will tilt the dipole as inspection of the

5

Rotational Spectroscopy

5.1 Linear, symmetric rotor, spherical rotor and asymmetric rotor molecules

For the purposes of studying the rotational spectra of molecules it is essential to classify them according to their principal moments of inertia.

The moment of inertia $I$ of any molecule about any axis through the centre of gravity is given by

$$ I = \sum_i m_i r_i^2 $$  \hspace{1cm} (5.1)

where $m_i$ and $r_i$ are the mass and distance of atom $i$ from the axis. There is one of these axes, conventionally labelled the $c$ axis, about which the moment of inertia has its maximum value and a second axis, labelled the $a$ axis, about which the moment of inertia has its minimum value. It can be shown that the $a$ and $c$ axes must be mutually perpendicular. These, together with a third axis, the $b$ axis, which is perpendicular to the other two, are called the principal axes of inertia and the corresponding moments of inertia $I_a$, $I_b$, and $I_c$ are the principal moments of inertia. In general, according to convention,

$$ I_c \geq I_b \geq I_a $$  \hspace{1cm} (5.2)

For a linear molecule, such as HCN in Figure 5.1(a),

$$ I_c = I_b > I_a = 0 $$  \hspace{1cm} (5.3)

where the $b$ and $c$ axes may be in any direction perpendicular to the internuclear $a$ axis. Considering the nuclei as point masses on the $a$ axis, it is clear that $I_a$ must be zero, since all the $r_i$ in Equation (5.1) are zero.

For a symmetric rotor, or symmetric top as it is sometimes called, two of the principal moments of inertia are equal and the third is non-zero. If

$$ I_c = I_b > I_a $$  \hspace{1cm} (5.4)

the molecule is a prolate symmetric rotor. Figure 5.1(b) shows the example of methyl iodide. Since the heavy iodine nucleus makes no contribution to $I_a$, which is therefore relatively
Figure 5.1  Principal inertial axes of (a) hydrogen cyanide, (b) methyl iodide, (c) benzene, (d) methane, (e) sulphur hexafluoride, (f) formaldehyde, (g) s-trans-acrolein and (h) pyrazine
small, the molecule is a prolate symmetric rotor. The benzene molecule, shown in Figure 5.1(c), is an oblate symmetric rotor for which

$$I_c > I_b = I_a$$  \hfill (5.5)

As for $I_c$ and $I_b$ in methyl iodide, it is not immediately obvious that $I_b$ and $I_a$ in benzene are equal, but simple trigonometry will prove this.

A symmetric rotor must have either a $C_n$ axis with $n > 2$ (see Section 4.1.1) or an $S_4$ axis (see Section 4.1.4). Methyl iodide has a $C_3$ axis and benzene a $C_6$ axis and, therefore, these are symmetric rotors whereas allene, shown in Figure 4.3(d), is also a symmetric rotor since it has an $S_4$ axis which is the $a$ axis: allene is a prolate symmetric rotor.

A spherical rotor has all three principal moments of inertia equal:

$$I_c = I_b = I_a$$  \hfill (5.6)

as is the case for methane and sulphur hexafluoride, shown in Figures 5.1(d) and 5.1(e). In fact, all molecules belonging to either the $T_d$ or $O_h$ point group (see Sections 4.2.8 and 4.2.9) are spherical rotors.

An asymmetric rotor has all principal moments of inertia unequal:

$$I_c \neq I_b \neq I_a$$  \hfill (5.7)

An example of an asymmetric rotor, a category which includes the majority of molecules, is formaldehyde, shown in Figure 5.1(f). However, for many asymmetric rotors, either

$$I_c \simeq I_b > I_a$$  \hfill (5.8)

and the molecule is known as a prolate near-symmetric rotor, or

$$I_c > I_b \simeq I_a$$  \hfill (5.9)

when it is known as an oblate near-symmetric rotor. An example of the former is $s$-trans-acrolein (Figure 5.1(g)) and an example of the latter is pyrazine (Figure 5.1(h)).

## 5.2 Rotational infrared, millimetre wave and microwave spectra

### 5.2.1 Diatomic and linear polyatomic molecules

#### 5.2.1.1 Transition frequencies or wavenumbers

In Section 1.3.5 (Equation 1.62) the expression

$$E_r = \frac{\hbar^2}{8\pi^2l}J(J + 1)$$  \hfill (5.10)
for the rotational energy levels \( E_r \) of a diatomic molecule, in the rigid rotor approximation, was introduced. In this equation, \( I \) is the moment of inertia \([\text{equal to } \mu r^2]\), where the reduced mass \( \mu \) is equal to \( m_1 m_2 / (m_1 + m_2) \) and the rotational quantum number \( J = 0, 1, 2, \ldots \). The same expression applies also to any linear polyatomic molecule but, because \( I \) is likely to be larger than for a diatomic molecule, the energy levels of Figure 1.12 tend to be more closely spaced.

In practice, what is measured experimentally is not energy but frequency, in the millimetre wave and microwave regions, or wavenumber, in the far infrared. Therefore we convert the energy levels of Equation (5.10) to what are known as term values \( F(J) \) having dimensions of either frequency, by dividing by \( h \), or wavenumber, by dividing by \( hc \), giving

\[
F(J) = \frac{E_r}{h} = \frac{\hbar}{8\pi^2 I} J(J + 1) = BJ(J + 1)
\]  

\[
F(J) = \frac{E_r}{hc} = \frac{\hbar}{8\pi^2 c I} J(J + 1) = BJ(J + 1)
\]  

(5.11)

(5.12)

The use of the symbols \( F(J) \) and \( B \) for quantities which may have dimensions of frequency or wavenumber is unfortunate, but the symbolism is used so commonly that there seems little prospect of change. In Equations (5.11) and (5.12) the quantity \( B \) is known as the rotational constant. Its determination by spectroscopic means results in determination of internuclear distances and represents a very powerful structural technique.

Figure 5.2 shows a set of rotational energy levels, or, strictly, term values, for the CO molecule.

The transition intensity is proportional to the square of the transition moment, which is

\[
R_r = \int \psi_r^* \mu \psi_r'' \, d\tau
\]

(5.13)

analogous to Equation (2.13). The rotational selection rules constitute the conditions for which the intensity, and therefore \( R_r \), is non-zero and are:

1. The molecule must have a permanent dipole moment (\( \mu \neq 0 \)).
2. \( \Delta J = \pm 1 \).
3. \( \Delta M_J = 0, \pm 1 \), a rule which is important only if the molecule is in an electric or magnetic field (see Equation 1.61).

Rule 1 shows that transitions are allowed in heteronuclear diatomic molecules such as CO, NO, HF and even \(^1\text{H}^2\text{H}\) (for which \( \mu = 5.9 \times 10^{-4} \text{ D} \) compared with, say, HF, for which \( \mu = 1.82 \text{ D} \)), but not in \( \text{H}_2 \), \( \text{Cl}_2 \) and \( \text{N}_2 \). Similarly, "unsymmetrical" linear polyatomic

\[ 1 \text{ D} \approx 3.33564 \times 10^{-30} \text{ C m.} \]
If we approximate, then the reduced rotational term values $F(J)$ are given by

$$F(J) = \frac{1}{(2J+1)} \exp\left(\frac{-E_J}{kT}\right) \frac{N_J}{N_0} \bar{v} \text{ cm}^{-1}$$

(5.11)

Because $J$ is likely to be more in the millimetre wave region, we convert the original dimensions giving

(5.12)

As of frequency (the transition) there seems to be a known as the condition of

(5.13)

Figure 5.2 Rotational term values $F(J)$ (horizontal lines): relative populations $N_J/N_0$ (calculated from Equation 5.15) and transition wavenumbers $\bar{v}$ (for the transitions indicated by the vertical arrows) for CO.
molecules (more specifically those having no centre of inversion; see Section 4.1.3), such as $O=C=S$, $H-C=:N$ and even $^1H-C\equiv C-H$ ($\mu \simeq 0.012$ D), have allowed rotational transitions whereas the 'symmetrical' molecules (those having a centre of inversion), such as $S=C=S$ and $H-C=:C-H$, do not.

So far as rule 2 is concerned, since $M$ is conventionally taken to refer to $J' - J''$, where $J'$ is the quantum number of the upper state and $J''$ that of the lower state of the transition, $M = -1$ has no physical meaning (although it emerges from the quantum mechanics). It is commonly, but incorrectly, thought that $M = +1$ and $M = -1$ refer to absorption and emission, respectively: in fact $M = +1$ applies to both. Transition wavenumbers or frequencies are given by

$$\tilde{v} \text{ or } v = F(J + 1) - F(J) = 2B(J + 1) \quad (5.14)$$

where $J$ is used conventionally instead of $J''$. The allowed transitions are shown in Figure 5.2 and are spaced, according to Equation (5.14), $2B$ apart. The $J = 1 - 0$ transition (a transition is written conventionally as $J' - J''$) occurs at $2B$. Whether the transitions fall in the microwave, millimetre wave, or far-infrared regions depends on the values of $B$ and $J$. The spectrum of CO spans the millimetre wave and far-infrared regions. Part of the far-infrared spectrum, from $15 \text{ cm}^{-1}$ to $40 \text{ cm}^{-1}$ with $J'' = 3, \ldots, 9$, is shown in Figure 5.3, and Table 5.1 lists the characteristically highly accurate frequencies and wavenumbers of the transitions with $J'' = 0$ to 6 observed in the millimetre wave region.

