

An Introduction to Molecular Spectra

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CHAPTER I

INTRODUCTION

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(a) THE ENERGY OF ATOMS AND MOLECULES

AN understanding of molecular structure must necessarily be built upon a reasonable knowledge of that simpler unit—the atom. An understanding of molecular spectra is also much more easily achieved from a prior knowledge of the principles of atomic spectra. The student is therefore advised before proceeding farther to refresh his memory at this point.*

Anyone who has examined with a direct-vision spectroscope the light from a bunsen flame into which certain salts have been introduced, or the light from the common neon discharge tube, will be familiar with the characteristic appearance of an atomic spectrum, viz. sharp bright lines on a dark background. Each of these radiated frequencies (ν) is the result of a particular electronic transition in a particular element, and is accounted for by the well-known Bohr equation $E' - E'' = h\nu$. Here E' and E'' are the total energies of the electron which makes the transition, when it is in the higher and the lower states respectively. Atomic spectroscopy has been concerned for many years (and in broad outline has completed its task) to take each of the chemical elements and record accurately the possible frequencies which can be emitted by electronic excitation. These data have then been sifted and expressed in mathematical formulae, and from these formulae can be inferred the so-called energy levels E' , E'' , &c., which the outermost electron in the atom is capable of occupying when displaced. The same can be done for singly ionized atoms, for doubly ionized atoms, &c., and from all these data has been constructed a picture of the architecture of each of the ninety-two chemical elements.

If with a direct-vision spectroscope the blue cone of a bunsen flame is examined, or the light from the incandescent vapour between the poles of a carbon arc burning in air, a different type of spectrum will be seen. The former is commonly called the 'Swan' spectrum, and it arises from a C_2 molecule. The latter is from a CN molecule, and causes the well-known violet colour of the vapour between the poles of an arc. Plate I of the Swan system should be carefully examined. It will be observed that instead of a number of sharp lines we have a pattern of bands or flutings. Such is characteristic of a molecular spectrum. Each of the bands in Plate I will be observed to be sharp on the red (or less refrangible) side and shade off towards the violet (or more refrangible) end of the spectrum. Briefly, we say this spectrum is degraded towards the violet. Other molecular spectra may degrade the opposite way. Sometimes, for reasons which will be understood later, no sharp band heads are formed, and the direction of degradation is not apparent. Another feature of Plate I which is

* A small monograph by the present author, *Atomic Spectra* (Methuen and Co., 1946), provides all that is essential for this purpose.

4 AN INTRODUCTION TO MOLECULAR SPECTRA

there is no change in the quantum number there is change in the rotational energy arising from a change of molecular size. Otherwise the Q branch would be a single strong line.)

The complete band system, such as Plate I depicts, thus arises from a single electronic transition associated with all the possible vibrational and rotational changes which can arise. Billions of atoms are participating in any light emission, and every possible combination of transitions will receive support according to certain statistical laws. The counterpart of such a band system in an atom is a single frequency arising from the electron transition only.

The units commonly used to express energy changes in atoms and molecules are either wave-numbers or volts. The wave-number ($1/\lambda$), for which the symbol ν will in future be used, is the number of waves per cm. Frequencies ν are much larger and in practice unwieldy. If wave-numbers are used, the energy is understood to be that of the corresponding quantum of radiation:

$$E_{\text{quanta}} = hc\nu_{\text{cm.}^{-1}}$$

from which we have

$$1 \text{ wave-number unit (cm.}^{-1}) = 1.9627 \times 10^{-16} \text{ erg.}$$

If volts are used, the energy of an electron which has been accelerated through this voltage is intended. The relation between ν (cm.⁻¹) and V (volts) is found from $h\nu = eV \times 10^9/c$ (1 volt = 8106 wave-number units).

(b) THE GENERAL STRUCTURE OF BAND SYSTEMS

It will form a useful introduction to the study of gross structure of band systems if we consider the Swan system of Plate I in some detail. The photograph shown is an enlargement of the spectrum obtained by using a medium-size dense flint-glass prism instrument. This well-known spectrum is radiated by a C_2 molecule; it can be observed in the light of a candle flame, in the blue cone of a bunsen burner, in the carbon arc burning in an atmosphere of hydrogen, when discharges are passed through hydrocarbons, and with great brilliance in a discharge tube having carbon electrodes and containing 20-30 mm. of argon, to which from time to time small quantities of hydrogen are admitted. The two thick energy levels on Plate I represent two electronic energy levels of the vibrationless C_2 molecule (or, strictly, they include the residual $\frac{1}{2}$ -quantum of vibrational energy). The lower one, $v'' = 0$, is associated with the ground state of the electron in the molecule; the upper one, $v' = 0$, represents the molecule with its outer electron in an excited state. We have already explained that each electronic state may be associated with various quanta of vibrational energy, and these levels are depicted in Plate I.

Since each band of a system has two vibrational quantum numbers and corresponds to a transition $v' \rightarrow v''$ from one level to another, the wave-numbers of the band origins, once determined, can be placed in a table such as that given on p. 5.

WAVE-NUMBERS OF ORIGINS OF SWAN BANDS
(Below) Estimated relative intensities on a scale (1-10)

$v'' \backslash v'$	0 (1618.23) (10)	1 (1109.57) (7)	2 (1271.33) (3)	3 (1546.19) (1)	4 (1824.83) (1)	5 (1601.51) (1)	6
0 (175.07)	19373.9 (10)	17756.7 (7)	16109.3 (3)	14589.3 (1)			
1 (175.37)	21127.9 (9)	19569.7 (6)	17914.0 (4)	16343.3 (4)	14795.1 (1)		
2 (1676.67)	22843.3 (2)	21225.1 (8)	19630.2 (1)	18058.7 (5)	16510.5 (3)	14985.7 (1)	
3 (1637.97)	22901.8 (4)	21306.9 (7)	19735.4 (4)	18187.2 (4)	16692.2 (3)	15160.8 (1)	
4		22944.9 (5)	21373.3 (4)	19825.1 (2)	18300.3 (2)	16788.8 (2)	

If molecules were simple harmonic vibrators, theory predicts that the only changes of vibrational quantum number which would take place would be ± 1 or 0. Since no molecule fulfils this condition in practice, we find that many values of $v' \sim v''$ occur. In the table given, the wave-number differences between adjacent rows necessarily correspond to the intervals between the adjacent v' levels on Plate I, and the wave-number differences between the columns correspond to the intervals between adjacent v'' levels on Plate I.

Once the band wave-numbers have been assigned satisfactorily in a table as shown, an expression can be found to represent the whole array. In the above case the formula following is a good representation:

$$\nu = 19373.9 + (1773.42 v' - 19.35 v'^2) - (1629.88 v'' - 11.67 v''^2).$$

The quadratic term, as we have mentioned, arises from the anharmonic character of the molecular vibration. If the C_2 molecule had been a true simple harmonic oscillator there would have been only three sequences of bands corresponding to $v' - v'' = \pm 1, 0$, and they would have been expressed by $\nu = 19373.9 + 1773.42 v' - 1629.88 v''$.

In Plate I we observe that bands corresponding to a particular change in v (i.e. a particular value of $v' - v''$) appear to form natural groups. These are technically called 'sequences'. Bands which arise from the same initial level are said to form a v'' -progression. Those which go to the same final level are said to form a v' -progression. Thus the bands marked * on Plate I are a v' -progression from $v' = 0$. Progressions are rows and columns of the above table; sequences are diagonals. Passing outwards from the band-system origin along a row, we observe that the wave-numbers diminish; in passing down a column they increase. This is, of course, expressed by the above formula for the Swan system. In general a formula of this type,

$$\nu_{v',v''} = \nu_{00} + (\omega' v' - \omega' x' v'^2) - (\omega'' v'' - \omega'' x'' v''^2), \quad (3)$$

therefore be represented by one of these 'fine' rotational levels, and the fine structure of a band (v' , v''), is accounted for by transitions from the rotational levels of the upper v' state to the rotational levels of the lower v'' state. Each rotational level is distinguished by a rotational quantum number K which measures the number of units of angular momentum ($h/2\pi$) the molecule possesses. Fortunately, theoretical considerations show that for rotational changes the quantum number

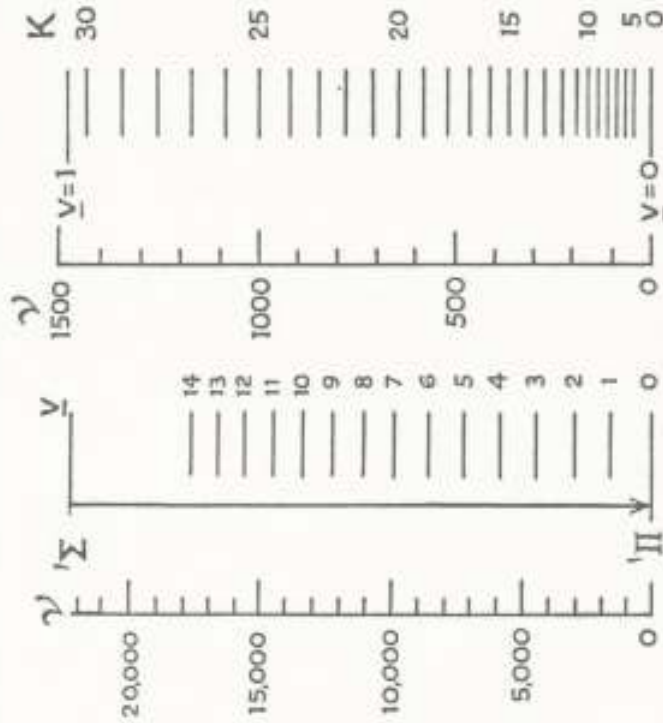


Fig. 1. Scale diagram of energy levels for the Angstrom system of CO, illustrating the relative magnitude of v' , v'' , and v_K in a typical case.

