

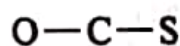
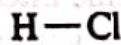
MICROWAVE SPECTROSCOPY

2.1 THE ROTATION OF MOLECULES

We saw in the previous chapter that spectroscopy in the microwave region is concerned with the study of rotating molecules. The rotation of a three-dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity—the principal axes of rotation. Thus a body has three principal *moments of inertia*, one about each axis, usually designated I_A , I_B , and I_C .

Molecules may be classified into groups according to the relative values of their three principal moments of inertia—which, it will be seen, is tantamount to classifying them according to their shapes. We shall describe this classification here before discussing the details of the rotational spectra arising from each group.

1. *Linear molecules.* These, as the name implies, are molecules in which all the atoms are arranged in a straight line, such as hydrogen chloride HCl or carbon oxysulphide OCS, illustrated below

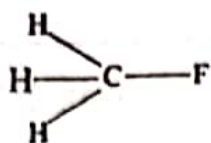


The three directions of rotation may be taken as (a) about the bond axis, (b) end-over-end rotation in the plane of the paper, and (c) end-over-end rotation at right angles to the plane. It is self-evident that the moments of (b) and (c) are the same (that is $I_B = I_C$) while that of (a) is very small. As an approximation we may say that $I_A = 0$, although it should be noted that this is only an approximation (see Sec. 2.3.1).

Thus for linear molecules we have:

$$I_B = I_C \quad I_A = 0 \quad (2.1)$$

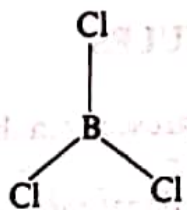
3. *Symmetric tops.* Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below:



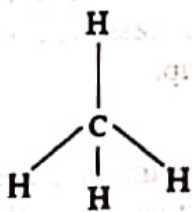
As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper are still identical and we have $I_B = I_C$. The moment of inertia about the C—F bond axis (chosen as the main rotational axis since the centre of gravity lies along it) is now not negligible, however, because it involves the rotation of three comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis can be imagined as a top, and hence the name of the class. We have then:

$$\text{Symmetric tops: } I_B = I_C \neq I_A \quad I_A \neq 0 \quad (2.2)$$

There are two subdivisions of this class which we may mention: if, as in methyl fluoride above, $I_B = I_C > I_A$, then the molecule is called a *prolate* symmetric top; whereas if $I_B = I_C < I_A$, it is referred to as *oblate*. An example of the latter type is boron trichloride, which, as shown, is planar and symmetrical. In this case $I_A = 2I_B = 2I_C$.



3. *Spherical tops.* When a molecule has all three moments of inertia identical, it is called a spherical top. A simple example is the tetrahedral molecule methane CH_4 . We have then:



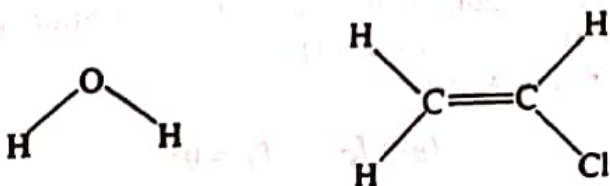
$$\text{Spherical tops: } I_A = I_B = I_C \quad (2.3)$$

In fact these molecules are only of academic interest in this chapter. Since they can have no dipole moment owing to their symmetry, rotation alone can produce no dipole change and hence no rotational spectrum is observable.

4. *Asymmetric tops.* These molecules, to which the majority of substances belong, have all three moments of inertia different:

$$I_A \neq I_B \neq I_C \quad (2.4)$$

Simple examples are water H_2O and vinyl chloride $\text{CH}_2=\text{CHCl}$.



Perhaps it should be pointed out that one can (and often does) describe the classification of molecules into the four rotational classes in far more rigorous terms than have been used above (see, for example, Herzberg, *Molecular Spectra and Molecular Structure*, vol. II). However, for the purposes of this book the above description is adequate.

2.2 ROTATIONAL SPECTRA

We have seen that rotational energy, along with all other forms of molecular energy, is quantized: this means that a molecule cannot have any arbitrary amount of rotational energy (i.e. any arbitrary value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned. The permitted energy values—the so-called rotational energy *levels*—may in principle be calculated for any molecule by solving the Schrödinger equation for the system represented by that molecule. For simple molecules the mathematics involved is straightforward for tedious, while for complicated systems it is probably impossible without gross approximations. We shall not concern ourselves unduly with this, however, being content merely to accept the results of existing solutions and to point out where reasonable approximations may lead.

We shall consider each class of rotating molecule in turn, discussing the linear molecule in most detail, because much of its treatment can be directly extended to symmetrical and unsymmetrical molecules.

2.3 DIATOMIC MOLECULES

2.3.1 The Rigid Diatomic Molecule

We start with this, the simplest of all linear molecules, shown in Fig. 2.1. Masses m_1 and m_2 are joined by a rigid bar (the bond) whose length is

$$r_0 = r_1 + r_2 \quad (2.5)$$

The molecule rotates end-over-end about a point C , the centre of gravity: this is defined by the moment, or balancing, equation:

$$m_1 r_1 = m_2 r_2 \quad (2.6)$$

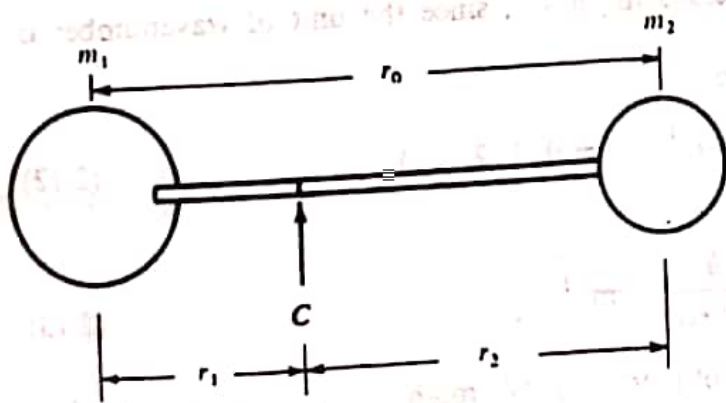


Figure 2.1 A rigid diatomic molecule treated as two masses, m_1 and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$.

The moment of inertia about C is defined by:

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\text{from Eq. (2.6)}) \\ &= r_1 r_2 (m_1 + m_2) \end{aligned} \quad (2.7)$$

However, from Eqs (2.5) and (2.6):

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

Therefore,

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad (2.8)$$

Replacing (2.8) in (2.7):

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \quad (2.9)$$

where we have written $\mu = m_1 m_2 / (m_1 + m_2)$, and μ is called the *reduced mass* of the system. Equation (2.9) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

By the use of the Schrödinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{joules} \quad \text{where } J = 0, 1, 2, \dots \quad (2.10)$$

In this expression h is Planck's constant, and I is the moment of inertia, either I_B or I_C , since both are equal. The quantity J , which can take integral values from zero upwards, is called the *rotational quantum number*: its restriction to integral values arises directly out of the solution to the Schrödinger equation and is by no means arbitrary, and it is this restriction which effectively allows only certain discrete rotational energy levels to the molecule.

Equation (2.10) expressed the allowed energies in joules; we, however, are interested in differences between these energies, or, more particularly, in the corresponding frequency, $\nu = \Delta E/h$ Hz, or wavenumber, $\bar{\nu} = \Delta E/hc$ cm^{-1} , of the radiation emitted or absorbed as a consequence of changes between energy levels. In the rotational region spectra are usually discussed in terms of wavenumber, so it is useful to consider energies expressed in these units. We write:

$$\epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \quad \text{cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad (2.11)$$

where c , the velocity of light, is here expressed in cm s^{-1} , since the unit of wavenumber is reciprocal *centimetres*.

Equation (2.11) is usually abbreviated to:

$$\epsilon_J = B J(J+1) \quad \text{cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad (2.12)$$

where B , the *rotational constant*, is given by

$$B = \frac{h}{8\pi^2 I_{BC}} \quad \text{cm}^{-1} \quad (2.13)$$

in which we have used explicitly the moment of inertia I_B . We might equally well have used I_C and a rotational constant C , but the notation of (2.13) is conventional.

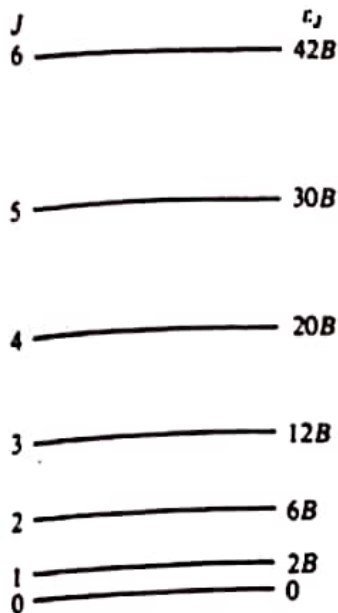


Figure 2.2 The allowed rotational energies of a rigid diatomic molecule.

