Table 3.1 Some molecular data for diatomic molecules determined by infra-red spectroscopy

Molecule	Vibration (cm^{-1})	Anharmonicity constant, x_e	Force constant $(N\ m^{-1})$	Internuclear distance $r_{eq.}$ (nm)
HF	4138·5	0·0218	966	0·0927
HCl†	2990·6	0·0174	516	0·1274
HBr	2649·7	0·0171	412	0·1414
HI	2309·5	0·0172	314	0·1609
CO	2169·7	0·0061	1902	0·1131
NO	1904·0	0·0073	1595	0·1151
ICl†	384·2	0·0038	238	0·2321

† Data refers to the ^{35}Cl isotope.

Although we have ignored transitions from $v = 1$ to higher states, we should note that, if the temperature is raised or if the vibration has a particularly low frequency, the population of the $v = 1$ state may become appreciable. Thus at, say, 600 K (i.e., about 300°C) $N_{v=1}/N_{v=0}$ becomes exp $(-2·4)$ or about 0·09, and transitions from $v = 1$ to $v = 2$ will be some 10 per cent the intensity of those from $v = 0$ to $v = 1$. A similar increase in the excited state population would arise if the vibrational frequency were 500 cm^{-1} instead of 1000 cm^{-1}. We may calculate the wavenumber of this transition as:

4. $v = 1 \rightarrow v = 2$, $\Delta v = +1$, normally very weak,

$$\Delta\varepsilon = 2\tfrac{1}{2}\bar{\omega}_e - 6\tfrac{1}{4}x_e\bar{\omega}_e - \{1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e\}$$

$$= \bar{\omega}_e(1 - 4x_e)\quad cm^{-1} \tag{3.15d}$$

Thus, should this weak absorption arise, it will be found close to and at slightly *lower* wavenumber than the fundamental (since x_e is small and positive). Such weak absorptions are usually called *hot bands* since a high temperature is one condition for their occurrence. Their nature may be confirmed by raising the temperature of the sample when a true hot band will increase in intensity.

We turn now to consider a diatomic molecule undergoing simultaneous vibration and rotation.

3.2 THE DIATOMIC VIBRATING-ROTATOR

We saw in Chapter 2 that a typical diatomic molecule has rotational energy separations of 1–10 cm^{-1}, while in the preceding section we found that the vibrational energy separations of HCl were nearly 3000 cm^{-1}. Since the

energies of the two motions are so different we may, as a first approximation, consider that a diatomic molecule can execute rotations and vibrations quite independently. This, which we shall call the Born–Oppenheimer approximation (although, cf. Eq. (6·1), this strictly includes electronic energies), is tantamount to assuming that the combined rotational–vibrational energy is simply the sum of the separate energies:

$$E_{total} = E_{rot.} + E_{vib.} \quad \text{(joules)}$$

$$\varepsilon_{total} = \varepsilon_{rot.} + \varepsilon_{vib.} \quad (\text{cm}^{-1}) \tag{3.16}$$

We shall see later in what circumstances this approximation does not apply.

Taking the separate expressions for $\varepsilon_{rot.}$ and $\varepsilon_{vib.}$ from Eqs (2.26) and (3.12) respectively, we have:

$$\varepsilon_{J, v} = \varepsilon_J + \varepsilon_v$$
$$= BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + \ldots$$
$$+ (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \quad \text{cm}^{-1} \tag{3.17}$$

Initially, we shall ignore the small centrifugal distortion constants D, H, etc., and hence write

$$\varepsilon_{total} = \varepsilon_{J, v} = BJ(J + 1) + (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \tag{3.18}$$

Note, however, that it is not logical to ignore D since this implies that we are treating the molecule as rigid, yet vibrating! The retention of D would have only a very minor effect on the spectrum.

The rotational levels are sketched in Fig. 3.5 for the two lowest vibrational levels, $v = 0$ and $v = 1$. There is, however, no attempt at scale in this diagram since the separation between neighbouring J values is, in fact, only some 1/1000 of that between the v values. Note that since the rotational constant B in Eq. (3.18) is taken to be the same for all J and v (a consequence of the Born–Oppenheimer assumption), the separation between two levels of given J is the same in the $v = 0$ and $v = 1$ states.

