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BULLETIN

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MOLECULAR SPECTRA IN GASES

Report of the Committee on Radiation in Gases

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F. WHEELER LOOMIS, LEIGH PAGE

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PREFACE

The preparation of this report has been beset with difficulties owing to the magnitude of the subject and the rapidity with which it is developing. At the present time, many new research workers are entering the field and our primary concern has been to give them an introduction to the subject combining an adequate historical background with as full an account of the present situation as possible. The authors have definitely abandoned, however, all attempt at encyclopedic completeness.

The preparation of the report has extended over several years, and much of it was written a year or two ago. Many alterations have been made in those parts which were finished first, in order to bring them into line with recent developments, but the various sections of the report are of necessity unequally up-to-date. All the chapters were completed before July, 1926, except Chapter VII, which was wholly rewritten during July and August.

The committee is deeply indebted to Professor R. S. Mulliken whose suggestions and criticisms have been numerous and invaluable.

EDWIN C. KEMBLE.

September 28, 1926.

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PREFACE TO SECOND PRINTING

Because of the important and extensive developments which have occurred in the field of band spectra since the first issue of this Report, and because of the rapidity with which the subject is being augmented at present, the Committee has not deemed it feasible to revise the Bulletin at this time. But it has seemed worth while to make a second printing, with certain changes and corrections, and with the addition of an index; and Professor Raymond T. Birge has kindly prepared a supplementary list of recent general references on molecular spectra which follows.

E. C. K.

May, 1930.

SUPPLEMENTARY REFERENCE LIST

Any attempt to bring the subject of band spectra up to date by means of a brief discussion would be futile. But there is given herewith a list of certain general references from which, collectively, the reader can obtain the desired information.

R. S. Mulliken, in Chemical Reviews, 6: 503 (1929), has written a very clear and non-mathematical account of recent developments, emphasizing especially the applications to chemical problems. This article may well be recommended as the best simple introduction to the entire subject of molecular spectra now available.

The theory of the structure of diatomic molecules has reached the point where it is possible to devise a systematic and logical nomenclature. Professor Mulliken has recently initiated discussions among the band spectroscopists of the world, regarding this matter, and as a result there has been obtained a very definite consensus of opinion on practically all important points. An article giving a complete nomenclature, with specific definitions in each case, is about to be published by Mulliken in the Physical Review.

He has written also a general summary of our present knowledge of band spectra. The first two parts of this review have appeared in Reviews of Modern Physics, 2: 60-115 (January, 1930). The third, and concluding portion, will appear in the April number.

The writer has published in the International Critical Tables V: 409-418, tables of constants for diatomic molecules, including all material available in December, 1927. This carries the data forward only one year, as compared to the table beginning on page 230 of this Report, but the I. C. T. table is almost twice as long. Since 1927, progress has been slower, and not many new molecules have been studied, although more accurate and much more extensive data have been obtained, in many cases. No complete table of band spectra data, bringing the material up-to-date, is now available.

The Faraday Society, in September, 1929, held a symposium on Molecular Spectra and Molecular Structure. More than forty papers were presented, and these are published in Trans. Faraday Soc., 25: 611-949 (1929). They are also published in book form by Gurney and Jackson. These papers cover a very wide field, and collectively give a general idea of the status of the subject at the present time.

R. Mecke, in Fortsch. d. Chem. Phys., etc., vol. 20: no. 3 (1929), has published a review entitled Bandenspektra und ihre Bedeutung für die

Chemie. This contains tables of constants, as well as a discussion of the theory. Essentially the same information is given by Mecke in the Geiger and Scheel Handbuch der Physik, 21: 493-573.

R. C. Johnson, in his monograph on Spectra (Methuen, 1928) devotes 28 pages to band spectra.

Atoms, Molecules, and Quanta (McGraw-Hill, 1930), by A. E. Ruark and H. C. Urey, contains 80 pages on band spectra, with numerous references to the original literature.

R. Ruedy, in the Sammlung Vieweg, has published a book of 124 pages entitled Bandenspektren auf experimenteller Grundlage.

Certain theoretical developments in molecular spectra, from the standpoint of the new mechanics, are contained in Quantum Mechanics, by E. U. Condon and P. M. Morse (McGraw-Hill, 1929), and also in Sommerfeld's Wellenmechanischer Engänzungsband (Vieweg, 1929).

RAYMOND T. BIRGE.

March 28, 1930.

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NOTATION

Some discrepancies in minor details of notation will be found from chapter to chapter in this report. The following major items, however, have been followed consistently:

Spectroscopic frequency	ν
Mechanical frequency (where it is to be distinguished from spectroscopic frequency)	ω
Energy	E
Upper energy level (prime)	$'$
Lower energy level (double prime)	$''$
Phase integral	J
Vibrational quantum number for diatomic molecule	n
Effective rotational quantum number (i. e., nuclear angular momentum in units $\frac{h}{2\pi}$)	m
Electronic angular momentum in units $\frac{h}{2\pi}$	s
True rotational quantum number (measuring resultant of m and s)	j
Electronic quantum numbers (in general)	e
Component of electronic angular momentum parallel to nuclear axis (in units $\frac{h}{2\pi}$)	σ
Component of electronic angular momentum perpendicular to nuclear axis (in units $\frac{h}{2\pi}$)	ϵ
Magnetic quantum number or component of j parallel to magnetic field	r
Empirical ordinal number of line in band series	M
Mass coefficient for diatomic molecules (i. e., product of masses divided by sum)	μ
Distance between nuclei	r
Equilibrium value of r	r_0
Moment of inertia for diatomic molecule	I
Equilibrium value of I	I_0
$\frac{h}{8\pi^2 I}$ (i. e., coefficient of hm^2 in formula for energy of diatomic molecule)	B
Electronic energy	E_e or E^e
Vibrational energy	E_n or E^n

Rotational energy	E_m or E^m
Vibrational energy "term" $\left(\text{i. e., } \frac{E_n}{h}\right)$	G
Rotational energy "term" $\left(\text{i. e., } \frac{E_m}{h}\right)$	F
Positive band branch $(j' = j'' + 1)$	R
Negative band branch $(j' = j'' - 1)$	P
Zero band branch $(j' = j'')$	Q

A *spectrum* includes all bands due to a given type of molecule.

A *system* includes all bands due to a given electronic transition.

An n' progression is a series of bands in which n'' is constant and n' varies.

An n'' progression is a series of bands in which n' is constant and n'' varies.

A *sequence* is a series of bands in which $n' - n''$ is constant.

CAPTION OF FRONTISPIECE

Fine Structure of Typical Electronic Bands

(a) AlO, λ4842 (0-0) band. Spectrogram by R. T. Birge, 2d order, 21 ft. grating, University of Wisconsin. Quantum analysis by W. C. Pomeroy. Illustrative of CN type of doublet (Chapter IV, Figure 8A). *P* and *R* branches only, medium weight molecule, small change in moment of inertia.

(b) Swan band, λ5165 (0-0). Spectrogram by R. T. Birge, 2d order, 21 ft. grating, University of Wisconsin. Quantum analysis by J. D. Shea. Illustrative probably of OH type of doublet plus normal singlet (Chapter IV, Figure 8C). *P* and *R* branches only, medium weight molecule, small change in moment of inertia.

(c) Runge bands of oxygen, λλ3370, 3516, and 3672 (0-14, 0-15, 0-16), degraded to red (*i. e.*, to the left). Spectrogram by C. Runge, 1st order, 21 ft. grating, University of Göttingen. CN type doublet (analysis of G. H. Dieke). *P* and *R* branches only, medium weight molecule, large change in moment of inertia.

(d) Comet-tail band (CO^+), λ3997 (3-0), degraded to red. Spectrogram by F. Baldet, Observatoire de Mendon. *P*, *Q*, and *R* branches, double electronic level, medium weight molecule, medium change in moment of inertia.

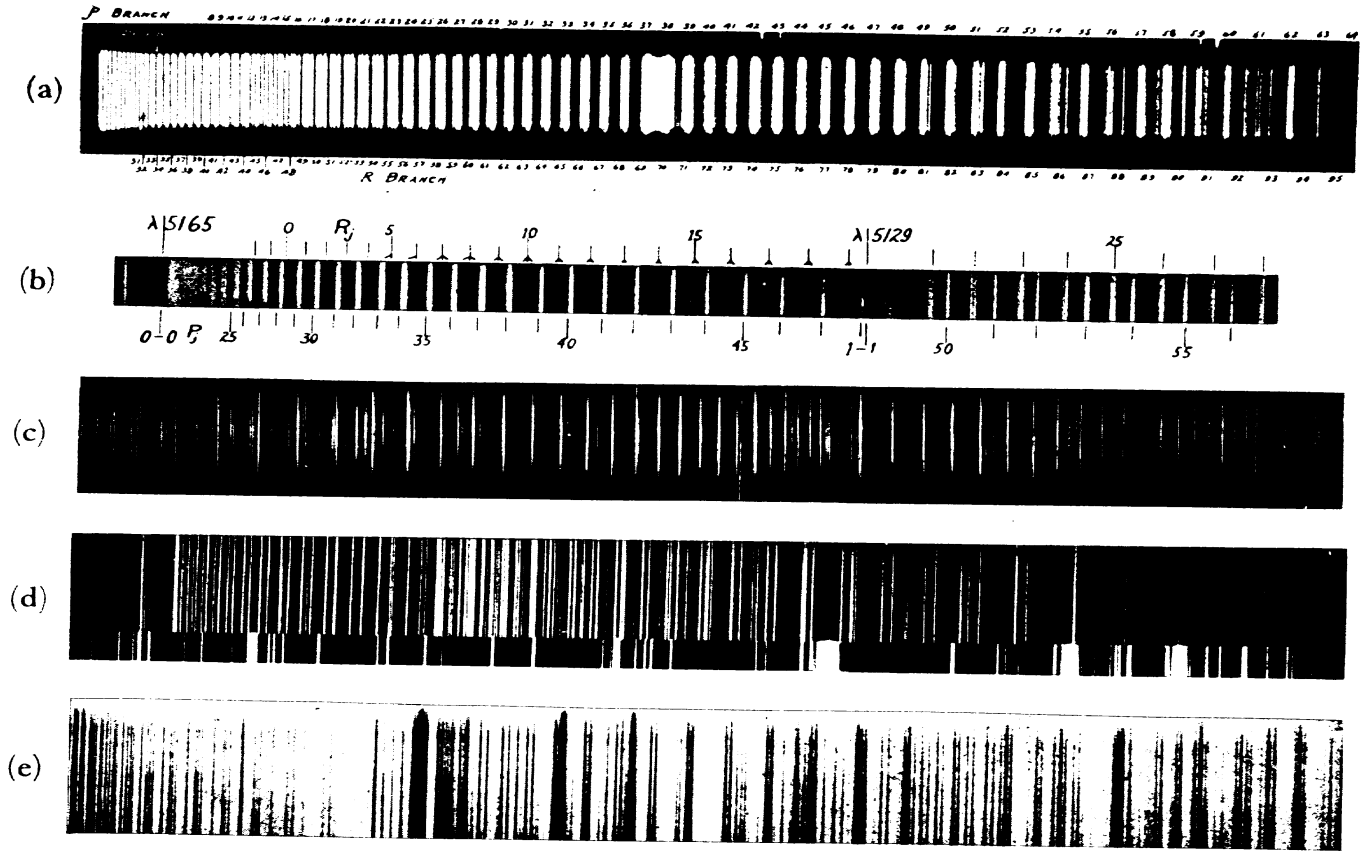
(e) MgH, λ5211 (0-0), degraded to violet. Spectrogram by W. W. Watson and P. Rudnick, 2d order, 21 ft. grating, University of Chicago. OH type of doublet (Chapter IV, Figure 8C). *P*, *Q*, and *R* branches. Light molecule.

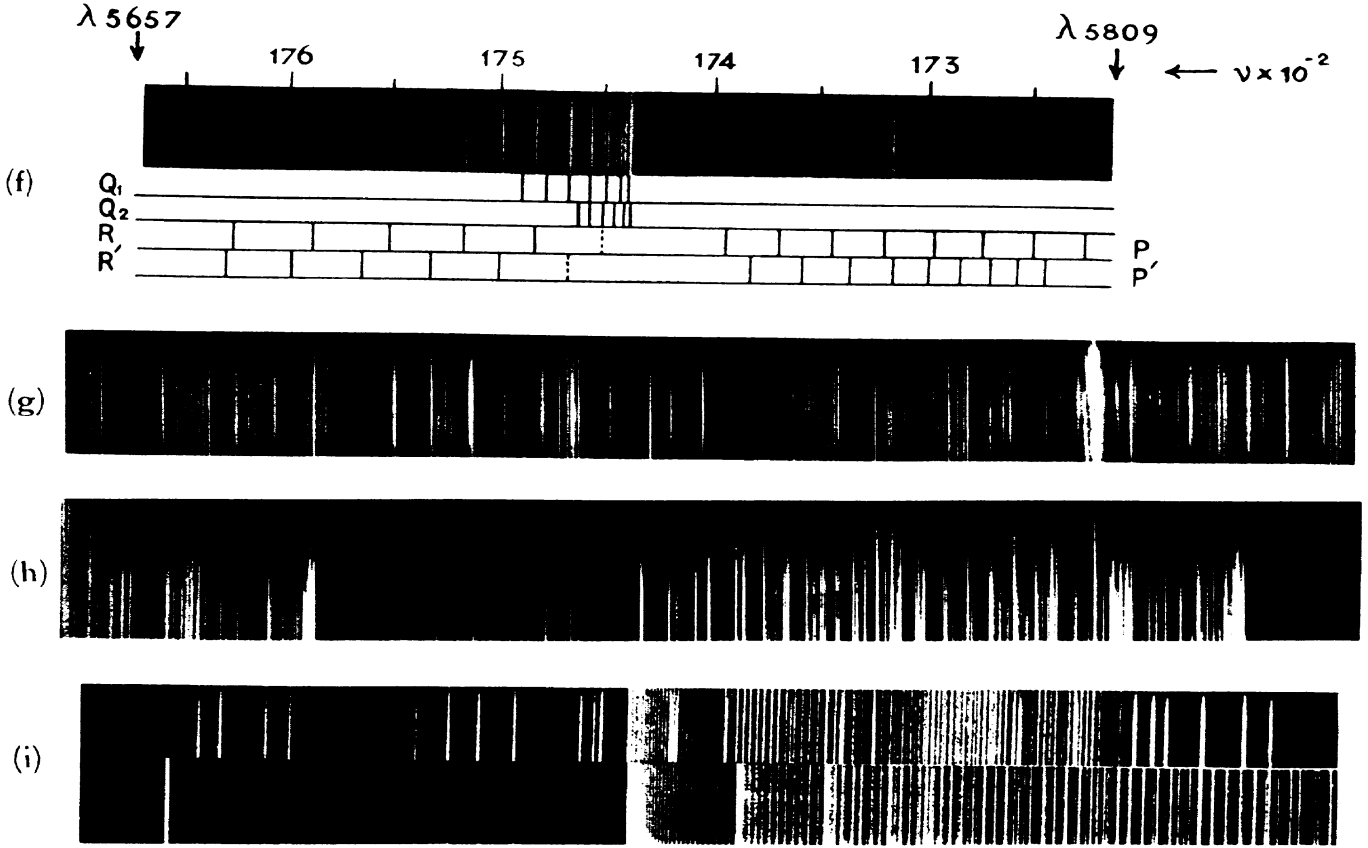
(f) Helium, λ5730 (0-0 band, *P-D* transition). Spectrogram by W. E. Curtis, 1st order, 10 ft. grating, Royal College of Science, London. (Published by permission of the Royal Society of London.) Two *P*, two *Q*, and two *R* branches. Light molecule, small change in moment of inertia.

(g) Hydrogen, ultra-violet bands, λ1100 to λ1650, degraded to red (*i. e.*, to the left). Spectrogram by G. H. Dieke and J. J. Hopfield, 1st order, 50 cm. grating, vacuum spectrograph. (Hydrogen-argon mixture.) *Q* branches only (quantum analysis of G. H. Dieke), very light molecule.

(h) Nitrogen, First Positive Group, λ6544 (7-5) and head of λ6468 (8-6) bands, degraded to violet. Spectrogram by R. T. Birge, 2d order, 21 ft. grating, University of Wisconsin. Fine structure analysis now in progress.

(i) CN, λ3883, in arc (below) and in active nitrogen (above). Spectrogram by W. E. Jevons, 1st order, 10 ft. grating, Imperial College of Science, London. Effect of low temperature (active nitrogen) on the distribution of rotational energy.


(a)
P BRANCH
R BRANCH
(b)
λ 5165
0
R_J
5
10
15
λ 5129
25
0–0 P_J
25
30
35
40
45
1–1
50
55
(c)
(d)
(e)


λ 5657
λ 5809
176
175
174
173
← ν × 10⁻²
(f)
Q1
Q2
R
R′
P
P′
(g)
(h)
(i)

CHAPTER I

INTRODUCTION

EDWIN C. KEMBLE

Although the theory of quanta has marvellously illumined all branches of physics connected in any intimate way with atomic and molecular processes, few subjects have been more strikingly clarified than that of band spectra. The extreme complexity of this type of spectrum, the difficulty of ascertaining with any certainty the nature of the emitting molecules, and the lack of any fundamental unifying law such as Ritz's combination principle for line series,[1] made progress exceedingly slow until about ten years ago. At the present time, however, many of the most fundamental questions involved in the study of gaseous band spectra have been answered and advances in this field are being made much more rapidly than ever before. It is now quite certain that band spectra are the characteristic spectra of molecules containing more than one atom, and that their emission is a quantum process like the emission of line spectra, but more complex, since it involves changes in the vibrational and rotational quantum numbers of the atomic nuclei as well as in the quantum numbers of the excited valence electron. One may also assert with considerable confidence that the individual lines which form the components of any one band series involve the same changes in electronic and vibrational quantum numbers and differ merely in the initial and final nuclear or molecular rotational quantum numbers. The theory enables us to calculate with precision the moments of inertia and vibrational frequencies of diatomic molecules from their spectra, and it is altogether reasonable to expect from the study of bands in the near future a great quantity of new information regarding molecular structure and the details of chemical reactions in gases.

The foundation for the present theory of band spectra was laid in 1892 by the elder Lord Rayleigh(1) when he pointed out that if an oscillator, which at rest emits and absorbs light of frequency ν_0, is caused to rotate with a frequency ν_r about an axis perpendicular to the direction of vibration, it should emit and absorb in about equal proportions the two frequen-

[1] This principle has only recently been employed with success in the study of bands.

cies $\nu_0 + \nu_r$ and $\nu_0 - \nu_r$.[2] He remarked that the absence of a corresponding broadening of spectrum lines due to molecular rotations constituted an outstanding difficulty in the theory of spectra. It is, indeed, self-evident that if the distribution of angular velocities of gas molecules followed the Maxwell-Boltzmann law, and if radiation were emitted in accordance with the classical electromagnetic theory, each emission and absorption frequency in a multi-atomic gas would be spread out into a continuous band whose width would depend on the moment (or moments) of inertia, but would always be large compared with the width of a normal spectrum line. The absence of such continuous bands in the spectra of gases[3] is one of the most incontrovertible evidences known that there is something radically wrong with the classical mechanics, or the classical electrodynamics, or both.

As early as 1904 Drude([2]) from the study of the dispersion of various crystals was led to the conclusion that the infra-red absorption and emission bands of most substances, including gases, must be due to the vibrations of electrically charged atoms and molecules rather than to the oscillations of the electrons inside the atoms, and in 1912 Niels Bjerrum([3]) called attention to the fact that the breadth of the as yet unresolved infra-red absorption bands of gases was of the order of magnitude to be expected from the superposition of molecular rotations on molecular vibrations.

The form and width of the band required by the Rayleigh-Bjerrum theory is most easily calculated for diatomic molecules. The generalized Maxwell-Boltzmann law then requires that in a group of n molecules in

[2] Let the scalar magnitude of the electric moment be $A + B\cos 2\pi\nu_0 t$. Choosing rectangular coordinates in the plane of the motion, let the angle between the center line of the molecule and the x-axis be $2\pi\nu_r t$. The components of the electric moment along the x and y axes are then

$$P_x = (A + B\cos 2\pi\nu_0 t)\cos 2\pi\nu_r t = A\cos 2\pi\nu_r t + \frac{B}{2}[\cos 2\pi(\nu_0 + \nu_r)t + \cos 2\pi(\nu_0 - \nu_r)t],$$

$$P_y = (A + B\cos 2\pi\nu_0 t)\sin 2\pi\nu_r t = A\sin 2\pi\nu_r t + \frac{B}{2}[\sin 2\pi(\nu_0 + \nu_r)t - \sin 2\pi(\nu_0 - \nu_r)t]$$

[3] There is now every reason to believe that all gaseous band spectra would be resolved into fine lines if examined at low pressures with spectroscopes of sufficient resolving power. Broad regions of continuous absorption or emission limited on the long-wave side only, are not classified as bands and are probably always associated with the last step in the process of the ionization of a molecule (monatomic or multiatomic) or with the first stage in the process of recombination.

thermal equilibrium at the temperature T the number having rotational frequencies between ν_r and $\nu_r + d\nu_r$ shall be

$$dn = \frac{4\pi^2 nI}{kT} e^{-\frac{2\pi^2 I \nu_r^2}{kT}} \nu_r d\nu_r \qquad (1)$$

where I is the moment of inertia and k is the gas constant for a single molecule. The quantity $dn/d\nu_r$ should be proportional to the absorption coefficient for either of the frequencies $(\nu_0 + \nu_r)$ or $(\nu_0 - \nu_r)$. Since $dn/d\nu_r$ is zero for $\nu_r = 0$, showing a maximum when ν_r has the value $\frac{1}{2\pi}\sqrt{\frac{kT}{I}}$, it follows that the absorption band should be a doublet with maxima separated by an interval

$$\Delta\nu = \frac{1}{\pi}\sqrt{\frac{kT}{I}} \qquad (2)$$

on a frequency scale.[4] The predicted doublet structure was found experi-

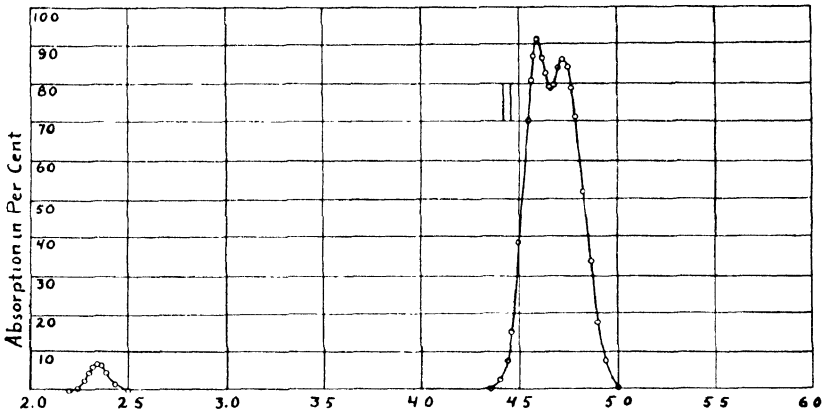


FIGURE 1.—Infra-Red Absorption Spectrum of CO (Burmeister).

mentally by Burmeister(4) and v. Bahr(5) [Cf. Figure 1]. The spacing of the maxima of the absorption doublets of HCl, HBr, and CO at 3.5μ, 3.9μ and 4.6μ, respectively, may be used to calculate the moments of inertia of these molecules and hence the nuclear separations r_0. Using

[4] Bjerrum's initial rough computation set the frequency difference equal to $\frac{1}{\pi}\sqrt{\frac{2kT}{I}}$. Cf. E. C. Kemble, Phys. Rev. N. S., 8: 689 (1916).

Burmeister's observations and equation (2) one obtains the plausible values of Table 1.

TABLE 1

Gas	Wave lengths of max. abs.		$I\times10^{40}$	$r_0\times10^{8}$
HCl	3.40μ	3.55μ	2 9	1.34
HBr	3.84	4.01	3.7	1.50
CO	4.60	4.72	14.7	1.14

Two other sources of evidence for this theory were the discovery that the separation of the maxima of the absorption doublets varies at least approximately as the square root of the absolute temperature ([5]), ([6]) as required by (2) and the rough verification of a correlation between the width of the absorption bands in the near infra-red and the width of the region of absorption which exists in the extreme infra-red spectrum of many gases. This absorption region in the extreme infra-red is believed to be a pure "rotation" spectrum. On the basis of the Rayleigh-Bjerrum theory its frequencies are to be identified with the frequencies ν_r of the rotations of the molecules. It should accordingly extend on a frequency scale from zero up to a value which is half the width on the same scale of the vibration-rotation band in the near infra-red. This theoretical prediction was shown by v. Bahr([5]) to be in accord with the meagre experimental data available on the extreme infra-red.

It seems desirable at this point to call attention to the three classes into which bands are naturally divided on the basis of the present theory. They are (a) the pure "rotation" bands in the extreme infra-red involving (in terms of the Rayleigh-Bjerrum theory) only the rotational frequencies of the molecules; (b) the "vibration-rotation" bands which involve both vibrational and rotational frequencies; and (c) the "electronic" bands involving the electronic frequencies in addition to the others. Bohr's correspondence principle correlates quantum transitions in which only the rotational quantum number changes with the rotational frequencies of the molecules, those in which both rotational and vibrational quantum numbers change with the vibration-rotation combination frequencies, and those in which the electronic quantum numbers also change with Fourier components of the motion which combine electronic and nuclear[*] frequencies. The quantum theory as now applied to band spectra therefore interprets the three classes of bands as due to jumps between molecular stationary states accompanied, respectively, by changes

[*] It is convenient to designate the frequencies associated with the rotation of the molecule as a whole and with the vibrations of the atoms as wholes, as nuclear frequencies since the kinetic energy of these rotations and vibrations is primarily nuclear kinetic energy.

in the rotational quantum numbers, rotational and vibrational quantum numbers, and in the last case rotational, vibrational, and electronic quantum numbers. The first two classes of bands are absent in the absorption spectra of the diatomic gaseous elements whose molecules presumably have no electric moment. In absorption spectra the three classes of bands commonly lie in well separated regions of the spectrum, viz., the extreme infra-red, the near infra-red, and the ultra-violet.[6] In emission, on the other hand, we have to do with transitions between highly excited states in which the electronic energy levels lie close together and the electronic frequencies are low. Hence, the electronic emission bands may extend down into the infra-red and overlap the rotation-vibration bands. The rotation and vibration-rotation spectra, however, are apparently confined under all circumstances to the infra-red region. The differences in the character of the three types of band will be considered later.

Simultaneously with the qualitative verification of Bjerrum's theory by Burmeister and v. Bahr came the discovery by the latter that the infra-red bands in question are not really continuous as required by the theory, but are resolvable into a fine structure.[7] This resolution was first effected for the water-vapor band at 6.3μ([5]), then for the HCl band at 3.5μ([7]). It was immediately evident that the existence of this fine structure must be regarded as conclusive evidence of the quantization of the rotational motion of the molecules. But since the Bohr form of the quantum theory had not yet won complete acceptance, it was at first supposed that the frequencies of the lines were to be interpreted in terms of the Rayleigh formula

$$\nu = \nu_0 \pm \nu_r. \tag{3}$$

The observations on HCl showed the central band lines to be spaced at approximately equal distances on a frequency scale and this fact was assumed by Bjerrum to be a direct proof that the angular velocity of a diatomic molecule is always an integral multiple of a certain unit of angular velocity.

The first suggestion regarding the quantization of the rotational motion of diatomic molecules was that of Nernst([8]) and Lorentz([9]) who proposed to set the energy equal to an integral multiple of Planck's constant h times its rotational frequency. This hypothesis leads to the formula

$$\nu_r = \frac{mh}{2\pi^2 I} \qquad m = 0,\ 1,\ 2,\ \ldots \tag{4}$$

[6] The electronic absorption band system sometimes extends down into the visible region. Br_2 and I_2 are familiar examples.

[7] See Figure 1, Chapter III.

in which I is the moment of inertia and ν_r is one of the possible frequencies of rotation. Later developments indicated that the energy should be set equal to an integral multiple of $\frac{1}{2}h\nu_r$ and hence that ([10]), ([11])

$$\nu_r = \frac{mh}{4\pi^2 I} \qquad m = 0,\ 1,\ 2,\ \ldots \tag{5}$$

Either of the formulas (4) or (5) when combined with (3) gives an expression for the absorption frequencies in general agreement with the observations. A more definite experimental test of the two rules is obtained by a comparison of the values of the moment of inertia I calculated from the spacing of the "quantum" lines by (4) and (5) with the value obtained in a wholly different way from (2).[8] The agreement in the case of HCl is within the limits of experimental error if the formula (5) is used, and the corresponding moment of inertia of the HCl molecule, viz., 2.7×10^{-40} gm. cm.^{2}, is reasonable.

One of the most important steps in the history of this subject was the extension of Bjerrum's theory by Heurlinger to the interpretation of electronic bands. As an introduction to a brief account of his work we shall indicate the two most striking differences between the typical electronic band spectrum [9] and the infra-red absorption spectra discussed above. These differences are more apparent than real, but have played an important part in the history of the theory. The first concerns the structure of the individual band. The lines of the typical electronic band are not spaced at approximately equal distances on a frequency scale as are those of the infra-red bands, but converge toward a head such as one of those shown in Frontispiece, figures (a), (b) and (d). The law of convergence is quite different from that which governs the series spectra of atoms, and if the lines are numbered from the head, the frequencies fit approximately into a simple empirical formula of the type

$$\nu = \nu_h + CM^2 \qquad M = 0,\ 1,\ 2,\ 3,\ \ldots \tag{6}$$

where ν_h is the frequency of the head and C is a constant characteristic

[8] Quite recently a further modification of the rule for the quantization of such rotational motions has been introduced and we now use (5) with the series of m values

$$m = j - \epsilon, \qquad j = 1,\ 2,\ 3,\ \ldots$$

where ϵ is a constant for electronically unexcited molecules and equal to $\frac{1}{2}$ for HCl. Cf. Chapter III, p. 55.

[9] By "typical electronic band spectrum" we mean one of the simple class illustrated in the frontispiece, which has outstanding regularities in structure lending themselves naturally to theoretical analysis. Many band spectra, perhaps owing to the superposition of numerous faint bands, are so confused and characterless as to defy analysis.

of the band. Formulas of this type were first devised by Deslandres([12]) and the quadratic term CM^2 is frequently called a "Deslandres" term. There may be one, two, or more, series of lines apparently diverging from a single head.

The second difference between the electronic and the infra-red bands comes from the arrangement of the former into systems. Each system is a two-dimensional set of bands of similar structure arranged in a regular way so that the frequencies of the heads fit approximately into a formula of the type

$$\nu_h = K + a'n' + b'n'^2 - (a''n'' + b''n''^2). \qquad n', n'' = 0, 1, 2, 3, \ldots \quad (7)$$

The different bands in a system usually overlap to a greater or less extent, as will be seen by reference to Frontispiece. Often a' and a'' are nearly equal. In this case those bands for which $n' - n''$ has a given value will lie close together, constituting what is called a "band sequence." The spectrum of a given molecule usually contains several systems.

The infra-red absorption spectra of diatomic gases also contain one series of bands whose centers have frequencies approximately in the harmonic ratio $1:2:3:\ldots$.[10] The first member is by far the strongest and the intensity drops so rapidly as one passes up the series that the third member can be observed only under the most favorable conditions([13]), ([14]). On theoretical grounds the development of a two parameter family of absorption bands in the infra-red is to be expected at high temperatures, and the discovery of a new band in heated HCl underlying the first member of the normal absorption series confirms this expectation([15]). The difference between this incipient infra-red "system" with its marked intensity differences and such a highly developed system as that shown in Figure 2, Chapter IV, is very striking, however, and of considerable theoretical importance.

Heurlinger's principal contribution([16]) consists in showing that the structure of some, at least, of the electronic bands is more like that of the infra-red bands of diatomic gases than a superficial view would indicate. He observes that if the moment of inertia of the molecule is treated as a variable (in view of the elastic nature of the interatomic bond) the fundamental equations of the Bjerrum theory (3) and (5) lead to a frequency formula of the type

$$\nu = \nu_0 \pm c_1 M + c_2 M^2 \pm \ldots \qquad M = 0, 1, 2, 3, \ldots \quad (8)$$

which differs only superficially from (6). ν_0 may denote either the frequency of the nuclear vibration or a combination of the frequency

[10] Cf. Figure 1.

of an electron with that of the nuclear vibration. If $|c_2|$ is small, as would be expected for a fairly rigid molecule, the lines will be nearly equidistant in the neighborhood of the frequency ν_0 where the parameter M [11] is zero. This assumption covers the case of the halogen hydride infra-red bands. The existence of a small quadratic term in the formula is in conformity with the empirical observations on these bands.

On the other hand, if $|c_2|$ is relatively large, the lines of one of the two branches will crowd together as M increases and the band will eventually double back on itself, forming a head. Figure 4, Chapter IV, shows a plot of the frequencies of the components of such a band plotted against M-values. This type of graph is known as a Fortrat diagram. The existence of a large value of $|c_2|$ must be ascribed to a large variation in the moment of inertia of the molecule, due, perhaps, to the fact that the molecules under consideration are in electronically excited states.

If the heads of bands with two branches are to be accounted for in this way, it is clear that the experimental facts must conform to two requirements, viz., (a) the head cannot be a point of discontinuity in the band structure, and (b) the intensities of the band lines must be distributed in a fairly symmetrical manner on either side of a point of minimum intensity which is the logical center of the band and has the frequency ν_0 of formula (8). The second of these theoretical predictions comes from the fact that the two lines corresponding to any given value of M are supposed to originate in the same group of molecules. An experimental study of a number of bands has shown that both of these requirements are fulfilled. One or more lines are missing at the point of minimum intensity and these help to give it a definite location. Additional evidence in favor of Heurlinger's choice of the band "center" is derived from a study of the fine structure of band components and from the small deviations of the experimental frequencies from those required by such simple formulas as (8). In a more complex type of band the two branches indicated by the elementary theory are supplemented by a third which diverges like the others from the intensity center and has the form

$$\nu = \nu_0 + c_2(M - \tfrac{1}{2})^2 \qquad M = 1,\ 2,\ 3,\ \ldots \tag{9}$$

Figure 7, Chapter IV, is a Fortrat diagram of such a band.

But despite its many early successes the semi-classical theory of Bjerrum has been displaced by an interpretation of band spectra based entirely on the Einstein-Bohr hypothesis that spectroscopic frequencies

[11] In Heurlinger's first theory the M of equation (8) was identified with the m of equation (5). As (8) is empirically correct, though later developments change its interpretation, we use the symbol M which, in this and later chapters, always stands for an empirical parameter.

are the measures of energy differences and are not identical with the frequencies of the motion of the emitting system. The abandonment of the initially successful Bjerrum theory has been brought about primarily by the necessity of unifying our interpretation of line and band spectra, but there is internal evidence against the older point of view to be obtained from the study of infra-red bands alone. A diatomic molecule can obviously have but a single vibrational frequency. It was assumed that this frequency was to be identified with that of the center of the strong band which is the first member of the series described on page 15. The first suggestion regarding the interpretation of the fainter bands was that they were due to harmonics in the vibrational motion of the atoms caused by the asymmetry of the restoring force brought into play by compression and extension of the molecule. This assumption seems to be the only one compatible with the Bjerrum theory and requires that the harmonic relationship between the frequencies of the centers of the bands be exact. On the other hand, it is a requirement of the Bohr form of band spectrum theory that this relationship be approximate only. Experiment shows that the frequency of the second band in the series is just a little less than double the frequency of the first, or "fundamental," thus definitely deciding against the Bjerrum theory([17]). It is nevertheless a striking and important fact that the predictions of this semi-classical theory are in substantial accord with the major experimental facts and, as it turns out, with the predictions of the Bohr form of theory. The numerous points of agreement are, of course, bound up with the intimate correlation between classical and quantum theories which is the basis of Bohr's correspondence principle.

The basic work in the application of the Bohr form of quantum theory to band spectra was done by Schwarzschild and Heurlinger. In a remarkable paper([18]) published on the day of his death Schwarzschild gave a beautiful treatment of the problem of the quantization of a conditionally periodic motion with applications to the Stark effect and to the problem of band spectra. The formula (5) contains implicitly the following expression for the energy of a quantized rotating non-gyroscopic diatomic molecule:

$$E = m^2h^2/(8\pi^2 I) \qquad m = 0,\ 1,\ 2,\ \ldots \qquad (10)$$

I denotes the moment of inertia about an axis perpendicular to the line joining the nuclei. The moment of inertia about the nuclear axis is treated as infinitesimal. An expression of the same form as (10) is easily derived for the energy of a molecule having three equal principal moments of inertia. After applying the quantum conditions to the more general case of the motion of a symmetrical rotating rigid body with principal

moments of inertia A, A, C, Schwarzschild showed that quadratic terms of the type appearing in Deslandres' empirical formulas for the frequencies of electronic band lines can be obtained by combining (10) with the Bohr-Einstein frequency formula

$$h\nu = E' - E''. \tag{11}$$

The resulting expression for the frequencies emitted in consequence of a jump from one rotational stationary state to another is

$$\nu = \frac{h}{8\pi^2 I}(m'^2 - m''^2). \tag{12}$$

If it is assumed that, in addition to the change in rotational energy, emission is accompanied by a change in electronic and vibrational energy of magnitude $h\nu_h$, the frequency formula

$$\nu = \nu_h + \frac{h}{8\pi^2 I}(m'^2 - m''^2) \tag{13}$$

is obtained. If either of the quantum numbers m' and m'' is treated as a constant (13) passes over into the Deslandres form (6), but Schwarzschild had no explanation of the reason for such a limitation on the values of m' or m''.

The difficulty was met by Heurlinger([19]) with the aid of Bohr's correspondence principle. It follows from this principle that only a few of the many conceivable transitions between stationary states may be expected to yield actual spectrum lines. It is not difficult to show that the Fourier analysis of the motion contains no combination tones corresponding to transitions in which $(m' - m'')$ has any other value than ± 1 or 0. Hence, only these jumps are to be regarded as permissible. Heurlinger pointed out that the three branches of such a band as that shown in Figure 7, Chapter IV, may be accounted for as due to these three possible types of transition. Without introducing explicit expressions for the energies of the stationary states he wrote down the general frequency formula

$$\nu = \phi(m', n'_1, n'_2 \ldots n'_s) - \phi(m'', n''_1, \ldots n''_s), \tag{14}$$

in which ϕ denotes E/h and $n_1, n_2, \ldots n_s$ are vibrational and electronic quantum numbers. If the energy of a molecule is independent of the sign of its rotational motion, it should be expansible in a power series in m containing even powers only. Heurlinger therefore assumed the formal expansions

$$\left.\begin{aligned} \phi(m', n'_1, \ldots n'_s) &= a'_0 + a'_2 m'^2 + \ldots \\ \phi(m'', n''_1, \ldots n''_s) &= a''_0 + a''_2 m''^2 + \ldots \end{aligned}\right\} \tag{15}$$

and derived from them formulas for the frequencies of the lines in the two branches of the simplest type of bands in which $m'-m''$ has the values $+1$ and -1 respectively. They are

$$\left.\begin{aligned}\nu &= (a'_0 - a''_0 + a'_2) + 2a'_2 m + (a'_2 - a''_2) m^2 + \ldots \\ \nu &= (a'_0 - a''_0 + a'_2) - 2a'_2 m + (a'_2 - a''_2) m^2 + \ldots\end{aligned}\right\} m = m'' = 0, 1, 2, \ldots \quad (16)$$

These expressions are of the same form as (8) which had previously been derived from the Bjerrum theory and shown to fit the major experimental facts. Heurlinger tested the new theory further by an indirect application of the Ritz combination principle and obtained fair agreement with the results of experiment.

The constants of Heurlinger's formulas receive an important theoretical interpretation if, following Lenz([20]), we introduce the formula (10) for the rotational part of the molecular energy. Then

$$a'_2 = \frac{h}{8\pi^2 I'} ; \qquad a''_2 = \frac{h}{8\pi^2 I''} ; \quad (17)$$

where I' and I'' are the moments of inertia for the states of greater and less energy respectively. The spacing of the lines near the center of the band on a frequency scale, viz., $2a'_2$, turns out to be identical with the spacing predicted by the semi-classical Bjerrum theory and the moments of inertia previously calculated from (5) or (2) (Table 1) are still valid. The coefficient of the quadratic term in the frequency formula is equal to $\frac{h}{8\pi^2}\left(\frac{1}{I'} - \frac{1}{I''}\right)$. This should be small for one of the infra-red absorption bands where the initial and final states differ only in vibrational and rotational quantum numbers. On the other hand a considerable change in the molecular moment of inertia may be expected as a result of a transition involving a change in electronic quantum numbers. Hence, the new theory predicts the existence of relatively large quadratic terms in the formulas for electronic bands and yields a satisfactory explanation of their tendency to form heads.[12]

To account for the formation of band systems the Heurlinger theory([21]) assumes a quantization of the energy of the nuclear vibration analogous to that used by Planck for his ideal linear oscillators. In view of the probable nonlinearity of the law of force governing the vibrational

[12] The electronic bands are generally observed in emission and the high temperatures which accompany emission accentuate the tendency to form heads by increasing the intensities of the lines associated with large rotational quantum numbers. Cf. Chapter IV, Section 2, part 2c.

motion of the molecules, Planck's energy formula cannot be exact and the more general series expansion

$$E_{\text{vib.}} = h(an + bn^2 + \ldots) \qquad n = 0, 1, 2, \ldots \tag{18}$$

is used. Here a is equal to the frequency of vibration for infinitesimal amplitudes and bn^2 is a presumably small correction term. In order to locate theoretically the positions of the centers of the different bands due to different final and initial values of n the small terms in m^2 may be dropped from equations (15) and the terms a'_0 and a''_0 may be replaced in view of (18) by

$$\left.\begin{aligned} a'_0 &= A' + a'n' + b'n'^2; \\ a''_0 &= A'' + a''n'' + b''n''^2. \end{aligned}\right\} \tag{19}$$

The general frequency formula (14) now yields

$$\nu_{\text{center}} = A' - A'' + a'n' + b'n'^2 - (a''n'' + b''n''^2), \tag{20}$$

which is identical in form with equation (7) previously deduced empirically by Deslandres for the band heads. As the centers and heads are never far apart, equation (20) is in obvious accord with the results of experimental measurement.

We have already noted that the infra-red vibration-rotation spectrum of a polar diatomic gas consists of a single series of bands whose frequencies are approximately in the ratio $1:2:3:\ldots$ and which decrease rapidly in intensity as one passes up the series. All these facts are simply accounted for by the Bohr-Heurlinger theory of molecular spectra. It is assumed that these bands are due to transitions which do not involve any changes in electronic quantum numbers. Hence the constants A', a', b' of equations (19) can be set equal to A'', a'', b'' for this special case. Furthermore, we may assume, in view of an elementary statistical calculation, that at ordinary laboratory temperatures practically all the molecules are in the lowest vibrational energy level, so that zero is the only value of n'' to be taken into consideration. (20) now degenerates into

$$\nu_{\text{center}} = an' + bn'^2. \qquad n' = 0, 1, 2, \ldots \tag{21}$$

As b is assumed small, equation (21) accounts for the approximately harmonic relationship between the frequencies of the band centers. The rapid decrease in intensity is taken care of by Bohr's correspondence principle, which associates the higher members of the series with weak overtones in the vibrational motion.[13]

[13] The absence of a corresponding rapid decrease in the intensities of the electronic bands correlated with successive values of $n' - n''$ is discussed in Chapter IV, Section 8 and in Chapter VII.

To sum up, though many serious difficulties have yet to be solved, the quantum theory in its present form gives a satisfactory account of the main features of the simpler molecular spectra in complete harmony with the Bohr theory of atomic spectra. There are no such accurate quantitative checks between theory and experiment in this field as that involved in Bohr's theoretical evaluation of the Rydberg constant, but this is to be expected in view of our lack of definite *a priori* knowledge of the structure of molecules and the forces binding the atoms together. The order of magnitude of molecular constants derived from the study of bands has always proved to be reasonable and the number of qualitative checks is so considerable that we can hardly doubt that the main lines of the theory are now permanent. The succeeding chapters of this report are devoted to a detailed discussion of the quantum interpretation of band spectra, the main lines of which have been sketched herein.

BIBLIOGRAPHY

[1] Rayleigh, Phil. Mag., (5) 34:410 (1892).
[2] Drude, Ann. Physik, (4) 14:677 (1904).
[3] Bjerrum, Nernst Festschrift, Halle, 1912.
[4] Burmeister, Verh. deut. physik. Ges., 15:589 (1913).
[5] Bahr, Verh. deut. physik. Ges., 15:710, 731 (1913).
[6] Spence and Holley, J. Optical Soc. Am., 7:169 (1923).
[7] Bahr, Verh. deut. physik. Ges., 15:1150 (1913).
[8] Nernst, Z. Elektrochem., 17:265 (1911).
[9] Lorentz, "La theorie du rayonnement et les quanta." (Report of First Solvay Conference.) Paris, 1912, p. 447.
[10] Ehrenfest, Verh. deut. physik. Ges., 15:451 (1913).
[11] Kemble, Phys. Rev., N. S., 8:689 (1916).
[12] Deslandres, Compt. rend., 103:375 (1886).
[13] Schaefer and Thomas, Z. Physik, 12:330 (1923).
[14] Brinsmade and Kemble, Proc. Nat. Acad. Sci., 3:420 (1917).
[15] Colby, Meyer and Bronk, Astrophys. J., 57:7 (1923).
[16] Heurlinger, Arkiv Mat., Astron. Fysik, 12:1 (1917). Dissertation, Lund, 1918.
[17] Kemble, Phys. Rev., 15:95 (1920).
[18] Schwarzschild, Sitzb. preuss. Akad. Wiss., 1:548 (1916).
[19] Heurlinger, Physik. Z., 20:188 (1919).
[20] Lenz, Verh. deut. physik. Ges., 21:632 (1919).
[21] Heurlinger, Z. Physik., 1:82 (1920).

CHAPTER II

QUANTUM DYNAMICS AND THE CORRESPONDENCE PRINCIPLE

LEIGH PAGE

SECTION 1. POSTULATES OF THE BOHR THEORY

Investigation of the structure of matter reveals the atom as a massive positively charged nucleus about which are circulating a number of electrons equal to the ordinal number of the element in the periodic table. In its normal condition the atom as a whole is uncharged. If, now, an atom which has lost one of its quota of electrons and therefore possesses a residual positive charge comes into the proximity of a second atom to which an extra electron has attached itself, the two will attract one another and may unite to form a molecule. A molecule which has a permanent electric moment, such as would be the case if it were composed of two ions of opposite sign, is called *polar*. Hydrochloric acid (HCl) is an example. On the other hand atoms may combine to form a molecule which, in its normal state, has no electric moment. Such a molecule, of which nitrogen (N_2) is an example, is known as *non-polar*.

In the study of atoms and molecules there are three regions of investigation. First, comes the nucleus and the laws governing its structure. Next, the region of the outer atom attracts attention. In investigating this region, the nucleus, on account of its comparatively minute dimensions, may be treated as a point charge, and, as its mass is much greater than that of one of the electrons revolving about it, it may in most cases be considered as immobile. The final region of interest is that occupied by the molecule. The center of mass of each atom coincides very exactly with its nucleus, but as the electrons in the outer atom are at distances from the nucleus comparable with the linear dimensions of the molecule itself, an ionized atom cannot be treated as a point charge except as a very rough approximation. Moreover, the overlapping of the atomic and molecular regions causes the structure of the outer atom to be appreciably modified when the atom enters into molecular combination. As different atoms have masses of the same order of magnitude, no one atom in a molecule can be considered as immobile, but all must be supposed to move about their common center of mass.

Each of these regions has a characteristic type of radiation associated with it. The gamma rays accompanying radioactive transformations are

the result of structural changes in the nucleus. With changes in the orbital configuration of the electrons outside the nucleus of an atom are associated the X-ray and optical spectra of the elements. Finally, when two or more atoms are combined into a molecule, alterations may occur in the velocity of rotation of the molecule as a whole or in the vibrations of the constituent atoms, which may be accompanied by changes in the configurations of the electrons in the outer portions of the atoms themselves. Changes in the energy of the structure due to these causes give rise to molecular or band spectra.

Classical electrodynamics is inherently incapable of accounting for either the stability of an atom or molecule, or for the emission from it of monochromatic radiation. On the basis of classical ideas, a negatively charged electron, coming into the region of influence of a massive positively charged nucleus, would be expected to revolve about the latter in an approximately elliptical orbit. While so moving, its acceleration would result in the emission of radiation, and the accompanying loss of energy would be evidenced by a decrease in the size of its orbit and an increase in the frequency of revolution. Thus the frequency of the electromagnetic waves emitted, which on the classical theory is identical with the frequency of revolution of the electron, would increase gradually with the time, giving rise to a continuous spectrum. Finally, the electron would fall into the nucleus, neutralizing its positive charge. The results to be expected in the case of a molecule consisting of two oppositely charged ions revolving about an axis through their common center of mass, are quite analogous.

Recognizing these limitations of the classical theory, Bohr concluded that the emission of monochromatic radiation and the stability of the atom or molecule are quantum phenomena. The theory which he proposed is based upon the following two fundamental postulates:

Postulate 1. Of all conceivable motions of the particles of which the atom or molecule is composed, this postulate selects certain ones and specifies that they and they alone are stable. Each such stable motion determines a definite value of the energy E of the atomic or molecular configuration. Thus, the stable states which the structure is capable of assuming may be specified by a series of energy levels. To calculate the quantitative value of the energy of a stable state, the following two auxiliary hypotheses are necessary:

(a) In stationary states the laws of classical mechanics hold good (Cf. 2), however much they may be deviated from in intermediate regions. The classical electrodynamics is adhered to, also, in these states, with the exception of the radiation reaction which the electromagnetic

equations, as usually interpreted([7]), ([8]), impose upon the orbital motion of a charged particle; for emission of radiation and its attendant reaction would negative the possibility of a state of motion of constant energy.

(b) The stable motions are selected from the infinitely greater number dynamically possible by a rule which will now be stated. Let the system (atom or molecule) have f degrees of freedom. Then its configuration is completely specified by f generalized coordinates $q_1, q_2 \ldots q_f$. Let L be the Lagrangian Function (normally the kinetic energy T less the potential energy V) expressed as a function of the q's and their time derivatives the $\dot{q}$'s. Then the momentum p_i conjugate to the coordinate q_i is defined as the partial derivative of L with respect to $\dot{q}_i$. This derivative gives p_i as a function of the q's and $\dot{q}$'s. In quantum dynamics the types of motion of chief importance are those in which each momentum p_i can be expressed as a function of the conjugate coordinate q_i alone, and the following discussion is limited to such types of motion.

Consider now the positive quantity

$$J_i = \oint p_i dq_i \tag{1}$$

known as the i^{th} *phase integral.* The path of integration is one which will bring the system back to its initial configuration after q_i has passed through a complete cycle of values or has increased by 2π. Two cases of importance arise. First, p_i may not contain q_i; that is, it is a constant. In this case q_i is known as a cyclic coordinate, and usually appears as an angle specifying an azimuth. When this is the case, the integral must be taken between the limits 0 and 2π. For example, if the polar coordinates ϕ and r are chosen to describe the motion of a single electron around a massive nucleus as in the case of the hydrogen or ionized helium atom, ϕ is a cyclic coordinate since the conjugate angular momentum p_ϕ remains constant during the motion. Second, p_i may be a function of q_i. In such cases, for the types of motion with which we are concerned, q_i appears under a radical sign, and p_i is real only for values of q_i lying between two fixed limits. This means that during the motion q_i oscillates to and fro between a fixed minimum and fixed maximum value. In this case the integral is to be extended from the minimum value of q_i to the maximum and back again. In the illustration just cited the radius vector r oscillates in the manner described from a minimum value at perihelion of the elliptical orbit to a maximum value at aphelion and back.

In general each of the f coordinates has a fundamental period different from that of any of the others. In such cases the rule for determining stationary states specifies that each of the f phase integrals given by

(1) is equal to a positive integral multiple of Planck's constant $h[6.56(10)^{-27}$ erg sec]. Provided this condition is fulfilled, the state of motion is one which can persist without radiation of energy. In degenerate cases, however, where two or more coordinates have the same period and therefore the number of such periods is less than the number f of degrees of freedom, those phase integrals corresponding to coordinates of the same period are to be added together and their sum put equal to a positive integral multiple of h. Thus, if the variation of mass with velocity is ignored, the coordinates ϕ and r used to describe the motion of the electron in the simple hydrogen atom have the same period and therefore only one quantum condition for specifying stationary states is afforded. As the energy in such a case is a function of the sum of the phase integrals, the energy of a stationary state is unambiguously determined even though the form of the electronic orbit is not. The necessity for stating the rule for quantizing the motion in such cases in the form indicated arises from the fact that in degenerate types of motion the phase integrals may be expressed in more than one set of coordinates. Placing each phase integral equal to a multiple of h leads to different orbits with each different choice of coordinates, though the energy is the same function of the sum of the phase integrals whatever set of coordinates may be used.

Postulate 2. With each of the stable states of the atom or molecule defined by the first postulate is associated a certain energy E of the system calculated on the basis of the classical laws of dynamics. Under conditions which have not yet been completely formulated a transition from one stationary state to another may occur. If this transition is from a state of greater to one of less energy, the principle of conservation of energy requires that an amount of energy equal to the difference between the energies of the two states shall be given out by the system; whereas, if the transition is in the opposite direction, an equal amount of energy must be taken in. Suppose this change in energy to be due to the emission or absorption of radiation of frequency ν. Then the second postulate of Bohr's theory puts the energy emitted or absorbed equal to $h\nu$. If the energy of the atomic or molecular configuration of greater energy content is denoted by E', and that of the configuration of less energy content by E'' then

$$h\nu = E' - E'' \tag{2}$$

specifies the frequency of the radiation emitted during a transition from E' to E'', or the frequency of the radiant energy which the system is capable of absorbing during a transition from E'' to E'.

The second postulate bears a striking resemblance to Ritz's combination principle. According to this principle, the frequency of a spectral line is expressible as the difference of two frequencies or spectral terms. Characteristic of each element are a number of such terms, from which the frequencies of the lines emitted or absorbed can be calculated by combining the terms into pairs and subtracting the smaller from the greater of each pair. While not every such difference gives the frequency of an observed line, yet the same term generally occurs in the expressions for the frequencies of a number of observed lines, and the number of terms needed is usually less than the number of lines observed. For all the lines in a single series the first term remains the same.

Bohr's second postulate gives an interpretation of the spectral term as the negative of the energy of the atomic configuration[1] divided by Planck's constant h. That this interpretation is correct is borne out by the fact that the energy which an electron must have to ionize an atom by impact agrees within the limits of experimental error with the negative energy of the most stable configuration of the atom as calculated from the limiting frequency of the principal series([3]).

SECTION 2. FIXATION OF STATIONARY STATES OF CONDITIONALLY PERIODIC SYSTEMS

Insomuch as the component charged particles constituting the atom or molecule generally have velocities small compared to that of light, the forces which they exert on one another can be taken as approximately the same as if they were permanently at rest in their instantaneous positions. Hence, it is necessary to take into account only the electrostatic attractions and repulsions specified by Coulomb's inverse square law. Consequently, the forces acting are derivable from a scalar potential function of the coordinates, and the dynamical methods developed for the solution of problems in celestial mechanics are directly applicable to the atomic problem.

In order to fix the stationary states, it is necessary to evaluate the phase integrals defined by equation (1) and to put each equal to an integral multiple of h. In the case of a cyclic coordinate measuring an azimuth, p_ϕ is constant and

$$J_\phi = 2\pi p_\phi.$$

In general, however, p_i is a function of q_i which may be determined most readily from the Hamilton-Jacobi partial differential equation.

[1] In the case of line spectra the energy of the atomic configuration is taken as negative, whereas in the case of band spectra the energy of the molecular configuration is taken as positive. The technical expression "spectral term" refers to the absolute magnitude of the energy regardless of sign.

The dynamics involved in this method of treating the problem will now be briefly outlined for the non-relativistic case.

The action S is defined as the time integral of twice the kinetic energy T integrated from a fixed initial instant 0 to a time t. If $d\tau$ is an element of time,

$$S=2\int_0^t T d\tau. \tag{3}$$

Now it may be shown by varying this quantity that

$$\delta S=\sum_i p_i\delta q_i-\sum_i p_i{}^0\delta q_i{}^0+t\delta E \tag{4}$$

where E is the total energy of the system, $p_i{}^0$ and $q_i{}^0$ the momentum and coordinate corresponding to the i^{th} degree of freedom at the time 0, and p_i and q_i the same quantities at the time t(1). Incidentally Hamilton's principle and the principle of least action are immediately deducible from this equation, which expresses the more general principle of varying action. Now suppose S to be given as a function of the q's and the energy E of the motion together with f constants such as the q^0's which specify the initial configuration. These $2f+1$ parameters completely determine S. Then it is evident from the expression for δS that

$$p_i=\frac{\partial S}{\partial q_i}, \qquad t=\frac{\partial S}{\partial E}. \tag{5}$$

We are now ready to consider the Hamilton-Jacobi partial differential equation. Let $H=T+V$ be the total energy expressed as a function of the p's and q's. The p's will occur only in the kinetic energy T since V is a function of the coordinates alone. As the system is conservative, H is equal to the constant E. Putting for p_i in H the partial derivative of S with respect to q_i, we have the Hamilton-Jacobi equation

$$H\left(\frac{\partial S}{\partial q_1}, \frac{\partial S}{\partial q_2} \ldots q_1, q_2, \ldots\right)=E. \tag{6}$$

In the case of the hydrogen atom this is simply

$$\frac{1}{2\mu}\left\{\left(\frac{\partial S}{\partial r}\right)^2+\frac{1}{r^2}\left(\frac{\partial S}{\partial \phi}\right)^2\right\}-\frac{e^2}{r}=E,$$

where μ is the mass of the electron and e its charge.

A complete solution of the Hamilton-Jacobi equation can generally be obtained only when the variables can be repeatedly separated so that a single variable and the corresponding derivative of S appear alone on the left hand side of the equation, all the other variables and derivatives being on the right hand side. If a variable is cyclic, as ϕ in the illustrative example, it is absent from the equation and hence the derivative of S with respect to this variable can always be separated from the other

variables. In the illustrative example this is effected by writing the equation in the form

$$\left(\frac{\partial S}{\partial \phi}\right)^2 = -r^2\left\{\left(\frac{\partial S}{\partial r}\right)^2 - 2\frac{\mu e^2}{r} - 2\mu E\right\},$$

and a complete solution is obtained by putting each side equal to a constant a_2 and integrating. In general, however, more than one variable will remain on the right hand side, and the process of separation has to be repeated. In this way a number of subsidiary equations equal to the number of variables is obtained, and as each such equation involves only a single q, it can be integrated. The value of S is obtained by adding together the solutions of the subsidiary equations and appending an additive constant a_0. From the nature of the process described it is evident that this expression contains a number of constants of integration, including a_0, equal to the number of variables. Hence, it is a complete solution of the Hamilton-Jacobi partial differential equation.

From the complete solution

$$S = S(q_1 \ldots q_f, E, a_2 \ldots a_f) + a_0, \tag{7}$$

it may be shown that the equations of motion can be obtained by simple differentiation with respect to the parameters $E, a_2 \ldots a_f$. For the purpose of computing the energies of the stationary states, however, it is unnecessary to know the equations of motion. For the phase integral is

$$\begin{aligned} J_i &= \oint p_i dq_i \\ &= \oint \frac{\partial S}{\partial q_i} dq_i, \end{aligned} \tag{8}$$

and for each i one of the subsidiary equations gives $\frac{\partial S}{\partial q_i}$ as a function of q_i and the constants $E, a_2 \ldots a_f$. In the illustrative example, the two phase integrals are

$$J_\phi = \oint \frac{\partial S}{\partial \phi} d\phi = \oint a_2 d\phi,$$

$$J_r = \oint \frac{\partial S}{\partial r} dr = \oint \sqrt{2\mu E + 2\frac{\mu e^2}{r} - \frac{a_2^2}{r^2}}\, dr.$$

Eliminating a_2 after performing the indicated integration, the energy E is obtained in terms of the phase integrals. This leads to the familiar expression for the energy of the hydrogen atom

$$\begin{aligned} E &= -\frac{2\pi^2\mu e^4}{(J_\phi + J_r)^2} \\ &= -\frac{2\pi^2\mu e^4}{h^2}\frac{1}{n^2}, \end{aligned}$$

where n is the total quantum number of the orbit.

In general, the parameters $a_2 \ldots a_f$ have to be eliminated from the f phase integrals (8), giving the energy E as a function of the J's. Then each J_i is to be put equal to h multiplied by an integer n_i. This procedure gives the energy of the stationary state in terms of the quantum numbers $n_1, n_2 \ldots n_f$. Although deduced on the basis of the classical dynamics, the procedure of this section applies equally well when the relativity variation of mass with velocity is taken into account provided that a more general definition of the action S is substituted for (3).

The phase integral (8) is a relation between J_i and the f parameters $E, a_2 \ldots a_f$. The f of these integrals can be used to eliminate $E, a_2 \ldots a_f$ from the expression (7) for S, giving S as a function of the q's and the J's, thus

$$S = S(q_1 \ldots q_f, J_1 \ldots J_f), \tag{9}$$

where the additive constant a_0 has been chosen as zero. Furthermore, if the parameters $a_2 \ldots a_f$ are eliminated from the f phase integrals, the energy E may be expressed as a function of the J's alone. This function of the J's will be denoted by $\bar{H}$. Now if we put w_j for the partial derivative of S with respect to J_j, it may be shown [2] that

$$\frac{dw_j}{dt} = \frac{\partial \bar{H}}{\partial J_j}. \tag{10}$$

[2] For, as S is expressed as a function of the q's and the J's alone

$$\delta S = \sum_i \frac{\partial S}{\partial q_i} \delta q_i + \sum_j \frac{\partial S}{\partial J_j} \delta J_j,$$

and

$$\frac{dS}{dt} = \sum_i p_i \dot{q}_i + \sum_j w_j \dot{J}_j.$$

Therefore as

$$\bar{H} = H = E,$$

$$\sum_i p_i \dot{q}_i - H = -\sum_j w_j \dot{J}_j - \bar{H} + \frac{dS}{dt}.$$

But

$$\sum_i p_i \dot{q}_i - H = 2T - H$$
$$= T - V.$$

Now Hamilton's principle requires that

$$\delta \int_0^t (T - V) d\tau = 0$$

provided the terminal configurations are the same for the varied and the original motion and corresponding configurations are reached at the same time. Hence,

$$\delta \int_0^t \sum_j (\dot{J}_j \delta w_j + w_j \delta \dot{J}_j + \frac{\partial \bar{H}}{\partial J_j} \delta J_j) d\tau - |\delta S|_0^t = 0.$$

As $\bar{H}$ is a function of the J's only, the right-hand member of this equation is a constant independent of the time. If ω is put for this constant and the equation is integrated,

$$w_j = \omega_j t + \delta_j, \tag{11}$$

where w_j, as it increases uniformly with the time, is known as an angle variable. From (10) it is seen that the increment in energy produced by arbitrary increments in the phase integrals is given by

$$\delta H = \omega_1 \delta J_1 + \omega_2 \delta J_2 + \ \ldots \ \omega_f \delta J_f. \tag{12}$$

Now it will be shown that when q_i goes from its minimum to its maximum value and back again, the other q's remaining unchanged, w_i increases by unity while the other w's are unaltered. For let S' and S'' be the initial and final values of the action respectively. Then from the equation (8) defining the phase integral

$$S'' - S' = J_i. \tag{13}$$

Differentiating partially with respect to J_i,

$$\frac{\partial S''}{\partial J_i} - \frac{\partial S'}{\partial J_i} = 1,$$

and, referring to the definition of w_i,

$$w''_i - w'_i = 1.$$

If, however, (13) is differentiated with respect to any other one of the J's such as J_j,

$$w''_j - w'_j = 0.$$

Hence, the important conclusion is reached that the q's are periodic functions of the angle variables w of period 1 and that the ω's are the fundamental frequencies of the motion.

In the simple case of the hydrogen atom

$$H = E = -\frac{2\pi^2 \mu e^4}{(J_\phi + J_r)^2},$$

Integrating the second term in the integral by parts and making use of the fact that the termini of the path are fixed,

$$\int_0^t \sum_j \left\{ \dot{J}_j \delta w_j - \left(\frac{dw_j}{dt} - \frac{\partial \bar{H}}{\partial J_j} \right) \delta J_j \right\} d\tau = 0,$$

from which it follows that

$$\dot{J}_j = 0,$$
$$\frac{dw_j}{dt} = \frac{\partial \bar{H}}{\partial J_j}.$$

and $$\omega_\phi = \frac{\partial E}{\partial J_\phi} = \frac{4\pi^2\mu e^4}{(J_\phi + J_r)^3} = \frac{\partial E}{\partial J_r} = \omega_r \qquad (14)$$

is the frequency of revolution of the electron.

As the q's are periodic functions of the angle variables w of period 1, they may be expressed as f-fold infinite Fourier series of the form

$$q_i = \sum_s C^i_{s_1, s_2 \ldots s_f} e^{2\pi i (s_1 w_1 + s_2 w_2 \ldots + s_f w_f)},$$

where the s's are positive and negative integers. The time comes in only in connection with the w's and there linearly, as shown by (11). Substituting the values of the w's given by this expression,

$$q_i = \sum_s D^i_{s_1, s_2 \ldots s_f} e^{2\pi i (s_1\omega_1 + s_2\omega_2 \ldots + s_f\omega_f)t}, \qquad (15)$$

where

$$D^i_{s_1, s_2 \ldots s_f} = C^i_{s_1, s_2 \ldots s_f} e^{2\pi i (s_1\delta_1 + s_2\delta_2 \ldots + s_f\delta_f)}.$$

While q_i is periodic in the w's, it is not periodic in t unless the ω's are commensurable. Hence, the motion is said to be *conditionally* or *multiply* periodic. It is only to such types of motion, whether of the "separable" type under discussion or not, that the quantum conditions are applicable. If the ω's are commensurable, the motion is spoken of as *degenerate*. More exactly, if there are g independent relations of the type

$$s_1\omega_1 + s_2\omega_2 \ldots + s_f\omega_f = 0,$$

the motion possesses a g-fold degeneration. For complete degeneration, f-1 such relations are required, because this number of relations permits the elimination of all but one ω from (15), and q is therefore completely periodic in t.

The hydrogen atom under consideration is an example of a completely degenerate system. Here there is only one frequency present, as ω_ϕ and ω_r are the same. Denoting this frequency by ω, the first two terms of the Fourier series expressing ϕ and r as functions of the time are

$$\phi = 2\pi\omega t - 2\epsilon \sin 2\pi\omega t \ldots,$$
$$r = a(1 + \epsilon \cos 2\pi\omega t \ldots),$$

where a is the semi major axis and ϵ the eccentricity of the elliptical orbit.

If, however, the relativity variation of mass with speed is taken into account, the motion of the electron in the hydrogen atom is no longer degenerate (provided it is considered as taking place in two dimensions only). For in this case, to a first approximation,

$$\overline{H} = E = -\frac{2\pi^2\mu e^4}{(J_\phi + J_r)^2}\left[1 + a^2h^2\left\{\frac{1}{J_\phi(J_\phi + J_r)} - \frac{3}{4}\frac{1}{(J_\phi + J_r)^2}\right\} \ldots\right],$$

where $$a = \frac{2\pi e^2}{hc},$$

and

$$\omega_\phi = \frac{\partial \bar{H}}{\partial J_\phi} = \frac{4\pi^2 \mu e^2}{(J_\phi + J_r)^3}\left[1 + \tfrac{3}{2}a^2h^2 \frac{J_r}{(J_\phi + J_r)^2} + \tfrac{1}{2}\frac{a^2h^2}{J_\phi^2} \cdots\right],$$

$$\omega_r = \frac{\partial \bar{H}}{\partial J_r} = \frac{4\pi^2 \mu e^4}{(J_\phi + J_r)^3}\left[1 + \tfrac{3}{2}a^2h^2 \frac{J_r}{(J_\phi + J_r)^2} \cdots\right].$$

Here ω_ϕ is greater than ω_r, ϕ goes through its cycle of values more rapidly than r, and the perihelion advances. The frequency σ of this advance is the difference between ω_ϕ and ω_r, or

$$\sigma = \tfrac{1}{2}\frac{a^2h^2}{J_\phi^2}\omega_r.$$

Since the elliptical orbit rotates slowly as the electron revolves around the nucleus, the path described by the electron, after a sufficiently long lapse of time, will fill completely the portion of the plane included between two circles whose centers are located at the nucleus and whose radii are equal to the minimum and maximum values of r. This is a characteristic of non-degenerate systems.

SECTION 3. THE CORRESPONDENCE PRINCIPLE

It has been shown that if the energy E of a conditionally periodic system of f degrees of freedom is expressed as a function of the f phase-integrals $J_1, J_2, \ldots J_f$, each of the fundamental frequencies $\omega_1, \omega_2, \ldots \omega_f$ of the motion is obtained by differentiating E partially with respect to the J of the same subscript.

Now, on the classical electromagnetic theory the mechanical vibration frequencies $\omega_1 \ldots \omega_f$ are at the same time optical frequencies; for the electric intensity in the radiation emitted by a charged particle is proportional to the acceleration of the particle, and the Fourier series for the components of acceleration contain the same fundamental frequencies as do the series expressions for the coordinates. Moreover, it has already been noted that in the terms of these series there appear not only the simple frequencies $\omega_1, \omega_2, \ldots \omega_f$ but also the combinations

$$s_1\omega_1 + s_2\omega_2 \ldots + s_f\omega_f.$$

Hence, on the classical theory, the optical frequencies to be expected are first the fundamental frequencies

$$\omega = \frac{\partial E}{\partial J_i},$$

second the overtones

$$\omega = s\frac{\partial E}{\partial J_i},$$

and third the combinational tones

$$\omega = \sum_i s_i \frac{\partial E}{\partial J_i},$$

the letter s in each case standing for an integer.

Now on the quantum theory, the phase integral J_i cannot change continuously, but only by the discrete amount $h(n'_i - n''_i)$, where n'_i is the i^{th} quantum number pertaining to the initial orbit and n''_i that pertaining to the final orbit. Putting s_i for the integer $n'_i - n''_i$ measuring the quantum change,

$$\frac{1}{h} = \frac{s_i}{\Delta J_i}.$$

Suppose, now, that all the phase integrals except J_i remain constant during the transition. Then if J_i changes by one quantum only, s_i is unity, and the second postulate of the Bohr theory gives for the frequency of the radiation emitted

$$\nu = \frac{\Delta E}{\Delta J_i},$$

which bears a striking resemblance to the expression obtained above for the fundamental frequency on the classical theory. If, however, J_i changes by more than one quantum,

$$\nu = s \frac{\Delta E}{\Delta J_i},$$

which, by analogy with the classical theory, may be called an overtone of the previous frequency, even though it is not an integral multiple of the same. Finally, if several J's change during the transition the frequency

$$\nu = \sum_i s_i \frac{\Delta E}{\Delta J_i}$$

is obtained, resembling in form the combinational tone on the classical theory. Comparing, then, the quantum theory with the classical theory, the following remarkable correspondence is observed:

	Classical theory	Quantum theory
Fundamental frequencies	$\omega = \frac{\partial E}{\partial J_i}$	$\nu = \frac{\Delta E}{\Delta J_i}$
Overtones	$\omega = s \frac{\partial E}{\partial J_i}$	$\nu = s \frac{\Delta E}{\Delta J_i}$
Combinational tones	$\omega = \sum_i s_i \frac{\partial E}{\partial J_i}$	$\nu = \sum_i s_i \frac{\Delta E}{\Delta J_i}$

Now, the greater the quantum numbers of the initial and final orbits, the more nearly does the difference quotient $\frac{\Delta E}{\Delta J_i}$ coincide with the derivative $\frac{\partial E}{\partial J_i}$. Hence, the fundamental frequency calculated on the quantum theory approaches asymptotically the fundamental given by the classical theory, and likewise with corresponding overtones and combinational tones.[1] For the simple hydrogen atom, for instance, (14) gives for the fundamental frequency as calculated on the classical theory

$$\omega = \frac{4\pi^2\mu e^4}{J^3}, \tag{16}$$

where J has been written for the sum of the two phase integrals J_ϕ and J_r. On the quantum theory the frequency emitted during a transition in which the quantum number changes by s units is

$$\begin{aligned} \nu &= \frac{E'-E''}{h} \\ &= \frac{2\pi^2\mu e^4}{h}\left[\frac{1}{J^2} - \frac{1}{(J+\Delta J)^2}\right] \\ &= \frac{4\pi^2\mu e^4}{J^3}\, s \left[\frac{1+\frac{\Delta J}{J}}{\left(1+\frac{\Delta J}{J}\right)^2}\right] \end{aligned} \tag{17}$$

[1] The quantum frequencies may also be regarded as mean values of the corresponding classical frequencies averaged over a continuous series of unquantized motions permitted by the classical theory and intermediate between the initial and final stationary states. (*Cf.* "Quantum Principles and Line Spectra," J. H. Van Vleck, Bull. Nat. Research Council 54: 28 (1925). Thus, if we treat the energy as a function of the J's, we may calculate the quantum frequency by means of a line integral in a space in which the J's are laid out as Cartesian coordinates.

$$\nu = \frac{E'-E''}{h} = \frac{1}{h}\int_{J''_i}^{J'_i} dE.$$

The path of integration is arbitrary. Introducing the classical frequencies, we have

$$\nu = \frac{1}{h}\int_{J''_i}^{J'_i} \sum_i \frac{\partial E}{\partial J_i}\, dJ_i = \frac{1}{h}\sum_i \int_{J''_i}^{J'_i} \omega_i dJ_i = \overline{\Sigma \tau_i \omega_i}$$

where τ_i is the integer $\frac{1}{h}(J'_i - J''_i)$ and the bar denotes a mean value defined by

$$\overline{\omega_i} = \frac{1}{J'_i - J''_i}\int_{J''_i}^{J'_i} \omega_i dJ_i.$$

This result is conveniently referred to as the "mean frequency theorem."

Consider now a one quantum leap. In this case s is unity, and comparison of (17) and (16) shows that the fundamental calculated on the quantum theory approaches asymptotically the fundamental given by the classical theory as J becomes very large. In the same way the quantum overtones approach the classical overtones. Now Bohr assumes that for large quantum numbers the quantum theory must yield statistical results in all cases identical with those obtained from the classical theory. Hence the k^{th} quantum overtone can occur only if the k^{th} overtone is present in the classically determined motion. Thus a transition in which J_i changes by sh is possible only if the harmonic of frequency $s\omega_i$ is present in the classically determined motion. Similarly, the combinational tone in which simultaneously J_i changes by s_1h, J_2 by s_2h, . . . J_f by s_fh, can arise only if the frequency $s_1\omega_1+s_2\omega_2$ . . . $+s_f\omega_f$ is present in the Fourier analysis of the motion as determined on the basis of the classical laws. Now these conditions governing the possibility of a transition, which must be true for the case of large quantum numbers if the quantum theory is to agree statistically with the classical theory, are assumed to be valid as well in connection with transitions in which small quantum numbers are involved. Furthermore, the asymptotic approach to the classical theory for high quantum numbers is assumed to hold for the amplitude and phase of the electric vector as well as for its frequency. Thus in addition to a selection principle determining the permissible changes in quantum number during a transition, it is possible to formulate a rule for determining the polarization of the radiation emitted and to obtain an estimate of the probability of a transition and therefore of the intensity of the light emitted.

Although the correspondence between the frequencies calculated on the quantum theory and those calculated on the classical theory is very striking, emphasis must be laid on the difference in the manner in which waves of these frequencies are radiated. On the classical theory *all* the frequencies involved in the motion of the system appear in the emitted radiations, the overtones as well as the combinational tones being radiated at the same time as the fundamentals. On the quantum theory, on the other hand, the entire energy is emitted in the form of monochromatic waves. A fundamental, *or* one of the overtones, *or* one of the combinational tones may be radiated, but not more than one during a single transition.

In order to understand the significance of the correspondence principle in detail, it is necessary to consider the expression for the electric moment of the atom or molecule expressed as a Fourier series. Evidently the fundamental frequencies involved are the same as those coming into the

expansions of the q's, so that the X component of the electric moment takes the form

$$P_x = \sum_s D_{s_1 s_2 \ldots s_f} e^{2\pi i (s_1\omega_1 + s_2\omega_2 \ldots + s_f\omega_f)t} \tag{18}$$

with similar expressions for the Y and Z components. On electromagnetic theory the amplitude of the X component E_x of the electric vector in the train of waves emitted is proportional to the second derivative of P_x with respect to the time. Denote this second derivative of the electric moment by Q. Then Q_x will differ from P_x only in that each coefficient $G_{s_1 s_2 \ldots s_f}$ will be greater than the corresponding coefficient $D_{s_1 s_2 \ldots s_f}$ in P_x by the factor

$$-4\pi^2 (s_1\omega_1 + s_2\omega_2 \ldots + s_f\omega_f)^2.$$

Now consider the transition in which on the quantum theory, J_1 changes by $s_1 h$, J_2 by $s_2 h$, . . . J_f by $s_f h$. Let $G'_{s_1 s_2 \ldots s_f}$ be the coefficient in the expansion of Q_x of the term of frequency $s_1\omega_1 + s_2\omega_2 \ldots + s_f\omega_f$ for the motion in the initial stationary state, and $G''_{s_1 s_2 \ldots s_f}$ the corresponding coefficient for the motion in the final stationary state. Then the correspondence principle may be interpreted to mean that the amplitude of E_x in the emitted radiation depends upon the average $\bar{G}_{s_1 s_2 \ldots s_f}$ of $G'_{s_1 s_2 \ldots s_f}$, $G''_{s_1 s_2 \ldots s_f}$ and of the values of G for classically permissible intermediate states. Just what average is to be taken is somewhat uncertain, but in the important case where $G'_{s_1 s_2 \ldots s_f}$, $G''_{s_1 s_2 \ldots s_f}$ and intermediate values are zero, it is not necessary to define exactly the process of averaging, for $\bar{G}_{s_1 s_2 \ldots s_f}$ vanishes whatever this process may be. Now the energy emitted by a single particle during the transition under consideration is quite definitely [4] the difference between the energies of the initial and final stationary states. Hence $\bar{G}_{s_1 s_2 \ldots s_f}$ measures the probability of the spontaneous occurrence of the assumed transition. Therefore, if $\bar{G}_{s_1 s_2 \ldots s_f}$ vanishes, the transition is interdicted.

The correspondence principle, therefore, furnishes a method of calculating the probabilities of the transitions allowed by the fundamental postulates in such a way as to make the quantum theory agree statistically with the classical theory for large quantum numbers. Then by a process of extrapolation an estimate is obtained of the probability of a transition even for the case of motions with which small quantum numbers are associated. Furthermore, as the polarization of the emitted radiation must agree with that predicted by the classical theory for large quantum numbers, the process of extrapolation employed indicates how the radiation should be polarized in the case of small quantum numbers.

[4] See, however, (2).

The correspondence principle will be illustrated by applying it to the simple hydrogen atom. If the initial and final orbits are circular and lie in the XY plane,

$$P_x = ae \cos 2\pi\omega t,$$
$$P_y = ae \sin 2\pi\omega t.$$

As s has only the value unity in the Fourier expansion, one quantum transitions alone are allowed, and give rise to circularly polarized waves advancing in the direction perpendicular to the plane of the orbit, and to plane polarized waves with the electric vector parallel to the plane of the orbit advancing in directions parallel to this plane.

If, however, either the initial or the final orbit is elliptical, then, if the major axis is taken in the X direction,

$$P_x = ae[\tfrac{3}{2}\epsilon + \cos 2\pi\omega t - \tfrac{1}{2}\epsilon \cos 4\pi\omega t + \ . \ . \ .],$$
$$P_y = ae[\sin 2\pi\omega t - \tfrac{1}{2}\epsilon \sin 4\pi\omega t + \ . \ . \ .],$$

and the presence of terms with all values of s indicates the possibility of transitions in which the quantum number changes by any integer. Whatever the transition may be, waves advancing in directions parallel to the plane of the orbit will be polarized with the electric vector parallel to this plane. The absence of a component of the electric moment in the Z direction precludes the possibility of radiation in which the electric vector is perpendicular to the plane of the orbit.

The most important application of the correspondence principle is to the case of a cyclic coordinate ϕ measuring an azimuth. It has already been noted that in the case of such a coordinate

$$\frac{\partial S}{\partial \phi} = p_\phi = \frac{J_\phi}{2\pi},$$

and therefore the action S has the form

$$S = \frac{1}{2\pi} J_\phi \phi + s(q_2 \ . \ . \ . \ q_f, J_\phi, J_2 \ . \ . \ . \ J_f),$$

where the second term on the right is not a function of $q_1 = \phi$.

Hence,

$$w_j = \frac{\partial S}{\partial J_j} = \frac{\partial s}{\partial J_j}, \qquad j = 2, 3, \ . \ . \ . \ f,$$
$$w_\phi = \frac{\partial S}{\partial J_\phi} = \frac{\phi}{2\pi} + \frac{\partial s}{\partial J_\phi}.$$

The first of these equations represents $f-1$ relations between $q_2 \ . \ . \ . \ q_f$ and $w_2 \ . \ . \ . \ w_f$. Solving them for the q's, it is seen that each q_j may be represented as a function of $w_2 \ . \ . \ . \ w_f$ and the constants $J_\phi, J_2 \ . \ . \ . \ J_f$, the variable w_ϕ being absent from these functions. Substituting these

functions for the q's appearing in the second term on the right of the second equation and solving this equation for ϕ,

$$\phi = 2\pi w_\phi + \psi(w_2 \ldots w_f, J_\phi, J_2 \ldots J_f). \tag{19}$$

Let the XY plane be that in which the azimuth ϕ of the system is measured, the origin coinciding with the center of mass of the system. Take a set of rectangular coordinates X', Y', Z' which are rotating around the Z axis at the same rate as that at which ϕ is increasing. Then the coordinates x', y', z' of each particle are functions of $q_2 \ldots q_f$ only, that is, their Fourier expansions involve the angle variables $w_2 \ldots w_f$ alone. Hence, the coordinates of the k^{th} particle are given by

$$x'_k + iy'_k = \sum_s A_{s_2 \ldots s_f} e^{2\pi i(s_2 w_2 \ldots + s_f w_f)},$$
$$z'_k = \sum_s B_{s_2 \ldots s_f} e^{2\pi i(s_2 w_2 \ldots + s_f w_f)},$$

and

$$x_k + iy_k = e^{i\phi} \sum A_{s_2 \ldots s_f} e^{2\pi i(s_2 w_2 \ldots + s_f w_f)},$$
$$z_k = \sum_s B_{s_2 \ldots s_f} e^{2\pi i(s_2 w_2 \ldots + s_f w_f)}.$$

The components of the electric moment of the system are obtained by multiplying the rectangular coordinates of each particle by the charge on that particle and summing up over the particles. If now ϕ is replaced by the right hand member of (19), and each w is replaced by $\omega t + \delta$, the components of the electric moment are seen to be

$$P_x + iP_y = e^{2\pi i \omega_\phi t} \sum_s D_{s_2 \ldots s_f} e^{2\pi i(s_2 \omega_2 \ldots + s_f \omega_f)t}, \tag{20}$$
$$P_z = \sum_s E_{s_2 \ldots s_f} e^{2\pi i(s_2 \omega_2 \ldots + s_f \omega_f)t}.$$

As ω_ϕ appears in P_x and P_y only with the coefficient unity, and in P_z only with the coefficient zero, the azimuthal quantum number can change only by one or zero. If the radiation emitted in a direction parallel to the XY plane is under consideration, a change of the azimuthal quantum number by one will give rise to plane polarized waves with the electric vector perpendicular to the Z axis, while a zero change in azimuthal quanta will result in plane polarized waves in which the electric vector is parallel to the Z axis. If all the charged particles move in a single plane, P_z is zero, and consequently a zero change in the azimuthal quantum number is interdicted.

In applying the above principle to systems made up of several particles, ϕ may be identified with the azimuth of any particle measured in a plane perpendicular to the resultant angular momentum. (See Born, Atommechanik, §17, Chapter 2.) The correlated and quantized angular momentum p_ϕ is then the total angular momentum of the system and not

the angular momentum of the individual particle whose azimuth is ϕ. In dealing with diatomic molecules the azimuth of the internuclear axis is usually identified with ϕ. If the electronic angular momentum is zero, the total angular momentum p_ϕ is the same as the nuclear angular momentum and the latter is quantized. The corresponding quantum number is designated as m and is subject to the principle of selection

$$m \begin{cases} \nearrow m+1 \\ \longrightarrow m \\ \searrow m-1 \end{cases}$$

On the other hand, if the electronic angular momentum is not zero, the nuclear angular momentum is not quantized though its value in units $\frac{h}{2\pi}$ is still frequently indicated by the symbol m. In this case the quantum number associated with the total angular momentum (sometimes called the true rotational quantum number) is in this report designated by the symbol j and is subject to the principle of selection

$$j \begin{cases} \nearrow j+1 \\ \longrightarrow j \\ \searrow j-1 \end{cases}$$

In this chapter the electronic angular momentum is assumed to vanish so that the symbol j need not be introduced.

SECTION 4. THE DUMB-BELL MOLECULE

The simplest type of periodic motion which a system consisting of two point masses may possess is a rotation about an axis through their center of mass and at right angles to the line joining them. If I is the moment of inertia of such a system and Ω its constant angular velocity, the angular momentum G is

$$G = I\Omega,$$

and if ϕ is the azimuth of the line joining the two masses, the phase integral becomes

$$J = \oint G d\phi = 2\pi I\Omega.$$

Therefore the kinetic energy T of the system is

$$T = \tfrac{1}{2} I\Omega^2 = \frac{J^2}{8\pi^2 I}. \tag{21}$$

In a stationary state the phase integral is equal to mh and hence the kinetic energy of the m^{th} state is

$$T = \frac{h^2}{8\pi^2 I} m^2. \tag{22}$$

The following two cases may arise:

(1) The moment of inertia I may depend upon the angular velocity, as in the case of an electron moving in a circular orbit around the nucleus of a hydrogen atom. For the m^{th} quantum orbit

$$I_m = \mu a_m^2 = \mu a_1^2 m^4,$$

where a_m is the radius of the m^{th} orbit and μ the mass of the electron. This gives for the kinetic energy from (22)

$$T = \frac{h^2}{8\pi^2 \mu a_1^2} \frac{1}{m^2} = \frac{2\pi^2 \mu e^4}{h^2} \frac{1}{m^2},$$

which has the form of a Balmer term in the formula for the line series of hydrogen.

(2) The moment of inertia may be constant, or nearly so, whatever the angular velocity may be. In this case (22) gives ([9])

$$T = \frac{h^2}{8\pi^2 I} m^2. \tag{23}$$

Consider, now, a polar molecule consisting of two rigidly connected atoms with an electric moment of constant magnitude. Such a system has a constant moment of inertia, and therefore its kinetic energy in the m^{th} stationary state is given by (23). As the moment of inertia is the same for all values of m, a transition from one stationary state to another involves no change in the potential energy of the system, and consequently the only energy to be considered is the kinetic energy T. Hence

$$E_m = \frac{h^2}{8\pi^2 I} m^2 = Bhm^2. \tag{24}$$

Applying the second postulate of the Bohr theory,

$$\nu = B(m'^2 - m''^2)$$

gives the frequency of the radiation emitted during a transition from the m'^{th} to the m''^{th} state, or absorbed during a transition in the reverse direction. Now, as ϕ is a cyclic coordinate, m can change by one unit only, a conclusion which can be reached directly in this simple case from a consideration of the components of the electric moment P of the molecule. For if the rotation is about the Z axis

$$\begin{aligned} P_x &= P \cos 2\pi(\omega t + \delta), \\ P_y &= P \sin 2\pi(\omega t + \delta), \\ P_z &= 0, \end{aligned}$$

and as the fundamental frequency ω appears in the Fourier expansions for the components of P only in the term in which s is unity, the quantum

number m can change during a transition by one only. Moreover, as ν must be positive m' must be greater than m''; therefore

$$m' = m'' + 1,$$

giving [5]

$$\nu = B(2m+1). \tag{25}$$

The spectrum described by this formula consists of evenly spaced lines and is known as a pure rotation spectrum. It can exist, however, only in connection with polar molecules. For if the atoms of which the molecule is constituted are electrically neutral, the electric moment of the system vanishes, and hence the emission or absorption of electromagnetic radiation is prohibited by the correspondence principle.

The frequency interval between successive lines is constant and equal to

$$\Delta\nu = 2B = \frac{h}{4\pi^2 I}. \tag{26}$$

From measurements of this interval the moment of inertia I of the molecule may be calculated.

The rotation spectrum affords an especially simple illustration of the asymptotic approach of the quantum frequency to the classical frequency as the quantum number increases in value. As no overtones or combinational tones are involved, only fundamental frequencies need be considered. Referring to the table on page 33, it is seen that

$$\omega = \frac{\partial E}{\partial J}$$

on the classical theory; and that

$$\nu = \frac{\Delta E}{\Delta J}$$

on the quantum theory. On Figure 1 the energy E is plotted against the phase integral J according to equation (21), and the stationary states are indicated by dots on the curve. On the classical theory, the frequency of the radiation emitted is given by the slope of the tangent to the curve. Thus, if a transition from state 2 to state 1 should occur, the frequency of the electromagnetic waves emitted by a polar molecule would be expected to decrease gradually from the value of the slope of the tangent at point 2 to the slope of the tangent at point 1. This would result in radiation covering a considerable range of frequencies. The quantum theory, on the other hand, puts the frequency equal to the

[5] The primes are dropped in formulas involving only the quantum numbers referring to a single state. The m in the formula is the same as the m'' used above.

slope of the chord joining the two points, or, in this case, to the slope of the tangent at the point on the curve where J has a value midway between its two extreme values. It is evident from the figure that as J increases, the curve straightens out and ultimately becomes indistinguishable from the broken line made up of the chords joining the points representing successive stationary states. Hence the classical and quantum frequencies become identical for very large values of the phase integral.

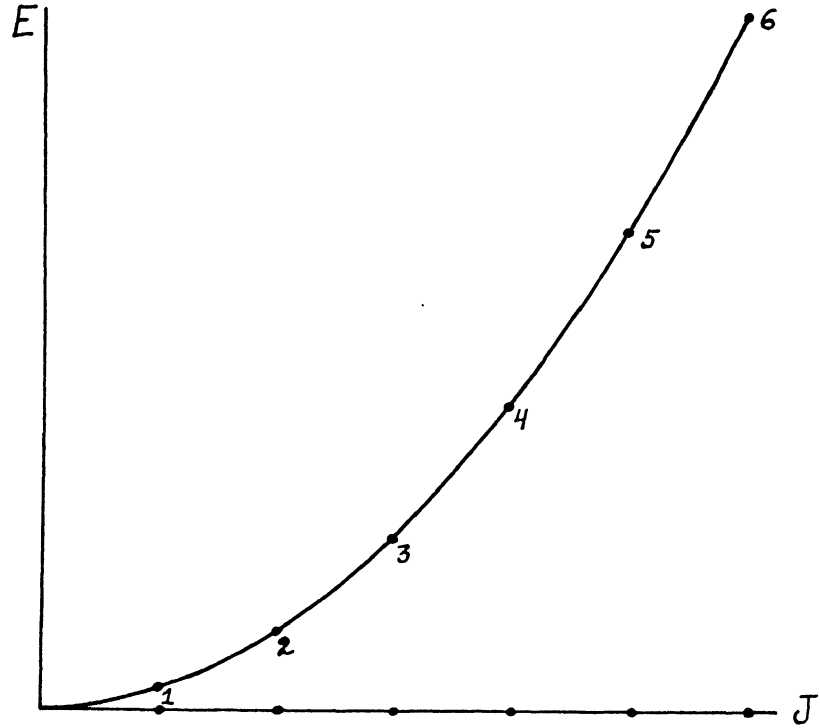


FIGURE 1.

SECTION 5. THE ANHARMONIC OSCILLATOR

The molecular radiation considered in the preceding section arises from a change in the energy of rotation of two rigidly connected atoms. It is to be expected, however, that the atoms in a diatomic molecule should be able to execute oscillations along the line joining them at the same time as they partake in the motion of rotation of the molecule. In this section such oscillations will be discussed on the assumption that they exist alone, unaccompanied by motion of rotation.

If the oscillation is simple harmonic, the electric moment varies with the time according to the equation

$$P_r = P \cos 2\pi(\omega t + \delta),$$

and the correspondence principle permits the associated quantum number to change by only a single unit during a transition. As the phase integral is

$$J = \oint p_r dr = 2\pi^2 \mu A^2 \omega,$$

where A is the amplitude of the vibration and $1/\mu$ the sum of the reciprocals of the masses of the two vibrating particles, the energy of the motion is

$$E = \pi \sqrt{k\mu} A^2 \omega = \frac{J}{2\pi} \sqrt{k/\mu},$$

where k is the coefficient of the force of restitution. In this case E is a linear function of J, and hence

$$\frac{\Delta E}{\Delta J} = \frac{\partial E}{\partial J} = \frac{1}{2\pi} \sqrt{k/\mu}. \tag{27}$$

Therefore, the fundamental frequency of the radiation emitted is the same on the quantum theory as on the classical theory, and as only one quantum transitions are permitted, no overtones can be present. Thus the frequency of the radiation which the simple harmonic Planck oscillator is capable of emitting or absorbing coincides with its frequency of vibration.

In many molecular spectra, however, overtones of the fundamental frequency are observed. Therefore the electric moment of the molecule must contain terms involving harmonics of the fundamental frequency. This means that the vibrations of the constituent atoms are not strictly simple harmonic, and therefore the forces of restitution are not accurately proportional to the displacements of the atoms from their positions of equilibrium. In the following preliminary discussion of the anharmonic oscillator, the molecule will be supposed to have no motion of rotation.

If r is the distance between the two atoms, the mutual potential energy V may be assumed to have the form

$$V = -\frac{e^2}{r}\left(1 + \frac{c_1}{r} + \frac{c_2}{r^2} + \frac{c_3}{r^3} \cdots\right), \tag{28}$$

where the terms involving c_1, c_2, c_3 . . . are due to the structure of the ions. Let r_0 be the equilibrium distance between the ions. Equating the gradient of V to zero for this value of r, a relation is obtained which may be used to eliminate the coefficient c_1 from (28). Finally, if ρ is used for the ratio of r to r_0 and ξ for the small quantity $\rho - 1$, and if c_2 and c_3

are assumed to be small, the expression for the potential energy may be put in the form [6]

$$V=-a\left(a+\frac{1}{\rho}-\frac{1}{2\rho^2}+b\xi^3+c\xi^4\ \ldots\right), \tag{29}$$

giving for the force of restitution

$$\begin{aligned}-\frac{\partial V}{\partial r}&=\frac{a}{r_0}\left(-\frac{1}{\rho^3}\xi+3b\xi^2+4c\xi^3\ \ldots\right)\\&\doteq-\frac{a}{r_0^2}(r-r_0).\end{aligned} \tag{30}$$

Hence if ω_0 is the natural frequency for very small amplitudes, the constant a has the meaning

$$\begin{aligned}a&=4\pi^2\omega_0^2\mu r_0^2\\&=4\pi^2\omega_0^2 I_0,\end{aligned} \tag{31}$$

as μr_0^2 is the moment of inertia I_0 of the molecule when there are no oscillations along the line joining the two atoms.

Now the kinetic energy of the vibration is

$$T=\frac{\mu}{2}\dot{r}^2=\frac{I_0}{2}\dot{\rho}^2$$

and therefore the momentum conjugate to ρ is

$$p_\rho=\frac{\partial T}{\partial\dot{\rho}}=I_0\dot{\rho}.$$

The Hamilton-Jacobi equation, then, is

$$\frac{1}{2I_0}\left(\frac{\partial S}{\partial\rho}\right)^2+V=E, \tag{32}$$

or

$$\frac{\partial S}{\partial\rho}=\sqrt{2I_0(E-V)},$$

and the phase integral [7] is

$$\begin{aligned}J&=\oint\frac{\partial S}{\partial\rho}\,d\rho\\&=\int\sqrt{2I_0(E-V)}\,d\rho.\end{aligned} \tag{33}$$

[6] The details of the following analysis may be found in Appendix 15, p. 833, of Sommerfeld's book on Atomic Structure and Spectral Lines (4th German edition).

[7] For an alternative procedure for evaluating (33) see E. C. Kemble, Proc. Nat. Acad. Sci., 7: 283 (1925).

Substituting the value of V given by (29), expanding by the binomial theorem in powers of the small quantity ξ, integrating and solving for E, it is found that[8]

$$E+a(a+\tfrac{1}{2})=J\omega_0-\frac{J^2}{4\pi^2 I_0}(\tfrac{3}{2}+\tfrac{15}{2}b+\tfrac{3}{2}c+\tfrac{15}{4}b^2)\ \ldots \qquad (34)$$

So far as the calculation of frequencies is concerned, only the difference in the energies of two stationary states is of import. Therefore the constant $a(a+\frac{1}{2})$ may be discarded, and the energy of the n^{th} stationary state is obtained by putting nh for J, giving

$$E^n=nh\omega_0(1-xn\ \ldots) \qquad (35)$$

where

$$x=\frac{h}{4\pi^2 I_0\omega_0}(\tfrac{3}{2}+\tfrac{15}{2}b+\tfrac{3}{2}c+\tfrac{15}{4}b^2).$$

The frequency of the radiation emitted or absorbed is obtained from the second Bohr postulate. If, for instance, the transitions are from states in which n has the values 1, 2, 3, etc., to a final state in which n is zero, the corresponding frequencies are

$$\omega_0(1-x), \qquad 2\omega_0(1-2x), \qquad 3\omega_0(1-3x), \text{ etc.},$$

representing the band centers in a system of bands. In the sense in which the term is used in the quantum theory, the second, third, etc., of these frequencies are overtones of the first, even though they are not integral multiples of the same. In fact, it is seen that the frequency interval between successive band centers decreases as the frequency increases.

SECTION 6 ROTATION-VIBRATION SPECTRA

In the preceding section the energy of a stationary state of a diatomic molecule was calculated on the assumption that the motion consists simply of anharmonic vibrations of the atoms along the line joining them. More generally the molecule would be expected to be in rotation about an axis through its center of mass at the same time that the atoms are executing these oscillations, a transition involving a change in the energy of rotation as well as in the energy of vibration. In this more general case a term due to the interaction between rotation and oscillation appears in the expression for the energy of the stationary state in addition to the expressions E_m given in (24) for the energy of rotation

[8] Sommerfeld seems to have a mistake in sign of the term in b^2 in the following expression.

alone and E^n in (35) for the energy of oscillation alone. For the Hamilton-Jacobi equation (32) becomes([5])

$$\frac{1}{2I_0}\left\{\left(\frac{\partial S}{\partial \rho}\right)^2+\frac{1}{\rho^2}\left(\frac{\partial S}{\partial \phi}\right)^2\right\}+V=E, \tag{36}$$

and, as V is a function of ρ only, the variables are separated if we write

$$\left(\frac{\partial S}{\partial \phi}\right)^2=-\rho^2\left\{\left(\frac{\partial S}{\partial \rho}\right)^2+2I_0V-2I_0E\right\}.$$

Putting each side equal to the constant p^2, the two phase integrals are seen to be

$$J_\phi=\oint p d\phi,$$

$$J_\rho=\oint \sqrt{2I_0E-2I_0V-\frac{p^2}{\rho^2}}\, d\rho.$$

Substituting the value of V given by (29), integrating, eliminating p and solving for E, and discarding the additive constant $a(a+\frac{1}{2})$, it is found that

$$E=I_\rho\omega_0\left(1-x\frac{J_\rho}{h}\right)+\frac{J_\phi^2}{8\pi^2I_0}-yJ^2{}_\phi J_\rho\ldots,$$

where the constant x has the same meaning as in the last section, and

$$y=\frac{3}{32\pi^4I_0{}^2\omega_0}(1+2b).$$

The energy of the stationary state characterized by m quanta of angular momentum and n quanta of vibrational momentum is obtained by putting mh for J_ϕ and nh for J_ρ. It may conveniently be written in the form:

$$E^n{}_m=nh\omega_0(1-xn)+B_0hm^2-a_nhm^2, \tag{37}$$

where

$$B_0=\frac{h}{8\pi^2I_0},$$

$$a_n=nh^2y$$

$$=an.$$

As ϕ is a cyclic coordinate, m can change during a transition by only one or zero, and the latter only in case the molecule has an electric moment at right angles to the plane of rotation. As ω_0 generally predominates over B_0, an increase in n during emission would lead to a negative value of the frequency, and is therefore excluded. Provided n decreases, however, m may either increase or decrease by unity without resulting in an increase in energy of the system.

Suppose the transition accompanying emission of radiation is from a state of energy E' to one of energy E''. Then the frequency calculated from (37) on the basis of the second postulate of the Bohr theory contains a term ν_n involving n' and n'' alone, which arises from the decrease in energy of the oscillatory motion. In addition there is a term containing m' and m'' which arises from the change in energy of the rotation, and finally a term involving both the n's and m's due to the change in the mutual energy of the two types of motion. Hence (37) leads to the expression

$$\nu=\nu_n+B_0(m'^2-m''^2)-(a'_n m'^2-a''_n m''^2) \tag{38}$$

for the frequency of the radiation emitted when the transition is from E' to E'', or absorbed when the transition is in the reverse direction.

If the molecule has no electric moment perpendicular to the plane of rotation, a transition in which m remains unchanged is excluded, and

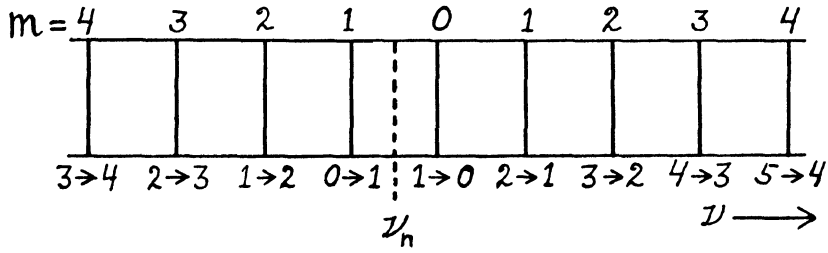


FIGURE 2.

hence either $m'=m''+1$ or $m'=m''-1$. As a first approximation a_n may be neglected as compared to B_0. Then if the energy of rotation decreases during the transition, the frequency of the emitted radiation is

$$\nu=\nu_n+B_0(2m+1) \tag{39}$$

where m has been put for m''. The series of lines obtained by giving positive integral values to m constitutes the positive (R) branch of the band. If, however, the energy of rotation increases as a result of the transition,

$$\nu=\nu_n+B_0(-2m+1), \tag{40}$$

constituting the negative (P) branch. For absorption, the transition, in each case, is in the reverse direction to that for emission.

The two branches merge into one another, as is shown in the diagram, the negative branch lying to the left of the center of the figure and the positive branch to the right. The line obtained by putting m equal to zero in (39), may be called the *zero line* of the series. The nuclear vibration frequency ν_n which determines the *origin*, does not coincide

with it, but lies half way between it and the first line of the negative branch. The frequency interval between adjacent lines is constant and the same as in the case of the single branch of the pure rotation spectrum.

If, now, the mutual term containing a_n is taken into account, the general form of the series of lines remains unaltered, but the frequency interval decreases in the direction of increasing frequency. For, as a'_n is greater than a''_n,

$$\nu = \nu_n + (B_0 - a'_n)(2m+1) - (a'_n - a''_n)m^2 \qquad (41)$$

for the positive branch, giving for the frequency interval between the k^{th} and $k+1^{th}$ line

$$\Delta\nu = 2(B_0 - a'_n) - (a'_n - a''_n)(2k+1),$$

and for the negative branch

$$\nu = \nu_n + (B_0 - a'_n)(-2m+1) - (a'_n - a''_n)m^2,$$

and

$$\Delta\nu = 2(B_0 - a'_n) + (a'_n - a''_n)(2k+1).$$

It may be noted that (41) may be used to represent the negative branch as well as the positive branch by substituting negative integers for m. Thus the two branches may be described by a single formula.

Rotation-vibration spectra of the type described (except for the absence of a line near the center) are observed in the near infra-red, and the closing together of the lines in passing from the long wave-length side of the band to the short wave-length side is in good accord with the theory.

While the theory just described gives a satisfactory account of the principal facts of the infra-red rotation-vibration bands of diatomic molecules, a close study of the empirical facts in connection with these bands and also in connection with the electronic bands discussed in the next section has made one important modification necessary. From the experimental standpoint this modification may be said to consist in the substitution of $j-\epsilon$ for m in energy formulas such as (37) where ϵ is a constant for each electronic energy level of the molecule, frequently approximately equal to one-half, and j is an integer. The simplest theoretical interpretation of this change in the energy formulas identifies ϵ with an assumed electronic angular momentum parallel to the nuclear angular momentum and j with the total angular momentum of the molecule (both in units $h/2\pi$). It may be shown theoretically that this change is in harmony with the fundamental principles stated at the beginning of this chapter provided that an electronic angular momentum $\epsilon h/2\pi$ perpendicular to the nuclear axis actually exists. We have reason to believe, however, from the study of line spectra and of the complex

Zeeman effect that the total angular momentum may have the series of values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ times $h/2\pi$ instead of the series of integral multiples of $h/2\pi$ usually assumed. This interpretation of the empirical facts involves a modification of postulate 1*b*, but since the differences between the values of the quantum number for total angular momentum are still integers the correspondence principle is unaffected.

SECTION 7. ELECTRONIC BANDS

In the pure rotation spectra, the motion of the molecule consists solely of a rotation about an axis through the center of mass. In the rotation-vibration spectra, this rotation is accompanied by a vibration of the two ions along the line joining them. To account for the ordinary bands of the visible and ultra-violet, it is necessary to assume that a change in the electronic configuration of the atoms accompanies the changes in the motions of rotation and vibration which occur during a transition. In fact, in the case of a non-polar molecule, an electric moment exists only by virtue of this electronic configuration, and therefore the correspondence principle requires it to change during a transition.

An alteration in electronic configuration will change the forces holding the atoms together and therefore change the equilibrium distance between them. Hence it is no longer legitimate to assume the moment of inertia I_0 in the final and initial states to be the same. Let the term in the frequency of the emitted radiation due to the change in energy of the electronic configuration be denoted by ν_e. Then if we neglect the mutual energy of rotation and oscillation([6]),

$$\nu = \nu_e + \nu_n + \frac{hm'^2}{8\pi^2 I'_0} - \frac{hm''^2}{8\pi^2 I''_0}. \tag{42}$$

For the positive (R) branch, if the electronic angular momentum vanishes, $m' = m'' + 1$, and hence

$$\nu = A_1 + 2B_0 m + Cm^2, \tag{43}$$

where m is put for m'' and

$$A_1 \equiv \nu_e + \nu_n + \frac{h}{8\pi^2 I'_0},$$

$$B_0 \equiv \frac{h}{8\pi^2 I'_0},$$

$$C \equiv \frac{h}{8\pi^2}\left(\frac{1}{I'_0} - \frac{1}{I''_0}\right),$$

from which it is evident that C is generally small compared to B_0. C may be either positive or negative.

The negative (P) branch, due to transitions in which the energy of rotation increases, is obtained by putting $m'=m''-1$, giving

$$\nu=A_1-2B_0m+Cm^2. \tag{44}$$

The molecule may, however, have an electric moment at right angles to the plane of rotation. Hence m may remain unaltered during a transition. This gives rise to the zero (Q) branch

$$\nu=A_0+Cm^2, \tag{45}$$

where

$$A_0\equiv\nu_e+\nu_n.$$

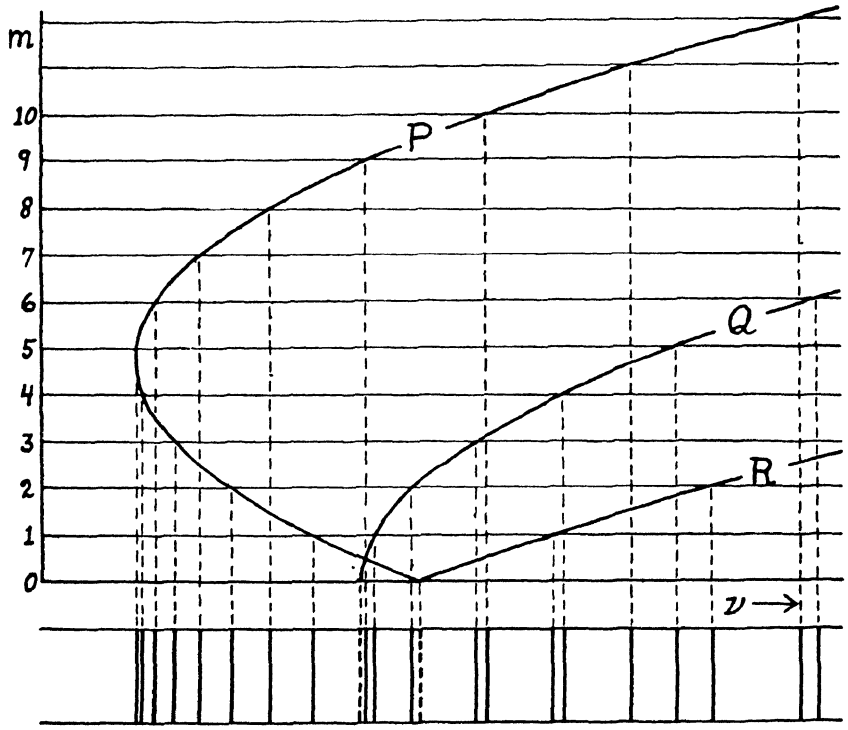


FIGURE 3.

Equations (43), (44) and (45) are parabolas in m. On the accompanying diagram ν is plotted against m for the three branches([4]), the points for which m is an integer being projected to the diagrammatic spectrum in the lower part of the figure. The zero branch meets the axis of abscissas at the frequency $\nu_e+\nu_n$, while the point of intersection of the other two branches lies at a distance $h/8\pi^2I'_0$ to the right of this frequency.

