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Class: Semester-6

Paper: C14T (Physical Chemistry)

Topic: Molecular Spectroscopy (Introduction, Rotational and vibrational spectroscopy)

Comments: Read as much as you can. The highlighted and the quoted portions are must read.

Reference: Fundamentals of molecular spectroscopy by C.N. Banwell

1.1 CHARACTERIZATION OF ELECTROMAGNETIC RADIATION

Molecular spectroscopy may be defined as the study of the **interaction of electromagnetic waves and matter**. Throughout this book we shall be concerned with what spectroscopy can tell us of the structure of matter, so it is essential in this first chapter to discuss briefly the nature of electromagnetic radiation and the sort of interactions which may occur; we shall also consider, in outline, the experimental methods of spectroscopy.

Electromagnetic radiation, of which visible light forms an obvious but very small part, may be considered as a simple harmonic wave propagated from a source and travelling in straight lines except when refracted or reflected. The properties which undulate—corresponding to the physical displacement of a stretched string vibrating, or the alternate compressions and rarefactions of the atmosphere during the passage of a sound wave—are interconnected electric and magnetic fields. We shall see later that it is these undulatory fields which interact with matter giving rise to a spectrum.

It is trivial to show that any simple harmonic wave has properties of the sine wave, defined by $y = A \sin \theta$, which is plotted in Fig. 1.1. Here y is the displacement with a maximum value A ,

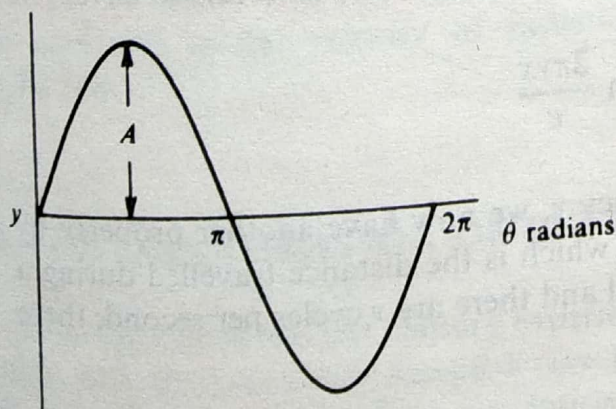


Figure 1.1 The curve of $y = A \sin \theta$.

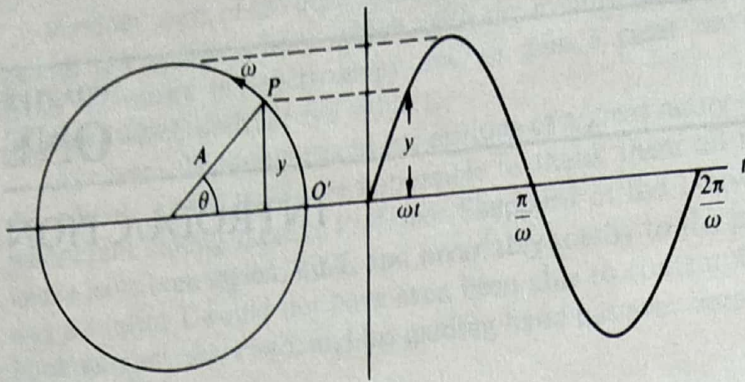


Figure 1.2 The description of a sine curve in terms of the circular motion of a point P at a uniform angular velocity of $\omega \text{ rad s}^{-1}$

and θ is an angle varying between 0 and 360° (or 0 and 2π radians). The relevance of this representation to a travelling wave is best seen by considering the left-hand side of Fig. 1.2. A point P travels with uniform angular velocity $\omega \text{ rad s}^{-1}$ in a circular path of radius A ; we measure the time from the instant when P passes O' and then, after a time t seconds, we imagine P to have described an angle $\theta = \omega t$ radians. Its vertical displacement is then $y = A \sin \theta = A \sin \omega t$, and we can plot this displacement against time as on the right-hand side of Fig. 1.2. After a time of $2\pi/\omega$ seconds, P will return to O' , completing a 'cycle'. Further cycles of P will repeat the pattern and we can describe the displacement as a continuous function of time by the graph of Fig. 1.2.

In one second the pattern will repeat itself $\omega/2\pi$ times, and this is referred to as the frequency (ν) of the wave. The SI unit of frequency is called the hertz (abbreviated to Hz) and has the dimensions of reciprocal seconds (abbreviated s^{-1}). We may then write:

$$y = A \sin \omega t = A \sin 2\pi \nu t \tag{i.1}$$

as a basic equation of wave motion.

So far we have discussed the variation of displacement with time, but in order to consider the nature of a travelling wave, we are more interested in the distance variation of the displacement. For this we need the fundamental distance-time relationship:

$$x = ct \tag{1.2}$$

where x is the distance covered in time t at a speed c . Combining (1.1) and (1.2) we have:

$$y = A \sin 2\pi \nu t = A \sin \frac{2\pi \nu x}{c}$$

and the wave is shown in Fig. 1.3. Besides the frequency ν , we now have another property by which we can characterize the wave—its wavelength λ , which is the distance travelled during a complete cycle. When the velocity is c metres per second and there are ν cycles per second, there are evidently ν waves in c metres, or

$$\underline{\nu \lambda = c} \quad \lambda = c/\nu \text{ metres} \tag{1.3}$$

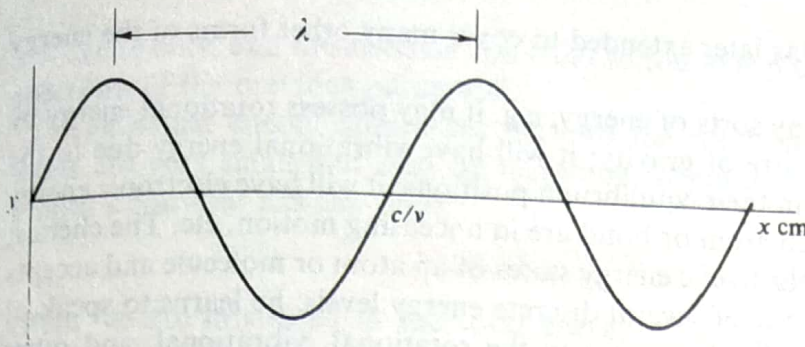


Figure 1.3 The concept of a travelling wave of wavelength λ .

so we have:

$$y = A \sin \frac{2\pi x}{\lambda} \quad (1.4)$$

In spectroscopy wavelengths are expressed in a variety of units, chosen so that in any particular range (see Fig. 1.4) the wavelength does not involve large powers of ten. Thus, in the microwave region, λ is measured in centimetres or millimetres, while in the infra-red it is usually given in micrometres (μm)—formerly called the *micron*—where:

$$1 \mu\text{m} = 10^{-6} \text{ m} \quad (1.5)$$

In the visible and ultra-violet region λ is usually expressed in nanometres (10^{-9} m), although occasional use is still made of the non-SI ångström unit where:

$$1 \text{ \AA} = 10^{-10} \text{ m} \quad \text{or} \quad 1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{ \AA} \quad (1.6)$$

There is yet a third way in which electromagnetic radiation can be usefully characterized, and this is in terms of the *wavenumber* $\bar{\nu}$. Formally this is defined as the reciprocal of the wavelength expressed in *centimetres*:

$$\bar{\nu} = 1/\lambda \text{ cm}^{-1} \quad (1.7)$$

and hence

$$y = A \sin 2\pi\bar{\nu}x \quad (1.8)$$

It is more useful to think of the wavenumber, however, as the number of complete waves or cycles contained in each centimetre length of radiation.

It is unfortunate that the conventional symbols of **wavenumber ($\bar{\nu}$)** and **frequency (ν)** are similar; confusion should not arise, however, if the units of any expression are kept in mind, since **wavenumber is invariably expressed in reciprocal centimetres (cm^{-1})** and **frequency in cycles per second (s^{-1} or Hz)**. The two are, in fact, proportional: $\nu = c\bar{\nu}$, where the proportionality constant is the velocity of radiation expressed in *centimetres* per second (that is $3 \times 10^{10} \text{ cm s}^{-1}$).

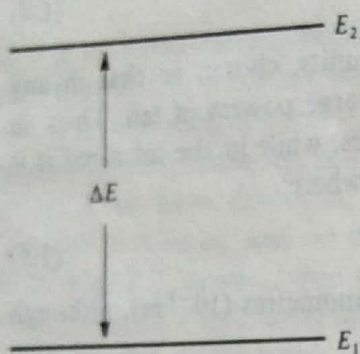
1.2 THE QUANTIZATION OF ENERGY

Towards the end of the last century experimental data were observed which were quite incompatible with the previously accepted view that matter could take up energy continuously. In 1900 Max Planck published the revolutionary idea that the energy of an oscillator is discontinuous and that any change in its energy content can occur only by means of a jump between

two distinct energy states. The idea was later extended to cover many other forms of the energy of matter.

A molecule in space can have many sorts of energy; e.g. it may possess rotational energy by virtue of bodily rotation about its centre of gravity; it will have vibrational energy due to the periodic displacement of its atoms from their equilibrium positions; it will have electronic energy since the electrons associated with each atom or bond are in unceasing motion, etc. The chemist or physicist is early familiar with the electronic energy states of an atom or molecule and accepts the idea that an electron can exist in one of several discrete energy levels: he learns to speak of the energy as being *quantized*. In much the same way the rotational, vibrational, and other energies of a molecule are also quantized—a particular molecule can exist in a variety of rotational, vibrational, etc., energy levels and can move from one level to another only by a sudden jump involving a finite amount of energy.

Consider two possible energy states of a system—two rotational energy levels of a molecule, for example—labelled E_1 and E_2 in the following diagram:



The suffixes 1 and 2 used to distinguish these levels are, in fact, *quantum numbers*. The actual significance of quantum numbers goes far deeper than their use as a convenient label—in particular, we shall later see that analytical expressions for energy levels usually involve an algebraic function of one or more quantum numbers. Transitions can take place between the levels E_1 and E_2 provided the appropriate amount of energy, $\Delta E = E_2 - E_1$, can be either absorbed or emitted by the system. Planck suggested that such absorbed or emitted energy can take the form of electromagnetic radiation and that the frequency of the radiation has the simple form:

$$\nu = \Delta E/h \quad \text{Hz}$$

i.e.

$$\Delta E = h\nu \quad \text{joules} \quad (1.9)$$

where we express our energies E in terms of the joule, and h is a universal constant—Planck's constant. This suggestion has been more than amply confirmed by experiment.

The significance of this is that if we take a molecule in state 1 and direct on to it a beam of radiation of a single frequency ν (monochromatic radiation), where $\nu = \Delta E/h$, energy will be absorbed from the beam and the molecule will jump to state 2. A detector placed to collect the radiation after its interaction with the molecule will show that its intensity has decreased. Also if we use a beam containing a wide range of frequencies ('white' radiation), the detector will show that energy has been absorbed *only* from that frequency $\nu = \Delta E/h$, all other frequencies being undiminished in intensity. In this way we have produced a spectrum—an *absorption spectrum*.

Alternatively the molecule may already be in state 2 and may revert to state 1 with the consequent emission of radiation. A detector would show this radiation to have frequency

$\nu = \Delta E/h$ only, and the **emission spectrum** so found is plainly complementary to the absorption spectrum of the previous paragraph.

The actual energy differences between the rotational, vibrational, and electronic energy levels are very small and may be measured in joules per molecule (or atom). In these units Planck's constant has the value:

$$h = 6.63 \times 10^{-34} \text{ joules s molecule}^{-1}$$

Often we are interested in the total energy involved when a gram-molecule of a substance changes its energy state: for this we multiply by the Avogadro number $N = 6.02 \times 10^{23}$.

