Unit 6.2 Rotational, Vibrational and Raman Spectroscopy (Marks 20)


Structure elucidation by IR spectroscopy – finger print region and group frequencies – effect of hydrogen bonding (alcohol, keto-enol) and coordination to metal.
Energy of a diatomic molecule

When two atoms combine to form a stable covalent molecule (e.g., HCl gas) they may be said to do so because of some internal electronic rearrangement. This is not the place to discuss the detailed mechanisms of chemical bond formation; we may simply look on the phenomenon as a balancing of forces. On the one hand there is a repulsion between the positively charged nuclei of both atoms, and between the negative electron ‘clouds’; on the other there is an attraction between the nucleus of one atom and the electrons of the other, and vice versa. The two atoms settle at a mean

![Diagram](image_url)

Figure 3.1 Parabolic curve of energy plotted against the extension or compression of a spring obeying Hooke’s law.
Energy of a diatomic molecule

Internuclear distance such that these forces are just balanced and the energy of the whole system is at a minimum. Attempt to squeeze the atoms more closely together and the repulsive force rises rapidly; attempt to pull them further apart and we are resisted by the attractive force. In either case an attempt to distort the bond requires an input of energy and so we may plot energy against internuclear distance as in Fig. 3.1. At the minimum the internuclear distance is referred to as the equilibrium distance \( r_{eq} \), or more simply, as the bond length.

The compression and extension of a bond may be likened to the behaviour of a spring and we may extend the analogy by assuming that the bond, like a spring, obeys Hooke’s law. We may then write

\[
  f = -k(r - r_{eq})
\]

(3.1)

where \( f \) is the restoring force, \( k \) the force constant, and \( r \) the internuclear distance. In this case the energy curve is parabolic and has the form

\[
  E = \frac{1}{2}k(r - r_{eq})^2
\]

(3.2)

This model of a vibrating diatomic molecule—the so-called simple harmonic oscillator model—while only an approximation, forms an excellent starting point for the discussion of vibrational spectra.
In Fig. 3.1 we have plotted the energy according to Eq. (3.2). The zero of curve and equation is found at \( r = r_{eq} \), and any energy in excess of this, for example, \( \varepsilon_1 \), arises because of extension or compression of the bond. The figure shows that if one atom \((A)\) is considered to be stationary on the \( r = 0 \) axis, the other will oscillate between \( B' \) and \( B'' \). If the energy is increased to \( \varepsilon_2 \) the oscillation will become more vigorous—that is to say, the degree of compression or extension will be greater—but the vibrational frequency will not change. An elastic bond, like a spring, has a certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion. Classically it is easy to show that the oscillation frequency is:

\[
\omega_{osc.} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \tag{3.3}
\]

where \( \mu \) is the reduced mass of the system (cf. Eq. (2.9)). To convert this frequency to wavenumbers, the unit most usually employed in vibrational spectroscopy, we must divide by the velocity of light, \( c \), expressed in \( \text{cm s}^{-1} \) (cf. Sec. 1.1), obtaining:

\[
\tilde{\omega}_{osc.} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \tag{3.4}
\]
Vibrational energies, like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system may be calculated from the Schrödinger equation. For the simple harmonic oscillator these turn out to be:

\[ E_v = (v + \frac{1}{2}) \hbar \omega_{osc.} \text{ joules} \quad (v = 0, 1, 2, \ldots) \]  

(3.5)

where \( v \) is called the \textit{vibrational quantum number}. Converting to the spectroscopic units, cm\(^{-1}\), we have:

\[ \varepsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2}) \tilde{\omega}_{osc.} \text{ cm}^{-1} \]  

(3.6)

as the only energies allowed to a simple harmonic vibrator. Some of these are shown in Fig. 3.2.

In particular we should notice that the \textit{lowest} vibrational energy, obtained by putting \( v = 0 \) in Eq. (3.5) or (3.6), is

\[ E_0 = \frac{1}{2} \hbar \omega_{osc.} \text{ joules} \quad [\omega_{osc.} \text{ in Hz}] \]

or

\[ \varepsilon_0 = \frac{1}{2} \tilde{\omega}_{osc.} \text{ cm}^{-1} \quad [\tilde{\omega}_{osc.} \text{ in cm}^{-1}] \]  

(3.7)

The implication is that the diatomic molecule (and, indeed, \textit{any} molecule) can never have zero vibrational energy; the atoms can never be completely
Figure 3.2 The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion.
at rest relative to each other. The quantity \( \frac{1}{2}h\omega_{osc.} \) joules or \( \frac{1}{2}\tilde{\omega}_{osc.} \) cm\(^{-1}\) is known as the zero-point energy; it depends only on the classical vibration frequency and hence (Eq. (3.3) or (3.4)) on the strength of the chemical bond and the atomic masses.

