Werner A. Bingel

Theory of Molecular Spectra

Translated by Express Translation Service, London

John Wiley & Sons Ltd 1969
Verlag Chemie

in which the molecule is a symmetric top with two equal moments of inertia. As an example, Fig. 20 shows qualitatively how the three principal moments of inertia of a bent AB_2 molecule depend on the bond

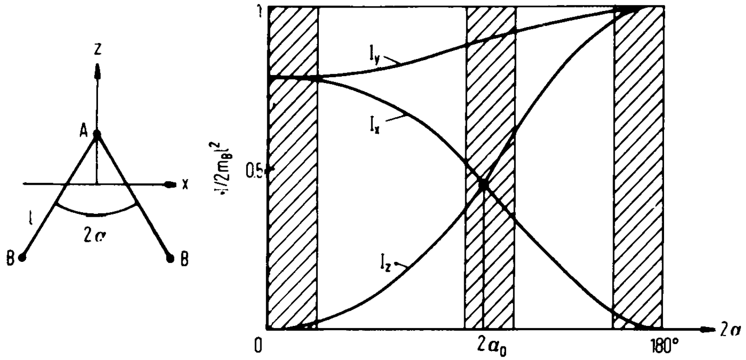

Fig. 20. Dependence of the principal moments of inertia I_x, I_y, and I_z of an AB_2 molecule on the bond angle 2α; l = internuclear distance.

angle 2α it shows that there are two regions around $\alpha = 0°$ and $2\alpha = 180°$ where the molecule approximates to an prolate symmetric top and a region around $2\alpha_0$ [$\tan \alpha_0 = \sqrt{m_A/(m_A + 2m_B)}$] where it approximates to an oblate symmetric top.

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5. Electronic Band Spectra of Diatomic Molecules

As was mentioned in Chapter 2, band spectra in the visible and UV regions are assigned to transitions between different electronic states of a molecule. When interaction between the three forms of motion is disregarded, then according to equation (5c) the energy of an electronic transition is

$$\Delta E = (V' - V'') + (E'_{vibr} - E''_{vibr}) + (E'_{rot} - E''_{rot}) \qquad (69)$$

[the quantity E_{el} in equation (5c) is identical with $V(R_e)$ in equation (25)]. Expressed in wave numbers, this energy becomes

$$\begin{aligned} \nu = \frac{\Delta E}{hc} &= (T'_e - T''_e) + G'(v') - G''(v'') + F'(J') - F''(J'') \\ &= \nu_e + \nu_{vibr} + \nu_{rot} \end{aligned} \qquad (70)$$

The electronic terms T'_e and T''_e are the energies of the potential minima of the two electronic states between which the transition takes place, i.e.

$$\begin{aligned} T'_e &= V'(R'_e)/hc \\ T''_e &= V''(R''_e)/hc \end{aligned} \qquad (71)$$

The vibrational and rotational terms are then built up on these purely electronic energies in accordance with equation (70); this is illustrated in Figs. 21 and 22. The rotational and vibrational terms for each of the two electronic states are again given by equation (47). Therefore the vibrational and rotational structure of an electronic transition is similar to that in a rotation-vibration spectrum, with the important difference that the rotational constants B'_v and B''_v and the vibrational constants ω'_e and ω''_e etc. are now characteristic of different electronic states. More precisely,

$$\begin{aligned} B'_v &= B'_e - \alpha'_e (v' + \tfrac{1}{2}), \\ B''_v &= B''_e - \alpha''_e (v'' + \tfrac{1}{2}). \end{aligned} \qquad (72)$$

Whereas the rotational constants of the upper and lower states in the rotation-vibration spectrum differ only in having different values for v' and v'', it is now possible, since $B'_e \neq B''_e$ and $\alpha'_e \neq \alpha''_e$, that $B'_v > B''_v$ even though $v' > v''$.

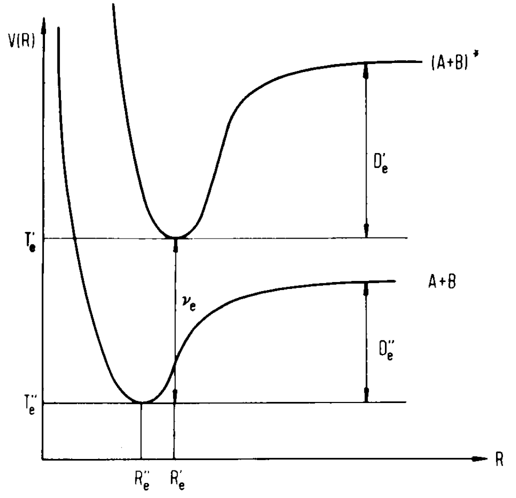

Fig. 21.

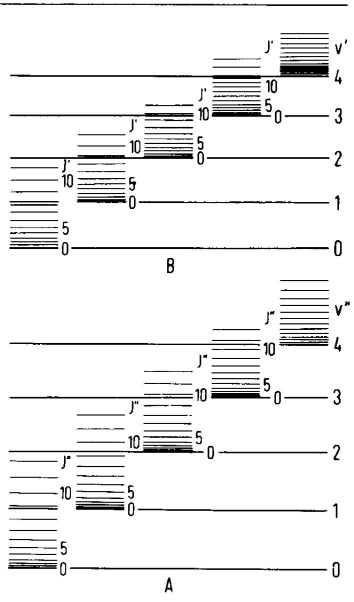

Fig. 22.

Fig. 21. Potential energy curves and characteristic quantities for an electronic transition in a diatomic molecule AB. T_e = electronic terms, D_e = dissociation energies, R_e = equilibrium distances, R = internuclear distances.

Fig. 22. Rotational and vibrational terms for a transition between two electronic states A and B.

5.1. Vibrational structure of electronic transitions

The totality of the lines in an electronic transition is built on a very complicated pattern. It is therefore convenient to examine the coarse structure first, taking into account only the rotationless states; this means that each band is replaced by its zero line. According to equations (47) and (70), this vibrational coarse structure is described by

$$\nu = \nu_e + \left[\omega'_e\left(v' + \frac{1}{2}\right) - \omega'_e x'_e\left(v' + \frac{1}{2}\right)^2\right] - \left[\omega''_e\left(v'' + \frac{1}{2}\right) - \omega''_e x''_e\left(v'' + \frac{1}{2}\right)^2\right] \tag{73}$$

$$= \nu_{oo} + [\omega'_o v' - \omega'_o x'_o v'^2] - [\omega''_o v'' - \omega''_o x''_o v''^2].$$

where

$$\nu_{oo} = \nu_e + \left(\frac{\omega'_e}{2} - \frac{\omega'_e x'_e}{4}\right) - \left(\frac{\omega''_e}{2} - \frac{\omega''_e x''_e}{4}\right) \tag{74}$$

is the wave number of the 0,0 transition (v' = v'' = 0). Equation (73), however gives the wave number of the v', v'' transition. The second anharmonic corrections $\omega_e y_e$ have been disregarded.

The wave numbers of the zero lines of the individual bands can generally be found only by rotational analysis. If no such analysis has been carried out, the band heads are used for a preliminary vibrational analysis.

The purpose of the vibrational analysis is to arrange all the observed bands (represented by their zero gaps or by their heads) into a scheme from which the v' and v'' values for each band can be found. The scheme of band heads (also called Deslandres table) for the emission spectrum of PN at 2500 Å is shown in Table 4.

Table 4. Band head scheme of the emission spectrum of PN at 2500 Å (after Herzberg[2]).

v' \ v''	0	Diff.	1	Diff.	2	Diff.	3	Diff.	4
0	39698.8	1322.3	38376.5	1307.8	37068.7				
Diff.	1087.4		1090.7		1086.8				
1	40786.2	1319.0	39467.2	1311.7	38155.5	1294.2	36861.3		
Diff.	1072.9		1069.0				1071.6		
2	41859.1	1322.9	40536.2				37932.9	1280.4	36652.5
Diff.			1061.2						1060.0
3			41597.4	1309.1	40288.3				37712.5
Diff.					1042.9				1043.9
4					41331.2				38756.4

For the rows of this scheme v' is constant and v'' increases from left to right, while in the columns v'' is constant and v' increases from top to bottom.

The bands in a given row form a v'' progression, the wave numbers of which, according to equation (73), are given by

$$\nu = \nu_{v'} - [\omega''_o v'' - \omega''_o x''_o v''^2]$$

where (75a)

$$\nu_{v'} = \nu_{oo} + \omega'_o v' - \omega'_o x'_o v'^2$$

In these v'' progressions, the bands proceed toward longer wave lengths (lower frequencies) with increasing v'', and the distance between bands decreases slightly.

The columns in Table 4 are called v' progressions, for which v'' is constant. In analogy to equation (75a), it is found from equation (73) that

$$\nu = \nu_{v''} + [\omega'_o v' - \omega'_o x'_o v'^2]$$

where (75b)

$$\nu_{v''} = \nu_{oo} - \omega''_o v'' + \omega''_o x''_o v''^2$$

In the v' progressions the bands proceed towards shorter wave lengths (higher frequencies) with increasing v', and the distance between bands again decreases slightly.

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In favourable cases, progressions of these types can be found fairly readily in the spectrum. The v'' progressions for the emission spectrum of N_2 are marked on horizontal lines in the lower part of Fig. 6, although in this case the sequences with $\Delta v = v' - v'' =$ constant are more obvious.

The correct arrangement of all the bands in a band-head scheme can generally be found only by trial and error. A useful check for the correctness of such an assignment is that the differences between the numbers in two adjacent columns must be all the same; this is also the case for the differences between two successive rows*). These differences are also shown in Table 4. Thus, for the first and second columns of the band head scheme, according to equation (75b), we have

$$\nu = \nu_{0''} + [\omega'_o v' - \omega'_o x'_o v'^2], \tag{75c}$$

$$\nu = \nu_{1''} + [\omega'_o v' - \omega'_o x'_o v'^2], \tag{75d}$$

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*) Stricly only for the zero gaps, but to a good approximation also for the band heads.

i.e. for the difference, irrespective of v',

$$\Delta\nu = \nu_{0''} - \nu_{1''} = \nu_{oo} - (\nu_{oo} - \omega''_o + \omega''_o x''_o)$$

$$= \omega''_o - \omega''_o x''_o = \Delta G''_{1/2}, \tag{75e}$$

When a correct band head scheme has been established in this way, it generally gives only the relative numbering in v' and v''; so the true values of v' and v'' may differ by an additive constant from the values assumed in the scheme; and to determine the absolute numbering, it is necessary to consider the intensity distribution over the various bands and the temperature-dependence of this distribution (see Chapter 6).