From Eq. (2.12) we can show the allowed energy levels diagrammatically as in Fig. 2.2. Plainly for $J=0$ we have $\epsilon_J = 0$ and we would say that the molecule is not rotating at all. For $J=1$, the rotational energy is $\epsilon_1 = 2B$ and a rotating molecule then has its lowest angular momentum. We may continue to calculate ϵ_J with increasing J values and, in principle, there is no limit to the rotational energy the molecule may have. In practice, of course, there comes a point at which the centrifugal force of a rapidly rotating diatomic molecule is greater than the strength of the bond, and the molecule is disrupted, but this point is not reached at normal temperatures.

We now need to consider *differences* between the levels in order to discuss the spectrum. If we imagine the molecule to be in the $J=0$ state (the *ground rotational state*, in which no rotation occurs), we can let incident radiation be absorbed to raise it to the $J=1$ state. Plainly the energy absorbed will be:

$$\epsilon_{J=1} - \epsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

and, therefore,

$$\bar{\nu}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1} \quad (2.14)$$

In other words, an absorption line will appear at $2B \text{ cm}^{-1}$. If now the molecule is raised from the $J=1$ to the $J=2$ level by the absorption of more energy, we see immediately:

$$\begin{aligned} \bar{\nu}_{J=1 \rightarrow J=2} &= \epsilon_{J=2} - \epsilon_{J=1} \\ &= 6B - 2B = 4B \text{ cm}^{-1} \end{aligned} \quad (2.15)$$

In general, to raise the molecule from the state J to state $J+1$, we would have:

$$\begin{aligned} \bar{\nu}_{J \rightarrow J+1} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[J^2 + 3J + 2 - (J^2 + J)] \end{aligned}$$

or

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J+1) \text{ cm}^{-1} \quad (2.16)$$

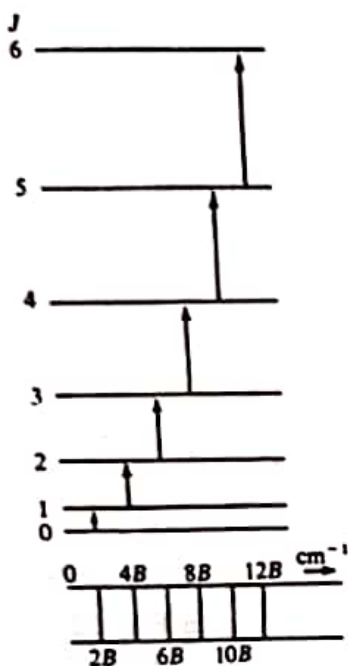


Figure 2.3 Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \dots \text{cm}^{-1}$, while a similar lowering would result in an identical emission spectrum. This is shown at the foot of Fig. 2.3.

In deriving this pattern we have made the assumption that a transition can occur from a particular level only to its immediate neighbour, either above or below: we have not, for instance, considered the sequence of transitions $J = 0 \rightarrow J = 2 \rightarrow J = 4 \dots$. In fact, a rather sophisticated application of the Schrödinger wave equation shows that, for this molecule, we need only consider transitions in which J changes by one unit—all other transitions being spectroscopically *forbidden*. Such a result is called a *selection rule*, and we may formulate it for the rigid diatomic rotator as:

$$\text{Selection rule: } \Delta J = \pm 1 \quad (2.17)$$

Thus Eq. (2.16) gives the *whole* spectrum to be expected from such a molecule.

Of course, only if the molecule is asymmetric (heteronuclear) will this spectrum be observed, since if it is homonuclear there will be no dipole component change during the rotation, and hence no interaction with radiation. Thus molecules such as HCl and CO will show a rotational spectrum, while N_2 and O_2 will not. Remember, also, that rotation about the bond axis was rejected in Sec. 2.1: we can now see that there are two reasons for this. Firstly, the moment of inertia is very small about the bond so, applying Eqs (2.10) or (2.11) we see that the energy levels would be extremely widely spaced: this means that a molecule requires a great deal of energy to be raised from the $J = 0$ to the $J = 1$ state, and such transitions do not occur under normal spectroscopic conditions. Thus diatomic (and all linear) molecules are in the $J = 0$ state for rotation about the bond axis, and they may be said to be not rotating. Secondly, even if such a transition should occur, there will be no dipole change and hence no spectrum.

Calculation of I masses & r by molecular spectroscopy.

To conclude this section we shall apply Eq. (2.16) to an observed spectrum in order to determine the moment of inertia and hence the bond length. Gilliam *et al.*† have measured the first line ($J = 0$) in the rotation spectrum of carbon monoxide as 3.84235 cm^{-1} . Hence, from Eq. (2.16):

$$\bar{\nu}_{0 \rightarrow 1} = 3.84235 = 2B \text{ cm}^{-1}$$

$$B = 1.92118 \text{ cm}^{-1}$$

or

Rewriting Eq. (2.13) as: $I = h/8\pi^2 Bc$, we have:

$$I_{\text{CO}} = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 2.99793 \times 10^{10} \times B} = \frac{27.9907 \times 10^{-47}}{B} \text{ kg m}^2$$

$$= 14.5695_4 \times 10^{-47} \text{ kg m}^2$$

where we express the velocity of light in cm s^{-1} , since B is in cm^{-1} . However, the moment of inertia is μr^2 (cf. Eq. (2.9)) and, knowing the relative atomic weights ($\text{H} = 1.0080$) to be $\text{C} = 12.0000$, $\text{O} = 15.9994$, and the absolute mass of the hydrogen atom to be $1.67343 \times 10^{-27} \text{ kg}$, we can calculate the masses of carbon and oxygen, respectively, as 19.92168 and $26.56136 \times 10^{-27} \text{ kg}$. The reduced mass is then:

Absolute masses of C & O

$$\mu = \frac{19.92168 \times 26.56136 \times 10^{-54}}{46.48303 \times 10^{-27}} = 11.38365 \times 10^{-27} \text{ kg}$$

Hence:

$$r^2 = \frac{I}{\mu} = 1.2799 \times 10^{-20} \text{ m}^2$$

and

$$r_{\text{CO}} = 0.1131 \text{ nm (or } 1.131 \text{ \AA)}$$

2.3.2 The Intensities of Spectral Lines

We want now to consider briefly the relative intensities of the spectral lines of Eq. (2.16); for this a prime requirement is plainly a knowledge of the relative probabilities of transition between the various energy levels. Does, for instance, a molecule have more or less chance of making the transition $J = 0 \rightarrow J = 1$ than the transition $J = 1 \rightarrow J = 2$? We mentioned above calculations which show that a change of $\Delta J = \pm 2, \pm 3$, etc., was forbidden—in other words, the transition probability for all these changes is zero. Precisely similar calculations show that the probability of all changes with $\Delta J = \pm 1$ is almost the same—all, to a good approximation, are equally likely to occur.

This does not mean, however, that all spectral lines will be equally intense. Although the intrinsic probability that a single molecule in the $J = 0$ state, say, will move to $J = 1$ is the same as that of a single molecule moving from $J = 1$ to $J = 2$, in an assemblage of molecules, such as in a normal gas sample, there will be different numbers of molecules in each level to begin with, and therefore different total numbers of molecules will carry out transitions between the various levels. In fact, since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial numbers of molecules in each level.

The first factor governing the population of the levels is the Boltzmann distribution (cf. Sec. 1.7.2). Here we know that the rotational energy in the lowest level is zero, since $J = 0$, so, if we

† Gilliam, Johnson, and Gordy. *Physical Review*, 78, 140 (1950).

have N_0 molecules in this state, the number in any higher state is given by:

$$N_J/N_0 = \exp(-E_J/kT) = \exp[-BhcJ(J+1)/kT] \quad (2.18)$$

where, we must remember, c is the velocity of light in cm s^{-1} when B is in cm^{-1} . A very simple calculation shows how N_J varies with J ; for example, taking a typical value of $B = 2 \text{ cm}^{-1}$, and room temperature (say $T = 300 \text{ K}$), the relative population in the $J = 1$ state is:

$$\begin{aligned} \frac{N_1}{N_0} &= \exp\left(-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right) \\ &= \exp(-0.019) \approx 0.98 \end{aligned}$$

and we see that there are almost as many molecules in the $J = 1$ state, at equilibrium, as in the $J = 0$. In a similar way the two graphs of Fig. 2.4 have been calculated, showing the more rapid decrease of N_J/N_0 with increasing J and with larger B .

A second factor is also required—the possibility of *degeneracy* in the energy states. Degeneracy is the existence of two or more energy states which have exactly the *same* energy. In the case of the diatomic rotator we may approach the problem in terms of its angular momentum.

