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THE OPTICAL BASIS OF THE THEORY OF VALENCY

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THE OPTICAL BASIS OF THE THEORY OF VALENCY

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R. DE. L. K.

GRONINGEN
May 1935

CHAPTER I

INTRODUCTION

1. THE FACTS OF CHEMISTRY

THE investigations of the chemist refer in general to quantities of matter sufficiently large to be weighed. Indeed, chemistry as a science may well be said to have had its beginning with the systematic use of the balance, and perhaps no other instrument has had so much influence upon its progress. *Chemical analysis* at an early date led to the classification of chemical substances as *elements* and *compounds* and uncovered the *laws of constant and multiple proportions*. These laws again were the immediate reason for the introduction of the concepts *atom* and *molecule* into chemical theory, finding on this basis an interpretation, at once simple and easily visualised. The usefulness of the pictures of molecular structure, developed especially in connection with the facts of organic chemistry, was further demonstrated by the discovery of the existence of *isomers*, showing that the geometrical concepts employed must have a high degree of reality.

New view-points were introduced into chemistry when one began to investigate systematically which compounds can occur in nature and which cannot be prepared, or in other words which combinations of atoms will give a stable molecule. Also the employment of *thermochemical methods* and the study of *dissociation equilibria* furnished a suitable measure for the stability of compounds in the *reaction energies* while independent evidence concerning chemical affinity was gained by measurements of *reaction velocities*. In order to systematise this field of experience, one spoke of *chemical forces* and one tried to describe their behaviour by means of the concept of *valence*. The use of valence dashes in chemical formulae and the notion of *saturation of valences* did much to clarify the general aspects of chemical union in spite of the numerous exceptions not amenable to this way of representation.

The discovery of *electrolysis* and the phenomena of *electrochemistry* shed new light upon the nature of chemical binding. They clearly demonstrated for the first time that electricity plays an important part in the structure of matter. The fundamental *laws of electrolysis* for the amount of matter dissociated by a given quantity of electricity in the electrolytic process could be regarded as an analogue of the laws of constant and multiple proportions by ascribing also to the electrical charge a corpuscular character. The great fertility of the theory of electrolytic dissociation with its central concept of the *ion* soon suggested that chemical forces must be of electrical origin. In ionogenic compounds, such as NaCl, it became plausible to imagine the binding of the atoms as arising from the electrostatic attraction between the positive and the negative ions. This idea of *heteropolar binding* was, however, not applicable to compounds with identical atoms, such as H_2, where another kind of binding, *homopolar*, had to be postulated, the nature of which long remained in the dark.

The further development of chemical theory as well as of the more modern forms of chemical investigation, such as *photochemistry*, went closely parallel with our increasing knowledge of atomic structure and the laws governing it. Physical methods of investigation were responsible for this progress, of which three deserve special mention: The *structure analysis with X-rays*, the observation of *collision phenomena* between atoms and fast corpuscles, notably α-particles and electrons, and the study of *spectra*. All three methods were capable of furnishing detailed information about the properties of the individual atoms and molecules in contrast to orthodox chemical methods, which only deal with matter in bulk, i.e. with the average properties of large numbers of atoms and molecules.

2. ATOMIC THEORY AND WAVE MECHANICS

According to our present notions atoms and molecules are composed of *electrons* and *nuclei*. The electrons all have the same negative charge of value $e = 4{\cdot}77 \,.\, 10^{-10}$ electrostatic units and the same mass $\mu = 9{\cdot}05 \,.\, 10^{-28}$ g. The nuclei have

positive charges equal to an integer Z times the elementary charge e. The *atomic number* Z distinguishes the different chemical elements and ranges for those known today from 0 to 92, the value 0 corresponding to the neutron which appears as a product in several artificial nuclear disintegrations. The nuclear masses, referred to hydrogen = 1·0078 as standard, i.e. the *atomic weights*, are approximately integers, and since the mass of the hydrogen nucleus is 1835 times as great as that of the electron, all the nuclear masses are large compared with the electronic mass. For a given atomic number Z there may occur nuclei, differing by a few units in atomic weight and spoken of as *isotopes*. It will appear later that for the chemical behaviour the nuclear charge is much more important than the nuclear mass so that in general isotopes are indistinguishable by ordinary chemical methods. Only for the very lightest elements, where the percentage difference in mass of the isotopes is large, the chemical differences may become noticeable. Thus the two hydrogen isotopes with atomic weights 1 and 2 respectively have different velocities of reaction. They also give two kinds of water, "light" and "heavy", with markedly different capacity for dissolving various salts. The phenomena of radioactivity and the experiments on the artificial disintegration of nuclei under the bombardment with fast particles have made it evident that the nuclei themselves are of composite structure.

Experience has shown that a quantitative description of the properties of atomic systems is not possible on the basis of the laws of classical physics. *Quantum physics* represents an attempt at a generalisation of these laws in the sense that a certain constant, Planck's constant, has a finite value $h = 6{\cdot}55.10^{-27}$ erg sec in contrast to classical physics, corresponding to the limit $h = 0$, just as relativistic physics is a generalisation of non-relativistic physics, the latter arising from the former by passing from a finite value of the velocity of light c to an infinite value. Quantum physics in its present form appears adequate for dealing with all questions in which the internal constitution of the electron and the atomic nuclei as well as the theory of relativity need not be taken into ac-

count. As none of these features is of importance in chemical phenomena, one may say that their interpretation by the advent of quantum physics has been reduced to a purely mathematical problem and will suffer just as little modification from a further development of physical principles as the mechanics of macroscopic bodies underwent from the discovery of the quantum laws.

In direct contrast to the properties of mechanical systems in classical physics the behaviour of atoms and molecules on the basis of quantum physics is characterised by the first postulate of Bohr:

A closed atomic system is capable of existing in a series of states, the *stationary states*, having energy values which in general form a discrete sequence and possessing a peculiar stability such that any change of energy of the system consists in a transition from one stationary state to another.

The attribute "closed" signifies that the constituent particles of the atomic system stay together, i.e. remain within a finite region of space. In this sense, e.g., an atom after ionisation or a molecule after dissociation is not to be considered as a closed system, since in the first case the ion and the electron, in the second case the dissociation products, if left to themselves, will recede further and further away from each other. For such systems the energy values of the stationary states as a rule are no longer discrete but form a continuous manifold.

Quantum mechanics permits the computation of the energy values characterising the stationary states by describing the atomic system by means of a differential equation, the *wave equation* of Schrödinger, of the form

$$(H - W)\Psi = 0. \qquad (2{\cdot}1)$$

H is an expression containing the co-ordinates of the particles of which the atomic system is composed and first- and second-order derivatives with respect to these co-ordinates. It is obtained from the classical Hamiltonian function of the system according to definite rules. W represents the energy. Ψ, finally, is a continuous function of the co-ordinates with continuous first derivatives, the *wave function*, which shall satisfy

equation (2·1) and must besides be single-valued and have an integrable square in the domain of the independent variables. The values of W for which solutions of the kind required exist are the energy values of the stationary states spoken of in Bohr's postulate.

Not only the constant W in equation (2·1) but also the wave function can be given a physical meaning. Let us imagine for simplicity that the atomic system described by equation (2·1) consists of a single particle in a given field of force, e.g. an electron in the field of a nucleus supposed fixed in space. While in classical physics it is, at least in principle, possible to determine simultaneously both position and velocity of the particle at a given instant, quantum physics disclaims this possibility. Indeed, the experiments that must be made to localise the electron all have such an influence on its motion that an uncertainty is introduced into the velocity and hence into the energy of the electron while conversely, if the energy of the electron is exactly determined, its position becomes uncertain. This may be realised qualitatively as follows: The only sources of information regarding the position and motion of the electron which we possess are its interaction with other particles such as we see it in collision phenomena or its interaction with light as it appears in the scattering of radiation. Of these methods the latter will be preferable for precise observations since in the collision experiments the lightest particles available are electrons having the same mass as the object of the investigation and hence radically changing its motion in the course of the experiment. But even the influence of radiation cannot be suppressed below a certain limit; for to increase the exactitude of the localisation of the electron the wave-length of the radiation to be scattered must be reduced (idea of the ultra-microscope). Now in the scattering process the electron suffers a recoil in a random direction, the transfer of momentum during the recoil increasing with decreasing wave-length of the radiation (Compton effect). In consequence here, too, a gain in the exactitude of localisation must be paid for by a loss in our knowledge of the velocity of the particle in question. A suitable way of describing this behaviour mathematically is

to associate with the electron as well as with any other particle a wave phenomenon, the waves of de Broglie, characterised by a function Ψ of the co-ordinates. The Ψ in equation (2·1) is just such a function, and equation (2·1) governs the behaviour of the de Broglie waves for the atomic system in question in a stationary state. Although, as mentioned, we cannot in our example speak of the exact position of the electron at every instant, and hence also not of an orbit of the particle, it is still possible to introduce a *probability* of finding the electron at various points of space. Wave mechanics assigns to the square of the absolute value of Ψ, $|\Psi|^2$, the rôle of probability so that $|\Psi|^2 d\tau$ is the chance of encountering the electron in the element of volume $d\tau$. For atomic systems containing several particles these notions can be generalised in a suitable way.

In many atomic systems there are other quantities besides the energy which take on definite values in the stationary states. Thus for an electron in a central field of force the square of the angular momentum of its orbital motion is such a quantity, having as possible values $l(l+1)h^2/4\pi^2$ with l zero or a positive integer, h denoting Planck's constant. To distinguish the different stationary states it is customary to number them by means of indices, the *quantum numbers*. In the example just mentioned l can conveniently serve as quantum number. In chapters III to VI we shall meet many other examples.

As stated already in section 1, among the atomic phenomena of special interest in connection with the exploration of atomic and molecular structure one must consider *collision processes* and *spectra*. The experimental method of investigating the former is to let a parallel beam of particles, e.g. electrons, of given velocity fall upon the atomic system and to study the distribution of the particles over the different directions in space as well as their velocities after having passed the atomic system. The wave-mechanical treatment of the problem consists in representing the incident particles by a plane de Broglie wave and to determine the scattering of this wave by the atomic system. The intensity of the scattered wave in a given direction is then proportional to the current of particles in that direction.

As regards the interpretation of spectra, the first postulate of Bohr has to be supplemented by his second postulate:

The possibility of the absorption or emission of radiation by an atomic system is bound to the possibility of energy changes of the system in such a way that the frequency ν of the radiation is related to the energy difference between initial and final states by the equation

$$h\nu = W' - W'', \tag{2·2}$$

where h is Planck's constant.

If the energy values W of the stationary states are known, this postulate permits the calculation of all frequencies ν that may occur in the spectrum. If they actually will occur depends upon whether the probability of a radiative transition between the two states W' and W'' is different from zero. In most atomic systems numerous transitions are forbidden by so-called *selection rules* so that the aspect of the spectrum is greatly simplified. Instead of computing the energy values and from them the spectral frequencies by theory, the problem usually is the converse, viz. that of obtaining the energy values from the experimentally determined spectrum and of trying to arrive at their theoretical significance.

The differences in energy of the stationary states of atomic systems may be measured in absolute units. Another way of expressing them is in Cal/gram-atom or Cal/gram-molecule by changing the absolute value of the energy difference into calories and multiplying by the number of atoms in a gram-atom. Often they are also stated in electron-volts, an electron-volt being the energy an electron obtains when moving in an electric field through a potential difference of 1 volt. Finally with every energy difference ΔW there is associated a definite frequency $\nu = \Delta W/h$ according to equation (2·2). Instead of the frequency one usually gives the wave number, obtained by dividing the frequency with the velocity of light c and measured in reciprocal cm. One has the following correspondence:

$$23{\cdot}07 \text{ Cal/gram-atom} = 1 \text{ electron-volt} = 8106 \text{ cm}^{-1}.$$

In fig. 1 the relation between the different energy scales is represented graphically.

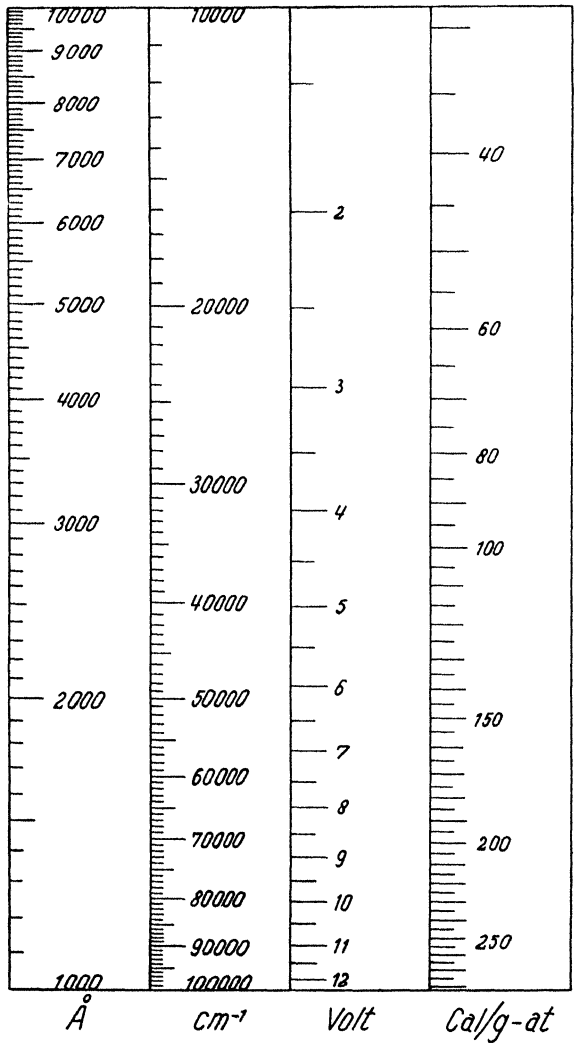


Fig. 1. Relation between wave-length in Ångströms and energy in cm^{-1}, electron-volts or Cal/gram-atom (gram-molecule).

3. ATOMIC MODELS AND THEIR LIMITATIONS

The purpose of all theoretical considerations is to establish a connection between experimental facts, i.e. between objects which can be visualised. They are constructions in trying to find an answer to the practical question: "What happens, if —?" Thus the organic chemist may ask if carbon, chlorine and hydrogen will unite at all to give a compound of the formula CCl_2H_2, and if so, whether there may result isomers of this same composition. Or the physical chemist may inquire if light of a certain frequency will dissociate photochemically a given vapour. The phenomena mentioned may be considered as "understood" or "explained" if it is possible to answer these questions in every detail before performing the experiments, and if the experiments confirm the answer given.

In looking for an answer to the first question one will resort to the concept of valence and to the pictures of stereochemistry. But while, as said above, the initial and final members in the chain of any theoretical reasoning are of a concrete nature, it is not *a priori* necessary that the intermediate members always have a character that lends itself to visualisation. In fact, for the second question this is no longer the case, and the development of wave mechanics has shown quite generally that a quantitative description of atomic phenomena can only be attained at the cost of their representation by means of pictures and models based upon the macroscopic concepts of daily life. All attempts, such as the interpretation of atomic properties by ascribing to the electrons definite orbits or the discussion of chemical union with the aid of valence dashes, were therefore doomed from the beginning to partial failure. Nevertheless, the operations with pictures and models undoubtedly have had, and still have, a marked heuristic value as long as their limitations are clearly kept in mind. Their usefulness may be compared with that of a railway map in which the stations are connected by straight lines. Such a map is convenient in determining the different possible ways by means of which a town B may be reached by train from a town A. It will also still tell us if A and B lie close together or

far apart. But nobody would try to base on such a map an exact estimate for the time required to reach B from A by measuring the total length of the connecting lines between A and B.

That classical physical concepts in spite of quantum mechanics may be employed with a certain degree of success in the interpretation of atomic phenomena is due to the fact that quantum mechanics includes classical mechanics as a limiting case, corresponding to $h = 0$. This brings with it that the geometrical proportions of atomic models in which the particles are supposed in certain respects to behave according to classical laws (e.g. in the old *atomic models* of Bohr) roughly agree with the geometrical proportions of the corresponding quantum-mechanical systems. Thus the orbit of the electron in the normal state of the hydrogen atom, as pictured originally by Bohr, has dimensions of the same order of magnitude as the region around the nucleus in which the electron, according to wave mechanics, will be found with a reasonable probability.

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CHAPTER II

THE INVESTIGATION OF ATOMIC AND MOLECULAR STRUCTURE BY MEANS OF X- AND CATHODE RAYS

4. GENERAL REMARKS

THE property of atoms and molecules which can be visualised most easily is the geometrical distribution of the positive and negative charges of which they are composed. Rigorously speaking the nuclei as well as the electrons are subject to the laws of wave mechanics so that, as we have seen in section 2, it is meaningless to ask for their exact localisation in a given stationary state of the atomic system. On account of their large mass in comparison with that of the electrons, however, the nuclei may be considered as fixed centres of force with an approximation sufficient in the discussion of many chemical problems. For the isolated atom one realises this by remembering that in the old atomic theory of Bohr, working with a model, the nucleus suffers displacements very small compared with the dimensions of the atom, and that according to wave mechanics the region in which a given particle may be found with a reasonable chance is just that same region where in the model the orbit of the particle is situated. In the case of a molecule, as will be explained more fully in chapters IV and V, there exists an equilibrium configuration of the nuclei. The nuclear motion will be composed of vibrations about this equilibrium configuration and of a free rotation of the configuration as a whole. The latter gives rise to centrifugal forces, which, however, on account of the relative slowness of rotation at ordinary temperatures conditioned by the large mass of the nuclei, have but a slight effect on the aspect of the molecule. The vibrations, too, will in general have little influence on the internuclear distances since at ordinary temperatures their amplitudes are small compared with the molecular dimensions. Disregarding hence for the present

these two forms of nuclear motion entirely, we shall be concerned with the determination of the *internuclear distances in the equilibrium configuration of the molecule.* For a polyatomic molecule they fix also the form of the nuclear structure, which in future we shall simply speak of as the *molecular form.*

Both in atoms and molecules the electrons, according to wave mechanics, may be found with a reasonable chance anywhere near the nuclei within a region, the dimensions of which are of the same order of magnitude as the dimensions of the electronic orbits in the models of Bohr, i.e. of the order of a few Ångströms. We do best to characterise the *average distribution of the electrons* by a function $w(x,y,z)$ of the co-ordinates, $w(x,y,z)\,d\tau$ being the probability of finding an electron in an element of volume $d\tau = dx\,dy\,dz$. As mentioned in section 2, w is connected in a simple way with the wave function of the atomic system in the stationary state under consideration.

5. CONNECTION BETWEEN THE NEGATIVE CHARGE DISTRIBUTION FOR AN ISOLATED ATOM AND THE SCATTERING OF X-RAYS

If a wave of radiation of frequency ν falls upon an atom, it modifies the charge density of the electrons, oscillating terms appearing in this quantity. In consequence the atom will emit scattered radiation, part of which, the *coherent scattered radiation*, has the same frequency ν as the incident wave while the rest, the *incoherent scattered radiation*, is composed of frequencies other than ν.

In the following considerations we shall assume that the frequency ν lies in the X-ray region. We shall also presuppose that the energy quantum $h\nu$ is large compared with the binding energies of the different electrons in the atom so that for our purpose we may regard them as practically free. If the nucleus of the atom is located at the origin of co-ordinates, and if the incident wave is plane polarised in the direction x while it is propagated in the direction z so that its electric field is given by

$$E_x = E_0 \cos 2\pi\nu\left(t - \frac{z}{c}\right),$$

where c is the velocity of light, then, as shown by Waller(61), the coherent radiation scattered in a given direction is equal to that emitted in the same direction on the basis of classical electrodynamics by a dipole at the origin, with the electric moment

$$P_x = -\frac{Fe^2E_0}{4\pi^2\mu\nu^2}\cos 2\pi\nu t, \qquad (5\cdot1)$$

also oscillating along the x-axis with frequency ν. Here e is the elementary charge, μ the electronic mass, while F, the *atomic form factor*, is given by

$$F(s) = 4\pi\int_0^\infty w(r)\frac{\sin sr}{sr}r^2dr. \qquad (5\cdot2)$$

In the last expression s is an abbreviation

$$s = \frac{4\pi\sin(\theta/2)}{\lambda}, \qquad (5\cdot3)$$

where θ denotes the angle between the direction of the incident radiation and the direction of scattering, the so-called angle of scattering, while $\lambda = c/\nu$ is the wave-length. r is the distance between an element of volume of the negative charge distribution and the nucleus, and it has been presupposed that the distribution function w depends upon r only, i.e. that it has spherical symmetry about the nucleus. For the electrons in closed shells (see section 14) this is always the case, while the few valence electrons outside of such shells usually do not play a rôle in actual scattering experiments, as we shall see presently.

Although the rigorous derivation of equation (5·1) on the basis of wave mechanics requires a considerable mathematical apparatus, this equation can be given the following simple geometrical interpretation: A free electron, located at the origin and scattering the incident wave, according to classical electrodynamics would have the scattering moment

$$p_x = -\frac{e^2E_0}{4\pi^2\mu\nu^2}\cos 2\pi\nu t. \qquad (5\cdot4)$$

In our atom, however, the electrons, which, as we had assumed, were to be considered as practically free with respect to the

incident radiation, are not concentrated at the origin but distributed over a volume, the linear dimensions of which are of the same order of magnitude of a few Ångströms as the wavelength of the radiation. If now, keeping the significance of w in mind, we ascribe to every element of volume $d\tau$ of the atom as scattering moment that of a free electron located there times $w(r)\,d\tau$, and if we take into account the difference in optical paths for the radiation scattered in a given direction by the various elements of volume, then the resultant scattering is just that given by the dipole in equation (5·1).

In order to prove this, we have drawn in fig. 2 the direction of propagation OZ of the incident wave and the direction of scattering OS, making the angle θ. We have also drawn the

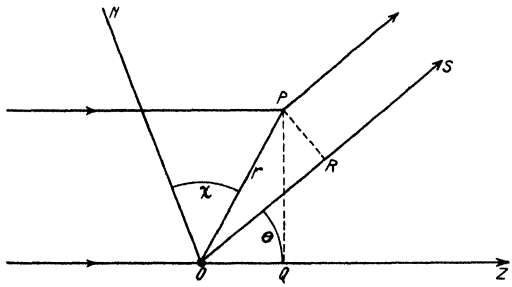


Fig. 2

bisectrix ON of the supplement of this angle. Take an element of volume at P. The path of the light scattered in the direction S by this volume element is shorter than that of the light scattered by a volume element at O by the amount $\Delta = OR - OQ$, Q and R being the perpendicular projections of P on OZ and OS. We now specify the position of P with the aid of polar co-ordinates r, χ, ψ, using the nucleus as origin and the direction ON as polar axis. r is the distance from the origin, χ is the angle between OP and ON, ψ is the azimuth of P around ON, measured from the plane through ON and OZ. From analytic geometry it follows that

$$\Delta = 2r\cos\chi\sin(\theta/2). \qquad (5\cdot5)$$

On the basis of our statement regarding the total scattering moment we have hence

$$P_x = \int_0^\infty \int_0^\pi \int_0^{2\pi} w(r) \cdot \left(-\frac{e^2 E_0}{4\pi^2 \mu \nu^2}\right) \cos 2\pi\nu \left(t + \frac{\Delta}{c}\right) \cdot r^2 \sin\chi \, dr \, d\chi \, d\psi.$$

The integration over ψ can be carried out immediately, giving a factor 2π, that over χ becomes possible after the substitution $\cos\chi = u$, $-\sin\chi \, d\chi = du$, leading to the result expressed by equations (5·1) and (5·2).

Equation (5·1) we may also write with the aid of equation (5·4) as

$$P_x = F p_x.$$

Since the scattered intensities are proportional to the squares of the dipole moments, it follows that the atom scatters F^2 times as much coherent radiation under an angle θ as a free electron on the classical theory. In this way one finds for the intensity of the coherent scattered radiation of the atom at a distance R

$$I_{\text{coh}} = \frac{F^2}{R^2} \cdot \frac{e^4}{\mu^2 c^4} \cdot \frac{1 + \cos^2\theta}{2} \cdot I_0 \qquad (5\cdot6)$$

if the incident radiation of intensity I_0 is unpolarised. In case the coherent scattering can be determined experimentally as a function of ν and θ, equation (5·6) furnishes us F in its dependence upon these quantities, or more accurately in its dependence upon the argument s given by equation (5·3). Now equation (5·2) permits us to determine $w(r)$ if $F(s)$ is known for all values of s. Looking upon the right-hand side of this equation as a Fourier integral, one immediately has the inverse formula

$$w(r) = \frac{1}{2\pi^2} \int_0^\infty F(s) \frac{\sin rs}{rs} s^2 ds. \qquad (5\cdot7)$$

It is interesting to note in this connection that according to equation (5·2) the values of $w(r)$ for large r, i.e. in the outermost regions of the atom, are of importance only for the values $F(s)$ for small s, i.e. at small scattering angles θ. This follows from the fact that $w(r)$ changes rapidly near the nucleus, i.e. for small r, and much less rapidly further away. For large s and r the factor $\sin sr$ under the integral of equation (5·2) will hence oscillate several times in a region of r in which $w(r)$ changes

little, with the consequence that in this region the positive and negative contributions to the integral cancel more or less completely. Since in actual scattering experiments one has always to work with an incident beam of finite diameter and divergence, it is not possible to obtain exact determinations of F for small scattering angles, and this is the reason that, as mentioned above, it is not warranted to assume a negative charge distribution with a character other than spherical even if electrons outside closed shells are present in the atom. Conversely it is practically not feasible to investigate the arrangement of the most loosely bound electrons of the atom by means of scattering experiments.

Just as the intensity of the coherent scattered radiation due to an atom can be expressed by equation (5·6), the intensity of the incoherent scattered radiation on the basis of the investigations of Waller[61] may be written as

$$I_{\text{incoh}} = \frac{G}{R^2} \cdot \frac{e^4}{\mu^2 c^4} \cdot \frac{1+\cos^2\theta}{2} \cdot I_0, \qquad (5\cdot8)$$

where G is a function, depending just as F on the kind of atom, the wave-length of the incident radiation and the angle of scattering. G too is connected with the negative charge distribution of the atom, but in a much more complicated way than F.

6. DETERMINATION OF THE NEGATIVE CHARGE DISTRIBUTION FOR AN ISOLATED ATOM FROM THE SCATTERING OF X-RAYS

For the determination of the atomic form factor F two experimental methods present themselves. In the one, which has been most widely used, the X-rays fall upon a *crystal*. Every atom in the crystal lattice functions as a source of scattered waves which interfere with each other. If the wave-length λ of the X-rays, the distance a between successive members of a family of lattice planes and the angle of incidence ϕ of the X-rays, measured from these lattice planes, obey the relation of Bragg

$$n\lambda = 2a \sin\phi \qquad (n \text{ integer}),$$

then the secondary wavelets, in so far as they are coherent, will all be in phase and hence give strong reflection. The absolute value of the reflected intensity will depend on the one hand upon the form factor of the individual atoms in the direction of reflection, on the other upon the number of scattering atoms and their spatial arrangement. If the latter circumstances are known from the geometry of the apparatus and from a crystal analysis, then the form factor of the individual atom may be computed from the reflected intensity, and from it by means of equation (5·7) the quantity $w(r)$. That the atom is contained in a lattice and that its $w(r)$ might differ from that of an isolated atom need not be a matter of concern, since the difference would only appear in the outermost regions of the atom which, as we have seen, are of little significance in scattering experiments. The advantage of the method described is that the incoherent radiation need not be corrected for since it does not contribute to the Bragg reflection; the disadvantage is that F is obtained after computations into which an insufficient knowledge of the crystalline condition and inadequate corrections for extinction may introduce errors.

The second method is applicable to atoms which can be worked with in the form of a *monatomic gas or vapour*. The scattering of such a substance is simply the sum of the scattering of the individual atoms composing it. If we let a narrow beam of X-rays pass through a cell containing the gas, we can get here the atomic form factor immediately from the angular intensity distribution, provided the incoherent scattering may be considered as negligible or can be corrected for. The directness of this method is an advantage over that previously discussed, the necessity of eliminating the effect of the incoherent radiation, the restriction to a limited group of substances and the long times of exposure required on account of the small density of the scattering material are distinct disadvantages.

Discussing first the results obtainable with crystals, we show in fig. 3 a graphical representation of the negative charge distribution in the Ca^{++}-ion as found by Havighurst(38) from

an investigation of crystals of CaF_2. As abscissa the distance from the nucleus is given in Ångströms. The ordinate does not represent the function $w(r)$ itself, but $U = 4\pi r^2 w$, i.e. the number of electrons per Ångström between concentric spheres around the nucleus. The points of the curve have been obtained from reflections at the 100-planes and 111-planes of the crystal. It

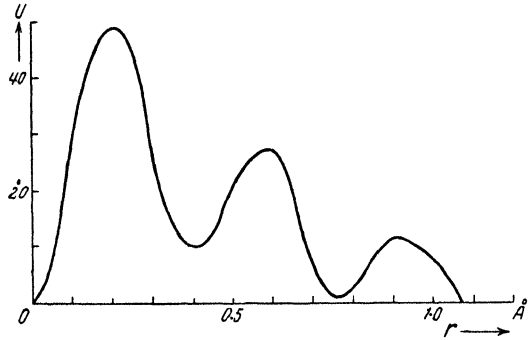


Fig. 3. Distribution of the negative charge in the Ca^{++}-ion of CaF_2 as function of the distance r from the nucleus.

ought to be noted that the curve drops practically to 0 at $r = 1{\cdot}05$ Å, a value of r which may be called the radius of the ion (see section 19). Furthermore, the curve has three maxima corresponding to the K-, L-, M-shells of the electrons in the atomic model (see section 16). Finally the total negative charge (area under the curve) corresponds to 18 electrons, signifying that the Ca-atom with atomic number 20 is doubly ionised. The two valence electrons have been given to the F-atoms, making them F^--ions so that the rest forms a spherically symmetrical rare gas configuration of the argon type. This is in conformity with the usual view that the chemical binding in CaF_2 arises from the attractive forces between oppositely charged ions, or, as one says, that it is of *heteropolar* character. Havighurst has also investigated the charge distribution of F in CaF_2 and of the atoms in LiF, NaF, NaCl. Among the other experimental researches of similar character ought to be mentioned those of Armstrong(8) (C), Bearden(10) (Al, NaCl), Froman(31) (KCl, MgO), James and Brindley(42) (KCl), James, Brindley and

Wood(43) (Al), James and Randall(44) (CaF_2), Wollan(63) (MgO). They all lead to curves of the same general aspect as that shown in fig. 3.

Passing on to the determination of F from the scattering of monatomic gases, we show in fig. 4 the curve by which Herzog(40) could represent his experimental results for argon,

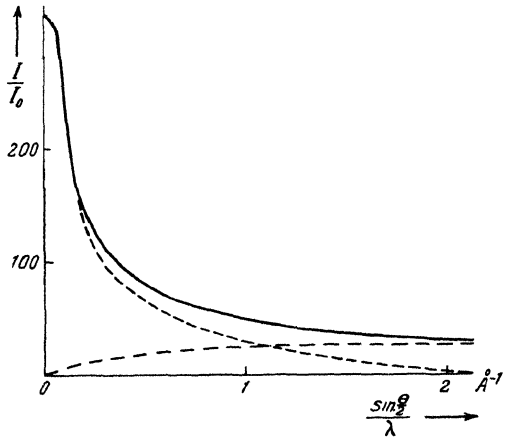


Fig. 4. Intensity of X-rays scattered by argon in its dependence upon the angle of scattering θ and the wave-length λ: —— total, – – – coherent, – · – · – incoherent scattering.

the abscissa being the quantity $\sin(\theta/2)/\lambda = s/4\pi$, the ordinate the ratio of the total scattered intensity I_{tot} to the incident intensity I_0, which has been split into the coherent and the incoherent part. This can at present be done most easily on the basis of theoretical considerations given by Heisenberg(39), and mentioned in section 7. One sees from fig. 4 that I_{coh}/I_0 decreases regularly with increasing abscissa; also that for small values of the abscissa the correction for the incoherent scattering is relatively small. From equation (5·6) it follows that the dependence of F upon s is of the same general character as that of I_{coh}/I_0, F decreasing regularly from its maximum value at $s = 0$ with increasing s. The charge distribution $U = 4\pi r^2 w$ for argon, as computed from the measured values of F by means of equation (5·7), is shown by the full-drawn curve in fig. 5.

Besides the work described, measurements on helium, neon and argon have been performed by Wollan(64) and on Hg-vapour by Scherrer and Stäger(59). Herzog(41) has discussed the results of Wollan on the basis of the theory of X-ray scattering with a view to the distribution of charge in the respective atoms.

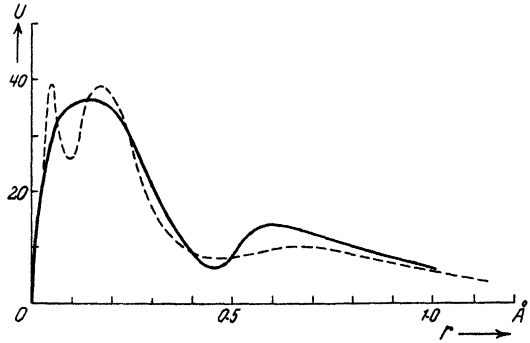


Fig. 5. Distribution of the negative charge in the Ar-atom as function of the distance r from the nucleus: —— obtained from X-ray scattering; – – – calculated by method of Hartree.

7. THEORETICAL DETERMINATION OF THE NEGATIVE CHARGE DISTRIBUTION FOR AN ISOLATED ATOM

As mentioned in section 2, the distribution function w is connected with the solution Ψ of the wave equation of the electrons moving in the field of the nucleus so that one can calculate w if Ψ is known. For all but the simplest atoms, however, a rigorous determination of Ψ encounters insurmountable mathematical obstacles. Nevertheless, it has been possible by three different methods of approximation to arrive at expressions for w which check quite satisfactorily with the X-ray determinations.

The first of these methods has been developed by Thomas(60) and has later been elaborated by Fermi(30). In it the electrons are supposed to form a gas in the field of the nucleus which can be treated on the basis of *quantum statistics*. This naturally requires that the number of electrons is sufficiently large so that the results are rather inaccurate for atoms of low atomic

number. The principal advantage of the method is that the distribution function w to which it leads is expressed for all atoms in one and the same formula

$$w(r) = \frac{C(Z)}{r^{3/2}} \phi^{3/2}\left(\frac{r}{\gamma}\right),$$

$$C(Z) = \frac{2^{9/2}\pi Z^{3/2} e^3 \mu^{3/2}}{3\hbar^3}, \quad \gamma = \frac{3^{2/3}\hbar^2}{2^{13/3}\pi^{4/3} Z^{1/3} e^2 \mu}.$$

Here Z is the atomic number, e the elementary charge and μ the electronic mass, h Planck's constant, r the distance from the nucleus. The function ϕ has been tabulated by Fermi(30). It decreases regularly from its maximum value 1 at $r = 0$ to the value 0 at large values of the argument.

The second method, employed especially by Pauling and Sherman(55), considers each electron as moving in a Coulomb field of force, replacing the action of the other electrons by a suitable diminution of the nuclear charge. The determination of this diminution, the *screening constant*, which must be chosen differently for each group of electrons in the atom, is discussed in detail by the authors just mentioned. The hydrogen-like wave equation for each electron may then be solved and the charge distribution calculated according to the principles sketched in section 2.

The third and most accurate method is that of the *self-consistent field*, due to Hartree(36). Here the interaction of the electrons is replaced by a central field, superposed upon the Coulomb field of the nucleus. The central field is chosen in such a way that the electrons, moving in the modified field of the nucleus according to wave mechanics, will just give rise to a charge distribution from which this central field would result on the basis of electrostatics. In contrast to the Thomas-Fermi distribution the last two methods have to be applied to every atom individually and are hence far more troublesome to handle.

In order to show how far the distribution function $w(r)$ as obtained from experiment by means of the considerations of sections 5 and 6 checks with the theoretical distributions, we have drawn in fig. 5, next to the experimentally determined

curve for $U = 4\pi r^2 w$, the curve calculated by Hartree's method. As one sees, the X-ray scattering does not permit the finding of all the details in the distribution function, the narrow minimum at r being smoothed out.

Each of the theoretical charge distributions will give rise to a definite dependence of the atomic form factor F upon its argument s according to equation (5·2). For the Thomas-Fermi distribution, again, an especially simple expression results for F. One finds

$$F(s) = Zf(Z^{-1/3}s), \qquad (7\cdot1)$$

where f is a function of one argument only. The derivation of equation (7·1) is, e.g., discussed by Bethe(11) while the values of f have been tabulated by Bewilogua(12). His results have been used in computing table 1, the wave-length occurring in the definition of s being measured in Ångströms. Equation (7·1) represents the atomic form factor for all atoms, for all wave-lengths and at all angles of scattering. To compare the F-values so obtained with those resulting from the other two methods, we show in fig. 6 the behaviour of F for the ions of the alkali metals. One notices that the three F-curves in each case do not lie very far apart and that the percentage deviation decreases as the atomic number becomes larger.

TABLE 1

x	$f(x)$	$\frac{1-f(x)}{x^2}$	x	$f(x)$	$\frac{1-f(x)}{x^2}$
0·00	1·000	1·01	3·67	0·284	0·053
0·33	0·922	0·70	4·00	0·264	0·046
0·67	0·796	0·459	4·33	0·240	0·040
1·00	0·684	0·316	4·67	0·224	0·036
1·33	0·589	0·232	5·00	0·205	0·032
1·67	0·522	0·172	5·33	0·189	0·029
2·00	0·469	0·133	5·67	0·175	0·026
2·33	0·422	0·106	6·00	0·167	0·023
2·67	0·378	0·087	6·33	0·156	0·021
3·00	0·342	0·073	6·67	0·147	0·019
3·33	0·309	0·062	—	—	—

The Thomas-Fermi distribution also leads to a formula for G, the quantity occurring in equation (5·8) for the incoherent

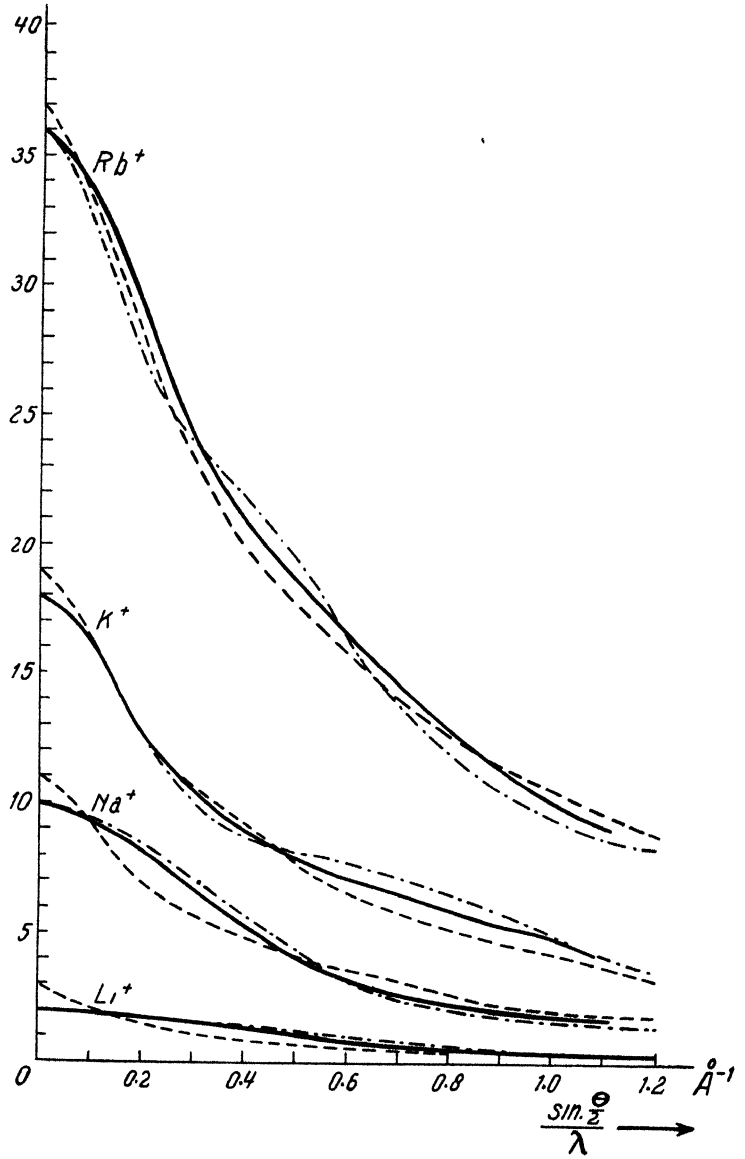


Fig. 6. Atomic form factor F of the alkali-ions in its dependence upon the angle of scattering θ and the wave-length λ, calculated by method of —— Hartree, · - · - · - · Pauling-Sherman, – – – Thomas-Fermi.

scattering. As shown by Heisenberg(39) and Bewilogua(12), it is given by

$$G(s) = Zg(Z^{-2/3}s), \qquad (7{\cdot}2)$$

g being again a function of the one argument as given numerically in table 2 so that by means of equations (5·8) and (7·2) and this table one can compute the incoherent scattered intensity for all atoms, for all incident wave-lengths and at all angles of scattering. The results have already been utilised in section 6 when splitting the total scattering for argon, represented in fig. 4, into its coherent and incoherent parts.

TABLE 2

x	$g(x)$	x	$g(x)$
0·00	0·000	2·84	0 880
0·28	0·319	3·41	0·909
0·57	0·486	3·98	0·929
1·14	0·674	4·55	0·944
1·71	0·776	5·12	0·954
2·27	0·839	5·68	0·963

In the following section, when discussing the X-ray scattering of a molecule, it will be necessary to presuppose the scattering of the composing atoms as known. From the preceding sections we know that we can use for this purpose the experimentally determined atomic F-curves, or, if these are not available, that we can calculate satisfactory atomic F-curves by one of the methods described. On account of its simplicity the method of Thomas is most easily used, giving F-values which in general are of sufficient accuracy.

8. DEPENDENCE OF THE X-RAY SCATTERING OF A MOLECULE UPON THE INTERNUCLEAR DISTANCES

We inquire now after the X-ray scattering of molecules and shall, to begin with, confine our attention to *diatomic molecules*. In accordance with the considerations of section 4 we regard the nuclei as fixed at their equilibrium distance ρ. We shall also presuppose that the negative charge distribution of the molecule arises from simple superposition of the charge distributions of the composing atoms in the isolated state. In reality,

of course, the arrangement of the most loosely bound electrons will be strongly perturbed by the binding forces, but for the reasons already mentioned in section 5 the error thus introduced is of minor significance in scattering experiments. On these assumptions it is possible to express the coherent scattering of the molecule in terms of the quantities characterising the scattering of the composing atoms and the internuclear distance ρ. In order to be able to compare the result of the calculation with scattering experiments on molecular gases, it is still necessary to average it over all possible orientations of the internuclear line of the molecules with respect to the direction of the incident X-rays, all orientations being equally

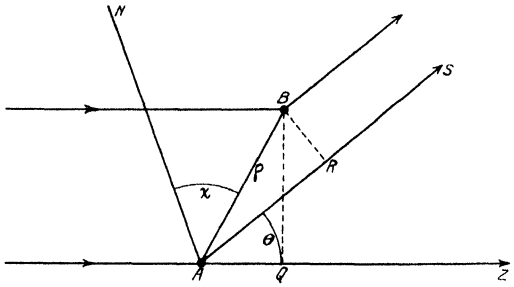


Fig. 7

probable. As shown by Debye(24), there results then for the coherent scattered intensity I_{coh} per molecule at a distance R from the molecule and under a scattering angle θ

$$I_{\text{coh}} = \frac{1}{R^2}\left(F_1^2 + 2F_1F_2\frac{\sin s\rho}{s\rho} + F_2^2\right)\cdot\frac{e^4}{\mu^2c^4}\cdot\frac{1+\cos^2\theta}{2}\cdot I_0, \quad (8{\cdot}1)$$

where F_1 and F_2 are the form factors of the two atoms while s again is given by equation (5·3). The incident radiation of intensity I_0 is supposed to be unpolarised.

The proof of equation (8·1) is easily given on the basis of considerations similar to those in section 5. Taking the incident X-rays again as propagated in the z-direction and as linearly polarised in the x-direction, and letting the nucleus of the first atom coincide with the origin A (see fig. 7), we may replace this atom in its coherent scattering effect, as we have seen there, by

the dipole (5·1) at the origin. In the same way the second atom may be replaced by a dipole at its nucleus B. The resulting scattering is that arising from these two dipoles, superposed with due regard to the difference in optical path $\Delta = AR - AQ$ for the light going over A and that going over B. Specifying AB by means of the polar angles, already introduced in the derivations of section 5, this difference is now in analogy to equation (5·5) given by

$$\Delta = 2\rho \cos\chi \sin(\theta/2), \tag{8·2}$$

the only change being that ρ is now a fixed quantity. The scattering moment of the molecules becomes then

$$\begin{aligned} P_x &= -\frac{e^2 E_0}{4\pi^2 \mu \nu^2}\left[F_1 \cos 2\pi\nu t + F_2 \cos 2\pi\nu\left(t+\frac{\Delta}{c}\right)\right] \\ &= -\frac{e^2 E_0}{4\pi^2 \mu \nu^2}\left[\left(F_1 + F_2 \cos\frac{2\pi\nu\Delta}{c}\right)\cos 2\pi\nu t \right. \\ &\qquad \left. - F_2 \sin\frac{2\pi\nu\Delta}{c} \sin 2\pi\nu t\right]. \end{aligned} \tag{8·3}$$

Just as the intensity of coherent scattering, for an isolated atom and unpolarised incident radiation, expressed by equation (5·6) is related to the scattering moment (5·1), so here the scattered intensity may be found from (8·3). It is the sum of the intensities which the term in this scattering moment with $\cos 2\pi\nu t$ and the term with $\sin 2\pi\nu t$ would give separately since these two terms are 90° out of phase. The scattered intensity thus becomes

$$\begin{aligned} I &= \frac{1}{R^2}\left[\left(F_1 + F_2 \cos\frac{2\pi\nu\Delta}{c}\right)^2 + F_2^2 \sin^2\frac{2\pi\nu\Delta}{c}\right]\cdot\frac{e^4}{\mu^2 c^4}\cdot\frac{1+\cos^2\theta}{2}\cdot I_0 \\ &= \frac{1}{R^2}\left[F_1^2 + 2F_1F_2\cos\frac{2\pi\nu\Delta}{c} + F_2^2\right]\cdot\frac{e^4}{\mu^2 c^4}\cdot\frac{1+\cos^2\theta}{2}\cdot I_0. \end{aligned}$$

If now we substitute for Δ the expression (8·2) and average over all orientations of the molecules, then we obtain equation (8·1).

The term $\sin s\rho/s\rho$ in equation (8·1) gives rise to maxima and minima in the coherent scattered intensity of the molecule if we represent it as a function of the scattering angle or of s. Since F_1 and F_2 may be regarded as known on the basis of

sections 6 and 7, the equation contains as the only unknown the *internuclear distance* ρ *of the molecule*. From the position of the maxima and minima in the scattering curve it is hence possible to determine ρ.

The generalisation of equation (8·1) to a *polyatomic molecule* is

$$I_{\text{coh}} = \frac{1}{R^2} \sum_{jk} F_j F_k \frac{\sin s\rho_{jk}}{s\rho_{jk}} \cdot \frac{e^4}{\mu^2 c^4} \cdot \frac{1+\cos^2\theta}{2} \cdot I_0, \quad (8{\cdot}4)$$

the sum to be extended over all pairs of atoms j and k (including the combination jj of each atom with itself), ρ_{jk} denoting the distance between the nuclei j and k. For $k=j$ the factor $\sin s\rho_{jk}/s\rho_{jk}$ is to be put equal to 1. Here there are several unknowns, namely the ρ_{jk}, and the scattering will only lead to a satisfactory determination of them if they are not too numerous. If they can all be obtained, then the *molecular form* is also known.

When applying the theory to scattering experiments on molecular gases, it must again be remembered that the actual scattering observed is the sum of the coherent and the incoherent scattering. The latter is composed additively of the incoherent scattering of the various atoms in the molecule, which may, e.g., be calculated by the method of Thomas and Fermi as described at the end of section 7.

9. DETERMINATION OF MOLECULAR SIZE AND FORM FROM X-RAY SCATTERING

In order that noticeable maxima and minima will appear in the curve showing the scattered intensity of a molecular gas or vapour as a function of the scattering angle or of the quantity s, defined by equation (5·3), it is essential that at least two of the atoms in the molecule have a sufficient scattering power. Since according to equation (7·1) the scattering power increases with the number of electrons in the atom, this means that at least two atoms must have a sufficiently high atomic number. Hydrogen atoms scatter so weakly that their presence does not cause noticeable fluctuations in the scattering curve. Hence their position in the molecule cannot be ascertained with accuracy by an X-ray analysis. The same applies to all

atoms the atomic number of which is small compared with that of the heaviest constituents of the molecule. In consequence in some cases the X-ray analysis may lead only to a partial determination of the molecular structure.

(*a*) *Internuclear distance of* N_2, O_2, Cl_2. As an example of X-ray scattering by a diatomic molecule we show in fig. 8

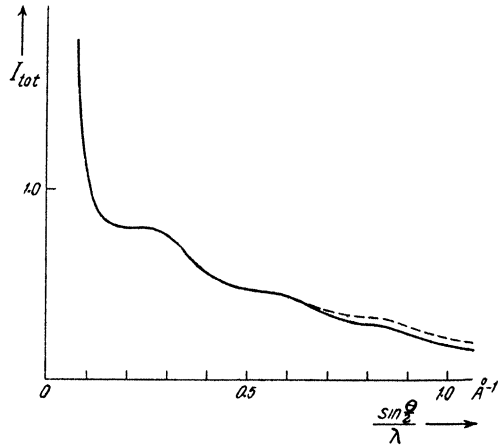


Fig. 8. Intensity of X-rays scattered by Cl_2 in its dependence upon the angle of scattering θ and the wave-length λ: —— theoretical, – – – experimental scattering (in so far as it deviates from the former).

the scattered intensity I_{tot} of *chlorine*, Cl_2, determined by Richter(58), as a function of s. One notices the decrease of I_{tot} with increasing s, caused by the fact that the atomic scattering as governed by F_1 and F_2 in equation (8·1) (which here are equal) decreases with s according to the results in sections 6 and 7. Furthermore the fluctuations in intensity, arising from the intramolecular interference, are clearly apparent. The scattering, calculated theoretically with the Hartree method for an internuclear distance $\rho_{Cl-Cl} = 2{\cdot}0$ Å, is shown by the full-drawn curve. The experimental results, in so far as they deviate from it, have been indicated by the dotted curve. As mentioned by Richter, computations with $\rho_{Cl-Cl} = 1{\cdot}9$ or $2{\cdot}1$ Å lead to a far worse agreement so that the above value of ρ_{Cl-Cl} may be taken as correct within perhaps 2 per cent.

Other diatomic molecules investigated are *nitrogen*, N_2, and

oxygen, O_2, both studied by Gajewski(32). Here, on account of the lightness of the atoms, the fluctuations in intensity are hardly visible. Good agreement between theory and experiment is obtained with $\rho_{N-N} = 1{\cdot}1$ Å, $\rho_{O-O} = 1{\cdot}2$ Å.

(*b*) *Internuclear distances of* CO_2, CS_2, NH_3, H_2O. In addition to the diatomic molecules just mentioned Gajewski(32) has also investigated some polyatomic molecules. For *carbon dioxide*, CO_2, and *carbon disulphide*, CS_2, the linear symmetric models with a distance $\rho_{C-O} = 1{\cdot}1$ Å and $\rho_{C-S} = 1{\cdot}5$ Å gave satisfactory agreement. In the compounds *ammonia*, NH_3, and *water*, H_2O, the scattering due to the H-atoms is so small that nothing definite can be said about their configuration.

(*c*) *Structure of* Cl-*substitution products of methane*. Bewilogua(13) has investigated the series of molecules CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl. The chemist has ascribed to these molecules a tetrahedral structure with the C-atom at the centre of the tetrahedron. For *carbon tetrachloride*, CCl_4, the tetrahedron should be regular so that there is only one unknown distance, e.g. ρ_{Cl-Cl}, characterising the molecule, ρ_{C-Cl} being equal to $\sqrt{6}\rho_{Cl-Cl}/4$. Fig. 9 (*a*) shows the experimental scattering curve, with which the theoretical curve can indeed be made to agree on the basis of the molecular form just described if ρ_{Cl-Cl} be put equal to 2·99 Å (error about 1 per cent). The corresponding value of ρ_{C-Cl} is 1·83 Å.

In the remaining molecules of the series the influence of the H-atoms is so small that it may be neglected in the discussion of the experimental results. Conversely, the experiments do not permit us to draw conclusions regarding the position of the H-atoms. The main cause of the fluctuations in the curves of *chloroform*, $CHCl_3$, and *methylene chloride*, CH_2Cl_2, as shown in fig. 9 (*b*) and (*c*), is the interference of the scattering from the Cl-atoms, while the interference of the scattering from Cl and C produces only a slight variation as may be seen from the curve for *methylchloride*, CH_3Cl, in fig. 9 (*d*). Only the relative position of the Cl-atoms in $CHCl_3$ and CH_2Cl_2 can hence be determined with some accuracy. For $CHCl_3$ the assumption that the three Cl-atoms form an equilateral triangle with $\rho_{Cl-Cl} = 3{\cdot}11$ Å and that the C-atom lies at about the same

distance from them as in CCl_4 gives satisfactory agreement with experiment. For CH_2Cl_2 one must take $\rho_{Cl-Cl} = 3{\cdot}23$ Å. The increase of ρ_{Cl-Cl} as the number of Cl-atoms in the molecule becomes smaller is ascribed by Bewilogua(13) to a spreading

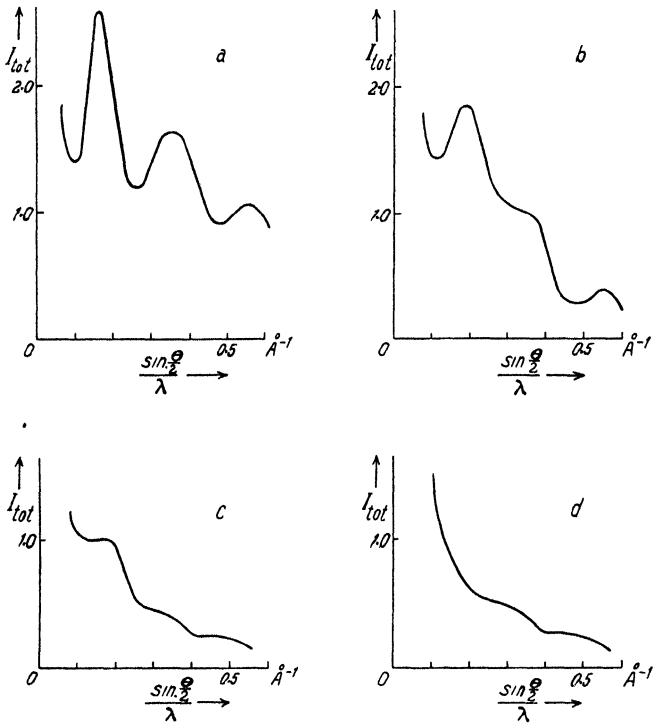
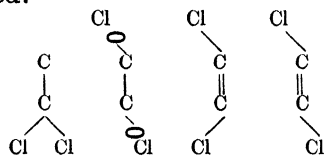


Fig. 9. Intensity of X-rays scattered by gaseous (*a*) CCl_4, (*b*) $CHCl_3$, (*c*) CH_2Cl_2, (*d*) CH_3Cl in its dependence upon the angle of scattering θ and the wave-length λ.

of the angle between the valences of the C-atom directed toward the Cl-atoms, the distance ρ_{C-Cl} remaining constant. While in the regular tetrahedron of CCl_4 this angle is 109·5°, the above values of ρ_{Cl-Cl} lead to angles of 116° and 124° for $CHCl_3$ and CH_2Cl_2 respectively if it is assumed that the distance ρ_{C-Cl} is the same as in CCl_4.

(*d*) *Structure of isomers.* Debye(25) and Ehrhardt(28) have also carried out investigations upon derivatives of ethane and

ethylene containing two chlorine atoms, i.e. on substances of the chemical formula $C_2H_4Cl_2$ and $C_2H_2Cl_2$. Each of these substances exists in isomeric forms which may be represented by the following structure formulae, in which the H-atoms have been omitted:



The circles (drawn in perspective) at the two Cl-atoms of 1, 2-dichlorethane indicate that the groups attached to the C-atoms with a single bond between them may have the possibility to rotate more or less freely with respect to each other.*

Discussing first 1, 1-*dichlorethane*, one arrives at the structure shown above on the basis of the ordinary notions of organic chemistry. Each C-atom, according to the theory of van 't Hoff, is located at the centre of a tetrahedron if the attached radicals are all equal. This was confirmed by the researches on CCl_4 cited under (*c*), a distance ρ_{C-Cl} of 1·83 Å resulting. If one or two of the Cl-atoms were replaced by H-atoms, the valence angle between the remaining Cl-atoms was found to increase. The scattering of 1, 1-dichlorethane we may compare with that of chloroform, $CHCl_3$, the only difference being that instead of one of the Cl-atoms there is now a second C-atom, the two H-atoms attached to the latter having again a negligible effect. Ehrhardt could interpret his results by assuming the distance ρ_{C-C} to be equal to 1·54 Å, which is twice the radius of the C-atom as found by Bragg (15) from X-ray investigations of crystal structure, by further taking the distance ρ_{C-Cl} to be the same as that found in CCl_4, viz. 1·83 Å, and by putting ρ_{Cl-Cl} equal to 3·15 Å. Comparison with the values for ρ_{Cl-Cl} mentioned under (*c*) shows that here too the

* Of $C_2H_4Cl_2$ there exists a third isomer, not considered here, in which both Cl-atoms are attached to the same C-atom.

spreading of the valence angle between the Cl-atoms has taken place to about the same extent as in $CHCl_3$.