If the same band system can be obtained for two isotopic molecules, the absolute numbering can be determined with the aid of the vibrational isotope effect. It was mentioned in Section 3.2 that the equilibrium conformations of two isotopic molecules agree to a very close approximation. More precisely, two such molecules have the same potential energy function V(R). In such a case not only are the positions of the potential energy minima (which determine the equilibrium configuration) identical, but the curvature of the potential energy curves at the minima (which determine the force constants according to equation (25)), are also the same. Thus two isotopic molecules, e.g. $^{10}B^{16}O$ and $^{11}B^{16}O$ have the same force constant and differ only in their reduced masses. From equations (29a) and (29b), therefore, the ratio of their vibration frequencies is

$$\frac{\nu'_i}{\nu'} = \frac{\omega_i}{\omega} = \sqrt{\frac{M}{M_i}} = \rho < 1. \tag{76}$$

The heavier isotope (index i) thus has the lower vibrational frequency. The wave number

$$\nu_e = [V'(R'_e) - V''(R''_e)]/hc$$

is also the same in the two cases. In the harmonic-oscillator approximation, therefore, the wave numbers of corresponding bands of two isotopic molecules are given by

$$\nu = \nu_e + \omega'_e\left(v' + \frac{1}{2}\right) - \omega''_e\left(v'' + \frac{1}{2}\right) \tag{76a}$$

$$\nu_i = \nu_e + \rho\omega'_e\left(v' + \frac{1}{2}\right) - \rho\omega''_e\left(v'' + \frac{1}{2}\right), \tag{76b}$$

i.e.

$$\frac{\nu_i - \nu_e}{\nu - \nu_e} = \rho. \tag{77}$$

This equation is also valid to a good approximation when the anharmonic terms in equation (73) are taken into account. Thus the whole band system of the heavier isotope is contracted by a factor ρ in relation to the whole band system of the lighter isotope, when both are measured from the wave number of the pure electronic transition. This is shown in Fig. 23, where the position of the pure electronic transition, which does not itself appear as a band in the spectrum, can be found extrapolation, and corresponding bands of the two isotopes can thus be found. The absolute numbering can the be determined from equations (76a) and (76b).

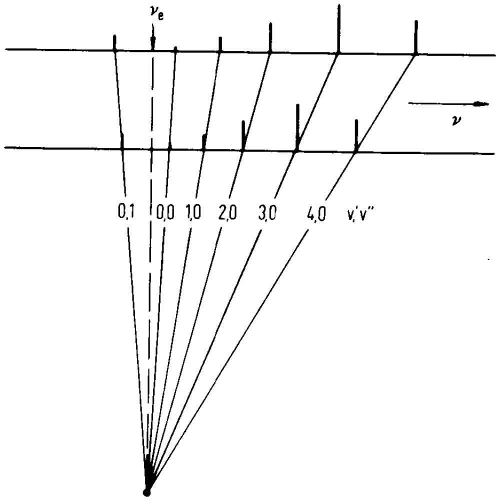

Fig. 23. Schematic representation of the vibrational isotope effect for two isotopic diatomic molecules. Top: band system of the lighter molecule; bottom: band system of the heavier molecule. ν_e = position of the pure electronic transition (extrapolated). The figures give the (v',v'') numbering of the bands.

However, this procedure is based on the assumption that the zero lines of the various bands are used for the wave numbers in equation (77). If the wave numbers of the band heads are used instead, a rotational isotope effect may be superimposed on the vibrational isotope effect (cf. Section 5.2), with the result that the evaluation becomes more difficult.

The procedure followed in practice is therefore:

1. Relative vibrational analysis.
2. Rotational analysis (see Section 5.2) to determine the wave numbers of the zero lines of all the bands and the rotational constants B'_v and B''_v.
3. Use of the vibrational isotope effect to determine the absolute numbering of the vibrational structure of the spectrum. This step may be omitted if the numbering is obtainable from the spectrum itself.
4. Determination of the vibrational constants ω'_e, ω''_e, $\omega'_e x'_e$, $\omega''_e x''_e$ from the constant differences in the zero gap-scheme [cf. equation (75e)].

5.2. Rotational structure of electronic transitions

We now consider the rotational lines of a given band, i.e. of a given v', v'' transition. The sum of the first two terms in equation (70) is then a constant, so that

$$\nu = (\nu_e + \nu_{vibr}) + \nu_{rot} = \nu_o + F'(J') - F''(J''). \tag{78}$$

As in the rotation-vibration spectrum, an R branch is obtained for $\Delta J = J' - J'' = +1$, with the wave numbers

$$\nu = R(J) = \nu_o + F'(J+1) - F''(J) = \nu_o + 2B'_v + (3B'_v - B''_v)J$$
$$+ (B'_v - B''_v)J^2, \quad J = J'' = 0, 1, 2, \ldots \tag{79a}$$

and a P branch for $\Delta J = J' - J'' = -1$:

$$\nu = P(J) = \nu_o + F'(J-1) - F''(J) = \nu_o - (B'_v + B''_v)J$$
$$+ (B'_v - B''_v)J^2, \quad J = J'' = 1, 2, \ldots \tag{79b}$$

For certain electronic transitions (cf. Chapter 7), there is also a Q branch with $\Delta J = J' - J'' = 0$, for which

$$\nu = Q(J) = \nu_o + F'(J) - F''(J) = \nu_o + (B'_v - B''_v)J + (B'_v - B''_v)J^2,$$
$$J = J'' = 0, 1, 2, \ldots \tag{79c}$$

As before, the P and R branches can be represented by a single formula

$$\nu = \nu_o + (B'_v + B''_v)m + (B'_v - B''_v)m^2, \tag{80}$$

where the quantum number m is given by

$$m = \begin{cases} J+1 \\ -J \end{cases} \text{for the} \begin{cases} R- \\ P- \end{cases} \text{branch} \qquad (81)$$

It is useful to compare the equations of this section for the rotational structure of electronic transitions with the equations (48) to (51) for the rotation-vibration spectrum. They are very similar, but differ in the following respects:

1. In equation (48), the quantity ν_0 is the wave number ν_{vibr} of the pure vibrational transition around which the band is built up. In the electronic transitions, on the other hand, according to equation (78), ν_0 is the wave number of the "vibronic" transition, i.e. the sum of the pure electronic transition ν_e and the vibrational transition ν_{vibr}. The extra additive term ν_e displaces the band from the IR into the visible region.
2. For certain electronic transitions a Q branch can also occur. The electronic transitions for which this is the case are described in Chapter 7.
3. In the rotation-vibration spectrum, the constants occurring in the term formulae belong to the same electronic state, namely the ground state of the molecule. The vibrational constants for the upper and lower states of the transition are identical, and the rotational constants in the upper and lower states differ only in their slight dependence on v [cf. equation (46)]. In the electronic transitions, on the other hand, the vibrational constants of the upper and lower states belong to two different electronic states and may therefore differ appreciably. The rotational constants of the upper and lower states can now differ widely owing to differences in the values of B_e and a_e in the two states; in particular, $B'_v > B''_v$ is possible as well as $B'_v < B''_v$. This leads to the formation of band heads in one of the three rotational branches.

Equation (80) is a second-order polynomial in the quantum number m. If m is regarded for the present as a continuously variable quantity, and if the first derivative $d\nu/dm$ is set equal to zero, then

$$m_{head} = - \frac{B'_v + B''_v}{2\,(B'_v - B''_v)} \qquad (82a)$$

$$\nu_{head} - \nu_0 = - \frac{(B'_v + B''_v)^2}{4\,(B'_v - B''_v)} \,. \qquad (82b)$$

Equation (82a) will not generally give an integral value for m. The true head is then at the nearest integral value of m. A plot of equation (80) taking into account equation (81) (J is plotted against ν) gives two parabolic sections for the P and R branches.

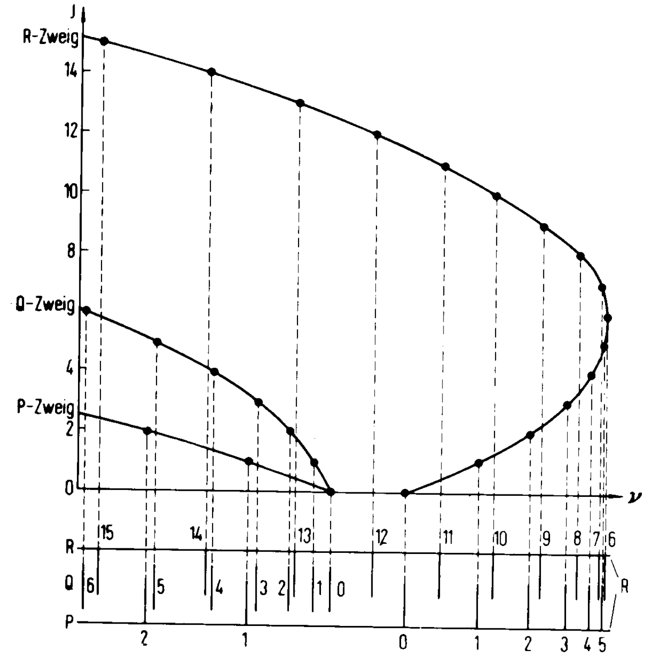

Fig. 24. Fortrat parabolas for a - Π-Σ transition.