However, the spectroscopist measures the various characteristics of the absorbed or emitted radiation during transitions between energy states and often, rather loosely, uses frequency, wavelength, and wavenumber as if they were energy units. Thus in referring to 'an energy of 10 cm^{-1} ', the spectroscopist means 'a separation between two energy states such that the associated radiation has a wavenumber value of 10 cm^{-1} '. The first expression is so simple and convenient that it is essential to become familiar with wavenumber and frequency energy units if one is to understand the spectroscopist's language. Throughout this book we shall use the symbol ϵ to represent energy in cm^{-1} .

It cannot be too firmly stressed at this point that the frequency of radiation associated with an energy change does *not* imply that the transition between energy levels occurs a certain number of times each second. Thus an electronic transition in an atom or molecule may absorb or emit radiation of frequency some 10^{15} Hz, but the electronic transition does not itself *occur* 10^{15} times per second. It may occur once or many times and on each occurrence it will absorb or emit an energy quantum of the appropriate frequency.

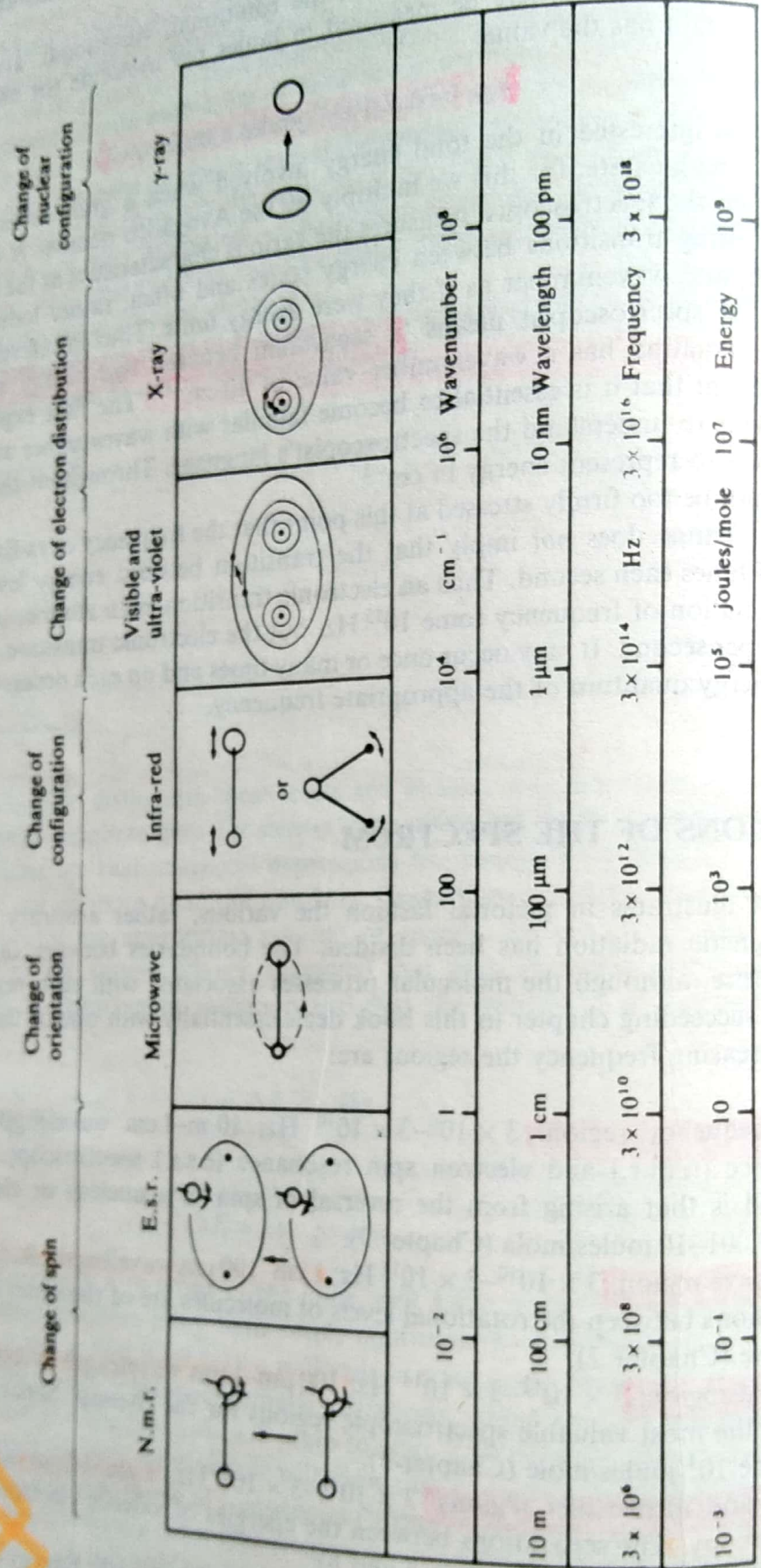
1.3 REGIONS OF THE SPECTRUM

Figure 1.4 illustrates in pictorial fashion the various, rather arbitrary, regions into which electromagnetic radiation has been divided. The boundaries between the regions are by no means precise, although the molecular processes associated with each region are quite different. Each succeeding chapter in this book deals essentially with one of these processes.

In increasing frequency the regions are:

1. **Radiofrequency region:** $3 \times 10^6 - 3 \times 10^{10}$ Hz; 10 m–1 cm wavelength. Nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) spectroscopy. The energy change involved is that arising from the reversal of spin of a nucleus or electron, and is of the order 0.001–10 joules/mole (Chapter 7).
2. **Microwave region:** $3 \times 10^{10} - 3 \times 10^{12}$ Hz; 1 cm–100 μm wavelength. Rotational spectroscopy. Separations between the rotational levels of molecules are of the order of hundreds of joules per mole (Chapter 2).
3. **Infra-red region:** $3 \times 10^{12} - 3 \times 10^{14}$ Hz; 100 μm –1 μm wavelength. Vibrational spectroscopy. One of the most valuable spectroscopic regions for the chemist. Separations between levels are some 10^4 joules/mole (Chapter 3).
4. **Visible and ultra-violet regions:** $3 \times 10^{14} - 3 \times 10^{16}$ Hz; 1 μm –10 nm wavelength. Electronic spectroscopy. The separations between the energies of valence electrons are some hundreds of kilojoules per mole (Chapters 5 and 6).
5. **X-ray region:** $3 \times 10^{16} - 3 \times 10^{18}$ Hz; 10 nm–100 pm wavelength. Energy changes involving the inner electrons of an atom or a molecule, which may be of order ten thousand kilojoules (Chapter 5).

↑
 E increase
 ↓
 E increase



λ increases ←
 Energy increases →

Figure 1.4 The regions of the electromagnetic spectrum.

6. γ -ray region: 3×10^{18} – 3×10^{20} Hz; 100 pm–1 pm wavelength. Energy changes involve the rearrangement of nuclear particles, having energies of 10^9 – 10^{11} joules per gram atom (Chapter 9).

One other type of spectroscopy, that discovered by Raman and bearing his name, is discussed in Chapter 4. This, it will be seen, yields information similar to that obtained in the microwave and infra-red regions, although the experimental method is such that observations are made in the visible region.

In order that there shall be some mechanism for interaction between the incident radiation and the nuclear, molecular, or electronic changes depicted in Fig. 1.4, there must be some electric or magnetic effect produced by the change which can be influenced by the electric or magnetic fields associated with the radiation. There are several possibilities:

1. The radiofrequency region. We may consider the nucleus and electron to be tiny charged particles, and it follows that their spin is associated with a tiny magnetic dipole. The reversal of this dipole consequent upon the spin reversal can interact with the magnetic field of electromagnetic radiation at the appropriate frequency. Consequently all such spin reversals produce an absorption or emission spectrum.
2. The microwave region. A molecule such as hydrogen chloride, HCl, in which one atom (the hydrogen) carries a permanent net positive charge and the other a net negative charge, is said to have a permanent electric dipole moment. H_2 or Cl_2 , on the other hand, in which there is no such charge separation, have a zero dipole. If we consider the rotation of HCl (Fig. 1.5, where we notice that if only a pure rotation takes place, the centre of gravity of the molecule must not move), we see that the plus and minus charges change places periodically, and the component dipole moment in a given direction (say upwards in the plane of the paper) fluctuates regularly. This fluctuation is plotted in the lower half of Fig. 1.5, and it is seen to be exactly similar in form to the fluctuating electric field of radiation (cf. Fig. 1.2). Thus interaction can occur, energy can be absorbed or emitted, and the rotation gives rise to a spectrum. All molecules having a permanent moment are said to be 'microwave active'. If there is no dipole, as in H_2 or Cl_2 , no interaction can take place and the molecule is 'microwave inactive'. This imposes a limitation on the applicability of microwave spectroscopy.

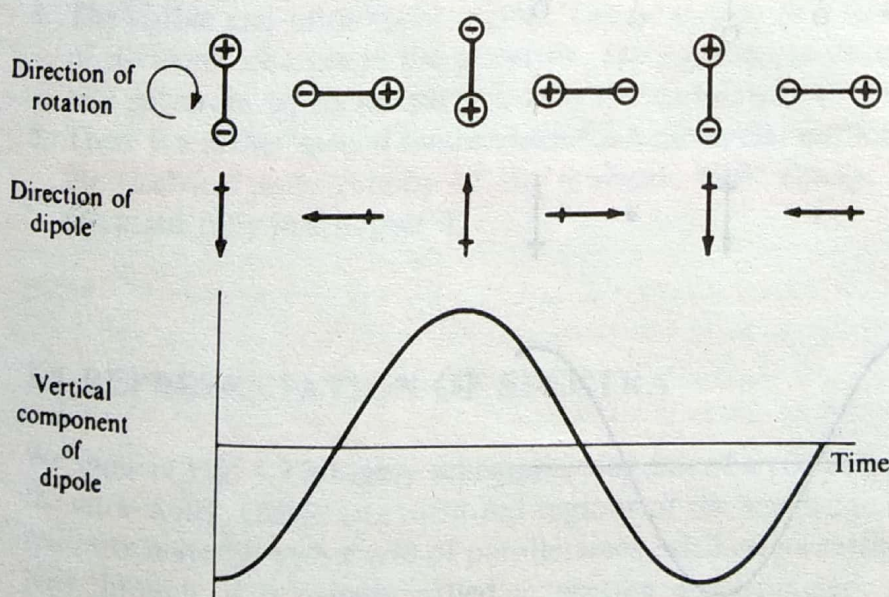


Figure 1.5 The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction.

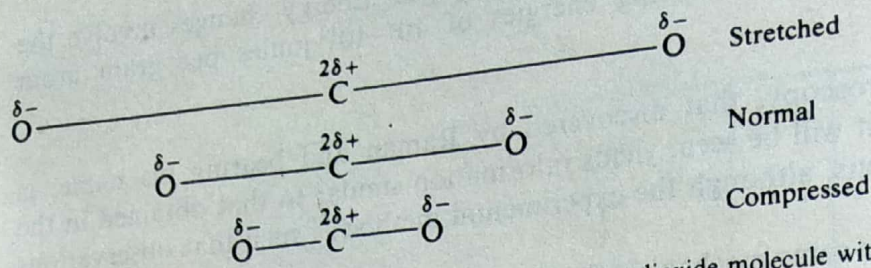
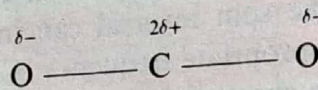


Figure 1.6 The symmetric stretching vibration of the carbon dioxide molecule with amplitude much exaggerated.

3. The infra-red region. Here it is a vibration, rather than a rotation, which must give rise to a dipole change. Consider the carbon dioxide molecule as an example, in which the three atoms are arranged linearly with a small net positive charge on the carbon and small negative charges on the oxygens:



During the mode of vibration known as the 'symmetric stretch', the molecule is alternately stretched and compressed, both C—O bonds changing simultaneously, as in Fig. 1.6. Plainly the dipole moment remains zero throughout the whole of this motion, and this particular vibration is thus 'infra-red inactive'.

