

### 6.1.5 Rotational Fine Structure of Electronic–Vibration Transitions

So far we have seen that the electronic spectrum of a diatomic molecule consists of one or more series of convergent lines constituting the vibrational coarse structure on each electronic transition. Normally each of these ‘lines’ is observed to be broad and diffuse or, if the resolution is sufficiently good, each appears as a cluster of many very close lines. This is, of course, the rotational fine structure.

To a very good approximation we can ignore centrifugal distortion and we have the energy levels of a rotating diatomic molecule (cf. Eqs (2.11) and (2.12)) as:

$$\varepsilon_{\text{rot.}} = \frac{h}{8\pi^2 I c} J(J + 1) = B J(J + 1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad (6.12)$$

where  $I$  is the moment of inertia,  $B$  the rotational constant, and  $J$  the rotational quantum number. Thus, by the Born–Oppenheimer approximation, the total energy (excluding kinetic of translation) of a diatomic

molecule is:

$$\varepsilon_{\text{total}} = \varepsilon_{\text{elec.}} + \varepsilon_{\text{vib.}} + BJ(J + 1) \text{ cm}^{-1} \quad (6.13)$$

Changes in the total energy may be written:

$$\Delta\varepsilon_{\text{total}} = \Delta\{\varepsilon_{\text{elect.}} + \varepsilon_{\text{vib.}}\} + \Delta\{BJ(J + 1)\} \text{ cm}^{-1} \quad (6.14)$$

and the wavenumber of a spectroscopic line corresponding to such a change becomes simply:

$$\bar{\nu}_{\text{spect.}} = \bar{\nu}_{(v', v'')} + \Delta\{BJ(J + 1)\} \text{ cm}^{-1} \quad (6.15)$$

where we write  $\bar{\nu}_{(v', v'')}$  to represent the wavenumber of an electronic-vibrational transition. This plainly corresponds to any *one* of the transitions, for example, (0, 0) or (1, 0), etc., considered in previous sections. Here we are mainly concerned with  $\Delta\{BJ(J + 1)\}$ .

The selection rule for  $J$  depends upon the type of electronic transition undergone by the molecule. We shall discuss these in more detail in Sec. 6.2.2; for the moment we must simply state that if both the upper and lower electronic states are  $^1\Sigma$  states (i.e., states in which there is no electronic angular momentum about the internuclear axis), this selection rule is:

$$\Delta J = \pm 1 \text{ only} \quad \text{for } ^1\Sigma \rightarrow ^1\Sigma \text{ transitions} \quad (6.16)$$

whereas for all other transitions (i.e., provided either the upper or the lower states (or both) have angular momentum about the bond axis) the selection rule becomes:

$$\Delta J = 0, \text{ or } \pm 1 \quad (6.17)$$

For this latter case there is the added restriction that a state with  $J = 0$  cannot undergo a transition to another  $J = 0$  state:

$$J = 0 \nleftrightarrow J = 0 \quad (6.18)$$

Thus we see that for transitions between  $^1\Sigma$  states,  $P$  and  $R$  branches only will occur, while for other transitions  $Q$  branches will appear in addition.

We can expand Eq. (6.15) as follows:

$$\bar{\nu}_{\text{spect.}} = \bar{\nu}_{(v', v'')} + B'J'(J' + 1) - B''J''(J'' + 1) \text{ cm}^{-1} \quad (6.19)$$

where  $B'$  and  $J'$  refer to the upper electronic state,  $B''$  and  $J''$  to the lower. When we considered vibration-rotational spectra in Chapter 3, we saw (cf. Sec. 3.4) that the difference between  $B$  values in different vibrational levels was very small and could be ignored except in explaining finer details of the spectra. But this is by no means the case in electronic spectroscopy: here we have seen, when discussing the Franck-Condon principle in Sec. 6.1.3, that equilibrium internuclear distances in the lower and upper electronic states may differ considerably, in which case the moments of inertia, and hence  $B$  values, in the two states will also differ. We cannot say a priori which of the

two  $B$  values will be greater. Quite often the electron excited is one of those forming the bond between the nuclei; if this is so, the bond in the upper state will be weaker and probably longer (cf. Fig. 6.3(b) or (c)) so that the equilibrium moment of inertia increases during the transition and  $B$  decreases. Thus  $B' < B''$ . The reverse is sometimes true, however, e.g., when the electron is excited from an antibonding orbital (see Sec. 6.2.2).