It is apparent from Figure 5.3 and the last column of Table 5.1 that the spacing of adjacent transitions is fairly constant and, as Equation (5.14) shows, the spacing is equal to $2B$.

### Table 5.1

Frequencies and wavenumbers of rotational transitions of CO observed in the millimetre wave region

<table>
<thead>
<tr>
<th>$\tilde{v}/\text{cm}^{-1}$</th>
<th>$J''$</th>
<th>$J'$</th>
<th>$v/\text{GHz}$</th>
<th>$\Delta v_{J''+1}/\text{GHz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.845 033 19</td>
<td>0</td>
<td>1</td>
<td>115 271 195</td>
<td>115 271 195</td>
</tr>
<tr>
<td>7.689 919 07</td>
<td>1</td>
<td>2</td>
<td>230 537 974</td>
<td>115 266 779</td>
</tr>
<tr>
<td>11.534 509 6</td>
<td>2</td>
<td>3</td>
<td>345 795 900</td>
<td>115 257 926</td>
</tr>
<tr>
<td>15.378 662</td>
<td>3</td>
<td>4</td>
<td>461 040 68</td>
<td>115 244 78</td>
</tr>
<tr>
<td>19.222 223</td>
<td>4</td>
<td>5</td>
<td>576 267 75</td>
<td>115 227 07</td>
</tr>
<tr>
<td>23.065 043</td>
<td>5</td>
<td>6</td>
<td>691 472 60</td>
<td>115 204 85</td>
</tr>
</tbody>
</table>

### Worked example 5.1

**Question.** By making measurements from Figure 5.3 determine the average separation of rotational transitions in $^{12}\text{C}^{16}\text{O}$ and hence estimate the bond length.

**Answer.** To obtain the best value of $2B$, the separation between adjacent rotational transitions, measure the total distance between the $J = 3$ and $J = 9$ transitions. This can be converted into cm$^{-1}$ using the scale at the bottom of the figure. The separation between the $J = 3$ and $J = 9$ transitions is approximately $2B$. Averaging the distance between adjacent transitions from Figure 5.3, the best estimate of $2B$ is $\ldots$. Therefore, the bond length is $\ldots$ A.
5.2 ROTATIONAL INFRARED, MILLIMETRE WAVE AND MICROWAVE SPECTRA

transitions is $12B$, giving $B = 1.929 \text{ cm}^{-1}$ (use four significant figures until the final stage, when only three will be justified).

$$B = \frac{h}{8\pi^2 c I} \quad \text{(with dimensions of wavenumber)}$$

where

$$I = \mu r^2$$

$$\therefore \quad r^2 = \frac{h}{8\pi^2 c \mu B}$$

For $^{12}\text{C}^{16}\text{O}$, the reduced mass

$$\mu = \frac{12.00 \times 16.00}{12.00 + 16.00} \text{ g mol}^{-1}$$

$$= 6.857 \times 10^{-3} \text{ kg mol}^{-1}$$

$$= \frac{6.857 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= 1.139 \times 10^{-26} \text{ kg}$$

$$\therefore \quad r^2 = \frac{h}{8\pi^2 c \mu B} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 1.139 \times 10^{-26} \text{ kg} \times 1.929 \text{ cm}^{-1}}$$

$$= 1.274 \times 10^{-20} \text{ m}^2$$

$$\therefore \quad r = 1.13 \times 10^{-10} \text{ m}$$

$$= 1.13 \text{ Å}$$
It will be seen in Section 5.2.1.4 that, since these rotational transitions of CO are associated with the zero-point \((v=0)\) level, the value of \(B\) obtained here is, in fact, \(B_0\) and not the equilibrium value \(B_e\). Equation (5.25) shows how these values are related.

Most linear polyatomic molecules have smaller \(B\) values and therefore more transitions tend to occur in the millimetre wave or microwave regions. Figure 5.4 shows a part of the microwave spectrum of cyanodiacetylene \((\text{H}-\text{C}=\text{C}=\text{C}=\text{C}=\text{N})\) which has such a small \(B\) value \((1331.331\ \text{MHz})\) that six transitions with \(J''=9\) to 14 lie in the 26.5 to 40.0 GHz region.

From Figure 5.3 it is apparent that transition intensities are not equal and, from Table 5.1, that the transition spacings show a slight decrease as \(J''\) increases. We will now consider the reasons for these observations.

### 5.2.1.2 Intensities

Apart from depending on the numerical value of the square of the transition moment of Equation (5.13), which varies relatively little with \(J\), intensities depend on the population of the lower state of a transition. The population \(N_j\) of the \(J\)th level relative to \(N_0\) is obtained from Boltzmann's distribution law. Equation (2.11) gives

\[
\frac{N_j}{N_0} = (2J + 1) \exp \left( -\frac{E_j}{kT} \right)
\]  

\(5.15\)

<table>
<thead>
<tr>
<th>Frequency/GHz</th>
<th>40.0</th>
<th>38.0</th>
<th>36.0</th>
<th>34.0</th>
<th>32.0</th>
<th>30.0</th>
<th>28.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J=14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(J=13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(J=12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(J=11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(J=10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(J=9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Figure 5.4* Part of the microwave spectrum of cyanodiacetylene. (The many 'satellite' transitions in each group are due to the molecule being in not only the zero-point vibrational state but also a multitude of excited vibrational states.) (Reproduced, with permission, from Alexander, A. J., Kroto, H. W. and Walton, D. R. M., *J. Mol. Spectrosc.*, 62, 175, 1967)

\[
\text{where } (2J + 1) \exp \left( -\frac{E_j}{kT} \right)
\]  

for \(B\) having.

5.3 shows the importance.

### 5.2.1.3 Centre

The small\(s\) values, \(5.1.\) compared in Section 5.1, consequently in the bond is not the apparent as the small values given by centre. Originally Equation

\[
\text{where } \alpha
\]  

\[
\text{where } D
\]  

\[
\text{which gives}
\]  

\[
\text{for } B\text{ having.}
\]
where \((2J + 1)\) is the degeneracy of the \(J\)th level. This degeneracy arises from the fact that, in the absence of an electric or magnetic field, \((2J + 1)\) levels, resulting from the number of values that \(M_J\) (see Equation 1.61) can take, are all of the same energy: in other words they are degenerate. Values of \((2J + 1)\), \(\exp(-E_r/kT)\) and \(N_J/N_0\) are given for CO in Figure 5.2 and illustrate the point that there are two opposing factors in \(N_J/N_0\). The \((2J + 1)\) factor increases with \(J\) whereas the \(\exp(-E_r/kT)\) factor decreases rapidly, so that \(N_J/N_0\) increases at low \(J\) until, at higher \(J\), the exponential factor wins and \(N_J/N_0\) approaches zero. The population therefore shows a maximum at a value of \(J = J_{\text{max}}\) corresponding to

\[
\frac{d(N_J/N_0)}{dJ} = 0
\]

which gives

\[
J_{\text{max}} = \left(\frac{kT}{2hB}\right)^{1/2} - \frac{1}{2}
\]

for \(B\) having dimensions of frequency. Figure 5.2 shows that \(J_{\text{max}} = 7\) for CO. In fact, Figure 5.3 shows that the observed maximum intensity is at about \(J'' = 8\) because there are other, less important, factors that we have neglected.

5.2.1.3 Centrifugal distortion

The small decrease in transition spacings with increasing \(J\), as shown for example in Table 5.1, compared with the constant spacings we expected is due to our original approximation in Section 1.3.5 of treating the molecule as a rigid rotor being not quite valid. In fact the bond is not rigid but is more accurately represented by a spring connecting the nuclei, as was apparent when we considered vibrational motion in Section 1.3.6. So it is not surprising that, as the speed of rotation increases (i.e. as \(J\) increases), the nuclei tend to be thrown outwards by centrifugal forces. The spring stretches, \(r\) increases and, therefore, \(B\) decreases. Originally, this \(J\)-dependent decrease of \(B\) was included by changing the term values of Equations (5.11) and (5.12) to

\[
F(J) = B[1 - uJ(J + 1)]J(J + 1)
\]

where \(u\) is an additional constant, but it is usually written in the form

\[
F(J) = BJ(J + 1) - DJ^2(J + 1)^2
\]

where \(D\) is the centrifugal distortion constant and is always positive for diatomic molecules. The transition wavenumbers or frequencies are now modified from Equation (5.14) to

\[
\tilde{v} \ (\text{or} \ v) = F(J + 1) - F(J) = 2B(J + 1) - 4D(J + 1)^3
\]
The centrifugal distortion constant depends on the stiffness of the bond and it is not surprising that it can be related to the vibration wavenumber \( \omega \), in the harmonic approximation (see Section 1.3.6), by

\[
D = \frac{4B^3}{\omega^2} \tag{5.21}
\]

### 5.2.1.4 Diatomic molecules in excited vibrational states

There is a stack of rotational levels, with term values such as those given by Equation (5.19), associated with not only the zero-point vibrational level but also all the other vibrational levels shown, for example, in Figure 1.13. However, the Boltzmann equation (Equation 2.11), together with the vibrational energy level expression (Equation 1.69), gives the ratio of the population \( N_v \) of the \( v \)th vibrational level to \( N_0 \), that of the zero-point level, as

\[
\frac{N_v}{N_0} = \exp \left( -\frac{\hbar \omega v}{kT} \right) \tag{5.22}
\]

where \( \omega \) is the vibration wavenumber and \( v \) the vibrational quantum number. Since this ratio is, for example, only 0.10 for \( v = 1 \) and \( \omega = 470 \text{ cm}^{-1} \) we can see that rotational transitions in excited vibrational states are generally very weak unless either the molecule is particularly heavy, leading to a relatively small value of \( \omega \), or the temperature is high; however, the negative exponential nature of Equation (5.22) means that increasing the temperature has only quite a small effect on populations.