However, there is another stretching vibration called the 'anti-symmetrical stretch', depicted in Fig. 1.7. Here one bond stretches while the other is compressed, and vice versa. As the

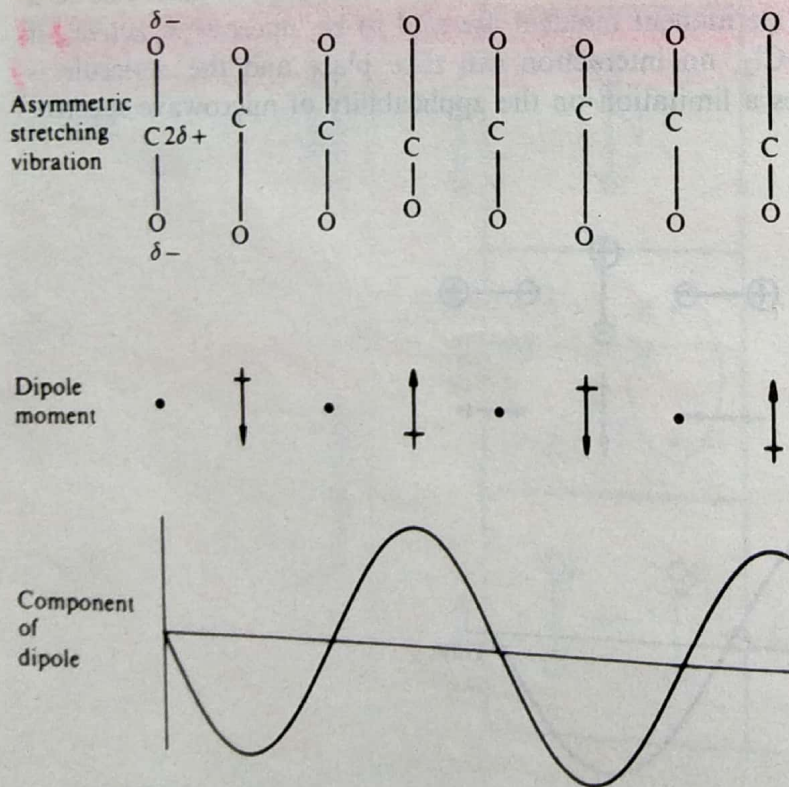


Figure 1.7 The asymmetric stretching vibration of the carbon dioxide molecule, showing the fluctuation in the dipole moment.

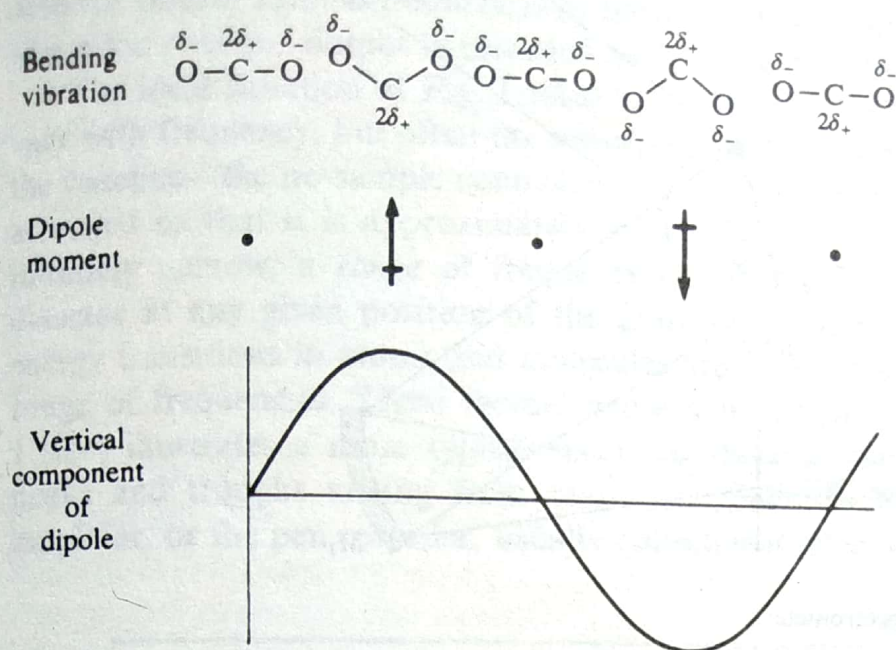


Figure 1.8 The bending motion of the carbon dioxide molecule and its associated dipole fluctuation.

figure shows, there is a periodic alteration in the dipole moment, and the vibration is thus 'infra-red active'. One further vibration is allowed to this molecule (see Chapter 3 for a more detailed discussion), known as the bending mode. This, as shown in Fig. 1.8, is also infra-red active. In neither of these motions does the centre of gravity move. Note particularly that the relative motions of the atoms are very much exaggerated in Figs 1.6, 1.7, and 1.8; in real molecules the displacement of atoms during vibrations is seldom more than about 10 per cent of the bond length.

Although dipole change requirements do impose some limitation on the application of infra-red spectroscopy, the appearance or non-appearance of certain vibration frequencies can give valuable information about the structure of a particular molecule (see Chapter 3).

4. The visible and ultra-violet region. The excitation of a valence electron involves the moving of electronic charges in the molecule. The consequent change in the electric dipole gives rise to a spectrum by its interaction with the undulatory electric field of radiation.
5. There is a rather special requirement for a molecular motion to be 'Raman active'; this is that the electrical polarizability of the molecule must change during the motion. This will be discussed fully in Chapter 4.

1.4 REPRESENTATION OF SPECTRA

We show in Fig. 1.9 a highly schematic diagram of a recording spectrometer suitable for use in the ultra-violet, visible and infra-red regions of the spectrum; since it uses a grating (a block of reflective material with a grid of parallel lines ruled on its surface) to select the frequencies which pass through, it is usually called a 'grating spectrometer'; another term frequently used is 'dispersive spectrometer' since the grating 'disperses' the radiation into its frequency components.

10 FUNDAMENTALS OF MOLECULAR SPECTROSCOPY

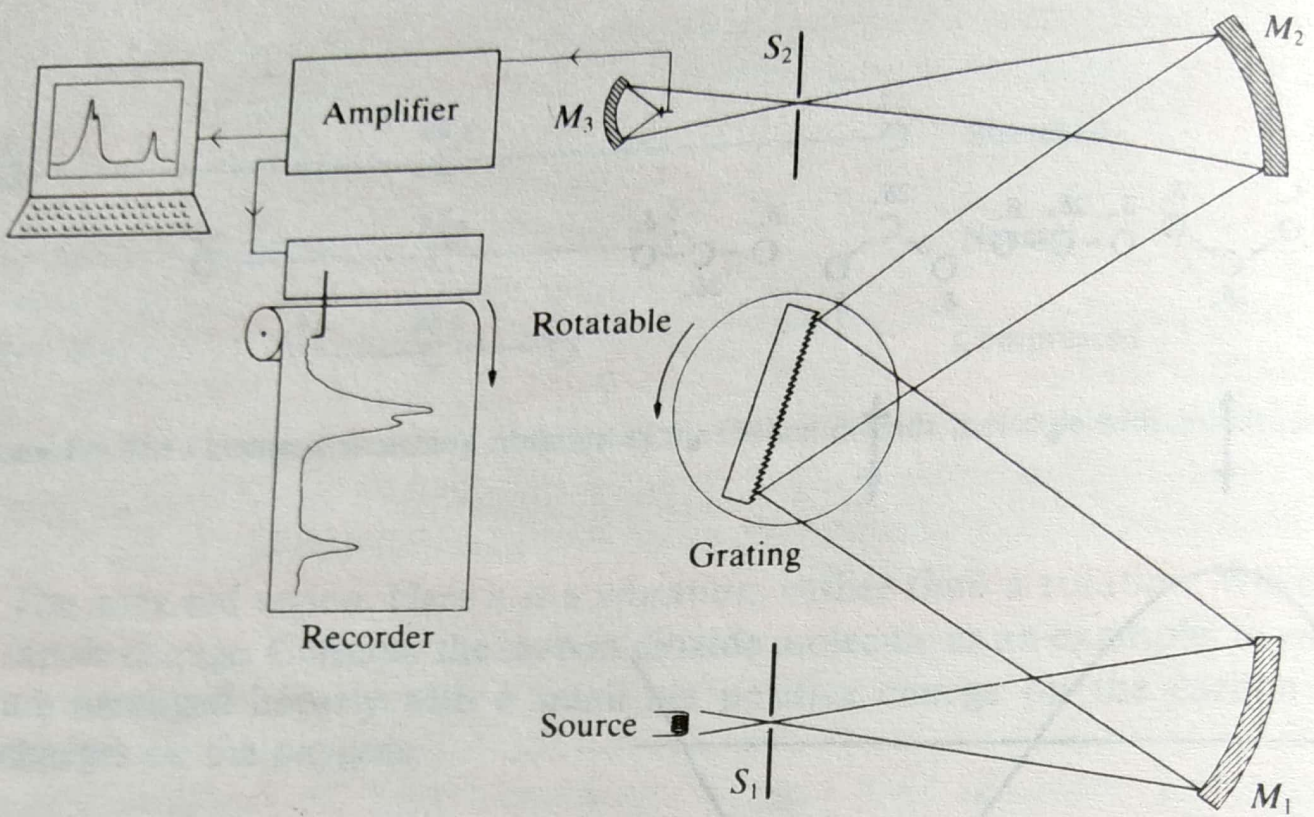
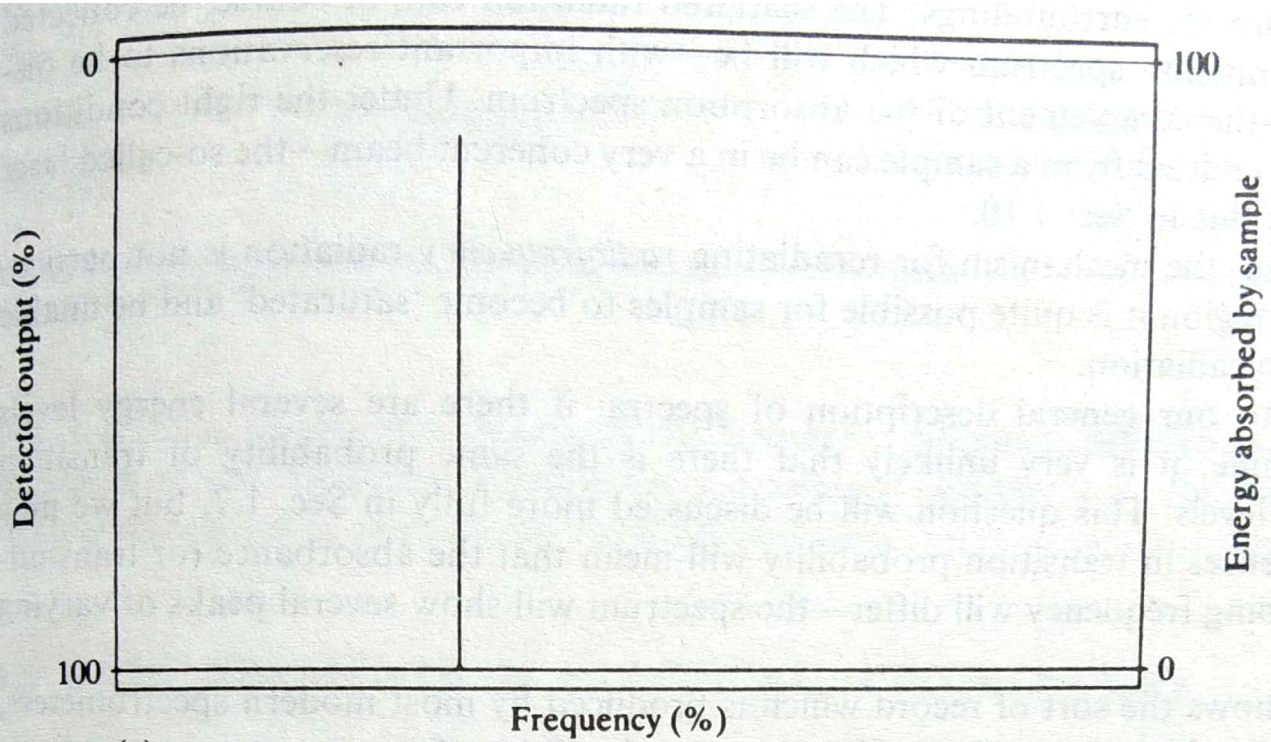
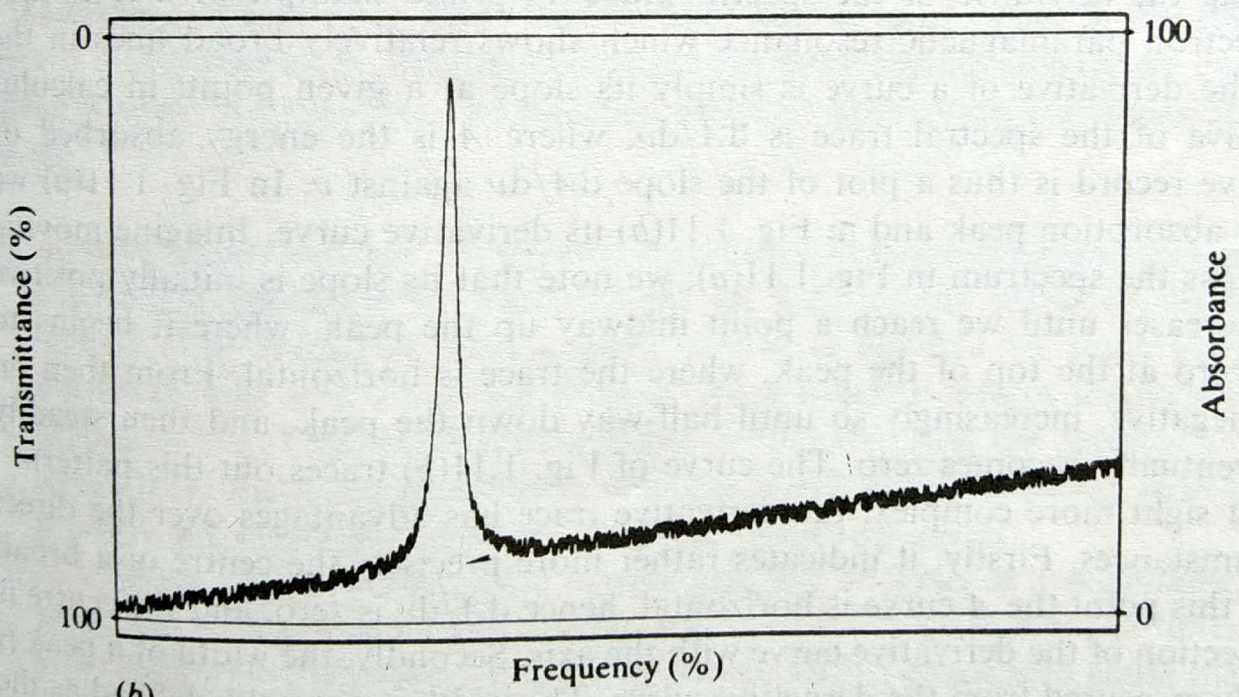


