11C.4 **Vibration–rotation spectra**

Each line of the high resolution vibrational spectrum of a gas-phase heteronuclear diatomic molecule is found to consist of a large number of closely spaced components (Fig. 11C.8). Hence, molecular spectra are often called **band spectra**. The separation between the components is less than $10\ cm^{-1}$, which
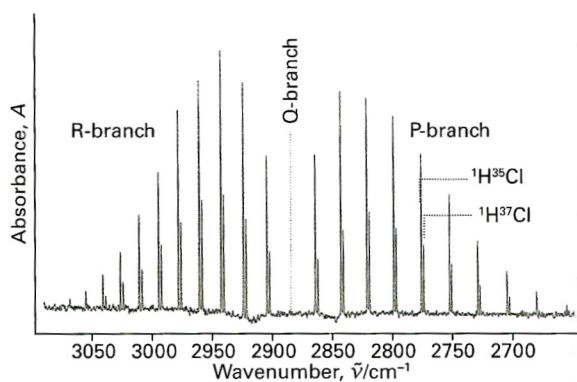

Figure 11C.8 A high-resolution vibration–rotation spectrum of HCl. The lines appear in pairs because $H^{35}Cl$ and $H^{37}Cl$ both contribute (their abundance ratio is 3:1). There is no Q branch (see below), because $\Delta J = 0$ is forbidden for this molecule.

suggests that the structure is due to rotational transitions accompanying the vibrational transition. A rotational change should be expected because classically a vibrational transition can be thought of as leading to a sudden increase or decrease in the instantaneous bond length. Just as ice-skaters rotate more rapidly when they bring their arms in, and more slowly when they throw them out, so the molecular rotation is either accelerated or retarded by a vibrational transition.

(a) Spectral branches

A detailed analysis of the quantum mechanics of simultaneous vibrational and rotational changes shows that the rotational quantum number J changes by ± 1 during the vibrational transition of a diatomic molecule. If the molecule also possesses angular momentum about its axis, as in the case of the electronic orbital angular momentum of the molecule NO with its configuration ... π^1, then the selection rules also allow $\Delta J = 0$.

The appearance of the vibration–rotation spectrum of a diatomic molecule can be discussed by using the combined vibration–rotation terms, $\tilde{S}$:

$$\tilde{S}(v, J) = \tilde{G}(v) + \tilde{F}(J) \qquad (11C.12a)$$

If anharmonicity and centrifugal distortion are ignored, $\tilde{G}(v)$ can be replaced by the expression in eqn 11C.4b, and $\tilde{F}(J)$ can be replaced by the expression in eqn 11B.9 ($\tilde{F}(J) = \tilde{B}J(J+1)$) to give

$$\tilde{S}(v, J) = (v + \tfrac{1}{2})\tilde{v} + \tilde{B}J(J+1) \qquad (11C.12b)$$

In a more detailed treatment, $\tilde{B}$ is allowed to depend on the vibrational state and written $\tilde{B}_v$.

In the vibrational transition $v + 1 \leftarrow v$, J changes by ± 1 and in some cases by 0 (when $\Delta J = 0$ is allowed). The absorptions then fall into three groups called **branches** of the spectrum. The **P branch** consists of all transitions with $\Delta J = -1$:

$$\tilde{v}_P(J) = \tilde{S}(v+1, J-1) - \tilde{S}(v, J) = \tilde{v} - 2\tilde{B}J$$
$$J = 1, 2, 3, \ldots \qquad \text{P branch transitions} \qquad (11C.13a)$$

This branch consists of lines extending to the low wavenumber side of $\tilde{v}$ at $\tilde{v} - 2\tilde{B}$, $\tilde{v} - 4\tilde{B}$, ... with an intensity distribution reflecting both the populations of the rotational levels and the magnitude of the $J - 1 \leftarrow J$ transition moment (Fig. 11C.9). The **Q branch** consists of all transitions with $\Delta J = 0$, and its wavenumbers are the same for all values of J:

$$\tilde{v}_Q(J) = \tilde{S}(v+1, J) - \tilde{S}(v, J) = \tilde{v} \qquad \text{Q branch transitions} \qquad (11C.13b)$$