K can only change by ± 1 or 0. (We shall find later that 'selection principles' of this kind govern many of the quantum numbers with which we are concerned in molecules.) As a result, a simple band may have three sets of lines. These are the so-called 'branches', and are named as follows:

$$\left. \begin{aligned} K + 1 \rightarrow K & \dots R \text{ branch (or Positive branch),} \\ K \rightarrow K & \dots Q \text{ branch (or Zero branch),} \\ K - 1 \rightarrow K & \dots P \text{ branch (or Negative branch).} \end{aligned} \right\} \quad (4)$$

Fig. 2 illustrates the transitions giving rise to these branches. One of the striking features of Plates II and III is the character of these

6. AN INTRODUCTION TO MOLECULAR SPECTRA

expresses with reasonable accuracy the bands of most systems. Here ω' and x' are constants for the upper electronic state and ω'' and x'' are constants for the final electronic state.

It will also be noticed that as we pass outwards from the origin of the band system there is a general tendency for the intensities to fall off. Although this is not invariably the case, it is often a helpful characteristic in trying to assign vibrational quantum numbers to a new band system.

A band system such as that shown in Plate I is very simple to analyse (i.e. to assign to a (v', v'') table as on p. 5). This is by no means always easy to do. Sometimes different sequences, instead of standing out separately, overlap a good deal. A little reflection will show from equation (3) that the sequences will stand out fairly clear of each other if $\omega' - \omega''$ is small compared to ω' or ω'' . In the Swan system of C_2 shown above, $1773.4 - 1629.9 = 143.5$ is a reasonably small quantity compared with either of them.

Comparing atomic and molecular radiation with each other, we observe that each line of an atomic spectrum is the counterpart of an elaborate band system in a molecule. When we recall the many hundreds of lines arising from various electron transitions in a typical atom, the question arises whether the spectrum of a typical molecule will not be an unmanageably complex affair of hundreds of complex band systems. Fortunately, in practice we find only a few electronic transitions taking place in molecules. In the helium molecule, which along with that of hydrogen is the most prolific in this respect, not more than a score or two of band systems have been found. Three or four known band systems is much more typical of the average molecule. This is because, as we shall see later in the book (Chapter III (α)), electronic transitions often result in the generation of substantial vibrational energy, and this may cause dissociation of the molecule, flinging the component atoms apart.

(c) THE FINE STRUCTURE OF BANDS

Even in Plate I, at some distance from the band heads, traces of the fine structure may be seen. In general, however, a powerful grating type of spectrograph is essential for the study of fine structure, and Plates II and III may be taken as examples of such photographs of two very simple bands. The band whose fine structure is shown in Plate II occurs also in Plate IV, which was taken by using a glass prism spectrograph, and the student will appreciate the marked contrast in resolving power of the two instruments.

We are now concerned to understand in general terms how fine structure arises. Chapters VIII and IX will deal in considerable detail with the many types which are found; here we consider only the basic principles. The vibrational levels of Plate I may be regarded as due to non-rotating molecules, and in reality a pile of rotational levels might be imagined associated with each of those levels. To make clear, however, the relative magnitudes of the different kinds of energy—electronic, vibrational, and rotational—we have constructed in Fig. 1 a scale diagram for a particular band system.

The state of a molecule taking into account its whole energy would

branches. The lines in any one branch are distributed in such a way that if the wave-number of each line is plotted against its rotational quantum number, they lie on a parabola. The *P* and *R* branches appear indeed to form parts of one and the same parabola. To account for this theoretically we may consider an idealized case—a rigid

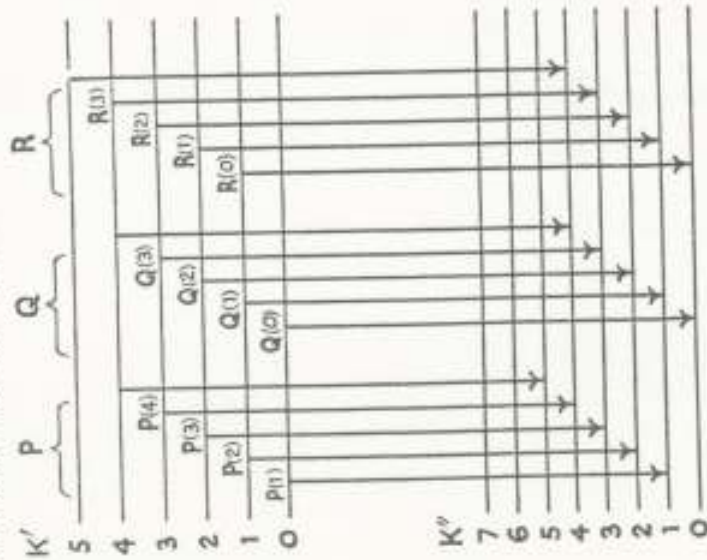


Fig. 2. Rotational transitions which will give rise to *P*, *Q*, and *R* branches in a simple band.

diatomic molecule rotating about a line perpendicular to the inter-nuclear axis and through the centre of gravity.

If *I* is the moment of inertia, and Ω the angular velocity

$$I\Omega = K \frac{h}{2\pi} \dots \dots \dots (5)$$

The rotational energy of the molecule is

$$E_K = \frac{1}{2} I \Omega^2 = K^2 \frac{h^2}{8\pi^2 I} \dots \dots \dots (6)$$

When an electronic transition takes place in a molecule, the molecular 'constants', such as the moment of inertia, frequency of nuclear vibration, &c., all change their values. This would be anticipated, in general, since the inter-nuclear distance represents an equilibrium between electrostatic repulsive forces of the nuclei and the binding

action of the negative electron-cloud. If an electron undergoes a transition from one orbit to another, its contribution to the binding forces of the molecule will change, and a new equilibrium must be established. If *I'* and *I''* are the values of the moment of inertia in the initial and final states of the molecule, and if $h\nu_0$ represents the energy output from electronic and vibrational change (the values of ν_0 being given by equation (3)), then the wave-numbers due to rotational transitions $K' \rightarrow K''$ will be given by

$$\nu = \nu_0 + \frac{h}{8\pi^2 I' C} K'^2 - \frac{h}{8\pi^2 I'' C} K''^2 \dots \dots (7)$$

If we substitute the permitted changes in *K* of (4) we have :

$$\begin{aligned} \nu &= \nu_0 + B' + 2B'K + CK^2 \dots \dots R \text{ branch,} \\ \nu &= \nu_0 + CK^2 \dots \dots Q \text{ branch,} \\ \nu &= \nu_0 + B' - 2B'K + CK^2 \dots \dots P \text{ branch,} \end{aligned} \dots (8)$$

where the following abbreviations are used :

$$B' = \frac{h}{8\pi^2 I' C}, \quad B'' = \frac{h}{8\pi^2 I'' C}, \quad C = B' - B'' \dots (9)$$

The formulæ (8) can best be understood with an actual case before us. In Plate II is a photograph of the (0,3) band of the Angstrom system of CO. The three branches have been picked out, and the diagram above the spectrogram is a graph of wave-number (ν) against rotational quantum number (*K*). It portrays in a clear manner the significance of the three branches, which, as we see from (8), correspond to a parabolic distribution of lines. (This is usually called a Fortrat diagram.)

We observe that the band of Plate II degrades to the high-frequency side. The condition that it should do so is that the coefficient *C* of (9) should be positive, for the term CK^2 is the dominating one for the large values of *K*. If *C* were negative, then the band would degrade to the low-frequency side. If *C* is positive, then it is the *P* branch which forms the head; if *C* is negative, it is the *R* branch (see equation (8)). On Plate III we have the spectrogram of the (13,13) band of the CN molecule—a very simple type of band which has no *Q* branch, and which is degraded to the less refrangible or low-frequency side. It may be of interest to note that for the Angstrom CO bands of Plate II, $B_0' = 1.942$ and $B_0'' = 1.538$ (i.e. $B' > B''$) and for the CN band of Plate III, $B_{13}' = 1.596$ and $B_{13}'' = 1.459$, i.e. $B' < B''$. We may summarize our remarks thus :

Direction of degradation to	Branch forming band	Changes in molecular constants		Inter-nuclear distance
		<i>B</i>	<i>I</i>	
High-frequency side	<i>P</i>	$B_0' > B_0''$	$I_0' < I_0''$	Increases Decreases
Low-frequency side	<i>R</i>	$B_0' < B_0''$	$I_0' > I_0''$	

We observe further from equation (8), as well as from Plates II and III, that, as regards the *P* and *R* branches, one branch is the continuation of the other branch for negative values of *K*.

The *P* and *R* branches intersect on the ν -axis at the point $\nu_0 + B'$ for $K = 0$. The *Q* branch intersect on the ν -axis at the point $\nu_0 + B'$ number close to, but not identical with, the above. The 'origin' of a band is defined by ν_0 the wave-number of the radiation arising from electronic and vibrational change only. The *Q* head, if present, marks this point. The point of intersection of the *P* and *R* branches at $\nu_0 + B'$ is often called the null line of the band, for the reason that it is absent from the band structure. We see therefore that a band's origin will always lie within the band structure at some distance from the band head. On low-dispersion spectrograms (Plate I) only the position of the head is measurable: the origin can as a rule be located only if highly resolved bands are available.