This is shown in Fig. 24 for a Π-Σ electronic transition. The Q branch – if occurs – can also be plotted in the same diagram. The resulting Fortrat parabolas are displayed in Figs. 25 and 26 for the two cases (a) $B'_v > B''_v$ and (b) $B'_v < B''_v$.

According to equation (82a), m_{head} is negative in case (a), i.e. the head lies in the P branch, and according to equation (82b) on the long-wavelength side of ν_0. Such a band is described as being shaded towards the violet.

In case (b), m_{head} is positive, i.e. the head lies in the R branch, and according to equation (82b) on the short-wave side of ν_0. Such a band is said to be shaded towards the red.

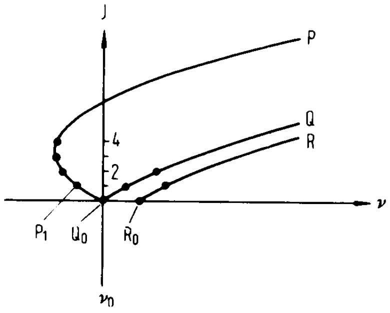

Fig. 25

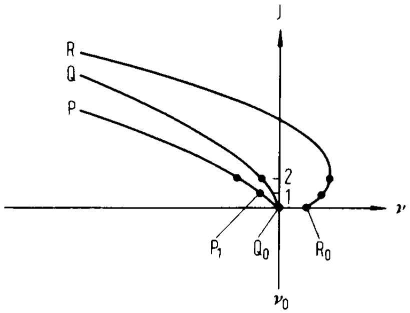

Fig. 26

Fig. 25. Fortrat parabolas (schematic) for $B'_v > B''_v$. J = rotational quantum number.
Fig. 26. Fortrat parabolas (schematic) for $B'_v < B''_v$. J = rotational quantum number.

A true band head cannot occur in the Q branch, since differentiation of equation (79c) with respect to J leads to the condition

$$(B'_v - B''_v)(1 + 2J) = 0$$

and the resulting values $J = -1/2$ does not occur in the Q branch. However, if $B'_v \approx B''_v$, then $B'_v - B''_v$ is small, and the Q branch starts almost perpendicular to the frequency axis, so giving the appearance of a Q head. Consequently, bands with Q branches often appear to be double-headed*). It can also be seen from equation (82b) that the distance of the head from the zero line increases as the denominator $B'_v - B''_v$ decreases. Thus the shading of the bands of an electronic transition can provide the first indication of the relative positions of the potential energy curves of the two electronic states involved. Since $B_e \gg a_e$, the sign of $B'_e - B''_e$ is generally the same as that of $B'_v - B''_v$. Thus for a band system shaded towards the violet, $B'_e > B''_e$ and, since $B_e \sim 1/R_e^2$, $R'_e < R''_e$, in this case, therefore, the minimum of the upper curve occurs at smaller R values than that of the lower curve. The situation is precisely the reverse for bands shaded towards the red. If however $B'_e \approx B''_e$, the shading may not be the same for all the bands in the system, i.e. it may be reversed within the system. This happens when the B_v curves have the form shown in Fig. 27.

Rotational analysis of the bands of a band system (electronic transition) could also be carried out by the procedure described in Section 4.2 for the rotation-vibration

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*) This is the case in the AlH band of Fig. 7.

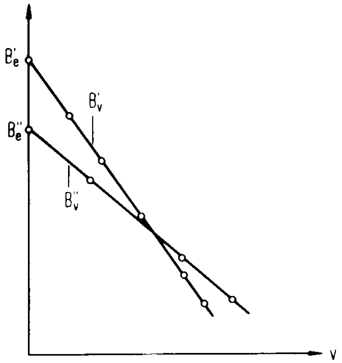

Fig. 27. Curves of B'_v and B''_v for band systems in which the shading reverses.

spectrum, i.e. by matching the wave numbers of all the lines with the theoretical expressions [equations (79a) to (79c)]. In practice, however, a more systematic analysis using combination differences is preferred, since that gives more accurate values for the rotational constants. As can be seen directly from Fig. 28, the combination difference

$$\Delta_2 F'(J) = R(J) - P(J) = F'_v(J+1) - F'_v(J-1) = 4B'_v\left(J + \frac{1}{2}\right) \quad (83)$$

between two rotational lines having the same lower level J" = J is equal to the distance between the rotational terms J' = J + 1 and J' = J - 1 in the upper electronic state. For a given J, this difference has the same value for different lower vibrational states, as is illustrated by the left-hand and right-hand sides of Fig. 28. Note that this is true even when the rotational lines can no longer be represented by equations (79a) to (79c), i.e. when the D terms in the rotational terms are no longer negligible or when the formulae are invalid for any other reason (rotational perturbations). Only the expression on the extreme right of equation (83) assumes the validity of equations (79a) to (79c).

The distances between the rotational levels J" = J + 1 and J" = J − 1 in the lower state can be obtained from the combination difference

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = F''_v(J+1) - F''_v(J-1) = 4B''_v\left(J + \frac{1}{2}\right) \quad (84)$$

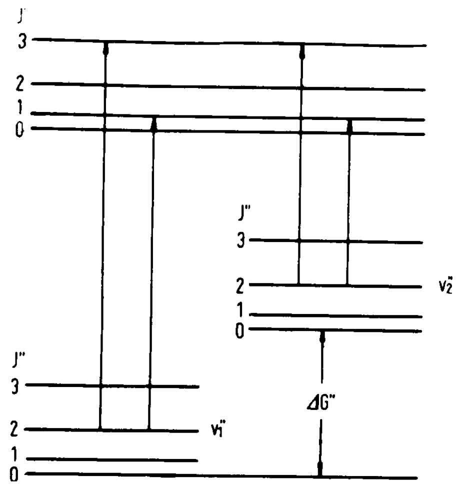

Fig. 28. Diagram illustrating the combination differences of equation (83). J = rotational quantum number, v = vibrational quantum number, ΔG" = distance between two vibrational levels v_1'' and v_2'' in the lower electronic state.

The two series of rotational terms F'(J') and F" (J") can be separated from one another by the use of the combination differences (83) and (84). A plot of $\Delta_2 F$ against J then gives a straight line of slope $4B_v$, passing through the point (0, -1/2). This graphical method averages out experimental (non-systematic) errors in the measurement of the wave numbers. Moreover, the rotational analyses of various v', v" bands of the same electronic transition can be fitted together. Thus for two bands having the same v', but different v" the combination difference $\Delta_2 F'$ must be the same, as has already been mentioned. For further details, such as the inclusion of the D terms, the combination differences for bands having Q branches, and the determination of the zero lines from the combination differences, the reader is referred to reference²⁾:

Before a rotational analysis using combination differences can be carried out, however, it is essential that the correct J numbering should be known. If the band is not completely resolved, if the zero gap is not clearly recognizable, or if rotational lines of different branches approximately coincide, the correct numbering must be deduced from those parts of the band that are well resolved. Another method for the determination of the absolute J numbering makes use of the rotational isotope effect. From the definition (8c) of the rotational constant B_e, it follows by equation

(76) that

$$B_e^i / B_e = M/M_i = \rho^2 \qquad (85)$$

It can also be shown that $\alpha_e^i = \rho^3 \alpha_e$ and $D_e^i = \rho^4 D_e$. A little calculation shows that to a good approximation

$$\nu_{rot}^i / \nu_{rot} = \rho^2 . \qquad (86)$$

Thus all the rotational lines of the heavy isotope are contracted by a factor of ρ^2 relative to the corresponding lines of the lighter isotope. It should be noted, however, that according to equation (78), the wave numbers ν_{rot} of the rotational lines in both cases must be measured from the corresponding zero lines ν_0, which are different for the two isotopes because of the vibrational isotope effect (cf. Section 5.1).

5.3. Potential energy curves of diatomic molecules

We were introduced to the concept of a potential energy curve in section 4.1, where some mention was also made of the different types of potential energy curves and their general form. In the present section we shall deal rather more fully with the potential energy curves of diatomic molecules. The general course of the potential energy curve for a stable electronic state is shown in Fig. 13. The curve has a minimum at $R = R_e$. It rises steeply for smaller R values, and - because of the last term in equation (24)-it tends towards + ∞ as $R \longrightarrow 0$. Thus within this range the two atoms of the molecule repel each other. The curve also rises when the R values exceed R_e, but the rise in this case is less rapid and the curve tends towards a finite value for $R \longrightarrow \infty$, the tangent then being horizontal; in this range the atoms attract each other. The difference

$$D_e = V(\infty) - V(R_e)$$

is the dissociation energy of the molecule, referred to the potential energy minimum.

However the energy required for the reaction

$$AB \longrightarrow A + B$$

in the gas phase is given by the distance D_o from the lowest level v = 0 to the dissociation limit. It is clear that

$$D_o = D_e - G(0),$$

where the zero-point energy G(0) is given by equation (41) (cf. Fig. 29).

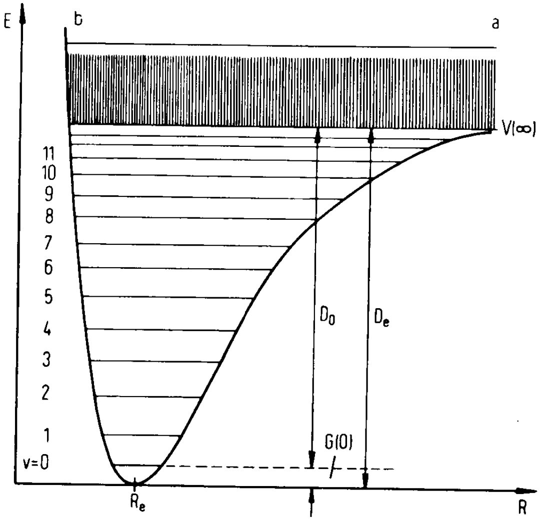

Fig. 29. Potential energy curve with vibrational levels, the dissociation limit $V\langle\infty\rangle$, and the subsequent continuum. R = internuclear distance, R_e = equilibrium distance, v = vibrational quantum number, D_0 and D_e = dissociation energies, G(0) = zero-point energy.