The prediction of zero-point energy is the basic difference between the wave mechanical and classical approaches to molecular vibrations. Classical mechanics could find no objection to a molecule possessing no vibrational energy but wave mechanics insists that it must always vibrate to some extent; the latter conclusion has been amply borne out by experiment.

Further use of the Schrödinger equation leads to the simple selection rule for the harmonic oscillator undergoing vibrational changes:

\[
\Delta v = \pm 1
\]  

(3.8)
Simple Harmonic Oscillator

To this we must, of course, add the condition that vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation, i.e. (cf. Chapter 1), if the vibration involves a change in the dipole moment of the molecule. Thus vibrational spectra will be observable only in heteronuclear diatomic molecules since homonuclear molecules have no dipole moment.

Applying the selection rule we have immediately:

$$\varepsilon_{v+1 \rightarrow v} = (v + 1 + \frac{1}{2}) \bar{\omega}_{osc} - (v + \frac{1}{2}) \bar{\omega}_{osc}.$$  

$$= \bar{\omega}_{osc} \text{ cm}^{-1} \tag{3.9a}$$

for emission and

$$\varepsilon_{v \rightarrow v+1} = \bar{\omega}_{osc} \text{ cm}^{-1} \tag{3.9b}$$

for absorption, whatever the initial value of $v$.

Such a simple result is also obvious from Fig. 3.2—since the vibrational levels are equally spaced, transitions between any two neighbouring states will give rise to the same energy change. Further, since the difference between energy levels expressed in cm$^{-1}$ gives directly the wavenumber of the spectral line absorbed or emitted

$$\bar{\nu}_{spectroscopic} = \varepsilon = \bar{\omega}_{osc} \text{ cm}^{-1} \tag{3.10}$$

This, again, is obvious if one considers the mechanism of absorption or emission in classical terms. In absorption, for instance, the vibrating molecule will absorb energy only from radiation with which it can coherently interact (cf. Fig. 1.8) and this must be radiation of its own oscillation frequency.
Anharmonic Oscillator

Real molecules do not obey exactly the laws of simple harmonic motion; real bonds, although elastic, are not so homogeneous as to obey Hooke’s law. If the bond between atoms is stretched, for instance, there comes a point at which it will break—the molecule dissociates into atoms. Thus although for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes—say greater than 10 per cent of the bond length—a much more complicated behaviour must be assumed. Figure 3.3 shows, diagrammatically, the shape of the energy curve for a typical diatomic molecule, together with (dashed) the ideal, simple harmonic parabola.
Anharmonic Oscillator

Figure 3.3 The Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.
Anharmonic Oscillator

A purely empirical expression which fits this curve to a good approximation was derived by P. M. Morse, and is called the Morse function:

\[ E = D_{eq.} \left[ 1 - \exp \left\{ a(r_{eq.} - r) \right\} \right]^2 \]  \hspace{1cm} (3.11)

where \( a \) is a constant for a particular molecule and \( D_{eq.} \) is the dissociation energy.

When Eq. (3.11) is used instead of Eq. (3.2) in the Schrödinger equation, the pattern of the allowed vibrational energy levels is found to be:

\[ \varepsilon_v = (v + \frac{1}{2})\tilde{\omega}_e - (v + \frac{1}{2})^2 \tilde{\omega}_e x_e \text{ cm}^{-1} \quad (v = 0, 1, 2, \ldots) \]  \hspace{1cm} (3.12)

where \( \tilde{\omega}_e \) is an oscillation frequency (expressed in wavenumbers) which we shall define more closely below, and \( x_e \) is the corresponding anharmonicity constant which, for bond stretching vibrations, is always small and positive.
Anharmonic Oscillator

Figure 3.4 The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.
Anharmonic Oscillator

\( \approx + 0.01 \), so that the vibrational levels crowd more closely together with increasing \( v \). Some of these levels are sketched in Fig. 3.4.

It should be mentioned that Eq. (3.12), like (3.11), is an approximation only; more precise expressions for the energy levels require cubic, quartic, etc., terms in \( (v + \frac{1}{2}) \) with anharmonicity constants \( y_e, z_e, \) etc., rapidly diminishing in magnitude. These terms are important only at large values of \( v \), and we shall ignore them.