Strictly, it is only band *origins* that are expressible by equation (3); but if these data are not available the band *heads* can usually be fitted to such a formula with fair accuracy. (Further detail is given in Chapter II, Sections (a) and (b).)

By fitting the fine-structure lines to equations (8), the moments of inertia of the emitting molecule are calculable for both the initial and final electronic states. The moment of inertia of a rotating diatomic molecule consisting of two masses m_1 and m_2 distant r apart is

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \frac{M_1 M_2}{M_1 + M_2} m_r r^2 \quad \dots \quad (10)$$

where M_1 and M_2 are nuclear masses (whole numbers) and m_r is the mass of an atom of unit atomic weight, viz.

$$m_r = \frac{\text{mass of H atom}}{\text{atomic weight of H}} = \frac{1.662 \times 10^{-24}}{1.0077} = 1.649 \times 10^{-24} \text{ gm.}$$

Thus if the chemical nature of the emitter is known, the internuclear distance can be calculated (often to an accuracy of 0.001 A.U.) from

$$r = \frac{16.774}{B} \left(\frac{M_1 + M_2}{M_1 M_2} \right),$$

where r is measured in A.U. and B is measured in cm^{-1} . In practice, however, the evaluation of the molecular constants B' , B'' , &c., is not done by fitting the fine-structure lines to the branch formulae (8), but by using certain mathematical relations between corresponding lines of different branches. These methods are collectively called the combination principle (see Chapter VIII, Section (c)).

(d) INFRARED BAND SPECTRA

We have seen in the preceding section what the structure of a simple type of 'electronic' band may be expected to be. The association of an electronic jump with vibrational and rotational changes has two major consequences: (1) because of the magnitude of ν_e , it usually causes bands to be in the visible or ultra-violet region, and (2) because of the change of size of the molecule it creates bands with the para-

metric type of branch. If no electronic transition takes place ($\nu_e = 0$), vibration-rotation bands may nevertheless occur. These are usually in the near infra-red region. This region can be investigated photographically up to about 12,000 A.U. ($= 1.2 \mu$), and beyond this the thermopile and galvanometer may be used. If prism spectrographs are employed the optical system has to be changed to deal effectively with different regions of the infra-red, such as quartz (1μ - 3.5μ), fluorite (1μ - 7μ), rocksalt (7μ - 15μ) or potassium bromide (12μ - 22μ).

In Fig. 3 we have represented the group of vibrational levels which is associated with the ground state of the C_2 molecule on Plate I.

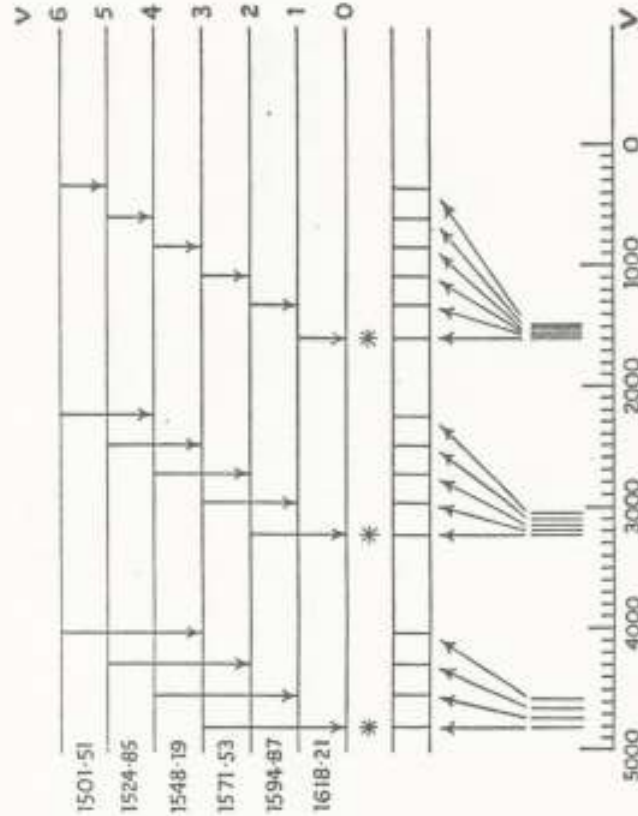


Fig. 3. Typical vibration-rotation band spectrum in emission.

Transitions between these would be expected to give rise to vibration-rotation bands, and all these bands should be expressible by the formula $\nu = 1629.88 (\nu' - \nu'') - 11.67 (\nu'^2 - \nu''^2)$. There are special reasons (see Chapter X) why molecules of the type X_2 , such as C_2 , N_2 , O_2 , Cl_2 , which have no electric moment, cannot give rise to vibration-rotation bands, but for purposes of illustrating the general features of such spectra we disregard the fact that the levels depicted in Fig. 3 are for a C_2 molecule. We have already remarked that the anharmonic vibrator can permit any change in v , so that arrows may be placed as shown to illustrate possible emission bands. The absorption spectrum of the cold gas or vapour would inevitably be simpler. The only bands to be expected are marked by * and would correspond to absorption of energy from the ground level $\nu'' = 0$ to various

higher levels. The absorption band ($1 \leftarrow 0$) is usually called the 'fundamental', while ($2 \leftarrow 0$), ($3 \leftarrow 0$), &c., may be called 'overtone', and are approximately multiples of the fundamental wave-number (in the above case 1018.21 cm^{-1}).

Infra-red bands commonly differ in appearance from electronic bands in not showing fine structure converging to the formation of a band head. The mean size of a molecule, and therefore the moment of inertia, is going to vary only slightly with vibrational amplitude, so that infra-red bands will almost invariably be headless. If $B' = B''$, so that equation (8), the coefficient $C = B' - B''$ will vanish, and the

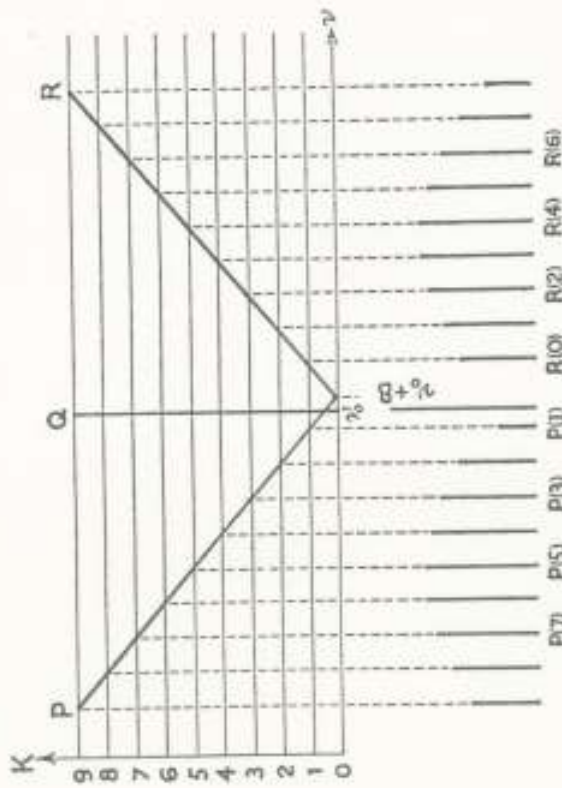


Fig. 4. Fortrat diagram for a simple vibration-rotation band where $C = 0$.

result will be a linear distribution of fine structure on both sides of the band origin. Examination of Plate VII, which is an *electronic* band system, will disclose a certain number of headless bands due to the fact that B' and B'' have become almost equal for these particular bands. This rather exceptional state of affairs for electronic bands is the rule for vibration-rotation bands. The formulae of equation (8) would degenerate in the special case $B' = B''$ to:

$$\begin{aligned} \nu &= \nu_0 + B' + 2BK & \dots & R \text{ branch,} \\ \nu &= \nu_0 & \dots & Q \text{ branch,} \\ \nu &= \nu_0 + B' - 2BK & \dots & P \text{ branch.} \end{aligned} \quad (11)$$

This corresponds to degeneration of the parabolas into straight lines as in Fig. 4.

The Q branch, if present, becomes a single strong line at the band origin.

The moment of inertia of a molecule, as we have remarked above, will be expected to vary only slightly with vibrational amplitude, compared with the magnitude of the change which commonly occurs because of electronic displacement. The effect of vibration will be to increase slightly the mean square of the inter-nuclear distance, and thus to increase the moment of inertia. The constant B of (11) thus very slowly diminishes as v increases, and to a close approximation the relationship is linear:

$$B_v = B_0 - \alpha v \quad \dots \quad (12)$$

The constant α is comparatively small: for the upper and lower electronic states of the C_2 molecule these values have been found to be $\alpha' = 0.03$ and $\alpha'' = 0.025$. Because the constant $C = B' - B''$, which is $\alpha(v'' - v')$ for vibration-rotation bands, is so small, these

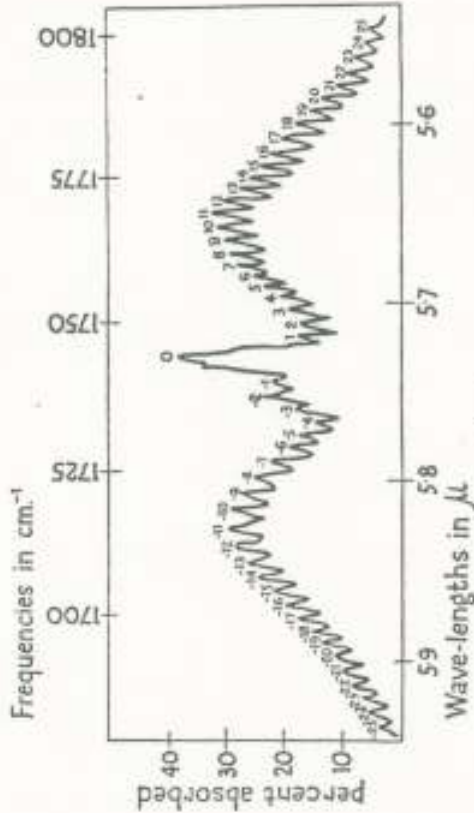


Fig. 5

bands will seldom if ever have a head. Because this has a negative value, however, the *tendency* to head formation will necessarily be in the R branch (see equation (8)).