The head of the band is the line nearest to the vertex of the parabola representing the negative branch in the case where C is positive. Putting the derivative of (44) equal to zero, the value of m corresponding to the head of the band is seen to be the whole number nearest to B_0/C.

The theory shows that the significant line in the band is not the line at the head, but the origin $A_0=\nu_e+\nu_n$ at the point when the zero branch meets the axis. In a system of bands, ν_e may be supposed to remain constant while ν_n changes. If the quantum number associated with the vibratory motion changes from n' to n'', reference to (35) shows that

$$A_0=\nu_e+n'\omega'_0(1-x'n')-n''\omega''_0(1-x''n''), \qquad (46)$$

where the natural frequency ω_0 of small oscillations has to be assumed different in the final and initial states on account of the change in electronic configuration. This is Deslandre's law of the band edges, although the present theory applies it not to the head of the band but to the origin.

If, now, $n'-n''$ is a constant, a sequence of bands is obtained lying close together. For instance, when $n'-n''=0$, the transitions

$$0\rightarrow 0,\ 1\rightarrow 1,\ 2\rightarrow 2,\ 3\rightarrow 3,\ 4\rightarrow 4,$$

each gives rise to one of a sequence of bands. The transitions

$$1\rightarrow 0,\ 2\rightarrow 1,\ 3\rightarrow 2,\ 4\rightarrow 3,\ 5\rightarrow 4,$$

likewise give rise to a second sequence. These sequences are well illustrated in the case of the cyanogen bands. (*Cf.* Figure 3, Chapter IV.) In view of the fact that ν_e is large compared to ω_0, n may increase as well as decrease during a transition resulting in emission of radiation.

BIBLIOGRAPHY

[1] Adams, Bull. Nat. Research Council, 39: 14 (1923).

[2] Bohr, Kramers and Slater, Phil. Mag., 47: 785 (1924).

[3] Foote and Mohler, "The Origin of Spectra," Chapter III. New York, Chemical Catalog Co., 1922.

[4] Fortrat, These, Paris, 1914, p. 109.

[5] Kratzer, Z. Physik, 3: 289 (1920).

[6] Lenz, Verh. deut. physik. Ges., 21: 632 (1919).

[7] Nordstrom, Proc. Acad. Sci. Amsterdam, 22: 145 (1920).

[8] Page, Phys. Rev., N. S., 24: 296 (1924).

[9] Schwarzschild, Sitzb. preuss. Akad. Wiss., 1916, p. 548.

CHAPTER III

INFRA-RED ABSORPTION BANDS

WALTER F. COLBY

The greatest ultimate detail and precision of measurement in infra-red bands has been attained in the case of the hydrogen halides in the vicinity of 3μ. The measurement of the strong band due to HCl at 3.4μ (Figure 1) has had a fairly long history and has led toward a general interpretation of absorption of this character. The history of this early work both in experiment and theory has been outlined in the introductory chapter.

In spite of the fact that these bands are due to an increase both of rotational and vibrational energy, they are in their main characteristics much more simple than most other bands. This is due partly to the fact that the molecule is diatomic. The nuclear vibration occurs along the line of nuclei and may be thought of in first approximation as simple harmonic. In regard to rotation the molecule has very restricted possibilities. If the moment of inertia about the line of nuclei is very small and if electronic angular momentum, at least about this axis, is excluded, then for moderate energy the rotation will be restricted to an axis normal to the line of nuclei. This restriction was assumed in the early work and later work has justified the assumption, at least for the hydrogen halides.

The main features of interest in the quantization of this motion have been described in Chapter II. It was there pointed out that with the help of the correspondence principle, one may prophesy permitted transitions from an analysis of the motion. If in this case the vibration had a component along the axis of rotation, we should expect a possible increase of vibration quantum number unaccompanied by a change in rotation quantum number. Such a transition should give rise to a so-called zero, or Q branch, of the band.

Figure 1 indicates the characteristic arrangement of lines in the hydrogen halide bands. Aside from the convergence on the short wave length side due to coupling, the two parts of the band at either side of the missing center are quite symmetrical. It was stated in Chapter II that these two parts are identified as the positive and negative, or R and P, branches of the band; that is, they consist (in absorption) of

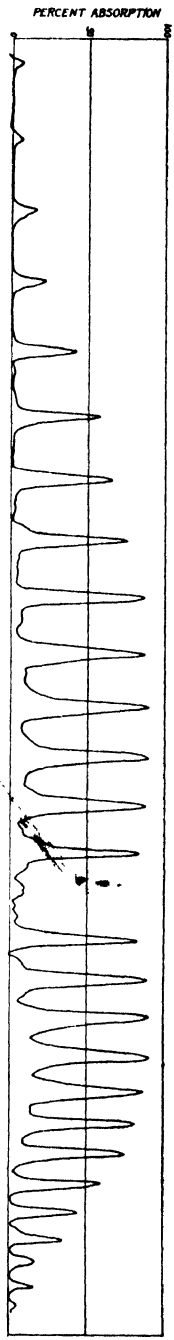


FIGURE 1.—Absorption Curve for HCl 6-Inch Tube

lines due to an increase of vibrational energy accompanied by an increase of rotational energy for the positive branch, and by a decrease of rotational energy for the negative branch. Those lines due to an increase of vibrational energy alone would be expected to lie between the observed branches and are missing for the hydrogen halides. Thus we may conclude that the nuclei move in the invariable plane.

Another favorable situation in these bands is the comparatively large spacing of the lines, an advantage which led to their early resolution with a prism. It has been shown that in first approximation the lines differ in frequency by $h/4\pi^2 I$ where I is the moment of inertia of the molecule about its axis of rotation. The mass coefficient of hydrogen and halide is nearly equal to the mass of the hydrogen and the moment of inertia is consequently small. Hence the wide spacing.

The moderate requirements of resolution and sensitivity together with the comparative simplicity of motion, have permitted both experiment and theory to advance further with the hydrogen halides than elsewhere in infra-red bands. In 1913, Burmeister(1) investigated a group of gases for absorption between 3μ and 15μ. He was able to resolve into doublets the fundamental bands of HCl, HBr and CO. Later in the same year, Eva von Bahr(2) published a paper in which she reported the resolution for the first time of the HCl band into its component lines. In 1917, Brinsmade and Kemble(3) analyzed further the fine structure of the fundamental band of HCl at 3.4μ and detected as doublets the first harmonics of HCl, HBr and CO. Imes(4) using a grating which gave him greater dispersion and resolution, was able to determine the fine structure of the two HCl bands and of the fundamentals of HBr and HF with considerable detail. Schaefer and Thomas(5) have since detected the second harmonics of CO and HCl and the first harmonic of HF but not their fine structure.

In the case of the strong band of HCl at 3.4μ, the precision of these wave-length measurements and the number of lines measured have been sufficient to warrant the empirical statement of frequencies as an ascending power series in the nuclear rotational quantum number m in which coefficients could be determined up to and including the cubic term. A knowledge of these coefficients assists in the analysis of the coupling of rotation and vibration and of the departure of the vibration from simple harmonic motion; in other words, they contain the constants of the force function of the system if that could be satisfactorily expressed as a function of the displacements of the nuclei from their rest positions. More simply, they permit one to build up approximate energy terms, a calculation which has been so fruitful in line spectra. The energy expression will contain only even powers of m and we may write

$$E_{n,\,m} = a + bm^2 + cm^4$$

where a, b and c contain the vibrational quantum number n. In the case of HCl there exist considerable data for the strong band at 3.4μ for which n changes from 0 to 1 and for the first harmonic at 1.7μ for which n changes from 0 to 2. With these results, one should be able to predict the constants of another band which would occur for the transition from 1 to 2. Such a band was calculated by Kratzer([6]). In 1923, Colby, Meyer and Bronk([7]) undertook the measurement of the 3.4μ band of HCl with the absorbing gas at 300° C. The gas was heated in order to increase the rotational energy of the molecules and thus occasion absorption corresponding to higher initial values of m. It was possible at 300° to extend the band on both sides to the twentieth member—forty lines in all. This large number of lines added greatly to the accuracy of determination of the empirical formula mentioned above.

In addition to new lines in the strong band, five lines were disclosed which apparently belonged to a weaker overlapping band. These new lines were only measurable at the higher temperature and must therefore be believed to have an initial state very infrequent under ordinary conditions. This would be the case for the vibrational transition 1 to 2 which, moreover, should fall close to the fundamental band 0 to 1. The individual lines, however, were displaced about one-third of their spacing from the positions predicted by Kratzer from the constants of the other two HCl bands. Such a discrepancy greatly exceeds experimental uncertainties. An explanation of this displacement came later and was in accord with a more satisfactory explanation of the missing first line of the positive branch.

It will be recalled that in the diagram of these bands shown in Chapter II, not only the line ν_n was absent but also another line of

slightly higher frequency, there described as a transition of m from 1 to 0 (0 to 1 absorption). The reverse transition, 1 to 0 absorption, is present—a fact very difficult to reconcile with the possibility of thermal equilibrium. This was an annoying difficulty for some time until it was finally proposed to alter the numbering so as to make the initial values of m odd multiples of $\frac{1}{2}$. This might be interpreted physically as due to an electronic angular momentum of magnitude $h/4\pi$, fixed in the molecule and directed along the invariable axis of the previous motion. In order that the total angular momentum should still be integral multiples of $h/2\pi$, the nuclear momentum must now have half values. Transitions will still be in units. This yields the following numbering for the absorption band:



FIGURE 2.—Diagram Correlating Quantum Transitions with Lines for HCl.

and places the missing ν_n at the center of the band.

The nuclear energy is again expressed by an equation of the form of (37) in which m is replaced by $(m-\frac{1}{2})$. For the case of absorption we have

$$\nu=\nu_n+B_0[(m-\tfrac{1}{2}+\Delta m)^2-(m-\tfrac{1}{2})^2] \\ -[a_{n''}(m-\tfrac{1}{2}+\Delta m)^2-a_{n'}(m-\tfrac{1}{2})^2],$$

where m indicates the total angular momentum of the initial (lower energy) state and $\Delta m=\pm 1$ for the positive and negative branches respectively.

If an empirical ordinal number, M, is used having positive and negative integral values starting with unity, we have for the two branches

$$\nu=\nu_n+\frac{a_{n'}-a_{n''}}{4}+2(B_0-a_n)M+(a_{n'}-a_{n''})M^2.$$

The electronic angular momentum now forms a reference direction with respect to which the nuclear momentum might be expected to be either positive or negative though always in the same line. Kramers and Pauli[8] have discussed this motion in detail. For a given total angular momentum, the energy is least when the electronic and nuclear angular momenta have the same direction. For greater values of the energy but the same angular momentum, the axis of electronic angular momentum will swing back and forth in a narrow loop about the

invariable axis. If the energy is great enough so that the electronic axis reverses with respect to the total angular momentum, the system finds itself in a condition of unstable equilibrium. Hence they excluded this as a stationary state. The intermediate states involving nutation do not fulfil the quantum conditions for this more general rotation if the molecule is diatomic. The state of zero total angular momentum is to be excluded as a limiting case of the unstable equilibrium. Thus the lines indicated in the preceding diagram are the only possible ones and as will be noted, every transition is permitted in both directions.[1]

It can readily be seen that the new numbering will alter the values of the energy terms previously computed. If from the revised values, the combination band, 1 to 2, is recomputed, the observed lines agree very closely with the calculated ones. This is a strong argument for the use of the half numbers.

Very little experimental work has been done with other diatomic molecules in this region. The bands found for carbon monoxide have not been resolved beyond a doublet, the positive and negative branches. The apparent absence of a zero branch is again evidence of rotation about an axis normal to the nuclear line.

As experimental evidence accumulates, one should perhaps expect to find cases where the motion is not so restricted as that just described. If, for example, due to some essential dissymmetry in the molecule, the electronic angular momentum should make an acute angle with the nuclear line, the invariable axis would then not be normal to the nuclear line nor parallel to the axis of electronic angular momentum. For a given total angular momentum and minimum energy, it would nevertheless make a fixed angle with the nuclear line. The nuclear vibration would then have a component along the invariable axis and a zero branch should be expected. Greater values of energy would again introduce nutation as described above. The motion then becomes doubly periodic and must fulfil two quantum conditions. This is, as before, impossible for the diatomic molecule. A more detailed discussion will be given for the polyatomic case.

[1] Very recent work on the problem of rotation for the diatomic molecule by Dennison and Kronig according to the Heisenberg and Schrödinger Mechanics requires the energy expression to be of the form

$$E = (j^2 + j)\,\frac{h^2}{8\pi^2 I}\,.$$

The use of integers in this formula yields the same empirical formulation as the use of half integers in the older formula. It is therefore possible to account for the HCl bands without the introduction of an electronic angular momentum. This is also in accord with recent work of Mullikan (see p. 102 of this report).

It has been shown in the introductory chapter that the distribution of intensities of the lines within a band of this type is symmetrical and that each branch apparently follows the Maxwell-Boltzmann distribution law for the rotation velocities of diatomic molecules in thermal equilibrium. This experimental observation was plausible until the recent introduction of half units of nuclear angular momentum into the theory. According to the older theory corresponding lines on the two sides of the center were supposed to originate in molecular transitions having the same initial state, one increasing and the other decreasing its angular momentum by one unit, e. g., $1\rightarrow 2$ and $1\rightarrow 0$. This assumption, together with the hypothesis that the two types of transitions ($\Delta m = +1$ and $\Delta m = -1$) were equally probable, explained the symmetry of the two branches; and statistical theory gave a satisfactory account of the intensity variation inside each branch.

A new theory of intensities is required, however, by the newer assignment of initial and final quantum numbers to the band lines. We now attribute corresponding lines in the two branches to a change in angular momentum whereby the original value for one transition is the same as the final value for the other and *vice versa*, e. g., $\frac{1}{2}\rightarrow\frac{3}{2}$ and $\frac{3}{2}\rightarrow\frac{1}{2}$. The number of molecules in the two different initial states will always be different and in the case just mentioned is very markedly different, so that the intensities of corresponding lines would not be the same if the two types of transition associated with the two branches were equally probable.

The problem has recently been discussed by Kemble from the standpoint of the Bohr correspondence principle. He finds that the amplitudes of the Fourier components of the motion associated with the two branches of the band are nearly the same, so that according to the usual formulation of Bohr's principle, the *emission* transitions for the two branches should be of nearly equal probability. It follows that the probabilities of *absorption* for any pair of corresponding lines should not be equal, but should be in the ratio of the *a priori* probabilities of the two final states. This modification of the theory leaves the intensity distribution unsymmetrical, however, and is not in accord with the experimental facts. He concludes that the method of calculating transition probabilities is wrong, and locates the source of difficulty in the fact that the molecular model is a degenerate system with fewer quantum conditions than degrees of freedom.

To avoid the complication of degeneracy, he assumes a slight perturbing force field which breaks each of the normal stationary states up into a group of subsidiary states of unit *a priori* probability and nearly equal energy. Such a field would split each of the original absorption

lines into a group of closely spaced components the sum of whose intensities should equal the original intensity. He recalculates the theoretical intensities on this basis and finds that they depend on the *a priori* probabilities of the initial and final states (degenerate) in such a way as to make the branches of the band approximately symmetrical when the more recent numbering of the lines is used. The result clears up the initial discrepancy between the observed intensities and the new assignment of quantum numbers to initial and final states but leaves the correct method of calculating transition probabilities for degenerate molecular systems uncertain.[3]

The correspondence principle predicts pure rotational bands in the far infra-red for molecules which possess an electric moment when at rest. This is doubtless the case for many diatomic molecules including the hydrogen halides. The only band which has been observed for this class of molecules is that due to hydrogen chloride which has recently been recorded by M. Czerny([22]).

With a very ingenious adaptation of Rubens' equipment, he has been able to measure the wave lengths of seven absorption maxima between 40μ and 100μ. As was expected from the near infra-red spectrum, these maxima form an approximate arithmetic progression. A small cubic term gives their slight convergence which is due to the change of moment of inertia of the molecule with angular velocity. The frequencies are satisfactorily given by the formula

$$\nu = 20.794m - 0.00164m^3.$$

These constants agree with those predicted from the near infra-red within a small systematic difference which is probably experimental in one or the other of these two technically difficult regions.

The most striking result of this excellent work is the fact that the formula for the frequencies has no constant term. If the rotational energy of the diatomic molecule were written

$$E = \frac{h^2 m^2}{8\pi^2 I}$$

the frequency should be given by

$$\nu = \frac{h}{8\pi^2 I}(2m+1).$$

If, however, one writes

$$E = \frac{h^2}{8\pi^2 I}(m-\tfrac{1}{2})^2,$$

then

$$\nu = \frac{h}{8\pi^2 I} 2m.$$

[3] A discussion of the recent application of the summation rules of Dorgelo and Burger to band line intensities will be found in Chapter IV, Section 6.

This work therefore leaves no doubt of the necessity of the use of half quanta in the formulation of these bands. Heisenberg's[23] recent work in Quantum Mechanics leads us to believe that the presence of $\frac{1}{2}$ in the energy expression may have a very fundamental significance and may need to be considered much more generally in the future.

The rotation and vibration of polyatomic molecules present considerably more intricate problems and, as one might expect, the bands are on the whole much more complicated. A great deal of experimental work has been done in this region for the greater part, however, without sufficient resolution to reveal the fine structure due to changes in the rotational state. Yet the work is of greatest importance in the study of molecular models as revealed by their normal modes of vibration. As has been pointed out, we may expect for harmonic oscillators, absorption or emission of radiation of the same frequency as that of the motion itself. For the anharmonic oscillator, overtones may also occur. If the molecule has several normal frequencies of vibration, we may expect emission or absorption of the frequencies approximately given by $\sum \tau_n \nu_n$. It is unfortunate that for many of the materials investigated by Coblentz[9] and others, the molecules, chiefly organic, have fundamental frequencies much lower than those included in the regions investigated. The importance of this information makes further observations greatly to be desired. For some of the simpler molecules, however, we possess sufficient data to draw some conclusions. Hettner[10] has contributed a very valuable list of combination frequencies, a list which contains most of the material for which sufficient data existed at that time. For example, for water vapor about ten bands are known between 7μ and 0.7μ, all of which he is able to account for as multiples and additive combinations of the two lower frequencies corresponding to the strong bands at 6.3μ and 2.7μ. These are all absorption bands. At room temperature one would not expect to find an appreciable number of molecules vibrating with frequencies which lie in this region. The normal state will therefore be vibrationless and difference combinations absent. The triangular model has three normal modes of vibration. Since two frequencies are sufficient to account for the observed bands, either one of the three frequencies has an integral relation to the others or it corresponds to a motion for which the electric moment remains unchanged. For five of these bands, those nearest the fundamentals, fine structure has been obtained, first by von Bahr[2], later by Hettner[11] and again by Sleator[12] with the help of a grating and with very considerable dispersion. E. R. Phelps[13] has continued the work of Sleator with an echelette grating designed for this region. He has added considerably

to the number of lines and to the resolution of the regions already mapped. Considerable resolution has been obtained for NH_3, CO_2, CH_4 and HCN.

Before discussing these bands in detail it will be necessary to analyze somewhat the main characteristics of this more general vibration and rotation. With the present meagre knowledge of molecular structure it is out of the question to hope for a complete solution of the problem of nuclear vibration. Wherever it is possible from the symmetry of the molecule and with the help of information derived from physical or chemical behavior, to set up energy expressions without too many undetermined constants, it may nevertheless be possible to solve for the normal vibration frequencies and identify them with observations. Triatomic molecules lend themselves to this treatment, particularly such molecules as CO_2 and H_2O. NH_3 has been similarly treated, likewise CH_4 which doubtless has a regular tetrahedral structure. On the analysis of the normal modes of vibration of these models, it has been possible to identify particular motions of the nuclei with definite observed band frequencies. The correspondence principle allows one also to predict the relative intensities of the bands and to check against observations. The simplified assumptions make the agreement between calculation and experiment only approximate but the results are nevertheless of great importance in the interpretation of outstanding differences among bands of the same molecule. For example, the direction of the electric moment called out by different vibrations is essential in accounting for the accompanying rotational transitions. In triangular models information may also be gained concerning the relative distances of the atoms—a most important point in a study of the rotation.

The problem of the quantization of general rotation was undertaken by Hettner even before the theory of stationary states had taken its present form. The problem has since been treated by Epstein([14]) and by Kramers([15]) who also included the case of an electronic angular momentum fixed in the body. The general rotation of an unsymmetrical body is doubly periodic. If the Eulerian angles θ, ϕ, and ψ indicate in the customary manner, θ, the angle between the principal axis (A) of the body and the invariable axis, ϕ, the angle between the principal axis (B) of the body and the nodal line, ψ, the angle between the nodal line and a radial line fixed in the invariable plane, the two quantum conditions may be written

$$J_\psi = 2\pi p_\psi = mh$$
$$J_\phi = p_\psi \int \cos\theta d\phi = ih$$

where p_ψ is the total angular momentum, m and i integral quantum numbers.

The general character of this quantization may be seen from the special case of a body which is symmetrical about the axis A. The above integral may then be evaluated and the spectrum described in detail. As is well known, the motion of the symmetrical rotator is one of steady precession. The angle θ is constant. Consequently,

$$p_\phi = \frac{ih}{2\pi}$$

where $p_\phi = p_\psi \cos\theta$, the component of p_ψ along the symmetry axis of the body. The expression for the energy is

$$2E = \frac{h^2}{4\pi^2}\left(\frac{i^2}{A} + \frac{m^2 - i^2}{C}\right)$$

where A is the moment of inertia about the axis of figure and C the moment of inertia about an axis normal to it. Spectral frequencies are then given by

$$h\nu = E_{m+\Delta m,\, i+\Delta i} - E_{m,\, i}.$$

$$\nu = \nu_n + \frac{h}{8\pi^2}\left(\frac{2m\Delta m}{C} + 2i\Delta i\left(\frac{1}{A} - \frac{1}{C}\right) + \frac{(\Delta m)^2 - (\Delta i)^2}{C} + \frac{(\Delta i)^2}{A}\right).$$

The character of the motion is not altered if the molecule has an electronic angular momentum which lies in the symmetry axis. The energy expression then becomes (approximately)

$$2E = \frac{h^2}{4\pi^2}\left(\frac{(i-s)^2}{A} + \frac{m^2 - i^2}{C}\right)$$

where $sh/2\pi$ is the electronic angular momentum. In this case

$$\nu = \nu_n + \frac{h}{8\pi^2}\left(\frac{2m\Delta m}{C} + 2i\Delta i\left(\frac{1}{A} - \frac{1}{C}\right) + \frac{(\Delta m)^2 - (\Delta i)^2}{C} + \frac{(\Delta i)^2}{A} - \frac{2s\Delta i}{A}\right).$$

One may think of the electronic angular momentum as producing a larger number of lines by separating pairs which otherwise fall together. Thus for $s=0$ the line $i=1$, $\Delta i=1$ falls on $i=-1$, $\Delta i=-1$, whereas for $s\neq 0$, they are separated by $sh/2\pi^2 A$. The lines $\Delta i=0$ remain unchanged.

Permitted transitions may be determined by analyzing the motion of the electric moment whose three components referred to the principal axes of the body may be written

$$\alpha = a\cos(2\pi\omega_n t)$$
$$\beta = b\cos(2\pi\omega_n t)$$
$$\gamma = 0.$$

The two components of the motion along the invariable axis and normal to it have the form

$$x = a\cos\theta\cos(2\pi\omega_n t) + \frac{b\sin\theta}{2}\cos 2\pi(\omega_n+\omega_i)t + \frac{b\sin\theta}{2}\cos 2\pi(\omega_n-\omega_i)t$$

$$y = \frac{a\sin\theta}{2}\cos 2\pi(\omega_n+\omega_m)t + \frac{a\sin\theta}{2}\cos 2\pi(\omega_n-\omega_m)t - \frac{b(1+\cos\theta)}{4}\cos 2\pi(\omega_n+\omega_m+\omega_i)t - \frac{b(1+\cos\theta)}{4}\cos 2\pi(\omega_n-\omega_m-\omega_i)t + \frac{b(1-\cos\theta)}{4}\cos 2\pi(\omega_n+\omega_m-\omega_i)t + \frac{b(1-\cos\theta)}{4}\cos 2\pi(\omega_n-\omega_m+\omega_i)t.$$

ω_n gives the frequency of vibration and is associated with n, ω_m the frequency of precession about the invariable axis, associated with the transitions of m, ω_i the frequency of rotation about the figure axis A referred to a set of axes rotating about the invariable axis with the angular velocity ω_m. This is related to the quantum number i. We see therefore that for $b=0$ (electric moment always in the symmetry axis) the following transitions are permitted

$$\Delta n=1\begin{cases}\Delta m=0 & \Delta i=0\\ \Delta m=\pm 1 & \Delta i=0\end{cases}.$$

No transitions of i are permitted in the vibration-rotational (near infrared) band ($\Delta n=1$). All three branches of the band should appear. ($\Delta m=\pm 1, 0$.)

For $a=0$, electric moment always parallel to the B axis, we have

$$\Delta n=1\begin{cases}\Delta m=0 & \Delta i=\pm 1\\ \Delta m=\pm 1 & \Delta i=\pm 1\end{cases}.$$

For the more general case where both a and b are different from zero, all the above transitions are permitted. The particular type of vibration involved appears here more important in determining the multiplicity of lines throughout the band than in determining the presence of the zero branch.

Turning again to the equation for the frequency of the lines and examining first the case where $A=C$ (sphere of inertia) we have for $s=0$

$$\nu=\nu_n+\frac{h}{8\pi^2}\left(\frac{2m\Delta m}{C}+\frac{(\Delta m)^2}{C}\right)$$

a series of lines with constant spacing $h/4\pi^2C$. It is obvious that if the molecule has spherical symmetry, any axis is a principal axis and it will always execute a simple rotation as was the case for the diatomic molecule. But if $s>0$ and fixed in the molecule, there is then a preferred axis which must not be expected in general to have the direction of the total angular momentum. Now

$$\nu=\nu_0+\frac{h}{8\pi^2}\left\{\frac{2m\Delta m}{C}+\frac{(\Delta m)^2}{C}-\frac{2s\Delta i}{C}\right\}.$$

If the electric moment lies in the direction of the electronic rotation $\Delta i=0$ and the new term disappears. If the electric moment is normal to the axis, $\Delta i=\pm 1$. Each of the previous lines separates into a pair displaced equally from the old position. The separation of the pair is $2sh/4\pi^2C$ and this becomes equal to the original spacing for $s=\frac{1}{2}$. Then the spacing is again constant and the same as before but the new lines lie midway between the old positions. For the electric moment oblique to the electronic axis, both systems of lines are present. For $s=\frac{1}{2}$, the spacing is now $h/8\pi^2C$.

The methane molecule is an illustration of the case described above. J. P. Cooley([16]) has been able to resolve some of these bands with great detail and to reveal characteristics which appeared clearly in no other bands of this type. The strong bands at 7.7μ and 3.3μ yield a large number (more than 40 at 7.7μ) of almost equidistant clearly defined single lines. At the center of each band is a strong absorption region covering two to three of the band lines. Its short wave length edge falls at the supposed center of the band. If the mass of the absorbing gas is increased, the maximum shifts to longer wave lengths indicating that it is an unresolved group of fine lines whose intensities rise more sharply on the short wave length side than on the long wave length side. All of these facts lead to the conclusion that we have here a zero branch. Another striking departure from the hydrogen halide bands is the fact that the spacing of the lines in the 3.3μ band is roughly twice that in the 7.7μ band.

An analysis of the probable behavior of this molecule has been made by D. Dennison([24]). We have every reason to believe from chemical data that the methane molecule has a regular tetrahedral structure with the H atoms at the vertices and the C at the centroid. Chemists have been able to find no evidence of a preferred direction in this system. Such a model would have no electric moment when at rest and this accords well with physical evidence. Dennison has analyzed the possible normal vibrations of such a system for infinitesimal displacements

and because of the symmetry has found that the nine degrees of freedom (15-6) yield only four distinct frequencies. Of these, two would involve no change of the electric moment and might not be expected to appear in the spectrum. The other two, however, may be expected to occur. Hettner has already shown that the strong bands of methane may be accounted for with the help of two fundamental frequencies. But there is evidence of very faint absorption which may be related to the other two frequencies and which may indicate a slightly preferred axis in the molecule, perhaps to be associated with an electronic rotation. The computed frequencies involve only three constants, but one may fit them to the four observed fundamentals with satisfactory agreement both in position and intensity. The occurrence of the zero branch should indicate that the electric moment does not always lie parallel to the invariable plane. The tetrahedral model has a sphere of inertia, i. e., all three moments of inertia are equal. In spite of this the bands have sharp equispaced lines with two spacing constants, one double the other. In the light of the previous discussion, this can only be explained on the basis that this molecule also has an electronic angular momentum of a half unit along an axis fixed in the molecule. The rotation of the molecule is therefore similar to that of the symmetrical rotator. Calling the frequency of vibration ν_n, neglecting the coupling of vibration and rotation and setting $A=C$, $s=\frac{1}{2}$, the previous formula becomes

$$\nu=\nu_n+\frac{h}{8\pi^2C}\,(2m\Delta m+(\Delta m)^2-\Delta i).$$

For the positive and negative branches $\Delta m=\pm 1$ and for the zero branch $\Delta m=0$. (The lines of the zero branch do not fall precisely together because of changes in the moment of inertia which are neglected here.) If the electric moment does not lie in the axis of electronic angular momentum nor normal to it, transitions $\Delta i=\pm 1$, 0 may all be allowed. This may be supposed to be the case for the richer spectrum at 7.7μ. The formula for the positive and negative branches then becomes

$$\nu=\nu_n\pm\frac{mh}{8\pi^2C}$$

a series of lines with the spacing $\frac{h}{8\pi^2C}$. But if we assume for the band at 3.3μ that the electric moment called out by this vibration lies either in the axis of electronic angular momentum or normal to it we have

the alternative possibilities of $\Delta i=0$ or $\Delta i=\pm 1$. This would give either the series

$$\nu=\nu_n \pm \frac{2mh}{8\pi^2 C}$$

or

$$\nu=\nu_n+\frac{h}{8\pi^2 C} \pm \frac{2mh}{8\pi^2 C}.$$

The spacing constant is then $\frac{h}{4\pi^2 C}$, double that just considered.

Returning to the more general case of axial symmetry and assuming now either that A is slightly greater or slightly less than C, Δi and i reappear in the frequency formula even for $s=0$. Where for the spherical model there was a series of equispaced lines, each of these lines now breaks up into a group whose multiplicity increases with m. For $\Delta i=\pm 1$, there are $2m+1$ equispaced components with spacing $\frac{h}{4\pi^2}\left(\frac{1}{A}-\frac{1}{C}\right)$. For $i=0$, there is a single line slightly displaced from the center of the $\Delta i=\pm 1$ lines. For $s>0$, the $\Delta i=0$ line is undisturbed but the $\Delta i=\pm 1$ groups separate into two groups each displaced equally from the old position.

Such a fine structure within the m lines might easily escape experimental resolution where A and C are nearly equal and result only in a broadening of the lines. The separation of the components depends on the departure of the ellipsoid of inertia from a sphere either toward a prolate or oblate spheroid. For A greater than C where A is the moment of inertia about the axis of symmetry, the limiting ratio of A to C is 2 which may occur when the nuclei of the molecule lie in a plane with axis of symmetry normal to the plane. The separation of components is then $h/8\pi^2 C$, half of the spacing of the m lines themselves. The interpretation of bands of this type becomes very difficult because of the wide overlapping of components from the various m lines. It may give rise to apparently two-fold spacing in a single band.

For C greater than A, there is no upper limit for the ratio of C to A. For C much larger than A, we have a most interesting case. The molecule is now to be thought of as a long and thin distribution about the axis of figure. The spacing of the i lines is great compared with that of the m lines, with the result that for a given vibrational transition we now have a series of bands, each associated with a single initial value of i. Each of these bands will contain lines for all initial values of m as was the case in the single fundamental band of HCl. For such an array of bands we may think of the band $\Delta i=0$ as the central one. On either side will occur the $\Delta i=\pm 1$ bands in pairs of probably comparable inten-

For the special transitions described above, the central band may

be absent or it may be the only one present. Since for small values of A the energy grows rapidly with i, there might be only one or possibly two pairs of the $\Delta i = \pm 1$ bands with observable intensity under ordinary conditions.

A striking example of this case has been pointed out by Dennison([25]), viz., the CO_2 molecule. Carbon dioxide has three chief regions of absorption at 2.7μ, 4.25μ and 14.7μ. The two shorter wave length regions were investigated in detail by Barker([17]) with a grating. He was able to resolve the band at 4.25μ into a doublet but could not get the fine structure. In the other region were two bands centering at 2.69μ and at 2.77μ (Figure 3). They appeared as doublets with some evidence of

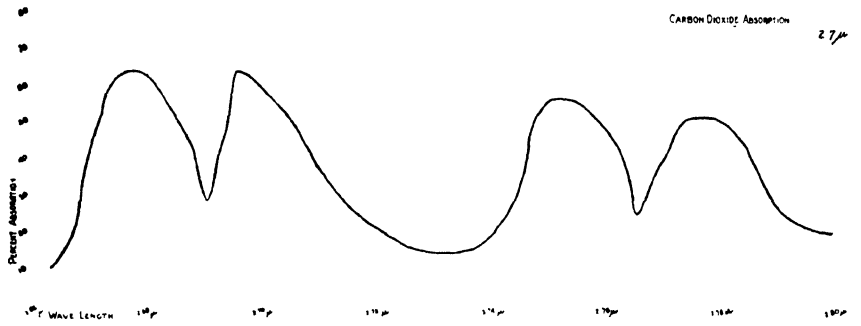


FIGURE 3.—Absorption Curve for CO_2.

fine structure. It was not possible to find any simple multiple relations of these frequencies to each other nor to the band at 14.7μ. Dennison has since solved the vibration problem for this isosceles triangle and has been able to fit its frequencies to these three spectral regions only by making the angle at the carbon very large. There is other evidence that this molecule is almost linear. Such a model is approximately symmetrical about an axis parallel to the line of the 0 atoms and the moment of inertia about this axis is small. Moreover an analysis of the vibrations showed that for the band at 4.25μ only the transition $\Delta i = 0$ is permitted. This is therefore a single band. For the band at 2.7μ, only $\Delta i = \pm 1$ is permitted and the pair of doublets is to be expected. It is possible to associate these two bands with the transitions of i, $0 \rightarrow 1$ and $1 \rightarrow 0$. Both of these initial states may be expected to occur abundantly under ordinary conditions if the moments of inertia are taken as those given by the spacing of the bands. Higher values of i should be comparatively infrequent. The absence of a zero branch is in accord with the analysis, since at no time will i have a value greatly different from zero.

The spectrum of NH_3 has recently been examined by Schierkolk([18]). He finds a considerable number of bands which have been associated with

each other in subsequent papers in different ways. A more certain knowledge of the band centers may assist in this classification. The bands show some similarity to those of methane, chiefly in the presence of a zero branch and two spacing constants. The molecule also has axial symmetry and its rotation may be quite similar in character to that of methane.

HCN was investigated by Barker([19]), but the fine structure was not revealed. A double band was found at about 7μ which seems to point to a degeneration toward the linear model. These bands have very interesting shapes and will doubtless yield much on further resolution.

The absorption spectrum of water vapor has the longest history of all, and the recent work of Sleator and Phelps has carried the resolution very far indeed. Nevertheless, the fine structure of these bands presents a bewildering array of lines with apparently unsystematic spacing and intensities. This is a case of rotation which is less accessible than those just discussed. It is quite possible that the two systems of m and i lines have spacing of the same order of magnitude. This may be complicated by the fact that the molecule has not axial symmetry. The stationary states for the unsymmetrical case are defined by the equations given above for m and i. The evaluation of the integral $\int \cos\theta d\phi$ now involves elliptic functions and the altered intensities and wave-lengths of i components are not simple to predict for a general case. A Fourier analysis of the nutation leads one to believe that only the transitions $\Delta i = \pm 1, 0$ need still be considered under ordinary conditions.

The only pure rotation band for a polyatomic molecule which we know in even approximate detail is that of water vapor which has been studied by Paschen and by Rubens and his co-workers. Absorption due, doubtless, to this class of band was found from 9μ to $100\ \mu$. In spite of incomplete resolution, definite maxima were obtained for nearly forty lines. Eucken([20]) found that these lines fitted the two series

$$\nu = \frac{p}{400}, \qquad \nu = \frac{p+\frac{1}{2}}{424}$$

with about equal success. The lack of resolution made a choice between them impossible. Moreover, intense lines chosen from the above set, particularly in the region 9μ to 20μ, fitted either of the two formulas

$$\nu = \frac{p}{173} \quad \text{or} \quad \nu = \frac{p+\frac{1}{2}}{180}$$

The equispaced intense lines may possibly be due to maximum within the m groups and have the spacing of the m groups; whereas the weaker lines may correspond to fine structure within the m groups and be approxi-

mately in step with them. It has been impossible, however, to interpret the band conclusively.

Very recently, Witt([21]) has made measurements of this band in the region 50μ to 180μ. He has used gratings of 1 mm. and $\frac{1}{2}$ mm. grating space and has been able to push the resolution very much further in this interesting region. He adds considerably to the number of lines found by Rubens. The formula $\frac{p+\frac{1}{2}}{400}$ which he uses, contains insufficient lines. $\frac{p+\frac{1}{2}}{600}$ succeeds better, but needs some readjustment in Rubens' shorter wave length region.

It is apparent that the fine structure of the m lines is still not completely resolved and that the overlapping makes the band a difficult one to analyze.

BIBLIOGRAPHY

[1] Burmeister, Verh. deut. physik. Ges., 15: 589 (1913).
[2] Bahr, Verh. deut. physik. Ges., 15: 1150 (1913).
[3] Brinsmade and Kemble, Proc. Nat. Acad. Sci., 3: 420 (1917).
[4] Imes, Astrophys. J., 50: 251 (1919).
[5] Schaefer and Thomas, Z. Physik, 12: 330 (1922).
[6] Kratzer, Z. Physik, 3: 289 (1922).
[7] Colby, Meyer and Bronk, Astrophys. J., 57: 7 (1923).
[8] Kramers and Pauli, Z. Physik, 13: 351 (1923).
[9] Coblentz, "Investigations of Infra-Red Spectra." Carnegie Institution of Washington, Publication 35. 1905.
[10] Hettner, Z. Physik, 1: 345 (1920).
[11] Hettner, Ann. Physik, 55: 476 (1918).
[12] Sleator, Astrophys. J., 46: 181 (1918).
[13] Sleator and Phelps, Astrophys. J., 62: 28 (1925).
[14] Epstein, Physik. Z., 20: 289 (1919).
[15] Kramers, Z. Physik, 13: 343 (1923).
[16] Cooley, Astrophys. J., 62: 73 (1925).
[17] Barker, Astrophys. J., 55: 391 (1922).
[18] Schierkolk, Z. Physik, 29: 277 (1924).
[19] Barker, Phys. Rev., N. S., 23: 200 (1924).
[20] Eucken, Jahrb. Radioakt. Elektronik, 16: 391 (1920).
[21] Witt, Z. Physik, 28: 236 (1924).
[22] Czerny, Z. Physik, 34: 227 (1925).
[23] Heisenberg, Z. Physik, 33: 879 (1925).
[24] Dennison, D., Astrophys. J., 62: 84 (1925).
[25] Dennison, D., Phil. Mag., 1: 195 (1926).

CHAPTER IV

ELECTRONIC BANDS

SECTION 1. GENERAL INTRODUCTION

RAYMOND T. BIRGE

In the previous chapters two different types of bands have been discussed in detail; namely, a type which logically can be ascribed to a simple change in the amount of rotational energy of the molecule, corresponding to a definite change in the value of the rotational quantum number, and a type which can be ascribed to a simultaneous change in nuclear rotational and nuclear vibrational energy, designated by changes in both the rotational and vibrational quantum numbers. In the present chapter we shall consider in some detail the third, more complex type of band, which has been designated in previous chapters as an electronic band. Many of the characteristic properties of electronic bands have now been given a logical explanation by the assumption of a simultaneous change in at least three different quantum numbers. A comparison of the properties of these bands on the one hand with the structure of rotation and vibration-rotation bands of the infra-red, and on the other hand with the structure of line spectra, has led to the conclusion that the three quantum numbers concerned here are connected respectively with nuclear rotational, nuclear vibrational, and electronic energy.

The change in the electronic energy is thus assumed, just as in the case of line spectra, to be due to the transition of an electron from one quantum orbit to another. To speak more correctly, we could say that there is a change in the energy of the molecule as a whole, due to the electron transition. In view of recent developments in connection with line spectra, it seems quite possible that two or more electrons may simultaneously change quantum states, but at the present time the only experimental data that we have concerning the electron change relate to the amount of energy connected with this change. As will appear later, it is now possible to evaluate a series of electron energy levels, in the case of a few molecules, but it is not yet possible to assign electronic quantum numbers to these various levels. Hence, it is really unnecessary even to refer to such quantum numbers. We shall, however, for the sake of analogy, introduce the hypothetical electronic quantum numbers

e', e'', referring respectively to the higher and lower energy levels. The energy associated with these numbers may be denoted by E'_e and E''_e, and the contribution to the emitted frequency, due to an electron transition, by ν_e where

$$\nu_e = \frac{E'_e - E''_e}{h}. \tag{1}$$

Therefore, in an electronic band, the frequency of a given line, ν, may be considered as a first approximation,[1] to be separable into three portions, connected respectively with the change in electronic energy, change in vibrational energy, and change in rotational energy, i. e.,

$$\nu = \frac{E' - E''}{h} = \nu_e + \nu_n + \nu_m = \frac{E'_e - E''_e}{h} + \frac{E'_n - E''_n}{h} + \frac{E'_m - E''_m}{h} \tag{2}$$

where

$$E' = E'_e + E'_n + E'_m \text{ and } E'' = E''_e + E''_n + E''_m. \tag{3}$$

The literature upon the subject of electronic bands is very extensive, and several accounts of the structure of such bands are available, references (1), (2), (3) having been written before the advent of the quantum theory, and (4), (5), (6), (7), (8) and (9) more recently. No detailed account has appeared, however, since the introduction of the quantum theory of molecular spectra.[2] Now in the case of line spectra, the introduction of the quantum theory involved no fundamental changes in viewpoint regarding the structure of such spectra as far as the numerical relations are concerned. This, however, is not the case as regards band spectra for which almost all of the previously known empirical facts appear in a quite different aspect. Hence it seems desirable to open the chapter with a general account of the more important empirical facts regarding band spectra, giving in each case, as far as convenient, the restatement of that fact in terms of quantum theory.

This section is followed by a discussion of the combination principle, as applied to electronic bands, and an analysis of the formulas for the energy levels, based mainly on Kratzer's theory of the non-harmonic oscillator. These formulas are then applied, first to the relations among the heads of a system of bands, and then to the relations among the lines of individual bands of various types. The chapter closes with a

[1] The method of representing the energy and energy change given here neglects the various mutual action terms which are considered in detail in Section 3, ahead. See equations (22), (24) and (27), page 107, for the more general form of the energy.

[2] Another brief account of the quantum theory, by Kratzer, has just appeared. Encyk. Math. Wiss. Band V, Teil 3, Heft 5 (1925).

brief summary of some of the more practical applications of the quantum theory of electronic bands, including much very recent work.

It may be noted, at this time, that the really exact relationships involved in the combination principle, as applied to band spectra have been discovered, almost without exception, since the advent of the quantum theory, and as a result of the predictions of that theory. This fact indicates the value of the theory, but the truth of the relations is of course quite independent of any theory.

No attempt is made to give a systematic account of known band spectra, such as has been done by Konen([3]). Instead of this, typical cases are cited which collectively constitute a general survey of our present knowledge of band spectra. Unfortunately the type of bands here discussed is very complex, and the amount of available results relatively meager. Although much work has been done on band spectra, it is in general necessary to repeat work done before 1918 in order to obtain complete data regarding the relations which we now know are of real significance. Much new work has, however, appeared during the writing of this report, and, as will be seen from the results given particularly in Section 8, the present status of the subject has now greatly improved.

SECTION 2. REVIEW OF CERTAIN EMPIRICAL FACTS WITH THEIR QUANTUM INTERPRETATION

PART 2A. INTRODUCTION

The great majority of electronic bands appear, under low dispersion, as broad lines, with an exceedingly sharp edge on one side, but with a gradual diminution of intensity on the other. With high dispersion each of these broad lines is resolved into a group of lines, whose distribution of position and intensity is such as to give, under low dispersion, the characteristic appearance just mentioned. Because of the faintness of most bands, only a small minority have as yet been obtained with sufficient dispersion to give anything like a complete resolution into lines. It is believed, however, that all these bands are actually composed of a large number of lines, each representing a monochromatic radiation. Moreover, there is good reason to believe that, with sufficiently high dispersion and resolving power, the lines of most band spectra as produced under ordinary laboratory conditions, would be found to be uniformly quite sharp and symmetrical. Actually many lines appear rather wide and non-symmetrical, but in a few cases where a detailed study has been made of this point it has been found possible to explain the result as the superposition of two or more lines of nearly coincident frequency, but usually of different intensity. In portions of a band where the lines

are more widely spaced, and hence the chance of such overlapping is relatively small, the lines are quite uniformly sharp and symmetrical.[3]

We have emphasized this general sharpness of band spectra lines for the following reason. In studying the numerical relations in band spectra, many lines appear to be irregular in position and in intensity. There is no question as to the fact that many lines in band spectra are quite irregular in position, such lines forming the so-called "perturbations." But when a line appears irregular in intensity, this phenomenon should be scrutinized with especial care. Thus in the case of the 3883 CN band, it has been found that all such irregularities in intensity are due merely to the overlapping of two or more lines. The complete analysis of this band into its component series immediately indicates which lines are really single, and in all such cases the intensity of the line is found to be as expected, even when the line in question is quite irregular as regards frequency. On the other hand, the work of Deslandres and d'Azambuja([10]) and more recently of Lindau([11]) on the second positive group of nitrogen, indicates that in many perturbations the intensity is quite irregular. We assume then, for the present, that all bands are composed of a number of sharp lines. In the typical band these lines can be arranged in series, the successive intervals between the lines of a series expressed in wave numbers diminishing in an arithmetic progression to a value of zero, or approximately zero.[4] The "head" of a band may be defined as the point where the frequency interval between successive lines becomes equal to zero. If the head is on the longer wave-length edge of the band, that band is said to be degraded or shaded to the violet. In other words the band is said to be degraded in the direction of increasing values of the frequency intervals ($\Delta\nu$), although it was historically the intensity change and not the relative values of $\Delta\nu$ that defined the direction of degradation. Of the known electronic bands, about equal numbers are degraded to the red and to the violet.[5] This is in contrast to the vibration-rotation

[3] All spectrum lines are slightly broadened, due to Doppler effect. This, however, is a *uniform* effect and very small in the case of most band spectra lines.

[4] Several spectroscopic texts state, quite incorrectly, that the frequencies themselves form an arithmetic progression.

[5] See Kayser's Handbook, 6: 1034-1054. Kayser's very interesting statement (p. 1034) that, in the great majority of cases, bands in the red are degraded to the red, while those in the violet are degraded to the violet, has as yet no theoretical interpretation and is probably not true. On the other hand, his statement that the bands of nearly all elements are degraded to the red is certainly not true. (See Section 8.) Many of the bands which he lists (p. 1035) as due to elements are according to recent investigations more probably due to compounds.

bands of the near infra-red where the quantum theory predicts that all bands will be found to be degraded to the red, as is in fact the case for all which have been accurately analyzed.

PART 2B. THE RELATIONS BETWEEN THE BANDS FORMING A SYSTEM

As has been indicated in the introductory chapter, electronic bands generally occur in clearly related groups, usually called "systems." In terms of the quantum theory, a system is defined as a collection of bands corresponding to a common transition between two major electron levels. Sets of bands in a system can be selected such that the frequency intervals between successive bands in the set change in an arithmetic progression. These sets can be chosen in two different ways, the frequency intervals increasing in opposite directions in the two sets. Deslandres, who did the pioneer work in this field, called one series of such sets "first progressions," and the other series "second progressions." An entire system of bands, often eighty or more in number, can thus be represented as a function of two parameters p and n. The parameter n varies in a first progression, p remaining constant. The parameter p varies in a second progression, n remaining constant.

The heads of a typical system of bands (the second positive group of nitrogen)[6] are shown in Figure 2, page 78, which presently will be considered in more detail. Each of the five horizontal rows constitutes a Deslandres' first progression, the frequency interval increasing to the right as indicated. The bands connected by the long dotted line, and indicated as "$\Delta\nu$ *2nd*," form a second progression, with the frequency interval ($\Delta\nu$) increasing in the direction of the arrow. If now each horizontal row is shifted until the various bands forming the indicated second progression are coincident, the various first progressions will be found to be identical. Conversely, all lines roughly parallel to the long dotted line form second progressions, and the intervals of the first progression give the necessary shifts to bring the several second progressions into coincidence. As an actual fact, when one uses the "head" of each band, the various progressions are usually not exactly identical. But the quantum theory indicates that it is the so-called "origin" of the band,[7] rather than the head, that should be used, and in the very few cases where such origins have been

[6] Deslandres used the word "group" for what is now usually called "system," and all names given by him thus include the word "group." We shall not use this latter word in any other sense, and so the two words are to be considered as synonymous.

[7] The definition of the term "origin" is given in Section 4, equation (72), p. 122.

definitely located, the Deslandres' progressions are found to be really identical. Conversely, the fairly accurate relations given by the heads indicate that as a rule the distance from the head to the origin, in each band of a system, is fairly constant. Practically all of the data on Deslandres' progressions given in this chapter are based on the position of the heads, because of lack of data as to the origins of the respective bands.

While the law of spacing of the bands in a Deslandres' progression is therefore the same as that for the spacing of the lines in a series of a particular band, i. e., an arithmetic progression in both cases, the distribution of intensity in the two cases is quite different. Thus the lines of a band series can normally be followed to a "head" where the spacing is zero, but the bands in a progression as indicated in Figure 2 have never been followed[8] to an analogous head. Deslandres, however, used an analogous numbering for the parameters in the two cases. Thus, since the frequency intervals form an arithmetic progression, the frequencies themselves are represented by a second degree parabola, in terms of the parameter. Deslandres gave the value zero to the line of a band series lying closest to the vertex of the parabola. In the case of the progressions, the portion of the parabola near the vertex is missing, but the experimental curve was extrapolated to this point, and the parameters numbered from there. Thus, in a band series, the Deslandres' parameter m_D has values 0, 1, 2, 3, etc., and each of these values corresponds, normally, to an observed line, while in the progressions of bands, the actually represented values of the parameters p and n normally range from 30 to 100 or more.[9]

Now in the quantum theory, n and p are replaced by the vibrational quantum numbers n' and n'' of the upper and lower energy levels. According to theory the intervals $\Delta\nu$ in each type of progression should decrease as the absolute value of the corresponding quantum number increases. Hence these quantum parameters are always numbered in a direction opposite to that of n and p. Moreover, unfortunately there can be no uniform correlation of n' with either p or n. As we shall see later, several distinct lines of evidence point quite conclusively to the fact that in all systems thus far analyzed in terms of quantum theory, bands with

[8] However, in the case of iodine, the heads have been followed until so closely adjacent as to be no longer resolvable. See p. 107 of reference (12). A similar situation has recently been found in oxygen. See note e' of Section 7.

[9] There is no such range in any particular band system, but among the many known systems one can find values extending over this range.

a common initial vibration state exhibit similar perturbations.[10] Deslandres designated a set of bands showing similar perturbations as a $f(n)$, and referred to the set as a first progression. He found, in addition, that first progressions were normally long, well-defined sets of bands, and that, with a fair degree of accuracy

$$f(n)=a+bn+cn^2. \tag{4}$$

On the other hand, the second progressions were normally short, and a plot of $f(p)$ showed that it often deviated radically from the simple parabolic form of equation (4). From the preceding relations, it follows that in general

$$\begin{aligned} n'&=c_1-p \\ n''&=c_2-n \end{aligned} \tag{5}$$

where c_1 and c_2 are constants. Let us designate a set of bands in a given system having a common *initial* vibration state as an n'' progression. An n'' progression thus includes bands showing similar perturbations, and normally constituting a Deslandres' first progression ($=f(n)$). Likewise, we designate a set of bands having a common *final* vibration state as an n' progression, so that an n' progression is normally a Deslandres' second progression ($=f(p)$). As will appear later, a certain set of vibration levels in the nitrogen band spectrum forms the initial levels for the first positive group, and also the final levels of the second positive group. Deslandres called this common set of levels a first progression,[11] because, in the second group, similar perturbations were found in the bands composing each progression.[12] Thus equations (5) are correct for the second positive group of nitrogen, but for the first positive group, we must write[13]

$$\begin{aligned} n'&=c_1-n \\ n''&=c_2-p \end{aligned} \tag{6}$$

[10] As will be shown presently, the initial state for one system of bands is sometimes the final state for another system (and theoretically may always be) The fact that the hitherto observed perturbations are found to be connected with the initial state indicates that in many cases the final state is the unexcited state of the molecule, for which the perturbations are doubtless very small, if not zero.

[11] It should be noted that, due to the fact that a progression of bands possesses a common terminal state--initial or final—the spacing of the bands themselves is likewise the spacing of a set of levels, so that the term "progression" may be applied either to a set of bands or to a set of energy levels. The same relations occur in line spectra, where, however, it is always the final state which is common to the lines of a series.

[12] The first group has not yet been analyzed satisfactorily into series.

[13] Fortrat, in his Report([6]), introduced the terms "family" and "class," referring them to Deslandres' $f(n)$ and $f(p)$ respectively. He then unfortunately

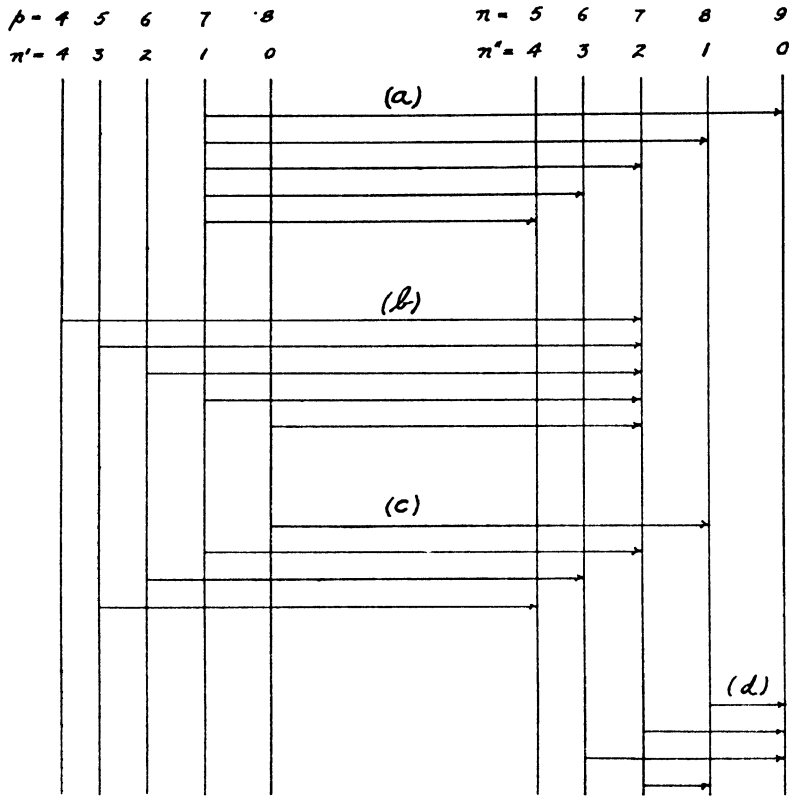


FIGURE 1 —Scheme of Vibrational Energy Levels.

(a) n'' progression $= f(n'')$.
This is usually a Deslandres' first progression $= f(n)$ and all bands show similar perturbations.

(b) n' progression $= f(n')$.
This is usually a Deslandres' second progression $= f(p)$.

(c) A sequence. $n'' - n' =$ constant.

(d) Vibration-rotation bands.
$1 - 0 =$ fundamental
$2 - 0$ and $3 - 0 =$ overtones.

Finally we shall adopt the term *sequence* for a set of bands having a common value of $n''-n'$ (or of $n-p$), and shall designate the sequence by the value of $(n''-n')$. Bands corresponding to successive values of n'' (and of n') but a common value of $n''-n'$ usually are adjacent to one another. Hence the grouping of bands by sequences is the most obvious one, especially as the intensity distribution in the sequence also tends to indicate such a grouping. Thus in the first positive group of nitrogen, the so-called green, yellow, and red "groups" of bands, actually form the three sequences, -4, -3, and -2, respectively. Where the Δn value of the sequence is small (especially 0, $+1$, and $+2$) the intensity usually decreases as n'' (and n') increase. The sequence can then be said to degrade to the red or violet, according to the direction in which the intensity decreases. But since in some sequences the intensity distribution is fairly symmetrical, it is convenient to *define* the direction of degradation as the direction of *increasing n*. Now it is very significant that apparently, without exception in the case of bands presumably due to diatomic molecules, a sequence degrades in the same direction as the bands composing it. The theoretical interpretation of this fact, as will appear later, is that an *increase* in the moment of inertia of a diatomic molecule, caused by an electron transition, is invariably accompanied by a *decrease* in the frequency of vibration of the dipole, and *vice versa*. This is to be expected if the electron transition causes a loosening of the bond between the two atoms.

The foregoing relations are indicated schematically in Figure 1, where a hypothetical assignment of values for p and n is assumed. The vertical lines in this figure represent two sets of vibrational energy levels, the right-hand set corresponding to the more stable state of the molecule. The horizontal distance between the vertical lines $n''=0$ and $n'=0$ is proportional to the energy associated with the common electronic change for a system of bands. Each horizontal line thus represents one band.[14] The spacing of the levels in the initial set is always different from that

used the first positive group of nitrogen in obtaining the quantum interpretation and arrived at the conclusion that a "family" indicates a common final state, and a "class" a common initial state. This led him to the quite erroneous conclusion that bands with a common *final* state have common perturbations.

[14] When such a figure is drawn to scale, the length of each horizontal line should be proportional to the frequency of the point in the band which we have referred to as the "origin" of the band. The origin of the particular band $0\rightarrow 0$ will be defined as the "origin" of the system, because its frequency is proportional to the change in electronic energy. Since the origins of very few bands are as yet known, the frequencies of the heads may be used as a first approximation. This causes a first order error in the separation of the two sets of levels, but only a second order error in the spacing of each set.

in the final set. In other words, the constants in the equations of the two Deslandres' progressions are not the same. This fact is interpreted by the quantum theory as evidence that the vibrational frequency of the molecule is altered by the change in electronic configuration which accompanies the emission of the bands, for the distance between any two successive levels of a set ($\Delta\nu$) will be shown later to be equal to the mean frequency of vibration of the molecule for these levels. According to Kratzer's theory of the non-harmonic oscillator the frequency of vibration should normally decrease as the amplitude increases. Hence the value of $\Delta\nu$ should decrease with increasing n' and n'', as previously stated.

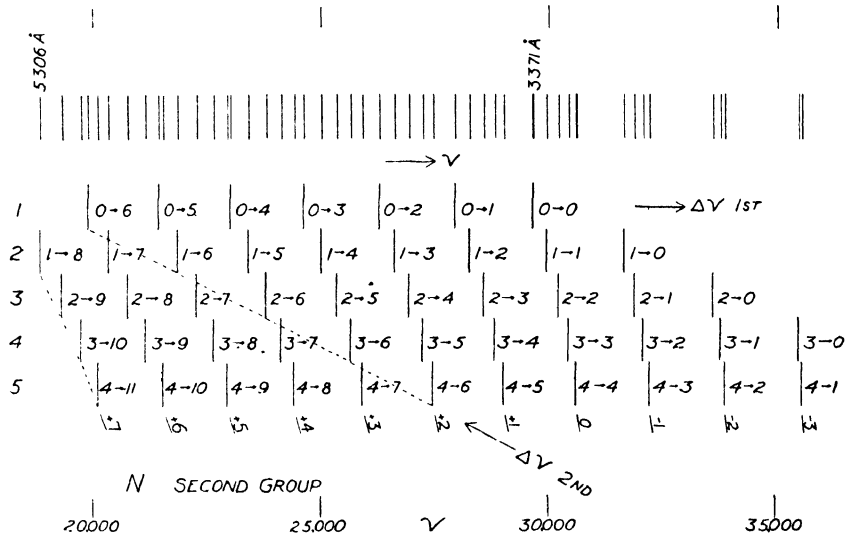


FIGURE 2.—Second Positive Group of Nitrogen. Band Heads Arranged in Progressions

Figure 1 shows clearly that the direction of degradation of a sequence depends on the relative values of the spacing of the initial and final vibration states, and hence on the relative frequency of the oscillator in these two states. If the mean oscillation frequency is smaller in the initial state, the sequence degrades to the red. This must always be true for the vibration-rotation bands if the frequency of vibration decreases with increasing amplitude, and is indicated in Figure 1(d), where the bands $1\rightarrow0$, and $2\rightarrow1$ [15] may be considered as the first two members of a sequence. In the case of such bands there is no electronic transition, and

[15] Recently found by Colby, Meyer and Bronk(13), in HCl, as discussed in Chapter III of this report.

hence the two sets of levels coincide, giving a single set, in which n' now represents merely the left-hand level, and n'' the right-hand level, in a given transition. Furthermore, the series of vibration-rotation bands designated as a fundamental with its overtones ($1\rightarrow0$, $2\rightarrow0$, $3\rightarrow0$) would be designated as the n' progression ($n''=0$), or more briefly as n' progression(0), and the fact that the frequencies of the overtones are less than expected in the case of true harmonics is in agreement with the figure. The sets of electronic bands here represented may be designated as n'' progression(1), n' progression(2) and sequence($+1$), the numbers indicating the common value of n', n'', and $n''-n'$, respectively.

Figure 1 indicates also the origin of the following two rules, which have been found useful in assigning vibrational quantum numbers.[16]

(A) When, in a Deslandres' progression, $\Delta\nu$ decreases in absolute magnitude as ν decreases, we have a $f(n'')$, with n'' increasing as $\Delta\nu$ decreases. This represents a single n'' progression and each band exhibits the same type of perturbations.

(B) When, in a Deslandres' progression, $\Delta\nu$ increases as ν decreases, we have a $f(n')$, with n' decreasing as $\Delta\nu$ increases. This represents a single n' progression.

Some of the relations just described are shown in another manner in Figure 2, which, as already mentioned, represents the heads of the bands of the second positive group of nitrogen, drawn to scale.[17] The actual values of the vibrational quantum numbers ($n'\rightarrow n''$) are given for each band,[18] the arrow indicating the process of emission. Each of the five horizontal rows represents the bands of one n'' progression, or in this case, of one Deslandres' first progression. The value of $\Delta\nu$ increases to the right (i. e., to the violet). The long dotted line indicates n' progression(6), or in this case, a Deslandres' second progression, with $\Delta\nu$ increasing to the red, as indicated. The steep dotted line indicates the sequence($+7$), and the values of the various sequences are shown below the last member of each. The range from $+7$ to -3 indicates that the vibrational energy may increase as well as decrease, in the process of

[16] Just as in the case of the direction of degradation of all vibration-rotation sequences, the validity of these rules depends upon the assumed law of force for the nuclear binding.

[17] See Fowler and Strutt(14), Plate 10, Figure 2a for a photograph of a portion of this system, under low dispersion. Figure 2 is from Birge(15).

[18] The assignment of vibrational quantum numbers for the first, second and fourth groups of nitrogen was made by Birge(15), before the American Physical Society, December 1923, for the second group by Hulthén and Johansson(16) and (17), before the Swedish Academy of Science, February 1924, and for the same system by Mecke and Lindau(18) in June 1924.

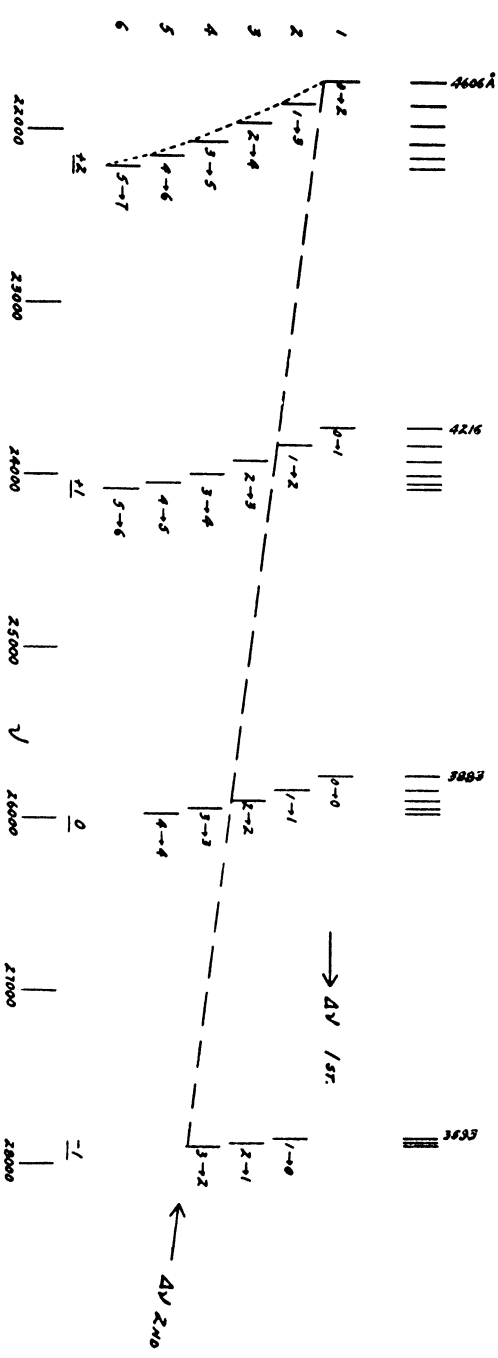


FIGURE 3.—Violet Group of CN. Similar to Figure 2.

emission. In the case of vibration-rotation bands, members only of negative sequences can exist, since in that case there is no electronic loss of energy to more than counterbalance a possible increase in vibrational energy, in the emission process. In this particular system there is a sharp upper limit to the initial vibration number (here $n'=4$), as if the molecule became unstable for more violent vibration, and the resulting successive diminution in the number of bands composing each negative sequence is a very significant feature of this type of spectrum.

From Figure 2 it will be noted that near the less refrangible end of the system, the successive sequences overlap somewhat; but near the violet end each sequence is quite distinct from its neighbors. These two conditions are found often in a much more exaggerated degree. Thus in the first positive group of nitrogen, each sequence is very long and overlaps considerably on the adjacent sequence.[19] The yellow sequence (-3) can be followed for at least five bands into the green sequence (-4), and each of these sequences consists of at least 15 observed bands. The other extreme is illustrated by the violet CN group, which is shown in Figure 3, in the same form as employed for Figure 2. We see here that the different sequences are so widely separated that a grouping together of the series of bands forming each sequence is a most natural one. In fact, it has been customary to speak of each of these sequences as a band composed of several "subheads." This nomenclature is unfortunate as it is convenient to reserve the word "subhead" or "subsidiary band" to denote the various heads or bands having the same vibrational quantum numbers, but compounded as a result of the existence of multiple initial or final electronic quantum numbers. It is impossible to decide whether a set of neighboring related bands are subheads in this technical sense, or successive members of a sequence, except upon the basis of a logical assignment of vibrational quantum numbers for the whole system.[20] Criteria for making such assignments will be discussed later.

[19] See drawing on p. 71 of Birge(19). The true vibration quantum numbers can be obtained from the equations $n''=50-p$, $n'=57-n$, for as already noted, equations (6) apply to this group. This assignment of quantum numbers indicates immediately the true position of the four bands which, in the drawing, are placed simultaneously in two different sequences.

[20] Thus the lines lying between λ3883 and λ3590 are referred to usually as the 3883 CN "band," with its five "subheads." This, however, is actually a sequence of five bands. On the other hand, each band of the first positive group of nitrogen has several true "subheads," by the above definition. See Birge(19) Plates 2 and 3 for this latter system under high dispersion, and Fowler and Strutt(14) Plate 10, Figure 1a, for the same system under low dispersion.

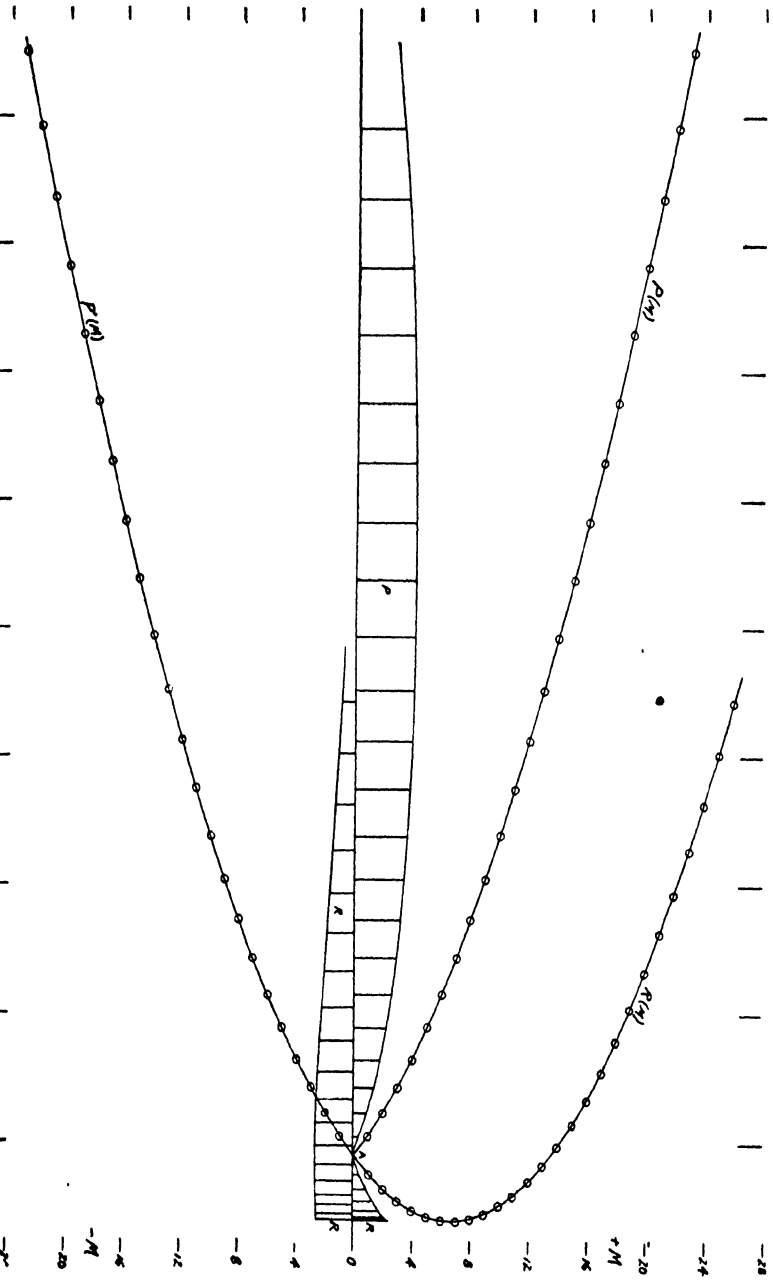


FIGURE 4.—λ4280 Band of CuH. $\nu : M$ Plot, with $P(M)$ Folded over to Give $P'(M)$. Relative Intensity of Lines also Indicated.

PART 2C. THE RELATIONS BETWEEN THE LINES FORMING A BAND

Let us now consider briefly the structure of the series of lines forming a "band," each line corresponding in general to a distinctive change of the rotational quantum number. Fortrat([20]) was the first investigator to suggest the correlation of lines which the quantum theory has since shown to be the correct one. In this arrangement as shown in Figure 4,[21] all of the lines of a band form one series, beginning at the point A. This point, as will be shown in Section 5, is practically coincident with the "origin" of the band. The series has two branches, the R or positive branch proceeding from A toward the violet, the P or negative branch toward the red. The lines of the two branches form essentially a continuous series, except that the line which should fall at A is missing and is sometimes referred to as the "null-line." The intensity of the lines of the two branches is roughly symmetrical with respect to the point A, rising rather rapidly to a maximum and then decreasing more slowly.

The lines of both branches can be represented, to a first approximation, by the parabola

$$\nu = A + 2BM + CM^2 \tag{7}$$

where $M=0$ for the missing line at A, and has successive integral values $+1$, $+2$, $+3$, etc., for the R branch, and -1, -2, -3, etc., for the P branch.[22] It is evident that when $M=-B/C$ the frequency interval between successive lines becomes zero. This point is defined as the "head" of the band. By the method of numbering M, B is always positive, but C may be positive or negative. If it is negative, the head is formed by the R branch, as in Figure 4, and all other lines of the band lie to the red, the band then being said to degrade to the red. If C is positive, the head lies in the P branch, and the band degrades to the violet.

If the intensity in the branch forming the head does not rise to its maximum value and fall again too rapidly, this branch returns across

[21] This figure is a drawing to scale as regards both position and intensity of the lines for a portion of the λ4280 Cu band, shown by Mulliken([21]), from the isotopic effect, to be due to CuH.

[22] Both branches are often plotted against positive values of M. As shown in Fig. 4, we shall, when necessary, use $P(M)$ to denote the frequency formula for the negative branch in terms of positive values of M, and $P'(M)$ to denote the formula for the same branch in terms of negative values. Thus $P'(M)$ is obtained from $P(M)$ by reversing the sign of every odd power term in M, if these functions are assumed to be polynomials in M. It is the mirror image of $P(M)$, formed by the axis $M=0$. If it is found that $P'(M)$ and $R(M)$ are identical functions, we say that $P'(M)$ is the smooth continuation of $R(M)$. In this case the function $R(M)$, which gives the real lines of the R branch with positive values of M, gives also the real lines of the P branch with negative values of M.

the origin, as indicated in Figure 4, so that on the left side of the origin one finds an intermingling of the lines of both branches. This returning branch tends to obscure the origin, since the initial lines in each branch are weak, while it frequently happens that the strongest lines of the branch occur in the immediate vicinity of the head. Moreover, in many if not most bands it would appear that A is so close to the head that it is impossible to resolve the lines between A and the head. Hence we have, historically, a quite different view-point regarding band structure, originally formulated by Deslandres. According to him a band was composed of two series, both proceeding from the head, although it was usually not possible to trace one of these series in the vicinity of the head. Thus, in Figure 4, all of the P branch and that portion of the R branch between A and the head form one Deslandres' series. This is the dominant series at some distance from the head and was often called the main or primary series.[23] The other Deslandres' series comprises the remaining portion of the R series, and since it dies out quickly, as it proceeds from the head, it was called the secondary series. For bands degraded to the violet it is of course the P branch which is thus divided between the two Deslandres' series.

Since Deslandres numbered the lines of each of his series from the head, in terms of what we shall call m_D, his equation can be written [24]

$$\nu = a + b(m_D + c)^2 \tag{8}$$

where c is less than 0.5 and constitutes the "phase" in Thiele's([24]) theory of band series. Unless the observations are very accurate, one can assume $c=0$, and we thus obtain the distinctive Deslandres' "term" bm^2_D. But according to the quantum theory, the distinctive term is $2BM$, in equation (7), where $2B$ gives the separation of successive lines, at the origin. As can be seen, this has no relation to Deslandres' term. We mention this fact because in the first formulation of the quantum theory of band spectra an attempt was made to obtain a second degree

[23] This series can normally be followed until it is lost in some adjacent strong band. Occasionally, however, a series seems to go to pieces, even when no such neighboring band is present, and when the exposure is sufficient to carry it further. This is true of all the series of the λ3883 CN sequence. These first become very irregular as regards frequency, and then disappear at about λ3640, although it should be possible to observe them for some distance further. A very striking example of the *sudden* disappearance of a series at a definite line is that of the calcium hydride band λ3534, recently discussed by Mulliken([22]), who ascribes the phenomenon to resulting instability of the molecule, when the rotational energy reaches a certain limiting value—in this case a relatively low value.

[24] See Birge([23]), pp. 86-89 for a critical review of Deslandres' original statement of this relation, and of the various forms in which it may be expressed.

term in the quantum parameter, to agree with Deslandres' term, and even considerably later this assumed requirement has caused some confusion.[25]

According to equation (7), both branches of the series can be represented by one formula. Recent work seems to indicate, however, that there is often a slight discontinuity at A, so that different formulas are needed for the two branches. Moreover, as has long been known, a simple parabolic formula is far from accurate. Thus the successive separation of lines, instead of being a linear function, was found by Birge([22]), to be accurately a hyperbola, in the case of the main (A_1) series of the 3883 CN band, the longest series thus far known. The lines of this band, at a point far distant from the head, instead of continually increasing in separation, actually begin to draw together again. This fact led to the theory that each band had a "tail" as well as a head. It has since been found that there is no experimental evidence in favor of such a theory, and no such phenomenon is to be expected, according to the quantum theory.

Now if the lines of a band are numbered symmetrically about the point A, of Figure 4, and if the intensity is plotted as a function of M, using positive and negative values, we obtain an intensity distribution precisely similar to that observed in the vibration-rotation bands.[26] This similarity is perhaps the strongest evidence in favor of an analogous interpretation of the two types of spectra. The actual *appearance* of the spectrum of the two types is usually quite different because the intensity in the vibration-rotation bands, due largely to the low temperature of the molecules concerned, reaches a maximum for low values of M, and then falls so rapidly that the "head" has never been reached in any such band. Therefore the missing line A is a conspicuous feature of these

[25] See Sommerfeld's "Atomic Structure," 4th Ed., p. 706.

[26] See Frerichs'([25]), Figure 1, for an illustration of such a plot, for electronic bands. The data for the intensities in Figure 4 are taken from Frerichs' work. It should be noted that while the distribution of intensity is quite similar in the P and R branches, the P branch is somewhat stronger. This is true in the case of nearly every electronic band thus far analyzed quantitatively. In the case of vibration-rotation bands, it is as yet impossible, because of difficulties of interpretation, to say whether a corresponding condition holds true. Fowler([26]) and Dieke([27]) in recent articles, predict that the P branch should be stronger in emission, and weaker in absorption. *Note added in proof.* This prediction has now been verified by Kemble and Bourgin (Nature 117: 789, June 5, 1926) for the fundamental HCl band, as obtained in absorption. The R branch is definitely stronger than the P branch, and the quantitative distribution of intensity in each branch is in good agreement with equation (179) or (182) of Section 6 ahead, under the assumptions given in footnote (151).

bands, while in the case of electronic bands, as already noted, this point is usually well concealed by the returning branch.[27] An arithmetic distinction between the two types is as follows. In the case of the vibration-rotation bands the frequency of the point of minimum intensity of a set of bands is given approximately by ν_n, $2\nu_n$, and $3\nu_n$, while in the case of electronic bands, a Deslandres' progression is given approximately by $\nu_e+\nu_n$, $\nu_e+2\nu_n$, $\nu_e+3\nu_n$, etc., or by $\nu_e-\nu_n$, $\nu_e-2\nu_n$, etc., where ν_e is many times as large as ν_n and, as already noted, has been interpreted as proportional to the energy change involved in an electron transition. The quantum interpretation of the P and R branches of an electronic band is, however, precisely similar to that of the P and R branches of the vibration-rotation bands, as discussed in earlier chapters.[28]

Certain electronic bands, even at ordinary excitation temperatures, have a head which is very weak, or entirely missing, so that the intensity distribution is quite similar to that of the vibration-rotation bands. In such cases it has been customary to speak of the two branches, R and P

[27] As already discussed in Chapters I and III, the distribution of intensity is a function of the temperature, and therefore the various types of intensity distribution just noted can be obtained in the same band, by merely varying the temperature. Thus in the λ3883 CN band, as usually obtained in the arc, the maximum of intensity occurs just at the head, which is therefore very pronounced. But in active nitrogen, where the temperature might be expected to be practically that of the room, the main A_1 series of Deslandres has a conspicuous "hole" at the true origin of the band. See Figure 4b, Plate 6, of Strutt and Fowler[28], as discussed by Birge[29].

[28] It may assist the reader if at this point we make the following brief statement regarding nomenclature. There is still some uncertainty as to the correct quantum designation of the lines of an electronic band, especially in the case of the more complex bands. Hence the matter of nomenclature is frequently the source of much confusion. The nomenclature used in this chapter will be defined more precisely in a later section. We will merely note at this time that Kratzer and many others use m for the number of quanta of angular momentum of the whole molecule in the final state (emission), which in this report is called j, writing $P(m)$ for the line $m-1\rightarrow m$, and $R(m)$ for the line $m+1\rightarrow m$. On the other hand, it is very common practice to use m also for the empirical parameter or "Laufzahl" which we have just designated as M, and to write $P(m)$ and $R(m)$, where we would write $P(M)$ and $R(M)$. In discussing the experimental facts it is very convenient to use this parameter M, whose values can usually be ascertained from a study of the intensity distribution. In order to distinguish it from our j, we write $P(M)$ and $R(M)$, in contrast to P_j and R_j. Thus, if j is not identical with M, P_j and $P(M)$ represent different functions. Moreover, it is possible for M and j to be identical for the R branch, while in the case of the P branch, let us say, $j=M+1$. This condition would be expressed as follows:

$$R(M)=R(j)=R_j. \qquad P(M)=P(j-1)=P_j.$$

as the "head" and "tail" of the band.[29] Examples of this type are the atmospheric oxygen bands, as shown so beautifully on Rowland's maps of the solar spectrum, and the C+H bands.[30] More recent examples are the bands of hydrogen[31] and helium[32] where the low value of M for maximum intensity is due primarily to the small moment of inertia of the molecule, rather than to low temperature.

As already mentioned, Deslandres assumed that, as a first approximation, the $\nu : m_D$ curve of a band series was a second degree parabola. It is probable that there is no band series in which this condition is strictly true for either the $\nu : m_D$ or $\nu : M$ curves, and frequently the deviations are very great.

Even in the case of CuH λ4280, where the deviations from a parabola are relatively small, a rigorous investigation[33] has indicated that it is necessary to use *different* functions for the two branches, and at least a fourth degree polynomial, in each case. Frerichs(25) attempted to fit both branches to a common fourth degree parabola, but the deviations are very great for values of $+M$ or $-M$ greater than 12. This requirement of different analytic functions for the two branches of a series seems to be a general one, although the magnitude of the discrepancy may be so small as to escape notice, without a rigorous least squares investigation. Thus, in Figure 4, the two branches R and P' of the λ4280 band *seem* to be continuous in every respect. But the actual equations required are,[34]

$$R(M) = 23{,}311.080 + 14.6072M - 1.07834M^2 - 0.001155M^3 + 0.0000364M^4. \quad (9)$$

$$P'(M) = 23{,}310.976 + 14.4439M - 1.09105M^2 - 0.003657M^3 + 0.0000138M^4. \quad (10)$$

[29] The head referring to the branch which returns, or tends to return, on itself.

[30] See Figure 3, Kayser's Handbuch, 5: 231; and Strutt and Fowler(28), Figure 7, Plate 6. In this λ4300 C+H band, the confused mass of lines between the head and tail forms a complex "Q" branch. This additional branch is discussed later in the chapter.

[31] Dicke(30), Kiuti(31), H. S. Allen(32), Richardson and Tanaka(33), Curtis(34) and others. See Part 5e ahead.

[32] Curtis(35), Plate 1. Here also a "Q" branch occurs between the P and R branches.

[33] Unpublished work by Birge and Shea, using their rapid method for obtaining the least squares' solution of a polynomial of any degree. See reference (36).

[34] In using the method of least squares, it is necessary first to smooth out any obvious irregularities in the measurements. For this band, the only change thus made was in the case of $P(21)$, where 22,563.06 was used in place of Frerichs' $22{,}562.86\nu$. In each branch the first 25 lines were used, i. e., to $P(25)$ and $R(25)$ inclusive.

The average residual is 0.023ν for the P branch, and 0.028ν for the R branch. The discontinuity in ν at $M=0$, is only 0.104ν, or $0.02A$ and *may*

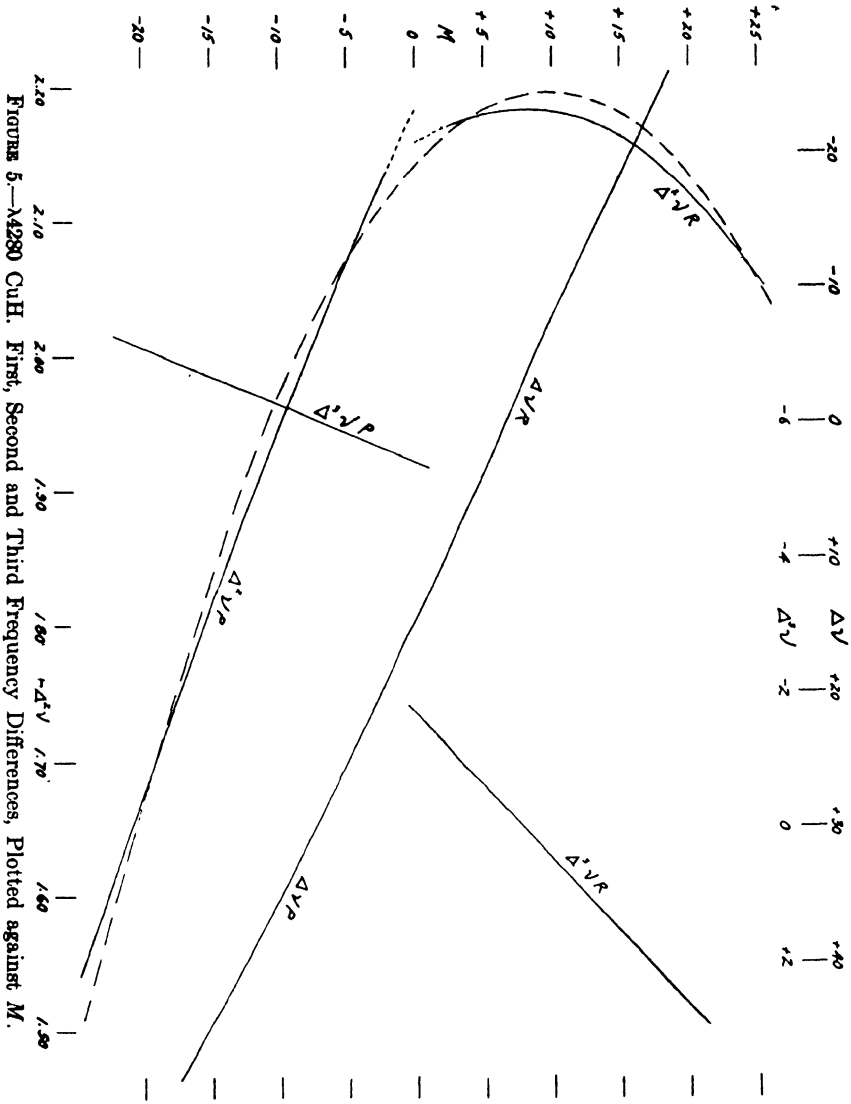


FIGURE 5.—λ4280 CuH. First, Second and Third Frequency Differences, Plotted against M.

be within the limits of experimental error. The differences between the two functions may be shown graphically by plotting the $\Delta\nu : M$, $\Delta^2\nu : M$, and $\Delta^3\nu : M$ curves, and this is done in Figure 5. As will be shown in a later section, these various differences, when plotted against the mean

value of M concerned, are essentially equal to the respective derivatives of the functions given by equations (9) and (10).

In Figure 5, the $\Delta\nu : M$ curves for R and P' are discontinuous at $M=0$ by only 0.163, and again this may be within the limits of error. But the $\Delta\nu : M$ curve for the R branch is almost linear, while that for the P branch has a pronounced curvature. This appears more prominently in the $\Delta^2\nu : M$ curves, where that for the R branch is roughly vertical, while that for the P branch has a large slope. According to Deslandres' law as given by equation (8), this $\Delta^2\nu$ curve should be a vertical line. In Figure 5, the continuous curves correspond to equations (9) and (10) while the broken curve is Frerichs' solution. Here again the two $\Delta^2\nu$ curves may be continuous at $M=0$, but if so, a very complex function would be required to represent simultaneously the two branches. The $\Delta^3\nu$ curves are linear, since a fourth degree polynomial was used, and it is again evident from the great discontinuity of these two curves, at $M=0$, how difficult it would be to obtain a common analytic function for the two branches.

Therefore, assuming that the P and R branches are to a certain degree discontinuous at $M=0$, we reach the interesting conclusion that while according to the original idea concerning band spectra, each band was composed of two series which were presumably discontinuous at the head of the band ($m_D=0$) it now appears that there are indeed two series (or branches), but the point of discontinuity, if present at all, is *not* at the head, but at or near the point of minimum intensity, $M=0$. It is to be emphasized that the most careful investigation has revealed no irregularity in a series as it turns back on itself to form the head of a band.[35] The theoretical aspects of the above relations are discussed at the end of Part 5b ahead.

We have mentioned two deviations from the simple parabolic formula for the $\nu : M$ curve—one the more complex functional form necessary—the other the fact that different equations are needed for the two branches P' and R. These irregularities concern the series as a whole. There remain further types of irregularity which concern particular lines; these are illustrated in Figure 6, which gives the residuals for the C_1 series of the 3883 CN band, as calculated by Birge([37]), from a hyperbolic formula for the $\Delta\nu : m_D$ curve. The so-called C_1 series is the main series of the band λ3862, commonly referred to as the third sub-head of the

[35] In most bands the lines are so crowded near the head that it is impossible to follow the series around this point of reversal, and no definite conclusion can be drawn as to the question of continuity. But in other bands, such as the λ3064 water band (probably due to OH), the lines are far less crowded and the absence of any discontinuity at the head can definitely be proved.

λ3883 band but actually the third band of the 3883 "sequence." The true point of minimum intensity, $M=0$, of the band is at $m_D=30$. Thus the C_1 series includes the entire R branch and a portion of the P branch, the band being degraded to the violet.

Figure 6 illustrates quite vividly the discontinuity at the point $M=0$. In this investigation (reference (37)), which was carried out previous to the advent of the quantum theory of band spectra, an attempt was made to fit the entire C_1 series into a single analytic formula. But it

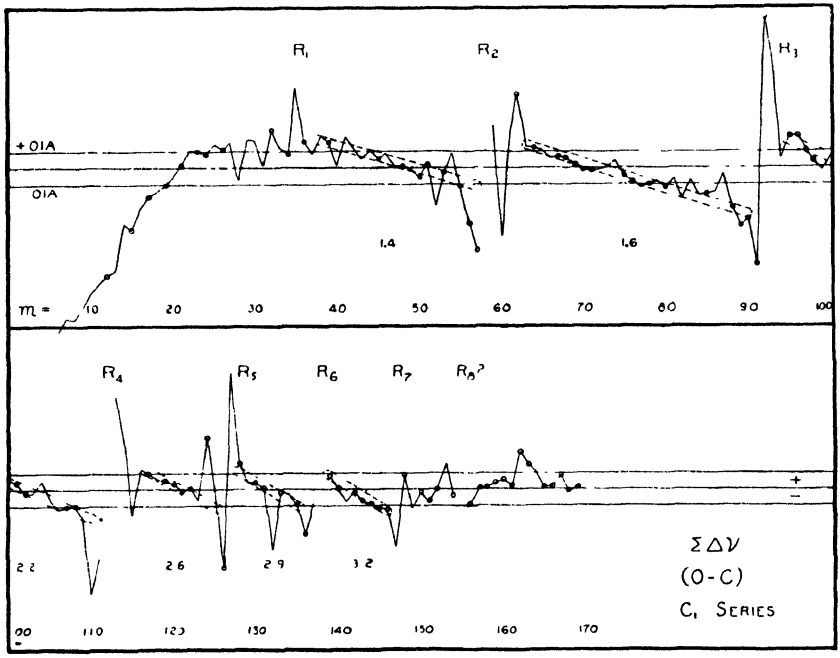


FIGURE 6.—λ3883 CN. Difference between Observed and Calculated Frequencies of C_1 Series. Deslandres Type of Nomenclature

was found that the portion of the series for which m_D is less than about 30, could not be brought into harmony with the remainder of the series. This is shown in Figure 6 by the large values of $(O-C)$ for this portion of the curve. In the case of the A_1 series (the main series of the true 3883 band), the deviation from a smooth curve is far less—so small in fact as to be practically unnoticeable, as is shown by a corresponding representation.[38]

[38] Figure 3, p. 97 of reference (23).

The outstanding irregularities in Figure 6 represent the "perturbations" so well known in many band series. In the case of the 3883 CN sequence, the perturbations increase in size and complexity from λ3883 (the 0→0 band) to λ3862 (the 2→2 band) here shown, and this increase with increasing value of n is always found. The figure illustrates an additional irregularity, evidently connected with the perturbations. The lines of the series do not fall on a smooth curve, such as that employed, but periodically deviate from it, beginning above the analytic curve after each perturbation, and ending below it, before the next perturbation is reached. The points marked with circles represent spectrum lines which are not confused with other lines, and which therefore are alone trustworthy. The dotted lines represent the limits of error ($\pm 0.003A$). This is the only known case of this type of what might be called "periodic" irregularity, but very few series have been examined with enough care to reveal such a condition, even if it did exist.

Two facts in connection with these perturbations are of importance in the quantum theory. One of these, found by Deslandres, as already mentioned, is that the bands forming a Deslandres' first progression possess perturbations of a similar character. The bands of such a series are now known, in all the cases examined, to have the same initial condition of vibration, and hence the perturbations may be assumed to be due to an irregularity in certain initial (higher energy) levels of the molecule. The other fact, discovered by Fortrat([20]), and stated more precisely by Heurlinger([38]), is that in the same band, the perturbations occur in pairs, the lines $R(M)$ and $P(M+1)$ showing similar irregularities of position and structure.[37]

This similarity of the perturbations formed the basis of Fortrat's division of the entire series into two branches, now called P and R.

[37] Heurlinger's([38]) work on the 3883 CN band indicates that the two related perturbations are qualitatively but not quantitatively similar. But a more detailed investigation of this band by the writer (unpublished), indicates that the agreement is quantitative. This agrees with the results of Bachem's([39]) investigation of the effect of a magnetic field upon these perturbed lines. In the case of the triplets of the second group of nitrogen, the quantum interpretation has not yet been carried far enough to decide whether certain corresponding perturbations are actually somewhat different, as is indicated by Lindau's([11]) results. It should be noted also, that the occurrence of similar perturbations at $R(M)$ and $P(M+1)$, where M has the meaning just given, furnishes a very precise method for obtaining the *relative* values of M for the two branches. It does not, however, give any information as to the *absolute* values, such as may be obtained from a study of the intensity distribution, but it is an important fact that in every case investigated, the *relative* numbering of M, as determined by these two criteria, is in agreement.

Heurlinger([38]) in his masterly analysis of the empirical facts of band spectra, adopted this idea, and added the additional criterion of the symmetrical distribution of intensity about the same point of division. With this work by Heurlinger as a basis, the application of the quantum theory to electronic bands was inevitable. Later it was realized by Kratzer([40]), that the two lines $R(M)$ and $P(M+1)$ comprising the two similar perturbations *must* be interpreted in such a way that they correspond to the same initial condition, as regards the *rotational* quantum number, as well as regards the *vibrational*. This necessitated the introduction of half-integral quantum numbers, in the case of series with one missing line.[38] The correctness of such a procedure has since been proved by more direct and convincing lines of evidence, but the perturbations must be credited with having initiated at least two of the most important advances in this field.

Part 2d. The "Q" Branch

Thus far we have tacitly assumed that each true quantum band consists of *one* series (the lines of which may be multiple in structure) composed of two branches R and P. By taking the point of zero intensity as an origin, and numbering the lines of the two branches with positive and negative values of M, as we have done, one may represent both branches by a single $\nu : M$ curve, although in general there may be a more or less pronounced discontinuity at $M=0$. As has been shown in Chapter II, these two branches correspond, on the quantum theory, to transitions in which the rotational quantum number (j) during emission increases by one unit (the P branch), or decreases by one unit (the R branch). In the same chapter it was shown that this quantum number which is taken to represent the resultant angular momentum of the molecule, can also remain constant, during the absorption or emission of radiation, if the resultant angular momentum is not in the same direction as the nuclear angular momentum. The zero change in the value of j gives rise to the so-called Q branch, or zero branch. Kratzer([41]) in a discussion of the correspondence principle, as applied to electronic bands, concludes, on the other hand, that the *presence* of a Q branch does not necessarily imply the existence of angular momentum about the figure axis. He concludes also that under special conditions any one of the three branches,

[38] Thus, if $M = j''$, for both branches, as had been supposed up to that time, $R(M)$ indicates the line $(M+1)' \rightarrow (M)''$, and $P(M+1)$ the line $(M)' \rightarrow (M+1)''$. The two lines are thus seen to have *no* condition in common, when we remember the difference in electron configuration in the initial and final states, making M' a quite different configuration from M''.

P, Q, and R, may be absent. The Q branch occurs in many bands, notably the λ3064 water band([38]), the C+H bands([42]), the Zn, Cd, and Hg hydride bands([43]), the Angstrom CO bands([44]), and the helium bands([35]). It does not occur in the analyzed bands of N_2 and O_2, but does occur in He_2 and H_2.

The observed relation of the Q branch to the R and P branches in the case of a band with *one* missing line between the P and R branches is

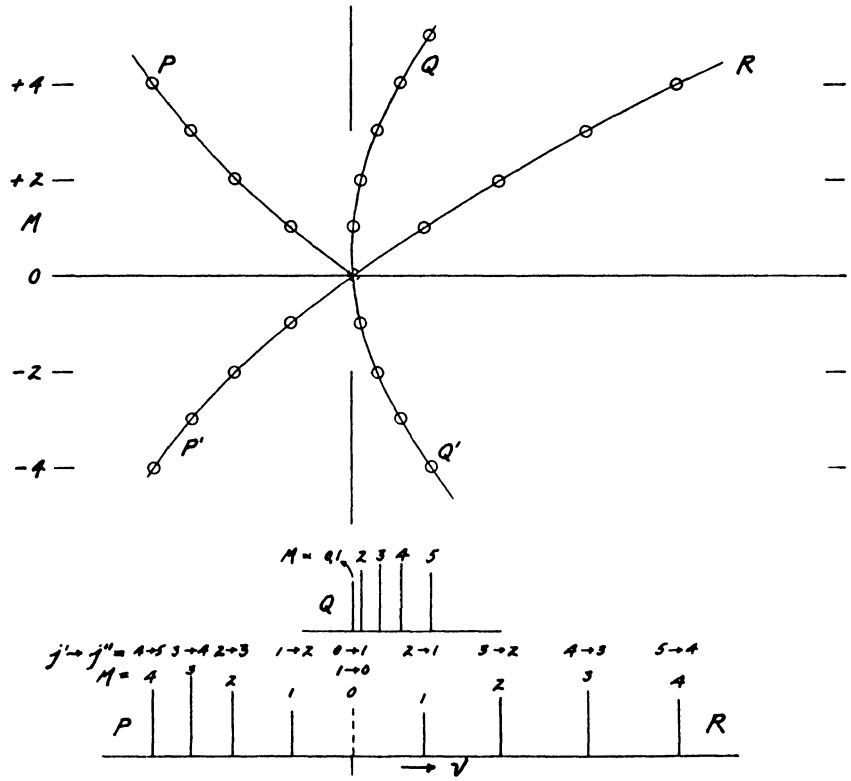


FIGURE 7.—Schematic Representation of P, P', Q, Q', and R Branches. ν Plotted against M. Spectral Lines and Relative Intensities also Indicated.

shown in Figure 7, which is drawn in a manner similar to Figure 4, except that Figure 7 relates to a band degraded to the violet. The λ5610 CO band([44]) is an actual example of the relations shown in this figure. The ordinates are values of M and we number the Q branch in the same manner as the other two, calling the first actual line $M=1$. The $\nu : M$ curve for this new branch is then a parabola with its vertex at $M=+\frac{1}{2}$. The first observable line of the Q branch—the $Q(1)$ line, coincides in

frequency with the missing line $M=0$ for R or P. The theoretical (missing) line $Q(0)$ also coincides with $Q(1)$. The frequency given by the vertex of the Q branch parabola defines the "origin" of a band, and hence is almost, but not exactly, coincident with the missing line between the P and R branches. Since the real $Q(1)$ line coincides with this missing line, we can of course not verify the fact that this latter line is actually missing, but can only assume it by analogy with bands in which the Q branch is absent. It may be noted that in order to make clearer the position of the vertex of the Q branch parabola, we have, in Figure 7, extrapolated this curve into the region of negative M's, calling the extrapolation Q'. Thus Q' and Q are symmetrical with respect to their vertex at $M=\frac{1}{2}$, but P' and P, as previously noted, are symmetrical with respect to $M=0$.

Figure 7 shows also the actual position and relative intensity of the lines of the three branches, for the hypothetical case of the maximum intensity at about $M=3$. While considerable work has been done on the distribution of intensity in the P and R branches, there are practically no published data for the case of the Q branch.[39] We assume, however, that the distribution in the Q branch is very similar to that in the P and R branches.

Part 2e. Intensity Relations

We have mentioned, in Part 2c of this chapter, the fact that the distribution of intensity in a given series is a function of the temperature, so that the general appearance of a given band can be radically altered by suitably varying the temperature. This variation is to be expected, on either classical or quantum theory, from the statistical distribution of rotational energy, and agrees essentially with the predictions of this theory when the conditions are such as to give thermal equilibrium. There is also a predicted variation of intensity of each entire band, compared to other bands of the system due to the distribution of vibrational energy. The predicted intensity variation, for a given change of temperature, is far less in this latter case and accordingly difficult to detect. It seems, however, to be actually present in certain cases where this question has been investigated.

But the experimental evidence indicates quite clearly that the relative intensity of the various bands of a system is a function of other conditions besides temperature; and as yet very little progress has been made

[39] Heurlinger's data, pp. 31 and 34, of (38) form one exception, but the intensities given are not sufficiently accurate for any theoretical deductions. See also Watson(45).

in the theory of this phenomenon even to the extent of identifying the controlling agencies. Finally, in the case of multiple bands, described in the next section, the relative intensity of the two or three components forming each line of the band can be made to vary, by mixing the gas being investigated with other gases. This may be connected with the distribution of energy among the various closely spaced electronic levels which seems to cause certain band multiplicities. All of these intensity variations can be discussed more conveniently after we have considered in more detail the actual quantum interpretation of the bands in question. We accordingly defer the matter to later sections of this chapter.

Part 2f. Multiple Bands

Thus far we have considered each band as though the series were composed of single lines. Such a condition is represented by the Angstrom CO bands([44]) and apparently by the negative carbon bands([46]) (due probably to CO^+), but is quite exceptional, the great majority of series being composed of doublets, triplets, or even higher multiplicities. These multiplicities can be divided, from a practical standpoint, into two distinct classes. Class one consists of a multiplicity in which the spacing of the component members is essentially independent of the value of M, but in class two the spacing is distinctly a function of M. It is probable that in many bands both classes are superimposed. In class one, the spacing, in several of the cases thus far noted, is large (even up to 3600ν in HgH) and thus one finds, experimentally, double-headed bands of constant doublet spacing, such as the β bands of nitrogen([14]), ($\Delta\nu=87$). In so-called "double-double-"headed bands, such as the γ bands of nitrogen([14]), the α bands of BO([47]), and the comet-tail bands([48]) (due probably to CO^+), and many others, the large constant separation (about 120ν for all three) of each of the close doublets doubtless belongs to this class.[40] The separation is due probably to a double electronic energy level, in either the initial or final state, or both, thus giving a double "origin" for the band. This may be interpreted as due to various possible space quantizations of a valence electron, in analogy to the interpretation of the doublets and triplets of line

[40] Baldet's recent analysis ([48]) of the comet-tail bands shows that these are really double bands of constant frequency separation. The two closely adjacent heads of each component of the doublet are due respectively to the turning point of the R branch (ordinary "head" of the band) and the head of the Q branch (the "origin" of the band). It is therefore probable that double-headed bands of constant frequency separation, and double-double-headed bands, differ only in the fact that the latter have a Q branch, while the former do not.

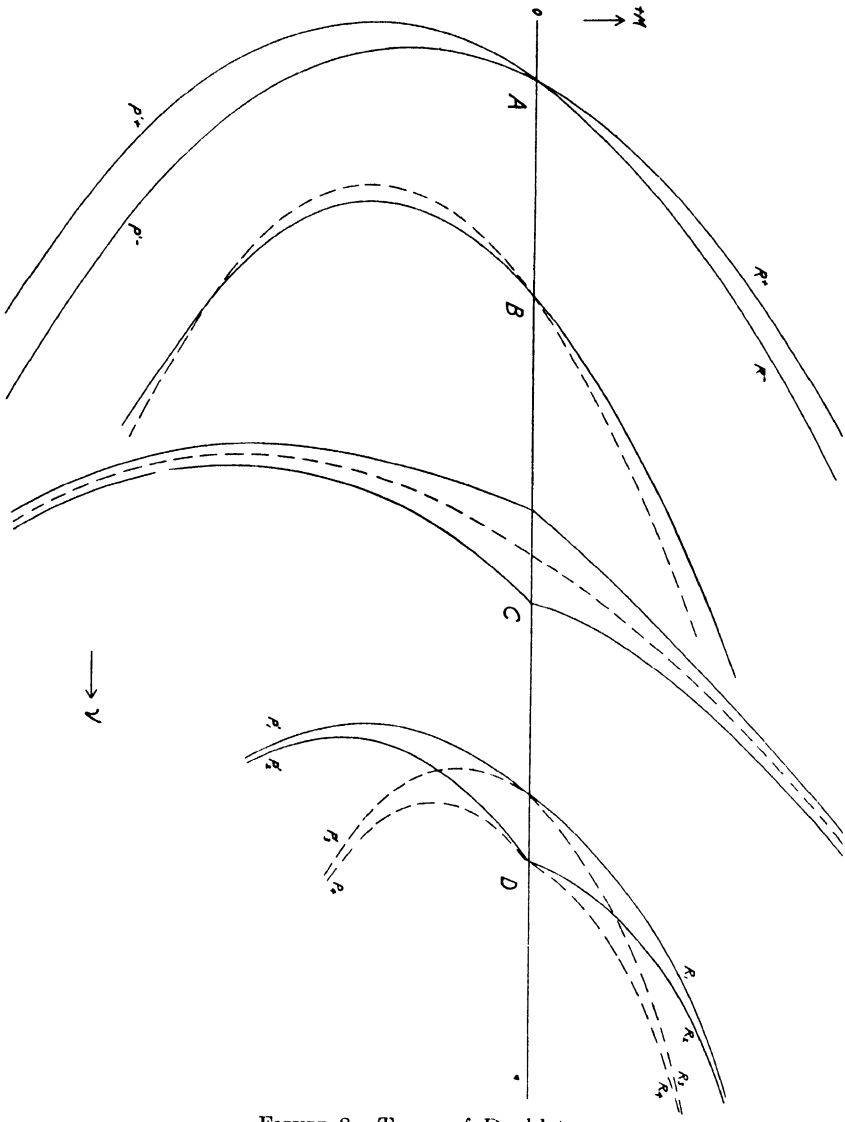


FIGURE 8.—Types of Doublets.

A The Hg and CN type of doublet, discussed in detail in Part 5c. Curve drawn to scale for Hg 4017 (degraded to the violet) except that the M scale is slightly displaced to make the doublet separation equal zero at $M=0$. See Figure 21 for a more accurate drawing.

B. The doubling due to a rotational isotopic effect, discussed in Chapter V.

C. The water-band (OH) type of doublet, discussed in detail in Part 5d. Curve drawn to scale for λ3064, except that this band degrades to the red.

D. Schematic drawing of C+H λ4300 (degraded to violet) with doubling greatly exaggerated. A combination of type *C* and type *A'* doubling. *A'* differs from *A* only in the fact that in *A'* the separation increases as M^2, while in *A* it increases as M. With the omission of the broken curves one obtains λ3900 C+H, except that this band is degraded to the red.

spectra. This idea has been suggested by Mulliken([49]), to whom is due also the general division into classes one and two, now being discussed.

The class two type of multiplicity, in which the spacing varies with M, has been the subject of considerable investigation. Obviously this class may include also class one, and from a theoretical standpoint it may be convenient to *define* any multiplicity in the "origin" of a band as an example of class one. This is not a practical working rule, since the calculated position of the origin, in a complex band, depends greatly upon the exact theoretical interpretation of the multiplicities, and in many bands it is not yet possible to state definitely whether or not the origin is multiple in character. For the present, class two will be considered from the experimental standpoint, ignoring the question as to whether it may, or may not, include class one.

Class two is divisible into several distinct types of multiplicity, some of which have been studied in detail, and are illustrated in Figure 8. In this figure only the P and R branches are shown, even when the band actually possesses a Q branch. The values of M as used are not always such as to agree with the true numbering of M for which the intensity is symmetrical with respect to $M=0$.

Taking up first the question of doublets, we find three different types, illustrated by curves A, B, and C.[41] Curve (A) is drawn to scale for the Hg λ4017 band, from the data of Liese([50]), as arranged by Kratzer([43]). In this type of band, each branch consists of doublets whose separation is, approximately, proportional to M. The doublets may be considered as the symmetrical opening out of two superimposed lines in such a fashion that P'^{+} is the smooth continuation of R^{-}, while P'^{-} is the smooth continuation of R^{+}. The quantum interpretation of such relations is discussed in Part 5c. Heurlinger calls such bands, "singlet" bands, since the doublet separation is zero at or near the origin.[42] The violet CN bands, according to Kratzer([43]), form further examples of this type of band. In these CN bands the doublet separation is about 0.002 as large as in the Hg band plotted in the figure, and within limits of error, the separation is the same in the two branches for equal values of M.[43] This equality of separation includes the perturbations, and since

[41] All of the curves of this figure are drawn as if the bands were degraded to the violet, but the actual λ3064 OH band (curve C) is degraded to the red.

[42] Since there may be some uncertainty as to the position of the origin, a more general statement would be—a band in which the doublet separation decreases as the origin is approached, and becomes zero at or near the origin, is defined by Heurlinger as a "singlet" band

[43] See p. 280 of reference ([29]) and Part 5c ahead, for further details concerning the doublet separation in the CN bands. It increases to a maximum value and then decreases toward zero, as M increases.

these occur at $R(M)$ and $P(M+1)$, as already noted, it would be more accurate to say that the equality of separation is with respect to $P(\frac{1}{2})$. Certain significant differences between the CN and Hg doublets are discussed in Part 5c.