If we rewrite Eq. (3.12), for the anharmonic oscillator, as:

\[
\varepsilon_v = \tilde{\omega}_e \{1 - x_e(v + \frac{1}{2})\}(v + \frac{1}{2})
\]

and compare with the energy levels of the harmonic oscillator (Eq. (3.6)), we see that we can write:

\[
\tilde{\omega}_{osc.} = \tilde{\omega}_e \{1 - x_e(v + \frac{1}{2})\}
\]

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing \( v \). If we now consider the hypothetical energy state obtained by putting \( v = -\frac{1}{2} \) (at which, according to Eq. (3.13), \( \varepsilon = 0 \)) the molecule would be at the equilibrium point with zero vibrational energy. Its oscillation frequency (in \( \text{cm}^{-1} \)) would be:

\[
\tilde{\omega}_{osc.} = \tilde{\omega}_e
\]
Anharmonic Oscillator

Thus we see that $\tilde{\omega}_e$ may be defined as the (hypothetical) equilibrium oscillation frequency of the anharmonic system—the frequency for infinitely small vibrations about the equilibrium point. For any real state specified by a positive integral $v$ the oscillation frequency will be given by Eq. (3.14). Thus in the ground state ($v = 0$) we would have:

$$\tilde{\omega}_0 = \tilde{\omega}_e (1 - \frac{1}{2} x_e) \text{ cm}^{-1}$$

and

$$\varepsilon_0 = \frac{1}{2} \tilde{\omega}_e (1 - \frac{1}{2} x_e) \text{ cm}^{-1}$$

and we see that the zero point energy differs slightly from that for the harmonic oscillator (Eq. (3.7)).

The selection rules for the anharmonic oscillator are found to be:

$$\Delta v = \pm 1, \pm 2, \pm 3, \ldots$$

Thus they are the same as for the harmonic oscillator, with the additional possibility of larger jumps. These, however, are predicted by theory and observed in practice to be of rapidly diminishing probability and normally only the lines of $\Delta v = \pm 1, \pm 2, \pm 3$, at the most, have observable intensity. Further, the spacing between the vibrational levels is, as we shall shortly see, of order $10^3 \text{ cm}^{-1}$ and, at room temperature, we may use the Boltzmann distribution (Eq. (1.12)) to show

$$\frac{N_{v=1}}{N_{v=0}} = \exp \left\{ - \frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300} \right\}$$

$$\approx \exp (-4.8) \approx 0.008.$$ 

In other words, the population of the $v = 1$ state is nearly 0.01 or some one per cent of the ground state population. Thus, to a very good approximation, we may ignore all transitions originating at $v = 1$ or more and
Anharmonic Oscillator

restrict ourselves to the three transitions:

1. $v = 0 \rightarrow v = 1$, $\Delta v = +1$, with considerable intensity.
   
   $$\Delta \varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0}$$
   
   $$= (1 + \frac{1}{2}) \bar{\omega}_e - x_e (1 + \frac{1}{2})^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - (\frac{1}{2})^2 x_e \bar{\omega}_e \right\}$$
   
   $$= \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

   \text{(3.15a)}

2. $v = 0 \rightarrow v = 2$, $\Delta v = +2$, with small intensity.
   
   $$\Delta \varepsilon = (2 + \frac{1}{2}) \bar{\omega}_e - x_e (2 + \frac{1}{2})^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - (\frac{1}{2})^2 x_e \bar{\omega}_e \right\}$$
   
   $$= 2 \bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}$$

   \text{(3.15b)}

3. $v = 0 \rightarrow v = 3$, $\Delta v = +3$, with normally negligible intensity.
   
   $$\Delta \varepsilon = (3 + \frac{1}{2}) \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - (\frac{1}{2})^2 x_e \bar{\omega}_e \right\}$$
   
   $$= 3 \bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}$$

   \text{(3.15c)}
Anharmonic Oscillator

These three transitions are shown in Fig. 3.4. To a good approximation, since \(x_e \approx 0.01\), the three spectral lines lie very close to \(\bar{\omega}_e\), \(2\bar{\omega}_e\), and \(3\bar{\omega}_e\). The line near \(\bar{\omega}_e\) is called the fundamental absorption, while those near \(2\bar{\omega}_e\) and \(3\bar{\omega}_e\) are called the first and second overtones, respectively. The spectrum of HCl, for instance, shows a very intense absorption at 2886 cm\(^{-1}\), a weaker one at 5668 cm\(^{-1}\), and a very weak one at 8347 cm\(^{-1}\). If we wish to find the equilibrium frequency of the molecule from these data, we must solve any two of the three equations (cf. Eqs. (3.15)):