Passing now to the two forms of *dichlorethylene*, we note that, according to the ordinary chemical notions, these molecules should have a plane structure. Fig. 10 shows the two tetrahedra around the C-atoms, which, according to van 't Hoff, should be joined along one common edge. There remain free then two corners at the top and two corners at the bottom, to which two H-atoms and two Cl-atoms may be attached. If the two Cl-atoms occupy the two left-hand corners, we have cis-dichlorethylene; if one of the Cl-atoms is located at the upper left-hand corner, the other Cl-atom at the lower right-hand corner, we have trans-dichlorethylene. Taking again the distance ρ_{C-C} equal to 1·54 Å, we should expect for ρ_{Cl-Cl} a value smaller in the cis-modification then in the trans-modification. Which of the two isomers, separated by a distillation process, is the cis- and which is the trans-modification had already been decided previous to the X-ray investigation on the basis of measurements of the electric moment performed by Errera(29). The trans-modification, possessing a centre of symmetry, should evidently have a vanishing electric moment in contrast with the cis-modification, and indeed a moment of $1{\cdot}85.10^{-18}$ esu. was found for one isomer, a vanishing moment for the other, making a classification possible. For the trans-molecule Ehrhardt's X-ray measurements gave $\rho_{Cl-Cl} = 4{\cdot}7$ Å, for the cis-molecule $\rho_{Cl-Cl} = 3{\cdot}7$ Å in harmony with the expectation.

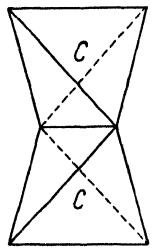


Fig. 10

We finally consider 1, 2-*dichlorethane*. As shown in fig. 11, the construction of van 't Hoff leads to two tetrahedra joined together in one point only. There exists then on this picture the possibility of a rotation of these two tetrahedra with respect to each other around an axis going through their junction and the

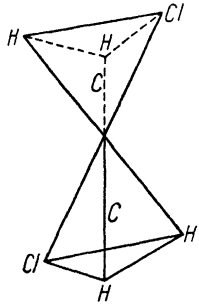


Fig. 11

two C-atoms. The problem arises as to which relative orientation of the tetrahedra is the most stable and as to how large is the binding to the equilibrium configuration. If the binding energy is small compared with the energy of thermal agitation kT (k = Boltzmann's constant, 'T = absolute temperature), then the two tetrahedra may be expected to rotate freely with respect to each other around the axis mentioned above, while for a binding energy large compared with kT torsional oscillations around the axis will result about the equilibrium position. On the basis of his scattering curve Ehrhardt was in the first place able to demonstrate with certainty the impossibility of a free rotation. For such a rotation, due to the variation in the mutual distance of the Cl-atoms which it produces, would flatten out the fluctuations in the scattering curve while in reality there are very noticeable maxima and minima. Fair agreement could be obtained between theory and experiment if the trans-position is assumed with $\rho_{Cl-Cl} = 4{\cdot}4$ Å, which is approximately the same value found for ρ_{Cl-Cl} in trans-dichlorethylene. A molecule with the two Cl-atoms in the trans-position should, however, have a vanishing electric moment just as trans-dichlorethylene, while experiment leads to a moment of about $1{\cdot}3.10^{-18}$ esu. This difficulty could be overcome by remembering that if the trans-configuration is an equilibrium position with a binding not too rigid, torsional oscillations will take place, and that a molecule with the two tetrahedra displaced at a given instant from the equilibrium position will have a non-vanishing moment. The assumption of torsional oscillations about the trans-configuration of suitable size to give the proper electric moment not only leaves undisturbed the agreement between the experimental and theoretical scattering curve but actually makes this agreement more nearly perfect.

Another investigation of isomers, the halogen derivatives of benzene, has been published by Pierce(57), who finds a plane structure for the C_6-ring with the halogen atoms in or near the plane. This result has also been obtained by Kaiser(45), who finds $\rho_{C-C} = 1{\cdot}42$ Å.

10. THE SCATTERING OF CATHODE RAYS BY AN ISOLATED ATOM

As we have mentioned in section 2, there are many atomic processes which can only be interpreted by associating with the elementary particles, nuclei and electrons, a wave-phenomenon. Thus, to account quantitatively for the scattering of a beam of electrons by atoms or molecules, we must represent this beam by a plane wave, the wave-length λ of which is related to the velocity of the particles by the equation of de Broglie

$$\lambda = \frac{h}{p}, \qquad (10{\cdot}1)$$

h being again Planck's constant, p the linear momentum of the particles, which for velocities v small compared with that of light is simply μv (μ = electronic mass). Just as a wave of radiation, such a material wave suffers scattering when it falls upon an atom. Here, too, there will in general be a scattered wave with the same wave-length λ as the incident wave, the *coherent scattered wave*, as well as scattered waves with modified wave-length, the *incoherent scattered waves*. Translated back into the particle language the former corresponds to electrons having suffered a deviation in their direction of motion by the presence of the atom without change of velocity, i.e. to the *elastically scattered electrons*. The latter, on the other hand, represent electrons which not only have had their direction of motion changed but which also have given energy to the atom, i.e. the *inelastically scattered electrons*.

Mott(52) and Bethe(11) have derived a simple expression for the intensity of the elastic scattering under the following two assumptions: (1) The incident electrons must have a kinetic energy large compared with their potential energy in the field of the scattering atom. (2) This atomic field is supposed to have spherical symmetry, corresponding to a spherically symmetric distribution function $w(r)$ of the negative charge in the atom (see section 5). If the intensity of the incident beam of electrons (number of electrons per cm^2 per sec) be called I_0, then at a

distance R from the scattering atom and under a scattering angle θ the coherent scattered intensity is given by

$$I_{\text{coh}} = \frac{1}{R^2} \cdot \frac{[Z - F(s)]^2}{s^4} \cdot \frac{64\pi^4 e^4 \mu^2}{h^4} \cdot I_0. \qquad (10{\cdot}2)$$

Here Z is the atomic number, $F(s)$ the atomic form factor as defined by equation (5·2) in section 5, s the abbreviation given there in equation (5·3) with λ now denoting the wave-length of the incident de Broglie waves.

At the expense of rigour equation (10·2) may be given a simple physical interpretation quite analogous to the considerations in connection with equations (5·1) to (5·6) for the coherent scattering of X-rays. If a plane de Broglie wave of amplitude Ψ_0 and wave-length λ, representing a stream of electrons of charge $-e$ and mass μ with a velocity related to λ by equation (10·1), is scattered by a point charge E, then, as shown by Gordon(34), the scattering is determined also in quantum mechanics by the well-known law first derived by Rutherford for the scattering of α-particles by atomic nuclei; i.e. the scattered intensity I in the direction θ and at a distance R from E is expressed in terms of the incident intensity I_0 by means of the formula

$$I = \frac{1}{R^2} \cdot \frac{1}{s^4} \cdot \frac{64\pi^4 E^2 e^2 \mu^2}{h^4} \cdot I_0.$$

Since the intensities are proportional to the squares of the amplitudes, the amplitude of the scattered wave is

$$\Psi = \frac{1}{R} \cdot \frac{1}{s^2} \cdot \frac{8\pi^2 E e \mu}{h^2} \cdot \Psi_0. \qquad (10{\cdot}3)$$

In the actual atom the scattering partially is due to the point charge Ze of the nucleus, partially to the charge $-Ze$ of the electrons distributed according to the distribution function $w(r)$. The former according to equation (10·3) gives a scattered amplitude

$$\Psi_1 = \frac{1}{R} \cdot \frac{Z}{s^2} \cdot \frac{8\pi^2 e^2 \mu}{h^2} \cdot \Psi_0.$$

In computing the effect of the latter it must be remembered again that there exists a difference in optical path Δ, given by

equation (5·5) for the various elements of volume $d\tau$, which gives rise to a difference in phase in the waves scattered by them. For the resultant scattering of the negative charge distribution one obtains in the notation of section 5

$$\Psi_2 = -\int_0^\infty \int_0^\pi \int_0^{2\pi} w(r) \cdot \frac{1}{R} \cdot \frac{1}{s^2} \cdot \frac{8\pi e^2 \mu}{h^2} \cdot \Psi_0 \cos \frac{2\pi\Delta}{\lambda} \cdot r^2 dr \sin\chi d\chi d\psi$$

$$= -\frac{1}{R} \cdot \frac{F(s)}{s^2} \cdot \frac{8\pi^2 e^2 \mu}{h^2} \cdot \Psi_0 .$$

The total scattered amplitude is then $\Psi_1 + \Psi_2$, and by taking the square one just obtains equation (10·2) for the scattered intensity.

Equation (10·2) expresses the intensity of the elastic scattering of a beam of electrons in terms of their velocity, of the atomic number of the scattering atom and of the scattering angle. As shown by Morse(53), the intensity of the inelastic scattering can be expressed in its dependence upon the same variables by means of the formula

$$I_{\text{incoh}} = \frac{1}{R^2} \cdot \frac{G(s)}{s^4} \cdot \frac{64\pi^4 e^4 \mu^2}{h^4} \cdot I_0 , \qquad (10\cdot4)$$

$G(s)$ being the function in equation (5·8) which also plays a rôle in the incoherent scattering of X-rays.

We proceed to a discussion of the relation of equations (10·2) and (10·4) with experiment. Just as equation (5·6), according to the considerations of section 6, is fundamental in determining the intensity of the beam of X-rays reflected by a *crystal* according to the equation of Bragg, so equation (10·2), next to the geometrical arrangement of the atoms in the lattice, governs the intensity of selective reflection of electron waves. If this has been measured for a sufficient number of velocities, equation (10·2) leads to a determination of $F(s)$. Conversely, if $F(s)$ is known from X-ray scattering or from the theoretical considerations of section 7, the coherent scattered intensity of the atom may be computed by means of equation (10·2) and compared with the intensity derived from the strength of selective reflection in crystals. In this way an independent check may be obtained on the F-values found

from X-ray investigations or by computation. Mark and Wierl(49) have carried out such a check for the metals Al, Ag, Au and found satisfactory agreement. For elements that can be worked with in the form of a *monatomic gas or vapour* there exists the additional possibility of directly comparing the total intensity of scattering of a beam of electrons with the sum of the expressions (10·2) and (10·4), entirely in analogy with the case of X-rays. Fig. 12 shows the scattering of electrons by the rare gases in its dependence upon the scattering angle as computed by Mott and Massey(6) and as measured by Arnot(9), there being good agreement.

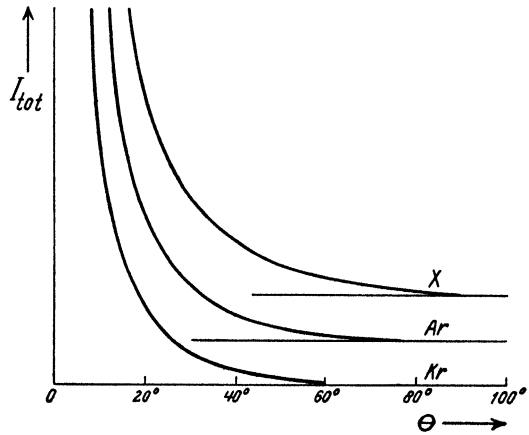


Fig. 12. Intensity of electrons scattered by krypton at 820 volts, by argon at 780 volts, by xenon at 800 volts as function of the angle of scattering.

As regards the general behaviour of I_{coh}, given by equation (10·2), with increasing s, it is of importance in connection with the applications of the following section to note that the decrease of I_{coh} in the case of electronic scattering is much steeper than in the case of X-ray scattering. This is most easily seen from table 1 in section 7, where next to the function $f(x)$, determining F in the case of a Thomas-Fermi distribution of charge according to equation (7·1), the expression $[1-f(x)]^2/x^2$ has been tabulated which, with this same distribution, will occur as a factor in equation (10·2). This strong falling off makes a determination of the atomic structure factors by

electronic scattering less accurate than that by X-ray scattering, a deficiency which in general is not compensated by the fact that the time of photographic exposure is a few seconds in the former case against many hours in the latter. Bewilogua(14) has discussed the relative advantages and disadvantages of the two methods.

11. DETERMINATION OF MOLECULAR SIZE AND FORM BY THE SCATTERING OF CATHODE RAYS

Once the scattering of electrons by the individual atom is known, it is possible to predict the scattering of a molecule of given dimensions if the mutual deformation of the negative charge distributions of the composing atoms may be taken as negligible. By a reasoning exactly the same as that which in the case of X-rays led from equation (5·6) to equations (8·1) and (8·4), we pass from equation (10·2) for the isolated atom to the formula for the coherent scattering of a molecule:

$$I_{\text{coh}} = \frac{1}{R^2} \sum_{jk} \frac{[Z_j - F_j(s)][Z_k - F_k(s)]}{s^4} \cdot \frac{\sin s\rho_{jk}}{s\rho_{jk}} \cdot \frac{64\pi^4 e^4 \mu^2}{h^4} \cdot I_0, \tag{11·1}$$

with ρ_{jk} again denoting the distance between the nuclei of the atoms j and k. The incoherent scattering of the molecules here too is the sum of the incoherent scattered intensities of the atoms, found from equation (10·4) with the values of $G(s)$ in table 2 of section 7.

The factors $\sin s\rho_{jk}/s\rho_{jk}$ in equation (11·1) have an oscillating character and tend to cause maxima and minima in the curve representing I_{coh} as a function of the scattering angle or of s. However, the steep decrease of the atomic scattering with increasing s, which we have stressed already in the previous section, usually prevents the formation of actual maxima and minima, leaving only points of inflection as they may be seen e.g. in fig. 13. The practical problem is to make the theoretical curve for I_{coh}, and especially the position of the inflection points, agree with the experimental data by a suitable choice of the ρ_{jk}.

Wierl(62) has performed extensive measurements on the electron scattering of vapours with the object of shedding light on the geometrical structure of their molecules. Fig. 14 shows a number of photographs taken by him of a beam of electrons after having passed through the scattering gas, the blackening of the plate as a function of the distance from the image of the

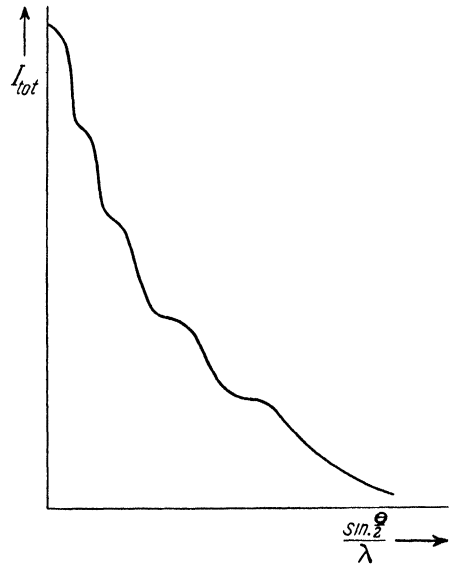


Fig. 13. Intensity of electrons scattered by gaseous CCl_4 in its dependence upon the angle of scattering θ and the wave-length λ.

central beam being a measure of the scattered intensity. We proceed to discuss his results and those of other authors in detail.

(*a*) *Diatomic molecules.* The only diatomic vapour investigated by Wierl was *bromine*, Br_2. Agreement between theory and experiment could be obtained with $\rho_{Br-Br} = 2{\cdot}28$ Å. Maxwell, Jefferson and Mosley(50) have also studied *iodine*, J_2, and find for ρ_{J-J} 2·64 Å.

(*b*) *Triatomic molecules.* Scattering curves were taken by Wierl for the gases CO_2, CS_2, N_2O, SO_2. On the basis of spectroscopic data (see section 36) and of their vanishing or

nearly vanishing dipole moments it is certain that *carbon dioxide*, CO_2, and *carbon disulphide*, CS_2, are both linear and symmetric of the type O—C—O and S—C—S, with the C-atom equidistant from the two other atoms. With $\rho_{C-O} = 1{\cdot}13$ Å in CO_2 and $\rho_{C-S} = 1{\cdot}58$ Å in CS_2 good agreement could be obtained on the basis of this assumption. Computations with a triangular model for CS_2 showed that the angle between the two legs drawn from the C-atom to the S-atoms, if it is not exactly 180°, must be at least greater than 160°. For *nitrous oxide*, N_2O, the results are rather inconclusive, since the scattering of N ($Z = 7$) does not differ much from that of O ($Z = 8$), so that a distinction between a configuration NON and NNO is hardly possible. This and other oxides of nitrogen have also been studied by Maxwell, Mosley and Deming(51). As may be concluded from its large electric moment, *sulphur dioxide*, SO_2, surely must be triangular. But the interference in the scattering curve due to the terms with ρ_{S-O} outweighs that due to the term with ρ_{O-O} to such an extent that only ρ_{S-O} could be determined, the value found being 1·37 Å. Brockway(18) by the same method has investigated *chlorine dioxide*, ClO_2. He finds for the distance $\rho_{O-Cl} = 1{\cdot}58$ Å, while the value of the angle between the lines joining the O-nuclei to the Cl-nucleus remains uncertain. Finally Braune and Knoke(17) have studied the *halides of mercury*, $HgCl_2$, $HgBr_2$, HgJ_2, which according to dipole measurements are linear and symmetrical, and find for the distance $\rho_{Hg-Cl} = 2{\cdot}20$ Å, $\rho_{Hg-Br} = 2{\cdot}40$ Å, $\rho_{Hg-J} = 2{\cdot}55$ Å.

(*c*) *Molecules of tetrahedral structure.* In the first place the *tetrachlorides of* C, Si, Ge, Ti *and* Sn were studied by Wierl(62). Agreement between theory and experiment could in all cases be attained by considering the four Cl-atoms arranged around these atoms as the corner points of a regular tetrahedron around its centre. The distances ρ_{Cl-Cl} giving the least deviation were the following: CCl_4 2·98 Å, $SiCl_4$ 3·29 Å, $GeCl_4$ 3·43 Å, $TiCl_4$ 3·61 Å, $SnCl_4$ 3·81 Å. The value found in the case of CCl_4 agrees perfectly with that furnished by the X-ray scattering (see section 9 (*c*)). The increase of ρ_{Cl-Cl} in the series must be ascribed to the increasing radius of the central atom.

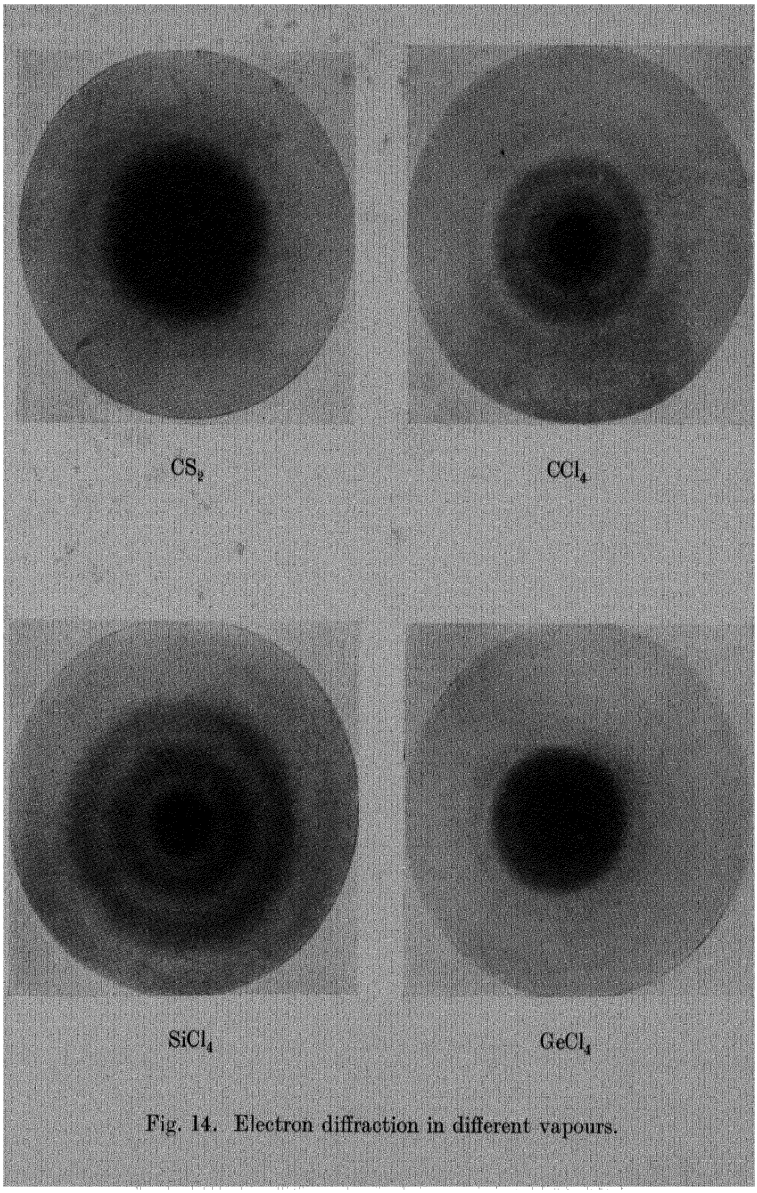


Fig. 14. Electron diffraction in different vapours.

The distances ρ_{X-Cl} from the central atom to a Cl-atom as computed from the above values are: CCl_4 1·82 Å, $SiCl_4$ 2·02 Å, $GeCl_4$ 2·10 Å, $TiCl_4$ 2·21 Å, $SnCl_4$ 2·33 Å. They may be compared with the distances resulting if the molecules are considered as built up of ions, regarded as rigid spheres of definite radius touching each other, as has been shown by Goldschmidt(33) to be practicable in many geometrical problems of crystal and molecular structure. For comparison we give the distances ρ_{X-Cl} resulting from Goldschmidt's ionic radii and from the ionic radii calculated by Pauling(54) on the basis of wave mechanics (see section 19) after a reduction of 7 per cent, corresponding to the fact that the co-ordination number in these compounds is 4 instead of 6: CCl_4 1·87 and 1·82 Å, $SiCl_4$ 2·05 and 2·06 Å, $GeCl_4$ 2·09 and 2·18 Å, $TiCl_4$ 2·28 and 2·32 Å, $SnCl_4$ 2·37 and 2·34 Å. In addition to the tetrachlorides mentioned, *carbon tetrabromide*, CBr_4, was investigated, the value $\rho_{Br-Br} = 3{\cdot}35$ Å being found.

In the second place the series CCl_4, $CHCl_3$ and CH_2Cl_2, which we have discussed already in section 9 (*c*) on the basis of X-ray scattering, was measured. Here too the results make it probable that upon substitution of H-atoms for one or two of the Cl-atoms a spreading of the angle between the valences from the C-atom to the remaining Cl-atoms occurs. Similar results are found by Dornte(26) for the bromine and iodine substitution-products.

In the third place the compounds *boron trichloride*, BCl_3, and *phosphorus trichloride*, PCl_3, were studied. In BCl_3 the scattering of B, on account of its low atomic number as compared to that of Cl, is relatively so slight that nothing can be said about its position. The configuration of an equilateral triangle for the three Cl-atoms with $\rho_{Cl-Cl} = 3{\cdot}03$ Å gave satisfactory agreement. In PCl_3 the P-atom is not negligible in its scattering effect. By trial and error the least deviation resulted if the molecule was supposed to be a regular pyramid with a distance $\rho_{Cl-Cl} = 3{\cdot}18$ Å and a distance $\rho_{P-Cl} = 2{\cdot}04$ Å.

(*d*) *Molecules of octahedral structure.* Braune and Knoke(16) and Brockway and Pauling(20) have studied the *hexafluorides of sulphur, selenium and tellurium*, SF_6, SeF_6, TeF_6, and have

shown that the S-, Se- or Te-atom is surrounded by the F-atoms, located at the corner points of a regular octahedron. For the distance from the central atom to the F-atom they find: SF_6 1·56 and 1·58 Å, SeF_6 1·67 and 1·70 Å, TeF_6 1·82 and 1·84 Å. These distances are somewhat less than the sum of the atomic radii as found by Pauling(54), the values for this sum being 1·65, 1·78 and 1·92 Å respectively (see section 19). It is interesting to note the good agreement between the values obtained by these investigators. It leads to an estimate of about 1 per cent for the accuracy of the distances determined.

(*e*) *Internuclear distance of the single, double and triple carbon bond. Organic chain compounds.* In order to determine the distance of two single, double or triple bound C-atoms, the compounds *ethane*, C_2H_6, *ethylene*, C_2H_4, and *acetylene*, C_2H_2, were subjected to an analysis by Wierl(62). On account of the low atomic number of C it is not justified to neglect the terms with ρ_{C-H} in equation (11·1), especially in the compounds with many H-atoms. On the other hand the effect of the H-atoms upon the scattering is too weak to determine this distance from the scattering curve. It was therefore assumed that the distance between the nucleus of a C-atom and that of an attached H-atom always has the same value of 1·1 Å which has been found from band spectra (see section 24). For ethane the ordinary model of stereochemistry as shown in fig. 15 with the tetrahedral angle between the valences gave satisfactory agreement if ρ_{C-C} for the single carbon bond was put equal to 1·52 Å. About the question of free rotation around this bond the experiments could not furnish any information since the terms with ρ_{H-H} in equation (11·1) are so insignificant that the position of the H-atoms attached to one C-atom relative to those attached to the other C-atom remains undetermined. An interpretation of the data for ethylene could be obtained on the basis of the plane model

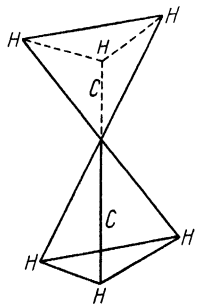
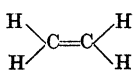
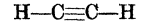


Fig. 15

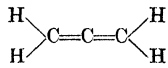


of stereochemistry with the tetrahedral angle between the valences from the C-atom to the two H-atoms and a distance $\rho_{C=C} = 1{\cdot}30$ Å for the double carbon bond, while for acetylene the rectilinear model

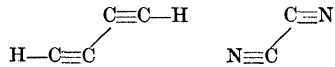


with $\rho_{C\equiv C} = 1{\cdot}22$ Å for the triple carbon bond proved adequate.

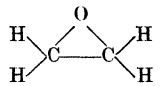
In order to test how far these distances are characteristic distances which occur also in other compounds, the substances *allene*, C_3H_4, *diacetylene*, C_4H_2, *cyanogen*, C_2N_2, and *ethylene-oxyde*, C_2OH_4, were investigated. The plane model for allene



with $\rho_{C=C} = 1{\cdot}31$ Å yielded satisfactory agreement. On the other hand, if for diacetylene and cyanogen one adheres to the values for ρ_{C-C} and $\rho_{C\equiv C}$ found above, rectilinear models give a theoretical scattering curve at variance with experiment. Wierl suggests the angular forms



with an angle of 30° and with the distances $\rho_{C-C} = 1{\cdot}51$ Å, $\rho_{C\equiv C} = 1{\cdot}20$ Å in the case of diacetylene, $\rho_{C-C} = 1{\cdot}47$ Å, $\rho_{C\equiv N} = 1{\cdot}18$ Å in the case of cyanogen. As stressed by Brockway[19], however, these conclusions are very uncertain. The measurements on ethylene oxide led to the configuration



with $\rho_{C-C} = \rho_{C-O} = 1{\cdot}49$ Å so that the two C-atoms and the O-atom lie at the corner points of an, at least approximately, equilateral triangle.

In this connection a research by Brockway and Pauling[21] on the compounds *methyl azide*, CH_3N_3, and *carbon suboxide*, C_3O_2, should also be mentioned. They arrive at the configurations



with, in the first case, distances $\rho_{C-N} = 1{\cdot}47$ Å, $\rho_{N=N} = 1{\cdot}26$ Å, $\rho_{N\equiv N} = 1{\cdot}10$ Å and a bending of 135°, and, in the second case, distances $\rho_{C=O} = 1{\cdot}20$ Å, $\rho_{C=C} = 1{\cdot}30$ Å.

With the value of $\rho_{C-C} = 1{\cdot}52$ Å for the single carbon bond an interpretation of the data for the series *ethane*, C_2H_6, *propane*, C_3H_8, *butane*, C_4H_{10}, *pentane*, C_5H_{12}, and *hexane*, C_6H_{14}, was attempted by Wierl(62). The burning question is whether the C-atoms in the chain all lie in a straight line or whether the valence dashes make the tetrahedral angle with each other so that the C-atoms lie along a zigzag line. Experience showed that in every case the angular chain furnished better results than the rectilinear chain. On the problem of the free rotation of the single carbon bond the investigation of these compounds could, however, not cast any new light, the difference between the theoretical scattering curves of a rigid model and one capable of rotation being too slight to permit any definite conclusions to be drawn.

(*f*) *Cyclical compounds.* The substances investigated by Wierl(62) were *benzene*, C_6H_6, *cyclohexane*, C_6H_{12}, and *cyclopentane*, C_5H_{10}. A discussion of the experimental material for benzene was attempted on the assumption that the C-atoms lie in a plane at the corner points of a regular hexagon. Agreement was obtained by taking the distance between neighbouring C-atoms as being equal to 1·39 Å. The scattering curve for cyclohexane was found to be typically different from that of benzene and led Wierl(62) to the inference that the model is not plane. If in harmony with the stereochemical picture the valences of the C-atoms were supposed to make with each other the tetrahedral angle, then the scattering data led to a value $\rho_{C-C} = 1{\cdot}51$ Å, i.e. practically the same value found in (*e*) for the single carbon bond. For cyclopentane a plane model with $\rho_{C-C} = 1{\cdot}52$ Å was found to be adequate. De Laszlo(48) has investigated the halogen derivatives of benzene, finding a plane structure with $\rho_{C-C} = 1{\cdot}41$ Å.

(*g*) *Structure of isomers.* The constitution of isomers and the problem of the free rotation of the single carbon bond has already been discussed in connection with the data of X-ray scattering on 1,1- and 1,2-dichlorethane and on cis- and trans-

dichlorethylene. These same substances have also been investigated by Wierl(62) with the aid of electron scattering. Taking the distance ρ_{C-C} in the *dichlorethanes* as 1·52 Å, the distance $\rho_{C=C}$ in the *dichlorethylenes* as 1·32 Å, the distance from a C-atom to an attached Cl-atom as 1·82 Å and to an attached H-atom as 1·10 Å on the basis of the results described in (*c*), (*e*), (*f*), it was possible to arrive at a rather accurate value for the distance ρ_{Cl-Cl} between the two Cl-atoms on the basis of the scattering curve. For cis- and trans-dichlorethylene the values 3·30 Å and 4·33 Å were found respectively for ρ_{Cl-Cl}, confirming the notion of their constitution. In the case of 1,2-dichlorethane scattering curves were computed on the following assumptions: (1) pure trans-position, (2) pure cis-position, (3) a half and half mixture of the cis- and trans-configuration, (4) the free rotation of the single carbon bond. The experimental data excluded the possibilities (2) and (4) but were not sufficiently accurate to decide between (1) and (3). In order to obtain more evidence the scattering of 1,2-*dibromethylene* was studied, and here the results were in favour of a strongly preferred trans-position in harmony with the conclusions drawn in section 9 (*d*) on the basis of X-ray scattering. The last mentioned and other related substances have also been studied by Dornte(27).

12. DETERMINATION OF MOLECULAR PROPERTIES FROM THE FINE STRUCTURE OF X-RAY ABSORPTION BANDS

If X-rays of given frequency ν fall upon an atom or molecule, they not only suffer scattering but also *absorption*. Consider an electron in one of the shells of the atom (see section 14) and denote the energy necessary for its removal by W_I. If we imagine the frequency ν of the incident X-rays as being gradually increased, then as soon as the energy quantum $h\nu$ exceeds W_I, the X-rays will be capable of throwing an electron out of the shell in question with a kinetic energy equal to the difference $h\nu - W_I$, the energy quantum being absorbed from the primary beam. The shell of electrons hence will give rise

to a continuous absorption band bounded on the side of lov frequencies or long wave-lengths, the *absorption edge* lying at a frequency ν_I given by $h\nu_I = W_I$. In practice the effect of the various electron shells is superposed so that the absorption spectrum in the frequency scale has the character shown in fig. 16, the absorption coefficient being used as ordinate.

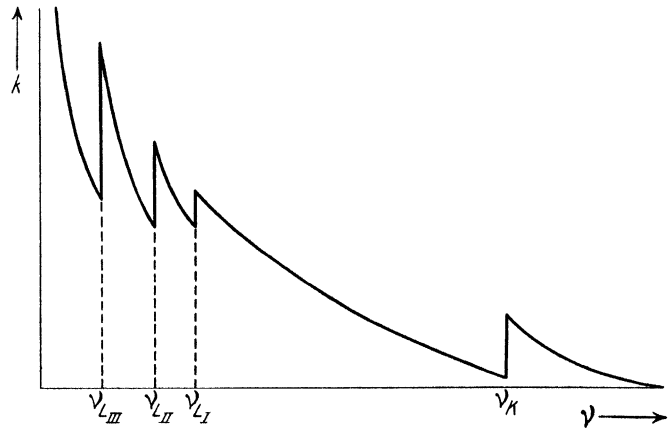


Fig. 16. Schematic representation of the absorption coefficient k of an atom in the X-ray region as function of the frequency ν. The K-, L_I-, L_{II}-, L_{III}-absorption edges lie at ν_K, ν_{L_I}, $\nu_{L_{II}}$, $\nu_{L_{III}}$.

Theory teaches and experiments, performed by Coster and van der Tuuk(22) and by Hanawalt(35) upon the X-ray absorption of the rare gases and of Hg-vapour, show that the absorption coefficient of the isolated atom, as indicated in fig. 16 decreases smoothly from its greatest value at an absorption edge when going to higher frequencies. In some cases a slight irregularity has been found in the immediate neighbourhood of the absorption edge and has been ascribed by Kossel(46) to the fact that the electron, instead of being removed completely from the atom with finite kinetic energy, may also be transferred to one of the unoccupied stationary states at the periphery of the atom.

As pointed out by Hanawalt(35), molecular gases or vapours in general show fluctuations in the absorption coefficient, extending to quite a distance from the absorption edge and

known as *fine structure*. Fig. 17 shows a photometer curve of the K-absorption edge of $GeCl_4$-vapour published by Coster and Klamer(23), who were the first to make accurate measurements of this structure for molecular gases.

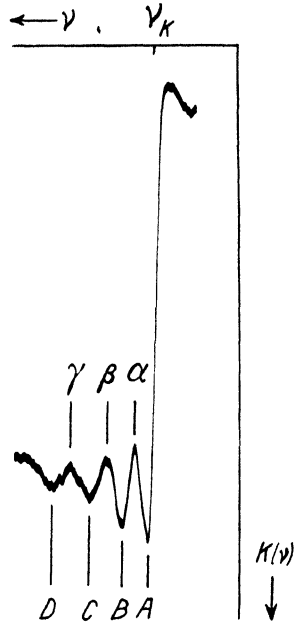


Fig. 17. K-absorption coefficient $K(\nu)$ of Ge in $GeCl_4$-vapour in its dependence upon the frequency ν. The K-absorption edge lies at ν_K. The maxima and minima of fine structure are clearly apparent.

An interpretation of the phenomenon was given by Kronig(47) on the basis of the wave theory of matter. The de Broglie wave which, in the example just mentioned, represents the electron ejected from the K-shell of the Ge-atom, suffers scattering at the four Cl-atoms, located according to the results of section 11 (*c*) at the corners of a regular tetrahedron with the Ge-atom at the centre. If the scattered waves reach the neighbourhood of the Ge-nucleus in such a phase as to augment the value of the wave function of the ejected electron there, then their effect is to increase the chance of absorption. If on the other hand they reduce this value by interference, then the chance of absorption is diminished. The reason is that in wave mechanics this chance depends upon the product of the wave functions of the electron before absorption (i.e. in the K-shell) and afterwards.

The phase near the Ge-nucleus of the waves scattered by the Cl-atoms in our example will depend upon their wave-length λ, the distance ρ_{Ge-Cl}, and the phase jump δ taking place in the scattering process. We can vary λ by changing the energy of the ejected electron, λ being related to its momentum by equation (10·1), or in other words by changing the frequency ν of the incident X-rays. As λ becomes larger, the scattered waves will alternately be in phase and out of phase and hence periodically

strengthen and weaken the absorption, which is just the phenomenon observed. With increasing energy of the ejected electron, i.e. with increasing distance of the incident X-ray frequency from the absorption edge, the scattering becomes less and hence the size of the fluctuations in the absorption coefficient diminishes. The effect of ρ_{Ge-Cl} upon the fluctuations is such that the larger this distance the closer the maxima and minima of the fine structure lie together since for a large distance a smaller change in λ is sufficient to make the scattered waves return with a given phase difference. The phase jump δ finally depends upon the atomic field of the scattering partners, in our example of the Cl-atoms.

An elaboration of Kronig's theory has been given by Petersen(56) in order to adapt it to numerical computations. Fig. 18 shows the curve for the K-absorption coefficient of Ge in $GeCl_4$ as calculated by Hartree, Kronig and Petersen(37). For the distance ρ_{Ge-Cl} the value 2·10 Å, as given in section 11 (*c*), has been taken while it has been assumed that the atomic fields are those of neutral atoms, $GeCl_4$ not being ionogenic. Only the position of the maxima and minima is directly comparable in figs. 17 and 18, since the ordinate in the photometer curve represents the blackening of the photographic plate and not the absorption coefficient itself. The theoretical maxima and minima A, A', A'' and α', α'' in the absorption coefficient are too close together to be resolved by the X-ray spectrometer. In the experimental curve there corresponds to them the one maximum A, in the left-hand slope of which careful observation discloses still a slight inflection point. The comparison between experiment and theory for the other maxima and minima is given in table 3. While for α the computed value is somewhat larger than the measured one, probably due to the close proximity of the absorption edge, the computed values of the following maxima and minima show slight deviations with respect to the measured ones, the deviations increasing systematically with increasing distance from the absorption edge. This discrepancy could be removed entirely by assuming for ρ_{Ge-Cl} a value about 1·5 per cent smaller than that of Wierl, i.e. 2·07 Å, which is within the limit

of accuracy of Wierl's value. Relying on the applicability of the fine structure method, as proved by its success for $GeCl_4$, Coster and Klamer determined by it the distance $\rho_{As-Cl} = 2{\cdot}20$ Å in $AsCl_3$, which molecule in all probability is a regular pyramid with the As-atom at the top.

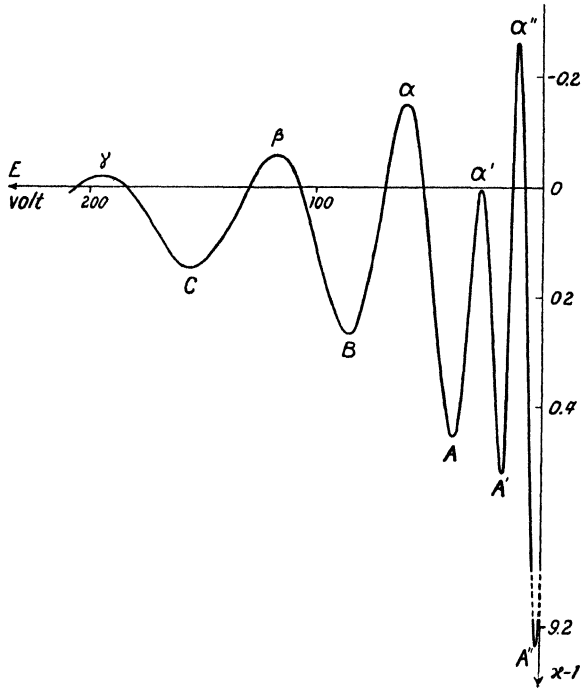


Fig. 18. Theoretical ratio κ of the K-absorption coefficient of a Ge-atom when contained in a $GeCl_4$-molecule and when isolated as function of the energy E of the ejected electron.

TABLE 3

MAXIMA AND MINIMA IN X-RAY FINE STRUCTURE OF $GeCl_4$

	α	B	β	C	γ
W_{exp} volts	50	86	120	160	203
W_{theor} volts	59	85	117	155	196

The advantages of this method over that of X-ray or cathode-ray scattering are the following: (1) the fact that the maxima and minima of the fine structure are much better defined than those in the scattering curve, making an exact determination more easy; (2) that an absorption curve with fine structure may be obtained for each atom in the molecule separately (at least if the absorption edge lies in an accessible region of the spectrum) furnishing more data than the one scattering curve; (3) that information may be gained about the state of ionisation of the atoms in the molecule on account of the circumstance that for the slow ejected electron it makes a difference in the scattering whether the atoms in the molecule are regarded as neutral or ionised. The last-mentioned circumstance justifies the hope that in cases where it is doubtful whether a compound is essentially heteropolar or homopolar a decision may be obtained by the present method.

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CHAPTER III

ATOMIC SPECTRA AND THE PERIODIC SYSTEM

13. GENERAL REMARKS

In chapter II we have focussed our attention exclusively upon the geometrical aspects of the structure of atoms and molecules, as it is revealed by the scattering of waves of radiation (X-rays) or waves of electrons (de Broglie waves). Of equal importance to the chemist, however, is the question of binding forces and binding energies governing this structure. In the case of the isolated atom, to which this chapter restricts itself, the problem takes the following form: In the first place one will try to find a suitable theoretical basis for subdividing the various electrons in the atom into groups. Next, one will investigate the way in which the energy necessary for the removal of an electron from the atom depends upon the group to which it belongs as well as upon the atomic number. Finally, one will inquire in how far the classification of the individual electrons suffices to characterise the state of the atom as a whole, and in case this classification proves inadequate, which additional features may serve to specify the atomic state uniquely. The chief progress attained by an adherence to this programme is not so much the accumulation of exact quantitative data referring to the individual atoms, but—much more important to the chemist—a systematic qualitative survey over the energetical relationships in passing from element to element. Indeed it appears that the crystallisation which chemical experience has found in the *periodic system* of the elements receives a satisfactory interpretation on the basis of the answers given by a co-operation of theory and experiment to the questions formulated above.

14. CLASSIFICATION OF THE ELECTRONS IN THE ATOM BY MEANS OF QUANTUM NUMBERS

It has been stressed in section 7 that a rigorous quantum-mechanical treatment of an atom with more than one electron is practically impossible, but that an approximation, sufficiently exact for the purpose of calculating the negative charge distribution in the atom, may be obtained if the interaction between the various electrons is replaced by a suitably chosen central screening of the nuclear field. As mentioned there, the screening may be introduced either by assuming for each electron a screening constant or by the more elaborate method of the self-consistent field. The usefulness of this viewpoint, however, extends much further than the application already given since it permits a classification of the individual electrons of the atom by means of *quantum numbers*.

For an electron in the Coulomb field due to a nucleus of charge Ze the wave equation (2·1) gives as energy values of the stationary states

$$W_n = -\frac{2\pi^2 Z^2 e^4 \mu}{h^2} \cdot \frac{1}{n^2}, \quad n = 1, 2, \ldots . \quad (14\cdot1)$$

These energy values are negative corresponding to the fact that energy has to be furnished to the electron in order to remove it from the atom. The positive integer n is called the *principal quantum number* and may be used to distinguish the different stationary states. According to equation (14·1) $n = 1$ corresponds to the state in which the electron is most strongly bound, i.e. the ground state of the system, while with increasing n the binding becomes less firm. A discussion of the solutions Ψ of the wave equation (2·1), which belong to the energy values (14·1), and of the charge distribution w, given according to section 2 by the square of Ψ, shows that in harmony with these results the chance of finding the electron in close proximity of the nucleus is greatest for $n = 1$, while for higher n the electron is encountered with larger preponderance in the more remote regions of space.

If a centrally symmetric screening is superposed upon the field of the nucleus, then not only are the energy levels dis-

placed with respect to the values given by equation (14·1), but they also suffer a splitting into sub-levels. Instead of the one stationary state with principal quantum number n there now appear n states with this quantum number. It is customary to distinguish them by a second quantum number l, the *azimuthal quantum number*, which takes on the values $0, 1, \ldots, n-1$. l has a simple physical significance, $l(l+1)h^2/4\pi^2$ representing, according to quantum mechanics, the square of the *orbital angular momentum* of the electron in its stationary state. One conveniently represents this angular momentum by a vector of length l, leaving off the factor $h/2\pi$. Also it is customary to designate the states with $l=0$, $l=1$, $l=2$, $l=3$, etc. as s-, p-, d-, f-, ... states and to add the principal quantum number as prefix. An electron in a state $2s$ in other words is one with quantum numbers $n=2$, $l=0$, an electron in a state $3d$ one with quantum numbers $n=3$, $l=2$, etc. For a given value of l the energy of the stationary states of the electron increases with n, while for a given value of n it increases with l. Moreover, for the more firmly bound states, all the sub-levels l belonging to a given value of n lie below all the sub-levels l belonging to $n+1$, in accordance with the fact that for these states the action of the nucleus predominates over that of the screening field so that all the sub-levels with the same n lie near the energy values (14·1). For states in which the electron is further away from the nucleus, however, it may actually happen that a state n with a high value of l is less firmly bound than a state $n+1$ with a low value of l. This is due to the circumstance that in these states the electron is on the average much nearer to the nucleus for small l than for large l.

If a magnetic field H is allowed to act upon an electron in a central field occupying a stationary state n, l, then this state will suffer a further splitting into sub-levels, the angular momentum taking in such orientations with respect to the direction of the magnetic field that its component in this direction has one of the values $-l, -l+1, \ldots, l-1, l$ measured in units $h/2\pi$. Graphically this phenomenon of *space quantisation* can be represented by the vector diagram of fig. 19. Altogether there are thus seen to be $2l+1$ possible orientations

of the vector l with respect to the direction of the external field. This, however, is strictly true only on the basis of non-relativistic wave mechanics. In reality it has been found necessary to assign to the electron in addition to its angular momentum of orbital motion another sort of angular momentum, the *spin angular momentum*, represented by a vector s of length $\frac{1}{2}$ in

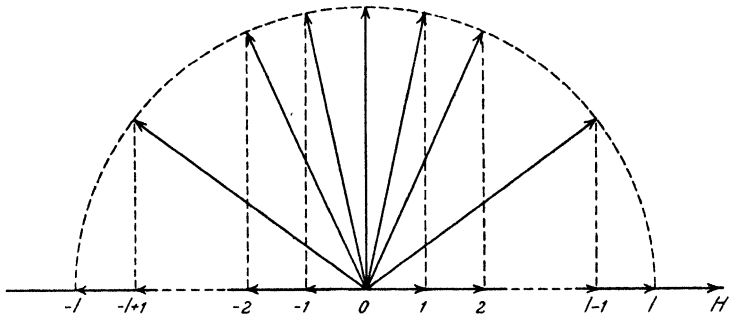


Fig. 19. Space quantisation.

units $h/2\pi$, which in an external magnetic field can only have the two values $-\frac{1}{2}$ and $\frac{1}{2}$ as component along the direction of the field. As shown by Dirac(11), it is a typical consequence of imposing the condition of relativistic invariance upon the wave equation. Disregarding the very weak coupling between spin and orbital motion and hence treating the vectors l and s as independent, we conclude that the stationary state n, l of the electron in the central field of the atom is an aggregate of $2(2l+1)$ states coinciding in the absence of external fields.

Next to the possibility of distinguishing the electronic states by means of quantum numbers as indicated, a principle discovered by Pauli(29) and known as the *exclusion principle* is of the utmost importance in the interpretation of atomic spectra. It states:

Two electrons of an atomic system cannot have the same quantum numbers; or, in every quantum state there is room for only one electron.

Let us apply this principle to the electrons in the central field of the atom. We have seen above that a stationary state n, l is really an aggregate of $2(2l+1)$ sub-states, all coinciding. The

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maximum number of electrons with quantum numbers n, l hence is $2(2l+1)$. Thus in $1s$-, $2s$-, $3s$-, ... states there is room for two electrons each, in $2p$-, $3p$-, $4p$-, ... states for six electrons each, in $3d$-, $4d$-, $5d$-, ... states for ten electrons each, in $4f$-, $5f$-, $6f$-, ... states for fourteen electrons each. Electrons fully occupying a stationary state n, l are said to form a *closed shell.*

15. SPECTRA OF ATOMS WITH ONE ELECTRON

Equation (14·1), which formed the starting point of our classification of electronic states in the isolated atom, finds its confirmation in the spectra of atoms with one electron. Depending upon whether the atomic number Z of the nucleus is 1, 2, 3, etc., we are dealing with the hydrogen atom, the atom of singly ionised helium, the atom of doubly ionised lithium, etc. Let us suppose for simplicity that $Z=1$. Then the frequency relation (2·2) of Bohr gives with the energy values (14·1) as possible frequencies of the spectral lines absorbed or emitted by the hydrogen atom

$$\nu = \frac{2\pi^2 e^4 \mu}{h^3}\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right),$$

n' and n'' being the principal quantum numbers of the higher and lower stationary state respectively. Introducing for the constant factor the abbreviation R, we have

$$\nu = R\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right),$$

$$R = \frac{2\pi^2 e^4 \mu}{h^3} = 3{\cdot}29 \,.\, 10^{15}\,\mathrm{sec}^{-1}, \qquad (15{\cdot}1)$$

R being called the *Rydberg constant.*

If we give n'' a definite value and allow only n' to vary, we get a *series* of spectral lines. Putting $n''=1, 2, 3$, etc., we obtain

$$\nu = R\left(1 - \frac{1}{n'^2}\right), \quad n' = 2, 3, 4, \ldots \text{ (*Lyman series*)}, \qquad (15{\cdot}2)$$

$$\nu = R\left(\frac{1}{4} - \frac{1}{n'^2}\right), \quad n' = 3, 4, 5, \ldots \text{ (*Balmer series*)}, \qquad (15{\cdot}3)$$

$$\nu = R\left(\frac{1}{9} - \frac{1}{n'^2}\right), \quad n' = 4, 5, 6, \ldots \text{ (*Paschen series*)}. \qquad (15{\cdot}4)$$

In each series, as n' increases, the frequencies converge toward a limiting value; to R in the Lyman series, to $\frac{1}{4}R$ in the Balmer series, to $\frac{1}{9}R$ in the Paschen series. The various transitions are most conveniently represented in a diagram as shown in fig. 20, in which the energy values of the stationary states are drawn as horizontal lines, the *energy levels*. Each frequency in the spectrum is then proportional to the length of the vertical line joining the initial and the final state. The actual aspect of the spectrum is shown in fig. 21 for the Balmer series, where the point of convergence of the spectral lines is clearly apparent.

The different series enumerated can be obtained in *emission* by exciting the hydrogen atom. They may be generated most easily by enclosing hydrogen gas in a discharge tube or a vacuum arc. The impacts of the electrons, when a current is passing through, partially dissociate the hydrogen molecules into hydrogen atoms, and the latter by further impacts are brought from the ground state $n=1$ into higher stationary states, making it possible for them to emit the spectral lines discussed above. The Lyman series may also be obtained in *absorption* if light passes through hydrogen gas partially or wholly dissociated into atoms in the ground state, the energy of the light being used to lift the atoms to higher stationary states. All the series are actually found to obey the equations (15·2), (15·3), (15·4) with a value of R agreeing within the experimental error with that given by equation (15·1). The Lyman series lies in the far ultra-violet near 1000 Å, the Balmer series in the visible, the Paschen series in the infra-red.

As mentioned already in section 14, the larger n, the further away the electron is removed from the nucleus. If we let n go to infinity, we remove the electron entirely from the atom, or, in other words we ionise the atom. We see hence that the convergence limit of the spectral series (15·2), (15·3), (15·4) corresponds to an *ionisation* of the hydrogen atom. The Lyman series represents in absorption a transfer of the electron from the ground state $n=1$ to a higher state n'. The limit of this series ν_l hence represents the removal of the electron from the ground state to infinity. The corresponding energy is $W_l = h\nu_l$.

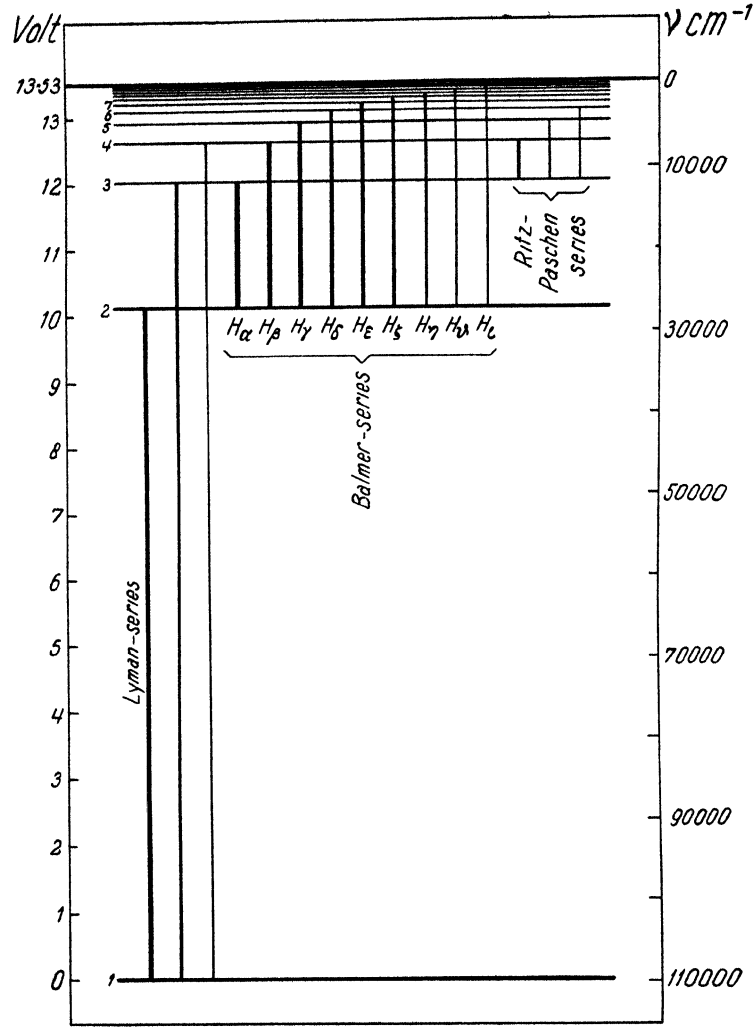


Fig. 20. Diagram showing energy levels and radiative transitions for the H-atom.

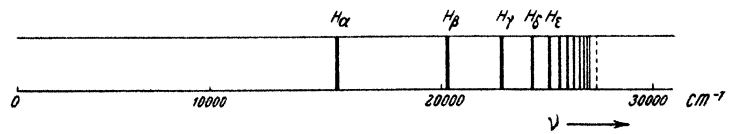


Fig. 21. Diagram showing aspect of the Balmer series in the frequency scale.

With the expression (15·1) for R this could be theoretically computed, but even if we did not know R from theory and only ν_l from experiment, we could still find W_l. This remark is of importance in the case of atoms with more than one electron, where an exact calculation of the energy values of the stationary states is mathematically very difficult so that the determination of the *ionisation energies* from the experimentally measured convergence limits of series is much more convenient.

In case the atomic number is not 1 but Z, all the energy values of the stationary states, and in consequence also the spectral frequencies, which are the difference of these energy values, according to equation (14·1) are simply multiplied by Z^2. The whole spectrum is thus seen to be displaced toward the ultra-violet. It also should be mentioned that the spectral lines considered, under high spectral resolution, show a fine structure due to the relativistic effects mentioned in section 14. As this, however, is not of interest in connection with chemical experiences, we shall not discuss it further here.

16. X-RAY SPECTRA

In the hydrogen atom there is only one electron, which normally will occupy the lowest stationary state $n=1$ but may be brought by electron impact or absorption of radiation into any of the higher stationary states $n>1$, from whence it can fall back again to lower stationary states under emission of radiation. For the atoms with atomic number $Z>1$ one must expect that normally the electrons will occupy the lowest stationary states n, l available with due regard to the exclusion principle (see section 14), which restricts the number of electrons in any stationary state n, l. The excitation of such atoms must consist in bringing one of the electrons from the state it occupies to one of the unoccupied states or in removing it entirely from the atom either by electron impact or by absorption of radiation.

We shall restrict ourselves for the present to the case that the electron in question originally occupied one of the inner

shells of the atom and that it is completely removed. After the excitation has taken place, one of the other electrons may make a transition from its stationary state to the empty place created. The frequency ν of the radiation arising from the transition will be rather high since the energy differences in the interior of the atom are large so that one will get in general an emission line in the X-ray region. In order to classify these *X-ray lines*, one has denoted the stationary states of an atom with a vacancy in one of its shells by special letters. If an electron with $n=1$, $l=0$ is removed, one says that the atom is left in the *K-state*. If an electron with $n=2$ is removed, one says that the atom is left in an *L-state*. Since for $n=2$, l may have the two values 0 and 1, one would at first expect that there are two L-states. In reality there are three, one of them, L_{I}, corresponding to $l=0$, the other two, L_{II} and L_{III}, both corresponding to $l=1$. The reason is that if an electron is removed from the shell with $n=2$, $l=1$, this shell can remain in two different conditions, depending upon how the spin angular momentum of the electrons mentioned in section 14, the influence of which upon the energy we had neglected, is coupled to their orbital angular momentum (see section 17). If an electron with $n=3$ is removed, one says that the atom is left in an *M-state*, there being altogether five M-states, of which one, M_{I}, corresponds to $l=0$, two, M_{II} and M_{III}, to $l=1$ and two, M_{IV} and M_{V}, to $l=2$. Analogously there are seven *N-states*, etc. The electron shells with $n=1, 2, 3, \ldots$ are in this connection often spoken of as *K-*, *L-*, *M-*, ... *shells*. The energy of the atom in the K-state W_K is much greater than that in an L-state W_L, the latter again much greater than that in an M-state W_M, etc. This one realises by remembering that in the interior of the atom the influence of the nucleus on an electron predominates so that the energy necessary for its removal is still approximately given by the expression (14·1) without the minus sign. One also sees from this that the energy increases rapidly with the atomic number Z. Of the three L-states L_{I} lies higher than L_{II} and L_{III} in accordance with the fact, already mentioned in section 14, that the binding of an electron with given n is stronger the lower the value of l. The X-ray

lines due to transitions for which the atom originally was in the K-, L-, M-, ... state are said to form the K-, L-, M-, ... *emission spectrum*. On the basis of the above results regarding the energy values and of the frequency relation (2·2), giving the frequency $\nu = W'/h - W''/h$ in terms of the energies W' and W'' of the atom before and after the transition, one sees that the K-lines have frequencies in the neighbourhood of the value $\nu_K = W_K/h$ and somewhat less than this, that the L-lines have frequencies in the neighbourhood of the three values $\nu_{L_I} = W_{L_I}/h$, $\nu_{L_{II}} = W_{L_{II}}/h$, $\nu_{L_{III}} = W_{L_{III}}/h$ and somewhat less than the greatest of these ν_{L_I}, etc. Also the K-lines have much greater frequencies, i.e. are harder than the L-lines, these again are much harder than the M-lines, etc. With increasing atomic number the various groups of lines retain their general aspect and only shift systematically toward higher frequencies as may be seen from fig. 22. This is what one would expect since the internal fully occupied regions of different atoms will show a strong general resemblance and only suffer a regular change as the atomic number is augmented. Also one understands why the state of chemical combination has hardly any influence upon the X-ray emission spectrum of an atom, the influence of neighbouring atoms being too weak to affect the motion of its internal electrons.