Bachem([39]) has found that in a magnetic field the two components of the doublets of the CN bands are drawn together and may become practically single lines. Moreover, the abnormally wide doublets composing a perturbation are abnormally sensitive to the effect of the field, so that the field tends to obliterate these abnormalities. With respect to this magnetic property, the doublets may be compared to the doublets of line spectra, which in the Paschen-Back effect are reduced to single lines, upon which the normal Zeeman splitting is superimposed. This normal splitting is absent in the series lines of band spectra. Magnetic relations such as these are considered in Chapter VII of this report.

Curve B represents the theoretical doubling of lines due to the rotational isotopic effect, in the case of two species, and is an adaptation of Mulliken's([51]) drawing, in his theoretical paper on this subject. No such doubling is actually observed in the spectrum except in the case of the $0-0$ band, for in other cases one has superimposed upon it a relative lateral displacement of the two curves B_1 and B_2, due to the vibrational isotopic effect. In the rotational isotopic effect the doublet separation is proportional to the frequency distance of each doublet from the origin (i. e., its horizontal distance, in Figure 8), while in curve A, the separation of each doublet is proportional to M (its vertical distance from the origin at $M=0$). In curve B, this doublet separation is 20 per cent of the distance of one component from the origin, and represents roughly the actual isotopic effect, assuming zero vibrational effect, in the case of two diatomic molecules in which the common atom has a mass of 10, and the two isotopes masses of 8 and 12.

A third type of doublet is illustrated by curve C. In this case the doublet separation for large values of M approaches asymptotically a constant value, but for small values of M it rapidly increases as M decreases, becoming a maximum for $M=0$ and generally giving the band a definite double "origin." Heurlinger called such bands "doublet" bands. Curve C is drawn to scale for the $\lambda 3064$ water band, from the data of Heurlinger([38]).[44] The correct quantum assignments for this band are discussed fully in Part 5d ahead. We may note here that by giving half integral values to M as has been done in plotting the figure, the P and R branches for each component coincide at $M=0$. The mean

[44] A second band of this same system ($\lambda 2811$) has recently been measured by Watson([45]).

position of each doublet is shown by the dotted line, which has a slight discontinuity of slope at $M=0$.

Deslandres and d'Azambuja([52]) found that the doublets of the λ3064 band become wider in a magnetic field. It does not necessarily follow that this is a different phenomenon from that shown by most bands where the doublets become united. One must first know the true quantum assignments of the lines forming the doublets.

If the dotted line in curve (C) is considered to be a real series, then this curve may be taken to represent in a general way certain "triplet" bands, such as those composing the second positive group of nitrogen. There is still considerable uncertainty as to the relative values of M for the three components of these triplets, but the middle component of the triplet is similar in every way to the mean position of the λ3064 doublets, while the two outer components of the triplet probably form a doublet of this same type. The mean position of the outer components does not, however, coincide with the middle component, and the relative position seems to be different, for different bands of the same system.

Curve D illustrates a still more complex type of band, of which the λ4300 C+H band is the best, and perhaps at the present time, the only known example. An inspection of this curve seems to indicate that we have here merely the combination of curves A and C. In fact in the λ3900 C+H band, which as Kratzer([53]) has shown corresponds to the same final condition of the molecule, the broken curves of Figure 8 are missing, giving a resulting plot precisely like curve C except that λ4300 degrades to the violet, and λ3900 to the red. An accurate analysis, discussed in Part 5d ahead, shows that one type of doublet is in fact precisely like that for the bands illustrated by curve C. But in the other type of doublet, the separation increases quite accurately proportional to M^2, while in curve A it increases proportional to M. Hence the theoretical interpretation is not the same, and we have here a fourth type of doublet, which we may call type A'. In the case of curve D the representation is purely schematic, the doubling being greatly exaggerated.

At the present time it would thus appear that a majority of the analyzed multiplicities of class two could be classified as singlets and doublets, or combinations of singlets and doublets. The doublets may be divided into the four classes illustrated by curves A, B, C, and a portion of D. The theoretical explanation of curve B is definitely known. The suggested explanation of the remaining curves is considered in some detail in Parts 5c and 5d of this chapter.

In conclusion it may be noted that the foregoing discussion does not by any means exhaust the question of multiplicities in bands. Thus, in the

second group of nitrogen one of the components of the triplet is itself a narrow doublet,[45] and in many cases the two components of this narrow doublet are of quite different intensity. Moreover, the line of greater intensity is alternately the red and violet component of successive doublets. Thus, if the faint component were not observed, the resulting strong lines would appear to form a series in which half the lines were slightly displaced.[46] This latter phenomenon is actually observed in the case of one component of the triplets found in the λ5165 Swan band. These triplets are otherwise much like those in the nitrogen bands. Again, the complex effects found in many bands, under the action of a magnetic field, indicate that many seemingly single lines may actually be quite complex.[47]

SECTION 3. THE MATHEMATICAL FORMULATION OF THE QUANTUM THEORY OF ELECTRONIC BANDS

PART 3A. THE COMBINATION PRINCIPLE AND THE SPECTRAL TERMS OF ELECTRONIC BANDS

The two fundamental postulates of the modern form of the quantum theory are: (1) any mechanism capable of absorbing or emitting radiation can exist in a series of discrete energy states E_1, E_2, E_3, etc.; (2) the mechanism can pass from one energy state to another, and if the energy absorbed or emitted during this transfer is in the form of radiation, the frequency of the radiation is proportional to the energy change of the mechanism.

$$\nu = \frac{1}{h}(E' - E'') = \frac{E'}{h} - \frac{E''}{h} = \nu' - \nu''. \tag{11}$$

The two frequencies ν' and ν'' are called spectral "terms," and the expression $\nu = \nu' - \nu''$ is merely the statement of the well-known Ritz combination principle. (See Chapter II.)

The modern form of the quantum theory thus interprets a spectral term as a number proportional to the energy of a possible state of an emitting or absorbing mechanism, and Bohr in fact introduced the above postulates mainly to obtain an agreement with the combination principle. But it is to be emphasized that this principle is an experimental *fact*, entirely independent of any theory, and one may undertake the necessarily laborious task of isolating and evaluating the entire set of terms

[45] Mecke(54) has recently concluded that a second component is also double, giving the band a quintuple structure.

[46] See Figures 2 and 3 of reference (10) and Figure 1 of reference (11).

[47] See references (55), and many other articles.

connected with a given spectrum without committing one's self to any particular theory. However, we must remember that the important matter in connection with any theory is not the question of its truth or falsity, but the question of its usefulness in correlating previously known facts, and in suggesting methods of obtaining new and significant facts.

Now in the case of line spectra, the main facts concerning the combination principle were known before the advent of the quantum theory, and as just stated, the theory was introduced to account for these facts. In the case of electronic band spectra, the order of events has been reversed. Previous to the introduction of the quantum theory, not a single accurate example of the combination principle was known in electronic bands, although the relations furnished by the Deslandres' progressions formed approximate examples. There are two main reasons for this dearth of information. (1) Electronic bands are so complex in structure that the labor involved in isolating and evaluating the spectral terms is so enormous as to be prohibitive, unless one has a definite idea how to proceed upon such a task. (2) The outstanding regularities in the structure of electronic bands, such as the heads, are actually of no theoretical significance, and hence the previous endeavors to link all of the numerical relations to these heads never led to an exact combination principle. On the other hand, the truly significant features of an electronic band, as far as the combination principle is concerned, are usually rather concealed. Hence the quantum theory of electronic bands has given a brilliant illustration of the usefulness of theories, for it has, besides many other achievements, indicated a systematic method for analyzing a band or system of bands into its spectral terms, and has in the very few years of its existence led to the discovery of literally thousands of accurate illustrations of the combination principle. There are still, however, relatively meager experimental results on which to base any general conclusions, due jointly to the complexity of the subject and to the scarcity of workers in this field.

We have given the preceding statements because it might appear that the logical method of procedure would be to consider in some detail the type of spectral terms found in electronic bands, and then to discuss possible methods of explaining such types. Actually, however, it is more convenient to present first a theoretical formulation of the spectral terms, and then to compare the results with experimental data. The chief reason for emphasizing the spectral terms, rather than the spectral lines, is that the formulation of the former is not only simpler, but gives immediately the latter, by the joint use of the combination principle and the cor-

respondence principle. That is to say, a series of spectral terms indicates the *possibility* of a very large number of spectral lines, but when these terms are interpreted on the quantum theory, only certain combinations of terms are permitted.

While the energy values or spectrum terms associated with the emission of the infra-red vibration-rotation bands are functions of the rotational quantum number j and the vibrational quantum number n, the corresponding terms for the electronic bands are functions of certain electronic quantum numbers, e_1, e_2, . . . (which will frequently be referred to collectively as e), in addition to j and n. In the infra-red vibration-rotation bands we have to do with a single "electronic energy

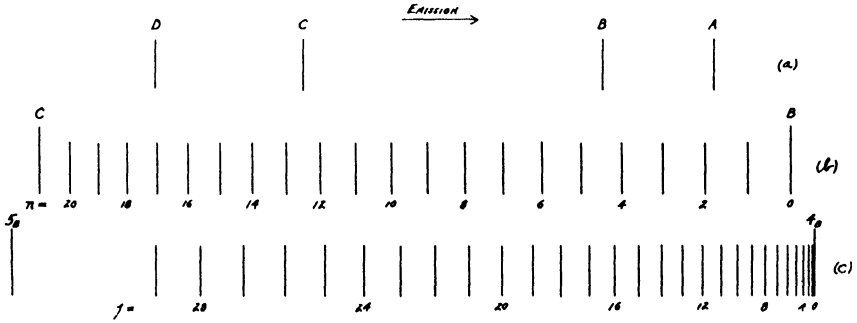


FIGURE 9.—Energy Levels of a Molecule.

(*a*) Set of electronic levels, drawn to scale for the neutral nitrogen molecule. $A - D = 55{,}110$ cm^{-1}.

(*b*) Set of vibrational levels attached to electronic level B, and constituting initial states of the first positive group of nitrogen. $20_B - 0_B = 28{,}477$ cm^{-1}.

(*c*) Partial set of rotational levels attached to vibrational level 4_B, and constituting final states of the λ3710 band of the second positive group of nitrogen. In the λ3371 band, this set has been followed to $j = 96$.

level" and the associated vibrational and rotational sub-levels. The emission of the electronic band spectrum of a given type of molecule, on the other hand, involves more or less numerous electronic energy levels, each accompanied by a full set of vibrational and rotational sub-levels.

As the energy of a given molecule is supposed to be determined by its quantum numbers, we may assume that some general formula of the type

$$E = f(e_1, e_2, \ldots, n, j) \tag{12}$$

must exist which will give all the term values when the quantum numbers are permitted to take on all integral values. But we have practically no knowledge of the nature of the electronic quantum numbers for molecules,

nor of the way in which the energy depends upon them.[48] Hence formulas are useful only in expressing the dependency of the energy on n and j for a fixed set of electronic quantum numbers. Each such set thus has its own empirical energy formula of the type

$$E_A = f_A(n, j), \qquad E_B = f_B(n, j), \ldots . \tag{13}$$

The energy values given by these formulas when n and j are set equal to zero, viz., $f_A(0, 0)$, $f_B(0, 0)$, etc., are sometimes called the electronic energy levels of the molecule. The principal electronic energy levels are rather widely spaced (usually 10,000 to 30,000ν) as indicated by A, B, C, D, in Figure 9 [49] and cover a total frequency interval sometimes as great as 125,000ν. At the present time, such a set of levels is known only for a few molecules, and with the exception of helium (to be discussed later) no conclusions can be drawn as to the law of spacing.[50] In the case of certain multiple bands, each primary electronic level is itself multiple, the $\delta\nu$ intervals for the subsidiary energy levels being usually rather small.

The values obtained by setting j equal to zero [51] in (13) are called vibrational terms or levels. These levels form a Deslandres' progression and are approximately equally spaced (usually 500 to 2500ν) as indicated by the formula

$$f(n, 0) = kn + c, \quad \text{(approx.)} \tag{14}$$

and cover a total frequency interval sometimes as great as 40,000ν. The set of vibrational levels associated with electronic level B is shown on a magnified scale in (b) of Figure 9. If the electronic level is itself multiple, *each* of the electronic sub-levels has its own set of vibration levels. The law of spacing $f(n, 0)$ of the vibrational levels is, of course, different for each electron level A, B, C, D, ...

If e = constant and n = constant, the resulting $f(j)$ consists of a set of so-called rotational terms or levels, spaced so as to give approximately a parabolic law

$$f(j) = k'(j - \epsilon)^2 + c'. \tag{15}$$

[48] Very recent advances in this subject are discussed in Section 8.

[49] This figure is intended as a schematic representation, but is actually drawn to scale, for the case of the neutral nitrogen molecule, except that the probable multiple character of certain sets of levels is not indicated, and the normal level is a fifth level, to the right of A. Compare with Figure 26. ahead.

[50] Important new information on this point is presented in Section 8 ahead.

[51] More accurately, the vibrational levels are given by the condition $m = 0$, as per equation (26) ahead, and the electronic levels by $m = 0$, and $n = 0$, as per equation (23) ahead.

Here the intervals vary from zero, or a very small number, up to possibly 400ν, and the set of levels covers a total frequency interval sometimes as great as $30{,}000\nu$. Thus each vibrational level has attached to it a set of rotational levels, and the spacing of the rotational levels, $f(j)$, is itself a function of the particular vibrational level to which it is attached, and thus indirectly, also of the electronic level to which the vibrational level is attached. A small portion of the set of rotational levels for $n=4$ of the general electron state B, is shown in (c) of Figure 9, on a further magnified scale.

In the simplest case of line spectra—that due to the hydrogen atom—we have a set of so-called electronic levels (actually multiple in character) which are spaced so as to follow the law $f(e)=\frac{k}{e^2}$. For other atoms, the spacing follows the more general law $f(e)=\frac{k}{[F(e)]^2}$, where F may be a rather complex function. The Bohr atom constitutes a *mechanism* which leads to such a set of spectral terms, when the terms are interpreted as energy levels.

Similarly we desire mechanisms which will yield a set of energy levels obeying at least approximately the laws of spacing just stated. As has been shown in Chapter II, the application of the quantum conditions

$$J_i=\int p_i dq_i=\tau_i h \tag{16}$$

to a harmonic oscillator, leads to a possible set of vibrational energy levels

$$E_n=nh\omega^0 \tag{17}$$

where n is an integer, and ω^0 is the frequency of the oscillator. Similarly, a rigid dipole,[52] rotating about an axis perpendicular to its figure axis with frequency ω_m possesses a set of rotational energy levels.

$$E_m=\frac{m^2h^2}{8\pi^2I} \tag{18}$$

where m is an integer, and I is the moment of inertia for the axis of rotation. The frequency of rotation ω_m is given by

$$\omega_m=\frac{mh}{4\pi^2I}. \tag{19}$$

If then we calculate the value of each actual level of what we have called a set of vibrational levels, *relative* to the electronic level to which the set

[52] The term " dipole " is in this report applied to a diatomic molecule, regardless of its polar or non-polar character. Some writers reserve this word for a strictly polar molecule, as judged by its electric moment.

is attached, we obtain approximately the law for a harmonic oscillator, and hence it is natural to interpret such sets of levels as due to the nuclear vibration of a diatomic molecule. If, further, we calculate the value of *each* level of what we have called a set of rotational levels, *relative* to the vibrational level to which it is attached, we obtain approximately the law for a rotating rigid dipole, except that m is in general not integral, and may be written as $(j-\epsilon)$, where j *is* an integer. Hence, assuming for the moment that ϵ=zero, it is natural to interpret such sets of levels as due to the nuclear rotation of a diatomic molecule.

It has already been shown that such interpretations lead to a satisfactory explanation of the near infra-red bands. We need only an additional assumption to explain the existence of a *number* of sets of vibrational levels (with their attached rotational levels), whose spacing gives us what has been called a set of electronic levels. Since the spacing of successive levels in this latter set (usually 10,000 to 30,000ν) is of the order of magnitude found in the spacing of electronic levels in line spectra, it is natural to give a similar interpretation. Hence a molecule is assumed to be capable of existence in a series of electronic energy states, just as is an atom.

Each line of an electronic band is thus assumed to be due to the energy emitted or absorbed as a result of a change in electronic energy of a molecule and this may or may not be accompanied by simultaneous changes in vibrational energy, and rotational energy. The addition of the electronic energy change greatly complicates the resulting phenomena, and in particular produces several important modifications in the theory as developed for near infra-red bands.

(1) When an electron changes from one energy state to another, the entire molecular configuration changes, thus causing every molecular constant (such as the moment of inertia, and the frequency of oscillation) to change in magnitude—sometimes very considerably.

(2) Since the emitted energy correlated with the electron change is so much larger than that due to the vibration change, this latter accompanying change may involve either emission or absorption of energy, whereas in the vibration-rotation bands of the near infra-red, since the vibrational change is the largest, it can occur only in one direction. In addition, the rotational change may take place in either direction, for electronic, just as for vibration-rotation bands.

(3) Due to the presence of electrons, we may have angular momentum associated with their motion, so that it is the *total* resultant angular momentum which should be quantized, rather than that due to the rotating dipole alone. This was found true in the case of vibration-

rotation bands, and led to the modification of equation (18) by the introduction of $(j-\epsilon)$, in place of m. But in electronic bands we have the possibility of the additional complication that the various electronic states may correspond to *different* amounts of electronic angular momentum, i. e., to different values of ϵ. This possible change in the value of ϵ, during emission, offers a wide latitude and considerable uncertainty in the interpretation of certain results, as will appear later.

In this connection we may note a further generalization of equation (18) which applies equally to vibration-rotation bands but which it has not yet been found necessary to use in the case of such bands. Kramers and Pauli([56]), assuming a model of the diatomic molecule in which the electronic angular momentum makes a fixed angle with the figure axis, but has a component $\sigma h/2\pi$ parallel to that axis in addition to the component $\epsilon h/2\pi$ perpendicular to the axis, find that equation (18) is still valid if m is calculated from the formula

$$m = \sqrt{j^2-\sigma^2}-\epsilon. \tag{20}$$

In the form

$$j^2 = (m+\epsilon)^2+\sigma^2 \tag{21}$$

equation (20) is immediately seen to represent the application of the Pythagorean law to the triangle formed by the resultant angular momentum and its components parallel and perpendicular to the axis of figure.

It is commonly assumed, in accordance with the Wilson-Sommerfeld quantum conditions, that j is an integer, though half integral values of j seem to be necessary to account for some of the facts regarding atomic spectra, and this alternative assumption will be considered later, for the case of at least one type of band. Furthermore, the experimental evidence suggests that ϵ is a rational fraction, though no theoretical explanation of this fact has been given.

Part 3b. Formulas for the Energy Levels of a Molecule

Assuming then the presence of a set of energy levels given by at least three distinct parameters, let us endeavor to obtain a more general expression for the energy connected with a definite level. If each type of energy (electronic, vibrational, and rotational) were independent of the other two, it would be relatively easy to obtain such an expression. But as already noted, a change of electronic configuration changes all the molecular "constants," sometimes by considerable amounts. Likewise, a change of vibrational energy changes the molecular "constants," but by a smaller amount. Finally, a change in rotational energy changes the same constants, but (usually) by a still smaller amount.

Thus in the previous expressions for E_n and E_m—equations (17) and (18)—the so-called constants ω^0 and I are in reality functions of the parameters e_s, n, and m (or j). As far as any direct experimental test is concerned, the total energy can be considered as divided only into the three parts

$$E=E(e,\ n,\ m)=E_e+\overset{*}{E}_n+\overset{*}{E}_m. \tag{22}$$

These three portions are defined as follows: If the molecular dipole is neither rotating ($m=0$), nor vibrating ($n=0$), then the total energy is a function of e only, i. e.,

$$E_e=E(e,\ 0,\ 0). \tag{23}$$

This gives what has just been called a set of electronic terms, or levels.

If the dipole is vibrating, but not rotating, the energy will be greater, due to the vibration, and the total *additional* energy is denoted by $\overset{*}{E}_n$, i. e.,

$$\overset{*}{E}_n=E(e,\ n,\ 0)-E_e. \tag{24}$$

Kratzer([4]) has formally divided the energy $\overset{*}{E}_n$ into two parts

$$\overset{*}{E}_n=E_n+E_{en} \tag{25}$$

calling E_{en} a term expressing mutual energy of vibration and electronic configuration; but such a division of the energy has no simple physical meaning, so long as we have no definite model of the molecule, and in this report no attempt will be made to distinguish between $\overset{*}{E}_n$ and E_n. The total energy is thus

$$E=E_e+\overset{*}{E}_n=E_e+E_n \tag{26}$$

and represents what we have called a vibrational energy level, while $\overset{*}{E}_n$ or E_n represents the separation of a vibrational energy level from its parent electronic level E_e.

If, finally, the dipole is both vibrating and rotating, then, due to the rotation, there will be an additional amount of energy $\overset{*}{E}_m$, given by

$$\overset{*}{E}_m=E(e,\ n,\ m)-E_n-E_e. \tag{27}$$

This additional energy represents, therefore, the separation of a rotational energy level from its parent vibrational level, the rotational level itself being given by the first term in equation (27), i. e., by equation (22). The term $\overset{*}{E}_m$ may be considered, formally, as made up of three portions

$$\overset{*}{E}_m=E_m+E_{nm}+E_{em} \tag{28}$$

where E_m is to be considered as a function of m, but not of n, while E_{nm}

is such a function that it becomes zero when *either n or m* equals zero, and may be considered to represent the mutual influence of rotation and vibration. In addition to E_m and E_{nm}, defined as just stated, E_m includes a further amount of energy which we represent by E_{cm}. Kratzer refers to this term as the effect of rotation upon the electronic configuration and attempts to evaluate it in a manner to be discussed presently.

The entire expression for the energy may then be divided formally into the five parts

$$E = E_e + E_n + E_m + E_{nm} + E_{cm}. \tag{29}$$

The formal character of this division of the energy is immediately evident when one considers that every molecular constant, such as ω^0 and I, is necessarily a function of the electronic configuration. Thus every coefficient of equation (29) is at least an implicit function of e and has in general a different value for the initial and final state of the molecule, in the case of electronic bands.

Kratzer(57), (43) and (4) has examined various terms in equation (29), both individually and collectively. The only strict calculation, based upon the usual quantum conditions, that has been made by Kratzer(57)[53] is for the case of a rotating non-harmonic vibrating dipole, with the term E_{cm} not specifically considered.[54] The result is as follows:

$$\begin{aligned} E &= E_n + E_m + E_{nm} \\ &= nh\omega^0(1 - xn + \ . \ . \ .) + \frac{m^2h^2}{8\pi^2 I_0}(1 - m^2u^2 + \ . \ . \ .) - m^2nah \end{aligned} \tag{30}$$

where [55]

$$\left.\begin{aligned} x &= (\tfrac{3}{2} + \tfrac{15}{2}b + \tfrac{3}{2}c + \tfrac{15}{4}b^2)u \\ u &= \frac{h}{4\pi^2 I_0 \omega^0} \\ a &= \tfrac{3}{2}\omega^0 u^2(1 + 2b + \ . \ . \ .). \end{aligned}\right\} \tag{31}$$

I_0 indicates, as usual, the moment of inertia for no vibration and infinitesimal rate of rotation. ω^0 denotes the frequency of vibration for

[53] Certain of the details of this work are given only in Sommerfeld(7).

[54] The quantization of a rotating dipole, vibrating non-harmonically, was first carried out by H. Sponer, using the Hamilton-Jacobi partial differential equation, in an unpublished dissertation (Göttingen 1920). The problem of the intensity distribution among the vibration states, and among the individual lines of the *P* and *R* branches was also considered. The work of Kratzer was quite independent and since it represents a somewhat greater development of the subject, is followed in this report.

[55] The expression for x is given correctly by Kratzer in equation (13) p. 297 of(57), where $c_3 = b$, $c_4 = c$; but in the "Atombau," the term $\frac{15}{4}b^2$ is given incorrectly with a negative sign.

no rotation and infinitesimal amplitude of vibration. b and c are constants of the assumed law of force of the molecule.

Kratzer([43]) later discussed in more detail the question of electronic energy. The term E_e was assumed, as in equation (23), a function of e only. In the term E_m there was introduced an important modification, as noted earlier in this section—namely the substitution of $j-\epsilon$, in place of m, if the resultant electronic momentum is taken as perpendicular to the figure axis. Thus, m as used in equation (30) is not confined to integral values. I_0 is of course always a function of e. Kratzer's main object in this paper was to evaluate the term E_{em}. This he succeeded in doing in a rather formal manner[56] obtaining

$$E_{em}=2\delta h(j-\epsilon)=2\delta h m. \tag{32}$$

In this expression ϵ is intrinsically positive when it is in the same direction as m, and negative when in the opposite direction. Kratzer in order to explain certain types of "doublets," assumes that ϵ may be either positive or negative, and finds that δ changes sign with ϵ. Hence he writes, more generally

$$E_{em}=\pm 2\delta h(j\mp\epsilon). \tag{32'}$$

For the present, ϵ and δ will each be considered to include its own intrinsic sign, so that equation (32') reduces to equation (32).

In thus assuming a possible double sign for ϵ, Kratzer ignores one of the demands of the theory of Kramers and Pauli([58]). These investigators found that the molecular motion was unstable, when ϵ and m had opposite signs. Arguments based on considerations of mechanical stability are, however, of doubtful value in quantum theory, and since Kratzer's assumption seems to be supported by certain experimental facts, too great weight need not be attached to the objections of Kramers and Pauli. Kratzer([41]) in a discussion of molecular models and band spectra, has taken this same position.

Retaining for the present Kratzer's expression for E_{em}, the entire energy of the molecule is given by equation (29) where

$$E_e=f(e) \text{ only} \tag{33}$$

$$E_n=nh\omega^0(1-xn+\ \ldots) \tag{34}$$

$$E_m+E_{nm}+E_{em}=\dot{E}_m=\frac{m^2h^2}{8\pi^2I_0}(1-u^2m^2+\ \ldots)-m^2nah+2\delta hm. \tag{35}$$

[56] Grave objections to the form of this solution, from the theoretical side, will be mentioned presently.

In comparing this last equation with the experimental results, it is customary to employ certain abbreviations, as follows,

$$\dot{E}_m = 2\delta hm + B_n hm^2 - B_0 hu^2 m^4 + \ldots \tag{36}$$

where

$$B_n = B_0 - an = \frac{h}{8\pi^2 I_n} \quad \text{(defining } I_n\text{)}. \tag{37}$$

$$B_0 = \frac{h}{8\pi^2 I_0}. \tag{38}$$

Equation (30), with the notation of equation (38), is merely equation (37) of Chapter II, since na, as defined by equation (31) of this chapter, is identical with a_n as defined in Chapter II.

In considering the physical significance of the various terms in (33) to (35), it is convenient to use a further equation of great theoretical importance, which has already been mentioned in Chapter II (p. 32). If a system possesses a number of periodic motions of frequency ω_i and if the energy can be expressed as a function of the various phase integrals $J_i (= \int p_i dq_i)$, then

$$\omega_i = \frac{\partial E}{\partial J_i} = \frac{1}{h} \frac{\partial E}{\partial \tau_i}. \tag{39}$$

The first equality is true according to the classical theory, and the second follows from it if the symbol τ_i is used to denote the classically permissible nonintegral values of J_i/h as well as the integral values of the quantum theory.[57]

Thus if the effective vibrational energy E_n is given in general by a function of the form

$$E_n = nh\omega^0 (1 + a_1 n + a_2 n^2 + a_3 n^3 + \ldots) \tag{40}$$

then

$$\omega^n = \frac{1}{h} \frac{\partial E}{\partial n} = \frac{1}{h} \frac{\partial E_n}{\partial n} = \omega^0 (1 + 2a_1 n + 3a_2 n^2 + \ldots) \tag{41}$$

[57] The relation

$$\omega_i = \frac{\partial E}{\partial \tau_i}$$

assumes that E is a continuous function of the τ's given by classical theory. Empirical observations give us only a finite number of values of E for corresponding quantized values of the τ's. If the number of points is sufficient to permit the setting up of a continuous function of the τ's interpolated between the discrete experimental values, the above equation may be applied to this empirically evaluated expression for E. Clearly, however, this procedure is inexact if the function E (τ_i) is not smooth, e. g., when perturbations occur.

where ω^n is the frequency of the nuclear vibration as a function of n, for *zero* rotation of the molecule.[58]

Similarly, since the resultant angular momentum of the molecule is conserved and consequently can be quantized, the frequency of rotation about the invariable axis, for any value of j and n, is given by

$$\omega_j(n) = \frac{1}{h}\frac{\partial E}{\partial j} = \frac{1}{h}\frac{\partial \overset{*}{E}_m}{\partial j}. \tag{42}$$

When σ in equation (20) is zero, the axis of j coincides with the perpendicular to the figure axis, and there is no precession. Hence ω_j becomes merely the frequency of revolution of the nuclei about that axis,[59] and may be written ω_m where $m = j - \epsilon$, as usual, and ϵ is assumed *constant*. Or we may write (42) as

$$\omega_m(n) = \frac{1}{h}\frac{\partial E}{\partial m} = \frac{1}{h}\frac{\partial \overset{*}{E}_m}{\partial m}. \tag{43}$$

Since m measures the amount of nuclear momentum, the frequency of revolution ω_m must necessarily equal zero when m is zero. But Kratzer's *first* power term in m, as given in equation (35) makes $\omega_m = 2\delta$ when $m = 0$. Hence any formula for rotational energy which contains a first power term in m (or j) necessarily conflicts with the very general equation (39). Moreover, Kratzer's ([43]) derivation of this $2\delta hm$ term in equation (35) is based on an alteration of the "inner energy" H_0 because of a perturbative term which gives rise to the Coriolis or rotational forces. But the "inner energy" H_0 is, to terms of first order, an adiabatic invariant unaffected by the perturbative potential.[60] Consequently any change in H_0 should be of the order $(m/M)^2$ where m/M is the ratio of the mass of the electron to that of the nucleus. As the rotational energy is of the order m/M compared to the electronic energy, this means that δ at best could be a small quantity of the order m/M, whereas, as appears in Part 5c ahead, Kratzer uses values as large as 2.5. Now it is shown by equation (65) ahead that any apparent first power term in m can be eliminated by a suitable change in the values of m from the customary integral or half-integral values. It is, however, convenient in handling the experimental data to assume at first these customary values, and then, if a finite value of δ results, to eliminate this by appropriate transformation. In the following discussion it is

[58] Since $\overset{*}{E}_m$ contains all the terms in m, and $m = 0$ for zero rotation, we can replace E by E_n, in equation (41).

[59] I. e., we associate the frequency of nuclear rotation with the quantum number j. See Born, "Atommechanik," pp. 117-119, for a discussion of this point

[60] See Bohr, "Quantum Theory of Line Spectra," p. 48.

necessary to assume that $\delta=0$, whenever equation (39) is employed; but in such cases it is to be understood that the real assumption is merely that the values of m have if necessary been so adjusted as to *make* $\delta=0$. In other equations, in which δ appears, the values of m have not been so adjusted.[61]

Equation (43), holding for the case of no precessional motion, not only evaluates the frequency of nuclear rotation, but gives also at least an average value for I, as a function of m and n. Thus, since ϵ is assumed constant, in $m=j-\epsilon$, the nuclear angular momentum is constant and is given by

$$\dot{\phi}I=\frac{mh}{2\pi} \tag{44}$$

where $\dot{\phi}$ denotes the instantaneous angular velocity. Let the average I be defined by the equation

$$\bar{I}=\frac{\dot{\phi}I}{2\pi\omega_m}. \tag{45}$$

Then

$$\bar{I}=\frac{mh}{4\pi^2\omega_m}=\frac{mh^2}{4\pi^2\dfrac{\partial E}{\partial m}}=\frac{mh^2}{4\pi^2\dfrac{\partial \overset{*}{E}_m}{\partial m}}. \tag{46}$$

From equation (36), under the stated condition of no precession ($\sigma=0$), and the necessary condition $\delta=0$, one obtains, for very small values of m,

$$\frac{\partial \overset{*}{E}_m}{\partial m}=2B_nhm. \tag{47}$$

Substituting this in equation (46), and using equation (37), we have

$$\bar{I}=\frac{h}{8\pi^2B_n}=I_n. \tag{48}$$

Thus the quantity I_n, defined by equation (37) represents actually the average value of the moment of inertia, as a function of n, for the case of vanishingly small rotation. Moreover, by equations (37) and (38),

$$\frac{1}{I_n}=\frac{1}{I_0}\left(1-\frac{8\pi^2I_0an}{h}\right), \tag{49}$$

proving that I increases with n, since a is found by experiment to be always positive.[62]

[61] The writer is indebted to Prof. J. H. Van Vleck and Prof. E. C. Kemble for much of the foregoing theoretical discussion of the "δ" term, and to the latter for the following discussion concerning $\bar{I}$.

[62] This result is at variance with Kratzer's statement on p. 319 of reference (4) that the vibration produces a decrease in the mean value of I. Boguslawski(58) obtained in 1914 a result agreeing in form with equation (49). See p. 76 of Born, "Atommechanik."

The above results show that, to a very close approximation, the E_{nm} term of equation (35) might be omitted, if I_n were substituted for I_0. Hence this mutual energy term can be thought of as resulting from the change of average value of the moment of inertia with vibration. But it may also be thought of as resulting from the change of the frequency of vibration with m. Thus the frequency of vibration, as a function of m and n is, by equations (29), (34) and (35), assuming $\delta=0$,

$$\omega^n(m)=\frac{1}{h}\frac{\partial E}{\partial n}=\omega^0(1-2xn+\ \ldots)-am^2. \tag{50}$$

Hence,

$$\omega^0(m)=\omega^0\left(1-\frac{am^2}{\omega^0}\right)=\omega^0(1-\gamma m^2), \tag{51}$$

the last member giving the form in which this relation is stated by Kratzer([4]). Thus again, to a very close approximation, the E_{nm} term of equation (35) may be omitted, provided ω^0 in (34) is replaced by $\omega^0(m)$, as defined by equation (51). Equation (50) shows that the frequency of vibration decreases as the amplitude of vibration increases. This is the usual deviation from Hooke's Law, and follows from any reasonable law of force.

Let us now use the equation (46) to evaluate $\overline{I}$ as a function of m, for $n=0$, in which case the *average* value $\overline{I}$, is of course a *constant* value. From equation (36), assuming $\delta=0$, and $n=0$,

$$I=I_m=\frac{mh^2}{4\pi^2(2B_0hm-4B_0hu^2m^3+\ \ldots)}=I_0(1+2u^2m^2+\ \ldots), \tag{52}$$

giving a quantitative measure of the "stretching" of the dipole, due to rotation. This result may be used to interpret the E_m term of equation (35). This term includes not only the ordinary kinetic energy of rotation (E_r), for the condition of zero vibration, but also the potential energy (U_r) stored up as a result of the above-mentioned expansion of the dipole. Since the angular momentum (p) is here constant and equal to $mh/2\pi$, the kinetic energy of rotation equals

$$E_r=\tfrac{1}{2}I_m(2\pi\omega_m)^2=\frac{\tfrac{1}{2}p^2}{I_m}=\frac{m^2h^2}{8\pi^2I_m}. \tag{53}$$

Therefore, from equations (53), (52) and (35),

$$E_m=E_r+U_r=\frac{m^2h^2}{8\pi^2I_0}(1-2u^2m^2+\ \ldots)+\frac{m^2h^2}{8\pi^2I_0}(u^2m^2+\ \ldots). \tag{54}$$

The last term of equation (54) thus evaluates the potential energy due to expansion of the dipole, and is of importance in determining the field of force of the molecule, as deduced from rotational energy data. This is discussed in Section 8 ahead.

It has been stated, earlier in this section, that from the experimental data one can determine a set of spectral terms, interpreted as energy levels, and that by finding the separation of each level from certain parent vibrational and electronic levels, it is possible to evaluate the three portions of the energy in equation (22). As a matter of fact, the experimental data yield directly[63] only the values of the separation of one level from another—i. e., the values of $\Delta \overset{*}{E}_m$ and of $\Delta \overset{*}{E}_n$ (or ΔE_n, by equation (26)).

We have derived an expression for $\overset{*}{E}_m$ as a $f(m)$, where m is given in general by equation (20). In this latter equation j indicates the resultant angular momentum of the molecule, and has hitherto been considered to be integral. This assumption is open to question as previously stated, but regardless of that matter, there seems to be convincing evidence that j can vary in the process of emission or absorption of radiation only by $+1$, -1, or 0. Equation (20) shows that if σ is not zero, the corresponding variation in m is not $+1$, -1, or 0. Hence the experimental data give us the values of $\Delta \overset{*}{E}_m$ and ΔE_n corresponding to integral changes in the parameters j and n, but to unknown changes in m, so long as σ is unknown.

[63] In anticipation of certain difficulties of interpretation in the case of the helium bands, the negative nitrogen bands, and others, the following statement may be made. Only in the case of bands having three branches (P, Q, and R) connected by the expected relations of the combination principle, is it possible from the data to evaluate a complete set of spectral terms, independent of any theory. In such a case either the P and Q, or R and Q branches, are sufficient to make the evaluation, the other pair giving an absolute check upon the work. If one branch is missing (usually, from appearances, the Q branch), there is in the first place a possible ambiguity in the interpretation of the two branches actually present. By assuming a value for ϵ' different from that for ϵ'', it is possible to make the theoretical Q branch ($\Delta j = 0$) appear in the spectrum exactly like a P or like an R branch. Hence apparent P and R branches may be interpreted theoretically as actual P and Q, or Q and R branches, as has been done by Dieke(59) in the case of the negative nitrogen bands. But in this case, as in the case of all bands having only two branches (apparently P and R) it is not in general possible to obtain the complete set of levels, in a purely arithmetic fashion. Instead, we find that alternate lines of each branch of each band of a system, or even of several systems, may be combined to give a set of levels, or terms. The remaining lines of all the bands concerned then yield *another* set of terms which may, as far as the *arithmetic* relations are concerned, be displaced *any* arbitrary distance with respect to the first set. Only in case we have "combination" bands, such as Mulliken(47) seems to have found in the BO band groups and Birge(60), in the case of the first negative group of carbon, comet-tail bands, and a new set of bands (all due to CO^+), is it potentially possible to obtain the actual relative displacement of the two sets of levels, independent of any theory. The details of this matter are given in Section 5 ahead, in connection with Figure 17.

Now as will be shown in the following section, by properly defining $\Delta\overset{*}{E}_m$ in relation to the initial and final values of j correlated with it, we have, very approximately

$$\frac{d\overset{*}{E}_m}{dj} = \Delta\overset{*}{E}_m \quad \text{for} \quad \Delta j = 1. \tag{55}$$

Hence it is possible, from the experimental data, to obtain the numerical values of $\frac{d\overset{*}{E}_m}{dj}$, as a $f(j)$, and also of $\frac{dE_n}{dn}$ as a $f(n)$, since n varies always by unity, between adjacent vibrational energy levels. In evaluating the molecular constants, δ, ϵ, σ, B_n, ω_m, ω^0, and x, these derivatives are of the highest importance.

In discussing them it is convenient to use the energy divided by h, since this, with the proper choice of origin, corresponds to the various spectral terms. We shall accordingly define

$$\frac{\overset{*}{E}_m}{h} = F, \qquad \frac{E_n}{h} = G \tag{56}$$

and can then say that $\frac{dF}{dj}$ and $\frac{dG}{dn}$ are the important quantities, for evaluating molecular constants.

We have now from equations (34) and (41)

$$\frac{1}{h}\frac{\partial E_n}{\partial n} = \frac{\partial G}{\partial n} = \omega^n = \omega^0(1 - 2xn + \ldots) = \Delta G_n \text{ (approx.)} \tag{57}$$

where ΔG_n is the experimental value of the separation of adjacent vibrational spectral terms. Hence one can obtain immediately the value of ω^n, the frequency of vibration for zero rotation, as a function of n. ω^0 is the special value of this quantity for infinitesimal amplitude, and $2x$ its initial percentage rate of variation with n.

From equations (36) and (43) we have

$$\frac{1}{h}\frac{d\overset{*}{E}_m}{dm} = \frac{\partial F}{\partial m} = (2\delta) + 2B_n m - 4B_0 u^2 m^3 + \ldots. \tag{58}$$

Because of the small magnitude[64] of u, it is only the first two terms

[64] u is defined in equation (31) and equals the spacing of adjacent lines in a band series, in the vicinity of the origin of a band $\left(= \frac{h}{4\pi^2 I_0}\right)$ divided by the spacing of adjacent bands in a Deslandres' progression $(= \omega^0)$. Another mode of expression is to say that it equals the frequency of rotation for one Bohr unit of angular momentum $\left[= \frac{h}{4\pi^2 I_0}\right.$ by equation (19)$\left.\right]$ divided by the frequency of vibration ω^0.

of equations (36) and (58) which are of real importance, especially when m is small. Hence we may write, for *small* values of m

$$F = 2\delta m + B_n m^2 \tag{59}$$

$$\frac{dF}{dm} = 2\delta + 2B_n m \tag{60}$$

where in general $m = \sqrt{j^2 - \sigma^2} - \epsilon$.

These last two equations are of fundamental importance for the determination of the molecular constants δ, ϵ, σ, B_n and ω_m, connected with rotational motion, just as is equation (57) for the vibrational constants ω^0 and x. It must be recalled, however, that only $\frac{dF}{dj}$ can be determined directly from experimental data. Therefore certain additional assumptions are necessary in order to make the evaluation. We shall confine the present discussion to certain special cases.

Let us first assume $\sigma = 0$ (no angular momentum about the figure axis). Then

$$\frac{dF}{dm} = \frac{dF}{dj} = \Delta F_j \text{ (approx.)} \tag{61}$$

where ΔF_j is the experimentally determined separation of adjacent rotational spectral terms. From equations (60) and (61) we have

$$\frac{dF}{dj} = 2\delta + 2B_n(j - \epsilon) \tag{62}$$

or

$$\frac{dF}{dj} = 2B_n\left(j - \epsilon + \frac{\delta}{B_n}\right) = 2B_n(j - {}^{*}\epsilon) \tag{63}$$

where

$${}^{*}\epsilon = \epsilon - \frac{\delta}{B_n}. \tag{64}$$

Now it should be noticed that from the *experimentally* determined value of $\frac{dF}{dj}$, as given in equation (63), we may deduce

$$F = B_n(j - {}^{*}\epsilon)^2 \tag{65}$$

and by defining $m = j - {}^{*}\epsilon$, we get rid of the first power term in m, or j, of equation (35), and hence of the difficulties concerning Kratzer's "δ." In other words, equation (65) differs from (59) only by a constant quantity, and this quantity is experimentally indeterminate. We may

therefore assume that (65) is the correct expression,[65] rather than (59), but for the sake of consistency, we shall in this section continue to present Kratzer's theory. Equation (63) is linear and from its slope we can immediately evaluate B_n. This quantity gives us, by equations (37), (48) and (49), the average value of the moment of inertia, as a function of n. According to Kratzer's theory, this quantity should vary linearly with n, and this Kratzer([40])([43])([61]) has found to be true, especially in the case of the violet CN bands. In connection with equation (63) it is to be noted that on Kratzer's theory, $\overset{*}{\epsilon}$ may have equal positive and negative values since δ changes sign with ϵ, according to equation (32′).

It is evident from equation (63) that ϵ and δ cannot be evaluated separately, since δ can always be combined with ϵ to give an effective $\overset{*}{\epsilon}$. But it is to be recalled that equation (62) or (60) holds only for small values of m, or of j. For larger values, where equation (58) takes the place of (60), δ still occurs, to the given degree of approximation, only in the constant term, while ϵ appears now in the form of higher powers of $(j-\epsilon)$ or m. Hence ϵ and δ can no longer be considered equivalent to an effective $\overset{*}{\epsilon}$. In the case of the Hg bands, Kratzer([43]) found certain numerical relations between various lines for larger values of m which apparently could be explained in terms of equation (58) only by assuming a definite value of ϵ. Hence from equation (62), δ could be evaluated. This constitutes Kratzer's experimental justification for his "δ" term.[66]

In the general case given by equation (63), we have $j=\overset{*}{\epsilon}$ when $\dfrac{dF}{dj}=0$. If the absolute values of j for the initial and final states associated with the various band lines were known, this would permit a graphical evaluation of $\overset{*}{\epsilon}$. If the j values are not known, it is still possible to determine the difference between $\overset{*}{\epsilon}$ and the nearest integer. Now it is usually assumed that ϵ is a proper fraction, and if we also assume that $\delta=0$, the above scheme leads to a definite value of ϵ and finally to the location of the absolute values of j. Another method of determining the absolute j values by assumptions concerning missing lines is discussed in Section 5 ahead.

[65] Some investigators use ρ, in place of $\overset{*}{\epsilon}$ in equation (65) but use ϵ for all higher (even-power) terms. In order, however, to avoid the objections to the "δ" term, we must write $m=j-\overset{*}{\epsilon}$ and hence must use $\overset{*}{\epsilon}$ in *all* terms. In order to avoid confusion we therefore employ the symbol $\overset{*}{\epsilon}$, rather than ρ, although the two are equivalent when terms in F above the second power are not considered.

[66] This work is discussed in detail in Part 5c of the chapter.

Let us next assume that neither ϵ nor σ is zero. Then we have, from equation (59)

$$\frac{dF}{dj} = 2\delta \frac{d}{dj}(\sqrt{j^2-\sigma^2}-\epsilon) + B_n \frac{d}{dj}(\sqrt{j^2-\sigma^2}-\epsilon)^2. \tag{66}$$

This is evidently *not* a linear equation, except for $\sigma=0$, when it reduces to equation (62). But since σ is small, it becomes rapidly linear, as j becomes large. Conversely, a rapid deviation from linearity of the $\frac{dF}{dj} : j$ plot, as j becomes small, should constitute definite evidence that σ is not equal to zero.[67] Now, in most of the bands thus far analyzed, no such deviation is found, and the analysis is thus greatly simplified. For the few cases where there seems to be evidence of curvature, it is convenient to expand equations (59) and (66) into an approximate form, as Kratzer([53]) has done in the case of the C+H bands. In order to obtain any determinate result it is necessary to assume $\delta=0$. Then equation (59) becomes

$$\begin{aligned} F &= B_n\left[j^2-\sigma^2+\epsilon^2-2\epsilon j\left(1-\frac{\sigma^2}{2j^2}+\ \ldots\right)\right] \\ &= B_n\left[-\sigma^2+(j-\epsilon)^2+\frac{\epsilon\sigma^2}{j}-\ \ldots\right]. \end{aligned} \tag{67}$$

Therefore we have

$$\frac{dF}{dj} = B_n\left[2(j-\epsilon)-\frac{\epsilon\sigma^2}{j^2}+\ \ldots\right]. \tag{68}$$

This last equation shows that the deviations of the value of $\frac{dF}{dj}$ from the linear curve are proportional, as a first approximation, to the inverse square of j, and have the same sign as ϵ. If from relations among the lines corresponding to higher values of m, we can again evaluate ϵ, equation (68) apparently allows the evaluation of σ to a close approximation. But in order to carry the scheme through, the value of B_n and the absolute values of j are needed, and in general these are not known for bands of this type. Hence Kratzer([53]) in his work on the C+H bands has apparently used a cut-and-try method, assuming a value of σ, and then comparing the observed and calculated results, especially in respect to what lines are missing. This question can be discussed to better advantage in a later section. (See Part 5c.) It should be noted in addition, that when σ is not zero, the $\frac{dF}{dj} : j$ curve is not linear for either

[67] Obviously, equation (60) is always linear, but since, from the experimental data when $\sigma \neq 0$, we know neither $\frac{dF}{dm}$ nor m, it cannot be plotted.

small or large values of j. Hence we cannot directly evaluate B_n from its slope. Instead we may use intermediate values of j to obtain an approximate value, and then, after a value of σ has been tentatively adopted use equation (68) in the region of rather small values of j, to obtain [68] a corrected value of B_n.

We have now considered the particular form of equations (59), (60) in the two special cases $\sigma=0$, and $\delta=0$. A third special case corresponds to $\epsilon=0$. If δ is not zero we obtain from equation (66), by a process similar to that employed in deriving equation (68)

$$\frac{dF}{dj}=2\delta+B_n\left(2j+\frac{\delta\sigma^2}{j^2B_n}+\ \ldots\right). \tag{69}$$

If now δ can be either positive or negative, as assumed by Kratzer, it is evident by comparing equations (68) and (69) that it is impossible to distinguish the case $\delta=0$, $\epsilon\neq0$, from the case $\delta\neq0$, $\epsilon=0$. Kratzer has assumed that the latter case is relatively improbable but that it occurs in the Cd bands. [Pp. 100-101 of reference ([43]).] From the standpoint of molecular structure, one would not expect δ to occur, implying an asymmetry with respect to two possible directions of rotation, unless there is a definite electronic structure capable of producing the asymmetry. But this latter is shown by the presence of ϵ.

Let us assume now that both ϵ and δ are zero. Then we have

$$\frac{dF}{dj}=2B_nj. \tag{70}$$

This equation is identical with (62), under the same conditions regarding ϵ and δ. In other words, in the case that the $\frac{dF}{dj}:j$ curve passes through the origin, it is not possible to decide whether or not σ is present. This conclusion may have a bearing on the question of whether j is to be

[68] Hulthén and Johansson([17]), assuming the form of equation (67) and assuming that the absolute values of j are known, have attempted to evaluate I as a function of n and of j, for the second positive group bands of nitrogen. But the values of j used by them are apparently not correct and the method is not, I believe, feasible except when $\sigma=0$. (See discussion at end of Part 5b ahead.) In fact a direct plot of the middle component of the triplet, using their data for these bands, yields a nearly linear $\frac{dF}{dj}:j$ curve, regardless of the absolute value of j, thus showing that $\sigma=$ zero for this component. From the slope of this curve, for the λ3371 band ($0\rightarrow0$) one obtains immediately, with considerable accuracy, $B'_0=1.82$, $B''_0=1.63$ [giving I'_0 and I''_0 by equation (37)], as compared to 1.88 and 1.68 given by these authors (i. e., $B/4$ and $B'/4$ of their notation, page 322 *l. c.*).

considered an integer, or a half-integer. For, as explained in Chapter II (p. 50), the presence of a Q branch suggests precessional motion, resulting from a real value of σ. Yet bands like the Angstrom CO bands, as analyzed by Hulthén([44]) have a Q branch, while the $\frac{dF}{dj} : j$ curve is linear even for large values of j and passes through the origin *only* if j is assumed to have half integral values. It has been assumed in the past that a linear $\frac{dF}{dj} : j$ curve indicated that $\sigma = 0$. We now see that this is not necessarily the case, but *if* σ is not zero, this curve should pass through the origin and from the experimental results for CO and other molecules, this occurs only with half-integral values of j—contrary to previous assumptions regarding this quantity. On the other hand, Kratzer([41]), as stated on page 92, concludes that the presence of a Q branch does not necessarily imply the existence of σ.[69]

In the general case where σ, δ, and ϵ are all not zero, equation (60) is incapable of indicating the evaluation of any of these quantities, and this case has not yet been assumed by any investigator.

The results of Part 3b may be summarized as follows: From the experimental data, by applying the combination principle, it is possible to calculate a set of spectral terms such as is shown in Figure 9. The data for a given band yield directly the spacing of successive rotational terms, as shown in (*c*) of Figure 9, this spacing being denoted by ΔF. Similarly, the spacing of successive bands of a Deslandres' progression is denoted by ΔG, and is indicated in (*b*) of Figure 9. By multiplying these quantities by h, we obtain the change of rotational energy $\Delta \overset{*}{E}_m$ for $\Delta j = 1$, or of vibrational energy ΔE_n for $\Delta n = 1$. These finite differences may be converted to derivatives, and the theoretical form of these derivatives and their corresponding integrals $\overset{*}{E}_m$ and $\overset{*}{E}_n$ has been studied by Kratzer, and others. The total energy E is given by equation (22), as the sum of the three portions E_e, $\overset{*}{E}_n$ and $\overset{*}{E}_m$ which can thus be experimentally determined, to within an additive constant. Kratzer's theoretical

[69] Mulliken (Proc. Nat. Acad. Sci. 12: 144 and 151, 1926) is the first investigator to make use of the above relations, by postulating relatively large values of σ in the case of certain bands, such as the Angstrom CO bands, which yield an apparently linear $\frac{dF}{dj}$ curve. (See also footnote at end of Part 5c.) The large values of σ seem necessary, in order to explain the missing lines, and conversely it now seems possible in certain cases from a study of the missing lines, to determine the absolute magnitude of σ. In conformity with the above relations, Mulliken also, for certain molecules (like CO) assumes half integral values of j. This very recent work of Mulliken is summarized briefly in Section 8.

formulas for these three portions are given by equations (33), (34) and (35). From equation (34) one can obtain the frequency of vibration as a function of n, as indicated in equations (39) and (41) while from equation (35) one can similarly obtain, except for the difficulty concerning "δ," the frequency of rotation, as indicated by equation (42). Most of the various molecular constants appearing in equation (35) can be evaluated only under special conditions. These conditions and the resulting equations giving the various constants appear in this section from equation (41) to equation (70). At least a mean value of the moment of inertia I can be evaluated for all values of n and j, and the actual calculations have been shown for the simple case of $\sigma=0$. The evaluation of the constants ϵ, σ and δ is more uncertain, and in many cases indeterminate. The absolute value of j, the resultant momentum, is dependent upon the value of ϵ and of σ, and so in turn is uncertain.

The entire theory of energy levels here presented applies equally in the case of near infra-red bands, but because of the simplicity of the bands analyzed thus far and the relative inaccuracy of the experimental data, in that region of the spectra, it has not yet been necessary to consider many of the refinements required in the case of electronic bands.

Aside from the question of the theoretical *frequencies* of the spectral terms or energy levels, there is the equally important question of the relative *weighting* of these terms, and of the probability of transition from one energy level to another—in other words, the whole question of the intensity of spectral lines. It seems more convenient, however, to discuss this matter incidentally, in connection with the analysis of the experimental facts. We accordingly now turn to such a discussion, considering first all matters concerned with nuclear vibration (i. e., assuming zero nuclear rotation), and then proceeding to the far more complex subject of simultaneous rotation and vibration.

SECTION 4. THE VIBRATION QUANTUM NUMBERS AND RELATIVE INTENSITIES OF THE BANDS FORMING A SYSTEM

In Section 3 we have given the mathematical formulation of the energy states of a diatomic molecule, according to the quantum theory. We shall now discuss in more detail the actual radiation resulting from a transition from one of these energy states to another. The frequency of such radiation has been given in equation (2), where the energy of the initial and final states was defined by equation (3). But in this definition all mutual action terms were omitted. The more general form of the energy of any quantum state is given by equation (22). Hence the

correct form of equation (2) becomes, by using also equations (26) and (56)

$$\nu=\nu_e+\nu_n+\nu_m=\frac{E'_e-E''_e}{h}+\frac{E'_n-E''_n}{h}+\frac{\overset{\bullet}{E}'_m-\overset{\bullet}{E}''_m}{h}$$
$$=\nu_e+(G'-G'')+(F'-F'') \qquad (71)$$

where E_e, E_n and $\overset{\bullet}{E}_m$ are defined by equations (33), (34) and (35), respectively. In these equations every constant, aside from h, has, in general, different values for the initial and final states. In equation (71), if $\nu_e=\nu_n=0$, we have the pure rotation bands of the far infra-red. If $\nu_e=0$, we have the vibration-rotation bands of the near infra-red. When ν_e is not zero, we have the electronic bands discussed in this chapter.

A constant value of ν_e gives a system of electronic bands. A constant value of ν_e and ν_n gives one band of a system, the variation in ν_m giving the various lines of the band. In the present section we shall discuss only the relations concerning the various bands of a system. These assume the simplest form when we let $\overset{\bullet}{E}'_m=\overset{\bullet}{E}''_m=0$, i. e., $\nu_m=0$. The frequency of the emitted radiation then defines the "origin" of a band. Hence, denoting this frequency by ν_0, we have

$$\nu_0=\nu_e+\nu_n=\frac{E'_e-E''_e}{h}+\frac{E'_n-E''_n}{h}=\nu_e+(G'-G''). \qquad (72)$$

The physical meaning of the origin of a band is then that frequency emitted when the molecule has no effective rotational energy in either the initial or the final condition. Actually such a radiation does not occur, but its theoretical frequency can easily be computed by extrapolation, in most cases.

Similarly we shall define the "origin" of a system of bands as the origin of that band which has no effective vibrational energy (E_n) in either the initial or final condition. Hence the origin of the system is given by ν_e.

We shall therefore proceed first to discuss the mathematical relations among the origins of the bands of a system. Since ν_e is a constant, these relations may be indicated in general by equation (72). Each E_n is given by equation (34) and we have, therefore [70]

$$\nu_0=\nu_e+(G'-G'')=\nu_e+(\omega^{0'}n'-\omega^{0'}x'n'^2+\ldots)$$
$$-(\omega^{0''}n''-\omega^{0''}x''n''^2+\ldots) \qquad (73)$$

[70] The possible values of n'' (or n') and of $(n''-n')$, in equation (73), are much more extensive than in the case of the near infra-red bands, as has previously been noted. Thus, in the case of iodine (see Figure 16 ahead) n' becomes as large probably as 59, and $(n''-n')$ also as large as 59.

Now we have mentioned in an earlier section that there is as yet scarcely any data as to the frequency of the origins of bands, so that in testing equation (73) we are forced to use the frequency of the heads. The compatibility of most of the results indicates that in general the distance from the head to the origin of any band in a system is roughly constant. When this is true, the substitution of heads for origins makes our calculated ν_e in error by just this constant quantity, but produces little error in the determination of the remaining constants of equation (73).[71]

The most convenient method of studying equation (73) is to keep either n' or n'' constant. The former condition gives an n'' progression of bands, as discussed in Section 2b, and ordinarily coincides with a first Deslandres progression. The equation of an n'' progression is, by equation (73)

$$\nu_{n''}=\nu_e+A_{n'}-(\omega^{0''}n''-\omega^{0''}x''n''^2+\ \ldots) \tag{74}$$

where $A_{n'}$ is positive, and as indicated, is a function of n'. Similarly, when n'' is a constant, we obtain an n' progression, which ordinarily coincides with a second Deslandres progression. The equation of an n' progression is, by equation (73)

$$\nu_{n'}=\nu_e+A_{n''}+(\omega^{0'}n'-\omega^{0'}x'n'^2+\ \ldots) \tag{75}$$

where $A_{n''}$ is negative, and as indicated is a function of n''.

But the various different Deslandres progressions, in a given system of bands yield average values, not of $\nu_{n'}$ or $\nu_{n''}$ but of the variation of these quantities, when the parameters of equations (74) and (75) change by unity. These differences of frequency, $\Delta\nu_n(=|\Delta G_n|)$, if properly defined, are almost identical in absolute magnitude with the first derivative of the frequency with respect to the parameter. We therefore *define* these finite differences, as follows,

$$\left.\begin{aligned}&\Delta\nu_{n+\frac{1}{2}}=\nu_{n+1}-\nu_n=\frac{d\nu}{dn}\ \text{ at } n+\tfrac{1}{2}\ \text{(approx.)}\\ \text{or}\\ &\Delta G_{n+\frac{1}{2}}=G_{n+1}-G_n=\frac{dG}{dn}\ \text{ at } n+\tfrac{1}{2}\ \text{(approx.)}\end{aligned}\right\} \tag{76}$$

so that each $\Delta\nu_n$ or ΔG_n is correlated with the *mean* value of n concerned,

[71] Blackburn(46) has recently measured the positions of the origins for the entire first negative group of carbon. The variations in the distance of the head from the origin, in the various bands, are very small and quite irregular, and thus apparently due entirely to experimental error.

and refers to a unit change in n. Hence we have from equation (73) approximately [72]

$$\Delta\nu_{n'} = \Delta G_{n'} = \omega^{0\prime} - 2\omega^{0\prime}x'n' + \ldots \tag{79}$$

and

$$\Delta\nu_{n''} = -\Delta G_{n''} = -(\omega^{0\prime\prime} - 2\omega^{0\prime\prime}x''n'' + \ldots) \tag{80}$$

[72] If equation (73) is of the second degree only, ΔG_n and $\frac{dG}{dn}$ are identical. This may be shown by direct substitution. Thus, more generally, let us write

$$\begin{aligned} y_n &= y_0 + An + Bn^2, \\ y_{n+1} &= y_0 + A(n+1) + B(n+1)^2. \\ \therefore \Delta y &= y_{n+1} - y_n = A + 2B(n+\tfrac{1}{2}), \\ \text{or, } \Delta y_n &= A + 2Bn = \frac{dy}{dn}. \end{aligned}$$

In the case of a fourth degree polynomial, which seems sufficiently accurate to represent any data on the Deslandres progression now available, let

$$\frac{dy}{dn} = a_0 + a_1 n + a_2 n^2 + a_3 n^3 + a_4 n^4.$$

But from the experimental data we obtain values of Δy_n and these, when fitted, usually by the method of least squares, to a fourth degree polynomial in n, give

$$\Delta y_n = a'_0 + a'_1 n + a'_2 n^2 + a'_3 n^3 + a'_4 n^4.$$

The following relations easily follow from a comparison of the above equations.

$$\left.\begin{aligned} a_0 &= a'_0 - 1\tfrac{1}{2}\, a'_2 + 2\tfrac{7}{40}\, a'_4 \\ a_1 &= a'_1 - \tfrac{1}{4} a'_3 \\ a_2 &= a'_2 - \tfrac{1}{2} a'_4 \\ a_3 &= a'_3 \\ a_4 &= a'_4. \end{aligned}\right\} \tag{77}$$

Thus the finite difference curve $\Delta G_n : n$ can be transformed into a true derivative, and this derivative, integrated with respect to n, and multiplied by h, gives immediately, by equations (75), (74), (73) and (56), the vibrational energy states, E'_n and E''_n of the system of bands under investigation. With the present obtainable accuracy of data as to the Deslandres progressions, it has been found that the corrections given by equations (77) are in general entirely negligible.

Finally, in the case of the effective rotational energy $\overset{*}{E}_m$, as discussed in the next section, we shall find that certain experimental data give directly the values of $y_{j+1} - y_{j-1} = 2\Delta y_j$. If these values are halved, and then fitted to a fourth degree polynomial in j (with constants a''_0, a''_1 etc.) the resulting equation may be transformed to the true equation for $\frac{dy}{dj}$ by the equalities

$$\left.\begin{aligned} a_0 &= a''_0 - \tfrac{1}{2} a''_2 + 1\tfrac{7}{15}\, a''_4 \\ a_1 &= a''_1 - a''_3 \\ a_2 &= a''_2 - 2a''_4 \\ a_3 &= a''_3 \\ a_4 &= a''_4. \end{aligned}\right\} \tag{78}$$

for any value of n.[73] Equations (74), (75), (76), (79) and (80) state analytically the relations illustrated schematically in Figure 1, and also the origin of the two rules (A) and (B), for the assignment of vibration quantum numbers, given on p. 79 of Part 2b. Thus in equation (80) $\Delta\nu_{n''}$ decreases in absolute magnitude as n'' increases, while by equation (74) $\nu_{n''}$ *decreases,* since the third term is small compared to the second. This gives rule (A) for an n'' progression. On the other hand, by equation (79) $\Delta\nu_{n'}$ decreases as n' increases, while by equation (75) $\nu_{n'}$ *increases.* This gives rule (B) for an n' progression. Finally, it should be noted that the *largest* absolute magnitude of $\Delta\nu$ (or ΔG) gives the spacing between the 0 and 1 vibrational levels and so is denoted $\Delta\nu_{\frac{1}{2}}$ (or $\Delta G_{\frac{1}{2}}$).

The preceding equations assume that ΔG decreases as n increases. This follows, as previously noted, from any reasonable law of force for the molecular vibration. The required condition is that the fourth power coefficient in the usual power series expansion of the potential energy be negative or not large in comparison with the third power coefficient.[74] It seem possible, however, in certain cases to obtain conclusive evidence for the correct assignment of vibrational quantum numbers, by an entirely independent method.

As an example let us consider the numerical relations given by the Deslandres progressions of the first, second, and fourth positive groups of nitrogen.[75] These are given to scale in Figure 10, which is plotted in the form of Figure 1, and of Figure 9.[76] This latter figure represents incompletely the same systems of bands, and, as noted, is drawn also to scale. Thus in Figure 10, the set of vibrational energy levels near the center ($n=0$ to 20) is represented in Figure 9 as set B (0_B to 20_B). The set on the left side of Figure 10 ($n=0$ to 4) is the set attached to the electronic level C of Figure 9 (the level C itself corresponding to $n=0$). Electronic level D is not shown in Figure 10. It forms the common initial

[73] ν_n and $\Delta\nu_n$ represent the frequency and increase in frequency, respectively, of the successive bands of a progression, for increasing n. Thus $\Delta\nu_n$ is normally positive for the n' progression, and negative for the n'' progression. On the other hand, G and ΔG represent the frequency of the spectral *term,* and the increase in frequency of successive terms, respectively, of vibrational energy levels, for increasing values of n. Thus ΔG is always positive. By equation (57), ΔG_n also equals approximately the frequency of vibration, as a function of n.

[74] See equations (4), (8) of Kemble(62).

[75] As interpreted by Birge(15).

[76] The horizontal lines of Figure 10 give the successive bands of each system arranged by sequences—hence essentially in the order in which they occur in the spectrum. A more compact form of this type of diagram has since been introduced by Mulliken(47).

level of the seven bands of the fourth group. On the right of Figure 10 we have a long set of vibrational levels ($n=0$ to 16) attached to level

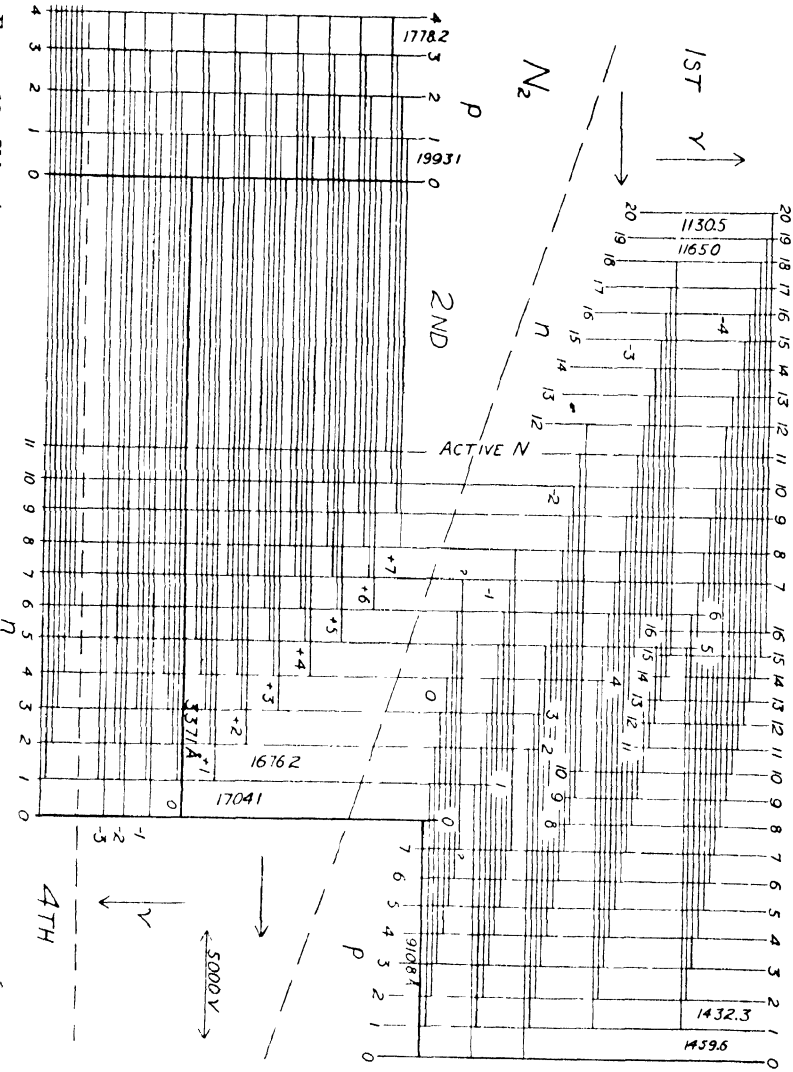


FIGURE 10.—Vibrational Energy Levels (Vertical Lines) and Bands (Horizontal Lines) of the First, Second, and Fourth Positive Groups of Nitrogen, from Birge(15)

A of Figure 9—so long in fact that the set overlaps on level B, and produces some confusion in Figure 10.

The levels of set B are thus common to all three of these systems of nitrogen bands, and thus constitute a common Deslandres progression. This proves that all three systems of bands are due to the same chemical

molecule, in merely different states of electronic excitation."[77] Figure 10, however, indicates the very significant fact that *all* of the levels of set *B* are *not* represented in *all* three groups. Only levels 0 to 6 appear in the fourth group, 0 to 11 in the second group, while the entire set, 0 to 20 appears in the first group. Moreover, the band λ3371 is the strongest in the second group, and the band λ9108 is the strongest in the first group.[78] These two bands involve the three levels marked zero, and in general the levels marked zero are associated with the strongest bands, and the intensity of the bands decreases as the designated number of the level increases.[79] If now we assume that each set of levels in Figure 10, because of its approximate equal spacing, represents a set of vibrational energy levels, then, according to the generalized Boltzmann distribution function,[80] the state of zero vibration is always the most probable state, and the bands associated with transitions from such a state should be especially intense. All of these facts point inevitably to the conclusion that the right-hand level of the middle set is really the zero vibration level. Similarly, the right-hand level for each of the other sets has been taken as the zero level.

This assignment of zero to the right-hand level indicates that the energy value of all the levels increases from right to left, while emission

[77] In view of a recent note by Duffieux (Nature 117, p. 302 (1926)) this point may be emphasized. One may say that the chemical origin of these three systems of bands is a matter of theory, and that it is conceivable that all three are due to an entity other than the neutral nitrogen molecule. It is, however, impossible to conclude that they are due to different entities, as Duffieux has done.

[78] According to Pfund's(63) recent energy curve of this system. (Figure 2 of his p. 195.)

[79] It is to be recalled that Figure 10 represents merely the experimental facts connected with the Deslandres progressions, and we are assuming, for the moment, that the numbering of the vertical lines indicated in the figure is a purely empirical one.

[80] This distribution function, in its quantum theory form, may be written

$$N_\tau = \frac{Nc^{-\frac{E_\tau}{k\bar{T}}}}{\sum_\tau c^{-\frac{E_\tau}{k\bar{T}}}} \qquad (81)$$

where N is the total number of molecules, N_τ the number in a given quantum state τ and the Σ is to be extended over all possible states. In a degenerate system, where a given quantum state consists actually of a number of coinciding states of a non-degenerate system, the number of such states gives the so-called "*a priori* probability" p_τ of the degenerate state, since each non-degenerate state is assumed to have unit *a priori* probability. An oscillator constitutes a non-degenerate system. Hence $p_\tau =$ unity.

thus takes place from left to right. The decrease in the spacing of set *B*, as well as in the other sets, as n increases, is then in agreement with Kratzer's theory. Figure 10 thus indicates that the fourth and second nitrogen groups have a common final set of vibrational energy levels,

n' \ n''	0	$\Delta\nu_{\frac{1}{2}}$	1	$\Delta\nu_{1\frac{1}{2}}$	2	$\Delta\nu_{2\frac{1}{2}}$	3	Average
0	29,655.6	(1,704.8)	27,950.8	(1,675.0)	26,275.8	(1,645.2)	24,630.6	
$\Delta\nu_{\frac{1}{2}}$	(1,993.0)		(1,994.4)		(1,993.8)		(1,993.0)	1,993.55
1	31,648.6	(1,703.4)	29,945.2	(1,675.6)	28,269.6	(1,646.0)	26,623.6	(55.03)
$\Delta\nu_{1\frac{1}{2}}$	(1,937.1)		(1,937.5)		(1,939.8)		(1,939.7)	1,938.52
2	33,585.7	(1,703.0)	31,882.7	(1,673.3)	30,209.4	(1,646.1)	28,563.3	(67.57)
$\Delta\nu_{2\frac{1}{2}}$	(1,870.0)		(1,870.8)		(1,870.7)		(1,872.3)	1,870.95
3	35,455.7	(1,702.2)	33,753.5	(1,673.4)	32,080.1	(1,644.5)	30,435.6	
Average		1,703.35		1,674.32		1,645.45		
		(29.03)		(28.87)				

FIGURE 11.—Frequencies of Heads of Bands of Second Positive Group of Nitrogen, Arranged for Calculation of n' and n'' Progressions. Values for Progressions in Parenthesis

and that this set is simultaneously the initial set for the first group. Now it is well known that all of the bands of the second group proceeding from any particular level of set *C* have similar perturbations. We thus have proof of the fact that the perturbations are connected with the initial energy state—at least in this particular system of bands. Deslandres accordingly designated the ***common*** set of levels as $f(n)$ and

hence sets C and A were designated in each case as $f(p)$. In this case then, Deslandres' $f(p)$ represents the initial energy states for the second group, and equations (5) are true, while his $f(p)$ represents the *final* energy states of the first group.

Unfortunately this first group has thus far defied analysis. Otherwise it would be interesting to investigate it for perturbations. The perturbations of the second group bands indicate that there are seemingly no irregularities in set B, while set A, representing a still more stable state of the molecule, should also be free from irregularities. Hence the first group bands should possibly show *no* perturbations. These ideas are in agreement with the numerical relations of the various progressions, as given in Figure 12 ahead. Set C is a typical set of initial vibration levels—short, and giving a $\Delta G : n'$ curve which requires several higher terms, in equation (79). But set B is an especially long set of levels, indicating an especially stable molecular form, and is represented by an almost linear $\Delta G : n''$ curve, as is also set A.

Figure 10 thus shows one method of indicating the quantum relations of bands, and especially of the relations between several systems of bands. On the other hand, the actual bands of a system composing each progression are better indicated by the type of representation of Figure 2. This figure illustrates another criterion for assigning vibration quantum numbers, provided we assume the theory of the non-harmonic oscillator. The criterion is the successive shortening of the sequences, at the violet end of the system. The shortening is very pronounced since the top horizontal row, forming n'' progression (0), represents in general the strongest bands. Thus it is the *strongest* band of a sequence that suddenly disappears, as we proceed to the violet. The strongest band of the last sequence which possesses a normal number of bands is therefore the (0, 0) band. All the other assignments then follow immediately by the application of rules (A) and (B) of Section 2b.

There is a third method for representing the Deslandres progressions of a given system of bands, and this is the type of representation usually employed by investigators. This is illustrated by Figure 11, where a small portion of the second positive group of nitrogen is given. The listed frequencies are in vacuum, from the data by Ames([66]). In this method of representation the horizontal rows represent first Deslandres' progressions or n'' progressions, giving the spacing for the final vibrational levels. The vertical columns represent second Deslandres' progressions or n' progressions, giving the spacing for the initial vibrational levels. The numbers in brackets give the frequency differences between adjacent members of the progressions. The constancy of the differences in each

horizontal row and vertical column is a verification of the combination principle and of the fact that the table is built up so that n' is constant along each horizontal row and n'' down each column. Thus, clearly, if n' is constant along each horizontal row, the frequency difference between adjacent bands of any such row is independent of the initial state and is equal to the interval between adjacent vibrational levels for the final state. Also, if n'' is constant down each column the horizontal differences between adjacent columns are the intervals between the same pair of final levels and must be the same.

The bands for $n'=4$ are omitted since Ames' data are poor, in this case. The variation among the various $\Delta\nu$'s which should be constant, is due partly to experimental error, and partly to the fact that the heads are used, in place of the "origins." In Figure 11 each diagonal represents a sequence. The fact that the upper left corner of the diagram is fully occupied then corresponds to the successive disappearance of the members of the sequences in Figure 2. The bands must be so arranged, in Figure 11, that in any horizontal row the frequencies decrease, and $\Delta\nu$ decreases, as one proceeds to the right, while in any vertical column, the frequencies increase and $\Delta\nu$ decreases, as one proceeds down the column. This fulfils the conditions of rules (A) and (B) of Section 2b.

As an example of the assignment of vibration quantum numbers by this method, we may consider Table II of p. 180 of Jevon's[65] analysis of the silicon oxide band heads. These are arranged in the general form of Figure 11, but with the usual Deslandres' assignment of p and n values. The direction of decrease of ν and of $\Delta\nu$, compared to Figure 11, shows that the correspondence is exact, Jevon's p parameter corresponding to n'', and his n parameter to n'. Deslandres would probably have interchanged p and n, since Jevon's $f(p)$ is the longer one. Evidently the 42643ν band is the (0, 0) band, and the correct quantum assignment is given by

$$\left.\begin{aligned} n'' &= 103 - p \\ n' &= 77 - n \end{aligned}\right\} \quad (82)$$

Another criterion for the assignment of vibrational quantum numbers results from the vibrational isotopic effect, whenever such an effect is present. As shown by Mulliken[51], this method should yield the *absolute* values of the vibrational quantum numbers, in contrast to all other methods which without additional assumptions yield only relative values. The assumptions made in this chapter are that the vibrational quantum numbers are integers and that the molecule is not permanently endowed with any finite amount of vibrational energy. This question will appear again later in the report.

Having thus made the assignment of vibrational quantum numbers for a given system of bands, we may calculate the average values of each ΔG_n, i. e., ω^n, for the two progressions, and plot these as a $f(n)$. Such a plot is shown in Figure 12, for a number of different band systems. Because of the amount of material that has recently become available for such plotting, the curves of Figure 12 are restricted to band systems believed to be due to carbon, nitrogen, or oxygen, and their intercombinations. These systems include, however, the majority of cases of identical progressions, which are of great value in determining the chemical identity of the emitting molecule. The notes accompanying this figure give the sources of information and other particulars. Heurlinger([67]) was the first investigator to apply the quantum theory to the question of amounts of vibrational energy, in the case of the bands of a system. On p. 89 of the reference cited, he gives equations corresponding to equation (73), which contain implicitly the assignment of vibrational quantum numbers for the violet and red CN groups, the first and fourth positive, and negative nitrogen groups, and in part for the second positive group. These equations are only approximate and in the case of the first positive nitrogen group his equation is incorrect. Kratzer([61]) later made a more careful study of the violet CN group as well as certain others.

Now, as already noted, graphs such as those shown in Figure 12, give the frequency[81] of the diatomic vibrator ω^n as a function of n. On the other hand, the area included between each of the curves of Figure 12 and the n axis, between $n=0$ and $n=n$, equals G_n and by equation (56) is proportional to the effective vibrational energy E_n.

An examination of Figure 12 reveals in general two different types of curves. In one the frequency ω^n (or ΔG_n) changes nearly proportional to n, while in the other it decreases more rapidly than n increases, giving a graph with a pronounced curvature. This latter type, in Figure 12, always represents the initial state of the molecule, and seems to indicate a relatively unstable state. It was this type of curve which Deslandres represented by $f(p)$. There are usually irregularities in the rotational energy levels, associated with this type of vibration, as revealed by the perturbations. The rapid curvature, in some cases, seems to point to a limiting value for n, as well as for the included area—i. e., for the energy of the oscillator.

Assuming that the $\omega^n : n$ curve actually runs to $\omega^n = 0$, the limiting value of the included area is proportional to the work required to separate

[81] We as usual give the frequency in terms of the so-called wave number (cm^{-1}) The true frequency is obtained by multiplying this number by 3×10^{10}

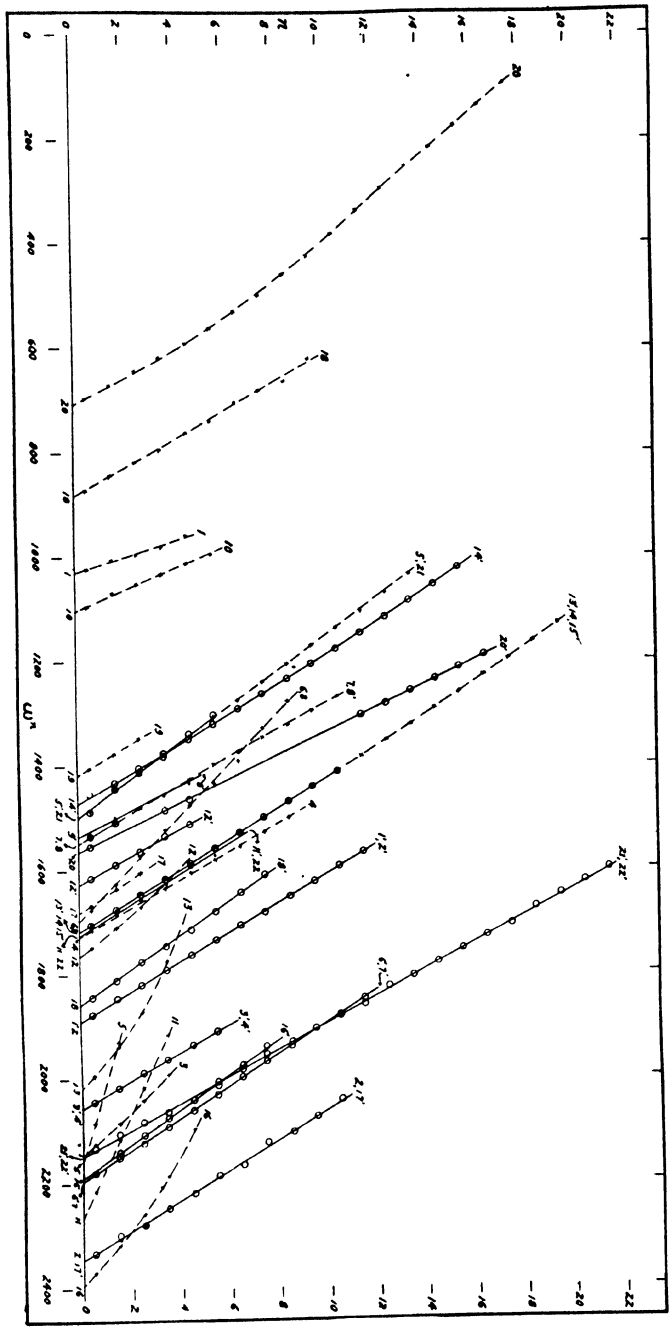


FIGURE 12

FIGURE 12.

Frequency of Vibration ω^n (in Wave Numbers) as a Function of the Vibrational Quantum Number n.

Broken curves, with usual numbers, refer to initial states for the emission process. Continuous curves with primed numbers refer to final states. Mecke(9) has independently made assignments of values of n, in a few cases where Birge(15)(68) is given as the source.

Curves 1, 1′. β bands of nitrogen (due to NO). Data from Fowler and Strutt(14), Birge(68) and Sponer and Hopfield(182). Assignments by Birge(68). The β and γ bands of nitrogen (NO) have a common final state (the stable state of NO) as recently proved by Sponer and Hopfield (loc. cit.).

Curves 2, 2′. γ bands (third positive group) of nitrogen (due to NO). Data by Schniederjost(69) and others. Assignments by Birge(68). Curve 2′ ($n=0$ to 6) equals curve 1′ ($n=3$ to 12). Curve 2 ($n=0$ to 3) almost equals curve 17′ ($n=0$ to 11). (See note at end of this chapter.)

Curves 3, 3′. Violet CN bands. Data arranged by Heurlinger(67), Kratzer(61)(43) and Birge(15). Assignments by Heurlinger(67). From data on origins, only the first point of curve 3 is known. Kratzer assumed a linear relation. The plotted curve is based on an apparent relation between the origin and the head of each band.

Curves 4, 4′. Red CN bands. Data and assignments as for 3, 3′. Curve 3′=4′.

Curves 5, 5′. Angstrom bands of carbon (due to CO). Data by Hulthén(44), and McLennan, Smith and Peters(160), as interpreted by Birge(72). Only first point of curve 5 may be real. Curve 5′ ($n=0$ to 6 with fair accuracy)=curve 21 ($n=0$ to 14).

Curves 6, 6′. First negative group of carbon (due to CO^+). Data by Blackburn(46) and especially Johnson(70). Assignments by Blackburn(46) and Birge(68). Curve 6′ ($n=0$ to 12)=curve 7′ ($n=0$ to 3). Curve 6 ($n=0$ to 9)=curve 8 ($n=0$ to 3).

Curves 7, 7′. Comet-tail bands (due to CO^+). Data by Baldet(48). Assignments by Birge(71). Curve 7 ($n=0$ to 11)=curve 8′ ($n=0$ to 2).

Curves 8, 8′. "Combination" bands, measured by Johnson(70) (due to CO^+). Assignments by Birge(60).

Curve 9′. High pressure CO bands. Data by Fowler(73). Assignments by Birge(71). Data (indicated by solid circles) very inaccurate. Linear least squares solution drawn.

Curve 10. Triplet system of carbon. Data by Merton and Johnson(74). Assignments by Birge(71).

Curves 11, 11′. Third positive group of carbon (due to CO). Data by Wolter(75) and Deslandres(76). Assignments by Birge(71). Curve 11′, indicated by solid circles, ($n=0$ to 7) equals curve 22 ($n=0$ to 4). Curve 11 is entirely spurious according to Wolter(75), but see note at end of this chapter.

Curves 12, 12′. Swan bands of carbon. Data on page 222, Vol. V, Kayser's "Handbuch." Assignments by Birge(15).

Curves 13, 13′. Nitrogen, second positive group (due to N_2). Compiled data. Assignments by Heurlinger(67), Birge(15), Hulthén and Johansson(17), Mecke and Lindau(18). Curve 13′ ($n=0$ to 11)=14 ($n=0$ to 20)=15′ ($n=0$ to 6).

Curves 14, 14′. Nitrogen, first positive group (due to N_2). Compiled data. Assignments by Birge(15).

Curve 15′. Nitrogen, fourth positive group (due to N_2). Data by Fowler and Strutt(14).

Curves 16, 16′. Nitrogen, negative bands (due to N_2^+). Compiled data (see note a′ of Section 7, ahead). Assignments by Fassbender(77) and Birge(68).

Curves 17, 17′. Nitrogen, ultra-violet bands ("resonance" system of N_2). Data and assignments by Birge and Hopfield(78), and unpublished work (see note at end of this chapter).

Curves 18, 18′. Oxygen, ultra-violet (first negative group) (due to O_2^+). Data by Johnson(79) and Ellsworth and Hopfield (note g′ of Section 7, ahead). Assignments by Birge(68), but see note g' (loc. cit.).

Curve 19. Oxygen, atmospheric absorption bands (due to O_2). Data compiled by Heurlinger(38). Assignment by Kratzer(61).

Curves 20, 20′. Schumann-Runge bands of oxygen (due to O_2). Compiled data. See note (c′) of Section 7 ahead.

Curves 21, 21′. Fourth positive group of carbon (due to CO). Compiled data, arranged and interpreted by Birge(72). See note g of Section 7, ahead. Curve 21′ ($n=0$ to 22)=curve 22′ ($n=2$ to 8).

Curves 22, 22′. Cameron bands of CO. See note i of Section 7, ahead.

the two atoms from the initial equilibrium position to infinity, and hence is proportional to the heat of dissociation D. Now as Kratzer([81]) pointed out, in answer to Tartakowsky([82]), the $\omega^n : n$ curve becomes asymptotic to the n axis, if the law of force between the two atoms becomes an inverse square or inverse cube law, for large values of the separation. The inverse square law may be expected in the case of polar molecules. On the other hand, if the limiting form of the law of force is represented by the inverse fourth or higher powers, the $\omega^n : n$ curve runs into the n axis at a finite value of n. This latter condition may be expected for non-polar molecules. Thus, for polar molecules $D = h \int_0^\infty \omega^n dn$, while for non-polar molecules $D = h \int_0^{n_0} \omega^n dn$, where n_0 is the value of n for which $\omega^n = 0$. At the present time, the only known cases where the $\omega^n : n$ curve can be followed almost to $\omega^n = 0$ are those for the excited states of the iodine bands and of the Schumann oxygen bands. The latter case is shown in curve 20 of Figure 12. The iodine curve has a precisely similar shape, and in both cases it is evident that a complex function is needed for its proper representation. The actual evaluation of the heat of dissociation, from spectroscopic data, is discussed in Section 8.

All of the graphs of Figure 12 show that ω^n is far from constant, indicating that the coefficient of the first degree term in n, in equations (41), (79) or (80) is of appreciable magnitude. But it is found on more detailed analysis that the graphs which are more nearly linear, such as graph 14, representing the common nitrogen progression, tend to become linear, for small values of n. Or, in analytic terms, the coefficient of the second degree term in n, in the three equations just cited—or of the third degree in the energy form—as given by equation (73) is zero, within limits of error, though higher degree terms in n must be retained. It is not possible to test the precision and generality of this statement until more accurate data are available. It appears to be true for the nitrogen progressions, within the limits of experimental error.

Passing now to the question of the distribution of intensity among the various bands of a system, one finds what appears at first to be a great variety of phenomena. Very recent work has, however, shown that in its major aspects, the intensity distribution of all known band systems can be definitely correlated with the change in the value of the moment of inertia of the molecule, between the initial and final electronic states for the system in question. The theoretical aspects of this are discussed in Section 8, but the recognition of the correlation has in itself greatly aided the empirical study of intensity distribution.[82]

[82] See Birge([68]) and Mulliken([83]) for previous empirical work.

The most common type of intensity distribution may be illustrated by the second positive group of nitrogen, as shown in Figure 13. In this figure the bands are arranged in the same manner as in Figure 11, except that intensities are recorded, in place of frequencies. A few weak bands near the longer wave-length end are indicated merely by a cross, as is also the extremely weak (4, 0) band at λ2692, recently found by Hulthén and Johansson([17]). This band forms the theoretical violet terminus of the system, and is omitted in Figure 2. The intensities correspond to the ordinary excitation of these bands by an induction

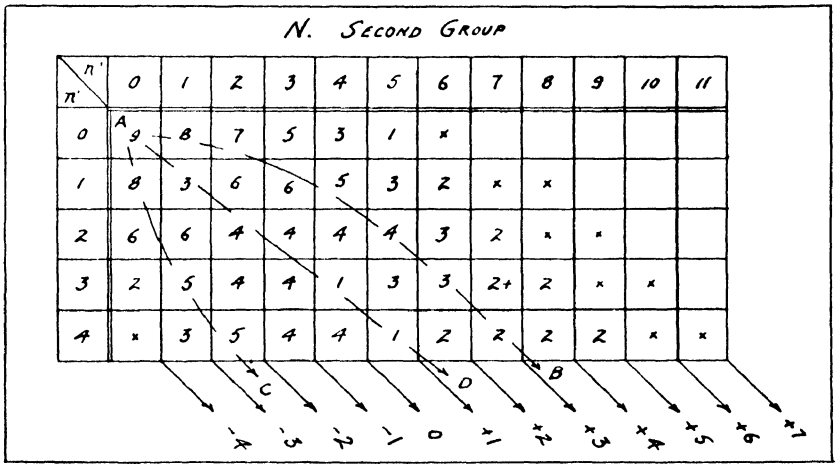


FIGURE 13.—Distribution of Intensity Among the Bands of the Second Positive Group of Nitrogen.

coil or transformer,[83] as judged from visual inspection of a number of spectrograms.

Each sequence lies along a diagonal line, and the constant defining each sequence is given at the bottom of the diagram. (Compare the same numbering in Figure 2.) We note from the diagram that the strongest band of the system is the (0, 0) band. The intensity can then be pictured by two ridges AB, and AC, running down from a maximum elevation at A.[84] Between these two ridges there is a trough, AD, almost coinciding with sequence (0). Thus every horizontal row, or n'' progression,

[83] The relative intensity of the bands in this system is very sensitive to changes in self-induction, capacity, and other experimental conditions. Hence it is very difficult to give a "normal" intensity distribution.

[84] Sometimes A is not the maximum elevation, and the ridges at first rise, and then fall. See Mulliken([47]) and ([83]).

except n'' progression (0), has two maxima of intensity, with a pronounced minimum between. Since, however, the bands of a sequence are adjacent in the spectrum, it is simpler[85] to note the intensity distribution in each sequence. The significant point here seems to be that while in the case of sequences 0, ± 1, and even ± 2, the first member of the sequence is the strongest, this is not true for sequences of higher

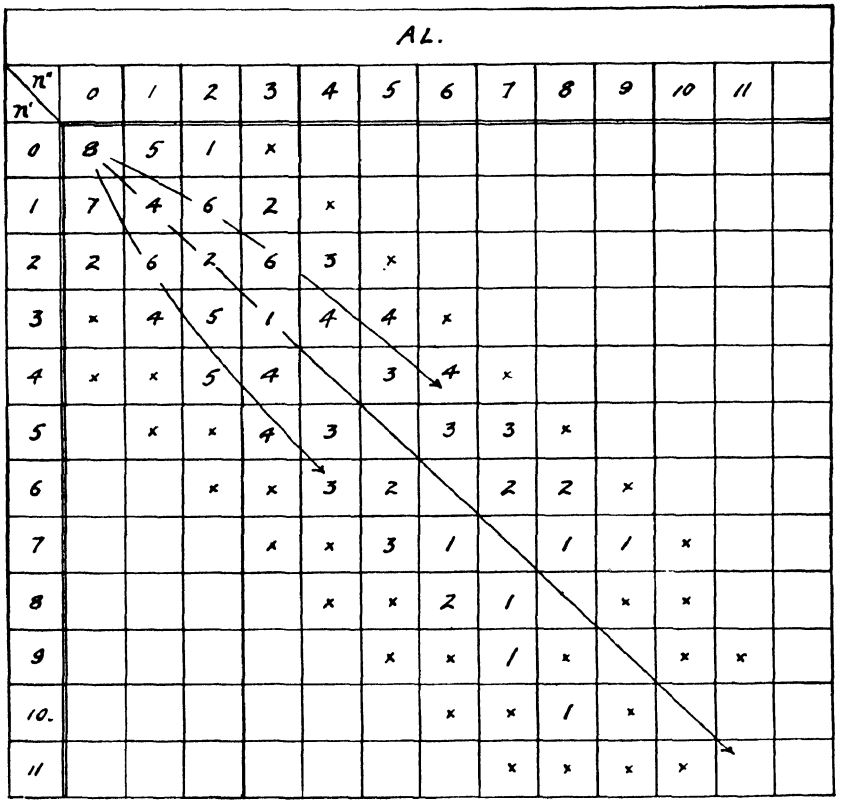


FIGURE 14.—Same as Figure 13, for the Aluminum Bands (AlO) of the Blue, Green and Yellow.

number, the maximum of intensity tending to shift down toward the center of the sequence.

This last tendency explains the distribution of intensity in the first positive group of nitrogen which, it now appears, is very similar to that

[85] There are at the present time practically no trustworthy data on relative intensities of bands. Because of the great spectral extent of any given n'' progression, the estimation of relative intensities from visual inspection of a photographic plate is highly uncertain.

in the second group. Valuable information concerning the first group is furnished by Pfund's([68]) energy curve for this system. It will be noted from Figure 10 (drawn previous to Pfund's work) that the positive sequences are missing, and this condition is true also as regards the red CN bands. But in both cases the missing sequences lie further to the red than the hitherto explored region. Pfund's curve shows clearly the extension of the first positive group to the red of λ9100, giving two more sequences +1, and +2. From the theoretically predicted position of the bands of these sequences, it is possible to obtain the intensity distribution in each sequence. The result is that the (0, 0) band at λ9100 is found to be the strongest of the entire system, while in the +1 sequence the first band is the strongest and in the +2 sequence, the first or second band, as in the second group. On the other hand, the strongest band in the −1 sequence is the (2, 1) band—the second of the sequence—while in the −2 sequence, the third band is the strongest, and in the −3 sequence the seventh band is the strongest. The −4 sequence has the peculiar intensity distribution of a maximum at probably the ninth band, and a secondary maximum at the fifteenth band. Because of this double maximum, Datta([84]) considers that we are here dealing with two different sequences. Such a distribution is, however, found in other instances, such as the β bands of nitrogen, and hence is not justification for such a division.[86]

As a further example of the normal distribution of intensity in a sequence, we cite the strong group of aluminum bands (probably due to AlO). The most complete experimental data are by Hagenback and Mörikofer([85]). The quantum assignments are λ4842 = (0, 0), λ5079 = (0, 1), λ4618 = (1, 0). From these all the other assignments immediately follow. The general intensity course is indicated very roughly in Figure 14, the figures having been made on the basis of a visual inspection of a small dispersion spectrogram, with an attempt to allow for the minimum sensitivity in the green. All bands marked with a cross have an intensity less than unity, on the assumed scale

The systems of bands just discussed are all examples of what the writer (reference ([68])) has termed the "normal" distribution of intensity in a band system. It appears now that this is merely the characteristic distribution accompanying a small change in moment of inertia. The maximum of intensity falls on a sort of narrow parabolic curve having the zero sequence for its axis, and consequently a minimum

[86] Datta's assignment of vibrational quantum numbers differs from that given by Birge as shown in Figure 10, and arguments in favor of Datta's assignment are not apparent to the writer.

of intensity is found for this zero sequence. This latter phenomenon is quite characteristic. Thus, in Figure 13, the (1, 1) band is very weak, compared to the (0, 0) band, and the same condition is true in Figure 14. However, in Figure 13, the (2, 2) and (3, 3) bands are again somewhat stronger, while in Figure 14 the intensity falls rapidly from (0, 0) to (4, 4). This rapid decrease in intensity is still more pronounced on a large dispersion spectrogram, even the (1, 1) band of aluminum being scarcely visible, and the (2, 2) band cannot be detected.

Lenz([86]) following a procedure originally outlined by Heurlinger([87]), has made an attempt to account for the distribution of intensity among the various sequences, by assuming a simple harmonic oscillator and considering the perturbations produced by the oscillation in the orbit of an encircling electron whose transition from one stationary state to

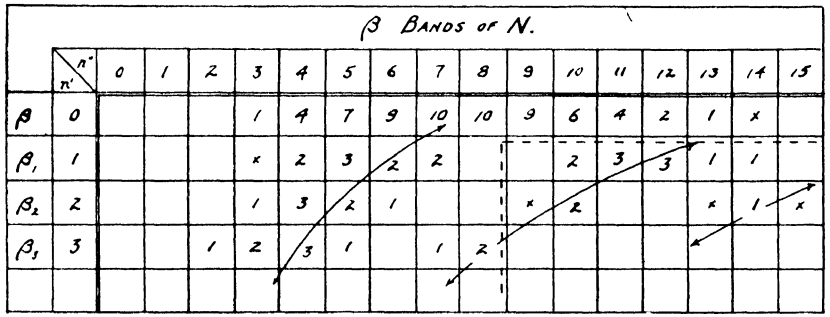


FIGURE 15.—Same as Figure 13, for β Bands of Nitrogen (Due to NO).

another causes the band emission. The intensity is then connected with the perturbations by means of Bohr's correspondence principle. His results give merely the variation of intensity from one sequence to another for some constant value of n'. They depend greatly on the assumed strength of the coupling between the electron and oscillator, and it would appear as if this mode of attack might furnish a possible explanation of the various known types of intensity distribution.

A second type of distribution, it now appears, is characteristic of a large change of moment of inertia. It is illustrated by the β bands of nitrogen, originally found in active nitrogen. The intensity distribution is shown in Figure 15. The figure contains, besides the bands listed by Fowler and Strutt([14]),[87] a number of others which have been found

[87] In this system the successive n'' progressions were designated by Fowler and Strutt as β, β_1, β_2, and β_3. The β progression shows an unusually great intensity, compared to the others, thus indicating an unusually large number of molecules in an initial state of zero vibration. But this is just what would be expected,

on spectrograms taken by E. P. Lewis. Because of the small intensity of the bands on the left side of the figure, the assignment of the values of n'' is uncertain. That given in the figure leads to the identification of the final state of the β bands with that of the γ bands.[88] The essential point about Figure 15 is the rise and fall of intensity as one proceeds along a horizontal row. In the case of n'' progression (2), there are unquestionably three different maxima of intensity, and one or more bands are definitely missing at each of the two intervening minima. In a very rough sort of way, there seems to be a tendency for the maximum of intensity to lie on rectangular hyperbolas about the (0, 0) origin.

This tendency is shown in a far more pronounced fashion in the case of the bands of iodine, as arranged by Mecke([12]). A portion of the bands of this system is shown in Figure 16, where merely the presence of each

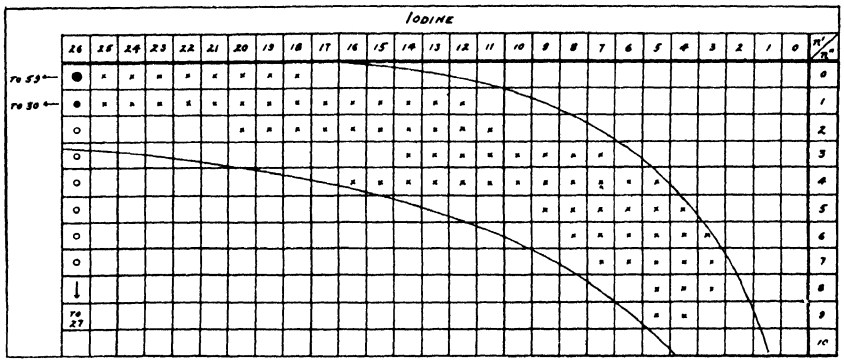


FIGURE 16.—Same as Figure 13, for the Iodine Bands, except that n' and n'' are Interchanged with Respect to the Horizontal and Merely the Appearance of Bands Indicated by Cross. Wood's Resonance Lines Form First Vertical Column, Running to $n'' = 27$.

band is indicated by a cross, as no definite values for the intensity are available to the writer.

The series of doublets originally found by Wood([87]) in his work on resonance spectra, corresponds to $n' = 26$, $n'' = 0$ to 27, and is denoted by

according to the Boltzmann intensity distribution, for the indicated intensities correspond to the bands as produced in active nitrogen which, from other evidence (see Birge([29])) seems to have a temperature scarcely above 100° C. On the other hand, as Fowler and Strutt remark (p. 383, *loc. cit.*) this dominance of the β series is entirely lost when the bands appear (faintly) in the ordinary air discharge. In this case evidently we have a high temperature and an intensity distribution quite similar to that of iodine.

[88] The actual molecule is NO. See Mulliken([47]). The correctness of the quantum assignments used here has recently been established by Sponer and Hopfield([182]).

circles. The exciting line corresponds to $n'=26$, $n''=0$, and the so-called "anti-Stokes" lines (corresponding to *negative* values of n'') have thus been omitted. This is in agreement with recent (unpublished) work by Loomis,[89] who finds that, with a sufficiently narrow exciting line, these anti-Stokes lines are absent, thus proving that they belong in reality to some other progression. A set of bands such as this, forming a "resonance series," constitutes what has been called in this report an n'' progression. Mecke([12]) calls them a "Querserie," while the set for $n''=$constant, here called an n' progression, he refers to as a "Längsserie." Mecke considered the assignment of vibrational quantum numbers in the case of iodine very doubtful. It would now appear that the newly assigned values of n'' are rather certain, but the values of n' are still somewhat doubtful. Aside from this point, it appears that in iodine, as in the β bands of nitrogen, the maximum of intensity tends to lie on a *wide,* rather than on a *narrow* parabola or hyperbola, having again the zero sequence as an axis. A third example of this distribution is the oxygen ultra-violet group, analyzed by Johnson([79]), and probably due to O_2^+. Recent work indicates that the band $\nu=26822$ should be omitted and that the true quantum numbers may be derived from Johnson's empirical parameters n and p, by the relations[90] $n'=33-n$, $n''=55-p$.

In these three cases, the vertex of the parabola representing the maximum of intensity tends to withdraw from the origin ($n'=0$, $n''=0$) as the parabola widens out. It is this phenomenon which introduces the uncertainty in the numbering of n' and n'', since all bands in the vicinity of the origin are so weak as to be as yet undetected.

All other band systems, for which the intensity distribution is even qualitatively known, seem to fall in one of the two classes, or at some intermediate point. The general relations may then be summarized as follows. Aside from the Boltzmann temperature factor, the distribution of intensity is such as to give in a general way a maximum of intensity along a parabola whose axis coincides with the zero sequence. The width of the parabola and the distance of its vertex from the "origin" of the system *increases* with *increased* change in the moment of inertia of the molecule, accompanying the electronic jump which characterizes the system. Franck (Trans. Faraday Society, 1925) has recently given a simple mechanical explanation of this correlation, which he first noted for the case of iodine, and Condon (March 1926 meeting of the American

[89] Full details of this work are given in Chapter VI of this report.

[90] See curves 18 and 18′ of Figure 12 and note (g′) of Section 7. The values of n' are fairly certain, but the true values of n'' may be given by $56-p$, or even 57 or higher numbers.

Physical Society) has extended the theory and tested it on a number of band systems. This is discussed in Section 8.

The Boltzmann temperature factor then modifies the initial distribution among the various n'' states, in the case of absorption spectra, or among the various n' states, in the case of emission spectra. Specific examples of this may be of interest. If the absorption spectrum of a cold gas or vapor is examined, *only* those bands comprising the n' progression for $n''=0$ may be expected to appear. If the change in the moment of inertia is rather small, the $0-0$ band may be the strongest, the intensity decreasing as n' increases. This phenomenon is illustrated by the ultra-violet absorption bands of cold CO, as photographed by Leifson, and interpreted by Birge([72]), (see Section 8). On the other hand, if the change in the moment of inertia is large the $0-0$ band may be too weak to detect, and the intensity may steadily increase as n' increases. This is illustrated by the Schumann bands of O_2 [see note (e') of Section 7]. For such a case the numbering of n' is very uncertain, unless the system can be obtained also in emission. This *has* been done for the O_2 system just noted. If the emission bands are produced at a relatively low temperature, the n'' progression corresponding to $n'=0$ will be particularly strong. If at the same time the change of the moment of inertia is large, the $0-0$ band will be very weak or missing, and the intensity will increase as n'' increases. These last two conditions are fulfilled in the case of the β bands of nitrogen, as obtained in emission in active nitrogen, the effective temperature of which is little above room temperature. The same system has been obtained in absorption in cold NO, by Leifson, as identified and interpreted by Sponer and Hopfield (see note d' of Section 7), and the phenomenon is then similar to that of the Schumann bands of O_2. On the other hand, as the temperature is raised, the Boltzmann factor causes the appearance of other n' progressions, in the case of absorption, or of other n'' progressions, in the case of emission. The first phenomenon has been observed in the Schumann bands of O_2 (see note e' of Section 7) and the second in the case of the β bands, as noted earlier in this section. The temperature distribution shown in Figures 13 and 14 is for emission at high temperature, that in Figure 15 for emission at low temperature, that in Figure 16 (with Wood's "resonance" progression omitted) for absorption at (relatively) high temperature. The first two figures are for small changes in the moment of inertia, the last two for large changes.

In addition to the intensity phenomena thus far discussed, there are variations in appearance for which no explanation has thus far been offered. A study of the intensity distribution in the violet CN bands,

(shown in Figure 3), as they appear in the arc (emission—high temperature), in the electric furnace (emission—moderate temperature), in active nitrogen (emission—low temperature), in the sun (absorption—high temperature), and in various type of stars (absorption—varying temperatures), reveals radical and unexpected variations of relative intensity. Figure 31, p. 192A, of Foote and Mohler's "Origin of Spectra," illustrating the second positive nitrogen group, as excited by high and low speed electrons, shows variations of relative intensity of which only a portion seems to have a temperature basis. Mulliken([47]),([83]), has discussed other similar cases. A final example is the effect of admixtures of foreign gases upon the first positive group of nitrogen, as studied by Rayleigh([88]). This phenomenon will be discussed in a later chapter.

As contrasted to the question of intensity distribution, the assignment of vibrational quantum numbers would seem rather trustworthy. If integral values of this quantum number are used, and if it is assumed that the molecule is not permanently endowed with some finite amount of vibrational energy, then the assigned values for the near infra-red bands are inevitable. But at the present time there has developed, in several quite diverse fields, the apparent necessity of introducing half-integral quantum numbers. Thus, in the case of all elements showing even multiplicity in the line spectra, Sommerfeld uses for the value of the resultant angular momentum of the atom $j=\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}$, etc. We shall find it possible to make a similar assumption regarding j, in the case of certain bands.[91]

Furthermore, Mulliken([47]), in the case of the BO bands, finds it necessary to use half-integral *vibrational* quantum numbers, in order to explain the vibrational isotopic effect. By this assumption, the molecule is permanently endowed with a half unit of vibrational energy, and if true in general, would necessitate the raising by a half unit of all values of n given in this report. This question is considered in greater detail in Chapter V, Section 4.

SECTION 5. THE QUANTUM STRUCTURE OF INDIVIDUAL BANDS

PART 5A. GENERAL DEDUCTIONS FROM THE COMBINATION PRINCIPLE

In Section 4 we have considered the special form of equation (71) when $\nu_m=0$. In this section we shall consider in some detail the various possible values of ν_m for a constant value of $\nu_e+\nu_n$—in other words the

[91] A systematic assignment of integral and half integral values of j has recently been made by Mulliken (Proc Nat. Acad. Sci. 12: 144 [1926], etc.), as discussed in Section 8.

structure of an individual quantum band. ν_m, it will be recalled, is the frequency of any given line relative to the origin of the band to which it belongs and is related to the initial and final rotational energy values by the equation

$$\nu_m = (\overset{*}{E}'_m - \overset{*}{E}''_m)/h = F' - F''. \tag{83}$$

Since, in the present section, this frequency *relative* to the origin is alone of interest, we may for convenience assume that the frequency of the origin $(\nu_e + \nu_n)$ is zero, so that ν_m becomes the actual frequency and is written merely as ν.