\[
\begin{align*}
\bar{\omega}_e(1 - 2x_e) &= 2886 \\
2\bar{\omega}_e(1 - 3x_e) &= 5668 \\
3\bar{\omega}_e(1 - 4x_e) &= 8347 \text{ cm}^{-1}
\end{align*}
\]

and we find \(\bar{\omega}_e = 2990 \text{ cm}^{-1}\), \(x_e = 0.0174\). Thus we see that, whereas for the ideal harmonic oscillator the spectral absorption occurred \textit{exactly} at the classical vibration frequency, for real, anharmonic molecules the observed fundamental absorption frequency and the equilibrium frequency may differ considerably.

The force constant of the bond in HCl may be calculated directly from Eq. (2.22) by inserting the value of \(\bar{\omega}_e\):

\[
k = 4\pi^2\bar{\omega}_e^2c^2\mu \quad \text{N m}^{-1}
\]

\[
= 516 \text{ N m}^{-1}
\]

when the fundamental constants and the reduced mass are inserted. These data, together with that for a few of the very many other diatomic molecules studied by infra-red techniques, are collected in Table 3.1.
### Table 3.1 Some molecular data for diatomic molecules determined by infra-red spectroscopy

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vibration (cm$^{-1}$)</th>
<th>Anharmonicity constant, $x_e$</th>
<th>Force constant (N m$^{-1}$)</th>
<th>Internuclear distance $r_{eq.}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>4138.5</td>
<td>0.0218</td>
<td>966</td>
<td>0.0927</td>
</tr>
<tr>
<td>HCl$^+$</td>
<td>2990.6</td>
<td>0.0174</td>
<td>516</td>
<td>0.1274</td>
</tr>
<tr>
<td>HBr</td>
<td>2649.7</td>
<td>0.0171</td>
<td>412</td>
<td>0.1414</td>
</tr>
<tr>
<td>HI</td>
<td>2309.5</td>
<td>0.0172</td>
<td>314</td>
<td>0.1609</td>
</tr>
<tr>
<td>CO</td>
<td>2169.7</td>
<td>0.0061</td>
<td>1902</td>
<td>0.1131</td>
</tr>
<tr>
<td>NO</td>
<td>1904.0</td>
<td>0.0073</td>
<td>1595</td>
<td>0.1151</td>
</tr>
<tr>
<td>ICl$^+$</td>
<td>384.2</td>
<td>0.0038</td>
<td>238</td>
<td>0.2321</td>
</tr>
</tbody>
</table>

$^+$ 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,

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

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

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.
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:

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

\[
\varepsilon_{\text{total}} = \varepsilon_{\text{rot.}} + \varepsilon_{\text{vib.}} \quad \text{(cm}^{-1}\text{)}
\]  

(3.16)

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

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

\[
\varepsilon_{J, v} = \varepsilon_J + \varepsilon_v
\]

\[
= BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + \ldots
\]

\[+(v + \frac{1}{2})\tilde{\omega}_e - x_e(v + \frac{1}{2})^2\tilde{\omega}_e \quad \text{cm}^{-1}\]

(3.17)
Initially, we shall ignore the small centrifugal distortion constants $D$, $H$, etc., and hence write

$$\varepsilon_{\text{total}} = \varepsilon_J, v = BJ(J + 1) + (v + \frac{1}{2})\bar{\omega}_e - x_e(v + \frac{1}{2})^2\bar{\omega}_e$$  

(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:

$$\Delta v = \pm 1, \pm 2, \text{etc.} \quad \Delta J = \pm 1$$  

(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.
Diatomic Vibrating-Rotator

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:

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

$$= BJ'(J' + 1) + \frac{1}{2}\tilde{\omega}_e - \frac{1}{4}x_e \tilde{\omega}_e - \left\{ BJ''(J'' + 1) + \frac{1}{2}\tilde{\omega}_e - \frac{1}{4}x_e \tilde{\omega}_e \right\}$$

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

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

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

2. $\Delta J = -1$, i.e., $J'' = J' + 1$ or $J' - J'' = -1$; and
   \[ \Delta \varepsilon_{J', v} = \bar{\omega}_o - 2B(J' + 1) \text{ cm}^{-1} \quad J' = 0, 1, 2, \ldots \]  
   \hspace{1cm} (3.20b)