It may be shown that the selection rules for the combined motions are the same as those for each separately; therefore we have:

$$\Delta v = \pm 1, \pm 2, \text{ etc.} \qquad \Delta J = \pm 1 \tag{3.19}$$

Strictly speaking we may also have $\Delta v = 0$, but this corresponds to the purely rotational transitions already dealt with in Chapter 2. Note carefully, however, that a *diatomic* molecule, except under very special and rare circumstances, may *not* have $\Delta J = 0$; in other words a vibrational change *must* be accompanied by a simultaneous rotational change.

In Fig. 3.6 we have drawn some of the relevant energy levels and transitions, designating rotational quantum numbers in the $v = 0$ state as J'' and in the $v = 1$ state as J'. The use of a single prime for the upper state
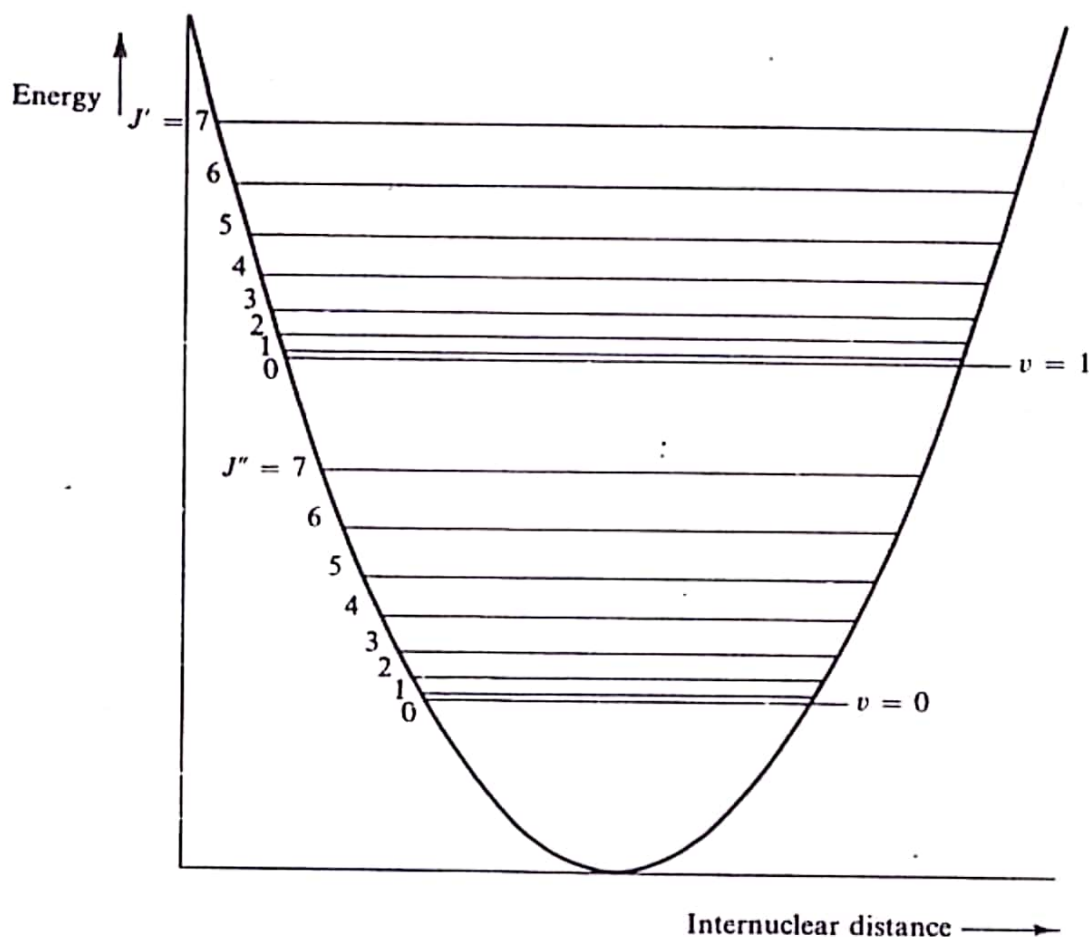
Figure 3.5 The rotational energy levels for two different vibrational states of a diatomic molecule.

and a double for the lower state is conventional in all branches of spectroscopy.

Remember (and cf. Eq. (2.20)) that the rotational levels J'' are filled to varying degrees in any molecular population, so the transitions shown will occur with varying intensities. This is indicated schematically in the spectrum at the foot of Fig. 3.6.