Fig. 5 shows a recording of a typical vibration-rotation band made by the use of a slit-thermopile and galvanometer.

We now come to the matter of pure-rotation bands. For most molecules in an ordinary state, ν_e and ν_v of equation (2) are both zero. If sufficiently stimulated by electrons or radiation or by thermal agitation at high temperatures, then electronic and vibrational energy may be imparted. The common absence of vibrational energy in ordinary molecules is supported by the evidence of specific heats which at ordinary temperatures are adequately accounted for by the translational and rotational energy of most molecules. Both these types of energy are governed by the temperature which gives to the molecules an appropriate (probability) distribution of linear velocities and angular velocities. If a gas is unexcited (i.e. in temperature

equilibrium with its surroundings), then there will be a constant interchange of energies between individual molecules, some going up and some going down the energy scale, but the net result so far as radiation of the gas to its surroundings is concerned will be zero. If, however, the gas is above the temperature of its surroundings, thermal radiation will be emitted. A continuous spectrum will presumably be radiated as the kinetic energy of translation falls, but discrete band lines will arise from the quantized rotational energy. The equation (7) becomes:

$$\nu = \frac{h}{8\pi^2 I_C} \{ (K + 1)^2 - K^2 \} = B(2K + 1) \quad (13)$$

This radiation is, of course, in the far infra-red region, and is difficult to analyse spectroscopically. Such a pure-rotation band, we observe, consists of one branch only of equidistant lines separated by the interval $h/4\pi^2 I_C$ (see Fig. 6). In a few favourable cases (HCl and HBr) some of these lines have been observed experimentally.

CHAPTER II

THE GROSS STRUCTURE OF BAND SYSTEMS

(a) REPRESENTATION OF BANDS

WE now amplify the matter introduced briefly in Chapter I (b). Using the Swan system of C_2 as an example, we saw that the gross-structure of a typical band system could be represented by equation (3). The typical vibrational term was taken to be the function

$$G(v) = \omega_0 v - \omega_0 x v^2 + \omega_0 y v^3 \dots \quad (14)$$

where as a rule no term higher than v^2 is necessary. The vibrational energy of the molecule is expressed by the values of $hG(v)$. The 'origin' of the band system was defined as the wave-number ν_0 . This is almost identical with the 'origin' of the (0,0) band but we shall see shortly that it is not quite the same.

According to the New Quantum Theory the typical vibrational term is

$$G(v) = \omega_0(v + \frac{1}{2}) - \omega_0 x(v + \frac{1}{2})^2 + \omega_0 y(v + \frac{1}{2})^3 \dots \quad (15)$$

where v takes values 0, 1, 2, 3, &c. It is sometimes said that the New Quantum Theory introduces half-integral quantum numbers, but this is not so. The quantum numbers remain integral; it is the expression for the vibrational energy of an oscillation which is modified. As a result of this, the vibrational energy never vanishes but has a minimum value $hG(0)$, where $G(0) = \frac{1}{2}\omega_0 - \frac{1}{8}\omega_0 x + \frac{1}{64}\omega_0 y$. This vibrational energy is residual, and cannot be removed from the molecule. It follows therefore that the (0,0) band of a system has its origin at

$$\nu^{00} = \nu_0 + G(0) - G'(0) = \nu_0 + (\frac{1}{2}\omega_0 - \frac{1}{8}\omega_0 x) - (\frac{1}{2}\omega_0 - \frac{1}{2}\omega_0 x')$$

which is not coincident with the system origin ν_0 . The nuclear vibration frequency is easily derived from the expression for the vibrational energy. Thus in cm^{-1}

$$\omega_0 = \frac{1}{hc} \frac{\partial E}{\partial v} = \frac{\partial G}{\partial v} \quad (17)$$

According to the Old Quantum Theory we should therefore have

$$\omega_0 = \omega_0 - 2\omega_0 x v + \dots \quad (18)$$

According to the New Quantum Theory we should have from (15) and (17)

$$\omega_0 = \omega_0 - 2x\omega_0(v + \frac{1}{2}) + 3y\omega_0(v + \frac{1}{2})^2 \dots \quad (19)$$

* The subscript e of ω_e is used to remind us that ω_e is the frequency of infinitesimal vibrations about the equilibrium position—a theoretical quantity, of course.

† A rigorous proof is rather too long to present. A simple proof follows from regarding v as continuously variable, when we should have for the energy of an oscillator of frequency ω_0 , $E = hc \int \omega_0 dv$.

So that we have for the vibration frequency (ω_0) in the lowest state, where $v = 0$,

$$\omega_0 = \omega_e - x_e \omega_e + \frac{1}{2} y_e \omega_e \dots \quad (20)$$

The theoretical frequency ω_0 , about the equilibrium position does not actually exist for the molecule: it is deduced from (19) by extrapolation of ω_v to $v = -\frac{1}{2}$.

We postpone to Section (c) the criteria by which a correct assignment of vibrational quantum numbers to bands can be made, but, assuming this has been done, we may consider how a satisfactory formula such as (5) is obtained to express the system. We take as an example the band-head data of BeO, a spectrum lying in the visible region and easily obtained by burning an arc in air between beryllium poles. In the two accompanying tables are shown, first, the experimental data to which quantum numbers (v' , v'') have been assigned, and secondly, the first differences between the wave-numbers of the band heads. Examining this table of first differences we note that $\Delta G''$ is not quite constant down a particular column, but is a function of v' , and similarly $\Delta G'$ along a particular row is a function of v'' . This lack of constancy arises through the use of data on band heads as distinct from band origins. A small term $k(v' + \frac{1}{2})(v'' + \frac{1}{2})$ is usually adequate to meet this difficulty, and the bands can be fitted to a formula:

$$\begin{aligned} \nu^{\text{H}} = \nu_e + [\omega_e'(v' + \frac{1}{2}) - \omega_e'x_e'(v' + \frac{1}{2})^2] \\ - [\omega_e''(v'' + \frac{1}{2}) - \omega_e''x_e''(v'' + \frac{1}{2})^2] - k(v' + \frac{1}{2})(v'' + \frac{1}{2}) \quad (21) \end{aligned}$$

For the sake of brevity we shall write $\Delta G(v + \frac{1}{2})$ for $G(v + 1) - G(v)$. From equation (21) we then derive

$$\begin{aligned} \Delta G'(v + \frac{1}{2}) = \omega_e' - 2\omega_e'x_e'(v' + 1) - k(v'' + \frac{1}{2}), \\ \Delta G''(v + \frac{1}{2}) = \omega_e'' - 2\omega_e''x_e''(v'' + 1) + k(v' + \frac{1}{2}). \quad (22) \end{aligned}$$

By taking the intervals between successive members in the same row or column in the second table we can find the best value of k . It is in this case 5.4. The third table is then prepared, giving the values of $\Delta G'(v' + \frac{1}{2}) + 5.4(v'' + \frac{1}{2})$ and $\Delta G''(v'' + \frac{1}{2}) - 5.4(v' + \frac{1}{2})$, in which table we now see that within the limits of experimental error there is constancy in particular rows or columns. Had this not been so, it would have indicated the necessity for terms in $y_e \omega_e'(v' + \frac{1}{2})^3$ or $y_e'' \omega_e''(v'' + \frac{1}{2})^3$. The mean values of the corrected differences are indicated at the top and side of the third table. They are expressed by the formulae:

$$\begin{aligned} \Delta G'(v' + \frac{1}{2}) + 5.4(v'' + \frac{1}{2}) = 1352.6 - 11.77 v', \\ \Delta G''(v'' + \frac{1}{2}) - 5.4(v' + \frac{1}{2}) = 1448.0 - 30.0 v''. \end{aligned}$$

Comparing these with (22), we see at once that

$$\begin{aligned} \omega_e' &= 1364.4, & \omega_e'x_e' &= 5.88, \\ \omega_e'' &= 1478.0, & \omega_e''x_e'' &= 15.0. \end{aligned}$$

To find ν_e we have from (21), putting $v' = 0$, $v'' = 0$,

$$\nu^{\text{H}} = \nu_e + \frac{1}{2}(\omega_e' - \omega_e'') - \frac{1}{2}(\omega_e'x_e' - \omega_e''x_e'') - \frac{1}{2}k,$$

which gives

$$\nu_e = 21231.5 + 55.9 = 21287.4 \text{ cm.}^{-1}.$$

Jenkins and Rosenthal obtained data on the origins of six bands by a fine-structure analysis. How different the constants may be, compared with those derived from data of low-dispersion photographs of the band heads, is shown by their formulae

$$\begin{aligned} \nu^{\text{H}} = 21254.05 + [1370.81(v' + \frac{1}{2}) - 7.76(v' + \frac{1}{2})^2] \\ - [1487.45(v'' + \frac{1}{2}) - 11.87(v'' + \frac{1}{2})^2]. \end{aligned}$$