These two expressions may conveniently be combined into:

\[ \Delta \varepsilon_{J', v} = \bar{v}_{\text{spect.}} = \bar{\omega}_o + 2Bm \text{ cm}^{-1} \quad m = \pm 1, \pm 2, \ldots \]  
\hspace{1cm} (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.
Diatomic Vibrating-Rotator

Equation (3.20a), then, represents the combined vibration-rotation spectrum. Evidently it will consist of equally spaced lines (spacing = 2B) on each side of the band origin \( \tilde{\nu}_0 \), but, since \( m \neq 0 \), the line at \( \tilde{\nu}_0 \) itself will not appear. Lines to the low-frequency side of \( \tilde{\nu}_0 \), 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 \( \Delta J \) values of 0 and \( \pm 2 \), in addition to \( \pm 1 \) 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:

\[
\Delta \tilde{\nu} = \tilde{\nu}_{\text{spect.}} = \tilde{\nu}_0 + 2Bm - 4Dm^3 \ \text{cm}^{-1} \quad (m = \pm 1, \pm 2, \pm 3, \ldots)
\]

(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 \( \tilde{\nu}_0 = \tilde{\nu}_e (1 - 2x_e) \)), but, by extending the selection rules to include \( \Delta \tilde{\nu} = \pm 2, \pm 3, \text{etc.} \), 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 \( \tilde{\nu}_e \) and the anharmonicity constant \( x_e \).
Figure 3.7(a) The fundamental absorption (centred at about 2143 cm$^{-1}$) and the first overtone (centred at about 4260 cm$^{-1}$) of carbon monoxide. The fine structure of the $P$ branch in the fundamental is partially resolved. (Gas pressure 650 mmHg in a 10 cm cell.)
Vibration of Polyatomic Molecules

In this section and the next, just as in the corresponding one dealing with the pure rotational spectra of polyatomic molecules, we shall find that although there is an increase in the complexity, only slight and quite logical extensions to the simple theory are adequate to give us an understanding of the spectra. We shall need to discuss:

1. The number of fundamental vibrations and their symmetry
2. The possibility of overtone and combination bands
3. The influence of rotation on the spectra.
Consider a molecule containing $N$ atoms: we can refer to the position of each atom by specifying three coordinates (e.g., the $x$, $y$, and $z$ cartesian coordinates). Thus the total number of coordinate values is $3N$ and we say the molecule has $3N$ degrees of freedom since each coordinate value may be specified quite independently of the others. However, once all $3N$ coordinates have been fixed, the bond distances and bond angles of the molecule are also fixed and no further arbitrary specifications can be made.

Now the molecule is free to move in three-dimensional space, as a whole, without change of shape. We can refer to such movement by noting the position of its centre of gravity at any instant—to do this requires a statement of three coordinate values. This translational movement uses three of the $3N$ degrees of freedom leaving $3N - 3$. In general, also, the rotation of a non-linear molecule can be resolved into components about three perpendicular axes (cf. Sec. 1.1). Specification of these axes also requires three degrees of freedom, and the molecule is left with $3N - 6$ degrees of freedom. The only other motion allowed to it is internal vibration, so we know immediately that a non-linear $N$-atomic molecule can have $3N - 6$ different internal vibrations:

$$\text{Non-linear: } 3N - 6 \text{ fundamental vibrations} \quad (3.24a)$$
Fundamental Vibrations and their Symmetry

If, on the other hand, the molecule is linear, we saw in Chapter 2 that there is no rotation about the bond axis; hence only two degrees of rotational freedom are required, leaving $3N - 5$ degrees of vibrational freedom—one more than in the case of a non-linear molecule:

**Linear:** $3N - 5$ fundamental vibrations \( (3.24b) \)

In both cases, since an $N$-atomic molecule has $N - 1$ bonds (for acyclic molecules) between its atoms, $N - 1$ of the vibrations are bond-stretching motions, the other $2N - 5$ (non-linear) or $2N - 4$ (linear) are bending motions.

Let us look briefly at examples of these rules. First, we see that for a diatomic molecule (perforce linear) such as we have already considered in this chapter: $N = 2$, $3N - 5 = 1$ and thus there can be only one fundamental vibration. Note, however, that the $3N - 5$ rule says nothing about the presence, absence, or intensity of overtone vibrations—these are governed solely by anharmonicity.