An analytical expression for the spectrum may be obtained by applying the selection rules (Eq. (3.19)) to the energy levels (Eq. (3.18)). Considering only the $v = 0 \rightarrow v = 1$ transition we have in general:

$$\Delta\varepsilon_{J,v} = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0}$$

$$= BJ'(J' + 1) + 1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e - \{BJ''(J'' + 1) + \tfrac{1}{2}\bar{\omega}_e - \tfrac{1}{4}x_e\bar{\omega}_e\}$$

$$= \bar{\omega}_o + B(J' - J'')(J' + J'' + 1) \quad \text{cm}^{-1}$$

where, for brevity, we write $\bar{\omega}_o$ for $\bar{\omega}_e(1 - 2x_e)$.

We should note that taking B to be identical in the upper and lower vibrational states is a direct consequence of the Born–Oppenheimer approximation—rotation is unaffected by vibrational changes.
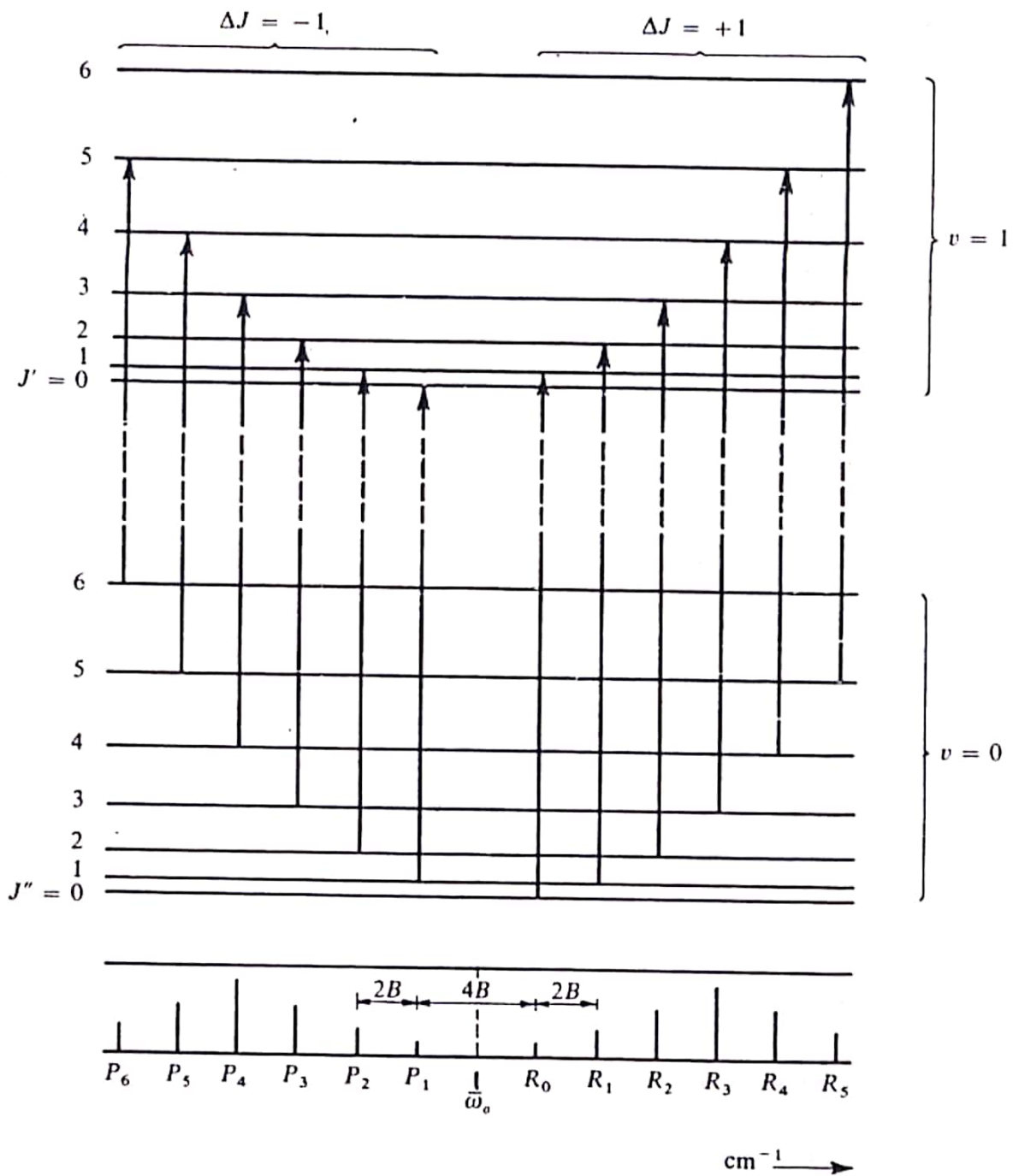
Figure 3.6 Some transitions between the rotational–vibrational energy levels of a diatomic molecule together with the spectrum arising from them.