Figure 1.9 Schematic diagram of a grating spectrometer.



(a)



(b)

Figure 1.10 The spectrum of a molecule undergoing a single transition: (a) idealized and (b) usual appearance.

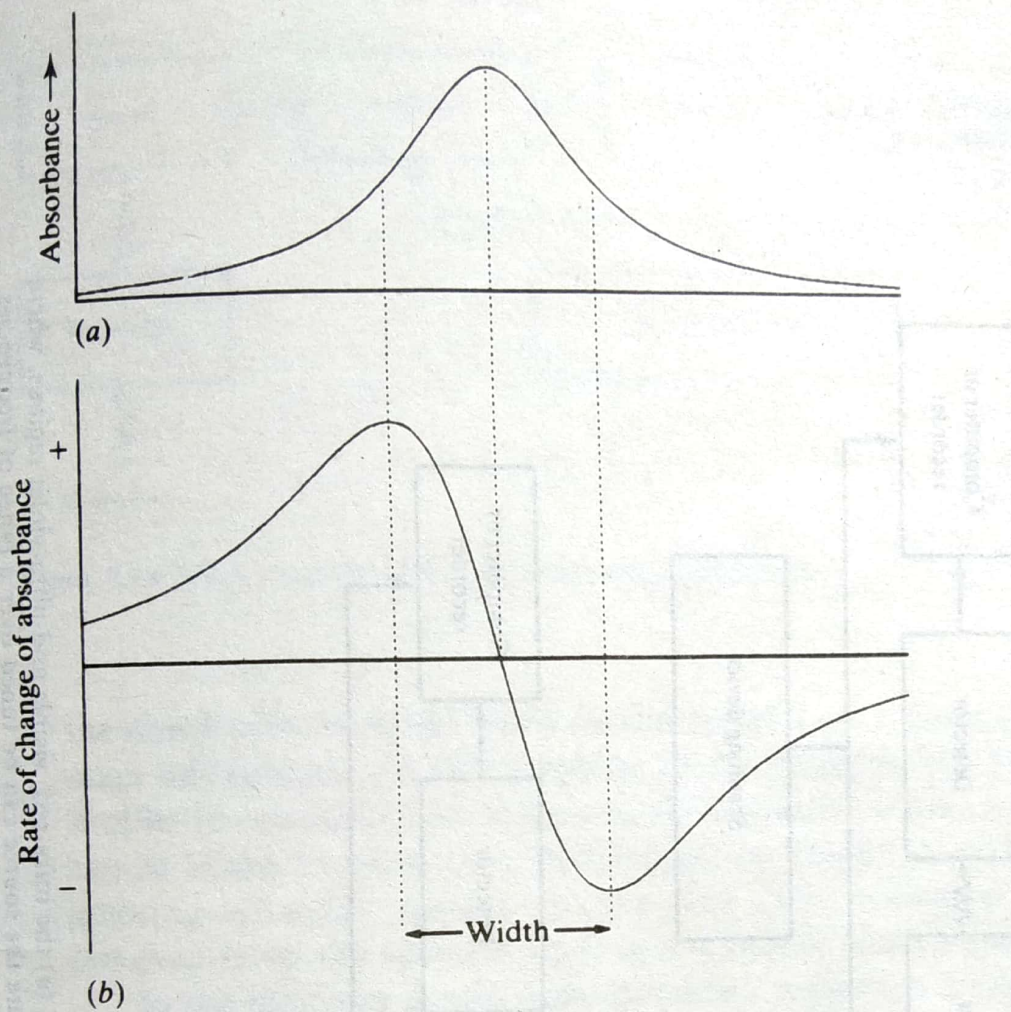


Figure 1.11 The relationship between absorption and derivative spectra: (a) a broad absorption band and (b) its derivative.

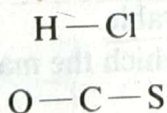
MICROWAVE SPECTROSCOPY

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.

- ✓ *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

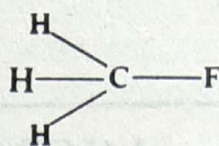


The three directions of rotation may be taken as (a) about the bond axis, (b) end-over-end rotation in the plane of the paper, and (c) end-over-end rotation at right angles to the plane. It is self-evident that the moments of (b) and (c) are the same (that is $I_B = I_C$) while that of (a) is very small. 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:

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

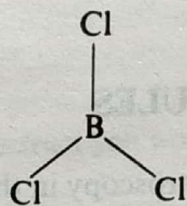
2. *Symmetric tops.* Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below:



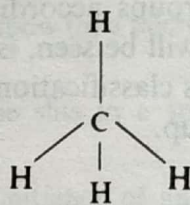
As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper are still identical and we have $I_B = I_C$. The moment of inertia about the C—F bond axis (chosen as the main rotational axis since the centre of gravity lies along it) is now not negligible, however, 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:



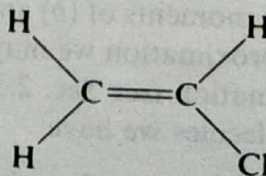
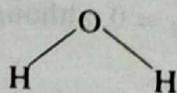
$$\text{Spherical tops: } I_A = I_B = I_C \quad (2.3)$$

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:

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

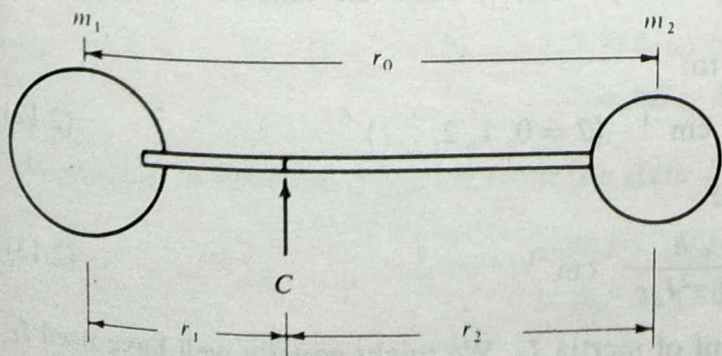


Figure 2.1 A rigid diatomic molecule treated as two masses, m_1 and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$.

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:

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

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:

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

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

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

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.

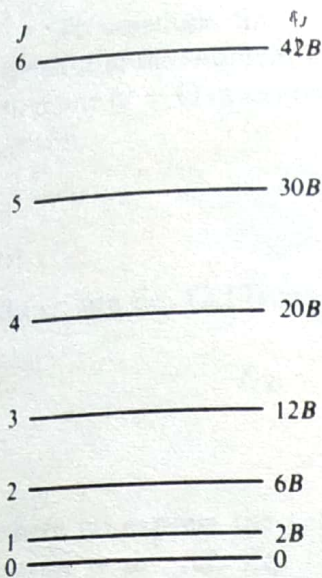


Figure 2.2 The allowed rotational energies of a rigid diatomic molecule.

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:

$$\begin{aligned} \bar{\nu}_{J \rightarrow J+1} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[J^2 + 3J + 2 - (J^2 + J)] \end{aligned} \quad (2.16)$$

or

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

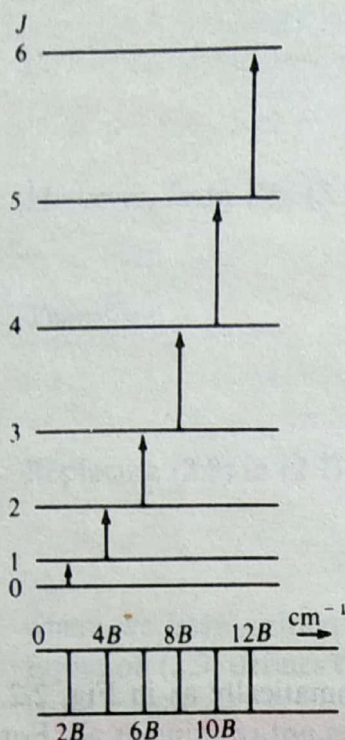


Figure 2.3 Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

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.