If the interval between band head and origin were constant through-

WAVE-LENGTH IN AIR } OF BANDS OF $v' \downarrow v''$ BeO

v'	0	1	2	3	4	5	6
v''	0	0	0	0	0	0	0
0	4705.67	21231.5	4170.03	4204.21	4474.69	4560.3	4535.0
1	21231.5	4427.31	4451.79	4754.46	4775.37	4517.3	4335.0
2	19780.4	21123.9	42456.6	21027.0	20934.9	22130.9	22042.1
3	5024.10	19695.1	4754.46	4496.47	4795.24	4813.04	4335.0
4	18357.3	18300.9	10623.0	20934.9	19498.2	20771.1	20709.5
5	5443.9	1462.7	5094.64	4754.46	4795.24	4813.04	4335.0
6	19400.6	21231.5	4204.21	4474.69	4560.3	4535.0	4335.0

18 AN INTRODUCTION TO MOLECULAR SPECTRA
 out a band system, then of course the formulae obtained from head-data or origin-data would differ only in the electronic term. In practice this is far from being true. Thus in the above example of BeO we have:

$$\nu_{or} - \nu^H = -33.35 + (6.4(v' + \frac{1}{2}) - 1.88(v'' + \frac{1}{2})^2) - [19.45(v' + \frac{1}{2}) + 3.13(v'' + \frac{1}{2})^2] + 5.4(v' + \frac{1}{2})(v'' + \frac{1}{2})$$

FIRST DIFFERENCES CONSTRUCTED FROM ABOVE DATA

ν''	0	1	2	3	4	5	6	7
$\Delta G''(0)$	1451.1	1451.1	1451.1	1451.1	1451.1	1451.1	1451.1	1451.1
$\Delta G''(1)$	1349.1	1450.7	1450.6	1437.3	1411.3	1390.3	1371.0	1352.6
$\Delta G''(2)$	1343.5	1425.8	1420.6	1407.2	1386.2	1365.0	1343.8	1322.6
$\Delta G''(3)$	1340.8	1425.8	1404.0	1378.4	1350.0	1320.0	1299.8	1278.8
$\Delta G''(4)$	1340.8	1425.8	1399.9	1374.3	1345.0	1315.0	1285.0	1255.0
$\Delta G''(5)$	1340.8	1425.8	1399.9	1374.3	1345.0	1315.0	1285.0	1255.0
$\Delta G''(6)$	1340.8	1425.8	1399.9	1374.3	1345.0	1315.0	1285.0	1255.0

19 THE INTERVAL BETWEEN BAND HEAD AND ORIGIN
 We proceed to consider upon what factors this variable interval depends.

(b) THE INTERVAL BETWEEN BAND HEAD AND ORIGIN

We should expect a variable interval of this kind to occur from the variation of moment of inertia with vibrational quantum number, expressed empirically by such formulae as (11). Let us consider this in detail.

Regarding a molecule as 'rigid' so far as the centrifugal effects of rotation are concerned (see Chapter IV (d) for a refinement), we have the fine structure of an electronic band given, according to the New Quantum Theory, by

$$\nu = \nu_0 + \frac{h}{8\pi^2 I' C} K'(K' + 1) - \frac{h}{8\pi^2 I'' C} K''(K'' + 1) \quad (23)$$

This may be compared with (7) on the Old Quantum Theory. The corresponding branches are:

$$\left. \begin{aligned} \nu &= \nu_0 + (B' + B'')(K + 1) + C(K + 1)^2 & (K + 1 \rightarrow K), \\ \nu &= \nu_0 - \frac{C}{4} + C(K + \frac{1}{2})^2 & (K \rightarrow K), \\ \nu &= \nu_0 - (B' + B'')K + CK^2 & (K - 1 \rightarrow K). \end{aligned} \right\} \quad (24)$$

Here $C = B' - B''$.

The R and P branches clearly form part of the same function, the sequence of lines in the neighbourhood of the origin ν_0 being labelled $R(2), R(1), R(0),$ null line, $P(1), P(2),$ &c. The value of K corresponding to the head of the P branch is given by $\frac{\nu_0}{\epsilon K} = 0$

$$K_H = \frac{B' + B''}{2(B' - B'')} \quad (25)$$

Upon substitution in the P branch formula we have for the interval between head and origin

$$\nu_{or} - \nu^H = \frac{(B' + B'')^2}{4(B' - B'')} \quad (26)$$

Now, as we have already seen, B' and B'' are functions respectively of v' and v'' . In place of (11), we should now write

$$B_v = B_0 - \alpha(v + \frac{1}{2}) \quad (27)$$

so that $B_v = B_0 + \alpha/2$ of the old expression.

Substituting expressions for B_v and $B_{v''}$ in (26), we have, using as abbreviations $C = B'_0 - B''_0$ and $\theta = \frac{2C}{B'_0 + B''_0}$, and bearing in mind in the expansion that $\alpha'(v' + \frac{1}{2}) - \alpha''(v'' + \frac{1}{2})$ is small compared with C ,

$$\begin{aligned} \nu_{or} - \nu^H &= C\theta^2 + \alpha'0(0 - 1)(v' + \frac{1}{2}) - \alpha''0(0 - 1)(v'' + \frac{1}{2}) \\ &+ \frac{\alpha'^2}{C} (\frac{1}{4} - 0 + 0^2)(v' + \frac{1}{2})^2 + \frac{\alpha''^2}{C} (\frac{1}{4} + 0 + 0^2)(v'' + \frac{1}{2})^2 \\ &- \frac{2\alpha'\alpha''}{C} (0^2 - \frac{1}{4})(v' + \frac{1}{2})(v'' + \frac{1}{2}) \quad (28) \end{aligned}$$

ν''	FIRST DIFFERENCES (CORRECTED)						
	$\Delta G''(v'' + \frac{1}{2}) - 5.4(v'' + \frac{1}{2})$	$\Delta G''(v'' + \frac{1}{2}) + 5.4(v'' + \frac{1}{2})$	$\Delta G''(v'' + \frac{3}{2}) - 5.4(v'' + \frac{3}{2})$	$\Delta G''(v'' + \frac{3}{2}) + 5.4(v'' + \frac{3}{2})$	$\Delta G''(v'' + \frac{5}{2}) - 5.4(v'' + \frac{5}{2})$	$\Delta G''(v'' + \frac{5}{2}) + 5.4(v'' + \frac{5}{2})$	$\Delta G''(v'' + \frac{7}{2}) - 5.4(v'' + \frac{7}{2})$
0	1448.4	1420.4	1371.9	1354.3	1339.1	1340.8	1341.0
1	1448.0	1448.6	1448.6	1417.7	1380.1	1340.8	1342.4
2	1418.1	1416.1	1390.5	1350.4	1328.2	1330.8	1330.4
3	1388.7	1388.3	1358.3	1321.4	1297.7	1300.5	1300.4
4	1359.3	1318.3	1287.0	1257.7	1227.0	1289.9	1287.0
5	1329.7	1287.0	1257.7	1227.0	1191.7	1257.7	1257.7
6	1297.8	1257.7	1227.0	1191.7	1151.7	1227.0	1227.0
7	1267.8	1227.0	1191.7	1151.7	1111.7	1181.7	1181.7

We observe that if $B_1'' + B_2'' > 2(B_1' - B_2')$ (i.e. if $3B_1'' > B_1'$ which will always be the case), $\theta > 1$. Moreover, θ is + or - according as C is + or -. We may therefore summarize signs of the various coefficients in (28) as follows:

	Constant	$v'' + \frac{1}{2}$	$v'' + \frac{3}{2}$	$v'' + \frac{5}{2}$	$v'' + \frac{7}{2}$
Degraded to ultra-violet	+	+	-	+	-
Degraded to infra-red	-	+	-	-	+

The expression for $\nu'' - \nu^H$ of the BeO bands (which are degraded towards the red) accords with these predictions as to signs. In Fig. 6 is shown diagrammatically how the interval $\nu'' - \nu^H$ will vary

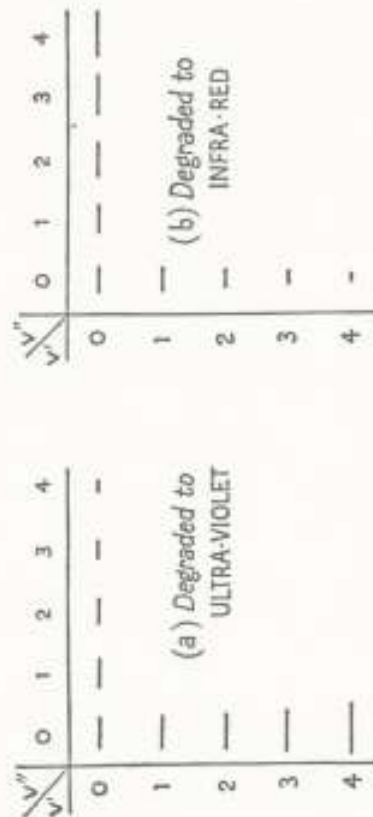


Fig. 6. Variation of the interval $\nu'' - \nu^H$ in band systems.

throughout typical band systems degraded (a) to the ultra-violet, and (b) to the infra-red.

Sometimes the nature of bands is such that even on low-dispersion plates the interval between band origin and band head is measurable. In such a case there is no reason why these data for four bands should not be substituted in (28) and the four equations solved to give C , θ , α' , and α'' . Thus B_1'' and B_2' could be approximately determined (without a fine-structure analysis). If a Q branch is present, the head of which (see (24)) is at the band origin, the interval $\nu'' - \nu^H$ should not be difficult to determine experimentally.