In principle, the Schrödinger equation (31) can also be solved for this potential energy function V(R) instead of the harmonic approximation of equation (25). The result is again a series of discrete vibrational levels E_v, which converge to the dissociation limit V(∞). Above the dissociation limit there is no discrete vibrational energy; the motion of the two atoms relative to one another is no longer quantized, and all energies above V(∞) are also quantum-mechanically possible. A motion of this nature, as illustrated by the horizontal line ab in Fig. 29, corresponds to a collision between the two atoms. Starting from the point a in the diagram, the atoms approach each other until they reach the classical turning point (point b in the diagram), where they come momentarily to rest, only to move apart again along the line from b 70a. Whether the number of discrete vibrational levels in the potential energy trough of Fig. 29 is finite or infinite depends on the behaviour of V (R) at large values of R. If the molecule AB dissociates into neutral atoms as R approaches ∞, the potential energy curve approaches its dissociation limit very rapidly, actually exponentially. In this case (which is by far the more frequent), only a finite number of vibrational levels can be contained in the potential energy trough.

If on the other hand the molecule dissociates into ions in accordance with

$$AB \longrightarrow A^+ + B^- \quad \text{or} \quad A^- + B^+$$

the curve approaches the dissociation limit much more slowly, the attraction being proportional to 1/R, corresponding to the Coulomb attraction of the ionised atoms of opposite charges. In this case there is an infinite number of discrete vibrational levels in the potential energy trough*). These converge on the dissociation limit which is now a true accumulation point.

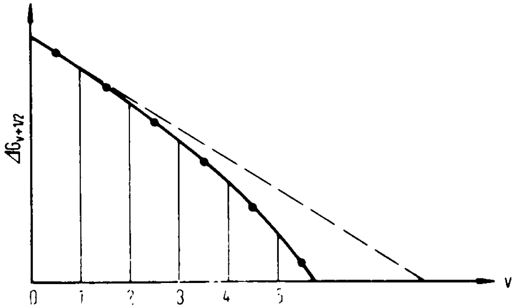

Fig. 30. General behaviour of $\Delta G_{v+\frac{1}{2}}$ (distance between adjacent vibrational levels) for the dissociation of a diatomic molecule into neutral atoms. v = vibrational quantum number.

It is easy to decide which of these two cases occurs by plotting the experimental differences $\Delta G_{v+\frac{1}{2}}$ of equation (44a) against $(v + \frac{1}{2})$. This gives the curves of Figs. 30 and 31. The broken lines show the behaviour of $\Delta G_v + \frac{1}{2}$ for the case in which this quantity can be described with sufficient accuracy for all values of v by

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*) At large values of R, van der Waals forces are superimposed on these valency forces, but the former vary as $1/R^6$; so they do not affect the above classification, since the change from an infinite to a finite number of vibrational levels occurs for large R if $V(R) \approx 1/R^2$.

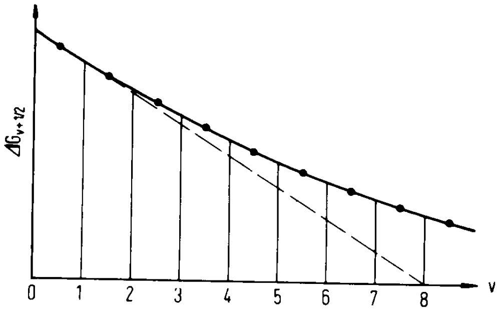

Fig. 31. General behaviour of $\Delta G_{v+\frac{1}{2}}$ for the dissociation of a diatomic molecule into ions.

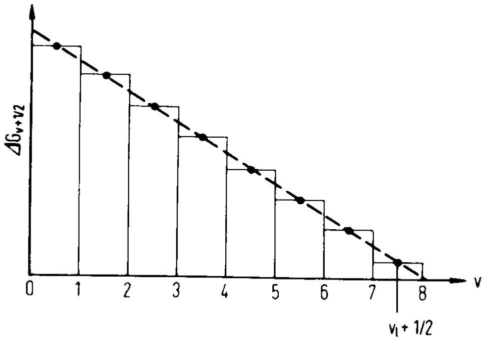

Fig. 32. Graphic representation of the Birge-Sponer extrapolation for dissociation energies. v_l = last vibrational quantum number.

equation (44a) (cf. Fig. 32). When this expression is equated to zero, the intersection of the straight line with the axis is found to be

$$v_l = \frac{\omega_o}{2\omega_o x_o} - \frac{1}{2},$$

where v_l is the last v value before the dissociation limit.

The dissociation energy D_o, referred to the lowest vibrational level v = 0 (cf. Fig. 29), is then obviously

$$D_o = \sum_{v=0}^{v_l} \Delta G_v + \frac{1}{2}.$$

This quantity is equal to the area under the step-curve of Fig. 32, and also equal to the area under the broken line. The area under the broken line is

$$D_o = \frac{1}{2} \cdot \omega_o \cdot \left(v_l + \frac{1}{2}\right) = \frac{\omega_o^2}{4\omega_o x_o}. \qquad (87)$$

Since the curves in Figs. 30 and 31 deviate downward and upward, respectively, from this line, equation (87) gives only an approximate value for the dissociation energy in these cases, namely too high a value in the first case and too low a value in the second. This linear extrapolation is known as the Birge-Sponer extrapolation.

More accurate values for the dissociation energy D_o are obtained if the vibrational distances $\Delta G_v + \frac{1}{2}$ are known up to the dissocitation limit. In this case the continuous curves of Figs. 30 and 31 are used instead of the Birge-Sponer line. The area under these curves then gives a good approximation to the dissociation energy, as can be shown by a method similar to that used in the case of the straight line. To obtain the dissociation energy D_e referred to the minimum of the potential energy curve, the zero-point energy of equation (41) must be added to D_o (see Fig. 29). Determination of dissociation energies has been discussed in detail by Gaydon[6].

The procedure just described for determination of the dissociation energy involves only quantities that can be determined experimentally, namely, the vibrational spacings $\Delta G_{v+\frac{1}{2}}$, and does not require prior knowledge of the true potential function V(R). However it must be clearly understood that there is strictly speaking no such thing as an experimentally determinable potential energy function. What can be measured is merely the distances $\Delta G_{v+\frac{1}{2}}$ between adjacent vibrational levels. Even if these are accurately known right up to the dissociation limit, they do not determine the potential energy curve V(R) uniquely, i.e. there are several (generally an infinite number) of potential functions for which the eigenvalues of the vibrational Schrödinger equation are identical.

If the experimental differences between rotational levels are used as well as the vibrational distances, an "experimental" potential energy curve can be found by a method known as the RKR (Rydberg, Klein, and Rees) method. This method makes use of the semiclassical or WBK approximation to a solution of the Schrödinger equation for the vibrational and rotational motion of a diatomic molecule. Many "experimental" potential energy curves have been calculated by this method in the last few years. Unfortunately the accuracy of this method has not yet been investigated throughly, so that it is not known how closely these potential energy thoro functions approximate to the true potential energy functions V(R). Owing to this uncertainty, it is wiser not to compare the quantum-mechanical calculations with experimental values at the level of potential functions V(R); it is better to calculate theoretical vibrational levels from theoretically calculated potential energy functions, and to use these vibrational levels to compare theory with experiment.

Since thus no closed expression for the true potential functions V(R) is known, one has to use empirical relationships that exhibit qualitatively the correct behaviour for $R \longrightarrow \infty$, $R \approx R_e$, and $R \longrightarrow 0$ and yet still permit free choice of parameters. These parameters are then selected for a given electronic state in such a way as to give the best possible agreement of the experimental vibrational constants ω_e, $\omega_e x_e$, D_e, R_e, etc. with those found from the empirical relationship.

The best-known empirical relationship of this type is the Morse potential

$$V(R) = D_e \left[1 - e^{-\beta(R - R_e)}\right]^2$$

$$\beta = \left(\frac{2\pi^2 cM}{D_e h}\right)^{1/2} \cdot \omega_e = 1.2177 \times 10^7 \, \omega_e \sqrt{\frac{M_a}{D_e}} \quad (\mathrm{cm}^{-1})$$

which contains three parameters (M_a = reduced mass in atomic weight units). For example, D_e, R_e and ω_e may be matched to the experimental values, but the anharmonicity correction $\omega_e x_e$ is then fixed by

$$\omega_e x_e = \frac{h}{8\pi^2 cM} \cdot \beta^2$$

and will usually not agree with the experimental value. To get the best possible representation of the experimental vibrational terms, it is therefore better to match the parameters R_e, ω_e, and $\omega_e x_e$; the value of D_e is then fixed, but will usually differ from the experimental value. Many other empirical relationships have therefore been discussed in the literature, some containing more than three parameters which permit better matching with the experimental data[2,6]. However, if a formula is to be established relating the parameters in V(R) to the vibrational constants the Schrödinger equation must have a closed solution for this potential and this greatly restricts the freedom of choice of empirical V (R).