Next, consider water, $\text{H}_2\text{O}$. This (Fig. 3.9) is non-linear and triatomic. Also in the figure are the $3N - 6 = 3$ allowed vibrational modes, the arrows attached to each atom showing the direction of its motion during half of the vibration. Each motion is described as stretching or bending depending on the nature of the change in molecular shape.

These three vibrational motions are also referred to as the *normal modes of vibration* (or *normal vibrations*) of the molecule; in general a normal vibration is defined as a molecular motion in which all the atoms move in phase and with the same frequency.
Fundamental Vibrations and their Symmetry

**Figure 3.9** The symmetry of the water molecule and its three fundamental vibrations. The motion of the oxygen atom, which must occur to keep the centre of gravity of the molecule stationary, is here ignored.
Fundamental Vibrations and their Symmetry

Further each motion of Fig. 3.9 is labelled either symmetric or antisymmetric. It is not necessary here to go far into the matter of general molecular symmetry since other excellent texts already exist for the interested student, but we can see quite readily that the water molecule contains some elements of symmetry. In particular consider the dashed line at the top of Fig. 3.9 which bisects the HOH angle; if we rotate the molecule about this axis by $180^\circ$ its final appearance is identical with the initial one. This axis is thus referred to as a $C_2$ axis since twice in every complete revolution the molecule presents an identical aspect to an observer. This particular molecule has only the one rotational symmetry axis, and it is conventional to refer the molecular vibrations to this axis. Thus consider the first vibration, Fig. 3.9(a). If we rotate the *vibrating* molecule by $180^\circ$ the vibration is quite unchanged in character—we call this a symmetric vibration. The bending vibration, $v_2$, is also symmetric. Rotation of the stretching motion of Fig. 3.9(c) about the $C_2$ axis, however, produces a vibration which is in antiphase with the original and so this motion is described as the antisymmetric stretching mode.
In order to be infra-red active, as we have seen, there must be a dipole change during the vibration and this change may take place either along the line of the symmetry axis (parallel to it, or $\parallel$) or at right angles to the line (perpendicular, $\perp$). Figure 3.10 shows the nature of the dipole changes for the three vibrations of water, and justifies the labels parallel or perpen-
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dicular attached to them in Fig. 3.9. We shall see later that the distinction is important when considering the influence of rotation on the spectrum.

Finally the vibrations are labelled in Fig. 3.9 as $\nu_1$, $\nu_2$, and $\nu_3$. By convention it is usual to label vibrations in decreasing frequency within their symmetry type. Thus the symmetric vibrations of $\text{H}_2\text{O}$ are labelled $\nu_1$ for the highest fully symmetric frequency (3651.7 cm$^{-1}$), and $\nu_2$ for the next highest (1595.0 cm$^{-1}$); the antisymmetric vibration at 3755.8 cm$^{-1}$ is then labelled $\nu_3$.

Our final example is of the linear triatomic molecule $\text{CO}_2$, for which the normal vibrations are shown in Fig. 3.11. For this molecule there are two different sets of symmetry axes. There is an infinite number of twofold axes ($C_2$) passing through the carbon atom at right angles to the bond direction, and there is an $\infty$-fold axis ($C_\infty$) passing through the bond axis
Fundamental Vibrations and their Symmetry

Figure 3.11 The symmetry and fundamental vibrations of the carbon dioxide molecule.
Fundamental Vibrations and their Symmetry

itself (this is referred to as $\infty$-fold since rotation of the molecule about the bond axis through any angle gives an identical aspect). The names symmetric stretch and antisymmetric stretch are self-evident, but it should be noted that the symmetric stretch produces no change in the dipole moment (which remains zero) so that this vibration is not infra-red active; the vibration frequency may be obtained in other ways, however, which we shall discuss in the next chapter.

For linear triatomic molecules, $3N - 5 = 4$, and we would expect four vibrational modes instead of the three shown in Fig. 3.11. However, consideration shows that $v_2$ in fact consists of two vibrations—one in the plane of the paper as drawn, and the other in which the oxygen atoms move simultaneously into and out of the plane. The two sorts of motion are, of course, identical in all respects except direction and are termed degenerate; they must, nevertheless, be considered as separate motions, and it is always in the degeneracy of a bending mode that the extra vibration of a linear molecule over a non-linear one is to be found.

It might be thought that $v_2$ of H$_2$O (Fig. 3.9(b)) could occur by the hydrogens moving simultaneously in and out of the plane of the paper. Such a motion is not a vibration, however, but a rotation. As the molecule approaches linearity this rotation degenerates into a vibration, and the molecule loses one degree of rotational freedom in exchange for one of vibration.