We note from (28) that the condition that the coefficient of $(v'' + \frac{1}{2})(v'' + \frac{3}{2})$ shall be large is that C is small. Such arises if F' and F'' are nearly equal. In the spectra of CaF, SrF, BaF, &c., where this is the case (see Plate VI), and where two or perhaps three long sequences constitute the system, it is for this reason very difficult to express them by an accurate vibrational function.

(c) THE ASSIGNMENT OF VIBRATIONAL QUANTUM NUMBERS

When a new band system has been found, the wave-lengths of the heads (or origins) measured, and corresponding wave-numbers *in vacuo* obtained from tables, the problem arises of assigning (v' , v'') values to the bands. In a case such as the Swan system of C_2 (see Plate I and the corresponding table), or in the case of BeO, this is quickly done, and there are many other band systems of this type. The (0,0) sequence can sometimes be picked out by the sharp intensity fall in this sequence. In many band systems the intensity distribution is not of this type (see Plates IV and V) and inspection of spectrograms is of little help. Sometimes the data are incomplete by reason of the spectrum lying partly in the infra-red or the far ultra-violet. In other cases (see BaF bands of Plate VI), the interpretation of the various heads may complicate the process. In this section are enumerated features that are a guide in assigning vibrational quantum numbers. Reference may be made by way of illustration to the two tables of the C_2 and BeO systems.

- (1) As v' increases ν increases; as v'' increases ν diminishes.
- (2) The first differences between adjacent rows or adjacent columns should be approximately constant. If $\Delta G'(v')$ is a function of v' , or $\Delta G''(v'')$ of v'' , this indicates an appreciable value of k (see (21) and (22)).
- (3) The second differences should be approximately constant, viz. $\Delta^2 G'(v') = 2\omega_e v' x''$ and $\Delta^2 G''(v'') = 2\omega_e v' x'$. If there is an appreciable drift, the third difference (see (15)) should be $6y_e \omega_e$.
- (4) Where Q branches are present, the direction of variation of the $v'' - v'$ interval as in Fig. 6 provides a check on the arrangement of the bands.
- (5) In many systems the (v' , v'') array has strong boundary progressions $v' = 0$ and $v'' = 0$. In contrast with this, observe the ultra-violet band system of the O_2 molecule shown on Plate V. The progression $v' = 0$ is well marked and the v'' -numbering is therefore reliable, but the $v'' = 0$ progression is faint, being far in the ultra-violet. The most that can here be done is to take prolonged photographic exposures with suitably sensitive plates to see if there is any evidence of a progression still farther in the ultra-violet than the last observed. If we were not dealing with an ionised molecule (but a neutral one), and if the lower electronic state of the band system was the normal state of the molecule, then the absorption spectrum of the cold gas would consist of such bands as (0,0), (1,0), (2,0), (3,0), &c., and this would fix unequivocally the correct assignment of v'' .
- The correctness of the assignment of initial quantum numbers can sometimes be conveniently determined by irradiation of the gas or vapour with a convenient monochromatic wave-length, and photography of the fluorescent spectrum. For example, if O_2 were irradiated with the strong Hg line λ 2536 ($= 39412 \text{ cm.}^{-1}$), this would permit the band (0 \rightarrow 0) at 38600 cm.^{-1} , but not the (1,0) band at 39601 cm.^{-1} to be emitted in fluorescence.
- (6) Another criterion is available if an isotope effect is present. If one of the atoms in the molecule has two isotopes, a duplication

of the gross structure of the band system results. The separation of corresponding bands of the two isotopes varies almost linearly with the wave-number separation of the band from the common system origin. (This is not quite identical with the origin of the (0,0) band: see (16).) The isotope effect is dealt with later in Chapter XI.

(7) When several band systems of the same molecule are known they are almost certain to share some of the electronic levels (and therefore the associated vibrational levels) in common. The correct assignment of v' or v'' values to a system is therefore assisted by the knowledge of other band systems that may be better developed or in a more convenient part of the spectrum. For example, the so-called Second Positive N_2 system has its heads expressed by

$$\begin{aligned} \nu^0 &= 29653 + [2044 \cdot 7(v' + \frac{1}{2}) - 26 \cdot 047(v' + \frac{1}{2})^2] \\ &\quad - [1732 \cdot 84(v'' + \frac{1}{2}) - 14 \cdot 437(v'' + \frac{1}{2})^2]. \end{aligned}$$

There is no doubt about the correctness of the assignment of (v' , v'') values here. The so-called First Positive N_2 system lies, however, to a substantial extent in the near infra-red, and some uncertainty as to the (v' , v'') assignment arises. Since some of the $\Delta G'(v')$ intervals of this system are clearly identical with $\Delta G'(v')$ intervals of the Second Positive system, the (v' , v'') values can be assigned confidently. Thus the First Positive system is then expressed by:

$$\begin{aligned} \nu^0 &= 9519 + [1732 \cdot 84(v' + \frac{1}{2}) - 14 \cdot 437(v' + \frac{1}{2})^2] \\ &\quad - [1460 \cdot 39(v'' + \frac{1}{2}) - 13 \cdot 93(v'' + \frac{1}{2})^2]. \end{aligned}$$

As another example take the 'High-Pressure Carbon' system of Plate IV. The assignment of vibrational quantum numbers, and the nature of the emitting molecule, were determined by observing that some of the band intervals were identical with those of $\Delta G'(v')$ of the Swan C_2 system. These two systems have in fact a common final electronic state, the normal state of this molecule.

(d) THE ORIGIN OF MULTIPLICITY IN BAND HEADS

Examination of the Plates IV-VI shows many examples of multiplicity in the gross band structure. The chief causes of this will be summarized here. They are: multiplicity of the electronic levels (i.e. ν_e), Q branches, Λ -type doubling, and isotopy.

Multiplicity of ν_e

Multiplicity in ν_e does not mean, however, a duplication or tripling of the gross structure, displaced by some constant interval. Electronic and vibrational motions interact, and the $\Delta \nu_e$ doublet interval which is obvious in the Comet-Tail (CO^+) system (${}^2\Pi \rightarrow {}^2\Sigma$) of Plate IV, or the ultra-violet O_2 bands (${}^2\Pi \rightarrow {}^2\Pi$) of Plate V, shows a small but definite change in value through the system. Again, the electronic and rotational motions are in some molecules strongly linked together, and large doublet or triplet intervals at the band origins may diminish rapidly with increase of rotational quantum number. An example of this is seen in Fig. 7. When this variation

takes place very rapidly, the gross structure (low-dispersion plates) usually shows no multiplicity of the heads (see Plate I). Where, as

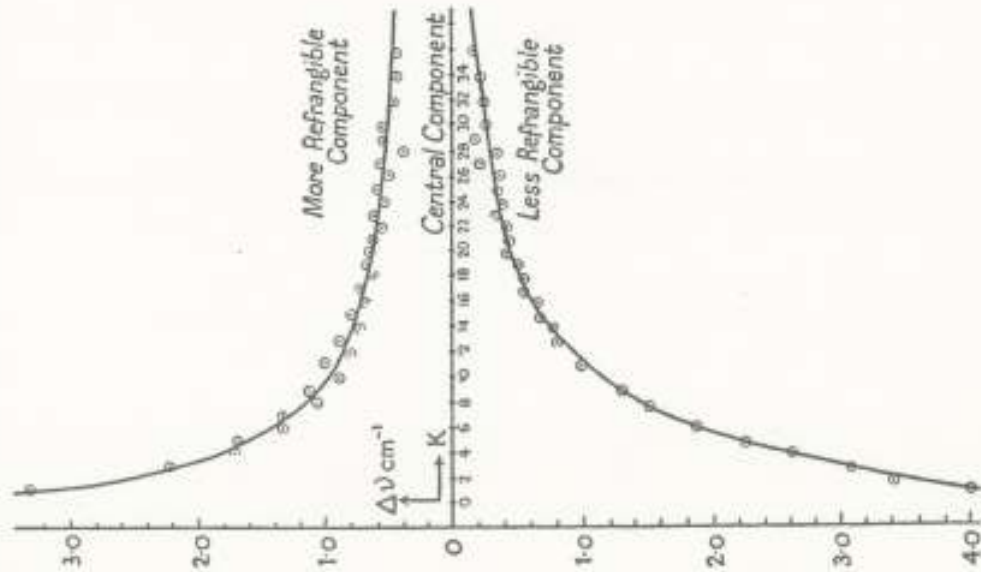


Fig. 7. Variation of the triplets of the R branch of $(0,0)$ system of the Swan $C_1^1\Pi \rightarrow {}^1\Pi$ system.

in the 'Triplet' System of CO (Plate IV), the variation is less rapid, the heads may be visible.

Q branches

Doubling arising from the presence of Q branches is usually easily distinguishable. As a typical case we observe the *minor* doublet interval in the Comet-Tail (CO^+) bands of Plate IV. The faint outer

head is an R head, the stronger inner one a Q head. Much, however, depends on the intensity distribution in the fine structure of the branches. Thus (in Plate II) the Angström CO bands have Q branches, but they are not apparent under the low dispersion on Plate IV. When the inter-nuclear distance remains practically the same in the initial and final states, it is clear from (26) that a Q branch, if present, may be widely separated from the corresponding P or R head. Plate VI of BaF shows this effect. In the green $(0,0)$ band (Spectrum II) the interval of about three bands of the sequence separates R and Q heads.