6. Intensities and Selection Rules

6.1. General

The intensity of a given transition is determined by the total transition moment

$$\mathbf{R} = \int \psi' \, \mathbf{M} \, \psi'' \, d\tau. \tag{88}$$

In this expression, ψ' and ψ'' are the total wave functions of the upper and the lower state between which the transition takes place. For dipole transitions, which are by far the most common transitions, **M** is the operator of the dipole-moment vector, which consists of an electronic and a nuclear component, as follows:

$$\mathbf{M} = \mathbf{M}^e + \mathbf{M}^k \tag{89}$$

According to the Born-Oppenheimer approximation (see p. 14), the ψ-functions can be written in the product form (5a)

$$\psi = \psi_{el} \cdot (\psi_v \cdot \psi_{rot}) = \psi_{el} \cdot \psi_k \tag{90}$$

Insertion of (89) and (90) into equation (88) then gives

$$\mathbf{R} = \int \psi_k' \psi_k'' d\tau_k \int \psi_{el}' \mathbf{M}^e \psi_{el}'' d\tau_{el} + \int \psi_k' \mathbf{M}^k \psi_k'' d\tau_k \int \psi_{el}' \psi_{el}'' d\tau_{el} \tag{91}$$

a) For rotational-vibrational transitions, the electronic state remains unchanged, so that $\psi_{el}' = \psi_{el}'' = \psi_{el}$. The last integral in equation (91) then becomes the normalization integral for the single electronic function ψ_{el}, the value of which, by analogy with equation (32), is unity. The transition moment of equation (19) then takes the form

$$\mathbf{R} = \int \psi_k' \psi_k'' \left(\mathbf{M}^k + \int |\psi_{el}|^2 \mathbf{M}^e d\tau_{el}\right) d\tau_k = \int \psi_k' \mathbf{M}(R) \psi_k'' d\tau_k. \tag{92}$$

Here **M**(R) is the vector of the dipole moment of the molecule in its electronic ground state, the dipole moment itself being the sum of a nuclear and an electronic component. The nuclear component is simply the dipole moment of the atomic nuclei a, which are regarded as point charges Z_a (nuclear charges); the electronic component is the dipole moment of the continuously distributed electron density for the ground state of the molecule. Both components depend on the relative positions of the nuclei, as is indicated in equation (92) by the argument R.

b) For electronic transitions, the last integral in equation (91) disappears because of the orthogonality of the wave functions ψ'_{el} and ψ''_{el} which are now different. Equation (91) therefore simplifies to

$$\mathbf{R} = \int \psi'_k \psi''_k \left| \int \psi'_{el} \mathbf{M}^e \psi''_{el} d\tau_{el} \right| d\tau_k = \int \psi'_k \mathbf{M}(R) \psi''_k d\tau_k . \tag{93}$$

In this equation, **M**(R) is the electronic transition moment, which is given by the inner integral in the first part of equation (93). This quantity again depends (via the wave functions) on the relative positions of the nuclei.

It can be seen that the total transition moment has the same form in both cases, namely, an integral over the product of the nuclear wave functions in the upper and the lower state and a moment vector **M**(R). The only difference is the explicit form of this vector. For rotational-vibrational transitions, it is the electric dipole moment of the molecule, while for electronic transitions it is the electronic transition moment. In both cases this moment has a fixed orientation with respect to the molecule-fixed axes x, y, z (z being the axis of the molecule), so that its space-fixed components have the form

$$M(R)_i = M(R) \cdot f_i, \quad i = X,Y,Z \tag{94}$$

Here M(R) is the magnitude of the moment, i.e. a scalar quantity. The second factor f_i depends on the orientation of the molecule-fixed axes with respect to the space-fixed axes. For example, if the moment lies along the axis of the molecule (only $\mathbf{M}(R)_z \neq 0$), the f_i in equation (94) are simply the direction cosines of the molecule-fixed z-axis with respect to the space-fixed axes x, y, z, i.e. in this case

$$f_X = \sin\vartheta \cdot \cos\varphi, \quad f_Y = \sin\vartheta \cdot \sin\varphi, \quad f_Z = \cos\vartheta, \tag{95}$$

where ϑ and φ are the polar angles of the figure axis. The rotational bands occurring in this case are called parallel bands. If the moment is perpendicular to the hold figure axis (perpendicular bands), other simple equations instead of equation (95). Finally, if the moment has components parallel to and perpendicular to the figure axis (hybrid bands), the total transition moment (93) can be represented by a linear combination of the simpler cases described above. [illegible]

In any case, (94) leads to a further simplification of equation (93) if the nuclear wave functions are resolved in accordance with equation (90) into their vibrational and rotational components

$$\mathbf{R}_i = \int \psi'_v M(R) \psi''_v d\tau_{vibr} \cdot \int \psi'_{rot} f_i \psi''_{rot} d\tau_{rot}, \quad i = X,Y,Z. \tag{96}$$

The components of the total transition moment are thus factorized into a vibronic component, which is independent of the index i, and a rotational component.

6.2. Selection rules for rotational and rotational-vibrational transitions

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To evaluate the vibrational component of equation (96), we expand the magnitude of the dipole moment as a function of the relative positions of the nuclei around the equilibrium positions. For diatomic molecules, in which the internuclear distance R is the only relative nuclear coordinate, this expansion has the form

$$M(R) = M(R_e) + \left(\frac{dM}{dR}\right)_e \cdot (R - R_e) + \ldots \tag{97}$$

Insertion of this expansion into the first factor of equation (96) gives:

$$M(R_e) \cdot \int \psi'_v \psi''_v d\tau_{vibr} + \left(\frac{dM}{dR}\right)_e \cdot \int \psi'_v (R - R_e) \psi''_v d\tau_{vibr} + \ldots \tag{98}$$

In pure rotational transitions, the molecule is in the vibrationless ground state in both the upper and the lower state i.e. $\psi'_v = \psi''_v = \psi_o$. The second integral in the expression (98) then is equal to zero on symmetry grounds, while the first becomes the normalization integral of the vibrational eigenfunction for v = 0, which has value 1 according to equation (32). Thus the only part of the expression (98) that remains is the factor $M(R_e)$, and the space-fixed components of the total transition moment (96) become

$$\mathbf{R}_i = M(R_e) \cdot \int \psi'_{rot} f_i \psi''_{rot} d\tau_{rot} + \ldots, \quad i = X,Y,Z. \tag{99}$$

The intensity of the transition is proportional to $R^2{}_X + R^2{}_Y + R^2{}_Z$ (cf. Section 6.5); thus if the transition is to have a finite intensity, at least one of the three components of equation (99) must be different from zero. This requires that

1. $M(R_e) \neq 0$. This is Part 1 of the selection rules of equations (9) and (9').

2. At least one of the integrals in equation (99) must be different from zero. This reflects Part 2 of the selection rules of equations (9) and (9'); however, we shall not deduce this explicitly, since we did not derive the rotational eigenfunctions in Chapter 3.

In later discussions we shall require the following distinction:

a) In linear, particularly diatomic, molecules the functions ψ_{rot} for the rotation spectrum depend only on the quantum numbers J and M_J [see equations (7a) and (7b)],and the procedure described above gives the selection rules

$$\Delta J = 0 \text{ and } \pm 1.$$

b) In symmetric top molecules, the functions ψ_{rot} for the rotation spectrum depend on the quantum number K as well as on J and M_J. If the permanent dipole moment lies along the figure axis ($\mu_a \neq 0, \mu_b = \mu_c = o$), calculation of the integral in equation (99), using the f_i of equation (95), gives the selection rules (9'a) to (9'c). S.23
(s.u. [illegible]34)

c) If the moment is perpendicular to the figure axis, one obtains instead

$$\Delta J = 0, \pm 1 \tag{9'd}$$

$$\Delta K = \pm 1 \tag{9'e}$$

This case is rare in pure rotation spectra, but is found in rotation-vibration spectra (see below).

d) For linear molecules, electronic transitions are governed by the selection rules (9'a) to (9'e), K being replaced by the component Λ of the orbital angular momentum of the electron along the internuclear axis.

The above derivation may be applied directly to polyatomic molecules, except that the second term in equation (97) has to be replaced by a sum of expressions of this form extending over all the normal coordinates, i.e.

$$M(Q_1, Q_2 \ldots) = M(R_e) + \sum_i Q_i \left(\frac{\partial M}{\partial Q_i}\right)_e + \ldots \tag{100}$$

It is immediately obvious that on insertion of equation (100) into equation (96), the only contribution is again from the first term, this contribution being the expression in equation (99).

In rotation-vibration spectra a vibrational transition takes place, so that the vibrational eigenfunctions ψ'_v and ψ''_v in the fisrt integral of the expression (98) belong to different vibrational states. However, they are then mutually orthogonal, and this integral disappears. The second remaining term in the expression (98), when inserted into equation (96), gives the total transition moment for rotational-vibrational transitions:

$$\mathbf{R}_i = \left(\frac{dM}{dR}\right)_e \cdot \int \psi'_v \cdot (R - R_e) \cdot \psi''_v d\tau_{vibr} \cdot \int \psi'_{rot} f_i \psi''_{rot} d\tau_{rot}, \tag{101}$$
$$i = X,Y,Z$$

Once again, at least one of the three components of equation (101) must be different from zero if the transition is to have a finite intensity, i.e. if it is to be "allowed". Transitions that fail to satisfy the selection rules, i.e. in which all three components of the total transition moment disappear, are known as forbidden transitions. Transitions of this type have vanishingly small intensities in the approximation used here. However such forbidden transitions can in fact occur in the spectrum but, owing to their forbidden character, their intensities are much lower than those of allowed transitions. For an allowed transition, therefore, the first factor in equation (101) must be different from zero, i.e.

$$\left(\frac{dM}{dR}\right)_e \neq 0 \text{ or } \left(\frac{\partial M}{\partial Q_i}\right)_e \neq 0, \tag{102}$$

when the expansion (100) is used instead of equation (97) for polyatomic molecules. This is the first part of the vibrational selection rules of equations (37) and (64). The second factor in equation (101), which is independent of i = X, Y, Z, must also be different from zero if the transition is to be allowed, i.e.

$$\int \psi'_v \cdot (R - R_e) \cdot \psi''_v d\tau_{vibr} \neq 0 \text{ or } \int \psi'_v \cdot Q''_i \cdot \psi''_v d\tau_{vibr} \neq 0. \tag{103}$$

As can be deduced by insertion of the explicit form of the vibrational wave functions of equation (34) or (63), this requirement gives the second part of the vibrational selection rules of equations (37) and (64). If the wave functions of the anharmonic oscillator are used in equation (103) instead of the functions of the harmonic oscillator, the integral is found to differ from zero also for changes in the vibrational quantum number Δv = 2,3 . . . ; however, its value generally decreases rapidly with increase in Δv. The ratio of the intensities of these overtones to that of the fundamental vibration Δv = 1 can also be calculated in this way. Finally, the requirement that the third factor in equation (101) should be different from zero for at least one value of i leads to the same rotational selection rules as were discussed above. Thus the rotational and vibrational selection rules are independent in the approximation used here.