The rotational constants \( B \) and \( D \) are both slightly vibrationally dependent so that the term values of Equation (5.19) should be written

\[
F_v(J) = B_vJ(J + 1) - D_vJ^2(J + 1)^2 \tag{5.23}
\]

and Equation (5.20) becomes

\[
\tilde{v} \text{ (or } v) = 2B_v(J + 1) - 4D_v(J + 1)^3 \tag{5.24}
\]

The vibrational dependence of \( B \) is given, to a good approximation, by

\[
B_v = B_0 - \alpha(v + \frac{1}{2}) \tag{5.25}
\]

where \( B_0 \) refers to the hypothetical equilibrium state of the molecule at the bottom of the potential energy curve of Figure 1.13 and \( \alpha \) is a vibration–rotation interaction constant. In order to obtain \( B_0 \) and hence the equilibrium bond length \( r_0 \), \( B_1 \) must be obtained in at least two vibrational states. If there is insufficient population of the \( v = 1 \) level to obtain \( B_1 \) then rotational spectroscopy can give only \( B_0 \).
and it is not in the harmonic

(5.21)

Equation (5.19), another vibrational transition (Equation (5.18)) gives the ratio of the ground level, as

\[ \frac{\nu_{\text{upper}}}{\nu_{\text{lower}}} \]

Since this ratio is particularly small, the rotational transitions are not well resolved. However, the temperature has been raised so that the term contribution is significant.

(5.22)

(5.23)

(5.24)

(5.25)

The vibrational dependence of the centrifugal distortion constant \( D_v \) is too small to concern us further.

5.2 ROTATIONAL INFRARED, MILLIMETRE WAVE AND MICROWAVE SPECTRA

5.2.2 Symmetric rotor molecules

In a diatomic or linear polyatomic molecule the rotational angular momentum vector \( \mathbf{P} \) lies along the axis of rotation, as shown in Figure 5.5(a), which is analogous to Figure 1.5 for electronic orbital angular momentum. In a prolate symmetric rotor, such as methyl iodide, shown in Figure 5.5(b), \( \mathbf{P} \) need not be perpendicular to the \( a \) axis. In general, it takes up any direction in space and the molecule rotates around \( \mathbf{P} \). The component of \( \mathbf{P} \) along the \( a \) axis is \( P_a \) which can take only the values \( K \alpha \), where \( K \) is a second rotational quantum number. The rotational term values are given by

\[ F(J, K) = BJ(J + 1) + (A - B)K^2 \]  

(5.26)

neglecting centrifugal distortion and the vibrational dependence of the rotational constants \( A \) and \( B \). These constants are related to \( I_a \) and \( I_b \) by

\[ A = \frac{h}{8\pi^2 I_a}, \quad B = \frac{h}{8\pi^2 I_b} \]  

(5.27)

when they have dimensions of frequency. The quantum number \( K \) may take values \( K = 0, 1, 2, \ldots, J \). The fact that \( K \) cannot be greater than \( J \) follows from the fact that \( P_a \) cannot be greater than the magnitude of \( \mathbf{P} \). All levels with \( K > 0 \) are doubly degenerate which can be thought of, classically, as being due to the clockwise or anticlockwise rotation about the \( a \) axis resulting in the same angular momentum. For \( K = 0 \) there is no angular momentum about the \( a \) axis and, therefore, no \( K \)-degeneracy.

For an oblate symmetric rotor, such as \( \text{NH}_3 \), the rotational term values are given by

\[ F(J, K) = BJ(J + 1) + (C - B)K^2 \]  

(5.28)

\[ (a) \quad (b) \]

\[ \text{Figure 5.5} \quad \text{The rotational angular momentum vector } \mathbf{P} \text{ for (a) a linear molecule and (b) the prolate symmetric rotor CH}_3\text{I where } P_a \text{ is the component along the } a \text{ axis} \]
analogous to Equation (5.26), where
\[
C = \frac{\hbar}{8\pi^2 I_c} \quad (5.29)
\]
when it has dimensions of frequency.

The rotational energy levels for a prolate and an oblate symmetric rotor are shown schematically in Figure 5.6. Although these present a much more complex picture than those for a linear molecule the fact that the selection rules
\[
\Delta J = \pm 1; \quad \Delta K = 0 \quad (5.30)
\]
include \(\Delta K = 0\) results in the expression for the transition frequencies or wavenumbers
\[
\nu \text{ (or } \tilde{\nu}) = F(J + 1, K) - F(J, K) = 2B(J + 1) \quad (5.31)
\]
This is the same as Equation (5.14) for a diatomic or linear polyatomic molecule and, again, the transitions show an equal spacing of 2B. The requirement that the molecule must have a permanent dipole moment applies to symmetric rotors also.

When the effects of centrifugal distortion are included the term values of a prolate symmetric rotor are given by
\[
F(J, K) = BJ(J + 1) + (A - B)K^2 - D_JJ^2(J + 1)^2 - D_KJ(J + 1)K^2 - D_KK^4 \quad (5.32)
\]
where there are now three centrifugal distortion constants $D_J$, $D_{JK}$ and $D_K$. There is an analogous equation for an oblate symmetric rotor and, for both types, the transition frequencies or wavenumbers are given by

$$v \text{ (or } v') = F(J + 1, K) - F(J, K) = 2(B_e - D_{JK}K^2)(J + 1) - 4D_J(J + 1)^3 \quad (5.33)$$

The term $-2D_{JK}K^2(J + 1)$ has the effect of separating the $(J + 1) \leftrightarrow J$ transition with different values of $K$. This is illustrated in Figure 5.7, which shows the eight components of the $J = 8 - 7$ transition of silyl isothiocyanate ($\text{H}_3\text{Si}-\text{N}=\text{C}=-\text{S}$), which has a linear SiNCS chain and is a prolate symmetric rotor.

5.2.3 Stark effect in diatomic, linear and symmetric rotor molecules

As we saw in Equation (1.61), space quantization of rotational angular momentum of a diatomic or linear polyatomic molecule is expressed by

$$(P_J)_z = M_J \hbar \quad (5.34)$$

where $M_J = J, J - 1, \ldots, -J$. Under normal conditions these $(2J + 1)$ components of each $J$ level remain degenerate but, in the presence of an electric field $\mathbf{E}$, the degeneracy is partly removed: each level is split into $(J + 1)$ components according to the value of $|M_J| = 0, 1, 2, \ldots, J$. This splitting in an electric field is known as the Stark effect and is small in a linear molecule. The energy levels $E_r$ of Equation (5.10) are modified to $E_r + E_\mathbf{E}$, where

$$E_\mathbf{E} = \frac{\mu^2 \mathbf{E}^2 [J(J + 1) - 3M_J^2]}{2\hbar BJ(J + 1)(2J - 1)(2J + 3)} \quad (5.35)$$

![Figure 5.7](image-url) Eight components, with $K = 0$ to 7 and separated by centrifugal distortion, of the $J = 8 - 7$ microwave transition of SiH$_3$NCS.
In this rather formidable equation there are two points to notice:

1. It involves $M_J^2$, and therefore the energy is independent of the sign of $M_J$.
2. It involves the molecular dipole moment.

Because of point 2, rotational microwave and millimetre wave spectroscopy are powerful techniques for determining dipole moments. However, the direction of the dipole moment cannot be determined. In the case of $\text{O=CO=S}$, for which $\mu = 0.715 \pm 0.0002 \text{D} [(2.3857 \pm 0.0007) \times 10^{-30} \text{C m}]$, a simple electronegativity argument leads to the correct conclusion — that the oxygen end of the molecule is the negative end of the dipole. However, in $\text{CO}$, the value of $0.112 \text{D} (3.74 \times 10^{-31} \text{C m})$ is so small that only accurate electronic structure calculations can be relied upon to conclude correctly that the carbon end is the negative one.

For a symmetric rotor the modification $E_\delta$ to the rotational energy levels in an electric field $\delta$ is larger than in a linear molecule and is given, approximately, by

$$E_\delta \simeq -\frac{\mu \delta K M_J}{J(J+1)}$$

(5.36)

Using the Stark effect, the dipole moment of, for example, $\text{CH}_3\text{F}$ has been found to be $1.857 \pm 0.001 \text{D} [(6.194 \pm 0.004) \times 10^{-30} \text{C m}]$.