In case the atom is excited by electron impact, it is clear that the K-lines for example can only appear if the impinging electrons have at least the energy W_K since otherwise they cannot remove an electron from the K-shell. Similar remarks apply to the L-, M-, ... lines, a circumstance confirmed by experiment. This comes out much more clearly still if the excitation is produced by absorption of radiation; i.e. in the *X-ray absorption spectrum* already referred to in section 12. In order to be able to remove an electron from the K-shell, the incident radiation must have a frequency greater than ν_K. The excess of the energy quantum $h\nu$ over W_K is used to expel the K-electron with a finite amount of kinetic energy. In the absorption spectrum the K-electrons will hence not contribute to the absorption coefficient for frequencies $\nu < \nu_K$, while for $\nu > \nu_K$ there is continuous absorption, the *K-absorp-*

tion band, sharply bounded at $\nu = \nu_K$, the *K-absorption edge*. Similarly one gets three L-absorption edges, corresponding to the electrons with $n = 2$, $l = 0$ or 1, the L_{I}-edge, belonging to $n = 2, l = 0$, being harder than the L_{II}- and L_{III}-edges, belonging to $n = 2$, $l = 1$. Furthermore, there are 5 M-edges, 7 N-edges,

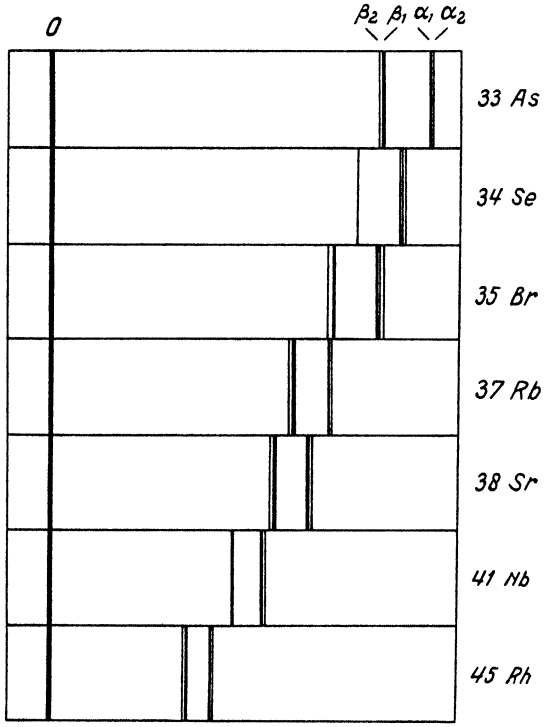


Fig. 22. Diagram of the K-series of the X-ray emission spectrum for elements of slightly different atomic number. The distance from the line O becomes smaller as the wave-length decreases (frequency increases).

etc. Fig. 16 in section 12 shows schematically the behaviour of the absorption coefficient.

In order to give a survey over the dependence upon the atomic number of the energy necessary for the removal of the different kinds of electrons from the atom, as it appears in the absorption edges, we have, following Bohr and Coster(7), represented in fig. 23 the square root of the frequencies of

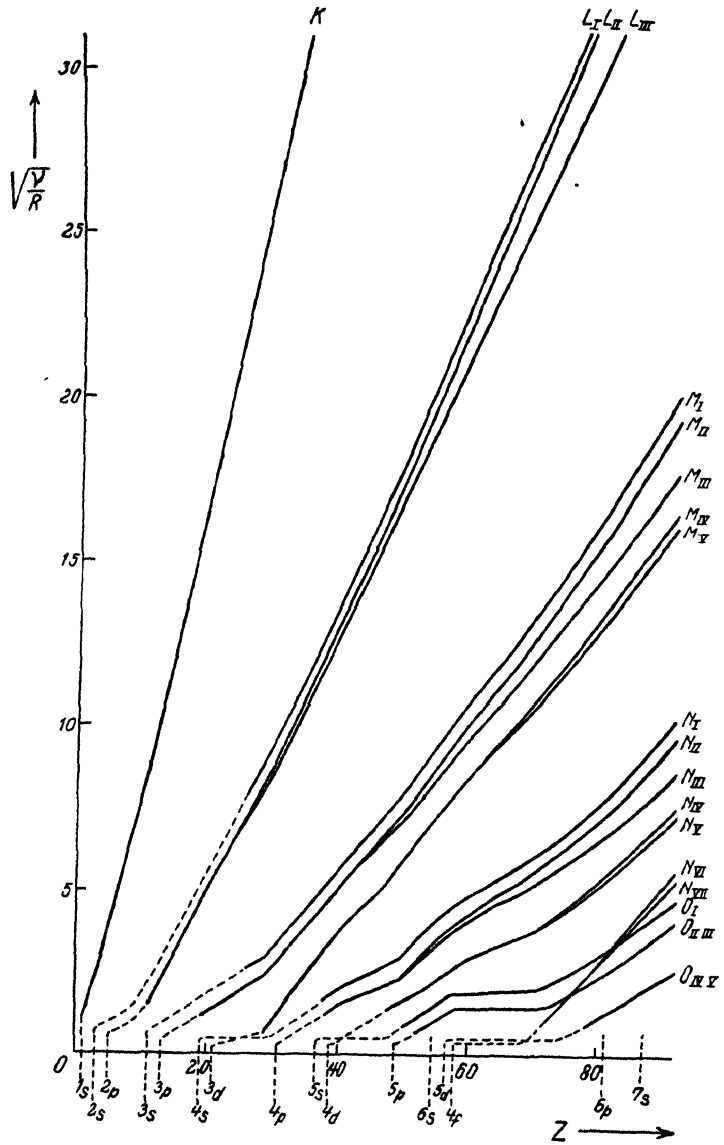


Fig. 23. Relation between the square root of the frequency ν of the X-ray levels, divided by the Rydberg constant R, and the atomic number Z.

these edges, divided by the Rydberg constant R (see section 15), as function of the atomic number Z. The choice of the square root as ordinate has the advantage that the graphical representation for each edge is approximately a straight line. It ought to be noted that L-, M-, N-, ... absorption edges are present only if the atomic number is high enough, since only then are there sufficient electrons to give a partially or completely occupied shell with $n = 2, 3, 4, \ldots$. In consequence in fig. 23 the corresponding curves commence at a certain minimum atomic number. Regarding the irregularities in the different curves we shall return to these in section 18.

As a general result of the experiences described in this section, we may say that the classification of the electrons in the interior of the atom, jointly with the exclusion principle, is entirely justified by the X-ray spectra, the only feature requiring further elucidation being the duplicity of some of the absorption edges. The following section deals with additional methods of classification which interpret this feature too.

17. OPTICAL SPECTRA OF ATOMS WITH MORE THAN ONE ELECTRON

The optical spectra of atoms with several electrons, in distinction to the X-ray spectra, arise from transitions of the outer, loosely bound electrons. To replace their interaction with the other electrons in the atom by a central shielding of the nuclear field and to regard them as moving independently in this field suffices to a lesser degree for a description of everything that is observed than in the case of the X-ray spectra since the influence of the nucleus is here not so predominant. A satisfactory interpretation of the different features of the optical spectra, excepting perhaps for the elements of very high atomic number, is arrived at by assuming an additional coupling of the electrons besides that represented by the central shielding of the nuclear field, the chief effect of which is to make the angular momenta of orbital motion of the in-

dividual electrons form a resultant vector L and their spin angular momenta to form a resultant vector S so that the configuration of the atom as a whole may be characterised by these two quantities. L must have one of the values 0, 1, 2, 3, ... in units $h/2\pi$, the corresponding atomic states being called S-, P-, D-, F-, ... states. S takes one of the values 0, 1, 2, 3, ... if the number of electrons in the atom is even and one of the values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$ if this number is odd. States with $S = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ are called singlet-, doublet, triplet, quartet-, ... states, the *multiplicity* $2S + 1$ being indicated by an upper left-hand index. Thus ${}^4P$ designates a quartet-P-state with $L = 1$, $S = \frac{3}{2}$, ${}^1D$ a singlet-D-state with $L = 2$, $S = 0$. To characterise the configuration of the atom more completely one will first indicate the quantum numbers of the individual electrons and then the resultant L and S. Thus

$$(1s)^2\,(2s)^2\,(2p)^6\,3s\,4d\,{}^3D$$

signifies a configuration of an atom with 12 electrons, of which two are in a state with $n = 1, l = 0$, two in a state with $n = 2, l = 0$, six in a state with $n = 2$, $l = 1$, one in a state with $n = 3$, $l = 0$ and one in a state with $n = 4$, $l = 2$, while the resultant $L = 2$ and the resultant $S = 1$. Atomic states for which Σl, the arithmetic sum of the l-values of the individual electrons, is even or odd are spoken of as *even* and *odd* atomic states, distinguished by an index g or u; thus ${}^1S_g$, ${}^2P_u$, etc.

In order to enable one to draw conclusions regarding the electronic configuration of atoms from their optical spectra, it is important to have an answer to the question: What are the possible values of the resultants L and S characterising an atomic state if the quantum numbers n, l of the individual electrons are given? As shown especially by Hund(2), quantum mechanics in conjunction with the exclusion principle gives an answer to this question. It leads in the first place to the following tables of atomic states resulting from a number of equivalent electrons (i.e. electrons with the same n and l). It teaches furthermore that if there are electrons in two different groups n, l, one must first find from the tables just given the possible resultants L_1, S_1 and L_2, S_2 of these groups and that

TABLE 4

ATOMIC STATES RESULTING

(*a*) From equivalent *s*-electrons

Number of electrons	Terms
ns	^2S
$(ns)^2$	^1S

(*b*) From equivalent *p*-electrons

Number of electrons	Terms
np	^2P
$(np)^2$	^1S ^1D ^3P
$(np)^3$	^2P ^2D ^4S
$(np)^4$	^1S ^1D ^3P
$(np)^5$	^2P
$(np)^6$	^1S

(*c*) From equivalent *d*-electrons

Number of electrons	Terms
nd	^2D
$(nd)^2$	^1S ^1D ^1G ^3P ^3F
$(nd)^3$	^2D ^2P ^2D ^2F ^2G ^2H ^4P ^4F
$(nd)^4$	^1S ^1D ^1G ^3P ^3F ^1S ^1D ^1F ^1G ^1J ^3P ^3D ^3F ^3G ^3H ^5D
$(nd)^5$	^2D ^2P ^2D ^2F ^2G ^2H ^4P ^4F ^2S ^2D ^2F ^2G ^2J ^4D ^4G ^6S
$(nd)^6$	^1S ^1D ^1G ^3P ^3F ^1S ^1D ^1F ^1G ^1J ^3P ^3D ^3F ^3G ^3H ^5D
$(nd)^7$	^2D ^2P ^2D ^2F ^2G ^2H ^4P ^4F
$(nd)^8$	^1S ^1D ^1G ^3P ^3F
$(nd)^9$	^2D
$(nd)^{10}$	^1S

one gets the final resultants L, S of the whole atom by vector addition of L_1 and L_2, S_1 and S_2 according to the rules

$$L = |L_1 - L_2|, |L_1 - L_2| + 1, \ldots L_1 + L_2 - 1, L_1 + L_2, \quad (17{\cdot}1)$$

$$S = |S_1 - S_2|, |S_1 - S_2| + 1, \ldots S_1 + S_2 - 1, S_1 + S_2, \quad (17{\cdot}2)$$

each of the L-values (17·1) being possible in conjunction with each of the S-values (17·2). If there are electrons present in three or more different groups, one has to combine first L_1 and L_2, S_1 and S_2 to form intermediate resultants according to the rules (17·1), (17·2) and these again with L_3, S_3, etc., in a similar way to the final resultants L and S. (The outcome is independent of the sequence of the addition processes.) A special consequence of this prescription is that electrons in closed shells, e.g. $(ns)^2$ or $(np)^6$ or $(nd)^{10}$, etc., do not contribute to the resultant L and S since according to the above tables they give for themselves a ^1S-state with $L = 0$, $S = 0$.

As an example we take the case of an atom with two electrons in $1s$-states, two electrons in $2s$-states, two electrons in $2p$-states and one electron in a $3d$-state. The electrons in s-states form closed shells. We may forget about them in computing the resultant L and S. The two electrons in $2p$-states according to table 4 give a ^1S-state ($L_1=0$, $S_1=0$), a ^1D-state ($L_1=2$, $S_1=0$) and a ^3P-state ($L_1=1$, $S_1=1$). The $3d$-electron gives a ^2D-state with $L_2=2$, $S_2=\frac{1}{2}$. We get by combination with the ^1S-state as possible values $L=2$, $S=\frac{1}{2}$, i.e. a ^2D-state; by combination with the ^1D-state $L=0$, 1, 2, 3, 4, $S=\frac{1}{2}$, i.e. ^2S, ^2P, ^2D, ^2F, ^2G; by combination with the ^3P-state $L=1$, 2, 3, $S=\frac{1}{2}$, $\frac{3}{2}$, i.e. ^2P, ^2D, ^2F, ^4P, ^4D, ^4F, altogether twelve different states of the atom as a whole.

From the optical spectra it is usually easy to find the values of the quantities L and S for an atomic state, especially if this be the ground state. For the vectors L and S are composed to give a resultant J according to the rule

$$J=|L-S|,\ |L-S|+1,\ \ldots\ L+S-1,\ L+S, \quad (17\cdot3)$$

so that the atomic state L, S will consist of a number of *multiplet-levels* more or less close together. In consequence the transitions between two different atomic states will give rise to groups of lines, the *multiplets*, as shown by the diagram of fig. 24. The J-values of the different multiplet-levels can usually be ascertained with the aid of the quantum mechanical selection rule forbidding changes of J by more than one unit as well as the transition $J=0\rightarrow J=0$. From the J-values in conjunction with the relation (17·3) and from a study of the *Zeeman effect*, i.e. the splitting which the multiplet components suffer in an outside magnetic field, a unique determination of the values L and S for the atomic state in question is obtained. The importance of the quantities L and S lies in the fact that they may help to classify the electronic configuration of the atomic state. If we know for example that an atom has as its ground state a ^4S-state and that there lie close to it and much lower than all the other states a ^2P- and a ^2D-state, then on the basis of table 4 it is rather certain that the ground state of the atom corresponds to a configura-

tion where all the electrons are in closed shells excepting three, which occupy equivalent *np*-states. In section 18 we shall make use of this method for obtaining information about the electronic configuration of isolated atoms. Also we see now how the duplicity of some of the X-ray states mentioned in the preceding section arises. For if we remove an electron from

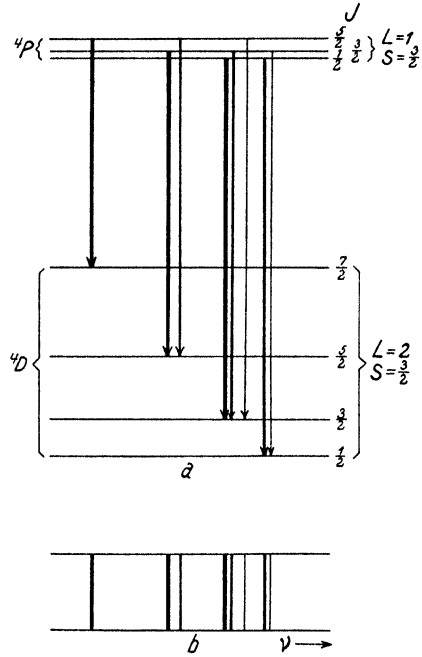


Fig. 24. Multiplet $^4P \rightarrow {}^4D$. (*a*) Diagram showing multiplet levels and radiative transitions. (*b*) Diagram showing aspect of the multiplet in the frequency scale.

a closed shell, then according to table 4 the atom is left in a ^2S-, ^2P-, ^2D-, ... state depending upon whether the shell has a value $l = 0, 1, 2, \ldots$. But a ^2P-, ^2D-, ... state consists of two component levels with $J = L \pm \frac{1}{2}$, while ^2S is single.

In section 15 we have seen that it is possible from the convergence limits of the series of spectral lines which the hydrogen atom absorbs and emits to determine the *ionisation energy* of this atom. The same method is applicable to more

complicated atoms too. In that way the ionisation energies for single and, in many cases, double and triple ionisation for the electrons most easily detached have been obtained from the optical spectra. The results are compiled in table 5 and graphically represented in fig. 25, where the abscissa signifies the atomic number, the ordinate the reciprocal ionisation energy. We shall refer to these results in the subsequent discussion of the periodic system and of the tendency of the atoms to form ions.

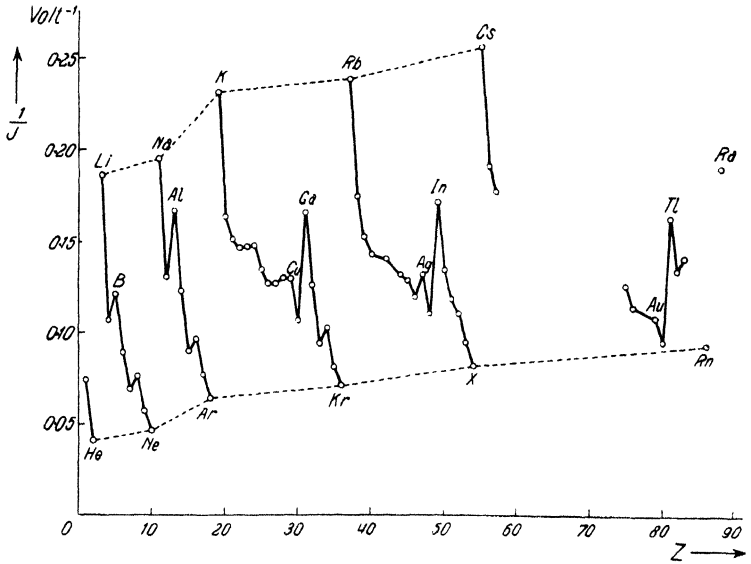


Fig. 25. Reciprocal ionisation energy of neutral atoms as function of the atomic number Z.

18. THE PERIODIC SYSTEM OF THE ELEMENTS

After the preparations of the preceding sections we are now in a position to establish a connection between the views developed there and the chemical experiences expressed in the periodic system of the elements. If the elements are arranged in the sequence of their atomic number, then it appears that their general properties show a periodic recurrence. Let us fix our attention upon the *rare gases*, all of which are characterised

by the fact that their atoms will not form compounds with the atoms of other elements nor will unite with each other. Moreover, the investigation of the optical spectra shows that these atoms are hard to ionise (see table 5) compared with the atoms of neighbouring elements and also hard to excite so that all the electrons in them form a particular stable configuration, which the spectrum analysis teaches to be a ^1S-state. Referring to table 4, this suggests that the rare gas atoms in their normal state have all their electrons in closed shells. Now this number of electrons is respectively: He 2, Ne 10, Ar 18, Kr 36, X 54, Rn 86. That leads to the following interpretation: In He the two $1s$-states are occupied, i.e. all states with $n=1$; in Ne the two $1s$-states, the two $2s$-states and the six $2p$-states, i.e. all states with $n=1$ and $n=2$. To get a closed shell configuration for Ar we must assume that its eight additional electrons fill the two $3s$-states and the six $3p$-states. The eighteen electrons added in going from Ar to Kr can be disposed of in closed shells by putting ten into the $3d$-states and the remaining eight into $4s$- and $4p$-states. In this way one has for all the rare gases considered thus far (excepting of course He) as external shell a configuration of two ns- and six np-electrons with $n=2$ for Ne, $n=3$ for Ar, $n=4$ for Kr, and since the chemical properties depend above all upon the outward regions of the atoms, the similarity of these gases is made especially plausible. In harmony with this result we shall assume the eight outermost electrons of X to occupy the $5s$- and $5p$-states, and we can then just fill completely with the other ten of the eighteen electrons added in passing from Kr to X the $4d$-states. We meet here for the first time an example of what we mentioned in section 14; viz. that electrons with a given n and small l, here the $5s$- and $5p$-electrons with $n=5$ and $l=0$ and 1, are more firmly bound than electrons with $n-1$ and large l, here the $4f$-electrons with $n=4$, $l=3$. Analogously in going from X to Rn we shall place the thirty-two additional electrons into the $4f$-states (taking care of fourteen of them), into the $5d$-states (taking care of another ten) and into the $6s$- and $6p$-states, giving again an outer configuration of the same type as above while the $5f$- and $5g$-states remain unoccupied. In

TABLE 5. IONISATION ENERGIES FOR THE REMOVAL OF THE FIRST THREE ELECTRONS IN VOLTS

																H	He
																13·53	24·47
																—	54·16
																—	—
Li	Be											B	C	N	O	F	Ne
5·37	9·28											8·25	11·22	14·48	13·56	17·34	21·47
75·28	18·14											25·01	24·28	29·47	34·93	34·81	40·77
121·86	153·10											37·75	47·65	47·17	54 63	62·35	63·2
Na	Mg											Al	Si	P	S	Cl	Ar
5·12	7·61											5·96	8·12	11 11	10·31	12·96	15·68
47·07	14·97											18·75	16·27	19·31	23 30	23·70	27·82
—	(81)											28·32	33·35	30·04	34·9	39·73	40·7
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4·32	6·09	6·57	6·80	6·76	6·74	7·40	7·83	7 81	7·64	7·69	9·35	5 97	7·85	10·5	9·70	(12·2)	13·94
31·7	11·82	12·80	13·60	14·7	16·6	15·70	15 12	17·3	18·13	20·2	17·89	18·9	15·86	20·1	—	—	26·4
46·5	50·8	24·64	27·6	(29·6)	(31)	(32)	—	—	—	29·5	—	30·58	31 97	28·19	33·9	—	—
Rb	Sr	Y	Zr	Nb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	X
4·16	5·67	6·5	6 92	—	7·06	—	(7·5)	(7·7)	(8 3)	7·54	8·95	5·76	7·37	8·35	8 96	10·44	12·06
27·3	10·98	12·3	—	—	—	—	—	—	(19·8)	21·4	16 84	18·79	14·52	18·8	—	—	21·1
—	—	20·6	20·00	—	—	—	—	—	—	—	(82)	27·91	30 49	24·7	—	—	—
Cs	Ba	La–Cp	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
3·88	5·19	5·5–7·0	—	—	—	7·85	8·7	—	—	9·19	10·39	6·08	7·38	7·25	—	—	10·70
23·4	9·95	—	—	—	—	—	—	—	—	—	18·67	20·30	14·97	19·5	—	—	—
—	—	—	—	—	—	—	—	—	—	—	(41)	29·7	31·91	25·9	—	—	—
—	Ra	Ac	Th	Pa	U												
—	5·18	—	—	—	—												
—	10·10	—	—	—	—												
—	—	—	—	—	—												

This table is taken from Landolt-Börnstein, *Physik.-chem. Tabellen*, 5 Aufl., II Ergänzungsband, supplemented from the following sources: B I(15), B II(14), C III(13), O III(15), F II(8), F III(8), Na II(39), P I(22), Cl II(28), Fe II(12), Cu III(33), Ge II(17), As I(32), As II(31), As III(34), Sc I(18), Se III(6), Rb II(26), Zr I(23), Zr III(24), Mo I(9), Ag II(19), In II(25), Sb II(10), Te I(38), J I(16), X II(21), Cs II(26), Re I(27), Os I(5), Rn I(35), Ra I(37), Ra II(36).

the table at the end of the book one finds for the rare gases the number of electrons in the different states, designated by their quantum numbers n, l, the symbols $1s$, $2s$, $2p$, etc., and the symbols K, L_{I}, $L_{\mathrm{II,\,III}}$, etc., in accordance with what has just been said. Also the nature of the most stable configuration of the atom as a whole, i.e. of the ground state, has been indicated for them by the symbol ^1S in the last column.

Although these electron distributions for the rare gas atoms are already rather probable on the basis of the preceding arguments, further confirmation is obtained by considering the other atoms. The elements following the rare gases are the *alkali metals*. Here there will be one electron in excess of those that can be placed in closed shells, and since all the alkali atoms have as ground state a ^2S-state (see last column in the table at the end of the book) lying much lower than any of the other states, one concludes from table 4 that the additional electron when most firmly bound is present in an ns-state, n being 2, 3, 4, 5, 6 for Li, Na, K, Rb, Cs respectively. That this electron is much more easily detached than all the other electrons, making the energy for single ionisation particularly small, as is seen in table 5, is now easily understood. The tendency of the alkali atoms to yield singly charged positive ions finds its explanation here too.

Upon the alkalies there follow the *alkaline earths* with as ground state again a low-lying ^1S-state. One will conclude that in addition to the ns-electron outside of closed shells already present in the preceding alkali there has been added a second equivalent ns-electron, making the ns-states a closed shell too. Table 5 shows the two outermost electrons to be much more easily detachable than the others, which belong to the preceding rare gas configuration. We understand therefore that the alkaline earths will easily give doubly charged positive ions.

We consider next with the aid of the table at the end of the book the elements $Z=5$ B to 9 F and the elements 13 Al to 17 Cl, forming the remainder of the two so-called *short periods*. Since for 4 Be the states $1s$ and $2s$ are completely filled while for 10 Ne the states $2p$ are also completely occupied, one will

conclude that for the intervening elements $2p$-electrons are successively added. Similarly between 12 Mg and 18 Ar the shell of $3p$-electrons is being completed. The ground states actually found from the spectra and indicated in the last column of the table at the end of the book are in accordance with the results of table 4 on the basis of this assumption.

Having thus settled the question of the electron distribution for the elements 1 H to 18 Ar, we pass on to the two *long periods* from 19 K to 36 Kr and from 37 Rb to 54 X, as well as to the *rare earth period* from 55 Cs to 86 Rn. Let us compare the seven elements preceding each of the three rare gases Kr, X, Rn with the seven elements in the two short periods preceding Ne and Ar respectively. It appears that all the elements removed an equal number of steps from a rare gas resemble one another. The resemblance is strongest for the immediate predecessors F, Cl, Br, J and still quite pronounced for O, S, Se, Te, for N, P, As, Sb, Bi and for C, Si, Ge, Sn, Pb. For B, Al, Ga, In, Tl, for Be, Mg, Zn, Cd, Hg and for Li, Na, Cu, Ag, Au the analogy restricts itself to more general features: equal number of valences, resemblance of the optical spectra and especially identity of the type of ground state, viz. ^2P, ^1S, ^2S respectively. One will interpret these facts by supposing that in the longer periods, just as in the short periods, the outermost p- and s-electrons are successively removed in going backwards from the rare gases until for Cu, Ag, Au there is just one ns-electron left outside closed shells. For the elements from 21 Sc to 28 Ni there must then evidently be a competition between the $4s$-states already fully occupied for 20 Ca and the $3d$-states. Similarly for the elements from 39 Y to 46 Pd there must be a competition between the $5s$- and the $4d$-states. The complicated optical spectra of these elements confirm this viewpoint, and from the L- and S-values of their ground states Hund(2) could determine uniquely the corresponding electron configurations.

The fact that some of the elements just discussed, especially those of the *triads* Fe, Co, Ni and Ru, Rh, Pd, resemble each other very much one will ascribe to the circumstance that one is concerned here with the completion of an inner shell,

affecting the chemical properties to a slighter degree than the filling in of outside states. This feature is even more pronounced for the rare earth period. Between 57 La and 79 Au the $4f$- as well as the $5d$-states become occupied. Now the 14 *rare earths* from 58 Ce to 71 Cp inclusive are very hard to separate chemically. Hence, one concludes that for them the fourteen $4f$-states are being filled in. Of the three outermost electrons probably one is in a $5d$-state, two in $6s$-states, just as for La, but this is not quite certain since the optical spectra of the rare earths have mostly not been analysed. To indicate this, a question mark has been put into the last column of the table at the end of the book, just as for some of the elements from 72 Hf to 78 Pt corresponding to the completion of the $5d$-states as well as for a few of the heaviest elements for which a similar state of affairs prevails.

An additional indication of the completion of inner shells for the elements 21 Sc to 28 Ni, 39 Y to 46 Pd and 57 La to 78 Pt may be found in the X-ray levels, as first pointed out by Bohr and Coster(7). An inspection of fig. 23 shows that in the ranges of atomic number in question the lines of the diagram show a sudden change of slope, especially the lines referring to the more loosely bound electrons, which naturally will be more affected by the type of binding of the other electrons than the K- and L-electrons, subject much more to the influence of the nucleus.

19. THE IONS

Besides the properties of the neutral atoms those of the ions are of the greatest importance to the chemist since ions not only play an important part in the structure of many molecules but also appear as constituents of solutions and crystals. As the most important properties characterising an ion we enumerate: (a) its charge; (b) its electronic configuration as expressed by the distribution of the electrons over the various states n, l; (c) its size.

Regarding the *charge of the ions*, we must distinguish between positive ions, created by detaching outside electrons from a neutral atom, and negative ions, arising from the addition of

one or more electrons to a neutral atom. The maximum charge of the ions that actually occur in a solution or crystal is 4 for positive ions and 2 for negative ions.

In the following discussion we shall denote with the words "outside electrons" those with the largest principal quantum number n. While for the neutral atoms the number of outside electrons changes from element to element, there is a tendency for the ions of successive elements actually occurring in chemical reactions to have identical *electronic configurations*. These in general are closed shell configurations and by preference such that the number of outside electrons is 8 or 18. In table 6 we have indicated the ions having these configurations. In addition to them there are a few ions with closed shells like Ga^+, In^+, Tl^+ and Ge^{++}, Sn^{++}, Pb^{++} having as outside electrons two s-electrons. Most of the other ions not having all electrons in closed shells are those of the transitional regions of the periodic system, where inner shells are being completed. These ions, e.g. those of the iron-group and of the rare earths, are paramagnetic and frequently give coloured solutions or crystals.

TABLE 6

ELECTRON DISTRIBUTIONS OF IONS WITH CLOSED SHELLS

Distribution numbers										n
									8	6
						8	8	18	18	5
				8	18	18	32	32	32	4
		8	18	18	18	18	18	18	18	3
	8	8	8	8	8	8	8	8	8	2
2	2	2	2	2	2	2	2	2	2	1
	O^{--}	S^{--}		Se^{--}		Te^{--}				
	F^-	Cl^-		Br^-		J^-				
(He)	(Ne)	(Ar)		(Kr)		(X)			(Rn)	
Li^+	Na^+	K^+	Cu^+	Rb^+	Ag^+	Cs^+		Au^+		
	Mg^{++}	Ca^{++}	Zn^{++}	Sr^{++}	Cd^{++}	Ba^{++}		Hg^{++}	Ra^{++}	
	Al^{3+}	Sc^{3+}		Y^{3+}		La^{3+}	Cp^{3+}			
				Zr^{4+}		Ce^{4+}			Th^{4+}	

Since wave mechanics teaches that atoms with all electrons in closed shells have a field of spherical symmetry, it is justifiable, at least for the great majority of ions, to express their size in terms of an *ionic radius*. This quantity is, of course, not sharply

defined, and its value depends upon whether one thinks in the first place of the geometrical limitation of the charge distribution or of the extension of the field of force. On the basis of wave mechanics and the electron distributions given above Pauling(30) has calculated the ionic radii for numerous ions, obtaining values which may be regarded as the most useful available at present. As mentioned already in section 7, he assigned to the electrons in each shell a definite screening constant S, considering them to move in a Coulomb field, due to a point charge $(Z-S)e$, where Z is the atomic number, and adjusting S so as to make the energy values of the stationary states agree with experience. Wave mechanics teaches then that for a given shell of electrons the extension of its charge distribution is inversely proportional to $(Z-S)$. In this way the ratio of the ionic radii of ions with the same electron configuration is determined. To obtain absolute values for these radii Pauling used the following method: he considered, e.g., the crystals NaF, KCl, RbBr, CsJ, in each of which the two ions have the same electron configuration, viz. that of a rare gas, and took as sum of the ionic radii of the partners in these substances the distance between the nearest neighbours. Knowing sum and ratio of the ionic radii he could compute their absolute values and thus also the absolute values of the ionic radii for all other ions with the same rare gas configuration. For ions of other than the rare gas type he used a similar procedure. In table 7 Pauling's values are given together with those obtained by Goldschmidt(20) from the lattice structure and lattice constants by arguments of a more geometrical character.

TABLE 7

IONIC RADII IN Å. UPPER VALUES ACCORDING TO PAULING (30), LOWER VALUES ACCORDING TO GOLDSCHMIDT (20)

(*a*) Rare gas ions (2 or 8 outside electrons)

		H^-	Li^+	Be^{++}	B^{3+}	C^{4+}	N^{5+}	O^{6+}	F^{7+}
		2·08	0·60	0·31	0·20	0·15	0·11	0·09	0·07
		1·27	0·78	0·34		0·2	0·1–0·2		
N^{3-}	O^{--}	F^-	Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}
1·71	1·40	1·36	0·95	0·65	0·50	0·41	0·34	0·29	0·26
	1·32	1·33	0·98	0·78	0·57	0·39	0·3–0·4	0·34	
P^{3-}	S^{--}	Cl^-	K^+	Ca^{++}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
2·12	1·84	1·81	1·33	0·99	0·81	0·68	0·59	0·52	0·46
	1·74	1·81	1·33	1·06	0·83	0·64	0·4	0·3–0·4	
As^{3-}	Se^{--}	Br^-	Rb^+	Sr^{++}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+}	Ma^{7+}
2·22	1·98	1·95	1·48	1·13	0·93	0·80	0·70	0·62	
	1·91	1·96	1·49	1·27	1·06	0·87	0·69		
Sb^{3-}	Te^{--}	J^-	Cs^+	Ba^{++}	La^{3+}	Ce^{4+}			
2·45	2·21	2·16	1·69	1·35	1·15	1·01			
	2·11	2·20	1·65	1·43	1·22	1·02			

(*b*) Ions with 18 outside electrons

Cu^+	Zn^{++}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}	Br^{7+}
0·96	0·74	0·62	0·53	0·47	0·42	0·39
	0·83	0·62	0·44		0·3–0·4	
Ag^+	Cd^{++}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}
1·26	0·97	0·81	0·71	0·62	0·56	0·50
1·13	1·03	0·92	0·74			
Au^+	Hg^{++}	Tl^{3+}	Pb^{4+}	Bi^{5+}	Po^{6+}	
1·37	1·10	0·95	0·84	0·74		
	1·12	1·05	0·84			

(*c*) Ions with 18+2 outside electrons

Tl^+	Pb^{++}
1·44	1·21
1·49	1·32

(*d*) Transitional ions

Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{2+}	Cr^{3+}	Fe^{3+}
0·80	0·75	0·72	0·69			
0·91	0·83	0·82	0·78	1·01	0·65	0·67

(*e*) Ions of rare earths (according to Goldschmidt)

Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}
1·18	1·16	1·15	1·13	1·13	1·11	1·09
Dy^{3+}	Ho^{3+}	Er^{3+}	Tu^{3+}	Yb^{3+}	Cp^{3+}	
1·07	1·05	1·04	1·04	1·00	0·99	

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CHAPTER IV

BAND SPECTRA AND CHEMICAL BINDING IN DIATOMIC MOLECULES

20. GENERAL REMARKS

After having learned how to characterise the state of an atom by means of quantum numbers one would naturally investigate the *interaction of two atoms* of the same kind or of different kinds in given stationary states. To describe this interaction one will inquire how the energy V of the two atoms, regarded as a single system, depends upon the distance ρ of their nuclei when these are held fixed in space. Two important cases must be distinguished. As the atoms approach, the energy V may first decrease, signifying attraction. If ρ becomes small enough, V must at last of necessity begin to increase again since at very small ρ the electrostatic repulsion of the nuclei exceeds all other effects so that V has a minimum for a certain value ρ_e. V may also steadily increase with decreasing ρ, corresponding to repulsive forces throughout. The first type of interaction permits the formation of a molecule with an equilibrium distance ρ_e of the nuclei, the second does not.

In order to obtain a survey over the energy relations for a given molecule, we might plot V as a function of ρ for all the possible configurations of the electrons, i.e. for all the *electronic states* of the molecule, obtaining diagrams as shown in fig. 26 (a) to (d). If the lowest point occurring in such a diagram is a minimum point M (fig. 26 (a) and (b)), we say that the molecule is *physically stable*, because once it is in the condition represented by this minimum, it can be made to leave it only by outside agencies, such as impacts or the absorption of radiation. In the contrary case (fig. 26 (c) and (d)) the molecule is said to be *physically unstable* since it will after some time spontaneously, under emission of radiation, get into the lowest repulsive curve and dissociate into separate atoms.

Physical stability must not be confused with chemical

stability. A molecule is said to be *chemically stable* if upon collision with molecules of its own kind it retains its identity such as, e.g., the molecules HCl or N_2. If that is not the case, it is said to be *chemically unstable*, as, e.g., the molecules CH or

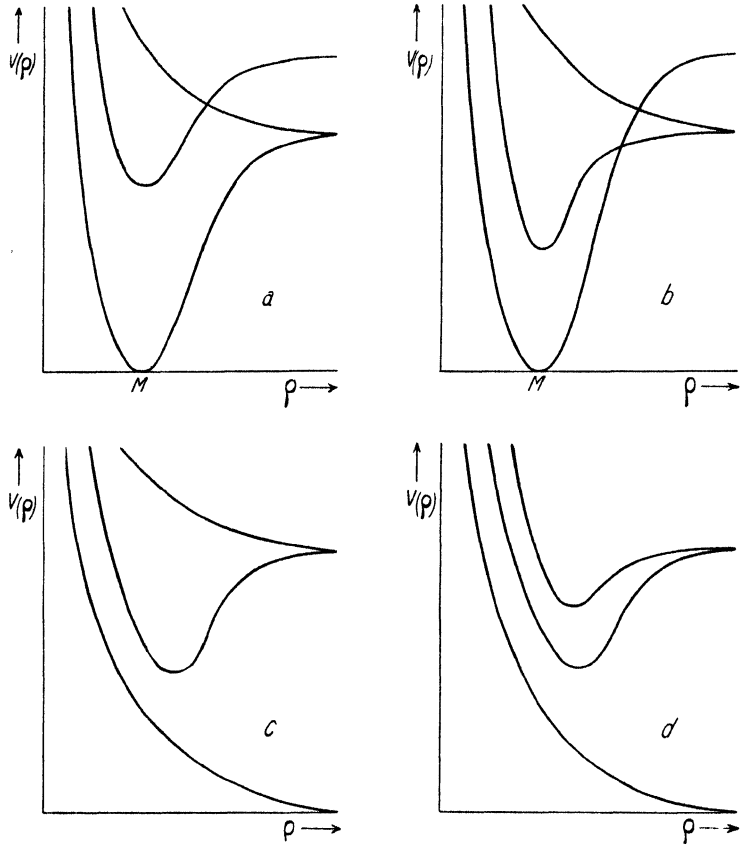


Fig. 26. Energy curves $V(\rho)$ of diatomic molecules, (*a*) and (*b*) for physically stable molecules; (*c*) and (*d*) for physically unstable molecules.

SO, which tend to give CH_4 and SO_2 with formation of free carbon or sulphur respectively, or as the molecule N_2^+, which tends to capture an electron to become neutral N_2.

Upon increasing the internuclear distance each one of the energy curves in fig. 26 approaches a horizontal line, corresponding to dissociation. The energy values of the various

asymptotes must hence be equal to the sum of the energy values of the two dissociation products. The electronic state of a physically stable diatomic molecule with the lowest minimum M (fig. 26 (a) and (b)) is called the *ground state* of the molecule. For a neutral molecule, the dissociation products arising from the ground state may either be two neutral atoms or a positive and a negative ion. In the former case the molecule is said to be *homopolar*, in the latter case it is called *heteropolar*. Examples of homopolar molecules are NaH, N_2, CO, SO, while NaCl is heteropolar.

The problem of investigating the interaction of atoms may be approached from a semi-empirical or from a purely theoretical side. Chemical analysis teaches that certain atoms unite with each other to form diatomic molecules while others do not. The investigation of band spectra supplements the results of chemical analysis in so far that it demonstrates the existence of numerous diatomic molecules not known to the chemist, either because the molecules are chemically stable but very easily dissociated (e.g. HgH) or because they are only physically but not chemically stable (e.g. OH, SO, N_2^+) or finally because they are not even physically stable (He_2). The band spectrum analysis, then, further permits the determination of the more important characteristics of the energy curves V with minima, and especially of the energy curve for the ground state of physically stable molecules, to which we shall restrict our attention for the time being. These characteristics are: (a) the distance ρ_e at which the minimum is situated, which is the *internuclear distance* of the molecule in its equilibrium state and has in some cases already been obtained by the methods of chapter II. (b) The distance D of the minimum below the horizontal asymptote to which the energy curve V approaches for large ρ. D is evidently the energy which must be supplied to the molecule in order to dissociate it into two atoms by gradual separation of the nuclei, the *physical dissociation energy*. In case of one or both the dissociation products are excited (as in fig. 26 (b)), it must be distinguished from the *chemical dissociation energy* which always refers to dissociation into two atoms in the ground

state. (*c*) The curvature of the energy curve in the minimum, directly connected with the *vibration frequency* for small vibrations of the molecule around the equilibrium point. (*d*) The way the energy curve approaches its horizontal asymptote for large ρ. Once these quantities are known, we can look for connections between them and with the chemical way of representing the binding by valences.

From the standpoint of theory let us first try to decide how many possible modes of interaction two atoms in given states have. We will next look for criteria making it possible to decide under what circumstances these modes of interaction include curves with a minimum. To arrive at such criteria it proves necessary to characterise the system of two atoms by new *quantum numbers* in addition to those already employed to describe the isolated atoms, and depending upon the way these quantum numbers have been introduced by different authors, various methods of approaching the problem have been worked out. While in this manner one will gain a deeper insight into the physical significance of chemical union than by the semi-empirical method, the latter retains its superiority when the object is to determine accurately the characteristics of the energy curves mentioned above since their purely theoretical calculation in all cases requires a great expense of mathematical labour.

21. THE LAW OF FORCE. VIBRATIONAL AND ROTATIONAL LEVELS

When the nuclei of the diatomic molecule are no longer regarded as centres of force held fixed in space, one has to deal with the system of nuclei and electrons as a whole. A great simplification, however, arises from the circumstance that the electrons have a much smaller mass than the nuclei and that in consequence the electronic frequencies are much higher than the nuclear ones, the electrostatic forces acting on both sorts of particles being of the same order of magnitude (see section 4). For this reason the electronic motion has the opportunity to adjust itself at every instant to the position of the nuclei as if these were centres of force at rest. Conversely the nuclei will

essentially be subject to forces averaged over the electronic motion so that for every electronic state we may describe their behaviour with the help of the potential energy functions of the preceding section without going into the details of the electronic motion.

In the immediate neighbourhood of the equilibrium position we may replace the curve V by a parabola and write

$$V = \frac{\kappa_2}{2!}(\rho - \rho_e)^2, \tag{21·1}$$

where κ_2 is the so-called *restoring force*, i.e. the force acting upon the nuclei when their distance is increased by one unit from its equilibrium value, assuming of course equation (21·1) to be valid over that range. The quantity κ_2 according to classical mechanics is connected with the frequency ω_e of small vibrations of the nuclei around the equilibrium point by

$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{\kappa_2}{M}}. \tag{21·2}$$

M is the reduced mass of the molecule,

$$M = \frac{M_1 M_2}{M_1 + M_2}, \tag{21·3}$$

where M_1 and M_2 are the masses of the two atoms.

That κ_2 and ω_e are related by equation (21·2) is most easily seen as follows. Denoting the displacements of the two nuclei along the internuclear line from their equilibrium positions of

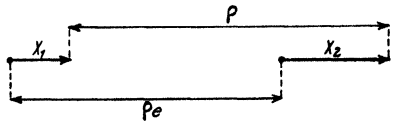


Fig. 27

rest by x_1 and x_2 (see fig. 27), one has as equations of motion under the influence of the potential energy (21·1)

$$M_1\ddot{x}_1 = \kappa_2(\rho - \rho_e) = -\kappa_2(x_1 - x_2),$$
$$M_2\ddot{x}_2 = -\kappa_2(\rho - \rho_e) = \kappa_2(x_1 - x_2).$$

Dividing respectively by M_1 and M_2 and subtracting gives

$$\ddot{x}_1 - \ddot{x}_2 = -\kappa_2\left(\frac{1}{M_1} + \frac{1}{M_2}\right)(x_1 - x_2).$$

Putting $x_1 - x_2 = x$ and introducing M by means of equation (21·3) leads to

$$\ddot{x} = -\frac{\kappa_2}{M} x.$$

This has as solution

$$x = \dot{x}_0 \cos 2\pi\omega_e (t - t_0), \qquad (21·4)$$

where ω_e is related to κ_2 by equation (21·2). Equation (21·4) signifies a vibration with frequency ω_e.

Quantum mechanics teaches that if the nuclei are restricted to move along the line joining them so that the possibility of rotation is excluded, the *simple harmonic oscillator* just considered has a single sequence of equidistant energy values W_v, the *vibrational levels*, given by the formula

$$\frac{W_v}{h} = \omega_e (v + \tfrac{1}{2}), \quad v = 0, 1, 2, \ldots. \qquad (21·5)$$

v distinguishes these levels and is known as the *vibrational quantum number*.

The investigation of the vibrational levels may be extended by carrying further the expansion for V in powers of $(\rho - \rho_e)$:

$$V = \frac{\kappa_2}{2!}(\rho - \rho_e)^2 + \frac{\kappa_3}{3!}(\rho - \rho_e)^3 + \frac{\kappa_4}{4!}(\rho - \rho_e)^4 + \ldots. \qquad (21·6)$$

This has been done by Fues(30). Instead of equation (21·5) we obtain then for the energy W_v of the vibrational levels, apart from a small additive constant independent of v,

$$\frac{W_v}{h} = \omega_e (v + \tfrac{1}{2}) - x_e \omega_e (v + \tfrac{1}{2})^2 + \ldots \quad v = 0, 1, 2, \ldots. \qquad (21·7)$$

Here ω_e and x_e are given by

$$\omega_e = \frac{1}{2\pi}\sqrt{\frac{\kappa_2}{M}}, \qquad x_e = \frac{h}{32\pi\sqrt{M\kappa_2}^3}\left(\frac{5}{3}\frac{\kappa_3^2}{\kappa_2} - \kappa_4\right). \qquad (21·8)$$

If κ_4 is positive, it will counteract the effect of κ_3. In practice, however, κ_3 is almost always sufficiently large to make $x_e > 0$. With increasing v the successive vibrational levels will then come closer together.

Finally, the vibrational levels must converge to the dissociation limit represented by the horizontal asymptote of the

curve V as shown in fig. 28, i.e. as v increases, the energy differences $\Delta W_v = W_v - W_{v-1}$ of successive levels v must at last approach zero for a value $v = v_{\max}$. If from experiment W_v is

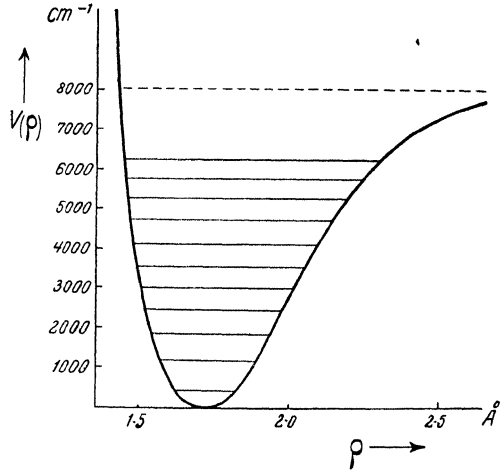


Fig. 28. Energy curve $V(\rho)$ and vibrational levels of the O_2-molecule in the ground state.

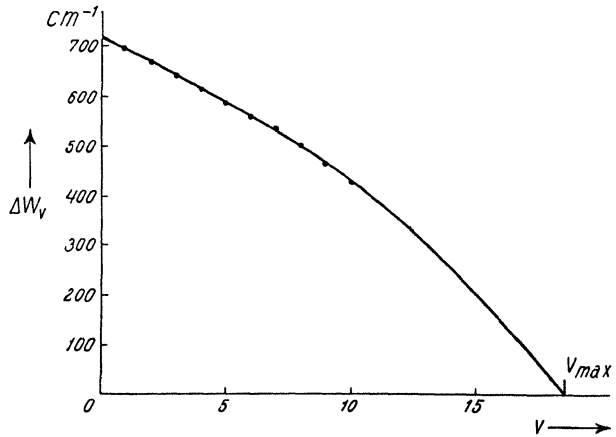


Fig. 29. Vibrational energy differences ΔW_v for the O_2-molecule in the ground state as function of the vibrational quantum number v.

known for the lower values of v over a sufficient range, then, following Birge and Sponer(21), the value $v_{\max}$ is found most easily by plotting ΔW_v against v for these values of v and

extrapolating the resulting curve until it cuts the v-axis (see fig. 29). The v-value of the intersection point is $v_{\max}$. Wave-mechanics teaches that if the function V with increasing ρ approaches its asymptote more rapidly than $1/\rho$, as it always does for a molecule disintegrating into neutral atoms or in other words a homopolar molecule, then the value $v_{\max}$ is finite; there is a limited number of vibrational levels. The energy D_0 required to dissociate the molecule from the vibrationless level $v=0$, which may be termed the *actual dissociation energy*, can evidently be obtained by a summation of the ordinates of the curve in fig. 29 for integral values of v:

$$D_0 = \sum_{v=1}^{v_{\max}} \Delta W_v. \qquad (21\cdot9)$$

It must be distinguished from the dissociation energy D as measured from the minimum of V to its asymptote since the vibrationless state $v=0$ does not coincide with this minimum but lies, according to equation (21·7), by an amount

$$W_0 = \tfrac{1}{2}h\omega_e(1+\tfrac{1}{2}x_e),$$

the *zero point energy* of vibration, above it so that

$$D = W_0 + D_0. \qquad (21\cdot10)$$

In contrast to D_0 the quantity D has a purely theoretical significance. For heteropolar molecules on the other hand $v_{\max}$ is infinite, and the method is not applicable.

If equation (21·7) is to be used for large values of v, then we should in general expect that higher powers in $(v+\frac{1}{2})$ would become important. Experience, however, has shown for many homopolar molecules, especially in their ground state, that equation (21·7) without higher powers is valid with good approximation up to energies close to the dissociation limit. It was therefore important that Morse (56) could prove equation (21·7) to follow rigorously for a potential energy of the form

$$V = D[1 + e^{-2a(\rho-\rho_e)} - 2e^{-a(\rho-\rho_e)}]. \qquad (21\cdot11)$$

This expression for V too has a minimum at ρ_e; the vibration frequency ω_e for small vibrations and the quantity x_e being related to a and D by

$$\omega_e = \frac{a}{2\pi}\sqrt{\frac{2D}{M}}, \quad x_e = \frac{h\omega_e}{4D}. \qquad (21\cdot12)$$

But, moreover, in contrast to the expression (21·6), equation (21·11) actually yields a curve of the type with minimum in fig. 26 over its whole range, D playing the rôle of the dissociation energy.

If instead of letting the nuclei vibrate along the line joining them we keep them at their equilibrium distance ρ_e, they may still rotate about an axis perpendicular to the internuclear line through the centre of mass of the molecule. Classically such a *rotator* can have any frequency of rotation. In the quantum theory, however, its modes of motion are restricted, the system having a set of *rotational levels* given by

$$\frac{W_J}{h} = B_e J(J+1) = -\tfrac{1}{4}B_e + B_e(J+\tfrac{1}{2})^2, \quad J = 0,\ 1,\ 2,\ \ldots, \tag{21·13}$$

where

$$B_e = \frac{h}{8\pi^2 M \rho_e^2} \tag{21·14}$$

and J is the *rotational quantum number*. It has a simple physical significance, $J(J+1)h^2/4\pi^2$ representing the square of the angular momentum of the nuclear rotation.

Returning to the expression (21·6) for V and allowing a simultaneous vibration and rotation of the molecule, it appears that upon each of the vibrational levels (21·7) there is built up a sequence of rotational levels with energies W_{vJ} which, apart from a small additive constant independent of v and J, are given by

$$\begin{aligned}\frac{W_{vJ}}{h} &= \omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 \\ &\quad + [B_e - \alpha(v+\tfrac{1}{2})](J+\tfrac{1}{2})^2 - D_e(J+\tfrac{1}{2})^4, \\ &\quad v = 0, 1, 2, \ldots, \quad J = 0, 1, 2, \ldots.\end{aligned} \tag{21·15}$$

Here ω_e, x_e and B_e are again given by equations (21·8) and (21·14), while

$$\alpha = -\left[6\frac{B_e^2}{\omega_e} + 4\left(\frac{B_e}{\omega_e}\right)^3 \frac{\rho_e^3 \kappa_3}{h}\right], \quad D_e = 4\frac{B_e^3}{\omega_e^2} \tag{21·16}$$

(D_e is not to be confused with the dissociation energy D). In equation (21·15) it must, of course, be presupposed that neither v nor J take very large values since otherwise higher powers in $(v+\frac{1}{2})$ and $(J+\frac{1}{2})$ would have to be added.

That the energy is not simply additively composed of the expressions (21·7) and (21·13) arises on the one hand from the fact that the vibration increases the average distance between the nuclei since these are a greater proportion of the time at $\rho > \rho_e$ than at $\rho < \rho_e$, the curve V being steeper to the left than to the right of the minimum. This has the same effect as if in equation (21·14) ρ_e were increased and hence the factor of $(J+\frac{1}{2})^2$ in equation (21·13) decreased, as expressed in equation (21·15) by the reduction of B_e to $B_e - \alpha(v+\frac{1}{2})$. On the other hand the centrifugal forces also increase the average distance of the nuclei and the term $D_e(J+\frac{1}{2})^4$ arises from this circumstance.

If the energy values W_{vJ} are known from experiment, then it is possible from them to determine the constants B_e, ω_e, x_e and α. Now from B_e we obtain directly ρ_e by means of equations (21·3) and (21·14). If the representation (21·11) for V is valid, i.e. if the vibrational levels are furnished with sufficient accuracy by a quadratic formula in $(v+\frac{1}{2})$ up to large values of v, then from the empirical values of ω_e and x_e we can by means of equations (21·3) and (21·12) compute directly the constants a and D in formula (21·11) so that the curve for V is then entirely known. If the representation of Morse is not applicable, then from the experimentally determined positions of the energy levels we can find the constants in the formula (21·6), describing the behaviour of the potential energy V in the neighbourhood of its minimum, while the dissociation energy determined by the method of Birge and Sponer according to equations (21·9) and (21·10) fixes the position of the horizontal asymptote so that the most important features of the function V are known.

Another method, due to Lotmar(55), of obtaining V in case the representation of Morse is inadequate is based upon a more general expression for V proposed by Rosen and Morse(63). It has the form

$$V(\rho) = -a\tanh\left(\frac{\rho+c}{d}\right) - b\,\mathrm{sech}^2\left(\frac{\rho+c}{d}\right) \quad (21\cdot17)$$

and contains four arbitrary constants a, b, c and d instead of the three arbitrary constants a, D and ρ_e in equation (21·11).

It can hence be adjusted to all the four experimental quantities ρ_e (directly obtained from B_e), ω_e, x_e and α. The position of the minimum of V is found by differentiating equation (21·17) with respect to ρ. The condition that it must lie at ρ_e gives the relation

$$\frac{\rho_e+c}{d}=\tanh^{-1}\left(\frac{a}{2b}\right). \qquad (21\cdot18)$$

The expressions for the vibrational frequency ω_e and for the quantity x_e in terms of a, b, c, d have already been given, partly incorrectly, by Rosen and Morse. Lotmar obtains

$$\omega_e=\frac{4b^2-a^2}{4\pi d\,(2Mb^3)^{\frac{1}{2}}}, \quad \omega_e x_e=\frac{h}{8\pi^2 M d^2}\left(1+\frac{3a^2}{4b^2}\right). \qquad (21\cdot19)$$

To find the connection between α and a, b, c, d we go back to equation (21·16) giving α in terms of B_e, ω_e and κ_3, the third derivative of V with respect to ρ in the minimum. Calculating this third derivative from equation (21·17) and substituting back into equation (21·16) finally leads to

$$\alpha=-\left[6\frac{B_e^2}{\omega_e}-24\left(\frac{B_e}{\omega_e}\right)^3\frac{\rho_e^3 a}{hd^3}\left(1-\frac{a^2}{4b^2}\right)^2\right]. \qquad (21\cdot20)$$

The four equations (21·18), (21·19), (21·20) are four equations for the four unknowns a, b, c, d. The function represented by equation (21·17) is of the same type as the simpler function (21·11) of Morse, approaching a horizontal asymptote for $\rho\to\infty$. The dissociation energy D is given in terms of a, b, c, d by means of

$$D=\frac{(a-2b)^2}{4b},$$

so that if a, b, c, d have been computed as just described, D may also be calculated.

For heteropolar molecules Hund(44) has pointed out that V approaches its asymptote as

$$-\frac{e_1e_2}{\rho}-\frac{1}{2}\frac{e_1e_2(\beta_1+\beta_2)}{\rho^4},$$

where e_1 and e_2 are the charges, β_1 and β_2 the polarisabilities of the two ions into which the molecule dissociates. The first term corresponds to the Coulomb attraction of the ions, the second

represents the energy of the deformation produced in each ion by the electric field of its partner.

A general method to find the function V from the position of the vibrational and rotational levels has been developed by Klein(51) and Rydberg(64), while Pöschl and Teller(62) have discussed the question in how far V is uniquely determined by a knowledge of these levels.

The object of the following sections will be to show how the vibrational and rotational levels of diatomic molecules, as well as certain other properties, can be obtained by an analysis of their spectra.