We can discuss the rotational fine structure quite generally by applying the selection rules of Eqs (6.16), (6.17), and (6.18) to the expression for spectral lines, Eq. (6.19). We may note, in passing, that the treatment given here for the  $P$  and  $R$  branch lines is identical with that given in Sec. 3.4 for the vibration-rotation spectrum, except that there we were concerned with  $B_0$  and  $B_1$ — $B$  values in lower and upper *vibrational* states. Here our concern is with  $B$  values in lower and upper *electronic* states,  $B''$  and  $B'$ , and we also consider the formation of a  $Q$  branch.

Taking the  $P$ ,  $R$  and  $Q$  branches in turn:

1.  $P$  branch:  $\Delta J = -1, J'' = J' + 1$

$$\Delta\varepsilon = \bar{\nu}_P = \bar{\nu}_{(v', v'')} - (B' + B'')(J' + 1) + (B' - B'')(J' + 1)^2 \text{ cm}^{-1}$$

where  $J' = 0, 1, 2, \dots$  (6.20a)

2.  $R$  branch:  $\Delta J = +1, J' = J'' + 1$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\nu}_{(v', v'')} + (B' + B'')(J'' + 1) + (B' - B'')(J'' + 1)^2 \text{ cm}^{-1}$$

where  $J'' = 0, 1, 2, \dots$  (6.20b)

These two equations can be combined into:

$$\bar{\nu}_{P, R} = \bar{\nu}_{(v', v'')} + (B' + B'')m + (B' - B'')m^2 \text{ cm}^{-1}$$

where  $m = \pm 1, \pm 2, \dots$  (6.20c)

positive  $m$  values comprising the  $R$  branch (i.e., corresponding to  $\Delta J = +1$ ) and negative values the  $P$  branch ( $\Delta J = -1$ ). Note that  $m$  cannot be zero (this would correspond in, e.g., the  $P$  branch, to  $J' = -1$  which is impossible) so that no line from the  $P$  and  $R$  branch appears at the *band origin*  $\bar{\nu}_{(v', v'')}$ . We draw the appearance of the  $R$  and  $P$  branches separately in Fig. 6.6(a) and (b) respectively, taking a 10 per cent difference between the upper and lower  $B$  values and choosing  $B' < B''$ . Note that, with this choice,  $P$  branch lines occur on the *low* wavenumber side of the band origin and the spacing between the lines increases with  $m$ . On the other hand the  $R$  branch appears on the *high* wavenumber of the origin and the line spacing decreases rapidly with  $m$ —so rapidly that the lines eventually reach a maximum wavenumber and then begin to return to low wavenumbers with increasing spacing.† It will be remembered that

† The returning lines of the  $R$  branch coincide with earlier lines if Eq. (6.20b) is obeyed exactly. For real molecules cubic and quartic terms become important at high values of  $m$ .



in Sec. 3.4, a similar decrease in spacing was observed in the  $R$  branch but this was much too slow for a convergence limit to be reached; the rapid convergence here is due simply to the magnitude of  $B' - B''$ . The point at which the  $R$  branch separation decreases to zero is termed the *band head*.