### 5.2.4 Asymmetric rotor molecules

Although these molecules form much the largest group we shall take up the smallest space in considering their rotational spectra. The reason for this is that there are no closed formulae for their rotational term values. Instead, these term values can be determined accurately only by a matrix diagonalization for each value of $J$, which remains a good quantum number. The selection rule $\Delta J = 0, \pm 1$ applies and the molecule must have a permanent dipole moment.

At a simple level, the rotational transitions of near-symmetric rotors (see Equations 5.8 and 5.9) are easier to understand. For a prolate or oblate near-symmetric rotor the rotational term values are given, approximately, by

$$F(J, K) \approx \tilde{B}J(J+1) + (A - \tilde{B})K^2$$

(5.37)

and

$$F(J, K) \approx \tilde{B}J(J+1) + (C - \tilde{B})K^2$$

(5.38)

respectively, where $\tilde{B}$ is equal to $\frac{1}{3}(B + C)$ for a prolate rotor and $\frac{1}{3}(A + B)$ for an oblate rotor. Centrifugal distortion has been neglected. Because the molecules concerned are only approximately symmetric rotors $K$ is not strictly a good quantum number (i.e. does not take integral values).
Examples of prolate near-symmetric rotors are the \( s\text{-}trans \) and \( s\text{-}cis \) isomers of crotonic acid, shown in Figure 5.8, the \( a \) axis straddling a chain of the heavier atoms in both species. The rotational term values for both isomers are given approximately by Equation (5.37) but, because \( A \) and \( B \) are different for each of them, their rotational transitions are not quite coincident. Figure 5.9 shows a part of a low-resolution microwave spectrum of crotonic acid in which the weaker series of lines is due to the less abundant \( s\text{-}cis \) isomer and the stronger series is due to the more abundant \( s\text{-}trans \) isomer.

Dipole moments of asymmetric rotors or, strictly, their components along the various inertial axes, may be determined using the Stark effect.

5.2.5 Spherical rotor molecules

We tend to think of a spherical rotor molecule, such as methane (see Figure 4.12a), as having no permanent dipole moment and, therefore, no infrared, millimetre wave or microwave

![Figure 5.8](image) The \( s\text{-}trans \) and \( s\text{-}cis \) isomers of crotonic acid

![Figure 5.9](image) Part of the microwave spectrum of crotonic acid. (Reproduced, with permission, from Scharpen, L. H. and Laurie, V. W., *Analyt. Chem.*, 44, 378R, 1972. Copyright 1972 American Chemical Society)
rotational spectra. However, rotation about any of the $C_3$ axes (i.e. any of the four axes in methane containing a C–H bond) results in a centrifugal distortion in which the other three hydrogen atoms are thrown outwards slightly from the axis. This converts the molecule into a symmetric rotor and gives it a small dipole moment resulting in a very weak rotational spectrum.

Part of the far-infrared rotational spectrum of silane ($\text{SiH}_4$) is shown in Figure 5.10. It was obtained by using a Michelson interferometer (see Section 3.3.3.2), an absorbing path of 10.6 m and a pressure of 4.03 atm ($4.08 \times 10^5$ Pa), these conditions indicating how very weak the spectrum is. The dipole moment has been estimated from the intensities of the transitions to be $8.3 \times 10^{-6} \text{ D} (2.7 \times 10^{-35} \text{ C m})$.

Neglecting centrifugal distortion, the rotation term values for a spherical rotor are given by

$$F(J) = BJ(J + 1)$$

(5.39)

This is an identical expression to that for a diatomic or linear polyatomic molecule (Equations 5.11 and 5.12) and, as the rotational selection rule is the same, namely, $\Delta J = \pm 1$, the transition wavenumbers or frequencies are given by

$$v \ (\text{or} \ \tilde{v}) = F(J + 1) - F(J) = 2BJ(J + 1)$$

(5.40)

and adjacent transitions are separated by $2B$.

All regular tetrahedral molecules, which belong to the $T_d$ point group (Section 4.2.8), may show such a rotational spectrum. However, those spherical rotors that are regular octahedral molecules and that belong to the $O_h$ point group (Section 4.2.9) do not show any such spectrum.
5.2 ROTATIONAL INFRARED, MILLIMETRE WAVE AND MICROWAVE SPECTRA

5.2.6 Interstellar molecules detected by their radiofrequency, microwave or millimetre wave spectra

Radiotelescopes are used to scan the universe for radiation in the radiofrequency region of the spectrum (see Figure 3.1). As illustrated in Figure 5.11 such a telescope consists of a parabolic reflecting dish which focuses all parallel rays reaching it onto a radiofrequency detector supported at the focus of the paraboloid. The surface of such a dish must be constructed accurately but only sufficiently so that the irregularities are small compared with the wavelength of the radiation, which is of the order of 0.5 m.

One of the uses of such a telescope is in detecting atomic hydrogen, which is found in large quantities, but with varying density, throughout the universe and which has an emission line with a wavelength of 21 cm. The emission occurs between closely spaced sublevels into which the \( n = 1 \) level (see Figure 7.8) is split. In 1963 the first molecule, OH, was detected with such a telescope. A transition with a wavelength of about 18 cm was observed in absorption and is electronic in character: it is a transition between components of \( A \)-doublets which are due to the ground electronic state being \( ^2\Pi \) and split into two components (see Section 7.2.6.2).

Both emission and absorption processes rely on the background radiation, which is present throughout the universe and which has a wavelength distribution characteristic of a black body and a temperature of about 2.7 K. This radiation is a consequence of the 'big bang' with which the universe supposedly started its life.

Since 1963 spectra of many molecules have been detected, mainly in emission but some in absorption. Telescopes have been constructed with more accurately engineered paraboloids in order to extend observations into the microwave and millimetre wave regions.

The regions of space where molecules have been detected are the nebulae which are found not only in our own galaxy but also in other galaxies. In our galaxy the nebulae are found in the Milky Way, which appears as a hazy band of light as a result of its containing millions of stars. Associated with the luminous clouds composing the nebulae are dark clouds of spectrum. The reason for this is that when, for example, SF\(_6\) (see Figure 5.1e) rotates about a \( C_4 \) axis (any of the F–S–F axes) no dipole moment is produced when the other four fluorine atoms are thrown outwards.
interstellar dust and gas. The presence of the dust particles is indicated by the fact that visible starlight passing through such a cloud is reddened as a result of preferential scattering, which is proportional to $\lambda^{-4}$, of the blue light by the dust particles. The nature of the dust particles is not known but they are about 0.2 $\mu$m in diameter. Since new stars are formed by gravitational collapse in the region of the nebulae, which must contain the raw material from which the new stars are formed, the detection of molecules in these regions is of the greatest importance. Molecules have been detected in several nebulae but the large cloud known as Sagittarius B2, which is close to the centre of our galaxy, has proved a particularly fruitful source.

The first polyatomic molecule was detected in 1968 with use of a telescope having a dish 6.3 m in diameter at Hat Creek, California, USA, designed to operate in the millimetre wave region. Emission lines were found in the 1.25 cm wavelength region due to NH$_3$. The transitions are not rotational but are between the very closely spaced $v_2 = 0$ and $v_2 = 1$ levels of the inversion vibration $v_2$ (see Section 6.2.5.4).

Table 5.2 lists some of the molecules which have been detected. It is interesting to note that some of them, such as the linear triatomics C$_2$H, HCO$^+$ and N$_2$H$^+$, were found in the interstellar medium before they were searched for and found in the laboratory. In all molecules, except OH and NH$_3$, the transitions observed are rotational in nature.

Identification of a molecule known in the laboratory is usually unambiguous because of the uniqueness of the highly precise transition frequencies. However, before frequencies detected in the interstellar medium can be compared with laboratory frequencies they must be corrected for the Doppler effect (see Section 2.3.2) due to the motion of the clouds. In Sagittarius B2 the molecules are found to be travelling fairly uniformly with a velocity of 60 km s$^{-1}$.