22. VIBRATION-ROTATION BANDS ON THE CLASSICAL THEORY

If the mechanical vibration of the simple harmonic oscillator by which we first represented the nuclear motion of the diatomic molecule in the preceding section is accompanied by an oscillation of the dipole moment of the molecule, then, according to classical physics, radiation will be emitted with the frequency ω_e of the oscillator. For small amplitudes of vibration we can take the oscillating part of the dipole moment as being proportional to the elongation x of the molecule introduced in the preceding section, let us say equal to qx. The amount of radiation emitted by the oscillator in unit time is then given by

$$E = \frac{1}{3}\frac{(2\pi\omega_e)^4}{c^3} q^2 x_0^2, \qquad (22{\cdot}1)$$

where c is the velocity of light, x_0 the amplitude of the elongation. Conversely, if radiation falls upon the oscillator, the frequency ω_e will be absorbed by it. The classical spectrum of the simple harmonic oscillator consists hence of the one line of frequency ω_e.

In order to get any emission or absorption at all it is of course necessary that $q \neq 0$. If we denote the dipole moment of the molecule for a distance of separation ρ of the nuclei by $p(\rho)$, then, according to its definition above, q is given by

$$q = \left(\frac{dp}{d\rho}\right)_{\rho=\rho_e}.$$

Now q may vanish for two reasons. Either p may be zero for all values of ρ. That is the case if the charge distribution of the molecule is symmetrical. Or it may happen that p goes through a maximum with increasing ρ and that the maximum lies at or near ρ_e. For homopolar non-symmetrical molecules p always has a maximum (curve a in fig. 30), while for hetero-

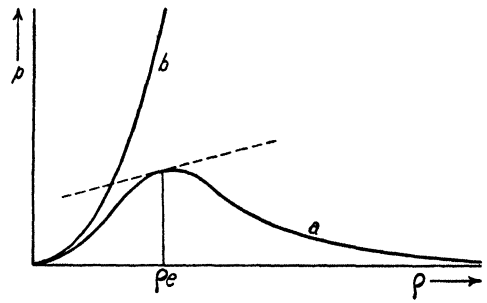


Fig. 30. Dipole moment of a diatomic molecule as function of the internuclear distance ρ, curve a for a homopolar non-symmetrical, curve b for a heteropolar molecule.

polar molecules p for large ρ is equal to $e\rho$, where e is the charge on the ions into which the molecule dissociates, so that p goes to infinity there (curve b in fig. 30), while q approaches the value e. If from the amount of radiation of frequency ω_e emitted by an oscillating diatomic molecule we arrive by means of equation (22·1) at a value of q much smaller than e, we may conclude that the molecule is homopolar, the equilibrium distance ρ_e being such that one is near the maximum of the curve a in fig. 30.

That for homopolar non-symmetrical molecules the dependence of the dipole moment p on ρ must be given by a curve of type a in fig. 30 can be seen as follows. If we imagine the nuclei to coincide so that $\rho = 0$, we have an atom, and atoms have never a dipole moment so that p vanishes there. If we imagine the nuclei to be entirely separate, $\rho = \infty$, we have by the definition of homopolar molecules (see section 20) two neutral atoms, also without dipole moments, so that the dipole moment p of the system as a whole vanishes again. Since p is a continuous function of ρ, p in between must have an extreme value. For

heteropolar molecules, on the other hand, we have for large ρ two separate ions of charge e and, by the definition of dipole moment, p is then simply $e\rho$.

If, instead of assuming the oscillation to be simply harmonic, we start from the more general anharmonic expression (21·6) for V, then the mechanical vibration will not be given by the equation (21·4), signifying the presence of the one frequency ω_e, but must be written as a Fourier series. For vibrations of small amplitude there will again be a term of the form (21·4) with the same frequency ω_e, but, in addition, terms appear with frequencies $2\omega_e$, $3\omega_e$, ... The first term, the *fundamental*, is accompanied by *harmonics*, in general of successively diminishing amplitude. In consequence, excepting when no oscillation of the dipole moment accompanies the mechanical vibration due to a symmetrical configuration of the charge distribution, the spectrum will consist both in emission and absorption of a series of lines with frequencies ω_e, $2\omega_e$, $3\omega_e$, ..., of which the first is much stronger than the second, this much stronger than the third, etc., the relative strength of the overtones and the fundamental depending upon the degree of anharmonicity of the binding.

Let us next consider the other limiting case of the preceding section, the rotator, in which the distance ρ between the nuclei is imagined to be kept fixed at its equilibrium value ρ_e. Such a rotator can emit or absorb radiation of the frequency with which it rotates, provided again that the mechanical rotation is accompanied by a rotating dipole moment. If the dipole moment of the molecule vanishes, due to the symmetry of its charge distribution, then there is no emission or absorption. In general, in a gas at room temperature T one will expect molecules with all possible frequencies of rotation. In consequence the gas will have a continuous emission or absorption spectrum, the so-called *rotation spectrum*, consisting of the one *rotation band*. Since for the temperature T a certain frequency of rotation will be most probable, the rotation spectrum has a maximum in its intensity distribution (see fig. 31).

We pass on to the most important case that the molecule may both vibrate and rotate. The frequencies which the mole-

cule will then emit or absorb are the summation- and difference-frequencies of the vibration and the rotation. They form together the *vibration-rotation spectrum* of the molecule. Instead of the sequence of lines ω_e, $2\omega_e$, $3\omega_e$, ..., the spectrum will now consist of a series of *vibration-rotation bands*, grouped around

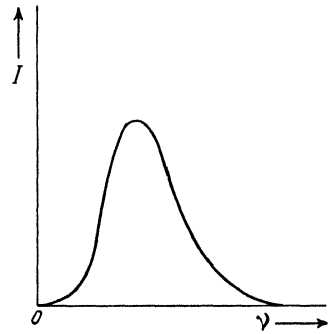


Fig. 31. Rotation band of a diatomic molecule on the classical theory.

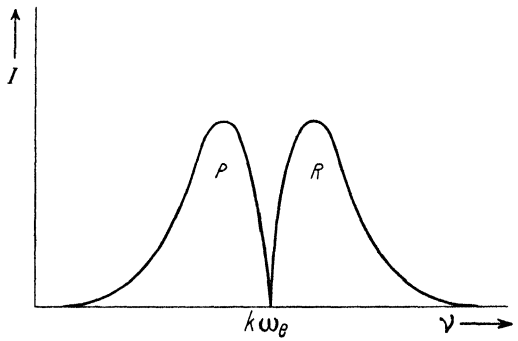


Fig. 32. Vibration-rotation band of a diatomic molecule on the classical theory.

these frequencies. Each band will be double. One branch, the *R-branch*, with frequencies $\omega_e + \omega_{\text{rot}}$ arises when the rotational frequency is added to the vibrational frequency, the other branch, the *P-branch*, with frequencies $\omega_e - \omega_{\text{rot}}$ arises when the rotational frequency is subtracted from the vibrational frequency. Both branches, as shown in fig. 32, have an intensity maximum for the same reason that the rotation band has such a maximum.

The significance of the preceding considerations, based on classical physics, lies in the circumstance that the quantum mechanical results to be discussed in the next section show a far-reaching analogy with them and can thus to a certain degree be visualised, always keeping in mind, of course, the remarks of section 3 regarding the limitations attaching to the use of pictures in the interpretation of atomic phenomena. That the analogy reaches farther here than in other cases is due to two particular circumstances. On the one hand the spectrum of the simple harmonic oscillator is identical in classical and in quantum physics, and on the other the rotations are often excited with high quantum numbers, in the region of which there is a sort of asymptotic approach of the results of quantum physics to those of classical physics.

23. VIBRATION-ROTATION BANDS ON THE QUANTUM THEORY

In the quantum theory the *rotation spectrum* of a diatomic molecule arises from transitions in which only the rotational motion of the molecule, characterised by the rotational quantum number J of section 21, changes. The corresponding frequencies are called rotational lines and form together a *rotation band*, which, in contrast to the classical results of the preceding section, is not continuous but discrete. Analogous to the classical results, however, is the fact that a rotation spectrum appears only if the molecule in question possesses a dipole moment, in other words if the electron cloud is distributed in such a fashion as not to make its electrical centre of gravity coincide with that of the two nuclei. Molecules with equal nuclei, homonuclear molecules, such as H_2, N_2, O_2, have a symmetrical charge distribution causing the dipole moment to vanish, and consequently no rotation spectrum is found for them. Conversely, the absence of such a spectrum is the strongest argument against the notion according to which the binding in these molecules is considered to be of the type H^+H^-, etc. In case the dipole moment differs from zero, the rotation lines actually occurring correspond to transitions in

which J changes by one unit, since a *selection rule* forbids all other transitions.

If we take the energy values of the stationary states of the molecule as being given by equation (21·15), then according to equation (2·2) there follows for the frequency $\nu_{J,J+1}$ of the rotational transition between the levels v, J and v, $J+1$

$$\nu_{J,J+1} = 2[B_e - \alpha(v+\tfrac{1}{2}) - \tfrac{1}{2}D_e](J+1) - 4D_e(J+1)^3.$$

Since in general α and D_e are small compared with B_e, we may in first approximation neglect the terms with α and D_e unless v or J take very high values. We see then that the rotational lines lie equidistantly with a difference in frequency $2B_e$. In this approximation B_e can be determined from the rotational spectrum. On account of the smallness of the correction terms it is in practice not possible to obtain α and D_e as well, and with them an exact value of B_e. But if α and D_e are known from other sources (see below), then B_e can be computed accurately, making a comparison possible with the B_e-values obtained by different methods.

The only diatomic molecules for which rotation spectra have been investigated are the halogen halides. The measurements were made in absorption and hence refer to molecules in the vibrationless state $v=0$. For at ordinary temperatures the energy of thermal agitation is too small to bring more than a negligible proportion of these molecules into higher vibrational states. The spectra lie in the far infra-red. The results are in accordance with the expectations, confirming the value of B_e already known from the vibration-rotation spectra to be discussed presently. For literature see (5) and (14).

Of much greater importance than the rotation spectra are the spectra of diatomic molecules corresponding to simultaneous changes of both the vibrational and the rotational quantum number, the *vibration-rotation spectra*. In analogy with the classical result they are present only in molecules for which the oscillation of the nuclei is accompanied by an oscillation of the dipole moment so that homonuclear molecules have no vibration-rotation spectra. The quantum

number J is again subject to the *selection rule* that it may only change by one unit.

For electronic states of diatomic molecules in which the electrons have a resultant angular momentum around the internuclear line (see section 25) J may also stay unaltered. Since the vibration-rotation spectra are all obtained in absorption and hence refer to the ground state, and since NO is the only diatomic molecule in the ground state of which the electrons have an angular momentum around the internuclear line, we disregard this special case in the subsequent investigation.

We shall denote the values of the vibrational quantum number of the two states which give rise to a line of the vibration-rotation spectrum by v' and v'', where $v' > v''$. All lines belonging to the same values of v' and v'' form together a *vibration-rotation band.* In such a band we must distinguish two groups of lines; those due to transitions between the states v', J and v'', $J+1$ forming the *negative or P-branch*, and those due to transitions between the states v', J and v'', $J-1$ forming the *positive or R-branch.*

If we assume the energy W_{vJ} to have again the form (21·15), then the frequency relation (2·2) gives for the frequencies of these branches:

$$\nu_{J,J+1} = c_0 - c_1(J+1) + c_2(J+1)^2 - c_3(J+1)^3, \qquad P\text{-branch} \tag{23·1}$$

$$\nu_{J,J-1} = c_0 + c_1 J \qquad + c_2 J^2 \qquad + c_3 J^3, \qquad R\text{-branch} \tag{23·2}$$

with the abbreviations

$$\left.\begin{aligned} c_0 &= \omega_e(v'-v'') - x_e\omega_e(v'-v'')(v'+v''+1) - \tfrac{1}{4}\alpha(v'-v''), \\ c_1 &= 2\left[B_e - \tfrac{1}{2}\alpha(v'+v''+1) - \tfrac{1}{2}D_e\right], \\ c_2 &= -\alpha(v'-v''), \qquad\qquad c_3 = -4D_e. \end{aligned}\right\} \tag{23·3}$$

Since, as mentioned already above, α and D_e are small compared to B_e, the terms with c_2 and c_3 in the equations (23·1) and (23·2) are small correction terms if v and J are not too large. Disregarding them, we get for the frequency of the lines in the P-branch (23·1) $c_0 - c_1(J+1)$, the smallest possible value of J

being 0. For the frequencies of the R-branch (23·2) we have then $c_0 + c_1 J$, the smallest value of J being here 1 since $J-1$ must be at least 0. We see hence that in both branches the lines in this approximation lie equidistantly with a difference in frequency c_1, or very nearly $2B_e$. Between the first lines of the P- and the R-branch, however, there is a double distance $2c_1$; one speaks of a *missing line*. The position of the missing line itself is approximately given by c_0, and this again, since x_e is small, is about equal to $\omega_e(v'-v'')$. The vibration-rotation bands corresponding to $v'-v''=k$ lie hence in the neighbourhood of a frequency k times as large as the frequency ω_e, around which the bands corresponding to $v'-v''=1$ are located.

The two branches in each band are entirely analogous to the two branches found for the vibration-rotation bands on the basis of the classical theory, excepting of course that their structure is discrete. Similarly, as in fig. 32, the intensity in each branch, beginning from the missing line, first increases, then goes through a maximum and finally decreases. The bands near ω_e with $v'-v''=1$ play the rôle of the *fundamental band*, the bands near $k\omega_e$ with $v'-v''=k$ that of the *harmonics*. Just as in the preceding section the former are by far the strongest, while the intensity of the latter rapidly diminishes with increasing k.

From a knowledge of the constants c_0, c_1, c_2, c_3, as they may be found by means of the relations (23·1) and (23·2) from the experimentally determined frequencies of the vibration-rotation lines, the quantities B_e, α, ω_e, x_e in the expression (21·15) for the energy of the vibration-rotation levels may successively be found. From the equations (23·3) there follows in the first place

$$2B_e = c_1 - c_2 \frac{v'+v''+1}{v'-v''} - \tfrac{1}{4}c_3;$$

furthermore

$$\alpha = -\frac{c_2}{v'-v''},$$

permitting α to be found; finally

$$\omega_e[1-x_e(v'+v''+1)](v'-v'') = c_0 - \tfrac{1}{4}c_2,$$

a relation involving the two unknowns ω_e and x_e. Applying this relation to two different vibration-rotation bands (different values of v' and v''), one has two equations from which ω_e and x_e may both be determined.

Vibration-rotation bands have been obtained for the halogen halides, for CO and NO. All the work has been done in absorption and hence refers to molecules originally in the vibrationless state $v'' = 0$. The spectra lie in the near infra-red. For each value of v' we get one band, for $v' = 1$ the fundamental band, for $v' = 2, 3, 4, \ldots$, the first, second, third, ..., harmonic bands, which in accordance with the expectation lie at about twice, three times, four times, ..., the frequency of the fundamental

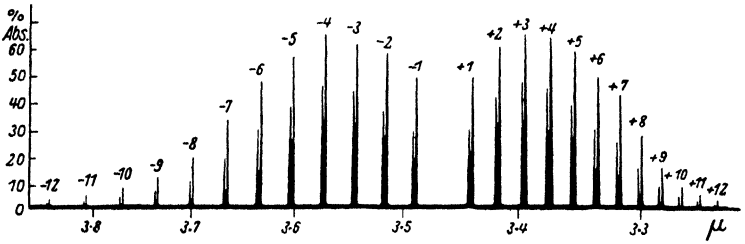


Fig. 33. Fundamental band of HCl in absorption according to Meyer and Levin (*Phys. Rev.* **34**, 44 (1929)).

band. The fundamental band is much stronger than the first harmonic, this again is much stronger than the second harmonic, etc. Fig. 33 shows the fundamental band of HCl. The missing line between the P- and R-branch is clearly recognisable, also the approximate equidistance and the change in intensity of the lines in each branch. Special attention should be drawn to the duplicity of the band lines, each of which consists of a strong and a weak component. This duplicity arises from the fact that chlorine is a mixture of two *isotopes* with atomic weights 35 and 37 respectively. There are hence two kinds of HCl molecules: HCl^{35} and HCl^{37}. Since the binding forces, depending only upon the charges of the constituent nuclei and electrons, are the same in both kinds of molecules while the reduced mass of HCl^{37} is larger than that of HCl^{35}, the vibration frequency ω_e will be smaller for the former. All the band lines of HCl^{37} are hence displaced toward lower frequencies

with respect to those of HCl^{35}. Now the weak components are due to HCl^{37}, since Cl^{37} is less abundant in ordinary chlorine than Cl^{35}, as shown already by the fact that the atomic weight of chlorine, 35·46, lies closer to 35 than to 37. Fig. 33 is thus seen to be in accord with the theoretical expectation regarding this *isotope effect* in the vibrational bands. For literature see (5), (14) and table 8.

As we have mentioned in section 22, the absolute intensity of the fundamental vibration band depends upon the quantity q, measuring the rate of change in dipole moment with the displacement of the nuclei from their equilibrium position. We have also pointed out that for heteropolar molecules q should have a value not far from the charge e on the ions into which the heteropolar molecule dissociates while very much smaller values of q plead for a homopolar character of the molecule. Now for the halogen halides q is indeed found to be only a small fraction of e, about $0{\cdot}2e$ for HCl, so that, as discussed by Bartholomé(19), these molecules in all likelihood are homopolar.

We have seen that homonuclear molecules have neither rotation nor vibration-rotation spectra, while for many other molecules these spectra are difficult to investigate experimentally on account of their location in the infra-red. For all these molecules information about the vibrational and rotational levels of their most stable electronic configuration, i.e. of the ground state, and about the energy curve V belonging to this configuration may be obtained from the spectra caused by transitions involving them and the vibrational and rotational levels of excited electronic states. These spectra are known as *electronic band spectra* and are usually situated in the visible or ultra-violet, making them easily accessible to investigation. Moreover, while the vibration-rotation spectra lead only to a determination of the energy values W_{vJ} for small v, since they are obtained in absorption from the level $v''=0$ and are sufficiently strong for observation only if v' is not too large (1, 2 and perhaps 3 and 4), the electronic band spectra also often give W_{vJ} for higher values of v, a fact important especially in connection with the calculation of the

TABLE 8

CONSTANTS OF DIATOMIC MOLECULES

Molecule	$M.10^{24}$ g	State	ω_e cm^{-1}	$x_e\omega_e$ cm^{-1}	B_e cm^{-1}	α cm^{-1}	K volts	D_0 volts	ρ_e Å	Literature
H_2	0·831	$^1\Sigma_g^+$	4417·9	131·32	60·8715	3·0671	9·9	4·465	0·7395	(49)
				Hydrides of group I						
LiH	1·453	$^1\Sigma^+$	1406·1	22·73	(7·38)	—	8·3	(2·47)	1·6	
NaH	1·592	$^1\Sigma^+$	1170·8	18·9	4·896	0·130	8·7	(2·24)	1·88	(43)
KH	1·620	$^1\Sigma^+$	984·3	14·5	3·415	0·083	8·8	(2·06)	2·24	(15)
CuH	1·636	$^1\Sigma$	1940·1	37·2	7·936	0·253	14·9	(3·2)	1·460	(35)
AgH	1·646	$^1\Sigma$	1760·0	34·05	6·453	0·203	15·1	(2·3)	1·614	
AuH	1·653	$^1\Sigma$	2302	42	7·21	0·188	23·0	(3·9)	1·52	
				Hydrides of group II						
BeH^+	1·495	$^1\Sigma^+$	2220·0	39·8	10·7887	0·3075	14·7	(2·80)	1·310	
BeH	1·495	$^2\Sigma^+$	2058·5	35·5	10·300	0·275	13·0	(2·40)	1·340	
MgH^+	1·595	$^1\Sigma^+$	1695·3	30·2	6·3782	0·1854	14·3	(2·09)	1·649	(34)
MgH	1·595	$^2\Sigma^+$	1493·45	31·25	5·79	0·18	12·1	(1·41)	1·73	
CaH	1·621	$^2\Sigma^+$	1316·7	19·2	4·277	0·098	12 6	(1·9)	2·02	
ZnH^+	1·637	$^1\Sigma^+$	(1916)	39	7·42	0·25	15·6	(2·03)	1·51	
ZnH	1·637	$^2\Sigma^+$	(1552)	—	(6·55)	—	12·5	0·91	(1·607)	
SrH	1·643	$^2\Sigma^+$	—	—	(3·6198)	—	—	—	(2·16)	
CdH^+	1·647	$^1\Sigma^+$	1775	37·3	6·070	0·187	16·1	(2·0)	1·664	(68)
CdH	1·647	$^2\Sigma^+$	1430·7	46·3	5·46	0·28	11·9	0·67	1 754	
BaH	1·650	$^2\Sigma^+$	(1137)	—	3·383	0·066	(11·8)	—	2 23	(31)
HgH^+	1·654	$^1\Sigma^+$	2016	40·8	6·57	0·19	19·2	(2·20)	1·59	
HgH	1·654	$^2\Sigma^+$	1432·7	108·8	5·58	0·373	11·8	0·37	1·729	

Hydrides of groups III, IV, V and VI										
BH	1·522	$^1\Sigma^+$	(2230)	(10)	12 098	0·459	(14)	(3·45)	1·226	
AlH^+	1·602	$^2\Sigma^+$	—	—	(6·763)	—	—	—	(1·60)	(17), (42)
AlH	1·602	$^1\Sigma^+$	1680·6	27·75	6 386	0·181	13 9	3·06	1·644	
CH	1·533	$^2\Pi$	2859	74	14·43	0·53	17·8	(4·0)	1·118	(36)
SiH	1·604	$^2\Pi$	(2012)	—	(7·40)	—	(17·0)	—	(1·527)	
NH	1·550	$^3\Sigma^-$	—	—	(15·30)	—	—	(4·2)	(1·08)	
PH	1·610	$^3\Sigma^-$	—	—	(8 411)	—	—	(3·2)	(1·43)	
BiH	1·654	$^1\Sigma^+$	1678·16	21 23	5·137	0·147	17·2	(4·01)	1·804	
OH	1·563	$^2\Pi$	3734·9	82·6	19·025	0·724	23·0	(4·9)	0·964	(50)
Hydrides of group VII; hydrogen halides										
HF	1·578	$^1\Sigma$	4037	50	20·925	0·763	23·9	—	0·864	
HCl^+	1·615	$^2\Pi$	(2608)	(20)	9·775	0·300	21·7	3·63	1·313	
HCl	1·615	$^1\Sigma$	2989·00	51 65	10·59090	0·30188	23·8	—	1·2717	(39)
NiH	1·635	$^2\Delta$	—	—	(7·701)	—	—	—	(1·48)	(32)
HBr	1·641	$^1\Sigma$	2649·74	45·23	8·4739	0 2289	25·0	—	1·4096	(61)
HJ	1·649	$^1\Sigma$	—	—	(6·4205)	—	—	—	(1·617)	
Halides of group I										
CuF	24·07	—	(620·59)	3·842	—	—	—	—	—	
CuCl	37·10	—	(417·02)	1·64	—	—	—	—	—	
CuBr	57·80	—	(314·10)	0 865	—	—	—	—	—	
CuJ	69·43	—	(265·13)	0·76	—	—	—	—	—	
AgCl	43·58	—	(343 6)	1·163	—	—	—	3·11	—	
AgBr	75·70	—	(250·2)	0·83	—	—	—	2·6	—	
AgJ	96·16	—	(206·27)	0·57	—	—	—	2 1	—	
AuCl	49·02	—	(382·8)	1·30	—	—	—	—	—	

TABLE 8—*contd*

Molecule	$M.10^{24}$ g	State	ω_e cm^{-1}	$x_e\omega_e$ cm^{-1}	B_e cm^{-1}	α cm^{-1}	K volts	D_0 volts	ρ_e Å	Literature
					Halides of group II					
BeF	10·07	$^2\Sigma^+$	1265·6	9·12	1·4877	0·01685	33·2	(6·0)	1·357	
MgF	17·49	$^2\Sigma$	(690·75)	3·95	(0·518)	—	—	(1·75)	(1·75)	(48)
CaF	21·99	$^2\Sigma$	(586·7)	(2·86)	(0·3225)	(0·0020)	(33·0)	—	(1·98)	
CaCl	30·78	—	(360)	—	—	—	—	—	—	
CaBr	44·02	—	(281)	—	—	—	—	—	—	
CaJ	50·23	—	(241)	—	—	—	—	—	—	
SrF	25·75	$^2\Sigma$	(500·1)	(2·13)	—	—	—	—	—	
SrCl	41·29	—	(298)	—	—	—	—	—	—	
SrBr	69·55	—	(215)	—	—	—	—	—	—	
BaF	27·52	$^2\Sigma$	(468·9)	1·79	—	—	—	—	—	
BaCl	46·04	—	(288)	—	—	—	—	—	—	
BaBr	82·85	—	(193)	—	—	—	—	—	—	
					Halides of groups III, IV and V					
TlCl	49·28	—	(284·8)	1·10	—	—	—	(3·79)	—	
TlBr	95·66	—	(192·5)	0·32	—	—	—	(3·20)	—	
TlJ	129·1	—	(150)	—	—	—	—	(2·56)	—	
SiF	18·67	—	(865·0)	4·55	(0·2904)	—	(79·5)	—	(2·259)	
SnCl	46·51	$^2\Pi$	(353)	1·1	—	—	—	—	—	
					Halogen molecules					
Cl_2	28·86	$^1\Sigma_g^+$	(564·9)	4·0	0·2438	0·0017	40·5	2·47	1·983	
BrCl	40·46	$^1\Sigma^+$	(421)	—	—	—	—	2·246	—	(24)
Br_2	65·89	$^1\Sigma_g^+$	(323·86)	1·15	0·08091	0·00028	40·0	1·961	2·28	
JCl	45·24	$^1\Sigma^+$	(384·6)	1·58	0·1146	0·00104	40·0	2·143	2·310	
JBr	80·87	$^1\Sigma^+$	268·4	0·78	—	—	—	1·808	—	(22)
J_2	104·65	$^1\Sigma_g^+$	(214·26)	0·592	0·03736	0·00012	38·0	1·535	2·660	

Alkali metal molecules										
Li_2	5·771	$^1\Sigma_g^+$	(351·60)	2·590	0·67286	0·00744	5·7	1·14	2·67	
LiK	9·793	—	(207)	—	—	—	—	—	—	
LiRb	10·67	—	(185)	—	—	—	—	—	—	
LiCs	10·97	—	(167)	—	—	—	—	—	—	
Na_2	18·96	$^1\Sigma_g^+$	(159·23)	0·726	0·15474	0·00082	5·1	0·76	3·070	
NaK	23·88	$^1\Sigma^+$	(123·29)	0·40	—	—	—	0·62	—	(53)
NaRb	29·88	—	(100)	—	—	—	—	—	—	
NaCs	32·33	—	(96)	—	—	—	—	—	—	
K_2	32·15	$^1\Sigma_g^+$	(92·64)	0·354	0·05621	0·00022	4·7	0·51	3·91	
Cs_2	109·5	—	(41·99)	0·080	—	—	—	0·45	—	(54)
Molecules of groups IV and V										
C_2	9·494	$^3\Pi$	1641·55	11·67	1·6335	0·0149	51·2	(5·5)	1·308	
CN	10·67	$^2\Sigma^+$	2068·792	13·176	1·8991	0·0173	70·0	7·09	1·169	
SiN	15·39	$^2\Sigma$	1151·68	6·56	0·7308	0·00567	56·2	—	1·568	
CP	14·27	$^2\Sigma$	1239·67	6·86	0·79863	0·00597	59·3	6·9	1·5583	(20)
N_2^+	11·54	$^2\Sigma_g^+$	2206·84	16·044	1·932	0·02	78·2	6·3	1·113	(58)
N_2	11·54	$^1\Sigma_g^+$	(2359·60)	14·445	2·007	0·018	86·3	7·35	1·094	(40), (69)
P_2	25·58	$^1\Sigma_g^+$	780·43	2·812	0·3142	0·00195	59·8	5·008	1·856	(38)
PN	16·47	$^1\Sigma$	1337·24	6·983	0·78621	0·00557	—	(6·3)	1·4869	(28)
Sb_2	91·83	—	(270)	—	—	—	—	—	—	(33)
Bi_2	172·2	—	172·71	0·3227	—	—	—	1·71	—	(16)
Oxides of groups II and III										
BeO	9·50	$^1\Sigma^+$	1486·87	11·70	1·6514	0·0189	41·5	(5·8)	1·3272	(41)
BO	10·75	$^2\Sigma^+$	1885·4	10·71	1·789	0·017	61·8	(6·6)	1·199	
AlO	15·56	$^2\Sigma$	977	7·0	0·6415	0·00575	46·2	—	1·614	
ScO	19·47	$^2\Sigma$	(971·55)	3·95	—	—	—	—	—	
YO	22·43	$^2\Sigma$	(852·5)	2·45	—	—	—	—	—	
LaO	23·66	$^2\Sigma$	(811·6)	2·23	—	—	—	—	—	

TABLE 8—*contd*

Molecule	$M.10^{24}$ g	State	ω_e cm^{-1}	$x_e\omega_e$ cm^{-1}	B_e cm^{-1}	α cm^{-1}	K volts	D_0 volts	ρ_e Å	Literature
					Oxides and Sulphides of groups IV					
CO^+	11·31	$^2\Sigma^+$	2217·1	15·5	1·954	0·019	78·0	(7·1)	1·114	(25)
CO	11·31	$^1\Sigma^+$	(2167·4)	12·70	(1·925)	—	78·3	(10·0)	(1·13)	(18)
CS	14·40	$^1\Sigma$	(1282·5)	6·00	—	—	—	—	—	(26)
SiO	16·80	$^1\Sigma$	1242·03	6·047	0·7238	0·00494	65·4	—	1·51	(65)
GeS	36·67	—	(575·8)	1·80	—	—	—	(5·65)	—	
PbO	24·48	$^1\Sigma$	(722·3)	3·73	0·3073	0·0019	52·7	—	1·918	
					Oxides and Sulphides of group V					
NO	12·31	$^2\Pi$	1906·5	14·44	1·684	0·0178	66·0	5·25	1·146	(58)
NS	16·11	$^2\Pi$	1220·0	7 75	—	—	—	—	—	
PO	17·41	$^2\Pi$	(1235)	7	—	—	—	—	—	
					Molecules of group VI					
O_2^+	13·19	$^2\Pi_g$	(1876·4)	16·53	1·597	0·009	67·5	6·45	1·14	(59)
O_2	13·19	$^3\Sigma_g^-$	1568·33	11·993	1·4456	0·0158	52·0	5·09	1·204	(27)
SO	17·60	$^3\Sigma$	1123·73	6·116	0·70894	0·00562	55·1	5·10	1·489	
S_2	26·45	$^3\Sigma_g^-$	(727·4)	2·75	0·4087	0·0007	40·0	4·45	1·603	
Se_2	65·30	—	387·8	0·63	—	—	—	—	—	(60)
Te_2	105·1	$^3\Sigma$	(250·9)	0·53	0·032	(0·001)	—	—	2·85	

dissociation energy according to the methods of section 21. We shall postpone the discussion of electronic band spectra until section 25 since it requires a more careful analysis of the electronic motion in the molecule. The results obtained from these spectra, regarding the energy curves V of diatomic molecules in their ground state, we shall, however, include in the general survey of the numerical data in the next section.

24. NUMERICAL DATA ON THE ENERGY CURVES V OF PHYSICALLY STABLE DIATOMIC MOLECULES IN THEIR GROUND STATE. CONNECTION WITH CHEMICAL BINDING

In table 8 we have collected data of the constants characterising the energy function V of various physically stable diatomic molecules in their ground state. Behind the symbol of the molecule there is given its reduced mass M, defined by equation (21·3). Then follows a Greek letter referring to its electronic state, the significance of which will be discussed later. The next columns contain the quantities ω_e, $x_e\omega_e$, B_e and α, all expressed in cm^{-1}. The constant K in the following column is calculated from

$$K = 2\pi^2\omega_e^2 M\rho_e^2. \qquad (24\cdot1)$$

It signifies the energy which would be required to double the internuclear distance if the harmonic law of force were valid over such a range and has been expressed in electron-volts just as the dissociation energy D_0 measured from the vibrational level $v=0$. The last but one column furnishes the values of the equilibrium distance ρ_e.

The molecules have been arranged according to their chemical character. The numerical data have been taken from the book of Jevons(5), as far as this author could take cognisance of the literature, and have been supplemented by results published since then (up to April 1935) indicated under the heading literature. Attention should be drawn to the fact that our quantity B_e must be distinguished from the quantity B_0 tabulated by Jevons, to which it is related by $B_e = B_0 + \frac{1}{2}\alpha$. In the cases that x_e is not known, the quantity

ω_e cannot be accurately determined. Similarly if α is not known, the value of B_e will be inexact. Such values of ω_e and B_e as well as values of these quantities and of D_0 inexact or doubtful for other reasons have been placed in parentheses. In case a molecule occurs in several isotopic forms (section 2), the data refer to the most abundant isotope.

In the first place it is striking that so many of the molecules in table 8 are not known to the chemist. In some cases, like C_2, this is due to the fact that the substance is not known in the gaseous state while more frequently the molecule is chemically unstable, having the tendency to unite with other atoms to form a polyatomic molecule, as, e.g., CH and SO, which will give CH_4 and SO_2, or to capture an electron, as, e.g., N_2^+. The cases of physically unstable molecules, as, e.g., He_2, are not contained in table 8.

We compare first the hydride molecules. Nearly all the hydrides of the elements in the two short periods of the periodic system are known and in addition some hydrides of the heavier elements. In fig. 34 we have plotted the quantity K as function of the atomic number, and we see a pronounced periodicity in this quantity, the hydrides of the elements in the same column of the periodic table having nearly the same value of K, which increases from about 10 to about 20 volts in going from the alkalies to the halogens. The dissociation energies are in general only roughly known. The small values of D_0 for ZnH, CdH, HgH are noticeable, probably connected with the fact that the metal atoms have all electrons in closed shells (see section 14). The quantity ρ_e, represented in fig. 35, shows again a pronounced periodicity with increasing atomic number and becomes larger for hydrides of the heavier elements in the same column of the periodic table on account of the increase of atomic radius. The large amplitude of vibration of the light H-nucleus causes the correction constants x_e and α to be exceptionally great.

Furthermore, it is interesting to discuss next to each other the alkali molecules and the halogen molecules. In each group the K-values are about the same, but while for the former, together with the D-values, they are especially small, about

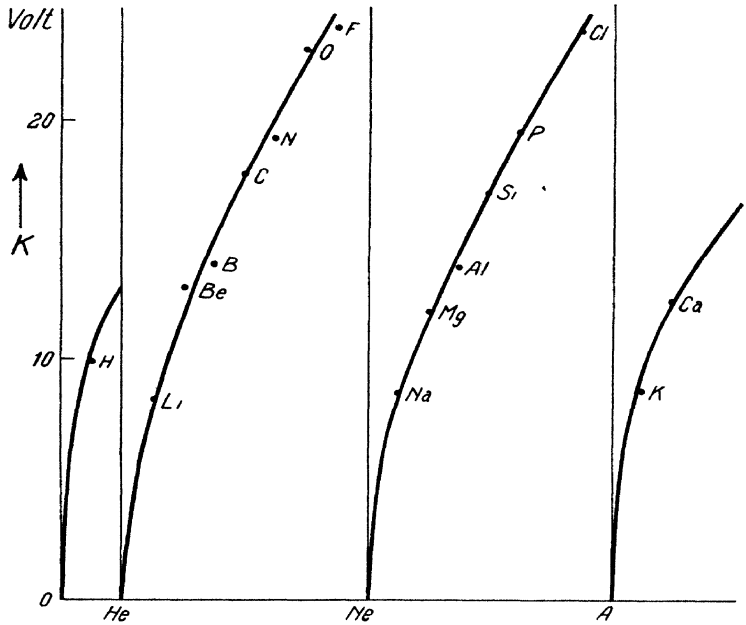
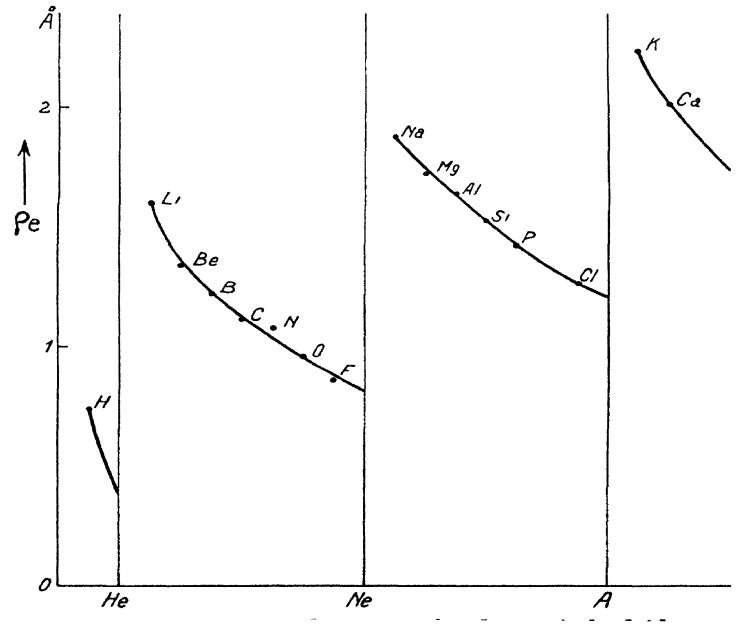


Fig. 34. Force constant K for diatomic hydrides.



5 volts, for the latter they are quite large, about 40 volts. Conversely, the values ρ_e are exceptionally large for the alkalies and of medium size for the halogens, showing an increase with atomic number in each group.

Among the molecules containing C, N and O the largest values of K and D_0 and the smallest values of ρ_e occur. This may be brought into connection with the fact that according to the ordinary chemical notions double and triple valence bonds are here often present. Thus for N_2 $K = 86{\cdot}3$ volts while for O_2 $K = 52{\cdot}0$ volts, in close parallelism with the triple and double valence bonds generally ascribed to these molecules. The K-value 78·3 volts of CO, which has the same number of electrons as N_2 and differs only in the nuclear charges, is nearly as large as that of N_2 so that one might be inclined to ascribe to it a triple bond too (see also section 29). The K-value, 51·2 volts for C_2, leads to the assumption that in this molecule one is dealing with a double bond.

Comparison of the values of ρ_e found in section 9 for Cl_2, N_2 and O_2 by means of X-ray diffraction and in section 11 for Br_2 and J_2 by electron diffraction shows a perfect agreement with the values here obtained.

25. ELECTRONIC STATES OF DIATOMIC MOLECULES. ELECTRONIC BANDS

Until now we have only investigated the different modes of vibration and rotation of a diatomic molecule in its ground state as they come to light in the vibrational and rotational levels. But, similarly, as in an atom the ground state is only one among many states, distinguished by the configuration of the electrons, thus, as we have mentioned already in section 20, a molecule has other *electronic states* in addition to its ground state, each of these being characterised by an energy curve V (see fig. 26). To every curve V with a minimum there belongs, just as in the ground state, a sequence of vibrational and rotational levels, the constants ω_e, B_e, etc., of which will, of course, in general be different from those for the ground state.

Hund(45) was the first to inquire if, in analogy to the case of an atom, it is possible to classify the electronic states of a

molecule by means of *quantum numbers*. For the atom we had introduced the quantum number L as a measure of the resultant orbital angular momentum of all the electrons since this quantity has a constant value. In the molecule the dissymmetry due to the presence of two nuclei destroys the constancy of L, but since the internuclear line is still an axis of symmetry, the component of the orbital angular momentum along this line will be a constant. Measured in units $h/2\pi$ we shall denote it by Λ, while molecular states with $\Lambda = 0, 1, 2, \ldots$ will be called Σ-, Π-, Δ-, ... states respectively. Just as for an atom, the resultant spin angular momentum of all the electrons may serve as a second quantum number, characterising a molecular state. It will again be denoted by S, and according to whether $S = 0, \frac{1}{2}, 1, \ldots$ we shall speak of singlet-, doublet-, triplet-, ... states of the molecule, denoting the multiplicity $2S+1$ by an upper left-hand index before the symbols referring to Λ. Thus ${}^2\Sigma$, ${}^1\Pi$, ${}^3\Delta$ stand for states with $\Lambda = 0$, $S = \frac{1}{2}$; $\Lambda = 1$, $S = 0$; $\Lambda = 2$, $S = 1$ respectively. Similarly as in the atomic case, S is integral or half-integral depending upon whether the total number of electrons in the molecule is even or odd. In addition to Λ and S, as shown by Hund (46), Kronig (52), Wigner and Witmer (70), certain symmetry properties of the wave functions associated with the molecular states may serve as a further means of classifying these. Thus for diatomic molecules in general one distinguishes two kinds of Σ-states, known as Σ^+ and Σ^-. The Σ^+-states are states the wave function of which, upon being reflected at a plane through the internuclear line, stays unchanged, while for the Σ^--states it changes its sign. Besides, for homonuclear diatomic molecules, all the states fall into two groups known as *even* or *odd*, indicated by the letters g and u; e.g. ${}^1\Sigma_g^+$, ${}^3\Pi_u$, etc. The even states are those for which the wave function upon reflection of all the co-ordinates at the midpoint of the internuclear line remains the same, while for the odd states it goes over into its negative.

The great importance of the quantum numbers Λ and S and of the symmetry properties lies in the fact that the radiative transitions of diatomic molecules are subject to *selection rules*

involving them. Thus Λ can only change by 0, ± 1, while bands corresponding to a change in S are absent or very weak. Finally Σ^+-states cannot combine with Σ^--states while for homonuclear molecules transitions between two even states or between two odd states are also prohibited.

Restricting ourselves first to singlet-states ($S=0$), we shall discuss the band spectra to be expected when not only the rotation and vibration but also the electronic configuration of the molecule changes, the so-called *electronic bands*, referred to already in section 23. For the vibration-rotation levels of the upper as well as of the lower electronic state we can write down an expression of the form (21·15), with this difference that for the upper state we have to add a certain constant $h\nu_e$, representing the excess of electronic energy with respect to the lower state. We distinguish the constants and quantum numbers of the upper state from those of the lower by denoting the first by a single, the last by a double accent. All transitions having the same values v' and v'' of the vibrational quantum numbers form together one band. In general such a band will consist of three branches, the first of these, the *P-branch*, corresponding to transitions between v', $J-v''$, $J+1$; the second, the *Q-branch*, to transitions between v', $J-v''$, J; the third, the *R-branch*, to transitions between v', $J'-v''$, $J-1$. If in equation (21·15) one neglects the terms with α and D_e, which are small corrections not affecting the general aspect of the band, one finds for the frequencies of the three branches on the basis of the frequency relation (2·2)

$$\left.\begin{aligned}
\nu_{J,J+1} &= \nu_0 - B_e'' - 2B_e''(J+\tfrac{1}{2}) + (B_e' - B_e'')(J+\tfrac{1}{2})^2, && P\text{-branch}\\
\nu_{J,J} &= \nu_0 + (B_e' - B_e'')(J+\tfrac{1}{2})^2, && Q\text{-branch}\\
\nu_{J,J-1} &= \nu_0 - B_e'' + 2B_e''(J+\tfrac{1}{2}) + (B_e' - B_e'')(J+\tfrac{1}{2})^2, && R\text{-branch}
\end{aligned}\right\} \quad (25\cdot1)$$

with

$$\nu_0 = \nu_e + \omega_e'(v'+\tfrac{1}{2}) - x_e'\omega_e'(v'+\tfrac{1}{2})^2 - \omega_e''(v''+\tfrac{1}{2}) + x_e''\omega_e''(v''+\tfrac{1}{2})^2.$$

In order to overlook the relative position of the various branches, it is most convenient to plot the relations (25·1) between ν as abscissa and $(J+\frac{1}{2})$ as ordinate (see fig. 36 (*a*)). We obtain then three parabolic curves, and by projecting

their intersection points with the horizontals corresponding to integral values of J upon the ν-axis, we find the whole band (see fig. 36 (b)).

Several circumstances ought to be noticed in connection with fig. 36 (a). From equation (25·1) it follows that the parabola called R-branch is the image of the continuation of the parabola called P-branch when it is reflected at the ν-axis. Furthermore, the parabolas will be opened either toward the high or the low frequency side depending on whether in equation

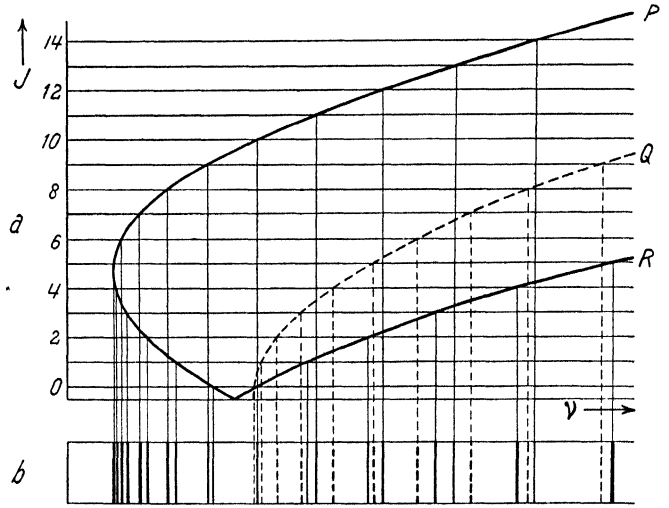


Fig. 36. Fortrat diagram for a singlet band of a diatomic molecule. (a) Diagram showing branch construction. (b) Diagram showing aspect of the band in the frequency scale.

(25·1) $B'_e > B''_e$ or $< B''_e$. In one of the branches—in fig. 36 (a) it is the P-branch—the lines crowd together near the top of the parabola, forming the *band head*. Finally, special attention must be paid to the smallest value J can take in each of the branches. For a singlet electronic state with orbital angular momentum Λ along the internuclear line the minimum value of J is not 0 but Λ. In consequence, one or more of the intersection points in fig. 36 (a) will have to be excluded so that there are one or more *missing lines*. An example of a singlet band is shown in fig. 36 (b). If the quantum number S does not vanish,

there arises a *multiplet structure* of the electronic levels of the molecule, making the aspect of the bands much more involved.

All the bands belonging to the same electronic transition, but distinguished by the vibrational quantum numbers v' and v'' of the initial and final levels, form together a *band system*. Although the question as to which transitions $v'-v''$, i.e. which bands, are represented with great intensity in a given band system is of spectroscopic rather than chemical interest,

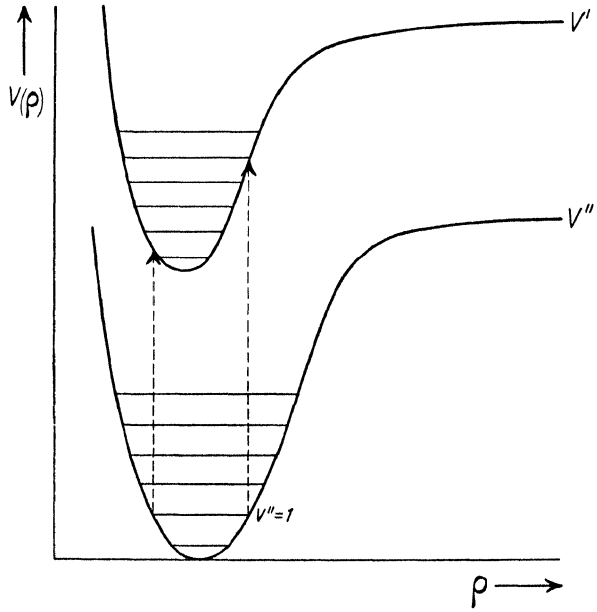


Fig. 37. Franck-Condon construction of the most probable transitions in a band system.

we shall go into it as a preparation for considerations which we shall have to make in chapter VI. Fig. 37 shows the energy function V governing the nuclear vibrations in two stable electronic states. Let us assume that we are dealing with the case of absorption bands corresponding to transitions from the vibrational levels v'' of the curve V'' to the vibrational levels v' of the curve V'. The energy values corresponding to the various vibrational levels are indicated for each curve by horizontal lines. Take, e.g., a molecule that initially has one

quantum of vibrational energy, $v''=1$. In the model that means that the vibration of the nuclei takes place between those values of ρ at which the curve V'' is intersected by the horizontal $v''=1$. Most of the time the nuclei spend near the extreme position $\rho_{\min}$ or $\rho_{\max}$ since there the vibratory motion reverses its direction. If now, under absorption of light, the molecule performs a transition to the curve V', this will most likely happen at $\rho_{\min}$ or $\rho_{\max}$ and hence the molecule after the transition will tend to vibrate along the curve V' in such a way that one of its extreme positions there is the same as one of the extreme positions of the original motion. This is indicated in fig. 37 by drawing vertical lines through $\rho_{\min}$ and $\rho_{\max}$ and finding their intercepts with the curve V'. The horizontal lines through these intercepts then give the energy values in the neighbourhood of which the vibrational levels v' after the transition will most probably fall. This semi-classical reasoning, first proposed by Franck[29], and later proved by Condon[23] to be essentially valid on the basis of wave mechanics too, is of course applicable to emission bands just as well.

The importance of the electronic bands for our purposes is a twofold one. As pointed out already in section 23, they in some cases supplement the information obtained from rotation and vibration-rotation bands regarding the vibration-rotation levels of the molecule in its ground state and in the great majority of cases are the only source of information regarding these. To employ them for that purpose it is, of course, necessary to take into account, in the relations (25·1) for the frequencies of the band lines, the correction terms previously neglected. But furthermore we gain from the number of missing lines of the bands and from the multiplet structure a knowledge of the quantities Λ and S for the electronic states involved in their emission while on the basis of the selection rules mentioned above further information about them and the symmetry properties may be obtained from the presence of certain electronic transitions and the absence of others. The conclusions about Λ and S may then often be confirmed by the relative intensity of the branches. To take an example: if the Q-branch is entirely absent, the transition must be one

between two Σ-states. In the second column of table 8 we have indicated the nature of the ground state for the different molecules enumerated so far as this is known from a band analysis.

26. THE MANIFOLDNESS OF THE ELECTRONIC STATES OF DIATOMIC MOLECULES

Discussing the optical spectra of atoms in section 17, we have seen that the nature of the stationary states of the isolated atom, characterised by the two quantum numbers L and S, could be predicted if the quantum numbers n, l of the individual electrons were known. We shall inquire now if it is possible to achieve a similar result for a diatomic molecule, i.e. if we can predict the nature of its electronic states, characterised by the quantum numbers Λ and S, on the basis of a more detailed knowledge of the constituent parts. Due to its more complicated structure there present themselves for a diatomic molecule, in contrast to the atomic case, three different ways of approaching this problem.

(*a*) As we have already repeatedly pointed out, the molecular electronic states may be considered as arising from the states of separate atoms upon letting these approach each other, the energy of the system being described as a function of the internuclear distance ρ by means of the curves V previously investigated in detail. From this point of view one will hence ask: What sort of molecular states arise, if two atoms, characterised by the quantum numbers L_1, S_1 and L_2, S_2 respectively, are brought together? Hund(46) and Wigner and Witmer(70) have developed a set of rules for dealing with this question. We shall confine ourselves here to obtaining an answer with the aid of the vector model used by the first of these authors, while the rigorous wave-mechanical justification given by Wigner and Witmer cannot be gone into here.

In the first place both the vectors L_1 and L_2, of which without loss of generality we may suppose that $L_1 \geqq L_2$, will suffer space quantisation (see section 14) with respect to the inter-

nuclear line so that their components Λ_1 and Λ_2 in that direction take the values

$$\Lambda_1 = -L_1,\ -L_1+1,\ \ldots,\ L_1-1,\ L_1,$$
$$\Lambda_2 = -L_2,\ -L_2+1,\ \ldots,\ L_2-1,\ L_2$$

respectively. The values of the resultant component of orbital angular momentum of the molecule along the internuclear line $\Lambda_1+\Lambda_2$ are obtained by combining each of the values Λ_1 with each of the values Λ_2. Those different from zero occur in pairs with positive and negative sign respectively, corresponding to the fact that the electronic rotation around the internuclear line may take place in either sense. Each pair hence signifies only one electronic state of the molecule which we shall characterise by the value of Λ equal to the positive member $\Lambda_1+\Lambda_2$ of the pair. We then get the following values represented directly, as far as possible, by the symbols Σ, Π, ..., introduced in section 25:

$$\begin{aligned} L_1+L_2,\ L_1+L_2-1,\ \ldots,\ &\Pi,\ \Sigma^+,\\ L_1+L_2-1,\ \ldots,\ &\Pi,\ \Sigma^-,\\ &\cdots\cdots\cdots\cdots\\ L_1-L_2,\ \ldots,\ &\Pi,\ \Sigma^+ \text{ or } \Sigma^-. \end{aligned}$$

For the Σ-states we have also indicated their character as Σ^+- or Σ^--states. For the last Σ-state we have the rule that it is Σ^+ or Σ^- depending on whether $L_1+L_2+\Sigma l_1+\Sigma l_2$ is even or odd, where Σl_1 and Σl_2 denote the sum of the quantum numbers l for the individual electrons in the two atoms. The spins S_1 and S_2 are coupled in the molecule to give the resultant spin according to the vector composition rule

$$S = |S_1-S_2|,\ |S_1-S_2|+1,\ \ldots,\ S_1+S_2-1,\ S_1+S_2.$$

Each of these values S combined with each of the values Λ found above stands for one molecular level. As an example we may take a N-atom in its ground state $(1s)^2(2s)^2(2p)^3\,{}^4S$ and an O-atom in its ground state $(1s)^2(2s)^2(2p)^4\,{}^3P$. The rule for Λ gives Π and Σ^+, the possible values of S are $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, so that we get as molecular states ${}^2\Pi$, ${}^2\Sigma^+$, ${}^4\Pi$, ${}^4\Sigma^+$, ${}^6\Pi$, ${}^6\Sigma^+$.

If the two atoms are of the same kind, we must distinguish between even and odd molecular states. If the two atoms

are in different states A and B, then either atom 1 may be in state A and atom 2 in state B or *vice versa*. As a consequence twice as many molecular states result as previously, each state occurring once as even, once as odd state. If the two atoms are in the same state $L_1 = L_2$, $S_1 = S_2$, then S takes the values $0, 1, \ldots, 2S_1$ while we have the following schemes for Λ:

if S is even

$$\begin{aligned}
&(2L_1)_g,\ (2L_1-1)_g,\ \ldots,\ \Pi_g,\ \Sigma_g^+,\\
&(2L_1-1)_u,\ \ldots,\ \Pi_u,\ \Sigma_u^-,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&\Pi_u,\ \Sigma_u^-,\\
&\Sigma_g^+;
\end{aligned}$$

if S is odd

$$\begin{aligned}
&(2L_1)_u,\ (2L_1-1)_u,\ \ldots,\ \Pi_u,\ \Sigma_u^+,\\
&(2L_1-1)_g,\ \ldots,\ \Pi_g,\ \Sigma_g^-,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\\
&\Pi_g,\ \Sigma_g^-,\\
&\Sigma_u^+.
\end{aligned}$$

Thus two N-atoms in their ground state ^4S give the states $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$.

(*b*) Instead of considering the molecule as being formed from atoms that approach each other, we may also first consider the two nuclei to coincide so that we have a single atom, and then separate them. While in the first case the molecular electronic states arose from the states of the constituent atoms they may in the second case be regarded as originating from those of the united atom.

The values Λ and S of the molecular electronic states arising from a given state L, S of the united atom are even easier to find than in (*a*). All we have to do is to subject L to space quantisation with respect to the internuclear line, giving as possible values of the component

$$\Lambda = -L,\ -L+1,\ \ldots,\ L-1,\ L,$$

so that the possible values of Λ are represented by

$$L,\ L-1,\ \ldots,\ \Pi,\ \Sigma^+ \text{ or } \Sigma^-,$$

the Σ-state being Σ^+ or Σ^- depending upon whether $L+\Sigma l$ is even or odd, while the S of the molecule is identical with the S of the united atom. Thus from the ground state $(1s)^2\,(2s)^2\,2p\,^2P$ of Al there arises a state $^2\Pi$ and $^2\Sigma^+$ of the molecule MgH if we imagine the Al-nucleus with atomic number 13 split into a Mg-nucleus with atomic number 12 and a H-nucleus of atomic number 1. It must be stressed here that while the dissociation of the molecule into separate atoms used in (*a*) for an interpretation of the molecular states can actually be carried out, e.g., by an increase of the vibration energy of the nuclei due to impacts, the formation of the united atom and its converse are purely fictitious processes introduced solely for the purpose of classifying the molecular states.

(*c*) A third method of arriving at the manifoldness of states in a diatomic molecule, due to Hund(47), Herzberg(3) and Mulliken(57) is an exact analogy of the method employed in the case of the isolated atom. One imagines the two nuclei fixed at a distance from each other and adds the electrons one by one, during which process the electrons will occupy the lowest available quantum states with due regard to the exclusion principle. This method has the marked advantage of immediately making clear why different molecules with the same number of electrons, so-called *isoelectronic* or *isosteric molecules*, have very similar properties. For just as in atoms and atomic ions with the same number of electrons like Ne, Na^+, Mg^{++}, the electrons in them will be bound successively in the same kind of quantum states. Thus, as table 9 shows, CO and N_2, both with 14 electrons, resemble each other very much in their physical behaviour. Other series of isoelectronic molecules are CN, N_2^+, BO, CO^+ with 13 electrons; CP, SiN, AlO, MgF with 21 electrons; CS, SiO with 22 electrons; NS, PO, SiF with 23 electrons. In each series, most of the members of which are not chemically stable and hence only known from their band spectra, the nature of the ground state is the same, while the spectroscopically determined quantities ω_e, D_0, ρ_e for this state have values not differing very much, as shown by table 10. From the standpoint of method (*a*) this similarity of isoelectronic molecules cannot be understood directly. Thus

N_2 arises from two N-atoms in their ground states ^4S, CO on the other hand from a C-atom in its ground state ^3P and an O-atom in its ground state ^3P.