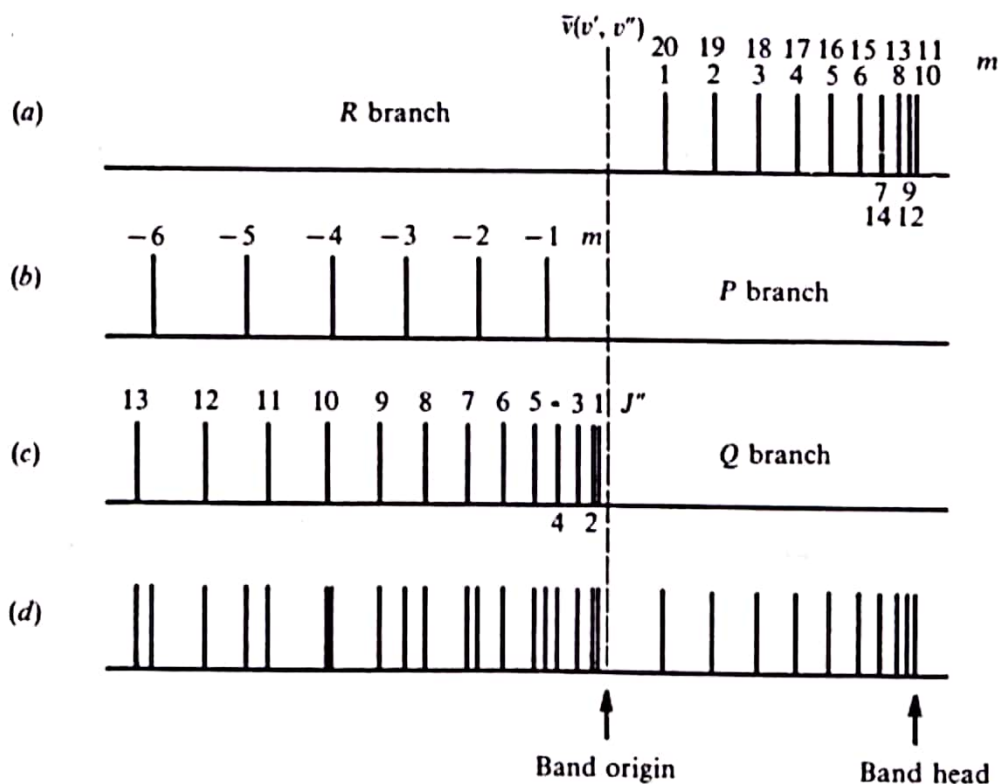
3.  $Q$  branch:  $\Delta J = 0, J' = J''$

$$\Delta\varepsilon = \bar{\nu}_Q = \bar{\nu}_{(v', v'')} + (B' - B'')J'' + (B' - B'')J''^2 \quad \text{cm}^{-1}$$

$$\text{where } J'' = 1, 2, 3, \dots \quad (6.21)$$

Note that here  $J'' = J' \neq 0$  since we have the restriction shown in Eq. (6.18). Thus again *no line will appear at the band origin*. We sketch the  $Q$  branch in Fig. 6.6(c), again for  $B' < B''$  and a 10 per cent difference between the two. We see that the lines lie to *low wavenumber* of the origin and their spacing increases. The first few lines of this branch are not usually resolved.

The complete rotational spectrum is shown in Fig. 6.6(d). We have seen in Sec. 2.3.2 that many rotational levels are populated even at room temperature; consequently, a large number of the  $P$  and  $R$  (and  $Q$ , where appropriate) lines will appear in the spectrum with comparable intensity. The spectrum is usually dominated by the band head, since here several of



**Figure 6.6** The rotational fine structure of a particular vibrational–electronic transition for a diatomic molecule. The  $R$ ,  $P$ , and  $Q$  branches are shown separately at (a), (b), and (c) respectively, with the complete spectrum at (d).

the *R* branch lines crowd together; for this reason, the *Q* branch is not very apparent if it occurs.

In the situation we have been discussing ( $B' < B''$ ), the band head appears in the *R* branch on the high wavenumber side of the origin; such a band is said to be *degraded* (or *shaded*) *towards the red*—i.e., the tail of the band where the intensity falls off points towards the red (low-frequency) end of the spectrum. If, on the other hand,  $B' > B''$ , then all our previous arguments are reversed. Briefly: (1) the *Q* branch spreads to *high* wavenumber, (2) the *R* branch (still, of course, on the *high* wavenumber side) consists of a series of lines with *increasing* separation, and (3) the band head appears in the *P* branch to *low* frequency of the origin. Such a band is *shaded to the violet*.

Normally, all the vibrational bands in any one electronic transition (e.g., the set of bands shown as a line spectrum in Fig. 6.1) are shaded in the same direction, while different electronic transitions in the same molecule may well show different shadings. Thus, observation of the shading may assist in the analysis of a complex spectrum. However, it may happen that different shadings are observed in bands belonging to the same electronic transition. This is because the  $B'$  and  $B''$  values are not altogether independent of the vibrational state (as we have already seen in Sec. 3.4) so that, if  $B' - B''$  is small, it may reverse sign for some higher vibrational levels. This behaviour is observed, for example, in the molecular fragment AlF, but is rare.