Table 5.2 Some interstellar molecules detected by their radiofrequency or millimetre wave spectra

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diatomics</strong></td>
<td>OH, CO, CN, CS, SiO, SO, SiS, NO, NS, CH, CH$^+$, SiC, NH, CP, HCl, CO$^+$, SO$^+$</td>
</tr>
<tr>
<td><strong>Triatomics</strong></td>
<td>H$_2$O, HCN, HNC, OCS, H$_2$S, N$_2$H$^+$, SO$_2$, HNO, C$_2$H, HCO, HCO$^+$, HCS$^+$, H$_2$D$^+$</td>
</tr>
<tr>
<td><strong>Tetramotis</strong></td>
<td>NH$_3$, H$_2$CO, HNCO, H$_2$CS, HNCS, N=C-C≡C, H$_2$O$^+$, C$_3$H (linear), C$_3$H (cyclic)</td>
</tr>
<tr>
<td><strong>5-Atomics</strong></td>
<td>N≡C-C≡C-H, HCOOH, CH$_3$NH, H–C≡C–C≡C, NH$_2$CN, C$_2$H$_2$ (linear), C$_3$H$_2$ (cyclic)</td>
</tr>
<tr>
<td><strong>6-Atomics</strong></td>
<td>CH$_3$OH, CH$_3$CN, NH$_2$CHO, CH$_3$SH, CH$_3$NC, HC$_2$CHO, H$_3$CNH$^+$, C$_4$H</td>
</tr>
<tr>
<td><strong>7-Atomics</strong></td>
<td>CH$_3$–C≡C–H, CH$_3$CHO, CH$_3$NH$_2$, CH$_2$=CHCN, N≡C–C≡C–C≡C–H, C$_6$H</td>
</tr>
<tr>
<td><strong>8-Atomics</strong></td>
<td>HCOOCH$_3$, CH$_3$–C≡C–C≡N</td>
</tr>
<tr>
<td><strong>9-Atomics</strong></td>
<td>CH$_3$OCH$_3$, CH$_3$CH$_2$OH, N≡C–C≡C–C≡C–C≡C–H, CH$_3$CH$_2$CN, CH$_3$C$_2$H</td>
</tr>
<tr>
<td><strong>11-Atomics</strong></td>
<td>N≡C–C≡C–C≡C–C≡C–C≡C–H</td>
</tr>
<tr>
<td><strong>13-Atomics</strong></td>
<td>N≡C–C≡C–C≡C–C≡C–C≡C–C≡C–H</td>
</tr>
</tbody>
</table>
5.2 ROTATIONAL INFRARED, MILLIMETRE WAVE AND MICROWAVE SPECTRA

Figure 5.12. The \( J = 1 \rightarrow 0 \) transition of cyanodiacetylene observed in emission in Sagittarius B2. (Reproduced, with permission, from Broton, N. W., MacLeod, J. M., Oka, T., Avery, L. W., Brooks, J. W., McGee, R. X. and Newton, L. M., Astrophys. J., 209, L143, 1976, published by the University of Chicago Press; © 1976 The American Astronomical Society)

60 km s\(^{-1}\) relative to a local standard of rest, which is taken to be certain stars close to the sun. In other clouds, there is a wider range of molecule velocities.

Figure 5.12 shows the \( J = 1 \rightarrow 0 \) transition of the linear molecule cyanodiacetylene (\( H-C\equiv C-C\equiv C-C\equiv N \)) observed in emission in Sagittarius B2 (Figure 5.4 shows part of the absorption spectrum in the laboratory). The three hyperfine components into which the transition is split are due to interaction between the rotational angular momentum and the nuclear spin of the \( ^{14}N \) nucleus for which \( I = 1 \) (see Table 1.3). The vertical scale is a measure of the change of the temperature of the antenna due to the received signal.

Table 5.2 shows that quite large molecules, of which the cyanopolyacetylenes form a remarkable group, have been detected. The presence of such sizeable molecules in the interstellar medium came as a considerable surprise. Previously, it was supposed that the ultraviolet radiation present throughout all galaxies would photodecompose most of the molecules, and particularly the larger ones. It seems likely that the dust particles play an important part not only in the formation of the molecules but also in preventing their decomposition.

In considering the molecules in Table 5.2 it should be remembered that the method of detection filters out any molecules with zero dipole moment. There is known to be large quantities of \( H_2 \) and, no doubt, there are such molecules as \( C_2 \), \( N_2 \), \( O_2 \), \( H-C\equiv C\equiv H \) and polyacetylenes to be found in the clouds, but these escape detection by radiofrequency, millimetre wave or microwave spectroscopy.
5.3 Rotational Raman spectroscopy

When electromagnetic radiation falls on an atomic or molecular sample it may be absorbed if the energy of the radiation corresponds to the separation of two energy levels of the atoms or molecules. If it does not, the radiation will be either transmitted or scattered by the sample. Of the scattered radiation most is of unchanged wavelength $\lambda$ and is the Rayleigh scattering. It was Lord Rayleigh in 1871 who showed that the intensity $I_s$ of scattered light is related to $\lambda$ by

$$I_s \propto \lambda^{-4}$$

(5.41)

For this reason blue radiation from the sun is scattered preferentially by particles in the atmosphere and the result is that a cloudless sky appears blue.

It was predicted in 1923 by Smekal and shown experimentally in 1928 by Raman and Krishnan that a small amount of radiation scattered by a gas, liquid or solid is of increased or decreased wavelength (or wavenumber). This is called the Raman effect and the scattered radiation with decreased or increased wavenumber is referred to as Stokes or anti-Stokes Raman scattering, respectively.

5.3.1 Experimental methods

The incident radiation should be highly monochromatic for the Raman effect to be observed clearly and, because Raman scattering is so weak, it should be very intense. This is particularly important when, as in rotational Raman spectroscopy, the sample is in the gas phase.

In outline, the method used is to pass the monochromatic radiation through the gaseous sample and disperse and detect the scattered radiation. Usually, this radiation is collected in directions normal to the incident radiation in order to avoid this incident radiation passing to the detector.

Until the advent of lasers the most intense monochromatic sources available were atomic emission sources from which an intense, discrete line in the visible or near-ultraviolet region was isolated by optical filtering if necessary. The most often used source of this kind was the mercury discharge lamp operating at the vapour pressure of mercury. Three of the most intense lines are at 253.7 nm (near-ultraviolet), 404.7 nm and 435.7 nm (both in the visible region). Although the line width is typically small the narrowest has a width of about 0.2 cm$^{-1}$, which places a limit on the resolution which can be achieved.

Lasers (see Chapter 9) are sources of intense, monochromatic radiation which are ideal for Raman spectroscopy and have entirely replaced atomic emission sources. They are more convenient to use, have higher intensity and are more highly monochromatic: for example, the line width at half-intensity of 632.8 nm (red) radiation from a helium–neon laser can be less than 0.05 cm$^{-1}$.

Figure 5.13 shows a typical experimental arrangement for obtaining the Raman spectrum of a gaseous sample. Radiation from the laser source is focused by the lens $L_1$ into a cell containing the sample gas. The mirror $M_1$ reflects this radiation back into the cell to increase the amount reaching it.
123 elements of the atoms scattered by the scattered light is

\[
(5.41)
\]

particles in the by Raman and of increased or the scattered or anti-Stokes to be observed intense. This is in the gas though the gaseous is collected in passing to were atomic region is kind was the of the most in the visible width of about are ideal for they are more for example, laser can be an spectrum into a cell to increase the amount of Raman scattering by the sample. Lens L_2 collects the Raman scattering reaching it directly, and also that reflected by mirror M_2, then directs and focuses it into a spectrometer where it is dispersed and detected.

Until the mid 1970s only lasers operating in the visible region of the spectrum, such as the helium–neon laser (Section 9.2.5) at 632.8 nm, and the argon ion laser (Section 9.2.6) at 514.5 nm, were used as sources of monochromatic radiation for Raman spectroscopy. However, many molecules are coloured and therefore absorb and fluoresce in the visible region. This fluorescence tends to mask the much weaker Raman scattering, thereby excluding many molecules from investigation by the Raman effect. Raman spectra are obtained, very often, with the sample in the liquid or solid phase when even a small amount of coloured impurity may produce sufficient fluorescence to interfere with the very weak Raman scattering of the main component of the sample.

Use of a laser operating in the infrared overcomes the problem of fluorescence, which normally occurs following the absorption of only visible or ultraviolet radiation (see Section 7.2.5.2). However, with an ordinary spectrometer having a diffraction grating as the dispersing element, the advantage of using an infrared laser is more than counteracted by the fact that the intensity of Raman scattering decreases as the fourth power of the wavelength, as Equation (5.41) indicates, making detection extremely difficult.

It was not until the development of Fourier transform infrared (FTIR) spectrometers (see Section 3.3.3.2) that the possibility of using an infrared laser routinely was opened up. The intensity advantage of an infrared interferometer, with which a single spectrum can be obtained very rapidly and then many spectra co-added, coupled with the development of more sensitive Ge and InGaAs semiconductor infrared detectors, more than compensate for the loss of scattering intensity in the infrared region.

The infrared laser which is most often used in this technique of Fourier transform Raman, or FT–Raman, spectroscopy is the Nd–YAG laser (see Section 9.2.3) operating at a wavelength of 1064 nm.
5.3.2 Theory of rotational Raman scattering

Electronic, vibrational and rotational transitions may be involved in Raman scattering but, in this chapter, we consider only rotational transitions.

The property of the sample which determines the degree of scattering when subjected to the incident radiation is the polarizability \( \alpha \). The polarizability is a measure of the degree to which the electrons in the molecule can be displaced relative to the nuclei. In general, the polarizability of a molecule is an anisotropic property, which means that, at equal distances from the centre of the molecule, \( \alpha \) may have different magnitudes when measured in different directions. A surface drawn so that the distance from the origin to a point on the surface has a length \( \alpha^{1/2} \), where \( \alpha \) is the polarizability in that direction, forms an ellipsoid. In general, this has elliptical cross-sections in the \( xy \) and \( yz \) planes, as shown in Figure 5.14, and the lengths of the axes in the \( x \), \( y \) and \( z \) directions are unequal. Like other anisotropic properties, such as the moment of inertia of a molecule (Section 5.1) and the electrical conductivity of a crystal, polarizability is a tensor property. The tensor can be expressed in the form of a matrix:

\[
\alpha = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\]  
(5.42)

where the \( \alpha_{ij} \) are the diagonal elements of the tensor.

where the \( \alpha_{ij} \) are the diagonal elements of the tensor.

where the \( \alpha_{ij} \) are the diagonal elements of the tensor.