TABLE 9

PHYSICAL PROPERTIES OF CO AND N_2

	CO	N_2
Melting point, abs.	66	63
Boiling point, abs.	83	78
Critical temperature, abs.	133	127
Critical pressure, atm.	33	33
Density in fluid state	0·793	0·796
Solubility in water at 0° C, in 1 gas/l	0·035	0·024
Viscosity. 10^6 at 0° C	163	166
Ground state	$^1\Sigma^+$	$^1\Sigma^+$
Vibration frequency in ground state, cm^{-1}	2167	2360
Dissociation energy in ground state, volts	(10·0)	7·34
Internuclear distance in ground state, Å	1·13	1·09

TABLE 10

SPECTROSCOPIC CONSTANTS OF ISOELECTRONIC MOLECULES

	CN	N_2^+	BO	CO^+	CS	SiO	
Ground state	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^1\Sigma$	$^1\Sigma$	
ω_e, cm^{-1}	2069	2207	1885	2217	(1283)	1242	
D_0, volts	7·09	6·3	(6·6)	(7·1)	—	—	
ρ_e, Å	1·169	1·113	1·199	1·114	—	1·51	
	CP	SiN	AlO	MgF	NS	PO	SiF
Ground state	$^2\Sigma$	$^2\Sigma$	$^2\Sigma$	$^2\Sigma$	$^2\Pi$	$^2\Pi$	—
ω_e, cm^{-1}	(1239)	1152	977	(691)	1220	(1235)	(865)
ρ_e, Å	—	1·568	1·614	—	—	—	(2·259)

In order to formulate more precisely the building up of a molecule by the successive capture of electrons in the field of the nuclei, one must ascribe quantum numbers to the individual electrons, just as in the atomic case. This can only be accomplished by again replacing the mutual interaction of the electrons by a suitable shielding of the nuclear field, imagining each electron to be subject to the nuclear attraction and the

smeared-out charge distribution of the other electrons. But while in the case of the isolated atom the shielding had central symmetry around the nucleus, it will only have rotational symmetry around the internuclear line in the case of a diatomic molecule. In the resultant field the component of orbital angular momentum along the internuclear line of every electron taken by itself, which, measured in units $h/2\pi$, we shall denote by λ, is a constant and will suitably serve as one of the quantum numbers required to characterise the electron. Electrons with $\lambda = 0, 1, 2, \ldots$ are spoken of as σ-, π-, δ-, ... electrons.

The quantum number λ is, of course, not sufficient to distinguish the various electrons. As additional quantum numbers one may choose the quantum numbers n and l which the electron gets in the limiting case of the united atom or that of the separate atom. In the first case one indicates the values n, l by placing the symbols $1s$, $2s$, $2p$, etc. before the symbols σ, π, etc.; thus $1s\sigma$, $2s\sigma$, $2p\pi$, etc. In the second case the symbols $1s$, $2s$, $2p$, etc. are placed behind the symbols σ, π, etc.; thus $\sigma 1s$, $\sigma 2s$, $\pi 2p$, etc.

If one knows the strength of binding for the various kinds of states of the electrons, one can fill up these states in the order of increasing energy. In doing so it is important, just as in the atomic case, to know how many electrons may be placed in a given kind of state. In a state with $\lambda = 0$, i.e. in a σ-state, the exclusion principle permits of putting two electrons on account of the two possible orientations of the electron spin, mentioned already in section 14. In a state with $\lambda \neq 0$, i.e. in a π-state, a δ-state, etc., there is room for four electrons, since in addition to the two possible orientations of the spin, there is the possibility of λ being ± 1 for a π-state, ± 2 for δ-state, etc.

Electrons with the same quantum numbers fully occupying the state in question are said to form a *closed shell*. In contrast to the atomic case, the closed shells in diatomic molecules consist either of two or of four electrons, depending on whether $\lambda = 0$ or $\lambda \neq 0$. In a closed shell of electrons both the component of the resultant orbital angular momentum Λ and the resultant spin S vanish so that a diatomic molecule with all

electrons in closed shells is in a $^1\Sigma$-state. In table 11 we have summarised the molecular states which are possible if there is outside of closed shells a σ-electron, a π-electron, a σ- and a π-electron, two equivalent π-electrons, etc.

Since in diatomic molecules the number of electrons required for the formation of a closed shell configuration is relatively so small, it is understandable why in molecules with an even number of electrons the ground states are $^1\Sigma$-states in the great majority of cases as shown by table 8.

TABLE 11

MOLECULAR STATES RESULTING FROM ELECTRONS OUTSIDE CLOSED SHELLS

σ	$^2\Sigma^+$			
π	$^2\Pi$			
$\sigma\pi$	$^1\Pi$	$^3\Pi$		
π^2	$^1\Sigma^+$	$^1\Delta$	$^3\Sigma^-$	
$\sigma\pi^2$	$^2\Sigma^+$	$^2\Sigma^-$	$^2\Delta$	$^4\Sigma^-$
π^3	$^2\Pi$			
$\sigma\pi^3$	$^1\Pi$	$^3\Pi$		

27. SEQUENCE AND STABILITY OF MOLECULAR STATES FROM THE LIMITING CASE OF SEPARATE ATOMS

The three methods described in the preceding section only give a partial answer to the question interesting the chemist; they allow him to predict the kind and number of molecular states. For an interpretation of chemical binding, however, we shall want to know in addition the sequence of these states and which of them have an energy curve with a minimum. Heitler and London(37) have approached this problem from the limiting case of the separate atoms. They consider the two constituent atoms in given stationary states, when at an infinite distance, as the starting point of a perturbation calculus, investigating how the energy of the system changes when the atoms come closer together. They find then the energy of the molecular states, arising from the given atomic states according to the rules given under (*a*) of the preceding section, as a function of the internuclear distance ρ. Their results are, of course, valid only if ρ is not too small since

otherwise the first approximation of the calculus, to which Heitler and London restrict themselves in order to keep the mathematical labour within reasonable bounds, is entirely insufficient. Nevertheless, one can see already in this region of ρ which of the molecular states correspond to attractive forces, and hence must have a function V with a minimum somewhere, and which correspond to repulsive forces excluding the possibility of molecule formation.

Heitler and London have actually applied their procedure numerically to two H-atoms in the ground state ^2S and to two He-atoms in the ground state ^1S. The same method has been used for a H-atom and a He-atom, for a H-atom and a Li-atom, for two Li-atoms, for two Be-atoms and for two Na-atoms, all in their ground state, which for Li and Na is ^2S, for Be ^1S. In the case of H_2 Heitler and London found that of the two states $^1\Sigma$ and $^3\Sigma$, resulting according to the rules under (a) of the preceding section, $^1\Sigma$ is attractive with a minimum, $^3\Sigma$ on the other hand repulsive, while for He_2 they got repulsion for the one possible molecular state $^1\Sigma$. LiH, Li_2, Na_2 were found to behave like H_2, Be_2 like He_2, while the one possible state $^2\Sigma$ of HeH turned out to be repulsive. All this is in agreement with the chemical and spectroscopic evidence, showing the existence of physically stable molecules H_2, LiH, Li_2, Na_2 with $^1\Sigma$-states as ground states (see table 8) and the impossibility of physically stable molecules He_2, Be_2 and HeH. Looking at our examples we see that when both atoms have non-vanishing spins S_1 and S_2, the lowest molecular state is the one where the spins compensate each other and actually corresponds to molecule formation, while if S_1 or S_2 or both are zero, the resulting molecular state is repulsive. Heitler and London generalised these results as follows:

If two atoms in states with spins S_1 and S_2 are brought together, the lowest molecular state will be one in which the spins compensate each other as far as possible, in other words a molecular state with resultant spin $S = |S_1 - S_2|$. If, and only if, such compensation actually takes place, i.e. if both S_1 and S_2 are different from zero, then will this molecular state have a function V with a minimum. $2S_1$ and $2S_2$ are to be identified

with the number of *valence dashes* originating from the two atoms, and their tendency toward mutual compensation in the molecule signifies what, expressed in chemical language, is termed *saturation of valences*.

We shall now discuss the experimental material with the object of ascertaining the limitations of the views of Heitler and London. We notice first that in the examples from which the above rules were obtained by generalisation all the atoms were in S-states ($L=0$). We hence consider first only atoms of this kind. Two atoms in S-states, according to the rules under (a) of the preceding section, give only Σ-states of the molecule with multiplicities $|S_1-S_2|$, $|S_1-S_2|+1$, ..., S_1+S_2, of which the first, according to Heitler and London, shall be the lowest.

(a) The *rare gases* have like He as ground state a ^1S-state with $S=0$ (see table at the end of the book). Theoretically and empirically they have the valence 0 and hence do not form molecules.

(b) The *alkalies* have as ground state a ^2S-state with $S=\frac{1}{2}$. In accordance with the expectation they unite with each other and with hydrogen to give fully saturated diatomic molecules in a $^1\Sigma$-state, like Li_2, LiNa, etc., LiH, etc., also known to the chemist. The molecules CuH, AgH, AuH, too, probably belong here.

(c) The *earth alkalies* and Zn, Cd, Hg have as ground state a ^1S-state and hence should not be capable of entering into chemical combination. Yet table 8 shows them to unite with H to give diatomic hydrides. The reason for this must be sought in the following circumstance. In the computation of Heitler and London the attention is confined to those stationary states of the atoms which serve as starting point of their approximation method. This is permissible only as long as the atoms do not get so near to each other that the energy change produced by their approach becomes comparable to the energy differences between the various stationary states of the atoms. For otherwise, according to wave mechanics, the properties of these atomic states will get "mixed". Now for the elements in the second column of the periodic table, in contrast to the rare

gases, excited triplet terms, with $S=1$ and hence bivalent, lie rather close to the ground state. Evidently through their presence the curve for V, originating from the atoms concerned in their ground state and being repulsive according to the simple theory, is depressed sufficiently by the presence of the excited states to have a minimum. The flatness of the curve for V as evidenced by small values of the dissociation energy, especially for ZnH, CdH, HgH (see table 8), is a reminder of its inherently repulsive character.

(*d*) The elements N and P have as ground state a ^4S-state with $S=\frac{3}{2}$ and should hence be trivalent. Accordingly they give with an H-atom diatomic molecules having as ground state a $^3\Sigma$-state, the spin $S=\frac{3}{2}$ of N and P being compensated as far as possible to a spin $S=1$ by the spin $S=\frac{1}{2}$ of the H-atom, so that the chemical formula should be written $\equiv$N—H, $\equiv$P—H. Accordingly these molecules are not saturated and are hence unknown to the chemist. The molecules N_2, P_2 and NP on the other hand are fully saturated, having a $^1\Sigma$-state as ground state with a threefold bond.

The rules of Heitler and London are also still applicable in most cases where one of the atoms is in an S-state, the other in a P-state. B, Al and the halogens have as ground state ^2P with $S=\frac{1}{2}$, C, Si and O, S have as ground state ^3P with $S=1$. With the ^2S-state of H the former should give, according to the rules under (*a*) of the preceding section, the molecular states $^1\Sigma$, $^1\Pi$, $^3\Sigma$, $^3\Pi$, the latter $^2\Sigma$, $^2\Pi$, $^4\Sigma$, $^4\Pi$. We should hence expect diatomic hydrides with a singlet-state as ground state in the first case, and with a doublet-state as ground state in the second case. This is indeed what is found, and, moreover, it is interesting to note that, according to table 8, BH, AlH and the halogen halides have $^1\Sigma$ as ground state; CH, SiH and OH on the other hand $^2\Pi$; furthermore, that AlH and the halogen halides, being saturated, can be prepared chemically; CH, SiH and OH with one free valence cannot. Other molecules belonging here are CN, SiN, CP, BO and AlO with a $^2\Sigma$-state as ground state and NO, NS and PO with a $^2\Pi$-state as ground state. Exceptions are again the oxides and halides of the alkaline earths.

When neither of the atoms is in an S-state, the rules of Heitler and London appear to lose their applicability entirely. The halogen molecules, it is true, have $^1\Sigma$-states as ground states, but C_2 has $^3\Pi$, O_2, S_2, Te_2 and SO $^3\Sigma$. Attempts to improve the theory by the introduction of an *orbital valence* (corresponding to $L \neq 0$) next to a *spin valence* (corresponding to $S \neq 0$) have not proved very successful. The discussion of polyatomic molecules on the basis of the notions developed in this section we postpone till the next chapter.

28. SEQUENCE AND STABILITY OF MOLECULAR STATES BY THE METHOD OF ELECTRONIC CONFIGURATIONS

The rules described under (*a*) and (*b*) of section 26 inform us about the manifoldness and energy of the molecular states in the limiting cases of the separate atoms and of the united atom, where the molecular states coincide with atomic states. They do not tell us anything about the energetic sequence of the molecular states in the important region of intermediate values of ρ. While Heitler and London, starting from the knowledge of the position of the molecular states in the case of the separate atoms, discussed their behaviour upon diminishing the internuclear distance ρ with the help of a rather laborious perturbation calculus, valid moreover only for large values of ρ, Hund, Herzberg and Mulliken tried to get a qualitative survey over the sequence of the molecular states for all values of ρ by developing rules to correlate the states in the two limiting cases. They also sought for criteria making it possible to predict when there would result a minimum in the function V giving rise to binding.

As regards the correlation it is in the first place necessary that the quantum numbers Λ and S of the states to be correlated are the same; thus a $^3\Pi$-state arising from the separate atoms in given states upon the approach of these atoms must stay a $^3\Pi$-state for all values of ρ and must hence be represented by an energy curve V which in the limiting case of the united atom also stands for a $^3\Pi$-state. In addition the symmetry properties of the molecular states discussed in

section 25 must be conserved during the correlation. Thus Σ^+-states in the one limiting case must be joined on to Σ^+-states in the other limiting case, while Σ^--states can only be connected with Σ^--states. For molecules with equal nuclei there is in addition the classification of all electronic states as even and odd. In the correlation even states can only be connected with even states, odd states with odd states.

These rules are, of course, not sufficient to establish a unique correlation. Hund(47), Herzberg(3) and Mulliken(57) have therefore taken recourse to the method of electronic configurations, described under (*c*) of section 26, in which the individual electrons are thought of as uncoupled and are each characterised by quantum numbers. On the basis of this viewpoint the quantum number λ for every electron must stay unchanged during the correlation just as above the quantum number Λ for the molecule as a whole had to remain unaltered. Besides, for molecules with equal nuclei and—with a certain lack of rigour—for molecules with nuclei of not too different atomic number, one can distinguish between even and odd electrons, indicating this property by writing, e.g., σ_g, π_u, etc., for a σ-electron with even wave function, a π-electron with odd wave function, etc. In the following considerations it will prove advisable to discuss separately the diatomic hydrides, the molecules with equal or approximately equal nuclei and the other molecules.

(*a*) *Correlation for the diatomic hydrides.* In the diatomic hydrides MH one of the nuclei, the H-nucleus, has a much smaller charge than the other nucleus M and besides penetrates quite deeply into the electronic structure of its partner. To classify the individual electrons by means of the quantum numbers they take in the limiting case of the united atom, hence has a physical significance here.

Before formulating general results we shall first consider as example the formation of CH. The united atom is here an N-atom. Its most stable electronic configuration according to the table at the end of the book is $(1s)^2(2s)^2(2p)^3$ from which, according to table 4, there result the ground state ^4S, a slightly higher ^2D-state and a still somewhat higher ^2P-state. If we

separate the C- and the H-nucleus slightly, then according to section 26 (*b*) the ^4S-state gives a $^4\Sigma$-state, the ^2D-state a $^2\Sigma^-$-, a $^2\Pi$- and a $^2\Delta$-state, the ^2P-state a $^2\Sigma^+$- and a $^2\Pi$-state. At the same time the orbital angular momenta l of the individual electrons will tend to be space quantised with respect to the internuclear line, their component in that direction λ being capable of the one value 0 for the s-electrons so that these now become $s\sigma$-electrons, while for the p-electrons λ may be 0 or 1 so that we have to distinguish between $p\sigma$- and $p\pi$-electrons. We get the three electron configurations $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 2p\pi$, $(1s\sigma)^2(2s\sigma)^2 2p\sigma(2p\pi)^2$ and $(1s\sigma)^2(2s\sigma)^2(2p\pi^3)$ since, according to section 26 (*c*), there cannot be more than two $2p\sigma$-electrons. Remembering that $(1s\sigma)^2$, $(2s\sigma)^2$ and $(2p\sigma)^2$ are closed shells, we find that the configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 2p\pi$, according to table 11, gives rise to a $^2\Pi$-state of the molecule, the configuration $(1s\sigma)^2(2s\sigma)^2 2p\sigma(2p\pi)^2$ to a $^2\Sigma^+$-, a $^2\Sigma^-$-, a $^2\Delta$- and a $^4\Sigma^-$- state, the configuration $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$ again to a $^2\Pi$-state. We are thus led to associate the six molecular states found above with definite electron configurations in the following way.

$$\text{N-atom } (1s)^2(2s)^2(2p)^3 \begin{cases} {}^2P_u \begin{cases} {}^2\Pi & (1s\sigma)^2(2s\sigma)^2(2p\pi)^3 \\ {}^2\Sigma^+ & (1s\sigma)^2(2s\sigma)^2 2p\sigma(2p\pi)^2 \end{cases} \\ {}^2D_u \begin{cases} {}^2\Sigma^- & (1s\sigma)^2(2s\sigma)^2 2p\sigma(2p\pi)^2 \\ {}^2\Delta & (1s\sigma)^2(2s\sigma)^2 2p\sigma(2p\pi)^2 \\ {}^2\Pi & (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 2p\pi \end{cases} \\ {}^4S_u - {}^4\Sigma^- & (1s\sigma)^2(2s\sigma)^2 2p\sigma(2p\pi)^2. \end{cases} \tag{I}$$

In this scheme there is only one ambiguity; one might interchange the electron configurations for the two $^2\Pi$-states. We shall justify later on the choice here given.

We now consider the limiting case of the C-atom and the H-atom. The C-atom has as its most stable electronic configuration $(1s)^2(2s)^2(2p)^2$, giving rise to the ground state ^3P, a slightly higher ^1D-state and a still higher ^1S-state. The hydrogen atom we shall take in the ground state ^2S. On bringing the atoms together we shall obtain, according to the rules of section 26 (*a*), the following molecular states; from

^3P: $^2\Sigma^-$, $^2\Pi$, $^4\Sigma^-$ and $^4\Pi$; from ^1D: $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$; from ^1S: $^2\Sigma^+$, which we may represent by the scheme

$$\left.\begin{array}{l} {}^2\Sigma^+ - {}^1S_g \\ \left.\begin{array}{l} {}^2\Pi \\ {}^2\Sigma^+ \\ {}^2\Delta \end{array}\right\} {}^1D_g \\ \left.\begin{array}{l} {}^4\Pi \\ {}^2\Sigma^- \\ {}^4\Sigma^- \\ {}^2\Pi \end{array}\right\} {}^3P_g \end{array}\right\} \text{C-atom } (1s)^2(2s)^2(2p)^2 + \text{H-atom } 1s\,{}^2S. \quad \text{(II)}$$

Comparing the two schemes we see that the state $^4\Pi$ of scheme II is not present in scheme I. This molecular state, arising from the separate atoms, must hence necessarily be joined on to a state of the united atom N with an excited electronic configuration and therefore lying much higher than the states ^4S, ^2D, ^2P previously considered. One will thus expect the curve V of this $^4\Pi$-state to have no minimum but to be repulsive. Similarly there is in scheme I only one $^2\Sigma^+$-state while in scheme II there are two. One of the latter must hence also be repulsive. It must be the one starting from ^1S since according to Heitler and London the C-atom in this state should have no valence. The other states one will be inclined to join in pairs, arguing that the electrons originally present in the C-atom will retain their quantum numbers n, l when the H-nucleus is made to coincide with the C-nucleus, while the electron of the H-atom will tend to occupy the most firmly bound sort of state not yet fully occupied in the resulting N-atom, viz. a $2p$-state. Regarding the two $^2\Pi$-states let us join the lower one in scheme I, arising from ^3P, with the lower one in scheme II, arising from ^2D. For the upper $^2\Pi$-states there is, however, this difficulty that we have assigned it in scheme I the electron configuration $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$ while the electron from the H-atom in the limiting case of the separate atoms is a σ-electron with $\lambda = 0$. If the electrons were entirely independent, their values λ would have to be conserved so that the H-electron could not become a $2p\pi$-electron

in the united atom. From this standpoint it would hence not be permissible to join the upper two $^2\Pi$-states; on the contrary one is led to suppose that the upper $^2\Pi$-state of scheme I in the limiting case of separate atoms will correspond to a C-atom in its normal state and an H-atom in an excited state, while the upper $^2\Pi$-state of scheme II in the limiting case of the united atom will go over into an excited electron configuration of N and hence be repulsive. On the basis of the fact that the electrons in reality are not completely uncoupled Mulliken,

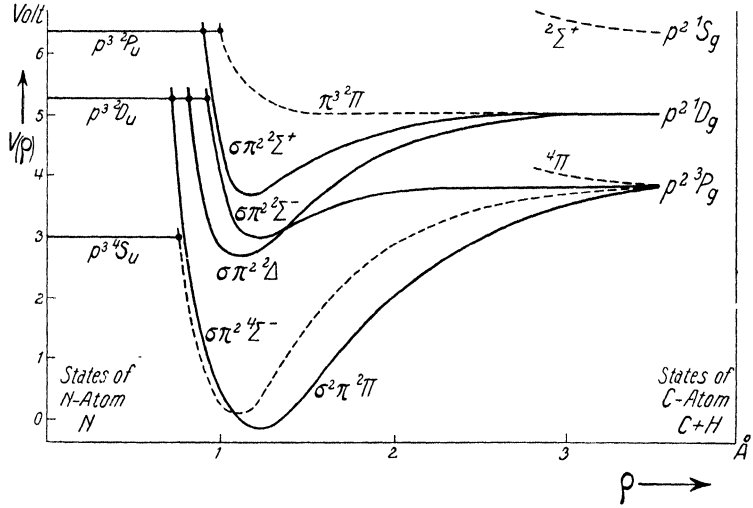


Fig. 38. Energy curves $V(\rho)$ for the molecule CH and their correlation to atomic states.

however, suggests that the two $^2\Pi$-states should nevertheless be joined.

In fig. 38 we have illustrated the conclusions just reached by the potential energy curves of CH obtained from the band spectroscopic data by means of the method of Morse (see section 21). The fully drawn curves represent states actually known, the dotted curves states to be expected according to the theory but not yet found. These are the states $^4\Pi$ and $^2\Sigma^+$ expected to be repulsive and hence not observable, the $^2\Pi$-state for which the correlation was doubtful and which, also on the viewpoint of Mulliken represented in the figure, should be

repulsive, and the state $^4\Sigma^-$. The latter probably has a curve V with pronounced minimum, but since it can only combine strongly with other quartet-states according to the selection rules for band spectra, it is not surprising that no bands involving it have as yet been discovered. On the right and left the atomic states for the separate and united atoms have been indicated, to which the energy curves V of the molecular states have been joined in agreement with the considerations given. The symbols p^2 and p^3 before the atomic states signify $(2p)^2$ and $(2p)^3$, i.e. the configuration of the atomic electrons not in closed shells. The symbols $\sigma^2\pi$, $\sigma\pi^2$, π^3 before the molecular states similarly signify $(2p\sigma)^2 2p\pi$, $2p\sigma(2p\pi)^2$, $(2p\pi)^3$ for these same electrons, the closed shell configuration $(1s\sigma)^2(2s\sigma)^2$ having been omitted. That the lower $^2\Pi$-state has the electron configuration $\sigma\pi^2$ and not π^3 can now also be justified. For this $^2\Pi$-state is experimentally found to be regular, meaning a certain sequence of its multiplet levels, and such a sequence can arise only from $\sigma\pi^2$, not from π^3.

The method employed in discussing the case of CH we may now generalise as follows for the other diatomic hydrides MH: Take the most stable electron configuration of the united atom and by the rules of section 26 (*b*) determine the different molecular states arising from each of the atomic states belonging to this configuration. Ascribe to the molecular states electron configurations in accordance with section 26 (*c*) (so far as this is possible). Then, according to section 26 (*a*), find the molecular states which each of the states of atom M, belonging to its most stable electronic configuration, gives when an H-atom in its ground state is added. Supposing that the electrons in the M-atom will retain their quantum numbers while the H-electron will tend to occupy as firm an orbit as possible in the united atom, join all states with equal $|\Lambda|$ and S and with equal symmetry in the two limiting cases. If there are several states of the same kind, join the lowest states on both sides, then the next higher, etc. Molecular states of the separate atom that cannot be correlated with molecular states of the united atom must go to excited electronic configuration of the united atom and will hence be repulsive. Utilise the experi-

mental data to control the assignment of electronic configurations in ambiguous cases.

In our example we saw that the electron of the H-atom, contained in a $1s$-state there, upon joining the two nuclei, became at least a $2p$-electron of the united atom (in the case of the repulsive states it would even have to become a $3s$- or $3p$-electron). This increase in its quantum number n is known as *promotion* of the electron. The concept of promotion will play an important part in the following considerations.

(*b*) *Molecules with equal or nearly equal nuclei.* For a molecule with equal (or nearly equal) nuclei, in passing from the limiting case of separate atoms to that of the united atom, half (or about half) of the electrons must undergo promotion, there being only half as many states of given quantum numbers n, l available in the united atom as in the separate atoms. Hund, Herzberg and Mulliken have tried to discuss the binding in such molecules by investigating the sequence of the different electronic shells as a function of the internuclear distance ρ. Herzberg, for this purpose, uses the correlation diagram shown in fig. 39. On the left and right are shown respectively the various types of states in which an individual electron may be bound in the case of the united atom ($\rho = 0$) and of the separate atoms ($\rho = \infty$), the notation being the one introduced in section 26 (*c*). The sequence of the states upwards is that of decreasing firmness of binding as it has been ascertained theoretically by Hund. That for $\rho = \infty$ one has a $\sigma_g 1s$- and a $\sigma_u 1s$-state of nearly the same energy, a $\sigma_g 2s$- and a $\sigma_u 2s$-state, also of nearly the same energy, etc., is due to the circumstance that the electron may be bound at either nucleus with the same energy so that the number of states $\sigma 1s$, $\sigma 2s$, etc., is doubled. The symmetry denoted by g and u has already been referred to in section 26 (*c*).

The procedure adopted in correlating states of individual electrons on left and right consists in conserving the value of λ and the symmetry, i.e. to join σ_g only to σ_g, π_u only to π_u, etc., and otherwise letting the correlation lines cross each other as little as possible. We then can read off immediately how a given type of electron in the case of separate atoms will be promoted

in the united atom. Thus an electron $\sigma_g 1s$ will not undergo promotion, remaining a $1s\sigma_g$ electron. A $\sigma_u 2s$ electron, however, will suffer promotion to $3p\sigma_u$. It is important to notice that an eventual promotion of an electron can become of physical significance only when the internuclear distance is so small that the description of the electron with the quantum numbers referring to the united atom begins to be justified. For the firmly bound electrons of the separate atoms, concentrated near the nuclei, that naturally happens at smaller

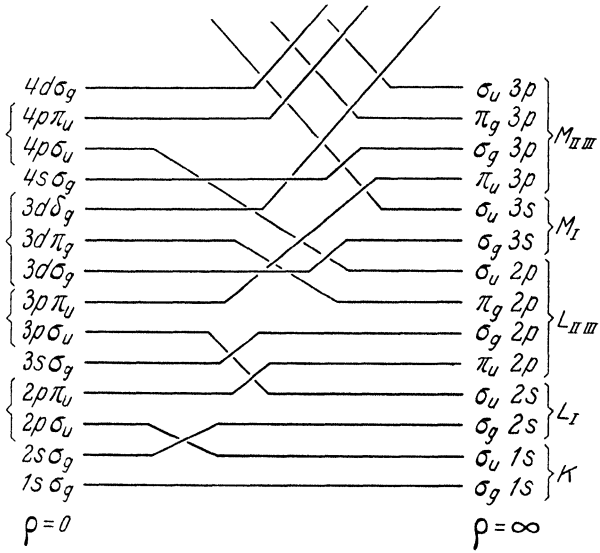


Fig. 39. Correlation diagram for the individual electrons in diatomic molecules with equal nuclei.

values of ρ than for the outer electrons. To indicate this, the crossings of the correlation lines in fig. 39 have been drawn more to the left for the lower states and more to the right for higher ones. The diagram of fig. 39, in addition to giving the correlation, indicates then also qualitatively how the energetic sequence of the different electronic shells will change when varying ρ.

To illustrate the use of the diagram of fig. 39 we consider as examples the interaction between two He-atoms, between two

Li-atoms and between two N-atoms, all in their ground state. A He-atom has as most stable electronic configuration $(1s)^2$. The four electrons of two He-atoms, when these are far apart, must hence be placed into the $\sigma_g 1s$- and the $\sigma_u 1s$-states, each of which can just take up two electrons. For large ρ we have thus the molecular state $(\sigma_g 1s)^2 (\sigma_u 1s)^2 \, {}^1\Sigma_g^+$ with all electrons in closed shells. Upon letting the nuclei approach and finally coincide we get from this configuration according to our diagram the configuration $(1s\sigma_g)^2 (2p\sigma_u)^2$ of the united atom, which is an excited configuration, $(1s\sigma_g)^2 (2s\sigma_g)^2$ being more stable. In analogy with the results for the hydrides in (*a*) we now understand that the interaction of the two He-atoms is repulsive. For two Li-atoms in their ground state $(1s)^2 \, 2s$ we have as possible molecular configuration for large ρ $(\sigma_g 1s)^2 (\sigma_u 1s)^2 (\sigma_g 2s)^2 \, {}^1\Sigma_g^+$, and this leads to $(1s\sigma_g)^2 (2s\sigma_g)^2 (2p\sigma_u)^2$ of the united atom, which is the most stable configuration of this atom. Similarly two N-atoms in their ground state $(1s)^2 (2s)^2 (2p)^3$ can give for large ρ the molecular configuration $(\sigma_g 1s)^2 (\sigma_u 1s)^2 (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 \, {}^1\Sigma_g^+$, which also leads to the most stable configuration of the united atom $(1s\sigma_g)^2 (2s\sigma_g)^2 (2p\sigma_u)^2 (2p\pi_u)^4 (3s\sigma_g)^2 (3p\sigma_u)^2$. It is hence not surprising that, in contrast to He, binding results in the last two cases, the ground state of the molecule being ${}^1\Sigma_g^+$ in accordance with table 8.

In order to formulate this state of affairs more precisely Herzberg and Mulliken distinguish between electrons, inactive and active in the molecule formation, depending upon whether their behaviour for the intermediate values of ρ actually encountered in a molecule is still practically the same as in the separate atoms or largely modified by their approach. E.g. in the case of Li_2 the first four electrons of the configuration $(\sigma_g 1s)^2 (\sigma_u 1s)^2 (\sigma_g 2s)^2 \, {}^1\Sigma_g^+$ are still practically in the condition of the K-electrons of the separate Li-atoms at the equilibrium distance $\rho_e = 2{\cdot}67$ Å of the molecule and hence do not affect the binding. Following Mulliken we shall denote such electrons simply by the letter of the shell to which they belong and speak of them as *non-bonding electrons*. For the active electrons, according to the definition of this concept, the quantum

numbers of the separate atoms no longer have any physical significance, but also those of the united atom are not usually realised even approximately. Mulliken therefore denotes these electrons by symbols like $x\sigma$, $y\pi$, etc., rather than by the symbols referring to the limiting cases of the separate or united atoms. He writes thus for the states of Li_2 and N_2 considered above:

$$Li_2: KK(z\sigma)^2\,{}^1\Sigma_g^+,$$
$$N_2: KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2\,{}^1\Sigma_g^+.$$

The active electrons fall into two groups, *bonding* and *anti-bonding electrons*. Anti-bonding electrons are those active electrons that contribute to make the electron configuration of the united atom an excited one, bonding electrons those that do not. In fig. 39 the correlation lines of the former for decreasing ρ go up, for the latter they go down. In He_2 we have a pair of bonding and a pair of anti-bonding electrons. In Li_2 there are four inactive electrons KK and a pair of bonding electrons. In N_2 the first four electrons KK are inactive, the following four probably only slightly active, and moreover half bonding, half anti-bonding, while the last six are all bonding electrons. One would be inclined in this picture to identify the number of pairs of bonding electrons diminished by the number of pairs of anti-bonding electrons with the number of valence bonds of chemistry. One thus gets for He_2 no valence bond, for Li_2 one valence bond, for N_2 three valence bonds in agreement with current notions.

For molecules with nearly equal nuclei the methods developed here are still approximately valid. There is only this difference that the distinction by the symmetry $g-u$ has no longer a rigorous physical significance. We shall discuss the question of binding for these molecules as well as for the other molecules with equal nuclei in section 29.

29. SURVEY OF ELECTRONIC CONFIGURATIONS OF DIATOMIC MOLECULES IN THEIR GROUND STATE

The method illustrated in section 28 (a) for the molecule CH can be applied to the other diatomic hydrides MH as well, leading in all cases to satisfactory agreement with experiment.

Just as for CH the electron configuration in these molecules is best described in terms of the quantum numbers referring to the united atom. In table 12 are given the electron configurations for the ground states, the electrons which already in the atom M occupied closed shells having been omitted.

TABLE 12

ELECTRON CONFIGURATIONS OF DIATOMIC HYDRIDES IN THE GROUND STATE

H_2	$(1s\sigma)^2\,{}^1\Sigma_g^+$	CdH	$(5s\sigma)^2\,5p\sigma\,{}^2\Sigma^+$
LiH	$(2s\sigma)^2\,{}^1\Sigma^+$	BaH	$(6s\sigma)^2\,6p\sigma\,{}^2\Sigma^+$
NaH	$(3s\sigma)^2\,{}^1\Sigma^+$	HgH^+	$(6s\sigma)^2\,{}^1\Sigma^+$
KH	$(4s\sigma)^2\,{}^1\Sigma^+$	HgH	$(6s\sigma)^2\,6p\sigma\,{}^2\Sigma^+$
BeH^+	$(2s\sigma)^2\,{}^1\Sigma^+$	BH	$(2s\sigma)^2\,(2p\sigma)^2\,{}^1\Sigma^+$
BeH	$(2s\sigma)^2\,2p\sigma\,{}^2\Sigma^+$	AlH	$(3s\sigma)^2\,(3p\sigma)^2\,{}^1\Sigma^+$
MgH^+	$(3s\sigma)^2\,{}^1\Sigma^+$	CH	$(2s\sigma)^2\,(2p\sigma)^2\,2p\pi\,{}^2\Pi$
MgH	$(3s\sigma)^2\,3p\sigma\,{}^2\Sigma^+$	SiH	$(3s\sigma)^2\,(3p\sigma)^2\,3p\pi\,{}^2\Pi$
CaH	$(4s\sigma)^2\,4p\sigma\,{}^2\Sigma^+$	NH	$(2s\sigma)^2\,(2p\sigma)^2\,(2p\pi)^2\,{}^3\Sigma^-$
ZnH^+	$(4s\sigma)^2\,{}^1\Sigma^+$	PH	$(3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^2\,{}^3\Sigma^-$
ZnH	$(4s\sigma)^2\,4p\sigma\,{}^2\Sigma^+$	BiH	$(6s\sigma)^2\,(6p\sigma)^2\,(6p\pi)^2\,{}^1\Sigma^+$
SrH	$(5s\sigma)^2\,5p\sigma\,{}^2\Sigma^+$	OH	$(2s\sigma)^2\,(2p\sigma)^2\,(2p\pi)^3\,{}^2\Pi$
CdH^+	$(5s\sigma)^2\,{}^1\Sigma^+$	HCl^+	$(3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^3\,{}^2\Pi$

Passing on now to other molecules, we have in the first place the upper part of table 13, containing molecules in which the electrons active in binding are those having in the separate atoms the principal quantum number $n = 2$. All these molecules have equal or nearly equal nuclei. The co-ordination of the symbols $z\sigma$, $y\sigma$, etc., to the quantum numbers in separate atoms with equal nuclei is indicated underneath this part of the table. Of the remaining molecules, only some of which have equal or nearly equal nuclei, those grouped together have band spectra resembling each other, and of the same type as the band spectra of one of the molecules or groups of molecules in the upper part of the table. Thus the spectra of Na_2, NaK, K_2 are like that of Li_2, those of SO, S_2, Te_2 like that of O_2. The explanation is to be found in the circumstance that after splitting off the configurations (RG) of the rare gases preceding the constituent atoms, which probably are inactive in the molecule formation, one retains for these molecules an equal number of active electrons (two for Li_2, Na_2, NaK, K_2, twelve for O_2, SO, S_2, Te_2). Moreover, the field exerted by the rare gas configurations in the molecules upon the active electrons

as long as they are outside will be very similar. Hence, we will write down for the active electrons similar quantum numbers, e.g. $(z\sigma)^2$ for Li_2, Na_2, NaK and K_2. The significance of z is, of course, different for them, just as in the isolated atoms Li, Na, K the one electron outside closed shells is an ns-electron with $n = 2, 3, 4$ respectively.

TABLE 13

ELECTRON CONFIGURATIONS OF DIATOMIC MOLECULES OTHER THAN HYDRIDES IN THE GROUND STATE

Li_2	$KK\,(z\sigma)^2\,{}^1\Sigma_g^+$
BeO	$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,{}^1\Sigma^+$
C_2	$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^3\,x\sigma\,{}^3\Pi$
BeF, BO, CO^+, CN, N_2^+	$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,x\sigma\,{}^2\Sigma^+$ (for $N_2^+\,{}^2\Sigma_g^+$)
CO, N_2	$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,{}^1\Sigma^+$ (for $N_2\,{}^1\Sigma_g^+$)
NO, O_2^+	$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,v\pi\,{}^2\Pi$
O_2	$KK\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,(v\pi)^2\,{}^3\Sigma_g^-$
$z\sigma \rightarrow \sigma_g 2s$ $y\sigma \rightarrow \sigma_u 2s$ $w\pi \rightarrow \pi_u 2p$ $x\sigma \rightarrow \sigma_g 2p$ $v\pi \rightarrow \pi_g 2p$	
Na_2, NaK, K_2	$(RG)\,(RG)\,(z\sigma)^2\,{}^1\Sigma^+$ (for Na_2, $K_2\,{}^1\Sigma_g^+$)
MgF, CaF, SrF, BaF, AlO, ScO, YO, LaO, SiN, CP	$(RG)\,(RG)\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,x\sigma\,{}^2\Sigma^+$
SiO, CS, PN, P_2	$(RG)\,(RG)\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,{}^1\Sigma^+$ (for $P_2\,{}^1\Sigma_g^+$)
NS	$K\,(RG)\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,v\pi\,{}^2\Pi$
SO, S_2, Te_2	$(RG)\,(RG)\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,(v\pi)^2\,{}^3\Sigma^-$ (for S_2, $Te_2\,{}^3\Sigma_g^+$)
Cl_2, BrCl, Br_2, ICl, IBr, I_2	$(RG)\,(RG)\,(z\sigma)^2\,(y\sigma)^2\,(w\pi)^4\,(x\sigma)^2\,(v\pi)^4\,{}^1\Sigma^+$ (for Cl_2, Br_2, $I_2\,{}^1\Sigma_g^+$)

Looking at the upper part of table 13 it is interesting to note how the different kinds of electron orbits are successively filled. As mentioned already in section 28 (b), the two $z\sigma$-electrons in Li_2 act as bonding electrons and correspond to one valence dash, the dissociation energy being rather small (1·14 volts). The molecule Be_2 is not known, since the following two electrons occupy the $y\sigma$-state, which is repulsive, and hence neutralise the action of the $z\sigma$-electrons. Next we have the $w\pi$-electrons and the $x\sigma$-electrons, both of the bonding type. They have approximately equal energy as shown by the electron configurations of BeO and C_2. On the basis of the

remarks at the end of section 28 we must speak here of a double valence bond, and accordingly the dissociation energy is also higher (5·5 volts for C_2) than for Li_2. In the following group, BeF, BO, etc., there is one more bonding electron so that it would be proper to speak of $2\frac{1}{2}$ valence bonds, while the dissociation energy lies between 6 and 7 volts. For N_2, discussed already in section 28 (*b*), as well as for CO we have three valence bonds and especially high dissociation energies (10 volts for CO). The electron $v\sigma$ added in going over to NO and O_2 is again of the anti-bonding type, with as consequence a smaller dissociation energy of about 6·1 volts, just as the electron added in going to O_2, further diminishing the dissociation energy to 5·09 volts and the number of valence bonds to two.

In some cases, where atoms in their ground state are only capable of repelling each other, molecules may be formed from the excited atoms. As soon, of course, as the energy of excitation is given up during an impact with other molecules or under emission of radiation, the molecule will dissociate spontaneously. These molecules are thus very short-lived, and known only from their spectra. The molecule He_2 is the most important example.

Other diatomic molecules not discussed hitherto, are the halides of the alkalies, of Cu, Ag, Au and of Tl. All these molecules in their ground state are heteropolar, as can be concluded from their spectra, the interpretation of which we postpone, however, to section 53 since they are not of a type previously mentioned.

Comparing now the theory of homopolar binding based upon the concept of electronic configuration with the theory of Heitler and London, we see that the former in several ways goes further in leading to an understanding of the empirical facts. The interpretation of the resemblence of isoelectronic molecules, and, more generally, of molecules with the same number of electrons active in binding, is perhaps the most important advantage. But also the possibility of dealing in a more satisfactory way with atoms in *P*-states and of getting a survey over the energy curves *V* arising from excited atoms should be

mentioned. The agreement of the two theories in many essential points must be sought in the fact that the electrons outside closed shells of the constituent atoms are the ones which function as bonding and anti-bonding electrons and at the same time those which contribute to the resultant spin of the atoms; the superiority of the theory of electronic configurations, on the other hand, is due to its using what may be termed an interpolation method, while the procedure of Heitler and London really is an extrapolation.

30. RAMAN EFFECT OF DIATOMIC MOLECULES

When radiation of a given frequency ν falls upon a diatomic molecule, it will be scattered. We consider first this scattering on the basis of classical theory. Let us imagine the nuclei of the molecule held fixed in space at their equilibrium distance ρ_e. The scattering arises then from the fact that the electrons in the molecule are periodically displaced in the rhythm of the incident light so that a dipole moment, also oscillating with frequency ν, is induced, giving rise to the emission of secondary waves of frequency ν, the *Rayleigh scattering*. If the electric vector of the incident radiation is given by

$$E = E_0 \cos 2\pi\nu t,$$

we may write for the induced dipole moment

$$p_i = \alpha_e E_0 \cos 2\pi\nu t, \qquad (30{\cdot}1)$$

where α_e, the polarisability of the molecule in its equilibrium position, is a measure for the ease with which its negative charge distribution can be deformed.

If we now allow the nuclei to vibrate along the line joining them, then we must remember that the polarisability will vary with the internuclear distance. For small elongations x of the molecule we may write for the polarisability

$$\alpha = \alpha_e + \alpha_1 x,$$

and this must be substituted into equation (30·1) for p_i instead of α_e. Taking the nuclear vibrations to be simple harmonic in first approximation, we have for x according to equation (21·4)

$$x = x_0 \cos 2\pi\omega_e t$$

so that we get

$$p_i = (\alpha_e + \alpha_1 x_0 \cos 2\pi\omega_e t)\, E_0 \cos 2\pi\nu t$$
$$= \alpha_e E_0 \cos 2\pi\nu t + \tfrac{1}{2}\alpha_1 x_0 E_0 [\cos 2\pi(\nu+\omega_e)t + \cos 2\pi(\nu-\omega_e)t].$$

The induced dipole moment contains now, in addition to the term already present formerly, new terms vibrating with the summation frequency $\nu+\omega_e$ and the difference frequency $\nu-\omega_e$. They give rise to scattered radiation with these frequencies, forming the *vibrational Raman spectrum*. Since there is no reason why α_1 should vanish for molecules with a symmetrical charge distribution, the vibrational Raman lines $\nu \pm \omega_e$ must appear also for such molecules in contrast to the vibration spectrum, which, as we saw in section 22, is absent for them.

If the vibration of the molecule is no longer simple harmonic, then, as mentioned in section 22, there appear in the expression for x also terms vibrating with frequencies $2\omega_e$, $3\omega_e$, ..., and hence in the vibrational Raman spectrum frequencies $\nu \pm 2\omega_e$, $\nu \pm 3\omega_e$, ... They will, however, in general be very weak, due to the small degree of anharmonicity.

We next consider what happens if, instead of allowing the nuclei of the diatomic molecule to vibrate along the line joining them, we let them rotate. In case the polarisability α_e is the same no matter what orientation the internuclear line has relative to the electric vector of the incident radiation, such a rotation will evidently not modify the induced dipole moment (30·1) and the scattering resulting from it. But since in reality one must distinguish between a polarisability α_π parallel to the internuclear line and another one α_σ perpendicular to it, which in general differ, the rotation will have the effect of giving rise in p_i to additional terms, vibrating with the frequency $\nu \pm 2\nu_{\text{rot}}$, where ν_{rot} is the rotational frequency. The appearance of $2\nu_{\text{rot}}$ instead of ν_{rot} is due to the circumstance that a rotation of the molecule through 180° is sufficient to bring about the original condition in the polarisability. One may say that the change in polarisability rotates twice as fast as the molecule. Since classically at room temperature all frequencies of rotation are present in a gas of diatomic mole-

cules, the *rotational Raman spectrum* will consist of two continuous branches to the right and left of the frequency ν, the one with $\nu - 2\nu_{\text{rot}}$ being known as the O-branch, the other with $\nu + 2\nu_{\text{rot}}$ as the S-branch. Here, too, there is no reason why this spectrum should be absent for molecules with a symmetrical charge distribution, in contrast to the rotation spectrum discussed in section 22.

Passing on to a molecule that may both vibrate and rotate, we expect a *vibration-rotation Raman spectrum* in which, besides each of the lines $\nu \pm \omega_e$, $\nu \pm 2\omega_e$, ..., in the vibration Raman spectrum, we get on both sides of these lines continuous branches of the type just discussed.

It remains now to translate these results into the quantum language. Here, as first pointed out by Smekal(67), the change in frequency of the scattered radiation must be accompanied by an energy change of the scattering molecule, i.e. by a quantum jump. The modified frequency ν' must be connected with the incident frequency ν by the relation

$$\nu' = \nu + \nu_{j'j''},$$

where $\nu_{j'j''}$ is the frequency corresponding to a transition of the scattering molecule from its stationary state j' to another stationary state j''. If j'' lies below j', the frequency shift $\nu_{j'j''}$ according to the frequency relation (2·2) is positive, otherwise negative. If the frequency shift $\nu_{j'j''}$ represents a change in rotational state only, we have a rotational Raman line, while if there is also a change in vibration, we obtain a vibrational Raman line. As regards the change of rotational quantum number J in going from j' to j'', the quantum mechanical analogue of the classical result is the selection rule that J may change only by ± 2 units (at least for molecules in $^1\Sigma$-states). In the vibrational Raman effect J may also stay unchanged, while the vibrational quantum number by preference will change there by one unit. If, on the basis of section 21, we take the vibrational and rotational energy for the ground state of the molecule as being given approximately by

$$\frac{W_{vJ}}{h} = \omega_e(v + \tfrac{1}{2}) + B_e(J + \tfrac{1}{2})^2,$$

we get for the rotational Raman spectrum

$$\begin{aligned} &\nu' = \nu - 2B_e(2J+3), && O\text{-branch},\\ &\nu' = \nu + 2B_e(2J+3), && S\text{-branch}, \end{aligned} \qquad J = 0, 1, 2, \ldots$$

while we have for the vibrational Raman spectrum

$$\begin{aligned} &\nu' = \nu - \omega_e - 2B_e(2J+3), && O\text{-branch},\\ &\nu' = \nu - \omega_e, && Q\text{-branch},\\ &\nu' = \nu - \omega_e + 2B_e(2J+3), && S\text{-branch}, \end{aligned} \qquad J = 0, 1, 2, \ldots$$

if we restrict our attention to the change of v by one unit and remember that at ordinary temperatures $v = 0$ for practically all molecules so that it can only change to $+1$. Of the frequencies in the vibrational Raman effect the one at $\nu - \omega_e$ is much stronger than the others since the molecules in all rotational states contribute to it, and therefore this is usually the only one observed.

The importance of the Raman spectrum lies especially in the fact that it also occurs for homonuclear molecules, which, according to sections 22 and 23, have no rotation and vibration-rotation spectra. Hence, it may be used to supplement the evidence derived from electronic bands, regarding the energy of vibrational and rotational levels in the ground state, and for a confirmation of the values of ω_e and B_e thus obtained. Researches of this sort have actually been carried out on HCl by Wood and on H_2, N_2, O_2, CO by Rasetti (for literature see (6) and (10)) and, more recently, on CO by Amaldi(18). Really essential, however, is the Raman effect in analysing the possible vibrations of polyatomic molecules, as we shall see in the next chapter. For such molecules very rarely have sharply defined electronic bands, while the rotation and vibration-rotation data usually are insufficient to arrive at a unique description of the molecular behaviour.

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CHAPTER V

BAND SPECTRA AND CHEMICAL BINDING IN POLYATOMIC MOLECULES

31. GENERAL REMARKS

It has been pointed out in section 20 that in the case of diatomic molecules the investigation of the chemical binding falls into two parts: viz. on the one hand the collection from band spectra of numerical data, characteristic for the different molecules, such as the equilibrium distances, the vibration frequencies, the dissociation energies of the different electronic states, and more especially of the ground state; on the other hand the interpretation, on the basis of wave mechanics, of the energy curves V, derived from these data, and their relation to the concepts of chemistry. For polyatomic molecules it is advisable to adhere to this same division of labour, although there are some notable differences compared with the case of diatomic molecules.

In the first place, as mentioned already in section 30, electronic bands with well-defined vibrational and rotational structure are known for hardly any polyatomic molecules, diffuse continuous spectra in general taking their place. (The reasons for this will be discussed in chapter VI.) As a consequence nearly all the information regarding polyatomic molecules must be obtained from rotation spectra, vibration-rotation spectra and Raman spectra. These, however, permit us to draw conclusions only about the vibrational and rotational levels of the ground state so that practically nothing is known about the excited electronic states. More precisely they refer only to the lowest vibrational levels since the vibrational quantum numbers, which for the majority of the molecules are 0 at ordinary temperatures, change at most a few units in these spectra. It is hence impossible in general to determine spectroscopically the dissociation energies and the nature of the dissociation products by the method used in section 21 for

diatomic molecules as this presupposes a whole sequence of vibrational levels to be known. As numerical data obtainable from the band spectra of polyatomic molecules there remain the *internuclear distances* in the equilibrium configuration, determining also the *shape* of the molecule, and the *vibration frequencies* about this equilibrium configuration.

The approach to the question of binding from the theoretical side is made more difficult by the fact that, excepting for rectilinear molecules, there no longer exists an axis of rotational symmetry, so that the introduction of quantum numbers with a simple physical significance for the molecule as a whole or for the individual electrons cannot be accomplished in so satisfactory a manner as for diatomic molecules. The field of chemical evidence to be explained, on the other hand, is much wider since for polyatomic molecules we not only have to account for the existence of compounds of a certain chemical composition and the non-existence of others, but also for the occurrence of *isomers*, the *directed* nature of the *valences* and the phenomena of *free* or partially free *rotation* of radicals around a chemical bond. It is therefore not surprising that the present stage of theory and experiment for polyatomic molecules is in many ways more summary and qualitative than for diatomic molecules.

32. NORMAL VIBRATIONS. VIBRATIONAL LEVELS. SYMMETRY PROPERTIES

Just as in the case of diatomic molecules the discussion of the motion of polyatomic molecules starts from the fact that we may replace with considerable approximation the influence of the electrons upon the nuclei and of the nuclei upon each other by a potential energy function V depending only upon the relative co-ordinates of the nuclei. For a certain configuration of the nuclei there must be equilibrium, i.e. V must have there a minimum or, what comes to the same thing, the forces acting upon all the nuclei must be zero. In analogy to the treatment of diatomic molecules we shall confine our attention at first to motions of the nuclei in which they stay near the *equilibrium*

configuration. We may write then for the restoring forces $X_1, Y_1, Z_2; X_2, Y_2, Z_2; \ldots$ acting upon the nuclei 1, 2, ... in the direction of three rectangular co-ordinate axes

$$\left.\begin{aligned} X_1 &= \kappa^{11}_{xx}x_1 + \kappa^{11}_{xy}y_1 + \kappa^{11}_{xz}z_1 + \kappa^{12}_{xx}x_2 + \ldots \\ Y_1 &= \kappa^{11}_{yx}x_1 + \kappa^{11}_{yy}y_1 + \ldots \\ Z_1 &= \kappa^{11}_{zx}x_1 + \kappa^{11}_{zy}y_1 + \ldots \\ X_2 &= \kappa^{21}_{xx}x_1 + \kappa^{21}_{xy}y_1 + \ldots \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right\}, \quad (32{\cdot}1)$$

where $x_1, y_1, z_1; x_2, y_2, z_2; \ldots$ are the displacements of the nuclei from their equilibrium positions in the three co-ordinate directions and the κs constant factors. In other words the forces may be taken to be linear functions of the displacements so that we can speak again of harmonic binding.

In spite of this simple character of the restoring forces the general motion of the nuclei will still be very involved. It is possible, however, to find certain simple types of motion, the *normal vibrations*, in which all the nuclei oscillate harmonically along straight lines through their equilibrium positions with the same frequency and with the same phase (passing at the same instant through their equilibrium positions and through their extreme positions). In such a type of motion it is evidently necessary that acceleration and displacement stand in the same ratio $-\lambda$ for all nuclei. (We write $-\lambda$, since the acceleration must be opposite to the displacement.) But the forces $X_1, Y_1, Z_1; X_2, \ldots$ are proportional to the accelerations, viz. equal to $M_1\ddot{x}_1, M_1\ddot{y}_1, M_1\ddot{z}_1; M_2\ddot{x}_2, \ldots$, where $M_1, M_2, \ldots$ are the masses of the nuclei. Taking this into account we get for a normal vibration from the equations (32·1)

$$\left.\begin{aligned} -\lambda M_1 x_1 &= \kappa^{11}_{xx}x_1 + \kappa^{11}_{xy}y_1 + \kappa^{11}_{xz}z_1 + \kappa^{12}_{xx}x_2 + \ldots \\ -\lambda M_1 y_1 &= \kappa^{11}_{yx}x_1 + \kappa^{11}_{yy}y_1 + \ldots \\ -\lambda M_1 z_1 &= \kappa^{11}_{zx}x_1 + \kappa^{11}_{zy}y_1 + \ldots \\ -\lambda M_2 x_2 &= \kappa^{21}_{xx}x_1 + \kappa^{21}_{xy}y_1 + \ldots \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right\}. \quad (32{\cdot}2)$$

If there are N nuclei, this is a system of $3N$ linear homogeneous equations with the $3N$ unknowns $x_1, y_1, z_1; x_2, \ldots$, which will have a solution different from zero only if the determinant of

the coefficients vanishes. Putting hence this determinant zero, we get an algebraic equation of the $3N$th degree for the unknown λ, giving $3N$ values of λ, which we shall call $\lambda_1, \lambda_2, \ldots$. Each of these values λ, which can be proved to be real and positive or zero, belongs to one normal vibration so that there are $3N$ normal vibrations. The normal vibration corresponding to λ_k, say, has a frequency given by

$$\omega_k = \frac{1}{2\pi}\sqrt{\lambda_k}. \qquad (32{\cdot}3)$$

This may be seen by writing down the equations of motion. We have

$$\ddot{x}_1 = \frac{X_1}{M_1} = -\lambda_k x_1, \quad \ddot{y}_1 = \frac{Y_1}{M_1} = -\lambda_k y_1, \ \ldots$$

with the solutions

$$x_1 = x_1^0 \cos 2\pi\omega_k (t - t_0), \quad y_1 = y_1^0 \cos 2\pi\omega_k (t - t_0), \ \ldots, \ (32{\cdot}4)$$

where ω_k is related to λ_k by equation (32·3) while $x_1^0, y_1^0, \ldots, t_0$ are constants. ω_k hence is the frequency of vibration. Substituting the expressions (32·4) into the linear equations (32·2), the cos drops out as a common factor, and the resulting equations determine the ratio of the amplitudes $x_1^0, y_1^0, \ldots$ and thereby also the relative sizes and directions of the displacements of the various nuclei at every instant, i.e. the form of the normal vibration. The absolute size of the amplitudes, however, is arbitrary since multiplication of all the expressions (32·4) by the same constant factor does not destroy their property of being a solution of the equations of motion with the character of a normal vibration.

The great importance of the normal vibrations of the molecule lies in the fact that, due to the linear character of the equations of motion, the most general form of motion of the nuclei is a simple superposition of the normal vibrations, each taken with a suitable amplitude. In the preceding considerations we have tacitly assumed that the values $\lambda_1, \lambda_2, \ldots$, and hence the frequencies $\omega_1, \omega_2, \ldots$, are all different. It may happen, however, that the determinantal equation, furnishing the values of λ, has multiple roots. Then there are several normal vibrations with the same frequency, which are said to

form together a *degenerate normal vibration*. The multiplicity of the corresponding root λ is called its *degree of degeneracy*. Thus one speaks of doubly, triply, ... degenerate normal vibrations. As an illustration from ordinary mechanics may be mentioned a point mass suspended on a string. Such a mass can oscillate as a pendulum in two perpendicular planes with the same frequency, and its general motion (always of course for small amplitudes of vibration) is a superposition of these two normal vibrations, which according to the above form together a doubly degenerate normal vibration. Examples of degenerate normal vibrations in the case of molecules we shall encounter later on when discussing the individual substances.

Among the normal vibrations of a molecule there are contained as special cases the three *translations* in the directions of the co-ordinate axes and the *rotations* of the system as a whole. To them there corresponds the value $\lambda = 0$ and hence according to equation (32·3) the frequency $\omega = 0$ since there are no restoring forces for these types of motion. The value $\omega = 0$ for both these forms of motion may at first sight seem strange. It must be remembered, however, that in our derivations we have supposed the nuclei never to deviate much from their equilibrium positions of rest in the course of their motion, and this really is the case only for infinitely slow translations and rotations. The translations and rotations are hence spoken of as *non-genuine normal vibrations*. All molecules have three translational degrees of freedom, while linear molecules have two, all other molecules three rotational degrees of freedom. For the former the root $\lambda = 0$ is fivefold, so that there remain for them $3N - 5$ *genuine normal vibrations*. For the latter the root $\lambda = 0$ is sixfold so that here we have $3N - 6$ genuine normal vibrations.