The defining equations for the energy and angular momentum of a rotator are:

$$E = \frac{1}{2} I \omega^2 \quad P = I \omega$$

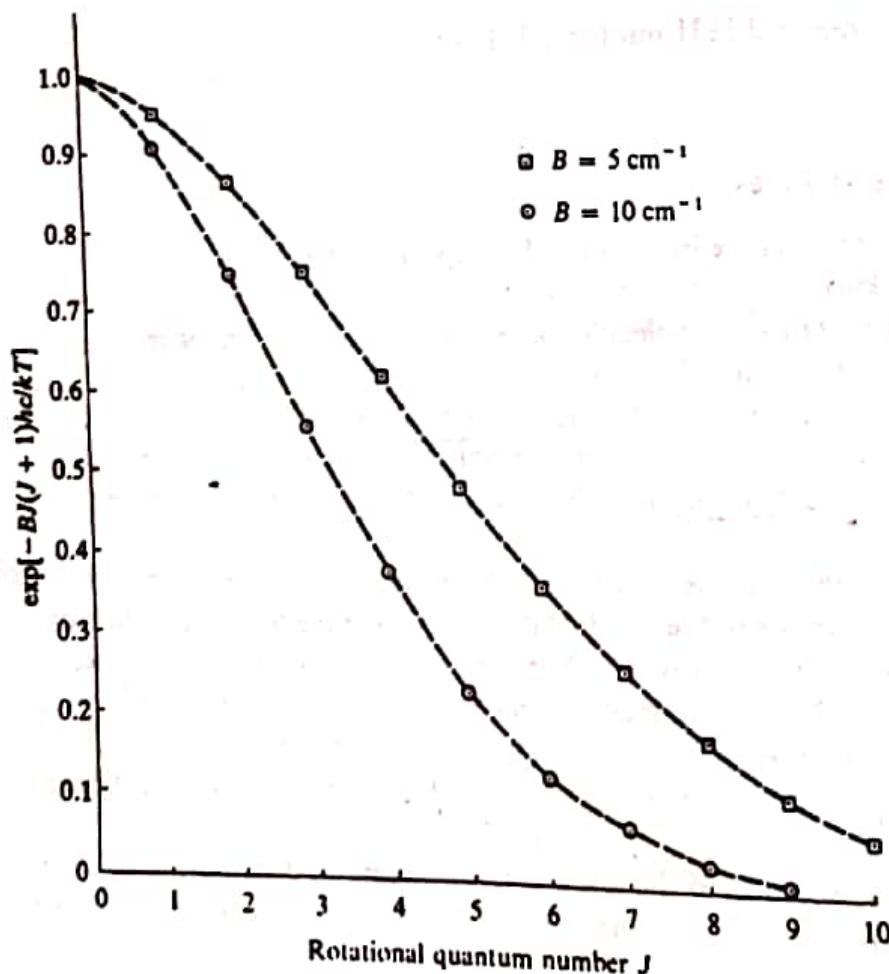


Figure 2.4 The Boltzmann populations of the rotational energy levels of Fig. 2.2. The diagram has been drawn taking values of $B = 5$ and 10 cm^{-1} and $T = 300 \text{ K}$ in Eq. (2.18).

where I is the moment of inertia, ω the rotational frequency (in radians per second), and \mathbf{P} the angular momentum. Rearrangement of these gives:

$$\mathbf{P} = \sqrt{2EI}$$

The energy level expression of Eq. (2.10) can be rewritten:

$$2EI = J(J+1) \frac{h^2}{4\pi^2}$$

and hence

$$\mathbf{P} = \sqrt{J(J+1)} \frac{h}{2\pi} = \sqrt{J(J+1)} \text{ units} \quad (2.19)$$

where, following convention, we take $h/2\pi$ as the fundamental unit of angular momentum. Thus we see that \mathbf{P} , like E , is quantized.

Throughout the above derivation \mathbf{P} has been printed in bold face type to show that it is a *vector*—i.e. it has *direction* as well as *magnitude*. The direction of the angular momentum vector is conventionally taken to be along the axis about which rotation occurs and it is usually drawn as an arrow of length proportional to the magnitude of the momentum. The number of different directions which an angular momentum vector may take up is limited by a quantum mechanical law which may be stated:

For integral values of the rotational quantum number (in this case J), the angular momentum vector may only take up directions such that its component along a given reference direction is zero or an integral multiple of angular momentum units.

We can see the implications of this most easily by means of a diagram. In Fig. 2.5 we show the case $J = 1$. Here $\mathbf{P} = \sqrt{1 \times 2} \text{ units} = \sqrt{2}$, and, as Fig. 2.5(a) shows, a vector of length $\sqrt{2}$ (= 1.41) can have only *three* integral or zero components along a reference direction (here assumed to be from top to bottom in the plane of the paper): +1, 0, and -1. Thus the angular

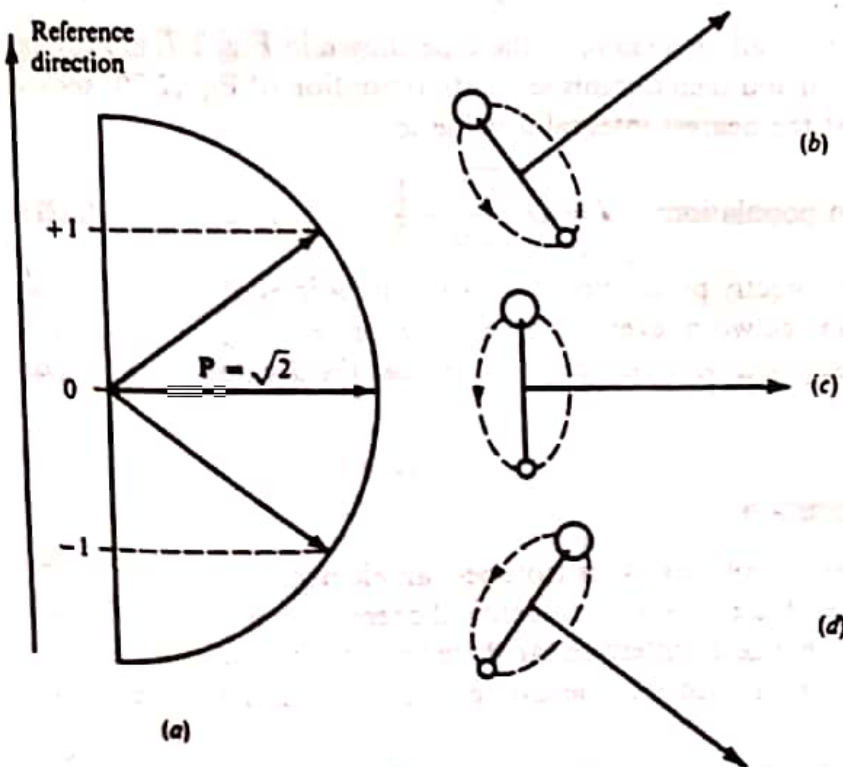


Figure 2.5 The three degenerate orientations of the rotational angular momentum vector for a molecule with $J = 1$.

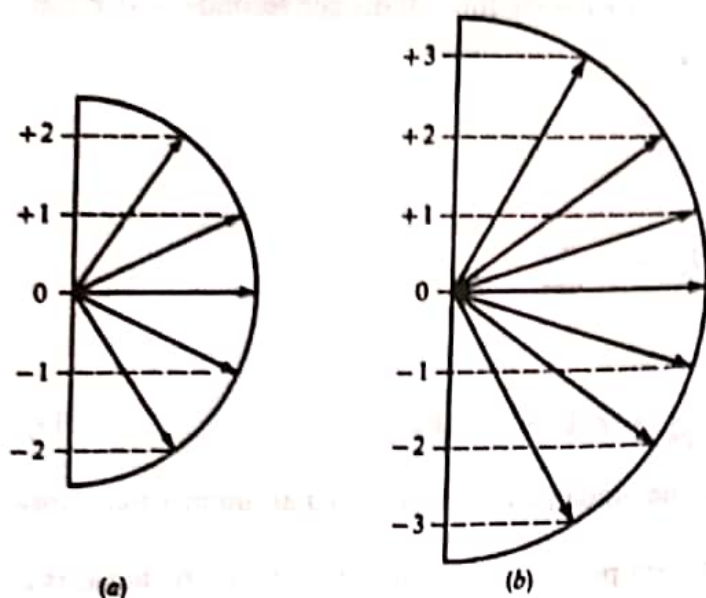


Figure 2.6 The five and seven degenerate rotational orientations for a molecule with $J = 2$ and $J = 3$, respectively.

momentum vector in this instance can be oriented in only three different directions (Fig. 2.5(b) to (d)) with respect to the reference direction. All three rotational directions are, of course, associated with the same angular momentum and hence the same rotational energy: the $J = 1$ level is thus threefold degenerate.