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where the \( \alpha_{ij} \) are the diagonal elements of the tensor.

where the \( \alpha_{ij} \) are the diagonal elements of the tensor.

Figure 5.14 The polarizability ellipsoid
5.3 ROTATIONAL RAMAN SPECTROSCOPY

where the diagonal elements $\alpha_{xx}$, $\alpha_{yy}$ and $\alpha_{zz}$ are the values of $\alpha$ along the $x$, $y$ and $z$ axes of the molecule. The matrix is symmetrical in the sense that $\alpha_{xy} = \alpha_{yx}$, $\alpha_{xz} = \alpha_{zx}$, and $\alpha_{yz} = \alpha_{zy}$ so that there are, in general, six different components of $\alpha$, namely $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xy}$, $\alpha_{xz}$ and $\alpha_{yz}$. Each of these can be assigned to one of the symmetry species of the point group to which the molecule belongs. These assignments are indicated in the right-hand column of each character table given in Appendix A and will be required when we consider vibrational Raman spectra in Section 6.2.3.2.

When monochromatic radiation falls on a molecular sample in the gas phase, and is not absorbed by it, the oscillating electric field $E$ (see Equation 2.1) of the radiation induces in the molecule an electric dipole $\mu$ which is related to $E$ by the polarizability

$$\mu = aE$$

(5.43)

where $\mu$ and $E$ are vector quantities. The magnitude $E$ of the vector can be written

$$E = A \sin 2\pi \tilde{v} t$$

(5.44)

where $A$ is the amplitude and $\tilde{v}$ the wavenumber of the monochromatic radiation. The magnitude of the polarizability varies during rotation and a simple classical treatment will serve to illustrate the rotational Raman effect.

The polarizability ellipsoid rotates with the molecule at a frequency $\nu_{\text{rot}}$, say, and the radiation 'sees' the polarizability changing at twice the frequency of rotation since, as can be seen from Figure 5.14, the ellipsoid appears the same for a rotation by $\pi$ radians about any of the cartesian axes. The variation of $\alpha$ with rotation is given by

$$\alpha = \alpha_{0,r} + \alpha_{1,r} \sin 2\pi c(2\tilde{v}_{\text{rot}}) t$$

(5.45)

where $\alpha_{0,r}$ is the average polarizability and $\alpha_{1,r}$ is the amplitude of the change of polarizability during rotation. Substitution of Equations (5.45) and (5.44) into Equation (5.43) gives the magnitude of the induced dipole moment as

$$\mu = \alpha_{0,r} A \sin 2\pi \tilde{v} t - \frac{1}{2} \alpha_{1,r} A \cos 2\pi c(\tilde{v} + 2\tilde{v}_{\text{rot}}) t$$

$$+ \frac{1}{2} \alpha_{1,r} A \cos 2\pi c(\tilde{v} - 2\tilde{v}_{\text{rot}}) t$$

(5.46)

All three terms in this equation represent scattering of the radiation. The first term corresponds to Rayleigh scattering of unchanged wavenumber $\tilde{v}$, and the second and third terms correspond to anti-Stokes and Stokes Raman scattering, with wavenumbers of $(\tilde{v} + 2\tilde{v}_{\text{rot}})$ and $(\tilde{v} - 2\tilde{v}_{\text{rot}})$ respectively.

Although in a classical system $\tilde{v}_{\text{rot}}$ can take any value, in a quantum mechanical system it can take only certain values, and we shall now see what these are for diatomic and linear polyatomic molecules.
5.3.3 Rotational Raman spectra of diatomic and linear polyatomic molecules

In a diatomic or linear polyatomic molecule rotational Raman scattering obeys the selection rule

\[ \Delta J = 0, \pm 2 \]  \hspace{1cm} (5.47)

but the \( \Delta J = 0 \) transitions are unimportant as they correspond to the intense Rayleigh scattering. In addition, the molecule must have an anisotropic polarizability, which means that \( \alpha \) must not be the same in all directions. This is not a very stringent requirement since all molecules except spherical rotors, whose polarizability is in the form of a sphere, have this property. As a result all diatomics and linear polyatomics, whether or not they have an inversion centre \( i \), show a rotational Raman spectrum.

The resulting spectrum is illustrated in Figure 5.15, and Figure 5.16 shows in detail the processes involved in the first Stokes and anti-Stokes transitions and in the Rayleigh scattering.

Molecules initially in the \( J = 0 \) state encounter intense, monochromatic radiation of wavenumber \( \tilde{\nu} \). Provided the energy \( h \tilde{\nu} \) does not correspond to the difference in energy between \( J = 0 \) and any other state (electronic, vibrational or rotational) of the molecule it is not absorbed but produces an induced dipole in the molecule, as expressed by Equation (5.43). The molecule is said to be in a virtual state which, in the case shown in Figure 5.16, is \( V_0 \). When scattering occurs the molecule may return, according to the selection rules, to \( J = 0 \) (Rayleigh) or \( J = 2 \) (Stokes). Similarly a molecule initially in the \( J = 2 \) state goes to...

---

**Figure 5.15** Rotational Raman spectrum of a diatomic or linear polyatomic molecule

The energy difference \( \Delta \tilde{\nu} \) must equal \( \hbar \Delta \omega \) for the transition to occur.

The molecule is said to be in a virtual state which, in the case shown in Figure 5.16, is \( V_0 \). When scattering occurs the molecule may return, according to the selection rules, to \( J = 0 \) (Rayleigh) or \( J = 2 \) (Stokes). Similarly a molecule initially in the \( J = 2 \) state goes to...

---

**Figure 5.16** Processes involved in the first Stokes and anti-Stokes transitions and in the Rayleigh scattering.

The energy difference \( \Delta \tilde{\nu} \) must equal \( \hbar \Delta \omega \) for the transition to occur.

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5.3 Rotational Raman Spectroscopy

Molecules

Eyes the selection

(5.47)

Intense Rayleigh. which means

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Figure 5.16, selection rules, to

= 2 state goes to

the virtual state \( V_1 \) and returns to \( J = 2 \) (Rayleigh), \( J = 4 \) (Stokes) or \( J = 0 \) (anti-Stokes).

The overall transitions, \( J = 2 \) to 0, and \( J = 0 \) to 2, are indicated by solid lines in Figure 5.16, and Figure 5.15 shows more of these overall transitions.

Conventionally, we take \( \Delta J \) to mean \( J \) (upper) \(- J \) (lower) so we need consider only \( \Delta J = +2 \). The magnitude of a Raman displacement from the exciting radiation \( \nu \) is given by

\[
|\Delta \nu| = F(J + 2) - F(J)
\]

(5.48)

where \( \Delta \nu = \nu - \nu_L \) (\( \nu_L \) is the wavenumber of the exciting laser radiation) is positive for anti-Stokes and negative for Stokes lines. When centrifugal distortion is neglected the rotational term values \( F(J) \) are given by Equation (5.12), and Equation (5.48) gives

\[
|\Delta \nu| = 4B_0J + 6B_0
\]

(5.49)

for molecules in the zero-point vibrational state. The spectrum shows two sets of equally spaced lines with a spacing of \( 4B_0 \) and a separation of \( 12B_0 \) between the first Stokes and anti-Stokes lines.

When centrifugal distortion is taken into account the rotational term values are given by Equation (5.19) and we have

\[
|\Delta \nu| = (4B_0 - 6D_0)(J + \frac{3}{2}) - 8D_0(J + \frac{3}{2})^3
\]

(5.50)

Series of rotational transitions are referred to as branches and they are labelled with a letter according to the value of \( \Delta J \) as follows:

\[
\begin{align*}
\Delta J &= \ldots -2, -1, 0, +1, +2, \ldots \\
\text{Branch} &= \ldots O, P, Q, R, S, \ldots
\end{align*}
\]

(5.51)
so that the branches in Figure 5.15 are both $S$ branches (although some authors refer to the anti-Stokes $S$ branch as an $O$ branch).

The intensities along the branches show a maximum because the populations of the initial levels of the transitions, given by Equation (5.15), also rise to a maximum.

Figure 5.17 shows the rotational Raman spectrum of $^{15}$N$_2$ obtained with 476.5 nm radiation from an argon ion laser. From this spectrum a very accurate value for $B_0$ of $1.857672 \pm 0.000027$ cm$^{-1}$ has been obtained from which a value for the bond length $r_0$ of $1.099985 \pm 0.000010$ Å results. Such accuracy is typical of high-resolution rotational Raman spectroscopy.