The translational energy of a molecule is of no interest in spectral problems since it does not change during radiative transitions. Just as for diatomic molecules in section 21 we shall for the moment disregard the rotational energy. The genuine normal vibrations, as we have seen, are simple harmonic and independent, the general motion of the molecule being a superposition of them, and the quantum theory teaches

then that each one contributes to the total vibrational energy W_v an expression of the type which we have encountered in section 21 for the harmonic oscillator. Hence we have for W_v

$$\frac{W_v}{h} = \sum_k \omega_k (v_k + \tfrac{1}{2}), \quad v_k = 0, 1, 2, \ldots, \tag{32·5}$$

where the v_k are the *vibrational quantum numbers* while the sum extends over all the genuine normal vibrations. If the amplitudes of vibration become large, the expression (32·5) has to be supplemented by terms with higher powers of the v_k just as was the case with diatomic molecules (see section 21). As the nature of these supplementary terms depends upon the type of molecule, we shall discuss them later in connection with various examples.

The nuclear configuration of many polyatomic molecules in the equilibrium state has symmetry properties. In the first place there may exist *symmetry planes* such that the mirror image of the molecule at such a plane cannot be distinguished from the molecule itself. Then there may exist *symmetry axes* such that upon rotating the molecule about the axis through an angle $2\pi/n$ the new configuration is indistinguishable from the original one. Depending upon whether $n = 2, 3, \ldots$, one speaks of a twofold, threefold, ... axis of symmetry. Finally there may exist a *centre of symmetry*, i.e. a point such that when the mirror image of all the nuclei with respect to this point is taken, the resulting configuration is indistinguishable from the initial state of the molecule. Symmetry planes, symmetry axes and symmetry centres are called *elements of symmetry*.

When the nuclei of the molecule perform a normal vibration, we shall naturally inquire how the various symmetry operations will affect the character of this vibration. It is obvious that the motion resulting from a normal vibration after performing a symmetry operation is again a normal vibration. For the nuclei will still all be oscillating with the same frequency and phase along straight lines through their equilibrium points. If the normal vibration is such that the configuration of the molecule, even in its deformed state, is not changed by a symmetry operation, then we call it *symmetrical* with respect

to this symmetry operation. A normal vibration symmetrical with respect to all possible symmetry operations we speak of as a *totally symmetrical* normal vibration. As an example we show in fig. 40 a linear symmetric triatomic molecule with two equal nuclei in the extreme positions. It has the plane through the central atom at right angles through the internuclear line as symmetry plane, and the internuclear line as symmetry axis (with $n = \infty$, since a rotation through an arbitrary angle around this axis leaves the molecule as it is). Also the midpoint

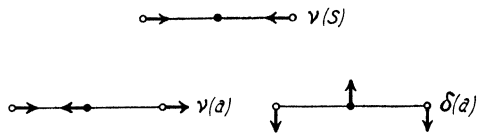


Fig. 40

is a symmetry centre. We see then that the normal vibration ν (*s*) represented by fig. 40 is totally symmetric. If on the other hand a certain symmetry operation changes the motion into its opposite, we say that the normal vibration is *anti-symmetrical* with respect to this symmetry operation. An example is the normal vibration ν (*a*) shown in fig. 40 which is anti-symmetrical with respect to reflection at the symmetry plane (and at the symmetry centre) mentioned above. Finally it may happen that by a symmetry operation a normal vibration is changed into another normal vibration. Since the latter must have the same frequency as the former, this can only happen in the case of degenerate normal vibrations. The normal vibration δ (*a*) of fig. 40 is an example. For a rotation of the deformed molecule around the symmetry axis previously mentioned gives a new form of motion, the nuclei vibrating now in a different plane.

33. MOLECULAR FORCE MODELS

For diatomic molecules the knowledge of the vibrational frequency permits us immediately to determine the force constant κ_2 in the expression (21·1) for $V(\rho)$, κ_2 and ω_e being connected by the equation (21·2). In a polyatomic molecule

we have not one but several force constants κ characterising the potential energy V for small displacements of the nuclei from their equilibrium configuration according to equation (32·1), and in general their number will be greater than the number of normal frequencies. That means that if the normal frequencies are known, the force constants are thereby not uniquely determined. Different systems of force constants may give exactly the same normal frequencies. If we nevertheless wish to determine the potential energy V for small displacements from the normal frequencies, we must make additional assumptions about the character of the forces.

One such assumption, of a very plausible nature, is that if in a molecule with an element of symmetry we perform a deformation accompanied by certain restoring forces, then the deformation arising from the first one by the symmetry operation will be accompanied by restoring forces arising from the original ones by the same symmetry operation. This assumption, of course, reduces the number of constants κ in the potential energy V.

Repeated attempts(54) have also been made to arrive at a potential energy function by presupposing that the forces between the different nuclei are central, i.e. directed along the lines joining them. Since for a molecule with N nuclei there are $\frac{1}{2}N(N-1)$ connecting lines, we would then have just as many force constants κ, while the number of normal frequencies, as we have seen, is in general $3N-6$. For $N=3$ and $N=4$ the number of κs would then be equal to the number of ωs so that a determination of the κs becomes possible, while for $N>4$, in the absence of symmetry properties the κs even here are no longer uniquely determined. In practice it has appeared, however, that the *central force model* is not very suitable for describing the vibratory motion of polyatomic molecules.

Mecke(4, 122) has therefore suggested what may be conveniently called a *valence force model*. In it the potential energy is assumed to be of the following kind: When the distance between two atoms joined by a valence bond is changed, there shall appear restoring forces along this valence bond, the *valence forces*; when, on the other hand, the angle between two

valence bonds ending on the same atom is changed by the displacement, there shall appear restoring forces at right angles to these valence bonds, the *deformation forces*. The potential energy then contains $3N-6$ constants, i.e. just as many constants as there are normal frequencies. In aliphatic compounds for example, where the atoms connected by valence bonds do not form rings, there are $N-1$ valence bonds which may be stretched and hence $N-1$ constants characterising the valence forces; and furthermore $2N-5$ independent angles between valence bonds with an equal number of constants characterising the deformation forces. For the types of molecules contained in table 14 one can easily ascertain this directly. Experience has shown the valence force model to be well adapted for dealing with the vibrations of most polyatomic molecules. In some cases, e.g. for the halogen derivatives of methane, there is evidence that atoms not joined by valence bonds affect each other in a more complicated way than by the deformation forces between the valence bonds.

The equality of the number of force constants and of the number of normal frequencies is not the only advantage of the valence force model. Another advantage is the following: The experimental investigations have shown that in general the valence force constants are by a factor of the order of magnitude 10 greater than the deformation force constants. A consequence of this is that the subdivision of the forces into valence and deformation forces brings about a classification of the normal vibrations into valence and deformation vibrations. In the *valence vibrations*, the frequencies of which we shall henceforth denote by the letter ν, the motion of the atoms takes place essentially in the direction of the valence bonds. In the *deformation vibrations*, on the other hand, the frequencies of which we shall call δ, the direction of displacement is essentially at right angles to the valence bonds. For complicated molecules (chain molecules) a type of normal vibration may occur which requires special attention, viz. a *torsional vibration* of two radicals with respect to each other around a valence bond. An example in table 14 is the molecule X_2Y_4, where a torsional vibration of the two groups XY_2 may take place

about the valence bond between the atoms X. Usually these torsional vibrations have low frequencies ω_t, lower even than the ordinary deformation vibrations, so that already at ordinary temperatures they will be excited by the thermal

TABLE 14

NORMAL VIBRATIONS OF SIMPLE POLYATOMIC MOLECULES

Type of molecule	Type of normal vibrations	Examples
$Y-X-Y$	$\nu\,(s)$, $\nu\,(a)$, $\delta\,(a)$ double	CO_2, CS_2
$Z-_1X-_2Y$	ν_1, ν_2, δ double	N_2O, HCN, OCS
$Y-_1X-_0X-_1Y$	$\nu_0\,(s)$, $\nu_1\,(s)$, $\nu_1\,(a)$ $\delta\,(s)$, $\delta\,(a)$ both double	C_2H_2, C_2N_2 (?)
	$\nu\,(\pi)$, $\nu\,(\sigma)$, $\delta\,(\pi)$	H_2O, H_2S, NO_2 SO_2, ClO_2, O_3
	$\nu\,(\pi)$, $\delta\,(\pi)$ $\nu\,(\sigma)$, $\delta\,(\sigma)$ both double	NH_3, PH_3, AsH_3 PCl_3, PBr_3, $AsCl_3$, $SbCl_3$, $BiCl_3$
(regular pyramid)		
	$\nu_1\,(\pi)$, $\nu_2\,(\pi)$, $\nu_2\,(\sigma)$ $\delta_2\,(\pi)$, $\delta\,(\sigma)$, $\delta'\,(\sigma)$	H_2CO, Cl_2CO (?) S_2Cl_2 (?), Cl_2SO (?)
	$\nu\,(s)$ $\delta\,(s)$ double $\nu\,(a)$, $\delta\,(a)$ both threefold	CH_4, C (hal)$_4$ $SiCl_4$, $SiBr_4$, $TiCl_4$ $SnCl_4$, $SnBr_4$
(regular tetrahedron)		
	$\nu_1\,(\pi)$, $\nu_2\,(\pi)$, $\delta_2\,(\pi)$ $\delta_1\,(\sigma)$, $\nu_2\,(\sigma)$, $\delta_2\,(\sigma)$ all three double	H_2C (hal), HC (hal)$_3$ $HSiCl_3$, $OPCl_3$ (?)
(tetrahedron)		
	$\nu_1\,(\pi)$, $\nu_2\,(\pi)$, $\delta_1\,(\pi)$, $\delta_2\,(\pi)$ $\nu_1\,(\sigma)$, $\nu_2\,(\sigma)$, $\delta_1\,(\sigma)$, $\delta_2\,(\sigma)$ ω_t	H_2C (hal)$_2$ F_2CCl_2
(tetrahedron)		
	$\nu_1\,(\pi s)$, $\nu_1\,(\pi a)$, $\nu_0\,(\pi s)$ $\nu_1\,(\sigma s)$, $\nu_1\,(\sigma a)$, $\delta_1\,(\pi s)$, $\delta_1\,(\pi a)$ $\delta\,(\sigma s)$, $\delta\,(\sigma a)$, $\delta'\,(\sigma s)$, $\delta'\,(\sigma a)$ ω_t	C_2H_4, C_2Cl_4

motion with considerable amplitudes or even may have gone over into a rotatory motion. To treat them as small displacements of the nuclei from the equilibrium configuration will then no longer be justified. To the importance of these torsional vibrations for some phenomena we have drawn attention already in section 9 (*d*).

In order further to distinguish the different normal vibrations we shall number the various valence bonds in the molecule. Then we shall call, e.g., the valence vibration in which the length of the valence bond 1 is the one most affected ν_1. For symmetrical molecules, where several bonds are equivalent, this method of classification can no longer be used since a normal vibration will affect all the equivalent bonds in the same way. Here, however, we can proceed as follows, depending upon whether the molecule possesses a centre or an axis of symmetry. In the case of a centre of symmetry we shall use the letters s and a to denote vibrations symmetrical and antisymmetrical respectively with respect to the centre; we write, e.g., $\nu(s)$ or $\delta(a)$. In the case of an axis of symmetry we can distinguish between parallel and perpendicular vibrations, depending upon whether the symmetrically located atoms all move symmetrically in planes through the axis so that their centre of gravity moves parallel to the axis, or whether this centre of gravity oscillates essentially at right angles to this axis. Parallel vibrations we shall denote by π, perpendicular ones by σ, so that we write, e.g., $\nu(\pi)$ or $\delta(\sigma)$.

In table 14, due to Mecke(6), are contained the equilibrium configurations of the simpler kind of molecules, the nature of the normal vibrations and the most important representatives of each type, which we shall discuss in detail later on. The remarks "double" and "threefold" refer to normal vibrations which on account of symmetry properties of the molecule are doubly or triply degenerate.

34. ROTATIONAL LEVELS

In the section 32 we have expressed in equation (32·5) the energy which the genuine normal vibrations of a polyatomic molecule contribute in the absence of rotation. Before considering the simultaneous presence of vibration and rotation we shall first discuss the simpler problem that all the nuclei are kept at their equilibrium distances and that the molecule rotates as a rigid body.

A rigid molecule possesses three mutually perpendicular axes A, B and C through its centre of gravity, the principal

axes of inertia, such that when the molecule is set rotating about them, they retain their position in space (absence of wobbling). The moments of inertia around these axes are known as the principal moments of inertia and will be denoted by I_A, I_B, I_C. The first possibility is that the molecule is linear. Then the two moments of inertia I about perpendicular axes at right angles to the internuclear line and going through the centre of gravity of the molecule are equal while the moment of inertia about the internuclear line vanishes. For the rotational energy levels we get here the same expression as in the case of diatomic molecules (see section 21), namely

$$\frac{W_J}{h} = BJ(J+1) = -\tfrac{1}{4}B + B(J+\tfrac{1}{2})^2, \qquad (34{\cdot}1)$$

where B is connected with the moment of inertia I by

$$B = \frac{h}{8\pi^2 I} \qquad (34{\cdot}2)$$

while J is the *rotational quantum number*. J has the same physical significance as for diatomic molecules, $J(J+1)h^2/4\pi^2$ representing the square of the angular momentum of the molecule. Another simple case investigated by Hund(95) and Elert(66) is that due to the symmetry of the molecule

$$I_A = I_B = I_C = I,$$

causing the rotation to be that of a *spherical top*, the energy of rotation being given by the same expression (34·1) as for linear molecules. If $I_A = I_B \neq I_C$, the molecule rotates as a *symmetrical top* with an energy, which according to Reiche and Rademacher(144), Kronig and Rabi(103) is given by

$$\frac{W_{JK}}{h} = AJ(J+1) + (C-A)K^2 = -\tfrac{1}{4}A + A(J+\tfrac{1}{2})^2 + (C-A)K^2, \qquad (34{\cdot}3)$$

$$J = 0, 1, 2, \ldots, \quad K = -J, \; -J+1, \; \ldots, \; J-1, \; J,$$

$$A = \frac{h}{8\pi^2 I_A}, \quad C = \frac{h}{8\pi^2 I_C},$$

where we now have two rotational quantum numbers J and K, of which the first has the usual meaning while K measures the angular momentum about the axis C in units $h/2\pi$. If

$I_A \neq I_B \neq I_C$, the molecule rotates as an *asymmetrical top*. No closed algebraic expression can then be given for the rotational levels but only rather complicated relationships, investigated by Kramers and Ittmann(102) and by Klein(101). We postpone their discussion until later (section 39) when we shall require them in connection with the interpretation of the infra-red spectrum of H_2O.

In the case of diatomic molecules, as we have seen in section 21, the expression for the energy levels when vibration and rotation are simultaneously present is in first approximation the sum of the energies for the linear oscillator and the rigid rotator. For larger values of the vibrational and rotational quantum numbers the anharmonicity and the change in the moment of inertia due to the centrifugal forces makes itself felt in the form of small correction terms (the ones with α and D_e in equation (21·15)). In the case of polyatomic molecules, as shown by Teller and Tisza(162) and by Placzek and Teller(137), there appears another much larger effect due to the circumstance that in the case of degenerate normal vibrations the direction of motion of the nuclei relative to the equilibrium configuration is not uniquely determined but may lie in different planes (example of the pendulum in space in the previous section). When the molecule rotates, the coupling forces between the nuclei will try to keep the direction of vibration relative to the rotating equilibrium configuration the same while the Coriolis forces arising from the rotation, on the contrary, tend to preserve the direction in space. The competition of these two agencies brings about that in general the direction of vibration is not carried around with the rotational frequency, but may either lag behind or run ahead of the rotation. The ratio of the frequency with which the plane of oscillation rotates to that with which the molecule rotates we shall denote by ζ. It can then be shown that $|\zeta| \leqq 1$.

We shall illustrate this effect with an example given by Teller(10). If we have three heavy atoms A_1, A_2, A_3 (fig. 41) forming an equilateral triangle and attached to each other by strong forces while the light atom B is attached by elastic forces independent of the direction of displacement to the

centre of the triangle, then B can vibrate in any direction with the same frequency while the atoms A practically stay in their original position. If we now let the triangle rotate while B originally vibrated in the vertical direction (fig. 41 (a)), it will keep this direction in spite of the rotation of the triangle. On the other hand, if we have three light atoms A_1, A_2, A_3 (fig. 42) not attached to each other but bound only to the much heavier central atom B, then the motion shown in fig. 42 (a) will be a normal vibration. But the same is the case with the motions shown in fig. 42 (b), (c), and since all three have the

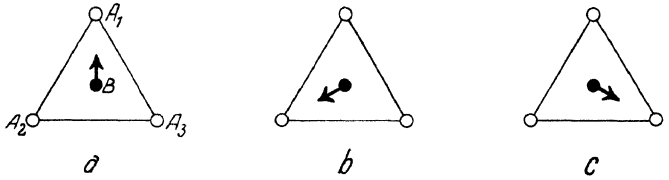


Fig. 41

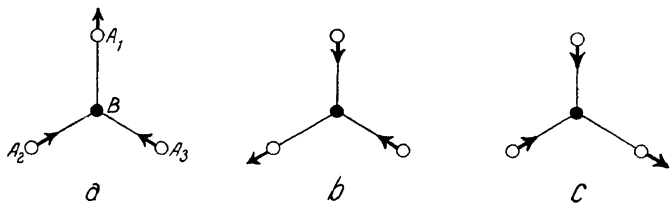


Fig. 42

same frequency for reasons of symmetry, we have here a motion of the same type of degeneracy as in fig. 41. In contrast, however, to the former case a rotation of the molecule will carry the plane of vibration with it now, the binding of each of the outer atoms to the central atom being exactly of the same kind as in a diatomic molecule so that $\zeta = 1$ while previously it was 0.

The effect just discussed does not influence the expression for the rotational energy in the case of linear molecules. For here the nuclei in the degenerate normal vibrations, as we saw in the example illustrated by fig. 40, move in planes at right angles to the internuclear line so that these planes are parallel

to the axis of nuclear rotation and hence carried around completely when the molecule turns. Nor is it of importance for asymmetrical top molecules because these have no degenerate normal vibrations. There remain then the spherical top molecules and the symmetrical top molecules. For the former only the triply degenerate normal vibrations are affected, for the latter all the doubly degenerate normal vibrations, with essentially this result that the separation of the rotational levels as given by the equations (34·1) and (34·3) appears to arise from moments of inertia different from the actual values.

35. VIBRATION-ROTATION SPECTRA AND RAMAN SPECTRA OF RECTILINEAR MOLECULES

The simplest polyatomic molecules are those the nuclei of which in the equilibrium configuration lie along a straight line. As we have seen in section 32, they have $3N-5$ genuine normal vibrations, N denoting the number of nuclei. As mentioned in section 33, following Mecke(4, 122), these may further be subdivided into *valence vibrations* in which the nuclei oscillate in the direction of the valence bonds, i.e. the direction of the internuclear line so that even the deformed molecule is linear, and *deformation vibrations* in which the displacements of the nuclei are at right angles to the internuclear line. In fig. 40 we have two examples of valence vibrations $\nu(s)$, $\nu(a)$, while $\delta(a)$ represents a deformation vibration. It can easily be seen that of the $3N-5$ normal vibrations for rectilinear molecules $N-1$ are valence vibrations, $2N-4$ deformation vibrations. The frequencies of these latter, however, are equal in pairs so that we may speak of $N-2$ doubly degenerate deformation vibrations. The reason for this, already mentioned in section 32 in connection with fig. 40, is that the deformation may take place in any plane through the internuclear line, and that the general deformation may be resolved into two independent deformation vibrations in mutually perpendicular planes in a similar way that the vibration of unpolarised light may be split into two linearly polarised components.

Considering next the vibration spectrum which the non-rotating molecule will emit according to classical theory it is important to distinguish between the molecules which, like the example shown in fig. 40, have a centre of symmetry and those which have not. For the latter we would expect, in analogy to the results for diatomic molecules in sections 22 and 30, that a change in the electric moment as well as in the polarisability accompanies each of the normal vibrations, the change having the same frequency as the mechanical motion. Hence, all the normal frequencies are *active*, i.e. occur, both in the vibration spectrum and in the Raman effect. For the molecules with a centre of symmetry, however, it is evident that for the normal vibrations symmetrical with respect to this centre (example fig. 40, $\nu(s)$) the electric moment, zero in the equilibrium configuration, remains zero even for the deformed molecules. Hence, these normal vibrations are *inactive* in the vibration spectrum. Conversely, the normal vibrations anti-symmetrical with respect to the centre (examples fig. 40, $\nu(a)$ and $\delta(a)$) will not give rise to a linear change in the polarisability; for the polarisability of the molecule in both extreme positions will be identical. In the Raman effect just those normal vibrations will hence be inactive which are active in the vibration spectrum. We see here for the first time, how the optical methods furnish a powerful means of obtaining information regarding the symmetry of polyatomic molecules.

If the binding of the nuclei may no longer be considered as linear in the displacements, there will occur, in addition to the *fundamental frequencies* ω_j, *harmonic* and *combination frequencies*, given approximately by

$$\nu = \Sigma \omega_j k_j, \qquad k_j = \text{integer}. \tag{35·1}$$

They naturally are much weaker in intensity than the fundamental frequencies. In molecules with a centre of symmetry a number of harmonic and combination frequencies, just as some of the fundamental frequencies, will be inactive as may be seen from a Fourier analysis of the motion. More precisely, in the vibration spectrum those frequencies are inactive for which the sum of the coefficients k_j in equation (35·1) belonging

to normal vibrations antisymmetrical with respect to the centre is even while in the Raman effect those are inactive for which this sum is odd.

It remains to inquire after the effect of rotation of the molecule upon the spectra. If only the valence vibrations are excited, there is no essential difference compared with the case of diatomic molecules so that we can take over the conclusions arrived at in sections 22 and 30. If, however, the deformation vibrations are excited, then the oscillating electric moment will also have a component at right angles to the internuclear line and hence along the axis of rotation. This brings about that in the emission or absorption spectrum of the molecule not only the frequencies $\omega \pm \nu_{\text{rot}}$ appear but also the unmodified vibrational frequency ω. By similar arguments in the Raman effect there will not only appear the frequency shifts $\pm 2\nu_{\text{rot}}$ but also $\pm \nu_{\text{rot}}$.

It is now easy to translate the classical results into the quantum language. Starting from equation (32·5) for the vibrational energy levels we get for the vibrational frequencies

$$\nu = \Sigma \omega_j \Delta v_j, \qquad (35{\cdot}2)$$

corresponding to transitions in which the vibrational quantum numbers change by amounts Δv_j. This formula is identical with equation (35·1), the Δv_j taking the place of the k_j. As pointed out by Dennison (55), the answer to the question as to which of these frequencies are active in the case of molecules with a centre of symmetry is the same as in classical theory.

In reality the frequencies (35·2) do not stand for isolated lines in the spectrum, but each one refers to a *vibration-rotation band*. For if we take into account the rotational energy as expressed in equation (34·1), we get for a given change in the vibrational quantum numbers a whole sequence of spectral lines corresponding to the various changes of the rotational quantum number. If one of the Δv, say Δv_j, is unity while the others vanish, we get a *fundamental band* in the neighbourhood of the frequency ω_j. If Δv_j is greater than one, while the remaining Δv vanish, we get a *harmonic band* in the neighbourhood of the frequency $\omega_j \Delta v_j$. If several of the Δv are different

from zero, we have a *combination band* in the neighbourhood of the frequency given by equation (35·2). The structure of the various bands is of the same kind as that discussed in section 22 for diatomic molecules. The reason is that apart from small correction terms the rotational energy according to sections 21 and 34 depends upon the rotational quantum number in the same way in both cases while also the selection rule that J may not change by more than one unit during radiative transitions is valid. One thus gets again a P-branch and an R-branch of almost equidistant lines. In case a deformation vibration is excited, there appears in addition a Q-branch corresponding to $\Delta J = 0$ and hence concentrated between the P- and the R-branch in the gap designated in section 23 as the "missing line". In the Raman spectrum we expect, next to changes of the v_j (subject to the selection rule of Dennison in the case of molecules with a centre of symmetry), changes of J by 0, ± 1, ± 2 units.

36. THE MOLECULES CO_2 AND CS_2

On no other polyatomic molecule, excepting perhaps H_2O, has so much work been done as on *carbon dioxide*, CO_2, the behaviour of which may now well be said to be fully understood. The character of the vibration-rotation spectrum leads definitely to the conclusion that this molecule is rectilinear and symmetrical, OCO, with the C-atom in the middle between the O-atoms. The rectilinear nature is confirmed by the fact that all the vibration-rotation bands, the rotational structure of which has been resolved, are of the same simple type already encountered for diatomic molecules and represented for HCl by fig. 33, some of the bands, however, having a Q-branch. As an example, we show two of the combination bands without Q-branch in fig. 43. For the symmetry of the molecule there are three independent arguments. In the first place the dipole moment of the molecule vanishes. Secondly we expect, according to the general results of the preceding section, four normal vibrations, viz. two valence vibrations in which the nuclei move along the line joining them, and one deformation vibration, to be counted twice on account of the degeneracy,

in which the nuclei move perpendicular to this line. If the equilibrium configuration of the nuclei is symmetrical, then the nature of these normal vibrations is just the one indicated in fig. 40, where the corresponding fundamental vibration frequencies have been denoted by $\nu_s(s)=\omega_1$, $\nu(a)=\omega_3$, $\delta(a)=\omega_2$, and according to the previous section we should find that ω_1 and, more generally, all combination frequencies for which $\Delta v_2+\Delta v_3$ is even should be absent in the vibration spectrum, as one indeed observes. If, on the other hand, the C-atom does not lie half-way between the O-atoms or if the

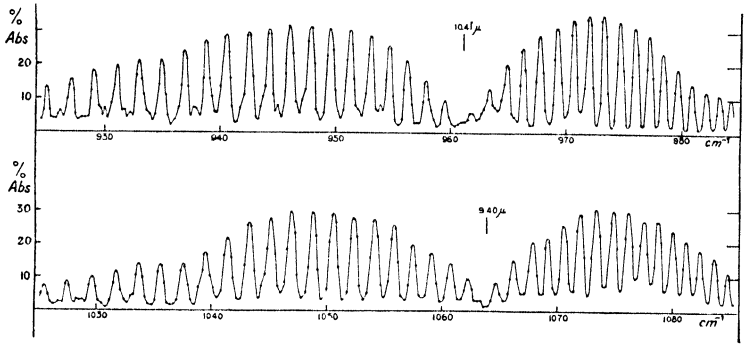


Fig. 43. Combination bands of CO_2 in absorption according to Barker and Adel (*Phys. Rev.* **44**, 185 (1933)).

molecule has the configuration COO, there would be no such limitation. Finally, a feature demanded by wave mechanics only for the symmetrical molecule and actually observed is the absence of alternate rotational lines in each band.

In order to account accurately for the position of the observed vibrational levels of CO_2, Adel and Dennison (13) have started from the following expression for the potential energy of the molecule:

$$\begin{aligned} V=&\tfrac{1}{2}h(\omega_1\sigma^2+\omega_2\rho^2+\omega_3\xi^2)\\ &+h(a\sigma^3+b\sigma\rho^2+c\sigma\xi^2)\\ &+h(d\sigma^4+e\rho^4+f\xi^4+g\sigma^2\rho^2+h\sigma^2\xi^2+i\rho^2\xi^2). \end{aligned} \quad (36{\cdot}1)$$

In this expression σ, ρ and ξ are given by

$$\sigma=2\pi\sqrt{\frac{\omega_1 M_O}{2h}}.q, \quad \rho=2\pi\sqrt{\frac{\omega_2 M}{h}}.r, \quad \xi=2\pi\sqrt{\frac{\omega_3 M}{h}}.z,$$

where M_O is the mass of an O-atom,

$$M = \frac{2M_O M_C}{2M_O + M_C},$$

with M_C representing the mass of the C-atom. q stands for the difference between the actual distance of the O-atoms from each other and their equilibrium distance, r for the perpendicular displacement of the C-atom from the equilibrium line of the molecule, z for the displacement of the C-atom from the centre of mass of the O-atoms measured parallel to the line joining these. The terms in the second and third lines of the expression (36·1) represent the anharmonic nature of the binding and are thus small correction terms of the sort that are neglected if the expression (32·5) is to hold accurately. They are, however, of great importance here, because, as appears from table 15, the valence vibration ω_1 has very nearly a frequency twice as great as that of the deformation vibration ω_2. There results then a strong *resonance* between the vibrational levels $v_1 = 1$, $v_2 = 0$, $v_3 = 0$ and $v_1 = 0$, $v_2 = 2$, $v_3 = 0$, due to the cubic and fourth degree terms in the expression (36·1) in spite of the fact that these terms in themselves are small. In consequence the vibrational levels are displaced considerably from the values given by the simple formula (32·5) and particularly the degeneracy of the deformation vibration is removed, an additional quantum number λ, measuring the angular momentum of the deformation vibration around the internuclear line, making its appearance, which in emission or absorption is subject to the selection rule $\Delta\lambda = \pm 1$ if Δv_2 is even, $\Delta\lambda = 0$ if Δv_2 is odd. Another consequence is that in the Raman effect the frequency ω_1, which, according to the elementary considerations of the preceding section, should be the only one present, is accompanied by the frequency $2\omega_2$, a circumstance first explained by Fermi(67) and discussed in greater detail by Dennison(56) and by Langseth and Nielsen(107). Using a perturbation calculus, Adel and Dennison could obtain satisfactory agreement between the vibrational levels which, according to wave mechanics, follow from the energy function (36·1) and the observed levels by assuming the values of the

constants given in table 15. For the constant d two values were found by different methods of computation.

To give an idea of the agreement between theory and experiment, table 16, taken from the paper of Adel and Dennison, shows the calculated energy values for the vibrational levels of CO_2, distinguished by the quantum numbers v_1, v_2, v_3, λ, up to 13,000 cm^{-1} together with the experimental energy values so far as these can be obtained from the observations. The agreement is very satisfactory.

TABLE 15

CONSTANTS OF THE CO_2-MOLECULE

$\nu(s)=\omega_1=1361$ cm^{-1}	$a=-36{\cdot}2$ cm^{-1}	$d=7{\cdot}8,\ 5{\cdot}3$ cm^{-1}	$g=-9{\cdot}9$ cm^{-1}
$\nu(a)=\omega_3=2378$,,	$b=72{\cdot}9$,,	$e=2{\cdot}0$,,	$h=7{\cdot}7$,,
$\delta(a)=\omega_2=673$,,	$c=-202{\cdot}1$,,	$f=2{\cdot}4$,,	$i=-12{\cdot}5$,,

TABLE 16

OBSERVED AND CALCULATED ENERGY VALUES FOR THE VIBRATIONAL LEVELS OF CO_2

v_1	v_2	v_3	λ	Energy cm^{-1} Calc.	Obs.	v_1	v_2	v_3	λ	Energy cm^{-1} Calc.	Obs.
0	1	0	1	667·9	667·5	0	6	1	0	6078	6079
						1	4	1	0	6233	6233
0	2	0	0	1286 3	1285·8	2	2	1	0	6352	6353
1	0	0	0	1387 9	1388·4	3	0	1	0	6512	6512
0	2	0	2	1335·8	1336·2	0	0	3	0	6974	6978
0	3	0	1	1933·2	1933 5	0	2	3	0	8188	—
1	1	0	1	2077·4	2077·1	1	0	3	0	8291	—
0	0	1	0	2350 1	2350·1	0	3	4	1	11050	—
						1	1	4	1	11193	—
0	2	1	0	3614	3610						
1	0	1	0	3716	3717	0	0	5	0	11496 5	11496·5
0	4	1	0	4852	4860	0	2	5	0	12672·4	12672·4
1	2	1	0	4982	4982	1	0	5	0	12774·7	12774·7
2	0	1	0	5109	5110						

The investigation of the rotational structure both of vibration-rotation bands and of the Raman effect leads to a determination of the constant B in equation (34·1) and hence according to equation (34·2) to a value for the moment of inertia I of the molecule in its equilibrium configuration. From

this the equilibrium distance ρ_{O-O} of the two O-atoms, which is twice the equilibrium distance ρ_{C-O}, is immediately found. From the combination bands Adel and Dennison(13) arrive at the value $I = 70{\cdot}1 \cdot 10^{-40}$ g.cm^2, in harmony with a value $I = 70{\cdot}2 \cdot 10^{-40}$ g.cm^2 obtained by Houston and Lewis(93) from the Raman effect. The corresponding value $\rho_{C-O} = 1{\cdot}15$ Å. This value again is in agreement with the value $\rho_{C-O} = 1{\cdot}1$ Å and 1·13 Å of sections 9 and 11, found by the X-ray and electron diffraction method respectively.

It is of interest to compare the CO-bond in CO_2 with the diatomic molecule CO. The distance $\rho_{C-O} = 1{\cdot}15$ Å in the former is practically identical with the distance $\rho_{C-O} = 1{\cdot}13$ Å in the latter. If the binding forces were acting only between the C-atom and the O-atoms, the binding energy between the C-atom and one of the O-atoms being given for small displacements by $\frac{1}{2}\kappa_2(\rho - \rho_{C-O})^2$ in analogy with equation (21·1), then we should have for the two valence vibrations

$$\omega_1 = \frac{1}{2\pi}\sqrt{\frac{\kappa_2}{M_O}}, \quad \omega_3 = \frac{1}{2\pi}\sqrt{\frac{\kappa_2(2M_O + M_C)}{M_O M_C}} \qquad (36{\cdot}2)$$

so that

$$\frac{\omega_3}{\omega_1} = \sqrt{\frac{2M_O + M_C}{M_C}}.$$

This ratio is 1·91 while the experimental ratio is 1·75. To compute the constant κ_2 we use the second equation (36·2) since in the normal vibration ω_3 both O-atoms are displaced in such a way that the distance between them remains constant, preventing their mutual forces from doing any work (which is the reason why we have chosen ω_3 rather than ω_1 to compute κ_2). We get thus $\kappa_2 = 14{\cdot}46 \cdot 10^5$ dynes/cm compared with $18{\cdot}78 \cdot 10^5$ dynes/cm in CO (from the data in table 8), showing that actually the restoring force between C and O in CO_2 is somewhat smaller than in CO. This is comprehensible since in CO we were led to assume a threefold valence bond (section 29) while here only half of the binding electrons which the C-atom contributes are available for the binding of each O-atom.

Adel and Dennison(13) have also tried to represent the potential energy of the CO_2-molecule by a function, analogous

to that introduced by Morse for diatomic molecules and given by equation (21·11). They put

$$V = [De^{-2\alpha(r_1+\epsilon)} - 2De^{-\alpha(r_1+\epsilon)}] + [De^{-2\alpha(r_2+\epsilon)} - 2De^{-\alpha(r_2+\epsilon)}] + Ae^{-Bq}. \quad (36\cdot3)$$

r_1, r_2, q specify the configuration of the molecule, q being the co-ordinate already previously introduced, while the significance of r_1 and r_2 appears from fig. 44, in which l denotes the equilibrium distance of the O-atoms. If desirable, we can of course express r_1 and r_2 in terms of the co-ordinates r and z used earlier. A, B, D, α, ϵ are constants characterising the molecule. The condition that the molecule be in equilibrium when the O-atoms are at distance l apart and the C-atom lies half-way between them imposes a relation upon the five constants so that only four of them are independent. Adel and Dennison then chose these four constants in such a way as to make the function (36·3) agree as far as possible with the function (36·1) in the neighbourhood of the equilibrium configuration. They find thus

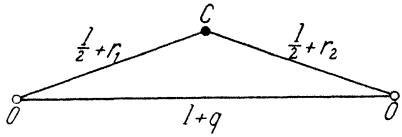


Fig. 44

$$A = 62600\,\text{cm}^{-1}, \quad B = 1\cdot086\,\text{Å}^{-1}, \quad D = 168350\,\text{cm}^{-1},$$
$$\alpha = 1\cdot81\,\text{Å}^{-1}, \quad \epsilon = 0\cdot061\,\text{Å}.$$

Assuming the expression (36·3) to be valid for all values of the co-ordinates, Adel and Dennison calculate the energy necessary for detaching one of the O-atoms from the CO_2-molecule and find for this 13·0 electron-volts or 300 cals per gram molecule. We shall return in section 46 to this dissociation process.

The experimental data for *carbon disulphide*, CS_2, are much more meagre than those for CO_2. The vibration-rotation bands have not been resolved so that the most cogent argument for the rectilinear form is not available, but this form is made practically certain by the vanishing dipole moment, the existence of only two strong frequencies in the infra-red spectrum and the general resemblance of the Raman effect to that of

CO_2. The work of Bailey and Cassie(21, 25, 45) and of Dennison and Wright(60) has yielded the following approximate values for the three fundamental frequencies:

$$\nu(s) = \omega_1 = 655, \quad \nu(a) = \omega_3 = 1523, \quad \delta(a) = \omega_2 = 397\,\text{cm}^{-1}.$$

Their sequence in the frequency scale is the same as in CO_2, but due to the greater mass of the S-atom they are notably smaller than for CO_2. A value $\rho_{C_S} = 1{\cdot}60\,\text{Å}$ for the internuclear distance has been estimated by Bailey and Cassie(21) from the separation of the intensity maxima of the *P*- and *R*-branch in the infra-red bands, while Jenkins(97) finds 1·53 Å from the rotational structure of electronic absorption bands in the ultraviolet (see section 46). This compares with the values 1·5 Å and 1·58 Å found in sections 9 and 11 by the X-ray and electron diffraction methods respectively.

Literature: CO_2, vibration-rotation spectrum (32, 34, 45, 118, 149), Raman spectrum (61, 93, 107, 109), theory (13, 56, 67, 127); CS_2, vibration-rotation spectrum (21, 25, 45, 60), Raman spectrum (42, 110), theory (56, 57).

37. THE MOLECULES N_2O, HCN AND OCS

The molecule *nitrous oxide*, N_2O, contains just as many electrons as CO_2. Hence, one would at first be inclined to expect that it too is rectilinear and symmetrical. The investigations of Plyler and Barker(139), however, have shown conclusively that the molecule is rectilinear and unsymmetrical, very probably of the type NNO, although an unsymmetrical configuration NON cannot be excluded in principle. The rectilinear character is confirmed again by the simple type of rotational structure of all the vibration-rotation bands, already discussed in the case of diatomic molecules like HCl (see section 23 and fig. 33) and also found for CO_2 (see previous section, fig. 43). That the molecule is unsymmetrical follows in the first place from the fact that all three normal frequencies ω_1, ω_2, ω_3 are active and, more generally, that the selection rule of Dennison for symmetrical triatomic molecules, according to which for the observable combination bands $\Delta v_2 + \Delta v_3$ must be odd, is not obeyed, in contrast to CO_2. In addition, if

the molecule were symmetrical, then according to wave mechanics the successive rotational lines in each band should be alternately weak and strong, at variance with the experimental results.

On the basis of the results of Plyler and Barker the latter author(31) has represented the vibrational levels of N_2O by a formula of the type

$$\frac{W_v}{h} = \omega_1 v_1 + \omega_2 v_2 + \omega_3 v_3 + x_{11} v_1^2 + x_{22} v_2^2 + x_{\lambda\lambda} \lambda^2 + x_{33} v_3^2 + x_{12} v_1 v_2 + x_{13} v_1 v_3 + x_{23} v_2 v_3 \quad (37{\cdot}1)$$

with the values of the constants given in table 17, the last three being average values. The values for ω_1, ω_2, ω_3 are perhaps not quite so accurate as those for CO_2 since they are based on a less elaborate expression for the potential energy function V of the molecule. From these data one may determine approximately κ_2 between N and N as well as between N and O. Plyler and Barker find $\kappa_2 = 24 . 10^5$ dynes/cm and $22 . 10^5$ dynes/cm respectively. This compares with $\kappa_2 = 22{\cdot}65 . 10^5$ dynes/cm in N_2 and $\kappa_2 = 15{\cdot}80 . 10^5$ dynes/cm in NO (from the data in table 8), showing that the restoring force between the two N-atoms is about the same in both cases, while that between N and O is notably larger in N_2O than in NO.

TABLE 17

CONSTANTS OF THE N_2O-MOLECULE

$\nu_1 \sim \nu\,(s) = \omega_1 = 1288{\cdot}7$ cm^{-1}	$x_{11} = -\ 3{\cdot}3$ cm^{-1}	$x_{12} = -\ 9{\cdot}9$ cm^{-1}
$\nu_2 \sim \nu\,(a) = \omega_3 = 2237{\cdot}9$,,	$x_{22} = -\ 2{\cdot}2$,,	$x_{13} = -\ 26{\cdot}7$,,
$\delta = \omega_2 = 588{\cdot}3$,,	$x_{\lambda\lambda} = \ \ 3{\cdot}0$,,	$x_{23} = -\ 13\ 5$,,
	$x_{33} = -\ 13{\cdot}8$,,	

From the rotational structure of the vibration-rotation bands Barker(31) has found for the moment of inertia of the molecule around an axis perpendicular to the internuclear line through the centre of gravity $I = 66{\cdot}0 . 10^{-40}$ g.cm^2, but this is of course not sufficient to compute both the internuclear distances ρ_{N-N} and ρ_{N-O}. As pointed out by the same author(30), the Raman effect confirms the conclusion regarding the configuration of the molecule.

Hydrogen cyanide, HCN, as shown by the investigations of Badger and Binder(17), of Choi and Barker(47) and of Adel and Barker(12) is a rectilinear molecule, too, with the same simple structure of the vibration-rotation bands encountered for CO_2 and N_2O. There are again three active vibrations: two valence vibrations ω_1 and ω_3, and the degenerate deformation vibration ω_2. Adel and Barker represent the vibrational levels by an equation of the type (37·1) with the values of the constants given in table 18. The hydrogen atom must occupy one of the end positions, but whether the molecule is HCN or HNC can at present not be decided with absolute certainty, although the chemical evidence favours HCN. Badger and Binder(17) find for the moment of inertia $I = 18{\cdot}79 \cdot 10^{-40}$ g.cm^2, Choi and Barker(47) $I = 18{\cdot}68 \cdot 10^{-40}$ g.cm^2, Herzberg and Spinks(88) $I = 18{\cdot}70 \cdot 10^{-40}$ g.cm^2, all on the basis of the rotational structure of the vibration bands.

TABLE 18

CONSTANTS OF THE HCN-MOLECULE

$\nu_1 \sim \nu\,(s) = \omega_3 = 3364{\cdot}8$ cm^{-1}	$x_{11} = 52{\cdot}0$ cm^{-1}	$x_{12} = -\ 0{\cdot}2$ cm^{-1}
$\nu_2 \sim \nu\,(a) = \omega_1 = 2037{\cdot}0$,,	$x_{22} = -\ 2{\cdot}9$,,	$x_{13} = -\ 15{\cdot}1$,,
$\delta = \omega_2 = 712{\cdot}1$,,	$x_{\lambda\lambda} = 3{\cdot}1$,,	$x_{23} = -\ 19{\cdot}6$,,
	$x_{33} = -\ 51{\cdot}3$,,	

For the molecule *carbonyl sulphide*, OCS, the experimental data are not very complete. A study of the infra-red absorption spectrum has been made by Bailey and Cassie(23, 45), of the Raman spectrum by Dadieu and Kohlrausch(53). Very likely this molecule is rectilinear in analogy with CO_2 and CS_2, but whether it is OCS or COS cannot at present be decided, chemical notions, however, pleading for the first. Only the possibility CSO must be excluded since the moment of inertia $I_e = 230 \cdot 10^{-40}$ g.cm^2 estimated from the separation of the intensity maxima in the P- and R-branches of the vibration bands is so large that it could only be obtained by having the S-atom at an end position.

To decide eventually between the possible sequence of the atoms in molecules like HCN and COS two methods might be used. One is the analysis of the fine structure in X-ray absorp-

tion bands discussed in section 12; for this fine structure, as we saw, depends for every atom upon the location of its partners relative to it. The other method, suggested by Adel(11), is the comparison of the vibration-rotation spectra of isotopic molecules, the difference in the frequencies of such molecules also depending upon the relative position of the constituent atoms. Thus if in OCS we substitute for the ordinary C-atom with atomic weight 12 the isotope with atomic weight 13, the change in the molecular frequencies will be different for COS and OCS. In the following section we shall meet an application of the method just mentioned.

Literature: N_2O, vibration-rotation spectrum (31, 139, 156), Raman spectrum (30, 38, 61, 108); HCN, vibration-rotation spectrum (12, 17, 29, 47, 88, 151), Raman spectrum (41, 99); OCS, vibration-rotation spectrum (23, 45), Raman spectrum (53).

38. THE MOLECULE C_2H_2

The molecule *acetylene*, C_2H_2, has been extensively studied by Mecke and his collaborators(46, 75, 76, 121, 123) and by Lochte-Holtgreven and Eastwood(114, 115). All of the vibration-rotation bands are of the simple type previously discussed so that the

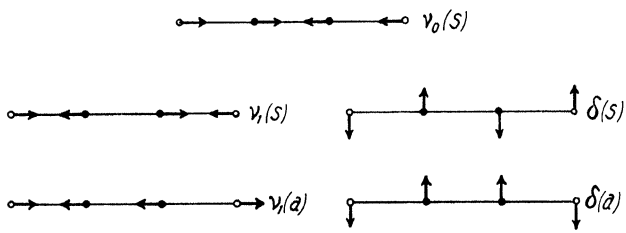


Fig. 45

molecule must be rectilinear. The fact that the dipole moment vanishes and that successive lines in each branch of these bands show an alternation of intensity (see fig. 46) is, according to wave mechanics, conclusive proof that the molecule is symmetrical, HCCH. There are then five normal vibrations of the types shown in fig. 45: three valence vibrations $\nu_0(s) = \omega_2$, $\nu_1(s) = \omega_3$, $\nu_1(a) = \omega_5$ and two degenerate deformation vibrations $\delta(s) = \omega_1$ and $\delta(a) = \omega_4$. Of these the symmetrical ones

ω_1, ω_2, ω_3 are inactive and hence should not appear as vibration-rotation bands. More generally, according to Dennison (see section 35), all combination bands should be absent for which $\Delta v_4 + \Delta v_5$ is even.

The interpretation of the observed vibration-rotation bands by the authors cited above is probably not entirely correct since in their classification some of the combination bands violate the rule of Dennison. More recently Sutherland(160) and Herzberg and Spinks(89) have tried to avoid this difficulty. They represent the vibration levels by a formula of the type

$$\begin{aligned}\frac{W_v}{h} = {} & \omega_1 v_1 + \omega_2 v_2 + \ldots + \omega_5 v_5 \\ & + x_{11} v_1^2 + x_{22} v_2^2 + \ldots + x_{55} v_5^2 \\ & + x_{12} v_1 v_2 + x_{13} v_1 v_3 + \ldots + x_{45} v_4 v_5,\end{aligned}$$

but at present there are not yet sufficient data available to determine all the constants in this expression. However, for ω_1, ω_2, ω_3, ω_4, ω_5 the values

$$\nu_0(s) = \omega_2 = 1974, \quad \nu_1(s) = \omega_3 = 3372, \quad \nu_1(a) = \omega_5 = 3288,$$
$$\delta(s) = \omega_1 \sim 618, \quad \delta(a) = \omega_4 = 729\,\mathrm{cm}^{-1}$$

are probably not far from correct.

The rotation structure of the vibration-rotation bands leads to a value of the moment of inertia $I = 23{\cdot}50 \cdot 10^{-40}$ g.cm^2(89). In order to obtain both the distances C—C and C—H, additional information is required. Herzberg, Patat and Spinks(86) for this purpose have determined the moment of inertia of C_2HD in which one of the H-atoms has been replaced by its isotope D of atomic weight 2. Since the internuclear distances will be the same for both molecules, we have now sufficient data for their determination. The above authors find for the isotope $I = 27{\cdot}90 \cdot 10^{-40}$ g.cm^2 and with the two values of I: $\rho_{C-C} = 1{\cdot}20$ Å, $\rho_{C-H} = 1{\cdot}06$ Å. This compares with a distance $\rho_{C-C} = 1{\cdot}22$ Å found by electron diffraction in C_2H_2 (see section 11) and a distance $\rho_{C-H} = 1{\cdot}118$ Å in the diatomic molecule CH (see table 8). The restoring force for the bond CH is $\kappa_2 = 2{\cdot}9 \cdot 10^5$ dynes/cm, that for the bond CC $\kappa_2 = 7{\cdot}4 \cdot 10^5$ dynes/cm; comparing with the values $\kappa_2 = 4{\cdot}42$ and $9{\cdot}47 \cdot 10^5$ dynes/cm in the diatomic molecules CH and C_2.

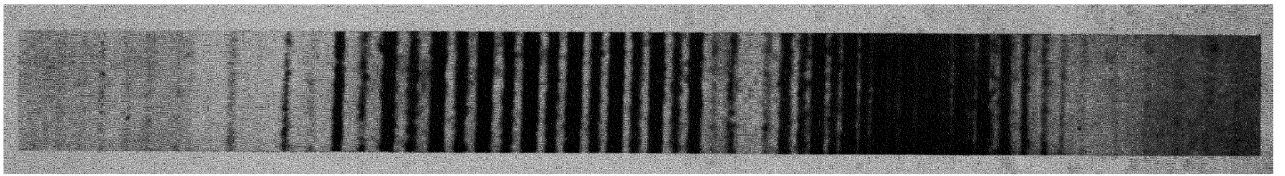


Fig. 46. The band λ 7886 of C_2H_2.

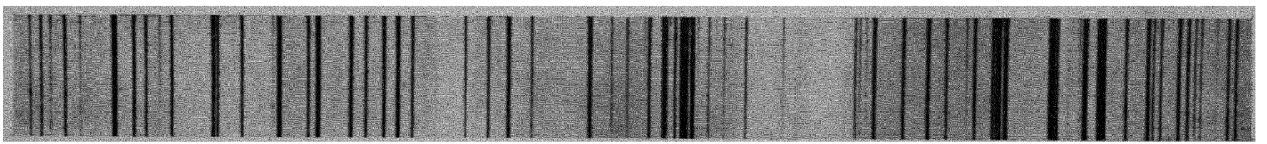


Fig. 47. The band λ 8230 of H_2O.

C_4H_2 and C_2N_2 probably also are linear. The experimental data available are, however, so complicated that they do not allow to draw any definite conclusions.

Literature: C_2H_2, vibration-rotation spectrum (46, 75, 76, 86, 89, 112, 114, 115, 119, 121, 123, 160), Raman spectrum (113); C_4H_2, vibration-rotation spectrum (36); C_2N_2, vibration-rotation spectrum (158, 171).

39. VIBRATION-ROTATION SPECTRA OF NON-LINEAR TRIATOMIC MOLECULES

In a triatomic molecule, the nuclei of which in the equilibrium configuration do not lie along a straight line, the nuclear vibrations may be regarded as arising from the superposition of three harmonic normal vibrations—$\nu(\pi)=\omega_1$, $\nu(\sigma)=\omega_3$, $\delta(\pi)=\omega_2$—as long as the deviations of the particles from the positions of rest are small. As the molecules for which data are available are of the type XY_2 and since very probably for all of them the distances of the two atoms Y to the atom X are equal, we shall confine ourselves to the case of an isosceles triangle as equilibrium configuration. The nature of the three normal vibrations is then shown by fig. 48. In the approximation in which anharmonic terms may be neglected the energy of the vibrational levels, characterised by the vibrational quantum numbers v_1, v_2, v_3, is again given by equation (32·5).

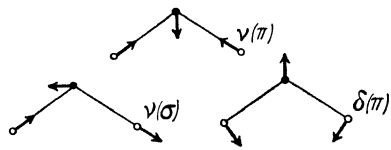


Fig. 48

The expression for the rotational energy, as mentioned already in section 34, is much more complicated than for linear molecules since the triangular configuration has in general three different moments of inertia $I_A < I_B < I_C$. In consequence there are three rotational constants

$$A=\frac{h}{8\pi^2 I_A}, \quad B=\frac{h}{8\pi^2 I_B}, \quad C=\frac{h}{8\pi^2 I_C}. \qquad (39\cdot1)$$

Also the one rotational quantum number J, measuring the angular momentum of the nuclear rotation, is no longer sufficient to distinguish the rotational states. To every value

of J there belong $2J+1$ sub-levels which may be characterised by a second quantum number K running from $-J$ to J, such that K increases with increasing energy of the sub-levels. Mecke(124) uses the notation J_K so that, e.g., the level 2_1 is the one having $J=2$, $K=1$. The rotational energy which must be added to the vibrational energy, given approximately by equation (32·5), cannot be expressed as a simple algebraic function of the quantum numbers J and K. There exist, however, algebraic relationships for the sum of the rotational energies of different rotational levels. In the first place the mean rotational energy of all the rotational levels with the same J is given by

$$\frac{W_J}{h} = \tfrac{1}{3}(A+B+C)\,J(J+1).$$

Furthermore, for the lower values of J and K one has the table 19. After a tentative classification of the rotational levels these relations may serve as a check for the correctness of the assignment of J and K since they only contain the three independent constants A, B, C, for a determination of which they are also very well suited.

We next discuss which transitions will occur in the spectrum of the molecule under consideration. In the first place, since all three normal vibrations are active, there is no restriction on the changes Δv of the vibrational quantum numbers. Hence, all fundamental, harmonic and combination bands will appear in the spectrum if the binding is not strictly harmonic. Next we have the usual selection rule that J may only change by ± 1 or 0. Finally we note that the rotational levels fall into four classes. To the first class belong those levels the rotational energy of which depends symmetrically upon the three rotational constants A, B and C (class ABC). The other three classes are formed by the levels the energy of which is symmetrical in only two of these constants (classes AC, AB, BC). We have then the following restrictions according to Dennison(55) and Mecke(124):

1. If the oscillating dipole moment of a normal vibration has a component along the principal axis of inertia A, then the

levels of class ABC can combine with the levels BC and the levels AC with the levels AB.

2. If it has a component along the axis B, then the levels ABC can combine with the levels AC and the levels BC with the levels AB.

3. If it has a component along the axis C, then the levels ABC can combine with the levels AB and the levels AC with the levels BC.

TABLE 19

SUM RULES FOR THE ROTATIONAL LEVELS OF SYMMETRICAL TRIANGULAR MOLECULE XY_2

Class	Sum of rotational energies/h	
ABC	0	0
	$2_{-2}+2_{+2}$	$4(A+B+C)$
	3_0	$4(A+B+C)$
	$4_{-4}+4_0+4_{+4}$	$20(A+B+C)$
	$5_{-2}+5_{+2}$	$20(A+B+C)$
	$6_{-6}+6_{-2}+6_{+2}+6_{+6}$	$56(A+B+C)$
AC	1_0	$(A+C)$
	2_0	$4B+(A+C)$
	$3_{-2}+3_{+2}$	$4B+10(A+C)$
	$4_{-2}+4_{+2}$	$20B+10(A+C)$
	$5_{-4}+5_0+5_{+4}$	$20B+35(A+C)$
	$6_{-4}+6_0+6_{+4}$	$56B+35(A+C)$
AB	1_{+1}	$(A+B)$
	2_{-1}	$4C+(A+B)$
	$3_{-1}+3_{+3}$	$4C+10(A+B)$
	$4_{-3}+4_{+1}$	$20C+10(A+B)$
	$5_{-3}+5_{+1}+5_{+5}$	$20C+35(A+B)$
	$6_{-5}+6_{-1}+6_{+3}$	$56C+35(A+B)$
BC	1_{-1}	$(B+C)$
	2_{+1}	$4A+(B+C)$
	$3_{-3}+3_{+1}$	$4A+10(B+C)$
	$4_{-1}+4_{+3}$	$20A+10(B+C)$
	$5_{-5}+5_{-1}+5_{+3}$	$20A+35(B+C)$
	$6_{-3}+6_{+}+6_{+5}$	$56A+35(B+C)$

The lines with $\Delta J=-1, 0, +1$ are again said to form P-, Q- and R-branches, but due to the complicated nature of the expression for the rotational energy these branches have not the simple appearance met with in rectilinear molecules.

For a rigid triangle the sum of the two smaller moments of inertia should be equal to the largest one

$$\Delta = I_C - (I_A + I_B) = 0. \qquad (39{\cdot}2)$$

If, however, there are vibrations and if I_A, I_B, I_C denote average moments of inertia, this relation will not be exactly fulfilled any more.

40. THE MOLECULES H_2O, H_2S, NO_2, SO_2, ClO_2, O_3

After a great amount of preliminary work by other authors Mecke and his collaborators (37, 68, 124) have succedeed in giving a satisfactory analysis of the vibration-rotation spectrum of H_2O. Their success depended essentially upon the fact that by means of sensitised plates they could photograph the combination bands in the near infra-red, thus obtaining a much higher resolution than was possible formerly. Fig. 47 shows one of these combination bands.

From the fact that H_2O has a large dipole moment, from the presence of three active vibration frequencies and from the complicated structure of the bands it follows that the molecule cannot be linear but must be triangular. The circumstance that the combinations between the rotational levels obey the restrictions to be expected for the isosceles triangular form, according to the previous sections, as well as the intensity alternation observed confirm the assumption that the two H-atoms are equidistant from the O-atom.

The vibrational levels could be represented by Mecke by the following formula

$$\frac{W}{ch} = [3670 - 70\,(v_1 + v_3)]\,v_1 + [1615 - 20\,(v_1 + v_2 + v_3)]\,v_2 + [3795 - 39\,(v_1 + v_3)]\,v_3,$$

an extension of equation (32·5), in which second powers of the vs arise from the anharmonic binding. We may therefore take as approximate values of the normal frequencies

$$\nu\,(\pi) = \omega_1 = 3670, \quad \nu\,(\sigma) = \omega_3 = 3795, \quad \delta\,(\pi) = \omega_2 = 1615\,\mathrm{cm}^{-1}.$$

The analysis of the rotational structure furnished on the basis of the relations of table 19 the values of A, B, C and hence by means of equation (39·1) the values of the moments of inertia:

$$I_A = 0{\cdot}995 \,.\, 10^{-40}, \quad I_B = 1{\cdot}908 \,.\, 10^{-40}, \quad I_C = 2{\cdot}980 \,.\, 10^{-40}\,\mathrm{g.cm}^2.$$

This gives for the quantity Δ, defined by equation (39·2),

$$\Delta = 0{\cdot}077 \,.\, 10^{-40}\,\text{g.cm}^2,$$

showing that the relation (39·2), for the reasons previously stated, is not exactly fulfilled. The largest moment of inertia I_C is the one about an axis perpendicular to the plane of the triangle. Regarding I_A and I_B it is important to decide which of them represents the moment of inertia about the bisectrix of the top of the isosceles triangle, i.e. the axis of symmetry of the molecule since otherwise a unique determination of the molecular shape and size is not possible. From the combination relations of the rotational levels based upon the symmetry properties of these levels Mecke could conclude that I_B represents the moment of inertia about the axis of symmetry. One can then calculate the distances $\rho_{\text{O—H}}$ in the isosceles triangle and the valence angle α at the top, which quantities determine the shape and size completely. For the vibrationless state one thus finds

$$\rho_{\text{O—H}} = 0{\cdot}97\,\text{Å}, \quad \alpha = 105^\circ,$$

while when the vibrations are excited these quantities, representing mean values, are slightly altered. The H_2O-molecule is thus seen to be nearly an isosceles *right* triangle in its equilibrium state; the two valence bonds from the O-atom to the two H-atoms form with each other approximately a right angle.