6.3. Selection rules in the Raman effect

The derivation of the selection rules for Raman transitions is very similar to that given above for dipole transitions. However, it is more complicated than for the IR spectrum, since the vector of the electric dipole moment is replaced by the tensor of the electric polarizability α of the molecule. Nevertheless this tensor can be transformed to principal axes so that only its diagonal elements α_{ii}, $i = x, y, z$ are involved. Moreover, for linear and symmetric top molecules, the two diagonal elements perpendicular to the figure axis z are equal to one another ($\alpha_{xx} = \alpha_{yy} = \alpha_\perp$), but different from the diagonal element $\alpha_{zz} = \alpha_{||}$. In this case the vector of equation (94) is replaced by the 'vector'

$$\alpha_i(R) = \alpha_\perp + (\alpha_{||} - \alpha_\perp) \cdot f_i(\vartheta,\varphi)^2, \quad i = X,Y,Z, \tag{104}$$

where f_i is given by equation (95). Insertion of this expression into the integral on the extreme right of equation (93) gives

$$\begin{aligned}\mathbf{R}_i = {} & \int \psi'_v \alpha_\perp \psi''_v d\tau_{vibr} \cdot \int \psi'_{rot} \psi''_{rot} d\tau_{rot} + \\ & + \int \psi'_v (\alpha_{||} - \alpha_\perp) \psi''_v d\tau_{vibr} \cdot \int \psi'_{rot} f_i^2 \psi''_{rot} d\tau_{rot} \,.\end{aligned} \tag{105}$$

which is the equivalent of eq. (96).

For pure rotational Raman-transitions, $\psi'_v = \psi''_v = \psi_o$, and with the expansions

$$\begin{aligned}\alpha_\perp(R) &= \alpha_\perp(R_e) + \alpha'_\perp(R_e) \cdot (R - R_e) + \ldots \\ \alpha_{||}(R) &= \alpha_{||}(R_e) + \alpha'_{||}(R_e) \cdot (R - R_e) + \ldots\end{aligned} \tag{106}$$

equation (105) simplifies to

$$\begin{aligned}\mathbf{R}_i = {} & \alpha_\perp(R_e) \cdot \int \psi'_{rot} \psi''_{rot} d\tau_{rot} + \\ & + [\alpha_{||}(R_e) - \alpha_\perp(R_e)] \cdot \int \psi'_{rot} f_i^2 \psi''_{rot} d\tau_{rot} \,,\end{aligned} \tag{107}$$

which is the equivalent of equation (99). Owing to the orthogonality of the rotational wave functions, the first integral differs from zero only if J' = J''.

Calculation of the second integral with the f_i from equation (95) and the eigenfunctions of the rotator shows that this integral differs from zero only if $\Delta J = J' - J'' = \pm 2$; the first integral disappears on grounds of orthogonality. The expression in square brackets before the second integral must also be different from zero in this case; in other words, the polarizabilities parallel and perpendicular to the axis of the molecule must be different. These are exactly the selection rules given in equation (19) and used in the subsequent text for rotational Raman spectra. Molecules such as CH_4, i.e. spherical tops with three equal moments of inertia, are included here as special cases: in such cases all the polarizabilities must have the same value on symmetry grounds, i.e. $\alpha_{||} = \alpha_\perp$, so that the bracketted expression before the second integral in equation (107) vanishes; these molecules consequently have no rotational Raman spectrum, as was mentioned at the end of Section 3.3.

In the rotation-vibration Raman spectrum, ψ'_v and ψ''_v are different vibrational eigenfunctions, which are orthogonal to one an other. Consequently, insertion of the expansions (106) leads to the following simplification of equation (105).

$$\begin{aligned}\mathbf{R}_i = {} & \int \psi'_v \cdot (R - R_e) \cdot \psi''_v d\tau_{vibr} \cdot \Big\{ \alpha'_\perp(R_e) \cdot \int \psi'_{rot} \psi''_{rot} d\tau_{rot} + \\ & + [\alpha'_\perp(R_e) - \alpha'_{||}(R_e)] \cdot \int \psi'_{rot} f_i^2 \psi''_{rot} d\tau_{rot} \Big\} .\end{aligned} \tag{108}$$

This equation is the analogue of equation (101). Since equation (108) is the product of a vibrational and a rotational integral, the vibrational and rotational selection rules are again independent. Moreover, the rotational integrals occurring in (108) are the same as in equation (107). We therefore obtain the same rotational selection rules $\Delta J = 0, \pm 2$.

The vibrational integral is the same as in equation (101) for the IR spectrum. The vibrational selection rules are thus also the same, namely, $\Delta v = \pm 1$. Finally, the factors before the integrals must differ from zero, i.e. the polarizabilities parallel to and perpendicular to the figure axis must change during the vibration. We have thus deduced all the selection rules of equation (54).

6.4. Selection rules for electronic transitions

We again return to equation (96), in which the quantity M(R) in the first integral is now the magnitude of the electronic transition moment. The second integral over the rotational wave functions is the same as for the rotation-vibration spectrum; which was discussed in detail in Section 6.2. The selection rules for the rotational quantum number J are thus the same as for the rotation vibration spectrum, i.e.

$$\Delta J = 0, \pm 1$$

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for electronic transitions with $\Delta\Lambda = 0, \pm 1$. According to equation (9'c), the possibility $\Delta J = 0$ does not occur when $\Lambda' = \Lambda'' = 0$. This also defines the transitions for which there is a Q branch and those for which there is no Q branch. The significance of the electronic quantum number Λ will be explained more fully in Chapter 7, in connection with the classification of the electronic states of diatomic molecules.

In the first factor of equation (96), we expand the magnitude of the transition moment, as in equation (97), as a function of the positions of the nuclei around the equilibrium position of that electronic state from which the transition takes place. This is the lower state for absorption spectra and the upper state for emission spectra. We again obtain the expression (98).
We shall first assume that the quantity $M(R_e)$, i.e. the magnitude of the transition moment, is different from zero for the equilibrium conformation of the initial state. Electronic transitions for which this is true are said to be allowed. The electronic transitions that are allowed in this sense will be discussed in Chapter 7. Here we simply note that the requirement $M(R_e) \neq 0$ again leads to selection rules, these rules applying to the "electronic" quantum numbers; we already know one of these rules for the quantum number Λ.

These electronic selection rules define those transitions of a molecule that are allowed as pure electronic transitions. For polyatomic molecules, there are also transitions that are forbidden as pure electronic transitions $[M(R_e) = 0]$, but are allowed as a result of non-totally symmetric vibrations. The electronic transition moment for such transitions is $M(R_e) = 0$, but the "vibronic" transition moment [the first integral in equation (96)] is different from zero. Which electronic transitions these are and which normal vibrations make them allowed can be deduced from the symmetry of the molecule alone, i.e. by the methods of group theory[5].

This mechanism is not possible in diatomic molecules, since the only normal vibration is totally symmetric (cf. Section 4.4). However, there are other mechanisms by which certain electronically forbidden transitions can occur in the spectrum with low intensities[2].

For allowed electronic transitions, therefore, the first term in (98) is different from zero. If the expansion (97) for the magnitude of the transition moment is at all reasonable, the second term in the expression (98) must be small compared with the first, so it can be neglected to a good approximation. In the discussion of the integral in the first term of (98), it must be noted that the vibrational wave functions ψ'_v and ψ''_v now belong to different electronic states ψ'_{el} and ψ''_{el} and are therefore no longer orthogonal. Even in the harmonic oscillator approximation, they have different values of both R_e and a [see equation (34)].

6.5. Intensities

As has been mentioned, the intensity of a transition is proportional to the square of the total transition moment. From equation (96), therefore, we construct the quantity $R^2{}_X + R^2{}_Y + R^2{}_Z$ and simultaneously sum over the possible values of the magnetic quantum numbers M'_J and M''_J [cf. equation (7b)]. This is necessary because in the absence of an external magnetic field, states with different M_J are degenerate with one another. A somewhat lengthy derivation then gives

$$\sum_{M'_J} \sum_{M''_J} (R_X^2 + R_Y^2 + R_Z^2) = \left| \int \psi'_v M(R) \psi''_v d\tau_{vibr} \right|^2 \cdot S^{J'\Lambda''}_{J'\Lambda''}. \qquad (109)$$

The S factor (the Hönl-London factor) in this equation arises as follows. The procedure described above (summation over all M'_J and M''_J and over the three components X, Y, and Z) affects only the second factor of equation (96). When all these operations have been carried out, the square of this factor gives the S factor of equation (109), which naturally also depends on the quantum numbers J and Λ of the upper and lower states. Like the second factor of equation (96), from which it is formed, the S factor differs from zero only when the rotational selection rules [equations (9'a) to (9'e)] are satisfied.

The first factor in equation (96) is affected by this procedure only in that its square now appears in equation (109). This quantity also has a special name; it is known as the band strength $p_{v'v''}$, while the whole expression of equation (109) is known as the line strength.

According to the above discussion, the band strength for an allowed electronic transition may be expressed in the simple form

$$p_{v'v''} = | M(R_e) |^2 \cdot | \int \psi_v' \psi_v'' d\tau_v |^2 = | M(R_e) |^2 \cdot q_{v'v''} \qquad (110)$$

where the square of the vibrational integral, i.e. the quantity $q_{v'v''}$, is known as the Franck-Condon factor.

As the final result of these rather tedious transformations, we have obtained in equations (109) and (110) an expression for the square of the total transition moment, that can be interpreted very easily. This quantity is a product of three factors, corresponding to the three forms of motion in a molecule. The first factor, the square of the electronic transition moment in the equilibrium configuration, gives a measure of the total intensity of the electronic transition. This is distributed over the various v', v" transitions in accordance with the Franck-Condon factor. In each transition, i.e. in each band, the intensity is again distributed over the various rotational lines in accordance with the Hönl-London factor. If, for example, one is interested in the relative intensity distribution of the lines in a band, one need only examine the S-factor since the band strength $p_{v'v''}$ is constant for this one band. On the other hand, to examine the distribution of relative intensity over the various vibrational transitions, one need only consider the various Franck-Condon factors for these vibrational transitions.