A feature of the $^{15}$N$_2$ spectrum is an intensity alternation of $1:3$ for the $J$ value of the initial level of the transition even: odd. This is an effect due to the nuclear spin of the $^{15}$N nuclei, which will now be discussed in some detail.

### 5.3.4 Nuclear spin statistical weights

When nuclear spin is included the total wave function $\psi$ for a molecule is modified from that of Equation (1.58) to

$$\psi = \psi_s \psi_e \psi_{ns}$$  \hspace{1cm} (5.52)
where $\psi_e$, $\psi_v$, and $\psi_r$ are the electronic, vibrational and rotational wave functions, respectively, and $\psi_{ns}$ is the nuclear spin wave function. We shall be concerned here mainly with the symmetry properties of $\psi_{ns}$ and $\psi_r$.

For a symmetrical ($D_{\infty h}$) diatomic or linear polyatomic molecule with two, or any even number, of identical nuclei having the nuclear spin quantum number (see Equation 1.47) $I = n + \frac{1}{2}$, where $n$ is zero or an integer, exchange of any two which are equidistant from the centre of the molecule results in a change of sign of $\psi$, which is then said to be antisymmetric to nuclear exchange. In addition the nuclei are said to be Fermi particles (or fermions) and obey Fermi–Dirac statistics. However, if $I = n$, $\psi$ is symmetric to nuclear exchange and the nuclei are said to be Bose particles (or bosons) and obey Bose–Einstein statistics.

We will now consider the consequences of these rules in the simple case of $^1\text{H}_2$. In this molecule both $\psi_v$, whatever the value of $v$, and $\psi_e$, in the ground electronic state, are symmetric to nuclear exchange: so we need consider only the behaviour of $\psi_r\psi_{ns}$. Since $I = \frac{1}{2}$ for $^1\text{H}_2$, $\psi$ and therefore $\psi_r\psi_{ns}$ must be antisymmetric to nuclear exchange. It can be shown that, for even values of the rotational quantum number $J$, $\psi_r$ is symmetric (s) to exchange and, for odd values of $J$, $\psi_r$ is antisymmetric (a) to exchange, as shown in Figure 5.18.

Equation (1.48) shows that, for $I = \frac{1}{2}$, space quantization of nuclear spin angular momentum results in the quantum number $M_f$ taking the values $\frac{1}{2}$ or $-\frac{1}{2}$. The nuclear spin wave function $\psi_{ns}$ is usually written as $\alpha$ or $\beta$, corresponding to $M_f$ equal to $\frac{1}{2}$ or $-\frac{1}{2}$.

![Figure 5.18](image)

Figure 5.18 Nuclear spin statistical weights (ns stat wts) of rotational states of various diatomic molecules; $a$, antisymmetric; $s$, symmetric; $o$, ortho; $p$, para; $\psi_r$, $\psi_{ns}$ and $\psi_e$, rotational, nuclear spin and electronic wave functions, respectively.
respectively, and both $^1$H nuclei, labelled 1 and 2, can have either $\alpha$ or $\beta$ spin wave functions. There are therefore four possible forms of $\psi_{ns}$ for the molecule as a whole:

$$\psi_{ns} = \alpha(1)\alpha(2); \beta(1)\beta(2); \alpha(1)\beta(2); \text{ or } \beta(1)\alpha(2) \quad (5.53)$$

Although the $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ wave functions are clearly symmetric to interchange of the 1 and 2 labels, the other two functions are neither symmetric nor antisymmetric. For this reason it is necessary to use instead the linear combinations $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ and $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$, where $2^{-1/2}$ is a normalization constant. Then three of the four nuclear spin wave functions are seen to be symmetric (s) to nuclear exchange and one is antisymmetric (a):

$$\psi_{ns} = \begin{cases} 
\alpha(1)\alpha(2) \\
2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
\beta(1)\beta(2) \\
2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]
\end{cases} \quad (5.54)$$

$$\psi_{ns} = \begin{cases} 
\alpha(1)\alpha(2) \\
2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
\beta(1)\beta(2) \\
2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]
\end{cases} \quad (5.55)$$

In general, for a homonuclear diatomic molecule there are $(2I+1)(I+1)$ symmetric and $(2I+1)I$ antisymmetric nuclear spin wave functions; therefore

$$\frac{\text{Number of (s) functions}}{\text{Number of (a) functions}} = \frac{I + 1}{I} \quad (5.56)$$

In order that $\psi_{ns}$ is always antisymmetric for $^1$H$_2$ the antisymmetric $\psi_{ns}$ are associated with even $J$ states and the symmetric $\psi_{ns}$ with odd $J$ states, as shown in Figure 5.18. Interchange between states with $\psi_{ns}$ symmetric and antisymmetric is forbidden so that $^1$H$_2$ can be regarded as consisting of two distinct forms:

1. para-hydrogen with $\psi_{ns}$ antisymmetric and with what is commonly referred to as antiparallel nuclear spins;
2. ortho-hydrogen with $\psi_{ns}$ symmetric and parallel nuclear spins.

As indicated in Figure 5.18, para-$^1$H$_2$ can exist in only even $J$ states and ortho-$^1$H$_2$ in odd $J$ states. At temperatures at which there is appreciable population up to fairly high values of $J$ there is roughly three times as much ortho- as there is para-$^1$H$_2$. However, at very low temperatures at which the population of all rotational levels other than $J=0$ is small $^1$H$_2$ is mostly in the para form.

All other homonuclear diatomic molecules with $I = \frac{1}{2}$ for each nucleus, such as $^{19}$F$_2$, also have ortho and para forms with odd and even $J$ and nuclear spin statistical weights of 3 and 1, respectively, as shown in Figure 5.18.

If $I = 1$ for each nucleus, as in $^2$H$_2$ and $^{14}$N$_2$, the total wave function must be symmetric to nuclear exchange. There are nine nuclear spin wave functions of which six are symmetric and three antisymmetric to exchange. Figure 5.18 illustrates the fact that ortho-$^2$H$_2$ (or $^{14}$N$_2$)
can have only even \( J \) and the \( \text{para} \) form only odd \( J \), and that there is roughly twice as much of the \( \text{ortho} \) form as there is of the \( \text{para} \) form at normal temperatures: at low temperatures there is a larger excess of the \( \text{ortho} \) form.

The effect of low temperatures affecting the \( \text{ortho} : \text{para} \) ratio is more important for light molecules, such as \( ^1\text{H}_2 \) and \( ^2\text{H}_2 \), than for heavy ones, such as \( ^{19}\text{F}_2 \) and \( ^{14}\text{N}_2 \). The reason is that the separation of the \( J = 0 \) and \( J = 1 \) levels is smaller for a heavier molecule and a lower temperature is required before a significant deviation from the normal \( \text{ortho} : \text{para} \) ratio is observed.

For the symmetrical linear polyatomic molecule acetylene

\[
^1\text{H} - ^{12}\text{C} \equiv ^{12}\text{C} - ^1\text{H}
\]

the situation is very similar to that for \( ^1\text{H}_2 \) since \( I = 0 \) for \( ^{12}\text{C} \). The main difference is that, since the rotational energy levels are much more closely spaced, a much lower temperature is necessary to produce acetylene predominantly in the \( \text{para} \) form.

For \( ^{16}\text{O}_2 \), \( I \) is zero and there are no antisymmetric nuclear spin wave functions for \( ^{16}\text{O}_2 \). Since each \( ^{16}\text{O} \) nucleus is a boson the total wave function must be symmetric to nuclear exchange. In the case of \( ^{16}\text{O}_2 \), with two electrons with unpaired spins in the ground state (see Section 7.2.1.1), \( \psi_e \) is antisymmetric, unlike the other molecules we have considered. Since \( I = 0 \) the nuclear spin wave function \( \psi_{ns} \) is equal to 1, which is symmetric to the exchange of nuclei. Therefore, as Figure 5.18 shows, \( ^{16}\text{O}_2 \) has only levels with the rotational quantum number having odd values and, in its rotational Raman spectrum, alternate lines with \( N'' \) even are missing. (In molecules such as \( ^{16}\text{O}_2 \), which have a resultant electron spin angular momentum due to unpaired electrons, the quantum number \( N \), rather than \( J \), distinguishes the rotational levels.)

### 5.3.5 Rotational Raman spectra of symmetric and asymmetric rotor molecules

For a symmetric rotor molecule the selection rules for the rotational Raman spectrum are

\[
\Delta J = 0, \pm 1, \pm 2; \quad \Delta K = 0
\]

resulting in \( R \) and \( S \) branches for each value of \( K \), in addition to the Rayleigh scattering.

For asymmetric rotors the selection rule in \( J \) is \( \Delta J = 0, \pm 1, \pm 2 \), but the fact that \( K \) is not a good quantum number results in the additional selection rules being too complex for discussion here.

### 5.4 Structure determination from rotational constants

Measurement and assignment of the rotational spectrum of a diatomic or other linear molecule result in a value of the rotational constant. In general, this will be \( B_0 \), which relates
to the zero-point vibrational state. If the rotational constant can be determined in one or more excited vibrational states \( B_e \), relating to the molecule in its unattainable equilibrium configuration, may be obtained by using Equation (5.25). For a diatomic molecule \( B_0 \) and \( B_e \) can be converted to moments of inertia, using Equation (5.11) or Equation (5.12), and thence to bond lengths \( r_0 \) and \( r_e \) since \( I = \mu^2 \). This begs the question as to whether we refer to \( r_0 \) or \( r_e \) as the bond length.