It is instructive to observe the type of error which may easily arise in interpreting the nature of band heads (Fig. 8). In some of the earliest plates taken of the BaF band system, triple band heads only were visible. Being an odd-electron molecule like BO, CN, CO^+ , and N_2^+ , an even multiplicity was expected, and analogy with the spectra of these other molecules indicated as the electron transition ${}^1\Pi \rightarrow {}^1\Sigma$ which should have Q branches. (This will be clear in later sections.) That the second interpretation in Fig. 8 is correct is shown by the following evidence: (a) the interval between the first and third heads varies through the system, as would be anticipated from Fig. 6 (for a system degraded to the red); (b) the interval between the first and second heads does not vary in this manner, and (c) while the expression of first and second heads by a formula requires a big coefficient of $(v' + \frac{1}{2})(v'' + \frac{1}{2})$, the third head requires no such term.

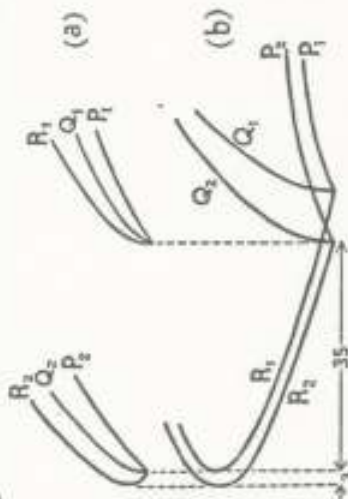


Fig. 8. (a) Incorrect, (b) correct, interpretation of bands of BaF system (${}^1\Pi \rightarrow {}^1\Sigma$).

Λ -type doubling

A brief note as to Λ -type doubling will here suffice, since its nature will be fully appreciated only when fine structure is studied in detail in Chapters VII, VIII, and IX. A good example is seen in Spectrum III of Plate VI, which is the $(1,0)$ sequence of the extreme red ${}^2\Sigma \rightarrow {}^2\Sigma$ system of BaF. It is characterized by a splitting of the rotational levels into two components, of which the separation increases with rotational quantum number. The effect of this will be seen from Fig. 9. Assuming only low-dispersion plates available, Λ -type doubling might possibly be confused with two R heads of an electronic doublet, as in Fig. 8 (b), especially if the Q branches are too faint to see. The differential diagnosis can, however, be made by examining heads known to be formed at lower K -values. Thus the $(1,0)$ band must have its head formed at a lower K -value than the $(0,0)$ band, for a system degraded to the red. For, since $B_1' = B_0' - \alpha'$,

we have $B_0'' - B_1' > B_0'' - B_0'$, and by (25) this result follows. At the lower K -value the separation of two heads arising from Λ -type doubling will be less. On the other hand, the separation of the two R heads would be greater (see Fig. 7) at the lower K -value. In a similar manner for a system degraded to the violet, for the $(0,1)$ band $B_0' - B_1'' > B_0' - B_0''$, so that by (25) the head is formed at a smaller value of K than in the $(0,0)$ band. Thus for the $(0,1)$ band the Λ -type doubling would be smaller, but the separation of two P heads would be greater.

There is another differential diagnosis to be made—between Λ -type doubling and an ordinary Q - R (or P - Q) branch doublet. Upon reference to Fig. 6 it will be seen that this interval varies in just the same way as does the Λ -type doubling. The following criteria must therefore be used:

(a) Express each of the heads in a vibrational formula such as (21). If both behave in a similar way and require a substantial coefficient k it is probably Λ -type doubling. On the other hand, if one of them is a Q head it should require no k to express it.

(b) The type of intensity distribution is some guide to the magnitude of the Q - R or P - Q interval to be expected. A dominant and very prolonged $(0,0)$ sequence indicates $\omega_1 \approx \omega_2$, and $B' \approx B''$, and therefore by (26) the Q - R or P - Q interval should be large.

(c) If an odd-electron atom is involved, Λ -type doubling in a ${}^2\Sigma \rightarrow {}^2\Sigma$ system is an almost certain diagnosis.

Isotopic Multiplicity

The subject of isotopy is dealt with in Chapter XI. No confusion should arise from this cause, since the multiplicity vanishes at the system origin and the pattern intervals vary almost linearly with wave-number separation from the origin. If the nature of the molecular emitter is known, the factor governing the isotopic separation can be calculated. Finally, the relative abundance of isotopes (if known) is a guide to the relative intensities of corresponding band heads. The existence of all three isotopes of corresponding band heads is shown in the SiN band systems. Similarly CuCl bands show

evidence of quadruple systems corresponding to the four possible molecules from Cu (63 and 65) and Cl (35 and 37).

(c) FORMATION OF 'TAILS' IN BAND SEQUENCES

In most band systems of which we may take Plate I as a type, the convergence of successive bands in a sequence is not very marked, and the intensity decrement down any sequence is such as to cause it to fade out after the first few members. Occasionally (as may be observed in Plate VII) the intensity appears to revive in higher members of a sequence which has converged, and, so to speak, doubled back on itself. These higher members of the sequence, moreover, may degrade in the opposite sense to the early members. This phenomenon we must now endeavour to understand. Turning to (21), which expresses the band heads of a system, let us write $v'' - v' = C$ and substitute for v' say. We obtain

$$v'' = \text{Const} + (v'' + \frac{1}{2})[\omega_1' - \omega_1'' + C(2\omega_1'x_1' + k)] - (v'' + \frac{1}{2})^2[\omega_2'x_2' - \omega_2''x_2'' + k] \quad (29)$$

This is a quadratic in $(v'' + \frac{1}{2})$ in which for most band systems the coefficient of $(v'' + \frac{1}{2})$ is substantially greater than that of $(v'' + \frac{1}{2})^2$. Several observations may be made from (29):

- (1) If $\omega_1' > \omega_1''$, successive members of a sequence are on the high-frequency side. If $\omega_1' < \omega_1''$, successive members are on the low-frequency side. Since I_0 is approximately constant (see Chapter IV (e)), it follows that if $\omega_1' > \omega_1''$, then $F' < F''$, and $B' > B''$, so that the bands will degrade to the violet, and vice versa. In other words, as Fig. 10 indicates, the early members of a sequence will always lie on that side of the leading head towards which the bands are degraded.
- (2) We observe that it is the magnitude of $\omega_1' - \omega_1''$ which principally controls the separation of successive members of a sequence. Where, as in the BaF (${}^2\Pi \rightarrow {}^2\Sigma$) system of Plate VI ($\omega_1' = 456.0$, $\omega_1'' = 468.0$), the vibrational change is small, the succeeding heads in each sequence are close together. The same approximation of ω_1' and ω_1'' leads consequently to that of F' and F'' , and therefore (see (26)) to a separation of the Q and R heads. Another associated feature (Chapter III (b)) is the concentration of energy largely in the $(0,0)$ sequence.
- (3) Since the coefficients of $(v'' + \frac{1}{2})$ and $(v'' + \frac{1}{2})^2$ have opposite signs, higher members of a sequence will theoretically converge to a limit, and still higher members will subsequently return upon themselves. We say 'theoretically' because the intensity fall down the sequence may cause the bands to fade out before this point is reached.

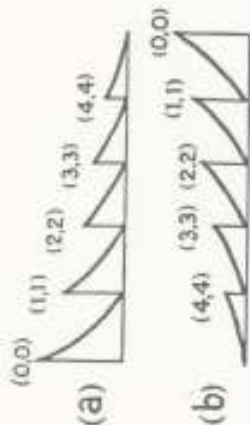


Fig. 10. Sequences (a) degraded to red, (b) degraded to violet.

If the intensity is sustained, however, we have what is commonly called a 'tail' formation. The critical value of v'' corresponding to this is given by $\frac{\partial^2 I}{\partial v''^2} = 0$ from (29), viz.

$$(v'' + \frac{1}{2})_{\text{crit}} = \frac{\omega_v' - \omega_v''}{2(\omega_v' x_v' - \omega_v'' x_v'' + k)} \quad (30)$$

For tails to be possible v'' must be a positive integer. We can formulate

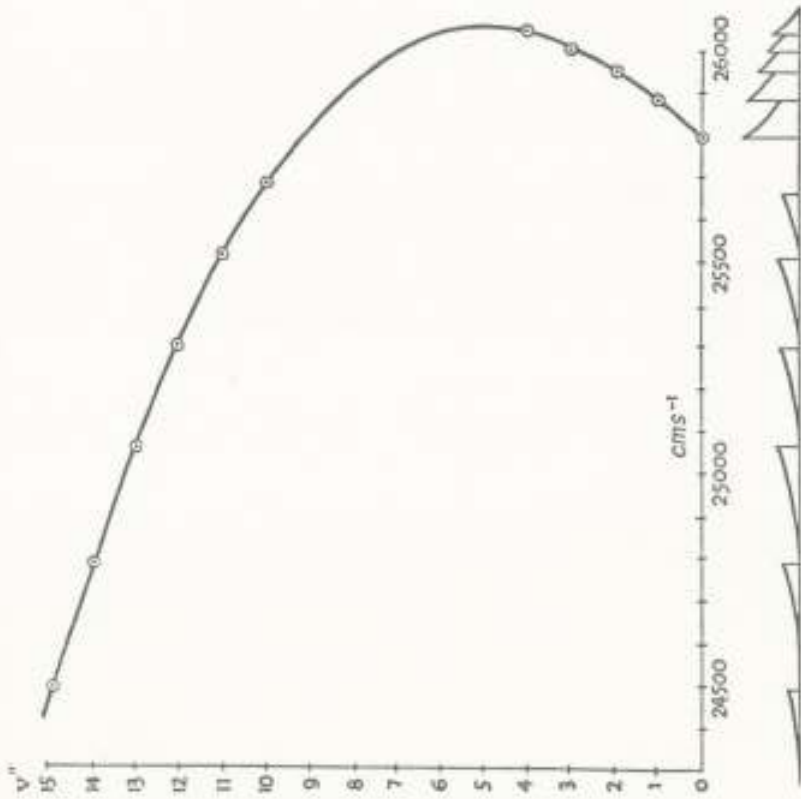


Fig. 11. Graph of v'' for the origins of the (0,0) sequence of CN bands.

a simple rule that covers the large majority of cases. Tails are possible when $(\omega_v' x_v' + k) - \omega_v'' x_v''$ has the same sign as $(\omega_v' - \omega_v'')$. By reason of the intensity fall down a sequence, a tail is more likely to be formed in practice if the above critical value of v'' is not too large. Thus we can say that favourable conditions are found if ω_v' and ω_v'' are not widely different while $\omega_v' x_v'$ and $\omega_v'' x_v''$ differ considerably. Also we note from (30) that when $C (= v'' - v')$ is negative, conditions will be more favourable than for C positive.