The intensity of a rotational line depends, not only on the line strength [equation (109)], but also on the number of molecules in the initial state (N_J' or N_J'') and on the wave number ν of the transition. For emission spectra we have²⁾:

$$I_{em} = C_{em} \cdot N_J' \cdot \nu^4 \cdot q_{v'v''} \cdot S_{J''\Lambda''}^{J'\Lambda'} / (2J' + 1) \qquad (111a)$$

and correspondingly for absorption spectra

$$I_{abs} = C_{abs} \cdot N_J'' \cdot \nu \cdot q_{v'v''} \cdot S_{J''\Lambda''}^{J'\Lambda'} / (2J'' + 1). \qquad (111b)$$

Note the difference in the dependence on ν (fourth power for emission and first power for absorption). The constants C_{em} and C_{abs} contain a pure numerical factor and the square of the electronic transition moment in equation (110), which has a fixed value for the entire electronic transition.

6.5.1. Relative intensities in the rotational structure of electronic transitions

If the excitation conditions are such that the distribution of the molecules over the various rotational states of the initial state corresponds to thermal equilibrium, we have*⁾:

$$N_J' = \text{const} \cdot (2J' + 1) \exp. \left\{ - \frac{B_v' hc}{kT} J' (J' + 1) \right\} \qquad (112)$$

τ

fund. temp.

and similarly for N_J''. The first factor (2J' + 1) apprears here because of the degeneracy in M_J'. The exponential factor is the well-known Boltzmann distribution. To obtain an idea of how these occupancies depend on J', we imagine for the moment that J' is a continuous variable and plot N_J' against J'. The two factors in equation (112) change in opposite directions; while the first factor increases linearly with J', the second (exponential) factor decreases monotonically from unity. The overall result is shown qualitatively in Fig. 33; the populations first increase with J' to a maximum at

$$J'_{max} = \sqrt{\frac{kT}{2B_v'hc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T(°K)}{B_v'(cm^{-1})}} - \frac{1}{2}$$

and then fall off rapidly.

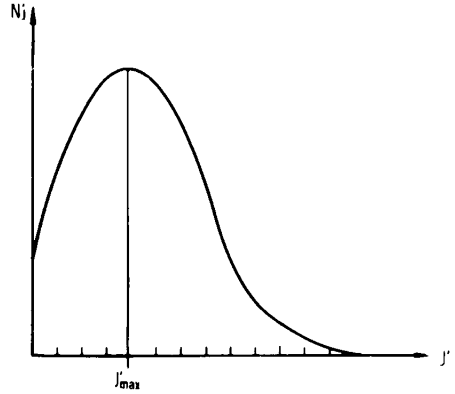

Fig. 33. Relative variation of the rotational occupation number N'_J at thermal equlibrium according to equation (112). J' = rotational quantum number, J'_{max} = value of J' at maximum (cf. text).

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*⁾ The constant is the reciprocal of the partition function and is therefore temperature-dependent. However, this is of no importance to the relative values of N'_J for a fixed T.

For Σ-Σ transitions (i.e. transitions in which Λ' = Λ" = 0, see Chapter 7), the S-factors are

$$S = \begin{cases} J'' \\ 0 \\ J''+1 \end{cases} = \frac{1}{2}\begin{cases} J'+J''+1 \\ 0 \\ J'+J''+1 \end{cases} \text{for the} \begin{cases} \text{P} \\ \text{Q-branch} \\ \text{R} \end{cases} \qquad (113)$$

The ratios

$$\frac{S}{2J'+1} = \frac{1}{2}\cdot\frac{J'+J''+1}{2J'+1} \quad\text{and}\quad \frac{S}{2J''+1} = \frac{1}{2}\cdot\frac{J'+J''+1}{2J''+1}$$

are practically constant (particularly for the higher J values) and equal to 1/2, so that the intensity of the lines in the P and R branches within a band is determined, to a close approximation, by the product $N'_J \cdot \nu^4$ for emission and by $N''_J \cdot \nu$ for absorption. According to equation (78) however, the wave number ν of the rotational lines is the sum of the very large ν_o and the very much smaller ν_{rot}. Within a band, therefore, ν may be replaced with reasonable accuracy by the constant quantity ν_o, so that the relative intensities of the lines in the P and R branches are ultimately given only by the quantities N'_J and N''_J (cf. Fig. 33). For the branch that does not form a head, this intensity distribution is evident merely on inspection of the spectrum. In the branch that forms the head, on the other hand, an intensity maximum is simulated by the convergence of the rotational lines in the vicinity of the head (cf. the photometric curve in Fig. 7).

For other electronic transitions with ΔΛ = 0 but Λ ≠ 0 or with ΔΛ = ±1, the intensity distributions in the P and R branches are essentially the same as in the Σ-Σ transitions, except that there is also a Q branch. The precise intensity distribution can naturally be deduced in all these cases from equation (111) and the corresponding expressions for the Hönl-London factors, but this will not be described in detail here (see reference[2]).

6.5.2. Relative intensities in the rotation-vibration spectrum

The distribution of the relative intensities of the lines in a rotation-vibration band is very similar to that in an electronic band. This is because the rotational component of equation (96) is the same in the two cases, as mentioned earlier. For linear molecules and parallel bands of symmetric top molecules, there is no Q branch, so that the intensity distribution is similar to that in the Σ-Σ electronic transitions described above. However, the wave number ν in equation (111) is now equal to $\nu_{vibr} + \nu_{rot}$ (the large term ν_e is missing), so that the variation of the wave number within a band is more extensive. On the whole, however, the distribution is that shown in Fig. 33: what does change markedly is the appearance of the band, because there is no longer a head as $B'_v \approx B''_v$.

6.5.3. Intensity distribution in the pure rotation spectrum

This can also be discussed on the basis of equation (111). In this case, however, the quantity $\nu = \nu_{rot}$ is subject very large variation, with the result that the intensity maximum is displaced ~~at~~ higher J values. For details, the reader is referred to the appropriate chapter of reference[2]. to

6.5.4. Relative intensities in the vibrational structure of electronic transitions

In accord with equation (11[illegible]), these intensities are determined by the Franck-Condon factor $q_{v'v''}$. Thus, in an electronic transition, the intensity of a band is high when this factor is large, or, as commonly described, when there is good overlap between the two vibrational wave functions. This is the wave-mechanical Franck-Condon principle. Good overlap occurs if both wave functions assume reasonably large values for the same argument; this is shown by the overlap integral

$$\sqrt{q_{v'v''}} = \int_{0}^{+\infty} \psi'_v(R) \cdot \psi''_v(R)\, dR \qquad (114)$$

the integrand of which depends on the product of the two wave functions.

This condition can also be demonstrated by insertion of the ψ_v of Fig. 15 into the potential energy curves of the two electronic states, as shown in Fig. 34. In the case shown in the diagram, the minima of the two potential curves do not occur at the same R ($R'_e > R''_e$). The overlap between the two wave functions ψ'_o and ψ''_o of the lowest vibrational level in each state is obviously very poor, since the value of one function is small when that of the other is large, so that their product is small for all values of R. The 0,0-transition in this case consequently has a very low intensity. The situation is most favourable for that vibrational finction ψ'_v (also shown) of the upper state, for which one of the two principal maxima (which are situated close to the classical turning points of the vibrational motion, cf. Fig. 15) exactly coincides with the single maximum of the vibrational function ψ''_0 of the lower state. The overlap is again small for vibrational levels of the upper state that lie appreciably above this optimum level, since the corresponding ψ'_v oscillates strongly in the range in which ψ''_0 has appreciable values, so that the integrand of equation (114) contains contributions with opposite signs, which largely cancel out.

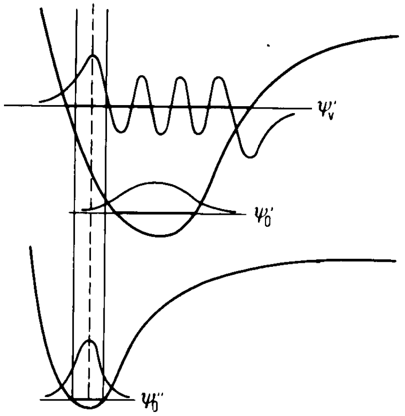

Fig. 34. Vibrational functions of the upper and the lower state in an electronic transition.

What we have deduced here on the basis of Fig. 34 for the most intense transition is the outcome of the classical Franck-Condon principle: The electron jump is so fast that the geometry of the molecule and the relative velocities of the nuclei do not change. It is easy to show that this requirement can be satisfied only if the transition takes place in the perpendicular direction from a turning point of the lower vibrational level to a turning point of the upper vibrational level. As our example shows, however, this classical Franck-Condon principle must be modified for transitions from the vibrationless level, the middle of the vibrationless level being used instead of the turning point. This follows naturally from the fact that ψ''_0 assumes its maximum value in the middle of the classically allowed range, where as the excited vibrational functions have their principal maxima close to the classical turning points (cf. Fig. 15). Apart from this modification, however, the classical Franck-Condon principle is very useful; it can be applied without difficulty also to electronic transitions of polyatomic molecules, for which an intuitive interpretation of the wave-mechanical Franck-Condon principle is no longer possible, since for polyatomic molecules the potential energy curves of diatomic molecules are replaced by potential surfaces in a higher-dimensional space.

The applicability of the classical Franck-Condon principle can be illustrated by the longest-wavelength absorption of the NH_2 radical. This molecule is bent in the ground state, but linear in the first excited state (see p. ~~213~~ ff.). In the electronic transition from the ground state, the molecule reaches the excited state in the bent form since according to the classical Franck-Condon principle the nuclear geometry should not change in an electronic transition ('perpendicular' transition).