Part of the answer is that, unless we require a high degree of accuracy, it does not matter very much. This is illustrated by the values for \( r_0 \) and \( r_e \) for \( ^{14}\text{N}_2 \) and \( ^{15}\text{N}_2 \), given in Table 5.3. Nevertheless, an important difference between \( r_0 \) and \( r_e \) in general is that \( r_e \) is independent of the isotopic species whereas \( r_0 \) is not. Table 5.3 illustrates this point also. It is because of the isotope-independence of \( r_e \) that it is this which is used in discussing bond lengths at the highest degree of accuracy.

The reason that \( r_e \) does not change with isotopic substitution is that it refers to the bond length at the minimum of the potential energy curve (see Figure 1.13), and this curve, whether it refers to the harmonic oscillator approximation (Section 1.3.6) or an anharmonic oscillator (to be discussed in Section 6.1.3.2), does not change with isotopic substitution. However, the vibrational energy levels within the potential energy curve, and therefore \( r_0 \), are affected by isotopic substitution: this is illustrated by the mass-dependence of the vibration frequency demonstrated by Equation (1.68).

These arguments can be extended to linear and non-linear polyatomic molecules for which zero-point structure, in terms of bond lengths and angles, is isotope-dependent but for which equilibrium structure is not.

As in diatomic molecules the structure of greatest importance is the equilibrium structure, but one rotational constant can give, at most, only one structural parameter. In a non-linear but planar molecule the out-of-plane principal moment of inertia \( I_c \) is related to the other two by

\[
I_c = I_a + I_b
\]

so there are only two independent rotational constants.

In, for example, the planar asymmetric rotor molecule formaldehyde, \( ^1\text{H}_2\text{CO} \), shown in Figure 5.1(f), it is possible by obtaining, say, \( A_e \) and \( B_e \) in the zero-point level and in the \( v = 1 \) level of all six vibrations to determine \( A_e \) and \( B_e \). Two rotational constants are insufficient, however, to give the three structural parameters \( r_e(\text{CH}) \), \( r_e(\text{CO}) \) and \( (\angle \text{HCH})_e \) necessary for a complete equilibrium structure. It is at this stage that the importance of
determined in one or tamable equilibrium molecule $B_o$ and $B_e$
 equation (5.12), and to whether we refer

it does not matter given in Table

is that $r_o$ is this point also. It is

refers to the bond and this curve, for an anharmonic isotopic substitution.

and therefore $r_o$, dependence of the

molecules for independent but for the equilibrium structure,

in a non-linear related to the other

(5.58)

$\text{H}_2\text{CO}$, shown in level and in the rotational constants are $D_0$ and $\langle \text{HCH} \rangle_o$ the importance of
dealing with equilibrium, rather than zero-point, structure is apparent. Determination of $A_e$ and $B_e$ for $^3\text{H}_2\text{CO}$, for which equilibrium structure is identical to that of $^1\text{H}_2\text{CO}$, would allow a complete structure determination, three structural parameters being found from four rotational constants.

However, even for a small molecule such as $\text{H}_2\text{CO}$, determination of the rotational constants in the $v = 1$ levels of all the vibrations presents considerable difficulties. In larger molecules it may be possible to determine only $A_0$, $B_0$ and $C_0$. In such cases the simplest way to determine the structure is to ignore the differences from $A_e$, $B_e$ and $C_e$ and make sufficient isotopic substitutions to give a complete, but approximate, structure, called the $r_o$ structure.

An improvement on the $r_o$ structure is the substitution structure, or $r_s$ structure. This is obtained using the so-called Kraitchman equations, which give the coordinates of an atom, which has been isotopically substituted, in relation to the principal inertial axes of the molecule before substitution. The substitution structure is also approximate but is nearer to the equilibrium structure than is the zero-point structure.

One of the largest molecules for which an $r_s$ structure has been obtained is aniline, shown in Figure 5.19. The benzene ring shows small deviations from a regular hexagon in the angles but no meaningful deviations in the bond lengths. As might be expected, by comparison with the pyramidal $\text{NH}_3$ molecule, the plane of the $\text{NH}_2$ group is not coplanar with the rest of the molecule.

### Worked example 5.2

**Question.**

(a) From the value for $B_0$ of 1.923 604 $\pm$ 0.000 027 cm$^{-1}$, obtained from the rotational Raman spectrum of $^{14}\text{N}_2^{15}\text{N}$, calculate the bond length $r_0$.

(b) Why does it differ from $r_0$ for $^{14}\text{N}_2$?
(c) Would the values of \( r_e \) differ?
(d) Would there be an intensity alternation in the spectrum of \(^{14}\text{N}^{15}\text{N}\)?
(e) Would \(^{14}\text{N}^{15}\text{N}\) show a rotational infrared spectrum?

**Answer.**
(a) For \(^{14}\text{N}^{15}\text{N}\), reduced mass \( \mu \) is given by

\[
\mu = \frac{14.003\text{ g mol}^{-1} + 15.000\text{ g mol}^{-1}}{14.003\text{ g mol}^{-1} + 15.000\text{ g mol}^{-1}} \times \frac{10^{-3}\text{ kg g}^{-1}}{6.022 \times 10^{23}\text{ mol}^{-1}}
\]

\[
= 1.202\ 600 \times 10^{-26}\text{ kg}
\]

\( \therefore \quad r_0 = \frac{\hbar}{8\pi^2 c \mu B_0}
\]

\[
6.626\ 069 \times 10^{-34}\text{ J s}
\]

\[
= \frac{8\pi^2 \times 2.997\ 925 \times 10^{10}\text{ cm s}^{-1} \times 1.202\ 600 \times 10^{-26}\text{ kg} \times 1.923\ 604\text{ cm}^{-1}}{1.210\ 065 \times 10^{-20}\text{ m}^2}
\]

\[
= 1.100\ 03 \times 10^{-10}\text{ m}
\]

\( \therefore \quad r_0 = 1.100\ 03 \times 10^{-10}\text{ m}
\]

\( = 1.100\ 03\ \text{Å} \)

Note that, since \( B_0 \) is given, effectively, to six significant figures, the calculation has been done to seven figures and rounded to six at the final stage.

(b) The calculated value of \( r_0 \) differs from that of \( r_0 = 1.100\ 105\ \text{Å} \) for \(^{14}\text{N}_2\) (Table 5.3) because the zero-point level is lower, within the same anharmonic potential (see Section 6.1.3), for the heavier isotopic species. Therefore the mid-point of the zero-point level is at a smaller value of the bond length. Note that this level of accuracy in the calculation is necessary to illustrate this point.

(c) The values of \( r_e \) would not differ because they refer to the minimum of the isotope-independent potential energy curve.

(d) There would be no intensity alternation in the spectrum of \(^{14}\text{N}^{15}\text{N}\) because there is no exchange of identical nuclei on rotation about an axis perpendicular to the bond.

(e) \(^{14}\text{N}^{15}\text{N}\) would not show a rotational infrared spectrum because \(^{14}\text{N}^{15}\text{N}\) has no dipole moment. (In fact, like all such isotopically unsymmetrical molecules, it has an extremely small dipole moment, but too small for an infrared rotational spectrum to be detected.)

### Exercises

5.1 Use Equation (5.16) to derive Equation (5.17). Compare values of \( J_{\text{max}} \) and the transition frequencies involving the values of \( J_{\text{max}} \) for HCN \((B \approx 44.316\text{ GHz})\) and \( \text{N} = \text{C}-(\text{C} = \text{C})_2-\text{H} \) \((B \approx 1.313\text{ GHz})\).
5.2 Rearrange Equation (5.20) into the form $y = mx + c$ so that $m$ involves $D$ only. Plot $y$ against $x$ using the data in Table 5.1 to obtain $B$ and $D$, in hertz, for carbon monoxide (use a computer or calculator that will work to nine-figure accuracy).

5.3 Make measurements of the transition wavenumbers in the rotational spectrum of silane from Figure 5.10 and hence determine the Si–H bond length.

5.4 Assuming reasonable bond lengths, estimate the frequency of the $J = 15 - 14$ transition in the linear molecule $\text{N} \equiv \text{C} -(\text{C} \equiv \text{C})_6 - \text{H}$. In which region of the electromagnetic spectrum does it lie?

5.5 Starting from an expression for rotational term values show that

$$|\Delta \tilde{v}| = (4B_0 - 6D_0)(J + \frac{3}{2}) - 8D_0(J + \frac{3}{2})^3$$

for rotational Raman transitions of a diatomic or linear polyatomic molecule.

5.6 The first three Stokes lines in the rotational Raman spectrum of $^{16}\text{O}_2$ are separated by 14.4 cm$^{-1}$, 25.8 cm$^{-1}$ and 37.4 cm$^{-1}$ from the exciting radiation. Using the rigid rotor approximation obtain a value for $r_0$.

Bibliography