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):

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

or

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

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

$$\begin{aligned} I_{CO} &= \frac{6.626 \times 10^{-34}}{8\pi^2 \times 2.99793 \times 10^{10} \times B} = \frac{27.9907 \times 10^{-47}}{B} \text{ kg m}^2 \\ &= 14.5695_4 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

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 ($H = 1.0080$) to be $C = 12.0000$, $O = 15.9994$, 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:

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

Hence:

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

and

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

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:

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

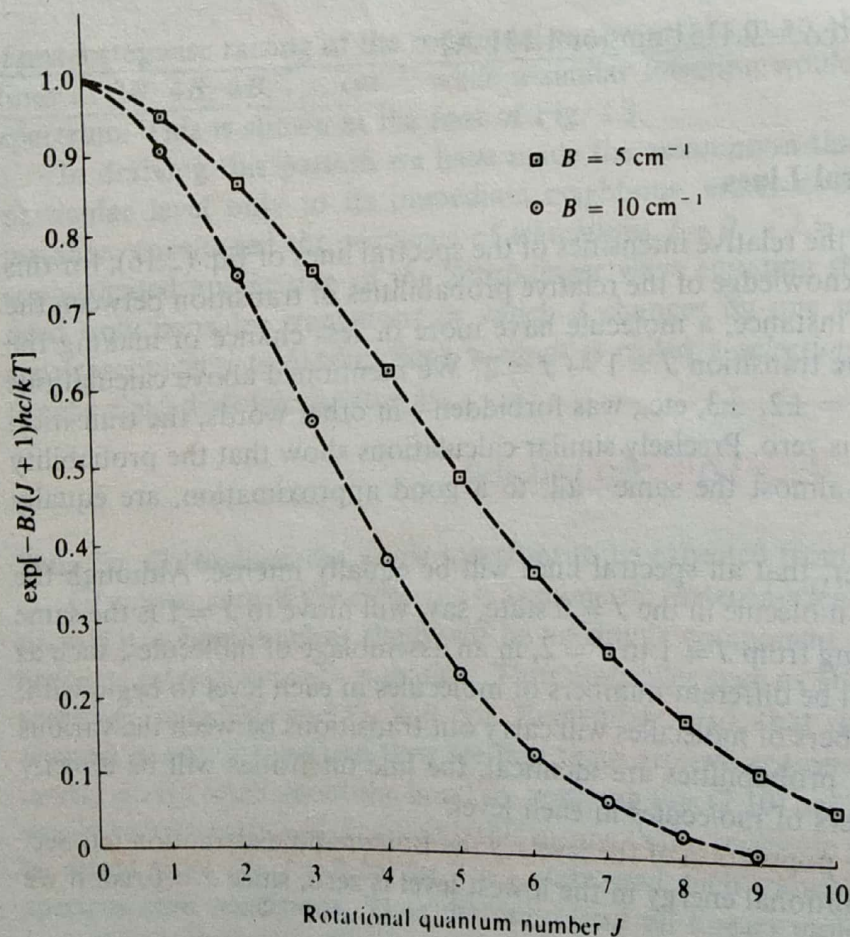


Figure 2.4 The Boltzmann populations of the rotational energy levels of Fig. 2.2. The diagram has been drawn taking values of $B = 5$ and 10 cm^{-1} and $T = 300 \text{ K}$ in Eq. (2.18).

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:

$$\mathbf{P} = \sqrt{2EI} \quad E = \frac{P^2}{2I}$$

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

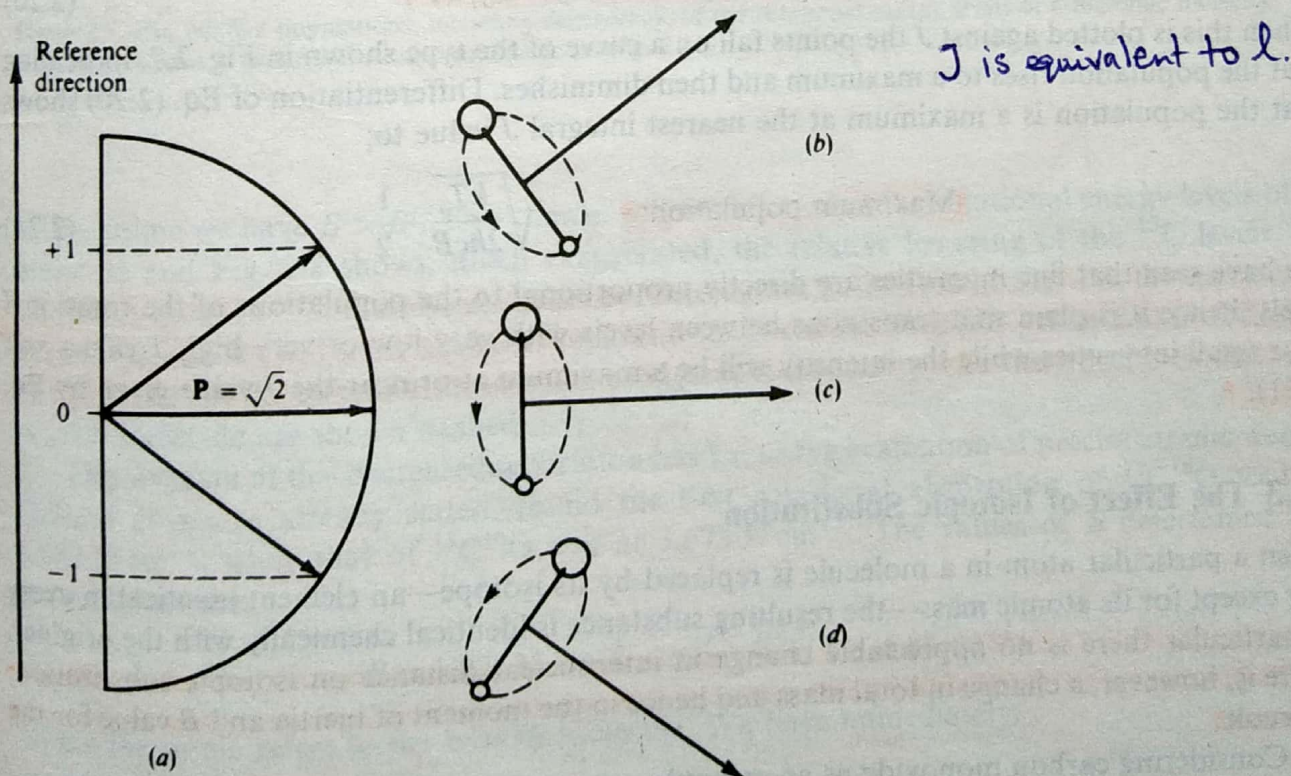


Figure 2.5 The three degenerate orientations of the rotational angular momentum vector for a molecule with $J = 1$.

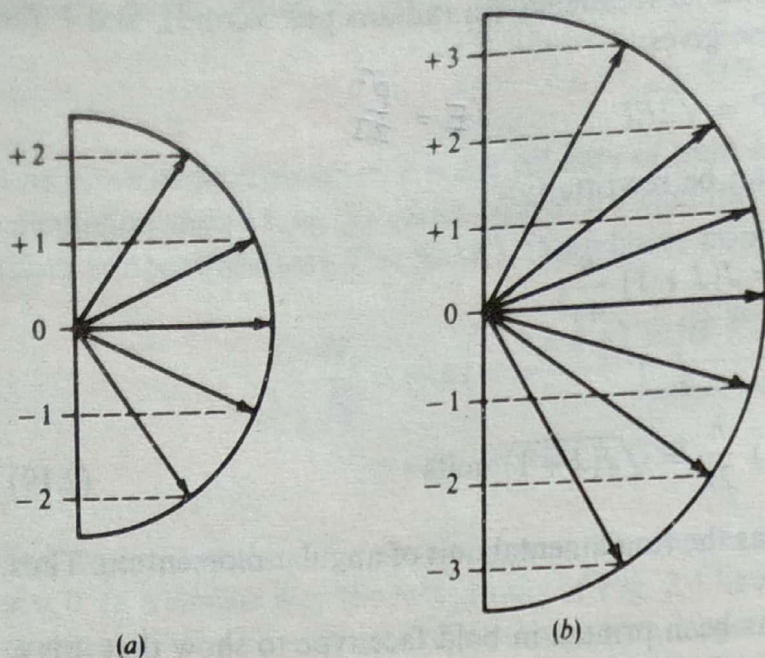


Figure 2.6 The five and seven degenerate rotational orientations for a molecule with $J = 2$ and $J = 3$, respectively.

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

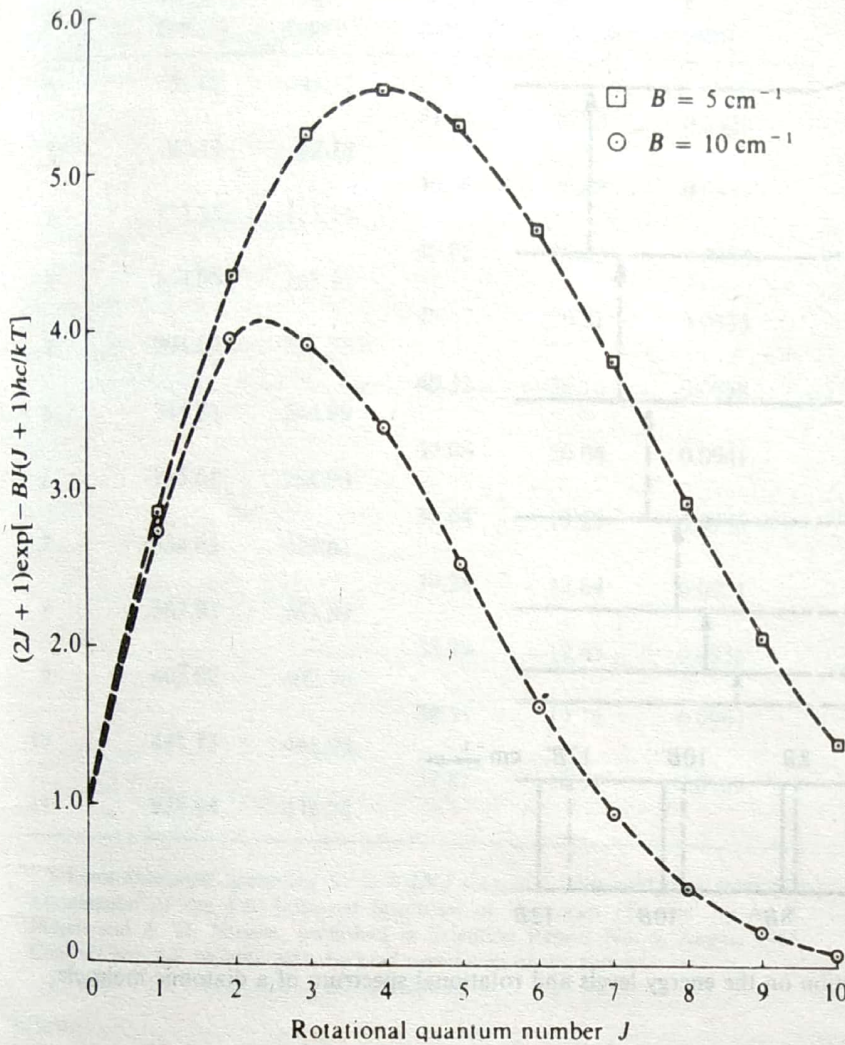


Figure 2.7 The relative populations, including degeneracy, of the rotational energy levels of a diatomic molecule. The diagram has been drawn for the same conditions as Fig. 2.4.