Figure 2.6(a) and (b) shows the situation for $J = 2$ ($P = \sqrt{6}$) and $J = 3$ ($P = 2\sqrt{3}$) with fivefold and sevenfold degeneracy, respectively. In general it may readily be seen that each energy level is $(2J + 1)$ -fold degenerate.

Thus we see that, although the molecular population in each level decreases exponentially (Eq. (2.18)), the number of degenerate levels available increases rapidly with J . The total relative population at an energy E_J will plainly be:

$$\text{Population} \propto (2J + 1) \exp(-E_J/kT) \quad (2.20)$$

When this is plotted against J the points fall on a curve of the type shown in Fig. 2.7, indicating that the population rises to a maximum and then diminishes. Differentiation of Eq. (2.20) shows that the population is a maximum at the nearest integral J value to:

$$\text{Maximum population: } J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad (2.21)$$

We have seen that line intensities are directly proportional to the populations of the rotational levels; hence it is plain that transitions between levels with very low or very high J values will have small intensities while the intensity will be a maximum at or near the J value given by Eq. (2.21).

2.3.3 The Effect of Isotopic Substitution

When a particular atom in a molecule is replaced by its isotope—an element identical in every way except for its atomic mass—the resulting substance is identical chemically with the original. In particular there is no appreciable change in internuclear distance on isotopic substitution. There is, however, a change in total mass and hence in the moment of inertia and B value for the molecule.

Considering carbon monoxide as an example, we see that on going from $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{16}\text{O}$ there is a mass increase and hence a decrease in the B value. If we designate the ^{13}C molecule

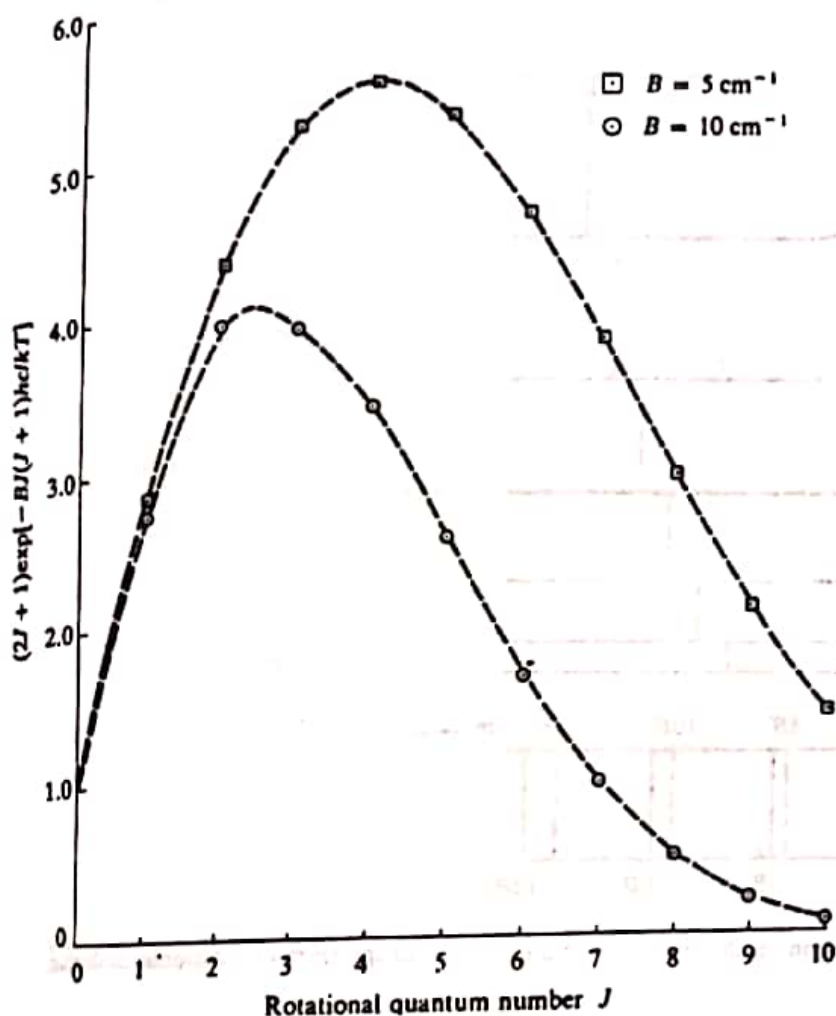


Figure 2.7 The relative populations, including degeneracy, of the rotational energy levels of a diatomic molecule. The diagram has been drawn for the same conditions as Fig. 2.4.

with a prime we have $B > B'$. This change will be reflected in the rotational energy levels of the molecule and Fig. 2.8 shows, much exaggerated, the relative lowering of the ^{13}C levels with respect to those of ^{12}C . Plainly, as shown by the diagram at the foot of Fig. 2.8, the spectrum of the heavier species will show a smaller separation between the lines ($2B'$) than that of the lighter, one ($2B$). Again the effect has been much exaggerated for clarity, and the transitions due to the heavier molecule are shown dashed.

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam *et al.*, as already stated, found the first rotational absorption of $^{12}\text{C}^{16}\text{O}$ to be at 3.84235 cm^{-1} , while that of $^{13}\text{C}^{16}\text{O}$ was at 3.67337 cm^{-1} . The values of B determined from these figures are:

$$B = 1.92118 \text{ cm}^{-1} \quad \text{and} \quad B' = 1.83669 \text{ cm}^{-1}$$

where the prime refers to the heavier molecule. We have immediately:

$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

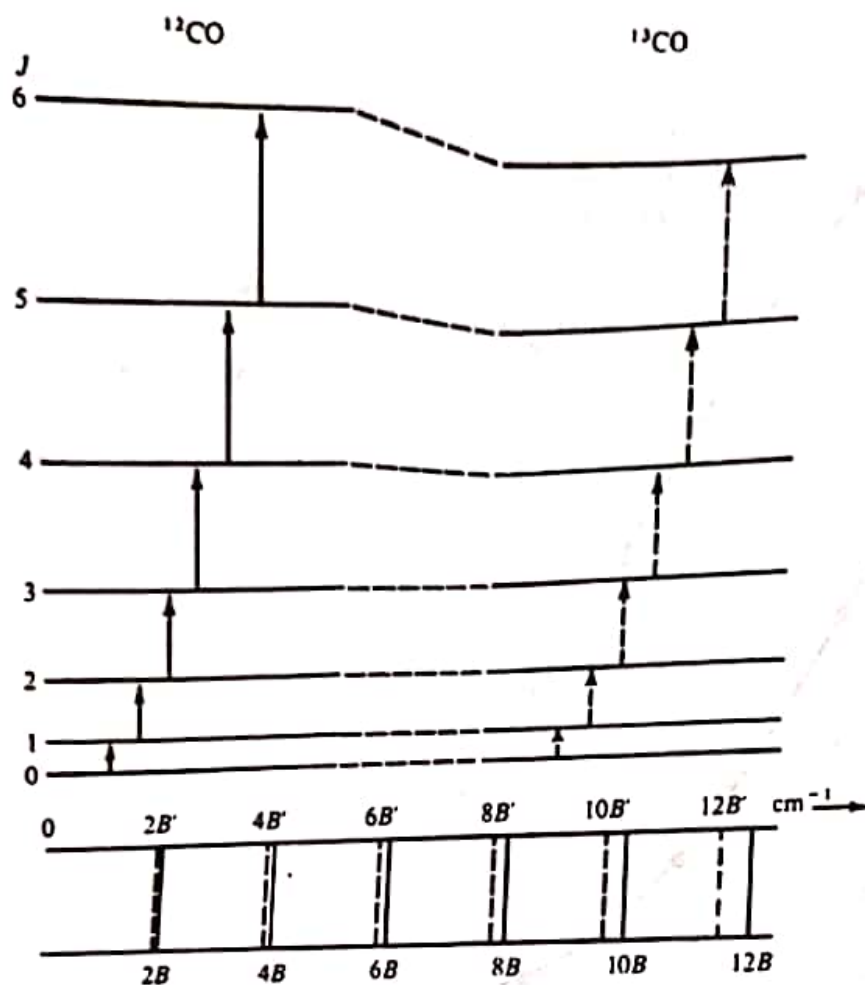


Figure 2.8 The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide.

where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00, we have:

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994m'}{15.9994 + m'} \times \frac{12 + 15.9994}{12 \times 15.9994}$$

from which m' , the atomic weight of carbon-13, is found to be 13.0007. This is within 0.02 per cent of the best value obtained in other ways.