Because of the great complexity of the phenomena now to be discussed, it seems simpler to calculate the band structure to be expected according to various theoretical assumptions, and then to compare these results with the structure of typical bands. But, as has previously been noted, the quantum analysis of a given band involves two distinct steps. (1) The evaluation of the spectral terms, (2) the quantum interpretation of these terms. Step (1) may again be subdivided into (1a), the evaluation of the finite differences of successive spectral terms, (1b), the evaluation of the spectral terms by appropriate summation of successive differences.[92] Step (1) is independent of quantum theory and is merely a test of the combination principle, but as a matter of fact the predictions of the quantum theory have been essential in order to indicate the method of procedure. We shall accordingly first discuss step (1a), beginning with a brief account of the predictions of the quantum theory which have led to a standardized process for obtaining the spacing of the spectral terms.

It has been shown in Chapter II (p. 43) that the vibrational quantum number n, in the case of a non-harmonic oscillator, can change by any integral amount. But in the case of the rotational quantum number j, the experimental evidence indicates that it changes only by the amounts $+1$, -1, or 0. The theoretical basis for this has been given in Chapter II (pp. 40 and 50). The vital step in the quantum interpretation of electronic bands was taken simultaneously by Heurlinger([89]) and by Lenz([90]), and consisted in the identification of the known P, Q, and R branches of electronic bands with changes in the rotational quantum number j of $+1$, 0, and -1, respectively, for the case of emission.

Without any further assumptions as to the emitting mechanism, it is possible to predict certain mathematical equalities, which form, essentially, a test of the combination principle. As indicated by equations (71) and (83), we denote by F' any spectral term corresponding to the initial

[92] Or, as discussed in Section 4, by transformation of the finite differences into derivatives, and then by integration.

condition of the molecule, and by F'' any term corresponding to the final condition so that $\nu = F' - F'' = \nu_m$. Let us further designate any spectral line by the value of j in the final state, in the case of emission, since this nomenclature [93] is now used by the majority of investigators. Accordingly we *define*

$$P_j = F'_{j-1} - F''_j \tag{84}$$

$$Q_j = F'_j - F''_j \tag{85}$$

$$R_j = F'_{j+1} - F''_j. \tag{86}$$

Thus $j'' = j$ for all three branches, while $j' = j-1$, j, and $j+1$ respectively.

It is sometimes convenient to express each line in terms of the effective quantum number m. In order to distinguish this nomenclature from the above, we write

$$P[m''] = F'[m'] - F''[m''], \text{ where } m' = m'' - c_P \tag{87}$$

$$Q[m''] = F'[m'] - F''[m''], \text{ where } m' = m'' + c_Q \tag{88}$$

$$R[m''] = F'[m'] - F''[m''], \text{ where } m' = m'' + c_R \tag{89}$$

As denoted by these three equations, m does not necessarily change by $+1$, 0, and -1, for the P, Q, and R branches respectively. Hence the statement of the value of m'' for any line does not always give any

[93] One of the greatest sources of confusion in the analysis of the detailed structure of electronic bands is the matter of nomenclature. From the previous sections it can be seen that there are numerous different ways of denoting a given line. We may, first, denote it by its initial quantum number, or by its final. Some investigators have used one, some the other, and some have used the initial for one branch and the final for the other. We shall adopt Kratzer's custom of denoting a line *always* by the *final* quantum number for the emission process, i. e., by the lower of the two energy levels. The next question concerns *which* quantum number to use. Each line has a *true* final rotational quantum number j'', measuring the total angular momentum, and an effective final rotational quantum number m'', measuring the nuclear angular momentum. The line may be denoted also by the purely arbitrary parameter or "Laufzahl" M, introduced in Section 2. Since at the beginning of an investigation, the values of j'' and of m'' are unknown, this arbitrary parameter is very convenient. Our convention as previously stated is to number the lines with integral values of M, in accordance with the symmetrical distribution of intensity, so that $P(0)$, $R(0)$ and $Q(0)$ represent missing lines, while $P(1)$, $R(1)$ and $Q(1)$ represent the first theoretically observable line in each branch. Methods for actually carrying out this numbering will be given presently. Now in all cases, so far as we know, the value of M, in each branch, differs from the true value of j'' by a constant quantity, although the constant is usually different for the different branches of the same band. Hence our general method of procedure will be to obtain experimental relations between the lines of a band, in terms of M, and then determine, for each branch, the connection between the value of M and the true quantum number of the final state, j''.

information as to the value of m'. The experimental data indicate that c_P and c_R are small positive quantities, equal to unity in certain simple cases, while c_Q is a small positive or negative quantity, equal to zero in certain simple cases. The method of representation in terms of m is most convenient in discussing ΔF, or F (i. e., $\Delta \overset{*}{E}_m$ or $\overset{*}{E}_m$) since we have seen, from the equations of Section 3, such as equation (59) that these quantities [94] are especially simple functions of m.

Finally, we shall continue to use the nomenclature $P(M)$, $Q(M)$, and $R(M)$ to designate the various lines in terms of M, and when plotting, we shall sometimes use negative values of M (or even for the other parameters j and m), denoting the graphs by P', Q' and R'.

If, now, the fundamental assumptions of the quantum theory regarding the origin of the P, Q, and R branches are true, as expressed by equations (84), (85), and (86), it follows that [95]

$$R_j - P_j = F'_{j+1} - F'_{j-1} = 2\Delta F'_j, \tag{90}$$

$$R_{j-1} - P_{j+1} = F''_{j+1} - F''_{j-1} = 2\Delta F''_j, \tag{91}$$

$$R_j - Q_j = Q_{j+1} - P_{j+1} = F'_{j+1} - F'_j = \Delta F'_{j+\frac{1}{2}}, \tag{92}$$

$$R_j - Q_{j+1} = Q_j - P_{j+1} = F''_{j+1} - F''_j = \Delta F''_{j+\frac{1}{2}}. \tag{93}$$

These four equations contain the various pairs of lines which not only test the combination principle, but enable us to isolate the initial and final spectral terms. Equation (93) is merely a rearrangement of terms in equation (92) and so both equations must be true, if one of them is. Moreover, the definitions of $R_j - P_j$ and of $R_{j-1} - P_{j+1}$ in equations (90) and (91) may be derived directly from equations (92) and (93). Thus, in (92),

$$\left.\begin{aligned} R_j - Q_j &= F'_{j+1} - F'_j = \Delta F'_{j+\frac{1}{2}}, \\ Q_j - P_j &= F''_j - F''_{j-1} = \Delta F''_{j-\frac{1}{2}}, \end{aligned}\right\} \tag{94}$$

and by addition we get equation (90).

[94] Just as in the case of the spectral lines, the spectral terms, F' and F'', or their spacing $\Delta F'$ and $\Delta F''$, can be expressed as functions of j or of m and as discussed in a footnote in Part 2c and now illustrated, we will distinguish these different functions by writing F_j or $F[m]$. It is convenient also to express $\Delta F'$ and $\Delta F''$ as a function of M where each value of M is derived from the R line entering into the determination of $\Delta F'$ or of $\Delta F''$, as explained later. In this case we write $\Delta F'(M)$, or $\Delta F''(M)$.

[95] In connection with equations (90) to (93) and many similar equations, attention may again be directed to equations (77) and (78) and accompanying discussion. $2\Delta F$, as obtained from the R and P branches is not mathematically twice the value of ΔF, as obtained from the R and Q, or Q and P branches, and neither is exactly twice the value of the derivative of F at the value of j noted in the subscript. But for the bands thus far analyzed these discrepancies are in all cases within limits of experimental error and hence need not be considered.

Now, if, in a given band, the equalities (92) and (93) are not found, it is certain that there is more than one set of initial levels (F') or of final levels (F'') or of both, and that the three different branches P, Q, and R, do not have common initial or final sets of levels, so as to make these equalities possible. Experimental evidence on this point will be presented later.

On the other hand, if the band has no Q branch, equations (90) and (91) are the only ones that can be tested, and for this purpose it is necessary to have data on a series of bands in a given system. Thus all of the bands forming an n'' progression must give identical values of $2\Delta F'_j$ while all bands forming an n' progression must give identical values of $2\Delta F''_j$. Equation (91) may be written

$$R_j - P_{j+2} = F''_{j+2} - F''_j = 2\Delta F''_{j+1}. \qquad (95)$$

By comparison of equations (90) and (95) we are led to expect the following phenomena. There should be certain sets of bands (called n'' progressions) in a given system for which the difference in frequencies of each line of the R branch (R_j) and a certain corresponding line of the P branch (P_j) give a series of values ($2\Delta F'_j$) which are identical for each band of the set. Then by taking the same lines of the R branch (R_j) with a different corresponding line of the P branch—the *second* line to the red in the P series as compared to the line previously used, i. e., P_{j+2} in place of P_j—we should obtain another set of values, $2\Delta F''_{j+1}$, which will be found identical for all bands of certain sets. These new sets are different from the previous sets, and constitute the various n' progressions of a system of bands.

By assuming Kratzer's theory of the non-harmonic oscillator, we have, in Section 4, equations (79) and (80), arrived at criteria for arranging the bands of a system in n'' and n' progressions. From the relative intensities of the bands in certain nitrogen groups in relation to the Deslandres' progressions, we have deduced an independent criterion for this assignment, as illustrated by Figure 10. We now, from the equalities among the various lines of each band given by the combination principle, obtain a third criterion for the classification of the bands of a system. If there are perturbations in the given system of bands, these form a fourth partially independent method for classifying the bands into progressions.[96] The isotopic effect, already mentioned, forms a fifth method.

[96] In practice, it is usually assumed by investigators that the perturbations are connected with the same initial state, so that a study of the character of the perturbations indicates which bands are to be classified as one n'' progression. Then one should find in any band similar perturbations in the P and R branches, and this immediately indicates that these two perturbed lines are to be used in

Now, when the lines are numbered with respect to a symmetrical intensity distribution, using the empirical parameter M, it is normally found experimentally that

$$R(M)-P(M-1)=2\Delta F'(M) \tag{96}$$

gives a set of identical values of $2\Delta F'$ for all bands forming any one n'' progressions and

$$R(M)-P(M+1)=2\Delta F''(M+1) \tag{97}$$

gives a set of identical values of $2\Delta F''$ for all bands forming any one n' progression.

In this case we have followed the convention agreed upon—to call the first real line of each branch, $R(1)$ and $P(1)$ respectively. If, in addition, each band of the system under consideration has a Q branch, and if, as agreed, we call the first real line of this branch $Q(1)$, then the following additional equalities are found experimentally to be true for *each* band of the system.

$$R(M)-Q(M) \quad =Q(M+1)-P(M)=\Delta F'(M+\tfrac{1}{2}), \tag{98}$$

or

$$R(M)-Q(M+1)= \quad Q(M)-P(M)=\Delta F''(M+\tfrac{1}{2}). \tag{99}$$

Moreover it is found that all bands of any one n'' progression give identical values of $\Delta F'(M+\frac{1}{2})$ in equation (98) and all bands of any n' progression give identical values of $\Delta F''(M+\frac{1}{2})$ in equation (99).

Let us, however, assume that we have made no analysis of the bands of the system into progressions, by means of the theory developed in

equation (95). From this are known all the other pairs of lines giving the values of $2\Delta F''_{j+1}$. Then by taking the second P line to the violet, and the same R line, we have the pairs of lines to be used in equation (90), and the values of $2\Delta F'_j$ thus found should be identical for all bands with similar perturbations. If this is found to be the case, it proves the original assumption that the perturbations are connected with the initial condition. If, however, it should happen that the perturbations were actually connected with the final state, then the set of values of $2\Delta F$ found by starting with a pair of perturbed lines would be values of $2\Delta F'$, and in order to get *any other* set of values $2\Delta F$ which would occur also in other bands, it would be found necessary to use the second P line to the *red*, with the same R line, thus getting a set of values of $2\Delta F''$ which would be found to be identical in all bands with similar perturbations

Thus the perturbations are an invaluable guide in starting the investigator on a test of the combination principle and in arranging bands in sets, but equations (90) and (95) must actually be used, in order to decide whether it is the initial or final state that is perturbed; or we may use any of the theoretical deductions of Section 4 to decide which state is perturbed. The perturbations thus form a connecting link between the theory of Section 4, and the theory of this section.

Section 4, and that the experimental evidence at our disposal consists solely of the relations given in equations (96) and (97), if the bands have no Q branch, and of the additional equalities of equations (98) and (99), if a Q branch occurs. Let us now consider what theoretical deductions can be drawn from this evidence, assuming the general quantum interpretation of the three branches, as expressed by equations (84) to (86), which lead in turn to equations (90) to (95) inclusive.

We first compare the experimental equations (96) and (97) with the theoretical equations (90) and (95). We see immediately that a certain R line has been used with two different P lines, separated by two units of M, whereas the theory indicates that the two P lines thus used are separated by two units in j. This leads to the important conclusion that the values of M which we have assigned to each P line (which values we may here call M_P) differ from the true final quantum number (j'') of each P line by a constant quantity. By transforming the experimental and theoretical equations so that the same P line is used with two different R lines, we can similarly deduce the result that the values of M applied to the R branch (here called M_R) also must differ from the true value of j'' of each R line by a constant quantity. Let us assume that

$$j = M_R + c \tag{100}$$

where, as in the previous equations of this section, we use merely j for the final quantum number j'', and where c is a constant to be determined.

Then by comparing equations (96) and (90) we see that this constant is not the same for each branch. If, by chance, M_R equals the true j'' for the R branch (as we shall find is actually the case), so that $c=0$ in equation (100), then, evidently we must set M_P equal to $j''-1$ in order to harmonize the two equations. Therefore, in general, for the P branch with the values of M_P actually used

$$j = M_P + 1 + c. \tag{101}$$

Next, by comparing equations (98) and (92) we see that for the Q branch

$$j = M_Q + c. \tag{102}$$

It should be noted, finally, that the designations $2\Delta F'$, and $2\Delta F''$, etc., used in equations (96) to (99) are purely arbitrary, but have been written down by analogy with equations (90) to (93). Thus, if the theory of these latter equations is true, the $2\Delta F'$of equation (96) must be interpreted as referring to a double interval in a set of initial rotational levels, while $2\Delta F''$ of equation (97) must have a similar relation to the final rotational levels.

By finding which bands give identical values of $2\Delta F'$ and of $2\Delta F''$ respectively, we then have an analysis of the bands of a system into progressions which is entirely independent of such a classification based on the methods of Section 4.

The parameters in the functions $2\Delta F'$, $2\Delta F''$, etc., given by equations (96) to (99) are likewise arbitrary. They have been introduced in such a manner, however, that the relation of the argument of ΔF in each such equation to the argument of R in the same equation is exactly the same as the relation of the corresponding arguments in the analogous equations (90) to (93). Hence, if we wish to express the ΔF values in terms of the j's as in equations (90) to (93), we must use the same transformation equation (100) as we would use in converting $R(M)$ into a function of j. Thus from our empirical designation $R(M)$, $Q(M)$, and $P(M)$ for the various lines we can obtain the true quantum designation $j' \rightarrow j''$, and from our empirical functions $2\Delta F'(M)$, $2\Delta F''(M+1)$, etc., of equations (96) to (99), we can obtain the true quantum functions $2\Delta F''_j$, $2\Delta F''_{j+1}$, etc., of equations (90) to (95), as soon as we know the value of c.

In order to determine c, we must make additional theoretical assumptions as to the intensity distribution, and these will be considered later, in connection with individual cases.

Meanwhile, it should be noted that the fact that M and j differ only by a constant is in itself an important clue to the theoretical structure of certain bands. Thus, in the second positive group of nitrogen, and in the Swan bands of carbon, there are, in one series, certain repeated irregularities of intensity. These were mentioned near the end of Part 2f. The phenomenon is such that several investigators have suggested that what had been called one series is really two series, each composed of the alternate lines of the original series. But now Lindau([11]) has shown that equations (96) and (97) are true [97] for the bands of nitrogen, using the questionable series in its original form. If the double series were

[97] It should be noted that Lindau made no attempt to evaluate the c of equations (100) and (101), and in fact did not carry the series close enough to the point of minimum intensity, except in two instances, to determine the *absolute* values of M by the method of intensity distribution. He determined the *relative* values by making the usual assumption that lines $R(M)$ and $P(M+1)$ have similar perturbations. This assumes, as already noted, that the perturbations are connected with the initial state, but the assumption was immediately justified by the verification of equations (96) and (97).

A preliminary study by the writer indicates that in some cases Lindau's absolute numbering of M (which should lead to $c=0$) is incorrect, and actually leads to values of c not only different for different bands, but different for the three component series (forming the triplets) of a single band. This result agrees with the still more recent work of Mecke([54]) on this band system.

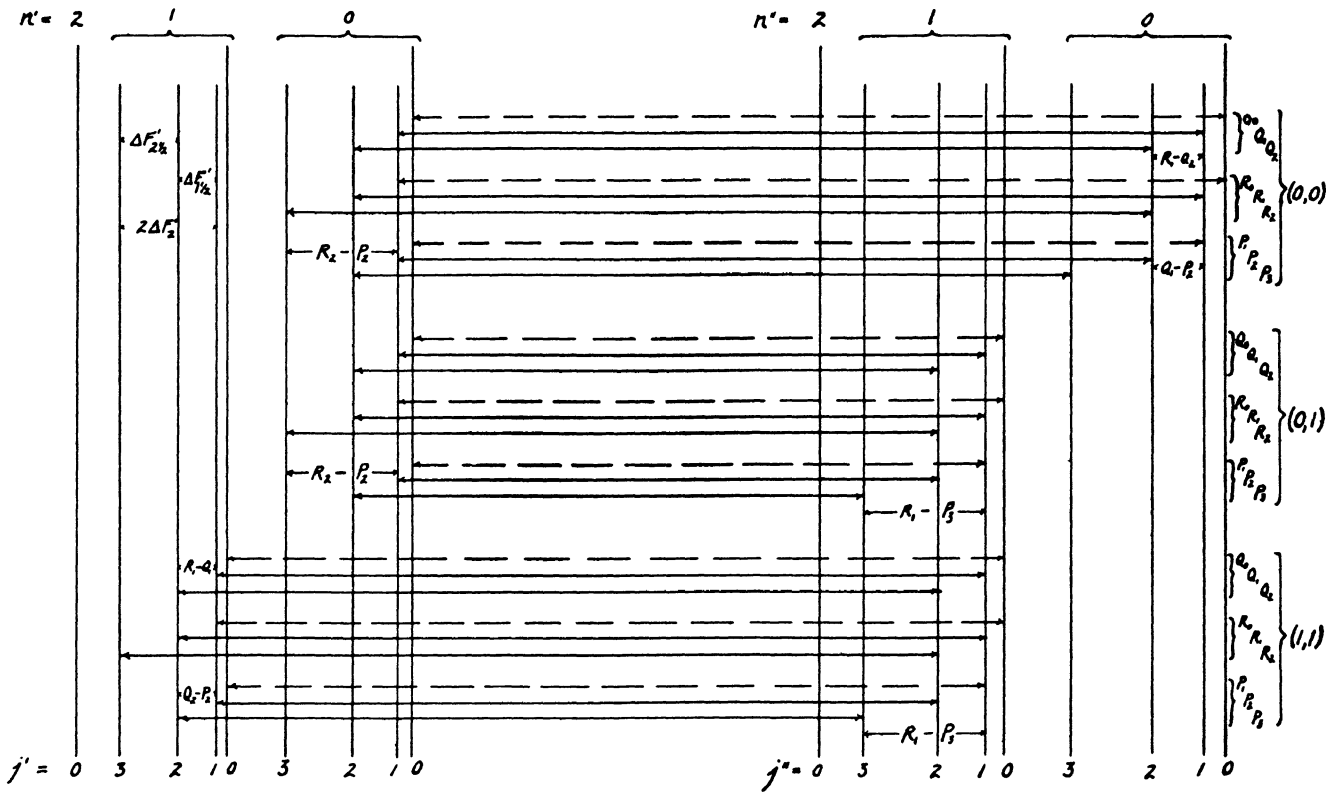


FIGURE 17.—Partial Sets of Rotational Energy Levels of Three Bands, and first Three Lines of each Branch, with Combination Principle Equalities.

assumed, the two P lines combined with the same R line in equations (96) and (97) would differ by only one unit in M, in contradiction to the theoretical expectation. J. D. Shea([91]) has shown the same relations for the Swan bands. However, in this case as in others in the preceding pages, the entire validity of the argument rests upon the assumed theoretical interpretation of the P, Q, and R branches as corresponding to $\Delta j=+1$, 0, and -1 respectively. As mentioned in a footnote of Section 3, it is possible, by assuming ϵ' different from ϵ'', to obtain an actual Q branch having the appearance of a P branch or of an R branch. This Dieke([59]) has done, in the case of the negative nitrogen bands. Thus the alternate lines of apparent P and R branches of these bands are interpreted as actual Q and R branches and P and Q branches, respectively. In this case, equations (92) and (93) for instance show that a certain R line (R_j) is to be combined with two different Q lines (Q_j and Q_{j+1}) differing by only *one* unit of j, to give values of $\Delta F'$ and $\Delta F''$ respectively, instead of with two P lines differing by *two* units in j, to give values of $2\Delta F'$ and $2\Delta F''$ respectively. Hence on Dieke's assumption, we are led to interpret the apparent P branch as in reality two branches, composed respectively of alternate lines. One is a true P branch, the other a true Q branch. Similarly, the R branch consists actually of two branches, one an R branch and the other a Q branch.

The preceding relations connected with the combination principle, as stated in equations (90) to (95) are shown graphically in Figure 17, assuming that $c=0$ in equations (100), (101), and (102). The rotational levels (vertical lines) are not drawn to scale, in order purposely to avoid the rapid confluence of the levels near $j=0$. The figure shows three vibrational levels, of which two are accompanied by several of the attached rotational levels, all for a given electron configuration, and a similar set of levels for another electron configuration. Taking for both configurations the vibrational quantum numbers as 0, 1, and 2, we have represented, by horizontal lines, the first three lines of each branch of the three bands (0, 0), (0, 1) and (1, 1). The first two bands belong to the same n'' progression ($n'=0$), and the last two to the same n' progression ($n''=1$).

In each branch the first possible line has $j=0$ for either the initial or final state, or both. In order to explain the experimental results, it has been customary to assume that the rotational state $j=0$ has zero probability. Hence this first possible line in each branch is missing, and is indicated in the figure by a broken line.

As drawn, the spacing of the vibrational levels is less in the initial state than in the final, corresponding to sequences degraded to the red.

This condition occurs, as has previously been noted, only in the case of bands degraded to the red. This latter condition is represented by a closer spacing of the rotational levels in the initial than in the final state (since $I'>I''$), for corresponding values of n. Also, in agreement with equations developed in Section 3, the spacing in the sets of rotational levels always decreases, as n increases. Finally, from the theory developed in Section 3, the spacing of the rotational levels increases at least approximately proportional to j, while the spacing of vibrational levels decreases slowly, as n increases. The diagram therefore shows qualitatively the relative spacing of the levels for a system of bands degraded to the red.

The illustrations of the combination principle are as follows: (1) The value of (R_1-P_3) for bands (0, 1) and (1, 1) is identical, because both bands have the same final vibrational state, while the two lines in question, R_1 and P_3, have the same initial rotational state, in each band. Therefore (R_1-P_3) gives $2\Delta F''_2$, in agreement with equation (91).

(2) The value of (R_2-P_2) for bands (0, 0) and (0, 1) is identical, for both bands have the same initial vibrational state, while the two lines R_2 and P_2 have the same final rotational state, in each band. Therefore, (R_2-P_2) gives $2\Delta F'_2$, in agreement with equation (90).

(3) The value of (R_1-Q_1) is identical with that of (Q_2-P_2) as illustrated in band (1, 1) since the final state is the same for the two lines of each pair, and the same two initial states occur in each pair. Therefore either of these two differences gives $\Delta F''_{1\frac{1}{2}}$, in accordance with equation (92).

(4) The value of (R_1-Q_2) is identical with that of (Q_1-P_2), as illustrated in band (0, 0), since the initial state is the same for the two lines of each pair, and the same two final states occur in each pair. Therefore, either of these two differences gives $\Delta F''_{1\frac{1}{2}}$, in accordance with equation (93).

This figure is convenient also for discussing more fully the remark made in a footnote of Section 3, to the effect that if all three branches of a set of bands are present, one can calculate a complete set of energy levels, such as that illustrated, by the combination principle alone independent of any theory; but if the Q branch is missing, one can in general compute only two independent sets of levels, by the respective use of alternate lines of the various series.

Assuming, first, the presence of all three branches, but using only the Q and R branches of, let us say, the (0, 0) band, one obtains from Q_1 the levels $j'=1$ and $j''=1$, of which one (let us say j') may be assigned any

arbitrary value. Then R_1 locates the level $j'=2$ and Q_2 the level $j''=2$. Thus, using the succession of lines Q_1, R_1, Q_2, R_2, etc., one may locate every level (except $j=0$) for the initial and final state of this band. Another band with the same initial state, such as (0, 1), then checks the values for this initial state, and simultaneously locates a new set of final levels, corresponding to $n''=1$. Thus we may build up the complete set of levels, for all of the bands of a system. If we have in addition, a series of electronic levels, *a, b, c,* etc., such that $a \rightarrow b$, and $b \rightarrow c$, etc., correspond to known band systems, then having obtained all of set *b* in terms of an arbitrary assumed value of some level of set *a,* we may similarly obtain all of set *c,* etc. Finally, by using the lines of the *P* and *Q* branches, instead of *R* and *Q,* in the order Q_1, P_2, Q_2, P_3, etc., one may obtain a completely independent evaluation of the entire set of levels.

But now let us assume that the *Q* branch is missing. In such a case only alternate lines of each of the two branches *P* and *R* have *any* level in common. Thus, starting as before with an assumed value of $j'=1$ for any given band, the series of lines P_2, R_2, P_4, R_4, etc., gives the evaluation of $j'=1$, 3, 5, etc., and $j''=2$, 4, 6, etc. By using other bands of the system, these same values of j may be evaluated for all values of n' and n'' actually represented. Thus *one-half* of the lines of the bands lead to the evaluation of the odd-numbered levels of the initial state, and the even-numbered, of the final state. If, now, we have a set of systems of bands, $a \rightarrow b$, $b \rightarrow c$, $c \rightarrow d$, etc., it is possible, by an obvious extension of the above calculations, to obtain the *odd*-numbered rotational levels related to *alternate* electronic levels, such as *a, c, e,* etc., and the *even*-numbered rotational levels of the remaining electronic levels *b, d,* etc. Finally, by using the remaining half of the lines of each branch of every band, one can obtain the even-numbered levels of the sets corresponding to *a, c, e,* etc., and the odd-numbered levels of the remaining sets. But there is *no* arithmetic connection between the *two* sets. To be sure, one can adjust the relative positions of the two sets so that, as in Figure 17, the combined effect is that of one set obeying certain relatively simple laws. This, however, is a matter of theory.

But now let us assume we have "combination" bands, due to the transition from electron level *a* to level *c* in addition to the two systems of bands $a \rightarrow b$, and $b \rightarrow c$. Then the odd-numbered levels of set *a* can be arithmetically connected with the even-numbered levels of set *c,* and *vice versa.* This gives the desired connection between the odd- and even-numbered levels of sets *a, b,* and *c.*

Unfortunately, such "combination" bands seem to be very rare, and in their absence, certain possible ambiguities of interpretation, in the case of complex bands, seem unavoidable.[98]

PART 5B. SPECTRAL DIAGRAMS

In the preceding portion of this section we have considered the general form taken by the combination principle, using only the most general assumptions as to the quantum origin of the P, Q, and R branches of a band as given by equations (84) to (86). We have considered, also, what has been found experimentally to be the actual form of this principle in terms of a convenient empirical numbering of the lines of a band, and have made several theoretical deductions from the empirical facts. In order, however, to obtain the true quantum numbers to be assigned to each line of a band—in other words, to make a real quantum analysis—it is now necessary to introduce some or all of the theoretical assumptions made in Section 3. In many cases, these assumptions are presumably correct. In other cases, there is as yet too little experimental evidence to draw any definite conclusions. In yet other cases, the whole matter is still in a highly speculative stage.

The simplest and most convenient method of procedure consists in using the theoretical equations for F' and F'', in Section 3, together with certain assumptions as to intensity distribution, in order to calculate the expected appearance of an entire band, and then to enquire whether known bands have such an appearance. We then indicate how the data should be handled in each case to obtain finally the theoretical equations for F' and F'' which we originally assumed. We shall accordingly begin with the simplest conceivable type of molecule, and pass progressively to more complex types, illustrating the results by means of a series of diagrams.

In plotting these diagrams, we give only the data relating to the immediate vicinity of the origin of the band; for, in general, only such data are needed in order to derive the essential facts regarding the quantum analysis of a band. Conversely, it is generally impossible to obtain the quantum analysis without such data, for it is then necessary

[98] As noted under Part 3b, two cases of "combination" band systems are now known, (1) in the BO bands, found by Mulliken(47), and (2) in the CO^+ bands, photographed by Baldet(92) and by Johnson(70) and identified by Birge(60). In the former case, none of the bands have as yet been photographed under high dispersion, while in the latter case the $a \rightarrow c$ (first negative group of carbon) and $b \rightarrow c$ (comet-tail bands) have been photographed under high dispersion and analyzed; but the new "combination" bands have not as yet been obtained under high dispersion.

to extrapolate the empirical equations into the region of the origin and this, in the case of all but the simplest types of bands, is a highly uncertain procedure.

Now for this region in which j and m are small, as has been shown in Section 3, the formulas become much simpler, except when neither σ nor ϵ vanishes, in which case the reverse is true. Aside from this latter case, the only formulas which are used are those for a straight line and for a second degree parabola.

In the diagrams, we begin at the left side by plotting F'_j and F''_j as a function of j, where j is the ordinate scale, and F the abscissa scale. j as usual is assumed to be an integer. We then shift F' up and down one unit to give the new equations F'_{j-1} and F'_{j+1}. Then by equations (84) to (86), we can graphically or analytically subtract F''_j from each of three functions F'_j, F'_{j-1} and F'_{j+1} to obtain respectively, Q_j, P_j and R_j. These resulting frequency values are then plotted in the center of the diagram as a function of j, using the *same* ordinate scale, as indicated by the form of equations (84) to (86). In order to show certain symmetries, we plot P, Q and R also in terms of negative values of j, denoting the curves as usual by P', Q', and R'.

From these $\nu : j$ plots of Q, R, and P we next obtain the actual appearance of the spectrum, as far as the relative frequency of each line is concerned. When it comes to the matter of intensity, it is necessary to introduce additional assumptions. The theoretical aspects of this question have already been discussed in Chapter III for vibration-rotation bands, and will be mentioned again later in this chapter. Meanwhile, it has been noted earlier that in all cases the intensity seems to be approximately symmetrical with respect to a point between the R and P branches, thus furnishing the basis for the values of M to be assigned to each line. As will appear more clearly from a study of these diagrams, the experimental [99] results are approximately satisfied by the following two empirical rules: (1) The intensity in each branch is distributed according to the general distribution function.

$$\text{Intensity} = \overline{m} e^{-k\overline{m}^2}, \tag{103}$$

where k is a function of I and of T, the absolute temperature, and $\overline{m}$ is the algebraic mean of m' and m'' for the line in question. (2) All lines for which either j' or j'' is zero, have zero intensity.

[99] These results, at the present time, are scarcely more than qualitative and consist in general of microphotometric curves of a number of electronic bands. More accurate quantitative material is greatly needed, in connection with several proposed theories of the intensity distribution in various types of bands. More searching data are needed, also, concerning the missing line, for as shown in Part 5d, rule (2) is found to break down in certain more complex bands.

The distribution function has such a form that for very small values of m, the intensity is nearly proportional to $\overline{m}$. But as is shown in foot note 104 in connection with the discussion of Cases I to IV (ahead), the distance of any line in the P or R branch from the origin of the band is approximately proportional to the algebraic mean value of m, for *small* values of m. Hence, there results the very convenient rule that, for small values of m, the lines of the P and R branches have an intensity proportional to their distance from the band origin. This, it may be noted, is exactly the original form of the classical theory [100] of near infrared bands, (assumed continuous), since the distance of any portion of the band from the central zero point is, on that theory, proportional to ω_m, the frequency of rotation, and the theoretical distribution of ω_m with temperature is given by equation (103) with $\overline{m}$ replaced by ω_m. This is only another example of the seemingly general "correspondence" between classical and quantum theory.

Each spectral line is accordingly drawn beneath the $\nu : j$ curve, and labelled with its theoretical value of $j' \rightarrow j''$. Its intensity is indicated by the length of the drawn line. Missing spectral lines are indicated by broken lines. At this point we drop the theoretical aspect and assume the viewpoint of the experimental investigator. We assume ourselves in possession only of the spectral lines with intensities as indicated, and wish to analyze these in such a manner as to obtain the theoretical F' and F'' functions. The details of this process will be given after we have discussed the theoretical treatment of Cases I to IV as given in Figures 18 and 19.

Case I. Figure 18 (Theoretical)

This illustrates the simplest conceivable type of molecule where the rotational energy E_m^* is given by equation (18) and where the molecular constants are the same in both the initial and final states. (This is of course a most improbable assumption, in the case of an electronic band.) Hence in equations (59) and (60)

$$F' = F'', \qquad \epsilon' = \epsilon'' = 0, \qquad \delta' = \delta'' = 0, \qquad \sigma' = \sigma'' = 0. \tag{104}$$

and equation (59) becomes

$$F = F' = F'' = B_0 m^2 = B_0 j^2 \tag{105}$$

and

$$\Delta F' = \Delta F'' = 2B_0 j. \tag{106}$$

[100] See Kemble, reference (93).

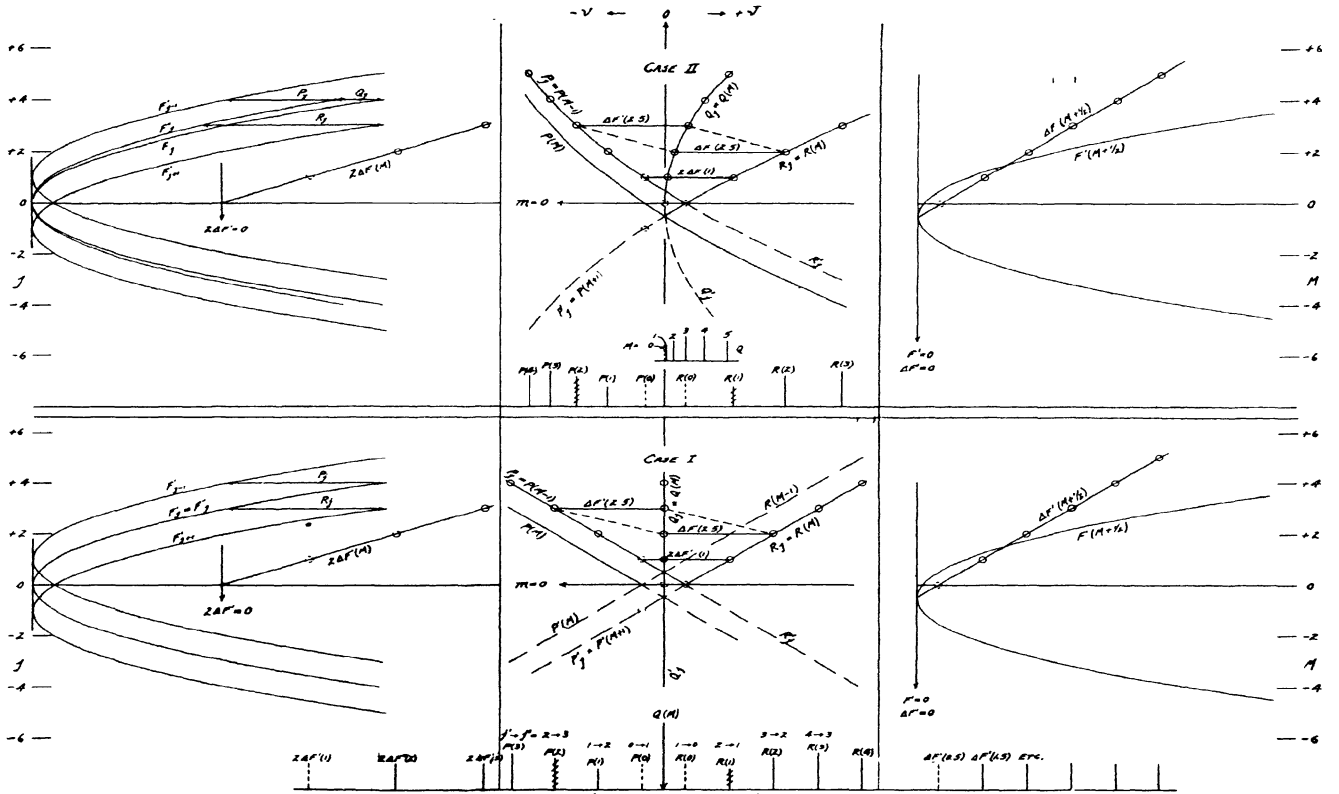


FIGURE 18.—Spectral Diagrams.

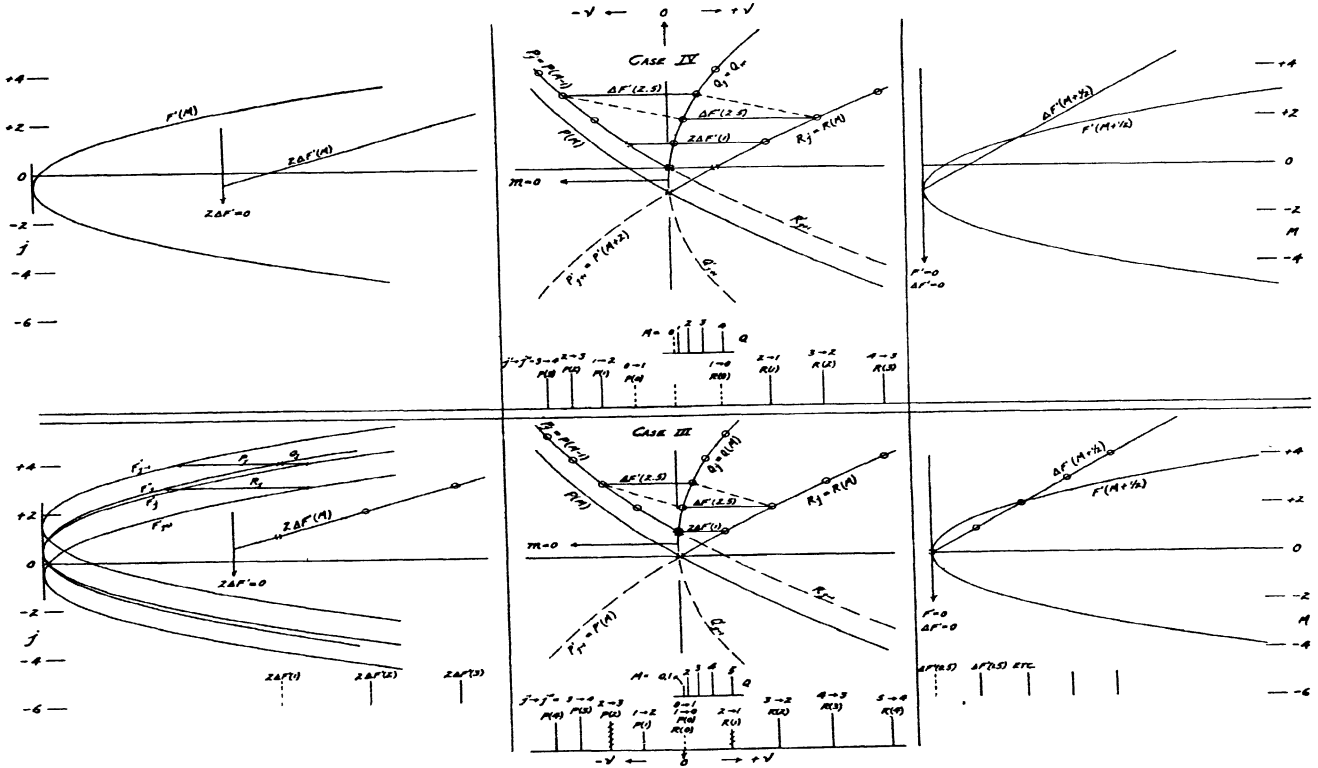


FIGURE 19.—Spectral Diagrams.—Cont'd.

Case III. $F' > F''$, $\epsilon' = \epsilon'' = +\frac{1}{2}$, $\delta = 0$, $\sigma = 0$. Case IV. $F' > F''$, $\epsilon' = \epsilon'' = -\frac{1}{2}$, $\delta = 0$, $\sigma = 0$.

See body of report for details.

In order now to plot all quantities in terms of the *final* quantum number j'', here designated j, we keep F''_j fixed and vary F'_j, as described above, and thus obtain

$$Q_j = F'_j - F''_j = B_0 j^2 - B_0 j^2 = 0, \tag{107}$$

$$R_j = F'_{j+1} - F''_j = B_0(j+1)^2 - B_0 j^2 = 2B_0(j+\tfrac{1}{2}), \tag{108}$$

$$P_j = F'_{j-1} - F''_j = B_0(j-1)^2 - B_0 j^2 = 2B_0(-j+\tfrac{1}{2}). \tag{109}$$

We see from these equations that P'_j is the extrapolation of R_j, since changing the sign of odd powers of j in P_j makes it identical with R_j. The Q branch, plotted with ν against j, is the vertical straight line, $\nu = 0$. The R_j and P_j graphs are straight lines of slope $+2B_0$ and $-2B_0$, meeting each other at $j=0$, $\nu = B_0$, and crossing the Q branch at $\nu = 0$, $j = -\frac{1}{2}$ and $+\frac{1}{2}$ respectively.

Beneath the $\nu : j$ curves for the three branches are plotted the actual spectrum lines, the Q branch being reduced to a single line $\nu = 0$. The R and P branches form a continuous sequence of equidistant lines, with interval $2B_0$. Above each spectral line is given its designation in terms of the empirical parameter M, i. e., $R(M)$, $P(M)$, and $Q(M)$. This is done for each of the cases I to IV, and these values of M will be discussed later. For Cases I, III and IV there is given above each line, also, the values of $j' \to j''$. These follow immediately from the P, Q, and R graphs.

If we now make the general assumption that only those lines are missing for which $j=0$ in either the initial or final state, we see that the $1 \to 0$ line of the R branch (i. e., R_0), the $0 \to 1$ line of the P branch (i. e., P_1), and the $0 \to 0$ line of the Q branch (i. e., Q_0) are missing. These three lines will be missing regardless of the functional form assumed for F' or F''. In the present case we find that in the continuous sequence of lines given by R_j and P'_j, there are *two* missing lines, R_0 and P_1. The Q branch forms a single strong line at $\nu = 0$, the origin of the band, and the two missing lines are situated on each side of this point at $\nu = \pm B_0$. On the other hand, if the perturbations are due to the initial conditions, then two lines such as $R_1(2 \to 1)$ and $P_3(2 \to 3)$ may show similar perturbations,[101] and such pairs of lines are equidistant from the missing line P_1, i. e., from $\nu = -B_0$.

Case II. Figure 18 (Theoretical)

This case is similar to Case I, except that we assume different functions for F' and F'', keeping F', for convenience, geometrically the same as for Case I. The actual plotted functions are

$$F' = B'_0 j^2 = \tfrac{45}{32} j^2 \tag{110}$$

and

$$F'' = B''_0 j^2 = \tfrac{40}{32} j^2 \tag{111}$$

[101] This pair of lines is indicated by cross-hatching, in Cases I, II, and III.

where the same linear scale is used for F and for j. The relative magnitude of B'_0 and B''_0 is that for a band degraded to the violet, and the per cent variation is quantitatively that frequently found in electronic bands. Hence the spectra plotted in this and succeeding diagrams can be considered to represent certain actual spectra, so far as the relative spacing of the lines is concerned.

As before, F'' is kept fixed, at the left side of the diagram, and F' placed in the three positions which will give the three branches of the series. The equations of these branches, letting $C_0 = B'_0 - B''_0$, are

$$Q_j = F'_j - F''_j = B'_0 j^2 - B''_0 j^2 = C_0 j^2, \tag{112}$$

$$R_j = F'_{j+1} - F''_j = B'_0 (j+1)^2 - B''_0 (j)^2 = C_0 j^2 + 2B'_0 (j + \tfrac{1}{2}), \tag{113}$$

$$P_j = F'_{j-1} - F''_j = B'_0 (j-1)^2 - B''_0 (j)^2 = C_0 j^2 + 2B'_0 (-j + \tfrac{1}{2}). \tag{114}$$

A comparison of equations (112), (113), (114) with equations (107), (108), (109), shows that every line of the three branches has a frequency $C_0 j^2$ greater in Case II than in Case I, due of course to the fact that we have used, for each branch, an F'' smaller by $C_0 j^2$ than that for Case I. Hence the three branches are now represented by parabolas, differing from the previous linear graphs by $C_0 j^2$, and hence tangent to these lines at $j = 0$. Thus the Q branch is now a parabola with its vertex at $j = 0$, $\nu = 0$, defining the "origin" of the band. In fact, the vertex of the Q branch parabola *always* locates the origin of a band, in cases where $\epsilon' = \epsilon''$, $\sigma = 0$, the only type discussed in Figures 18 and 19. The relations in more complex cases will be discussed individually.

As in Case I, P'_j is the continuation of R_j, as is evident from a comparison of equations (114) and (113); and P_j and R_j cross at $j = 0$, $\nu = B'_0$. This is the frequency of R_0 while P_1 (the other missing line) is at $\nu = -B''_0$. Hence the two missing lines are at equal distances from $\nu = +C_0/2$, instead of from the origin, as in Case I. Moreover, R_j and P_j intersect Q_j at $j = -\frac{1}{2}$ and $j = +\frac{1}{2}$, respectively, as in Case I, but at $\nu = C_0/4$ instead of at the origin.[102]

For this case the frequencies of two similar perturbations are given by equation (113) for pairs of values of j (using positive and negative values) such that $\frac{j_1 + j_2}{2} = -1$. That is to say, the perturbations are no longer symmetrical, in terms of frequency, with respect to any given frequency, but are symmetrical in terms of j from $j = -1$, on the $R_j P'_j$ curve, as plotted.

[102] The corresponding curves for bands degraded to the red are obtained by making C_0 negative, so that the parabolas of Case II lie on the *left* side of the straight lines of Case I, and the intersection of R_j and Q_j is just to the red of the origin, instead of to the violet, as drawn here.

The spectral lines obtained in Case II are similar to those of Case I, save that the spacing of the lines of the R and P branches increases uniformly to the violet, while the Q branch has become a real series. It is unnecessary to give the $j' \to j''$ values for the Q branch, since $j = j' = j''$ always. The intensity distribution assumed for this branch is the same as that for the R and P branches—in lieu of definite experimental or theoretical evidence on this point. The $j' \to j''$ values for the P and R branch lines are identical with those in Case I, and therefore are not given.

Case III. Figure 19 (Theoretical)

This case differs from the preceding in that we assume $\epsilon' = \epsilon'' = +\frac{1}{2}$, i. e., $m = j - \frac{1}{2}$ for both initial and final conditions.[103] Therefore equation (59) becomes

$$F'_j = B'_0 m'^2 = B'_0 (j - \tfrac{1}{2})^2, \tag{115}$$

$$F''_j = B''_0 m''^2 = B''_0 (j - \tfrac{1}{2})^2. \tag{116}$$

These equations, compared with equations (110), (111), show that m (or $j - \frac{1}{2}$) has replaced j. Making the same change in equations (112), (113), (114), we obtain

$$Q_j = C_0 m^2 = C_0 (j - \tfrac{1}{2})^2, \tag{117}$$

$$R_j = C_0 m^2 + 2B'_0 (m + \tfrac{1}{2}) = C_0 (j - \tfrac{1}{2})^2 + 2B'_0 j, \tag{118}$$

$$P_j = C_0 m^2 + 2B'_0 (-m + \tfrac{1}{2}) = C_0 (j - \tfrac{1}{2})^2 + 2B'_0 (-j + 1). \tag{119}$$

In obtaining these expressions graphically, we first plot equations (115) and (116). These parabolas are shifted up one-half unit in j, as compared to the parabolas of equations (110), (111), since the vertex is at $j = \frac{1}{2}$ instead of at $j = 0$. The same shift applies in Case III to all parabolas on the left side of the diagram. Hence the R_j, P_j and Q_j curves also are identical with those of Case II, except that they are shifted up one-half unit in j. This shift, however, destroys the symmetry of the P' and P curves, with respect to the $j = 0$ axis. Hence now P'_{j-1} is the smooth continuation of R_j, as can be verified from equations (119) and (118). Moreover, this shift produces a profound change in the actual appearance of the spectrum, for our fundamental assumption is that each spectral line corresponds only to *integral* values of j' and j''. Thus, while the $\nu : j$ curves of Case II are moved up one-half unit, to obtain those of Case III, the observed points must remain opposite the same values of j, and hence must move *down* the $\nu : j$ curves by one-half

[103] Obviously this is equivalent to assuming $\epsilon' = \epsilon'' = 0$ and $j =$ half-integer. This alternative assumption is considered in Part 5c ahead.

unit. This movement along the $\nu : j$ curves shifts the P and R branches closer together, so that the two missing lines R_0 and P_1 now coincide in position. This position as given by equations (118) and (119) is $\nu = C_0/4$. This is also the frequency of Q_0 and Q_1. The P_j and R_j curves cross at $j = +\frac{1}{2}$, (i. e., $m = 0$), $\nu = B'_0$, while the vertex of Q_j is at $j = +\frac{1}{2}$, $\nu = 0$.

Since Case III, representing a series with *one* missing line, seems to be a type commonly found in the case of diatomic molecules, it may be well to note that P_j crosses Q_j at $j = +1$, $\nu = C_0/4$ and R_j crosses it at $j = 0$, $\nu = C_0/4$, while the missing lines R_0, Q_0 and P_1 all coincide at this same point $\nu = C_0/4$, which is thus not identical with the origin $\nu = 0$.

Just as for Case II, the perturbations are not equidistant in terms of frequency from any given point. In Case III, they are equidistant in terms of j from $j = -\frac{1}{2}$, on the $R_j P'_{j-1}$ curve, and are thus given by equation (118) for pairs of values of j such that $\frac{j_1 + j_2}{2} = -\frac{1}{2}$.

Case IV. (Theoretical)

This case differs from Case III in that we assume $\epsilon' = \epsilon'' = -\frac{1}{2}$, instead of $+\frac{1}{2}$. Equation (59) becomes

$$F'_j = B'_0 m'^2 = B'_0 (j + \tfrac{1}{2})^2, \tag{120}$$

$$F''_j = B''_0 m''^2 = B''_0 (j + \tfrac{1}{2})^2. \tag{121}$$

Hence, as in Case III, we use equations (112), (113), (114), replacing j by m, i. e., by $j + \frac{1}{2}$, thus obtaining

$$Q_j = C_0 m^2 = C_0 (j + \tfrac{1}{2})^2, \tag{122}$$

$$R_j = C_0 m^2 + 2B'_0 (m + \tfrac{1}{2}) = C_0 (j + \tfrac{1}{2})^2 + 2B'_0 (j + 1), \tag{123}$$

$$P_j = C_0 m^2 + 2B'_0 (-m + \tfrac{1}{2}) = C_0 (j + \tfrac{1}{2})^2 + 2B'_0 (-j). \tag{124}$$

The graphical solution in this case differs from Case II in the same manner that Case III differs from Case II, except that all the parabolas are shifted down one-half unit in j, instead of up and it seems unnecessary to repeat them. In this case it is P'_{j+1} which is the smooth continuation of R_j. The shift causes the R and P branches to draw apart, so that the two missing lines R_0 and P_1 occupy the positions of R_1 and P_2 of Case III. Hence between R_0 and P_1 there is a third missing line, corresponding to the transitions $-1 \to 0$ and $0 \to -1$. Thus every line in each of the three branches, for Case IV, coincides in frequency with a line of Case III, but the value of j' and of j'' in Case IV, designating a given line, is always one unit lower than in Case III. In other words, there is no difference between Cases III and IV except that one is a "one missing line" case, and the other a "three missing line" case. In Case IV, the

pairs of similar perturbations on the $R_jP'_{j+1}$ curve are given by the pairs of j values $\frac{j_1+j_2}{2} = -1\frac{1}{2}$, using equation (123).

If now, in Case III, ϵ is slightly less than 0.5, all of the plotted lines in Figure 19 will be slightly displaced *away* from the origin—the single missing line breaking up into two adjacent missing lines. A similar decrease in the *absolute* value of ϵ, in Case IV will cause all the plotted lines of Figure 19 to move slightly *nearer* the origin. Hence the combination of Cases III and IV with these changes in ϵ gives a series of doublets, the center doublet being composed of two missing lines, and the first doublet on each side of one missing and one real line. We have seen in equation (64) that the introduction of "δ," due, according to Kratzer, to the mutual influence of electronic and rotational energy, is equivalent effectively to a small decrease in the absolute magnitude of ϵ. Hence we have a possible explanation of a series of doublets, and in fact Kratzer introduced this quantity δ, in order to explain such doublets. This matter is considered more fully in Part 5c.

In concluding the theoretical discussion of Cases I to IV, we may summarize the relations as follows: Excluding Case I, which is introduced merely to define the tangent linear graphs of the other cases, we find, from equations (105) to (124) that in terms of m, the equations for all three cases are identical. Because of this fact it is common practice to write and plot the equations for the Q, R, and P branches in terms of m.

Since in Case II, $j=m$, these common equations are actually equations (110) to (114), of Case II, with j replaced by m, and the graphs of these equations are actually the graphs of Case II, with j replaced by m.[104] Moreover, the introduction in these new equations of j $(=m+\epsilon)$ in place of m merely shifts all of the graphs up or down. Hence the frequency values of the various intersections are independent of the value of ϵ. Thus R_m and P_m (or R_j and P_j) intersect Q_m (or Q_j) at $\nu=C_0/4$, while the vertex of Q_m (or Q_j) is at $\nu=0$, defining the origin of the band. R_m and P_m (or R_j and P_j) intersect one another at $m=0$, $\nu=B'_0$. Two similar perturbations are given by equation (113), with j replaced by m, for pairs of values of m given by $\frac{m_1+m_2}{2} = -1$.

[104] Equations (113) and (114), with j replaced by m, give in analytic form, the basis of a previous statement in connection with equation (103), to the effect that, for small values of m, the distance of any P or R line from the origin is proportional to the mean value of m' and m'' for the particular line. Thus in equation (113), R_m indicates the transition $m+1\rightarrow m$, giving $m+\frac{1}{2}$ as the mean value. P_m indicates the $m-1\rightarrow m$ transition, giving $m-\frac{1}{2}$ as the mean value. Neglecting the small C_0m^3 term, $R_m = 2B'_0(m+\frac{1}{2})$ and $P_m = -2B'_0(m-\frac{1}{2})$.

On the other hand, the appearance of the spectrum depends decidedly upon the value of ϵ' and of ϵ''. Beginning with $\epsilon'=\epsilon''=\frac{1}{2}$, the P and R branches form a continuous sequence of lines, with one missing. As ϵ' and ϵ'' decrease, the two branches move apart so that they cannot be plotted as a continuous sequence, until ϵ' and ϵ'' equal zero. In that case the sequence is continuous, with two missing lines. It is again continuous at $\epsilon'=\epsilon''=-\frac{1}{2}$, with three missing lines. All of the cases just discussed are for the condition $\epsilon'=\epsilon''$, so that $\Delta m=\Delta j$, in any transition. The phenomena introduced when $\epsilon'\neq\epsilon''$ will be considered presently, in connection with the CN and Hg doublets.

Cases I to IV. (Experimental)

Let us consider now that we have found, experimentally, spectra corresponding to those plotted in Cases I to IV, in respect both to the frequency of the lines of the various branches, and to the presence or absence of lines. We wish to analyze these spectra in such a manner as to obtain, either graphically or analytically, the appropriate functions F'_j and F''_j.

To do this, we first label each line with its value of M, in the form $P(M)$, $R(M)$ or $Q(M)$, using values of M such that $M=1$ for the first real line. Lines showing similar perturbations should then correspond to $R(M)$ and $P(M+1)$, the relation announced by Heurlinger[38].

Figures 18 and 19 show immediately that in all cases $R(1)=R_1$, $P(1)=P_2$, $Q(1)=Q_1$, so that equations (100) to (102) are satisfied, with $c=0$. If, then, it is possible to decide, experimentally, just what lines are and are not missing, it is possible to obtain definite information as to the values of j' and j'', on the assumptions made here concerning missing lines. Unfortunately, in the case of high temperature sources, the lines corresponding to small values of M are exceedingly weak, so that it is often very difficult, if not impossible, to decide whether a line is really missing or only too faint to be detected with the experimental resources available.

Because of this difficulty, let us, for the moment, assume the values of M given in Figures 18 and 19. We now plot the curves $P(M)$, $R(M)$ and $Q(M)$, as a function of M, using the same ordinate scale for M as for j.[105] The scale for M is indicated on the right side of the diagrams. In each case the experimental $R(M)$ and $Q(M)$ curves, drawn on this basis, are identical with the R_j and Q_j curves, already drawn. But the

[105] We here, for convenience, note the relations between j and M, *as shown* in Figures 18 and 19, although the experimenter is assumed, at this stage, to be unaware of the correct values of j' and j''.

$P(M)$ curve lies one unit beneath the P_j curve, so that this latter curve represents $P(M-1)$.

Let us now test the combination principle for the particular spectrum under consideration, by the use of equations (96) to (99). The values of $2\Delta F''(M)$, in equation (96) appear in Figures 18 and 19 as the difference of the two curves already drawn, $R(M)$ and $P(M-1)$. The sample value $2\Delta F''(1)$ is indicated for each case. The resulting curves are drawn on the left side of the diagram, using a new abscissæ scale for $2\Delta F''$. In each case the curve is linear.

If the relative numbering for the different branches is correct, identical $2\Delta F'' : M$ curves should be obtained for all bands of an n'' progression. Assuming that this is found to be the case, Figure 18 shows that for Cases I and II, we may write

$$2\Delta F''(M) = kM \quad \text{or} \quad F'' = \frac{k}{4} M^2 + \text{constant}. \tag{125}$$

A comparison of equation (125) with (60), (59) and (61) indicates[106] that we may assume $\delta' = 0$, $M = m = j$, and $k = 4B'$. We thus obtain equations (105) and 110), the theoretical equations for F'' for these two cases.

If, now, the relative numbering of M were correct, but the absolute numbering incorrect, the $2\Delta F'' : M$ curve would be given by

$$2\Delta F''(M) = k(M + c) \tag{126}$$

where c is an integer, equal to the error in numbering. Since in all cases it is desirable to present as simple an explanation as possible for a given set of facts, it would be natural to renumber the lines in such a manner as to make $c = 0$. This is equivalent to making $c = 0$ in equations (100) to (102). The simplest method for ensuring this result is to make the $P(M-1)$ and $R(M)$ curves intersect always within the limits $M = \pm\frac{1}{2}$ (i. e., at $m = 0$, $\nu = B'_0$, the theoretical intersection of P_j and R_j).

A similar use of the data, in Case III, gives

$$2\Delta F''(M) = k(M - \tfrac{1}{2}) \tag{127}$$

[106] As noted in the discussion of equation (70), of Section 3, a linear equation for ΔF, as a function of j, passing through the origin, is satisfied by $\epsilon = 0$, $j =$ integer, while σ may have *any* value. The simplest assumption is, of course, $\sigma = 0$; but, as stated in the footnote at this place in Section 3, Mulliken has recently used this possible latitude regarding the value of σ as the basis of a quite different explanation of missing lines. The present discussion thus gives the simplest possible assumption for Cases I and II, but by no means the only possible one. This ambiguity does not, however, arise in connection with Cases III and IV.

and by comparison with equation (60) we infer that

$$M-\tfrac{1}{2}=m=j-\epsilon', \qquad k=4B'.$$

Here, again, the simplest interpretation of the results is obtained by assuming $j=M$, $\epsilon'=\frac{1}{2}$.

For Case IV, we find

$$2\Delta F'(M)=k(M+\tfrac{1}{2}), \tag{128}$$

from which we infer that $\epsilon'=-\frac{1}{2}$, and as usual $k=4B'$.

Returning again to the combination principle, as given by equation (98), we see that in Figures 18 and 19 we have $R(M)$ and $Q(M)$, ready to be subtracted, to give $\Delta F'(M+\frac{1}{2})$. The sample result $\Delta F'(2.5)$ for $M=2$ is indicated for each case. From equation (98) we have

$$Q(M)-P(M-1)=\Delta F'(M-\tfrac{1}{2}). \tag{129}$$

Using these two curves, with $M=3$, we obtain $\Delta F'(2.5)$, and this result is indicated on Figures 18 and 19, for each of the four cases.

On the right side of the diagrams are plotted the resulting values of $\Delta F'(M+\frac{1}{2})$, for each of the four cases. Cases I and II give

$$\left.\begin{aligned} &\Delta F'(M+\tfrac{1}{2})=k'(M+\tfrac{1}{2}),\\ \text{or}\quad &\\ &\Delta F'(M)=k'(M). \end{aligned}\right\} \tag{130}$$

This agrees with equation (125), if $k'=k/2$, as will be found, experimentally, to be the case. Case III gives

$$\left.\begin{aligned} &\Delta F'(M+\tfrac{1}{2})=k'(M),\\ \text{or}\quad &\\ &\Delta F'(M)=k'(M-\tfrac{1}{2}), \end{aligned}\right\} \tag{131}$$

agreeing with equation (127), while Case IV gives

$$\left.\begin{aligned} &\Delta F'(M+\tfrac{1}{2})=k'(M+1),\\ \text{or}\quad &\\ &\Delta F'(M)=k'(M+\tfrac{1}{2}), \end{aligned}\right\} \tag{132}$$

agreeing with equation (128). On Figures 18 and 19 are shown also the graphs for $F'(M+\frac{1}{2})$, resulting from integration, after the substitution of a derivative for the finite difference $\Delta F'$. In each case, raising $F'(M+\frac{1}{2})$ by one-half unit in M, to give $F'(M)$, results in a parabola identical with F'_j when $M=\mathrm{j}$.

These results may be summarized as follows: The P and R branches should be numbered so as to give a symmetrical intensity distribution, in terms of M, for small values of M. Pairs of lines with similar perturbations, according to all cases thus far investigated, will then correspond

to $R(M)$ and $P(M+1)$. The numbering of the Q branch must then be made in such a manner that equations (98) and (99) hold true. This makes the *relative* numbering of M, for all three branches, in accordance with equations (100) to (102). The values of $\Delta F'(M+\frac{1}{2})$ or of $2\Delta F'(M)$ may then be obtained analytically, from equations (96) to (99), or graphically, as indicated in Figures 18 and 19. The resulting functions according to the combination principle must be identical for all bands in the same Deslandres progression. Finally, in order to make $c=0$ in equations (100) to (102) so that M in $2\Delta F'(M)$ may be replaced by j, the absolute numbering of M should be so chosen as to make the $P(M-1)$ and $R(M)$ curves intersect at as small a value of M as possible. This will make the $2\Delta F'(M)$ curve pass as close to the origin as possible. The value of M for $\Delta F'=0$ should not fall outside the range $M=\pm\frac{1}{2}$. This procedure is based on the assumption that we wish to confine ϵ within the range of values $\pm\frac{1}{2}$. In the great majority of cases tested experimentally, the foregoing procedure is consistent with a numbering of the first real line of each branch as $M=1$, and with the assumption that the missing lines are those for which either j' or j'' equals zero.

The calculation of $\Delta F''$ and F'' cannot be shown graphically on Figures 18 and 19. The proper combinations of lines, for this calculation, are given by equations (97) and (99). Starting with the $R(M)$, $Q(M)$ and $P(M-1)$ curves needed for obtaining $\Delta F'$, the simplest procedure [107] seems to be as follows. Raise $R(M)$ one unit to give $R(M-1)$. Lower $P(M-1)$ one unit to give $P(M)$, and $Q(M)$ one unit to give $Q(M+1)$. Then subtract $P(M)$ from $R(M-1)$ to give $2\Delta F''(M)$, which may be plotted in the manner employed for $2\Delta F'(M)$, in Figures 18 and 19. The subtraction of $Q(M+1)$ from $R(M)$ gives $\Delta F''(M+\frac{1}{2})$, while $Q(M)-P(M-1)$ gives $\Delta F''(M-\frac{1}{2})$, the procedure again being the same as in Figures 18 and 19, where, however, only the $\Delta F'(M+\frac{1}{2})$ results are shown.

Illustration of Case III.

It seems probable, at the present time, that at least the great majority of bands due to diatomic molecules are represented by Case III, aside from the multiplicity of the lines. The combination principle, in the form given by equation (98), was first tested on electronic bands by Hulthén([44]), using the Angstrom CO bands. Hulthén derived an explicit expression only for F', from the data on three bands giving identical

[107] An alternative procedure, using equations (96) and (97) as written, is given in the illustration immediately following.

values for $\Delta F'(M+\frac{1}{2})$. In the present nomenclature[108] his final result is

$$F''=1.943(j-\tfrac{1}{2})^2. \tag{133}$$

This equation shows that these bands form an example of Case III, as far as the initial condition is concerned. Hulthén then assumed $n'=2$ for these three bands, from an assumed intensity relationship. But according to the intensity relations given in Section 4, it is more probable that $n'=0$. Therefore,[109] by equations (37) and (115), $I'_0=14.26\times10^{-40}$ gm. cm.^{2} Hulthén did not represent, analytically, the final state, for $n''=0$.

The structure of these CO bands is especially simple. A much more typical example of Case III is furnished by the CuH bands, for which there are available accurate experimental data, by Frerichs([25]), and by Bengttson([95]). The problem of the best method of handling data of this type, so as to obtain a suitable theoretical formulation, is very involved, and until recently but little work has been done upon it. In reality, two distinct problems are concerned in this question. The first is, what particular functional form will best represent the data, or, conversely, will any of the proposed theoretical expressions properly represent the data? The second is, having decided upon the proper functional form, what are the most probable values of the rotational molecular constants, as deduced from a given set of experimental data? The real difficulties lie in the first problem. The second, while possibly tedious in its actual application, involves merely previously known methods for the reduction of observations.

[108] Hulthén's actual result contains an additional term, $-\frac{1}{2}$, due to the manner in which he summed the $\Delta F''$ values. As has been suggested, an integration is far more convenient, and should be taken with $m=0$ as the lower limit of the definite integral.

[109] As already shown by equation (37) and the discussion, B_n yields a true average value of the moment of inertia of the molecule as a function of n. But in the case of the (0, 0) band, one obtains B'_0 and B''_0, which by equation (38) give the true value of the moment of inertia, perpendicular to the figure axis, for the initial and final state of the molecule respectively, for no vibration, and infinitely slow rotation. Using the most probable values of h and of c [see Birge([94])], equation (38) becomes

$$I_0=\frac{h}{8\pi^2B_0c}=\frac{27.70\times10^{-40}}{B_0}\text{ gm. cm}^2 \tag{134}$$

where B_0 is expressed in wave numbers. In the previous equations of this chapter, the form is such as to require frequency in sec^{-1} units, but in stating numerical values, the more customary "wave numbers" (cm^{-1}) have been used. These latter, as indicated in equation (134), must be multiplied by c, before being inserted in the usual formulas.

Three methods of handling the data will be given here, in rather brief form. The full details of these methods will be published elsewhere, in the near future. What may be called method one has been carried through by the writer for the case of the λ4280 (0, 0) CuH band, but has not been published. Method two has been applied to several bands, and preliminary statements have been published [references (96) and (97)]. Method three is now being applied to the Swan bands by J. D. Shea, to the AlO bands by W. C. Pomeroy, and to the CuH bands by the writer. Preliminary results for the Swan bands and for CuH have been published [references (98) and (99)] and the final results for AlO have just been obtained, reference (97A).

All three methods involve finding analytic expressions for F' and F'', by means of the combination principle, from the experimental data for the P and R branches. Method one yields expressions for F' and F'' which, when used in equations (84) and (86), give satisfactory calculated values of the various spectrum lines. The analytic form of F' and F'' is, however, essentially empirical, and the molecular constants deduced from it are not especially trustworthy, particularly as regards the higher power terms. Method two uses a strictly theoretical formulation of F' and F'' and is a very rapid method for obtaining surprisingly accurate values of certain molecular constants, chiefly B' and B'' (and hence of I' and I''). Method three is much more involved, but is designed as a critical test of the proper functional form for F' and F'', as well as a method for obtaining the most probable values of all of the rotational molecular constants. The weakness of both methods two and three lies in the fact that the expressions for F' and F'', when used in equations (84) and (86), are likely to show small systematic deviations between observed and calculated values of the actual spectral lines. From the theoretical standpoint, however, the real problem is not that of representing spectral lines by accurate analytic expressions, but rather it is that of finding expressions for F' and F'' from which deductions can be drawn as to the structure of molecules. Judged by this latter criterion, methods two and three have led to some interesting conclusions, which are mentioned in later sections.

Method One.—The first step in method one is to obtain, usually by the method of least squares, a suitable empirical formulation of the P and R branches. In the case of the λ4280 CuH band this has been done, in equations (9) and (10), and the results are plotted in Figure 4. Attention has been drawn to the fact that it would appear at the present time that *different* numerical coefficients must be used for the P and R branches, in all cases. For this particular band, a fourth degree poly-

nomial is entirely satisfactory, although one of any lower degree is quite unsatisfactory. Equations (9) and (10) are now to be transformed, and then combined, analytically, to give finally expressions for F' and F''. The first step is to transform $P'(M)$ to $P(M)$, by changing the sign of every odd power term in M. The second is to obtain from $P(M)$ the expressions $P(M-1)$ and $P(M+1)$, in the form of new functions of M. This is done by substituting $(M-1)$ and $(M+1)$ in $P(M)$, and multiplying out. In the case of polynomials, standard expressions for the coefficients of the various powers of M in the new equations, in terms

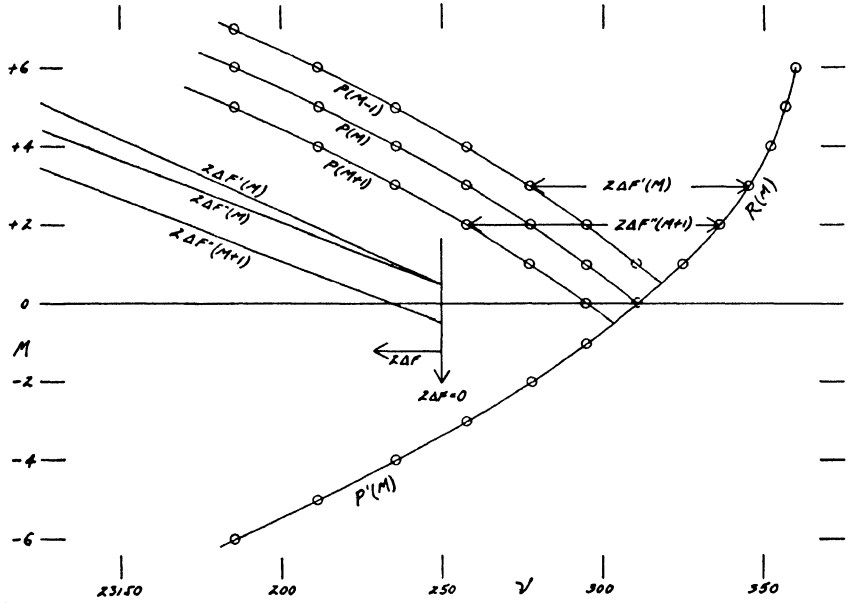


FIGURE 20.—λ4280 CuH Band. Curves to Illustrate Method One of Calculating the Rotational Energy Function.

of those of $P(M)$, are easily obtainable and greatly facilitate the work. Using equations (96) and (97) we next *analytically* subtract $P(M-1)$ and $P(M+1)$ from $R(M)$, to obtain $2\Delta F'(M)$ and $2\Delta F''(M+1)$. $2\Delta F''(M+1)$ may then be transformed into $2\Delta F''(M)$. The results are

$$\left.\begin{aligned} 2\Delta F'(M) &= -13.246+26.8581M+0.02359M^2 \\ &\qquad -0.004757M^3+0.0000226M^4 \\ 2\Delta F''(M) &= -15.581+31.2043M+0.01639M^2 \\ &\qquad -0.004957M^3+0.0000226M^4 \end{aligned}\right\} \quad (135)$$

A quantitative plot of a small portion of the various functions just discussed is given in Figure 20. By halving the expressions of equation

(135) and applying the corrections given by equations (78), one obtains $\frac{dF'}{dM}$ and $\frac{dF''}{dM}$. One then assumes that $c=0$, in equations (100) and (101), so that, as previously discussed, M may be replaced directly by j.

The resulting expressions for j show that ϵ is very closely 0.5, i. e., that if we write $j=m+0.5$, the resulting $f(m)$ will pass very close to the origin. These expressions are also nearly linear, especially where j is small, and it is therefore evident that $\sigma=0$, and that $\frac{dF}{dj}=\frac{dF}{dm}$, as in equation (61). Substituting $(m+0.5)$ for j one obtains

$$\left.\begin{aligned}\frac{dF'}{dm} &= 0.0913+13.4414m+0.00822m^2-0.002356m^3 \\ &\qquad +0.0000113m^4 \\ \frac{dF''}{dm} &= 0.0110+15.6109m+0.00447m^2-0.002456m^3 \\ &\qquad +0.0000113m^4\end{aligned}\right\}. \tag{136}$$

The results indicate that Kratzers "δ," of equation (60) is very small, but apparently real in the case at least of the initial state. As discussed in Section 3, we shall interpret this situation as due to a true value of ϵ (written $\overset{*}{\epsilon}$) slightly different from 0.5, and shall for convenience write

$$m=j-\overset{*}{\epsilon}=j-0.5-a=k-a, \tag{137}$$

where j is an integer, and k a half-integer.[110] When Kratzer's ϵ equals 0.5, a equals $-\delta/B_n$, by equation (64).

In equations (136), $m=j-0.5$ and is therefore to be replaced by k. A new m, defined by equation (137), is then to be formed, by choosing a value of a which will eliminate the constant term in (136). The results are

$$\left.\begin{aligned}\frac{dF'}{dm} &= 13.4413m+0.00825m^2+\text{etc.}, \\ \frac{dF''}{dm} &= 15.6109m+0.00448m^2+\text{etc.},\end{aligned}\right\} \tag{138}$$

the remaining terms being identical with those of (136). This transformation was made by means of the equalities

$$m'=k'+0.006793, \qquad m''=k''+0.000705. \tag{139}$$

[110] Obviously, the "a" introduced in equation (137), and used repeatedly in the remaining portion of this chapter, is not related to Kratzer's "a," as defined by equation (37). In the rare cases where ambiguity might arise, Kratzer's "a" may be written as $\bar{a}$.

The final expressions for F' and F'' are, by integration of (138),

$$\left.\begin{aligned} F' &= 6.7206m^2 + 0.275\times10^{-2}m^3 - 5.89\times10^{-4}m^4 + 2.26\times10^{-6}m^5 \\ F'' &= 7.8054m^2 + 0.149\times10^{-2}m^3 - 6.14\times10^{-4}m^4 + 2.26\times10^{-6}m^5 \end{aligned}\right\}, \quad (140)$$

where $m = k - a$ and the values of a' and a'' are given by equation (139).

The question of the interpretation of these equations is best postponed until after the presentation of methods two and three.

Method Two.—Method two is partly graphic, and is believed to be the most rapid method for obtaining a fairly accurate value of the moment of inertia. In this method the individual numerical values of the P and R branch lines are used in equations (96) and (97) to obtain the numerical values of $2\Delta F'$ and $2\Delta F''$. In the case of the λ4280 CuH band, the resulting sets of values, which are listed by Frerichs([25]), have approximately constant first differences, especially for small values of M, and thus again it is evident that $\sigma = 0$. It is evident, also, that if these sets of values are considered as $f(k)$, where k is a half-integer, a particular choice of k will give curves passing at least very close to the origin. With the k thus chosen, one may compute and plot $\Delta F'/k$ and $\Delta F''/k$, as a function of k. The resulting curves are quite accurately parabolas, with the vertex at $k = 0$.

The discussion of Section 3 has shown that F should be an even-powered function of m, and in connection with the determination of the constants of the law of force for the molecular dipole, as will be explained in Section 8, it was found necessary to assume *only* even powers in m, in order to obtain any solution whatever. We accordingly write for the rotational energy function, for the case of no vibration,

$$F = B_0m^2 + D_0m^4 + F_0m^6 + H_0m^8. \quad (141)$$

Kratzer and other investigators have considered only the first two terms of this equation. By comparison of equations (36), (56) and (141), $D_0 = -u^2B_0$. Also from equation (31),

$$D_0 = -\frac{4B_0^3}{\omega^{0^2}}. \quad (142)$$

This connection between the *rotational* energy constant D_0, and the *vibrational* energy constant ω^0,[111] is of considerable importance, and will be mentioned again.

[111] B_0 evaluates the moment of inertia and hence the nuclear separation, for the condition of zero vibration and zero rotation. It is therefore technically neither a rotational nor a vibrational energy constant. But to evaluate it, one must use data for rotational energy. Most of the difficulties connected with method three are due to this fact.

From equation (141), assuming $m=k-a$, one obtains, to a very close approximation, when a is small,

$$\Delta F/k=2B_0-\frac{2B_0a}{k}+4D_0k^2+6F'_0k^4+\ldots \qquad (143)$$

If both a and F_0 are very small, as in the case of most bands, equation (143) represents essentially a parabola with vertex at $k=0$. The effect of the term in a is mainly evident for very small values of k, and that of the term in F_0 for very large values of k. By eliminating such values from consideration, one may easily obtain, from the plotted $\Delta F/k$ curve, quite reliable values of B_0 and of D_0. The results for λ4280 CuH are, $B'_0=6.7445$, $B''_0=7.8105$, $D'_0=-4.55\times10^{-4}$, $D''_0=-5.08\times10^{-4}$. These may be compared with the coefficients of m^2 and m^4 in equations (140).

The superiority of method two is immediately evident when we consider the relation given by equation (142). Using the known values of $\omega^{0\prime}$ and $\omega^{0\prime\prime}$ (see table of constants, Section 7), one obtains from equation (142) the "calculated" values, $D'_0=-4.48\times10^{-4}$, $D''_0=-5.26\times10^{-4}$, which agree closely with the results of method two, but are quite different from those obtained in method one. By means of method two, Birge[96] obtained equally good agreements between calculated and observed values of D_0 for the (0, 0) band of the violet CN group, the negative bands of nitrogen (N_2^+), and the second positive nitrogen group (N_2). The mean position of the doublets was used for the first two, and the middle component of the triplet, for the last. In the case of CuH, CN, and N_2^+, it was not possible, by method two, to detect the presence of a. But for N_2, m is definitely different from a half-integer, and the results obtained are $a'_0=+0.0451$, $a''_0=+0.0564$. The values of the moments of inertia obtained in this way, for the (0, 0) bands of CN, N_2^+, and N_2, are given in Section 7. For CuH the more accurate results of method three are used.

The foregoing agreement in the observed and calculated values of D_0 leads to certain interesting theoretical conclusions which are considered in Part 5e, and in Section 8.

Method Three.—This method is based essentially upon assumed theoretical relations between the rotational and vibrational energy constants, and was suggested by Kemble[62]. The first relation of this character is due to Kratzer and is given in equation (142). Birge[96], by assuming equation (141), obtained similar expressions for F_0 and H_0. These are given in Section 8, equations (198), (199). They involve, besides B_0,

only constants connected with the vibrational levels of the molecule.[112] From the plotted $\Delta F/k$ curves for $n=0$ and $n=1$, one can obtain fairly accurate values of B_0 and B_1 and thus of D_0, F_0, and H_0. The more accurate values of B_0 and B_1 are then obtained by successive approximations. The process is involved and the most expeditious procedure, under the circumstances, is now being investigated. The essential points are as follows: If, in equation (141), one knows the values of D_0, F_0, and H_0, then one may write,

$$\frac{dF}{dm} - 4D_0m^3 - 6F_0m^5 - 8H_0m^7 = 2B_0m, \tag{144}$$

where $m=k-a$, and a is usually very small. Assuming a *constant* and very small, and using the relations of equation (78), one obtains, to a high degree of accuracy,

$$2\Delta\overset{*}{F} = 2\Delta F - 8D_0k^3 - 12F_0k^5 - 16H_0k^7 = (4B_0+8D_0)(k-a). \tag{145}$$

All the terms on the left side of the equation (defining $2\Delta\overset{*}{F}$) are known, at least to a close approximation. If the above assumptions are true, $2\Delta\overset{*}{F}$ should be found a linear function of k, and from its least squares solution, the most probable values of B_0 and a are obtainable. A similar process, with slight modifications, can be employed for B_1 and the new values of B_0 and B_1 can then be used to obtain more accurate values of D_0, F_0, and H_0, and so, by successive approximations, of B_0 and a.

The actual numerical values of $2\Delta\overset{*}{F}$ show, in some cases, a distinct trend from linearity, and this may be interpreted as due to a *variable* a. The trend has been found much larger in the initial, excited state of the molecule, than in the final state, especially if this latter is the normal state. Now if a is assumed a function of k (or of j), then equation (141), expanded as a function of k (or of j) contains odd as well as even powers. This explains the presence of apparent odd power terms in the function for the rotational energy, for hitherto m has been taken as equivalent to our k, or j.[113] Hence the present conclusions on this subject are that

[112] One of these constants, Kratzer's "a" of equation (37) equals $B_0 - B_1$ and measures the increase in mean nuclear separation, with increasing vibrational energy. Unfortunately, however, it can be evaluated only by means of rotational energy data.

[113] Thus in equation (59), if m, instead of being the exact integer or half-integer postulated by Kratzer, is assumed equal to $(k-a)$, or $(j-\overset{*}{\epsilon})$, where a and $\overset{*}{\epsilon}$ are *constant*, then the first degree term can be eliminated, as shown in the resulting equation (65). Similarly, higher odd power terms in m, in the equation of rotational energy, may be eliminated by the further assumption that $m=k-a$, where

$$a = a_0 + \zeta_0k^2 + \theta_0k^4, \text{ etc}, \tag{146}$$

and k, instead of m, is an exact half-integer.

the rotational energy function $F=f(m)$ may contain only even powers of m, and the coefficients of the higher power terms may be calculated from theoretical considerations. In order to attain this result, it may be necessary to set $m=k-a$, where a is itself a function of k. This variable a may be taken as an indication of a varying amount of electronic angular momentum. Such a variation is to be expected, owing to the warping of the electron orbits by rotation, and is believed by the writer to be the actual evidence of the mutual effect of rotation and electronic configuration, formulated by Kratzer as the first degree "δ" term.

The results for CuH, by method three, are subject to further revision, but stand at present as

$$\left.\begin{aligned} F' &= 6.7603m^2-4.507\times10^{-4}m^4+0.9676\times10^{-8}m^6, \\ \text{where } m &= k-5.914\times10^{-3}-5.816\times10^{-5}k^2, \\ F'' &= 7.8153m^2-5.278\times10^{-4}m^4+2.318\times10^{-8}m^6, \\ \text{where } m &= k+0.00010. \end{aligned}\right\} \quad (147)$$

It was found unnecessary to consider the H_0m^8 term. These values of B'_0 and B''_0 should be correct to less than 0.05 per cent. They are certainly correct to 0.1 per cent, and show that the values obtained by method two are in error by 0.24 and 0.06 per cent respectively, while those by method one are in error by 0.59 and 0.13 per cent respectively. Because of the small (probably zero) value of a for the final state, the first two methods give fairly accurate values of B''_0, while the larger value of a' leads to inaccuracies in B'_0. Incidentally, these results show that the odd power terms obtained in method one have no theoretical significance.

A more striking example of the use of method three is furnished by results for the AlO bands. The calculations for the (0, 0) (λ4842) band have just been completed by W. C. Pomeroy([97A]). He finds that equation (141) is accurately true for the entire band (maximum $m=140.5$) with the "calculated" values of D_0, F_0 and H_0, and with $m=k-a$ where $a'=+0.0074$, $a''=+0.010$. A direct calculation of D_0 from vibrational data and from rotational data gives results agreeing to 0.2 per cent. (See note b* of Section 7.)

It may be noted, in conclusion, that *any* value of a' or of a'', other than zero, leads to a "break" between the $R(M)$ and $P'(M)$ curves at $M=0$, and to the necessity of employing *different* numerical coefficients for the two branches. In other words, any value of m, other than an exact integer or half-integer, in a rotational energy function of the form given by equation (141) leads to such a break, and this phenomenon seems to be present, in greater or less degree, in every band where the

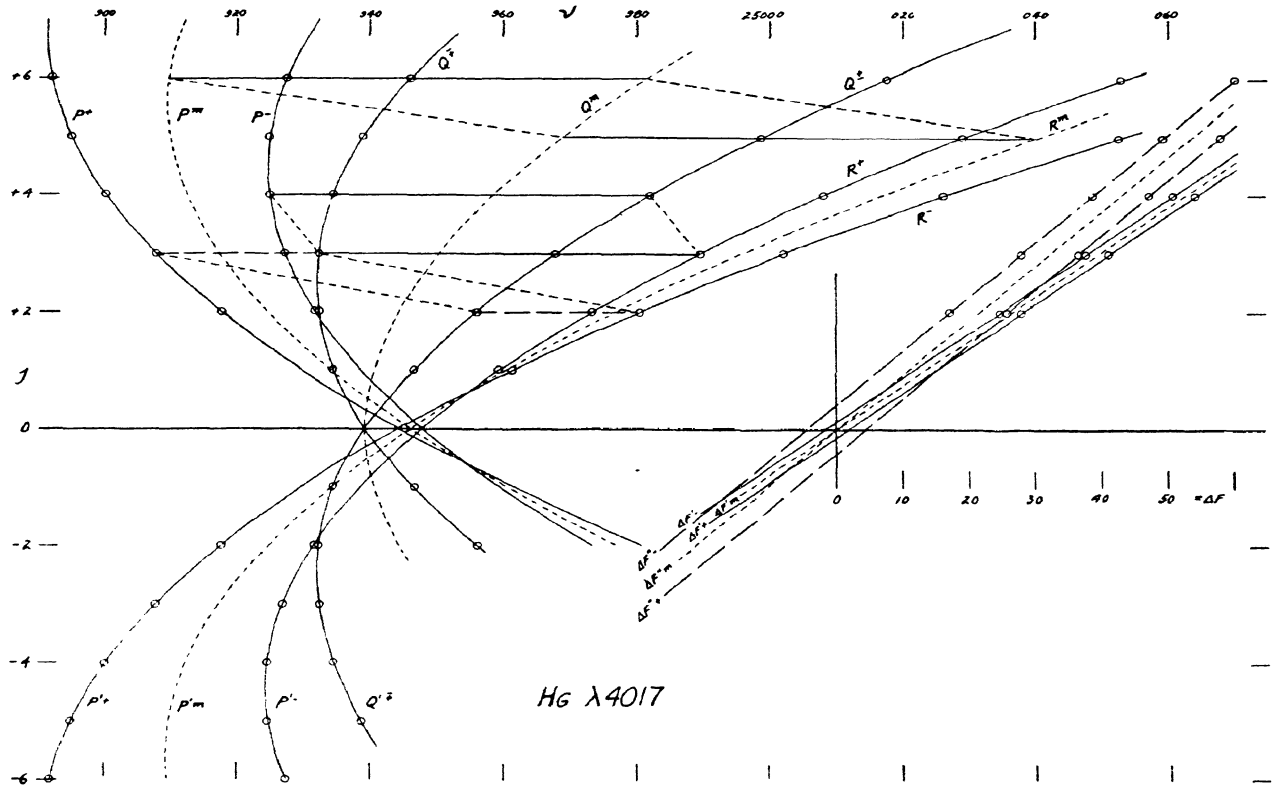


FIGURE 21.—λ4017 Mercury Hydride Band (0, 0). $\nu : j$ Curves for First Few Lines of Each Branch Mean Values of the Doublets Indicated by Broken Curves. Also $\Delta F'_j$ and $\Delta F''_j$ and Mean Values.

matter has been carefully examined. On the other hand, an accurate evaluation of a, even by method three, is very difficult, and in the case of AlO, just cited, the probable error in a' and a'' is fully as great as the quantities themselves.[114]

PART 5c. DOUBLETS OF THE Hg AND CN TYPE

In Figure 8, Curve A, we have illustrated one common type of doublet for which the doublet splitting becomes zero at or near the "origin" of the band. Since there is still some uncertainty as to the theoretical interpretation of this type of doublet, an attempt will be made to present the experimental facts from a somewhat empirical standpoint, as far as the doublet character of the series is concerned.

The most interesting known example of this type of doublet is furnished by the Zn, Cd, and Hg bands (probably due to the hydride), since here the doublet separation is very large and *all* lines of the various series can actually be measured. It is probable that the λ4017 band of Hg is the 0, 0 band of the system, and this band, previously used for Curve A of Figure 8 (omitting the Q branch), will now be considered in more detail.

In Figure 21 are plotted the first few lines of the six branches found in the band using the frequencies in air, as given by Liese(50). The basis of the designations R^+, R^-, P^+, P^-, $Q^\pm$, and $Q^\mp$ appears from equations (154) to (159) ahead. Previous investigators have used varying designations, and the relations are shown in the following table. Several of the

TABLE

This chapter	R^+	R^-	P^+	P^-	$Q^\pm$	$Q^\mp$	F''^+	F'^-	F'''^+	F''^-
Liese(50)	B_2	B_1	A_1	A_2	A_1	B_3				
Hulthén 1922(100)	R_2	R_1	P_1	P_2	R_3	P_3				
Kratzer(43)	R_2	R_1	P_2	P_1	Q_2	Q_1	F_2	F_1	f_2	f_1
Hulthén 1925(101)	R_1	R_2	P_1	P_2	Q_1	Q_2	F_1	F_2	f_1	f_2

series, as given by Liese, who used the Deslandres' scheme, include one branch and several lines of another branch, according to the quantum interpretation. The table gives also the designations of the rotational energy function.

Combination relations between the lines of the Zn, Cd, and Hg bands were found first by Hulthén(100), using the data of Liese(50), and were later interpreted in detail, in accordance with the quantum theory, by

[114] Compare footnote at end of Part 5c.

Kratzer([43]). New measurements and computations for all of the Hg bands have recently been made by Hulthén([101]). In terms of the present nomenclature, the observed combinations are

$$R_j^- - Q_j^+ = Q_{j+1}^- - P_{j+1}^+, \tag{148}$$
$$R_j^+ - Q_{j+1}^+ = Q_j^- - P_{j+1}^-, \tag{149}$$
$$R_j^- - Q_{j+1}^- = Q_j^+ - P_{j+1}^+, \tag{150}$$
$$R_j^+ - Q_j^- = Q_{j+1}^+ - P_{j+1}^-, \tag{151}$$

where (150) and (151) are derived from (148) and (149) by mere interchange of terms, just as equation (93) is derived from (92). We note that aside from the double character of each branch, as indicated by the + or − index, equations (148) and (151) are merely equation (92), and that (149) and (150) are equation (93). Moreover, if (148) and (151) are added together, the resulting equation is equation (92), in terms of the *mean* position of each doublet. Similarly, equations (149) and (150) give (93) in terms of the mean position. On Figure 21 are indicated the equalities of equations (148), (151), and of their sum, for $j=2$, 3, and 5 respectively, by means of parallelograms, as was done in Figures 18 and 19. The mean position of each doublet is indicated by the dashed curves R^m, P^m and Q^m.

These curves of mean positions are especially significant for, as can be seen from Figure 21, they are *in every respect* identical with Case II, Figure 19.[115] The two missing lines of the continuous $R^mP'^m$ curve are each formed from a missing doublet, while the Q^m curve has its vertex at $j=0$ with a missing line at that point. The resulting values for what may be called $\Delta F'^m$ and $\Delta F''^m$ are shown by dashed curves, on the right side of Figure 21. The *relative* numbering of the P, Q, and R branches adopted here is due to Kratzer([43]), and is such as to be in conformity with equations (92) and (93). That used earlier by Hulthén([100]) can be indicated on Figure 21 by raising the R^+ graph one unit, and lowering P^- one unit.

In agreement with Case II, we have; therefore, for *small* values of j,

$$\Delta F'^m = 2B'j \quad \text{or} \quad F'^m = B'j^2, \tag{152}$$
$$\Delta F''^m = 2B''j \quad \text{or} \quad F''^m = B''j^2. \tag{153}$$

The question then becomes, how are these very simple functions to be modified, in order to account for the doublets? It will be noted that

[115] This indicates that the frequency of the lines represented by these curves, relative to each other, is the same as in Case II. It does not mean, necessarily, that the frequency of *all* the lines, relative to the "origin" is the same as in Case II, as we shall see in a moment.

the doublet separation in the P, Q, and R branches, for a given value of j, is not the same, but the separation is such that P'^{+}, P'^{-} and $Q'^{\mp}$ (i. e., as plotted against negative values of j) are respectively the smooth continuations of R^{-}, R^{+}, and $Q^{\pm}$. It can be shown, analytically, that this relation is accurately true, at least for small values of j, in the case of the bands under consideration. Such a relationship may be fulfilled by assuming two F' and two F'' functions, each pair of the type $F^{\pm}=f(j\pm a)$, where the argument $(j+a)$ or $(j-a)$ occurs only in even powers. Thus $j-a$, for negative values of j, is numerically the same as $j+a$, for positive values of j. Finally, Kratzer[43] found that in order to satisfy the actual combinations just noted in equations (148) to (151), it was necessary and sufficient to assume

$$R_j^{+}=F'^{+}_{j+1}-F''^{+}_{j}, \tag{154}$$
$$R_j^{-}=F'^{-}_{j+1}-F''^{-}_{j}, \tag{155}$$
$$P_j^{+}=F'^{+}_{j-1}-F''^{+}_{j}, \tag{156}$$
$$P_i^{-}=F'^{-}_{j-1}-F''^{-}_{i}, \tag{157}$$
$$Q_j^{\pm}=F'^{+}_{j}-F''^{-}_{j}, \tag{158}$$
$$Q_j^{\mp}=F'^{-}_{j}-F''^{+}_{i}. \tag{159}$$

From these assumptions it follows that the equalities given by equations (148) and (149), for example, are equal, respectively, to $F'^{-}_{j+1}-F'^{+}_{j}$ and $F''^{-}_{j+1}-F''^{+}_{j}$. The quantities evaluated by these two equations do not therefore isolate the various term differences for the rotational energy, and cannot be added to obtain the actual values of F'^{-}, F'^{+}, F''^{-} and F''^{+}. These four functions *can* be obtained, however, by using the P and R combinations only, as given by equations (90) and (91). Thus we have, corresponding to (90),

$$R_j^{+}-P_j^{+}=F'^{+}_{j+1}-F'^{+}_{j-1}=2\Delta F'^{+}_{j}, \tag{160}$$
$$R_j^{-}-P_j^{-}=F'^{-}_{j+1}-F'^{-}_{j-1}=2\Delta F'^{-}_{j}, \tag{161}$$

with two similar expressions corresponding to equation (91). The values of $\Delta F'^{+}_{j}$ and $\Delta F'^{-}_{j}$ evaluated by equations (160) and (161), as well as the values of $\Delta F''^{+}_{j}$ and $\Delta F''^{-}_{j}$, are plotted on the right side of Figure 21. For the small values of j shown, we find in the case of the λ4017 band

$$\left.\begin{aligned}
\Delta F'^{+}&=2\times 6.55\,(j+0.130)=2B'_0(m^{+})\\
\Delta F'^{-}&=2\times 6.55\,(j-0.130)=2B'_0(m^{-})\\
\Delta F''^{+}&=2\times 5.37\,(j+0.405)=2B''_0(m^{+})\\
\Delta F''^{-}&=2\times 5.37\,(j-0.405)=2B''_0(m^{-}).
\end{aligned}\right\} \tag{162}$$

These results, when substituted in equations (154) to (159) explain the relative *appearance* of the six different branches, which depends, not on

the value of Δj, but on the value of Δm. Thus in the case of the two Q branches, while $\Delta j=0$, $\Delta m=+0.54$ and -0.54 for Q^+ and Q^- respectively. For P^+ and P^-, $\Delta m=+1.28$ and $+0.72$, respectively, and for R^+ and R^-, $\Delta m=-0.72$ and -1.28, respectively. Thus Q^+ appears like a P branch, and Q^- like an R branch, and were so designated by Hulthén([100]).

A further point of interest here is in regard to the location of the "origin," the frequency of which, beginning with Section 5, has arbitrarily been taken as zero. For Cases I to IV, as discussed in Part 5b, i. e., for any case where $\epsilon'=\epsilon''$, $\sigma=0$ (or $a'=a''$ as used here), the head of the Q branch has the frequency $\nu=0$, while the R_j and P_j graphs intersect at $\nu=B'$, either point thus enabling the origin to be located. In the present case, however, it appears by substitution in equations (154) to (159) that *every* spectral line represented by the *mean* curves R^m, Q^m and P^m of Figure 21 is greater than the corresponding theoretical frequencies of Case I to IV by $(B'a'^2-B''a''^2)$. Hence the origin may be located if we proceed as usual and apply this correction.

The experimental values of the various functions of equation (162), for *all* known values of j, are listed either by Kratzer([43]) or by Hulthén([101]), and as expected, they indicate curves deviating considerably from linearity for larger values of j, especially as the value of n increases. [See Figure 2 of Hulthén([101]).] The essential point here is, however, that there are evidently *two* sets of initial rotational energy states, and *two* sets of final states,[110] which we have designated as + and − respectively, and that while R^+ and P^+ are due to the transition between two "+" states (and similarly R^- and P^- between two "−" states), each of the Q branches must be considered as the transition between a "+" and a "−" state.

In the case of doublets such as the above, the constants a' and a'' can be evaluated most simply from the values of the doublet separations, as pointed out by Birge([102]). Thus, if

$$\left.\begin{aligned} F'^{+} &= B'(j+a')^2 \\ F'^{-} &= B'(j-a')^2 \\ F''^{+} &= B''(j+a'')^2 \\ F''^{-} &= B''(j-a'')^2 \end{aligned}\right\}, \tag{163}$$

we have, using equations (154) and (155),

$$R_j^- - R_j^+ = 4j(a''B''-a'B') - 4a'B'. \tag{164}$$

[110] There is, however, only *one* initial and *one* final electronic energy level, giving a *single* "origin," since the doubling vanishes with the rotation. This doubling is then purely of class two character, as defined in Part 2f of this chapter.

It is convenient to let $\gamma = aB$, so that this equation becomes

$$R_j^- - R_j^+ = 4j(\gamma'' - \gamma') - 4\gamma'. \tag{165}$$

Similarly, we may obtain from equations (156) and (157)

$$P_j^+ - P_j^- = -4j(\gamma'' - \gamma') - 4\gamma'. \tag{166}$$

If, then, we use negative values of j, there results

$$P_j'^+ - P_j'^- = 4j(\gamma'' - \gamma') - 4\gamma', \tag{166'}$$

which is identical with equation (165). This must necessarily be so, since $P_j'^+$ and $P_j'^-$ are the smooth continuations of R_j^- and R_j^+, respectively. It is convenient thus to plot the doublet separation as a continuous function of j, using equation (165) and negative values of j for the P branch.

This is a linear equation in j, from which γ' and γ'' can be calculated with great accuracy. The slope of the ΔF curves then evaluates B' and B'', so that a' and a'' may be obtained. In this manner the writer[102] has obtained for the λ4017 Hg band.[117]

$$\gamma' = +0.852 \pm 0.03, \qquad \gamma'' = 2.175 \pm 0.03,$$

which with the values of B'_0 and B''_0 noted in equation (162), give

$$a' = +0.130 \pm 0.005, \qquad a'' = +0.405 \pm 0.006,$$

as used in this same equation.

Several special cases of equation (165) are of interest. If $\gamma'' = 0$, the doublet separation is zero at $j = -1$, while if $\gamma' = 0$, the separation is zero at $j = 0$. If $\gamma' = \gamma'' = \gamma$, the separation is constant and equal to -4γ (i. e., R^+ and P'^- lie parallel to, and on the high frequency side of R^- and P'^+).[118] This, however, is a distinctly different type of constant separation, as far as the theoretical interpretation is concerned, from that defined as class one, in Part 2f of this chapter.

Before considering Kratzer's explanation of the Hg doublets, it seems convenient to discuss the doublets of the violet CN group bands. Here the doublet separation is far smaller. Within limits of error the separation for equal values of j for the two branches is the same. The actual

[117] The graph of the doublet separation for this band is quite accurately linear for j less than 10.

[118] It should be noted that in this case of constant doublet separation, the *red* component of the R branch is to be combined with the *violet* component of the P branch, to obtain ΔF^-, and *vice versa* for ΔF^+. But if there is a point of zero doublet separation near $j = 0$, as in Figure 21, the two *red* components are to be taken together. Whether they give ΔF^- or ΔF^+ depends upon the relative magnitude of γ' and γ''.

separation cannot be measured below $j=28$, and increases from that point to a maximum at $j=75$, and then diminishes until again too small to measure.[119] In the region of small values of j, the width of the unresolved doublets is consistent with the assumption that the separation is proportional to j. The actual point of zero separation is, however, indicated definitely by the perturbations. These occur as usual at R_j and P_{j+2}, and in certain cases are in the form of an abnormally great doublet separation, equal for the two doublets in question. Hence it is a double *initial* state which causes the doubling of the lines, i. e., $\gamma''=$ zero.[120]

But the *mean* position of each doublet in the violet CN bands, when plotted, gives a *typical* Case III of Figure 19.[121] Hence the two $\Delta F'$ functions are, for *small* values of j, of the form

$$\Delta F'^{+}=2B'(j-\tfrac{1}{2}+\alpha')=2B'(k+\alpha'), \tag{167}$$

$$\Delta F'^{-}=2B'(j-\tfrac{1}{2}-\alpha')=2B'(k-\alpha'). \tag{168}$$

Therefore equation (165) may be used also in this case, if k is substituted for j. We have then as a general formula holding for doublets of this type, whose mean positions correspond to *any* of the Cases I to IV of Figures 18 and 19,

$$R_j^- - R_j^+ = P_j'^{+} - P_j'^{-} = 4k(\gamma''-\gamma') - 4\gamma', \tag{169}$$

where $k=j-\epsilon$. Thus for the CN bands, the doublet separation is zero at $k=-1$ (the point midway between the two perturbations at k and $-(k+2)$) and by equation (169), $\gamma''=0$. For the 3883 CN band, $\gamma'=+0.00225$ from which, since $B'=1.959$, $\alpha'=+0.00115$, $(\alpha''=0)$.[122] The $\Delta F'^{+}$ and $\Delta F'^{-}$ curves are parallel and separated by $4\gamma'$ or 0.009 cm^{-1}.

The above treatment is essentially an empirical formulation of the experimental facts, and may be summarized as follows. The doublets

[119] See p. 280 of Birge(29).

[120] It is quite possible that the final state also is double, but if so, the quantum transitions are such that this doubling does not affect the doublet spacing of the lines. On the other hand Pomeroy(97A) has just found that in the case of the analogous AlO bands, the observed doublets must be attributed to a double *final* state.

[121] As in the case of the Hg mean curves, all frequencies of these mean curves are higher by $B'\alpha'^2 - B''\alpha''^2$ (which becomes merely $B'\alpha'^2$ in this case), than those of Case III, and this fact must be noted, in an accurate location of the "origin."

[122] See reference (102). For this case $\gamma=\delta$ of Kratzer, and equation (15) of Kratzer(43) is equation (169) above, except for sign, since his $\Delta=R^+-R^-$. These results are therefore quite different from Kratzer's published values of $\delta'=0.05$, $\delta''=0.05-0.0011$. His values, as shown by Figure 2 of reference (43), lead to a doublet separation which becomes zero for a large negative value of j, and therefore predict an entirely non-symmetrical doubling for the two branches.

of the type found in the Hg or in the CN bands yield, in general, a double set of rotational energy terms for both initial and final states of the molecule. This doubling, for small values of j, may be represented by a two-fold rotational energy term of the form $F^{\pm}=B(k\pm a)^2$. For the Hg bands, k has integral values, for both initial and final state, and may be identified with j. All lines having $j=0$ for initial or final state are missing. For the violet CN bands, k has half-integral values and may be written as $(j-\frac{1}{2})$, with the same rule for missing lines. The doublet separation, expressed as a $f(k)$ is given by the linear equation (169), holding accurately only for small values of k. This equation applies to both P and R branches, provided negative values of k are used for the P branch. In it $\gamma'=a'B'$, $\gamma''=a''B''$, and thus a' and a'' may be easily and accurately evaluated. For the CN bands, $a''=0$ and a' is very small, while for the Hg bands both a' and a'' are finite and large.

In this connection we may consider the suggestion mentioned earlier, that in bands illustrating Case III, such as the CN bands, j itself may have half-integral values, just as it seems to have in certain atoms, according to the evidence of line spectra. With such an assumption $k=j$ always, and one may write the rotational energy as $B(j\pm a)^2$. This suggests as a qualitative explanation of these doublets, an electronic effect which may be positive or negative according to the direction of revolution of the nuclear dipole, with respect to the electronic configuration. There is, however, only one electronic configuration for either initial or final state. On this assumption $j\pm a=m$, so that the frequency of nuclear revolution is zero, when $m=0$, as it should be, while $j=\mp a$, indicating permanent resultant electronic momentum of amount a, perpendicular to the figure axis. For larger values of j, we may then assume any even-powered function of $(j\pm a)$.[123]

This explanation differs from that of Kratzer([43]) for both the Hg and the CN bands. Kratzer's explanation has already been mentioned in connection with the theoretical discussion of Case IV, and, by comparison with equations (36), (56), (63) and (64), is equivalent to writing the rotational energy in the form

$$F^{\pm}=B_n(j\mp\overset{*}{\epsilon})^2-B_0u^2(j\mp\epsilon)^4+\ \ldots, \qquad (170)$$

where $\overset{*}{\epsilon}=\epsilon-\dfrac{\delta}{B_n}$, and δ represents a so-called mutual effect of nuclear rotation and electronic configuration, in addition to the permanent electronic momentum given by ϵ. For the Hg bands this equation, assuming $\overset{*}{\epsilon}=a$, differs numerically from the above assumptions only in

[123] See, however, footnote at end of this part.

the substitution of ϵ for ϵ^*, in all higher power terms, as necessarily must be done, from Kratzer's formulation of δ (equation 36). Kratzer assumes that $\epsilon'=0.5$, for the Hg λ4017 band, giving $\delta'=2.42$, since $a'=0.130=\epsilon'-\frac{\delta'}{B'_0}$. The basis for this assumption as to ϵ' is the curious experimental fact that

$$\Delta F'^{-}_{j}-\Delta F'^{+}_{j-1}=\text{constant} \qquad (171)$$

for all values of j. (Table 8 of Kratzer[43].) For by assuming in the

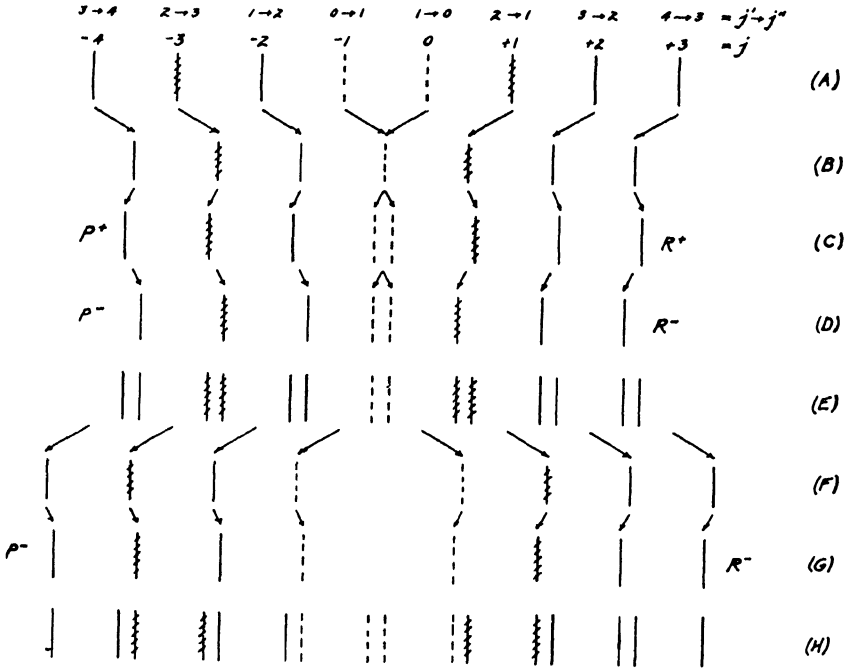


FIGURE 22.—Schematic Representation of Violet CN Bands Type of Doublet, Illustrating Two Proposed Theories Concerning Its Origin.

expression for ΔF, as obtained from equation (170), that $\epsilon=0.5$, all higher power terms in $\Delta F'^{-}_{j}$ and $\Delta F'^{+}_{j-1}$ are numerically identical, while the linear terms have a constant difference of 4δ. When now the final molecular state for λ4017 is considered, it is found necessary to assume $\epsilon=0.25$, from the observed values of $\Delta F''^{-}$ and $\Delta F''^{+}$. Kratzer's published value of δ'' $(+0.411)$ corresponds, however, essentially to $\epsilon=0.5$, as noted by the writer([102]),[124] while $\epsilon=0.25$ yields $\delta''=-0.833$. A more

[124] Hulthén([101]) also has noted that Kratzer's published constants do not agree with his data, and the error, due to the omission of a factor of -2, has been rectified in a recent detailed discussion of these bands by Ludloff([103]).

extended investigation, using the complete data now made available by Hulthén([101]) seems necessary in order to decide whether or not the relation given in equation (171) is purely accidental, and whether the assumption of a function of $(k \pm a)$, especially if odd powers are included, would not be equally satisfactory.

Kratzer's explanation of the CN doublets, as contrasted with the alternative suggestion preceding, is best shown by means of a diagram, applying only to small values of j. For simplification we will assume $\gamma' = \gamma''$ and $B' = B''$, so that $a' = a''$ ($= 0.1$ assumed), thus giving a series of doublets of constant separation and equally spaced. This is shown in Figure 22. In this figure, (A) gives the series of single equidistant lines for which $m = j$. (B) gives the result when $m = j - \epsilon = j - 0.5$, for both initial and final states. (C) gives $m = j - 0.5 + 0.1 = k + 0.1 = k + a$, for both states. (D) gives $k - a$. The combination of (D) and (C) gives (E), the $(k \pm a)$ form suggested above. (C) as noted gives $j - 0.5 + 0.1 = j - 0.4 = j - \frac{2}{5}$ of Kratzer. (F) gives $j + 0.5$. (G) gives $j + 0.5 - 0.1 = j + 0.4 = j + \frac{2}{5}$. The combination of (C) and (G) gives (H), which is Kratzer's assumption of $(j \pm \frac{2}{5})$.