This branch, when it is allowed (as in NO), appears at the vibrational transition wavenumber $\tilde{v}$. In Fig. 11C.8 there is a gap at the expected location of the Q branch because it is
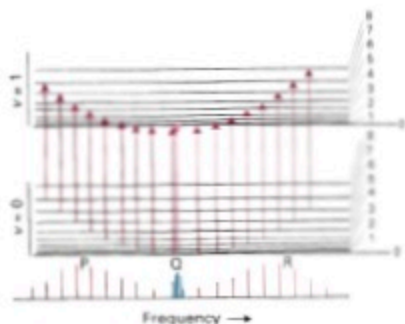

Figure 11C.9 The formation of P, Q, and R branches in a vibration–rotation spectrum. The intensities reflect the populations of the initial rotational levels and magnitudes of the transition moments.

forbidden in HCl because it has zero electronic angular momentum around its internuclear axis. The **R branch** consists of lines with $\Delta J = +1$:

$$\tilde{v}_R(J) = \tilde{S}(v+1, J+1) - \tilde{S}(v, J) = \tilde{v} + 2\tilde{B}(J+1)$$
$$J = 0, 1, 2, \ldots \qquad \text{R branch transitions} \qquad (11C.13c)$$

This branch consists of lines extending to the high-wavenumber side of $\tilde{v}$ at $\tilde{v} + 2\tilde{B}$, $\tilde{v} + 4\tilde{B}$, ...

The separation between the lines in the P and R branches of a vibrational transition gives the value of $\tilde{B}$. Therefore, the bond length can be deduced in the same way as from microwave spectra (Topic 11B). However, the latter technique gives more precise bond lengths because microwave frequencies can be measured with greater precision than infrared frequencies.

Brief illustration 11C.2

The infrared absorption spectrum of $^1H^{81}Br$ contains a band arising from $v = 0$. It follows from eqn 11C.13c and the data in Table 11C.1 that the wavenumber of the line in the R branch originating from the rotational state with $J = 2$ is

$$\tilde{v}_R(2) = \tilde{v} + 6\tilde{B} = 2648.98\,cm^{-1} + 6 \times (8.465\,cm^{-1})$$
$$= 2699.77\,cm^{-1}$$

Table 11C.1 Properties of diatomic molecules*

	$\tilde{v}/cm^{-1}$	R_e/pm	$\tilde{B}/cm^{-1}$	$k/(N\,m^{-1})$	$\tilde{B}_0/(10^2\,cm^{-1})$
$^1H_2$	4400	74	60.86	575	3.61
$^1H^{35}Cl$	2991	127	10.59	516	3.38
$^1H^{81}Br$	2308	161	6.51	314	2.46
$^{35}Cl_2$	560	199	0.244	323	2.00

* More values are given in the Resource section.

(b) Combination differences

A more detailed analysis of the rotational fine structure shows that the rotational constant decreases as the vibrational quantum number v increases. The origin of this effect is that the average value of $1/R^2$ decreases because the asymmetry of the potential well results in the average bond length increasing with vibrational energy. A harmonic oscillator also shows this effect because although the average value of R is unchanged with increasing v, the average value of $1/R^2$ does change (see Problem P11C.13). Typically, $\tilde{B}_1$ is 1–2 per cent smaller than $\tilde{B}_0$.