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:

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

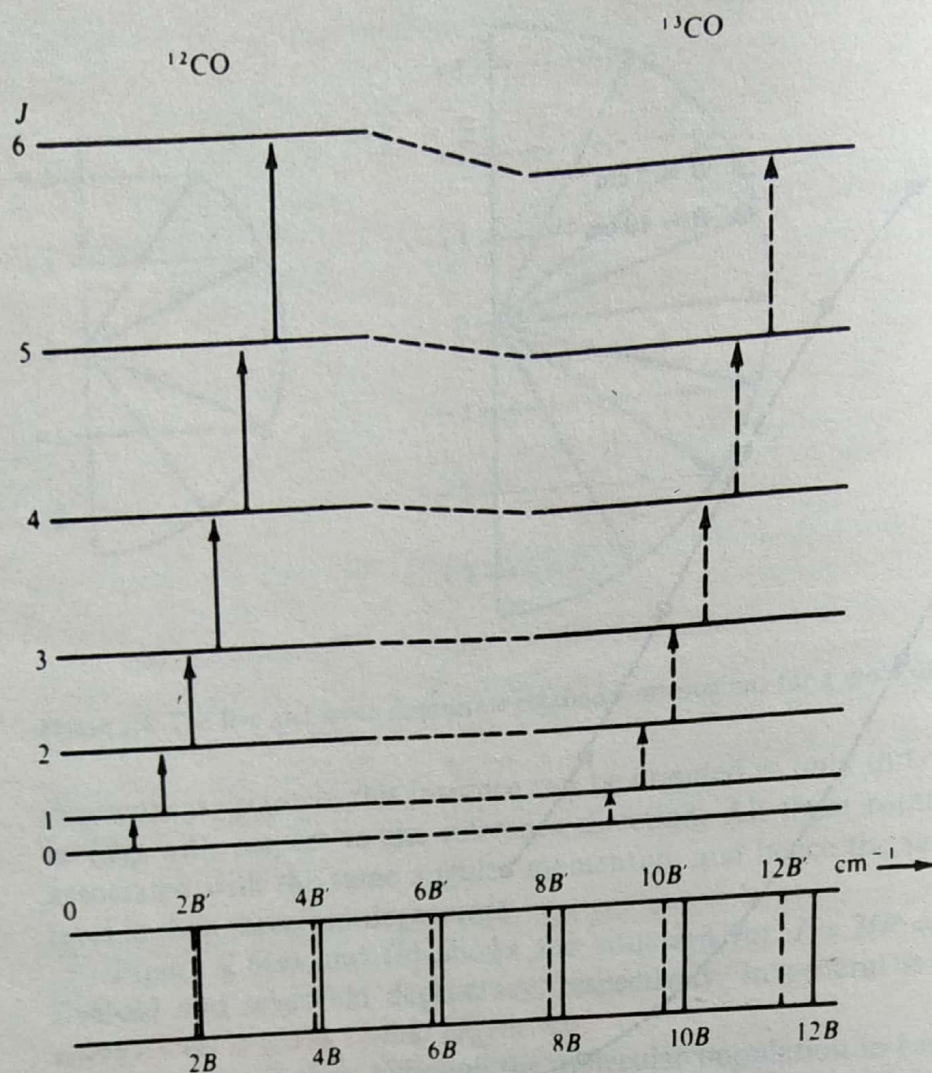


Figure 2.8 The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide.

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	$\bar{\nu}_{\text{obs.}} \dagger$ (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			

† 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.

‡ 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:

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

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

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:

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

but

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

and therefore $\langle r \rangle_{\text{av.}} = \sqrt{1/103.5} = 0.0985 \text{ nm}$. 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 $r_{\text{av.}}$ being greater than $r_{\text{eq.}}$.

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:

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

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:

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

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.

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

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.
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	...		
1 → 2	0.8109	2×0.4055	0.2027
2 → 3	1.2163	0.4054	0.2027
3 → 4	1.6217	0.4054	0.2027
4 → 5	0.0271	0.4054	0.2027

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

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

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	107.3 ± 0.2
CH ₃ Cl	Sym. top	{ 0.109 59 ± 0.000 05 (CH) 0.178 12 ± 0.000 05 (CCl)	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.

2.7 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.

INFRA-RED SPECTROSCOPY

We saw in the previous chapter how the elasticity of chemical bonds led to anomalous results in the rotational spectra of rapidly rotating molecules—the bonds stretched under centrifugal forces. In this chapter we consider another consequence of this elasticity—the fact that atoms in a molecule do not remain in fixed relative positions but vibrate about some mean position. We consider first the case of a diatomic molecule and the spectrum which arises if its only motion is vibration; then we shall deal with the more practical case of a diatomic molecule undergoing vibration and rotation simultaneously; finally we shall extend the discussion to more complex molecules.

3.1 THE VIBRATING DIATOMIC MOLECULE

3.1.1 The Energy of a Diatomic Molecule

When two atoms combine to form a stable covalent molecule, for example HCl, they may be said to do so because of some internal electronic rearrangement. We shall not here discuss the detailed mechanisms of chemical bond formation, but we can simply look on the phenomenon as a balancing of forces. On the one hand there is a repulsion between the positively charged nuclei of both atoms, and between their negative electron 'clouds'; on the other there is an attraction between the nucleus of one atom and the electrons of the other, and vice versa. The two atoms settle at a mean internuclear distance such that these forces are just balanced and the total energy of the whole system is a minimum. Squeezing the atoms more closely together will cause the repulsive force to rise rapidly, while pulling them apart is resisted by the attractive force. Any attempt to distort the bond length requires an input of energy and we may plot energy against internuclear distance as in Fig. 3.1, where we have 'anchored' the chlorine atom on one axis and imagine pushing and pulling the hydrogen atom closer to or further from the chlorine—a bigger push or pull results in raising the energy more. At the energy minimum the internuclear distance is referred to as the equilibrium distance r_{eq} , or more simply as the bond length.

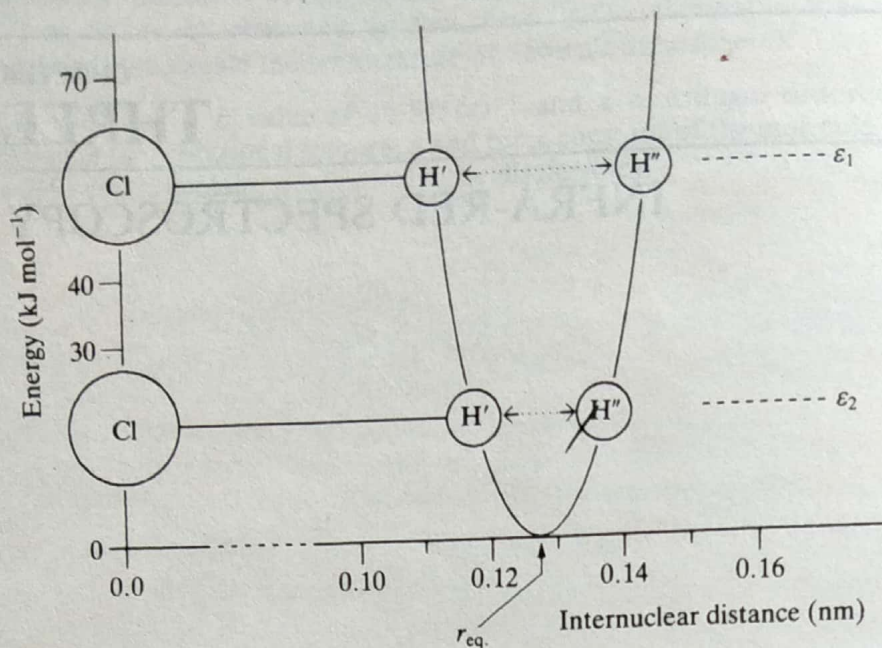


Figure 3.1 The energy of HCl as the bond is compressed or extended.

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

$$m \frac{d^2 r}{dt^2} = f = -k(r - r_{eq.}) \quad (3.1)$$

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

$$E = \frac{1}{2} k(r - r_{eq.})^2 \quad (3.2)$$

This model of a vibrating diatomic molecule—the so-called simple harmonic oscillator model—while only an approximation, forms an excellent starting point for the discussion of vibrational spectra.

3.1.2 The Simple Harmonic Oscillator

In Fig. 3.1 we have plotted the energy in the form of Eq. (3.2), i.e. **as a parabola**. The zero of curve and equation is at $r = r_{eq.}$, and any energy in excess of this, for example at ϵ_2 , arises because of extension or compression of the bond. The figure shows that if one atom (Cl) is considered to be stationary on the $r = 0$ axis, the other (H) will oscillate between H' and H'' . In the case of HCl, it is a good approximation to say that, during vibrations, the heavy chlorine atom stays virtually still and it is the much lighter hydrogen which moves. However, only the distance between the two atoms is important and for any diatomic molecule we can always imagine ourselves to be sitting on one atom and watching the other move—from our point of view the atom we are on is stationary and can be assumed fixed on the $r = 0$ axis. Thus diagrams like Fig. 3.1 apply to *any* diatomic molecule.

If the energy of the HCl molecule of Fig. 3.1 is increased to ϵ_1 the oscillation will become more vigorous—that is to say the degree of compression and extension will be greater—but the vibrational frequency will not change. An elastic bond, like a spring, has a certain intrinsic vibrational frequency, dependent on the mass of the system and the force constant, but is independent of the amount of distortion. Classically it is simple to show that the oscillation frequency is:

$$\omega_{\text{osc.}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \quad \bar{\omega} = \bar{\nu} \quad (3.3)$$

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

$$\bar{\omega}_{\text{osc.}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad (3.4)$$

Vibrational energies, like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system may be calculated from the Schrödinger equation. For the simple harmonic oscillator these turn out to be:

$$E_v = (v + \frac{1}{2})h\omega_{\text{osc.}} \text{ joules} \quad (v = 0, 1, 2, \dots) \quad (3.5)$$

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

$$\epsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2})\bar{\omega}_{\text{osc.}} \text{ cm}^{-1} \quad (3.6)$$

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

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

$$E_0 = \frac{1}{2}h\omega_{\text{osc.}} \text{ joules} \quad (\omega_{\text{osc.}} \text{ in Hz})$$

or

$$\epsilon_0 = \frac{1}{2}\bar{\omega}_{\text{osc.}} \text{ cm}^{-1} \quad (\bar{\omega}_{\text{osc.}} \text{ in cm}^{-1}) \quad (3.7)$$

The implication is that the diatomic molecule (and, indeed, *any* molecule) can never have zero vibrational energy; **the atoms can never be completely at rest relative to each other.** The quantity $\frac{1}{2}h\omega_{\text{osc.}}$ joules or $\frac{1}{2}\bar{\omega}_{\text{osc.}}$ cm^{-1} is known as the *zero-point energy*; it depends only on the classical vibration frequency and hence (Eq. (3.3) or (3.4)) on the strength of the chemical bond and the atomic masses.

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

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

$$\Delta v = \pm 1 \quad (3.8)$$

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

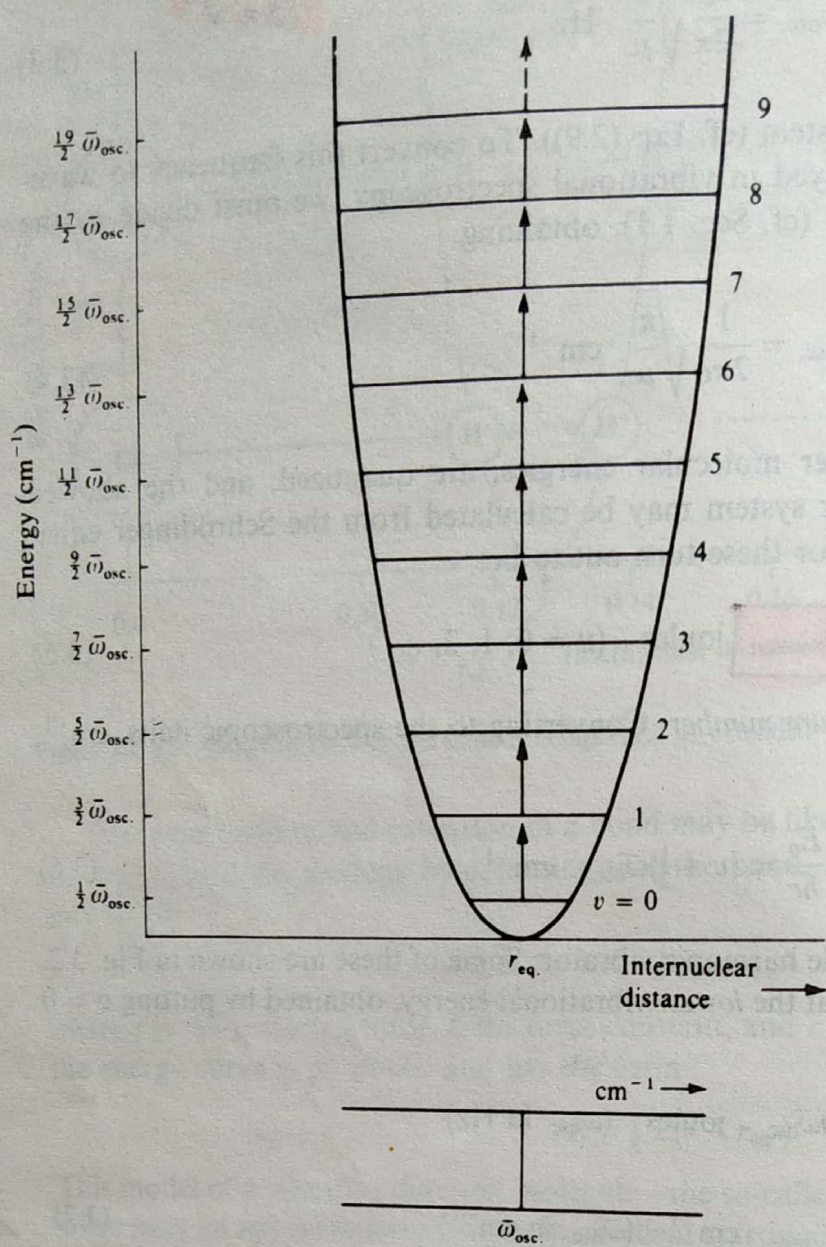


Figure 3.2 The vibrational energy levels and allowed transitions between them for a diatomic molecule undergoing simple harmonic motion.