One distinction between (E) and (H) is that in (H), besides the missing central doublet, there is one component missing for each adjacent doublet, thus giving these doublets half-normal intensity, if unresolved. But all measurements thus far made show clearly that these first doublets have *normal* intensity, and this would seem to be a definite objection to Kratzer's theory. Dieke([27]) has, however, been able to overcome this difficulty, as discussed in Section 6. A further distinction arises in connection with the perturbations. If we assume, for instance, that state $j' = 2$ is irregular in position, then the cross-hatched lines in each set will be irregular. Set (E) corresponds to the experimental facts, while set (H) does not. If, however, we assume that the perturbation is connected with a definite value of m', rather than of j', then either theory will give set (E), as far as the perturbations are concerned.[125]

In obtaining a physical explanation of this type of doublet, as contrasted with a purely formal explanation, there seem to be at present only two guiding facts. (1) The doublet separation of the two spectral *lines* is due to the two-fold character of the initial, or of the final, or of both rotational energy *terms* of the molecule. The doublet separation

[125] Hulthén, in his recent analysis of the Hg bands([101]), finds the expected numerical relations for the R and P branch perturbations, but curious results for the Q branch perturbations that do not agree with any previous theory as to their formation. The discrepancy has, however, now been explained by Ludloff([103]) as due to an incorrect assignment of these particular Q branch lines.

of the *terms* is a function of the nuclear rotation, and vanishes for zero rotation. (2) The doublet separation of the terms is a function of the magnetic field, and vanishes, or tends to vanish, for strong fields. This latter point was mentioned in Part 2f of this chapter, and is treated in more detail in Chapter VII.

The explanation just considered is that the total doublet separation is due to a variation of rotational energy, for a given value of j, with the direction of revolution of the dipole with respect to the permanent electronic configuration. Kratzer's explanation is that this effect, which is represented by the assumed value of ϵ, is very large, while another effect (large in some cases) tending to cancel the first effect, as shown by $\epsilon^* = \epsilon - \frac{\delta}{B_n}$, is due to the mutual influence of rotational energy and electronic configuration. There must naturally be such an effect but it should be very small, while in the form postulated by Kratzer, it is large and leads to a contradiction with the very fundamental equation $\omega_i = \frac{dE}{dJ_i}$, as already discussed in Section 3. Hulthén([101]) has just recently suggested a third, quite different, type of explanation, which the writer is not prepared to discuss critically. Dieke([104]), ([27]), also has discussed the CN doublets, and has suggested a modification of Kratzer's theory.[126]

[126] As has been noted in earlier sections of this chapter, Mulliken, in a series of papers in the Proc. Nat. Acad. Sci. (Vol. 12, p. 144, etc.) has very recently presented a systematic interpretation of electronic bands. In the case of the HgH, CdH, and ZnH bands, he adopts the interpretation just given, as shown by equation (162), i. e., j an integer, and $\epsilon' = \pm 0.13$, $\epsilon'' = \pm 0.405$. He assumes, however, that the *resultant electronic* momentum s of *all* molecules is an integer or half-integer, in analogy with atoms. For these bands he assumed $s_e (= \sqrt{\sigma^2 + \epsilon^2})$ to be 0.5 for both initial and final states. Hence, $\sigma' = 0.483$, $\sigma'' = 0.294$. Now as shown by the linearity of the ΔF curves of Figure 21, we *apparently* have $\sigma = 0$. Actual calculations, using Mulliken's new constants, show, however, that the calculated deviation from linearity at the last observed point ($j = 2$) is too small to be proved or disproved with present existing data.

It may be noted, in addition, that Hulthén([101]) has measured a fainter set of HgH bands, in the vicinity of λ3500. In a recent note [reference ([163])], he interprets the two sets of HgH bands as due to a double electronic level in the initial state, of *wide* spacing (3683 cm^{-1}). Now, as Mulliken states in the above noted articles, the $\Delta F''^{\pm}$ for this second initial level (designated P_2) is given by $2 \times 6.61(j \pm 0.00)$. For such a case, σ may have any arbitrary value, and cannot be detected from frequency measurements. In accordance with his system. Mulliken assumes $s = \sigma = 1.5$. Such an assumption *does*, however, affect the number of missing lines, for as shown by equation (20), j can never be less than σ, in absolute value. For the older HgH bands, either the arbitrary rule, $j = 0$ gives missing lines, or the new rule $j > \sigma$, leads to the same predictions (j' or $j'' \geq 1$) and this is in agreement with the known experimental

PART 5D. DOUBLETS OF THE WATER-BAND (OH) TYPE

In Figure 8, Curve *C*, we have indicated a second type of doublet, characterized by the fact that for large values of j the doublet separation, to a first approximation becomes asymptotically constant, while for small values of j, the separation increases rather rapidly, as j decreases. This type of doublet is illustrated by the ultra-violet water vapor bands (of which λ3064 is the strongest), by the C+H bands (λ4300 and λ3900), and by the two outer components of the triplets of the second positive group of nitrogen (of which λ3371 is the strongest band). The type of rotational energy function derived theoretically by Kramers and

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facts. For the new bands, the data are somewhat incomplete, but apparently may be explained only by the assumed value of σ'. In the next section it will appear that the $j = 0$ rule for missing lines definitely breaks down for the λ3064 OH band, and it would seem at the present time that an appreciable σ must be invoked, in many cases, in order to explain the missing lines.

In the case of the CN bands, Mulliken's system demands *integral* values of j, in agreement with Kratzer. This requires for the initial state $m = j \pm 0.49885$, if (H) of Figure 22 is assumed. But we may equally well assume $m = j \pm 0.50115$, giving a set of doublets of precisely the same frequencies, and differing from (H) only in that the two outer components of the doublets adjacent to the center should be missing, in place of the two inner components. From the absence of a Q branch in these bands, Mulliken concludes that $\sigma' = \sigma'' = 0$, and that $s(= \epsilon$, here) may consequently deviate *very* slightly from exact integral or half-integral values. He then explains the one missing line by assuming that the direction of rotation of the molecule can never reverse during the radiation process (i. e., that ϵ cannot change from plus to minus, or more generally, that the direction of precession of the molecule cannot reverse). Such an explanation has already been suggested by Kratzer, in the case of certain missing lines in the C+H bands [pp. 315-316 of reference (53)].

In the preceding interpretation, it is tacitly assumed that $m' = j' \pm 0.49885$, so that the *mean* position of the violet CN doublets is given by $m = j \pm 0.50$. But as noted at the end of Part 5b, the apparent "break" in the $R(M)$ and $P'(M)$ curves at $M = 0$ (an undoubted fact for the violet CN bands, the CuH bands, and probably many others), indicates definitely that m for the *mean* doublet position is *not* an exact integer or half-integer for either the initial or the final state. For the violet CN bands this means that, with j an integer, $m' = j' + \epsilon'_1$, and $j' - \epsilon'_2$, where ϵ'_1 and ϵ'_2 are slightly *different*, but both nearly equal to 0.50. Similarly, in the case of the AlO bands (see note b* of Section 7 ahead), there are *two* values of ϵ for the *final* state, one corresponding to the parallel position of ϵ and m, the other to the anti-parallel position.

This explanation of the violet CN bands the writer now accepts in preference to his own earlier suggestion that $j = k =$ half-integer (reference 102), as given in the main body of this section. On the other hand, Mulliken's system requires *half-integral* values of j for the simple CuH and HCl bands, and accordingly for *these* cases $j = k$, $\epsilon = a =$ zero, or almost zero. The general theoretical basis for these assumptions is given at the end of Section 8, ahead.

Pauli([56]), in which m is given by equation (20) if used for either initial or final state, seems at first glance capable of representing such doubling provided we use the double sign before ϵ, as suggested by Kratzer, i. e.,

$$F' = B(\sqrt{j^2 - \sigma^2} \pm \epsilon)^2. \qquad (172)$$

We shall in the future refer to equation (172) as the Kramers and Pauli formula, even though these authors ruled out the positive sign, on grounds of mechanical instability.

Kratzer([53]) has applied this equation with apparent success to the C+H bands. On the other hand, Mecke([54]) states that this formula will *not* apply, in the case of the second positive group of nitrogen, while Dieke([105]) makes the same statement regarding the water bands. Now a plot of the ΔF values for representative bands of these three systems shows that all three are essentially similar in structure. Since the Kramers and Pauli formula is the only one as yet proposed which is based on a definite molecular model, it seems worth while to consider with some care just what this formula demands, and how actual spectra deviate from these demands, if such be the case.

For this purpose we shall consider chiefly the λ3064 water band (probably due to OH), since for this band there is no question as to the series assignment of every line, nor as to which lines are present or missing. This band possesses also historical interest, for Heurlinger used it in his first test of equations (92) and (93), after giving his original quantum interpretation of the P, Q, and R branches. As is well known, these equations, embodying the combination principle, are found true for this band, for very small values of j, but a " quantum defect " immediately sets in, and increases rapidly in size, as j increases. In this situation the matter rested until Watson([45]) measured and analyzed the series of the λ2811 band of this same system. Each of these bands is accompanied by a fainter band, and with the then available data for the four bands, Dieke([105]) and Birge([106]) independently showed that equations (90) and (91) were accurately true, for each component of the doublet, when the red components of the R and P branches were taken together, and likewise the violet components. The expected equalities were based on a reasonable assignment of vibrational quantum numbers to the four bands in question (λ3064 = 0, 0; λ3126 = 1, 1; λ2811 = 1, 0; λ2875 = 2, 1). Furthermore, as Dieke points out, *each* side of equation (93) has equal values for the two bands (λ3064 and λ2811), where this is to be expected, but the two sides of the equation are *not* equal to each other except for very small values of j, as just noted. This may be interpreted by the assumption of a double set of rotational energy levels (just as in the

case of the Hg and CN doublets) which are concerned with the doublet lines of the P and R branches. The Q doublets employ this same double set for the initial condition, but a *new* double set for the final condition. Watson(107) has, however, recently measured the previously known satellites of the Q branch lines, and has found that these satellites give the usual combination relations with the R and P branches. The difference between each main Q branch line and its satellite thus measures the "quantum defect" found by Heurlinger.

The spacing of the new final set of levels ($\Delta\overset{*}{F}''$) differs only slightly from the spacing of the regular final set ($\Delta F''$), according to the values listed by Dieke. The difference, for small values of j, is proportional to j. Hence, as Dieke(105) suggests, $\overset{*}{F}''$ may be represented by the same functional form as F'', with merely a slightly different value of B'' (0.1 to 0.2 per cent), thus indicating a slightly different moment of inertia for the two sets of final states, but no other distinction.[127]

Turning now to the matter of the functional form required for F' and F'', we recall that the combination principle gives the relative values of j for the P and R branches, for each component, but does not give the relative values of j for the two components. In order to simplify the discussion, we shall, in the case of all bands of this type, assume at first the *same* value of j for the various components forming the "natural" doublet or triplet, i. e., the doublet or triplet whose spacing becomes asymptotically constant for large values of j. Likewise, we shall assign absolute values of j in such a manner as to obtain as nearly as possible Case II or Case III of Figures 18 and 19.

Figure 23 gives a plot of the first few lines of the series of the λ3064 water band, using the data as arranged by Heurlinger(38) together with the $\Delta F'$ and $\Delta F''$ graphs, from the analysis of Dieke and Birge. The mean values of all doublets are shown also, by broken curves. The values of j are the same as Heurlinger's values of the "Laufzahl" m adopted by all subsequent investigators. The six branches (P^v, R^v, P^r, R^r, Q^v, and Q^r)[128] have been extrapolated by the writer, to $j=0$. The extrapolation is quite certain, to the limit of accuracy of the figure. All lines of all series are present down to and including $j=2$.

[127] If we had two spectral lines with the same initial state, but two final states differing only in respect to the value of B'', the separation of the two lines would increase as the second power of j. There are no such pairs of lines in the OH bands, but the pairs R_1R_3, P_1P_3, and Q_1Q_3 of the λ4300 C + H band, form an example of this type of multiplicity, which was called type A', in the discussion of Curve D, Figure 8. This will be mentioned again later.

[128] r denotes the red, and v the violet component, $P^v = P_2$, $P^r = P_1$, of Heurlinger, and similarly for the other branches.

Considering first the ΔF graphs, we find that the two functions $\Delta F''^{v}$ and $\Delta F''^{r}$ are too closely the same to be distinguishable in the figure. $\Delta F''^{v}$ is larger than $\Delta F''^{r}$ by the small *constant* amount $\nu = 0.2$. Both func-

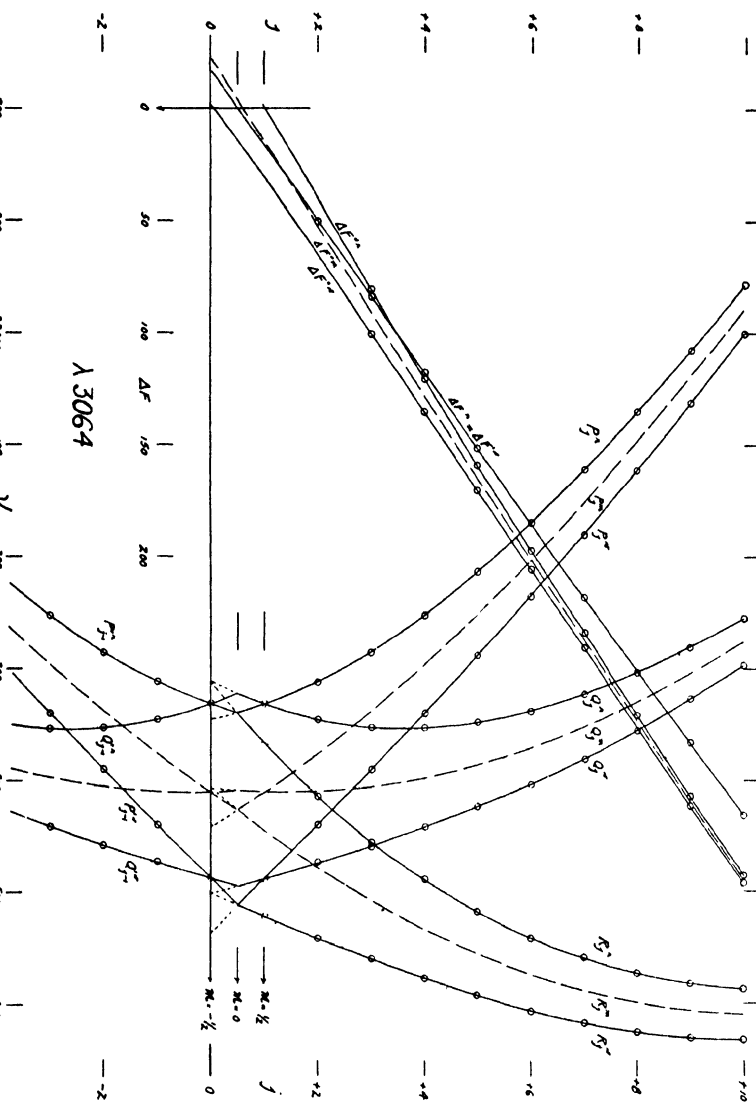


FIGURE 23.—λ3064 Water Band (0, 0). $\nu : j$ Curves for First Few Lines of Each Branch. Mean Values of the Doublets Indicated by Broken Curves. Also $\Delta F'_j$ and $\Delta F''_j$ and Mean Values.

tions equal zero for $j = +0.50 \pm 0.01$. They are thus precisely similar to, and may be explained in the same manner as, the corresponding functions for the CN violet bands, for which as already noted, the con-

stant separation is 0.009cm^{-1}. Aside from this trifling separation,[129] we have, as far as the initial state is concerned, an example of Case III of Figure 19, for each component of the doublet, separately. In agreement with this, as shown by equation (90), R^v intersects P^v, R^r intersects P^r, and R^{mean} intersects P^{mean} at $j=+0.5$. Also, since all of the P, Q, and R combinations of equations (92) and (93) hold for *small* values of j, each Q graph intersects the corresponding P graph at $j=+1$, and the corresponding R graph at $j=0$.[130] The $\Delta F'$ curves approach linearity for small values of j, and deviate from linearity in the usual manner, for large values. There is no more need here to assume a "sigma" in the Kramers and Pauli formula, than in the case of the violet CN bands.

In the case of the λ4300 C+H bands the conditions are somewhat more complex, but again there seems to be no real indication of a "sigma" effect in the initial states, although Kratzer employed a value of $\sigma'=0.5$, in representing these states. This matter will be considered later.

On the other hand, the two $\Delta F''$ graphs for λ3064 definitely show something at least analogous to the "sigma effect," in that they become asymptotically identical for large values of j, but deviate with increasing rapidity for small values. Within limits of error, $\Delta F''^r=0$ for $j=+1$, while almost within limits of error $\Delta F''^v=0$ for $j=0$. These simple values of j take on added significance when we find, in the case of the λ3371 nitrogen band, that for *both* the initial and the final states, the three ΔF functions become zero, for the simple values $j=1.5$, 0.5, and -0.5, respectively (using the same value of j for the "natural" triplets),[131] but become identical for large values of j. For the λ4300 C+H

[129] Due to it, the doublet separation of the "natural doublets" cannot be *exactly* constant, for large values of j, but must vary slowly and constantly with j.

[130] In agreement with Figure 19, Case III, we have folded over the P and Q graphs on the $j=+0.5$ axis. The P'_{j-1} and R_j intersections are then discontinuous in slope, at $j=+0.5$, even for the mean value, as already noted in the discussion of Curve C, Figure 8. The one striking divergence from Case III is, however, the fact that in the $P'_{j-1}R_j$ graph there are *two* missing lines, at $j=0$ and $+1$, while in Case III there is *one* missing line, at $j=0$. This divergence must evidently be due to the fact that the final state conditions are quite different from those assumed in Case III.

[131] Zeit(108) measured this band and arranged the lines in series, according to the older Deslandres' scheme, except in the vicinity of the head of the band. Birge(15), using Zeit's data, traced the series through the head, back to the "origin," and thus showed that the band had the expected quantum structure. Independently, Lindau(11) and Hulthén and Johansson(16), (17), measured a number of other bands of this system, and proved the combination principle. The latter investigators carried the series, in general, much closer to the origin than did Lindau. On the basis of their results, a portion of the assignments by Birge are incorrect; however, because of the crowding of the lines near the head of each band, the

band, however, each pair of functions ($\Delta F''_1$, $\Delta F''_2$, and $\Delta F''_3$, $\Delta F''_4$) becomes zero for the less significant values of $j = \frac{5}{2}$ and $\frac{3}{2}$ respectively, the two members of each pair becoming identical for large values of j, but the two pairs not identical.[122]

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analysis, even with the aid of the combination principle, is somewhat uncertain. The exact form of the ΔF curves in this case can therefore not be considered as necessarily final, but in the case of the water bands, the lines are so widely spaced that there is no question as to the correct series assignment, nor as to the form of the resulting ΔF curves. The writer has not studied the C + H bands with sufficient care to venture an opinion in their case.

The values of j for λ3371 of nitrogen, to give the ΔF intersections just quoted, are in all cases greater by unity than the values of "m," given by Hulthén and Johansson(17).

[122] It has been noted, in the discussion of Curve D, Figure 8, that the λ4300 C + H band consists of a combination of what we have called Type A′ and Type C doublets. The quantum structure of this band has been studied in great detail by Kratzer(53). Because presumably of its theoretical importance, and because the writer does not agree with all of Kratzer's conclusions, the following brief summary is given.

Corresponding to the four-fold multiplicity of each branch, (P, Q, and R), we assume, as a starting point, four different initial and four different final rotational energy functions. Thus R_1, P_1 and Q_1 are connected with $\Delta F'_1$ and $\Delta F''_1$, in the usual manner. In the case of the initial functions, we find for all four, as a first approximation $F' = B'(j - \frac{1}{2})^2$, the same functional form as for the initial state of the OH bands. Within limits of error, $\Delta F'_1 = \Delta F'_3$, $\Delta F'_2 = \Delta F'_4$. But, within limits of error, the *difference* between $\Delta F'_{1,3}$ and $\Delta F'_{2,4}$ is *linear*, and is about -0.10 for $j = 22$, and $+0.27$ for $j = 0$. This type of difference can be explained only by assuming two different values of B', and also two different values of α'. Thus we may write, for the initial states of λ4300,

$$\left.\begin{aligned} F'_{1,3} &= B'_1(j - \tfrac{1}{2} + \alpha'_1)^2 + \ \ldots \\ F'_{2,4} &= B'_2(j - \tfrac{1}{2} + \alpha'_2)^2 + \ \ldots \end{aligned}\right\} \qquad (173)$$

From the numerical values quoted, one obtains

$$\alpha'_1 - \alpha'_2 = +0.008, \qquad B'_1 - B'_2 = -0.009$$

approximately.

Kratzer, however, assumes that the $F'_{1,3}$ and $F'_{2,4}$ values are given by the double Kramers and Pauli formula, with $\epsilon' = \frac{1}{2}$, $\sigma' = \frac{1}{2}$. As shown in Figure 24 ahead, the separation of the two $\Delta F'$ curves, with the values of j used here, should then be zero for all large values of j, and increase with sudden and enormous rapidity, for very small values. The writer cannot see how this assumption of an actual σ' is justified by the experimental facts. Mulliken (private communication) has independently concluded that $\sigma' = 0$, for this band, from the evidence furnished by missing lines.

For the *final* rotational states, the relations are very definite. Here we have $\Delta F''_1 - \Delta F''_2 = 0$, and $\Delta F''_3 - \Delta F''_4 = 0$, for all large values of j, with these two differences increasing from zero with great rapidity, as j becomes small. Hence this indicates at least qualitatively, an example of the double Kramers and Pauli formula, for each pair of functions. Kratzer assumed $\epsilon'' = \frac{1}{2}$, $\sigma'' = 1$, for

In considering the type of spectral doublet found in the λ3064 OH band, the approximately constant frequency difference for large values of j suggests the case mentioned in the preceding part, where if $\gamma'=\gamma''$, ($a'B'=a''B''$) one obtained such a constant separation, the two ΔF graphs having also the same constant separation ($=4\gamma$). But as noted there, this separation is obtained when one in obtaining the values of ΔF combines the *red* component of the R branch with the *violet* component of the P branch, and *vice versa*. Now in the OH bands, the writer finds it possible to make such a combination, and to satisfy the combination principle, as far as the values of $\Delta F''$ are concerned. But this method breaks down for $\Delta F'$. On the other hand, combining the two red components leads, as already noted, to a consistent fulfilment of the combination principle. But for this method of combination, the two ΔF graphs are identical, when the doublet separation becomes constant. Hence $\gamma=0$ and there is no possibility of explaining in this way any constant

each, and Mulliken (private communication) also has adopted these values. On the other hand, $\Delta F''_1 - \Delta F''_3 = 0$ and $\Delta F''_2 - \Delta F''_4 = 0$ for $j=0$, and this value increases from zero, linearly with j. We thus have a definite case of a two-fold value of B'', for each pair, and this was assumed by Kratzer.

Now in connection with the definition of the various types of spectral doublets, in Figure 8, (Types A, A', B, and C) it must be remembered that in general the observed separation of the two spectral lines is due to a combination of the differences of the two *initial* rotational energy functions concerned, of the two *final* functions, and of the two possibly different electronic levels in either initial or final state. Hence it is only when *one* of these effects is operating alone that one can correlate immediately the observed doublet difference with the character of a two-fold energy state.

Such a condition is exemplified here, for in the case of the R_1R_3, P_1P_3, or Q_1Q_3 doublets, forming the type A' doublets of Curve D, Figure 8, the *initial* state has been found to be precisely the same, and therefore the doublet separation indicates, independently, the character of the double final state. As noted by Kratzer, $R_1 - R_3 = P_1 - P_3 = Q_1 - Q_3$, and these differences are given accurately by a quadratic in j (the definition of a type A' doublet), thus verifying the above relation between $\Delta F''_1$ and $\Delta F''_3$. For $R_1 - R_3 = (B_1 - B_3)[f(j)]^2$. Aside, then, from the effect of the presence of σ, in $f(j)$, an effect which is manifest only for very small values of j, the doublet separation should be accurately proportional to j^2. On the other hand, the R_1R_2 or P_1P_2 doublets are due almost entirely to the "sigma effect" of the double Kramers and Pauli formula for the final state, since the effect due to the two different initial functions F'_1 and F'_2, already evaluated, is very small. Hence these doublets represent, very closely, a true example of type C.

Finally it may be noted that this λ4300 band has overlying it another band of similar structure, the two being possibly the 0, 0 and 1, 1 bands of a system. The closely adjacent position of the two bands adds greatly to the difficulty of the actual series analysis, made so brilliantly by Heurlinger and Hulthén[109] and by Hulthén[42].

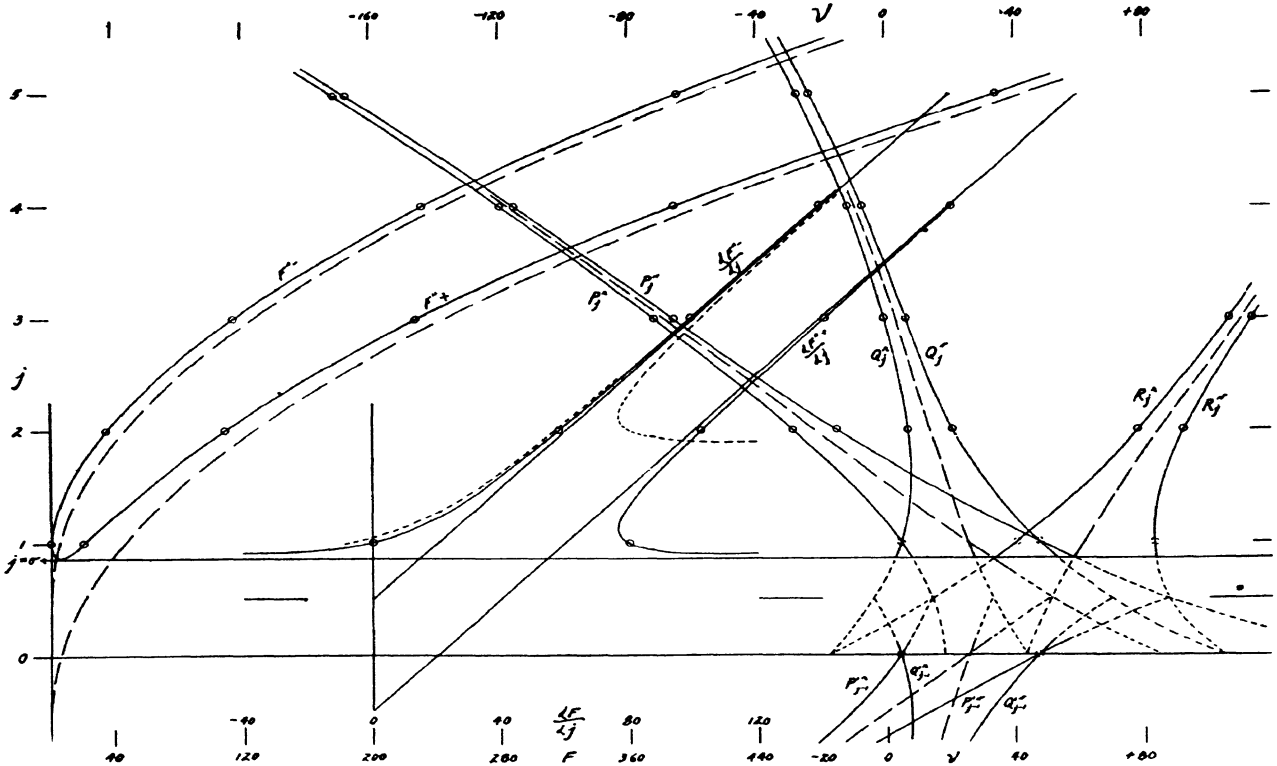


FIGURE 24.—Graphical Representation of the Double Kramers and Pauli Formula for Small Values of j only. Plot of F and of its Derivative. Also a Hypothetical Band, Using the Above Formula for the Final State Only. $\nu = 0$ for the "Origin" of the Band.

separation other than zero. In other words, if we assume the validity of equation (172), then in the limiting region of large values of j the presence of σ does not affect the doublet separation and the relations derived for this separation in Part 5c still apply. But these, as noted, cannot lead to a constant doublet separation other than zero except in the case of bands for which the combination principle equalities indicate that the red component of the P branch is to be combined with the violet component of the R branch, and *vice versa*. In the C+H bands the doublet separation of the two type C doublets evidently does approach zero, but in the other bands cited it remains quite large.

Mecke([54]) has represented this limiting separation, analytically, by adding a constant term E to the ordinary rotational energy function. [See equation (177) ahead.] By giving E various values for the various components, it is possible to obtain any constant doublet separation which is desired. This is essentially equivalent to assuming a double or triple "origin" for these bands, the spacing of the multiple origin equaling the constant spacing of the doublets and triplets for large values of j. Thus we may assume that the limiting real constant separation in the OH and N_2 bands is an example of the "class one" type of multiplicity attributed in Part 2f to a multiple electronic energy level, as evidenced by a multiple "origin." This separation is then superimposed upon a "class two" type of doubling, which is a function of j and which *may* be capable of being represented by the Kramers and Pauli formula. According to Kratzer, it is so capable, in the λ4300 C+H band, which therefore has a single "origin." It should be noted, in this connection, that the points of intersection of the P and R branches, which, in all previously discussed cases, can conveniently be used to locate the "origin" of a band, as noted in connection with the several cases, cannot be so used here, since in general this point of intersection involves imaginary values of F' or F''' and may be located, as we have done, only by an arbitrary extrapolation. Hence the only *general* method of locating the origin of a band is to evaluate by means of the combination principle, and appropriate summation, expressions for F' and F''' of acceptable theoretical form, and then from the known spectral frequencies $\nu = \nu_0 + F' - F'''$, as per equations (71) and (72), to evaluate ν_0, the desired frequency. The actual value of this frequency is thus obviously dependent upon the theory adopted, and is very uncertain, in the present case.

In order now to test the validity of the Kramers and Pauli formula, we indicate in Figure 24 a set of relations calculated on the basis of this formula. The theoretical equation has been taken as closely as convenient

to the apparent actual equation for the λ3064 band, in order to facilitate comparison. That is, we have assumed for the final state

$$F''^{\pm} = B''(\sqrt{j^2 - \tfrac{3}{4}} \pm \tfrac{1}{2})^2. \qquad (174)$$

This double function is plotted on the left side of Figure 24. For large values of j, the two curves for F^+ and F^- become parallel to the functions obtained by placing $\sigma = 0$, in equation (174). We shall call these the parent functions. They are shown by broken lines. In the center of the figure are given the " derivative " curves $\left(\frac{dF}{dj}\right)^+$ and $\left(\frac{dF}{dj}\right)^-$, together with their parent functions—here straight lines. All values of the functions, for j less than σ, are of course imaginary. Because of the rapid change of slope of the derivative curves, for j close to σ, the experimentally determined values of $\Delta F'$ may be quite different from the true derivative. Numerical calculation of the former shows, however, that the first effective difference appears at $j = 2$, and a reasonable extrapolation of the ΔF^- curve is shown by the dashed curve just to the left of the $\left(\frac{dF}{dj}\right)^-$ curve. It will be noted that the discrepancy in the determination of the value of j for which $\left(\frac{dF}{dj}\right)^-$ equals zero [133] is not very great.

The two derivative curves are given by the equation

$$\left(\frac{dF}{dj}\right)^{\pm} = 2Bj \pm \frac{2Bj\epsilon}{\sqrt{j^2 - \sigma^2}}. \qquad (175)$$

We have then the essential result that the *mean* curve passes through the origin. But as shown by Figure 23, the actual mean curve passes through a point one-half unit *above* the origin. Hence, in order to agree in any way with the Kramers and Pauli formula, we must *lower* by one unit the values of j which we have assigned to the *violet* components, in each branch of the λ3064 band. This will of course lower the $\Delta F'^+$ curve by one unit. Since this band has already been plotted in the most symmetrical fashion, in Figure 23, we may more conveniently leave this plot as it is, and in order to obtain the corresponding theoretical formulation, *raise* the $\left(\frac{dF}{dj}\right)^+$ curve of Figure 24, by one unit. This gives

[133] This value of j is important, if the Kramers and Pauli formula is true, for according to this formula, j then equals $\sqrt{\sigma^2 + \epsilon^2} = s$, the resultant electronic momentum of the molecule. The fact that this value is essentially unity, for the λ3064 band, therefore might be considered significant. Also, if we assume that $\epsilon = \frac{1}{2}$, then necessarily $\sigma^2 = \frac{3}{4}$ as used in equation (174).

$\left(\frac{dF}{dj}\right)^{+}_{j-1}$ which is shown in Figure 24 by a dashed curve. In the case of the C+H bands, Kratzer obtains this result by writing

$$F''^{+}=B''^{+}(\sqrt{(j-1)^2-\sigma^2}+\tfrac{1}{2})^2, \qquad (176)$$

where, however, this indicates merely a renumbering of the lines in terms of the "Laufzahl" (Kratzer's "m" or our "M") and not a modification of the Kramers and Pauli formula.

We now assume for F' the same type of function found for λ3064, i. e., $F'=B'(j-\frac{1}{2})^2$, and calculate the frequencies of the lines of a hypothetical band. The results are plotted on the right side of Figure 24, with then the same value of j for the natural doublets. (Note that the scale of Figure 24 is twice as large as for Figure 23.) As already mentioned, the doublet separation becomes asymptotically equal to zero, as j increases, although since the curves of Figure 24 are carried only to $j=5$, this fact does not appear so clearly. The curves for the P, Q, and R branches have been extrapolated to zero, even though the rotational energy term is imaginary for such a value. Because of the form assumed for F', the P and R branches *must* intersect at $j=+0.5$ (and the other intersections similar to Figure 23), even though the *frequency* of the intersecting point is purely arbitrary, depending upon the extrapolation. As in the case of Figure 23, the mean values for the P, Q, and R doublets are indicated by broken curves, and in further analogy, the P and Q curves have been folded over on the $j=+\frac{1}{2}$ axis,[134] to give P'_{j-1} and Q'_{j-1}, as in Case III.

We are now in a position to examine the question of missing lines. As already noted, it is definitely known that all lines are present for which $j=2$, in Figure 23, but all lines are missing, for which $j=1$. The true values of j for the violet components of each branch are to be taken as less by unity than those indicated in Figure 23, and these true values are hereafter used in the designation of individual lines. In accordance with the preceding discussion, we assume ϵ' and $\epsilon''=+\frac{1}{2}$ and $-\frac{1}{2}$ for violet and red components respectively, while $\sigma'=0$, $\sigma''=\sqrt{\frac{3}{4}}$.

In the case of the analogous C+H bands, Kratzer([53]) has assumed as usual that $j=0$ gives one condition for missing lines, while obviously

[134] It is possible to use such a common axis for the folding, and preserve the symmetry, only when the $\Delta F'$ curves all equal zero for the same value of j—here $+\frac{1}{2}$. In contrast, in the case of λ3371 of nitrogen, the points of intersection of the P and R curves, as already noted, are $j=+1\frac{1}{2}$, $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively, and therefore, in order to preserve the symmetry, each P curve must be folded over at its own intersection with the corresponding R curve, the resulting folded curves being P'_{j-3}, P'_{j-1} and P'_{j+1} for the three components of the triplet, respectively.

$j<\sigma$ leads to an imaginary value of m, in equation (172), and hence to missing lines. But in the case of the λ3064 OH band, the $j=0$ rule definitely breaks down, for $P_1{}^v$ (32,440.49 cm^{-1}) is present, although $j'=0$. Incidentally, this proves that $\sigma'=0$ since otherwise m' would be imaginary for this line. Mulliken (private communication) finds a similar condition for the λ3900 C+H band, and therefore σ' must be zero for this band also, contrary to Kratzer's assumption.

On the other hand, the lines $R_1{}^r$ and $Q_1{}^r$ are absent, and with the values of ϵ and σ just assumed, there is no obvious explanation for this fact. Thus these lines correspond to $j'=2$, $j''=1$, and $j'=j''=1$, respectively. If $\sigma''=\sqrt{\frac{3}{4}}$, as Figure 23 quite definitely indicates, they correspond to $m'=1.5$, $m''=0$, and $m'=0.5$, $m''=0$, respectively. The only distinctive value here is the $m''=0$ of the final state, but none of the assumptions concerning intensity distribution, discussed in Section 6 ahead, give zero intensity for a line corresponding to zero rotation of the molecule in the *final* state. Mulliken (private communication) avoids this difficulty by assuming $\sigma''=$unity, or essentially unity, in analogy with the C+H bands. The lines just considered then correspond to a reversal of the direction of rotation of the molecule, and therefore fall in the same category as the missing line in the violet CN bands.[135]

[135] The question of missing lines is considered at many places in this report. The present status of the matter may be summarized as follows. The $j=0$ exclusion rule evidently breaks down in certain cases. The realization of this fact is, however, of such recent occurrence that in the main body of the report the older interpretation is in general assumed, and footnotes are added where necessary to give the newer interpretations. These new interpretations are mainly the result of Mulliken's recent work, and as pointed out in Section 3, and at the end of Part 5c, many missing lines can now be explained by assuming a fairly large value of σ (0.5 or 1.5) in cases where it had not previously been realized that any real σ existed.

The rule, $j<\sigma$ gives missing lines, will not account for the one missing line of the violet CN bands, the CuH bands, the HCl bands, and other bands of this common type. Mulliken has suggested for this case the criterion that the nuclear rotation cannot reverse direction, during the radiation process. It may be pointed out, however, that in the case of bands composed of *single* lines, such as the HCl and CuH bands, both Kemble and Dieke have implicitly explained this one missing line by deriving theoretical formulas for the *distribution* of intensity in the P and R branches which *predict* zero intensity for this line. These formulas are given by equations (179) and (182) of Section 6 ahead, and are discussed there. The two equations are equivalent, under certain conditions, and are in essential agreement with the observed intensity distribution, as given empirically in equation (103) of Part 5b. Equation (182) takes on a slightly different form, when applied to the unresolved doublets of the CN bands, as interpreted by Kratzer and by Mulliken, and the argument accordingly does not apply in such cases.

It thus appears that the Kramers and Pauli formula is fairly satisfactory, so far as missing lines are concerned. Unfortunately, the same statement cannot be made in regard to the predicted frequencies. Aside from the essentially constant doublet separation for large values of j, which may be considered, as already noted, as due to a double electronic level, it is evident that in the λ3064 band, the increasing doublet separation for small values of j begins to manifest itself at higher values of j, but increases more slowly than is predicted by the formula.[136] This is even more true in the λ3371 nitrogen band, where the increased separation is quite evident even for $j=20$, and the continued increase for the R branch triplets[137] is very slow and almost uniform down to the smallest values of j. The discontinuities in slope of the $P'R$ curves, in the λ3371 band, are very small, compared to the enormous discontinuities of Figure 24. It would thus appear that the Kramers and Pauli formula, although with suitable modifications qualitatively of the form needed to explain the band structure now under discussion, is quantitatively unsuitable.

A new formula for the rotational energy terms of the nitrogen bands, with only a formal theoretical basis, has been proposed by Mecke([54]), as follows:

$$\left.\begin{aligned} F_1(m) &= E_1 + B(\sqrt{m^2+A}-\epsilon)^2 \\ F_2(m) &= E_2 + Bm^2 \\ F_3(m) &= E_3 + B(\sqrt{m^2+A}+\epsilon)^2 \end{aligned}\right\}, \qquad (177)$$

where m is a half integer, $\epsilon=1$, $A=81$, in the case of the second positive group of nitrogen. The values of the other constants are not given. By this numbering of m, which Mecke uses in place of j, the three $\Delta F : m$ curves coincide for small values, a relation that could be obtained, in our previous notation, by lowering F_1 one unit; and raising F_3 one unit, with $m=j-\frac{1}{2}$.

[136] The doublet separation in the "natural" doublets of λ3064 is really due then to three separate causes, (1) the small constant difference in the initial $\Delta F'^v$ and $\Delta F''^r$ (using the same value of j for the two lines in question), giving a separation proportional to j, and equalling about 4 cm^{-1}, for $j=20$; (2) an assumed constant effect (due to a double electronic level) which, except for effect (1) would indicate an essentially constant doublet separation for large values of j; (3) an effect manifesting itself only for small values of j, and given at least qualitatively by the double form of the Kramers and Pauli formula for the *final* state, providing one uses different values of j for the two lines concerned. (In that case it is of course necessary to make a corresponding change in j for the initial rotational energy functions.)

[137] In the case of the P branch triplets, the separation increases just as in the R branch, down to the "head" of the band. From that point to the origin it rapidly *decreases*, according to the series assignment of Hulthén and Johansson([17]), while it continues to increase, according to the assignments by Birge([15]).

These equations, regardless of theory, indicate for the nitrogen bands, according to Mecke, the type required to fit the experimental facts. Meanwhile, as long as there is uncertainty in this matter of the rotational energy formula, it is not possible to evaluate the double or triple "origins" of such bands, and consequently it is not possible to decide just what portion of the multiplet spacing is due to a multiplicity of electronic configuration, and what portion is due to other causes.

PART 5E. THE HYDROGEN AND HELIUM BANDS, AND OTHER BANDS DUE TO SYMMETRICAL MOLECULES

Some of the most puzzling, and possibly for that reason the most interesting phenomena, evidenced by band spectra occur in the case of diatomic molecules composed of two like atoms such as N_2, N_2^+, O_2, C_2, He_2 and H_2. These phenomena, to be described presently, seem to be, to greater or less extent, an invariable accompaniment of this type of molecule, as noted by Mecke([110]). Conversely, no such phenomena have been observed in the case of any band known to be due to a diatomic molecule composed of unlike atoms. If this turns out to be an invariable rule, it should be of great service in the determination of the chemical origin of bands.[138]

As examples of symmetrical molecules, we shall discuss in some detail the bands due to N_2^+, He_2, and H_2, the order given corresponding to order of increasing complexity.

The negative bands of nitrogen have recently been photographed under high dispersion, and analyzed according to the quantum theory by Fassbender([77]). The bands of this system are in all respects similar to the violet CN bands, with the following single exception. The successive lines of the P and R branches (there is no Q branch) are alternately strong and weak, this variation applying to *both* components of the doublet. Thus, if one plots an intensity curve, using only alternate lines, there is obtained the usual variation of intensity with j (or m). If one plots the other half of the lines, a similar curve is obtained, but the ordinates of one curve are roughly twice those of the other. Such curves are given on p. 90 of reference ([77]).

[138] Thus, for instance, the Al band system, of which λ4842 is the strongest band, must be due either to AlO or Al_2. The bands are exactly like the violet CN bands, showing no trace of the phenomena in question, and therefore must be due to AlO, a conclusion which Mulliken([49]) has reached on other lines of evidence. Similarly, the first negative group of carbon bands has commonly been attributed to C_2^+, although it is now believed to be due to CO^+ (see references ([71]) and ([49])). This system, also, does not show these new phenomena, and therefore cannot be due to C_2 or C_2^+.

Figure 25 illustrates schematically the phenomena in these bands, as well as in certain helium bands to be considered later. In the lower half of the figure is shown the continuous sequence of lines of the P and R branches (one line being missing), with the alternating intensity

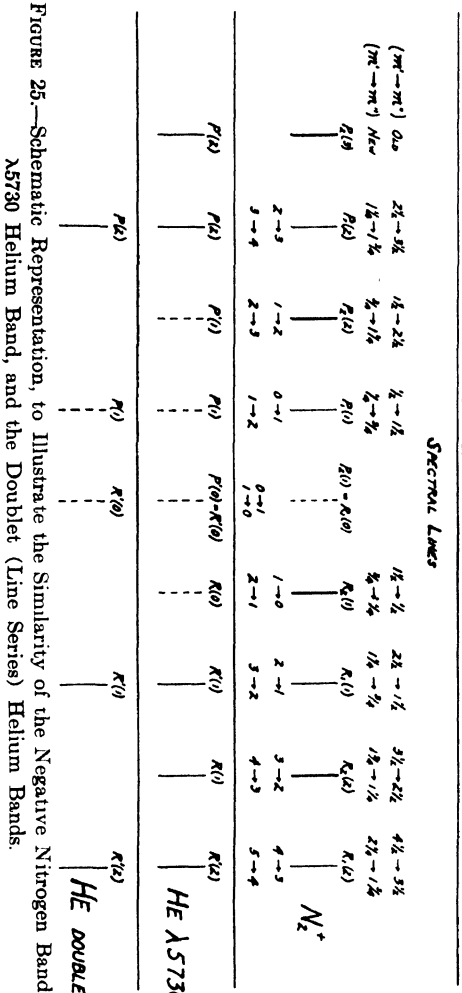


FIGURE 25.—Schematic Representation, to Illustrate the Similarity of the Negative Nitrogen Bands, λ5730 Helium Band, and the Doublet (Line Series) Helium Bands.

indicated. The continuous change of intensity due to temperature distribution is here ignored. Above these lines are given the values of m' and m'' according to the usual assumptions. They are marked $m' \rightarrow m''$ (old). Beneath the lines are given the double set of values of $j' \rightarrow j''$ used by Kratzer to account for the CN doublets. Only the lower set has

been used by the writer, as discussed in Part 5c. With either set of values, the central line, $P_2(1)$ or $R_1(0)$, is missing. The designation of the various lines is that proposed by Dieke([59]). In the upper half of the figure is shown a portion of the initial and of the final rotational energy levels, spaced arbitrarily at equal intervals. The alternating intensity of the N_2^+ lines may be accounted for by an alternation in probability of either the initial or final set of levels. It is shown, in the figure, for both sets. In addition there are given the transitions corresponding to the two lines on each side of the central missing line, as well as the transitions for two Q branch lines which occur in the helium bands, but not in nitrogen. Each transition is designated according to the nomenclature used in the lower half (R_1R_2, etc.) and also according to Kratzer's([111]) notation for the λ5730 helium band. Above the energy levels are given the usual values of m and of j marked "old." Again, only the lower set of values of j has been used by the writer, in the case of the CN bands.

As can be seen from Figure 25, the strong lines can be considered as associated with the values $m'=1\frac{1}{2}$, $3\frac{1}{2}$, etc., *or* with $m''=\frac{1}{2}$, $2\frac{1}{2}$, etc., while the weak lines are associated with the remaining alternate levels. It has seemed difficult to explain this apparent alternation in the *a priori* probability of successive quantum states. Hence, Dieke([59]) suggested an entirely different interpretation, to which reference has already been made in Parts 3b and 5a. He merely halves all previous values of m, for both initial and final states, obtaining the values marked in Figure 25 as "new." One may now make various assumptions as to the values of j to be associated with the various values of m. The validity of these assumptions can be tested by an examination of the "missing" lines, although as we have previously noted, there is some question as to the correct criterion. We shall for the present adopt the usual rule that $j=0$ gives a missing line.

Four sets of possible values of j are indicated in the upper half of Figure 25 and are designated as A, B, C, and D, respectively. Each scheme may be assumed for either initial or final state. Thus the true state of affairs may be a combination of scheme A in the initial state with scheme B in the final state, etc. Using the same scheme for *both* states, it may be noted that scheme A predicts *one* missing line [$P_2(1)$ or $R_1(0)$]. Scheme B (and also scheme D) predicts *five* missing lines, centered on the line just mentioned, and thus including all the P and R lines shown in the upper half of Figure 25, while scheme C predicts *three* missing lines, also centered on the same line. It may be noted further that scheme A gives $\epsilon=+\frac{3}{4}$ and $+\frac{1}{4}$ where $m=j-\epsilon$. In the

nitrogen bands, $\epsilon = \frac{3}{4}$ gives a weak initial or a strong final state, with the reverse conditions for $\epsilon = \frac{1}{4}$. Similarly, scheme B gives $\epsilon = -\frac{1}{4}$ and $-\frac{3}{4}$, while scheme C gives $\epsilon = \pm\frac{1}{4}$ and scheme D, $\epsilon = \pm\frac{3}{4}$. The realization of two different values of ϵ, with presumably different *a priori* probabilities, is the chief reason for Dieke's hypothesis.

To explain the doublets of the negative nitrogen bands, Dieke uses a combination of schemes A and B, one scheme for each component. Thus both components of the central doublet should be missing, and one component of the *two* adjoining doublets on either side. This is analogous to Kratzer's interpretation of the CN doublets, his values of j (given at the top of Figure 25) indicating one missing doublet, and one component of the adjoining doublet on either side. The same objection holds in the case of both band systems. Fassbender's intensity curves are precisely like those for the CN bands, the intensity of lines near the central missing line being proportional to the value of M, as previously discussed, with only the line $M = 0$ missing.[139] The writer suggests the use of scheme A only, with the doublets explained in a manner similar to that proposed for the CN doublets.

For either scheme A or B, we have the following results. The apparent R branch for which $\Delta m = -\frac{1}{2}$ is to be broken into two branches R_1 and R_2 for which $\Delta j (= j'' - j') = -1$, and 0, respectively. The apparent P branch for which $\Delta m = +\frac{1}{2}$ is to be broken into two branches P_1 and P_2 for which $\Delta j = 0$, and $+1$, respectively.[140] Without attempting for the

[139] Dieke(27), (104), has applied the intensity rules of Burger and Dorgelo (see Sommerfeld's Atombau, 4th Edition, pp. 649-659) to the case of band spectra, and has obtained results which avoid the above difficulty. For according to these rules, the sum of the intensities of all lines corresponding to transitions from a given initial state is proportional to the *a priori* probability of that state. Therefore, if certain transitions are prohibited, the others are relatively that much stronger, and in the case cited above this leads to the prediction that the single remaining component in the first line should have an intensity equal to the sum of the intensities of the two normal components of other lines (aside from the customary temperature effect). Dieke's work on intensity is discussed more critically in Section 6, ahead.

[140] Dieke(58) has proposed that the names P, Q and R be used to designate the *appearance* of a branch, just as Heurlinger originally intended these letters, while positive, negative, and zero be used for transitions for which $j' - j'' = +1$, -1, and 0 respectively. The writer thinks that in general the names P, Q, and R should indicate both meanings. That is, unless otherwise specified, an R branch should be taken to mean a positive branch, a P branch to mean a negative branch, etc. But in the present case it is convenient to use Dieke's nomenclature. Hence the R branch is actually a combination of a positive and a zero branch, while the P branch is a combination of a zero and a negative branch.

moment any critical discussion of this new formulation, let us consider the phenomena in other similar cases.

In the second group of nitrogen, we have apparent triplet lines, as already discussed at length in Part 5d. Higher dispersion shows that one member of these triplets (the violet member R_1P_1) is actually double, and the doublet components are of unequal intensity, with the violet component alternately the stronger and weaker.[141] The combination principle has been found to hold for the strong members, in the P and R branches, taken together, although this leads to staggered values for ΔF. The mean doublet position gives a smooth ΔF curve. If the weak member were entirely suppressed one would have a series of lines alternately slightly displaced, and such a phenomenon occurs in one component of the triplet, in the Swan bands, where Shea([91]) has found that the combination principle similarly holds. The phenomenon in the case of the atmospheric, and of the Runge (ultra-violet) bands of oxygen is generally similar to that in the case of helium, and has been summarized by Mecke (p. 233 of reference ([9])). We turn, therefore, to the case of helium, which typifies the second stage of complexity for the phenomena under discussion.

The very fact that helium has a band spectrum is an interesting example of the usefulness of the quantum theory of band spectra. Thus, from the structure of the bands, we can be sure that they are due to a diatomic molecule, while the experimental evidence indicates that only helium is needed for their production. Hence we have proof of at least the temporary existence of the He_2 molecule.

This band spectrum has been measured and analyzed in detail by Curtis([35]), ([113]) and Curtis and Long([114]), and certain bands have been further interpreted by Kratzer([111]). Other published articles have considered a possible molecular model, but that topic will not be treated here. A reproduction of the greater portion of the known bands is given by Curtis([115]), while the more recent articles by Curtis contain enlargements and diagrams of various individual bands. All of the helium bands are characterized by a strong Q branch, which is a dominating feature in their appearance. In the λ5730 band there are two R, two P, and two Q branches, each pair of equal intensity, but requiring different formulas. In all other bands there is only one R, one P, and one Q branch, according to recent work. The band spectrum of helium consists,

[141] When nitrogen is mixed with argon, however, *all* members of the triplet show the alternating intensity characteristic of the negative nitrogen bands. See curves XIII, XIV, XVI, and XX of Toussaint([112]).

first, of two series of double-headed bands all degraded toward the red, one series consisting of the bands λλ4650, 3680, 3350, 3200, 3120, 3070, 3036, and 3012, as extended by Curtis and Long([114]), and the other of the bands λλ5130, 4000, 3630, and 3460. There are also two strong bands at λ6400 and λ5730 and a weaker one at λ4550, which do not belong in any series and which may be called the "non-conforming" bands. All of the above bands are degraded to the red, with the exception of λ5730. A number of additional bands have not as yet been studied.

Fowler([116]) made the first examination of the helium bands, and arranged the two series of bands just noted. He made the very important discovery that successive bands in each series obeyed a *line series* law. He found that the less refrangible head of the doublet could be satisfactorily fitted by an ordinary Hicks formula (and almost as well with the simpler Rydberg formula), but that the other head could not be well fitted, even with a four constant formula. We know now, thanks to the analysis by Curtis, that the less refrangible head is really the head of the Q branch, or branches, and therefore locates the origin of the band. The other head is merely the turning point of the R branch, and has no theoretical significance, so that the inability to fit it into a simple formula is not surprising, as has been noted by Curtis([113]). The fact that the successive *origins* follow a line series law is, however, of fundamental importance. It indicates that *each band* constitutes a separate *system,* with its *own* electronic transition, and that the series of electronic energy levels in the helium molecule is quite analogous to a set of spectral terms of an atom. This certainly might be expected, and the failure to observe long series of such levels in other molecules must be due to their more complex character.[142]

Curtis([35]) first analyzed the three "non-conforming" bands. The results showed many apparent discrepancies with the quantum theory, and Curtis was not able to prove the combination principle. Kratzer([111]) later found the combination principle equalities, and on this basis made a searching analysis of these three bands. Curtis([113]) in a still later paper gave an analysis of the first three ("double") bands of the first "line" series, and of the first four of the second series. In a very recent paper, Curtis and Long([114]) have extended the first series to eight members and have re-analyzed the entire series, using an interpretation virtually the same as that adopted by Kratzer for the three non-conforming bands. Dieke([59]) has indicated the close similarity of the doublet bands and of the non-conforming λ5730 band to the negative nitrogen bands already discussed.

[142] In line spectra, the more complex the atom, the shorter the sequences of spectral terms. New evidence on the above matter is discussed in Section 8.

The phenomena are so complex that only an incomplete statement can be given here. Considering first the λ5730 band, the only helium band of those analyzed which is degraded to the violet, we find six branches, two P, two R, and two Q branches. Although the lines of the two similar branches are of equal intensity and interlace roughly, quite different formulas are required for the two, as already noted. The relations for this band are shown in the diagram on p. 56 and the reproduction on Plate I, of Curtis([35]). Dieke has noted the points of resemblance to the N_2^+ bands, and these are shown in the lower half of Figure 25. There are *four* lines absent in the $P-R$ sequence as indicated in the figure. The designations are those proposed by Kratzer([111]) and used by Dieke([59]). Curtis' $R(M)$ = Kratzer's $R(M-1)$, Curtis' $Q_1(M)$ = Kratzer's $Q_1(M+1)$. Otherwise, Curtis' designations agree with Kratzer's. The lines $Q_1(1)$ and $Q_2(1)$ are shown in the upper half of Figure 25. $Q_1(2)$ is the first real line of this branch, while $Q_2(1)$ is the first real line of the other.

In order to account for the missing lines, using the $j=0$ criterion it is necessary to assume scheme B for the initial states. For the final, we may have either scheme A or scheme C. The former seems objectionable since it makes the R branch a true negative branch, Δj *increasing* by one unit, while Δm *decreases* by a half unit. We therefore assume scheme C for the final state. Kratzer([111]) originally postulated scheme C for both initial and final states, and his values of j, throughout the entire article, correspond to this. Later in the article he discusses various methods of enumeration, one of which is scheme D,[143] and decides that no decision can be made between them.

In the case of all the *doublet* helium bands, the phenomena are much simpler. In this case there is only one P, one Q, and one R branch. The relative position of the P and R branches can be obtained by wiping out all the *strong* lines of the N_2^+ bands. This analogy was pointed out by Dieke([59]) and is shown at the bottom of Figure 25. The lines $R'(0)$ and $P(1)$ are missing. In addition there is the one Q branch, corresponding to Q_1 in Figure 25, of which $Q_1(1)$ is the first real line. In order to account for the missing lines it is now necessary to assume scheme C for *both* initial and final states, except that for the final state only one-half the energy levels—those corresponding to $\epsilon = +\frac{1}{4}$—are used. This result seems more rational than any of the preceding for we have only the one numerical value of $\epsilon = \frac{1}{4}$. In this case also there is no artificial division

[143] By this scheme, which does not agree with the data on missing lines, the values of j, from right to left are 1, 0, 2, 1, etc., and for several lines Δj and Δm have opposite signs. The writer believes that this should be avoided, if possible.

of the branches into two sets of lines and the assumption of $\epsilon=\frac{1}{4}$ seems almost inevitable with the quarter-quantum interpretation. This formulation has been adopted by Curtis and Long([114]) in their recent paper on these doublet bands.

The remaining helium bands, λ6400 and λ4550, have been analyzed by Curtis([35]) and discussed by Kratzer([111]). In each there is one P, one R, and one Q branch.[144] All three branches (called R, P' and Q) are strong, and correspond in every way to the branches marked R, P', and Q_1, in the λ5730 band. Thus the R and P' sequence comprises just those lines *not* found in the doublet helium bands. The first real lines of each branch are $R(1)$, $P'(1)$ and $Q(1)$. An examination of Figure 25 shows that scheme C must again be used for both initial and final states, except that the value $\epsilon'=+\frac{1}{4}$ is alone needed, as contrasted to $\epsilon''=+\frac{1}{4}$ for the doublet bands. Kratzer([111]) found that the three "non-conforming" helium bands had a common final state, with $I''=0.944\times10^{-40}$, on the present interpretation. λ6400 and λ4550 he assumed belong to the same system, but differ in the initial vibrational quantum number. λ5730, which is degraded in a direction opposite to the other two bands, must have a different electronic initial condition, i. e., it belongs to another band system. As already noted, each of the doublet bands forms the sole representative of an entire system. The analysis of Curtis([113]) indicates that each (line) series of doublet bands has a common final state, while Curtis and Long([114]) conclude that different radiating electrons are concerned with the two different series.[145]

Reviewing now all of the facts presented in Part 5e, it might appear that the use of quarter-integral values of ϵ, in the case of the helium bands, first suggested by Kratzer([111]), is most probable. With this assumption, the close analogy of these bands to the relations in the N_2^+ bands favors Dieke's interpretation of the latter, as shown in Figure 25. Yet there is one important and probably vital distinction. In the helium bands there is *no* case of a series composed of lines of alternating intensity.

[144] This is in agreement with new work by Curtis (private communication) who finds that the weak and rather irregular P branch previously assigned to these bands actually belongs to other faint bands. Curtis now assumes the strong λ6400 and λ4546 bands to be (0, 0) bands, and the new bands to be (1, 1). If this interpretation is correct, it constitutes the first valid evidence of the actual existence of vibration, for the helium molecule.

[145] Mulliken (Proc. Nat. Acad. Sci. 12: 158, 1926) on the basis of the new developments presented in Section 8, has recently found the true interpretation of these bands. The λ6400 and λ4550 bands belong to different systems and are in each case the (0, 0) band. The entire system of electronic energy levels corresponding to the known helium bands is strikingly similar to that of the helium atom. (See Section 8 for further details.)

Neither are there any two series which can be combined into a single formula. Mecke([9]) therefore suggests as an alternative hypothesis, the older interpretation of the N_2^+ bands, with the alternating intensity left essentially unexplained. Then for the helium bands he assumes that each series is composed actually of lines of alternating intensity, but that every alternate line is so weak that it has not yet been observed. Mecke makes a similar assumption in the case of the atmospheric (absorption) bands of oxygen, and the Runge (emission) bands of oxygen. This assumption has at least the strength of consistency, since we thus assume alternating intensity in the series of *every* symmetrical molecule. Another argument in favor of Mecke's assumption is that it would preserve the older value of the moment of inertia, in the case of the N_2^+ bands, while Dieke's assumption gives a value just one-fourth as large.[146]

Rather convincing evidence on this point is now available, for Birge([96]), has found in the case of N_2^+, that the "observed" and "calculated" values of D_0 agree to within a few per cent, when calculated by Method Two, as discussed at the end of Part 5b, using the older interpretation of these bands. The new interpretation by Dieke would give a "calculated" D_0 just four times as large as the "observed" D_0. Moreover, the very striking similarity in the numerical values of the moment of inertia, for molecules of similar mass, and the relation between the values of the moment of inertia and of the vibration frequency, shown by Table 1 of Section 8, hold true only if half-integral values of m, rather than quarter-integers, are used for the N_2^+ and O_2 bands. The values of I_0 given in the table of Section 7 are based on such an assignment. On the other hand, consistency then demands that only half-integers be used for the helium bands. This procedure gives values of I_0 for helium just four times as large as those listed by Kratzer([111]) and by Curtis and Long([114]). The apparent objection to this change is that it immediately contradicts all the explanation of the missing lines, as just given for the various helium bands. However, as already noted in Part 5d, the rule $j=0$ for missing lines definitely fails in certain cases, and therefore one of the advantages of the use of quarter-quantum numbers disappears. On the other hand, by consistently adopting half-integral (i. e., not quarter-integral) values of the effective quantum number m, Mulliken (Proc. Nat. Acad. Sci. 12: 144, 1926, etc.) has given a new interpretation of various electronic bands, which yields uniformly satisfactory results. All of the values of I_0 and r_0 listed in Section 7 are based on half-integral, rather than on quarter-integral quantum numbers.

[146] Since the numerical values of the rotational energy terms $\left(\frac{m^2h}{8\pi^2I}\right)$ are known, halving the value of m necessarily divides the value of I by four.

Slater (Nature, 117: 555, April 1926), has just suggested a possible theoretical explanation of the alternating intensities found in symmetrical, or essentially symmetrical molecules, and the theory of this is discussed in Section 8. His explanation leads to the assumption that in a perfectly symmetrical molecule the alternate lines will be entirely missing, as seems to be true for O_2 and He_2, but that in a slightly non-symmetrical molecule, like N_2^+, the alternate lines are merely weaker. Only in an entirely non-symmetrical molecule, like HCl, would there be no weakening of alternate lines.

One theoretical aspect of this problem may be mentioned here. As discussed by Mecke([54]), and particularly by Mulliken([49]), the question of the electronic multiplicity in band spectra seems to be definitely related to the number of free valence (i. e., easily excited) electrons in a molecule, just as in the corresponding phenomena of line spectra and atoms. This is discussed in some detail in Section 8. But the phenomena described in the preceding pages are seemingly independent of the number of valence electrons. Hence the seat of the phenomena must be in the inner electronic configuration which presumably characterizes a symmetrical molecule, as contrasted to a non-symmetrical, or polar, molecule. This point has been mentioned by Mecke([117]).

The third, and most complex, type of spectrum due to a symmetrical molecule, is that illustrated by the secondary or many-lined spectrum of hydrogen. Since at the present time the analysis of this spectrum has not progressed to the stage where it casts any real light on the problems mentioned above, it may be considered separately. It is probable that this spectrum is a composite, and may have as its source any two or more of a number of possible molecular species, such as H_2, H_2^+, H_3, H_3^+, etc. A number of investigators are now working on the hydrogen spectrum, and many papers on the subject have appeared during the past few years; but as the conclusions of various investigators are very conflicting, even in regard to the most fundamental points, we shall merely summarize as briefly as possible the main points at issue, and discuss incidentally some of the possible reasons for the present situation.

The recognition of the secondary spectrum of hydrogen as a band spectrum is due initially to Fulcher([118]). It has now been established beyond question that this spectrum is due to the molecular form, and not the atomic. The most complete published measurements of the spectrum are given by Merton and Barratt([119]). These investigators publish, in addition to a list of about 750 lines between $\lambda 6540$ and $\lambda 3368$, also the behavior of each line under high and low pressure, condensed discharge, etc. Such information is an invaluable clue in unraveling

such a complex spectrum where in general it is possible to obtain many purely fortuitous numerical relations. This is especially true when the measurements are not of the highest accuracy. Merton and Barratt photographed this spectrum with a dispersion of only 10A per mm., giving possible errors of measurement of 0.01 to 0.02A. Gehrcke and Lau([120]), however, publish a photograph extending from λ6800 to λ3650, taken with a dispersion of 2A per mm., but they have apparently made no wave-length measurements. Such measurements are greatly needed. About 565 additional lines have been measured recently by Tanaka([128]).

Among the papers dealing with the series analysis of the spectrum we may mention in addition to those just quoted, articles by Allen([32]); Bury([120A]); Croze([121]); Curtis([34]); Dieke([30]), ([122]); Gehrcke and Lau([123]), ([124]); Kiuti([31]); Richardson and Tanaka([33]), ([125]); Takahashi([126]); Richardson([127]); Sandeman([129]); Nicholson([129A]); and Curtis([129B]). Much work has been done also on the specific heat of hydrogen at low temperatures, leading to an attempted evaluation of the molecular constants. Among the papers dealing with such an evaluation may be mentioned those by Kemble and Van Vleck([130]), by Tolman([131]), and by Dieke([131A]). Finally, the subject of an exact molecular model for hydrogen has naturally attracted much attention, since H_2 is the simplest of all molecules. Among the more recent papers on this topic are those by Allen([132]), Born([133]), Eucken([134]), Marshall([135]), Niessen([136]), Nordheim([136A]), Pauli([137]) and Urey([138]).

The secondary spectrum of hydrogen, so far as investigated, extends from about λ7700 to the extreme ultra-violet. That there is a close connection between this spectrum and the Balmer series is shown by a curve drawn by Glitscher and reproduced on p. 210 of Sommerfeld's "Atomic Structure" (English translation). This integrated intensity curve shows a number of maxima bearing a definite relation to the Balmer lines. This would indicate an analogous phenomenon to that shown by the doublet bands of helium. In that case, also, the line series law followed is rather similar to that of the actual helium line series, but the connection is not as close as in the case of hydrogen.

Fulcher([118]) found two groups of low-pressure lines, showing *no* Zeeman effect, one in the red and the other in the green, which obeyed a band spectrum law. That is, the red group could be arranged in seven parallel series of from six to four lines each, the lines of each series being separated by an almost constant wave-length interval. The green group is similarly composed of three series of four lines each. ($\Delta\lambda = 100$A for the red group, and 118A for the green.) These two groups are usually referred to as the first and second Fulcher bands, and the seven series are designated S_1, S_2, S_3, etc. Since all seven series run parallel, one

finds repeated sets of seven lines, with the same relative spacing within the set. Beginning at the red side, the first three lines, S_1, S_2, S_3, form an evident triplet, with spacing $\Delta\nu = 20$ and 14 approximately. Then after an interval of 60 frequency units, there occurs the quartette S_4 to S_7 with spacing $\Delta\nu = 5$, 7, and 37 approximately. S_3 is the strongest line of the seven, and the S_3 series has been extended to the red, four additional members, by Gehrcke and Lau([123]). These investigators also find a third "band" in the blue. The two Fulcher bands may be considered as related to H_α at $\lambda 6563$, according to Glitscher's curve. The third band has the same relation to H_β that the first has to H_α.

In addition to these three bands Richardson and Tanaka([33]) using only high pressure lines, have found *P*, *Q*, and *R* branches which have the proper intensity distribution and for which the usual combination principle holds. They have evaluated the *F'* and *F''* functions and calculate $I' = 0.624 \times 10^{-40}$, $I'' = 0.480 \times 10^{-40}$, $\nu_0 = 17{,}307$. In a later paper([125]), they give a number of sets of series, some of which they consider quite definite, others extremely doubtful. These series yield values of I varying between the values just given and that for the second Fulcher band, $I = 0.12 \times 10^{-40}$ (see ahead). They are actively at work on this problem at the present time and it is impossible to give the present status of the matter. Croze([121]) lists long series of lines, including those forming the Fulcher bands, but according to Dieke([30]) most of these additional lines represent only fortuitous regularities.

One may now take the seven series of the first Fulcher band to be a *P* branch of at least seven-fold multiplicity, while the series of the second Fulcher band (composed only of S_1, S_2, S_3) form a three-fold *R* branch. Kiuti([31]) believed he had found a singlet *Q* branch related to the strongest component (S_3) of the *P* and *R* branches just cited. But the relations are far from exact, as pointed out by Allen([32]) and Curtis([34]), and furthermore the lines of Kiuti's *Q* branch are strengthened at high pressure, instead of at low pressure. There seems to be little doubt that Kiuti's correlation is not justified.

If one assumes that the two Fulcher bands are indeed *P* and *R* branches, respectively (whether related or not), then it seems to the writer that the multiplicity must be ascribed to a multiple electronic level, as in the case of all bands with multiple "origins." Curtis, however, assumes that we have here a "sequence" of bands such as $1 \to 0$ $2 \to 1$, etc, each band composed of a singlet series. In regard to the actual relations holding for the series of the first band, Allen([32]) finds that by the use of half-integers for m, in the case of S_1 to S_3, and integers for the other four series, all seven series yield nearly the same values

of B' and B''. Curtis([34]) finds that by interchanging the whole and half-integers, the agreement is even better. From this analysis, Curtis obtains,[147] for the first band, $I'=0.179\times10^{-40}$, $I''=0.186\times10^{-40}$, and for the second band $I'=0.125\times10^{-40}$, $I''=0.129\times10^{-40}$. Because of the great difference between the constants for the two bands, they cannot be considered as forming the R and P branches of a single band. We are thus confronted with the peculiar situation of two or more bands each consisting of a *single* branch, and that of most *complex* character.

The multiplicity of each branch also has a structure of its own. Allen([32]) found that the S_1-S_3 triplet could be extended to the red into at least a quintette or sextette, and that these five or six lines themselves fitted a parabolic formula, thus giving what Allen called "vertical" series. Dieke([30]) independently found these new relations and suggested that these were the *true* series, the sextette being a true Q branch. Dieke found further that by using only S_4 and S_7, additional lines to the *violet* could be found which gave collectively an R branch, with the proper relation to his Q branch. On this interpretation, the former multiplicity becomes the true band structure, while the former succession of sets of seven lines becomes a succession of bands. The new interpretation gives a series of numerical relations agreeing in nearly all respects with that predicted by the Kratzer formulas, and from them Dieke calculates $I''=0.82\times10^{-40}$, a value over four times that of the previous interpretation. Dieke then interprets his series of bands as due to various vibration changes—the older interpretation of the line multiplicity. In this case, the greater spacing of Dieke's so-called successive bands makes the alternative suggestion of a multiple electronic level rather improbable.

In a second paper, Dieke([122]) presents a very strong argument in favor of his general interpretation of the series, as against the older interpretation. Goos([139]) and McLennan and Shrum([140]) had meanwhile made intensity measurements at varying temperatures. Dieke finds that according to his interpretation there occurs the expected redistribution of intensity with temperature among the rotational quantum states. With the older interpretation there is *no* redistribution. This latter fact really means, according to Dieke, that the redistribution of intensity among the *vibrational* quantum states with temperature is very small—in agreement with the facts for other band systems. *Important new information* concerning hydrogen is given in footnote 148a, and in note (j') of Section 7.

Meanwhile Gehrcke and Lau([120]), ([123]), ([124]), have obtained sets of lines which are placed like object and mirror image with respect to a

[147] Lenz([90]) made the first rough calculation of this quantity, obtaining 0.19×10^{-40}

given frequency. But in the last paper([124]) the sets thus presented constitute a complete rearrangement of those given in the earlier paper([123]), using many of the original lines, and many additional lines. Hence in both cases the relations may be fortuitous.

In all of the foregoing analysis, the numerical relations are not as exact as might be desired. The first Fulcher band gives the best regularities. It would appear that, aside from the previously noted actual experimental errors, there are many real irregularities, indicating possibly a rather loosely constructed molecule. One point in this connection may be of interest. Kemble and Van Vleck([130]), from specific heat data, have calculated the moment of inertia and vibration frequency of the hydrogen molecule in its stable condition. The values are admittedly only approximate, but nothing more is needed here. Now, as Kemble([141]) has noted,[148] with this data one can calculate immediately the amplitude of vibration, for any given number of quantum units of vibrational energy. The writer finds that this amplitude, in the case of molecules like N_2 is only six per cent of the original nuclear separation, for one unit of energy, the amplitude increasing of course as the square root of the energy, hence approximately as $\sqrt{n}$. But for hydrogen, the amplitude for a single unit is 34 per cent of the nuclear distance. Hence, unless the hydrogen molecule can withstand an unusually large deformation, it is no more likely to have over one unit of vibrational energy than is the nitrogen molecule to have over 30 to 35 units—much greater than the actually observed limit. Even iodine, with a maximum observed $n=59$, has essentially no greater per cent amplitude than has hydrogen with $n=1$. For this reason, the assumption of comparatively large values for n, as made by Curtis and Dieke in the case of the hydrogen spectrum, requires the possibility of a relatively large deformation of the molecule.

In conclusion it may be noted that none of the above spectrum lines are connected with the normal state of the hydrogen molecule, since cold hydrogen gas is entirely transparent to all of them. The work of Duffendack([142]), and others, on the voltage required to produce these secondary spectrum lines (about 13 volts) indicates that the fundamental band system lies in the extreme ultra-violet. Urey's([138]) interpretation of the ionization potential work of Olsen and Glöckler is also along this line.

A noteworthy addition to our knowledge of the hydrogen spectrum has just been made by Witmer([142A]). He finds on plates taken by Lyman, using a mixture of hydrogen (small proportion) and argon (large proportion), a series of twelve bands, running from λ1063 to λ1635. Each band is degraded to the red and the entire set forms definitely

[148] See also pp. 15-16 Buchwald "Korrespondenzprinzip."

a single Deslandres progression with $n'=$constant. Since the band of highest frequency coincides with the "resonance" lines of argon, it would appear that the excitation energy is limited to the corresponding voltage (11.6 volts), and the transitions are thus from this common initial level (which Witmer takes to be $n'=0$) to the various final vibrational levels. The resulting constants are $\omega^{0''}=4260$, $x''\omega^{0''}=112.5$ cm^{-1}. The observed $\omega^n : n$ curve runs almost to $\omega^n=0$, and shows in fact that the last observed band, corresponding to $n''=11$, is almost the last possible band of this progression. The area of the curve thus obtained is equivalent to 4.34 volts (100,100 calories) which according to the theory developed in Section 4, equals the heat of dissociation of hydrogen. This value agrees with the best chemical data now available.

Witmer further finds from these bands a value of ν_e corresponding to 11.61 volts. Then using the Glitscher diagram already mentioned, he obtains a series of electronic levels given by a Rydberg formula, with a limiting value of 15.2 volts. This should correspond to the ionization potential of the molecule, and although uncertain to several tenths of a volt, is probably more reliable than the direct measurements. The original paper should be consulted for further details.[148a]

[148a] *Note added in proof.* Rapid progress in the analysis of the hydrogen spectrum has continued since Part 5e was written. Hopfield and Dieke (Nature, 118: 592, 1926) have for the first time obtained the absorption spectrum of the hydrogen molecule. With this and with much new material on the emission spectrum, Dieke and Hopfield (Z. Physik, 40: 299, 1926) have been able to analyze almost completely the ultra-violet spectrum of hydrogen. Three electronic levels, which may be called *X*, *A*, and *B*, are evaluated. *A* lies 11.1 volts (90,083 cm^{-1}) above *X*, and *B* lies 12.2 volts (99,039 cm^{-1}) above *X*. The vibrational constants are

	X	*A*	*B*
ω^0	4248	1337	2377
$\omega^0 x$	114.5	18	67

where the data run from $n=0$ to $n=11$, 10, and 5, for levels *X*, *A*, and *B*, respectively. (Dieke and Hopfield adopt the new quantum mechanics, and their published values of ω^0 and of ν_e therefore correspond to $n=-0.5$ in the notation used here and elsewhere in this report.)

Witmer's initial level turns out to be $n'=3$ of state *A*, but the absorption spectrum proves that his n numbering of the final states is correct and that the heat of dissociation is thus definitely 4.3 to 4.4 volts. Continuous absorption begins at 14.53 volts (λ849.4) and this gives 4.38 volts for the heat of dissociation, assuming that the products of dissociation are in this case one normal and one 10.15 volt excited hydrogen atom. (See Section 8 ahead for details concerning such a process.) Within limits of error this voltage (14.53) is the point of confluence of the vibrational energy levels of state *A* and also of state *B*. Dieke and Hopfield therefore conclude that the radiating electron moves in a 2_1 path in state *A*, in a 2_2 path in state *B*, and in a 1_1 path in the normal state *X*. Witmer,

SECTION 6. THE INTENSITY DISTRIBUTION AND ITS VARIATION WITH TEMPERATURE

As mentioned in Part 2e, the relative intensity of the various lines of a band varies with temperature, and if the conditions are such as to give approximate temperature equilibrium, the distribution of intensity may be predicted. On the basis of the classical theory, the intensity with which a certain frequency is emitted is given by the amplitude of the corresponding term in the Fourier development of the motion, and by the number of molecules which are capable of emitting the frequency in question. According to the quantum theory, the intensity, in the case of emission, is given by the number of molecules in the initial state and the probability of the transition (A'') from this state to the final state. The relative number of molecules (N_m) with an energy E_m is given by the Maxwell-Boltzmann distribution function

$$N_m = p_m e^{-\frac{E_m}{kT}}, \tag{178}$$

where p_m is the probability *a priori* of the particular state. (Compare equation (81) and discussion.) For large quantum numbers, the transition probabilities (A'') can be calculated by means of Bohr's correspondence principle from the coefficients of the Fourier development of the motion. For small quantum numbers, the correspondence principle applied in its usual form can give us only approximate values for the intensities.

Kemble([93]) was the first investigator to calculate the relative intensities of the lines of one band, and he found that good agreement with the observations could be obtained by the use of whole rotational quantum numbers. If, however, as the development of the theory has made necessary, half-integral quantum numbers were used, his results were in sharp disagreement with the observations.[140] The formula postulates an intensity distribution non-symmetrical with respect to the missing line, while the observed distribution is strictly symmetrical for small values of m, as

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in a very recent article (Phys. Rev., N. S., 28: 1223, Dec. 1926) accepts this interpretation, and recalculates the ionization potential as 15.86 volts, a value agreeing more nearly with the most probable experimental value of 16.2 volts (Kwei, Phys. Rev. N. S., 26: 537 (1925)). See also note (j') of Section 7.

The hydrogen bands seem to consist of Q branches only. It is therefore not possible to calculate the moment of inertia, but only its change during the radiation process. The rule that the moment of inertia increases when the frequency of vibration decreases is here obeyed (contradicting preliminary work which seemed to indicate a violation of the rule). As yet it has been impossible to correlate these ultra-violet bands with the Fulcher bands.

[140] See Kemble([143]).

noted in connection with equation (103). The relative intensities of the lines of *one* branch also do not agree with the observations.

In two recent papers Kemble([144]), ([145]), gets a much better agreement between the theoretical formulas and the observed intensities by removing the degeneration of the motion by means of an external magnetic field. He then applies the correspondence principle to each non-degenerate motion and adds the intensities of the Zeeman components in order to obtain the intensity of each band line. He thus finds, for emission,

$$\text{Intensity} = \text{const. } \bar{p}_m e^{-\frac{E'}{kT}}, \tag{179}$$

where $\bar{p}_m$ is the average *a priori* probability of the initial and final states. This procedure is a great improvement; the only uncertainty arises from the fact that there is very little known experimentally about the behavior of molecules in a magnetic field. As already mentioned, it must be kept in mind that the nature of the correspondence principle enables one to obtain only approximate values of the intensities for small quantum numbers. By Kemble's method of calculation, the approximation is, however, much closer than when the correspondence principle is applied directly to the degenerate system. The results which Fermi([146]) obtained by analogous calculations in the case of multiplet lines clearly illustrate this. He showed that a much better approximation to the true intensity results if one calculates first the Zeeman components and then adds them; but that even then the correspondence principle is inadequate to give the exact values for small quantum numbers.

There has, however, been suggested recently a new method of obtaining the exact intensities, which is based on a more general application of the correspondence principle, and which, as was shown by Heisenberg([147]) leads to the summation rules found experimentally by Burger and Dorgelo([148]). If, for instance, we bring a radiating atom into a magnetic field, the motion of its electrons is only slightly changed by the induced Larmor precession. This indicates, on the basis of the classical theory, that the total intensity which is emitted by the atom in that particular state is practically independent of the strength of the magnetic field and of the angle between the magnetic axis of the atom and the field—the two factors which determine the magnitude of the Larmor precession. Heisenberg now assumes, as suggested by the correspondence principle, that for quantum radiation also, the sum of the intensities of the lines which come from a certain magnetic quantum level is independent of the amount of the Larmor precession, i. e., of the strength of the field, and of the angle between the magnetic axis and the field, as specified by the magnetic quantum number r.

Now the emission of the lines of a given band presents an analogous case. The motion of the electrons is in general only slightly changed by the rotation of the nuclei and this indicates that the sum of the transition probabilities of the lines issuing from a certain level should be independent of the rotational quantum number; i. e., that the summation rules of Burger and Dorgelo are valid also for band spectra.[150] In the case of bands with only a positive and a negative branch, one can derive the exact formulas for the intensities of the band lines. This was shown independently by Fowler([26]) and by Dieke([27]). Thus, if u_j and w_j are the factors in the intensity formulas for the lines $j \to j+1$ and $j+1 \to j$ which are independent of temperature, and if p_j is the *a priori* probability of state j, then an application of the summation rules yields the equations

$$\left.\begin{aligned} u_1 &= p_1 = w_1, \\ w_1 + u_2 &= p_2 = u_1 + w_2 \end{aligned}\right\} \tag{180}$$

These equations are sufficient to calculate the u_j and w_j. The result is, if one assumes that $p_j = 2j-1$,

$$u_j = w_j = 2j, \tag{181}$$

so that the intensities of the lines $j \to j+1$ and $j+1 \to j$ are given by

$$I_{j \to j+1} = 2j \cdot e^{-\frac{E'_m}{kT}} \quad \text{and} \quad I_{j+1 \to j} = 2j \cdot e^{-\frac{E'_{m+1}}{kT}}. \tag{182}$$

If the *a priori* probabilities were chosen differently, we should find that the intensities of all the lines of one branch do not lie on a smooth curve, but that all even-numbered lines, for example, are a little weaker than should be expected from the intensities of the odd-numbered lines. The intensity distribution is, for small values of m, symmetrical with respect to the missing line, in agreement with the observations.[151] The presence of the Boltzmann factor causes the P branch in emission to be a little stronger than the R branch, as is actually observed in the CN, CuH, and N_2^+ bands. For absorption, the R branch should be the stronger one. In this respect, equation (182) differs from equation (103) and seems to be more accurate than (103).

[150] These rules may thus be expected to hold only for small values of m, such that the electronic motion in the molecule is not appreciably changed by the nuclear rotation.

[151] Equations (182) and (179) become identical, if the *a priori* probability p_j of state j is taken equal to $2j-1$. For the common case $m = j - 0.5$, both equations become $I = 2\overline{m} \cdot e^{-\frac{E'_m}{kT}}$, in essential agreement with the empirical equation (103).

If a Q branch is present also, the intensities are not determined by the summation rules alone, but special assumptions as to the model of the molecule must be made.[153]

Dieke considered also the case of bands with a fine structure. If Kratzer's explanation is accepted, we find that in the case for instance of the CN doublets the factor $2j$ in (182) must be replaced by $2j-1$. There should be, therefore, a difference in the intensity distribution of bands with single lines and with (unresolved) doublets. If the same intensity distribution occurs in both classes of bands, as seems now to be the case, this can be regarded as evidence that Kratzer's explanation of the fine structure (as due to "false" doublets) must be modified. On the other hand, from the derivation of the above intensity formulas, it follows immediately that the unresolved doublets in the vicinity of the missing line must have normal intensity, even though one component is missing. Hence the objection to Kratzer's theory, based on this point, as given in Part 5c, is no longer valid. This was noted, at the time, and was mentioned again in Part 5e.

Kemble, in a recent paper([149]), has objected to the application of the summation rule to band intensities because of an apparent conflict with the correspondence principle. The objection was based on Fowler's conclusion that according to the summation rule the P and R branches must have equal intensities even when there is a Q branch. Hönl and London([148A]), however, have shown that this conclusion is incorrect and that in the case of bands with a Q branch the summation rule may yield differing intensities for the P and R branches in accord with the correspondence principle.[153] Kemble has therefore withdrawn his objection.

The relative intensity of the various branches of an electronic band, as predicted by the correspondence principle, is briefly as follows. The R and P branches are to be correlated with circular Fourier components of the electronic motion[154] in the invariable plane, one rotating in the same sense as the nuclei (R branch), and the other in the opposite sense (P branch). The Q branch, on the other hand, is to be associated with a linear Fourier component vibrating perpendicular to the invariable plane (i. e., parallel to the j axis). These three components have the same frequency when observed with reference to a system of coordinates rotating with the nuclei and unite in the most general case to form an

[153] See Fowler([26]) and Hönl and London([148A]).

[153] Recent work by Mulliken (forthcoming paper in the Physical Review) shows that there is much experimental evidence for the Hönl-London summation rule formulas.

[154] Strictly speaking, these Fourier components are "combination tones" containing the nuclear vibrational frequency as well as the electronic frequency.

elliptical orbit in that coordinate system. (This statement follows from the relationship between the principle of selection, $\Delta j = 0$, or ± 1, and the harmonic analysis of the motion.) It is thus evident that in general the two circular components correlated with the R and P branches will be of unequal amplitude, and hence these two branches will be of unequal intensity.

In fact, if the two circular components are of equal amplitude, they will unite to form a rectilinear motion in the invariable plane, from which we conclude that the Fourier component of the resultant electronic motion correlated with the band system in question represents a rectilinear motion. But this seems actually to be the situation in the case of many of the most familiar band systems, such as the violet CN bands, the first negative group of carbon, the first negative group of nitrogen, etc. In all these cases we now believe (see Section 8 ahead) that the electronic transition is similar to that denoted as an S to S transition, in the case of atoms. Such a transition, for which $\Delta k = 0$, is to be correlated with a linear Fourier component perpendicular to the plane of the electronic precession. Hence the component of such a motion in the invariable plane is likewise linear, and breaks up into two equal circular components, as just noted. The essential equality of the P and R branches of these well-known band systems is thus in entire accord with the correspondence principle.[155]

The whole question of intensity distribution is now put in a new light by the recently developed quantum mechanics of Heisenberg and Born, and the related "wave mechanics" of Schrödinger. These new theories allow unique calculations of intensity in the cases to which they have been applied, in contrast to the older rules, which do not yield unique solutions.

Without attempting any further analysis of this theoretical work, we shall turn to the experimental material, confining our attention to bands with one missing line. For such bands $\overline{m}$ in equation (103) equals the empirical parameter M and also equals j as used in equation (182). All of the micro-photometric curves thus far published seem to show that equation (103) is experimentally true, for *very* small values of M. We shall merely assume that it is true for at least moderately small values of M (including $M_{max.}$) It is the equation derived by Kemble([93]) from classical theory, and is also, by chance, the quantum formula resulting from the older interpretation of the CN band lines (integral values of m). As such it was used in 1922 by Birge([89]), in a comparison of theory and experiment.

[155] This is discussed by Mulliken in the paper cited in footnote (153) and had been deduced independently by the writer.

The violet CN bands have been obtained in emission, in active nitrogen, by Strutt and Fowler([88]), in the furnace in emission at 2300°, 2500° and 2700° C., and in absorption at 2900° C., by King([150]), in the arc in emission, with varying current and voltage, and in the sun's reversing layer, in absorption. Birge found that the line of maximum intensity, in the R branch, corresponded to $M=8$, in active nitrogen, to $M=23$, in the 2500° and 2700° furnace, to $M=28$ in a 4 ampere arc, and $M=30$ in a 13 ampere arc. Now with $\bar{m}$ replaced by M, equations (81) and (103) give

$$I=cMe^{-\frac{M^2h^2}{8\pi^2IkT}} \tag{183}$$

where there is considered only the rotational energy, and that in the very simple form of equation (18). From (183) there results, by differentiation,

$$M_{max.}=\frac{2\pi}{h}\sqrt{kIT}. \tag{184}$$

From the definition of B_0, in equation (38), and the known values of k and h, one obtains, for the 0, 0 band

$$T=2.862B_0M^2_{max.}. \tag{185}$$

Obviously these equations can be only approximately true, since the moment of inertia I is assumed constant, regardless of the amount of rotational energy. The error thus introduced is, however, in the case of equation (184) or (185), probably less than the present experimental error in the determination of $M_{max.}$ (one to two units). It is therefore of interest to note that the value of $M_{max.}$ found by Birge gives 70° C. for the temperature of active nitrogen, while conversely the known furnace temperatures give 22.9 and 23.7 for the predicted values of $M_{max.}$ Equation (184) thus appears in this case to be experimentally correct, within the rather wide limits of experimental error. Assuming its correctness, one obtains for the arc under the current conditions mentioned, 3900° C. and 4500° C. respectively, and for the sun, 4000° C. (about 1000° below the usual estimates). In this latter case, however, a direct observation of $M_{max.}$ is not possible, and the result quoted is based on the fact that, at various observable values of M, the relative intensity of this band in the sun is the same as that in the 4 ampere arc. Birge found, however, that equation (183) predicted intensities several times as large as observed, for very *large* values of M, in the case of the 13 ampere arc. Hence the deduced solar temperature may be considerably in error.

Other experimental results are summarized by Fowler([26]), all based on published micro-photometric curves of spectrum plates. It is probable that the values of $M_{max.}$ from this type of data, are reasonably accurate, but little can be concluded as to the exact form of the intensity distribution, in view of the uncertainty as to the properties of the photographic plate. Using equation (184), one obtains temperatures of 2000° C. and up, for various metal arcs, for *emission* spectra. It may be of interest to note that the distribution of intensity in the λ3371 N_2 band, as obtained by E. P. Lewis([151]), with self-induction, corresponds to about 8000° C.!

In the above discussion we have *assumed* a statistical (thermal) distribution of rotational energy, and any deviation from such a condition will cause more or less error in the temperatures deduced. Yet it would appear that even in the case of emission, the distribution in many instances at least approximates a thermal distribution, so far as the rotational energy is concerned.

In the matter of vibrational energy, as dependent on temperature, only the following brief statement is given. This effect concerns the relative intensity of entire bands. The writer([29]) has stated that the relative intensity of the bands of the zero sequence (0−0, 1−1, etc.) of CN, is practically unaffected by temperature. The temperature effect is theoretically rather small, but from later work it would appear that it is present.

Thus one may find two closely adjacent lines (each a doublet), one belonging to the 0−0, and the other to the 1−1 band, which have equal intensity in the solar spectrum (assumed 4000° C.) but unequal intensity in King's absorption furnace spectrum (roughly 2900° C.). For such a case there can be little dispute as to the correct theoretical expression, for we are concerned here only with the *form* of the exponent, in equation (81). By using the zero sequence, it is immaterial whether we use the initial (n') or the final (n'') vibrational quantum number, in the expression for vibrational energy ($nh\omega^0$ by equation (17)). On the other hand, for moderately large values of M, it is impossible to distinguish from intensity measurements between m', m'', or $\bar{m}(=M)$. in the expression for rotational energy. Under these limitations, the expression for the *relative* intensity (R) of two lines ($M_1 n_1$) and ($M_2 n_2$), as a function of temperature, is

$$R = Ae^{-\frac{h}{kT}\left\{\frac{h}{8\pi^2 I}(M_1^2 - M_2^2) + (n_1 - n_2)\omega^0\right\}}. \qquad (186)$$

The two closely adjacent lines tested were $M_1 = +58$, $n_1 = 1$, $M_2 = +73$, $n_2 = 0$, in the λ3883 CN "sequence." With $R = 1$ for the sun, it is

theoretically 1.21 for the 2900° furnace, and this agrees with the observations, as nearly as can be judged. But if the vibrational energy term were neglected, R should be 1.53; and this is certainly in disagreement with the observations. Hence a thermal vibrational energy effect is at least present. But as stated earlier in this chapter, the major cause, or causes, in the matter of the distribution of vibrational energy in electronic bands, is certainly not temperature, in the case at least of *emission* spectra.

SECTION 7. TABLE OF CONSTANTS

General Notes

This table of molecular constants, chiefly for electronic band systems of diatomic molecules, is reasonably complete, up to the date of compilation (March 1926, with revisions up to November 1926), but does not claim to be entirely so. A very few values for vibration-rotation bands, and of triatomic molecules have been added for sake of comparison. In many cases, the constants here listed are merely those previously published by other investigators. In other cases, however, they have been computed by the writer directly from the original data, and in practically all cases an attempt has been made to verify in a general way the correctness of the analysis and of the numerical values here given.

The first column gives the usual name of the system, the second, the probable carrier. This latter is rather definitely known in the great majority of cases. The third column gives the direction of degradation of the bands composing the system. In all cases, as previously noted, bands degraded to the red have $\omega^{0\prime} < \omega^{0\prime\prime}$ (and necessarily $I'_0 > I''_0$) and *vice versa* for those degraded to the violet.

The fourth column gives the origin of the system ν_e, in terms of the wave number in vacuum. If the wave number of the true origin of the $0-0$ band is known, it is followed by (O). Otherwise the wave number of the head is given, followed by (H). In the case of certain isolated bands, the $n'n''$ values are unknown. In the case of the helium line series bands, each band is the sole representative of a system, and should be listed separately. Only the least refrangible band of each series is, however, given. See footnote (t).

The fifth and seventh columns give $\omega^{0\prime}$ and $\omega^{0\prime\prime}$, the frequency of vibration (in terms of wave numbers) for infinitesimal amplitude for the higher and lower energy condition respectively. These two, of course, become identical for near infra-red bands, ν_e becoming zero. When only two bands of a progression are known, the single resulting value of ω^n is given in parenthesis. Similarly, columns six and eight give $\omega^{0\prime}x'$ and

$\omega^{0''}x''$, the negative of the coefficients of n'^2 and n''^2, in equation (73). Twice these quantities, by equations (79) and (80) gives the negative of the rate of change of frequency of vibration with n. When these equations are not linear, the direction of deviation from linearity is indicated by $-$ or $+$ in these same two columns. Thus the usual deviation is an increasing rate of variation of ω^n with n, and is represented by the negative sign.

Column nine gives the reference to articles, and also to the special notes accompanying the table. If one investigator only has worked out the quantum analysis, that reference alone is given, since it usually contains references to all necessary previous work. Where there are seemingly conflicting results or conclusions, all the references are given, with a notation as to the values here adopted.

Columns ten and eleven, when multiplied by 10^{-40}, give the moment of inertia in *gram* · cm^2, for the band whose origin is given in column four. These values are obtained from B'_0 and B''_0 by equation (134), and in practically all cases the B's have been obtained from the data by application of the combination principle—equations (96) to (99). Columns twelve and thirteen, when multiplied by 10^{-8}, give the resulting values of the nuclear separation in *cm.*, with the carrier assumed in column two, using

$$r_0 = \sqrt{\frac{I_0}{\mu}} \tag{187}$$

where $\mu = 1.650 \times 10^{-24} \frac{m_1 m_2}{m_1 + m_2}$, and m_1 and m_2 are the atomic weights of the two atoms. 1.650×10^{-24} grams is the mass of a hypothetical atom of unit atomic weight.

Column fourteen gives the references and notes applying to columns (10) to (13).

Special Notes

(A) See note added in proof, at end of Section 8.

(a) Hulthén and Zumstein, in a recent article on "The Absorption Spectra of Some Hydride Compounds in the Ultra-Violet" ([151A]), have for the first time obtained in absorption the AgH, AlH, AuH, and CuH bands. Their work proves that these bands are due to the hydride, as hitherto assumed on internal evidence (size of moment of inertia, etc.). It also verifies the $n'n''$ assignments hitherto assumed for CuH and AlH, and for the first time makes possible definite $n'n''$ assignments for AgH and AuH. In the case of AgH the values of ω' and ω'' are calculated by the writer from their published data, and are relatively inaccurate. The

values of I'_0 and I''_0 are calculated by the writer directly from the data of Bengtsson and Svensson([152]), for the λ3330 (0, 0) band, and differ somewhat from the values of B' and B'' given by these investigators. The new absorption data by Hulthén and Zumstein are somewhat less accurate.

(b) Calculated directly from Erickson and Hulthén's([153]) published data. See also note (a).

(b*) As noted in Part 5c, and at the end of Part 5b, this system consists of doublets of the violet CN type, due, however, to a double level in the *final* state. The rotational energy functions for the (0, 0) band are given, according to Pomeroy([97A]), by

$$F' = 0.6019m^2 - 1.1630 \times 10^{-6}m^4 + 0.44 \times 10^{-12}m^6,$$

where $m = k - 0.0074$,

$$F''^{\pm} = (0.6386 \pm 6.0 \times 10^{-6})m^2 - (1.1094 \times 10^{-6} \pm 3.1 \times 10^{-11})m^4 - 0.53 \times 10^{-12}m^6 - 5.2 \times 10^{-18}m^8,$$

where $m = k - 0.01 \pm 0.00482$.

(c) $\omega^{0'}$ and $\omega^{0'}x'$ calculated by the writer from new data by Hulthén and Zumstein. [See note (a).] Also, all values of I_0 and r_0, using the λ3652 (0, 0) band. Values of $\omega^{0''}$ and $\omega^{0''}x''$ from Bengtsson([154]).

(d) For the three BO band systems, Mulliken([47]) presents definite evidence in favor of half-integral values of the *vibrational* quantum number n, and this interpretation has been adopted here. Thus in the case of *all other* band systems listed in this table, the origin of the so-called 0−0 band *coincides* with the origin of the system (ν_e). But for the BO systems, the corresponding band is designated $\frac{1}{2}-\frac{1}{2}$, and its origin is accordingly obtained by substituting $n' = \frac{1}{2}$, $n'' = \frac{1}{2}$, in equation (73) of this chapter, i. e., in equations (8), (9), and (10) of Mulliken([47]). These latter equations are not entirely correct, as Dr. Mulliken has kindly pointed out to the writer. Thus the a bands have double-double heads, and Mulliken originally assumed that these represented four R branch heads. Equation (8) of Mulliken([47]) was obtained from equation (1) not only by shifting the value of n' and n'' by 0.5, but also by shifting from the observed R head to a calculated position of the assumed origin. It is, however, probable that these four heads represent two R branch heads, and two Q branch heads, just as in the case of the comet-tail bands. The second and fourth heads of Mulliken's equation (1) thus represent very closely the origin of the $\frac{1}{2}-\frac{1}{2}$ band, and need only the shift to 0−0 to give the true double origin of the system. The resulting revised constants, as given in the table, indicate that the two observed heads of the "combination" bands are actually Q branch heads, as originally assumed by Mulliken.

When half-integers are assumed for n, the true origins of the various BO systems are practically identical for the two isotopes, and arithmetic means are used in the table, the values of ν_e for the combination bands being calculated from the ν_e of the α and β bands. On the other hand, the actual origins of the $\frac{1}{2}-\frac{1}{2}$ bands are definitely different for the two isotopes, and this fact constitutes the strong evidence in favor of Mulliken's interpretation. It may be noted, finally, that the numerical relations of ν_e and ω^0 to the observed frequencies, given here for the BO bands, are probably those required by the new quantum mechanics. (See end of Section 8.)

(d*) The quoted values of I_0 and r_0 are more recent, and slightly more accurate, than those given in reference ([98]). C_2 is assumed as the carrier, but there is no certainty on this point, as yet.

(e) Origin assumed as second and fourth heads, in analogy with comet-tail bands, but uncertain whether the band quoted is the $0-0$ band.

(e*) Values of $\omega^{0\prime}$ and $\omega^{0\prime\prime}$ calculated by equation (142) from Kratzer's([53]) values of B_0 and D_0. $\omega_{12}{}^{0\prime\prime}=2797$, $\omega_{34}{}^{0\prime\prime}=2815$.

(f) New data and calculations giving $2B'=3.9180$, $2B''=3.7824$ [see Birge([96])]. Kratzer([43]) gives $2B'=3.918$, $2B''=3.783$.

(g) The vibration frequency for the stable state of CO is known both from the fourth positive group of carbon (electronic), and from the infra-red bands at 4.67μ, 2.35μ and 1.573μ. The results agree well within limits of error, the positions of the infra-red bands, as *calculated* from the data on the *electronic* bands being 4.679μ, 2.354μ and 1.578μ.

The moment of inertia for the stable state is known only from the infra-red bands (14.9×10^{-40}), but from the usual relations between I_0 and ω^0, it is to be expected that the initial state of the Angstrom CO bands ($\omega^0=2158$, $I_0=14.3$) and the final state of the fourth group ($\omega^0=2150$) will give about the same value of I_0, thus roughly checking the infra-red value.

The value of I''_0 for the Angstrom bands is from $B''_0=1.600$, extrapolated from Hulthén's([44]) observed values, $B''_3=1.529$, $B''_2=1.551$, and $B''_1=1.576$; the last value having been calculated by the writer from Hulthén's published data for $\lambda4835$. Recent measurements by Jassé([162A]) are in agreement with these conclusions.

The constants quoted for the initial state of the fourth positive group and for the final state of the Angstrom CO bands are calculated from the data for the former system, reference ([72]), since the data for the final state of the Angstrom bands—references ([159]), ([44]), and especially ([160])—are less accurate, although agreeing with that for the fourth group within limits of error. All of the CO constants given in the table agree

with reference([72]) (Phys. Rev.) and occasionally differ in minor respects from those shown in Figure 26 (ahead).

(h) Assuming Mulliken's([49]) values of $B'_0=1.80$, and $B''_0=1.97$, to be correct.

(i) Cameron([162B]) has obtained this new band system. Each band has five heads, the most refrangible of which is given in the table, with the spacing 37.8, 18.3, 17.2, and 29.8 cm^{-1}. Johnson([162C]) has noted that this system has as its initial level, the final level of the third positive group of carbon. This latter system also consists of bands with five heads of the same spacing as the Cameron bands. Johnson found, also, that it was possible to assume an extrapolation of the Cameron bands such that their final state is well within limits of error the same as the final state of the fourth positive group, as analyzed by Birge([72]). This relation is undoubtedly correct, and although the expected $n''=0$ sequence ($\lambda\lambda$2060.4, 1990.2, 1925.3, 1866.1, etc.) does not appear on Leifson's absorption spectrum of CO, it has very recently been found by J. J. Hopfield in absorption in cold CO. For a critical discussion of all these relations, see Birge([72]) (Phys. Rev.).

(i*) Wolter's data([75]) are used for the n'' progression, and the values of $\omega^{0''}$ and $\omega^{0''}x''$ are accurate and trustworthy. The n' progression (curve 11 of Figure 12) is from Deslandres' data([76]) and is entirely spurious, according to Wolter. A reproduction of one of these bands is given by Wolter and on p. 254 of Konen([3]).

(j) These data, except ν_e, are taken directly from the two preceding systems.

(k) $\omega^{0''}$ calculated from known value of Dm^4 term. See equation (142) and Birge([96]).

(l) Calculated from data of Kratzer([43]), using Hulthén's([163]) interpretation.

(m) Recalculation of Frerichs'([25]) data.

(n) New calculation of Frerichs' data, giving $B'_0=6.7603$, $B''_0=7.8153$ as discussed near end of Part 5b (page 175).

(o) Mulliken([83]) gives also the equations and measurements of the corresponding $Cu^{65}I$ bands. All five systems have a common final state, within limits of error.

(p) ω from specific heat data, and therefore extremely uncertain. Values of ν_e and of I_0 are in accord with Curtis'([34]) interpretation which, as discussed in Part 5e, is very uncertain. Dieke's([122]) interpretation gives I_0 about four times as large, and *is* the correct interpretation, according to the very recent work reported in note (j').

(q) See discussion in Part 5e.

(r) New calculations, assuming half-integers for m.

(s) Kratzer([111]) concludes that the λ6400 and λ4546 bands (degraded to the red) belong to the same system, with n' differing by two units; and that λ5730 (degraded to the violet) has the same final state as the others, but belongs to a different system. The data for the two "line series" bands indicate, however, that only the non-vibrational state of the helium molecule can exist; and Mulliken([185]) has, on the basis of new developments, now re-interpreted all of these bands. This is discussed in Section 8. The values of I_0 and r_0 here listed are obtained by multiplying by four the values given in references ([35]) and ([111]). This is in keeping with the new interpretation of the bands of symmetrical molecules, first suggested by Mecke, and now adopted by Mulliken and by the writer, as already discussed in Part 5e.

(t) Each band of the series is the sole representative of a "system" of bands. The entire main series is given by the line series formula

$$\nu_0 = 34{,}301.82 - \frac{109{,}678.3}{(m + 0.928075 - 0.000449/m)^2},$$

where $m = 2$ to 8 inclusive. The second series is given by

$$\nu_0 = 31{,}958.14 - \frac{109{,}678.3}{(m + 0.964366)^2},$$

where $m = 2$ to 5 inclusive. Mulliken's interpretation of these bands is given in Section 8.

(u) Hulthén's([101]) data give 1203.7, 965.6, and 632.4 for the ω'' values of the final state, an unusually rapid variation with n, indicating a very unstable molecule.

(v) Calculated from Hulthén's([101]) data. The two sets of HgH bands form an electronic doublet, just as in the case of CdH and ZnH. See Hulthén([163]).

(w) The values quoted are recalculated from the data of Mecke([12]) and Wood([87]), with $n'' = n_e - 4$ and $n' = n_a$, in accordance with the recent work of Loomis, as mentioned in Section 4. The initial state, as there noted, requires a complex function for its proper representation. The values of I'_0 and I''_0 are based on Loomis' data for B'_{29} and B''_0, as given in equation (43) of Chapter VI, ahead, and on the recent calculations by Loomis (Phys. Rev., N. S., 29: 112, 1927).

(x) Values of I_0 as given by Smith([166]) and of resulting r_0 calculated by the writer, using the apparent 0−0 band. As the combination principle was not used in obtaining I_0, its value is uncertain.

(y) Calculations by the writer on the basis of the Hulthén and Johansson([17]) series assignments, giving $2B'_0=3.634$, $a'_0=+0.0451$, $2B''_0=3.262$, $a''_0=+0.0564$, as discussed on pages 119 and 173.

(z) These bands seem to have at least five heads. That quoted is the least refrangible.

(a') The recent data of Merton and Pilley([168]) show definitely that the initial state corresponds to a curved $\omega^n : n$ graph, as shown in 16 of Figure 12. The constants quoted are from these data (for the heads), except in the case of ν_c, where Fassbender's([77]) value is used.

(b') New calculation of Fassbender's([77]) data, giving $2B''_0=3.844$, $2B'_0=4.148$. See Birge([96]). If Dieke's interpretation were adopted, B_0 would be four times as large, as discussed in Part 5e.

(c') Second and fourth heads assumed as origins, in analogy to comet-tail bands. Values of $\omega^{0'}$ and $\omega^{0'}x'$ not identical with the final state of the ultra-violet N_2 bands, as explained in note at end of Section 8.

(d') Final state same as for γ bands and constants from averages of β and γ bands, as discussed in Section 4 (see Figure 15). ν_c calculated on this basis. Sponer and Hopfield([182]) have found $n''=0$, $n'=2$ to 5 on Leifson's([169]) absorption spectrum of NO, thus proving the correctness of these assumptions.

(e') Füchtbauer and Holm([172]), by using varying temperature brought out successive n' progressions, and thus established the chief relations for these Schumann absorption bands. The intensity distribution is similar to that for the iodine bands, making the n' numbering uncertain. Mulliken (unpublished work) has now found that the Runge([80]) emission bands of oxygen are a portion of this same system, those actually measured by Runge corresponding to $n'=0$, $n''=11$ to 17. Bands corresponding to lower values of n'' are on Runge's plates, but have not been measured. From this new relation it appears that the n' numbering of Füchtbauer and Holm([172]) should be raised by two units. Hopfield and Leifson([173]), ([169]), have measured in absorption bands which the writer has identified as corresponding to $n''=0$, $n'=9$ to 18. The resulting $\omega^n : n$ curve for the excited state (curve 20 of Figure 12) is thus known from $\omega=708$ at $n'=0$, to $\omega=94$ at $n'=17.5$. The curve has a point of inflection, and is precisely like the curve for the excited state of the iodine bands. The constants quoted give as usual only the first two terms of the required power series equation. The evaluation of the heat of dissociation of oxygen from this curve is discussed in Section 8.

(f') Values of I_0 in accordance with Mecke([9]), as discussed in Part 5e. The only alternative possibility (quarter-integers for m) would give I_0 one-fourth as large. Actual values of I_0 are due to Mulliken (see

note e'). The agreement of I''_0 for the Runge bands, on Mulliken's interpretation, with that for the atmospheric bands, is a proof of the correctness of this interpretation. Thus the Schumann bands and the atmospheric bands, since both appear in absorption in cold oxygen, must have as a common lower level the normal state of the molecule, and now the Runge bands evidently have this same common final state, as far as the moment of inertia is concerned, while their derived vibration frequencies prove that they are a portion of the Schumann band system.

(g') This system, as noted in Section 4, has the characteristic intensity distribution for a large change of moment of inertia (which may be predicted because of the large change from $\omega^{0\prime}$ to $\omega^{0\prime\prime}$). Both Mecke([9]) and Birge([68]), omit the λ3727 band of Johnson([79]), in giving the quantum interpretation, since this band seems to be of a different character and is 3A out of position. Mecke omits also the λ2318 band, and thus obtains $\omega^{0\prime\prime}=1826.8$. But recent work by Ellsworth and Hopfield([173A]) shows the presence not only of this band, but of a number of others of this same $n''=0$ progression. Moreover, there are additional bands to the violet, too faint to measure, so that the true value of $\omega^{0\prime\prime}$ as well as of ν_e is in all probability larger than that listed. See footnote (173) of Section 8, and Birge and Sponer([187]).