It is noteworthy that the data quoted above were obtained by Gilliam *et al.* from $^{13}\text{C}^{16}\text{O}$ molecules in natural abundance (i.e. about 1 per cent of ordinary carbon monoxide). Thus, besides allowing an extremely precise determination of atomic weights, microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

2.3.4 The Non-rigid Rotator

At the end of Sec. 2.3.1 we indicated how internuclear distances could be calculated from microwave spectra. It must be admitted that we selected our data carefully at this point—spectral lines for carbon monoxide, other than the first, would not have shown the constant $2B$ separation predicted by Eq. (2.16). This is shown by the spectrum of hydrogen fluoride given

Table 2.1 Rotation spectrum of hydrogen fluoride

J	$\bar{\nu}_{\text{obs.}} \uparrow$ (cm^{-1})	$\bar{\nu}_{\text{calc.}} \ddagger$ (cm^{-1})	$\Delta \bar{\nu}_{\text{obs.}}$ (cm^{-1})	B ($= \frac{1}{2} \Delta \bar{\nu}$)	r (nm)
0	41.08	41.11	41.11	20.56	0.0929
1	82.19	82.18	40.96	20.48	0.0931
2	123.15	123.14	40.85	20.43	0.0932
3	164.00	163.94	40.62	20.31	0.0935
4	204.62	204.55	40.31	20.16	0.0938
5	244.93	244.89	40.08	20.04	0.0941
6	285.01	284.93	39.64	19.82	0.0946
7	324.65	324.61	39.28	19.64	0.0951
8	363.93	363.89	38.89	19.45	0.0955
9	402.82	402.70	38.31	19.16	0.0963
10	441.13	441.00	37.81	18.91	0.0969
11	478.94	478.74			

\uparrow Lines numbered according to $\bar{\nu}_J = 2B(J+1) \text{cm}^{-1}$. Observed data from 'An Examination of the Far Infra-red Spectrum of Hydrogen Fluoride' by A. A. Mason and A. H. Nielsen, published in Scientific Report No. 5, August 1963, Contract No. AF 19(604)-7981, by kind permission of the authors.

\ddagger See Sec. 2.3.5 for details of the calculation.

in Table 2.1; it is evident that the separation between successive lines (and hence the apparent B value) decreases steadily with increasing J .

The reason for this decrease may be seen if we calculate internuclear distances from the B values. The calculations are exactly similar to those of Sec. 2.3.1 and the results are shown in column 6 of Table 2.1. Plainly the bond length increases with J and we can see that our assumption of a *rigid* bond is only an approximation; in fact, of course, all bonds are elastic to some extent, and the increase in length with J merely reflects the fact that the more quickly a diatomic molecule rotates the greater is the centrifugal force tending to move the atoms apart.

Before showing how this elasticity may be quantitatively allowed for in rotational spectra, we shall consider briefly two of its consequences. Firstly, when the bond is elastic, a molecule may have vibrational energy—i.e. the bond will stretch and compress periodically with a certain fundamental frequency dependent upon the masses of the atoms and the elasticity (or force constant) of the bond. If the motion is simple harmonic (which, we shall see in Chapter 3, is usually a very good approximation to the truth) the force constant is given by:

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \quad (2.22)$$

where $\bar{\omega}$ is the vibration frequency (expressed in cm^{-1}), and c and μ have their previous definitions. Plainly the variation of B with J is determined by the force constant—the weaker the bond, the more readily will it distort under centrifugal forces.

The second consequence of elasticity is that the quantities r and B vary during a vibration. When these quantities are measured by microwave techniques many hundreds of vibrations

occur during a rotation, and hence the measured value is an average. However, from the defining equation of B we have:

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

$$B \propto 1/r^2 \quad (2.23)$$

or

since all other quantities are independent of vibration. Now, although in simple harmonic motion a molecular bond is compressed and extended an equal amount on each side of the equilibrium distance and the average value of the distance is therefore unchanged, the average value of $1/r^2$ is *not* equal to $1/r_e^2$, where r_e is the equilibrium distance. We can see this most easily by an example. Consider a bond of equilibrium length 0.1 nm vibrating between the limits 0.09 and 0.11 nm. We have:

$$\langle r \rangle_{av.} = \frac{0.09 + 0.11}{2} = 0.1 = r_e$$

but

$$\left\langle \frac{1}{r^2} \right\rangle_{av.} = \frac{(1/0.09)^2 + (1/0.11)^2}{2} = 103.05 \text{ nm}^{-2}$$

and therefore $\langle r \rangle_{av.} = \sqrt{1/103.5} = 0.0985 \text{ nm}$. The difference, though small, is not negligible compared with the precision with which B can be measured spectroscopically. In fact the real situation is rather worse. We shall see in Chapter 3 that real vibrations are not simple harmonic, since a real bond may be stretched more easily than it may be compressed, and this usually results in $r_{av.}$ being greater than $r_{eq.}$.

It is usual, then, to define three different sets of values for B and r . At the equilibrium separation, r_e , between the nuclei, the rotational constant is B_e ; in the vibrational ground state the average internuclear separation is r_0 associated with a rotational constant B_0 ; while if the molecule has excess vibrational energy the quantities are r_v and B_v , where v is the vibrational quantum number.

During the remainder of this chapter we shall ignore the small differences between B_0 , B_e , and B_v —the discrepancy is most important in the consideration of vibrational spectra in Chapter 3.

We should note, in passing, that the rotational spectrum of hydrogen fluoride given in Table 2.1 extends from the microwave well into the infra-red region (cf. Fig. 1.4). This underlines the comment made in Chapter 1 that there is no fundamental distinction between spectral regions, only differences in technique. Since hydrogen fluoride, together with other diatomic hydrides, has a small moment of inertia and hence a large B value, the spacings between rotational energy levels become large and fall into the infra-red region after only a few transitions. Historically, indeed, the moments of inertia and bond lengths of these molecules were first determined from spectral studies using infra-red techniques.

2.3.5 The Spectrum of a Non-rigid Rotator

The Schrödinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \quad J$$

or

$$\epsilon_J = E_J/hc = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \quad (2.24)$$

where the rotational constant, B , is as defined previously, and the *centrifugal distortion constant*, D , is given by:

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1} \quad (2.25)$$

which is a positive quantity. Equation (2.24) applies for a simple harmonic force field only; if the force field is anharmonic, the expression becomes:

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \dots \text{ cm}^{-1} \quad (2.26)$$

where H , K , etc., are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D and most modern spectroscopic data are adequately fitted by Eq. (2.24).

From the defining equations of B and D it may be shown directly that:

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2} \quad (2.27)$$

where $\bar{\omega}$ is the vibrational frequency of the bond and k has been expressed according to Eq. (2.22). We shall see in Chapter 3 that vibrational frequencies are usually of the order of 10^3 cm^{-1} , while B we have found to be of the order of 10 cm^{-1} . Thus we see that D , being of the order 10^{-3} cm^{-1} , is very small compared with B . For small J , therefore, the correction term $DJ^2(J+1)^2$ is almost negligible, while for J values of 10 or more it may become appreciable.

Figure 2.9 shows, much exaggerated, the lowering of rotational levels when passing from the rigid to the non-rigid diatomic molecule. The spectra are also compared, the dashed lines connecting corresponding energy levels and transitions of the rigid and the non-rigid molecules. It should be noted that the selection rule for the latter is still $\Delta J = \pm 1$.

We may easily write an analytical expression for the transitions:

$$\begin{aligned} \epsilon_{J+1} - \epsilon_J = \bar{\nu}_J &= B[(J+1)(J+2) - J(J+1)] \\ &\quad - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \end{aligned} \quad (2.28)$$

where $\bar{\nu}_J$ represents equally the upward transition from J to $J+1$, or the downward from $J+1$ to J . Thus we see analytically, and from Fig. 2.9, that the spectrum of the elastic rotor is similar to that of the rigid molecule except that each line is displaced slightly to low frequency, the displacement increasing with $(J+1)^3$.