The rotational spectrum of H_2O has been investigated repeatedly, most recently by Kühne(105). There is, however, little agreement between different observers, probably in part due to insufficient resolution, so that a discussion would be premature.

The molecule *hydrogen sulphide*, H_2S, is of the same type as H_2O. The vibration-rotation spectrum of H_2S has recently been reinvestigated by Nielsen and Barker(131), by Mischke(125) and by Cross(51). Bands of the same character as in H_2O are found, leading to

$$I_A = 2{\cdot}267 \,.\, 10^{-40}, \quad I_B = 3{\cdot}076 \,.\, 10^{-40}, \quad I_C = 5{\cdot}845 \,.\, 10^{-40}\,\text{g.cm}^2,$$

$$\rho_{\text{S—H}}\, 1{\cdot}35\,\text{Å}, \quad \alpha = 92^\circ.$$

Three other triatomic molecules, probably of the symmetric

triangular type, are NO_2, SO_2 and ClO_2. For *nitric oxide*, NO_2, Bailey and Cassie(27) first suggested the symmetric rectilinear form since they only found two active vibration frequencies in the infra-red. Schaffert(150), however, repeating the experiments, in which care must be taken to distinguish the absorption due to N_2O_4 from that due to NO_2 by diminishing the amount of the former through raising the temperature, found three vibration frequencies at 1373, 641 and 1628 cm^{-1}. In addition a study of the rotational structure of electronic absorption bands in the ultra-violet, carried out by Hermann(82), makes it also probable that in the ground state the molecule is not rectilinear. For *sulphur dioxide*, SO_2, similarly, the existence of three vibration frequencies, points to a triangular form. There is, however, still disagreement between the values for these frequencies as found by different authors from the vibration-rotation spectrum and from the Raman effect. The latter leads to the values 1146, 525, 1340 cm^{-1}. The first two values were also found by Chow(48) as vibrational frequency differences of electronic absorption bands of SO_2 in the ultra-violet. A still greater uncertainty exists for *chlorine dioxide*, ClO_2, the vibration-rotation spectrum of which was studied by Bailey and Cassie(25), while Ku(104) investigated the electronic absorption bands. From these he gets for the three normal frequencies of the ground state 954, 529 and 1105 cm^{-1}. Bailey and Cassie(26) also studied *chlorine monoxide*, Cl_2O.

Besides the molecules just discussed, *ozone*, O_3, should be mentioned in this connection. It is of special chemical interest since it usually has been supposed to have an equilateral triangular form. If this is so, the molecule should have a doubly degenerate and a non-degenerate normal vibration, of which the former should be active in absorption or emission and inactive in the Raman effect, while for the latter the converse would be true. The experimental investigations, however, appear to show that there are three active vibrations in absorption. This can only be accounted for by the assumption that the nuclear equilibrium configuration is triangular but not equilateral. Further work will be required to clear up this question entirely.

Literature: H_2O, rotation spectrum (91, 105, 170, 172), vibration-rotation spectrum (37, 68, 124, 138, 140), Raman spectrum (98, 142), theory (44); H_2S, vibration-rotation spectrum (51, 125, 131, 146), Raman spectrum (41); NO_2, vibration-rotation spectrum (27, 73, 74, 150, 161); SO_2, vibration-rotation spectrum (18, 24, 25, 28), theory (90); ClO_2, vibration-rotation spectrum (24, 25); Cl_2O, vibration-rotation spectrum (26); O_3, vibration-rotation spectrum (39, 71, 92).

41. VIBRATION-ROTATION SPECTRA AND RAMAN SPECTRA OF PYRAMIDAL MOLECULES; NH_3, PH_3, AsH_3

Molecules XY_3 in which the atoms Y form an equilateral triangle while the atom X is located vertically above the centre of the triangle so that the molecule is a regular pyramid should have comparatively simple rotation and vibration-rotation spectra. There are four normal vibrations (see fig. 49).

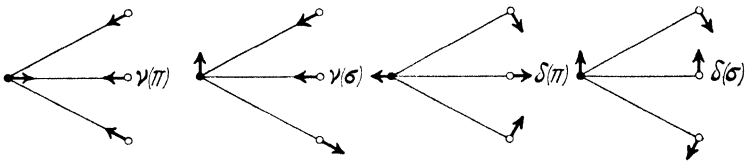


Fig. 49

Two of these, $\nu(\pi)$, $\delta(\pi)$, represent motions in which the X-nucleus moves along the axis of symmetry while the Y-atoms are displaced symmetrically in planes through it so that the electric moment oscillates parallel to the axis of symmetry (parallel type of vibrations). The two others, $\nu(\sigma)$, $\delta(\sigma)$, which are doubly degenerate (see section 32), yield an oscillating electric moment perpendicular to the axis of symmetry (perpendicular type of vibrations). All four normal vibrations are active, appearing in the vibration-rotation spectrum as well as in the Raman effect. Since two of the moments of inertia I_A and I_B of the molecule are equal while the third I_C will in general be different, the rotation of the molecule should be that of a symmetrical top. The rotational energy is then obtained from equation (34·3).

In the vibration-rotation spectrum the parallel type of vibration bands has a particularly simple rotational structure since for it K may not change at all while J, as always, may

not change by more than one unit. As the dependence of the rotational energy on J according to equation (34·3) is the same as in the case of rectilinear molecules, these bands will also consist of simple P-, Q- and R-branches corresponding to $\Delta J = -1, 0, +1$, the rotational separation of the band lines depending only on I_A. For the perpendicular type of bands K may change too, causing them to have a much more involved aspect so that in the infra-red they are hard to resolve. For the pure rotation spectrum K and J are governed by the same rule as in the parallel type of the vibration-rotation bands.

An interesting feature of the molecular configuration considered is that the atom X will have two equivalent equilibrium positions, the second one being the mirror image of the first at the plane through the atoms Y. As pointed out by Hund(95), this will give rise in wave mechanics to a sort of beat frequency with which the nucleus X will pass through the potential threshold between the equilibrium positions with, as consequence, a doubling of the various vibrational levels. This frequency, and hence the doublet separation, will be the greater the lower the threshold and the nearer the atom X to the plane of the atoms Y, i.e. the flatter the pyramid. The size of the doublet separation may thus furnish valuable information regarding the dimensions of the molecule.

The most important example of the kind of molecule just discussed is *ammonia*, NH_3. That it is actually a symmetrical top molecule is made plausible by the fact that some, but not all, of its vibration-rotation bands are of the simple three-branch type while the pure rotation spectrum confirms this view. The non-vanishing dipole moment as well as the presence of this latter spectrum exclude the possibility of three H-atoms in the form of an equilateral triangle with the N-atom in the same plane at the centre. There remains then the symmetrical pyramidal form discussed above and a plane configuration $H—N\begin{smallmatrix}H\\H\end{smallmatrix}$ in which the first H-atom is at a different distance from the N-atom than the other two H-atoms. This last possibility is excluded by the intensity alternation of

the bands as well as by the circumstance that the duplicity of the vibrational levels postulated above is actually observed.

Regarding the values of the four normal frequencies there is still considerable disagreement between different authors. Among the more recent investigations those of Badger(15), of Dennison and Hardy(57), of Lueg and Hedfeld(117) and of Unger(163) should be mentioned. The identification of the double bands near 3335 and 950 cm^{-1} as the two parallel type vibrations $\nu(\pi)$ and $\delta(\pi)$ seems to be certain while one of the perpendicular type vibrations lies at 1630 cm^{-1}. The identification of the second perpendicular type vibration, however, is still doubtful.

An investigation of the rotational structure of some of the parallel type vibration-rotation bands led Badger(15), Dennison and Hardy(57), and Lueg and Hedfeld(117) to a determination of I_A. The same constant followed also from the pure rotation spectrum, as investigated by Badger and Cartwright(19) and by Wright and Randall(172), as well as from the rotational structure of the Raman effect studied by Dickinson, Dillon and Rasetti(61) and by Amaldi and Placzek(14). As most probable value $I_A = 2{\cdot}78 \,.\, 10^{-40}$ g.cm^2 was found.

The doubling of the vibrational levels which Dennison and Hardy(57), following Hund(95), first interpreted as due to the two equilibrium positions of the N-nucleus has led to a determination of the moment of inertia I_C about the axis of symmetry. By assuming for the potential energy of the N-nucleus in its dependence upon the distance h of this nucleus from the H_3-plane, measured along the axis of symmetry, a convenient function, adjusted to the observed parallel vibration frequencies of the molecule, and by investigating for which value of the equilibrium distance h_e the nucleus passes through the potential barrier with the beat frequency observed in the doubling Rosen and Morse(147) derived a value $h_e = 0{\cdot}365$ Å. Wright and Randall(172), on the basis of more careful measurements, obtained the value 0·388 Å. This in conjunction with the value of I_A gives for the moment of inertia $I_C = 4{\cdot}33 \,.\, 10^{-40}$ g.cm^2, leading to the following values for the internuclear dis-

tance ρ_{N-H} and for the angle α between the valence bonds from the N-atom to the H-atoms

$$\rho_{N-H} = 1{\cdot}01\,\text{Å}, \quad \alpha = 106°.$$

The pyramid is thus seen to be rather flat, but the valence bonds are by no means coplanar.

Other molecules also of the pyramidal type are *phosphine*, PH_3, and *arsine*, AsH_3. For PH_3 the value $I_A = 6{\cdot}221 \cdot 10^{-40}$ g.cm^2 has been made certain by the measurements of Wright and Randall(172). Finally, the molecules PCl_3, PBr_3, $AsCl_3$, $SbCl_3$, $BiCl_3$ should be mentioned in this connection, the Raman spectrum of which has been investigated.

Literature: NH_3, rotation spectrum (19, 172), vibration-rotation spectrum (15, 20, 33, 35, 57, 117, 145, 157, 163), Raman spectrum (14), theory (147); PH_3, vibration-rotation spectrum (69, 145, 172); AsH_3, vibration-rotation spectrum (145); other pyramidal molecules (3, 9).

42. THE MOLECULE H_2CO

Formaldehyde, H_2CO, on the basis of its spectra has an equilibrium configuration as shown in fig. 50. In the same figure the six normal vibrations, all non-degenerate and active, may be

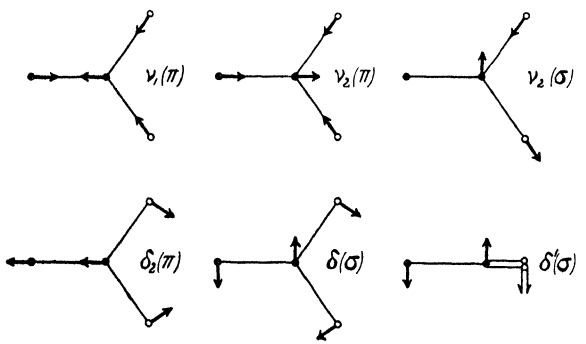


Fig. 50

seen. Five strong frequencies found in the Raman effect may probably be identified with five of the normal frequencies.

The rotation of the molecule has a rather simple character because the mass of the two H-nuclei is so much smaller than that of C and O. Consequently, the rotation about the axis of

symmetry is fast compared to the rotation about perpendicular axes and there is a certain analogy with the rotation of diatomic molecules with an electronic angular momentum about the internuclear line. From the rotational structure of electronic absorption bands Dieke and Kistiakowsky (62, 63) could determine the three principal moments of inertia, finding the values $24{\cdot}33$, $21{\cdot}39$ and $2{\cdot}94 . 10^{-40}$ g.cm^2.

Molecules with a similar configuration are probably Cl_2CO, S_2Cl_2 and $OSCl_2$.

Literature: H_2CO, vibration-rotation spectrum (130, 133), theory (129).

43. VIBRATION-ROTATION SPECTRA AND RAMAN SPECTRA OF TETRAHEDRAL MOLECULES; CH_4, HALOGEN SUBSTITUTION PRODUCTS OF CH_4

Practically all known molecules consisting of five atoms have tetrahedral structure. There will be nine normal vibrations, but for reasons of symmetry some of these may have identical frequencies. If the symmetry is that of a regular tetrahedron,

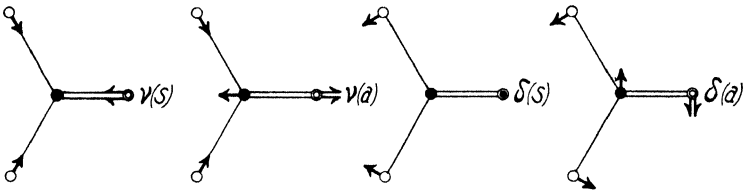


Fig. 51

there will be a non-degenerate vibration $\nu(s)$, symmetrical with respect to the centre, a doubly degenerate symmetrical vibration $\delta(s)$ and two triply degenerate antisymmetrical vibrations $\nu(a)$ and $\delta(a)$ (see fig. 51). If there is only a threefold symmetry axis, one obtains three non-degenerate parallel type vibrations (see section 33) $\nu_1(\pi)$, $\nu_2(\pi)$, $\delta_2(\pi)$, and three doubly degenerate perpendicular type vibrations $\delta_1(\sigma)$, $\nu_2(\sigma)$, $\delta_2(\sigma)$. If there is only a twofold axis of symmetry or no symmetry at all, all the nine normal frequencies are different from each other.

Methane, CH_4, is the most important representative of the regular tetrahedral structure. That it has a centre of symmetry is supported by its vanishing dipole moment and the absence of a rotational spectrum. Just as for linear molecules with a centre of symmetry we have for any other molecules with a centre of symmetry, that the normal vibrations symmetrical with respect to this centre are inactive in emission or absorption. The very strong frequency 2915 cm^{-1} which only appears in the Raman spectrum must hence be identified with one of the normal vibrations $\nu(s)$, $\delta(s)$. More particularly it can be proved to be the vibration $\nu(s)$ in which the outside atoms move in a radial direction with respect to the central atoms. The reason for this identification is the absence of rotational structure in the Raman line, in harmony with the circumstance that the rotation of the molecule vibrating in the way described will not affect its polarisability. Another frequency appearing both in the Raman and infra-red spectrum has the value 3022 cm^{-1} and must be identified with $\nu(a)$.

The rotational structure of the absorption bands as studied by Dennison and Ingram(58), Moorehead(126), Norris and Unger(132), Vedder and Mecke(166) is greatly influenced by the interaction of vibration and rotation as discussed at the end of section 34. Great care must therefore be taken in evaluating the moment of inertia from the separation of the rotational lines. Taking the effect just mentioned into account Placzek and Teller(137) arrive at the value $I = 5{\cdot}3 \cdot 10^{-40}$ g.cm^2, while Dennison and Johnston(59) find $I = 5{\cdot}47 \cdot 10^{-40}$ g.cm^2, corresponding to the distance $\rho_{C-H} = 1{\cdot}11$ Å.

Other molecules of regular tetrahedral structure that have been studied spectroscopically are CCl_4 and CBr_4. Also molecules in which halogen atoms have been substituted for only one, two or three of the H-atoms in CH_4 as well as analogous derivations with Si, Ti, Ge, Sn instead of C have been investigated, partly in the liquid state.

Literature: CH_4, vibration-rotation spectrum (50, 58, 59, 126, 132, 166); other tetrahedral molecules (3, 9, 40, 81, 87, 106, 148, 153, 164).

44. THE MOLECULES C_2H_4, C_6H_6 AND OTHER ORGANIC SUBSTANCES

Ethylene, C_2H_4, possesses twelve non-degenerate normal vibrations of which eleven are shown in fig. 52 while the twelfth is the torsional vibration of the two end groups about the

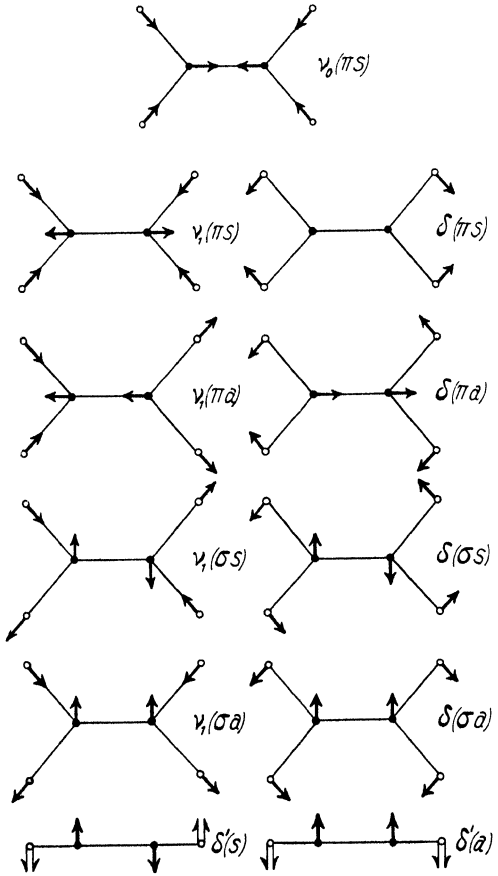


Fig. 52

double carbon bond. Since the molecule has a centre of symmetry, the vibrations fall into two groups, symmetrical and antisymmetrical with respect to the centre, of which the former are inactive in emission or absorption, the latter in the Raman

effect. The frequency of the torsional vibration is not known. For the other frequencies Mecke(6) gives the values

$\nu_0(\pi s) = 1623$, $\nu_1(\pi s) = 3019$, $\nu_1(\pi a) = 2988$, $\nu_1(\sigma s) = 3240$,
$\nu_1(\sigma a) = 3107$, $\delta(\pi s) = 1342$, $\delta(\pi a) = 1444$, $\delta(\sigma s) \sim 970$,
$\delta(\sigma a) \sim 1100$, $\delta'(s) \sim 940$, $\delta'(a) = 950$ cm^{-1}

Rather uncertain estimates of the moments of inertia of the molecule from the rotational structure in the absorption spectrum and the Raman spectrum have been made by Badger and Binder(17), by Scheib and Lueg(152) and by Levin and Meyer(112).

The molecule of *benzene*, C_6H_6, is of particular interest to the chemist. If the molecule is a regular hexagon, then from symmetry arguments one should again expect that the frequencies active in absorption should be inactive in the Raman effect and *vice versa*. This expectation, however, has not been confirmed by experiment. If the reason must be sought in a deviation from the regular form or perhaps in resonance phenomena such as we encountered for CO_2 in section 36 is not yet certain.

A number of other organic molecules has been studied, especially with the aid of the Raman effect. The theoretical interpretation, however, is in most cases difficult due to the complicated nature of the molecules.

Literature: C_2H_4, vibration-rotation spectrum (16, 17, 112, 152), Raman spectrum (61).

45. NUMERICAL DATA ON THE STRUCTURE OF POLYATOMIC MOLECULES. CONNECTION WITH CHEMICAL BINDING

In table 20 we have given a survey of the structure of the more important polyatomic molecules for which sufficiently reliable data are available. In the column for the vibrational frequencies the geometrical character of the vibrations may be seen by reference to the figures in the text mentioned in each case. Doubtful values have been placed in round parentheses. The values in square brackets are the calculated frequencies for infinitely small amplitudes. In the columns for

TABLE 20

CONSTANTS OF POLYATOMIC MOLECULES

Molecule	Form	Vibrational frequencies cm^{-1}	Moments of inertia $\times 10^{40}$ g.cm^2	Internuclear distances Å	Literature section
CO_2	Linear symmetric O—C—O	Fig. 40 $\nu(s) = 1340$ [1361] $\nu(a) = 2350$ [2378] $\delta(a) = 667$ [673]	$I = 70{\cdot}1$	C—O = 1·1 (X) = 1 13 (E) = 1·15 (B) = 1·15 (R)	36
CS_2	Linear symmetric S—C—S	Fig. 40 $\nu(s) = 655$ $\nu(a) = 1523$ $\delta(a) = 397$	($I = 255$)	C—S = 1·5 (X) = 1·58 (E) = 1·56 (B)	36
N_2O	Linear unsymmetric N—N—O	Fig. 40 $\nu_1 = 1285$ [1288 7] $\nu_2 = 2224$ [2237·9] $\delta = 589$ [588·3]	$I = 66{\cdot}0$	—	37
HCN	Linear H—C—N	Fig. 40 $\nu_1 = 3290$ [3364·8] $\nu_2 = 2100$ [2037·0] $\delta = 735$ [712·1]	$I = 18\ 72$	—	37
OCS	Linear S—C—O	Fig. 40 ($\nu_1 = 859$) ($\nu_2 = 2079$) ($\delta = 541$)	($I = 230$)	—	37
C_2H_2	Linear symmetric H—C—C—H	Fig. 46 $\nu_0(s) = 1974$ $\nu_1(s) = 3372$ $\nu_1(a) = 3288$ ($\delta(s) = 615$) $\delta(a) = 729$	$I = 23{\cdot}50$	C—H = 1·06 (B) C—C = 1·22 (E) = 1·20 (B)	38.
H_2O	Isosceles triangle O α H H $\alpha = 105°$	Fig. 47 $\nu(\pi) = 3670$ $\nu(\sigma) = 3795$ $\delta(\sigma) = 1615$	$I_A = 0{\cdot}995$ $I_B = 1{\cdot}908$ $I_C = 2{\cdot}980$	O—H = 0·97 (B)	40
H_2S	Isosceles triangle S α H H $\alpha = 92°$	Fig. 47	$I_A = 2{\cdot}267$ $I_B = 3{\cdot}076$ $I_C = 5{\cdot}845$	S—H = 1·35 (B)	40
NO_2	Isosceles triangle N O O	Fig. 47 $\nu(\pi) = 1373$ $\nu(\sigma) = 1628$ $\delta(\sigma) = 641$	—	—	40
SO_2	Isosceles triangle S O O	Fig. 47 $\nu(\pi) = 1146$ $\nu(\sigma) = 1340$ $\delta(\sigma) = 525$	—	S—O = 1·37 (E)	40

TABLE 20—*contd*

Molecule	Form	Vibrational frequencies cm^{-1}	Moments of inertia $\times 10^{40}$ g.cm^2	Internuclear distances Å
ClO_2	Isosceles triangle 	Fig. 47 $\nu(\pi) = 954$ $\nu(\sigma) = 1105$ $\delta(\sigma) = 529$	—	Cl—O = 1·57 (*E*)
O_3	Isosceles triangle 	Fig. 47 $\nu(\pi) = 1044$ $\nu(\sigma) = 1355$ $(\delta(\sigma) = 435)$	—	—
NH_3	Regular pyramid  $\alpha = 106°$	Fig. 49 $\nu(\pi) = 3335$ $\delta(\pi) = 950$ $\nu(\sigma) = ?$ $\delta(\sigma) = 1630$	$I_A = 2·78$ $I_C = 4·33$	N—H = 1·01 (*B*)
PH_3	Regular pyramid	Fig. 49	$I_A = 6·22$	—
H_2CO	Coplanar 	Fig. 50 Identification uncertain	$I_A = 2·94$ $I_B = 21·39$ $I_C = 24·33$	—
CH_4	Regular tetrahedron 	Fig. 51 $\nu(s) = 2915$ $(\delta(s) = 1530)$ $\nu(a) = 3020$ $\delta(a) = 1320$	$I = 5·47$	C—H = 1·11
C_2H_4	Coplanar 	Fig. 52 $\nu_0(\pi s) = 1623$ $\nu_1(\pi s) = 3019$ $\nu_1(\pi a) = 2988$ $\nu_1(\sigma s) = 3240$ $\nu_1(\sigma a) = 3107$ $\delta(\pi s) = 1342$ $\delta(\pi a) = 1444$ $(\delta(\sigma s) = 970)$ $(\delta(\sigma a) = 1100)$ $(\delta'(\sigma s) = 940)$ $\delta'(\sigma a) = 950$ $\omega_t = ?$	—	—

Other molecules of linear structure: $HgCl_2$, $HgBr_2$, HgI_2, C_2N_2; see section 11.

Other molecules of pyramidal structure: BCl_3, PCl_3, PBr_3, $AsCl_3$, $SbCl_3$, $BiCl_3$; see 11 and 41.

Other molecules of the type H_2CO: Cl_2CO, S_2Cl_2, $OSCl_2$.

Other molecules of regular tetrahedral structure: CCl_4, CBr_4, $SiCl_4$, $SiBr_4$, $TiCl_4$ $SnCl_4$, $SnBr_4$; see sections 9, 11 and 43.

Other molecules of tetrahedral structure: H_3C hal, H_2C $(hal)_3$, HC $(hal)_3$; see se 11 and 43.

Molecules of octahedral structure: SF_6, SeF_6, TeF_6; see section 11.

the internuclear distances the data obtained from X-ray and electron diffraction (X and E) have been placed next to those furnished by band (B) and Raman (R) spectra. The last column refers to the sections where the various molecules have been discussed in more or less detail and where the literature may be found.

Just as in the case of diatomic molecules discussed in section 24, it is possible to find notable similarities both as regards internuclear distances and binding constants among molecules of analogous constitution. Table 21 illustrates this for two groups of molecules. The molecules in the first group are isoelectronic with N_2 and CO, already discussed in section 26, those in the second group isoelectronic with O_2. Thus HCN may be imagined to arise from N_2 by splitting one of the N-nuclei into a C-nucleus and a H-nucleus. H_2CO from O_2 by splitting one of the O-nuclei into a C-nucleus and two H-nuclei. As frequencies for the polyatomic molecules there have been taken those that correspond to a normal vibration in which the two radicals oscillate essentially as a whole with respect to each other (e.g. the normal vibration $\nu_0\,(s)$ in fig. 46 for C_2H_2). The internuclear distances are those between C, N and O respectively. Table 21 shows clearly the greater strength of binding for the triple bond, as expressed by the greater value of the vibration frequency, a circumstance mentioned in connection with diatomic molecules at the end of section 24.

TABLE 21

SPECTROSCOPIC CONSTANTS OF ISOELECTRONIC MOLECULES

Molecule	ω cm^{-1}	ρ Å	Molecule	ω cm^{-1}	ρ Å
N≡N	2360	1·09	O=O	1568	1·20
C≡O	2167	1·13	H_2C=O	(1770)	(1·19)
HC≡N	2037	(1·15)	H_2C=CH_2	1623	(1·25)
HC≡CH	1975	1·21			

The constancy of the internuclear distances of certain bonds such as C—C, C=C, C≡C, C—H and others in different compounds we have already referred to in chapter II. The optical data confirm the results obtained there. Also it is of interest

to point out that the small mass of the H-atom entails that the C—H bond may be said to have a rather well-defined vibration frequency in the neighbourhood of 3000 cm^{-1}. This is due on the one hand to H having only one valence and on the other to the small mass of H as compared with that of other atoms. The first circumstance entails that the H-atom will always occupy in the molecule an end-on position, the second that there will be a normal vibration in which only the H-atom (or the H-atoms) vibrates while the other atoms are practically at rest. Table 22 shows the slight effect which the nature of the other atoms has on the vibration frequency of the C—H bond as it appears in the absorption spectrum.

TABLE 22

OBSERVED FREQUENCY OF THE C—H BOND IN DIFFERENT COMPOUNDS

Molecule	HCN	C_2H_2	H_2CO	CH_4	$CHCl_3$	$CHBr_3$	C_2H_4	C_6H_6
ω cm^{-1}	3290	3277	(2945)	3020	3016	3021	2988	3030

46. ELECTRONIC BANDS OF POLYATOMIC MOLECULES

Until now we have only considered the rotation and vibration-rotation spectra of polyatomic molecules. The information to be gained from *electronic bands* is here much more limited than in the case of diatomic molecules. As mentioned already in section 31, the reason for this is a twofold one: on the experimental side the diffuse character of the electronic spectra in most cases, due to causes which we shall discuss in the next chapter; on the theoretical side the greater difficulty of finding suitable means to classify the electronic states.

In the case of rectilinear molecules the angular momentum of the electrons about the internuclear line will evidently be a constant just as for diatomic molecules and may be specified by a quantum number Λ. In addition for all molecules the resultant electronic spin S may be used to help to characterise the electronic states. Finally in molecules with elements of symmetry the electronic states will fall into different classes according to the behaviour of the electronic part of the wave function with respect to the different symmetry operations.

Various *selection rules* will again govern the changes in the quantum numbers and in the kind of symmetry in radiative transitions, discussed in detail by Mulliken (128).

Electronic bands in the case of rectilinear molecules have been studied in absorption for the following cases: CO_2 (78, 111, 143), CS_2 (97), N_2O (111), C_2H_2 (100), without, however, making it possible to draw any very definite conclusions. In most cases the bands, situated in general in the ultra-violet and far ultra-violet, are diffuse, but for CO_2 also bands with discrete structure have been observed in emission by Schmid (154), resembling in many ways the bands of diatomic molecules so that in both the electronic states of these bands the molecule probably is rectilinear.

Another feature of interest in this connection is the fact that the rectilinear molecules CO_2, CS_2, N_2O, HCN, OCS and C_2H_2 must have $\Lambda = 0$, $S = 0$ in their ground state since all these gases are diamagnetic. In other words their ground state is a $^1\Sigma$-state. From this it may be concluded that in the dissociation processes

$$CO_2 \rightarrow CO + O,$$
$$CS_2 \rightarrow CS + S,$$
$$N_2O \rightarrow NO + N \quad \text{or} \quad N_2O \rightarrow N_2 + O,$$
$$HCN \rightarrow CH + N,$$
$$OCS \rightarrow CS + O$$

upon being performed by slowly separating the two dissociation products, those at the end cannot both be in their ground state. For the ground states are, according to table 8 and the periodic table at the end of the book: $^1\Sigma$ for CO and CS; $^2\Pi$ for NO and CH; ^3P for O and S and ^4S for N. The two dissociation products in each of the above equations have hence different multiplicities or S-values S_1 and S_2 so that, upon being brought together, they never could give the singlet ground state with $S = 0$ of the triatomic molecules on the left since S is obtained from S_1 and S_2 according to the vector addition rule

$$S = |S_1 - S_2|, \quad |S_1 - S_2| + 1, \quad \ldots, \quad S_1 + S_2$$

(see section 26).

For CO_2 and N_2O Herzberg (84) has considered more carefully the various possibilities for the dissociation processes men-

tioned. His conclusions are embodied in figs. 53 and 54. In fig. 53 we have on the left the energy levels for N_2O with large distance N—N with energies obtained additively from those of N and NO, while on the right are shown the energy levels for N_2O with large distance N—O corresponding to dissociation into N_2 and O. The ground state of the molecule is joined on to the lowest states of the dissociation products that can give together $S = 0$. The distance 41 cal of the level $N_2(^1\Sigma) + O(^3P)$ above the ground state of the molecule is obtained from the thermochemically known reaction

$$2N_2O \rightarrow 2N_2 + O_2 + 35\,\text{cal}$$

and from the known energy of dissociation 117·5 cal of O_2. The distance 88 cal of the level $N(^4S) + NO(^2\Pi)$ above the same ground state follows from the level $N_2(^1\Sigma) + O(^3P)$ and the energies of dissociation 169·5 cal and 121·0 cal of N_2 and NO. The situation for CO_2, represented in fig. 54 is quite analogous. The position of the energy level $CO(^1\Sigma) + O(^3P)$ of CO and O in their ground states 125 cal above the ground state of the molecule CO_2 follows by the same reasoning as in the case of N_2O. The significance of the results here obtained for the problem of dissociation will be discussed in section 60.

In the case of triangular triatomic molecules some interesting electronic band systems have been obtained in absorption for NO_2[52,82,83,119], SO_2[48,49,70,116,168] and ClO_2[104,165]. NO_2 has a very involved spectrum, partially discrete, partially diffuse, extending from 7000 Å into the ultra-violet. For SO_2 a spectrum with well-defined vibrational structure lies between 2500 and 3400 Å. In the case of ClO_2 Ku[104] could represent the ultra-violet absorption band system by a vibrational formula from which we have derived already in section 40 the normal frequencies in the ground state. The ultra-violet absorption of O_3 has also been studied[173].

The electronic spectrum of NH_3 in the ultra-violet has been studied repeatedly[43,64,111]. It is entirely diffuse. The same applies to the electronic spectrum of CH_4[65,111]. Also that of C_2H_4 has only slight structure[141]. We shall discuss certain peculiarities in chapter VI in connection with photochemical

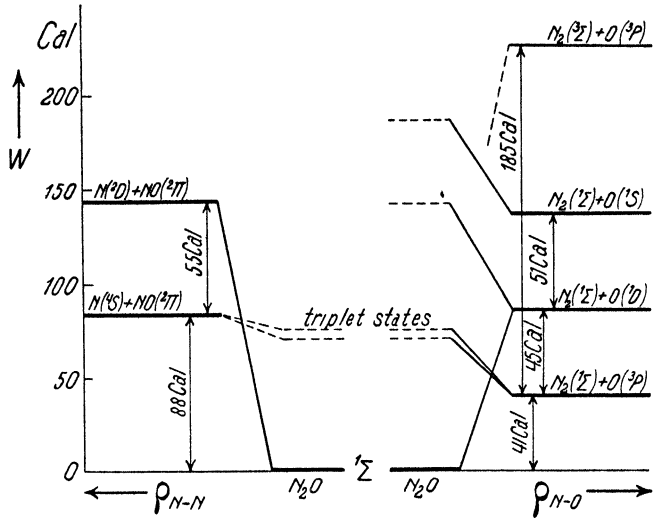


Fig. 53. Diagram showing electronic states of N_2O and their correlation to the states of the dissociation products.

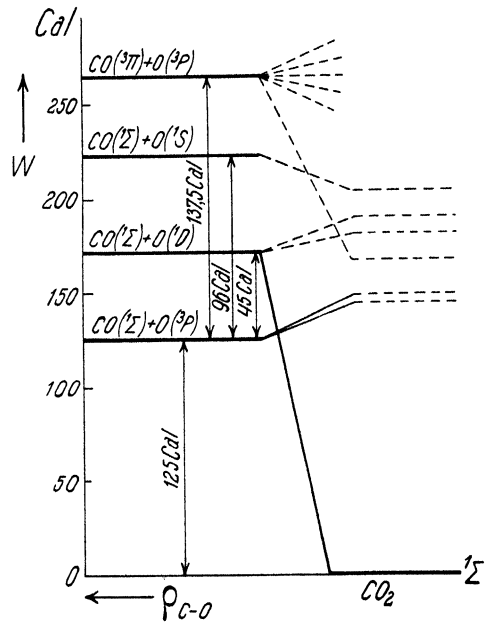


Fig. 54. Diagram showing electronic states of CO_2 and their correlation to the states of the dissociation products.

processes. The electronic spectrum of H_2CO on the other hand has a discrete structure as mentioned already in section 42. It has been investigated by several authors (71, 80, 85), most recently and extensively by Dieke and Kistiakowsky (62, 63). The conclusions regarding shape and size as well as the normal frequencies in the ground state which may be drawn from this spectrum we have enumerated before (see section 42).

47. THE PROBLEM OF BINDING IN POLYATOMIC MOLECULES

We have discussed in the preceding part of the chapter the spectroscopic evidence regarding the geometrical configuration (molecular size and shape as determined by the internuclear distances and the valence angles) and the strength of binding (as it appears in the nuclear vibration frequencies) of the simpler polyatomic molecules. The ordinary chemical notions were in general confirmed by this evidence while in many cases additional information, not derivable from chemical experiences, was obtained (e.g. the triangular form of H_2O). We are now confronted with the problem, already dealt with for diatomic molecules in chapter IV, of interpreting the chemical and spectroscopic evidence in terms of the properties of the electrons that give rise to the binding forces. Before discussing the different view-points proposed, we shall summarise briefly the situation as it appears from the chemical side.

The most complete formulation, from the standpoint of the chemist, of the facts concerning valence in a great variety of compounds is the one due to G. N. Lewis. Its essential features are the following:

The various atoms in a compound have the tendency to give up, or take on, or share electrons in such a way as to be surrounded by a *shell of eight electrons* (rare gas configuration). When electrons are shared, they may be shared equally, as in H_2 and N_2, or unequally, as in NaCl, so that one has all possible stages between the case where the molecule, even in its equilibrium state, is a partnership of two neutral atoms or of two ions.

A *single valence bond* is regarded as due to a *pair of outside electrons* shared by two atoms. As just stressed, this sharing may be symmetrical or unsymmetrical. The valence which an atom has in a molecule is the number of electron pairs which it shares with other atoms in the molecule. The valence thus defined agrees with the *coordination number* as introduced into chemistry by Werner and the *covalence* of Langmuir. In the case of heteropolar molecules which one may consider as built up of ions, Lewis speaks of *polar number* rather than valence so that, e.g. in $Ca^{++}Cl_2^-$, the polar number of Ca is 2. Langmuir employs the term *electrovalence*. In general it is so that the two partners each contribute one electron to a valence bond, but there are exceptions where one partner furnishes both. *Double* and *threefold valence bonds* are ascribed to the sharing of two and three pairs of electrons.

By the advent of atomic theory these empirical notions of Lewis have obtained a theoretical foundation. On the basis of the developments described in chapter III, resting mainly on the classification of the atomic electrons by means of quantum numbers and the exclusion principle of Pauli (see section 14), it became intelligible why the group of eight electrons (and the less stable group of eighteen electrons) should play so predominant a rôle in chemistry. An insight into the significance of electron sharing, however, was only afforded by quantum mechanics. With a view to the empirical data we may regard it more precisely as the task of the theory to give an interpretation of the concept of valence which not only refers to the possibility of an atom to enter into compounds but also signifies an opportunity which the atom on the average makes use of so far as circumstances permit. Let us therefore look first for an explanation of valence as a property of the individual isolated atom and afterwards discuss the deviations from the standard behaviour to which the different character of the partners gives rise.

Depending upon the method of approach we may distinguish three theories of chemical binding, all of which are intimately connected with the notions of Lewis. The first of these, due to Heitler and London (77), we have already discussed

for the case of diatomic molecules in section 27. It starts from the states of the separate atoms entering into a compound and tries to interpret the saturation of valences and the electron pair bond by the neutralisation of the electron spins in these atoms. The second theory, developed by Pauling(134) and Slater(155), does not start from the states of the separate atoms as a whole but from the states of the individual electrons of the atoms. It furnished for the first time an understanding of the *directed nature of the valence bonds*, i.e. their tendency to form definite angles with each other, such as the tetrahedral angle in quadrivalent carbon. The last method which we owe to the work of Hund(96) and Mulliken(128) has also been discussed already for diatomic molecules in section 28. It begins directly with the properties of the electrons in the molecule rather than with those of the electrons in the separate atoms. We shall consider the three theories with their relative merits and disadvantages in the next sections. In comparing them with the notions as introduced by Lewis it will be instructive to keep in mind that there are three essential elements in his ideas: (*a*) the tendency of the atoms to give rare gas configurations of eight electrons, a feature also stressed in other valence theories such as that of Kossel; (*b*) the tendency of certain electrons, to which the bonding power is ascribed, of being geometrically localised between the partners which they tie together; (*c*) the tendency of these bonding electrons to occur in pairs, as evidenced by the circumstance that the great majority of stable molecules have an even number of electrons. It will appear then that the three theories mentioned above put the emphasis on these features in a different way.

48. THE HEITLER-LONDON THEORY OF CHEMICAL BINDING

In section 27 we have discussed for the case of diatomic molecules the theory of chemical binding as developed by Heitler and London(77), which starts from the states of the separate atoms. We saw there that the mutual cancellation of the electron spins of the two atoms concerned, which Heitler and London consider as the physical mechanism behind the chemical

experience known as saturation of valences, actually occurs in most cases of molecule formation where the constituent atoms are in S-states. Before going into the limitations of the theory and its connection with the idea of electron pairs proposed by Lewis we shall investigate its applicability to polyatomic molecules, pointing out some new features that appear only if the number of atoms in the molecule is greater than two (1).

If in a polyatomic molecule built up from atoms in S-states we let the electron spins of the constituent atoms compensate each other in pairs, we should be inclined, in analogy with the case of diatomic molecules, to write down as structure formula one in which to every electron pair there corresponds a valence dash. Thus if we take the four electrons outside the K-shell of a quadrivalent C-atom in the state ^5S and compensate the spin of one of them by the spin of the electron of an H-atom in its normal ^2S-state, the spin of the three others by the spins of the three $2p$-electrons of an N-atom in its normal ^4S-state, we get the molecule hydrogen cyanide

$$\mathrm{H{-}C{\equiv}N} \qquad (48{\cdot}1)$$

with the resultant spin 0. The state of a molecule described by such a structure formula is known as a *pure valence state*. It is easily seen that in the example just given the compensation process expressed by the formula (48·1) is the only one which will lead to a resultant spin 0.

Take on the other hand the isonitril group, according to ordinary chemical notions written as

$$\mathrm{H{-}N{=}C{=}} \qquad (48{\cdot}2)$$

with two free valences, i.e. with a resultant spin 1. Of the three valence electrons of the N-atom one has its spin compensated by the spin of the electron of the H-atom, two by the spins of two valence electrons of the C-atom while two valence electrons of the C-atom have uncompensated spins. We might, however, also have obtained the resultant spin 1 of the group by the following compensation processes

$$\overline{\mathrm{H\ \ N{=}C{-}}} \qquad (48{\cdot}3)$$

$$\quad\ |$$

and $$\mathrm{{-}H\ \ N{\equiv}C{-}} \qquad (48{\cdot}4)$$

The two structure formulae, (48·3), (48·4), are at variance with chemical usage. The perturbation calculus of Heitler and London for this case shows, however, that the actual stationary state of the group CNH corresponds to a "mixture" of the three pure valence states, (48·2), (48·3), (48·4), in this sense that the quantum-mechanical wave function of the binding electrons is a linear superposition of the wave functions associated with each of the above pictures. The justification of the formula (48·2) lies in the fact that in the wave function associated with a stable molecule the part which it contributes predominates over the parts arising from the other "idiotic" structure formulae.

The case that a given value of the resultant spin can only be realised by one pure valence state is by far the simplest. The perturbation calculus of Heitler and London teaches then that the binding energy of the molecule will be essentially the sum of the binding energies corresponding to the individual bonds. Apart from diatomic molecules, the most important case is that of a polyatomic molecule $ABC\ldots$ in which the spin S_A is greater than or equal to the algebraic sum of the spins S_B, S_C, ... Next to HCN, already discussed, NH_3, PH_3, AsH_3, CH_4, SiH_4 and the radicals NH_2, CH_3 should be mentioned. In those cases where the same resultant spin can be obtained by various ways of reaction it must in general be expected that the energies of the different bonds are not simply additive.

The defects of the theory appear in the first place when it attempts to deal with atoms not in S-states, a circumstance already mentioned in section 27 in connection with diatomic molecules. An interpretation of the numerous compounds between oxygen, sulphur and the halogens seems at present hardly possible. Also the quadrivalent nature of the C-atom in many of its compounds must be ascribed to the existence of a low ^5S-term which hitherto is entirely hypothetical (see the example of HCN previously discussed). The preferential occurrence of bonding electrons in pairs as postulated by Lewis finds a simple explanation. But the theory leaves no room for cases where both the bonding electrons are furnished by one and the same partner. Also it does not cover the numerous

compounds, of which the hydrogen molecular ion H_2^+ is the simplest representative, where unpaired electrons contribute essentially to the binding. Finally the restriction of the calculations to a first approximation makes many results doubtful, especially when near the normal states of the interacting atoms there lie other states; a shortcoming pointed out already under (*c*) in section 27.

49. THE SLATER-PAULING THEORY OF CHEMICAL BINDING

To avoid the last one of the defects just mentioned Slater(155) and Pauling(134), instead of using as starting point of a perturbation calculus separate atoms in definite stationary states, investigate the interaction of atoms with given electronic configurations. This means that the mutual influence of the electrons at first is taken into account only in so far as it may be represented by a screening of the nuclear field (a Thomas-Fermi field, screening constants, or a Hartree field, see section 7) while the coupling of the different angular momentum vectors is neglected. In this approximation all stationary states of an atom with the same electron configuration coincide energetically. In the case of the light elements, where the principal quantum numbers also of the outermost electrons are small, it may even prove advisable to forget about the difference in energy for the electrons with the same principal but different azimuthal quantum number (e.g. 2*s*- and 2*p*-electrons), this difference in some cases being small compared with the energy changes due to chemical binding.

The next step in the procedure is to consider the charge distribution due to the electrons outside closed shells as furnished by the square of the wave functions of these electrons (see section 2). An *s*-electron always gives a spherical charge distribution (see fig. 55 (*a*)), as does also a closed shell. To a *p*-electron, on the other hand, there correspond three possible charge distributions, due to the circumstance, already mentioned in section 14, that a *p*-state really must be regarded as three coincident states. The three wave functions associated with it according to wave mechanics may then be chosen in

such a way that the first gives a charge distribution with the x-axis as axis of rotational symmetry and with a concentration of charge before and behind the yz-plane (see fig. 55 (b)), while the other two wave functions give analogous distributions with respect to the y- and z-axes. We shall hence denote the three sub-states as p_x, p_y and p_z.

The sign of the interaction energy, not taken into account already in the screening of the nuclear field, of the electrons in the same atom and in different atoms depends essentially upon the relative orientation of their spin vectors. For equivalent

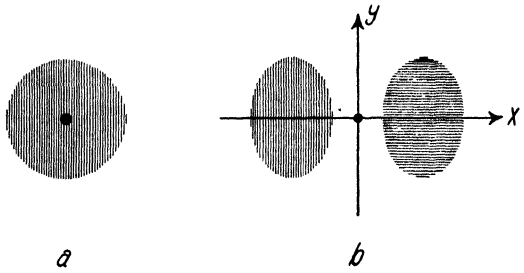


Fig. 55. Charge distribution (a) for an s-electron, (b) for a p-electron.

electrons in the same atom quantum mechanics teaches that a parallel orientation of their spins gives a negative, an anti-parallel orientation a positive interaction energy. Experience confirms this, showing that in general the lowest atomic state belonging to a given electronic configuration has the largest possible resultant spin S (highest possible multiplicity). Thus if we have two np-electrons outside closed shells, the lowest atomic state will have $S=1$. A consequence of the greatest importance for the following considerations is that on the basis of the exclusion principle (see section 14) they cannot then be both np_x-electrons or np_y-electrons, or np_z-electrons, but that e.g. one must be an np_x-electron, the other an np_y-electron. Similarly three np-electrons will have the tendency to give a resultant spin $\frac{3}{2}$, one electron becoming an np_x-electron, another one an np_y-electron, the third an np_z-electron. On the contrary for two electrons in different atoms Slater, following Heitler and London, assumes the interaction energy to be

negative for antiparallel, positive for parallel orientation of the spin vectors. As regards the magnitude of this interaction energy it will be primarily determined by the degree of overlapping of the charge distributions spoken of before.

For atoms having only s-electrons outside closed shells the Slater-Pauling theory in its results does not go essentially beyond the work of Heitler and London. In the case of p-electrons, however, one obtains in a rather simple way an interpretation of the *directed nature of the valence bonds*. As an illustration take an atom A with two equivalent p-electrons outside

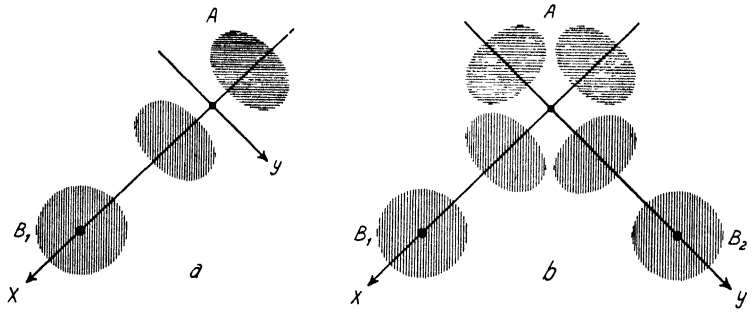


Fig. 56. Charge distributions giving rise to the binding of two atoms B_1 and B_2 with an s-electron each by an atom A with two p-electrons. (a) Binding of the first atom B_1. (b) Binding of the additional atom B_2 under a valence angle of 90°. In the equilibrium configuration B_1 and B_2 must be close enough to A to make their charge distributions overlap with that of A.

closed shells and two atoms B_1 and B_2 each with one s-electron outside closed shells. We only take into account these outside electrons since the closed shells usually have radii small enough compared with the internuclear distances in the actual molecule to preclude any noticeable overlapping of their charge distributions. Take the line joining the nuclei A and B_1 as x-axis. Then according to the above, in order to get strong binding between these two atoms, we must let the spin of the s-electron of B_1 compensate the spin of one of the p-electrons of A, and moreover we must chose as this p-electron the one described by the wave function p_x (see fig. 56 (a)). Now the other p-electron of A will not be in the state p_x, but in p_y, say. Then, in order to get strong binding of B_2, we must not only

compensate the spin of this electron by the spin of the s-electron of B_2, but we must also locate the nucleus of B_2 somewhere near the y-axis, so as to give a proper overlapping of the charge distributions (see fig. 56 (b)). In other words the most stable molecular configuration will be one in which the two lines AB_1 and AB_2 form approximately a right angle. The extension to an atom A with three equivalent p-electrons outside closed shells and three atoms B_1, B_2, B_3, each with an s-electron outside closed shells, is obvious. Here the three valence bonds AB_1, AB_2, AB_3 will tend to form right angles so that one now gets instead of the triangular molecule of the previous example a molecule in the shape of a regular pyramid.

The water molecule is an example of the first case. The O-atom, it is true, has four equivalent $2p$-electrons outside closed shells. Wave mechanics, however, teaches that a shell with r unoccupied places behaves in many respects like a shell with r occupied places, and since there is room for six $2p$-electrons, we are justified in mentioning H_2O in this connection. Examples of the second kind are NH_3, PH_3, AsH_3. As we have seen in the beginning of this chapter, the shape of all these molecules indeed is in accordance with the conclusions arrived at above.

Of the greatest interest in this connection is the C-atom. The isolated C-atom has two $2s$- and two $2p$-electrons. The binding strength of the $2s$-electrons is not very much different from that of the $2p$-electrons, the difference in energy being comparable to the energy changes in chemical union. Hence, it will not surprise if the C-atom enters into many compounds with one $2s$-electron and three $2p$-electrons. But with this latter configuration a charge distribution can be shown to be especially stable in which the greatest density occurs at the corner points of a regular tetrahedron. By the arguments already employed in the case of water other atoms will then attach themselves to the C-atom in the points thus distinguished. In this way of presenting the state of affairs the quadrivalence of carbon in many compounds is ascribed to the presence of four outside electrons with approximately the same binding energy rather than to a particular ^5S-term of the

C-atom as in the Heitler-London theory (see section 48), and, moreover, the tetrahedral arrangement of the bonds is explained.

Summarising, we may say that the present theory goes beyond that of Heitler-London in permitting us to deal also simply with atoms not in S-states and in furnishing an interpretation of the directed nature of valence bonds. Comparing it with the notions of Lewis, we see immediately that here too the idea of the electron pair plays an essential rôle in so far as it is necessary for the binding of two atoms to have the charge distributions of two electrons, one in each atom, overlap properly. The bonding power of unpaired electrons or the binding in case one of the partners furnishes all the bonding electrons cannot be dealt with by this method either. The mathematical procedure is again a perturbation calculus starting from atoms in the limiting case of infinite separation, but the criticism of its applicability is not as severe as for the Heitler-London theory since all low-lying atomic states are taken equally into account.

50. THE HUND-MULLIKEN THEORY OF CHEMICAL BINDING

In contrast to the theories previously described this theory does not start from separate atoms in definite stationary states or with definite electronic configurations but considers the electrons to be fed, one at a time, without mutual interaction into the nuclear framework, in which the distances and angles are assumed to have their equilibrium values while a suitable shielding of the nuclear charges representing the ultimate effect of the electron cloud is introduced from the beginning. Each electron is then captured in the state of lowest energy not yet occupied by other electrons. Here, too, the preferential occurrence of the bonding electrons in pairs is intelligible since, due to the two possible orientations of the spin, each type of "orbit" can contain two electrons. But there is room in this treatment also for the case of unpaired electrons (in molecules with an uneven number of electrons). Another advantage, to which

attention has been called in dealing with diatomic molecules on the basis of this method in section 28, is the ease with which the physical and chemical similarity of *isosteric molecules* is understood. Such a similarity is also met with in the case of polyatomic molecules. Examples are N_2O and CO_2, both rectilinear molecules with 22 electrons, for which we have compiled a number of typical properties in table 23.

TABLE 23

PHYSICAL PROPERTIES OF CO_2 AND N_2O

	CO_2	N_2O
Melting point, abs.	216	171
Boiling point, abs.	195	183
Critical temperature, abs.	305	308
Critical pressure, atm.	77	75
Density in fluid state	1·031	0·996
Solubility in water at 0° C, in 1 gas/1	1·780	1·305
Viscosity. 10^6 at 0° C	148	148
Ground state	$^1\Sigma$	$^1\Sigma$
Vibration frequencies in ground state for infinitely small amplitudes, cm^{-1}	1361 2378 673	1289 2238 588
Moment of inertia in ground state, 10^{40} g.cm^2	70·1	66·0

In the Hund-Mulliken picture there is ascribed to every electron an independent wave function with symmetry properties with respect to the symmetry operations which the nuclear framework permits. Such individual wave functions have been termed *orbitals* by Mulliken.

The rôle which the various electrons play in the binding of the molecule may again be related to the concept of *promotion* introduced in section 28. Electrons which, upon letting two nuclei coincide, are brought into stationary states higher than the lowest unoccupied ones in the resulting system will act as anti-bonding electrons while the other electrons are of the bonding type. The electrons in the innermost shells of the atoms will, of course, in general have non-bonding character.

Van Vleck(167) has compared from the quantitative viewpoint the advantages and disadvantages of the Slater-Pauling method and the Hund-Mulliken method for *methane*, CH_4. He also shows, by applying both methods, that the regular tetra-

hedral model is the most stable configuration of the nuclei. For molecules of the type CH_3X, CH_2X_2, CHX_3 there will result in general tetrahedra which are no longer regular unless the bonds C—H and C—X are of equal strength. This is in accord with the experimental results on the spreading of the valence angle for different halogen substitution products of CH_4, discussed in sections 9 (*c*) and 11 (*c*). Van Vleck considers also the interesting case of CH_4^+ in which one of the bonding electrons has been removed and comes to the conclusion that this molecule must be either a very flat tetrahedron or even coplanar.

Penney(135) has used the theoretical procedures outlined to investigate the problem of free rotation about the single and double bond between two C-atoms. The calculations have been carried out for *ethylene*, C_2H_4, and for *ethane*, C_2H_6. For C_2H_4 the overlapping of the wave functions in the Pauling-Slater method as well as the orbitals of the Hund-Mulliken method lead to the result that the coplanar configuration of the nuclei is the most stable and that the valence angle between the bonds from a C-atom to the two H-atoms is probably quite large, about 130°. (This angle in the regular tetrahedron is 109·5°; see section 9 (*c*).) The coplanar structure is in accordance with the ordinary chemical notions. The large angle shows again that the valence directions are not as rigidly attached to an atom as has often been supposed. Penney also estimates the energy required to twist the two CH_2-groups with respect to each other around the double bond from the coplanar position into the perpendicular position and finds for it about $\frac{1}{2}$ electron-volt. Since the energy of thermal agitation at ordinary temperatures is about 0·02 volt, we see that a passage of the molecule from the one equilibrium position to the other, where the two end groups are again coplanar but turned with respect to each other through 180°, is a rather rare event. The possibility of preparing isomers of dichlorethylene which do not change over into each other must be due to similar circumstances. The notion that a double bond between two C-atoms handicaps free rotation is thus made comprehensible. The less explicit calculations of Penney for C_2H_6 point out that for the

single bond the maxima to be overcome when turning the two groups CH_3 with respect to each other are much less pronounced.

A good deal of theoretical work has also been expended on *benzene*, C_6H_6. Especially the publications of Hückel(94) and of Penney(136) should be mentioned here. The principal result of the latter author is that of all ring compounds built from n groups CH in the form of regular polygons the one with $n=6$, i.e. benzene, is by far the stablest. The stability should change only slightly if some or all of the H-atoms are replaced by other monovalent atoms or radicals as is actually shown by chemical experience. Penney studies also rings built from n groups CH_2 and concludes that while for $n=3$, 4 and 5 the C-atoms should lie in one plane, the rings should be buckled for $n>5$. This is borne out by the experiments on electron diffraction on cyclopentane and cyclohexane discussed in section 11 (f).

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CHAPTER VI

OPTICAL AND THERMAL DISSOCIATION

51. GENERAL REMARKS

In the two previous chapters we have confined our attention to band spectra of discrete structure. Very often, however, there appear next to them *diffuse spectra*, in some cases in absorption, in others in emission. These spectra fall into different categories, strictly *continuous spectra* without any structure and *predissociation spectra* in which the discrete band lines have a breadth much greater than the natural breadth (due to radiation damping and of the order of a few thousandths of an Å) so that the rotational structure of the bands is obscured or may even disappear entirely, leaving only a vibrational structure. The continuous spectra appearing in emission are in general connected with the presence of electronic states of the repulsive type or of very slight stability and often furnish the only means of investigating such states. The absorption continua are associated either with the dissociation of a molecule into atoms or with the ionisation of the molecule and supply an important method of measuring exactly the dissociation energies. The predissociation spectra may serve this same purpose and sometimes also allow the determination of the nature of the dissociation products when these are not known otherwise. Hence, it is justified to consider the various kinds of *optical dissociation* processes in greater detail.

Next to them it is of interest to consider the phenomena of *thermal dissociation* in the light of the information regarding molecular structure which we have obtained from band spectra. Particularly the theoretical determination of the *degree of dissociation*, not only in its dependence upon temperature and pressure which is predicted by the laws of mass action, but also as regards its absolute value, is a problem which may be faced, at least for the simpler molecules, on the basis of band spectroscopical data.