We shall take as an example of 'tail' formation the violet CN

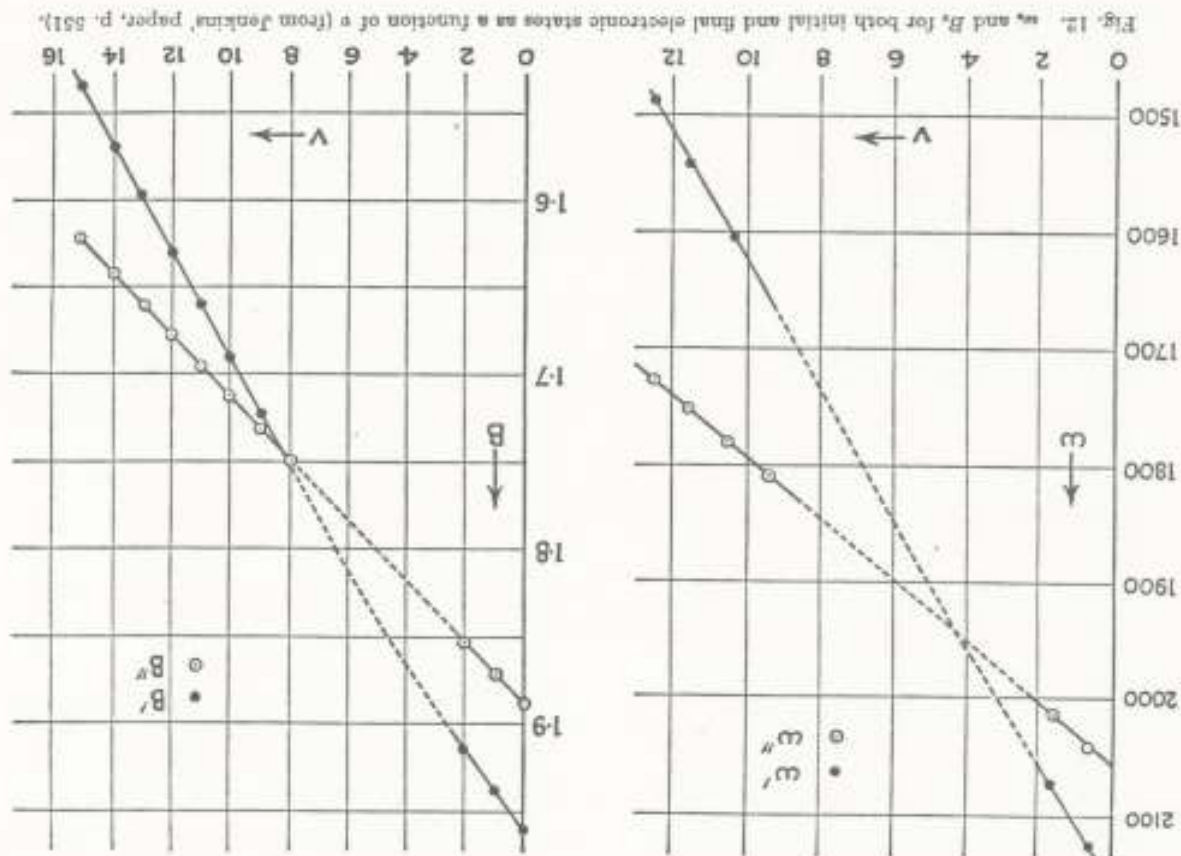


Fig. 12. ω_v' and B_v' for both initial and final electronic states as a function of v (from Jenkins' paper, p. 551).

($^3\Sigma \rightarrow ^3\Sigma$) system which was studied in detail by F. A. Jenkins.* Photographs taken by him in the second order of a 20-ft. grating are shown in Plate VII. The main system degrades to short wavelengths: spectrum (C) shows the (0,1) sequence at λ 4216, spectrum (B) shows at the left, part of the (0,0) sequence at λ 3883, and spectrum (A) shows the (1,0) sequence at λ 3585. On the long-wave side of the (1,0) sequence are a number of headless bands, which are now known to be higher members of this sequence which has doubled back on itself. Similarly, spectrum (B) shows on the long-wave side of the (0,0) sequence, a number of bands degraded to the long wavelength side which are now known to be higher members of this sequence which has doubled back (and changed its direction of degradation). In Fig. 11 the band origins of the (0,0) sequence have been plotted against v'' . It is in fact a parabola such as would be expected by graphing equation (29). Intermediate members of the sequence are of course obscured by the strong early members.

By making a fine-structure analysis of the 'tail' bands, Jenkins was able to show that the final vibrational function $\omega''; v''$ was virtually a linear extrapolation of that previously derived from analysis of the violet system. The function $\omega'; v'$ is not, however, linear (see Fig. 12). In a similar way it is seen that the rotational constants B_v' of the final electronic state are very closely expressed by a linear formula $B_v'' = 1.8944 - 0.0181 v''$, but to express B_v' would require a cubic in v' .

The intersection of these two rotational term functions in Fig. 12 shows why the early members of the violet bands are degraded to the short-wave side (for $B_v' > B_v''$) while the so-called 'tail' bands are degraded to the long-wave side (for $B_v' < B_v''$). Bands in the neighbourhood of the intersection ($B_v' = B_v''$) will be headless. Such bands as (9,8) at λ 3616, and (10,9) at λ 3638 are clearly seen on Plate VII A. It is not, of course, inevitable that tail bands should degrade in the opposite direction to that of low- v members of the system. In the event of the B_v' and B_v'' functions intersecting at a larger value of v than the observed tail bands, they would all have degraded in the same direction.

Numerous other examples of tail formations have been investigated, e.g. in N_2^+ bands by Herzberg,[†] and in the CaF and SrF bands by Johnson and Harvey.[‡]

* *Phys. Rev.*, vol. 31, p. 535 (1928).

† *Ann. d. Phys.*, vol. 86, p. 189 (1928).

‡ *Proc. Roy. Soc.*, vol. 122, p. 161 (1929), and vol. 133, p. 356 (1931).

CHAPTER III

THE DISTRIBUTION OF INTENSITY IN A SYSTEM

(c) THE FRANK-CONDON THEORY

THE nuclei of a particular diatomic molecule have, as we know, a characteristic inter-nuclear distance r_e corresponding to stable equilibrium, and anharmonic oscillations are possible about this position. The equilibrium position must obviously correspond to that of minimum potential energy of the nuclei, and the restoring force when they are replaced from this position must arise as the resultant of (1) a force of mutual repulsion of the two nuclei, and (2) a binding force arising from the electron-cloud.

There is no difficulty in appreciating that the potential energy function $U(r)$ plotted as a function of r has a certain general form which is shown in Fig. 13. We have here constructed hypothetical $U(r)$ curves for two electronic states of a molecule. The general form of the curve follows from the following considerations: (1) there must be a minimum at r_e , the equilibrium inter-nuclear distance; (2) as r increases considerably, $U(r)$ must rise asymptotically to a value equal to the energy of dissociation (D) of the molecule; (3) as r diminishes considerably, $U(r)$ must rise rapidly corresponding to the strong inter-nuclear repulsion. A few typical vibrational energy levels associated with the lower electronic state are shown. Consider a typical vibrational level ab . As r oscillates from the value at a to that at b , it is clear that the kinetic energy of the nuclei is measured at any point k en route by the distance kc of the curve below k . Since the total energy of this particular vibration is constant in the absence of a quantum jump, clearly a fall kc of the nuclear potential energy involves a gain of this amount of kinetic energy.

Frank's original ideas^{*} were directed to explaining the mechanism of photochemical dissociation (i.e. how a molecule could dissociate by absorption of a photon of suitable energy), but his conceptions apply equally to the reverse process of chemical association accompanied by light emission, to the problem of intensity distributions in both absorption and emission spectra, and to an understanding of continuous spectra. Condon[†] later developed Frank's ideas quantitatively, in the first instance from the old quantum standpoint, and later using wave-mechanics.

Consider a typical level ab of the lower electronic state. At some point of its oscillation in this energy level suppose a photon is absorbed and the molecule is transferred to the upper electronic state. Owing to the rapidity of this electronic change compared with the period of vibration of the nuclei, the nuclei possess the same distance and kinetic energy immediately after the transition as they had before. The net effect is the instantaneous substitution of one law of force

* *Trans. Faraday Soc.*, vol. 21, p. 535 (1925).

† Condon, *Phys. Rev.*, vol. 28, p. 1182 (1926); vol. 32, p. 865 (1928).