Now we can have:

1. $\Delta J = +1$, i.e., $J' = J'' + 1$ or $J' - J'' = +1$; hence

$$\Delta\varepsilon_{J,\, v} = \bar{\omega}_o + 2B(J'' + 1) \text{ cm}^{-1} \qquad J'' = 0, 1, 2, \ldots \qquad (3.20a)$$

2. $\Delta J = -1$, i.e., $J'' = J' + 1$ or $J' - J'' = -1$; and

$$\Delta\varepsilon_{J,\, v} = \bar{\omega}_o - 2B(J' + 1) \text{ cm}^{-1} \qquad J' = 0, 1, 2, \ldots \qquad (3.20b)$$

These two expressions may conveniently be combined into:

$$\Delta\varepsilon_{J,\,v} = \bar{v}_{\text{spect.}} = \bar{\omega}_o + 2Bm \quad \text{cm}^{-1} \qquad m = \pm 1, \pm 2, \ldots \quad (3.20c)$$

where m, replacing $J'' + 1$ in Eq. (3.20a) and $J' + 1$ in Eq. (3.20b) has positive values for $\Delta J = +1$ and is negative if $\Delta J = +1$. Note particularly that m *cannot be zero* since this would imply values of J' or J'' to be -1. The frequency $\bar{\omega}_o$ is usually called the *band origin* or *band centre*.

Equation (3.20c), then, represents the combined vibration–rotation spectrum. Evidently it will consist of equally spaced lines (spacing $= 2B$) on each side of the band origin $\bar{\omega}_o$, but, since $m \neq 0$, the *line at $\bar{\omega}_o$ itself will not appear*. Lines to the low-frequency side of $\bar{\omega}_o$, corresponding to negative m (that is, $\Delta J = -1$) are referred to as the P branch, while those to the high-frequency side (m positive, $\Delta J = +1$) are called the R branch. This apparently arbitrary notation may become clearer if we state here that later, in other contexts, we shall be concerned with ΔJ values of 0 and ± 2, in addition to ± 1 considered here; the labelling of line series is then quite consistent:

Lines arising from $\Delta J =$	-2	-1	0	$+1$	$+2$	
called:	O	P	Q	R	S	branch

The P and R notation, with the *lower J* (J'') value as a suffix, is illustrated on the diagrammatic spectrum of Fig. 3.6. This is the conventional notation for such spectra.

It is readily shown that the inclusion of the centrifugal distortion constant D leads to the following expression for the spectrum:

$$\Delta\varepsilon = \bar{v}_{\text{spect.}} = \bar{\omega}_o + 2Bm - 4Dm^3 \quad \text{cm}^{-1} \qquad (m = \pm 1, \pm 2, \pm 3, \ldots)$$
$$(3.21)$$

But we have seen in Chapter 2 that B is some 10 cm^{-1} or less, while D is only some 0·01 per cent of B. Since a good infra-red spectrometer has a resolving power of about 0·5 cm^{-1} it is obvious that D is negligible to a very high degree of accuracy.

The anharmonicity factor, on the other hand, is not negligible. It affects not only the position of the band origin (since $\bar{\omega}_o = \bar{\omega}_e(1 - 2x_e)$), but, by extending the selection rules to include $\Delta v = \pm 2, \pm 3$, etc., also allows the appearance of overtone bands having identical rotational structure. This is illustrated in Fig. 3.7(a), where the fundamental absorption and first overtone of carbon monoxide are shown. From the band centres we can calculate, as shown in Sec. 1.3, the equilibrium frequency $\bar{\omega}_e$ and the anharmonicity constant x_e.