However, since the equilibrium configuration of the molecule in the excited electronic state is linear, the only vibrational transitions that should appear in the absorption spectrum with appreciable intensities are those in which so many quanta of the bending vibration are excited in the upper electronic state that the molecule assumes the bent geometry of the ground state even in the excited electronic state. In fact, the absorption spectrum contains only transitions in which the bending vibration ω_3 (Fig. 19) is strongly excited (i.e. $v'_3 \gg 1$); the 0,0-transition does not appear in the spectrum at all (cf. Section 9.2).

The wave-mechanical Franck-Condon principle is preferable for a quantitative comparison of the relative intensities. The absorption intensities are given by equation (111b) on summation over all the rotational quantum numbers J" of the lower vibrational level v". This gives

$$I_{abs.} = const. \cdot N''_v \cdot \nu \cdot p_{v'v''}. \qquad (115)$$

The occupation number N''_v of the lower vibrational levels at thermal equilibrium, in analogy to equation (112), is given by*)

$$N''_v = const.\ exp. -\frac{\omega_e hc}{kT} \cdot v'' \qquad (116)$$

In contrast to the distribution over the various rotational states, the population

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*) The constant in this equation is the reciprocal of the partition function and thus temperature-dependent. However, this is of no importance to the relative values of N''_v for fixed T.

N''_v of the vibrational levels decreases monotonically with increasing quantum number v". The numerical value of the exponent is such that even the first vibrational level v" = 1 is practically unoccupied at room temperature (300 °K). Calculation from equation (116) shows that the ratio N_1/N_o for the H_2 molecule has a value of 2.16×10^{-9}, while the value for Cl_2 is 6.92×10^{-2}. Thus in the latter case, for every 100 molecules in the state v" = 0, there are 7 in the first excited vibrational state, and correspondingly fewer in the more highly excited vibrational states. At room temperature, therefore, the transition takes place mainly from the vibrationless level of the ground state to those levels of the excited state that lie 'perpendicularly' above the former in the sense of the classical Franck-Condon principle. However, the wave-mechanical Franck-Condon principle modifies this result, since all the vibrational levels of the upper state whose turning points fall in the vertical region of Fig. 34 bounded by the two turning points of ψ''_o occur with appreciable intensities. If the left-hand branch of the potential energy curve of the upper state is already very steil steep in this region, a large number of v' levels fall within this region. This leads to long v' progressions. On the other hand, if the two potential energy curves lie practically one above the other ($R'_e \approx R''_e$), the only band having an appreciable intensity is the 0,0-band, Finally, if the minimum of the upper state occurs at a smaller R value than that of the ground state, the right-hand turning point of the vibrational level of the upper state must be taken; however, this case is encountered only infrequently, since it requires that the bonding in the excited electronic state of such a molecule is stronger than that in the ground state.

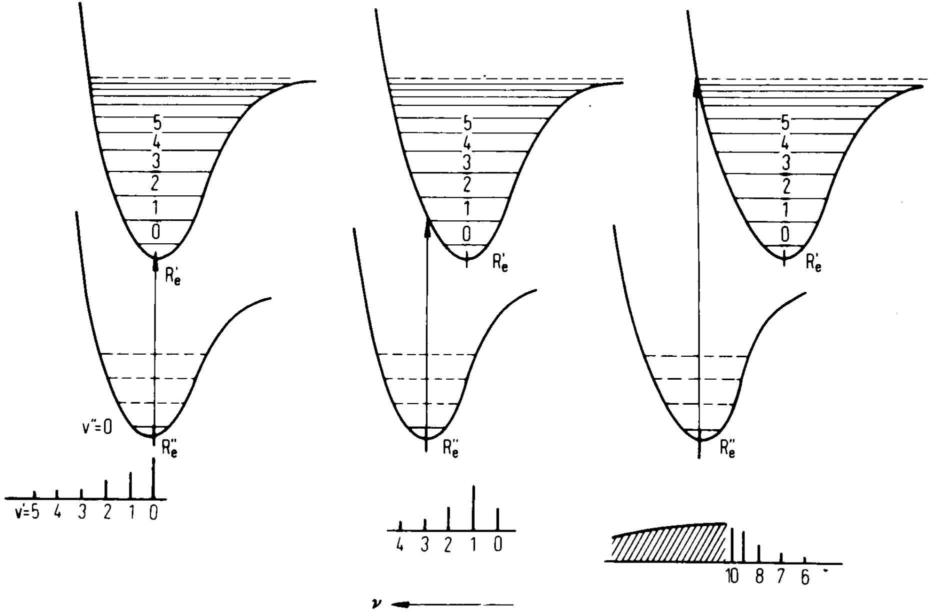

Fig. 35. Intensity distribution in absorption, as explained by the Franck-Condon principle. For the left-hand curve, $R'_e = R''_e$; for the second curve, $R'_e > R''_e$; and for the right-hand curve $R'_e > R''_e$.

The cases just discussed are shown in a simplified form in Fig. 35. In the third case the potential energy curve of the upper state is situated so far to the right that the Franck-Condon region even includes part of the continuous states above the dissociation limit. As can be seen from the schematic spectrum at the bottom, the v' progression is followed by a dissociation continuum in which the molecule, dissociates into separate atoms after having been excited into the upper state.

The situation is generally more complicated in emission spectra. If the excitation conditions are such that the molecules in the excited state are in thermal equilibrium with respect to the vibrational levels, the populations N'_v are given by a relation similar to equation (116). In this case, just as in absorption, only the lowest vibrational level v' = 0 will be appreciably occupied, and the reasoning given for the absorption spectrum can be applied to the emission spectrum also.

If, on the other hand, the excitation is by electron impact or by light absorption (fluorescence), the distribution of the molecules over the excited vibrational states may differ considerably from the equilibrium distribution. In particular, it is quite possible in this case for higher vibrational levels of the excited state also to be appreciably occupied. If one considers the intensities of all v', v" transitions that

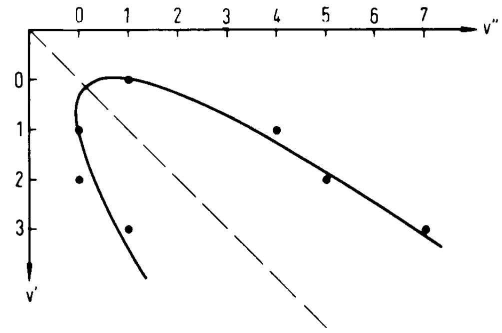

Fig. 36. The Franck-Condon parabola drawn in the head scheme of a band system. The relative positions of the potential energy curves are assumed to be the same as in Fig. 37.

occur, then those most intense in the band-head scheme (Table 4) lie close to a parabola, the Franck-Condon parabola, which is shown in Fig. 36. This means that for each v' level there are two v" levels to which strong transitions take place. The reason for this is that the excited vibrational levels have two turning points, from which perpendicular transitions can take place to generally different v" levels, as shown in Fig. 37. The strongest transitions in Fig. 37 are indicated by dots in Fig. 36. These lie very close to the Franck-Condon parabola.

To summarize, the Franck-Condon principle is easy to apply in its qualitative form, and is a very useful aid to the interpretation of the spectra of diatomic and polyatomic molecules.

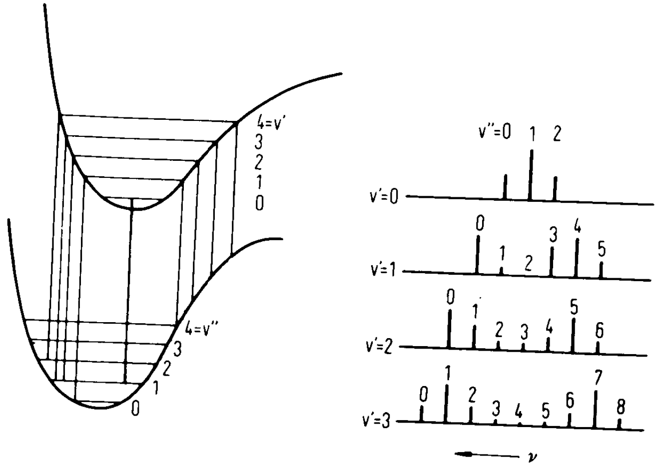

Fig. 37. Intensity distribution in emission, as explained by the Franck-Condon principle.

7. Electronic States of Diatomic Molecules

So far we have introduced the difference $\nu_e = T'_e - T''_e$ in equation (70) only as an abbreviation for the position of an electronic transition that was empirically determined. We shall now try to classify the electronic terms T_e of diatomic molecules by the introduction of electronic quantum numbers.

However, owing to the complexity of the quantum-mechanical treatment of the motion of several electrons in the field of the fixed nuclei, the electronic energy cannot be expressed as an explicit function of the electronic quantum numbers and the internuclear distance R, as was possible for rotational and vibrational motion.

7.1. Electronic states and quantum numbers

The existence of the quantum number L of the total orbital angular momentum of the electrons in an atom follows from its high symmetry, which is, in fact, that of a sphere. Diatomic (and linear polyatomic) molecules have only cylindrical symmetry. Whereas rotations about any axis are possible for an atom rotation in a molecule of this type is possible as a symmetry operation only around one axis namely the line joining the nuclei. As quantum mechanical treatment shows, there is then no good quantum number that corresponds to the total angular momentum L of the electrons; only its component L_z along the line joining the nuciei is quantized, the possible values for this component being $M_L \cdot \hbar$.

These different symmetries of atoms and molecules can be correlated by an imaginary experiment. The molecule AB, with nuclear charges Z_a and Z_b, is imagined to be formed from the united atom (cf. p. 36), with the nuclear charge $Z_a + Z_b$, by separation of the charges to a distance R from each other, as illustrated in Fig. 38. The united atom is assumed to be situated at the electrical centre of gravity of the nuclear charges on the line joining the nuclei. To a first approximation, the perturbation potential V is that of an electric quadrupole which produces

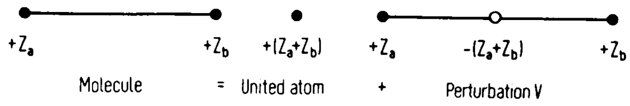

Fig. 38. Formation of a diatomic molecule from the united atom. Z_aZ_b = nuclear charges.