Applying the selection rule we have immediately:

$$\begin{aligned} \epsilon_{v+1 \rightarrow v} &= (v + 1 + \frac{1}{2})\bar{\omega}_{osc.} - (v + \frac{1}{2})\bar{\omega}_{osc.} \\ &= \bar{\omega}_{osc.} \text{ cm}^{-1} \end{aligned} \tag{3.9a}$$

for emission and

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

for absorption, whatever the initial value of v .

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

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

This, again, is obvious if one considers the mechanism of absorption or emission in classical terms. In absorption, for instance, the vibrating molecule will absorb energy only from radiation

with which it can coherently interact (cf. Fig. 1.8) and this must be radiation of its own oscillation frequency.

3.1.3 The Anharmonic Oscillator

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

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

$$V(r) - E = D_{eq} [1 - \exp\{a(r_{eq} - r)\}]^2 \quad (3.11)$$

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

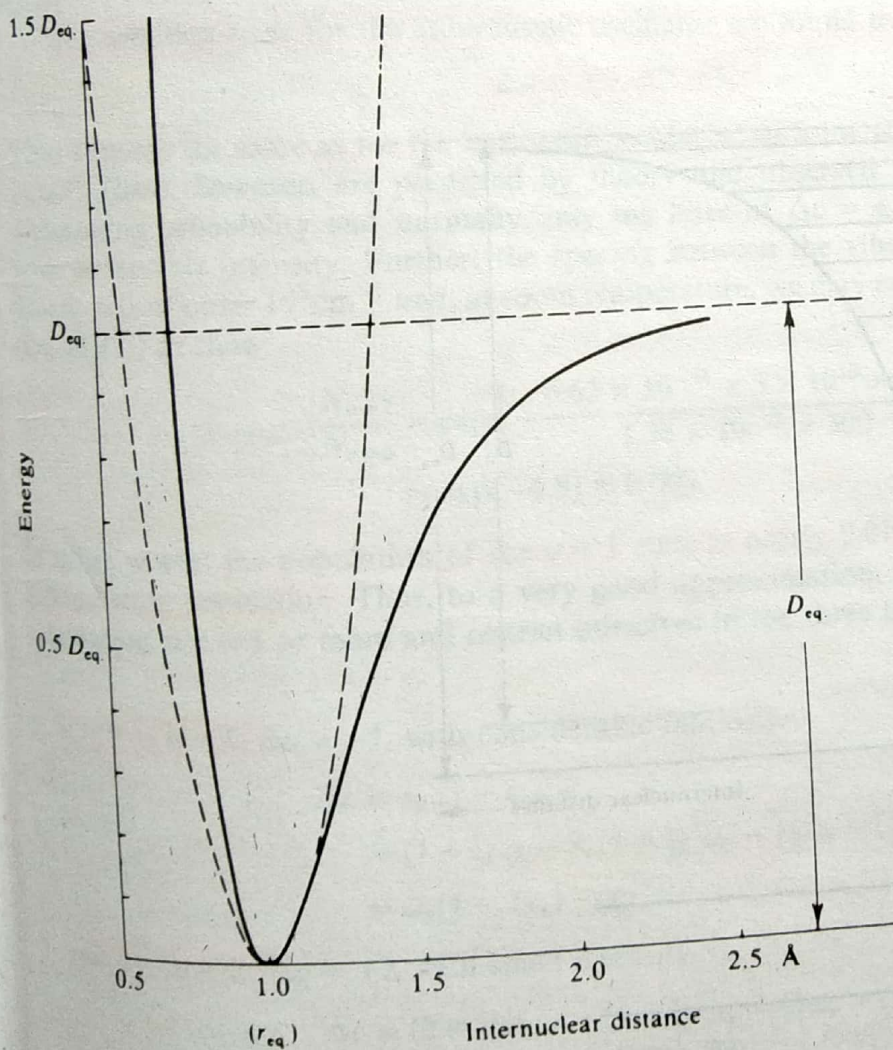


Figure 3.3 The Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

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

$$\epsilon_v = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})^2 \bar{\omega}_e x_e \text{ cm}^{-1} \quad (v = 0, 1, 2, \dots) \quad (3.12)$$

where $\bar{\omega}_e$ is an oscillation frequency (expressed in wavenumbers) which we shall define more closely below, and x_e is the corresponding anharmonicity constant which, for bond stretching vibrations, is always small and positive ($\approx +0.01$), so that the vibrational levels crowd more closely together with increasing v . Some of these levels are sketched in Fig. 3.4.

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

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

$$\epsilon_v = \bar{\omega}_e \{1 - x_e(v + \frac{1}{2})\} (v + \frac{1}{2}) \quad (3.13)$$

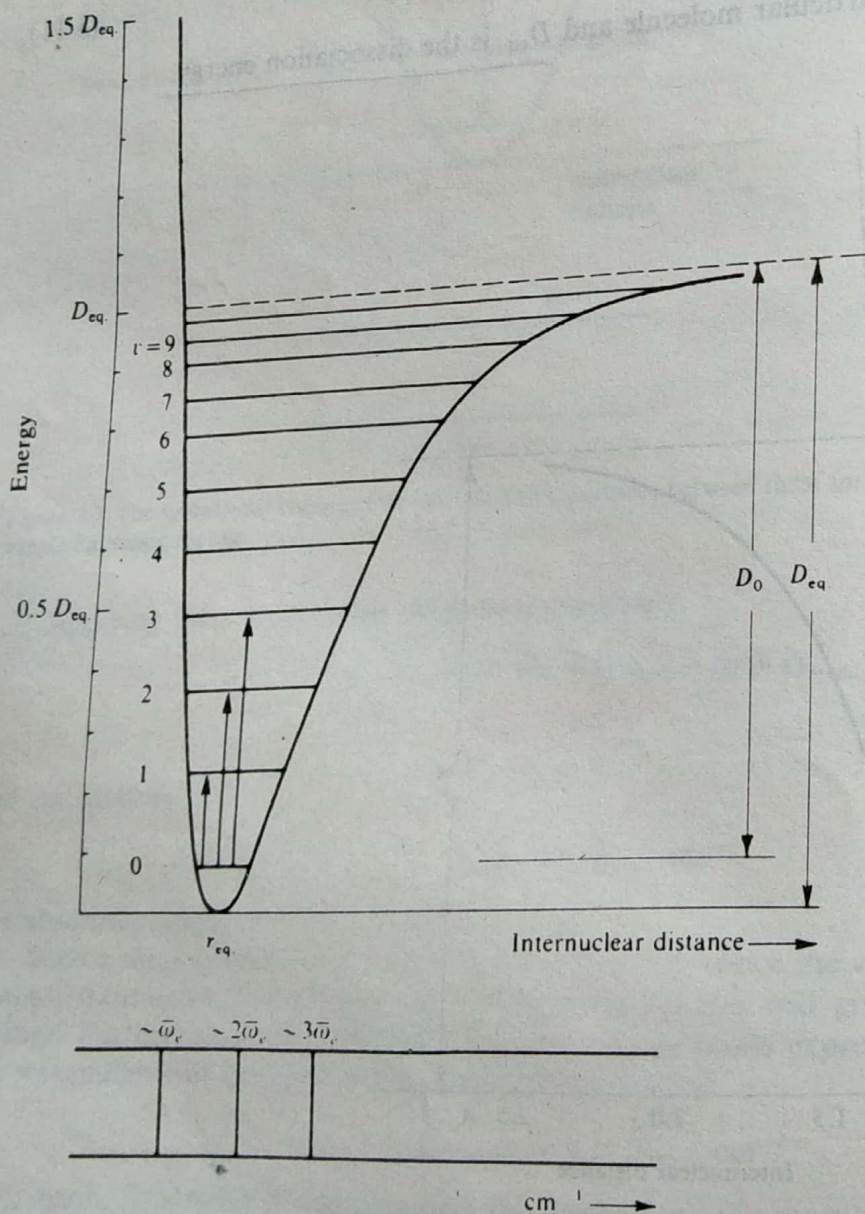


Figure 3.4 The vibrational energy levels and some transitions between them for a diatomic molecule undergoing inharmonic oscillations.

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

$$\bar{\omega}_{\text{osc.}} = \bar{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\} \quad (3.14)$$

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

$$\bar{\omega}_{\text{osc.}} = \bar{\omega}_e$$

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

$$\bar{\omega}_0 = \bar{\omega}_e \left(1 - \frac{1}{2} x_e \right) \quad \text{cm}^{-1}$$

and

$$\epsilon_0 = \frac{1}{2} \bar{\omega}_e \left(1 - \frac{1}{2} x_e \right) \quad \text{cm}^{-1}$$

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

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

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

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

$$\begin{aligned} \frac{N_{v=1}}{N_{v=0}} &= \exp \left\{ - \frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300} \right\} \\ &\approx \exp(-4.8) \approx 0.008 \end{aligned}$$

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

1. $v = 0 \rightarrow v = 1$, $\Delta v = +1$, with considerable intensity.

$$\begin{aligned} \Delta \epsilon &= \epsilon_{v=1} - \epsilon_{v=0} \\ &= \left(1 + \frac{1}{2} \right) \bar{\omega}_e - x_e \left(1 + \frac{1}{2} \right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2} \right)^2 x_e \bar{\omega}_e \right\} \\ &= \bar{\omega}_e (1 - 2x_e) \quad \text{cm}^{-1} \end{aligned} \quad (3.15a)$$

2. $v = 0 \rightarrow v = 2$, $\Delta v = +2$, with small intensity.

$$\begin{aligned} \Delta \epsilon &= \left(2 + \frac{1}{2} \right) \bar{\omega}_e - x_e \left(2 + \frac{1}{2} \right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2} \right)^2 x_e \bar{\omega}_e \right\} \\ &= 2 \bar{\omega}_e (1 - 3x_e) \quad \text{cm}^{-1} \end{aligned} \quad (3.15b)$$

3. $v = 0 \rightarrow v = 3$, $\Delta v = +3$, with normally negligible intensity.

$$\begin{aligned}\Delta\varepsilon &= (3 + \frac{1}{2})\bar{\omega}_e - \{\frac{1}{2}\bar{\omega}_e - (\frac{1}{2})^2 x_e \bar{\omega}_e\} \\ &= 3\bar{\omega}_e(1 - 4x_e) \text{ cm}^{-1}\end{aligned}\quad (3.15c)$$