(h') Origin probably double.

(i') Calculated from the analysis of Dieke([105]) and Birge([106]), using Watson's([45]) data.

(j') (*Note added in page proof.*) A very important paper by Richardson has just appeared (Proc. Roy. Soc., 113A: 368 (1926). Richardson obtains an almost complete theoretical analysis of parts of the secondary spectrum of hydrogen. He finds that the Fulcher bands each form a sequence of bands, the true band series being the "vertical series" of Allen and Dieke. *Accurate* values for the frequencies of vibration are obtained. Richardson finds not only one complete band system, composed of sequences in the green, red, and deep red, the origin lying at 16,611 cm^{-1}, but also a whole series of such systems, evaluating a set of electronic energy levels such as Witmer (see page 214) has assumed for H_2. *The "terms" of this set of levels are almost identical with those of the principal doublet series of the helium atom.* If this analogy between the *hydrogen molecule* and the *helium atom* is general, it gives, in the writer's opinion, the explanation of the still lacking contact between the visible and ultra-violet band systems of hydrogen. In analogy to the helium atom, the ultra-violet band levels probably all belong to the *singlet* system, while Richardson's levels all belong to the doublet (true triplet) system. The original paper should be consulted for numerous additional results.

1 Name	2	3	4 ν_e	5 ω''	6 $\omega''x'$	7 ω'''	8 $\omega'''x''$	9 References	10 $I_0' \times 10^{40}$	11 $I_0'' \times 10^{40}$	12 $r_0' \times 10^8$	13 $r_0'' \times 10^8$	14 References
Silver bands	AgH	R	29,898 (O)	(1490)		(1690)		(152)(a)	4.57	4.38	1.665	1.630	(152)(a)
Aluminum hydride bands	AlH	R	23,477.0 (O)	(1082)		(1625.1)		(153)(b)	4.58	4.41	1.690	1.658	(153)(b)
Aluminum bands	AlO	R	20,635.3 (O)	864.4	3.75	970	7.0	(85)(15)(97)	46 02	43.38	1.665	1.617	(97)(97A)(b*)
Gold bands	AuH	R R	27,342.1 (O) 33,230.0 (O)	1630. (1548)	79.	2249 4 2249.4	34.0 34.0	(154)(155)(c)	4.74	3.93	1.69	1.54	(154)(155)(c)
Beryllium fluoride bands	BeF	R	33,215 (H) 33,180 (H)	1157	8	1250	12	(49)(156)	.....	.....	....	....	.....
Beryllium oxide bands	BeO?	R	21,231.6 (H)	1354	8.9	1465	12.7	(157)(9)	.....	.....	....	....	.....
BO α group	$B^{11}O$	R	23,960.4 (O) 23,834.2 (O)	1259.1	10.6	1885.4	11.71	(47)(d)	14+	12	1.2	1.1	(49)
BO α group	$B^{10}O$	R	23,960.4 (O) 23,834.2 (O)	1298.0	11.7	1940.5	12.39	(47 (d)	14+	12	1.2	1.1	(49)
BO β group	$B^{11}O$	R	43,167.4 (O)	1280.3	10.07	1885.4	11.71	(47 (d)	14—	12	1.2	1.1	(49)
BO β group	$B^{10}O$	R	43,167.4 (O)	1316.7	10.53	1940.5	12.39	(47, d)	14—	12	1.2	1 1	(49)
BO "combination" bands	$B^{11}O$	V	19,333.2 (O) 19,207.0 (O)	1280.3	10.07	1259.1	10.6	(47) d)	14—	14+	1.2	1.2	(49)
BO "combination" bands	$B^{10}O$	V	19,333.2 (O) 19,207.0 (O)	1316.7	10.53	1298.0	11.7	(47) l)	14—	14+	1.2	1.2	(49)
Calcium hydride band	CaH	V	28,353.38 (O)	.....	.....	.....	.....	(22)(A)	5.773	6.546	1.886	2.009	(22)
Swan bands	C_2?	V	19,379.2 (O)	1766	18.0—	1626	12.7	(158)(15)(91)	15.84	17.08	1.265	1.311	(38)(91)(98)(d*)
Triplet carbon bands	C+H?	R	15,540 (O) 15,623 (O)	1105	9.8	(1714)		(74)(71)(e)	.....	.....	....	....	.....
C+H band λ 4300	CH	V	23,163.3 (O)	(2851)		(2797) and (2815)		(53)(e*)	1.90	1.95	1.11	1.13	(53)
C+H band λ 3900	CH	R	25,715 (O)	.....	.....	.....	....	(53)(155)	2.21	1.95	1.20	1.13	(53)
Violet cyanogen bands	CN	V	25,797.8 (O)	2143.9	20.25—	2055.64	13.75	(67)(43)	14.140	14.647	1.151	1 172	(43)(f)
Red cyanogen bands	CN	R	14,430 (O?) 14,374	1728.5	13.5	2055.64	13.75	(67)(43)	.....	.....	....	....	.....
Fourth positive group of carbon	CO	R	64,721 (H)	1497.28	17.24	2149.74	12.703	(72)(g)	.....	.....	....	....	.....
Angstrom CO bands	CO	V	22,164 (O)	2158	76	1497.28	17.24	(159)(44)(9) (160)(72)(g)	14.26	17.31	1.122	1.236	(44)(72)(g)
Infra-red CO	CO	R	zero	2143	9 7	same	same	(161)(g)	14.9	same	1.15	same	(162)(g)
Third positive group of carbon	CO	V	35,288 (H)	(2214)		1724.78	14.47	(76)(75)(71)(i*)(A)	.....	.....	....	....	.....

1 Name	2	3	4 ν_e	5 ω''	6 $\omega''x'$	7 ω'''	8 $\omega'''x''$	9 References	10 $I_0' \times 10^{40}$	11 $I_0'' \times 10^{40}$	12 $r_0' \times 10^8$	13 $r_0'' \times 10$	14 References
Cameron CO bands	CO	R	48,530 (H)	1723.2	14.6	2151.1	12.7	(i)	.....	.....	....	....	.....
First negative group of carbon	CO^+	R	45,637.7 (O)	1697.8	24.33	2197.03	15.17	(46)(71)(70)	15.4	14.05	1 17	1.11	(46)(49)(h)
Comet-tail bands	CO^+	R	20,471 6 (O) 20,346.1 (O)	1550.46	14.07+	2198.6	15.00	(48)(71)(60)	17.7?	14.05	1.25?	1.11	(48)(49)
Baldet-Johnson "combination" bands	CO^+	V	25,285 (O) 25,158 (O)	1697.8	24 33	1550.46	14.07+	(70)(60)(j)	.....	.....	....	....	.....
High pressure bands of carbon	?	V	22,972.7 (H)	.....	.....	1537.3	11.88	(74)(71)	.....	.....	....	....	.....
Cadmium bands	CdH	V	22,278 (O) 23,279 (O)	.....	.....	1374	.....	(43)(163)(k)(A)	4.647 4.594	5.201 5.201	1.679 1.669	1.776 1.776	(43)(163)(l)
Copper bands	CuH	R	23,311.15 (O)	1655.70	44.63	1963 68	37.36	(95)(25)(m)	4.097	3.544	1.58?	1.471	(95)(25)(n)
Copper iodide A bands	$Cu^{63}I$	R	19.707.65 (H)	211 91	2.283	264.63	0.713	(83)(o)	.....	.....	....	....	.....
Copper iodide B bands	$Cu^{63}I$	R	21,748.3 (H)	241.8	1.88	265.4	1.0	(83)(o)	.....	.....	....	....	.....
Copper iodide C bands	$Cu^{63}I$	R	21,851.41 (H)	229.17	0.447	263.86	0.653	(83)(o)	.....	.....	....	....	.....
Copper iodide D bands	$Cu^{63}I$	R	22,929.66 (H)	.....	.....	264.2	0.64	(83)(o)	.....	.....	....	....	.....
Copper iodide E bands	$Cu^{63}I$	R	23,982.71 (H)	228.28	0.954	263.81	0.671	(83)(o)	.....	.....	....	....	.....
Fulcher bands. First band	H_2	V	17,050 (O) ?	(4880)		.....	.....	(34)(30)(p)(j')	0.179	0.186	0.46	0.47	(34)(p)
Fulcher bands. Second band	H_2	V	19,485 (O) ?	(4880)		.....	.....	(34)(130)(p)(j')	0.125	0.129	0.39	0.394	(34)(p)
Hydrogen-Richardson & Tanaka	H_2	R	17,307 (O) etc.	.....	.....	.....	.....	(33)(j')	0.62 etc.	0.48 etc.	....	....	(33)(125)(q)
HF near infra-red (absorption)	HF	R	zero	(3962)		same	.....	(57)(r)	1.35	same	0.924	same	(57)(r)
HCl near infra-red (absorption)	HCl	R	zero	2940.8	53.6	same	.....	(164)(r)	2.645	same	1.279	same	(164)(r)
HBr near infra-red (absorption)	HBr	R	zero	(2559)		same	.....	(57)(r)	3.305	same	1.418	same	(57)(r)
Helium λ 6400	He_2	R	15,623.9 (O)	.....	.....	.....	.....	(35)(111)(s)	3.840	3.784	1.078	1.070	(35)(111)(s)
Helium λ 4546	He_2	R	21,992.7 (O)	.....	.....	.....	.....	(35)(111)(s)	3.888	3.784	1.086	1.070	(35)(111)(s)
Helium λ 5780	He_2	V	17,436.6 (O)	.....	.....	.....	.....	(35)(111)(s)	3.664	3.784	1.054	1.070	(35)(111)(s)
Helium main line series	He_2	R	21,507.4 (O)	.....	.....	.....	.....	(114)(t)	3.876	3.636	1.084	1.050	(114)(t)
Helium second line series	He_2	R	19,477.1 (O)	.....	.....	.....	.....	(114)(t)	3.856	3.608	1.080	1.046	(114)(t)
Mercury bands (Liese, etc.)	HgH	V	24,933.9 (O)	(1940)		1308	104.	(101)(u)(A)	4.220	5.142	1.597	1.763	(43)
New mercury bands (Hulthén)	HgH	V	28,617.1 (O)	(1986)		1308	104.	(101)(u)(A)	4.181	5.142	1.589	1.763	(101)(v)
Iodine bands	I_2	R	15,598.29 (H)	127.5	0.85—	213.67	0.592—	(12)(w)	951.6	742.6	3.015	2.663	(w)
Lithium hydride bands	LiH	..	.....	.....	.....	.....	.....	.....	.....	6	....	2.0	(166)

1 Name	2	3	4 ν_e	5 $\omega^{\circ\prime}$	6 $\omega^{\circ\prime}x^{\prime}$	7 $\omega^{\circ\prime\prime}$	8 $\omega^{\circ\prime\prime}x^{\prime\prime}$	9 References	10 $I_e^{\prime}\times10^{40}$	11 $I_e^{\prime\prime}\times10^{40}$	12 $r_e^{\prime}\times10^{8}$	13 $r_e^{\prime\prime}\times10^{8}$	14 References
Potassium (absorption)	K_2	R	15,406.1 (O)	.....	.....	.....	... .	(166)(x)	212	184	2.56	2.39	(166)(x)
Magnesium hydride bands	MgH	V	19,280 (O)	.....	.....	.....	.....	(38)(167)	.....	4.6	....	1.70	(167)
First positive, of nitrogen	N_2	V	10,979.0 (H)	1718.40	14.437—	1474.87	13.982—	(15)	.....	.....	....	....	.....
Second positive, of nitrogen	N_2	V	29,653.1 (H)	2018.66	26.047—	1718.40	14.437—	(67)(15)	15.24	16.98	1.149	1.212	(17)(18)(96)(y)
Fourth positive, of nitrogen	N_2	V	44,218 (H)	.....	.....	1718.40	14.437—	(14)(67)(15)(z)	.....	.....	....	....	.....
Ultra-violet, of nitrogen	N_2	R	66,956.6 (H)	1679.2	13.85—	2345.16	14.445	(78)(66)(A)	.....	.....	....	....	.....
First negative, of nitrogen	N_2^+	V	25,565.9 (O)	2392.3	22.8—	2187.4	16.3	(77)(68)(168)(a′)	13.35	14.41	1.075	1.117	(77)(b′)
Third positive, of nitrogen or γ bands	NO	V	44,072 (O) 44,193 (O)	2352	13—	1888.31	13.88	(69)(68)(66)(c′)(A)	.....	.....	....	....	.....
β bands, of nitrogen	NO	R	45,475 45,387 (H)	1031	7.5?	1888.31	13.88	(14)(68)(d′)	25.5 24.1	16.6 16.0	1.44 1.40	1.16 1.14	(A)
Sodium (absorption)	Na_2	R	20,262.4 (O)	.....	.....	.....	.....	(166)(x)	29	25	1.23	1.15	(166)(x)
Sodium potassium mixture	NaK	R	17,043.3 (O)	.....	.....	.....	.....	(166)(x)	78	66	1.81	1.66	(166)(x)
Schumann (and Runge) oxygen bands	O_2	R	49,359.3 (H)	708.	13—	1565.37	11.37	(170)(171)(169) (9)(172)(80)(e′)	34.22	19.2	1.609	1.20	(80)(155)(f′)
Atmospheric, oxygen	O_2	R	13,117.6 (O)	1418.86	14.05	.....	.....	(38)(61)	.....	19.2	....	1.20	(9)(155)
First negative, of oxygen	O_2^+	R	38,308 38,108 (H)	885.2	13.7	1859.9	16.53	(79)(68)(9)(g′)	.....	.....	....	....	.....
Water vapor bands (emission)	OH	R	32,410 (O)	3085	97	(3570)		(45)(105)(106)(h′)	1.630	1 43	1.022	0.957	(45)(105)(106)(i′)
Infra-red, of water vapor	H_2O	R	zero	(1595) and (3742)		same	.....	(174)	3.013 3.024 3.157		....	....	(174)
Silicon nitride bands	$Si^{28}N$	R	24,234.2 (O)	1016.3	17.7+	1145.0	6.57	(175)	37.8	37.2	1.567	1.554	(175)
Silicon oxide bands	SiO	R	42,643 (H)	844	5.8	1236	6.0	(65)(9)	.....	.....	....	....	.....
Tin chloride bands	SnCl	V	31,262.5(H) 33,622.6(H)	431.3 431.3	1.2 1.2	353.5 351.4	1.0 1.2	(176) (176)	.....	.....	....	....	.....
Zinc bands	ZnH	V	23,263.6 (O) 23,504.0 (O)	.....	.....	1552	.....	(163)(A)	3.874 3.708	4.234 4.234	1.538 1.505	1.608 1.608	(43)(1)

SECTION 8. THE STRUCTURE OF MOLECULES

In this, the concluding section of the chapter, a brief survey is given of some of the applications of the study of the structure of electronic bands. Much of the work about to be discussed is not only very recent, but is constantly being augmented. Much of it has appeared since the earlier portions of the chapter were written and, in many cases, only minor necessary changes have been made in these earlier sections, with a reference to the present section for a fuller discussion.

The most important result of the analysis of band structure is undoubtedly the information obtained as to the value of certain molecular constants; notably, the frequency of vibration and the moment of inertia of certain diatomic molecules. This information has been collected in Section 7. Certain outstanding relations among these numerical values seem worthy of notice.

As has been pointed out by Birge([68]) and by Mecke([155]), an increase in ω^0 is invariably correlated with a decrease in I_0, and *vice versa*. Mecke([155]) has gone a step further and has given a table which seems to indicate that the proportional change in these two quantities is, roughly, even quantitatively the same. There is, undoubtedly, a striking similarity in the change of ω and of I_0, especially for molecules of the same type, but the correlation can hardly be called quantitative. Using the more complete results given in Section 7, the following table (Table 1) lists these relations, in a form differing from Mecke's([155]) Table 2

TABLE 1

(1) Name	(2) $\frac{\omega_{mean}}{\omega^{0\prime}-\omega^{0\prime\prime}}$	(3) $\frac{I_{mean}}{I_0''-I_0'}$	(4) $\omega_m \times I_m$	(5) $\omega'' \times I''$
AgH	− 7.9	− 23.5	7,120	7,400
AlH	− 2.49	− 26.4	6,080	7,170
AlO	− 8.73	− 16.9	41,000	42,100
AuH	− 3.13	− 5.36	8,410	8,840
BO (α)	− 2.51	− 6.5	20,450	22,600
Swan (C_2?)	+ 12.1	+ 14.1	28,700	27,700
violet CN	+ 23.8	+ 28.4	30,200	30,100
Angstrom CO	+ 2.77	+ 5.18	28,850	26,000
negative C	− 3.97	− 10.9	28,700	30,850
CuH	− 7.18	− 6.91	6,800	6,750
Iodine	− 1.98	− 4.05	144,300	158,700
2d pos. N	+ 6.23	+ 9.83	30,100	29,200
N_2^+	+ 11.0	+ 13.1	31,850	31,500
Schumann (O_2)	− 1.327	− 1.78	30,350	30,100
SiN	− 8.40	− 62.5	40,550	42,600

only in minor aspects. Column 1 gives the name of the band system, column 2 the ratio of the *mean* value of $\omega^{0\prime}$ and $\omega^{0\prime\prime}$ to the value of

$(\omega^{0\prime} - \omega^{0\prime\prime})$. Column 3 gives the ratio of the *mean* value of I' and I'' to the value of $(I'' - I')$.[156] Because of the invariable relation just mentioned, the sign of both the ratios is the same, but as may be seen, the numerical values are sometimes quite different.

Another relation, pointed out by Mecke([155]), is given in columns four and five of this same table. This concerns the product of the moment of inertia and the frequency of vibration, using the mean values for column four, and the final state values for column five. In most cases, but not in all, this final state is the normal state of the molecule. The relations shown in these columns are very striking. Thus, all of the hydrides give essentially the same product (6000 to 9000), while the molecules C_2, CN, CO, CO^+, N_2, N_2^+, and O_2, all of which are of about the same mass, and the same mass distribution, give products confined within the narrow range 26,000 – 31,500. This certainly seems to indicate that the moments of inertia adopted for these various molecules are at least relatively correct. Thus, in the case of CN and CO, because of the simplicity of the band structure, there seems to be but one possible interpretation with its resulting value of I_0. But in the case of N_2^+, O_2, and other non-polar molecules, the use of quarter-quantum numbers has been suggested, as already discussed in Part 5e.* The present data are all based on half-integral values of m, and a change to quarter-integral values would give a number in column (4) or (5) just one-fourth as large. The table certainly presents strong evidence against any such change, unless it is made for *all* molecules.

In order to obtain additional evidence as to the *absolute* values of the moments of inertia, we may consider the field of force of the molecule. The discussion in Section 3 has shown that the frequency of vibration of the dipole depends upon the strength of the nuclear binding, and its change with the amplitude of vibration depends upon the deviation from an elastic law of the force acting on the two nuclei, when displaced from their normal separation. It was also shown (as in equation 52) that when the dipole rotates, the moment of inertia increases. The amount of this increase naturally depends not only upon the rapidity of rotation, but also upon the strength of the nuclear binding. It is thus evident that from a study of the frequency of vibration, as a function of n, as well as of the moment of inertia, as a function of m, it should be possible to obtain information as to the law of force of the molecule, in the neighborhood of the equilibrium position. The first method of attack (that using

[156] If I'' had been used in place of I_{mean}, this ratio would have been equal to B'_0/C_0 which, from the theory given in Part 5b, measures the number of lines from the origin to the head of the 0 — 0 band.

vibrational data) has been formulated by Kratzer([57]), Kemble([88]), and Born and Hückel([177]). The results of these investigators may be given, in a slightly modified form, as follows:

Let r represent the nuclear separation in general, and r_0 the special equilibrium value. Let us now assume that the force called into play by any variation of r from r_0, so long as $(r-r_0)$ is small, may be represented by

$$F=k_1(r-r_0)+k_2(r-r_0)^2+k_3(r-r_0)^3+\text{etc.} \tag{188}$$

Then it may be shown that the constants of this equation are given,[187] using the most compact form, by

$$k_1=c^2\mu(2\pi\omega^0)^2, \tag{189}$$

$$k_2=-\frac{3k_1}{2r_0}\left(\frac{a\omega^0}{6B_0^2}+1\right), \tag{190}$$

where $I_0=\mu r_0^2=\dfrac{h}{8\pi^2B_0c}$, as per equation (134).

$$k_3=\frac{1}{3k_1}\left(\frac{10k_2^2}{3}-\frac{8k_1^3x}{ch\omega^0}\right). \tag{191}$$

Here h, ω^0, B_0, a, x, and μ have their usual meaning (see equations 30, 31, 38, and 187) and c is the velocity of light.[186] In these equations B_0, a, and ω^0 are in cm^{-1}, k_1 in dyne-cm^{-1}, k_2 in dyne-cm^{-2}, k_3 in dyne-cm^{-3}, μ in grams, F in dynes, $(r-r_0)$ in cm. (x has no dimensions).

Equations (189) to (191) show that in order to evaluate the coefficients in equation (188) one must know not only ω^n as a function of n (i.e., ω^0 and x), but also the value of B_0 and its change with n (i. e., a). The fact that one has a dipole makes the force different for equal positive and negative values of $(r-r_0)$. This difference is indicated by the presence of even powers in equation (188). But the amount of this variation is connected in turn with the *average* value of the nuclear separation, for any given value of n. To know this we must know B_n as a $f(n)$. Thus while we are evaluating the constants of the law of force from the properties of the dipole for a series of positions in which it is *vibrating,* but *not rotating,* we must actually use constants (B_0 and a) which can be obtained only from an analysis of rotational energy data.

[187] These equations agree with Kemble's results. In the equation for "x," as written on p. 4 of Born and Hückel([177]), the "48" should be replaced by "96." The equation for W, on p. 3, from which "x" is derived, is correct. The error is repeated by Hund (Z. f. Phys. 32: 1, 1925) where on p. 3 his equation for $\phi_0(\cdot)$ should have "32" in place of "16."

[186] The numerical values adopted in this report are $c=2.9986\times10^{10}$ cm/sec, $h=6.556\times10^{-27}$ erg. sec.

This point was mentioned in connection with Method Three, at the end of Part 5b.

One may also evaluate the constants of equation (188) by means of rotational energy data *alone*. This has recently been pointed out by Birge([96]). The derivation is based upon the fact that one may evaluate the potential energy of the dipole U_r, produced by the swelling of the dipole as it rotates. The first approximate expression for this has been given as a $f(n)$ in equation (54) of Section 3. But

$$F=\frac{dU_r}{dr}=\frac{dU_r}{dm}\frac{dm}{dr}. \tag{192}$$

Now $I_m=\mu r^2=f(m)$, as given in equation (52). Hence we may obtain r as a $f(m)$, and from this dr/dm or dm/dr. By repeating the differentiation with respect to r, using $\frac{d}{dr}=\frac{d}{dm}\frac{dm}{dr}$, and then placing $m=0$ (i. e., $r=r_0$), one obtains the successive k's, since

$$k_1=\left(\frac{d^2U_r}{dr^2}\right)_{r=r_0}=U''_0, \qquad k_2=\tfrac{1}{2}\left(\frac{d^3U_r}{dr^3}\right)_{r=r_0}=\tfrac{1}{2}U'''_0, \text{ etc.} \tag{193}$$

Writing the rotational energy of a *non-vibrating* molecule in the form of equation (141)[150] the results, in their most compact form, are

$$k_1=-\frac{2hcB_0^2}{D_0r_0^2}, \tag{194}$$

$$k_2=-\frac{3k_1}{2r_0D_0^2}(3D_0^2-B_0F_0), \tag{195}$$

$$k_3=-\frac{k_1}{2r_0^2D_0^4}(18F_0B_0D_0^2-25D_0^4-9F_0^2B_0^2+4H_0D_0B_0^2). \tag{196}$$

In these equations all the units are the same as for equations (188) to (191), i. e., B_0, D_0, F_0, and H_0 in cm^{-1}.

In general, the rotational data yield a far less exact evaluation of the k's than do the vibrational data. This is to be anticipated, for in the case of CN, for instance, the maximum available value of $\frac{r-r_0}{r_0}$, as obtained by rotational data, is about three per cent, but from vibration it is about

[150] This equation contains only even powers of m. It has been shown in Section 3 that the inclusion of a first degree term in m in the rotational energy function contradicts the very fundamental equation (39). Similarly, the presence of a third degree term leads to $k_1=0$, although higher odd powers do not affect k_1. A fifth power gives $k_2=0$, but higher odd powers are without effect. It is thus evident that equation (141) must be restricted to even powers in m, and any apparent odd powers may be interpreted as due to the warping of electronic orbits, as discussed at the end of Part 5b.

15 per cent. However, using equations (189) and (194), Birge[96] showed that the two values of k_1 agreed within a few per cent, for the CN, CuH, N_2 and N_2^+ molecules. For CN values of k_2 were obtained, using equations (190) and (195), and these also agreed within the rather large limits of error.[100]

The results for N_2 and especially for N_2^+ have an immediate theoretical significance, for if quarter-quantum numbers had been used, as had been suggested by Dieke[59], the value of k_1, as derived from equation (194) would have been just four times as large, while the value as derived from equation (189) would have been unchanged. Hence this comparison of the constants of the law of force, as derived from rotational and from vibrational data, furnishes a method of establishing the correctness of the *absolute* values of the moments of inertia. The results prove that it is necessary to use half-quantum numbers for the N_2 and N_2^+ bands, and then the data in Table 1 indicate that the values of I_0 for O_2 and for other non-polar molecules are also correct. Data of sufficient accuracy for making a direct test are not in general as yet available.

By equating the two expressions for the respective k's, given in equations (189) to (191) and (194) to (196), one obtains

$$D_0 = -\frac{4B_0^3}{\omega^{0^2}} = -u^2 B_0, \tag{197}$$

$$F_0 = \frac{D_0^2}{B_0}\left(2 - \frac{a\omega^0}{6B_0^2}\right), \tag{198}$$

$$H_0 = \frac{1}{B_0^2 D_0}\left(3B_0 F_0 D_0^2 - 5D_0^4 + B_0^2 F_0^2 - \frac{8D_0^3 B_0^2 x}{3\omega^0}\right). \tag{199}$$

These equations give the " calculated " values of D_0, F_0, and H_0, which are the basis of Method Three, as discussed at the end of Part 5b. Equation (197) is the same as equation (142), and was derived by Kratzer[57], by considering only the first two terms of equation (141). Equations (195), (196), (198) and (199) were derived by Birge[96].

[100] It is to be anticipated that when the molecule rotates, the electronic orbits are more or less warped. This warping will in turn play a rôle in determining the law of force. Similarly, when the molecule vibrates, the electronic orbits will be warped, but in a different manner. Hence the force acting on the two nuclei, when at a given separation r, will depend on whether this separation has been achieved as a result of rotation, or of vibration. In other words, the constants of the law of force may be expected to have more or less different values, as determined from vibration and from rotation. But the value of k_1, depending only upon infinitesimal displacement, must be the same, while in order to detect any reasonable discrepancy in the k_2 values, experimental data must be used of far greater accuracy than any at present available.

We turn now to an entirely different matter—the question of the general system of electronic energy levels of a molecule. The curves of Figure 12, and the constants listed in Section 7, together with the accompanying discussion, have indicated that in many cases two or more systems of bands are found to have a common set of vibrational energy levels. Provided that the data are sufficiently accurate to be certain that the $\omega'' : n$ curves, as obtained from the two systems, are really identical,[161] this relation is certain evidence that the two systems in question are due to the same molecule, and from data of this character one obtains the relative position of at least three electronic energy levels of the molecule. In the case of BO and CO^+, the correctness of such a relation has been further checked by the finding of " combination " bands, as previously discussed.

As a result of this line of investigation, there are now known five electronic energy levels for CO, four levels for N_2 and NO, and three for molecules such as BO, CN, CO^+, and O_2. (See Figure 26 ahead.) For helium, two long series of levels are known, each given by a *Rydberg* formula as discussed in Part 5e. It is of great interest to investigate as to whether a similar formula holds in the case of other molecules. To test this matter, one needs a number of related electronic levels, for which a limit can be calculated, and thus the spectral " terms," in the manner employed by line spectra.[162] Unfortunately such data are available only for helium. Now in many cases the position of electronic levels relative to the normal state of the molecule is known (by obtaining bands in absorption, etc.). Hence, if the ionization potential of the molecule is known,[163] the separation of each level from this limiting value can be calculated, and from this the " denominator " of the term ($D = \sqrt{R/\nu}$). The Rydberg formula corresponds to a series of values of D each differing by an integer.

Birge([72]) has recently obtained the three electronic energy levels for CO associated with the fourth positive group of carbon, and the Angstrom

[161] Thus it was for a time thought that the initial state of the red CN bands (curve 4 of Figure 12) was identical with the common nitrogen progression (curve 13', 14, 15' of Figure 12) and that therefore the CN bands must be due to nitrogen. The curves, as drawn in Figure 12, show clearly the error of such an assumption.

[162] See A. Fowler " Report on Line Spectra."

[163] Values of the ionization potentials of molecules are particularly scarce. (See pp. 111-127, of National Research Council Bulletin 48, " Critical Potentials," 1924). Some work has recently been done on the excitation potentials of various band systems (see Duffendack([177A]) for a general account); but it would appear from the discrepancies of certain of the recent results of different observers that the experimental difficulties are very great.

CO bands (CO, levels X, A, and B, of Figure 26). The ionization potential is known both from direct and indirect observation and with 14.2 ± 0.3 volts as the most probable value, the "denominators" of the three levels are 0.976 ± 0.02, 1.48 ± 0.10, and 1.97 ± 0.15. It is evident that the first and third levels may be a portion of a Rydberg series, and that the intermediate second level bears the usual relation of a P level to the adjacent S levels, found in the case of atoms in the first two columns of the periodic table. Sponer([178]), in her work on the excitation potentials of the various nitrogen band systems, had previously noted that the N_2 levels given by A, C, and D of Figure 9, can be fitted to a Ritz formula, giving a series limit of 16.3 volts, in fair agreement with the value of the ionization potential obtained directly. Olson and Glockler([179]) have obtained a series of critical potentials in hydrogen that can be interpreted as a series of electronic energy levels of the molecule, and which closely follow a line series law.[164] The above relations have been noted and discussed by Birge([180]), in connection with the following additional analogies between atoms and molecules.

Mulliken([49]) has shown that there are multiple electronic levels in molecules similar to those in atoms. This has been discussed in Part 2f of the present chapter. Thus, in the molecules CO^+, BO, CN, and NO, there is a double level which may be designated as a double "P" level. Mulliken([83]) found such a double level also in the alkaline earth halides, and noted that the doublet separation was of the same order of magnitude as in a certain "corresponding" atom having the same number of valence electrons. Mecke([181]) independently investigated these alkaline earth halides, and applied the Landé formula for the doublet separation of the alkalies. In this way he obtained an "effective quantum number" and an "effective nuclear charge" for these molecules, and by analogy with atoms, deduced from these data that the valence electrons of the molecules actually penetrated close to the two nuclei. Then Hulthén([163]) found doublet separations in HgH, CdH, and ZnH which were roughly the same as the $1^3P_2 - 1^3P_1$ separation of the Hg, Cd, and Zn atoms.[165]

Now in the case of molecules like CO, N_2, etc., it is quite probable that certain molecular electronic orbits should be different from those in either atom. For such molecules, Mulliken([49]) has assumed that each atom retains its own K electrons, but that the remaining electrons may possibly form a "shell" of eight electrons, as in the atomic rare gas configuration,

[164] The work of Witmer([142A]) on the spectrum of hydrogen, as mentioned in Part 5e, leads to a similar set of levels.

[165] Notation of Russell and Saunders (Astrophys. J. 61: 38, 1925).

the two remaining electrons (in CO and N_2) being the valence electrons. It does not seem necessary to assume that all of the eight electrons encircle both nuclei, to form a shell practically identical with that found in atoms. We may assume merely that the eight electrons form some sort of a firmly-bound symmetrical group,[166] while the two remaining electrons (in the case of CO or N_2) are more loosely bound and therefore possess a set of energy levels similar to those correlated with the valence electrons in atoms. From this standpoint, CO and N_2 may be termed "two-valence" molecules and may be compared with the atom, Mg. Similarly CO^+ and N_2^+ may be compared with Mg^+, NO with Al, O_2^+ with Si^+, and O_2 with Si. On such a basis the three single levels of CO just cited may be designated as 1^1S, 1^1P, and 2^1S, in analogy with Mg.[167] In the case of NO the recent work of Sponer(66) and of Sponer and Hopfield(182) has shown that the lower level is double, as in the case of the valence (^2P) level of Al, while the two closely adjacent excited levels are similar to the ^2S and ^2D levels of Al. (NO, levels *X*, *A*, and *B* of Figure 26.) Mulliken first suggested (private communication) that it was the lower, rather than the higher level that was double, in the case of the γ bands of NO.

On the basis of evidence such as that just cited, Birge(180) announced the following generalization—"The energy levels associated with the valence electrons of molecules agree in all essential aspects with those associated with the valence electrons of atoms." The levels may be designated *S*, *P*, *D*, etc., and similarly lettered levels obey line spectra laws, and have the same multiplicity as in the "corresponding" atom. In deciding whether a level is an *S*, *P*, or *D* level, the following additional relation has been noted, for molecules of the type under discussion. As Mulliken(49) has suggested in the case of BO, CN, CO^+ and similar molecules, the molecule appears to be less stable for the *P* state than for

[166] Mulliken in a later paper (Proc. Nat. Acad. Sci., 12: 338, 1926) reaches a similar conclusion.

[167] The fine structure analysis of the Angstrom CO bands by Hulthén(44) proves that the 1*P* and 2*S* levels are single, and it is a natural assumption that the lowest (1*S*) level is also single. If this assumption is correct, the fine structure of the fourth positive group of carbon may be predicted to be similar in every respect to that for the Angstrom CO bands.

Furthermore, the two new levels recently found by Johnson (see note i of Section 7), giving the initial states of the new Cameron bands and of the third positive carbon group, respectively, are evidently, by similar analogy with Mg, the 1^3P_{123} and 1^3S levels. (See CO levels *a* and *b* of Figure 26.) Johnson finds the 1^3P_{123} level five-fold. The writer believes it to be six-fold, due to three *Q* branch and three *R* or *P* branch heads, and hence truly a triple electronic level. The 1^3S level is evidently single.

the S states above and below it. This is indicated by the smaller value of ω^0 for the P state. Birge([180]) expressed this more definitely as follows: In an atom a series of S levels (or of P or D) corresponds to a set of electronic orbits for which the "penetration" is roughly the same. The calculations on atomic force fields have shown that any constant penetration of a set of orbits into a fixed distribution of charge leads to the Rydberg formula as a representation of the energy of the set, and a constant azimuthal quantum number, but varying total quantum number (as in a set of S orbits) corresponds to such a set of orbits of roughly constant penetration. The values of ω for each of the molecular electronic orbits for which it seems possible to assign letter designations, indicate that for molecules like CO, N_2, NO, etc., *all* S levels correspond more or less to a large but constant value of ω, P levels to a *smaller* value, and D levels to a *still smaller* value.

More recent work by Mulliken has shown that these *relative* values for the S, P, and D levels are not a general characteristic. Thus, in HgH, CdH, etc., the ω for the excited P level is much larger than for the normal S level. The essential point is, however, that the value of ω is roughly the *same* for various S levels, but has a *different* roughly constant value for P levels, etc. Birge([180]) suggested that the relative values of ω for the S, P, and D levels might be taken as a measure of the penetration of the electron, and that the observed numerical relations just quoted could thus be explained in terms of actual electronic orbits. It is probable that this is too literal an interpretation. More generally, we may conclude that a set of S levels *does* correspond to some roughly constant penetration of the orbit of the valence electron, just as in the case of atoms, and that there is some definite configuration of the remaining electrons which alone is in stable equilibrium with this particular penetration of the valence electron. The entire configuration of the molecule then leads to some roughly constant value of the frequency of vibration ω. When, however, the valence electron is in a P level, it has a different penetration, and to this there corresponds a different configuration of the remaining electrons leading in turn to a different value of ω. Whether this new value of ω is greater or less than the former depends upon the type of molecule under discussion, and no general rule can as yet be given.[188]

[188] This *difference* in value of ω^0 (and hence of I_0) for the S, P, and D levels gives the real theoretical significance of the direction of degradation of bands. Thus all bands due to a given molecule, or to molecules of a given type, are not degraded in the same direction, as Kayser seems to have assumed. (See Part 2a.) On the contrary, an $S - P$ transition gives one direction of degradation, a $P - S$ transition the opposite direction. Because of the near equality of values of ω^0 and I_0 for successive S, or of P states, the direction of degradation of $S - S$ or $P - P$ transitions cannot be predicted.

Since the paper by Birge([180]) appeared, Mulliken([183]), ([184]), ([185]), has been working along the same line, and has found many new relations which support the general conclusions. In particular, he finds (reference([185])) that the bands forming the main "line series" of helium may be considered to originate in the set of levels $3P$, $4P$, $5P$, etc., and to have $2S$ for a common lower level.[189] The calculated value of $2P$ shows that the $2S-2P$ band would be at 20,900 A, and so is not known. Then the "non-conforming bands" λ6400, λ4546, and λ5730 (see Part 5e) can be represented by $2P-3S$, $2P-4S$, and $2P-3D$. The known limit of the P levels allows the calculation of the denominators of each of these atomic levels, and the results are given in the accompanying Table 2, together with the denominators of the corresponding terms in the helium atom. The correspondence between the atom and molecule is very striking

TABLE 2

Total quantum number	Molecule He_2 "Main" series			Atom He "Doublet" series		
	S	P	D	S	P	D
2	1.788	1.928		1.689	1 937	
3	2.810	2.928	3.013	2 697	2.933	2.997
4	3.818	3.928		3 700	3.932	3.997
5		4.928		4.701	4 932	4.997
6		5.928				
		etc.				

and shows clearly that the helium molecule consists of two very loosely bound He atoms, each having its electronic orbits virtually unchanged. The essential absence of all observed vibration proves the weakness of the binding in this case. Mulliken, similarly, shows the analogy between the "second" line series of the molecule, and the "singlet" series of the helium atom.

The lowest term of the singlet ("crossed" orbit) series of the atom ($1S$) has a denominator 0.744 and corresponds to the normal state of the atom (1_1 orbit). It should particularly be noted that the corresponding term in the molecule does not occur so far as is now known. The lowest term of the "singlet" series of the molecule has the denominator 1.853, corresponding evidently to a 2_1 orbit for the radiating electron. As in the case of the helium atom, the 2_1 orbit of the "parallel" configuration

[189] An earlier, but less successful, attempt to correlate the electronic energy levels of He and He_2 was made by Takahashi([126]).

gives a spectral term still lower (denominator 1.788), and so this configuration, which corresponds to the so-called "*metastable*" state of the helium atom, is apparently the *normal* configuration of the helium molecule, and yields an ionization potential of 4.24 volts. These deductions conform with the known fact that one electron in the helium atom must be excited from its normal 1_1 state to at least a 2_1 state, in order that the helium molecule may form.

Returning now to the more stable diatomic molecules, we give, in Figure 26, the known facts regarding the energy levels of CO, CO^+, N_2 N_2^+, O_2, O_2^+, and NO. Each electronic energy level is given an arbitrary designation, following out the scheme used by Birge([186]), ([72]) and ([60]), in the case of N_2, CO, and CO^+, respectively. The frequency of vibration, for infinitesimal amplitude, is given at the right of each electronic configuration, preceding the letter designation of the level.[170]

In addition, all of the known vibrational levels connected with each electronic level are shown. On the left of the figure is given the scale in cm^{-1}, running from 0 to 200,000, and the corresponding scale in volts, running from 0 to 24. All of the data used in plotting these vibrational levels are given more accurately in Figure 12, and the relations between Figures 26 and 12, and the band systems listed in Section 7, are given in the caption of Figure 26.

Now, as noted in Section 4, the curves of Figure 12 may be extrapolated to the point $\omega^n=0$ $(n=n_0)$ and if the extrapolation is correct, the included area, when multiplied by "h," i. e.,

$$D=h\int_0^{n_0}\omega^n dn, \tag{200}$$

gives the maximum vibrational energy possible for each given electronic configuration, and represents physically the energy required for dissociation of the two atoms. The extrapolation of the curves of Figure 12 to the point $\omega^n=0$, is equivalent to the extrapolation of the vibrational levels of Figure 26 to the point where the spacing of successive levels becomes zero. This point is shown on Figure 26, for each electronic level for which data are available. These results are due to Birge and Sponer([187]) who used them for a direct determination of the heat of dissociation of the molecules indicated.

The first attempt to obtain a heat of dissociation from band spectra data was made in the case of iodine, and the general problem has been

[170] In the case of the B' level of CO^+, 1697 8, as given in Section 7, is a slightly better value than 1704.4. Similarly, for A' of N_2^+, 2392.3 is better than 2396.0. Certain changes in Figure 26 resulting from very recent work are discussed in a note at the end of this section.

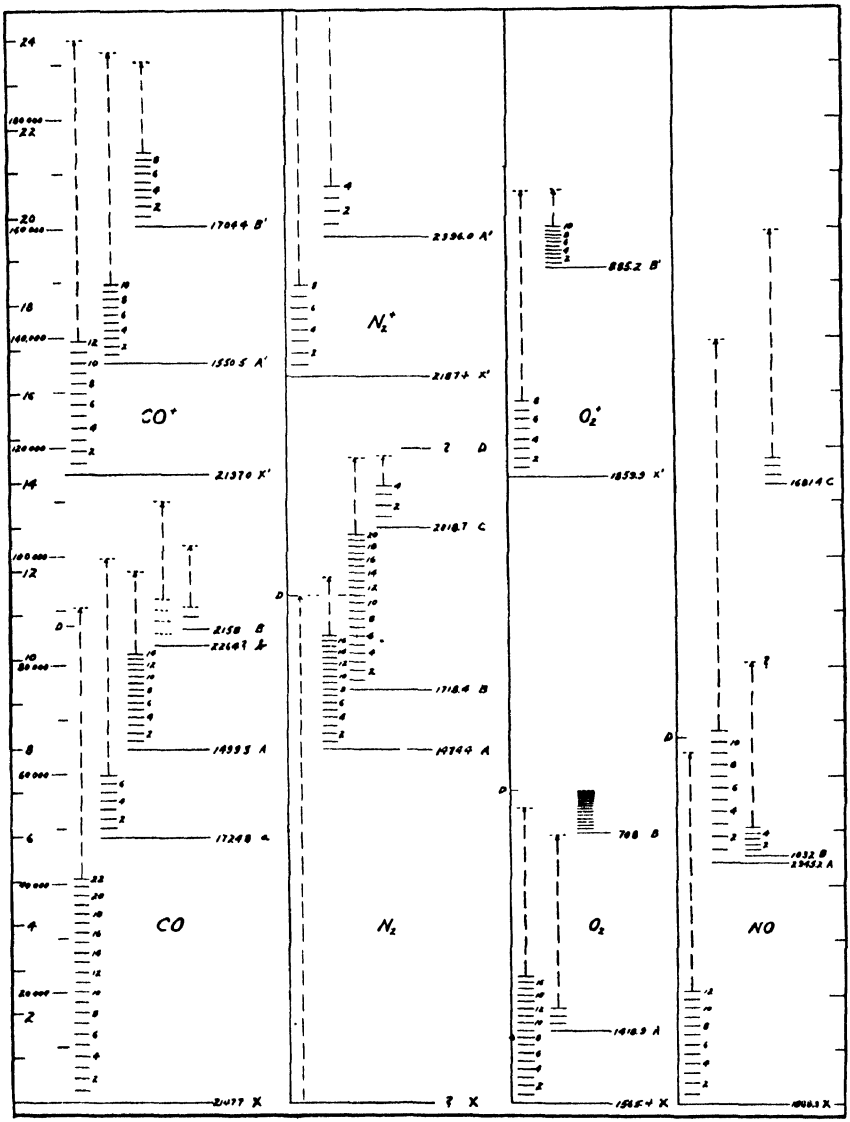

CO+
CO
N2+
N2
O2+
O2
NO
21370 X'
17064 B'
15505 A'
2158 B
22649 b
14959 A
17248 a
2177 X
2396.0 A'
21874 X'
2218.7 C
1718.4 B
14744 A
? X
1859.9 X'
885.2 B'
708 B
1616.9 A
1565.4 X
16814 C
1032 B
1943.2 A
1018.3 X

FIGURE 26.

FIGURE 26.

Electronic and Vibrational Energy Levels of Certain Molecules.

The designations (X, A, B, etc.) of each electronic level are purely arbitrary. The probable true quantum designation and the curve of Fig. 12 giving the ω^m values for each of these levels are as follows (see note at end of this chapter for certain revisions),

CO
$X=1\ ^1S=$curve 21′, 22′.
$a=1\ ^3P=$curve 11′, 22 (triple, $\Delta\nu=?$).
$A=1\ ^1P=$curve 5′, 21.
$b=1\ ^3S=$curve 11.
$B=2\ ^1S=$curve 5.

CO+
$X'=1\ ^2S=$curve 6′, 7′.
$A'=1\ ^2P=$curve 7, 8′ ($\Delta\nu=126$).
$B'=2\ ^2S=$curve 6, 8.

N_2
$X=1\ ^1S=\omega^m$ unknown.
$A=1\ ^3P=$curve 14′ ($\Delta\nu=20$ and 40 ?).
$B=1\ ^1P$? curve 13′, 14, 15′.
$C=2\ ^3P=$curve 13 ($\Delta\nu=2$ and 2 ?).
$D=3\ ^3P$? no vibration known.

N_2^+
$X'=1\ ^2S=$curve 16′.
$A'=2\ ^2S=$curve 16.

O_2
$X=$? =curve 20′.
$A=$? =curve 19.
$B=$? =curve 20.

O_2^+
$X'=1\ ^2P=$curve 18′ ($\Delta\nu=$about 200)
$B'=1\ ^2D=$curve 18 ($\Delta\nu=?$).

NO
$X=1\ ^2P=$curve 1′, 2′ ($\Delta\nu=121$).
$A=1\ ^2S=$curve 2, 17′.
$B=1\ ^2D=$curve 1 ($\Delta\nu=33$).
$C=$? =curve 17.

The known band systems connected with these electronic levels are

CO
$A-X$ Fourth positive group of carbon.
$a-X$ Cameron CO bands.
$B-A$ Angstrom CO bands.
$b-a$ Third positive group of carbon.

CO+
$A'-X'$ Comet-tail bands.
$B'-X'$ First negative group of carbon.
$B'-A'$ "Combination" bands of Baldet-Johnson.

N_2
$A-X$ Predicted ultra-violet bands of nitrogen.
$B-A$ First positive group of nitrogen.
$C-B$ Second positive group of nitrogen.
$D-B$ Fourth positive group of nitrogen.

N_2^+
$A'-X'$ First negative group of nitrogen.

O_2
$A-X$ Atmospheric bands of oxygen.
$B-X$ Schumann-Runge bands of oxygen.

O_2^+
$B'-X'$ First negative (ultra-violet) bands of oxygen.

NO
$A-X$ Third positive group (γ bands) of nitrogen.
$B-X$ β bands of nitrogen.
$C-A$ Ultra-violet bands of nitrogen.

reviewed by Franck([188]). The iodine band system is precisely like that given by the Schumann-Runge O_2 bands (transition $B-X$ of O_2 in Figure 26. Curves 20 and 20′ of Figure 12). The nuclear binding is far weaker in the initial (excited) state than in the final state and, as discussed in Section 4, such a condition allows a large change in the value of the vibrational quantum number n, when light is absorbed. Thus, starting with the cold gas, for which $n''=0$, one may obtain by absorption of light, values of n' corresponding to $\omega^n=0$, or even larger. In other words, the set of *absorption* bands ($0-1$, $0-2$, $0-3$, etc.) can be followed in the spectrum until it is no longer possible to separate them. Then, just beyond the last resolvable band, continuous absorption sets in. Dymond([189]) has shown clearly that the absorption of light of any part of this continuous spectrum corresponds to dissociation of the molecule. Now the long wave-length limit of this region is equivalent to 2.47 ± 0.01 volts;[171] but the chemically measured heat of dissociation of iodine is only 1.5 volts. Franck([188]) and Dymond([189]) explain this as due to the fact that the iodine molecule, when in an electronic excited condition, dissociates into one normal and one excited atom. The excited atom in this case must possess about one volt of energy, and Franck([188]) gives evidence that the lower level of the iodine atom is in fact a double P level of about one volt separation.[172] Hence the excited iodine atom is in a metastable P state.

These results have been extended by Birge and Sponer([187]). The probable form of the $\omega^n : n$ curve, for non-polar molecules, has been discussed in Section 4. In the case of the *normal* state of the molecule, the $\omega^n : n$ curve is *always strictly linear,* within the experimental range. Its linear extrapolation to the point $\omega^n=0$ gives an area which should measure the heat of dissociation of the molecule, providing the extrapolation is correct, and assuming that the molecule dissociates into two normal atoms. The numerical results obtained by Birge and Sponer([187]) could be checked with each other and also with various chemical data and seemed to indicate the validity of these assumptions.

When the molecule is in an electronic excited state, one cannot predict the products of dissociation. The limiting values of the vibrational plus electronic energy, are, however, often almost identical with the limiting value of the vibrational energy of the normal state, as indicated in Figure 26. In all such cases it is significant that at least one oxygen atom is

[171] One volt = 23,070 gram calories per gram mol.

[172] Turner (Phys. Rev. 27: 397, 1926) has since found a recurring doublet separation of 7600 cm^{-1} (0.94 volts) in the arc spectrum of iodine, and uses this to obtain as a more accurate value of the heat of dissociation of iodine, $2.47 - 0.94 = 1.53$ volts.

present in the molecule. Now the lower level of the oxygen atom has been shown by Hopfield([190]) to be a triple P level, of 0.01 and 0.02 volts spacing. Hence, if the products of dissociation include an excited oxygen atom in one of these metastable P states (in analogy with iodine), the extra energy (0.02 or 0.03 volts) would be too small to recognize. Thus, from the "B" level of O_2, one obtains, with great accuracy, a total energy for dissociation of 7.05 volts. The first level of the oxygen atom above the valence P level represents 9.1 volts excitation. Therefore the products of dissociation, in the case of this excited molecule, must be neutral oxygen atoms, or, at the most, oxygen atoms in these very low-lying metastable P states; and the true heat of dissociation must be 7.02 ± 0.05 volts. The extrapolation of the $\omega^n : n$ curve for the "X" normal level of O_2 gives 6.65 volts, and this indicates the probable error of such an extrapolation.

In the case of NO, the extrapolated energy value for state "A" is greater than the most probable value of the actual heat of dissociation (8.3 volts) by 8.9 volts. In this case it thus appears likely that one of the products of dissociation is an oxygen atom in the 9.1 volt excited state.

The value of the heat of dissociation of nitrogen has been assumed by Sponer([178]) as 11.4 volts. This is the energy of "active nitrogen" [see Birge([186]) and ([191])], corresponding to $n=11$ of state "B" of N_2, as indicated on Figure 26. Sponer assumes that this amount of energy is released by the *association* of two neutral nitrogen atoms, in a three-body collision. The long-discussed question of the identity of active nitrogen does not properly concern the present report; but it may be noted that this value of 11.4 volts checks with other evidence, as discussed by Birge and Sponer([187]). Other values of heats of dissociation obtained in this work are: CO, 10.8 volts; CO^+, 9.8 volts; N_2^+, 9.1 volts; O_2^+, 6.5 volts; NO, 8.3 volts. All of these are uncertain to 0.5 volts.[173]

[173] In this connection, attention may be called to the fact that there is a close relation between heats of dissociation and ionization potentials. Thus, if a neutral molecule AB dissociates into two neutral atoms A and B, and the ionized molecule AB^+, into A and B^+, then the change from AB into $A+B^+$, may occur (at least hypothetically) in two different ways, but the total energy must be the same since the initial and final products are the same. Thus, if

$$AB \xrightarrow{I_m} AB^+ \xrightarrow{D'} A + B^+,$$

and

$$AB \xrightarrow{D} A + B \xrightarrow{I_a} A + B^+,$$

then

$$I_m + D' = D + I_a. \tag{201}$$

In the case of CO, all four quantities have been determined independently, if

We pass now to another topic, that of the theoretical distribution of intensity among the bands of a given system. This question has already been discussed empirically in Section 4, where it was pointed out that the distribution of intensity was very definitely correlated with the change in the frequency of vibration, or of the moment of inertia, of the molecule which occurred at the instant of emission of the radiation. Franck([188]) in his discussion of the photo-chemical activity of molecules, gives a purely mechanical explanation of the correlation of large possible changes of vibrational quantum number, with large changes of the moment of inertia, pointed out in Section 4. This theory has since been extended and tested by Condon([193]) and is, briefly, as follows: In the case either of electronic impact or of light absorption, the electronic jump in the molecule presumably takes place almost instantaneously, compared to the slow vibration of the nuclei. If the gas is initially cold and so in its normal state with no vibration, and if the electronic jump results in a greatly changed strength of binding (and hence of a greatly changed moment of inertia) the two nuclei originally in equilibrium, suddenly "find themselves" far from equilibrium, and hence possessed of a large amount of potential energy. This energy immediately sets up a vibration, and this may be great enough to dissociate the molecule. Such a condition seems to exist in the iodine and in the Schumann-Runge oxygen bands, and explains the region of continuous absorption at the short wave-length limit of these band systems.

The Franck explanation, according to Condon's results, undoubtedly explains the correlation of large change of n with large change of I_0. It is, however, necessary to assume other factors, in order to obtain the entire observed intensity distribution. Thus, if a gas is initially cold, with all the molecules in the state $n''=0$, Franck's explanation would give only one possible value of n'. This value would be $n'=0$ for infra-red bands, for which there is no electron transition. But the intensity

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one assumes that the dissociation of CO^+ gives C and O^+. Equation (201) using the results of Birge and Sponer([187]) becomes

$$14.2+9.8=10.8+13.56, \quad \text{or} \quad 24.0=24.36.$$

The discrepancy is well within the limits of error. Similarly, equation (201) can be used to calculate any one of the four quantities, if the other three are known, and the value of the ionization potential of O_2 ($I_m=14.1$ volts) used in plotting Figure 26 was obtained by this indirect method. It should be recalled that, as indicated in note g' of Section 7, the n numbering of the X' level of O_2^+ should probably be raised several units, and additional vibrational levels added *below* that marked $n=0$. The true value of I_m would then be *less* than 14.1 volts (and the value of D' *more* than 6.5 volts) by just these added levels, and hence more in accord with the value of 13 volts for I_m recently obtained by Hogness and Lunn([192]). All of the above relations are discussed fully by Birge and Sponer([187]).

distribution for such bands (0−1, 0−2, 0−3) is at least qualitatively that expected on the correspondence principle. In the case of the β bands of NO, as observed in the active nitrogen afterglow (see Figure 15) $n'=0$ for the initial state of nearly all the molecules, but n'' has a range from 3 to 14. Hence we may assume that the Franck explanation gives the *most probable transition* (i. e., most probable value of Δn) with the neighboring values of Δn possible, but less probable. It is difficult at present to see how such an explanation can be correlated with the work of Lenz([86]), as discussed in Section 4, but the new treatment undoubtedly brings out significant relations that the older treatment did not. Much more experimental data are needed, especially of a quantitative nature, in order to reach a definite conclusion.

One of the phenomena which was left unexplained, in the earlier sections, is that of the alternating intensities in lines emitted by essentially symmetrical diatomic molecules. Slater([194]) has recently suggested the following explanation. If a diatomic molecule is perfectly symmetrical, two positions of the molecule differing by 180° in phase cannot be distinguished. Hence the correct period for the $\int pdq=jh$ may be 0 to π, instead of 0 to 2π. On that hypothesis, the angular momentum is restricted to 0, 2, 4, etc., Bohr units. In other words, alternate rotational energy levels of the older scheme are missing. This is exactly the apparent situation in the case of the He_2 and the atmospheric and the Runge oxygen bands. In the case of the N_2^+ bands, the alternate levels give weaker lines, indicating merely a smaller *a priori* probability. Slater notes that there must be some transition from exactly symmetrical to entirely non-symmetrical molecules, given by a change of *a priori* probability of the alternate levels from zero to the normal value.

It might be thought that the alternate strong lines were due to changes of two units in the rotational quantum number, instead of the usual one unit change. The two similar poles (nuclei) of a symmetrical molecule would give an electric field fluctuating at twice the fundamental frequency of the rotator. By Bohr's correspondence principle this would permit $\Delta j=\pm 2$, in addition to ± 1. In the special case of $B'=B''$, the new spectral lines thus possible would coincide with alternate old lines, but would be placed symmetrically with respect to the *origin* of the band. This, however, is contrary to fact. The stronger lines *never* correspond to symmetrical *transitions* (such as 2→1 and 1→2) but *always* to the *same* initial (or final) *state*, such as 2→1 and 2→3. Actually B' is never equal to B'' and the new lines would not coincide with any of the old. Hence this second explanation is quite untenable.

We may appropriately close this section with a very brief reference to Mulliken's recent results in systematizing electronic bands (references

183, 184, 185, 185A, 185B, 185C). Particular results of this work have already been noted at various places in the present chapter. The general results are as follows:

Following Birge(180), a definite designation is given to each electronic level, similar to that in the case of atoms. The *resultant electronic* momentum correlated with each such level is denoted by s [$=\sqrt{\epsilon^2+\sigma^2}$ in terms of the Kramers and Pauli formula, equation (20)]. This s is substantially identical with Sommerfeld's inner quantum number j for the corresponding atomic energy level.[174] In some cases, however (i. e., CH) each atom may have its own individual s, uncombined with that of the other atom. Although the vector s, according to the Kramers and Pauli formula, may form any angle with the vector m (giving the nuclear momentum), the actual tendency is for s to be nearly parallel to m (making ϵ the chief component) or nearly perpendicular to m (making σ the chief component).

Since, according to Sommerfeld, j has integral values for atoms with an even number of valence electrons, and half-integral values for atoms with an odd number, the same situation is postulated for the " corresponding " molecule. This gives the value of s for the molecule. The *resultant* angular momentum of the *entire* molecule is, however, given by j, the vector sum of s and m. In the very common case that s and m are essentially parallel (σ=zero or very small), it is known that m has half-integral values. Hence, there results the rule that j has *integral* values for molecules with an *odd* number of electrons, and half-integral values for those with an even number. Mulliken. postulates this as a general rule, independent of the mutual direction of s and m. Hence m has essentially half-integral values only for special types of bands.

$\Delta j=0$, or ± 1, only, and the actual occurrence of the corresponding Q, P, and R branches is determined by the correspondence principle. This is the usual selective principle for the inner quantum number j of line spectra. On the other hand, as emphasized also by Birge(180), the selective principle for the azimuthal quantum number k does not operate in the case of molecules (possibly due to the fact that the second atom of a molecule causes a strong electric field acting like a Stark effect in the case of a single atom). Thus, transitions from S to S orbits are freely permitted, as in the case of the violet CN bands, and the first negative groups of carbon and of nitrogen. Each transition from a given type of electronic orbit to another given type, results in an electronic band system of a definite structure. Hence, all band systems between similar types of electronic levels have identical structure, and it is hoped,

[174] See Sommerfeld " Atombau " 4th edition pp. 575-594.

in the near future, to be able to state the character of the initial and final levels, from the observed band structure, just as now can be done for atomic lines, from the observed complex Zeeman effect.

Mulliken, as a result of the above ideas, has already reached rather definite conclusions as to the value of j and of s (and even of ϵ and σ separately) for most of the known band systems. It is hardly possible, as yet, to give a critical estimate of these conclusions, except in certain specific cases, as already discussed earlier in the chapter. The writer believes, however, that they are substantially correct and that this work marks a distinct advance in the theoretical interpretation of molecular spectra.

CONCLUSION

The results presented in this and preceding chapters of the report, show that the observed relationships found in molecular spectra can be used to obtain a considerable amount of information, quantitative as well as qualitative, regarding the structure of certain types of molecules. Certain discrepancies still remain, and some at least are likely to augment in number, rather than diminish, with increased experimental data. Similar discrepancies are known to exist in the case of atoms, and although they often are very small, numerically, they are of such a fundamental character that there is now a wide-spread conviction that it is necessary to re-formulate the fundamental postulates of the quantum theory in such a way as to employ "quantum" rather than "classical" mechanics for the description of the stationary states. A notable beginning for such a system of quantum mechanics has recently been made by Heisenberg, Born, Jordan, and others; but as yet this new theory has not been developed to the point where it can be applied in any detail to the questions of molecular structure. For that reason, it has purposely been ignored in the preceding discussion. It must be remembered also that the difference between the new and the old mechanics, although very fundamental in character, is usually very small, numerically, and it is doubtful if the two could be distinguished save in exceptional cases, in the present state of knowledge regarding molecular spectra. For example, the values of ω^0 have been obtained, in Figure 12, by the extrapolation of the curves to $n=0$. It is probable that the new mechanics will indicate that a value of ω corresponding on the curves as now drawn to $n=-0.5$, should be used in the various formulas in place of our value of ω^0. The actual change in the value of ω would then be $x\omega$ of columns 6 and 8 of the table of Section 7.

It is thus most probable that some new form of mechanics must be employed, to obtain a consistent interpretation of molecular spectra; but

it is also probable that the general interpretation of such spectra presented in the preceding pages, and the numerical magnitudes of the various molecular constants quoted in Section 7, are at least essentially correct.[175]

[175] *Note added in proof.* The main object of this added note is to call attention to certain recent work which contradicts or modifies statements made in Chapter IV. No attempt is made to discuss in a general way work which has appeared during the printing of this report.

Sponer (Nature, 118: 696, 1926) has obtained the absorption spectrum of the nitrogen molecule, using Hopfield's vacuum spectrograph. The spectrum consists of two progressions of bands, one stronger than the other. The strong progression is merely the $n'' = 0$ progression of the ultra-violet bands of nitrogen, analyzed by Birge and Hopfield([78]), and extends this system to $n' = 10$ (as compared to $n' = 3$ of curve 17 of Figure 12). More accurate measurements of the γ bands of NO, by Sponer and Hopfield (unpublished) show that the identity assumed by Sponer([66]) for the vibrational intervals of these two systems (curve 2, 17′ of Figure 12) is not true. The revised data for the γ bands are given in Section 7. Still later work by Hopfield and the writer (unpublished) has shown that these nitrogen bands form the true resonance system of nitrogen and correspond in every way to the fourth positive group of carbon, the resonance system of CO. Level C of NO, in Figure 26, is therefore spurious, and with its removal there disappears the only evidence in favor of double electron jumps in molecules. The vibrational levels of state X of N_2 are, however, now known (i. e., the plotted level A of NO, of Figure 26, or curve 17′ of Figure 12) and the extrapolation to $\omega'' = 0$ gives 11.75 volts for the heat of dissociation. This is a direct confirmation of Sponer's assumption as to the identity of active nitrogen (giving $D = 11.4$ volts) and in the opinion of the writer, makes this assumption practically a certainty.

On the other hand, the recent work by Hopfield and the writer shows that the *weak* absorption bands obtained by Sponer occur in the *discharge tube* and *not* in the vacuum spectrograph (which was filled with nitrogen for this work), and accurate measurements show that they are merely the known absorption bands of CO, evidently occurring as an impurity in the discharge. It seems probable at the present time that levels A, B, C, and D, of N_2, in Figure 26, represent the triplet system (small letter levels of CO) while the initial and final levels of the ultra-violet bands represent the singlet system. As in the case of CO, transitions between these two systems are not in general to be expected. The A-X transition of N_2 thus corresponds to the a-X transition of CO and may possibly be obtained by mixing nitrogen with neon.

In Figure 26, four vibrational levels are shown for level b of CO. As recorded in note i* of Section 7, these are spurious, according to Wolter([75]). Duffendack and Fox (Nature, 118: 12, 1926) have, however, shown that the $n' = 4$ level is actually the $n' = 0$ level of a new system of CO bands, which they call the 3A bands. This system is accordingly given by

$$\nu = 43{,}556 - (1724.78n'' - 14.47n''^2)$$

and thus locates a new electronic level of CO at 92,086 cm^{-1} in Figure 26. The $n' = 0$ and 1 levels of the third positive group of carbon may be real, and give the single value of ω' (2214) listed in Section 7. In a later article, Duffendack

BIBLIOGRAPHY

[1] Kayser, Handbuch der Spectroscopie, 2:470-495 (1902) (general).
[2] Baly, Spectroscopy, 1912 ed., pp. 612-623 (general).
[3] Konen, Das Leuchten der Gase und Dampfe, pp. 199-278, 313-318 (1913) (general).
[4] Kratzer, Ergebnisse der exakten Naturwiss., 1:315-334 (1922) (general, quantum theory).
[5] Hulthén, Physica, 1:365-376 (1921) (general, quantum theory).
[6] Fortrat, J. phys. radium, (6) 5:33-50 (1924) (general, quantum theory).
[7] Sommerfeld, Atombau, 4th ed., Chap. IX (1924) (general, quantum theory).
[8] Dieke, Physica, 4:193-218 (1924) (general, quantum theory).
[9] Mecke, Physik. Z., 26:217 (1925) (general, quantum theory).
[10] Deslandres and d'Azambuja, Compt. rend., 157:671 (1913) (nitrogen, second group).
[11] Lindau, Z. Physik., 26:343 (1924) (nitrogen, second group).
[12] Mecke, Ann. Physik, 71:104 (1923) (iodine).

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and Fox (Science, 64:277, 1926), by measurement of excitation potentials, obtain a beautiful confirmation of the entire energy level scheme of CO, as given in Figure 26. See also Ann B. Hepburn, Phys. Rev., N. S., 29:212 (1927).

Hulthén, in an article on "The Bandspectrum of Calcium Hydride," Phys. Rev., N. S., 29:97 (1927), obtains several new systems of bands, all having the same final state. This final level is assumed to be a ^2S state, while the new initial electronic states are believed to be $^2P_1$, $^2P_2$, and another ^2S state. The double system of ZnH, CdH, and HgH bands listed in Section 7 forms probably the $^2S - {}^2P$ transition, and the corresponding CaH bands are quite similar in structure.

Jenkins, Barton, and Mulliken (Phys. Rev., N. S., 29:211 (1927) have photographed the β bands of NO under high dispersion and have obtained the quantum analysis. Their preliminary values of the moment of inertia for each of the two electronic levels of initial and final state are given in Section 7. The values of I''_0 must apply also to the γ bands, as these have the same final state. The fine-structure analysis of the β bands indicates that level B of NO, in Figure 26, is a ^2P level, instead of a ^2D level, as given in the caption of that figure. This is the first proved case of a $P - P$ transition in band spectra, although $S - S$ transitions seem quite common (i. e., violet CN bands, first negative group of carbon, first negative group of nitrogen, etc., according to the interpretation of Mulliken[49]). The intensity relations in various types of spectra, as predicted by the correspondence principle, are discussed by Mulliken in a companion paper (Phys. Rev., N. S., 29:211 (1927).

In addition to the references already quoted on the subject of the correspondence of the electronic levels in atoms and molecules, we may list a paper by Mecke (Z. Physik, 36:795, 1926), discussing particularly the doublet levels in various hydride and oxide molecules. The very important theoretical paper by Hund (Z. Physik, 36:657, 1926) on the general subject of molecular structure is discussed fully in Chapter VII, Section 5, of this report.

[13] Colby, Meyer and Bronk, Astrophys. J., 57:7 (1923) (HCl).
[14] Fowler and Strutt, Proc. Roy. Soc., 85A:377 (1911) (nitrogen, and active nitrogen).
[15] Birge, Phys. Rev., N. S., 23:294 (1924) (nitrogen).
[16] Hulthén and Johansson, Arkiv. Mat. Astron. Fysik, 18 (1924) (nitrogen, second group).
[17] Hulthén and Johansson, Z. Physik, 26:308 (1924) (nitrogen, second group).
[18] Mecke and Lindau, Physik. Z., 25:277 (1924) (nitrogen, second group).
[19] Birge, Astrophys. J., 39:50 (1914) (nitrogen, first group).
[20] Fortrat, These, Paris (1914) (Zeeman effect and general).
[21] Mulliken, Nature, 113:489 (1924) (CuH).
[22] Mulliken, Phys. Rev., N. S., 25:509 (1925) (CaH).
[23] Birge, Astrophys. J., 46:85 (1917) (Deslandres' laws, A_1 series λ3883 CN).
[24] Thiele, Astrophys. J., 6:65 (1897) and 8:1 (1898) (theory).
[25] Frerichs, Z. Physik, 20:170 (1923) (CuH).
[26] Fowler, R. H., Phil. Mag., 49:1272 (1925) (theory of intensity).
[27] Dieke, Nature, 115:875 (1925); Z. Physik, 33:161 (1925) (intensity, theory).
[28] Strutt and Fowler, Proc. Roy. Soc., 86A:105 (1912) (CN, etc., in active nitrogen).
[29] Birge, Astrophys. J., 55:273 (1922) (intensity and temperature).
[30] Dieke, Proc. Acad. Sci. Amsterdam, 27:490 (1924) (hydrogen).
[31] Kiuti, Proc. Phys. Math. Soc. Japan, 5:9 (1923) (hydrogen).
[32] Allen, Proc. Roy. Soc., 106A:69 (1924) (hydrogen).
[33] Richardson and Tanaka, Proc. Roy. Soc., 106A:663 (1924) (hydrogen).
[34] Curtis, Proc. Roy. Soc., 107A:570 (1925) (hydrogen).
[35] Curtis, Proc. Roy. Soc., 101A:38 (1922) (helium).
[36] Birge and Shea, Phys. Rev., N. S., 24:206 (1924), Univ. of California, Pub. in Math. vol. 2, No. 5 (1926) (least squares).
[37] Birge, Phys. Rev., N. S., 11:136 (1918) (C_1 series, λ3883 CN).
[38] Heurlinger, Dissertation, Lund (1918) (general).
[39] Bachem, Z. Physik, 3:372 (1920) (Zeeman effect, CN).
[40] Kratzer, Sitzb. math.-physik. Klasse Baeyer. Akad. Wiss. München, 1922:107 (half-quantum numbers, CN).
[41] Kratzer, Naturwissenschaften, 11:577 (1923) (theory).
[42] Hulthén, Dissertation, Lund (1923) (C+H, etc.).
[43] Kratzer, Ann. Physik, 71:72 (1923) (HgH, CdH, ZnH, CN, and theory).

[44] Hulthén, Ann. Physik, 71: 41 (1923) (Angstrom CO bands).
[45] Watson, Astrophys. J., 60: 145 (1924) (OH).
[46] Blackburn, Proc. Nat. Acad. Sci., 11: 28 (1925) (first negative group of carbon).
[47] Mulliken, Phys. Rev., N. S., 25: 259 (1925) (BO, isotopes).
[48] Baldet, Compt. rend., 180: 271, 820 (1925) (comet-tail bands).
[49] Mulliken, Phys. Rev., N. S., 26: 561 (1925) (multiplicities, emitters of bands).
[50] Liese, Z. wiss. Phot., 11: 349 (1912) (HgH).
[51] Mulliken, Phys. Rev., N. S., 25: 119 (1925) (isotopes, theory).
[52] Deslandres and d'Azambuja, Compt. rend., 157: 814 (1913) (OH, Zeeman effect).
[53] Kratzer, Z. Physik, 23: 298 (1924) (C+H).
[54] Mecke, Z. Physik, 28: 261 (1924) (systematization of bands).
[55] Fortrat, Compt. rend., 157: 991 (1913); Compt. rend., 158: 334 (1914); Ann. phys., 3: 282 (1915) (Zeeman effect, etc.).
[56] Kramers and Pauli, Z. Physik, 13: 351 (1923) (theory).
[57] Kratzer, Z. Physik, 3: 289 (1920) (theory, HCl).
[58] Boguslawski, Physik. Z., 15: 569 (1914) (theory).
[59] Dieke, Z. Physik, 31: 326 (1925) (N_2^+ theory).
[60] Birge, Nature, 116: 207 (1925) (CO^+ groups).
[61] Kratzer, Ann. Physik, 67: 127 (1922) (CN and theory).
[62] Kemble, J. Optical Soc. Am., 12: 1 (1926) (HCl, law of force and heat of dissociation).
[63] Pfund, J. Optical Soc. Am., 9: 193 (1924) (nitrogen, first group).
[64] Ames, Phil. Mag., 30: 48 (1890) (nitrogen, second group).
[65] Jevons, Proc. Roy. Soc. 106A: 174 (1924) (silicon oxide).
[66] Sponer, Nature, 117: 81 (1926) (NO).
[67] Heurlinger, Z. Physik, 1: 82 (1920) (theory).
[68] Birge, Phys. Rev., N. S., 25: 240 (1925) (intensity distribution).
[69] Schniederjost, Z. wiss. Phot., 2: 265 (1904) (γ bands, nitrogen).
[70] Johnson, Proc. Roy. Soc., 108A: 343 (1925) (carbon groups).
[71] Birge, Nature, 116: 171 (1925) (carbon groups).
[72] Birge, Nature, 117: 229 (1926); Phys. Rev., N. S., 28: 1157 (1926) (CO groups).
[73] Fowler, A., Mon. N. Roy. Astron. Soc., 70: 484 (1910) (CO bands).
[74] Merton and Johnson, Proc. Roy. Soc., 103A: 383 (1923) (carbon groups).
[75] Wolter, Z. wiss. Phot., 9: 361 (1911) (carbon, third positive group).
[76] Deslandres, Ann. chim. phys., (6) 15: 5 (1888) (carbon, third positive group).
[77] Fassbender, Z. Physik, 30: 73 (1924) (N_2^+).

[78] Birge and Hopfield, Nature, 116:15 (1925) (ultra-violet group of nitrogen).
[79] Johnson, Proc. Roy. Soc., 105A:683 (1924) (O_2^+).
[80] Runge, Physica, 1:254 (1921) (oxygen group).
[81] Kratzer, Z. Physik, 26:40 (1924) (theory).
[82] Tartakowsky, Z. Physik, 24:98 (1924) (theory).
[83] Mulliken, Phys. Rev., N. S., 26:1 (1925) (CuI, isotopes).
[84] Datta, Phil. Mag., 48:673 (1924) (nitrogen, first group, theory).
[85] Hagenback and Mörikofer, Arch. phys. nat., (5) 3:301 (1921) (aluminum).
[86] Lenz, Z. Physik, 25:299 (1924) (intensity, theory).
[87] Wood, Phil. Mag., 26:828 (1913) and 35:236 (1918) (iodine, resonance).
[88] Rayleigh, Proc. Roy. Soc., 102A:453 (1923) (nitrogen, first group).
[89] Heurlinger, Physik. Z., 20:188 (1919) (original quantum theory).
[90] Lenz, Verh. deut. physik. Ges., 21:632 (1919) (original quantum theory).
[91] Shea, Phys. Rev., N. S., 25:716 (1925) (Swan bands).
[92] Baldet, Compt. rend., 178:1525 (1924). *See also* Nature, 116:360 (1925) (new CO^+ bands).
[93] Kemble, Phys. Rev., N. S., 8:689 (1916) (intensity, theory).
[94] Birge, Nature, 111:811 (1923) (value of "h").
[95] Bengtsson, Z. Physik, 20:229 (1923) (CuH).
[96] Birge, Nature, 116:783 (1925) (law of force from rotation).
[97] Pomeroy and Birge, Phys. Rev., N. S., 27:107 (1926) (AlO bands).
[97A] Pomeroy, Phys. Rev., N. S., 27:640 (1926); Phys. Rev., N. S., 29:59 (1927) (AlO bands).
[98] Shea and Birge, Phys. Rev., N. S., 27:245 (1926) (Swan bands).
[99] Birge, Phys. Rev., N. S., 27:245 (1926) (molecular constants).
[100] Hulthén, Z. Physik, 11:284 (1922) (HgH).
[101] Hulthén, Z. Physik, 32:32 (1925) (HgH).
[102] Birge, Phys. Rev., N. S., 25:240 (1925) (Hg and CN doublets).
[103] Ludloff, Z. Physik, 34:485 (1925) (HgH).
[104] Dieke, Physica, 5:178 (1925) (CN doublets).
[105] Dieke, Nature, 115:194 (1925) and Proc. Acad. Sci. Amsterdam, 28:174 (1925) (OH).
[106] Birge, Phys. Rev., N. S., 25:240 (1925) (OH).
[107] Watson, Nature, 117:157 (1926) (OH satellites).
[108] Zeit, Z. wiss. Phot., 21:1 (1921) (nitrogen, λ3371).
[109] Heurlinger and Hulthén, Z. wiss. Phot., 18:241 (1919) (C+H).
[110] Mecke, Z. Physik, 31:709 (1925) (N_2^+).
[111] Kratzer, Z. Physik, 16:353 (1923) (helium).

[118] Toussaint, Z. Physik, 19: 271 (1923) (nitrogen, intensity).
[118] Curtis, Proc. Roy. Soc., 103A: 315 (1923) (helium).
[114] Curtis and Long, Proc. Roy. Soc., 108A: 513 (1925) (helium).
[115] Curtis, Proc. Roy. Soc., 89A: 146 (1913) (helium).
[116] Fowler, A., Proc. Roy. Soc., 91A: 208 (1915) (helium).
[117] Mecke, Physik. Z., 25: 597 (1924) (intensity anomalies).
[118] Fulcher, Astrophys. J., 37: 60 (1913) (hydrogen).
[119] Merton and Barratt, Trans. Roy. Soc. London, 222A: 369 (1922) (hydrogen).
[120] Gehrcke and Lau, Sitzb. preuss. Akad. Wiss., 1922: 453 (hydrogen).
[120A] Bury, Phil. Mag., 50: 1139 (1925) (hydrogen).
[121] Croze, Ann. phys., (9) 1: 35 (1914) (hydrogen).
[122] Dieke, Z. Physik, 32: 180 (1925) (hydrogen). *See also* Phil. Mag., 50: 173 (1925).
[123] Gehrcke and Lau, Sitzb. preuss. Akad. Wiss., 1923: 242 (hydrogen).
[124] Gehrcke and Lau, Ann. Physik, 76: 673 (1925) (hydrogen).
[125] Richardson and Tanaka, Proc. Roy. Soc., 107A: 602 (1925) (hydrogen).
[126] Takahashi, Japan. J. Physics, 2: 95 (1923) (molecular structure).
[127] Richardson, Proc. Roy. Soc., 108A: 553 (1925) (hydrogen). *Also* 109A: 35, and 239 (1925); 111A: 714 (1926); *also,* Nature, 118: 116 (1926) (hydrogen).
[128] Tanaka, Proc. Roy. Soc., 108A: 592 (1925) (hydrogen).
[129] Sandeman, Proc. Roy. Soc., 108A: 607 (1925) and 110A: 326 (1926) (hydrogen).
[129A] Nicholson, Mon. N. Roy. Astron. Soc., 85: 449 (1925) (hydrogen).
[129B] Curtis, Phil. Mag., (7) 1: 695 (1926) (hydrogen).
[130] Kemble and Van Vleck, Phys. Rev., N. S., 21: 653 (1923) (hydrogen, specific heat).
[131] Tolman, Phys. Rev., N. S., 22: 470 (1923) (hydrogen, specific heat).
[131A] Dieke, Physica, 5: 412 (1925) (hydrogen, specific heat).
[132] Allen, Proc. Roy. Soc. Edinburgh, 43: 180 (1923) (H_2 model).
[133] Born, Naturwissenschaften, 10: 677 (1922) (H_2 model).
[134] Eucken, Naturwissenschaften, 10: 533 (1922) (H_2 model).
[135] Marshall, Proc. Roy. Soc. Edinburgh, 42: 247 (1922) (H_2 model).
[136] Niessen, Ann. Physik, 70: 129 (1923) (H_2 model).
[136A] Nordheim, Z. Physik, 19: 69 (1923) (H_2 model).
[137] Pauli, Ann. Physik, 68: 177 (1922) (H_2 model).
[138] Urey, Proc. Nat. Acad. Sci., 11: 618 (1925); Phys. Rev., N. S., 27: 216 (1926) (H_2^+ model).
[139] Goos, Z. Physik, 31: 229 (1925) (hydrogen, intensity).

[140] McLennan and Schrum, Trans. Roy. Soc. Canada, (3) 18: 177 (1924) (hydrogen, intensity).
[141] Kemble, Phys. Rev., N. S., 8: 701 (1916) (harmonic bands).
[142] Duffendack, Astrophys. J., 60: 122 (1924) (H_2, critical potentials).
[142A] Witmer, Proc. Nat. Acad. Sci., 12: 238 (1926) (H_2 and theory).
[143] Kemble, Phys. Rev., N. S., 21: 713 (1923) (intensity theory).
[144] Kemble, Proc. Nat. Acad. Sci., 10: 274 (1924) (intensity theory).
[145] Kemble, Phys. Rev., N. S., 25: 1 (1925) (intensity theory).
[146] Fermi, Physica, 4: 340 (1924) (intensity in Zeeman effect).
[147] Heisenberg, Z. Physik, 31: 617 (1925) (correspondence principle).
[148] Burger and Dorgelo, Z. Physik, 23: 258 (1924) (intensity, multiplets).
[148A] Hönl and London, Z. Physik, 33: 803 (1925) (intensity of Q branch).
[149] Kemble, Z. Physik, 35: 286, 1925 (intensity theory).
[150] King, Astrophys. J., 53: 161 (1921) (CN in furnace).
[151] Lewis, Astrophys. J., 40: 148 (1914) (N_2, self-induction).
[151A] Hulthén and Zumstein, Phys. Rev., N. S., 28: 13 (1926) (hydrides).
[152] Bengtsson and Svensson, Compt. rend., 180: 274 (1925) (AgH).
[153] Erickson and Hulthén, Z. Physik, 34: 775 (1925) (AlH).
[154] Bengtsson, Arkiv. Math., Astron. Fysik, 18: (1924) (AuH).
[155] Mecke, Z. Physik, 32: 823 (1925) (compiled data and relations).
[156] Datta, Proc. Roy. Soc., 101A: 187 (1922) (BeF).
[157] Glaser, Ann. Physik., 68: 73 (1922) (BeO).
[158] Kayser, Handbuch der Spectroscopie, 5: 226 (1910) (Swan bands).
[159] Kayser, Handbuch der Spectroscopie, 5: 227 (1910) (Angstrom CO bands).
[160] McLennan, Smith and Peters, Trans. Roy. Soc. Canada, (3) 19: 39 (1925) (Angstrom CO bands).
[161] Schaefer and Thomas, Z. Physik, 12: 330 (1923) (CO, infra-red).
[162] Lowry, J. Optical Soc. Am., 8: 647 (1924) (CO, infra-red).
[162A] Jassé, Compt. rend., 182: 692 (1926) (Angstrom CO bands).
[162B] Cameron, Phil. Mag., 1: 405 (1926) (New CO bands).
[162C] Johnson, Nature, 117: 376 (1926) (CO bands).
[163] Hulthén, Nature, 116: 642 (1925) (ZnH, CdH, HgH).
[164] Colby, Astrophys. J., 58: 303 (1923) (HCl).
[165] Watson, Phys. Rev., N. S., 25: 887 (1925) (LiH).
[166] Smith, Proc. Roy. Soc., 106A: 400 (1924) (Na_2, K_2, NaK).
[167] Watson and Rudnick, Astrophys. J., 63: 20 (1926) (MgH).
[168] Merton and Pilley, Phil. Mag., 50: 195 (1925) (N_2^+).
[169] Leifson, Astrophys. J., 63: 73 (1926) (extreme ultra-violet absorption spectra).
[170] Block, L. and E., Compt. rend., 158: 1161 (1914) (O_2 absorption).

[171] Duclaux and Jeantet, Compt. rend., 173: 581 (1921) (O_2 absorption).
[172] Füchtbauer and Holm, Physik. Z., 26: 345 (1925) (O_2 absorption).
[173] Hopfield and Leifson, Phys. Rev., N. S., 25: 716 (1925) (O_2 absorption).
[173A] Ellsworth and Hopfield, Phys. Rev., N. S., 27: 639 (1926), and Phys. Rev., 29: 79 (1927) (O_2^+ bands).
[174] Sleator and Phelps, Astrophys. J., 62: 28 (1925) (H_2O).
[175] Mulliken, Phys. Rev., N. S., 26: 319 (1925) (SiN, isotopes).
[176] Jevons, Proc. Roy. Soc., 110A: 365 (1926) (SnCl, isotopes).
[177] Born and Hückel, Physik. Z., 24: 1 (1923) (theory).
[177A] Duffendack, Astrophys. J., 61: 209 (1925) (energy levels).
[178] Sponer, Z. Physik, 34: 622 (1925) (N_2 excitation potentials and "active nitrogen").
[179] Olson and Glockler, Proc. Nat. Acad. Sci., 9: 122 (1923) (H and H_2 excitation potentials).
[180] Birge, Nature, 117: 300 (1926) (structure of molecules).
[181] Mecke, Naturwissenschaften, 13: 755 (1925) (electronic doublets).
[182] Sponer and Hopfield, Phys. Rev., N. S., 27: 640 (1926) (NO absorption bands).
[183] Mulliken, Proc. Nat. Acad. Sci., 12: 144 (1926) (systematic relations, I).
[184] Mulliken, Proc. Nat. Acad. Sci., 12: 151 (1926) (systematic relations, II, ZnH, CdH, HgH).
[185] Mulliken, Proc. Nat. Acad. Sci., 12: 158 (1926) (electronic states of He_2).
[185A] Mulliken, Proc. Nat. Acad. Sci., 12: 338 (1926) (molecule formation).
[185B] Mulliken, Phys. Rev., N. S., 28: 481 (1926) (systematic relations).
[185C] Mulliken, Phys. Rev., N. S., 28: 1202 (1926) (systematic relations).
[186] Birge, Nature, 114: 642 (1924) (nitrogen, and "active nitrogen").
[187] Birge and Sponer, Phys. Rev., N. S., 28: 259 (1926) (heats of dissociation from band spectra).
[188] Franck, Trans. Faraday Soc., 21: Part 3 (1925) (heats of dissociation and photo-synthesis).
[189] Dymond, Z. Physik, 34: 553 (1925) (iodine, and heat of dissociation).
[190] Hopfield, Astrophys. J., 59: 114 (1924) (oxygen atom energy levels).
[191] Birge, Nature, 117: 81 (1926) ("active nitrogen").
[192] Hogness and Lunn, Phys. Rev., N. S., 27: 642 (1926) (O_2 and O_2^+ ionization and dissociation).
[193] Condon, Phys. Rev., N. S., 27: 640 (1926) and 28: 1182 (1926) (intensity distribution).
[194] Slater, Nature, 117: 555 (1926) (alternating intensities in non-polar molecules).

CHAPTER V

THE ISOTOPE EFFECT

F. W. Loomis

SECTION 1. INTRODUCTION

Soon after the discovery of isotopic elements their line spectra were compared by a number of observers([2]) and found to be sensibly identical, as is to be expected in the light of present theories of atomic structure—since a line spectrum is believed to be emitted by electrons revolving about a nucleus which is nearly stationary and whose mass therefore cannot greatly affect their motion. The effect of the nuclear mass is not, however, entirely absent, even in line spectra, the most famous example being the minute differences between the wave lengths of certain lines of hydrogen and ionized helium which would exactly coincide if it were not for the differences in nuclear mass.

In this case, as in the most general case which can be treated as a two-particle problem, the masses of the particles, M and M', enter the equations only through the effective mass, $\mu = MM'/(M+M')$. It will be seen from this expression that the difference between the values of μ, corresponding to slightly different values of M, will be small if M' is small in comparison to M. Hence the possible values of μ in the case of line spectra, where M' is the mass of an electron and M that of a nucleus, differ very little; and, while the consequent wave length differences are measurable in the case of He *versus* H, they become less than the resolving power of spectroscopes for the isotopes of even comparatively light elements. The above argument is rigorous only for atoms with a single electron, but it seems probable that in atoms with several electrons their attractions of the nucleus more or less cancel each other, rendering its motion and hence the isotope effect even smaller than the above. However, Aaronberg([1]) and Merton([16]) have found differences between wave lengths of certain lines from isotopic samples of lead and thallium, which, while barely measurable, are nevertheless about eighty times as great as would be calculated on the basis outlined above. These differences have not been fully explained, but Bohr([7]) has suggested that they may be due to a difference in the structure of the nucleus affecting an electron which penetrates especially near it.

Realizing that much larger effects were to be expected in cases where the two particles are of more nearly equal mass, the writer in 1920 sought the effect among the spectra of isotopic molecules and found it

in the data of Imes on the absorption spectrum of HCl, where it was also noticed by Kratzer.

Recently Mulliken has worked with electronic spectra, where greater accuracy is possible and more spectra available, and has found and measured the theoretically predicted isotope effect in the spectra of BO, CuH, SiN, and CuI.

Detailed consideration of these cases will be postponed until a general theory of the isotope effect has been outlined in the next section.

SECTION 2. THEORY OF THE ISOTOPE EFFECT IN BAND SPECTRA

The isotope effect is measured by the isotopic displacement $\nu_2-\nu_1$, the difference in frequency between like numbered lines of the two isotopes, where the subscript 1 is used to denote the more abundant isotope, corresponding to the stronger lines. An expression for the isotopic displacement can be deduced by simply examining the way in which mass enters any theoretical expression for the frequency.

Just as in earlier chapters it was convenient to divide the frequency somewhat arbitrarily into electronic, vibrational, and rotational terms, $\nu=\nu^e+\nu^n+\nu^m$, where

$$\nu^e=\frac{E^{e'}-E^{e''}}{h},\qquad \nu^n=\frac{E^{n'}-E^{n''}}{h},\qquad \nu^m=\frac{E^{m'}-E^{m''}}{h},$$

it is here convenient to divide the isotope effect into electronic, vibrational, and rotational effects,

$$\nu_2-\nu_1=(\nu_2^e-\nu_1^e)+(\nu_2^n-\nu_1^n)+(\nu_2^m-\nu_1^m). \tag{1}$$

The Electronic Effect

The arguments advanced above as to the smallness of the isotope effect in line spectra apply with equal force to the electronic term in the isotope effect of band spectra, for this term $(\nu_2^e-\nu_1^e)$ depends upon the difference in energies of the two species in states where the nuclear vibration and rotation quantum numbers are zero, and hence where the nuclei are stationary except for slight unbalanced attractions of the electrons as in line spectra. It seems quite safe, then, to conclude that $\nu_2^e-\nu_1^e$ will in no case be much larger than the effect calculated for a hydrogen-like line spectrum, which is quite negligible in comparison with the rotational and vibrational effects treated below.

Consequently, since the vibrational and rotational displacements vanish when the vibrational and rotational terms do, the origins of band systems of a pair of isotopes must coincide. This furnishes a rigorous test, independent of other theory, for the correct location of origins.

Vibrational Effect

Equation (37) of Chapter II contains all the terms of importance for the isotope effect. Consider first the part which represents the vibrational energy

$$E^n = h n \omega_0 (1 - xn) \tag{2}$$

where

$$x = \frac{h}{4\pi^2 I_0 \omega_0} \left(\tfrac{3}{2} + \tfrac{1}{2}^5\, b + \tfrac{3}{2}\, c + \tfrac{1}{4}^5\, b^2 \ldots\right) \tag{3}$$

and is small. It will be seen, since b and c are constants of the potential energy function and hence do not contain the mass, that the mass enters only through I_0 and ω_0, which are proportional to μ and $\mu^{-\frac{1}{2}}$ respectively. Thus the first, or linear, term in E^n is proportional to $\mu^{-\frac{1}{2}}$ and the second, considerably smaller quadratic term, to μ^{-1}. The vibrational isotopic displacement can now be calculated by expressing separately the vibrational part of the frequencies emitted during a given transition by isotopes 1 and 2, and subtracting. Thus

$$\nu_1{}^n = \frac{E_1{}^{n'} - E_1{}^{n''}}{h} = [(\omega'_0)_1 n' - (\omega''_0)_1 n''] - [(\omega'_0)_1 x'_1 n'^2 - (\omega''_0)_1 x''_1 n''^2]. \tag{4}$$

Letting [1]

$$\rho = \sqrt{\mu_1/\mu_2}, \tag{5}$$

$\nu_2{}^n$ can be written as

$$\nu_2{}^n = \rho[(\omega'_0)_1 n' - (\omega''_0)_1 n''] - \rho^2[(\omega'_0)_1 x'_1 n'^2 - (\omega''_0)_1 x''_1 n''^2] \tag{6}$$

and

$$\nu_2{}^n - \nu_1{}^n = (\rho - 1)[(\omega'_0)_1 n' - (\omega''_0)_1 n''] - (\rho^2 - 1)[(\omega'_0)_1 x'_1 n'^2 - (\omega''_0)_1 x''_1 n''^2]. \tag{7}$$

For approximate purposes the second term can be neglected and the expression for the vibrational isotope effect becomes

$$\nu_2{}^n - \nu_1{}^n = (\rho - 1)\nu_1{}^n. \tag{8}$$

Equation 8 describes the chief characteristics of the vibrational isotope effect. The isotopic displacement is zero at the origin of a band system, where $\nu_1{}^n = 0$. If $\rho - 1$ is positive, the displacement will be positive on the high frequency side of the origin (ν^n positive) and negative on the low frequency side (ν^n negative). Corresponding band systems of two isotopes are identical in pattern of band origins, but differ in the scale of that pattern. This scale is greater, in the ratio ρ, for the lighter isotope, so that every band of the lighter isotope lies farther from the origin than the corresponding band of the heavier isotope. The distance $|\nu_2{}^n - \nu_1{}^n|$ between the origins of corresponding bands of two isotopes increases

[1] The notation follows Mulliken(88).

approximately linearly with the distance, ν^m, in either direction from the origin; and may reach fairly large values, since $\rho-1$ is commonly of the order of the magnitude of 1 per cent.

Figure 1 illustrates the characteristics of the vibrational isotope effect in a comparatively simple case in which the sequences do not overlap. Each vertical line represents the position, on a frequency scale, of the origin of a particular band, corresponding to the values n' and n'' indicated above it. The full lines indicate the more abundant isotope 1, the broken lines isotope 2. The situation pictured is much like that in the CuI bands, except that the magnitude of the isotopic displacement is exaggerated about fourfold.

Actual photographs of band spectra of course appear much more complicated than in Figure 1, due chiefly to the structure of the bands, and to the overlapping of band sequences on band systems. And, of

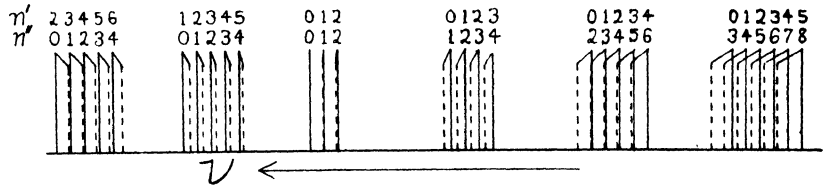


FIGURE 1.

course, it is the band heads and not the origins which strike the eye. In the spectra of compounds having more than two isotopes, each line will be split into a more complex isotope pattern.

ROTATIONAL EFFECT

Consider now the last part of equation (37) of Chapter II which represents the rotational energy.

$$E^m = h[B_0 m^2 - a n m^2] \tag{9}$$

where

$$B_0 = h/8\pi^2 I_0 \quad \text{and} \quad a = 3h^2(1+2b)/32\pi^4 I_0^2 \omega_0.$$

Again the mass enters only through I_0 and ω_0 and here the first and principal term is proportional to μ^{-1} and the second term to $\mu^{-\frac{1}{2}}$.

$$\nu_1^m = \frac{E_1^{m'} - E_1^{m''}}{h} = [(B'_0)_1 m'^2 - (B''_0)_1 m''^2] - [a'_1 n' m'^2 - a''_1 n'' m''^2] \tag{10}$$

$$\nu_2^m = \rho^2[(B'_0)_1 m'^2 - (B''_0)_1 m''^2] - \rho^3[a'_1 n' m'^2 - a''_1 n'' m''^2] \tag{11}$$

$$\nu_2^m - \nu_1^m = (\rho^2-1)[(B'_0)_1 m'^2 - (B''_0)_1 m''^2] - (\rho^3-1)[a'_1 n' m' \quad a''_1 n'' m''^2] \tag{12}$$

which, neglecting the small last term, becomes

$$\nu_2^m - \nu_1^m = (\rho^2 - 1)\nu_1^m. \tag{13}$$

A good idea of the nature of the rotational isotope effect can be obtained by considering a hypothetical band of simple type with three branches, and neglecting all but the $B_0 m^2$ term of equation (9) for E^m. Then for the positive and negative and for the null branches, for which $m' - m'' = \pm 1$ and 0, respectively,

$$\nu_1^m = B'_1 \pm 2B'_1 m + (B'_1 - B''_1)m^2 \quad \text{or} \quad (B'_1 - B''_1)m^2 \tag{14}$$

and

$$\nu_2^m = \rho^2 \nu_1^m. \tag{15}$$

The result is pictured in Figure 2 which shows ν plotted against m for the three branches of an imaginary typical band having half integral

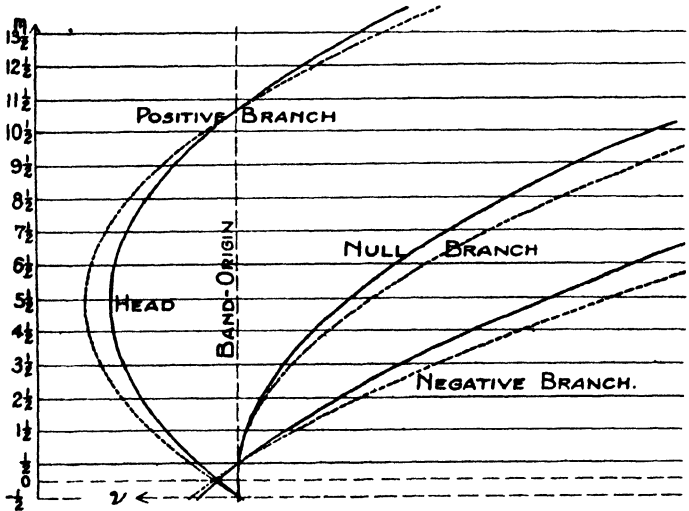


FIGURE 2.

rotational quantum numbers and no vibrational displacement, a (0, 0) band. The continuous line parabolas represent the more abundant, and the broken line parabolas the less abundant, of the two isotopes, which have been assumed to have an isotopic displacement coefficient, $\rho^2 - 1$, of 20 per cent. The rotational effect for the lines in a band is seen to be very similar to the vibrational effect for the bands in a system. The pattern is the same for each isotope, but the spacing is greater, approximately in the ratio ρ^2, for the lighter isotope. A band in which the vibrational effect was present would differ from the above by having the entire set of lines for one isotope displaced along the frequency axis, in a direction depending on the sign of the underlying vibrational effect.

SECTION 3. INFRA-RED ABSORPTION SPECTRUM OF HCl

Figure 3, which is the absorption curve reported by Imes([11]) for HCl in the region of the so-called "first harmonic" band ($n'=2$, $n''=0$) at 1.76μ, quite definitely shows each structure line of the band to be really a doublet, consisting of a strong line, accompanied by a fainter satellite of longer wave length. Imes pointed this out (*l. c.*, p. 275), and remarked: "The apparent tendency of some of the maxima to resolve into doublets may be due to errors of observation, but it seems significant that all the secondary maxima are on the long-wave side of the principal maxima which they accompany." This, together with the absence at that time of any theory to lead one to expect these satellites, may be taken as excellent evidence that they are real, and not experimental irregularities in the absorption curve.



FIGURE 3.

It was pointed out by Loomis([15]) and independently by Kratzer([14]) that these doublets are undoubtedly due to the isotopic nature of HCl.

It can be seen by inspection, that the relative intensities are about right; for chlorine, whose chemical atomic weight is 35.46, has been found by Aston([2, 3]) to consist of two isotopes of atomic weights 35 and 37, which must therefore occur in the ratio of 3.5 : 1; and this appears to be roughly the ratio of the intensity of each line to that of its satellite.

Moreover, the sign of the displacement is correct, for the fainter line has the lower frequency, as it should if it is to correspond to the heavier isotope.

In calculating the magnitude of the isotopic displacement to be expected, only the vibrational term is worth considering. Here

$$\rho-1=\tfrac{1}{2}(\rho^2-1)=\tfrac{1}{2}\frac{M'(M_1-M_2)}{M_2(M_1+M')}=\tfrac{1}{2}\frac{1.008(35-37)}{37\times 36.008}=-0.000749.$$

Hence

$$\nu_2^n-\nu_1^n=(\rho-1)\nu_1^n=-0.000749\times 5682=-4.26\ \text{cm}^{-1},$$

which agrees excellently with the average doublet interval measured from the curve of Figure 3, viz., -4.5 ± 0.3 cm^{-1}.

This agreement with calculations from the theory, in sign and magnitude as well as approximately in relative intensity, is sound evidence

that the doublets are truly isotopic in origin, especially since they occur in these simple bands whose theory is practically complete.

Calculation of the isotopic displacements to be expected in other vibration rotation spectra makes it seem unlikely that other instances of this sort of isotope effect will be found without a considerable improvement in experimental technique; unless it should be in the "fundamental" of HCl, in which the conditions are only a little less favorable than in the "first harmonic."

SECTION 4. BORON MONOXIDE

The discovery of further examples of the isotope effect came several years later, after considerable progress had been made in the theory and systematization of electronic band spectra. In 1923 Mulliken([17, 18]) after a search of the literature on the subject reported a case in the spectrum photographed by Jevons([12]) in 1914 and attributed by him to BN. Jevons had arranged the band heads into an α and β, β_1 and β_2 systems, which have a band structure of the simple sort typical of a diatomic molecule.

Now Aston ([2, 4]) has found boron to consist of two isotopes of atomic weights 11 and 10, which, since the chemical atomic weight is 10.82, must occur in the proportion of 4.6 : 1. We should therefore expect, in accordance with Section 2, that its band spectrum, whether emitted by BO or BN, would consist of comparatively strong systems of bands due to B^{11}, with each of which should be associated a fainter system, due to B^{10}, having the same origin but spaced out from the origin at wider intervals. And indeed, Jevons' β_1 and β_2 systems have just this relation to his β system, the β_1 bands lying on the low and the β_2 bands on the high frequency side of the origin. But he made no reference to any bands which could be attributed to a light isotope α system.

Mulliken([20, 23]), however, has made new photographs of this spectrum under improved experimental conditions, and has succeeded in showing that the whole spectrum can be analyzed into an α, a β, and a new combination system, $\alpha\beta$, each with its appropriate α', β' and $\alpha'\beta'$ companion system due to the lighter isotope. Part of the β system is reproduced in Plate I(a), which shows the well separated band heads and structure lines of both isotopes. Plate I(b) is the $2\frac{1}{2}$-$2\frac{1}{2}$ band, showing weak $B^{10}O$ structure lines among the strong $B^{11}O$ lines. Not only has he located an α' head corresponding to each α head, and a β' head to each β head, and $\alpha'\beta'$ heads to many of the $\alpha\beta$ heads, but he has found his measurements sufficiently accurate, on account of the very favorable value of ρ, to settle the following two important points:

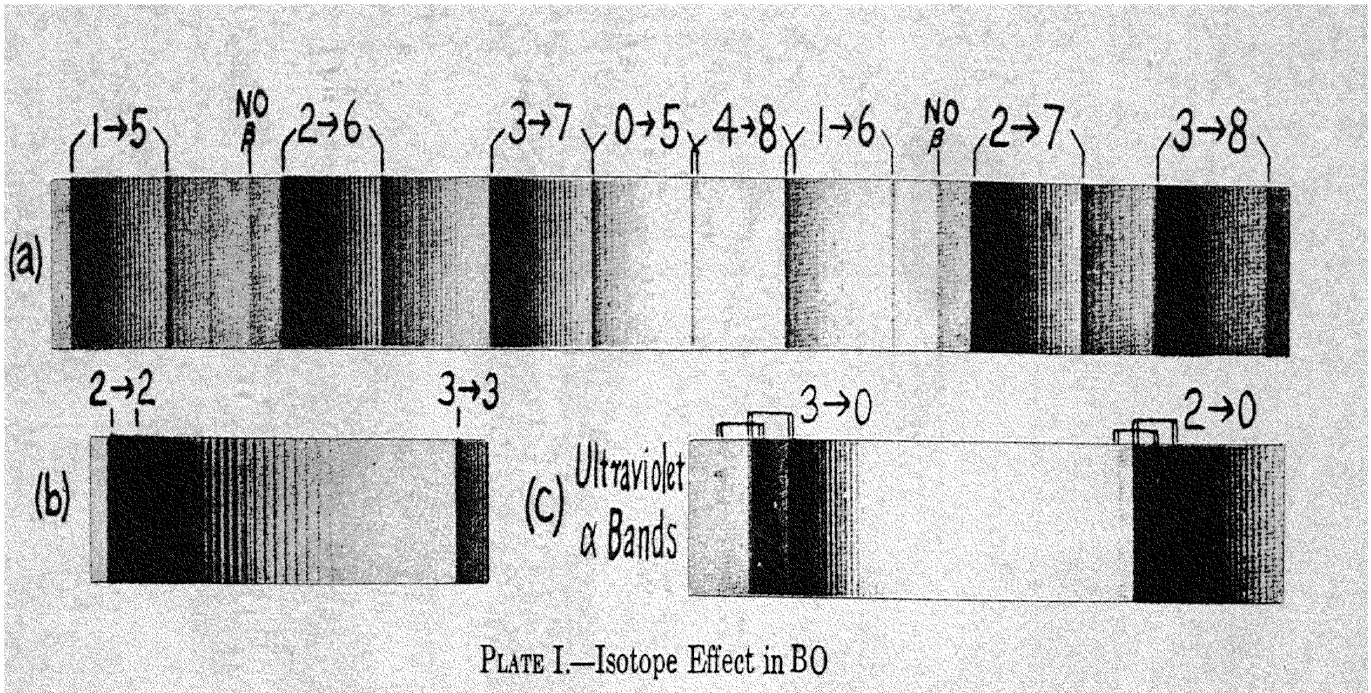


PLATE I.—Isotope Effect in BO

(a) Location of the system origin; half-quantum numbers. When the band origins are expressed as a power series in n' and n'', the values of the coefficients of all powers below the highest, and especially of the constant term, will depend on the assumed location of the system origin. If it were assumed to coincide with some band origin, the criteria of Heurlinger and Kratzer (Chapter IV) would suffice to decide which one. But it turns out, when quantum numbers are assigned in this way, that the constant, i. e., electronic, terms in both the α and β systems differ from those in the α' and β' systems by considerably more than the experimental error. These differences are far too large to be attributable to an electronic isotope effect. And they cannot be diminished by any renumbering of bands which retains integral quantum numbers. But if the vibrational quantum numbers are assumed to be integers plus $\frac{1}{2}$, then the difference between the electronic terms for the two isotopes becomes small enough to be attributable to experimental errors. The criterion that the electronic isotope effect must be zero is sufficiently cogent to force us to accept these vibrational half-quantum numbers. The equations for the α and α' heads and the β and β' origins are now:[2]

$$\begin{aligned}
\nu_\alpha &= \left\{\begin{matrix}23974.5\,;\ 23961.2\\ 23848.3\,;\ 23835.0\end{matrix}\right\} + (1258.5n' - 10.6n'^2) - (1884.9n'' - 11.68n''^2)\\
\nu_{\alpha'} &= \left\{\begin{matrix}23972.9\,;\ 23959.6\\ 23846.7\,;\ 23833.4\end{matrix}\right\} + (1297.3n' - 11.7n'^2) - (1939.0n'' - 12.21n''^2) \qquad (16)\\
\nu_\beta &= 43166.2 + (1280.3n' - 10.07n'^2) - (1885.7n'' - 11.77n''^2)\\
\nu_{\beta'} &= 43168.6 + (1316.7n' - 10.53n'^2) - (1941.5n'' - 12.58n''^2)
\end{aligned}$$

(b) Identification of the emitter. It appears from equation (6) that the value of ρ for the emitter of these bands can be found from the ratio

TABLE 1

Term	ρ	ρ^2
n' (α)	1.0308	1.104
n''(α)	1.0287	1.045
n' (β)	1.0284	1.046
n''(β)	1.0296	1.069
Weighted[24] mean	1.0293 ± 0 0003	1.062 ± 0.008
Theoretical, BO	1.0292	1.059
Theoretical, BN	1.0276	1.056

of the linear terms, and the value of ρ^2 from the ratio of the quadratic terms in n' and n'' in the equations (16). The values so obtained are given in Table 1, together with the theoretical values on the assumptions that BO and BN are the emitters.

[2] The data for locating the band origins are given in the table in Section 7 of Chapter IV. See also footnote (d) of that section.

The differences between the experimental values of ρ and ρ^2 and the theoretical ones for BN are enough larger than the probable error to render it extremely improbable that BN can be the emitter, although it was so reported by Jevons on plausible experimental grounds; especially since the agreement with the theoretical values for BO is so excellent. This evidence, fairly conclusive in itself, led Mulliken to undertake further study of the conditions of excitation, details of which are to be found in his papers([19, 20]) and which, despite some criticism by Jevons([13]), seem also to point conclusively to BO as the emitter. It is safe to say that this would hardly have been discovered, in the face of Jevons' *prima facie* case for BN, had it not been for the quantitative evidence of the isotope effect.

All the structure lines of three β bands of both isotopes were measured, found to check roughly with the predicted isotope effect, and analyzed enough to furnish data for a small correction needed to convert the measurements, which were made on band heads, into data on band origins.

SECTION 5. COPPER HYDRIDE

Another instance in which measurements of the isotopic displacement have settled the question of the emitter of a spectrum is the copper bands reported by Frerichs([9]) which are probably due to CuH, he considers, on account of the large spacing of the structure lines and corresponding small moment of inertia. Mulliken([19]) points out that measurements of the isotope effect are conclusive on this point, for, in the (0, 0) and (1, 1) bands which he investigated, the separations of the doublets, which Frerichs had noted, agree with the predicted isotopic displacements between $Cu^{63}H$ and $Cu^{65}H$, where $1-\rho=0.00024$, but not at all with those of any other possible emitters, such as CuO whose $1-\rho=0.0031$.