A knowledge of D gives rise to two useful items of information. Firstly, it allows us to determine the J value of lines in an observed spectrum. If we have measured a few isolated transitions it is not always easy to determine from which J value they arise; however, fitting Eq. (2.28) to them—provided three consecutive lines have been measured—gives unique values for B , D , and J . The precision of such fitting is shown by Table 2.1 where the wavenumbers are calculated from the equation:

$$\bar{\nu}_J = 41.122(J+1) - 8.52 \times 10^{-3}(J+1)^3 \text{ cm}^{-1} \quad (2.29)$$

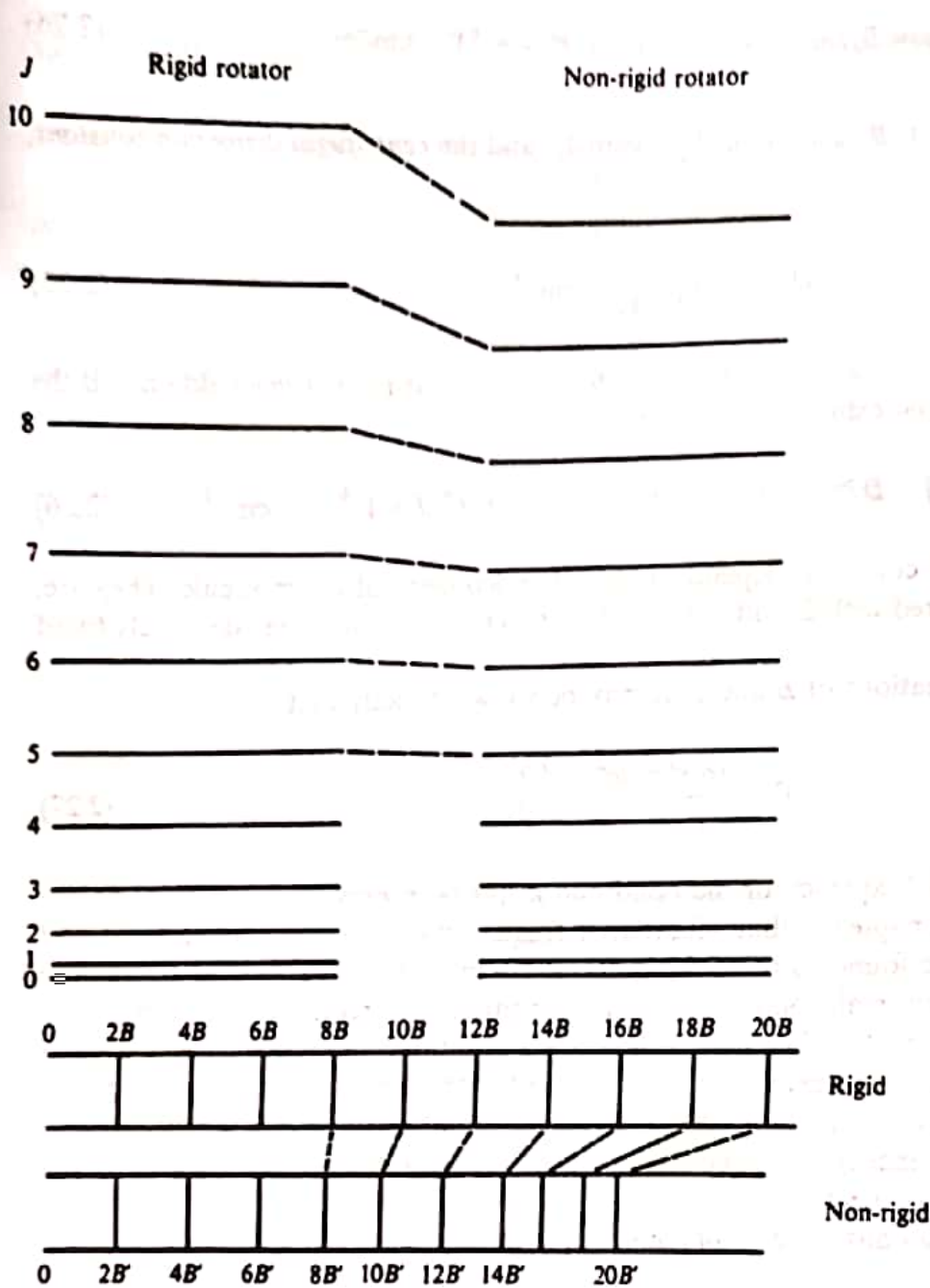


Figure 2.9 The change in rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule. Energy levels on the right are calculated using $D = 10^{-3}B$.

Secondly, a knowledge of D enables us to determine—although rather inaccurately—the vibrational frequency of a diatomic molecule. From the above data for hydrogen fluoride and Eq. (2.27) we have:

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16.33 \times 10^6 (\text{cm}^{-1})^2$$

i.e.

$$\bar{\omega} \approx 4050 \text{ cm}^{-1}$$

In the next chapter we shall see that a more precise determination leads to the value 4138.3 cm^{-1} ; the 2 per cent inaccuracy in the present calculation is due partly to the assumption of simple harmonic motion and partly to the very small, and hence relatively inaccurate, value of D .

The force constant follows directly:

$$k = 4\pi^2 c^2 \bar{\omega}^2 \mu = 960 \text{ N m}^{-1}$$

which indicates, as expected, that H—F is a relatively strong bond.

2.4 POLYATOMIC MOLECULES

2.4.1 Linear Molecules

We consider first molecules such as carbon oxysulphide OCS or chloroacetylene $\text{HC}\equiv\text{CCl}$, where all the atoms lie on a straight line, since this type gives rise to particularly simple spectra in the microwave region. Since $I_B = I_C$; $I_A = 0$, as for diatomic molecules, the energy levels are given by a formula identical with Eq. (2.26), i.e.

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 + \dots \text{ cm}^{-1} \quad (2.30)$$

and the spectrum will show the same $2B$ separation modified by the distortion constant. In fact, the whole of the discussion on diatomic molecules applies equally to all linear molecules; three points, however, should be underlined:

1. Since the moment of inertia for the end-over-end rotation of a polyatomic linear molecule is considerably greater than that of a diatomic molecule, the B value will be much smaller and the spectral lines more closely spaced. Thus B values for diatomic molecules are about 10 cm^{-1} , while for triatomic molecules they can be 1 cm^{-1} or less, and for larger molecules smaller still. $B \propto \frac{1}{I}$
2. The molecule must, as usual, possess a dipole moment if it is to exhibit a rotational spectrum. Thus OCS will be microwave active, while OCO (more usually written CO_2) will not. In particular, it should be noted that isotopic substitution does not lead to a dipole moment since the bond lengths and atomic charges are unaltered by the substitution. Thus $^{16}\text{OC}^{18}\text{O}$ is microwave inactive.
3. A non-cyclic polyatomic molecule containing N atoms has altogether $N - 1$ individual bond lengths to be determined. Thus in the triatomic molecule OCS there is the CO distance, r_{CO} , and the CS distance, r_{CS} . On the other hand, there is only one moment of inertia for the end-over-end rotation of OCS, and only this one value can be determined from the spectrum. Table 2.2 shows the data for this molecule. Over the four lines observed there is seen to be no

Table 2.2 Microwave spectrum of carbon oxysulphide

$J \rightarrow J+1$	$\bar{\nu}_{\text{obs.}} (\text{cm}^{-1})$	$\Delta\bar{\nu}$	$B(\text{cm}^{-1})$
0 → 1	...	2×0.4055	0.2027
1 → 2	0.8109	0.4054	0.2027
2 → 3	1.2163	0.4054	0.2027
3 → 4	1.6217	0.4054	0.2027
4 → 5	0.0271		

appreciable centrifugal distortion, and, taking the value of B as 0.2027 cm^{-1} , we calculate:

$$I_B = \frac{h}{8\pi^2 Bc} = 137.95 \times 10^{-47} \text{ kg m}^2$$

From this one observation it is plainly impossible to deduce the two unknowns, r_{CO} and r_{CS} . The difficulty can be overcome, however, if we study a molecule with different atomic masses but the same bond lengths—i.e. an isotopically substituted molecule—since this will have a different moment of inertia.

Let us consider the rotation of OCS in some detail. Figure 2.10 shows the molecule, where r_O , r_C , and r_S represent the distances of the atoms from the centre of gravity. Consideration of moments gives:

$$m_O r_O + m_C r_C = m_S r_S \quad (2.31)$$

where m_i is the mass of atom i . The moment of inertia is:

$$I = m_O r_O^2 + m_C r_C^2 + m_S r_S^2 \quad (2.32)$$

and we have the further equations:

$$r_O = r_{CO} + r_C \quad r_S = r_{CS} - r_C \quad (2.33)$$

where r_{CO} and r_{CS} are the bond lengths of the molecule. It is these we wish to determine. Substituting (2.33) in (2.31) and collecting terms:

$$(m_C + m_O + m_S)r_C = m_S r_{CS} - m_O r_{CO}$$

or

$$M r_C = m_S r_{CS} - m_O r_{CO} \quad (2.34)$$

where we write M for the total mass of the molecule. Substituting (2.34) in (2.32):

$$\begin{aligned} I &= m_O (r_{CO} + r_C)^2 + m_C r_C^2 + m_S (r_{CS} - r_C)^2 \\ &= M r_C^2 + 2r_C (m_O r_{CO} - m_S r_{CS}) + m_O r_{CO}^2 + m_S r_{CS}^2 \end{aligned}$$

and finally substituting for r_C from Eq. (2.34):

$$I = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O r_{CO} - m_S r_{CS})^2}{M} \quad (2.35)$$

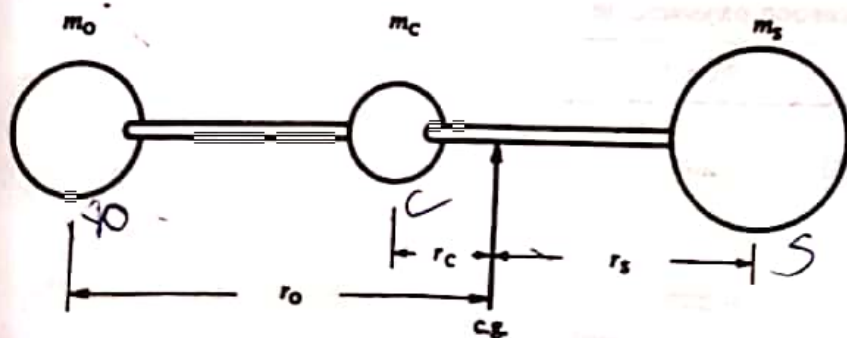


Figure 2.10 The molecule of carbon oxysulphide, OCS, showing the distances of each atom from the centre of gravity.