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

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

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

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

$$\begin{aligned}k &= 4\pi^2 \bar{\omega}_e^2 c^2 \mu \\ &= 516 \text{ Nm}^{-1}\end{aligned}$$

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

Although we have ignored transitions from $v = 1$ to higher states, we should note that, if the temperature is raised or if the vibration has a particularly low frequency, the population of the $v = 1$ state may become appreciable. Thus at, say, 600 K (i.e. about 300°C) $N_{v=1}/N_{v=0}$ becomes $\exp(-2.4)$ or about 0.09, and transitions from $v = 1$ to $v = 2$ will be some 10 per cent the intensity of those from $v = 0$ to $v = 1$. A similar increase in the excited state population

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

Molecule	Vibration (cm^{-1})	Anharmonicity constant x_e	Force constant (Nm^{-1})	Internuclear distance r_{eq} (nm)
HF	4138.5	0.0218	966	0.0927
HCl†	2990.6	0.0174	516	0.1274
HBr	2649.7	0.0171	412	0.1414
HI	2309.5	0.0172	314	0.1609
CO	2169.7	0.0061	1902	0.1131
NO	1904.0	0.0073	1595	0.1151
ICl†	384.2	0.0038	238	0.2321

† Data refers to the ^{35}Cl isotope

would arise if the vibrational frequency were 500 cm^{-1} instead of 1000 cm^{-1} . We may calculate the wavenumber of this transition as:

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

$$\begin{aligned} \Delta \epsilon &= 2\frac{1}{2}\bar{\omega}_e - 6\frac{1}{4}x_e\bar{\omega}_e - (1\frac{1}{2}\bar{\omega}_e - 2\frac{1}{4}x_e\bar{\omega}_e) \\ &= \bar{\omega}_e(1 - 4x_e) \text{ cm}^{-1} \end{aligned} \quad (3.15d)$$

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

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

3.2 THE DIATOMIC VIBRATING ROTATOR

We saw in Chapter 2 that a typical diatomic molecule has rotational energy separations of $1\text{--}10 \text{ cm}^{-1}$, while in the preceding section we found that the vibrational energy separations of HCl were nearly 3000 cm^{-1} . Since the energies of the two motions are so different we may, as a first approximation, consider that a diatomic molecule can execute rotations and vibrations quite independently. This, which we shall call the Born–Oppenheimer approximation (although, cf. Eq. (6.1), this strictly includes electronic energies), is tantamount to assuming that the combined rotational–vibrational energy is simply the sum of the separate energies:

$$\begin{aligned} E_{\text{total}} &= E_{\text{rot.}} + E_{\text{vib.}} \quad (\text{joules}) \\ \epsilon_{\text{total}} &= \epsilon_{\text{rot.}} + \epsilon_{\text{vib.}} \quad (\text{cm}^{-1}) \end{aligned} \quad (3.16)$$

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

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

$$\begin{aligned} \epsilon_{J,v} &= \epsilon_J + \epsilon_v \\ &= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \dots \\ &\quad + (v + \frac{1}{2})\bar{\omega}_e - x_e(v + \frac{1}{2})^2\bar{\omega}_e \text{ cm}^{-1} \end{aligned} \quad (3.17)$$

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

$$\epsilon_{\text{total}} = \epsilon_{J,v} = BJ(J+1) + (v + \frac{1}{2})\bar{\omega}_e - x_e(v + \frac{1}{2})^2\bar{\omega}_e \quad (3.18)$$

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

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

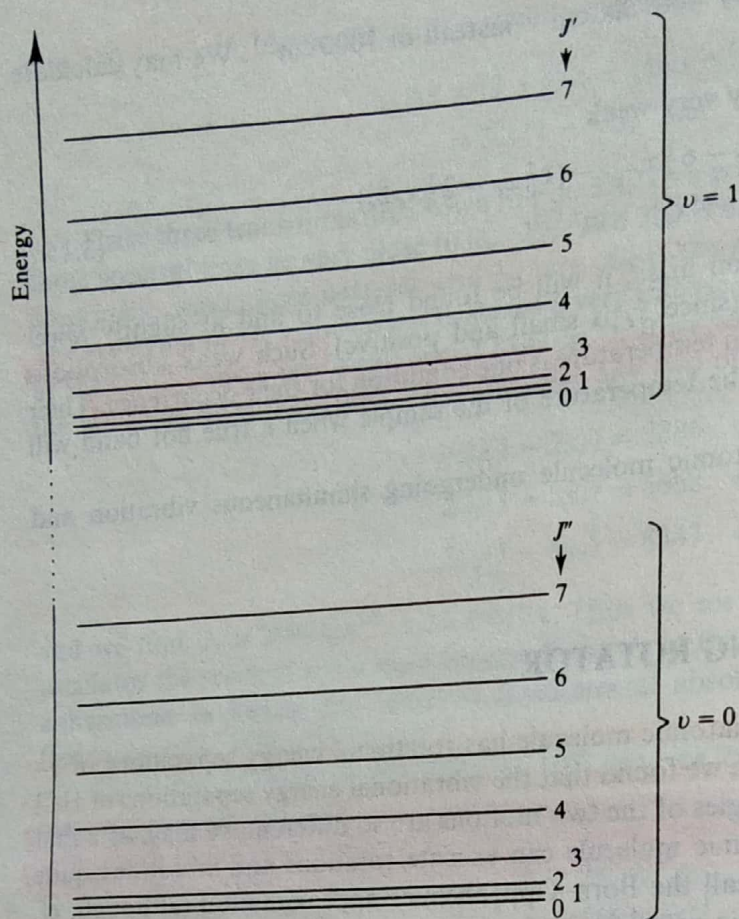


Figure 3.5 Some of the rotational energy levels for the first two vibrational states of a diatomic molecule.

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

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

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

In Fig. 3.6 we have drawn some of the relevant energy levels and transitions, designating rotational quantum numbers in the $v = 0$ state as J'' and in the $v = 1$ state as J' . The use of a single prime for the upper state and a double for the lower state is conventional in all branches of spectroscopy.

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

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

$$\begin{aligned} \Delta \epsilon_{J,v} &= \epsilon_{J',v=1} - \epsilon_{J'',v=0} \\ &= BJ'(J'+1) + \frac{1}{2}\bar{\omega}_e - 2\frac{1}{4}x_e\bar{\omega}_e - \{BJ''(J''+1) + \frac{1}{2}\bar{\omega}_e - \frac{1}{4}x_e\bar{\omega}_e\} \\ &= \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1} \end{aligned}$$

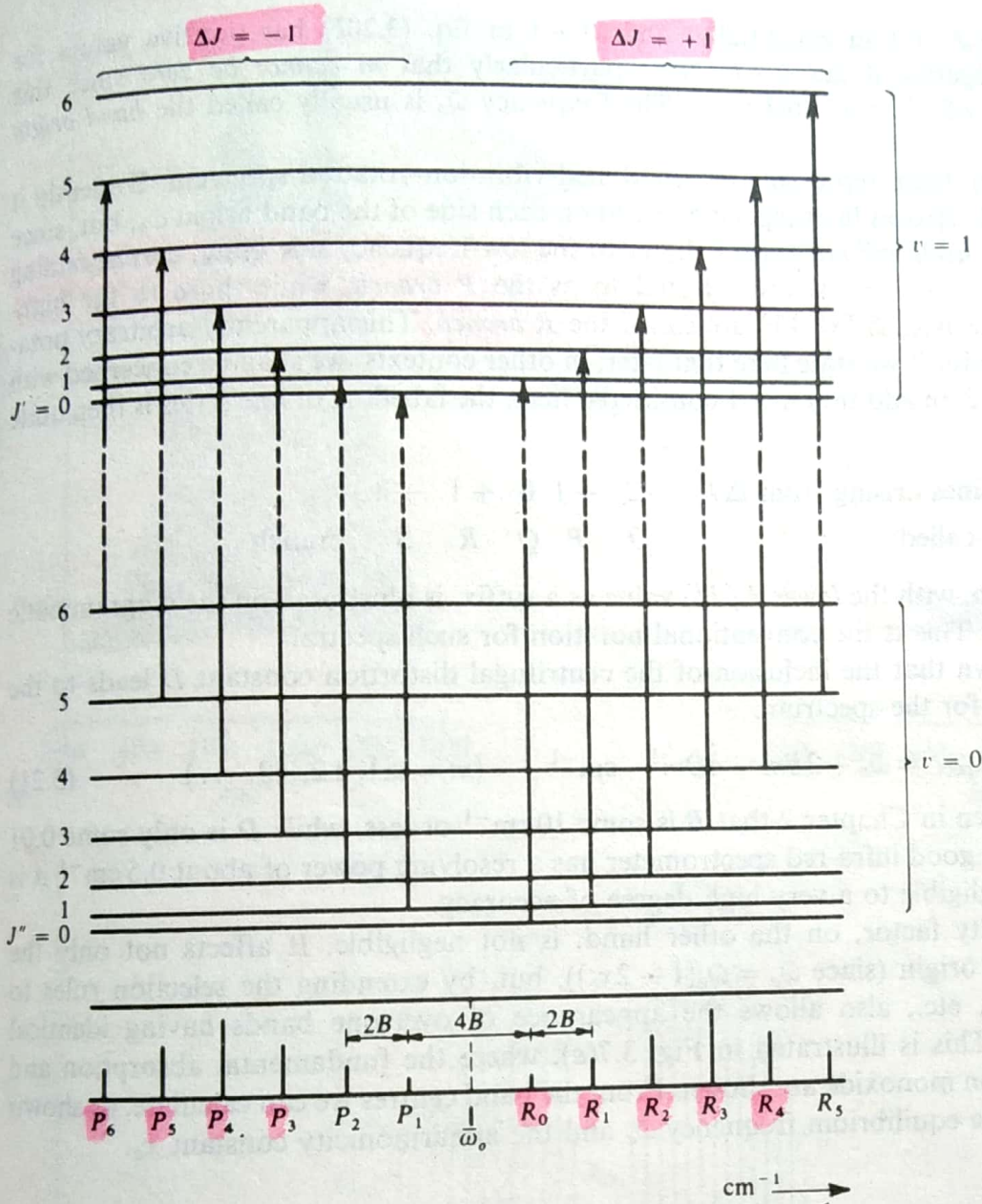


Figure 3.6 Some transitions between the rotational-vibrational energy levels of a diatomic molecule, together with the spectrum arising from them.

where, for brevity, we write $\bar{\omega}_0$ for $\bar{\omega}_e(1 - 2x_e)$.

We should note that taking B to be identical in the upper and lower vibrational states is a direct consequence of the Born-Oppenheimer approximation—rotation is unaffected by vibrational changes.

Now we can have:

1. $\Delta J = +1$, that is $J' = J'' + 1$ or $J' - J'' = +1$; hence

$$\Delta \epsilon_{J,v} = \bar{\omega}_0 + 2B(J'' + 1) \text{ cm}^{-1} \quad J'' = 0, 1, 2, \dots \quad (3.20a)$$

2. $\Delta J = -1$, that is $J'' = J' + 1$ or $J' - J'' = -1$; hence

$$\Delta \epsilon_{J,v} = \bar{\omega}_0 - 2B(J' + 1) \text{ cm}^{-1} \quad J' = 0, 1, 2, \dots \quad (3.20b)$$

These two expressions may conveniently be combined into:

$$\Delta \epsilon_{J,v} = \bar{\nu}_{\text{spect.}} = \bar{\omega}_0 + 2Bm \text{ cm}^{-1} \quad m = \pm 1, \pm 2, \dots \quad (3.20c)$$

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

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

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

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

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

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

However, we have seen in Chapter 2 that B is some 10 cm^{-1} or less, while D is only some 0.01 per cent of B . Since a good infra-red spectrometer has a resolving power of about 0.5 cm^{-1} it is obvious that D is negligible to a very high degree of accuracy.

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