SECTION 6. SILICON NITRIDE

The study of the isotope effect in SiN has led to the discovery of a new isotope of silicon. For although Aston([2, 4]) made mass spectrograph measurements on silicon and found species with atomic weights 28 and 29, he reported that the existence of Si^{30} was doubtful on account of the presence of hydrogen compounds. But Mulliken's photographs([18, 21, 26]) of its spectrum show that each principal band head, in the regions where resolution is possible, is accompanied by a pair of fainter heads; and values of ρ computed for these subsidiary heads show that if the principal ones are due to $Si^{28}N$, then these are due to $Si^{29}N$ and $Si^{30}N$. Aston([5]) has since confirmed the existence of Si^{30} with the mass spectrograph.

SECTION 7. COPPER IODIDE

Recently Mulliken[25] unravelled the spectrum of CuI, arranging the heads due to the more abundant $Cu^{65}I$ into five band systems with a common final electronic term, and expressing them as power series of the form (4). He was then able to calculate, by equation (6), expressions for the corresponding $Cu^{63}I$ heads and to compare the calculated with the observed positions. The agreement with theory is perfect, for every $Cu^{63}I$ head is found within the experimental error of its calculated position and all calculated heads which might be expected to have sufficient intensity are found, and no others. Mulliken's success with this spectrum, which consists of complicated overlapping band systems and had baffled several previous investigators, is undoubtedly largely due to his use of the vibrational isotope effect as a guide.

SECTION 8. MAGNESIUM HYDRIDE

Watson[27] has recently reported further evidence for vibrational half-quantum numbers from measurements of isotopic displacements in the

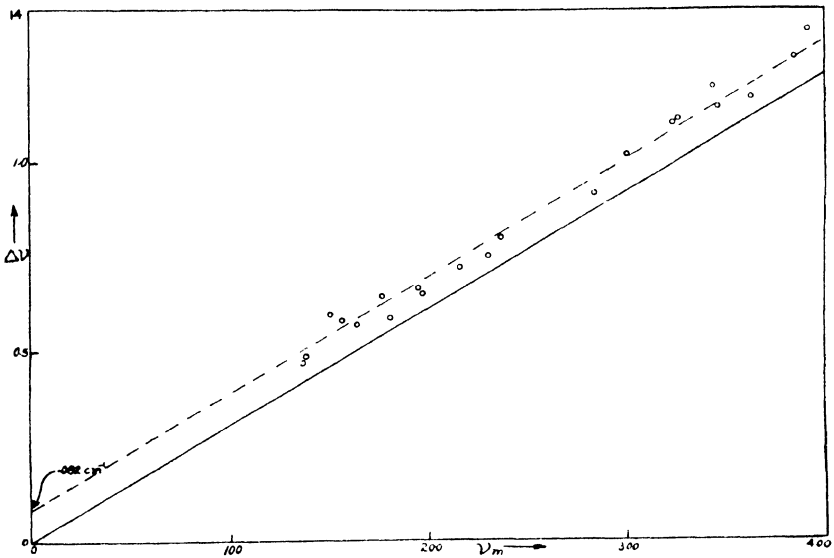


FIGURE 4.—Isotope Effect in MgH λ5211 Band

λ5211 band of MgH. When first measured by Watson and Rudnick[28], this band was numbered (0, 0); but Watson[27] now points out that the data agree much better with the numbering $(\frac{1}{2}, \frac{1}{2})$.

Figure 4 shows the isotopic displacements, $\Delta\nu$, between the lines of the most abundant isotope, Mg^{24}, and the corresponding lines of Mg^{26}. Lines

due to Mg^{25} are omitted to avoid confusing the figure and also because they are less accurately measured. The solid line represents the displacement to be expected, according to equation (13), on the assumption that this is the (0, 0) band and hence that the effect is purely rotational. The broken line represents the same rotational displacement with an additional vibrational displacement of 0.082 cm^{-1} which is that calculated from (7) on the assumption that this is the $(\frac{1}{2}, \frac{1}{2})$ band. The average excess of the observed displacements over the theoretical rotational displacement is -0.073 and -0.029 cm^{-1} for isotopes 26 and 25 respectively, as compared with theoretical values of -0.082 and -0.042. Within the limits of experimental error this is satisfactory agreement.

SECTION 9. CONCLUSION

It will be seen that the isotope effect has been found useful in the discovery of one new isotopic species, Si^{30}, and in the identification of the emitters of the spectra of BO and CuH. And in each case it has served as a key to the arrangement of structure lines into bands and of bands into band systems, to the location of band and systems origins, and to the assignment of rotational and vibrational quantum numbers.

But the most interesting aspect of the isotope effect and the one which promises to be of most value in future work is that it furnishes data for the testing of theories of band spectra, additional to and independent of the frequencies, or energy terms, which, with usually dubious estimates of intensities, have formed practically the whole of the experimental evidence; since essentially, the isotopic displacement gives the derivative of the frequency of each line, head or origin with respect to mass. In this way the isotope effect can serve to confirm the broad outlines of the theory of band spectra, through its general agreement with predictions, and to furnish a decisive answer to such specific questions as the use of half-quantum numbers; in fact, it furnishes the only experimental evidence to date on the question of the vibrational half-quantum numbers which are demanded by the recent theories of Heisenberg([10]) and Born and Jordan([8]).

Discovery of new isotopes is on the whole simpler with the mass spectrograph, and Aston has already progressed so far that probably not much remains to be contributed by the study of the isotope effect, though it may furnish some evidence on the relative abundance and relative weights of different isotopes of the same elements.

But so many elements have been found to be isotopic([6]), (30 of the 56 so far investigated, not counting the radioactive elements), and so

many of their compounds must be carriers of band spectra, that it is safe to prophesy for the isotope effect an increasingly important part in the study of band spectra and in the development of their theory.

BIBLIOGRAPHY

[1] Aaronberg, Astrophys. J., 47: 96 (1918).
[2] Aston, "Isotopes," 2d ed. London, Arnold, 1924.
[3] Aston, Nature, 104: 393 (1919).
[4] Aston, Nature, 105: 547 (1920).
[5] Aston, Nature, 114: 273. (1924).
[6] Aston, Phil. Mag., 49: 1198 (1925).
[7] Bohr, Nature, 109: 745 (1922).
[8] Born and Jordan, Z. Physik, 34: 858 (1925).
[9] Frerichs, Ann. Physik, 71: 102 (1924).
[10] Heisenberg, Z. Physik, 33: 879 (1925).
[11] Imes, Astrophys. J., 50: 251 (1919).
[12] Jevons, Proc. Roy. Soc., 91A: 120 (1915).
[13] Jevons, Nature, 113: 744, 785 (1924); Proc. Roy. Soc., 106A: 174 (1924).
[14] Kratzer, Z. Physik, 3: 460 (1920); 4: 476 (1921).
[15] Loomis, Nature, 106: 179 (1920); Astrophys. J., 52: 248 (1920).
[16] Merton, Proc. Roy. Soc., 96A: 388 (1920).
[17] Mulliken, Science, N. S., 58: 164 (1923).
[18] Mulliken, Nature, 113: 423 (1924).
[19] Mulliken, Nature, 113: 489 (1924).
[20] Mulliken, Nature, 114: 349 (1924).
[21] Mulliken, Nature, 116: 14 (1925).
[22] Mulliken, Phys. Rev., N. S., 25: 119 (1925).
[23] Mulliken, Phys. Rev., N. S., 25: 259 (1925).
[24] Mulliken, Phys. Rev., N. S., 25: 275 (footnote) (1925).
[25] Mulliken, Phys. Rev., N. S., 26: 1 (1925).
[26] Mulliken, Phys. Rev., N. S., 26: 319 (1925).
[27] Watson, Nature, 117: 692 (1926).
[28] Watson and Rudnick, Astrophys. J., 63: 20 (1926).

CHAPTER VI

FLUORESCENT BAND SPECTRA

F. W. Loomis

SECTION 1. INTRODUCTION

The only band spectrum which has been intensively investigated in fluorescence is that of iodine. The complex iodine fluorescent spectrum excited by white light has been known and studied for a long time, but the researches of chief theoretical importance are those of R. W. Wood([11, 12]) who used for excitation, light which was monochromatic or nearly so. The spectrum which resulted was very much simplified, consisting of a series of equally spaced doublets of constant interval; but it stood absolutely unexplained until the application of the Bohr postulates and the modern quantum theory of band spectra by Lenz([3]) who showed that this spectrum constituted a clear example of the working of the Bohr selection principle for rotational quantum numbers.

SECTION 2. EXPERIMENTS WITH MONOCHROMATIC EXCITATION

For the most part Wood used the green mercury line at 5460Å for excitation. This line, as it comes from a quartz mercury arc at high current densities, is broad enough to cover seven measurable iodine lines, which are extraordinarily numerous in this region; but by using an arc designed to run at low current densities, with comparatively cold mercury vapor, and made of glass which cut out the ultra-violet lines, he obtained light so monochromatic that it covered only one iodine line.

The resulting fluorescent spectrum is shown in part on Plate Ia. It consists of a series of 27 doublets of 5 wave numbers separation and with an approximately constant spacing of 200 wave numbers. The line of shortest wave length coincides exactly with the exciting line and is called the resonance line.

SECTION 3. THEORY OF THE FLUORESCENT SERIES

These results are entirely in accord with present theories of band spectra. For, if the exciting light is sufficiently monochromatic to cover only one absorption line, then all the molecules which emit the fluorescent spectrum must be in the same initial state; that is, must have common

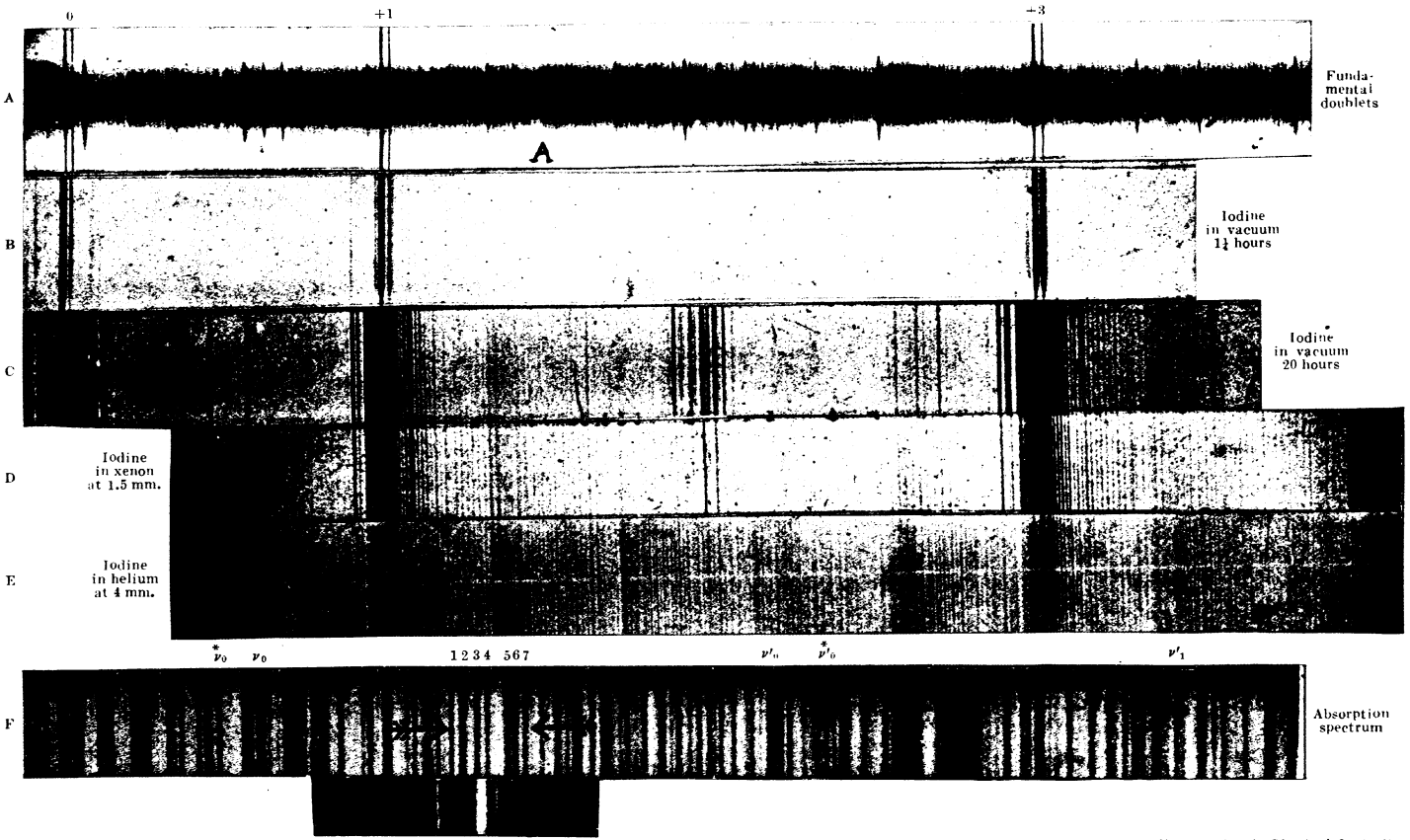


PLATE 1

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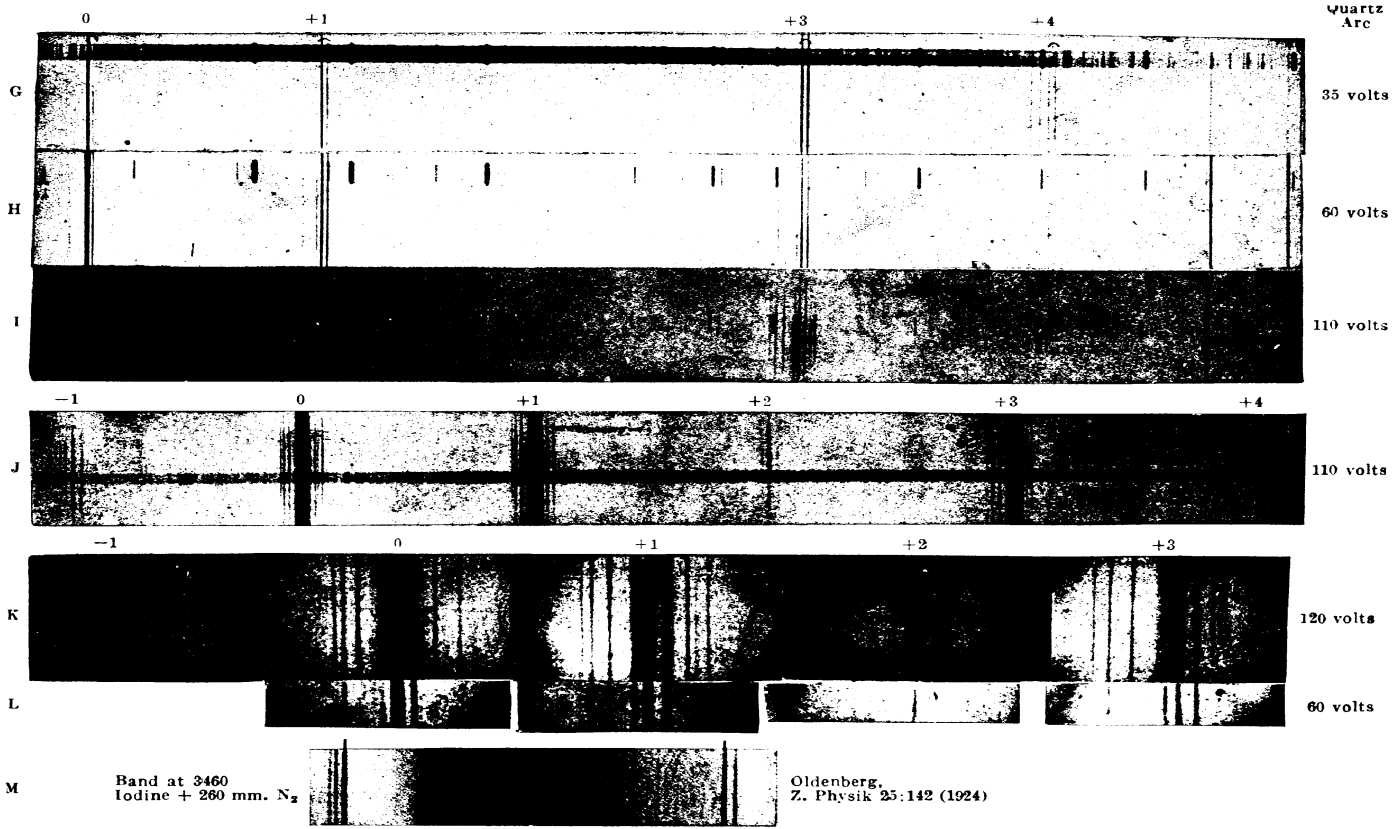


PLATE II

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e', n' and j'. And the possible final states are limited by the correspondence principle to

$$j''=j'\mp 1. \tag{1}$$

($j''=j'$, corresponding to a Q branch, which is possible in many spectra, apparently does not occur in iodine. See, however, Section 4 below.) As the vibrational motion is non-harmonic all values of n'' are possible. But it seems that the molecules excited by λ5460 must always revert to the original unexcited electronic state, since there is only one fluorescent series and it contains a line which coincides with the exciting line.

Equation (37) of Chapter II

$$E=E^e+E^n+E^m=E^e+h[\omega_0 n(1-xn)]+h[(B_0-\alpha n)m^2] \tag{2}$$

will serve as a basis for quantitative discussion. Here, in the simpler band types

$$m=j-\epsilon, \tag{3}$$

where ϵ is usually small and may depend on the electronic state but not on n or j. Since the upper level, E', is constant throughout a fluorescent series, as is also $E^{e''}$, the expression for any series, say the i^{th}, can be written

$$\nu_i=C_i-\omega''_0 n''_i(1-x''n''_i)-(B''_0-\alpha''n''_i)m''_i{}^2. \tag{4}$$

This represents a series of doublets because m'' can take on the two values corresponding by (3) to the two values of j'' in (1); i. e.,

$$m''=(m'+\epsilon'-\epsilon'')\mp 1 \tag{5}$$

while n'' can take on any integral value.

Let $\bar{n}$, $\bar{j}$ and $\bar{m}$ be the values of n'', j'' and m'' corresponding to the resonance line; i. e., the values of n, j and m of the fluorescent molecule before it was excited. Other values of n'' can be represented by

$$n''=\bar{n}+p. \tag{6}$$

Then, since the correspondence principle applies both to absorption and re-emission,

$$j'=\bar{j}\pm 1 \quad \text{and} \quad j''=j \quad \text{or} \quad \bar{j}\pm 2. \tag{7}$$

(Wherever there is a double sign, $\pm$ or $\mp$, the upper one will consistently, throughout this chapter, correspond to the case where the *excited* line is on an R branch.) Hence by (3)

$$\begin{aligned} m''=j''-\epsilon''=\bar{j}-\epsilon'' \quad &\text{or} \quad \bar{j}-\epsilon''\pm 2 \\ =\bar{m} \quad &\text{or} \quad \bar{m}\pm 2. \end{aligned} \tag{8}$$

The doublet separation will then be the difference between the two values of the last term in (4) which correspond to the two values of m'' in (8)

$$\Delta\nu_i = \nu(\bar{m}_i \pm 2) - \nu(\bar{m}_i) = -(B''_0 - \alpha'' n''_i)(\pm 4\bar{m}_i + 4). \qquad (9)$$

It will be seen, since B''_0 and α'' are constant throughout a fluorescent series, and $\alpha'' \ll B''_0$, that the doublet separation, while nearly constant, should really decrease slowly and linearly along the series. That it actually does so, can be seen from Figure 1, page 278, which is like Mecke's Figure 2([6]) and represents the doublet separation in four different fluorescent series, plotted against p, the ordinal number of the doublet counted from the resonance line. In fact Kratzer and Sudholt([2]) have calculated B''_0 by comparing the theoretical expression (9) for $\Delta\nu_i$ with the numerical values expressed in the empirical equations of the form

$$\Delta\nu_i = d_i - \eta_i p, \qquad (10)$$

taking α'' from Mecke's([7]) analysis of the absorption spectrum. Since n'' and p are equal within a few units at most (in fact it will be shown below that their difference, $\bar{n}$, is zero for all the fluorescent series formulated by Mecke) it is clear that

$$d_i = -4B''_0(\pm\bar{m}_i + 1) \qquad (11)$$

$$\eta_i = -4\alpha''(\pm\bar{m}_i + 1) \qquad (12)$$

$$B''_0 = \alpha'' d_i/\eta_i. \qquad (13)$$

Table 1 gives the empirical formulas for the four doublets which can be followed along the series, and the values of B_0'' deduced from them.

TABLE 1

Series	Doublet interval	d/η	B_0''
$\Delta\nu_0$	$4.43 - 0.0175p$	253	.030
$\Delta\nu'_0$	$-(5.20 - 0.0231p)$	225	.027
$\Delta\nu_1$	$11.85 - 0.053p$	223	.027
$\Delta\nu_2$	$16.08 - 0.057p$	282	.034
Average			.030

The values here tabulated constitute a revision of those given by Kratzer and Sudholt, using a corrected value of α'' (see footnote 1) and corrected expressions for the doublet intervals. The revision of the doublet intervals was needed because Mecke identified each interval of order zero with the distance from the outer member of the doublet to the center of the broad exciting mercury line. The width of the mercury line, which measures the spectral range of the various resonance members of the doublets of order zero, is so large that this is not a very satisfactory approximation.

SECTION 4. THE ABSORPTION SPECTRUM

Before going on to study the more complex fluorescent spectra, we shall need the information obtained from analysis of the absorption spectrum. Mecke([7]) has reported a series expression of the form

$$\nu(n_1, n_2) = \nu_0 + (a_2 n_2 + b_2 n_2^2 + c_2 n_2^3) - (a_1 n_1 + b_1 n_1^2 + c_1 n_1^3) \quad (14)$$

which represents all the band heads in the region 5000 – 7000 Å. From the variation of intensity along the n_2 series (n_1 constant), and from their insensitiveness to temperature changes, and from the relative smallness of the linear term, he concludes that n_2 corresponds to n', the upper level vibrational quantum number but increases as n' decreases. As $n_2 = 26$ seems to be a limiting value (see Figure 16 of Chapter IV), he concludes that it is the zero of n' and sets $n' = 26 - n_2$. Whether this is correct need not concern us here, as n' is constant in fluorescence. Similarly, from the way in which the intensities of the lines of the n_1 series (n_2 constant) vary with temperature he concludes that n_1 corresponds to and increases with n'', the vibration quantum number in the unexcited state. Now the coefficients of n_1, n_1^2, and n_1^3, are sensibly the same as those of p, p^2 and p^3 in the expression (20) for Wood's fluorescent doublets, and it is therefore justifiable to identify Mecke's n_1 with the p of Wood's fundamental series. Mecke, however, concludes from the occurrence of four antistokes members in Pringsheim's experiments, discussed below, that the zero of n'' must be at least at $n_1 = p = -4$. But, while it is true that the zero of a series having antistokes members must be at least as low as the lowest member, the fundamental series, for which $p = n_1$, apparently does not contain any antistokes members; while the frequencies of the antistokes lines which appear in Wood's reproductions do not fit any of the series (21) into which Mecke has analyzed the fluorescent spectrum. The correct assignment should therefore be $n'' = n_1 = p$ for the fundamental series and others having no antistokes members. For other series $n'' = p + \bar{n}$, where $\bar{n}$ is the number of antistokes members. Using this numbering, the series formula which represents all Mecke's band heads becomes:

$$\nu(n', n'') = 15597.70 + (126.59n' - 0.755n'^2 - 0.0033n'^3) - (213.76n'' - 0.596n''^2 - 0.0021n''^3). \quad (15)$$

Mecke has also measured the individual lines of four bands in the red, where the lines are less numerous and resolution easier than in the neighborhood of the green mercury line. He has found that they can be expressed in the form

$$\nu = \nu_H + CM^2 \quad (16)$$

where ν_H is the frequency of the head, M represents the ordinal number starting from the head, and $C(4, 8) = -0.008$. The values of C vary from band to band, however, as indeed they should, since by (2)

$$C = B' - B'' = (B'_0 - \alpha' n') - (B''_0 - \alpha'' n'') \tag{17}$$

and it appears [1] that

$$C(4, 9) - C(4, 8) = C(5, 9) - C(5, 8) = 0.00012 = \alpha''. \tag{18}$$

$$C(4, 9) - C(5, 9) = C(4, 8) - C(5, 8) = 0.00017 = \alpha'. \tag{19}$$

It is worthy of note that Mecke's values of C, α' and α'', above, do not depend on the correctness of the absolute numbering, either in M, n' or n''.

It should be mentioned, however, that Mecke considers that his red absorption bands consist of Q branches only. This, if true, definitely disproves Lenz's theory, which attributes the doublets to pairs of lines from the R and P branches ($j'' = j' \mp 1$). And, indeed, Mecke found no trace of lines from a second branch between any of the four red bands he measured. But it is entirely possible that the lines of the R and P branches of the bands he measured overlap within the limits of his resolution, which is only sufficient to resolve the lines for which $M > 30$. In fact, the position of the band heads in the green is calculated from fluorescent spectrum data in Section 6, and it turns out that the head occurs within two lines of the origin. This accounts for the similarity of the R and P branches and indicates that if the R and P lines happen to coincide at all they will coincide fairly closely throughout that band. Moreover, Mecke has measured Wood's reproduction of the iodine absorption spectrum, taken with high resolution, in the neighborhood of the green mercury line, and analyzed it into three overlapping series, two of which are very similar and look like parts of R and P branches, though Mecke considers them probably electronic doublets. Comparison with the fluorescent spectrum (see Section 6) leaves no possible doubt that they are actually R and P branches.

SECTION 5. EFFECT OF MIXTURES OF OTHER GASES

The series of doublets resulting from monochromatic excitation can be thought of as picked out from the very complex emission bands by the limitation to a single initial state. That this is the case is checked by several variations of Wood's experiments in which the rest of the bands begin to appear.

[1] Mecke gives $\alpha'' = 0.00011$ and $\alpha' = 0.00015$, but a computation from his data by the author, using the method of least squares, makes it appear that 0.00012 and 0.00017 are better values. There is also an error of $+4$ in Mecke's numbering.

If iodine is mixed with helium at 4 mm. pressure or with xenon at 1.25 mm., complex bands appear as shown in Plates Ie and Id. This is interpreted by Lenz[3] as due to "collisions of the second kind" between helium or xenon atoms and excited iodine molecules, in which a transfer of energy takes place between kinetic energy of translation and the energy of rotation and vibration of the iodine molecules; leaving the latter still in the same electronically excited state, but with a range of values of n' and j', each of which will correspond to a series of doublets on re-emission. Two or three new bands appear on each side of each band of the original (n'') series at intervals of about 81 wave numbers; indicating that the vibration quantum numbers of the excited molecule, n', have been changed by collisions of the second kind, from 26, which is the value of n' in the fundamental series of doublets, to 28, 27, 25, 24, etc. The interval between successive n' terms in Mecke's absorption series is 80.7 in the region $n'=26$, and its agreement with the spacing of these new fluorescent bands indicates that the upper electronic levels in fluorescence and absorption are the same.

The same thing must take place to some extent, even in the absence of a foreign gas, when iodine molecules collide with each other; but, owing to the comparatively low vapor pressure of iodine, such collisions will be rarer during the life of an excited iodine molecule, and the corresponding lines will be fainter. However, they are clearly shown in Plates IB and IC, which are the fluorescent spectra of pure iodine, monochromatically excited and exposed for one and for twenty hours respectively, so that the original doublets are over-exposed.

SECTION 6. EXCITATION WITH THE BROAD LINE FROM THE QUARTZ ARC

A somewhat similar, but less complete and less regular, filling out of the bands occurs when the green mercury line is made wider by using a quartz mercury arc at high current densities. The resulting spectrum, excited by the green mercury line at its widest, when it covered seven iodine absorption lines, is shown in Plates IIJ and IIK. It has been analyzed by Wood[11, 12] and Mecke[7] into ten series of doublets, including the one discussed above which they call the fundamental series. These series all consist of doublets whose separation decreases slowly and linearly with the ordinal number, p. See Figure 1. And each series contains a resonance line, i. e., one coinciding with some part of the exciting green mercury line. Wood has named the component of any doublet which is on the same side as the resonance line, the "main line"; and the other component the "companion line." And he has assigned an arbitrary

number, p, to the doublets, starting with 0 for the one which contains the resonance line and running to $p=27$ for the longest wave-length doublet observed. Obviously, the main line is due to a return to the original rotational state, $m''=m$; while for the companion line, $m''=m\pm 2$. And the doublet of 0 order is due to a return to the original vibrational state, $n''=n$; while the p^{th} doublet corresponds to $n''=n+p$. In five of the series the main line is the short-wave component of the doublet, in the other five it is the long-wave component. Which it shall

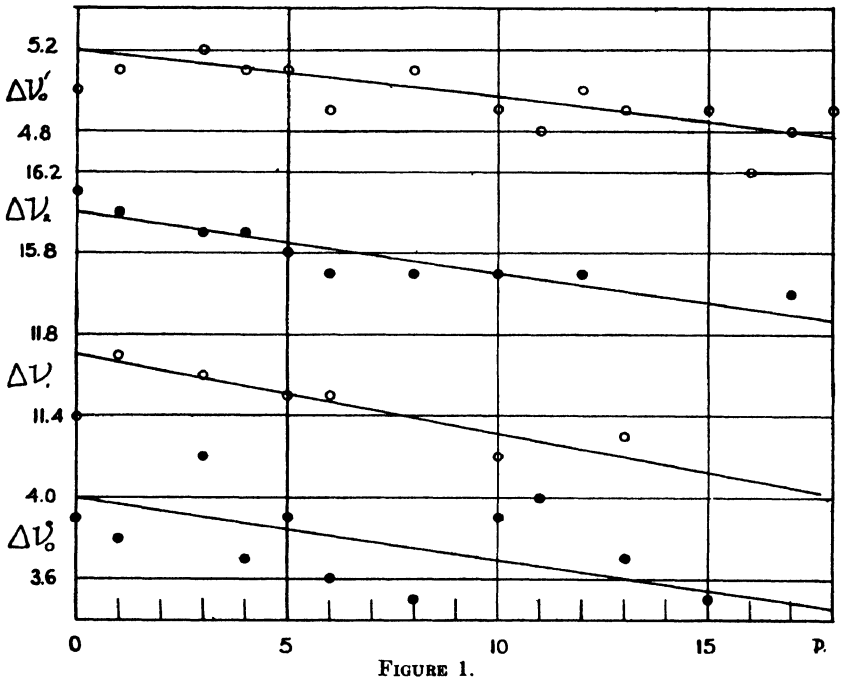


FIGURE 1.

be in any particular series will depend on whether the absorption line by which it is excited belongs to an R or a P branch.

The complete formulation of these series follows. It is due to Mecke(7), with revision by Kratzer and Sudholt(2), who computed the linear term in the doublet interval, and by the writer, who has computed the small constant terms from the slight differences in the positions of the absorption lines, all within the green mercury line, which excite the various series. See Section 7. Denote by

$$F(p)=18307.5-213.667p+0.592p^2+0.00207p^3 \qquad (20)$$

the expression which represents the main line of the so-called fundamental series. Then the entire group of series is given by

$$\left.\begin{aligned}
\nu_0 &= F(p) - 0.53 \qquad + (\ 4.43 - 0.0175p) \\
\overset{*}{\nu}_0 &= F(p) + 0.26 \qquad + (\ 4.24 \ldots\ldots\ ) \\
\nu_1 &= F(p) - 0.65 + 0.66p + (11.85 - 0.053p\ ) \\
\nu_2 &= F(p) - 0.17 + 1.33p + (16.08 - 0.057p\ ) \\
\nu_3 &= F(p) \qquad + 1.95p + (19.0 \ldots\ldots\ ) \\
\nu'_0 &= F(p) \qquad - (\ 5.20 - 0.0231p) \\
\overset{*}{\nu}'_0 &= F(p) - 0.84 \qquad - (\ 5.16 \ldots\ldots\ ) \\
\nu'_1 &= F(p) + 0.46 + 0.75p - (12.8 \ldots\ldots\ ) \\
\nu'_2 &= F(p) \qquad + 1.5p \ - \qquad\quad (?) \\
\nu'_3 &= F(p) \qquad + 2.2p \ - (19.7 \ldots\ldots\ )
\end{aligned}\right\} \qquad (21)$$

where the quantities in parentheses represent the doublet intervals and if omitted leave the expressions for the main lines but if included give the companion lines.

It will be seen, that, since the coefficients of p, p^2 and p^3 in (20) are sensibly the same as those of n'', n''^2, n''^3 in (15), all the fluorescent series belong to the group of n'' series; that is, each series has a single upper state and a lower electronic state identical with that in the normal unexcited molecule. The small linear terms in (21) are accounted for below.

The expressions (21) represent twenty series of lines. Now the green mercury line, if it is narrower than the interval between successive lines in a branch in the region it covers, can at most give rise to four series of lines from one band; i. e., a series of doublets excited by a line in the R branch and another by one in the P branch. And this is the case in all except the ν_0 series; for the intervals between successive lines near 5460Å, calculated from results below, are about 0.8, 2.2, 3.1, and 3.8 cm^{-1} in the ν_0, ν_1, ν_2 and ν_3 series respectively, while the width of the mercury line is about 1.3 cm^{-1}. We conclude that the series (21) belong to at least four bands which overlap the green mercury line; that, because of the sign of the doublet separation, the series labelled ν' are excited by lines belonging to an R branch, those labelled ν by a P branch; and that the ν_0 and the $\overset{*}{\nu}_0$ series are excited by successive lines in the same band.

Kratzer and Sudholt(2) have accounted for the linear terms, which they call $\gamma_i p$, in the expressions for the main lines, as follows. The main lines of the i^{th} series are given by

$$\nu_i(n''_i, \bar{m}_i) = C_i - \omega''_0 n''_i (1 - x'' n''_i) - (B''_0 - \alpha'' n''_i)\bar{m}_i^2 \qquad (22)$$

which can be changed into a function of p by substituting from (6).

$$\nu_i(p, \bar{m}_i) = \nu_i(\bar{n}_i, \bar{m}_i) - \omega''_0 p + \omega''_0 x''(p^2 + 2\bar{n}_i p) + \alpha'' p \bar{m}_i^2. \qquad (23)$$

Subtracting from this a similar expression for $\nu'_0(p, \bar{m}'_0)$, the main lines of the fundamental series, and denoting the resonance line of the i^{th} series by

$$\nu_i(\bar{n}_i, \bar{m}_i) = F(0) + g_i \tag{24}$$

we get for the difference between the main lines in the p^{th} order

$$\nu_i(p, \bar{m}_i) - \nu'_0(p, \bar{m}'_0) = g_i + p[2\omega''_0 x''(\bar{n}_i - \bar{n}'_0) + a''(\bar{m}_i^2 - \bar{m}_0'^2)], \tag{25}$$

since $g'_0 = 0$. Now by comparing Mecke's absorption series (15) with the theoretical expression (4) or (22) it appears that $\omega''_0 x'' = 0.596$. And by (18) $a'' = 0.00012$. Hence,

$$\gamma_i = 1.192(\bar{n}_i - \bar{n}'_0) + 0.00012(\bar{m}_i^2 - \bar{m}_0'^2). \tag{26}$$

The last term in (26) has been calculated by Kemble and Witmer [1], assuming that the successive fluorescent series in (21) are excited by lines of bands having successive values of n'. That this assumption, rather than the alternative, the variation of n'', is correct, is highly probable; first, because none of the series (21) seems to have any antistokes members; and, second, because this assumption leads to results, below, which fit the facts, while the alternative does not. In equation (15) the band which lies nearest the green mercury line and which presumably gives rise to the fundamental series is ($n' = 26$, $n'' = 0$). We shall denote n' for the other bands by

$$n' = 26 + i \tag{27}$$

and the origin of band $(26+i, 0)$ by ${}_0\nu_i$. Then the frequency of the main line in the zero order (the resonance line) of the i^{th} series will be

$$\nu_i(p=0, \bar{m}_i) = F(0) + g_i = {}_0\nu_i + B' \pm 2B'\bar{m}_i + C\bar{m}_i^2 \tag{28}$$

where

$$C = B' - B''.$$

Subtracting from this a similar equation for the resonance line of the fundamental series

$$\nu'_0(p=0, \bar{m}'_0) = F(0) = {}_0\nu_0 + B' + 2B'\bar{m}'_0 + C\bar{m}_0'^2 \tag{29}$$

one obtains

$$g_i = {}_0\nu_i - {}_0\nu_0 \pm 2B'm_i - 2B'\bar{m}'_0 + C(\bar{m}_i^2 - \bar{m}_0'^2) \tag{30}$$

which can be solved for the second term in (26) yielding

$$a''(\bar{m}_i^2 - \bar{m}_0'^2) = \frac{a''({}_0\nu_i - {}_0\nu_0)}{-C} + \frac{a''g_i}{C} \mp \frac{2a''B'\bar{m}_i}{C} + \frac{2a''B'\bar{m}'_0}{C}. \tag{31}$$

The first term on the right-hand side of (30), which is much the largest, can be calculated entirely from Mecke's data on absorption. For, since

the origins are sensibly coincident with the heads, ${}_0\nu_i - {}_0\nu_0$ can be calculated from (15). And, by equations (17-19),

$$C(26, 0) = C(4, 8) - 22a' - 8a'' = -0.013; \qquad a'' = 0.00012. \quad (32)$$

The g_i can be taken from equations (21) and the $\bar{m}$'s, as well as $B' = B'' + C = 0.024$, from Table 3, with more than sufficient accuracy for the calculation of the other terms, which are small. The value of the last term, so calculated, is -0.015. The resulting values of $a''(\bar{m}_i^2 - \bar{m}_0'^2)$ are shown in column 6 of Table 2 for comparison with the observed values of γ_i in column 7. The agreement of the last two columns is close enough

TABLE 2

i	${}_0\nu_i - {}_0\nu_0$	$\frac{a''({}_0\nu_i - {}_0\nu_0)}{-C}$	$\frac{a''g_i}{C}$	$\mp\frac{2a''B'm_i}{C}$	$a''(\bar{m}_i^2 - \bar{m}_0'^2)$	γ_i
0	0.	0.000	+0.005	−0.014	−0.03	0
0*	0.	0.000	−0.002	−0.013	−0.03	0
1	79.65	0.736	+0.006	−0.036	+0.69	0.66
2	157.25	1.452	−0.002	−0.049	+1.39	1.33
3	232.78	2.15	?	−0.058	+2.08	1.95
0′	0.	0.000	0.000	+0.015	0.00	0
0*′	0.	0.000	+0.008	+0.015	+0.01	0
1′	79.65	0.736	−0.004	+0.038	+0.76	0.75
2′	157.25	1.452	....	....	...	(1.5)
3′	232.78	2.15	?	+0.060	+2.2	2.2

to make it certain that $\bar{n}_i - \bar{n}'_0 = 0$ in (25) and (26). And this accounts for the fact, to which Mecke called attention without offering an explanation, that γ_i is proportional to i; for, since the bands are approximately equally spaced, ${}_0\nu_i - {}_0\nu_0$, the variable factor in the principal term in (31), will be proportional to i. Moreover, since none of the series (21) appear to contain any antistokes members, it is probable that the common value of $\bar{n}$ is the least possible. We shall, for simplicity, call this minimum value 0, though it is more probable that $\frac{1}{2}$ is correct.

The values of γ_i could be checked by calculating $\bar{m}_i$ and $\bar{m}'_0$ directly from (11), using the average value of B''_0 in Table 1, and would be found to agree only fairly well. But γ_i is much larger, and consequently more accurately known, than η_i, so that it is preferable to use the equations so obtained to deduce a presumably more accurate value of B''_0. From (11)

$$\bar{m}_i = \mp\left(\frac{d_i}{4B''_0} + 1\right) \quad (33)$$

$$a''(\bar{m}_i^2 - \bar{m}_0'^2) = a''\frac{d_i^2 - d_0'^2}{16B_0''^2} + a''\frac{d_i - d'_0}{2B''_0} = \gamma_i. \quad (34)$$

Table 3 gives in the second and fifth columns the value of B''_0 calculated from (34), and in the third and sixth columns, the values of $\bar{m}_i$ calculated from (33) using the average value of $B''_0 = 0.0366$. The

TABLE 3

i	B_0''	$\bar{m}_i$	i'	B_0''	$\bar{m}'_i$	m''_H
0		31.3	0′		34.5	1.94
0*		30.0	0*′		34.2	1.48
1	.0367	81.9	1′	.0367	86.4	2.48
2	.0366	110.8	2′			
3	.0362	131.	3′	.0349	134.	
	Average*			.0366		1.97

* Weighted according to number of doublets in the series.

discrepancy between these values of B''_0 and those in Table 1 is rather unsatisfactory, but is undoubtedly attributable to the large experimental errors in the determination of the η_i which enter (13).

It is of interest to calculate the location of the band heads, m''_H, which, of course, depends on the ratio of the coefficients of the linear and quadratic terms in (28).

$$m''_H = \frac{-B'}{C}. \tag{35}$$

Substituting $B' = B'' + C$ from (28) and taking $C = -0.013$ from (32) and $B''_0 = 0.0366$ from Table 3 we obtain

$$m''_H = \frac{B'' + C}{-C} = 1.82. \tag{36}$$

m''_H can be calculated in another and independent way from B''_0 and the d_i. For, subtracting the two equations represented by the upper and lower signs in (28)

$$g'_i - g_i = 2B'(\bar{m}'_i + \bar{m}_i) + C(\bar{m}_i'^2 - \bar{m}_i^2) \tag{37}$$

or

$$(m''_H)_i = \frac{B'}{-C} = \frac{\bar{m}'_i - \bar{m}_i}{2} - \frac{g'_i - g_i}{2(\bar{m}'_i + m_i)C}$$
$$= \frac{-d'_i - d_i}{8B''_0} - 1 - \frac{2(g'_i - g_i)B''_0}{(-d'_i + d_i)C}. \tag{38}$$

The values of $(m''_H)_i$ calculated by (38) are given in the seventh column of Table 3, and are seen to agree well with the value in (36). Had B''_0 been taken, from Table 1, as 0.030, the value of m''_H from (36) would have been 1.3 and the average value from (38) 2.5; which is unsatisfactory. This confirms our opinion that 0.0366 is the better value of B''_0.

SECTION 7. CORRELATION OF THE FLUORESCENT AND ABSORPTION SPECTRUM

We can now identify, in Wood's reproduction, Plate IF, of the iodine absorption spectrum, the lines which excite the stronger fluorescent series (21). Mecke(7) has measured this reproduction and found that most of the strong lines fit into three series, Ia, Ib, and II, shown in Figure 2. Now the fluorescent series ν_0, ν'_0, ν''_0 and ν'''_0 must,

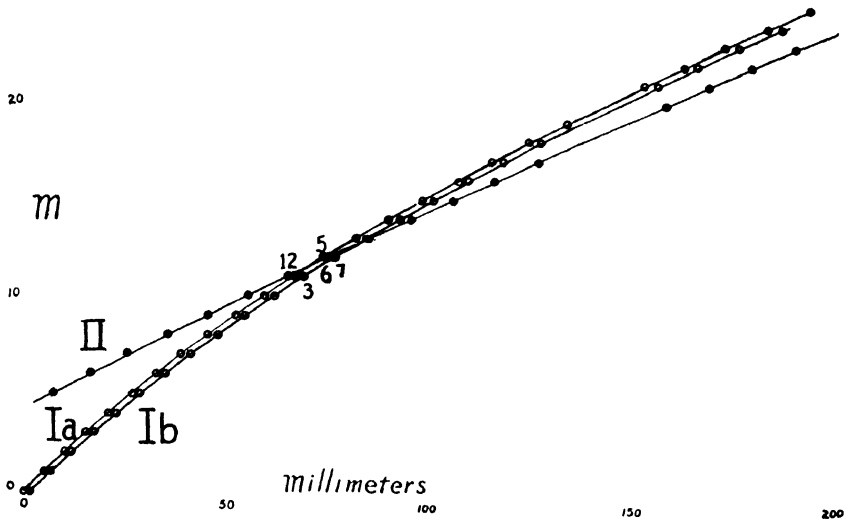


FIGURE 2.

on our theory, belong to the same band, since they all have $\gamma=0$. And this is quite possible, since the spacing,

$$\frac{d\nu}{dm} = \pm 2B' + 2Cm'' = -0.82 \text{ cm}^{-1}, \tag{39}$$

calculated from Table 3 and equation (32), between successive lines in either the R or P branch of the band $i=0(26,0)$ is small enough to allow two lines of each branch to fall within the wide green mercury line. It is an obvious step to identify Mecke's series Ia and Ib with the P and R branches of this band. They have the right spacing, about 7.45 mm. on the reproduction, which corresponds to $d\nu/dm = -0.83$ cm^{-1}. And they supply the four absorption lines within the green mercury line, which are needed to account for the four series of doublets. One of them, Ib 11, is Wood's absorption line 3 which nearly coincides with the narrow green mercury line, and which certainly excites the fundamental series ν'_0. Now series ν'_0 and ν'''_0 have a negative doublet interval and their main

lines must therefore belong to the R branch. It follows that series Ib is the R branch, and that Ib 12, the other line in this series within the green mercury line, excites $\mathring{\nu}'_0$. Lines Ia 11 and Ia 12 must excite series ν_0 and $\mathring{\nu}_0$. That they are to be assigned as in Table 4, and not in the alternative manner, is proved by the fact that this assignment gives corrected doublet intervals $\Delta\nu_0 = 4.43$, $\Delta\mathring{\nu}_0 = 4.24$, which agree, while the alternative assignment does not.

It is natural to expect that the next strongest absorption series in the $\lambda 5460$ region will be the R and P branches of the band (27, 0) $i=1$, to which ν'_1 and ν_1 belong. The spacing between successive lines in either branch of this series calculated by (39) should be 2.11 cm^{-1}, whereas Mecke finds the single series, II, with a spacing of 10.0 mm. corresponding to 1.12 cm^{-1} or about half what one should expect. The natural conclusion is that alternate lines of this series II belong to the R, the others to the P branch. Series ν_1 should be assigned to line II 12, rather than to II 11, which also lies within the green mercury line, because this gives a corrected doublet interval in the zero order which agrees well with the $\Delta\nu_1$ in higher orders, whereas the alternative assignment does not. This leaves II 11 to excite series ν'_1.

Series ν_2 is assigned by Wood to absorption line number 4 because it is the first new series to come out when the green mercury line, which lies between absorption lines 3 and 4, is broadened, either by raising the potential from 30 volts, which excites only the fundamental series, to 60 volts, or by using end-on emission. We can now be sure of this point because line 4 is the only absorption line shown on the reproduction within the green mercury line, which has not been assigned by Mecke to his series Ia, Ib, or II.

Mecke's series ν'_2 is probably illusory. It is based on only 5 main lines and no companion lines, although the intensity of the two components of a doublet should be equal. Moreover, most of the supposed main lines fit about equally well into other series. Moreover, an extrapolation of the relative positions of adjacent P and R lines in the zero and first bands (series I and II) indicates that no line of the R branch of the second band can lie within Hg 5460.

No lines within Hg 5460 are left to account for series ν_3 and ν'_3 which must be excited by absorption lines either too faint to be detected, or in coincidence with others, or possibly by absorption line 0 which is in coincidence with a satellite of Hg 5460.

The above assignments are summarized in Table 4.

Having identified the main lines in the absorption spectrum, it is easy to pick out the corresponding companion lines by adding or subtracting

the known doublet interval. The resulting correspondence is also shown in Table 4. The fact that both main lines in the Ib series turn out to have companion lines in the Ia series, and *vice versa*, and that the companion line of II_q 11, an odd-numbered line, is II 22, an even-numbered line, is a good check on our interpretation of these three series.

Wood([11], p. 85) has investigated the rotation of the plane of polarization of mercury arc light passed through iodine vapor parallel to a strong magnetic field and has reported that the direction of rotation in the neighborhood of five of the absorption lines is as shown in the seventh column of Table 4, where a + sign indicates the normal direction of rotation, the same as for the D lines of sodium. It will be seen that we

TABLE 4

CORRELATION OF ABSORPTION WITH FLUORESCENT LINES IN THE ZERO ORDER

Series	Exciting (main) line						Companion line				
	Branch	Wood's number	Mecke's number	Position on reproduction	$\nu - 18307.5$	Magnetic rotation	Branch	Wood's number	$\nu - 18307.5$	Mecke's number	Position on reproduction
ν_0	P	5	Ia 12	73.5	− 0.526	+	R	5	+ 3.9	Ib 6	34.5
ν_0*	P	2	Ia 11	66.4	+ 0.255	+	R	4	+ 4.6	Ib 5	28.3
ν_1	P	6	II 12	74.9	− 0.650	+	R	3	+ 11.4	....	....
ν_2	P	4	....	70.4	− 0.174	+	R	2	+ 16.1	....	....
ν_3	P	..	....	....	....	..	R	1	....	....	....
ν_0'	R	3	Ib 11	68.7	0.000	—	P	7	− 5.0	Ia 17	114.5
ν_0*′	R	7	Ib 12	76.2	− 0.838	..	P	8	− 6.1	Ia 18	123.5
ν_1'	R	1	II 11	64.9	+ 0.460	..	P	9	− 12.2	II 22	178.6
ν_2'	R	—	—	—	—	..	P	—	—	—	—
ν_3'	R	..	....	....	....	..	P	..	....	....	....

have been forced to assign to a P branch every line which shows + magnetic rotation, and to an R branch the line which shows − magnetic rotation. For the interpretation of this result the reader is referred to Chapter VII.

Having identified in the absorption spectrum both lines of the fluorescent doublets, we know which lines in the R and P branches have the same m', and can easily deduce which have the same m''. We are now in a position to plot the corresponding frequency differences

$$\nu_R(m') - \nu_P(m') = 4B''(m''_R + 1) = \nu_b(b) - \nu_a(b+6) = 4B''[m''(b) + 1] \quad (40)$$

and

$$\nu_R(m'') - \nu_P(m'') = 4B'(m'_R - 1) = \nu_b(b) - \nu_a(b+4) = 4B'[m'(b) - 1] \quad (41)$$

against b, the arbitrary number which Mecke has assigned to lines in the R branch; to find $4B'$ and $4B''$ from the slopes of the graphs; and to

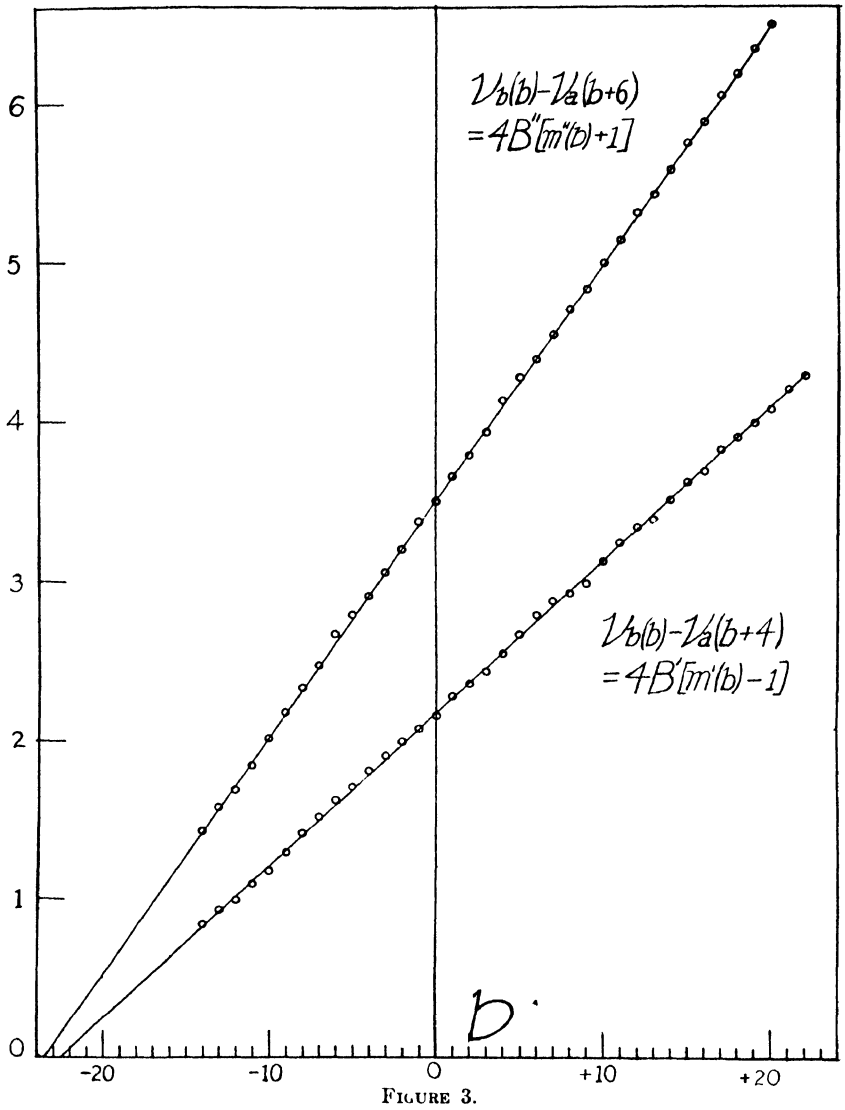


FIGURE 3.

determine the absolute numbering of the lines from the line number at which the frequency differences extrapolate to zero. See Figure 3.

This the author has done, using the wave lengths of the fluorescent lines as reported by Wood to determine the scale of his absorption spec-

trum reproduction, on which comparison lines are lacking; with the following results:

$$B'=0.0248 \qquad B''=0.0384 \qquad C=B'-B''=-0.0136. \tag{42}$$

Results much better than the above have, however, been obtained by analyzing some plates of the iodine absorption spectrum taken by Wood and Klingaman for a forthcoming paper([13]) and kindly made available to the author in advance of publication. The analysis has not yet been completed but it has already proved possible to identify some 100 or 200 lines in each of seven bands overlapping the green mercury line and to deduce therefrom accurate values of the constants of the iodine molecule, of which the following are of interest here:

$$\begin{aligned} B'(29) &= 0.023368 \pm 0.000005 \\ B''(0) &= 0.037300 \pm 0.000003 \\ C(29,0) &= -0.013932 \\ B'(0) \text{ extrapolated}^2 &= 0.0391 \\ I'_0 &= 951\times10^{-40} \text{ g. cm}^2. \\ I''_0 &= 742\times10^{-40} \text{ g. cm}^2. \\ r'_0 &= 3.01\times10^{-8} \text{ cm}. \\ r''_0 &= 2.66\times10^{-8} \text{ cm}. \end{aligned} \tag{43}$$

The absolute values of m' for the zero order fluorescent lines are given in Table 5, together with their probable errors. Also, the frequencies of the companion lines reported by Wood are given in column 4 for comparison with the frequencies of the corresponding absorption lines in column 5.

TABLE 5

Band	i	m'		Frequency of companion line: in fluorescence	Frequency of companion line: in absorption
(26, 0)	0	29 551	± 0 055	18311.4	18311 37
	0*	28.551		18312.1	18312 04
	0′	34 551		18302 5	18302.36
	0*′	35 551		18301.4	18301 36
(27, 0)	1	80.515	± 0.03	18318.9	18318 82
	1′	85 515		18295.3†	18295.22
(28, 0)	2	108.5		18323 6	18323.45
	2′	none		.....	.....
(29, 0)	3	129 5		18326 3	18326 23
	3′	134.5		18387 9	off plate

† Wood gives 18294.8. The value in the table is from a remeasurement of his reproduction.

Figure 3 shows the frequency differences which occur in equations (40) and (41) plotted, for band (26, 0), against Mecke's b. The frequencies

[2] For the method of extrapolation see a paper by the writer in the Physical Review for January 1927.

were measured on Wood and Klingaman's plates. The numbers in (43) are based on more data than are shown here, including measurements of several other bands, some of which were followed to values of m as high as 150. In these bands cubic terms had to be added to equations (40) and (41).

The values of m' in Table 5 are evidence for the doctrine of "half-quantum numbers"; or at least they definitely disprove the earlier hypothesis of integral numbers and are consistent with half-integral ones.

The relation of the fluorescent doublets of zero order to their absorp-

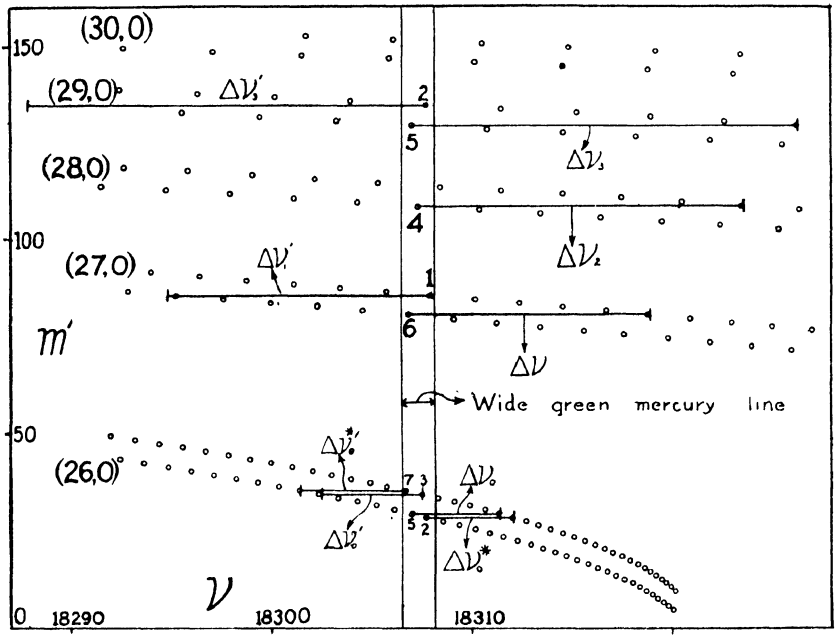


FIGURE 4.

tion bands is shown in Figure 4 wherein m' is plotted against observed values of ν in the region near Hg5460 for the bands (26, 0), (27, 0), (28, 0), (29, 0), (30, 0), the first four of which are responsible for the fluorescent series 0, 1, 2 and 3 respectively. The fluorescent doublets are indicated by horizontal lines.

It should be noted that the unravelling of the complex iodine absorption spectrum, and particularly the assignment of absolute quantum numbers, would probably have been impossible without the clues furnished by data on fluorescence. For, particularly in the green, the lines are so crowded and belong to so many overlapping bands that other methods of number-

ing them are out of the question. A perturbation of sufficient magnitude, for instance, would probably result in misidentifying the line. And the origins come so far within the unresolved regions near the heads that the "missing line" could not be located.

SECTION 8. ANTISTOKES DOUBLETS AND THE EFFECT OF TEMPERATURE

The occurrence, in Wood's experiments with the quartz arc, of two groups having greater frequency than the exciting light, the so-called antistokes groups, $p=-1$ and -2, means that some iodine molecules must be able to radiate more energy than they absorb, and must therefore have possessed energy equivalent to at least two quanta before being struck by the mercury light. It is natural to attribute this to thermal energy since two quanta is about the average state of vibration at the temperature of Wood's experiments. This has been confirmed by some experiments which Pringsheim([10]) has made with fluorescent iodine vapor at varied temperatures. He found that, while the doublets of any particular series changed all together with the varying temperature, keeping the same relative intensity, the several doublet series varied with respect to each other, some being weakened and some enhanced by rise of temperature. He even found new series to appear at high temperatures, one at least of which showed antistokes members as high as $p=-4$. This is significant, for it means that the molecules which emitted them must have had four vibrational quanta before absorption, i. e., must have belonged to a class which is comparatively rare at low temperatures and becomes more common as the temperature is raised. Presumably, on the other hand, those series which are weakened by rise of temperature are due to molecules which before absorption have low thermal energy, and which therefore become relatively rarer at higher temperatures.

SECTION 9. INTENSITIES AND THE CORRESPONDENCE PRINCIPLE

The long fluorescent series of lines with a common initial state offers a splendid opportunity for the study of relative probabilities of transition. The intensities of the doublets vary in an irregular manner, orders 2, 7, 14, 21, 24 and 26 being missing from the fundamental series according to Wood([11], p. 39) and the estimated intensities of the doublets from 0 to 19 being given by Lenz([4]) as 10, 9, 1, 3, 8, 2, 9, 0, 8, 3, 2, 7, 0, 7, 0, 2, 1, 0 . . . . This irregularity cannot be accounted for by reabsorption of the fluorescent light, for it is highly improbable that both components of each doublet should coincide with other absorption lines

and be effected equally. But Lenz([4]) has applied the correspondence principle to a simplified molecular model emitting a band spectrum, and has shown that the combination tones in the electronic motion due to a non-linear coupling with the nuclear vibration may, if certain constants have suitable values, be such as to correspond to very irregular variation with n'' of the probability of transition. For instance, he gives one set of calculated values as : 0.97; 0.03; 1.02; 0.055; 0.77; 0.88; 0.003; 0.75; 1.62; 1.36; 0.69; 0.16; 0.063; 0.013; 0.0023; 0.0003; 0.00004. This is qualitatively very similar to the above set of observed values, even to the characteristic occurrence of very weak lines between two strong ones. For further discussion see Chapter IV Section 8, and Chapter VII, Section 1.

SECTION 10. ULTRA-VIOLET EXCITATION

Iodine fluorescence has been studied by McLennan([5]) using various sources of ultra-violet light for excitation. The resulting spectra are much more complex than Wood's and have not yet been analyzed in detail; but a number of interesting qualitative relations have been noted. The fluorescence begins in the ultra-violet with series apparently similar to those excited by the green mercury line, but merges into a complex band spectrum in the visible. This band spectrum, quite unlike the fluorescence in Wood's experiments, does not depend either in position or intensity distribution on the particular source of ultra-violet light used to excite it; provided the source supplies strong light in the region 1800-2000A. Undoubtedly the essential difference between Wood's and McLennan's experiments is that absorption of the green mercury line leaves the iodine molecule in a state from which only a direct return to the normal electronic level is possible; but the greater amount of energy available after ultra-violet excitation makes possible a return to the normal level by several stages. The series of doublets in the ultra-violet would then correspond to the direct return to the normal electronic level, as in Wood's experiments. But molecules which fell first to an intermediate electronic level would occupy a series of vibrational and rotational states which would be initial states in the subsequent fall to a still lower level. In other words, they would emit a group of bands in the second stage. And this group would be independent of the original excited state, and hence of the exact line used for excitation.

SECTION 11. IONIC RECOMBINATION SPECTRUM

Another interesting aspect of the iodine fluorescence excited by ultra-violet light is the continuous band at 3460 Å which has been studied by

Oldenberg([9]) and which he attributes to the recombination of the ions I^+ and I^-. His reasons are as follows. In the first place, on the addition of a foreign gas this band behaves quite differently from the ordinary band spectrum fluorescence. The effect on the ordinary fluorescent spectrum of adding any other gas such as He, Ne, H_2, O_2, or CO_2, but especially N_2 is, as explained in Section 5, to transfer energy by collisions of the second kind between excited iodine molecules and molecules of, say, N_2. This, if the N_2 pressure is not too great, merely results in a multiplicity of initial states for fluorescence and a more complex fluorescent spectrum; but at large N_2 pressures so much of the energy is transferred to the N_2 and dissipated, that the fluorescent spectrum is completely extinguished. On the other hand, the 3460 band is not weakened, possibly even brightened, by the addition of foreign gases even at atmospheric pressure. The only effect on it is to shift its intensity towards the low frequency edge at high pressures and to cause it to separate into continuous partial bands. (See Plate IIM.) It seems certain that the initial state for bands which behave in this way must be some sort of ions; for any sort of excited molecule must surely become a prey to collisions of the second class, while a pair of ions cannot lose their energy of separation until they come near enough to recombine. Other conceivable pairs of ions are eliminated by various considerations such as insufficient energy, etc., ([9]). That the final state in the emission of this band is an iodine molecule follows from the resolution into partial bands by pressure of foreign gases. The interval between these partial bands is about 95 wave numbers, which is the order of magnitude of the intervals between successive bands in the n' series and indicates that the molecule left after the recombination of the ions and the emission of the 3460 bands is still excited. The continuity of this band in pure iodine, and of the partial bands into which it is resolved by pressure, is undoubtedly due to the continuous range of kinetic energies possible in the separated state of the ions, which is the upper level in emission. Oldenberg does not offer any plausible explanation of the effect of pressure in bringing out the structure, which of course is the opposite of the usual effect. But it seems likely that it is due to a limitation, by collisions, of the speeds with which the ions approach each other, and hence of the range of energies in the initial state. This is confirmed by the fact that a rise of temperature causes these bands to fade out again; and that while different foreign gases need to be at different pressures to bring them out, the bands are always at the same positions.

The rather sharp low frequency edge of this band, corresponding, of course, to high final vibration quantum numbers, is attributed by

Oldenberg to an approaching instability of the molecule; the evidence for which is the considerable drop in the frequency interval between the bands near this edge. An apparently analogous phenomenon has been noticed by Mulliken([8]) in the spectrum of CaH.

BIBLIOGRAPHY

[1] Kemble and Witmer, Phys. Rev., N. S., 28: 633 (1926).
[2] Kratzer and Sudholt, Z. Physik, 33: 144 (1925).
[3] Lenz, Physik. Z., 21: 691 (1920).
[4] Lenz, Z. Physik, 25: 299 (1924).
[5] McLennan, Proc. Roy. Soc., 88A: 289 (1913); 91A: 23 (1914).
[6] Mecke, Z. Physik, 7: 73 (1921).
[7] Mecke, Ann. Physik, 71: 104 (1923).
[8] Mulliken, Phys. Rev., N. S., 25: 509 (1925).
[9] Oldenberg, Z. Physik, 25: 136 (1924).
[10] Pringsheim, Z. Physik, 7: 206 (1921).
[11] Wood, "Researches in Physical Optics," part II. New York, Columbia Univ. Press, 1919.
[12] Wood, Phil. Mag., 35: 236, 252 (1918).
[13] Wood and Klingaman, not yet published.

CHAPTER VII

MOLECULAR MODELS, GYROSCOPIC MOTION, THE ZEEMAN EFFECT, AND RELATED TOPICS

EDWIN C. KEMBLE

SECTION 1. THE FORCES WHICH GOVERN MOLECULAR VIBRATIONS

PART 1A. THE DUMB-BELL MODEL

The first model of the molecule to which the student of band spectra is usually introduced consists of a pair of heavy particles (nuclei) with a mutual potential energy $V(r)$ dependent only on their separation (cf. Chapter II, Section 5). In this model we may consider that the electronic orbits associated with the atoms have been replaced by a weightless spring with a somewhat complicated law of force. In justification of the use of this artificial picture one may observe that, whatever the nature of the orbits, a very slow relative displacement of the nuclei produced by external forces applied directly to them will be reversible (Ehrenfest's adiabatic principle) and will require an amount of work depending only on the initial and final values of the internuclear distance r. The energy supplied in this manner in order to change the internuclear distance from its equilibrium value to any other is to be identified with the potential energy of the spring. It actually goes partly into mutual potential energy of nuclei and electrons and partly into kinetic energy of the electrons. The " potential " energy function governing such slow displacements will also govern the rotary and vibratory motions of the nuclei provided that the vibratory variations in r take place slowly enough to permit the electron orbits to adjust themselves to the instantaneous value of r.

It seems probable that the above idealization of the molecule will cease to work when the frequency of the internuclear vibration becomes comparable with one of the electronic frequencies. The action of an external light wave on an atom presents an interesting analogy. If the wave has a frequency low compared with that of the first absorption line of the atom, the polarization produced by this varying external influence, as recorded by dispersion, is sensibly the same as for a static field. On the other hand, if the frequency of the light wave is close to that of an absorption line, the atom not only ceases to react statically, but ceases also to react in accordance with the Newtonian mechanics.

This observation lends point to the study made by Birge [1] of the effective potential energy functions governing the vibratory and rotary motions of molecules, for in dealing with the rotational energy levels for the state of zero vibration we are observing the effective potential energy under essentially static conditions. In the cases examined by Birge, the two energy functions seem to be the same, but the foregoing argument would suggest that the result would be different in the case of a molecule in which there is an electronic frequency as low as the vibrational frequency. Presumably there is such a low frequency in case the energy level whose effective potential energy is under consideration is a member of an electronic multiplet.

It is of interest to inquire regarding the effect on the electronic orbits of changing internuclear distance. The most obvious result of such a change is a distortion of shape such as that which accompanies the polarization of an atom in an external electric field. An effect of even greater importance from some points of view, however, is the change of kinetic energy and frequency. It is a well-known theorem of the classical mechanics that in a system of particles attracting or repelling each other according to the inverse square law the total energy is equal to the negative of the mean kinetic energy. Assuming, for the moment, the validity of the classical mechanics for the stationary states of a molecule, we may apply the theorem to the electrons alone if we imagine the nuclei held rigidly in place at some arbitrary relative distance r by forces external to the system.[2]

The mean kinetic energy of the electrons is then equal to the negative of their total energy or to the work required to remove them all to rest at infinity. The value of this energy as a function of r can be obtained by subtracting the nuclear potential energy from the effective potential energy $V(r)$ of the spring of the equivalent dumb-bell model. Denoting the atomic numbers by Z_1 and Z_2, we thus obtain the expression

$$E^e = -\overline{T} = V(r) - \frac{e^2 Z_1 Z_2}{r} + \text{const.} \qquad (1)$$

for the kinetic energy in question. As the product $Z_1 Z_2$ is large, the variation of $\frac{e^2}{r} Z_1 Z_2$ with r is probably always much larger than the variation in $V(r)$ for any internuclear distance to be considered in connection with a band spectrum problem. Reference to the $V(r)$ graph for

[1] Chapter 4, Section 8, p. 236.

[2] An inspection of the proof of the theorem (cf. Van Vleck, "Quantum Principles and Line Spectra," p. 20) shows that it is applicable if some of the particles are held fixed provided that the mutual energy of the fixed particles is not included in counting up the "total" energy. [This statement is incorrect. Aug., 1930.]

the HCl molecule given by Kemble([1]) gives convincing evidence on this point. The curve shows V plotted against r_0/r. The function $e^2Z_1Z_2/r$ when plotted against the same independent variable would give a straight line with a slope 17 times the limiting slope of the $V(r)$ curve for infinite r or zero r_0/r. Hence the mean kinetic energy of the electrons must increase as r decreases and we may infer that the frequencies of the electronic motions also increase as the atoms in a molecule are brought closer together.

The latter inference is supported by introducing the quantum conditions in the form

$$\overline{T}_k = \tfrac{1}{2} n_k h \omega_k \tag{2}$$

in which $\overline{T}_k$ and n_k denote respectively the mean kinetic energy and the quantum number associated with the frequency ω_k. According to the adiabatic principle the n's will be unchanged during a slow variation in r and, as the quantum numbers may always be chosen in such a way as to be intrinsically positive, it is clear that

$$\sum_k n_k \frac{\partial \omega_k}{\partial r} = \frac{2}{h} \frac{\partial \overline{T}}{\partial r} < 0. \tag{3}$$

Thus the assumption that the classical mechanics may be used to describe the stationary states leads to the conclusion that *in general* the frequencies of the electrons increase with decreasing nuclear separation. Individual frequencies may, however, depart from the general rule.

Fortunately there is another line of attack which gives us information about the variation with r of the electronic frequencies associated with the various band systems. The band spectrum data enable us to determine the first terms in the power series expansion for the apparent potential energy $V(r)$ in the neighborhood of the equilibrium point([1]). In some cases the general course of the entire curve may be determined for both the upper and lower energy levels connected with a band system. Figure 1a shows a pair of such curves drawn up for a band system in which the more excited state has about the same moment of inertia (equilibrium value of r) and vibrational frequency as the less excited, while Figure 1b shows a case in which the upper energy level has a larger moment of inertia and a lower vibrational frequency. The difference between the ordinates of such a pair of curves for any given value of r has the following simple interpretation.

Let the nuclei be assumed to be held fixed by external forces so that they cease to form a part of the system to which the quantum conditions are applied. Then let the electronic transition $e' \rightarrow e''$ associated with the band system take place with r subject to constraint. The energy change,

in accordance with (1), must be equal to the difference in the corresponding ordinates of the two $V(r)$ curves. By the mean frequency theorem [1] it is also proportional to a mean value of the electronic frequency ω_e associated with the transition. Hence

$$V'(r) - V''(r) = \sum \int_{e''}^{e'} \frac{\partial E}{\partial e}\, de = h\bar{\omega}_e \qquad (4)$$

where the sum is to be extended over all the electronic quantum numbers involved and $\bar{\omega}_e$ is the mean obtained by averaging ω_e over a continuous series of classically permissible non-quantized orbits or states intermediate between these determined by e' and e''. (ω_e itself is, of course, not necessarily one of the fundamental electronic frequencies, but may be a combination tone formed from them). Hence the variation in $\bar{\omega}_e$ with r is measured by the $V' - V''$ curve. It is easy to see graphically that when

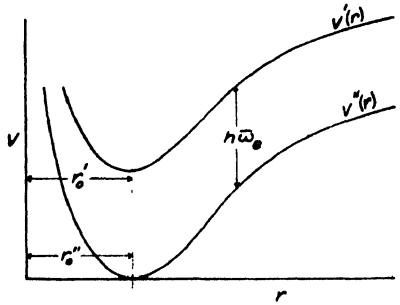


FIGURE 1a.

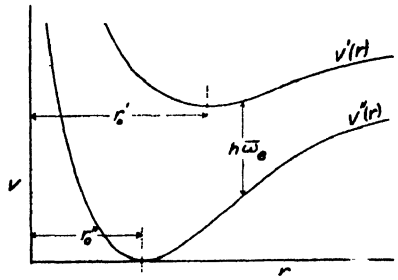


FIGURE 1b.

r_0 (the equilibrium value of r) is greater for the excited state, $V' - V''$ must decrease with increasing r in the neighborhood of the points $r = r'_0$ and $r = r''_0$; while, if r_0 is least in the excited state, $V' - V''$ must increase with increasing r. We may conclude that if the moment of inertia of a molecule is increased by excitation, the corresponding mean electronic frequency $\bar{\omega}_e$ (and probably also ω'_e and ω''_e) must decrease with increasing nuclear separation, and vice versa.

Empirically we find that the moment of inertia may either increase or decrease when a molecule passes from a lower to a higher electronic energy level. Equation (3) indicates that the former case should be the more common and the experimental facts seem to corroborate this prediction.

The variation in the electronic frequency with r thus correlated with the V' and V'' curves is to be identified with the variation postulated by Lenz([2]) in his attempt to explain by the correspondence principle the

[1] Cf. Chapter II, Section 3.

large changes in vibrational quantum number which accompany an electronic transition. He found that if the restoring force governing the motion of a linear oscillator of frequency ω_e is subjected to periodic fluctuations with the frequency ω^n of the nuclear vibration, the perturbed motion is expressible as a sum of periodic terms with the frequencies $\Omega_e + \tau\omega^n$ where τ is a positive or negative integer and Ω_e is the unperturbed value of ω_e. These components are to be correlated with transitions for which $n' - n'' = \tau$. Their amplitudes a_τ are Bessel's functions of order τ and argument $\frac{\lambda}{\omega^n}$ where λ is the maximum difference between ω_e and its mean value Ω_e. If $\frac{\lambda}{\omega^n}$ is small, the amplitude a_0 is the largest and the transition for which $n' - n'' = 0$ should be most prominent, but if $\frac{\lambda}{\omega^n}$ is large, the coefficients vary irregularly as τ increases from 0 to $\frac{\lambda}{\omega^n}$ beyond which point they drop gradually to zero. The occurrence of transitions with large values of $n' - n''$ is thus to be correlated with a large variation in the electronic frequency.

Our present point of view goes beyond that of Lenz in showing that such large changes in frequency should accompany transitions in which there is a large change in the molecular moment of inertia. This is the same condition as that required by Franck's "mechanical" theory for large changes in n and is in accordance with the observed facts.[4] λ may be taken, as a first approximation, equal to the product of the amplitude of the nuclear vibration and $\frac{1}{h}\frac{\partial}{\partial r}(V' - V'')$. If $\frac{\partial}{\partial r}(V' - V'')$ is treated as constant and if V is treated as a quadratic function of $r - r_0$ near the equilibrium point, the following rough approximation for the change in internuclear distance may be derived

$$r'_0 - r''_0 = -\frac{\frac{\partial}{\partial r}(V' - V'')}{\frac{\partial^2 V}{\partial r^2}}. \tag{5}$$

A simple calculation shows further that for a vibrational motion of quantum number n

$$\frac{\lambda}{\omega^n} = \sqrt{4nP} \tag{6}$$

where P is the number of vibrational quanta required to make the amplitude $r'_0 - r''_0$. The crudity of the approximations involved in deriving (6) will be evident if we observe that the variation in the vibrational

[4] Cf. Chapter IV, Section 8, p. 248.

frequency ω^n from one electronic state to the other is neglected. In the case of iodine where large values of $n'-n''$ are especially prominent, $\frac{\lambda}{\omega^n}$ works out to be $10\sqrt{n}$ if we base the estimate on the vibrational frequency in the lower electronic level, but $8\sqrt{n}$ if we use the vibrational frequency for the upper level. These values are ample to account for the large changes in the vibrational quantum number actually observed.

On the other hand, since the Bessel's function of order zero and argument $\frac{\lambda}{\omega^n}$ is not necessarily small compared with Bessel's functions of higher order with the same argument, this theory is not able to account for the complete absence of transitions in which $n'-n''$ is small as does the theory of Franck. It is not unreasonable to hope, however, that this difficulty may be overcome by the application to the problem of the new quantum mechanics of Heisenberg and Born.

Part 1b. Polar Molecules

The typical polar molecule of the chemists is composed of positive and negative ions, its formation having been accompanied by the transfer of one or more electrons from one atom to another. Molecules of this type have normally such large electric fields that they are difficult to vaporize and have not been studied to any great extent in the gaseous form. The non-metal hydrides, however, form an exception to this rule due to the small size of the hydrogen ion which may permit it to imbed itself in the outer portion of the electron-sphere of the negative ion to which it is attached; thus reducing the electric moment to a moderate value.

There can be no doubt, in view of the work of Born, Debye, and others on the properties of solid ion-aggregates and of ions in solution, that molecules of this type are held together by electrostatic forces. At very large distances each ion may be regarded as a point charge and the attractive force is governed by the Coulomb inverse square law. When the distance between the ions is smaller, the polarization of each by the electric field of the other must be taken into account. As a first approximation, the induced atomic dipole moment may be assumed to be given by an equation of the form

$$P = \alpha E$$

where E is the external electric field (assumed uniform) and α is a constant called the atomic polarizability. The value of α may be determined from dispersion measurements([3]). As the electric force at a point on the axis of a dipole and distant r cm. from it is $\frac{2P}{r^3}$, and as the inducing field

is approximately e/r^2, the additional attractive force due to P is

$$F_P = \frac{2ae^2}{r^5}.$$

A natural step forward consists in the investigation of the extent to which the properties of molecules of this type can be accounted for in terms of an ion-model consisting of a charged polarizable sphere with a repulsive field varying as some large inverse power of r. The recent work of Hund([4]) in this direction is notable since it shows that the triangular form required for the molecules of H_2O and H_2S by several lines of evidence may be accounted for by an ion model of spherical symmetry. It would seem at first glance as if a symmetrical rectilinear arrangement of the atoms in these molecules would be required by the assumption of symmetrical force fields and that the triangular form must indicate "directed valence." Happily for the simplicity of the theory, this is not the case. In shifting from the symmetrical rectilinear arrangement to a suitable isosceles triangle, the increment in the mutual potential energy of the hydrogen nuclei is offset by the decreased mutual energy of the hydrogen nuclei and the oxygen or sulphur ion brought about by the polarization of the latter. If the polarizability of the negative ion is large enough, the triangular configuration is therefore the stable one. In the same way Hund shows that if the polarizability of the N^{---} ion in NH_3 is large enough, the stable configuration is a polar one of tetrahedral form.

A rough approximation to the energy of dissociation into ions for polar molecules can be made either by treating the ions as rigid polarizable spheres or as polarizable spheres carrying a repulsive force field varying as some large inverse power of the distance. In the case of H_2O, for example, Hund, using data based on Eucken's determination of the moments of inertia and C. P. Smyth's measurement of the electric moment, calculates the heat of dissociation into ions from the model and obtains good agreement with the value computed from thermochemical data. The method is a crude one, however, and Hund in a later paper([5]) makes use of the band spectrum data on the course of the potential energy curve in the neighborhood of equilibrium value of r. This is combined with the theoretical curve for large values of r determined from the charges and polarizability to yield a more reliable estimate of the heat of dissociation.[5]

Most discussions of the forces exerted on each other by the atoms or ions which compose a molecule or by atoms and ions in collision, assume

[5] Hund finds that in the case of HCl the potential curve determined in this way is in harmony with Born's calculation of the energy of dissociation from thermochemical data and the grating energies of chlorine salts. The more recent work of Kemble([1]), however raises serious doubt as to the validity of Hund's conclusion.

a repulsive force varying inversely as some large power of r, without discussing the origin of this force. In the case of the polar halides, the repulsive force at short distances may be accounted for by assuming that the H nucleus penetrates the outer boundary of the electron-swarm which surrounds the nucleus of the negative ion. If so, it enters a region in which the outermost electrons no longer attract it strongly so that the repulsive force between the two nuclei exceeds the net attractive force of the electron-swarm and the H^+ ion. The hypothesis is plausible in view of the small size of the H^+ ion and permissible from the standpoint of the distances involved. In HCl, for example, the internuclear distance is 1.28×10^{-8} cm. and the mean radius of the sphere occupied by the outermost group of the chlorine electrons is estimated to be about 0.95×10^{-8} cm. The latter figure refers to a Cl^- ion undistorted by external action. The measurements of the electric moment of the HCl molecule show that the Cl^- ion * has an induced electric moment equal to that of a proton and electron about 10^{-8} cm. apart, and since most of this moment must come from the loosely attached 3_1 and 3_2 electrons, it is possible that orbits of these electrons are sufficiently distorted to pass around the H nucleus.

The foregoing explanation of the repulsive force is not wholly satisfactory, however, since it is not applicable to the repulsive force exerted at short distances by two atoms or ions both of which have electron shells. It seems to the writer fairly certain that in most cases there is no appreciable penetration of the outer shells. Such a penetration would involve an apparently hopeless distortion of the orbits in which electrons originally belonging to one atom would jump over to the other. Moreover, if such a penetration occurs, there is apparently nothing to arrest it until it has become large enough so that the outer electrons of one atom pass around the core of the other. The possibility that some of the electron orbits do enclose both nuclei and are thus shared by both atoms is a familiar suggestion for such non-polar and semi-polar molecules as N_2 and CO. The hypothesis of the sharing of valence electrons is not plausible for such crystalline salts as NaCl, however, and cannot possibly be regarded as a universal characteristic of the formation of molecules. In fact it is open to serious question for such typical non-polar molecules as H_2 and I_2. The evidence will be discussed in Part 1c.

We are thus led to the conclusion that in many molecules each atom retains its own electron orbits and that the two electron spheres do not interpenetrate. To account for the absence of penetration we must postulate the existence of a force of repulsion between the electron shells of

* The moment of the molecule as a whole is equal to that of charges $+e$ and $-e$ separated by the internuclear distance minus the moment induced in the Cl^- ion.

atoms and ions strong enough at short distances to overcome the attractive force and ultimately to maintain the identity of colliding atoms at whatever relative speed they may strike each other.

The mention of collisions in connection with this force of repulsion should serve as a warning that we are here concerned with a question which does not lie wholly within the realm of the classical mechanics and the Bohr theory of stationary states. The repulsive force between the atoms in a molecule can hardly be considered as distinct from the repulsive force exerted by free atoms in collision, and the latter, in turn, can hardly be differentiated in principle from the repulsive forces exerted in collisions between free electrons and atoms. But impacts of the last mentioned type lie clearly outside the realm of ordinary mechanics. The experiments of Ramsauer, Townsend, and others show that atoms are transparent to electrons moving with very low velocities, though they act as if rigid in impacts with electrons of intermediate speed. When the energy of the impacting electron reaches the first excitation potential of the atom there is a sudden transition from the elastic to the inelastic type of collision and finally, when it reaches a very high value (cathode and beta rays), the atom once more becomes relatively transparent.

Perhaps the most hopeful suggestion bearing on this puzzling situation is the "mechanical correspondence principle"([6]), ([7]), ([8]), ([9]), first formally enunciated by Pauli. This principle asserts the existence of a correlation between the transitions which accompany an actual collision between an electron and an atomic system, or between two atoms or molecules, and the changes which would occur if the classical mechanics were valid, such that in the limiting region of large quantum numbers the actual statistical result of the collisions asymptotically approaches that to be expected from the classical mechanics. This point of view has been applied with success to the study of atomic collisions by Born, Jordan, and Nordheim.([8]), ([9]). It harmonizes obviously with the success of the classical theory of the scattering of alpha particles on which the nuclear conception of the atom is based.[7]

[7] It is of interest to note that the mechanical correspondence principle suggests the probability that changes in the nuclear energy which result from the impact of an electron with a diatomic molecule must be essentially incidental to the electronic changes produced by the collision The argument rests on the fact that the period of vibration of the typical diatomic molecule (10^{-14} seconds) is large compared with the time of collision with an electron of moderate energy. For example, the velocity of an electron with five volts of energy is about 10^8 cm./sec. and the duration of the collision with an atom, estimated as the time required to travel 10^{-8} cm. would be 10^{-16} seconds. As this is only a hundredth part of the period of vibration, the change in the internuclear distance during the collision will normally be quite small. It follows that if the electron actually strikes only one

If there is such an asymptotic agreement between the results of actual collisions and the predictions of the classical theory, we may suppose that each of the forces actually operative between atoms in collision has a classical analogue. The first steps toward understanding the repulsive forces between atoms or molecules may therefore be made on a classical basis.

In his crystal lattice theory, Born has used a static atom model with the outer electrons arranged at the corners of a cube. Two neutral cubic atoms of this type repel each other when placed face to face and oppositely charged ions of similar construction and orientation will do the same at very short distances. They attract, however, when placed corner to face and the average force between neutral atoms for all orientations is

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atom (as will usually be the case) the other will have little part in the encounter. From the classical point of view each atom would therefore be expected to react to the colliding electron as if free and the transfer of momentum from the electron to the atom struck should therefore be subject to the same restrictions as those which operate during the collision between an electron and a free atom. The fraction of its energy which an electron can convert directly into nuclear kinetic energy should therefore be very small (of the order of magnitude of the ratio of the mass of the electron to that of the atom). The argument thus leads to the conclusion that changes in the vibrational quantum numbers of molecules produced by electronic collisions must be incidental to the electronic changes just as vibrational changes are incidental to electronic changes in Franck's theory (Chapter IV, Section 8) of the absorption of light by molecules (collisions between light quanta and molecules). The existence of an analogy between the effects produced by colliding electrons and colliding light quanta is not new (cf. Birge and Sponer(10).

The validity of the theoretical conclusion is supported by the experimental observation that the dissociation of molecules does not begin when the energy of the impacting electrons reaches a value equal to the work of dissociation.

An important corollary is that when an electron with energy below the first electronic excitation potential strikes a molecule the energy loss should be of the same order of magnitude as if the electron had struck a free atom. In other words, the collision should be essentially elastic though the electron has sufficient energy to change the vibrational quantum number by many units. In such impacts, changes of a few units of rotational angular momentum may easily occur though the corresponding energy transfer would be quite small. Thus, if an electron, under favorable conditions, strikes a molecule at a distance of 10^{-8} cm from the center of gravity and has its velocity reversed, it may deliver to the molecule an angular momentum of the order of magnitude of $\sqrt{V}$ (in units $h/2\pi$), where V is the energy of the electron in volts. Unfortunately, it appears (private communication from Professor K. T. Compton) that there is some experimental evidence for the occurrence of inelastic collisions between electrons and molecules at voltages below the first electronic excitation potential. It seems highly desirable, in view of the above considerations, that further experimental work be done to determine, if possible, the magnitude and frequency of the energy losses of electrons under these conditions.

zero. The device used to account for the force of repulsion at short distances is therefore unsatisfactory.

A suggestion due to Debye([11]), however, is more promising. He calls attention to the fact that if a free negative charge is brought near to the orbit of a second electron rotating about a nucleus, the free electron will tend to execute forced oscillations with the period of the orbital motion and of such phase that its distance from the orbit is least when the rotating electron is at the nearest point of its path. Hence the average force of repulsion between the two electrons is greater than it would be if the free electron were stationary. A similar excess repulsion would be produced by the changes in the speed of the orbital electron due to the proximity of the free electron. The former would tend to slow down as it approached the latter, spending more time in the part of its orbit near the free electron than in the opposite part. Thus the time average of the repulsive force would be increased. The resulting added force of repulsion increases very rapidly with decreasing distance. Evidently the same considerations will lead to a similar repulsion between atoms or molecules.

The above argument neglects the changes in the shapes of the electron orbits due to the external forces. These changes in shape should work in the opposite direction to the effect considered above, and are to be correlated with the polarizability of an atom or ion previously mentioned. To complete the discussion a general proof should be given that the attractive force due to the change in orbital shape under the influence of a neighboring ion or dipole varies less rapidly with distance than the repulsive force due to the Debye effect. This proof is lacking at present, as the discussion of atomic polarizability by Born and Heisenberg is based on the empirically measured dielectric constants of gases rather than on an analysis of the effect of external fields on the electron orbits. The detailed study of various possible models of the H_2^+ ion by Pauli([6]) and Niessen([12]) as well as the examination by Nordheim([13]) of the mutual perturbations of two hydrogen atoms as they slowly approach each other shows, however, that the attractive force should actually exceed the repulsive force at large distances according to the classical mechanics. On the other hand, these authors have not attempted to separate the contributions of the change in orbital shape and of the Debye effect to the total force.

Although the above considerations suggest classical analogues to the attractive and repulsive forces which must exist at large and small distances respectively, it does not seem possible to carry through a complete theory by applying the classical mechanics to the stationary states. This is indicated by the work of Nordheim on the hydrogen molecule just

mentioned([13]). He has examined the forces between two hydrogen atoms as they approach each other adiabatically in various orientations which conform to the quantum conditions. It turns out that from the standpoint of the classical perturbation theory there can be no equilibrium position for those relative orientations which have the greatest energetic stability. Before the atoms get close enough for the repulsive forces to balance the attractive forces, a sudden discontinuous change in the character of the orbits takes place and the electrons cease to revolve solely about their parent nuclei.

It seems reasonable to suppose that right here we face the breakdown of the classical mechanics as a satisfactory means for the description of the quantized states of an atomic system. Bohr has called attention to the fact that the stability of the excited penetrating orbits in the alkali metal atoms (and others) is not to be accounted for on a purely classical basis([14]). The orbits in question have such a small negative energy that a slight perturbation or exchange of energy between the valence electron and one of the interior electrons would suffice to throw the former into an hyperbolic orbit and thus to produce spontaneous ionization. The energy transfer required for this purpose would be exceedingly small compared with the mutual energies of the inner group electrons which the valence electron approaches at its perihelion point. If the suggested perturbations actually took place, the orbits would lose the simple multiply periodic character which is a necessary concomitant of the existence of phase integrals and quantum numbers. Hence we may infer that one of the outstanding differences between quantum mechanics and the classical mechanics consists in a tendency on the part of orbital electrons to "ignore" the detailed variations in the forces which act on them and to follow that multiply periodic motion which best fits the average field in which they find themselves. The actual orbits are thus simpler than those required by a strict application of the classical mechanics. A similar conclusion may be drawn from the study of Ramsauer's experiments on the long free paths of slow electrons in argon and krypton.

Returning now to the problem of the repulsive forces between atoms and molecules, we observe that the sudden transition from one type of orbit to another to which Nordheim's classical theory calculations lead is incompatible with the maintenance of a multiply periodic motion and it therefore seems probable that the laws of quantum mechanics prevent the transition and maintain inviolable the fundamental character of the orbits even when the atoms are pressed closely together as in a collision. If we grant the existence of quantum forces of the nature of constraints which permit the deformation of an orbit but prevent it from "breaking," the Debye forces should suffice to account for the repulsion which

atoms exert on each other at short distances. It is altogether improbable that the stability of atoms and molecules in collision can be accounted for without the aid of such forces or of mechanical laws which take their place.

PART 1c. NON-POLAR MOLECULES

We shall confine our attention in this section to diatomic molecules and primarily to the symmetrical molecules of the elements. The fundamental problem in setting up a model of a non-polar molecule is to account for the attractive force which holds it together. In the case of polar molecules composed of oppositely charged ions this force is supplied primarily by the net charges on the ions. In the case of a molecule ion, in which one atom is charged and the other neutral, the charge on the former and the polarization which it induces in its companion may be sufficient to account for the attractive force. Some other explanation must be sought for the neutral symmetric molecule, however.

The hypotheses regarding the origin of the attractive force for non-polar molecules fall into two primary classes in one of which the link between the atoms is supplied by electrons which are thought to be shared in some way by the atoms, while in the other each electron is thought to move in an orbit attached to one atom only, as in the polar molecules. There are two possible ways in which shared electrons might serve to bind molecules together. The first of these is an arrangement in which the shared electrons move in the plane which forms the perpendicular bisector of the internuclear axis. The well-known hydrogen molecule models of Bohr and Langmuir belong to this class. Electrons so placed attract both the atoms toward themselves and thus act as a binding cement. The crossed orbit model of the hydrogen molecule proposed by Born is bound together in essentially the same manner.

Bohr's model of the hydrogen molecule in which two electrons each with angular momentum $h/2\pi$ rotate in a common circular orbit in the median plane of the molecule is open to several objections but not all of these seem to the writer as serious as commonly supposed. The diamagnetic behavior of hydrogen, for example, is frequently cited as evidence against this Bohr model since the electronic angular momentum must be correlated with a magnetic moment according to the classical electromagnetic theory. Moreover, calculations based on the classical mechanics using this model give the wrong heat of dissociation. The uncertainties introduced into the quantum theory by the introduction of the Uhlenbeck-Goudsmit spinning electron and the new quantum mechanics are so great, however, that these objections can hardly be considered decisive. A more serious difficulty comes out of the recent work

of Witmer([15]) in analyzing the ultra-violet Lyman bands of hydrogen. His investigations show that the heat of dissociation of hydrogen may be identified with the limit approached by the vibrational energy when the vibrational frequency approaches zero. The implication is that the hydrogen molecule breaks up into two normal atoms when it dissociates as a result of taking up too much vibrational energy. Dissociation through the absorption of vibrational energy should yield the same products and require the same amount of work as dissociation through the slow adiabatic separation of the nuclei by an external force, but clearly the adiabatic separation of the nuclei of the Bohr model would leave the electrons moving in ever widening circular orbits in the median plane so that the final product would be two ionized hydrogen atoms instead of two normal atoms. Hence the writer regards Witmer's conclusion as definitely incompatible with the Bohr model. The models of Langmuir and Born are open to the same objection and the failure of models of this type for the neutral hydrogen molecule tends to discredit the related Langmuir model of the molecule ion recently revived by Urey([16]).

The idea that symmetrical molecules might be held together by the sharing of electrons seems to be due to G. N. Lewis, and is essential to the Lewis-Langmuir static atom theory. The conception has been so fruitful in correlating chemical facts that it is natural to try to translate it into the dynamical language of the Bohr theory.[8] According to the static atom theory the outer electrons in atoms tend to form groups of eight of cubic shape and have great stability when this tendency is fulfilled. The groups of eight may be completed in a molecule in either one of two ways. In the typical non-polar molecule from two to four electrons play a double rôle, entering simultaneously into the structure of each of two groups of eight, one associated with each atom. In a few cases, such as that of nitrogen, the two atoms are thought to join forces in such a way that their valence electrons form a single group of eight which surrounds both nuclei and the inner groups of electrons. The logical dynamical equivalent of the static shared electrons of the Lewis-Langmuir theory would seem to consist in orbital electrons revolving about both nuclei. Such "binuclear" orbital electrons would tend to act as interatomic cement if the electrons spent most of their time in the region between the nuclei. We may regard the molecule as made up of two positively charged ions and two or more shared electrons. The ions will repel each other continuously, but when the shared electrons are in the above-mentioned region they will exert

[8] The application of this idea to BO, CN, N_2^+, CO^+ by Mulliken([17]) has played an important part in the development of our ideas regarding the relation between electronic energy levels in atoms and molecules.

a strong force drawing the ions together. If the orbits are symmetric and elliptic and lie in a plane through both nuclei, it is evident that the electron velocity will be a minimum at a point half way between the nuclei, and, hence, that electrons should spend the major portion of their time in the region in which they are effective in holding the ions together. It is also evident that the attractive force will rapidly decrease as the orbits decrease in eccentricity.

The analysis of the various possible models of the hydrogen molecule ion by Pauli([6]) and Niessen([12]) is of interest in connection with the general problem of shared orbits. As there is only one electron, definite conclusions are attainable as to the types of orbit permissible according to the classical dynamics. Pauli divides the orbits into two fundamental classes, viz., those in which the electron has an angular momentum parallel to the molecular axis, and those in which there is no such angular momentum and which therefore lie in meridian planes. There are orbits of both classes in the plane which forms the perpendicular bisector of the internuclear axis. As these orbits have already been briefly considered and are not binuclear we need not discuss them here.[9] The remaining types of electron path without axial angular momentum include orbits which pass around both nuclei and completely fill a zone between two ellipses and others which enclose one nucleus only. The last-mentioned type must eventually strike the nucleus and is discarded on that account. The symmetrical orbits enclosing both nuclei turn out to be incapable of holding them together. This suggests that even in the heavier neutral molecules, such binuclear electrons are poor cement; but it is quite possible that several such electrons might prove "strong" enough where one is a failure. Another difficulty with orbits passing around both nuclei comes out of the rapid precessional motion characteristic of penetrating atomic electron paths. On account of this precession it would seem that an electron coming out of one atom and plunging into the other would emerge from the second atom at a point so far removed from the first that it would be unlikely to return to its starting point until it had made two or more loops around the second atom. The path would be very complicated indeed and it is hard to see how such an electron could act as a binding force between atoms or how it could be equivalent to other electrons with simpler orbits in building up a stable group.[10]

[9] Pauli discards these median plane orbits and also all those with zero σ on account of their dynamical instability, but the writer considers the importance of this requirement doubtful.

[10] From the spectroscopic standpoint, the most important evidence for the sharing of electrons is Mulliken's correlation of the spectra of Na, Mg, and Al, respectively, with the spectra of certain corresponding molecular species (e. g., BO, CO, NO)([17]). This correlation was established on the basis of the shared electron theory, but Dr Mulliken in a recent important paper on molecular

The space orbits with axial angular momentum for H_2^+ are of both symmetric and asymmetric types. Equilibrium of the nuclei is possible in either case. The symmetric orbits unite a rotary motion around the molecular axis with a vibrational motion parallel to the axis in such a way as to fill out a barrel-shaped zone bounded by two ellipsoids of revolution with the nuclei as foci and cut off at the ends by confocal hyperboloids. In the asymmetric case the electron revolves in a distorted orbit about one nucleus only. A special quantized orbit of the symmetric class is regarded by Pauli as the most promising model of the molecule ion. Orbits of this general type should make strong connecting links between the atoms in heavier diatomic molecules such as O_2 and N_2, but on account of their peculiar shape it is doubtful whether they could act as the equivalent of simpler orbits in building up such stable groups as are suggested by the Lewis-Langmuir theory.

In connection with the Bohr model of the hydrogen molecule we have already mentioned the apparent possibility of dissociating hydrogen adiabatically into two normal H atoms. This possibility stands as an equally forceful objection to any model of the molecule in which the electrons are shared by the two atoms. The work of Birge and Sponer([10]) (cf. Chapter IV, Section 8) indicates that other molecules previously thought to be bound together by shared electrons may also be dissociated adiabatically into normal atoms without an electron jump. The conclusion is not absolutely certain, but their evidence shows that the heat of dissociation calculated on this basis cannot differ greatly from the true heat of dissociation. Hence it is important to inquire whether, or not, the experimental facts regarding the homopolar molecules cannot be accounted for in terms of models in which there are no symmetric orbits.

Any explanation of the attractive force between the atoms in a nonpolar molecule consistent with the possibility of an adiabatic dissociation into normal atoms must depend on the electric field due to the polarization of the atoms whether that polarization be of the simple dipole type or of the quadrupole type([19]). Each individual electron in an atom in conjunction with a corresponding charge element in the nucleus may be regarded as a dipole whose magnitude and direction varies with the time. If two electrons execute similar orbits with the same period and a suitable phase relationship their dipole moments may cancel, but there will still be a varying electric field of the quadrupole moment type. The field due to a quadrupole fades away more rapidly with the distance from the

formation([18]) has pointed out the possibility that a similar correlation may originate in the interaction between the two atoms in each of the molecules under discussion which does *not* involve the formation of orbits about both nuclei. Hund's theory (Section 5) shows in part how such an interaction might take place.

atom than the field due to a dipole and is therefore likely to be less effective in producing an attraction between atoms. Fields corresponding to poles of still higher order may arise from symmetric groups of electrons whose orbits have the same frequency.

The force exerted by one dipole on another varies inversely with the cube of the distance and depends on the time averages of the products of corresponding components $p_x p'_x$, $p_y p'_y$, $p_z p'_z$. Each of the components will be expressible as a Fourier's series and in the case of a precessing orbit the mean value of each will be zero. Hence the time average of the product vanishes unless the two dipoles have the same frequency. The major forces of attraction between two neutral atoms will therefore arise as the result of the interaction of synchronous terms in the Fourier expansion for the electric moment of each. These synchronous terms may be due to the existence of two equivalent electrons, one in each atom, or to an induced or perturbative polarization in one resulting from a primary polarization in the other.

As an example of binding through the mutual interaction of naturally synchronous orbits the work of Nordheim([13]) on the adiabatic approach of two normal hydrogen atoms may be mentioned. He has shown that all of the various modes of approach which satisfy the quantum conditions involve definite phase relations. The greatest attractive force is obtained when the electrons rotate in opposite directions in the same plane, their phases so adjusted that when either atom is polarized along the molecular axis the other is polarized in the same way. It is therefore at least plausible to attribute the strong binding of the atoms in such symmetric molecules as N_2, O_2, F_2 to phase relations between equivalent exterior electrons. The absence of a correspondingly strong binding in the case of the diatomic molecules of the alkali metals is not so easy to explain, but if our present point of view is correct, it must be due in some way to the rapid precessional motion of the valence electrons in these strongly electro-positive atoms.

As the polarization which one molecule induces in another has been used by Debye to account for the attraction which produces the Joule-Thomson effect, it seems plausible to suppose that the atoms in a molecule may be held together by this type of synchronous polarization. The formation of molecules by the union of excited and unexcited helium and mercury atoms may be interpreted as evidence in favor of this assumption. We may, perhaps, suppose that in the normal atoms of these elements the two most loosely bound electrons (in helium the only two) are moving in equivalent orbits of such phase that together they give the atom a quadrupole instead of a dipole moment. This is not able to hold a molecule together, but when one of the electrons is excited, the periods

of the valence electrons are no longer the same and their dipole moments do not combine to form a quadrupole moment. Hence they can act inductively on a normal atom and so form a loose molecule. These conjectures are, however, as yet very uncertain.[11]

Calculations by Mensing([20]) seem to indicate that the magnetic forces between magnetic atoms are not strong enough to play an important part in molecular formation.

SECTION 2. GYROSCOPIC MOTION—RIGID MOLECULE THEORY

PART 2A. PROOF OF KRAMERS AND PAULI FORMULA FOR ROTATIONAL ENERGY OF DIATOMIC MOLECULES

The gyroscopic properties of molecules may be investigated in several ways. One may, for example, consider the probable effect of electronic angular momentum on band structure and attempt to deduce the values of this momentum for the various molecular states from the corresponding empirical band spectra. The experimental study of the magnetic susceptibility of gases and of the Zeeman effect for band lines gives additional data for the determination of the electronic angular momenta. The problem may also be attacked from a purely theoretical point of view either by a direct application of the quantum principles to various hypothetical molecular models or by an examination of the problem of the formation of molecules from the constituent atoms in the light of perturbation theory. Of course it is highly desirable that all these methods of investigation shall be used simultaneously so that each may supplement the other.

In the earlier chapters of this report (especially Chapter IV) considerable attention has been given to the correlation of the observed band structures with the gyroscopic properties of molecules. As this correlation is based on the Kramers and Pauli formula (Chapter IV, Equations 18 and 20) for the rotational energy of a gyroscopic molecule it seems worth while to give here a simple derivation of that formula. The proof given by Kramers and Pauli([21]) is based on a treatment of the more complicated general case of a multi-atomic molecule([22]) and may be shortened by restricting the discussion from the beginning to diatomic molecules.

The formula is based on the assumption that to a first approximation the electronic angular momentum [12] $\mathbf{s}$ is constant in magnitude and

[11] Note added after completion of chapter: Dr. Mulliken calls my attention to the fact that if an excited He atom has sufficient polarizing power to unite with normal He, hydrogen and sodium atoms ought also to unite with normal He, which, so far as we know, does not occur.

[12] In this chapter vectors are indicated by bold-faced type.

subject to a rigid constraint which gives it a fixed angle with the molecular axis. The constant total angular momentum **j** is then the vector sum of **s** and the nuclear angular momentum **m** (all expressed in units $h/2\pi$). **m** is by definition perpendicular to the molecular axis (provided that the nuclei are not themselves gyroscopic). The first step in the derivation of the energy formula is to show that the three angular momentum vectors **m, s, j** all lie in a common plane with the molecular axis.

If **s** happens to be parallel to the nuclear axis there is nothing to prove, for **j**, being the vector sum of **m** and **s** must lie in the plane which they define. If **s** is not parallel to the nuclear axis we may prove the point by differentiating the vector equation

$$\mathbf{s}=\mathbf{j}-\mathbf{m}=\mathbf{j}-\frac{2\pi\mu}{h}[\mathbf{r}\dot{\mathbf{r}}]$$

in which **r** is the vector distance between the nuclei and μ is the mass coefficient $\frac{m_1 m_2}{m_1+m_2}$. Since **j** is constant,

$$\frac{d\mathbf{s}}{dt}=-\frac{2\pi\mu}{h}[\mathbf{r}\ddot{\mathbf{r}}].$$

In other words, as the torque reaction of the nuclei is necessarily perpendicular to the nuclear axis, $\frac{d\mathbf{s}}{dt}$ is also perpendicular to that axis. But since it is rigidly attached to the nuclei, **s** with the nuclear axis defines a rigid body which rotates about some line in the plane of **m** and the nuclear axis. The angular velocity of this rigid body may be resolved into vector components $\mathbf{u}'$ and $\mathbf{u}''$ parallel to **m** and the nuclear axis respectively. Then

$$\frac{d\mathbf{s}}{dt}=[\mathbf{u}'\mathbf{s}]+[\mathbf{u}''\mathbf{s}].$$

If **s** had a component perpendicular to the plane of **m** and the nuclear axis, it is readily seen that this component would unite with $\mathbf{u}'$ to yield a component of $\frac{d\mathbf{s}}{dt}$ parallel to the nuclear axis. As this is impossible, we conclude that the nuclear axis must lie in a common plane with **s**, **m**, and **j**.

Evidently the angle between **s** and **m** is fixed so that the vector triangle formed by **s**, **m**, and **j** is invariable except for its rotation about **j** as an axis. If the nuclei do not vibrate, the motion is a pure precession about **j**. In any case there can be no nutation. In spherical coordinates r, θ, ϕ referred to **j** as an axis, the expression for the nuclear kinetic energy is

$$T=\tfrac{1}{2}\sum_{k=1,2} m_k(\dot{r}_k^2+r_k^2\sin^2\theta\dot{\phi}^2)=\tfrac{1}{2}\mu(\dot{r}^2+r^2\sin^2\theta\dot{\phi}^2). \qquad (7)$$

The expression for the kinetic energy of the nuclei in terms of the radial momentum p_r and the nuclear angular momentum

$$p_m = \mu r^2 \sin\theta\dot{\phi} \equiv \frac{mh}{2\pi} \quad (m \text{ not integral}) \tag{8}$$

is of the same form as for the non-gyroscopic case. If we assume that the electronic energy in any given electronic state is a function of r only, it follows that the radial quantum condition leads to the same relation between the energy, the radial quantum number n, and the nuclear angular momentum as when **s** is zero. The molecular energy is therefore given by an expression of the form

$$E = E_\epsilon + E_n + B_n m^2 + D_n m^4 \ . \ . \ . \tag{9}$$

where B_n and D_n have the same meanings as in the non-gyroscopic case

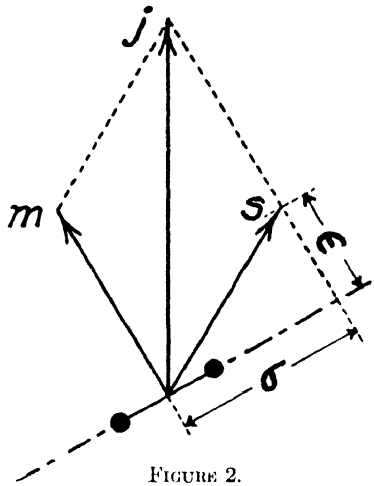


FIGURE 2.

(Cf. equation (141), Chapter IV) but m is not in general integral. The value of **m** is determined by the fact that it is the vector difference of **j** and **s**. If the symbol σ and ϵ are used to designate the fixed components of **s** parallel and perpendicular to the nuclear axis respectively, it follows that m may be calculated from the Kramers and Pauli formula

$$m = \sqrt{j^2 - \sigma^2} - \epsilon \qquad j = \text{integral}. \tag{10}$$

PART 2B. EXPERIMENTAL CONFIRMATION

The experimental verification of formulas (9) and (10) has been discussed at length in Chapter IV. The situation may be briefly summarized as follows. The simpler band types are in essential accord with (9) and the special cases of (10) obtained by setting either σ or ϵ equal to zero

for both the initial and final states. Multiplet bands of the OH type in which each branch consists of doublets or triplets with a separation which increases near the origin, are obviously in qualitative accord with the general Kramers and Pauli formula when both σ and ϵ have values appreciably greater than zero. The discussion in Chapter IV, Part 5d, shows that the use of the Kramers and Pauli formula as advocated by Mulliken helps to account for the missing lines near the origin, but that there is difficulty in fitting the frequency observations accurately on this basis. It is probable that the assumption of values of σ and ϵ which vary slightly with the nuclear angular momentum([23]) would suffice to account for the discrepancies in the frequency calculations.