Considering now the isotopic molecule, ^{18}OCS , we may write m'_0 for m_0 throughout Eq. (2.35):

$$I' = m'_0 r_{\text{CO}}^2 + m_{\text{S}} r_{\text{CS}}^2 - \frac{(m'_0 r_{\text{CO}} - m_{\text{S}} r_{\text{CS}})^2}{M'} \quad (2.36)$$

and we can now solve for r_{CO} and r_{CS} , provided we have extracted a value for I' from the microwave spectrum of the isotopic molecule. Note that we do *not* need to write r'_{CO} , since we assume that the bond length is unaltered by isotopic substitution. This assumption may be checked by studying the molecules $^{16}\text{OC}^{34}\text{S}$ and $^{18}\text{OC}^{34}\text{S}$, since we would then have four moments of inertia. The bond distances found are quite consistent, and hence justify the assumption.

The extension of the above discussion to molecules with more than three atoms is straightforward; it suffices to say here that microwave studies have led to very precise determinations of many bond lengths in such molecules.

2.4.2 Symmetric Top Molecule

Although the rotational energy levels of this type of molecule are more complicated than those of linear molecules, we shall see that, because of their symmetry, their pure rotational spectra are still relatively simple. Choosing methyl fluoride again as our example we remember that

$$I_B = I_C \neq I_A \quad I_A \neq 0$$

CH_3F

There are now two directions of rotation in which the molecule might absorb or emit energy—that about the main symmetry axis (the C—F bond in this case) and that perpendicular to this axis.

We thus need two quantum numbers to describe the degree of rotation, one for I_A and one for I_B or I_C . However, it turns out to be very convenient mathematically to have a quantum number to represent the total angular momentum of the molecule, which is the sum of the separate angular momenta about the two different axes. This is usually chosen to be the quantum number J . Reverting for a moment to linear molecules, remember that we there used J to represent the end-over-end rotation of a molecule; however, this was the only sort of rotation allowed, so it is quite consistent to use J , in general, to represent the total angular momentum. It is then conventional to use K to represent the angular momentum about the top axis—i.e. about the C—F bond in this case.

Let us briefly consider what values are allowed to K and J . Both must, by the conditions of quantum mechanics, be integral or zero. The total angular momentum can be as large as we like, that is J can be 0, 1, 2, ..., ∞ (except, of course, for the theoretical possibility that a real molecule will be disrupted at very high rotational speeds). Once we have chosen J , however, K is rather more limited. Let us consider the case when $J = 3$. Plainly the rotational energy can be divided in several ways between motion about the main symmetry axis and motion perpendicular to this. If all the rotation is about the axis, $K = 3$; but note that K cannot be greater than J since J is the total angular momentum. Equally we could have $K = 2, 1, \text{ or } 0$, in which case the motion perpendicular to the axis increases accordingly. Additionally, however, K can be negative—we can imagine positive and negative values of K to correspond with clockwise and anticlockwise rotation about the symmetry axis—and so can have values $-1, -2, \text{ or } -3$.

In general, then, for a total angular momentum, J , we see that K can take values:

$$K = J, J-1, J-2, \dots, 0, \dots, -(J-1), -J \quad (2.37)$$

which is a total of $2J + 1$ values altogether. This figure of $2J + 1$ is important and will recur.

If we take first the case of a rigid symmetric top—i.e. one in which the bonds are supposed not to stretch under centrifugal forces—the Schrödinger equation may be solved to give the allowed energy levels for rotation as:

$$\epsilon_{J,K} = E_{J,K}/hc = BJ(J+1) + (A-B)K^2 \quad \text{cm}^{-1} \quad (2.38)$$

where, as before,

$$B = \frac{h}{8\pi^2 I_{BC}} \quad \text{and} \quad A = \frac{h}{8\pi^2 I_{AC}}$$

Note that the energy depends on K^2 , so that it is immaterial whether the top spins clockwise or anticlockwise: the energy is the same for a given angular momentum. For all $K > 0$, therefore, the rotational energy levels are doubly degenerate.

The selection rules for this molecule may be shown to be:

$$\Delta J = \pm 1 \quad (\text{as before}) \quad \text{and} \quad \Delta K = 0 \quad (2.39)$$

and, when these are applied to Eq. (2.38), the spectrum is given by:

$$\begin{aligned} \epsilon_{J+1,K} - \epsilon_{J,K} &= \bar{\nu}_{J,K} = B(J+1)(J+2) + (A-B)K^2 \\ &\quad - [BJ(J+1) + (A-B)K^2] \\ &= 2B(J+1) \quad \text{cm}^{-1} \end{aligned} \quad (2.40)$$

Thus the spectrum is independent of K , and hence rotational changes about the symmetry axis do not give rise to a rotational spectrum. The reason for this is quite evident—rotation about the symmetry axis does not change the dipole moment perpendicular to the axis (which always remains zero), and hence the rotation cannot interact with radiation. Equation (2.40) shows that the spectrum is just the same as for a linear molecule and that only one moment of inertia—that for end-over-end rotation—can be measured.

Equations (2.38) and (2.40) both apply to a rigid molecule. A real molecule, as we have seen, has elastic bonds and the picture inevitably becomes more complicated when the possible distortions of each individual bond in the symmetric top are allowed for. The details need not concern us here, but the microwave spectra of such molecules have, in the past, given very precise estimates of their bond lengths and angles. Table 2.3 collects some representative data for these, and for some linear and asymmetric top molecules (see the next section); this table illustrates the great precision which has been achieved.

Table 2.3 Some molecular data determined by microwave spectroscopy

Molecule	Type	Bond length (nm)	Bond angle (deg)
NaCl	Diatomic	0.236 06 ± 0.000 01	—
COS	Linear	{ 0.116 4 ± 0.000 1 (CO) 0.155 9 ± 0.000 1 (CS)	—
HCN	Linear	{ 0.106 317 ± 0.000 005 (CH) 0.115 535 ± 0.000 006 (CN)	—
NH ₃	Sym. top	0.100 8 ± 0.000 4	—
CH ₃ Cl	Sym. top	{ 0.109 59 ± 0.000 05 (CH) 0.178 12 ± 0.000 05 (CCl)	107.3 ± 0.2 108.0 ± 0.2
H ₂ O	Asym. top	0.095 84 ± 0.000 05	(HCH)
O ₃	Asym. top	0.127 8 ± 0.000 2	104.5 ± 0.3 116.8 ± 0.5

2.4.3 Asymmetric Top Molecules

Since spherical tops show no microwave spectrum (cf. Sec. 2.1(3)), the only other class of molecule of interest here is the asymmetric top. These molecules, having three different moments of inertia, also have much more complicated rotational energy levels and spectra. No simple general expression corresponding to Eqs (2.24) or (2.28) can be derived for them, and they are usually treated by approximative methods, much computation being required before agreement between observed and calculated spectra is achieved. However, such methods have been very successful for small molecules and much accurate bond length and bond angle data have been derived. Some examples are included in Table 2.3 above.

2.5 TECHNIQUES AND INSTRUMENTATION

It is not proposed to give more than a brief outline here of the techniques of microwave spectroscopy since detailed accounts are available elsewhere, and the technique is rarely used as a routine analysis tool now as it has been largely superseded by other methods. Figure 2.11 shows, very diagrammatically, how the various components discussed below are linked together.