52. THE CONTINUOUS EMISSION SPECTRA OF H_2 AND He_2

The spectrum of electric discharges through hydrogen shows pronounced continua. These are of two types. Under conditions of excitation which are favourable to a high degree of dissociation so that there is an abundance of atomic hydrogen and a predominance of the atomic spectrum (Lyman series, Balmer series, Paschen series, see section 15) there occur continua adjoining the various series limits on the short wave-length side. Since the series limits, according to section 15, correspond to the difference in energy of the electron when removed from the nucleus and when contained in a stationary state of the atom, the continua just mentioned can be interpreted as being the radiation which an electron with finite kinetic energy emits upon being captured by the nucleus. Similar continua have been observed also for He and for the metallic vapours of the elements in the first and third column of the periodic table.

Returning to the case of hydrogen, there appears another continuum, much more easily obtainable than the first and associated with the ordinary molecular spectrum, the so-called many-line spectrum of the hydrogen molecule. Of the numerous interpretations suggested by different authors the one proposed by Winans and Stueckelberg(30) is now generally accepted. According to them the continuum arises from the fact, already mentioned in section 27, that two H-atoms in their normal state ^2S according to Heitler and London can react in two different ways. They can attract each other, giving a molecular state $(1s\sigma)^2\,{}^1\Sigma_g$ (for the significance of this and similar symbols see sections 25 and 26) with a minimum of its potential energy curve, corresponding to the formation of a stable H_2-molecule, or they can repel each other according to a repulsive energy curve belonging to a $1s\sigma\,2p\sigma\,{}^3\Sigma_u$-state. Now hydrogen molecules in excited triplet states, especially in the state $1s\sigma\,2s\sigma\,{}^3\Sigma_g$, according to the selection rules mentioned in section 25, which make radiative transitions between triplet and singlet states very improbable, have, as practically the

only way of giving up their excess energy, the possibility of jumping on to the repulsive energy curve $1s\sigma\,2p\sigma\,{}^3\Sigma_u$ under emission of radiation. Depending upon the vibrational level of the upper state in which the molecule originally was contained

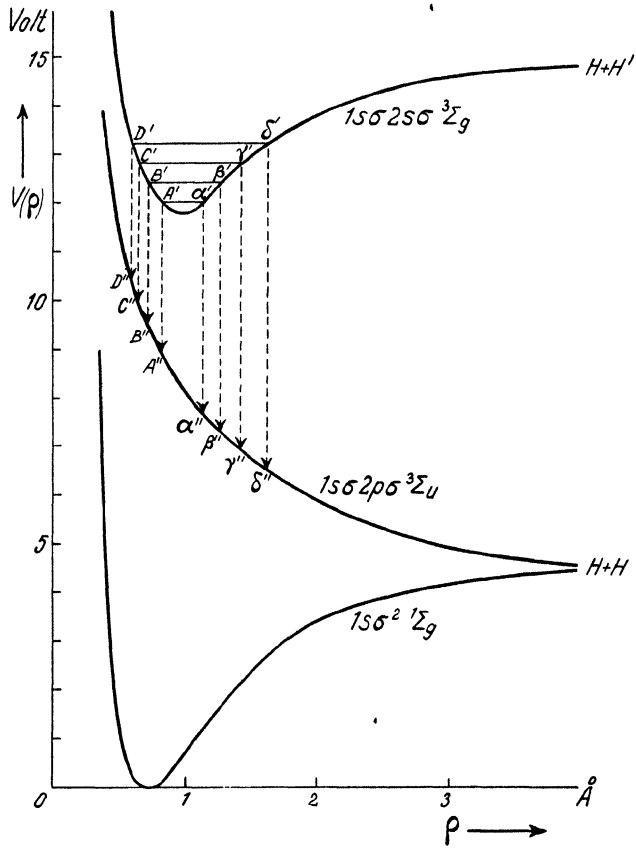


Fig. 57. Origin of the continuous spectrum of the H_2-molecule.

and upon the internuclear distance at which the electronic transition takes place a smaller or larger quantum of energy is emitted.

Fig. 57 illustrates this state of affairs. The vertical dotted lines are drawn through the points at which the vibratory motion of the molecule in the upper state reverses its sense in

the classical model since, according to the principle of Franck and Condon (see section 25), the electronic transitions by preference take place for these values of the internuclear distance, in the neighbourhood of which the molecule remains longer than elsewhere. The length of the dotted lines is a measure for the energy transformed into radiation and hence for the frequency emitted. Since the molecule may not only perform transitions at the points of reversal but also in between, though with smaller probability, one gets a continuous spectrum extending from small frequencies as represented by $D'D''$ to large frequencies as represented by $\delta'\delta''$. The excess of energy of the molecule in the points A'', B'', etc., above the horizontal asymptote to which the repulsive curve approaches for large values of the internuclear distance and which corresponds to dissociation into two normal H-atoms appears as kinetic energy of the atoms after dissociation.

Similar continua, probably also due to transitions of the molecule to repulsive electronic states, have been found for He_2. For a detailed review of the experimental investigations concerning them and the hydrogen continua see the report by Finkelnburg(1).

53. THE CONTINUOUS ABSORPTION OF THE HALOGENS, THE HYDROGEN AND ALKALI HALIDES

The *halogen molecules*, Cl_2, Br_2, J_2, show in absorption discrete bands in the visible spectrum converging toward a limit on the short wave-length side, beyond which continuous absorption sets in. As shown especially by the work of Kuhn(22), the maximum of the absorption lies in all cases in the continuous spectrum, but there is a progression noticeable in going from J_2 to Cl_2, such that for J_2 the maximum lies still rather close to the limit of convergence, about 400 Å away from it, while for Br_2 it is 900 Å, for Cl_2 even 1400 Å removed from the limit.

The interpretation of these facts can be given with the aid of fig. 58 and the Franck-Condon rule discussed in section 25. Most of the molecules at room temperature will be present in the vibrational level $v''=0$ of the ground state. Now if

the upper state has the minimum of its energy curve not directly above that of the ground state but at a much larger value of the internuclear distance (fig. 58), as is actually the case for the halogens, then the transitions to the discrete vibrational levels of the upper state according to Franck and Condon will be rather improbable while the transitions bringing the molecule to the portion of the energy curve

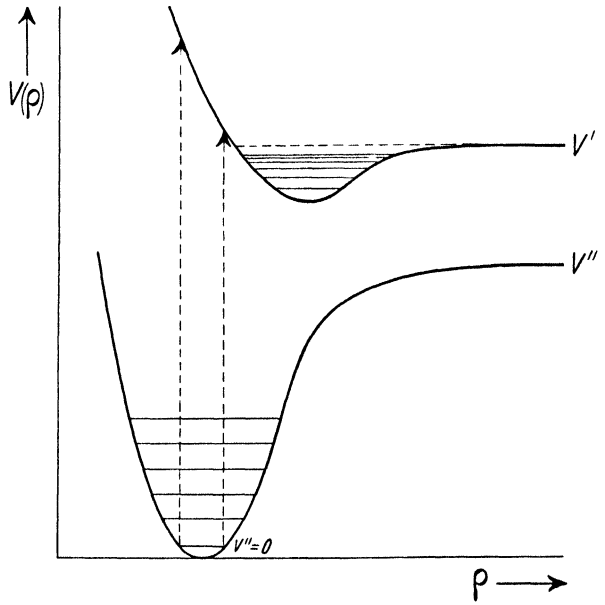


Fig. 58. Franck-Condon construction as applied to the continuous absorption of the halogen molecules.

directly above the minimum of the ground state will occur very often. But as shown in fig. 58 these transitions give sufficient energy to the molecule to enable it to dissociate. The discrete vibrational levels of the upper state converge to the horizontal asymptote of its energy curve, corresponding to dissociation (see section 21), and above this asymptote the energy is no longer quantised since the molecule may dissociate into atoms with any amount of excess kinetic energy. Hence the converging sequence of discrete bands with a continuous spectrum of predominating intensity adjoining. Since

for the halogens the convergence limit of the vibrational levels of the upper state is actually observable and not only known from extrapolation, very exact values can be obtained here for the dissociation energies (see table 8).

For the *hydrogen halides* and for the *alkali halides* only continuous absorption is observed. This may be due to the fact that the energy curve of the upper state has a minimum which is displaced still more towards large values of ρ with respect to the minimum of the ground state than in the halogen molecules, making transitions to the discrete vibrational levels of the upper state, according to Franck and Condon, practically impossible. Or it may be that the energy curve of the upper state has no minimum but is repulsive. For the alkali halides, as shown especially by the work of Sommermeyer(28) and Schmidt-Ott(27), very probably the latter is the case, and more particularly the energy curves of the upper state appear to be horizontal there up to rather small values of ρ (see fig. 59). This may be concluded as follows. Due to the small size of the vibrational frequency of these rather heavy molecules and to the high temperature required to bring them into the gaseous condition there will be molecules present in all the lower vibrational levels of the ground state. Now the continuous absorption shows a sequence of maxima converging toward the long wave-length side, and these can be interpreted as corresponding to the transitions from the various vibrational levels of the ground state which are most probable according to Franck and Condon, as indicated by the dotted lines in fig. 59. But in order to keep these maxima apart from each other, it is necessary that the energy curve of the upper state has not a very strong curvature in the region where the upper end points of the dotted lines are located as otherwise there is too much leeway in the energy after the transition.

For several of the alkali halides more than one region of continuous absorption has been found so that one must have recourse to a number of repulsive curves as shown for CsJ in fig. 59. From the energy differences between the horizontal parts of these curves one can conclude that these correspond to dissociation into neutral atoms in various stages of excita-

tion. The energy curve of the ground state, on the other hand, very probably leads for increasing internuclear distance to a dissociation into ions so that the alkali halides are to be regarded as heteropolar compounds. For from the construction of fig. 59 it appears that the distances between the

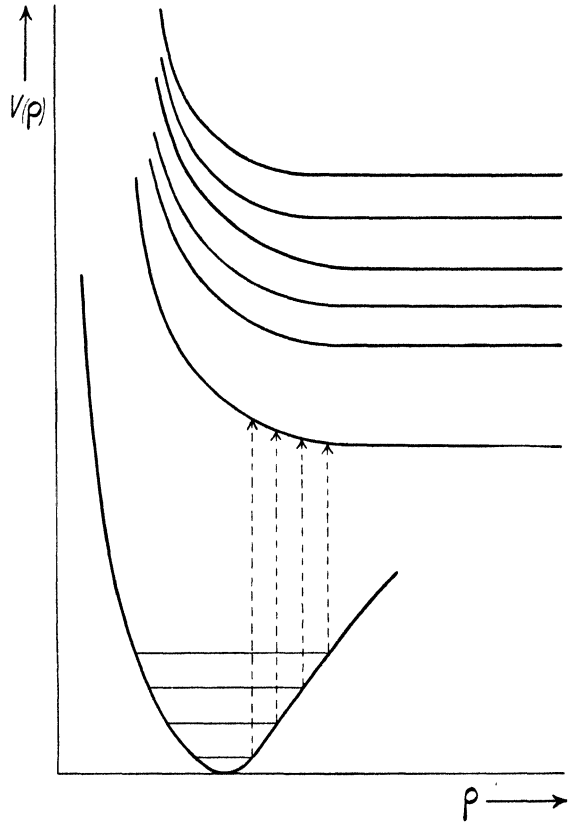


Fig. 59. Origin of the continuous spectra of the molecule CsJ.

maxima of the intensity fluctuations in the absorption continua are approximately the frequency differences of successive vibrational levels, i.e. the vibrational frequency in the ground state. This frequency, on the other hand, has been computed theoretically by Born and Heisenberg(8) on the assumption that the alkali halides are composed of polarisable ions. The

agreement between their theoretical values and the experimental values of Sommermeyer strongly supports the assumption of the heteropolar character of these molecules. Since the ionisation energy of the alkali atoms is greater than the electron affinity of the halogen atoms, the energy curve of the ground state must for sufficiently large ρ cross at least that excited energy curve which corresponds to neutral atoms in their normal state. The convergence of the vibrational levels of the ground states makes it likely that such a crossing actually will occur so that we have here another argument in favour of the heteropolar nature of the alkali halides. That the hydrogen halides, on the other hand, are probably homopolar we have already pointed out in section 23. For a detailed discussion of the experimental data concerning the continuous spectra of the halogens and the hydrogen and alkali halides see the reports by Sponer(6) and Finkelnburg(1).

54. THE POLARISATION MOLECULES

A number of metal vapours, notably those of Zn, Cd and Hg, show continuous emission and absorption bands which must arise from the molecules Zn_2, Cd_2, Hg_2. An interpretation can be given by ascribing to these molecules in the ground state an energy curve with a very flat minimum. Fig. 60, taken from a report of Finkelnburg(1), where these molecules are discussed in detail, shows for Hg_2, on which very complete data are available, the various energy curves involved, their connection with the atomic states in the limiting case of very distant nuclei and the transitions possible between them. The absence of quantisation for the vibrational motion in the ground state entails the continuous character of these spectra.

The same applies to certain bands occurring in metal vapours (Na, K, Rb, Hg, In, Tl) in the presence of rare gases, which Oldenberg and Kuhn(25) ascribe to diatomic compounds between the metal and rare gas atoms. Here, too, the binding in the ground state must be very loose.

The theory of Heitler and London, sketched in section 27, would let one expect that the atoms Zn, Cd, Hg in their ground state should not be capable of molecule formation since the

ground state is a ^1S-state, with vanishing resultant spin, leading only to repulsive interaction. Also the rare gas atoms have as ground state a ^1S-state and should hence not be able to unite with metal atoms. If, however, the perturbation calculus of Heitler and London is carried one approximation further, as has been done especially by Eisenschitz and

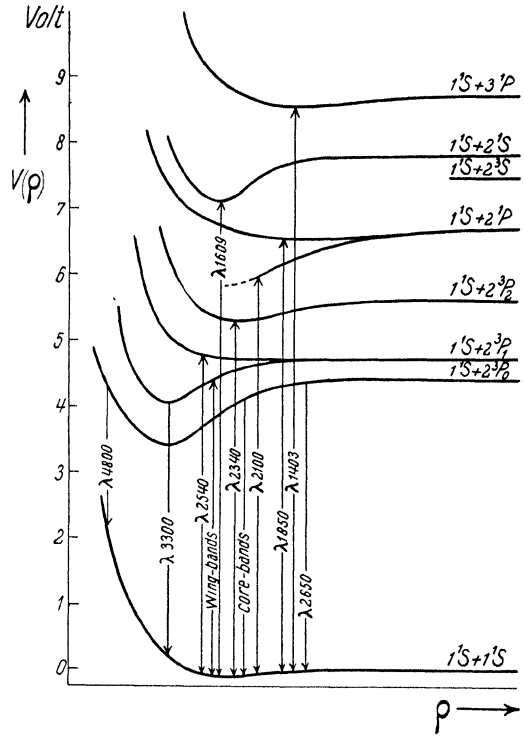


Fig. 60. Origin of the continuous spectra of the Hg_2-molecule.

London(11), it appears that at large internuclear distances, where the repulsive forces of the first approximation have already practically gone to zero, weak attractive forces occur even for these pairs of atoms, giving rise to a flat minimum of the energy curve there. These forces may be termed *polarisation forces* or *van der Waals forces* since they are the cause of the van der Waals correction in the equation of state of the vapour which makes possible the liquefaction at sufficiently

low temperatures and high pressures. The molecules just discussed for the same reason are spoken of as *polarisation molecules* or *van der Waals molecules*.

It is of interest in this connection to consider once more the hydrides of the elements in the second column of the periodic table discussed already in relation to the Heitler-London theory in section 27. We mentioned there that these molecules are not in harmony with the rule forbidding atoms in ^1S-states (here the earth alkalies and Zn, Cd, Hg) to enter into chemical union with other atoms. Thus the situation for them formally is the same as for the molecules discussed above so that we might call these hydrides van der Waals molecules too. Indeed, the "admixture" of the wave functions of excited states to the wave function of the ground state, which in section 27 we made responsible for the deviation from the behaviour to be expected according to Heitler and London, is just what is taken into account by the second approximation of Eisenschitz and London. But there is this difference that for molecules like Hg_2, due to the large atomic sizes bringing about repulsive interaction which outweighs the van der Waals attraction already for rather large values of ρ, the minimum in the energy curve lies far out so that in its neighbourhood the approximation method, starting from separate atoms, is still significant while the small H-nucleus easily penetrates deeply into the electron cloud of the partner so that the equilibrium distance is small enough to make the whole Heitler-London method lose its significance here. This appears also in the values of the depth of the minimum in the ground state, which for Hg_2 is about 0·07 volt while for HgH (where it is smaller than for any other hydride) it is still 0·37 volt. Hence, the hydrides of the elements in the second column of the periodic table may be regarded as a sort of intermediate case between ordinary valence binding and van der Waals binding.

55. PREDISSOCIATION IN DIATOMIC MOLECULES

We consider a stable electronic state of a diatomic molecule, characterised by the energy curve B with the horizontal asymptote QQ in fig. 61. Besides it let the molecule possess

another electronic state, characterised by the energy curve A with the horizontal asymptote PP. In fig. 61 (a) and (b) it is assumed that the state A too is a stable state, while fig. 61 (c) and (d) correspond to a repulsive state A. Evidently, when

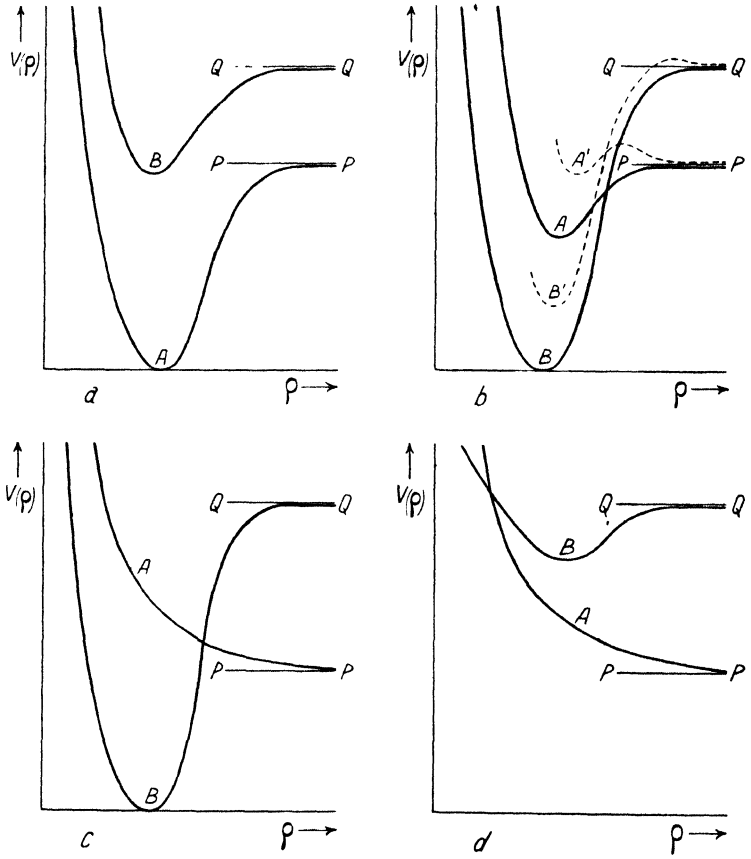


Fig. 61. Different types of energy curves $V(\rho)$ for a diatomic molecule giving rise to predissociation.

the molecule is in one of the vibration-rotation levels of the curve B which lie above the horizontal asymptote PP, it has energetically the possibility of changing its electronic configuration into that associated with the curve A, the energy thus becoming available being used to dissociate the molecule

into two separate atoms. One speaks of a radiationless transition of the molecule from the discrete vibrational levels of curve B into the continuous manifold of energy values above the asymptote PP of curve A.

The question arises now: Will such transitions occur and if so, how great will be their probability? As shown by Kronig[20], the two curves A and B must satisfy certain prerequisites to make transitions of the kind described possible at all. In the first place the multiplicity of the states A and B should be the same while their quantum number Λ (see section 25) should not differ by more than one unit. (These two rules, especially the last, are not quite rigorous since they are based on the assumption of weak interaction between electronic spin, electronic angular momentum and nuclear rotation.) Further if both the states A and B are Σ-states, they must be either both Σ^+ or Σ^-. Finally for homonuclear molecules the states A and B must be either both even or both odd.

Another important factor, considered by Franck and Sponer[12] and by Herzberg[16], is the relative position of the curves A and B. Of the vibration-rotation levels of B with $J=0$, i.e. in the non-rotating molecule, only for those which lie at about the same height as an intersection point of the two energy curves A and B and simultaneously above PP is the chance of radiationless transitions considerable. For the vibration-rotation levels of B with $J \neq 0$ we must first add to the energy curves A and B the potential energy of the centrifugal forces

$$\frac{h^2 J(J+1)}{8\pi^2 M \rho^2},$$

giving instead of the drawn-out curves A and B the dotted curves A' and B'. Here the condition for a large transition probability is that an intersection point of these dotted curves lies at about the same height as the vibration-rotation level in question while PP must lie beneath. The rules just given may be understood by a reasoning analogous to the Franck-Condon principle in the case of radiative transitions (see section 25). For in the classical model the point of reversal of the vibrational motion for one of the levels fulfilling the condition just

given lies near the intersection point, and since the molecule tarries long near this position, the chance of jumping over from the curve B (or B') to the curve A (or A') is great. In the case of fig. 61 (a), where there is no intersection point, radiationless transitions should practically not occur while in the cases of fig. 61 (b), (c) and (d) such transitions will be likely to take place if all the selection rules previously enumerated are fulfilled.

We must now inquire what the influence of the processes just considered upon the aspect of a band spectrum will be, in which the vibration-rotation levels of the electronic state B function as initial or final levels. If B is the final state (i.e. in emission, if B is the lower state, in absorption, if B is the higher state), the radiationless transitions will give rise to broadening of the spectral lines. For the radiationless transitions shorten the lifetime of the stationary states and hence, similarly as the radiative transitions, introduce according to quantum mechanics an uncertainty into the corresponding energy values. As shown by Kronig(20), this broadening may under favourable circumstances become comparable to the rotational separation of the band lines, thus wiping out the rotational structure and making the bands diffuse. If B is the initial state (i.e. in emission, if B is the higher state, in absorption, if B is the lower state), there is the additional effect that the radiationless transitions will drain the molecules away from the levels concerned so that the intensity of radiative transitions from these same levels is diminished or even reduced practically to zero. The band lines are then not only broadened but also abnormally weak or they may even be absent entirely.

The experimental phenomena just described were discovered by Henri and Teves(15) who called them *predissociation*, a term which is now generally applied to this whole complex of problems. That radiationless transitions are responsible for the observed diffuseness of the bands was first recognised by Bonhoeffer and Farkas(7) and by Kronig(20). The latter author also gave a treatment on the basis of wave mechanics. Since a discussion of individual spectra is not the object of this book,

we give in figs. 62 to 64 a few characteristic examples of spectra in which predissociation plays a rôle. For a more detailed discussion of the experimental data the reader is referred to the reports of Kronig(4) and Herzberg(3).

56. CALCULATION OF DISSOCIATION ENERGIES FROM PREDISSOCIATION; EXAMPLE OF N_2

The phenomenon of predissociation in many cases makes possible the determination of *dissociation energies*. In the example of fig. 61 (*b*) predissociation of the state B will set in for the vibration-rotation levels directly above the asymptote PP so that from the point where the diffuseness or weakening of a band spectrum involving the state B occurs the energy value of PP relative to the molecular energy curves is accurately determined. In the example of fig. 61 (*c*) the predissociation may begin directly above PP or become noticeable only at higher energies depending upon whether the intersection point of the curves A and B lies close to PP or further away. In the first case diffuseness or weakening of the band lines will set in suddenly for the levels directly above PP so that this asymptote is again precisely known, in the second case the diffuseness or weakening increases rather gradually above PP to a maximum value for the levels at the height of the intersection point so that for PP only an upper limit can be given. This last remark applies also to the example of fig. 61 (*d*). If now it is known which energy levels of the separate atom correspond to the asymptote PP, then knowing the position of PP fixes the system of molecular levels relative to that of atomic levels. If we furthermore know the dissociation products for a given molecular state we obtain directly the energy of dissociation of this state.

We shall illustrate these considerations by the results for the molecule N_2. The N-atom possesses three low-lying states, the ground state ^4S, above this a state ^2D and still higher a state ^2P. Two N-atoms at a large distance hence give the six levels $^4S+{}^4S$, $^4S+{}^2D$, $^4S+{}^2P$, $^2D+{}^2D$, $^2D+{}^2P$ and $^2P+{}^2P$, drawn as dotted lines in fig. 65. The molecule N_2 possesses a system of

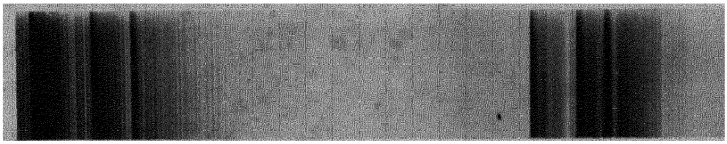


Fig. 62. Emission spectrum of N_2. Sudden termination of bands due to predissociation.

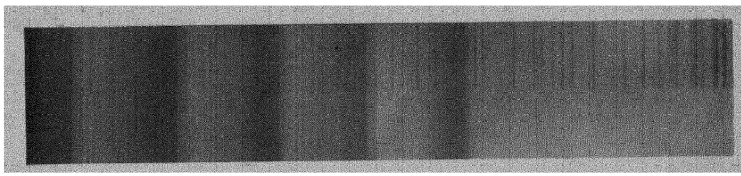


Fig. 63. Emission spectrum of S_2. Sudden termination of band system due to predissociation.

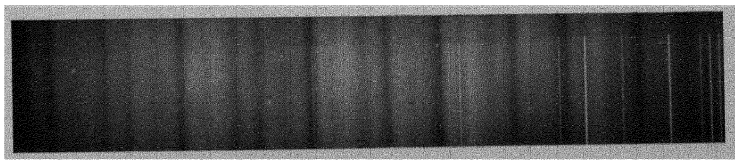


Fig. 64. Absorption spectrum of the vapour of chromyl chloride, CrO_2Cl_2. (The dark regions are those of strong absorption.) Diffuseness due to predissociation.

triplet states and a system of singlet states, the ground state $X\,^1\Sigma_g^+$ belonging to this latter system. In fig. 65 we have drawn on the right-hand side the energy values of the minima of the energy curves for the stable triplet states. Their position relative to the atomic levels, already suggested by Kaplan (19),

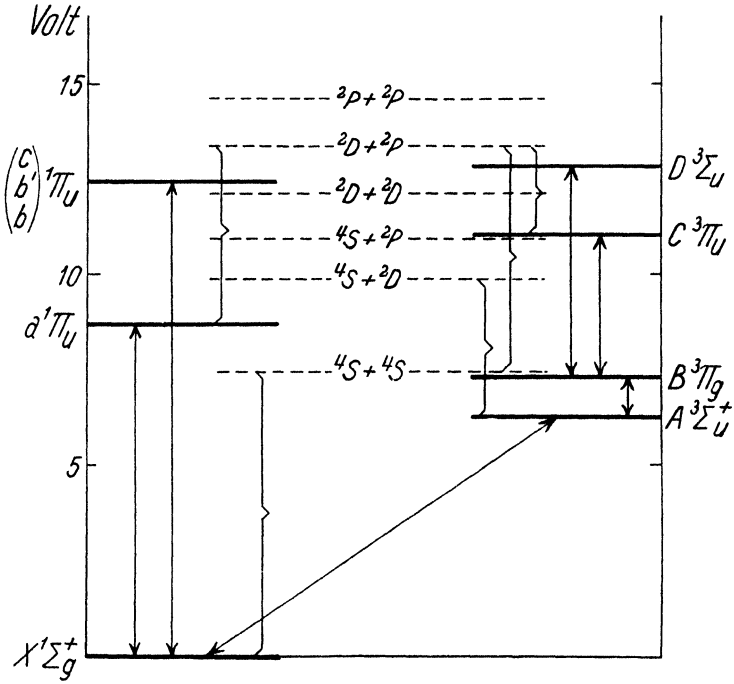


Fig. 65. Energy levels of the N_2-molecule. To the left are shown the singlet states to the right the triplet states. The dotted lines refer to the states of the atoms after dissociation. Arrows indicate the observed radiative transitions, brackets the correlation of molecular to atomic states.

has been fixed with certainty by the work of Coster, Brons and van der Ziel (10) who studied the predissociation in the rotation-vibration levels of the state $C\,^3\Pi_u$, and of van der Ziel (31) who investigated very carefully the predissociation of $B\,^3\Pi_g$. The latter investigation proved that the state causing predissociation in $B\,^3\Pi_g$ cannot possibly be a Σ-state, and since the atomic levels $^4S+^4S$ only give Σ-states, the predissociation in $B\,^3\Pi_g$ must be caused by $^4S+^2D$ or one of the

higher combinations. In fig. 65 $^4S+^2D$ has been taken since then the position of the predissociation limit for $C\,^3\Pi_u$ can be accounted for in a satisfactory way as being due to $^2D+^2D$ while only with this choice a reasonable value results for the dissociation energy of the molecule. This latter predissociation has been studied in detail by Büttenbender and Herzberg(9).

The position of the singlet states of the molecule with respect to the triplet states has been determined by Herzberg and Sponer(17) from the intercombination bands $A\,^3\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$. Since the ground state dissociates into the atomic states $^4S+^4S$, its dissociation energy is known. The best value(9) is

$$D_0 = 7{\cdot}35 \text{ volts} = 169{\cdot}5 \text{ cals.}$$

57. PREDISSOCIATION OF POLYATOMIC MOLECULES

In diatomic molecules we have one vibrational degree of freedom and one corresponding co-ordinate, the internuclear distance ρ. The energy of the molecular states is then a function of ρ that can be represented by the energy curves $V(\rho)$. For polyatomic molecules the simplest case is when there are three vibrational degrees of freedom, viz. for a triatomic molecule of triangular shape. The vibrational motion can then be specified by three co-ordinates for which we may use, e.g., the three internuclear distances ρ_1, ρ_2, ρ_3. The energy of a molecular state $V(\rho_1, \rho_2, \rho_3)$ is a function of these. Let us now first imagine that we could have the intermediate case that V depends upon two parameters ρ_1 and ρ_2 only (e.g. in the case of a triatomic triangular molecule by imagining two of the nuclei to be rigidly attached to each other). Following Franck, Sponer and Teller(13) the situation resulting can be described as follows: Instead of an energy curve $V(\rho)$ we have now for every molecular state an energy surface $V(\rho_1, \rho_2)$. Predissociation can take place in a state B if its energy surface is intersected by the energy surface of another state such that in a region where we have still discrete vibration-rotation levels of B we are already in the energy continuum corresponding to dissociation of the state A.

More precisely the two energy surfaces A and B will intersect each other along a curve. The chance of predissociation for a vibration-rotation level of B will be great—apart from the fulfilment of selection rules perhaps introduced by the symmetry properties of the molecule—if its energy is about the same as that of a point on the intersection curve. For then the vibratory motion of the molecule represented by a sort of Lissajous figure on the surface $V(\rho_1, \rho_2)$ of B will come somewhere near the line of intersection with the surface $V(\rho_1, \rho_2)$ of A, making it easy for the molecule to jump from the former to the latter surface.

The circumstance that the intersection point with a definite energy in the case of one vibrational degree of freedom is now replaced by an intersection curve, the various points of which may have energies that in general will differ considerably, entails that the predissociation may be expected to extend over a much wider energy interval and hence over a much broader region in the spectrum of the system in question.

For molecules with more than two vibrational degrees of freedom recourse must be had to a geometrical representation in a space with more than three dimensions. The reasoning is the same as before, but one may expect that the differences with the case of diatomic molecules become still more accentuated. Hence, it is quite comprehensible why discrete electronic band spectra should occur only as an exception for polyatomic molecules (see sections 31 and 46), the excited electronic states being apt to suffer from predissociation over the whole or almost the whole range of their vibration-rotation levels.

Another complication typical for polyatomic molecules is that the dissociation products in so far as they are molecules themselves retain energy not only in the form of electronic excitation but also as vibrational and rotational energy. These facts, too, tend to make the points in the spectra where predissociation sets in less well defined and more difficult to interpret.

Henri(2) has investigated the predissociation in the absorption spectra of a number of polyatomic molecules, at the same

time studying the *photochemical processes* by which it is accompanied. The principal compounds analysed were carbon disulphide, CS_2; nitric oxide, NO_2; sulphur dioxide, SO_2; formaldehyde, H_2CO; acetaldehyde, CH_3COH. The chemical changes in the effective regions of wave-lengths are the following, according to Henri:

$$CS_2 \rightarrow CS + S,$$
$$NO_2 \rightarrow NO + O,$$
$$SO_2 \rightarrow SO + O,$$
$$H_2CO \rightarrow HCO + H,$$
$$CH_3COH \rightarrow CH_4 + CO.$$

Predissociation in the absorption spectrum of NH_3 in its connection with photochemical disintegration has already been recognised by Bonhoeffer and Farkas(7). The predissociation in NO_2 and SO_2 has been discussed in greater detail by Franck, Sponer and Teller(13) on the basis of the view-point described above.

58. DISSOCIATION BY ROTATION

A diffuseness or weakening of discrete band lines, instead of being due to predissociation, may also arise from a different cause to which Oldenberg(24) has first called attention. The energy curves $V(\rho)$ which govern the nuclear vibration of a diatomic molecule in a given electronic state as ordinarily spoken of refer to the non-rotating molecule. For a stable molecular state they have the shape shown in fig. 66 (a). If the molecule rotates, i.e. if $J \neq 0$, then, as pointed out already in section 55, we must add to this curve the term

$$\frac{h^2 J(J+1)}{8\pi^2 M \rho^2},$$

which may be regarded as the potential of the centrifugal forces. As J is augmented, one gets successively from the curve of fig. 66 (a) the curves of fig. 66 (b), (c) and (d), with a maximum next to the minimum and finally without minimum. The energy of the vibration-rotation levels with the same value v_0 of the vibrational quantum number increases then with J as shown in fig. 66. But, what is more important, these levels will

exist even for energy values above the asymptote (ρ-axis) corresponding to dissociation as shown by fig. 66 (*c*). For in the energy trough to the left of the maximum in fig. 66 (*c*) we have in practice still a quantised vibrational motion, the only difference as compared to the cases shown in fig. 66 (*a*) and

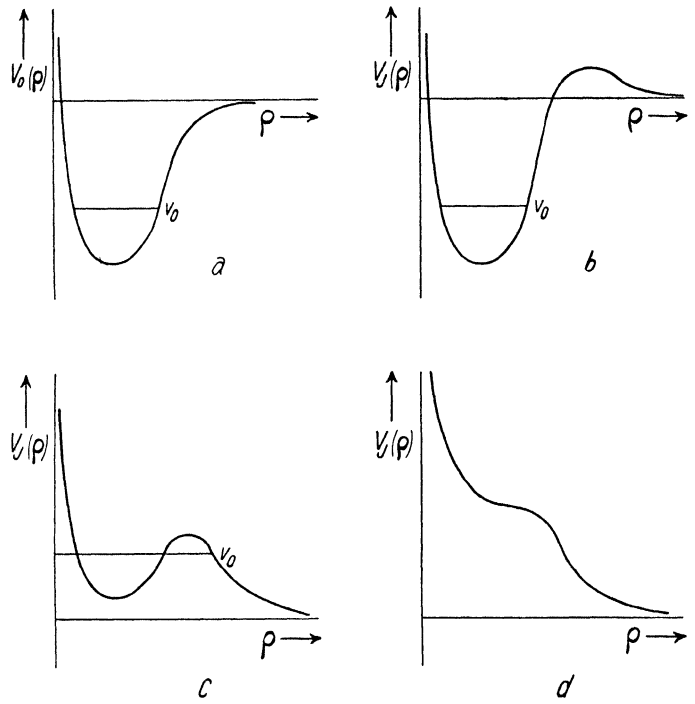


Fig. 66. Influence of rotation on an energy curve $V(\rho)$ of a diatomic molecule. Dissociation by rotation.

(*b*) being that the nuclei now have a certain chance of penetrating the potential barrier above the horizontal line v_0 and flying apart. As shown by Kronig[21], the order of magnitude of the probability for this dissociation process, which may be termed *dissociation by rotation*, is easily estimated. When the rotational quantum number J is so large that we have the case represented by fig. 66 (*d*), then of course there exist no longer discrete levels.

The molecule for which the phenomenon just spoken of has been studied most extensively is HgH. Dissociation by rotation takes place here in the ground state and finds expression in an increasing diffuseness and a final termination for higher J-values of the bands involving the ground state. Müller(23) has compared the observed and theoretical diffuseness and finds good agreement. For AlH similar phenomena are observed, due to the dissociation of an excited state by rotation. This example is particularly interesting because Hulthén and Rydberg(18), in order to explain quantitatively their results, had to assume that already in the non-rotating molecule (i.e. in fig. 66 (a)) the curve $V(\rho)$ possesses a maximum to the right of its minimum. We shall see in section 60 that the existence of such maxima plays a rôle in the problem of the activation energies.

59. DETERMINATION OF DISSOCIATION CONSTANTS FROM SPECTROSCOPIC DATA

The general laws of thermodynamics allow us to predict the form of the functional relationship between the degree of dissociation of a gaseous compound and the temperature and pressure. They leave undetermined, however, certain constants in these relationships. From a knowledge of the energy levels which the molecules of the compound can occupy, as it is furnished by the spectroscopic methods described in chapters IV and V, it is possible to evaluate these constants too so that the degree of dissociation can be computed numerically from thermodynamics in conjunction with spectroscopic data. A comparison with experiment may then serve as a test for the assignment of energy levels.

In order to make clear the nature of the procedure, we shall consider here the simplest type of dissociation equilibrium,

$$AB \longleftrightarrow A + B,$$

in which a gaseous compound AB dissociates into the monatomic vapours A and B. The law of mass action states that for a given temperature T the product of the partial pressures p_A and p_B of the vapours A and B, divided by the partial

pressure p_{AB} of the vapour AB, is a constant K, the *dissociation constant*:

$$\frac{p_A p_B}{p_{AB}} = K. \qquad (59{\cdot}1)$$

It is the object to determine K in its dependence upon T. The problem will be solved if we can obtain the relative chances of the atoms A and B for being free and for being bound together in a molecule.

Let us consider first the free atoms A. We may safely assume that they are all in the normal state since in general the states where the electrons are excited lie so high that the thermal agitation is not sufficient to lift an appreciable fraction of the atoms into them. The atoms will then only differ in their translational energy. We inquire: How many stationary states are there with translational energy between w and $w+dw$ if the atoms are confined to a volume V? Quantum mechanics teaches that between these energy limits there are

$$\frac{2\pi (2M_A)^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw$$

different ways of translatory motion, M_A signifying the mass of the atoms A. This would be the number of states asked for if the normal state of the atoms were simple. We have seen, however, in section 14 that often a state with given energy actually is an aggregate of coincident sub-states which may be separated from each other by suitable outside agencies such as applied magnetic or electric fields. If we denote the number of sub-states contained in the normal state of the atom A by g_A, we get for the total number of *states* with translational energy between w and $w+dw$

$$dG_A = g_A \frac{2\pi (2M_A)^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw.$$

The total number of *atoms* A with translational energy between w and $w+dw$ is then given, according to Boltzmann's distribution law, by

$$dN_A = dG_A . \exp\frac{f_A - w}{kT} = g_A \frac{2\pi (2M_A)^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw . \exp\frac{f_A - w}{kT},$$

where f_A is the free energy per atom of the gas of free atoms A. The total number of free atoms A results by integration over

w from 0 to ∞. It is found to be

$$N_A = g_A \frac{(2\pi M_A kT)^{\frac{3}{2}}}{h^3} V . \exp \frac{f_A}{kT}. \qquad (59{\cdot}2)$$

A similar expression is obtained for N_B, the total number of free atoms B.

We consider next the molecules AB. Again we may presuppose that they are present only in their normal electronic state. We shall assume this to be a $^1\Sigma$-state as is the case for almost all chemically stable diatomic molecules (see table 8). There are then no electronic sub-states. The energy of the molecule on the assumption just made is composed of the translational energy of the molecule as a whole, the vibrational energy and the rotational energy. With a precision sufficient for the present purpose these three parts are additive. The translation may again be specified by requiring its energy to lie between the limits w and $w+dw$. The number of ways in which the translation may take place between these limits for molecules confined to the volume V is in analogy with the expression above $\frac{2\pi (2M_{AB})^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw$,

$M_{AB} = M_A + M_B$ denoting the total mass of the molecule.

The vibration is specified by a vibrational quantum number v. If we confine our attention to the lowest vibrational levels, which at temperatures not excessively high are the only ones excited to an appreciable extent, then according to equation (21·5) we may write approximately for the vibrational energy $h\omega_e (v+\frac{1}{2}), \qquad v = 0, 1, 2, \ldots$

with ω_e denoting the vibrational frequency for small amplitudes of motion. The vibrational energy is here measured from the minimum of the potential energy curve which governs the binding of the atoms for the normal state of the molecule. For the free atoms the energy of relative motion, on the other hand, is measured from the horizontal asymptote corresponding to dissociation of the molecule. In order to refer the energy in both cases to the same zero-point, we must hence write $w_{\text{vib}} = -D + h\omega_e (v+\frac{1}{2}), \qquad v = 0, 1, 2, \ldots,$

D, as introduced in section 20, signifying the energy difference between the asymptote and the minimum. We may combine $-D$ with the constant term $\frac{1}{2}h\omega_e$ to give $-D_0$, the actual energy of dissociation from the lowest vibrational level, defined in section 21, and get then

$$w_{\text{vib}} = -D_0 + h\omega_e v, \qquad v = 0, 1, 2, \ldots. \qquad (59{\cdot}3)$$

To every value of v there corresponds one type of vibrational motion.

The rotation is specified by a rotational quantum number J. According to equation (21·13) we have for the rotational energy

$$w_{\text{rot}} = hB_e J(J+1), \qquad J = 0, 1, 2, \ldots, \qquad (59{\cdot}4)$$

B_e being defined by equation (21·14). Again it must be presupposed that the rotational levels excited by the thermal agitation have reasonably low values of J since otherwise the validity of equation (59·4) is impaired by the deformation of the molecule due to centrifugal forces (see section 21). To a given value of J, i.e. to a given value of the rotational energy there belong $2J+1$ coinciding sub-states because the angular momentum of the molecule, of which J is a measure, may take $2J+1$ different orientations in an outside field (see section 14).

The total number of *states* of the molecules AB with translational energy between w and $w+dw$, with vibrational quantum number v and with rotational quantum number J is now seen to be

$$dG_{AB}(v, J) = (2J+1)\frac{2\pi(2M_{AB})^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw$$

while their energy according to equations (59·3) and (59·4) is

$$W = w + w_{\text{vib}} + w_{\text{rot}}.$$

The *total number of molecules* in these states is according to Boltzmann's distribution law

$$\begin{aligned} dN_{AB}(v, J) &= dG_{AB}(v, J) \,.\, \exp\frac{f_{AB} - W}{kT} \\ &= (2J+1) \,.\, \exp\frac{-hB_e J(J+1)}{kT} \,.\, \exp\frac{D_0 - h\omega_e v}{kT} \\ &\quad \,.\, \frac{2\pi(2M_{AB})^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw \,.\, \exp\frac{f_{AB} - w}{kT}, \end{aligned}$$

f_{AB} being the free energy per molecule of the gas of molecules

AB. The total number of molecules AB in all states is now obtained by summing over J and v and by integrating over w from 0 to ∞:

$$N_{AB} = \sum_{J=0}^{\infty} (2J+1) \cdot \exp \frac{-hB_e J(J+1)}{kT} \cdot \sum_{v=0}^{\infty} \exp \frac{D_0 - h\omega_e v}{kT} \cdot \int_0^{\infty} \frac{2\pi (2M_{AB})^{\frac{3}{2}}}{h^3} V w^{\frac{1}{2}} dw \cdot \exp \frac{f_{AB} - w}{kT}.$$

The summation over J may in general be replaced by an integration since the temperature usually is so high that the energy difference of successive rotational levels is small compared with kT. It furnishes then the factor

$$\frac{kT}{hB_e}.$$

The sum over v gives $\dfrac{\exp \dfrac{h\omega_e}{kT}}{\exp \dfrac{h\omega_e}{kT} - 1}$.

The integral is the same as that previously encountered when discussing the free atoms. We finally get

$$N_{AB} = \frac{kT}{hB_e} \cdot \frac{\exp \dfrac{h\omega_e}{kT}}{\exp \dfrac{h\omega_e}{kT} - 1} \cdot \frac{(2\pi M_{AB} kT)^{\frac{3}{2}}}{h^3} V \cdot \exp \frac{f_{AB} + D}{kT}. \quad (59{\cdot}5)$$

We now make use of the thermodynamic condition that in the dissociation equilibrium the free energy of the compound AB per molecule must be equal to the sum of the free energies of the vapours A and B per atom; or

$$f_{AB} = f_A + f_B. \quad (59{\cdot}6)$$

Since the partial pressures p_A, p_B and p_{AB} according to the gas laws are given respectively by

$$kTN_A/V, \quad kTN_B/V, \quad kTN_{AB}/V,$$

we have with the definition (59·1)

$$\log K = \log \frac{p_A p_B}{p_{AB}} = \log \frac{kTN_A N_B}{VN_{AB}}$$
$$= \log N_A + \log N_B - \log N_{AB} + \log \frac{kT}{V}.$$

Substituting for N_A the expression (59·2), for N_B the analogous expression, for N_{AB} the expression (59·5) and eliminating f_A, f_B and f_{AB} by means of equation (59·6) we find

$$\log K = -\frac{D_0}{kT} + \frac{3}{2}\log\left(\frac{2\pi M_A M_B kT}{h^2 M_{AB}}\right) + \log hB_e + \log\left[1-\exp\left(-\frac{h\omega_e}{kT}\right)\right] + \log g_A g_B. \quad (59\cdot7)$$

As an example we shall apply our considerations to the dissociation of J_2-vapour according to the equation

$$J_2 \longleftrightarrow 2J.$$

This dissociation process has been investigated theoretically by Gibson and Heitler(14). Here the two atoms A and B are identical, which brings with it that $M_A = M_B = M$, $M_{AB} = 2M$ and that $g_A = g_B = g$. But furthermore there must be added to the right-hand side of equation (59·7) a term $\log 2$. It arises from the fact that the molecule J_2 is symmetrical so that already a rotation through 180° instead of 360° makes its new position indistinguishable from its old one. On the basis of wave mechanics the expression for N_{AB} is thereby reduced with a factor $\frac{1}{2}$. One says that the molecule J_2 has the *symmetry number* 2. The quantities ω_e, B_e and D_0 are known from band spectra. The quantity $g_A = g_B$ is here equal to 4 since the ground state of the iodine atom is a state $^2D_{\frac{3}{2}}$ (see section 17) with $J = \frac{3}{2}$, permitting four different orientations of the atom in an outside field. In table 24 we give the values of K over the temperature range from 800° C to 1200° C as computed by Gibson and Heitler(14) and as observed by Starck and Bodenstein(29). The agreement is very satisfactory.

TABLE 24

DISSOCIATION CONSTANT OF J_2-VAPOUR AS FUNCTION OF THE TEMPERATURE

t° C	K_{comp}	K_{exp}
800	0·0113	0·0114
900	0·0479	0·0474
1000	0·165	0·165
1100	0·494	0·492
1200	1·22	1·23

60. REACTION VELOCITIES, ACTIVATION ENERGIES

Chemical reactions in which only gaseous substances are involved are often strongly influenced by the walls of the vessel where they take place. Such influences of the walls, due in general to adsorption of the reagents or contamination with foreign substances having catalytic effects, are of course very involved and make it difficult to interpret the results obtained. It is therefore important that one has succeeded in finding gaseous reactions which proceed independently of the walls of the vessel if these are suitably chosen while in other cases it has been possible to eliminate the effect of the walls in different ways(26). The following remarks apply to this kind of reaction.

Very often one finds that the equilibrium between the various components of a gaseous reaction is not reached instantaneously but may require a considerable time to be attained. As the temperature increases, the condition of equilibrium is approached more rapidly. Let us now try to interpret these results for a simple case, viz. the reaction already considered in the previous section,

$$AB \longleftrightarrow A + B.$$

Let us imagine that the diatomic vapour AB to begin with is entirely undissociated, which may be accomplished, e.g., by rapidly raising its temperature from a low value to the higher value at which the dissociation equilibrium is to be studied. The dissociation can take place, when two molecules AB or a molecule AB and an atom A or B formed already by dissociation of another molecule collide with an energy of relative thermal motion equal to or greater than the dissociation energy. The *reaction velocity* will be determined by the efficiency of such impacts. If nearly every impact with the necessary energy brings about dissociation, the equilibrium at pressures not too low will be established more or less instantaneously. If, however, only one impact in a billion is effective, then evidently it may take a measurable or even a very long time till one has equilibrium.

In fig. 67 we have drawn the energy curves $V(\rho)$ for the ground state of the molecule AB in three different cases. In fig. 67 (a) it is assumed that the ground state dissociates into the atoms A and B both in their ground state and that the curve $V(\rho)$ approaches its asymptote from below. The dissociation of J_2, investigated in the previous section is an example. In fig. 67 (b) it is again assumed that the ground state of the molecule dissociates into normal atoms but that the curve $V(\rho)$ has a maximum to the right of its minimum. That such maxima may occur we have mentioned in section 58. In fig. 67 (c) finally it is assumed that at least one of the dis-

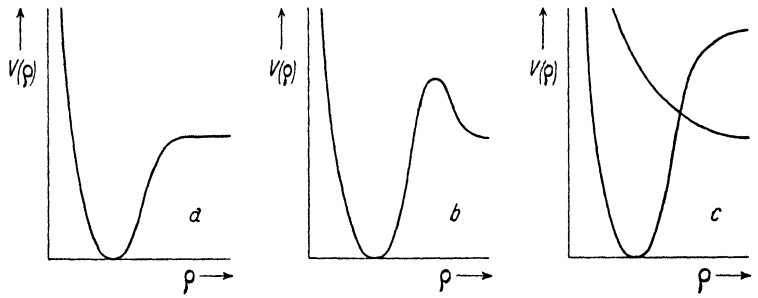


Fig. 67. Energy curves $V(\rho)$ of a diatomic molecule giving rise to an activation energy.

sociation products of the molecular ground state is an excited atom, while from normal atoms we only get a repulsive energy curve of the molecule, crossing the energy curve with the minimum. This situation we encountered for the polyatomic molecules N_2O and CO_2 in section 46.

While in the case of fig. 67 (a) it is sufficient for dissociation if a molecule AB is hit by another molecule or atom having a kinetic energy with respect to the first one equal to or only slightly greater than the dissociation energy, dissociation in the cases illustrated by fig. 67 (b) and (c) will only take place with reasonable probability for energies of the impinging particles much greater than this lower limit. For in fig. 67 (b) the nuclei of the molecule AB have to be carried over the hill in the curve $V(\rho)$ while in fig. 67 (c) they have to be brought to the intersection point of the two curves, where they may jump

from the attractive to the repulsive curve, finally flying apart. But such high relative velocities of the impinging particles are very rare, the less frequent the lower the temperature.

The energy of the hill or intersection point above the horizontal asymptote corresponding to normal atoms may be called the *activation energy*. It naturally is of importance also in the inverse processes where two atoms A and B cannot enter into chemical combination unless their relative kinetic energy is sufficient to overcome the potential barrier (in these inverse processes, in order that chemical union may actually take place, it is in general necessary to have a third atom present to carry away the excess energy of the other two when these have approached each other beyond the barrier).

Similar considerations as we have given them here apply to polyatomic molecules. Only there the situation will be much more complicated, due to the many internal degrees of freedom. Instead of two energy curves for the various molecular states, recourse must be had to the energy surfaces introduced in section 57.

A particularly interesting object for the study of reaction velocities is the heavy isotope of hydrogen of atomic weight 2 and represented by the symbol D. Let us compare, e.g., the molecules HCl and DCl. The energy curves $V(\rho)$ for the ground states of these two molecules will be essentially the same. But the vibrational frequency ω_e of the heavy molecule DCl is much smaller than that for the light molecule HCl (the experimental values are 2990 and 2091 cm^{-1} respectively). In consequence the vibrational level $v=0$, which lies by the amount of the zero-point energy $\frac{1}{2}h\omega_e$ above the minimum of the curve $V(\rho)$, lies further below the asymptote corresponding to dissociation for DCl than for HCl. In other words the energy of dissociation D_0 is greater for DCl than for HCl. Analogous remarks apply to other hydrogen compounds. For the reasons just set forth (and to a certain degree also on account of the less rapid thermal motion) it is comprehensible that the heavy hydrogen compounds react in general more slowly than those of ordinary hydrogen (see section 2). For a more detailed treatment of these questions which really fall

outside the scope of this book the reader is referred to the volume on Light and Heavy Hydrogen by A. Farkas(5).

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TABLE OF ELECTRON CONFIGURATIONS

Shell orbit	K $1s$	L_{I} $2s$	$L_{II,III}$ $2p$	M_{I} $3s$	$M_{II,III}$ $3p$	$M_{IV,V}$ $3d$	N_{I} $4s$	$N_{II,III}$ $4p$	$N_{IV,V}$ $4d$	$N_{VI,VII}$ $4f$	O_{I} $5s$	$O_{II,III}$ $5p$	$O_{IV,V}$ $5d$	P_{I} $6s$	$P_{II,III}$ $6p$	$P_{IV,V}$ $6d$	Q_{I} $7s$	Ground state
1 H	1																	^2S
2 He	2																	^1S
3 Li	2	1																^2S
4 Be	2	2																^1S
5 B	2	2	1															^2P
6 C	2	2	2															^3P
7 N	2	2	3															^4S
8 O	2	2	4															^3P
9 F	2	2	5															^2P
10 Ne	2	2	6															^1S
11 Na	2	2	6	1														^2S
12 Mg	2	2	6	2														^1S
13 Al	2	2	6	2	1													^2P
14 Si	2	2	6	2	2													^3P
15 P	2	2	6	2	3													^4S
16 S	2	2	6	2	4													^3P
17 Cl	2	2	6	2	5													^2P
18 Ar	2	2	6	2	6													^1S
19 K	2	2	6	2	6		1											^2S
20 Ca	2	2	6	2	6		2											^1S
21 Sc	2	2	6	2	6	1	2											^2D
22 Ti	2	2	6	2	6	2	2											^3F
23 V	2	2	6	2	6	3	2											^4F
24 Cr	2	2	6	2	6	5	1											^7S
25 Mn	2	2	6	2	6	5	2											^6S
26 Fe	2	2	6	2	6	6	2											^5D
27 Co	2	2	6	2	6	7	2											^4F
28 Ni	2	2	6	2	6	8	2											^3F
29 Cu	2	2	6	2	6	10	1											^2S
30 Zn	2	2	6	2	6	10	2											^1S
31 Ga	2	2	6	2	6	10	2	1										$^2P_?$
32 Ge	2	2	6	2	6	10	2	2										^3P
33 As	2	2	6	2	6	10	2	3										^4S
34 Se	2	2	6	2	6	10	2	4										^3P
35 Br	2	2	6	2	6	10	2	5										^2P
36 Kr	2	2	6	2	6	10	2	6										^1S
37 Rb	2	2	6	2	6	10	2	6			1							^2S
38 Sr	2	2	6	2	6	10	2	6			2							^1S
39 Y	2	2	6	2	6	10	2	6	1		2							^2D
40 Zr	2	2	6	2	6	10	2	6	2		2							^3F
41 Nb	2	2	6	2	6	10	2	6	4		1							?
42 Mo	2	2	6	2	6	10	2	6	5		1							^7S
43 Ma	2	2	6	2	6	10	2	6	6		1							?
44 Ru	2	2	6	2	6	10	2	6	7		1							^5F
45 Rh	2	2	6	2	6	10	2	6	8		1							^4F
46 Pd	2	2	6	2	6	10	2	6	10									^1S
47 Ag	2	2	6	2	6	10	2	6	10		1							^2S
48 Cd	2	2	6	2	6	10	2	6	10		2							^1S
49 In	2	2	6	2	6	10	2	6	10		2	1						^2P
50 Sn	2	2	6	2	6	10	2	6	10		2	2						^3P
51 Sb	2	2	6	2	6	10	2	6	10		2	3						^4S
52 Te	2	2	6	2	6	10	2	6	10		2	4						^3P
53 J	2	2	6	2	6	10	2	6	10		2	5						^2P
54 X	2	2	6	2	6	10	2	6	10		2	6						^1S
55 Cs	2	2	6	2	6	10	2	6	10		2	6		1				^2S
56 Ba	2	2	6	2	6	10	2	6	10		2	6		2				^1S
57 La	2	2	6	2	6	10	2	6	10		2	6	1	2				^2D
58 Ce	2	2	6	2	6	10	2	6	10	1	2	6	1	2				?
59 Pr	2	2	6	2	6	10	2	6	10	2	2	6	1	2				
60 Nd	2	2	6	2	6	10	2	6	10	3	2	6	1	2				
61 Il	2	2	6	2	6	10	2	6	10	4	2	6	1	2				
62 Sm	2	2	6	2	6	10	2	6	10	5	2	6	1	2				
63 Eu	2	2	6	2	6	10	2	6	10	6	2	6	1	2				
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	2				
65 Tb	2	2	6	2	6	10	2	6	10	8	2	6	1	2				
66 Dy	2	2	6	2	6	10	2	6	10	9	2	6	1	2				
67 Ho	2	2	6	2	6	10	2	6	10	10	2	6	1	2				
68 Er	2	2	6	2	6	10	2	6	10	11	2	6	1	2				
69 Tu	2	2	6	2	6	10	2	6	10	12	2	6	1	2				
70 Yb	2	2	6	2	6	10	2	6	10	13	2	6	1	2				
71 Cp	2	2	6	2	6	10	2	6	10	14	2	6	1	2				
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	2				^3F
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2				^4F
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4	2				^5D
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5	2				^6S
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6	2				^5D
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7	2				?
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	1				?
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1				^2S
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2				^1S
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1			^2P
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2			^3P
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3			^4S
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4			^3P
85 —	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5			^2P
86 Em	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6			^1S
87 —	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		1	^2S
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		2	^1S
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2	?
90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2	?
91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	3	2	?
92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	4	2	?

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