As previously mentioned (footnotes 8 and 10) Birge([31]), Mecke([30]), and especially Mulliken([17]), ([24]), ([25]) have made a systematic study of the relation between electronic energy levels in atoms and molecules. They find a similarity between the energy level schemes of many molecules and corresponding atoms which permits the classification of the electronic states of molecules in terms of the symbols *S, P, D, F,* etc. (Russell-Saunders notation) used to designate the various types of atomic energy level. An examination by Mulliken of the relationship between these term types and the values of σ and ϵ which are required to account for the band structures by means of the Kramers and Pauli theory has led to very interesting and important results. He finds that in the case of electronic energy levels of the sharp series type (azimuthal quantum number k equal to unity) σ is zero or approximately zero, while ϵ is zero or approximately one-half according as the corresponding atomic level belongs to a singlet or doublet system. In other words, for electronic levels of the sharp series type, ϵ is equal to the inner quantum number of the corresponding atomic level as assigned by Sommerfeld. On the other hand, in the case of molecular electronic energy levels analogous to principal or diffuse series atomic levels the value of ϵ is usually quite small, while σ is to be set equal to the corresponding value of Sommerfeld's inner quantum number. Cases in which both σ and ϵ have values as large as a half (OH type mentioned above) are ascribed by him to the independent orientation of the electronic angular momentum of one atom parallel to the nuclear axis and that of the other atom perpendicular to the nuclear axis. These systematic results lend support to the Kramers and Pauli theory.

Part 2c. Objections to Rigid Molecule Theory

There are, however, certain theoretical objections to the Kramers and Pauli formula which must be taken into consideration. First among these we may mention the objections stated by Kramers and Pauli them-

selves regarding the use of negative values of ϵ (the vector values of m and ϵ antiparallel) which correspond to dynamically unstable motions. (Cf. Chapter IV, p. 188.) In view of the uncertainty regarding the importance of dynamical stability for quantized motions this objection seems not to be crucial. Certainly the use of negative values of ϵ is required if the formula (10) is to be correlated with the experimental facts.

A second objection to the rigorous application of the formula is, that it assumes a molecular rigidity which is hardly to be expected,[13] The electronic angular momentum and its orientation with respect to the nuclear axis are assumed to be constant. If the angle between the electronic angular momentum **s** and the nuclear axis is less than 90°, however, the rotation of the nuclei will create a torque tending to orient **s** perpendicular to that axis. This torque is given by the well-known formula for the precession of a gyroscope

$$\begin{aligned} Torque &= 2\pi\omega \times [component\ of\ angular\ momentum\ perpendicular \\ &\qquad to\ axis\ of\ precession] \\ &= 2\pi\omega S \sin(\mathbf{S}, \mathbf{j}) \end{aligned} \tag{11}$$

in which ω is the precessional frequency or frequency of nuclear rotation and **S** is the electronic angular momentum in absolute units.[14] The component $(S\sin(\mathbf{S}, \mathbf{j}))$ of **S** perpendicular to the vector total angular momentum is equal to $\frac{\sigma}{j} \cdot \frac{mh}{2\pi}$ and the frequency ω is $\frac{1}{h} \frac{\partial E}{\partial j}$. Hence

$$Torque = 2\sigma Bh \frac{m^2}{m+\epsilon}. \tag{12}$$

This torque grows indefinitely with j and m so that a gradual change in the angle between **S** and the nuclear axis with large values of j is to be expected. This objection does not invalidate the formula as a satisfactory approximation for low values of j.

Another difficulty with the Kramers and Pauli theory is that it assumes that when the nuclei of the molecule are held fixed the electronic angular momentum will remain fixed in direction. The rigid orientation of the vector **s** with respect to the nuclear axis precludes the possibility of a torque tending to make **s** either parallel or perpendicular to that axis such as would be required to produce a precession of **s** around the line joining the nuclei. This assumption is reasonable if the angle between **s** and the nuclear axis is zero or 90°, but for other angles a precession is to be

[13] Kramers and Pauli call specific attention to this point.

[14] As a result of the precession, the end point of the vector **S** traces out a circle of radius equal to the component of **S** perpendicular to the axis of precession **j**. The linear velocity of this end point along the circle is equal to the time derivative of the vector **S** and hence to the torque.

expected. The practical inevitability of such a precession may be made evident in several ways.

For example, we may observe that if a single electron has a motion quantizable in either cylindrical coordinates or in spherical coordinates, the absence of a precession implies the equality of two of the three frequencies associated with the three coordinates. In other words, the motion is degenerate. Such degeneracy is to be expected in the case of an electron moving in a central force field, but is removed when an external electric or magnetic field is applied. In the case of an electron or a group of electrons moving in the neighborhood of two fixed nuclei, the force field would have axial symmetry like the field of an atom in the Stark effect, but not spherical symmetry. Only in case the vector **s** is either parallel or perpendicular to the nuclear axis, might limiting degeneracy be expected which would remove the precession.[15] This general conclusion is supported by the work of Nordheim on the hydrogen molecule and the study of more complicated molecular models by Mensing.

If the orbit does precess about the nuclear axis we may infer the existence of a torque tending to orient **s** either parallel or perpendicular to the nuclear axis. This torque and the corresponding "potential" energy presumably depend on the angle between **s** and the nuclear axis.

Another inference which may be drawn from the study of the electronic motion with the nuclei held fixed, is that under these circumstances the component of the electronic angular motion parallel to the axis will be definitely quantized so that σ is an exact integer (or half integer).[16]

Kramers and Pauli also call attention to the failure of their theory to give a satisfactory account of the Zeeman effect for band lines. This aspect of the situation will be considered in detail later on.

SECTION 3. THE APPLICATION OF PERTURBATION THEORY TO MOLECULAR MOTION

In view of the preceding objections to the Kramers and Pauli theory, it is highly desirable that their arbitrarily chosen model be replaced by an examination of the behavior to be expected from the actual complex system of electron orbits and nuclei. As the direct solution of the whole dynamical problem is hopelessly difficult, the most promising mode of attack is through the method of successive approximations (perturbation theory) so skilfully developed by Born and his collaborators. There have been two sorts of application of this method to the problem of the molecule. One of these is the study of the electronic motion to be expected

[15] Cf. Footnote on p. 147 of Born's Atommechanik (Berlin, 1925).

[16] This follows from Bohr's study of systems with axial symmetry. Cf. also Born, Atommechanik, page 28.

with nuclei fixed by examining the mutual perturbations of the electrons in two atoms assumed to be initially far apart but permitted to approach each other slowly and "adiabatically." The results obtained in this way by Nordheim and Mensing have been mentioned several times already and need not be restated here.

The second application of this method to molecular motion consists in a study of the effect of setting the nuclei free on the motion and energy of a multiatomic molecule, as carried through by Born and Heisenberg([26]). The standard mode of procedure developed by Born and his collaborators for the solution of problems in perturbation theory involves the development of the Hamiltonian function, the action function, and the energy in powers of some small parameter λ. The equations are first solved neglecting terms containing powers of λ greater than zero, then as a second approximation the first degree terms in λ are considered, and so on. Born and Heisenberg choose the ratio m/M of the mass of an electron to that of one of the nuclei as the parameter λ. In the series expansion for the Hamiltonian function

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \ldots . \tag{13}$$

H_0 is the electronic energy for fixed nuclei. H_1 has a mean value zero when averaged over the unperturbed motion and hence has to be eliminated from the problem by a suitable change of variables. H_2 then consists of three parts of which one gives in first approximation the vibrational energy of the molecule, another the rotational energy, while the third is a constant term of no great importance for our present purpose.

In order to get a first approximation for the energy of a perturbed system it is customary to add to the unperturbed energy H_0 the mean value of the perturbative energy (or of the first term of the series expansion) averaged over the unperturbed motion.[17] In this case the mean value of the rotational energy terms in H_2 is

$$E^r{}_2 = \tfrac{1}{2}\left\{ \frac{(\mathbf{D}_x - \bar{\mathbf{S}}_x)^2}{A_x{}^0} + \frac{(\mathbf{D}_y - \bar{\mathbf{S}}_y)^2}{A_y{}^0} + \frac{(\mathbf{D}_z - \bar{\mathbf{S}}_z)^2}{A_z{}^0} + \sum_{x,y,z} \frac{1}{A_x{}^0}(\overline{\mathbf{S}_x{}^2} - \bar{\mathbf{S}}^2{}_x) \right\} \tag{14}$$

where $\mathbf{D}$ and $\mathbf{S}$ denote the total angular momentum and the electronic angular momentum respectively, $A_x{}^0$, $A_y{}^0$, $A_z{}^0$ being the principal moments of inertia. The bars over $\mathbf{S}_x$, $\mathbf{S}_y$, etc., denote mean values. The

[17] The theorem was first applied to quantum theory problems by Bohr (Memoirs of the Danish Academy of Sciences, Series 8, Vol. IV, No. 1). See Born "Atommechanik," Chapter 4, and Van Vleck "Quantum Principles and Line Spectra," Bulletin of the National Research Council, No. 54, articles 62 and 64.

above expression differs only by a constant term from that which was derived by Kramers and Pauli for the rotational energy of their multiatomic model and hence may be regarded as a theoretical justification of their rigid molecule theory. Unfortunately the proof is limited to multiatomic molecules whose atoms do not lie on a single straight line and also by restriction to moderate values of the nuclear angular momentum.

The writer has found it possible, however, to apply their method to diatomic molecules. In making the computation, which is somewhat long for reproduction here, the nuclei are assumed to be held at a fixed distance apart by a rigid constraint. The coordinates used for the nuclei are the colatitude θ and the longitude ϕ. As the center of gravity of the nuclei is assumed to be at the origin, the radial distances of the nuclei are constant. The positions of the electrons are specified by means of Cartesian coordinates referred to axes which rotate with the nuclei. If the axis of the system of spherical coordinates θ, ϕ is identified with the direction of the vector total angular momentum, the Hamiltonian function may be thrown into the form

$$H = H_0 + \frac{1}{2I}\left\{\mathbf{S}_y^2 + [\sqrt{p_\phi^2 - \mathbf{S}_z^2} - \mathbf{S}_x]^2\right\}. \tag{15}$$

Here H_0 is the Hamiltonian function for the electronic motion with fixed nuclei, p_ϕ is the total angular momentum of the molecule, and $\mathbf{S}$ is the instantaneous electronic angular momentum. $\mathbf{S}_z$ is the component of $\mathbf{S}$ along the nuclear axis to be identified with $\frac{\sigma h}{2\pi}$. $\mathbf{S}_x$ and $\mathbf{S}_y$ are components of $\mathbf{S}$ perpendicular to the nuclear axis and lying respectively in and at right angles to the plane defined by the nuclear axis and the total angular momentum vector. It may be proved that if $\mathbf{S}_z$ is constant in the perturbed motion, as it must be in the unperturbed motion, $\mathbf{S}_y$ vanishes. If we make this arbitrary assumption and at the same time substitute $\frac{jh}{2\pi}$ and $\frac{\epsilon h}{2\pi}$ for p_ϕ and $\mathbf{S}_x$ respectively, we obtain an expression for the energy, formally the same as that given by Kramers and Pauli, viz.,

$$H = H_0 + B[\sqrt{j^2 - \sigma^2} - \epsilon]^2. \tag{16}$$

The agreement is somewhat superficial, however, as H_0 is the energy of the electronic motion as perturbed by the nuclear motion, while $\mathbf{S}_x$, $\mathbf{S}_y$, and $\mathbf{S}_z$ in (15) and σ and ϵ in (16) are not constants, but instantaneous components of the electronic angular momentum evaluated for the actual perturbed motion.

Now according to the theorem used in deriving (14), we obtain an approximate value of the energy E by averaging the right-hand member of (15) over the unperturbed motion, i. e., we replace $\mathbf{S}_y^2$ by its mean

value $\mathbf{S}_y^2$ evaluated for the motion with fixed nuclei, $\mathbf{S}_x^2$ by $\overline{\mathbf{S}_x^2}$, and so on. In this way the formula

$$E=\overline{H}=E_0+\frac{1}{2I}\left(\overline{\mathbf{S}_y^2}+\overline{\mathbf{S}_x^2}-\overline{\mathbf{S}_z^2}+p_\phi^2-2\overline{\mathbf{S}_x\sqrt{p_\phi^2-\mathbf{S}_z^2}}\right) \tag{17}$$

is obtained. Now when the nuclei are held fixed, $\mathbf{S}_z$ is constant. Also, the component of $\mathbf{S}$ perpendicular to the nuclear axis will normally execute a more or less rapid precession about the nuclear axis unless $\mathbf{S}_z$ vanishes. Hence it is a natural step to set $\mathbf{S}_x$, and hence $\mathbf{S}_x\sqrt{p_\phi^2-\mathbf{S}_z^2}$ equal to zero. If this is done, (17) takes the form

$$E=E_0+\frac{1}{2I}\left(\overline{\mathbf{S}_x^2}+\overline{\mathbf{S}_y^2}-\overline{\mathbf{S}_z^2}+p_\phi^2\right). \tag{18a}$$

On the other hand, if $\mathbf{S}_z$ is equal to zero for the unperturbed motion and if there is no precession, we may assume $\mathbf{S}_y$ to be zero for the unperturbed motion also, thus deriving the alternative formula

$$E=E_0=\frac{1}{2I}\left(\overline{\mathbf{S}_x^2}-\overline{\mathbf{S}^2}_x+(p_\phi-\overline{\mathbf{S}_x})^2\right). \tag{18b}$$

Thus we *seem* to be able to show that the Kramers and Pauli type formula always holds as a first approximation, but with either ϵ zero (Equation (18a)) or σ zero (Equation (18b)).

There is a flaw in the argument, however, due to the fact that although the perturbational terms in the energy vanish when λ becomes zero (infinite nuclear masses) the derivatives of these perturbational terms which give the corresponding forces need not vanish at the same time. Hence the motion of the electrons with respect to the coordinate axes x, y, z, does not necessarily approach the motion characteristic of H_0 alone when λ approaches zero. Under these circumstances the mean value theorem used in deriving (14) and (17) requires modification. The real situation may be demonstrated most easily by dropping the perturbation theory equations for the moment and considering a model diatomic molecule of a type somewhat more general and more close to physical reality than that of Kramers and Pauli.

SECTION 4. DIATOMIC MOLECULAR MODEL WITH ELASTICALLY MOUNTED GYROSCOPE

Let us consider a molecular model consisting of a pair of rigidly connected nuclei to which is attached a symmetrical gyroscope with an elastic mounting. This mounting permits the axis of the gyroscope to assume any angle θ with the nuclear axis, but creates a potential energy U which is a function of θ. The gyroscope will then be subject to a torque

$$Q(\theta)=-dU/d\theta$$

which is always perpendicular to the plane defined by the gyroscopic and nuclear axes and which may tend either to increase or decrease the angle θ. We further assume, as does Kramers([22]) in the paper on the quantization of rotating molecules on which the Kramers and Pauli formula is based, that the angular momentum of the gyroscope $sh/2\pi$ is constant in magnitude.

With fixed nuclei the gyroscope will then execute a motion of pure precession about the nuclear axis, a nutation being impossible since it would involve a torque in the plane of the gyroscope and the nuclear axis which does not exist. The quantization of this precessional motion, like the quantization of the precession of an atom in a magnetic field, will fix the possible angles which **s** may make with the nuclear axis so that the component of **s** parallel to the axis will be an integer or half integer.

The model is frankly artificial in ignoring the details of the actual electronic motion and in its assumption of a constant electronic (i. e., gyroscopic) angular momentum. It behaves with nuclei fixed, however, in approximately the same way as an actual system of electrons would be expected to behave. Hence it seems reasonable to suppose that the behavior with nuclei free will approximate more closely to the behavior of an actual molecule than does the Kramers and Pauli model.

The simplest type of motion with free nuclei will be that in which the vectors **s**, **m**, **j** and the nuclear axis lie in a common plane. There will then be a pure precession of **s** and **m** about **j**. In this case **s** does not precess about the nuclear axis and its component parallel to that axis is not quantized. A more complicated type of motion involving a double precession of **s** about the nuclear axis, and of the nuclear axis about **j**, is also possible. The component of **s** parallel to the nuclear axis is then quantized and the nuclear axis executes a nutation synchronous with the precession of **s** in addition to its own precession. We shall consider in detail only the simpler type of motion.

If the motion is one of pure precession the torque required to rotate the vectors **m** and **s** about **j** is supplied by the potential energy $U(\theta)$. The angle θ is determined so that the torque $Q(\theta)$ balances the torque reactions of the vectors **m** and **s**. We proceed to the derivation of an equation for the determination of θ as a function of j and s.

If the torque Q tends to draw the vector **s** towards the nearest nucleus,[18] there are two cases to be considered as illustrated in Figures 3a and 3b.

[18] The above clause is, perhaps, ambiguous. It would be more accurate to say "If the torque Q is so directed that it would draw a rigid bar in the place of **S** toward the nucleus, etc." Owing to the gyroscopic character of **S** the actual effect of Q is to produce a precession without changing the angle between **S** and the nuclear axis.

In case 1 (Figure 3a) which corresponds to the positive value of ϵ in the Kramers and Pauli theory, j is greater than s; while in case 2 (Figure 3b) we have a negative ϵ and j less than s. Two other cases are possible if the torque Q tends to push **s** away from the adjacent nucleus (i. e., if U is a maximum when **s** points along the nuclear axis).

Let ϕ denote the angle between $\overrightarrow{BA}$ and **j** measured in the same direction as θ. Let I denote the moment of inertia of the molecule (due to the nuclei) about its own center of gravity. Then $I \sin^2\phi$ will be the

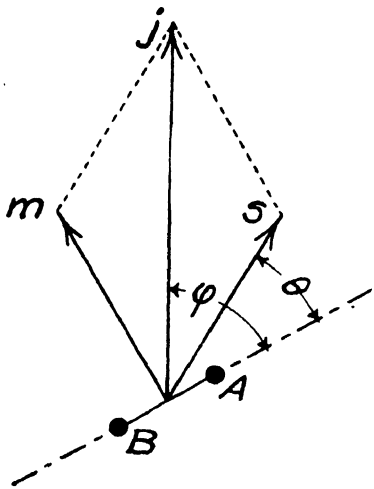


FIGURE 3a.—Case 1

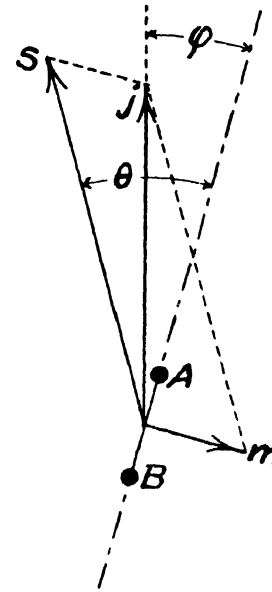


FIGURE 3b.—Case 2.

effective moment of inertia about the axis of precession **j**. Let ω be the frequency of precession. The kinetic energy of the nuclei is

$$\tfrac{1}{2} I \sin^2\phi (2\pi\omega)^2$$

and the nuclear angular momentum is

$$\frac{mh}{2\pi} = \pm I(2\pi\omega)\sin\phi. \tag{19}$$

Hence the kinetic energy of the nuclei may be expressed in the form

$$T_{nuclei} = \frac{m^2h^2}{8\pi^2 I} = Bhm^2 \tag{20}$$

as in the non-gyroscopic case. The torque $Q(\theta)$ must balance the torque

reaction given by the equation (11) above or by the right-hand member of the equation

$$Q(\theta) = -\frac{dU}{d\theta} = 2\pi\omega \times \textit{component of } \mathbf{m} \textit{ perpendicular to } \mathbf{j}$$
$$= \pm 2\pi\omega \left(\frac{mh}{2\pi}\right) \cos\phi. \qquad (21)$$

Combining the above with (19) we obtain

$$Q(\theta) = \frac{m^2h^2}{4\pi^2 I \tan\phi} = \frac{2hBm^2}{\tan\phi}. \qquad (22)$$

In each case $\tan\phi$ is positive so that Q must also be positive.

In order to evaluate θ as a function of j we must express the right-hand member of (22) in terms of j and θ. The relations

$$\frac{m}{s} = \pm(\cos\theta \tan\phi - \sin\theta); \qquad (23)$$

$$\tan\phi = \sqrt{\frac{j^2}{s^2\cos^2\theta} - 1}, \qquad (24)$$

follow directly from the vector diagram of Figures 3a-b. Combining these with (22) we obtain

$$\frac{Q}{2hBs^2} = \cos^2\theta \tan\phi - 2\sin\theta\cos\theta + \frac{\sin^2\theta}{\tan\phi} \qquad (25)$$

or

$$\frac{Q}{2hBs^2} = \cos^2\theta \sqrt{\frac{j^2}{s^2\cos^2\theta} - 1} - 2\sin\theta\cos\theta + \frac{\sin^2\theta}{\sqrt{\frac{j^2}{s^2\cos^2\theta} - 1}}. \qquad (26)$$

The above equation may be solved graphically by plotting the left- and right-hand members as functions of θ or $\cos\theta$. The right-hand member we designate as $F(\theta, j/s)$. A plot of F against $\cos\theta$ for various values of j/s is shown in Figure 4. The positive values of $\cos\theta$ go with cases 1 and 2 illustrated by Figures 3a and 3b. The negative values go with the other two cases mentioned above in which the torque Q tends to push s away from the nearest nucleus. Curves A and B of Figure 4 show possible forms of $\frac{Q(\theta)}{2hBs^2}$. From the intersections of the two classes of curves one may read off the values of $\cos\theta$ correlated with various values of j for any assumed torque function $Q(\theta)$ with any given values of B and s. Then (23) and (24) may be used to determine m as a function of j. Finally, the energy values may be calculated from

$$E = E_0 + Bhm^2 + U(\theta). \qquad (27)$$

In this last equation E_0 denotes the energy for stationary nuclei and θ

equal to zero, the potential energy U being measured relative to the angle $\theta=0$.

We have no information on which to base an exact determination of the forms of the function $U(\theta)$ and of its derivative $Q(\theta)$. Clearly $U(\theta)$ must be a maximum or minimum $\theta=0$ and $\theta=\pi$. Also, a reversal of the sense of the rotations around the nuclear axis would reverse the sign of $\cos\theta$, but should not change the energy([27]). Hence we may infer that

$$U(\theta)=U(\pi-\theta),$$

and that U is a maximum or minimum when $\theta=\frac{\pi}{2}$. Consequently Q vanishes when $\mathbf{s}$ is either parallel or perpendicular to the nuclear axis.

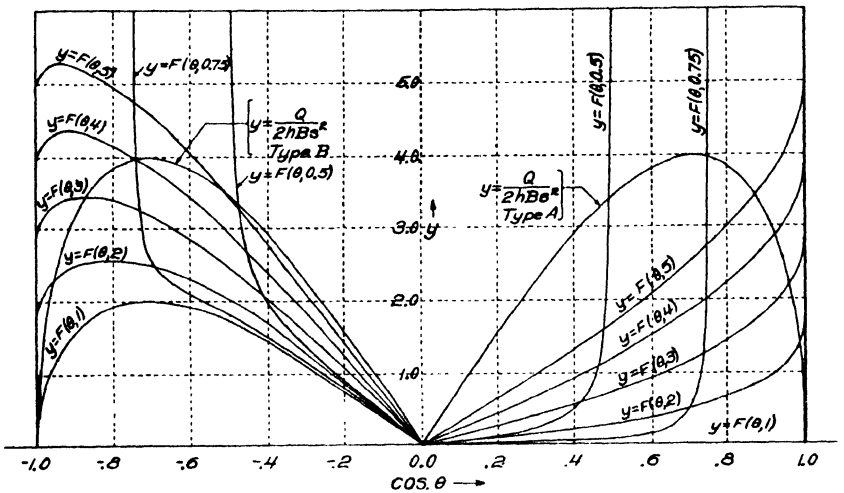


FIGURE 4.

The simplest possible assumption regarding the torque function would then be that it has the form

$$Q(\theta)=\pm A\sin 2\theta. \tag{28}$$

Curves A and B of Figure 4 are drawn in accordance with (28) using the plus and minus signs respectively. (Figures 3a and 3b show the possible orientations of $\mathbf{s}$, $\mathbf{j}$, and the nuclear axis for the torque curve A only.)

From Figure 4 it will be seen that θ may be zero for any value of j/s. Also, if j/s is not too large, there will be another possible value of θ. This second value of θ approaches zero (Curve A) or π (Curve B) as a limit when j/s approaches unity. If s is greater than 2, j can have integral values less than s for which the angle between $\mathbf{s}$ and the nuclear axis may be shown to approximate one of the values given by

$$\cos\theta=j/s. \tag{29}$$

In other words, the angles of inclination for values of j/s less than unity tend to approximate those determined by the quantum conditions for fixed nuclei. If j/s is less than unity, $0 < |\sin \phi| < |\sin \theta|$. Equations (24) and (25) show that, as $\cos \theta$ approaches j/s, $\tan \phi$ approaches zero and the torque reaction becomes infinite. Hence, if the applied torque is not too small, $\cos \theta$ will approximate the value (29) and at the same time the angle ϕ between **j** and the nuclear axis will become very small. Under these circumstances the nuclei must rotate in very small circles about **j** as an axis and the nuclear angular momentum is nearly perpendicular to **j**. Though the angular velocity of the nuclei may be large, the orbits are small and the motion approximates that for fixed nuclei.

Now consider the effect of increasing the nuclear masses towards infinity as a limit. As B varies inversely with the nuclear masses the ordinates of the $Q/2hBs^2$ curve will increase with the masses. If j is less than s, the angle ϕ will approach zero and the radii of the nuclear orbits will also approach zero. At the same time $\cos \theta$ approaches more and more closely the value given by (29). Thus the indefinite increase in the nuclear masses carries each of the states for which j/s is less than unity over into a definite corresponding state with fixed nuclei for which $\cos \theta$ is quantized and has a value between 0 and s.

Turning to values of j/s greater than unity, we observe that the critical value of j, beyond which $\cos \theta$ can have only the single value 0, grows with the nuclear masses. Consider any of the curves of $F(\theta, j/s)$ on Figure 4 for which j/s is greater than unity. If the product of nuclear mass into torque is large enough, there will be two intersections of this curve with the curve for $\frac{Q(\theta)}{2hBs^2}$. As the nuclear masses continue to increase, one of these intersections will move to the right if the torque curve is of type A and the corresponding value of θ will approach zero as a limit. If the torque curve is of type B, θ will approach π as a limit. Thus the states for which j/s is greater than unity may be divided into two classes. In the one class the vector **s** is always perpendicular to the nuclear axis. In the other the vector **s** makes an angle with the nuclear axis which depends on the function $\frac{Q(\theta)}{2hBs^2}$ and approaches zero or π as the nuclear masses increase indefinitely.

The transition from fixed nuclei to free may be regarded as equivalent to a reduction of the nuclear masses from infinity to the value appropriate to the actual chemical constitution of the molecule without removing any actual external constraint. Let σ_0 denote the value of σ or $|s \cos \theta|$ for one of the initial states with fixed nuclei. From the above discussion we may conclude that when the nuclei are set free

(a) the state for which σ_0 vanishes gives birth to an infinity of states for all of which σ is equal to zero;

(b) each state for which σ_0 is intermediate between 0 and s becomes the parent of a single state with j less than s (other states with larger values of j doubtless occur, but with the double precession previously mentioned);

(c) the states for which σ_0 is equal to s give birth to a class of states finite in number for which j is greater than s and σ is intermediate between s and zero, and in addition, to a class of states for which $j_{min} < j < \infty$ and $\sigma = 0$.

More complicated possibilities are to be expected if the torque function $Q(\theta)$ has a more complicated form than that here assumed.

Hund([27]) has recently called attention to the fact that the precessional frequency of the electronic motion with fixed nuclei is likely to be quite high on account of the large departure from central symmetry of the field in which the electrons move. It follows that $\frac{Q}{2hBs^2}$ must be much greater than unity for most values of θ and hence that $\cos\theta$ will not depart appreciably from its values for fixed nuclei unless j is very large. Let us assume, for example, a molecule whose precessional frequency for fixed nuclei (Ω) and an angle θ of 60° is equal to the rotational frequency with j equal to 200. This would make the precessional frequency of the same order of magnitude as the frequency of vibration of the nuclei. Let s have the value 2. Then from Equation (11)

$$\Omega(60°) = \frac{Q(60°)}{sh \sin 60°}.$$

When j is 200 the frequency of rotation of the molecule is sensibly the same as if it were non-gyroscopic. Hence the rotational frequency is

$$\omega(200) = \frac{200h}{4\pi^2 I} = 200 \times 2B.$$

Equating these frequencies and solving for $Q/2hBs^2$, we obtain

$$\frac{Q(60°)}{2hBs^2} = \frac{200 \times .866}{s} = 86.6.$$

An examination of Figure 4 shows at once that if $Q/2hBs^2$ has such a large value as this at $\theta = 60°$, the complete curve must rise very rapidly from the points $\theta = 0$, $\theta = \frac{\pi}{2}$, $\theta = \pi$ at which the torque vanishes. It follows that if j has a moderate value greater than unity, θ must approximate one of the three values 0, $\frac{\pi}{2}$, π. In other words, the distortion of the molecule due to nuclear rotation will be small and it will behave in

essentially the same way as the rigid model of Kramers and Pauli.[19] Such a large torque function also involves a wide range of j values for which θ may be greater than zero. The critical value of j at which $\mathbf{s}$ must become perpendicular to the nuclear axis may be shown to be of the order of magnitude of 200.

This elastically mounted gyroscopic model, it must be frankly admitted, does not yield a satisfactory explanation of the empirical facts regarding the more complex band types. Its study does shed light on the perturbation problem of the preceding section, however, and may be made the basis for the development of a modified model which is more promising.

Returning to the perturbation theory problem, we observe that our study of the model shows pretty definitely that the electronic motions with free nuclei must approach corresponding motions with fixed nuclei as a limit when the nuclear masses are indefinitely increased. The mean value theorem for the approximate determination of the perturbational energy is not always directly applicable, however. This theorem is valid only if the motion of the electrons with respect to the rotating x, y, z axes approaches the motion corresponding to the unperturbed Hamiltonian function H_0 when the nuclear masses are indefinitely increased. The latter motion involves a precession if σ_0 is less than s, while the former need not. In the perturbed motions which we have discussed, the nuclei, the x, y, z axes, and the electronic angular momentum vector all precess together. Thus $\mathbf{s}$ has an absolute precession, but does not rotate with respect to the x, y, z axes. The mathematical explanation of this peculiar situation is found by calculating the contributions of the perturbational terms in the Hamiltonian function to the time derivatives of $\mathbf{S}_x$, $\mathbf{S}_y$, $\mathbf{S}_z$. Denoting the values of these derivatives $\dot{\mathbf{S}}_x$, $\dot{\mathbf{S}}_y$, $\dot{\mathbf{S}}_z$ for fixed nuclei (calculated from H_0 alone) by $(\dot{\mathbf{S}}_x)_0$, $(\dot{\mathbf{S}}_y)_0$, $(\dot{\mathbf{S}}_z)_0$, the following formulas may be derived:

$$\begin{aligned}
\dot{\mathbf{S}}_x &= (\dot{\mathbf{S}}_x)_0 + \frac{\mathbf{S}_x\mathbf{S}_y\mathbf{S}_z}{I\sqrt{p_\phi^2 - \mathbf{S}_z^2}}; \\
\dot{\mathbf{S}}_y &= (\dot{\mathbf{S}}_y)_0 + \frac{\mathbf{S}_z}{I\sqrt{p_\phi^2 - \mathbf{S}_z^2}}\left\{\sqrt{p_\phi^2 - \mathbf{S}_z^2} - \mathbf{S}_x\right\}^2. \qquad (30) \\
\dot{\mathbf{S}}_z &= (\dot{\mathbf{S}}_z)_0 - \frac{\mathbf{S}_y}{I}\sqrt{p_\phi^2 - \mathbf{S}_z^2}
\end{aligned}$$

Our study of the model shows that $\sqrt{p_\phi^2 - \mathbf{S}_z^2}$ may approach zero as the

[19] The above discussion tacitly assumes that the electronic angular momentum $\mathbf{s}$ is due solely to the orbital motion of the electrons. Hund's recent application to band spectra of the Uhlenbeck and Goudsmit hypothesis of a spinning electron opens up the possibility of a much less rigid type of model than that just described.

nuclear masses are indefinitely increased if p_ϕ is less than $\mathbf{S}$, so that $\dot{\mathbf{S}}_z$, $\dot{\mathbf{S}}_y$ do not approach $(\dot{\mathbf{S}}_x)_0$, $(\dot{\mathbf{S}}_y)_0$ as limits.

Under these circumstances we may reasonably assume, however, the legitimacy of calculating the energy of the perturbed system by adding to the unperturbed energy the mean value of perturbational part of the Hamiltonian function averaged over the limiting motion which the system actually approaches as the nuclear masses increase indefinitely. In other words, we may use (17) if we understand $\overline{\mathbf{S}_x^2}$, $\overline{\mathbf{S}_y^2}$, etc., to denote mean values of the corresponding components of angular momentums referred to an axial system x, y, z which rotates with the limiting rotational speed of the nuclei. If the perturbed motion involves a double precession, it is easy to see that in the limit as the nuclear masses increase, the vector $\mathbf{S}$ continues to revolve about the z axis so that $\mathbf{S}_x$ vanishes and we have the simple Kramers and Pauli formula with ϵ equal to zero and σ less than s. If the perturbed motion involves only a simple precession and $p_\phi > |\mathbf{S}|$, we infer that in the limit $\mathbf{s}$ becomes either parallel or perpendicular to the nuclear axis so that again we have the Kramers and Pauli formula with ϵ or σ equal to zero. The general formula (17) is to be used only in connection with those special states involving a simple precession for which $p_\phi < |\mathbf{S}|$. As these states are isolated, the practical conclusion is that ϵ or σ must vanish for any complete series of rotational energy levels.

SECTION 5. ELECTRON SPIN AND BAND STRUCTURE

In a recent paper of very great importance Hund([27]) has applied to band spectra the conception of electron spin([28]) which is proving so fruitful in the interpretation of the multiple energy levels in atomic spectra. According to this current theory the angular momentum of spin of an individual electron is one-half a Bohr unit while the corresponding magnetic moment is that of a full Bohr magneton, $\frac{eh}{4\pi mc}$. Thus the ratio of angular momentum of spin to corresponding magnetic moment is only half as great as for the angular momentum and magnetic moment due to orbital motion. This hypothesis is of fundamental importance for the explanation of the magneto-mechanical effects and the anomalous Zeeman effect([29]).

In the case of atoms, the mutual energy of orientation of the orbits relative to one another is thought to be large. Hence the corresponding torques create a rapid precession of the angular momentum vectors of the individual electrons around their resultant $\mathbf{k}$, which is therefore quantized. The electron spins, in turn, orient themselves first with respect to one another in such a way that all are either parallel or anti-parallel

to any one. Then there is a precession of the resultant angular momentum of spin $\mathfrak{s}$ and the resultant orbital angular momentum **k** about the invariable axis leading to the quantization of the total angular momentum **j**. Different values of $\mathfrak{s}$ due to different orientations of the spins relative to one another give the different systems of series (singlet, doublet, triplet, etc.) while different orientations of $\mathfrak{s}$ with respect to **k** give the different terms in a multiplet. Both **k** and $\mathfrak{s}$ vanish for any complete electron group.

Since the similarity between the multiple electronic energy levels associated with line and band spectra has been stressed recently by several workers([24]), ([25]), ([30]), ([31]) it is only reasonable to assign the two types of multiplicity to the same origin, viz., the existence of different orientations of the angular momentum of spin $\mathfrak{s}$ with respect to the resultant electronic orbital angular momentum **k**. As the coupling between **k** and $\mathfrak{s}$ is thought to be of a magnetic character the change in mutual energy due to different orientations of $\mathfrak{s}$ with respect to **k** should be of the same order of magnitude for molecules as for atoms. This is in accordance with the empirical observation that the spacing of electronic multiplets in band spectra for small values of the nuclear angular momentum is of the same order of magnitude as the spacing of certain corresponding atomic multiplets. Since the orientation energy of **k** and $\mathfrak{s}$ is small, the torque tending to orient $\mathfrak{s}$ parallel to **k** is small and the molecule should therefore be of a non-rigid character.

Hund's conception of the motion and quantization of a diatomic molecule is based on the assumption that the electron orbits in such a molecule may be regarded as modifications of the plane orbits to be expected in a central force field. The distortion may be ascribed to the following perturbing influences.

(1) The interactions between the various orbital angular momenta $\mathbf{k}_r$ of the exterior orbits tending to produce a quantization of their resultant **k**.

(2) The effect on the orbital motion of the double nucleus which transforms the spherical symmetry of the atomic force field into axial symmetry. This type of perturbation will evidently present strong analogies with the Stark effect.

(3) The interaction between the resultant orbital angular momentum **k** and the resultant angular momentum of spin $\mathfrak{s}$. The mutual energy is assumed to be proportional to the cosine of the angle between the two vectors as in the atomic case.

(4) The interaction between the nuclear rotation and the electronic angular momentum.[20]

The effect of these various interactions on the motion will depend on their relative order of magnitude. The reader is referred to the original paper for a detailed consideration of the various possibilities. Here we note only the general conclusions.

It seems probable first of all that interactions (1) and (2) are strong compared with (3) and (4). The relative importance of (1) and (2) is uncertain, but these two types of perturbation will lead in any case to a quantization of the component of the orbital angular momentum parallel to the nuclear axis which we designate by the symbol σ_k.[21] The component of the orbital angular momentum perpendicular to the nuclear axis may remain approximately constant in magnitude while precessing around that axis or may fluctuate rapidly in absolute value as well as direction. In either case its mean value for fixed nuclei will normally be zero. As noted in the preceding section, one would expect that the case where the electronic orbital angular momentum $\mathbf{k}$ is normal to the nuclear axis would be an exception to the above rule. Hund, however, gives an argument based on the quantum mechanics, which the writer does not clearly understand, purporting to show that it is not possible for the electronic angular momentum to orient itself perpendicular to the nuclear axis.

It is assumed that the spin vectors $\mathbf{s}_\tau$ unite to form a quantized resultant $\mathbf{s}$ as in the case of atoms. If the orbital angular momentum $\mathbf{k}$ were constant in direction, the vector $\mathbf{s}$ would precess about it, but the torque exerted on $\mathbf{s}$ by $\mathbf{k}$ being small, $\mathbf{s}$ cannot follow rapid fluctuations in $\mathbf{k}$. Hence, in estimating the interaction between $\mathbf{s}$ and $\mathbf{k}$, we may replace $\mathbf{k}$ by its mean value over a period long enough for $\mathbf{s}$ to precess around it. Now there are two natural ways of forming a mean value for $\mathbf{k}$. One would be to take the mean over a period long compared with the orbital frequencies but short compared with the time of nuclear rotation. The mean found in this way would have the direction of the nuclear axis and would be identical with σ_k in absolute value. The second mean would be that over a full period of the nuclear rotation and would yield a vector in the direction of the resultant $\mathbf{j}_k$ of the orbital and nuclear angular momenta.

[20] Hund lists as the fourth of his perturbing actions the influence of the orbital angular momenta $\mathbf{k}$ on the rotation through the modification in the moment of inertia. The writer fails to understand this statement but finds that if it is replaced by item 4 above, the rest of the article becomes intelligible.

[21] Hund uses the symbol l for orbital angular momentum and i_l for the component parallel to the nuclear axis.

Hund supposes that if the nuclear angular momentum is small and the nuclear period of rotation long, the spin vector is quantized with respect to the first of these two means. Then if $\mathfrak{s}$ is inclined to the nuclear axis, it precesses around that axis and its parallel component $\sigma_{\mathfrak{s}}$ must be an integral multiple of $h/2\pi$ (or, to $(\tau+\frac{1}{2})\frac{h}{2\pi}$ where τ is an integer). The interaction of the nuclear angular momentum $\mathbf{m}$ and the mean electronic angular momentum would finally lead to a slow superposed precession of $\mathbf{m}$ and $\sigma(=\sigma_k+\sigma_{\mathfrak{s}})$ about their resultant $\mathbf{j}$.

On the other hand, if m is large enough and the nuclear period is very short, there is first of all a precession of $\mathbf{m}$ and σ_k about their resultant $\mathbf{j}_k$ and superposed on this a slow precession of $\mathfrak{s}$ and $\mathbf{j}_k$ about their resultant $\mathbf{j}$.

In the first case ($\mathbf{m}$ small, $\mathfrak{s}$ precessing about the nuclear axis) the different possible values of $\sigma_{\mathfrak{s}}$ give a series of electronic energy levels with energy differences of the same order of magnitude as those obtained in an atomic multiplet as a result of different orientations of $\mathfrak{s}$ with respect to $\mathbf{k}$. In the second case (m large, $\mathfrak{s}$ precessing about $\mathbf{j}$), the energy differences due to different orientations of $\mathfrak{s}$ with respect to $\mathbf{j}$ are very small since the component of σ_k parallel to $\mathbf{j}$ which determines the orientation energy drops off very rapidly as m increases and the angle θ (Figure 3a) approaches 90°. A gradual transition from one type of motion to the other due to the increase in m and j would lead to a contraction of the spacing of the levels in the multiplet similar to the contraction in the spacing of the plus and minus ϵ levels in the Kramers and Pauli theory and similar to the contraction actually observed in the doublets of the bands discussed in Part 5d of Chapter IV.

Thus, in the case of the OH bands (Figure 23, Part 5d, Chapter IV) the double branches may be attributed to the existence of a double lower electronic energy level whose components get closer and closer together as the nuclear speed increases, owing to the fact that $\mathfrak{s}$, which is parallel or anti-parallel to σ_k for small values of m swings away from the nuclear axis and becomes almost perpendicular to it for large values of m. Hund shows that the spacing of the components of such an electronic multiplet should be inversely proportional to j_k for large values of j if the distortion of the electronic orbits by the nuclear rotation is neglected.[22] Actually the doublet spacing in these OH bands does not decrease so rapidly as $1/j_k$. The failure of Hund's contraction law may be accounted for, however, by the distortion of the orbital motion by the nuclear rotation (Cf. Part 6c, p. 345). This distortion would create a small component of orbital

[22] The components which draw together in this way have equal values of j_k, but not equal values of j. In other words these are really false doublets.

angular momentum perpendicular to the nuclear axis and therefore nearly parallel to $\mathbf{j}_k$. This component of angular momentum through its magnetic field would increase the orientation energy of $\mathbf{s}$ relative to $\mathbf{j}_k$ and would tend to keep the doublet spacing more nearly constant than Hund's calculation would suggest.

No very satisfactory explanation is given of the existence of the second superposed type of doubling in the upper energy levels of the OH and similar bands.[23]

The contraction of electronic multiplets with increasing nuclear angular momentum is to be expected only in cases in which the nuclear rotational frequencies are large compared with the frequency differences between the members of the multiplet. In this respect the contraction is similar to the Paschen-Back effect. Hence the distortion of the molecule by rotation should have little effect on the shapes of bands associated with multiple energy levels whose members are far apart, as in the case of the ZnH, CdH, and HgH bands.

Hund's theory harmonizes very well in a general way with Mulliken's conclusions([24]), ([25]) (Cf. Part 2b), provided that in applying the symbols S, P, D, etc., to molecular electronic energy levels we interpret them as indices of the orbital angular momentum parallel to the nuclear axis (σ_k) rather than of the total orbital angular momentum as in the case of atoms. (It is doubtful from the standpoint of the Hund theory whether the total electronic angular momentum is sufficiently constant in most molecules to be quantized in the usual way.) Thus, if we define S, P, D, F, etc., as symbols denoting energy levels for which σ_k is 0, 1, 2, 3—respectively, and identify the index r in ${}^rS$, ${}^rP$, ${}^rD$—with $2s+1$, the multiplicity of each molecular term type for zero m will be identical, according to Hund, with that of the corresponding atomic term type and may be expected to have a spacing of the same order of magnitude. Mulliken's conclusions regarding the difference in the orientation of the electronic angular momentum for different term types then follow from the dynamical theory. For example, in the case of electronic energy levels of the sharp series type (${}^1S$ or ${}^2S$) Mulliken finds that σ vanishes and ϵ is either zero or $\pm\frac{1}{2}$. This is exactly what would be predicted by Hund's theory for such levels. Since σ_k is zero for states of this type there is no torque to hold $\mathbf{s}$ in line with the nuclear axis and in accordance with Section 4 it might be expected to orient itself at right angles to that axis forming a positive or negative ϵ.

[23] This second type of doubling with a spacing which increases with j, is responsible, as explained in Part 5d of Chapter IV for the failure of the PQR combination principle. It is a doubling of the energy levels which does not produce additional spectrum lines owing to a principle of selection.

In Part 6c of this chapter, reason is given for supposing that even when σ_k vanishes a very small orbital angular momentum parallel to $\mathbf{m}$ and proportional to m is developed by the nuclear rotation. The angular momentum of spin $\mathbf{s}$ should orient itself with respect to the corresponding residual magnetic field in exactly the same way that it orients itself with respect to the nuclear axis when σ_k does not vanish and the nuclear rotation is slow. Hence the molecular S levels should show a multiplicity of essentially ϵ type similar to the multiplicity of the P and D levels but on a very small scale vanishing with the nuclear rotation. Thus the dynamical theory and Mulliken's empirical scheme agree in giving the molecular S levels a fine structure not observed in the corresponding atomic levels and indicative of the multiplicity r of the associated system of electronic levels.

Mulliken and Hund also agree in identifying the value of σ for principal or diffuse series terms (distortion by nuclear rotation neglected) with the inner quantum number of the corresponding atomic level and in assigning a zero ϵ to terms of this type. The theory of electron spin furthermore gives an explanation of the difference noted by Mulliken([18]) between the multiplicity of molecular levels and the multiplicity of the levels of the constituent atoms. For example, in the case of CuH we have the union of two doublet atoms to form a molecule of singlet type due to the anti-parallel orientation of the two $\mathbf{s}$ vectors which neutralize each other as do the $\mathbf{s}$ vectors of the two valence electrons in normal Mg.

To be sure, Mulliken's conclusions are based in part on the assumed universal validity of the Kramers and Pauli formula, which fails, according to Hund, in those cases where the electronic multiplets contract with increasing values of j. This assumption is the cause of the discrepancy between Mulliken's interpretation of the OH type band and Hund's. Most of Mulliken's evidence, however, is valid in the light of the work of Hund and gives it real support.

The new theory is by no means able to give an immediate solution to all the important problems related to the fine structure of bands, but the complete working out of Hund's suggestions and the correlation of the theory with the complex empirical situation must of necessity take time. The theory represents the logical outgrowth of the application to molecules of those conceptions which have proved the key to the understanding of line spectra, and workers in the field of molecular spectra will await its more detailed development with hopeful interest.

SECTION 6. THE ZEEMAN EFFECT IN BAND SPECTRA

PART 6A. INTRODUCTION. THE ZEEMAN EFFECT IN LINE SPECTRA

One of the most important means for the investigation of atomic dynamics and atomic structure has been the experimental and theoretical

study of the perturbing effects of magnetic and electric fields on line spectra. In view of our initial ignorance regarding the laws of atomic dynamics it has been essential to the progress of the science that we test our hypotheses on relatively simple problems. These perturbing effects may be discussed without a detailed consideration of the normal structure of the atom and hence have given just the sort of research field needed for orientation regarding fundamental principles.

Bohr's postulates and the Wilson-Sommerfeld quantum conditions scored a striking success in the remarkably accurate account which they gave of both the Zeeman and Stark effects for hydrogen. Their failure to give an adequate explanation of the complex Zeeman effect in the elements of higher atomic number is largely responsible for the development of the new mechanics of Heisenberg and Born and for the formulation of the spinning electron hypothesis of Uhlenbeck and Goudsmit.([28]). The recent combination of these two new developments into a complete theory of the anomalous Zeeman effect and of the complex structure of spectrum lines([29]) forms a climax to a long series of interesting advance steps in this field.

The corresponding effects of magnetic and electric fields on band lines have not yet received very extensive study. It seems probable that the magnetic field will soon prove a probe of great importance for the development of our ideas regarding molecular structure as well as atomic structure, but work in this direction has been held back thus far largely on account of the experimental difficulties involved.[24]

An exact theoretical account of the empirical observations regarding the Zeeman effect in line spectra requires the use of the new matrix mechanics of Heisenberg and Born, but fortunately an illuminating approximate theory may be formulated in terms of the better known "conventional" quantum theory of Bohr. Our discussion of the Zeeman effect for band lines will be based on this approximate treatment of the corresponding effect in line spectra. Hence it is convenient to preface our discussion of the band spectrum case with a brief review of the theory for atomic spectra.

Equation (11) of this chapter forms a natural starting point. The application of a magnetic field to an atomic or molecular system creates a torque on that system equal to the vector product of the magnetic moment $\mathbf{M}$ into the field strength $\mathbf{H}$. This torque would orient a bar magnet parallel to the field, but as the moment $\mathbf{M}$ is associated with an angular momentum p_φ the primary effect in the case of an atom or mole-

[24] Band lines are usually insensitive to magnetic influence except near the origin where the low intensity and overlapping of different branches present serious obstacles to the experimental determination of the Zeeman pattern.

cule is to produce a precession of the system around the vector **H** as an axis. The magnetic field may also distort the atom or molecule and in some cases effectively disrupts it into two systems, but for the present we shall assume that the field is weak compared with the forces which hold the system together so that the latter reacts essentially as a rigid whole. Let θ denote the angle between **M** and **H** and let ω_H denote the precessional frequency. Then in accordance with (11)

$$\omega_H = \frac{\text{torque}}{2\pi p_\phi \sin\theta} = \frac{MH}{2\pi p_\phi} = \kappa H, \tag{31}$$

where κ is simply an abbreviation for $\frac{M}{2\pi p_\phi}$. The frequency ω_H is seen to be independent of the orientation of the system with respect to the field. In accordance with the correspondence principle (Chapter II, Section 3) we may immediately write

$$\frac{\partial E}{\partial J_r} = \frac{1}{h}\frac{\partial E}{\partial r} = \omega_H \tag{32}$$

where r is the quantum number associated with the precessional motion and J_r is the corresponding phase integral. The integration of (32) yields

$$E = E_0 + rh\omega_H = E_0 + rh\kappa H. \tag{33}$$

If r is set equal to an integer,[25] or to an integer plus one-half, we obtain a series of equally-spaced magnetic energy levels. The uniform spacing of these levels flows out of the uniformity of the corresponding frequency just as in the case of the Planck ideal linear oscillator.

To get a physical interpretation of the quantum number r, one may note that the atom or molecule is, in a sense, the equivalent of a small bar magnet of moment M. Hence it should have an energy relative to the field of magnitude[26]

$$E - E_0 = -MH\cos\theta. \tag{34}$$

Comparing (33) with (34) we see that

$$r = -\frac{M\cos\theta}{\kappa h} = -\frac{2\pi p_\phi \cos\theta}{h}. \tag{35}$$

In the conventional atomic model without electron spin, the angular momentum p_ϕ is set equal to an integral multiple of $h/2\pi$. Thus

$$p_\phi = jh/2\pi. \qquad j = 0, 1, 2, 3, \ldots \tag{36}$$

[25] Strictly speaking (32) should be written in the form $\frac{\partial E}{\partial J_r} = \pm\omega_H$ and r should be limited to positive values. It is convenient, however, to eliminate the double sign by the arbitary introduction of negative values of r.

[26] This amount of energy is actually supplied to the system by electromagnetic induction during the building up of the field H.

j is identified with the azimuthal quantum number of the emitting electron in the case of hydrogen and with the vector sum of the azimuthal quantum numbers of all the electrons in the heavier elements. Combining (35) and (36) we obtain

$$r = -j\cos\theta = j\cos(\mathbf{j}, \mathbf{H}). \tag{37}$$

Thus r is the component of $\mathbf{j}$ in the direction of the field and has the maximum and minimum values $\pm j$. The number of magnetic sublevels in each group is accordingly $2j+1$.

The correspondence principle shows that only those transitions may be expected to occur for which $r'-r''=\pm 1, 0$. Hence the frequencies of the Zeeman pattern are given by the formula

$$\begin{aligned}\nu &= \frac{E'_0 - E''_0}{h} + (r'\kappa' - r''\kappa'')H \\ &= \nu_0 + i\kappa' H + r''(\kappa' - \kappa'')H, \qquad i = \pm 1,\ 0.\end{aligned} \tag{38}$$

If κ' and κ'' are equal, the above formula gives a simple triplet of lines. Otherwise the pattern which it predicts is complicated. Now according to the classical electromagnetic theory the conventional atomic model under consideration should have the magnetic moment

$$M = \frac{cp_\phi}{2mc} = \frac{jeh}{4\pi mc}. \tag{39}$$

Here m denotes the mass of the electron. κ then takes on the constant value $\frac{e}{4\pi mc}$ which we denote by the symbol κ_n. The frequency formula (38) reduces to

$$\nu = \nu_0 + i\kappa_n H, \qquad i = \pm 1,\ 0. \tag{40}$$

Thus the conventional atomic model gives a "normal" Zeeman triplet like that observed for hydrogen. This statement is equally true, as a matter of fact, if the matrix mechanics is used to study the influence of a magnetic field on this model.

Though the Zeeman effect as observed for the lines of atoms and ions containing two or more electrons is usually much more complex, it still has a great similarity to the "normal" effect produced in hydrogen and required by the above theory.

In a weak field, each of the original energy levels splits into a number of equally-spaced sublevels as in the normal effect. The spacing of these sublevels varies from one primary level to another, though it is always a rational fraction of the normal spacing. The same principle of selection for transitions between the magnetic sublevels holds for the complex effect as for the normal effect and we may infer that we have to do with a precessional motion of the atom around the magnetic lines of force

similar to the normal precession, but with a different angular velocity. This inference is further supported by the fact that the same polarization rules hold for the abnormal as for the normal case. The anomalous value of the precessional frequency may be referred to a corresponding anomalous value of the ratio of magnetic moment to angular momentum.

Additional and more direct evidence for the existence of an anomalous ratio M/p_ϕ is to be found in the magneto-mechanical experiments of Barnett([32]) and of Einstein and de Haas([33]). The value of this ratio deduced from these experiments is about twice the value $\frac{e}{2mc}$ required for orbital electrons by (39), and agrees closely with the value $\frac{e}{mc}$ deduced by Abraham([34]) for an electron with a uniform surface charge spinning on its own axis. The spinning electron theory of Uhlenbeck and Goudsmit([28]) is an application of this old idea to the explanation of the complex structure of spectrum lines[27] and the Zeeman effect. It accounts for the variety of abnormal ratios M/p_ϕ found in the complex Zeeman effect as the result of the separate compounding of orbital and spin angular momenta on the one hand and of orbital and spin magnetic moments on the other. The application of classical mechanics to the stationary states of the modified atomic model of Uhlenbeck and Goudsmit leads to the formula

$$\frac{\kappa}{\kappa_n} \equiv g = 1 + \frac{j^2 + \mathfrak{s}^2 - k^2}{2j^2} \tag{41}$$

where $\mathfrak{s}$, k, j are the quantum numbers associated with the resultant angular momentum of spin, the resultant orbital angular momentum, and the total angular momentum respectively. g is Landé's "Aufspaltungsfaktor" which measures the spacing of the magnetic sublevels associated with any given parent level. Thus the spinning electron accounts for the fact that the spacing of the magnetic sublevels varies from one parent level to another and is always a rational fraction of the normal spacing.

In order to obtain quantitative values of g in harmony with the empirical observations it is necessary to use the peculiar relation between angular momentum and corresponding quantum number which comes out of the matrix mechanics. We must suppose, in fact, that the magnitude of the orbital angular momentum is not $kh/2\pi$, but $\sqrt{k(k+1)}\frac{h}{2\pi}$

[27] Cf. Section 5, p. 326. The theory of Uhlenbeck and Goudsmit is really a revival of the magnetic electron theory of Compton([35]) and Parsons, but has a different motivation and eliminates Compton's objectionable assumption that the electron is of a size comparable with the dimensions of the 1_1 orbits in the heavier elements.

with similar formulas for the spin angular momentum and total angular momentum. Then (41) is replaced by

$$\frac{\kappa}{\kappa_n} \equiv g = 1 + \frac{j(j+1)+\mathfrak{s}(\mathfrak{s}+1)-k(k+1)}{2j(j+1)} \tag{42}$$

in accordance with the empirical data([36]).

If the magnetic field applied to a radiating monatomic gas is increased until the outer Zeeman components of the adjacent lines in a multiplet group approach each other closely, the magnetic displacements cease to be proportional to the field strength and the original weak field pattern is perturbed. The groups of components coming from the several original members of the multiplet group become asymmetrical, and finally, when the magnetic displacements become large compared with the spacings of the components of the multiplet, the pattern for the entire group is simplified into a single normal triplet. This simplification is accomplished partly through the fading out of some of the outer components and partly through the convergence of the outer components on the three lines of the ultimate triplet. The central member of the high field triplet is located at a sort of center of gravity of the original multiplet. This process of mutual perturbation followed by simplification with increasing field is called the Paschen-Back effect. According to theory the components of the high field triplet should have a fine structure comparable in scale to that of the original multiple line. As yet there is no definite experimental confirmation of this theoretical requirement([37]).

The explanation of this effect is to be found in the fact that the natural frequency of precession of the spin vector $\mathfrak{s}$ (or $\sqrt{\mathfrak{s}(\mathfrak{s}+1)}$) is twice as great as the frequency of precession of the orbital angular momentum $\mathbf{k}$ (or $\sqrt{k(k+1)}$). When the magnetic field is small, the atom reacts as a rigid whole and executes a precession with the compromise frequency $g\kappa_n H$. But the field has a tendency to make the two vectors precess with *different* frequencies and when the torques which it exerts on $\mathfrak{s}$ and $\mathbf{k}$ become comparable with the torques exerted by $\mathfrak{s}$ and $\mathbf{k}$ on each other, the atom is distorted and the motion is no longer a superposition of a uniform precession about $\mathbf{H}$ on a primary precession of $\mathbf{k}$ and $\mathfrak{s}$ about $\mathbf{j}$. Finally, when the field is very strong, the coupling between $\mathfrak{s}$ and $\mathbf{k}$ is completely broken and each executes its own independent Larmor precession, orienting itself with respect to the external field as if alone. Thus the reduction of a complex Zeeman pattern to a normal triplet in high field is due to the fact that the orbital angular momentum executes a normal Larmor precession when disengaged from the influence of the spin vector $\mathfrak{s}$. The independence of the two precessional motions and of the orientation of

the two angular momentum vectors does not destroy the mutual energy of $\mathfrak{s}$ and $\mathbf{k}$, however. This mutual energy is the cause of the residual high field fine structure.

PART 6B. THEORY OF ZEEMAN EFFECT FOR BANDS

The observations which have been made on the Zeeman effect for band lines are rather bewildering. Many of the lines are quite insensitive to the influence of a magnetic field. In other cases, where the unperturbed band lines are double or triple, they are displaced by an amount proportional to the square of the field, without being resolved into a fine structure, in such a way as to produce a contraction of the original spacing which bears a strong resemblance to the Paschen-Back effect for line spectra. In still other cases the lines are diffusely broadened. Many of these effects are evidently second order phenomena more closely related to the Paschen-Back effect than they are to the Zeeman resolutions of atomic line spectra in weak fields. We must therefore be prepared to seek their explanation in the distortion of the molecule by the magnetic field. In many cases, however, the displacements of the magnetic components of band lines are proportional to the first power of the field strength as they should be for an undistorted molecule. It is therefore important to inquire what effects we should expect for band lines when the molecular distortions are neglected. The answer to this query in the form of a theory of the first order Zeeman effect for molecular spectra would seem to be the logical point of departure for the study of the important second order phenomena.

The first attempt at the development of such a theory is due to Lenz([38]). He deals briefly with the case of a diatomic molecule having an electronic angular momentum $\frac{\sigma h}{2\pi}$ parallel to its axis of figure and derives the following (correct) expression for the magnetic energy of such a molecule when oriented with the axis of resultant angular momentum either parallel or antiparallel to the field:

$$E - E_0 = \pm \kappa_n \frac{hH\sigma^2}{j}. \tag{43}$$

Unfortunately, Lenz's discussion is based on the Rubinowicz principle of selection and not on the Bohr correspondence principle. He states that on account of the principle of selection all orientations of the resultant angular momentum of the molecule relative to the external field other

than the parallel and antiparallel ones, are to be excluded. This assumption is quite out of harmony with our present ideas of space quantization and practically vitiates the whole discussion.

A brief discussion of the application of the conventional quantum theory to the problem of the Zeeman effect for rigid diatomic molecules has been given by Kramers and Pauli([21]) and their work is here somewhat amplified by the writer. As the experimental data are very puzzling, it seems sufficient for the purpose of initial orientation to assume the normal value $\frac{2mc}{e}$ for the ratio of the electronic angular momentum to magnetic moment.[38]

The physical reason for expecting a Zeeman effect for molecular spectra is essentially the same as for atomic spectra. The molecule like the atom has, in general, a magnetic moment and therefore precesses in a magnetic field. The magnetic moment is determined by the electronic angular momentum **s**. It is convenient to consider the components perpendicular and parallel to **j** separately. The perpendicular component rotates around **j** with the nuclei. The magnetic field acting on it gives rise to a torque which changes direction as the nuclei rotate and averages to zero over the period of that rotation. It produces a small amplitude motion of the end point of the vector **j** in a plane perpendicular to the field with the frequency of the nuclei. On the other hand, the interaction between the field and the component of the magnetic moment parallel to **j** yields a steady torque $MH \cos(\mathbf{s}, \mathbf{j}) \sin(\mathbf{H}, \mathbf{j})$ perpendicular to **H** and **j** which causes a slow uniform precession of **j** about **H** superposed on the above-mentioned higher frequency oscillation. This precession is slow compared with the Larmor frequency for atoms, since the presence of a relatively large nuclear angular momentum usually reduces the ratio of magnetic moment to angular momentum for the molecule as a whole to a small value. The precessional frequency is independent of the orientation, however. Thus equation (31) holds as in the atomic case if we replace M by $M \cos(\mathbf{j}, \mathbf{s})$, and the value of κ becomes

$$\kappa = \frac{M \cos(\mathbf{j}, \mathbf{s})}{2\pi p_\phi} = \kappa_n \frac{s \cos(\mathbf{j}, \mathbf{s})}{j}$$
$$= \kappa_n \left(\frac{j^2 + s^2 - m^2}{2j^2} \right) = \kappa_n \left(\frac{\sigma^2 + \epsilon \sqrt{j^2 - \sigma^2}}{j^2} \right) \qquad (44)$$

[38] Kramers and Pauli leave this ratio indeterminate. The contribution of the nuclei to the magnetic field is, of course, negligible.

Owing to his accidental oversight of the discussion by Kramers and Pauli, the writer gave a brief summary of his own work in a recent paper([39]) read to the American Physical Society (April meeting, 1926) without giving due credit to their earlier work.

Equations (32) to (38) are also correct for molecules as well as for atoms. Introducing the above value of κ we may throw (33) into the form

$$E=E_0+rh\kappa_n H\left[\frac{\sigma^2+\epsilon\sqrt{j^2-\sigma^2}}{j^2}\right]. \tag{45}$$

Since the maximum and minimum values of r are $+j$ and $-j$ respectively (Eq. (37)), it is clear that the number of sublevels will increase as j increases just as in the case of atomic spectra. The very large values of j which occur in band spectra therefore imply the existence of very complex Zeeman patterns. The spacing of the magnetic sublevels decreases, however, as the number of levels grows, owing to the factor j^2 in the denominator of the second term of (45). As in the case of line spectra, the magnetic quantum number r will take on integral or half-integral values according as j is integral or half-integral.

If ϵ or σ changes during the transition which gives rise to the band, the maximum and minimum values of the magnetic energy given by $h\kappa_n H\left(\frac{\sigma^2+\epsilon\sqrt{j^2-\sigma^2}}{j}\right)$ will be quite different for the initial and final states. Hence the maximum displacement of any Zeeman component from the unperturbed line will be determined essentially by the difference between the values of $\frac{\sigma^2+\epsilon\sqrt{j^2-\sigma^2}}{j}$ for the two states involved. For large values of j this reduces to ϵ, so that the extreme width of the Zeeman pattern for the outer lines should be $\epsilon'-\epsilon''$ times that of the normal pattern for singlet lines. On the other hand, if ϵ and σ are constant, it is evident that the width of the pattern will approach zero as j increases indefinitely. Thus the band lines near the origin will be the only ones to give a pattern of appreciable breadth unless ϵ changes during the transition. The scale of the pattern near the origin, however, where j is not very different from σ, will approach that which is characteristic of atoms.

In the recent paper([27]) to which reference has been made so often above, Hund gives two formulas for the magnetic resolution of the energy levels in conformity with his theory of molecular spectra. The first of these formulas is applicable to cases in which the spin vector $\mathfrak{s}$ is quantized with respect to the nuclear axis (i. e., the perturbing effect of the nuclear rotation on the vector $\mathfrak{s}$ is small). In his case the components of $\mathbf{k}$ and $\mathfrak{s}$ perpendicular to the internuclear axis average to zero and the effective electronic angular momentum and magnetic moment are parallel to that axis. Then

$$s_{eff}=\sigma_k+\sigma_{\mathfrak{s}}=\sigma.$$

Since the ratio of magnetic moment to angular momentum is twice as great for electron spin as for orbital motion, we have

$$M_{eff}=\kappa_n(\sigma_k+2\sigma_{\hat{s}})h=\kappa_n(\sigma+\sigma_{\hat{s}})h. \tag{46}$$

Equation (44) becomes

$$\kappa=\frac{M_{eff}\cos\theta}{jh}=\kappa_n\frac{(\sigma_k+2\sigma_{\hat{s}})}{j}\,\frac{(j^2+\sigma^2-m^2)}{2\sigma j}=\kappa_n\frac{(\sigma+\sigma_{\hat{s}})\sigma}{j^2} \tag{47}$$

where θ denotes the angle between the nuclear axis and $\mathbf{j}$ as heretofore.[38a] Finally the energy equation takes the form

$$E=E_0+\frac{rh\kappa_nH(\sigma+\sigma_{\hat{s}})\sigma}{j^2}. \tag{48}$$

If we set $\sigma_{\hat{s}}$ equal to zero in (48), and ϵ equal to zero in (45), the equations reduce to the same form as they ought.

Hund's second Zeeman effect formula

$$E=E_0+\frac{rh\kappa_nH}{j^2}\left\{\frac{\sigma_k^2}{2j_k^2}(j^2+j_k^2-\hat{s}^2)+(j^2+\hat{s}^2-j_k^2)\right\} \tag{49}$$

is applicable when the nuclear angular momentum is so large that $\hat{s}$ precesses about $\mathbf{j}$ instead of about the nuclear axis. Here again the spacing of the magnetic levels decreases indefinitely as the nuclear angular momentum and j increase.

Both (48) and (49) are subject to modification in the light of the quantum mechanics.

As an illustration of the actual Zeeman patterns to be expected let us consider a special case. Let

$$\hat{s}=0; \qquad \epsilon'=\epsilon''=0;$$
$$\sigma'=0; \qquad \sigma''=1.$$

This is the case of the Angstrom CO bands as interpreted by Mulliken. Either by (45) or (48) we should have

$$\nu=\nu_0+\frac{r''}{j''^2}\kappa_nH. \tag{50}$$

Thus the Zeeman pattern is in this case conditioned entirely by the lower of the two electronic energy levels concerned. The outer components obtained by setting r'' equal to j'' are displaced by an amount κ_nH/j'' from the unperturbed line. The first observed line of each branch should show the same Zeeman pattern.

[38a] *Note added in proof.* An article by J. H. Van Vleck in the November 1926, Physical Review (p. 980) states that according to the new quantum mechanics j^2 in the denominator of (47) should be replaced by $(j^2-\frac{1}{4})$ if the conventional empirical values of j are used, but by $j(j+1)$ if the correct j values of the new theory are used.

In the light of the intensity discussion given below it will be seen that the higher members of the R and P branches, when partially resolved, should appear as somewhat diffuse doublets in the perpendicular [39] polarization and as broad singlets in the parallel polarization. The Q branch lines, on the other hand, should show the reverse effect, doublets in parallel polarization and broad singlets in perpendicular polarization.

Magnetic Rotation. In many cases where there are no observations showing a direct Zeeman effect, we have data on the closely related Faraday effect, or rotation of the plane of polarization of light passing near absorption lines in a magnetic field. R. W. Wood and his collaborators have shown that this rotation may be observed and its sense determined when there is no direct evidence of a resolution of the line into components or of an appreciable broadening([40]). The sense of the observed rotations is sometimes the same as that for line spectra and sometimes the opposite, so that it becomes important to inquire when our theory predicts positive rotations and when negative. Now in the normal Zeeman effect and in the complex effect for line spectra the components $r'=r''+1$ which emit right-handed circularly polarized light in the direction of the lines of force have higher frequencies than the left-handed components $r'=r''-1$. The sense of the rotation of the plane of polarization of light traveling along the lines of force is then right-handed.[39] To get a reversed, or left-hand rotation of the plane of polarization for light traveling along the lines of force, the appearance of left-handed circularly polarized emission components on the high frequency side of the pattern is requisite. As the most cursory examination of our frequency formulas indicates that circular components of each sign should be found on both sides of the unperturbed line, it is clear that the answer to our question about the sign of the rotation of the plane of polarization involves the solution of the problem of the relative intensities of the components.

Sommerfeld and Heisenberg([41]) have dealt with the question of the intensities of the Zeeman components in line spectra on the basis of the correspondence principle, while H. Hönl([42]) and independently R. de L. Kronig([43]) have derived formulas for the intensities from the summation rule of Ornstein and Burger([44]). From the correspondence principle standpoint, the problem of the intensity distribution in the weak field Zeeman pattern of a band line is exactly the same as for an atomic line. Hence the formulas for line spectra may be applied directly to the molecular case under consideration. The summation rule formulas are in

[39] Electric vector vibrating perpendicular to the field.

[39] This statement applies to light frequencies lying just outside the limits of the Zeeman pattern.

qualitative agreement with those derived from the correspondence principle, but undoubtedly describe the facts more accurately. (There is, of course, always a certain amount of ambiguity about correspondence principle formulas for intensity.) As recent advances in the interpretation of line spectra indicate that the Sommerfeld system of inner quantum numbers (j values) has greater physical significance than that of Landé, we give here the formulas in terms of the former as stated by Hönl. Let Σ^+, Π, Σ^- denote the respective relative intensities in the transverse effect of components due to transitions of the types $r'=r''+1$, $r'=r''$, and $r'=r''-1$. The Π components give radiation with the electric force vibrating parallel to the lines of force in the transverse effect and contribute nothing to magnetic rotation. The Σ^+ and Σ^- components emit perpendicular vibrations in the transverse effect and right- and left-handed circularly polarized light along the lines of force. The relative intensities depend on the value of $j'-j''$ for the parent line and hence are different for the P, Q, and R branches. We give the formulas in terms of the mean values of j and r for initial and final states. They are

$$R \text{ branch } \Sigma^+:\Pi:\Sigma^- = \tfrac{1}{2}(\bar{j}+\bar{r})(\bar{j}+\bar{r}-1):(\bar{j}+\tfrac{1}{2})^2-\bar{r}^2:\tfrac{1}{2}(\bar{j}-\bar{r})(\bar{j}-\bar{r}+1); \quad (51)$$

$$Q \text{ branch } \Sigma^+:\Pi:\Sigma^- = \tfrac{1}{2}(\bar{j}-\bar{r}+\tfrac{1}{2})(\bar{j}+\bar{r}+\tfrac{1}{2}):\bar{r}^2:(\bar{j}-\bar{r}+\tfrac{1}{2})(\bar{j}+\bar{r}+\tfrac{1}{2}); \quad (52)$$

$$P \text{ branch } \Sigma^+:\Pi:\Sigma^- = \tfrac{1}{2}(\bar{j}-\bar{r})(\bar{j}-\bar{r}+1):(\bar{j}+\tfrac{1}{2})^2-\bar{r}^2:\tfrac{1}{2}(\bar{j}+\bar{r})(\bar{j}+\bar{r}-1). \quad (53)$$

A number of general conclusions may be drawn from these intensity relations. Let us consider first the magnetic rotation to be expected from the R branch. In this case the greatest values of Σ^+ and Σ^- are associated with the values $\bar{r}=\bar{j}$, and $\bar{r}=-\bar{j}$, respectively. If a change in the magnetic moment M accompanies the electronic transition which produces the band, the term $r''(\kappa'-\kappa'')H$ in (38) will overshadow the term $i\kappa'H$, and the strong components with extreme values of $\bar{r}$ will be farthest from the center of the pattern. If $\kappa'-\kappa''>0$, the strong line (Σ^+) $r''+\frac{1}{2}=\bar{r}=\bar{j}$ will lie on the high frequency side of the pattern, while the line $r''-\frac{1}{2}=\bar{r}=-\bar{j}$ (Σ^-) will lie on the low frequency side of the pattern. As the right-handed components lie on the high frequency side of the left-handed components in the case of atomic spectra, we conclude that if $\kappa'-\kappa''>0$ the R branch lines will show *normal* magnetic rotation.

The inversion of the intensity formula (53) with respect to (51) leads to the association of the greatest values of Σ^+ and Σ^- with $\bar{r}=-\bar{j}$ and $\bar{r}=+\bar{j}$, respectively, for the P branch. Hence the P branch should always

show the opposite rotation to the R branch and if $\kappa'-\kappa''>0$ the P branch will be *abnormal.*

In the case of the Q branch the strongest Σ^+ and Σ^- components are evidently associated with the small values of $\bar{r}$ which give lines close to the center of the pattern. The intensities are independent of the sign of $\bar{r}$ and the magnetic rotation should be much smaller than in the R and P branches. Writing (38) in the form

$$\nu=\nu_0+\bar{r}(\kappa'-\kappa'')H+i\frac{(\kappa'+\kappa'')}{2}H, \tag{54}$$

we see that the right-handed components for which $i=+1$ lie on the high frequency side of the left-handed components with the same $\bar{r}$ and same intensity if $\kappa'+\kappa''$ is positive. Hence the direction of rotation for the Q branch depends on the sign of $\kappa'+\kappa''$ and should be positive under ordinary circumstances.

Part 6c. Experimental Results and Their Interpretation

The earliest investigations of the effect of a magnetic field on band spectra made by the following—Zeeman([45]), Becquerel and Deslandres([46]), Michelson([47]), and Purvis([48]), all gave a negative result. The relative insensibility of most band lines to the influence of magnetic fields revealed by these observations is what would be expected from the theory sketched above which shows that normally only the lines next the origin should exhibit a Zeeman pattern of sufficient breadth to be observed. The failure to note an effect near the origin is easily accounted for as a result of the low intensity of the early lines in each branch and the difficulty of observation which frequently results from the overlapping of the more intense lines of the branch returning from the head. At the time these observations were made the existence of an origin at a point displaced from the head was, of course, unknown.

The first discovery of an effect due to the action of a magnetic field on band lines was made by R. W. Wood([40]), who in 1905 established the existence of the "bright line magnetic rotation spectrum" of sodium vapour. In Wood's experiments, the rotation of the plane of polarization of wave lengths very near those of certain band absorption lines was used to detect the presence of an inverse Zeeman effect too small to observe in any other way. Plane polarized light (continuous primary spectrum) after passing through the absorbing gas in a magnetic field was analyzed by a Nicol's prism set with its principal plane perpendicular to that of the polarizer. Only those wave lengths rotated through an appreciable angle were transmitted by the system. Under these circum-

stances, the transmitted light proved to have the structure of a line spectrum and was designated by Wood as a magnetic rotation spectrum.

The lines in this spectrum are much less numerous than the lines in the absorption or white light fluorescence spectrum and we may conclude that only a few of the band lines (according to our theory those near the band origins) are magnetically sensitive to a high degree. In some parts of the spectrum, especially in the blue-green, there are distinct band heads and in this region the strong magnetic rotation lines lie just beyond the band heads, i. e., on the relatively transparent side of the head([49]). These rotation lines are probably due to the combined effect of all the absorption lines in the neighborhood of the head. As the analysis of the absorption bands of sodium vapour by Smith([51]) shows that the origins of these bands are very close to the heads, the existence of strong rotation at the head is in harmony with our theoretical conclusion that the lines near the origin should show a maximum magnetic sensitivity.

Similar magnetic rotation spectra have been found in the vapours of potassium, bromine, and iodine([50]). The rotation is particularly strong for bromine and in this case practically all the absorption lines yield corresponding magnetic rotation lines.

Wood has been able to determine the sign of the rotation of the plane of polarization for the stronger rotation lines. It is predominantly normal in the sodium bands which form about the D lines and which are probably due to a molecular electronic transition related to the atomic transition which produces the D lines. On the otner hand, in the red part of the spectrum there are a large number of cases of rotation with the reverse sign. These were at first interpreted as evidence of the existence of positive electrons([52]), but this view is clearly permissible no longer.

The theoretical conclusion that the P and R branches should normally show opposite magnetic rotations is of interest in view of Wood's determination of the sign of the magnetic rotation for six iodine absorption lines which lie under the broad green line emitted by the mercury arc. He found that two of the six lines showed abnormal or negative rotations. The recent analysis of the fine structure of the absorption spectrum of iodine in the region adjacent to the mercury green line by Loomis([53]) (Cf. Chapter VI, page 285) establishes a definite correlation between five of the absorption lines whose rotation has been observed and the P and R branch series of the overlapping bands in this region. The situation is somewhat confused by the accidental superposition of R and P branch lines of different bands, but when due account is taken of the intensities of the various overlapping series, the analysis leads to the

definite conclusion that the P branch lines show normal rotation and the R branch lines abnormal rotation.

The existence of *any* Zeeman effect in the case of these iodine bands is surprising at first glance in view of their general character, especially as the lines under consideration correspond to large values of j (from 30 to 115). The bands consist of P and R branches only and all the lines are single. Bands of this type are attributed by Mulliken to electronic transitions of the ${}^1S \rightarrow {}^1S$ type. The absence of a Q branch indicates that σ vanishes for both upper and lower levels. This might conceivably come about because $\sigma_{\mathfrak{s}}$ and σ_k neutralize each other, but, if that were the case, the electronic levels should be multiple as a result of the presence of neighborboring electronic states due to other orientations of $\mathfrak{s}$ with respect to the nuclear axis. Hence we may conclude in the light of Hund's theory, that σ_k vanishes for initial and final states. Under these circumstances $\mathfrak{s}$ should set itself perpendicular to the nuclear axis and the existence of bands of the type of the violet CN bands (doublets vanishing at the origin) shows that a fine structure due to the orientation of $\mathfrak{s}$ parallel or anti-parallel to $\mathbf{m}$ is to be expected. As no such fine structure is observed we conclude that $\mathfrak{s}$ vanishes also. In other words, both the initial and final levels are of the ${}^1S$ type (sharp series, single line system). This conclusion conforms with the fact that I_2 has an even number of electrons and so is capable of developing a singlet system.[21] It is surprising, however, in view of the magnetic behavior of the iodine lines.

The author ventures the following explanation. The CN doublets show that there is a certain amount of energy of orientation for $\mathfrak{s}$ relative to $\mathbf{m}$ when σ_k is zero and ϵ_k vanishes at zero m. In view of the origin of the angular momentum $\mathfrak{s}$ in electron spin, we may attribute this energy to a small residual magnetic field parallel to $\mathbf{m}$. Such a field is to be expected as a result of a molecular analogue of the Barnett magnetization by rotation effect. As indicated in Section 4 of this chapter, an electronic angular momentum vector parallel to the nuclear axis will tend to swing away from that axis into parallelism with $\mathbf{m}$ as the molecule is set into rotation. Now, although the resultant orbital angular momentum parallel to the nuclear axis vanishes, this is due to the mutual cancellation of the components of angular momentum of the individual electrons parallel to that axis. These individual electronic angular momenta all tend to twist into parallelism with $\mathbf{m}$ and thus form an ϵ_k. The distortional electronic angular momentum thus created and the corresponding mag-

[21] The reader should compare the above rather dogmatic statement regarding the CN doublets with the more detailed account given in Chap. IV, Part 5c. The discussion here given dates more than two months after the closing of Chap. IV and a much longer time after the writing of Part 5c of that chapter.

netic field are presumably proportional to m for small values of m. Hence the orientation energy of $\mathfrak{s}$ should be proportional to m.[32]

If we add the orientation energy of $\mathfrak{s}$ to the usual quadratic rotational energy term, we obtain

$$F(m) = Bm^2 \pm \delta m, \tag{55}$$

where δ is a small constant. Here

$$m = j \pm \mathfrak{s} - \epsilon_k = j \pm \tfrac{1}{2} - bm$$

b is another small constant. Solving for m and assuming that j is integral, we have

$$m = \frac{j \pm \frac{1}{2}}{1+b} = \frac{\tau}{1+b}, \quad \tau = \tfrac{1}{2}, 1\tfrac{1}{2}, 2\tfrac{1}{2}, \ldots .$$

Let $\overset{*}{B}$ and $\overset{*}{\delta}$ be defined by

$$\overset{*}{B} = \frac{B}{(1+b)^2}; \qquad \overset{*}{\delta} = \frac{\delta}{1+b}$$

Then (55) takes the form

$$F(m) = \overset{*}{B}\tau^2 \pm \overset{*}{\delta}\tau. \tag{55a}$$

The frequency formulas for the R and P branches now become

$$\begin{aligned} \nu_R &= \overset{*}{B}' + 2\overset{*}{B}'\tau + (\overset{*}{B}' - \overset{*}{B}'')\tau^2 \pm [\overset{*}{\delta}' + (\overset{*}{\delta}' - \overset{*}{\delta}'')\tau] \\ \nu_P &= \overset{*}{B}' - 2\overset{*}{B}'\tau + (\overset{*}{B}' - \overset{*}{B}'')\tau^2 \mp [\overset{*}{\delta}' - (\overset{*}{\delta}' - \overset{*}{\delta}'')\tau]. \end{aligned} \tag{56}$$

The doublet intervals are accordingly linear functions of τ or m to a first approximation. To explain the failure of the linear law for large values of m, the simple assumption that ϵ_k is proportional to m must be dropped.[33]

Turning now to iodine molecules, we note that they also should show the same rotational effect and that the distortional magnetic field should

[32] Birge (Chapter IV, Part 5b) has already found evidence from a detailed analysis of the rotational term formulas for the CuH bands of the existence of a variation in ϵ with m which he attributes to a "warping of the electron orbits by rotation." Our present point of view supports his interpretation of the empirical data for CuH and checks the sign of the effect, for the distortional ϵ is necessarily positive in accordance with Birge's result (Equation 147 of Chapter IV). Another application of the same idea will be found in Section 5, p. 329 of this chapter.

[33] The linear term in m here introduced into the energy formula is apparently open to the same objection as that raised by Birge with reference to Kratzer's linear term (cf. Chapter IV, Section 3, p. 111), for its presence violates the theoretical rule that $\frac{\partial E}{\partial m}$ should vanish with m. The writer has not yet fully straightened out this point, but in view of the magnetic nature of the term in question is of the opinion that the objection is in this case not insuperable.

produce a Zeeman effect which does not disappear for large values of m and j. In view of Equation (44) since σ is zero we may write

$$\kappa = \frac{\kappa_n \epsilon_k}{j} = \frac{a\kappa_n m}{j} = \beta$$

where a and β are small constants. (38) becomes

$$\nu = \nu_0 + (r'\beta' - r''\beta'')H. \tag{58}$$

In the case of the R branch, $j' = j'' + 1$ and we may set r' equal to $\pm j'$ and r'' equal to $\pm j''$ to get the strong exterior lines which determine the width of the Zeeman pattern and also the sign of magnetic rotation. For them

$$\nu = \nu_0 \pm H[\beta' + (\beta' - \beta'')j'']. \tag{59}$$

The upper sign goes with the right-handed circular polarization (Σ^+ component). Equation (59) shows that the Zeeman pattern grows in width as j if $\frac{(\beta' - \beta'')j''}{\beta'}$ is large compared with unity and that the sense of the rotation is normal or abnormal according as β' is greater or less than β''. The work of Wood and Loomis shows that in the case of the visible iodine absorption bands we must suppose that β'' is greater than β'. This again, is surprising at first glance since we should expect the more excited state to be more deformable and hence to have the greater β. But since the moment of inertia of I_2 is 28 per cent greater in the excited state than in the unexcited, the angular velocity connected with any given value of m must be 28 per cent lower in the excited state. Hence the lower energy level should be more sensitive to changes in m than the upper level even if somewhat less sensitive to changes in angular velocity.

The foregoing theory involves the assumption that in iodine and other apparently diamagnetic gases there is really a second order paramagnetism superposed on the inductive diamagnetic effect which is alone considered in the accepted theory. The writer sees no reason to suppose that the contribution of the suggested paramagnetic effect to the susceptibility of the gas need be large enough to conflict with the observed negative sign of that quantity.

The existence of a direct Zeeman effect for band lines was first proved by Dufour([54]) who found it in certain rather peculiar bands in the spectra of the fluorides and chlorides of calcium, barium, and strontium. The structure of the individual bands was not resolved by Dufour, but he found by suitable examination along the lines of force that each head was doubled in a magnetic field. Each component showed partial circular polarization. The relative positions of the two circular components were

such as to indicate a positive magnetic rotation of the plane of polarization for one group of bands, but a negative rotation for two others. Each band was resolved into a quartet when viewed transversely. The displacements were proportional to the field strength and of the order of magnitude of the normal displacements in the spectrum of atomic hydrogen.

The effects described by Dufour are quite different in character from those subsequently discovered in other hands and also from the effects predicted by our first order theory. Apparently *all* the lines are resolved into quadruplets of about the same breadth, a result which seems to demand that the orientation of the electronic angular momentum in the field be essentially independent of the orientation of the plane of the nuclear rotation. The situation bears a close analogy to the final stage of the Paschen-Back effect in line spectra, especially when we consider that the magnetic displacements are much larger than the spacing of adjacent band lines, indicating that the magnetic precessional motions are more rapid than the slower nuclear rotations. The action of a magnetic field on these bands deserves further study.

Another phenomenon resembling the Paschen-Back effect in line spectra is the previously mentioned contraction of doublet and triplet band lines in a magnetic field first observed by Fortrat([55]). This drawing together of the original non-magnetic components is essentially a second order effect usually unaccompanied by any tendency on the part of the lines to broaden or develop a polarized fine structure. Fortrat's observations on certain rather broad doublet band lines suggested the formula

$$dn = \frac{aH^2}{n} \tag{60}$$

for the contraction dn of doublet components having a normal spacing n on the frequency scale. Here a is a constant for any given line and varies slowly with the term number of the doublet.

More recent precise measurements by Bachem([56]) on the narrow doublets of the violet CN band $\lambda 3883$ have shown that the law of contraction should be written

$$\frac{n\,dn}{\left(1-\frac{dn}{n}\right)} = aH^2. \tag{61}$$

In this form the law indicates a displacement at first proportional to the square of the field, but at a rate which gradually decreases so that the components actually meet only for an infinite field.

The occasional doublets of abnormal width (perturbations) show an abnormal sensitivity to magnetic influence and are regularized by the field.

It seems possible that this gradual contraction of doublet and triplet lines by a magnetic field is a true Paschen-Back effect in the sense that it indicates a gradual loosening of the bond which links the angular momentum of spin $\mathbf{s}$ to the rest of the molecule. According to the theory of the CN doublets sketched above, we have to do with molecular states in which $\mathbf{s}$ is oriented with respect to the rest of the molecule only by the residual magnetic field due to the rotation of the molecule as a whole. Under these circumstances it is reasonable to suppose that a small external field should be sufficient to cause the independent orientation $\hat{\mathbf{s}}$ and $\mathbf{m}$ relative to the magnetic lines. It should be observed, however, that the absence of a first order magnetic fine structure makes the observed phenomenon essentially different from the Paschen-Back effect for atomic lines. Moreover, the theory of the Paschen-Back effect for line spectra requires that the members of the strong field triplets shall have a multiplet fine structure of the same order of magnitude as the original multiplet structure, and though the data do not as yet permit the confirmation of this requirement([37]) it is probable that this residual multiplet structure does actually exist. A corresponding fine structure is to be expected in the case of the CN bands, for if the field is strong and $\mathbf{s}$ orients itself parallel or antiparallel to the lines of force independent of the orientation of the plane of the nuclear motion, this does not eliminate the mutual energy of $\mathbf{s}$ and $\mathbf{m}$. On the contrary it should lead to the replacement of the two initial orientations of $\mathbf{s}$ relative to $\mathbf{m}$ by $2j+1$ such orientations corresponding to the $2j+1$ values of the magnetic quantum number r. Hence the final effect should be to replace the original doublet by a very fine Zeeman pattern equal in width to the original doublet, but having its greatest intensity in the center so that it would look like a single line somewhat less broad than the original doublet. This seems not to be the effect actually observed.

In other bands the existence of a magnetic resolution proportional to the field strength for lines near the origin has been established. The Zeeman patterns are not usually of the type indicated by our theory, however, and the first order effect is commonly accompanied by disturbing second order phenomena. Unfortunately the bands which have been studied are with one or two exceptions of a complicated structure which we are just beginning to understand.

The CH band $\lambda 3900$ has been studied by Hulthén([58]). This band consists of three doublet branches having a maximum separation at the origin indicating a variation in the angle which $\mathbf{s}$ makes with the nuclear

axis due to variation in m. When observed transversely, the higher frequency component of each of the three branches (P_2, Q_2, R_2) is split by the magnetic field into an asymmetric doublet. The stronger component is displaced toward the red and the weaker one about twice as far toward the blue, as indicated in the accompanying figure. The red component of the original doublet (P_1, Q_1, R_1) undergoes a simple displacement towards its companion line. The displacements are all directly proportional to the field strength and of the order of magnitude of the normal displacement $\kappa_n H$. The separation of the magnetic components of P_2, Q_2, R_2 decreases somewhat as the term number increases, but approaches the value $2\kappa_n H$ as the term number approaches zero.

The asymmetry in the displacements of the magnetic components is accompanied by an asymmetry of intensities, the exterior component

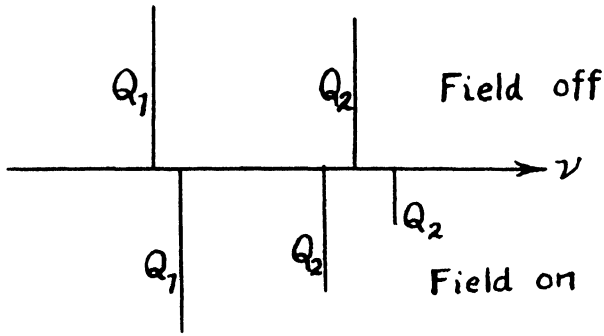


FIGURE 5.—Magnetic Resolution of First Doublet in Q Branch λ3900 CH Band after Hulthén.

being the weaker. The intensity difference is small for the earlier lines of each branch but with increasing term number the weaker component gradually fades out and beyond the tenth line is no longer observable. It is accentuated by an increase in the field strength as if it were a function of the ratio of the magnetic displacement to the original separation of the doublet components.

The fading out of the exterior magnetic component or satellite bears a strong resemblance to the fading out of the exterior magnetic components in the Paschen-Back effect. It reduces the effect of the field on the doublets of higher term number to a simple contraction like that observed in the λ3883 cyanogen band but with displacements varying linearly with the field strength.

The Zeeman effect for the λ3900 CH band has also been studied by Fortrat([59]) who reports that some of the lines are split into quadruplets

with two components vibrating parallel to the field and two perpendicular to the field. (He describes this as the λ3872 Swan band, but his table of wave-numbers shows that it is the λ3900 CH band.) Fortrat reports that the displacements cease to be proportional to the field strength when the latter becomes strong enough to appreciably weaken the exterior magnetic components. He has made observations of the same general character regarding the Zeeman effect for the zinc, cadmium, and mercury bands.

An even more complicated situation of the same general character is reported by Fortrat([60]) for the λ3064 band of OH. This band (Cf. Chapter IV, Part 5d) is of the same general structure as the λ3900 CH band studied by Hulthén([58]). Satellites are split off by the magnetic field and these sometimes develop in intensity with increasing term number. In one branch (Q_1) a satellite increases in intensity from the first line to the ninth and then decreases and finally disappears simultaneously with the appearance of a second exterior satellite which in turn increases rapidly in intensity with increasing term number to a maximum and then fades out again. The displacements show no general tendency to diminish toward zero with increasing term number.

The magnetic behavior of the zinc, cadmium, and mercury bands has been studied by Hulthén([58]). He reports in detail on the λ4326, λ4268, and λ4260 bands of ZnH only. The lines of the R_1, R_2, Q_2 branches adjacent to the origin split into doublets with a spacing which decreases as the term number increases and approaches a twice normal value when extrapolated to the origin itself. The first members of the P_1, P_2, Q_1 series are too close to the head to study. The higher members of the Q_1 series show a persistent doubling which has a half normal separation for the fifteenth line, but the higher members of the other series are magnetically insensitive. The doublets are somewhat asymmetric and in some cases diffuse.

In the case of the helium band λ4659, attributed by Mulliken to a transition of the $^1P \rightarrow {}^1S$ type, Curtis and Jevons([61]) have found a magnetic broadening of the early lines in each branch which has a maximum value (about two-thirds normal) for the lines adjacent to the origin.

These observations confirm the theory to the extent of showing that a Zeeman resolution of the order of magnitude of that found in line spectra occurs frequently in the weak band lines next the origin. They show further that this splitting of the lines is usually accompanied by other effects of a sort not easy to interpret, but evidently due in part to a distortion of the electron orbits by the field. The increase in the complexity of the Zeeman pattern with increasing term number which the theory demands has not been definitely established, the experimental difficulties involved in securing a satisfactory check on this point being

very great. Dr. R. S. Mulliken working in partial collaboration with the author has very recently obtained some plates showing the Zeeman effect for the λ5610 Angstrom CO band [34] taken particularly for the purpose of testing this question.[35] The first line of the Q branch is apparently a doublet in parallel polarization and a triplet in perpendicular polarization, the other Q branch lines being apparently double in the parallel polarization, but broad singlets in perpendicular polarization. The P branch lines, on the other hand, are single in the parallel polarization and broad, apparently double, in the perpendicular polarization. The R branch lines are diffusely broadened and show more evidence of complex structure than either Q or P lines, but are so weak and blurry even with a long exposure that it is not possible to resolve their fine structure in detail. In all cases the spacing of the components decreases as j increases. The R and P branches both show greater breadth of resolution in the perpendicular polarization than in the parallel, while the Q branch shows the reverse effect. This is in accordance with the theory when we take intensities into account. The low frequency components of the apparent doublets are the more intense and the separation of the components is less than the normal separation even for the first lines of the three branches. On the whole, the evidence in favor of the theoretical complexity is strong and the empirical results for this band are in better conformity with the theory than in any other case known to date.[35a]

[34] Cf. theoretical discussion on p. 340.

[35] These plates were taken in the first order with a 21-foot Rowland grating at the Jefferson Physical Laboratory at Harvard University.

[35a] *Note added in proof.* Measurements of the spacing of the Zeeman components of the first lines of the P and Q branches show that they are approximately half normal triplets and thereby definitely confirm the Van Vleck formula based on the new quantum mechanics. (Cf. footnote added in proof, p. 340.) The formula (50) cannot be fitted to the observations.

As previously stated, the upper electronic level is non-magnetic, so that the Zeeman pattern shows directly the multiplicity of the lower level. The triplet character of the lines under consideration shows that for them $j'' = r_{max.} = 1$ and thus verifies the conclusion drawn from the new mechanics that the correct j values for gyroscopic as well as non-gyroscopic molecules are smaller by a half integer than the conventional values determined from the Kramers and Pauli formula. Using the new j values, Van Vleck's modification of (50) becomes

$$\nu = \nu_0 + \frac{r''\kappa_n H}{j''(j''+1)}$$

For the lines under consideration $\frac{r''}{j''(j''+1)}$ takes the values $\pm\frac{1}{2}$, 0 so that a half normal triplet is predicted.

In general, the agreement between the theory of the Zeeman effect for band lines and the empirical facts is by no means satisfactory, and it is clear that a revision or extension of the theory taking into account the distortion of the electron orbits by the field will be needed to account for many of the observations. On the other hand, the theory is qualitatively verified in a number of ways and the evidence as to its essential validity is particularly good in those cases (such as the Angstrom CO bands) where we probably have to do with a fairly rigid molecule.

In connection with the discussion of the Zeeman effect for band lines it may be well to call attention to the fact that our theory of the magnetic behavior of molecules is in conflict with Pauli's calculation of the relation between the magnetic moments of paramagnetic molecules and their susceptibilities([62]). Pauli's theory, which reconciles the empirical susceptibilities of O_2 and NO with the hypothesis that all magnetic moments are integral multiples of $h/2\pi$, is based on two assumptions. One of these postulates the orientation of the electronic angular momentum and magnetic moment perpendicular to the nuclear axis, while the other postulates that the space quantization of the electronic angular momentum is independent of the nuclear angular momentum. The latter assumption, particularly, is highly improbable unless the magnetic field be strong enough to produce a molecular Paschen-Back effect. A revision of Pauli's calculation is therefore desirable.

SECTION 7. THE STARK EFFECT AND THE DIELECTRIC CONSTANTS OF DIPOLE GASES

The theoretical problem of the effect of an electric field on the rotational states of polar non-gyroscopic molecules has been studied by Hettner([63]), Pauli([64]), and Pauling([65]). Hettner's work was primarily directed to the determination of the nature of the Stark effect to be expected, while that of Pauli and Pauling had for its object the evaluation of the relation between dipole moment and dielectric constant. The more important conclusions regarding the Stark effect may be deduced without introducing mathematical complications.

The scale of the fine structure pattern produced in an electric field depends on the energy of the molecules with respect to the field. If there is a first order effect (separation of components proportional to the field strength), the perturbation theory of the classical mechanics (Cf. Section 3, p. 316) states that the corresponding energy may be calculated by taking the time average of the mutual energy of the molecule and the field over the unperturbed orbit. In the case of a polar molecule, the instantaneous mutual energy is proportional to the component of the molecular electric moment parallel to the field, and if the molecule is

diatomic and nongyroscopic the mean energy vanishes on account of the circular character of the unperturbed orbit. Hence we have to do with a second order effect except when the unperturbed molecule is not rotating, if, indeed the rotationless state is included among the permitted stationary states.[36] The energy of such a rotationless molecule will be equal to the product of its electric moment into the field strength and this energy will produce a proportional displacement of any band line due to a transition between the rotationless state and any other state. At the time of the publication of Hettner's paper, the hypothesis of non-integral values of the nuclear angular momentum was not generally accepted and it was commonly supposed that one of the lines of each of the vibration-rotation bands of the halogen hydrides was due to a transition involving a rotationless final state. In the case of HCl the effect predicted for this line (the first of the P branch) was large enough to be observable and the experiment was tried with a negative result by Barker([66]). The absence of any Stark effect for this line was interpreted as evidence that no rotationless state exists and hence as a support for the half-integral quantum number hypothesis.[37]

The theoretical relation between the dielectric constant and the dipole moment has had an interesting history. It was first evaluated by Debye([68]) on the basis of the classical statistical mechanics. He obtained the formula

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2} = \frac{N\mu^2}{3kT} + N\beta \qquad (62)$$

in which ϵ is the dielectric constant, μ is the dipole moment, N is the number of molecules per unit volume, k is the absolute entropy constant, and T the absolute temperature. β is a small constant which gives the contribution of the induced electric moment due to the distortion of the electron orbits by the field. Pauli([64]) carried through a similar calculation for the quantum theory using integral quantum numbers, but excluding the rotationless state. His result was of the same form as Debye's

[36] The reason for the absence of a first order Stark effect in the line spectra of the elements of higher atomic number than hydrogen is essentially the same. The precessional motion of the electron orbits takes the place of the nuclear rotations in averaging out the mutual energy of atom and field.

[37] Kramers and Pauli([21]) have shown that in the case of a gyroscopic polar molecule ($\sigma>0$) a first order Stark effect is to be expected for all band lines not too far from the origin. It is doubtful, however, whether the effect is large enough to be easily observable. Steubing([67]) has tried the effect of an electric field on the band spectra of the several non-polar molecules and one partially polar molecule (CO). He found an apparent change in the relative intensities of different parts of the spectrum but observed no displacement or resolution of the lines.

but the coefficient of $\frac{N\mu^2}{kT}$ was 1.5367 instead of $\frac{1}{3}$. Later Pauling([65]) revised Pauli's work by introducing the half-integral quantum numbers which have been the normal stock in trade of band spectrum workers during the last few years. According to Pauling the coefficient of $\frac{N\mu^2}{kT}$ is a function of IT (here, as usual I denotes moment of inertia) and varies between the upper limit 4.570 for very low temperatures and zero for very high temperatures. The large discrepancies between these results are due to the fact that only the molecules with the lowest rotational energies contribute appreciably to the first term in the right-hand member of (62).

Pauling used the statistical weight series 2, 4, 6, 8, ... for the successive rotational states and reports that the series 1, 3, 5, 7 . . . . leads to an impossible negative electric polarization. (The statistical weights give the number of different orientations which the molecules may take up in the electric field.) This is not surprising since orientations in which the nuclear angular momentum is nearly perpendicular to the field yield negative contributions to the polarization analogous to the negative polarization of atoms by the interatomic electric fields used by Debye to account for the repulsion between atoms and molecules at short distances (Cf. Part 1b, p. 303). But recent measurements of the relative intensities of the lines in the infra-red vibration-rotation spectrum of HCl by Dr. D. G. Bourgin([68A]) in collaboration with the author indicate that the correct statistical weight series is 1, 3, 5, 7, ... ! This set of statistical weights is also required by the summation rule theory of infra-red intensities([69]), ([70]).

Happily the conflict between these divergent results has been resolved almost before its existence was known. The new matrix mechanics of Heisenberg and Born has been applied to the problem of the polar diatomic molecule by Mensing([71]), Schrödinger([72]) and others. They find that the correct relationship between angular momentum and rotational energy is not that given by the conventional Bohr theory (a conclusion foreshadowed by earlier work of Heisenberg). Thus the angular momentum is zero for the lowest rotational energy level, though the rotational energy itself does not vanish. This conclusion invalidates the work of Pauling, but Kronig([73]), Mensing and Pauli([74]), and Van Vleck([75]) have worked out the problem of the relation between dipole moment and dielectric constant on the basis of the quantum mechanics and arrived at a formula in essential agreement with the "classical" one of Debye. The new theories harmonize with the negative result of Barker's experiment (Stark effect for HCl) in spite of the fact

that they assign the angular momentum zero to the lowest rotational state of the molecule. The original interpretation of Barker's experiment is thrown overboard, however, and we ought perhaps to regard that experiment as a verification of the quantum mechanics as distinguished from the classical mechanics.

BIBLIOGRAPHY

[1] Kemble, E. C., J. Opt. Soc. Am., 12: 1 (1926).
[2] Lenz, W., Z. Physik., 25: 299 (1924).
[3] Born, M., and Heisenberg, W., Z. Physik., 23: 388 (1924).
[4] Hund, F., Z. Physik., 31: 81 (1925).
[5] Hund, F., Z. Physik., 32: 1 (1925).
[6] Pauli, W. Jr., Ann. Phys., 68: 177 (1922).
[7] Bohr, N., Z. Physik., 13: 130 (1923).
[8] Born, M., Jordan, P., and Nordheim, L., Naturwiss., 13: 967 (1925).
[9] Nordheim, L., Z. Physik., 36: 496 (1926).
[10] Birge, R. T., and Sponer, H., Phys. Rev., 28: 259 (1926).
[11] Debye, P., Physik. Z., 22: 302 (1921).
[12] Niessen, K. F., Dissertation, Utrecht (1922).
[13] Nordheim, L., Z. Physik., 19: 69 (1923).
[14] Bohr, N., Proc. Phys. Soc., 35: 296 (1923).
[15] Witmer, E. E., Proc. Nat. Acad. Sci., 12: 238 (1926).
[16] Urey, H. C., Proc. Nat. Acad. Sci., 11: 618 (1925); Phys. Rev., 27, 216 (1926).
[17] Mulliken, R. S., Phys. Rev., 26: 561 (1925).
[18] Mulliken, R. S., Proc. Nat. Acad. Sci., 12: 338 (1926).
[19] Herzfeld, K. F., in Band 22 of Geiger and Scheel's "Handbuch der Physik" (Berlin, 1926), Chapter 5, Article 39.
[20] Mensing, L., Z. Physik., 34: 602 (1925).
[21] Kramers, H. A., and Pauli, W., Jr., Z. Physik., 13: 351 (1923).
[22] Kramers, H. A., Z. Physik., 13: 343 (1923).
[23] Birge, R. T., Phys. Rev., 27: 245 (1926) (Abstract).
[24] Mulliken, R. S., Proc. Nat. Acad. Sci., 12: 144 (1926).
[25] Mulliken, R. S., Phys. Rev. (in press).
[26] Born, M., and Heisenberg, W., Ann. Physik., 74: 1 (1924).
[27] Hund, F., Z. Physik., 36: 657 (1926).
[28] Uhlenbeck, G. E., and Goudsmit, S., Naturwiss., 47: 953 (1925). *Cf. also* Bichowsky, F. R., and Urey, H. C., Proc. Nat. Acad. Sci., 12: 80 (1926).
[29] Heisenberg, W., and Jordan, P., Z. Physik., 37: 263 (1926).
[30] Mecke, R., Z. Physik., 28: 261 (1924); 31: 709 (1925); Naturwiss., Aug. 7 and Sept. 4 (1925).

[31] Birge, R. T., Nature, 117: 300 (1926).
[32] Barnett, S. J., Science, 30: 413 (1909); Phys. Rev., 6: 239 (1915). *Cf. also* "The Angular Momentum of the Elementary Magnet," by S. J. Barnett, in Bulletin No. 18 of the National Research Council, August, 1922, pp. 235-250.
[33] Einstein, A., and de Haas, W. J., Verh. d. d. Phys. Ges., 17: 152 (1915).
[34] Abraham, M., Ann. Physik., 10: 151, 169, 171 (1903).
[35] Compton, A. H., Phys. Rev., 14: 20 (1919); Phil. Mag., 41: 279 (1921).
[36] Landé, A., Z. Physik., 5: 231 (1921); 15: 189 (1924).
[37] Sommerfeld, A., "Atombau und Spektrallinien," Fourth Ed. Braunschweig (1924), pp. 676-677.
[38] Lenz, W., Verh. d. D. Phys. Ges., 21: 632 (1919).
[39] Kemble, E. C., Phys. Rev., 27, 799 (1926) (Abstract).
[40] Wood, R. W., Phil. Mag., 10: 408 (1905); 12: 329 (1906).
[41] Sommerfeld, A., and Heisenberg, W., Z. Physik., 11: 131 (1922).
[42] Hönl, H., Z. Physik., 31: 340 (1925).
[43] Kronig, R. de L., Z. Physik., 31: 885 (1925).
[44] Ornstein, L. S., and Burger, H. C., Z. Physik., 28: 135 (1924); 29: 241 (1924).
[45] Zeeman, P., Verslag. Akad. Wettenschappen Amsterdam, 5, 248 (1896); Astroph. J., 5, 332 (1897); Phil. Mag., 43, 226 (1897).
[46] Becquerel, H., and Deslandres, H., Compt. rend., 127; 18 (1898).
[47] Michelson, A. A., Nature, 59: 440 (1899).
[48] Purvis, J. E., Camb. Phil. Soc., 13: 354 (1906).
[49] Wood, R. W., and Hackett, F. E., Astrophys. J., 30: 339 (1909).
[50] Wood, R. W., and Ribaud, G., Phil. Mag., 27: 1009 (1914); J. de Phys., 4: 584 (1914).
[51] Smith, H. G., Proc. Roy. Soc., A 106: 400 (1924).
[52] Wood, R. W., Phil. Mag., 15: 274 (1908).
[53] Loomis, F. W., Phys. Rev. (in press).
[54] Dufour, A., Le Radium, 5: 291 (1908); Physik. Z., 10: 124 (1909).
[55] Fortrat, R., Ann. Phys., 3: 345 (1915).
[56] Bachem, A., Z. Physik., 3: 372 (1920).
[58] Hulthén, E., Thesis, Lund (1923).
[59] Fortrat, R., Ann. Phys., 19: 81 (1923).
[60] Fortrat, R., J. de Phys. et le Rad., 5: 20 (1924).
[61] Curtis, W. E., and Jevons, W., Nature, 116: 746 (1925).
[62] Pauli, W. Jr., Physik. Zeits., 21: 615 (1920).
[63] Hettner, G., Z. Physik., 2: 349 (1920).
[64] Pauli, W. Jr., Z. Physik., 6: 319 (1921).

[65] Pauling, L., Proc. Nat. Acad. Sci., 12: 32 (1926); Phys. Rev. 27: 568 (1926).
[66] Barker, E. F., Astrophys. J., 58: 201 (1923).
[67] Steubing, W., Physik. Zeits., 23: 427 (1922); 26: 915 (1925).
[67A] Datta, S., Astrophys. J., 57: 114 (1923).
[68] Debye, P., Physik. Zeits., 13: 97 (1912).
[68A] Kemble, E. C., and Bourgin, D. G., Nature, 117: 789 (1926).
[69] Fowler, R. H., Phil. Mag., 49: 1272 (1925).
[70] Dieke, G. H., Z. Physik., 33: 161 (1925); Nature, 115, 875 (1925).
[71] Mensing, L., Z. Physik., 36: 814 (1926).
[72] Schrödinger, E., Ann. Physik., 79: 489 (1926).
[73] Kronig, R. de L., Proc. Nat. Acad. Sci., 12: 488 (1926).
[74] Mensing, L., and Pauli, W. Jr., Physik. Zeits., 27: 509 (1926).
[75] Van Vleck, J. H., Nature, 118: 226 (1926).

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