1. *The source and monochromator.* The usual source in this region is the klystron valve which, since it emits radiation over only a very narrow frequency range, is called 'monochromatic' and acts as its own monochromator. The actual emission frequency is variable electronically, and so a spectrum may be scanned over a limited range of frequencies using a single klystron. One slight disadvantage of this source is that the total energy radiated is very small—of the order of milliwatts only. However, since this is all concentrated into a very narrow range of frequencies, the electric field generated at these frequencies is more intense than might be expected from the radiative power. This means that a sharply tuned detector can be sufficiently sensitive to detect the signal.
2. *Beam direction.* This is achieved by the use of 'waveguides'—hollow tubes of copper or silver, often of rectangular cross-section—inside which the radiation is confined. The tubing may be gently tapered or bent to focus or direct the radiation. Atmospheric absorption is considerable, so the whole system must be efficiently evacuated.
3. *Sample and sample space.* Normally the sample is gaseous and is retained in a piece of evacuated waveguide by very thin mica windows. Very small pressures are sufficient to obtain a spectrum, and many substances which are normally thought of as liquid or solid have sufficient vapour pressure to allow them to be studied by the technique.
4. *Detector.* It is possible to use a radio receiver as detector, provided it can be tuned to the appropriate high frequency; however, a simple crystal detector is found to be more sensitive

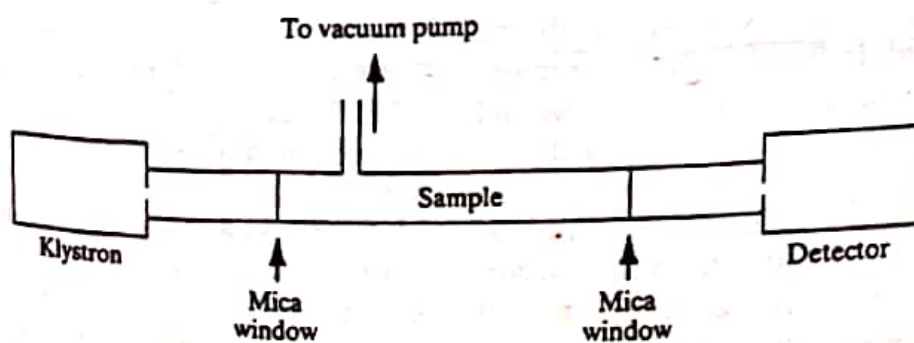


Figure 2.11 Schematic diagram of a microwave spectrometer.

and easier to use. This detects the radiation focused on it by the waveguide, and the signal it gives is amplified for display on an oscilloscope or for permanent record on paper.

2.6 CHEMICAL ANALYSIS BY MICROWAVE SPECTROSCOPY

Improvements and simplifications in the techniques of microwave spectroscopy are now allowing it to move away from being purely a specialist research instrument towards becoming a technique for routine analysis. Even though effectively limited to gaseous samples, it has much to offer in this respect, since it is a highly sensitive (0.01 mmHg pressure is adequate) and specific analytical tool.

The microwave spectrum of a substance is very rich in lines since many rotational levels are populated at room temperatures, but since the lines are very sharp and their positions can be measured with great accuracy, observation of just a few of them is sufficient, after comparison with tabulated data, to establish the presence of a previously examined substance in a sample. The technique is also quantitative, since the intensity of a spectrum observed under given conditions is directly dependent on the amount of substance present. Thus mixtures can be readily analysed.

It is the *whole* molecule, by virtue of its moment(s) of inertia, which is examined by microwave spectroscopy. This means that the technique cannot detect the presence of particular molecular groupings in a sample, like $-\text{OH}$ or $-\text{CH}_3$ (cf. the chapters on infra-red, Raman, and magnetic resonance spectroscopy later), but it can readily distinguish the presence of isotopes in a sample, and it can even detect different conformational isomers, provided they have different moments of inertia.

One fascinating area where microwave analysis is being used is in the chemical examination of interstellar space. Electronic spectroscopy has long been able to detect the presence of various atoms, ions, and a few radicals (for example $-\text{OH}$) in the light of stars but recently use of microwaves has extended the analysis to the detection of simple stable molecules in space. Some 80 or so molecules have already been characterized in this way, the earliest among them (water, ammonia, and formaldehyde) giving new impetus to speculations regarding the origins of biological molecules and of life itself. Such observations concern the emission of microwaves by these molecules and, by comparing the relative intensities of various rotational transitions, particularly in the spectrum of ammonia, accurate estimates can be made of the temperature of interstellar material.

2.7 THE MICROWAVE OVEN

One area where microwave radiation has become very familiar in recent years is the kitchen, in the shape of the microwave oven. While obviously not nearly as sophisticated as a spectrometer, its mode of operation depends entirely upon the absorption by the food of the microwave radiation in which it is bathed. In fact, it is the water molecules only which absorb the radiation and so become raised into high rotational states—the biological molecules in food are far too large to be able to rotate. As with many other excited states, the excess rotational energy of the water molecules is re-emitted as heat and the food becomes cooked.

The efficiency of the oven lies in the fact that this heating is *internal*. In a conventional hot oven a piece of meat or a cake is heated from the outside, and it must be left to cook until its centre has been raised to a sufficiently high temperature. In microwave heating, however, water molecules throughout the whole bulk of the food are simultaneously excited and 'heated', so cooking times are drastically reduced.

The effect of such concentrated microwave radiation on the human body, unfortunately, is similar—whatever is exposed to the radiation is rapidly heated and cooked from the inside! It is essential, therefore, to ensure that the door seal on a microwave is in good condition, so that no radiation is allowed to leak out.

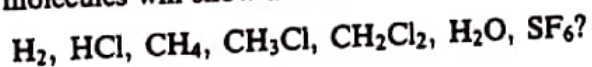
BIBLIOGRAPHY

- Chantry, G. W.: *Modern Aspects of Microwave Spectroscopy*, Academic Press, 1979.
 Ebsworth, E. A. V., D. W. H. Rankin, and S. Craddock: *Structural Methods in Inorganic Chemistry*, 2nd ed., Blackwell Scientific Publications, 1991.
 Gordy, W., and R. L. Cook: *Microwave Molecular Spectra (Techniques of Organic Chemistry, vol. 9)*, John Wiley, 1970.
 Gordy, W., W. V. Smith, and R. Trambarulo: *Microwave Spectroscopy*, John Wiley, 1966.
 Ingram, D. J. E.: *Spectroscopy at Radio and Microwave Frequencies*, 2nd ed., Butterworth, 1967.
 Kroto, H. W.: *Molecular Rotation Spectra*, Wiley-Interscience, 1975.
 Sugden, T. M., and N. C. Kenney: *Microwave Spectroscopy of Gases*, Van Nostrand, 1965.
 Townes, C. H., and A. L. Schawlow: *Microwave Spectroscopy*, McGraw-Hill, 1955.
 Wollrab, J. E.: *Rotational Spectra and Molecular Structure*, Academic Press, 1967.

PROBLEMS

(Useful constants: $h = 6.626 \times 10^{-34}$ J s; $k = 1.381 \times 10^{-23}$ J K⁻¹; $c = 2.998 \times 10^8$ m s⁻¹; $8\pi^2 \times 78.956$; atomic masses (in kg): $^1\text{H} = 1.673 \times 10^{-27}$, $^2\text{D} = 3.344 \times 10^{-27}$, $^{19}\text{F} = 31.55 \times 10^{-27}$, $^{35}\text{Cl} = 58.06 \times 10^{-27}$, $^{37}\text{Cl} = 61.38 \times 10^{-27}$, $^{79}\text{Br} = 131.03 \times 10^{-27}$, $^{127}\text{I} = 210.7 \times 10^{-27}$.)

2.1 Which of the following molecules will show a microwave rotational spectrum:



2.2 The rotational spectrum of $^{79}\text{Br}^{19}\text{F}$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the rotational constant, B , and hence the moment of inertia and bond length of the molecule. Determine the wavenumber of the $J = 9 \rightarrow J = 10$ transition, and find which transition gives rise to the most intense spectral line at room temperature (say 300 K). Calculate the number of revolutions per second which the BrF molecule undergoes when in (a) the $J = 0$ state, (b) the $J = 1$ state, and (c) the $J = 10$ state.
 Hint: Use $E = \frac{1}{2}I\omega^2$ in conjunction with Eqs (2.10) and (2.13), but remember that here ω is in radians per second.

2.3 The rotational constant for H^{37}Cl is observed to be 10.5909 cm^{-1} . What are the values of B for H^{37}Cl and for $^2\text{D}^{35}\text{Cl}$?

2.4 A microwave spectrometer capable of operating only between 60 and 90 cm^{-1} was used to observe the rotational spectra of HI and DI. Absorptions were measured as follows:

HI (cm^{-1})	DI (cm^{-1})
64.275	65.070
77.130	71.577
89.985	78.094
	84.591

Find B , I and r for each molecule, and determine the J values between which transitions occur for the first line listed above for each. Do your results support the usual assumption that bond length is unchanged by isotopic substitution?

2.5 Sketch a diagram similar to that of Fig. 2.7, using $B = 5 \text{ cm}^{-1}$ and a temperature of 1600 K. (Note: Find the maximum and calculate two or three points on either side only—do not attempt to carry out the calculation for every value of J .)

2.6 A space probe was designed to seek CO in the atmosphere of Saturn by looking for lines in its rotational spectrum. If the bond length of CO is 112.8 pm, at what wavenumbers do the first three