The result of $\tilde{B}_1$ being smaller than $\tilde{B}_0$ is that the Q branch (if it is present) consists of a series of closely spaced lines; the lines of the R branch converge slightly as J increases, and those of the P branch diverge. It follows from eqn 11C.12b with $\tilde{B}_v$ in place of $\tilde{B}$

$$\tilde{v}_P(J) = \tilde{v} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

$$\tilde{v}_Q(J) = \tilde{v} + (\tilde{B}_1 - \tilde{B}_0)J(J+1) \tag{11C.14}$$

$$\tilde{v}_R(J) = \tilde{v} + (\tilde{B}_1 + \tilde{B}_0)(J+1) + (\tilde{B}_1 - \tilde{B}_0)(J+1)^2$$

To determine the two rotational constants individually, the method of **combination differences** is used, which involves setting up expressions for the difference in the wavenumbers of transitions to a common state. The resulting expression then depends solely on properties of the other states.

As can be seen from Fig. 11C.10, the transitions $\tilde{v}_R(J-1)$ and $\tilde{v}_P(J+1)$ have a common upper state, and hence the difference between these transitions can be anticipated to depend on $\tilde{B}_0$. From the diagram it can be seen that $\tilde{v}_R(J-1) - \tilde{v}_P(J+1) = \tilde{S}(0,J+1) - \tilde{S}(0,J-1)$. The right-hand side is evaluated by using the expression for $\tilde{S}(v,J)$ in eqn 11C.12b (with $\tilde{B}_0$ in place of $\tilde{B}$) to give

$$\tilde{v}_R(J-1) - \tilde{v}_P(J+1) = 4\tilde{B}_0(J+\tfrac{1}{2}) \tag{11C.15a}$$

Therefore, a plot of the combination difference against $J+\tfrac{1}{2}$ should be a straight line of slope $4\tilde{B}_0$ and intercept (with the vertical axis) zero; the value of $\tilde{B}_0$ can therefore be determined
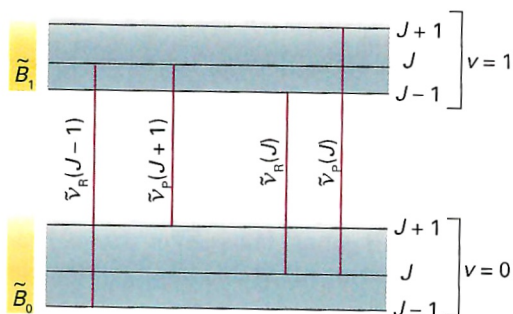
from the slope. The presence of centrifugal distortion results in the intercept deviating from zero, but has little effect on the quality of the straight line.

The two lines $\tilde{v}_R(J)$ and $\tilde{v}_P(J)$ have a common lower state, and hence their combination difference depends on $\tilde{B}_1$. As before, from Fig. 11C.10 it can be seen that $\tilde{v}_R(J) - \tilde{v}_P(J) = \tilde{S}(1,J+1) - \tilde{S}(1,J-1)$ which is

$$\tilde{v}_R(J) - \tilde{v}_P(J) = 4\tilde{B}_1(J+\tfrac{1}{2}) \tag{11C.15b}$$

Brief illustration 11C.3

The rotational constants of $\tilde{B}_0$ and $\tilde{B}_1$ can be estimated from a calculation involving only a few transitions. For $^1H^{35}Cl$, $\tilde{v}_R(0) - \tilde{v}_P(2) = 62.6\ cm^{-1}$, and it follows from eqn 11C.15a, with $J = 1$, that $\tilde{B}_0 = 62.6/4(1+\tfrac{1}{2})\ cm^{-1} = 10.4\ cm^{-1}$. Similarly, $\tilde{v}_R(1) - \tilde{v}_P(1) = 60.8\ cm^{-1}$, and it follows from eqn 11C.15b, again with $J = 1$ that $\tilde{B}_1 = 60.8/4(1+\tfrac{1}{2})\ cm^{-1} = 10.1\ cm^{-1}$. If more lines are used to make combination difference plots, the values $\tilde{B}_0 = 10.440\ cm^{-1}$ and $\tilde{B}_1 = 10.136\ cm^{-1}$ are found. The two rotational constants differ by about 3 per cent of $\tilde{B}_0$.

Figure 11C.10 The method of combination differences makes use of the fact that certain pairs of transitions share a common level.