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Molecular spectroscopy

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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, 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

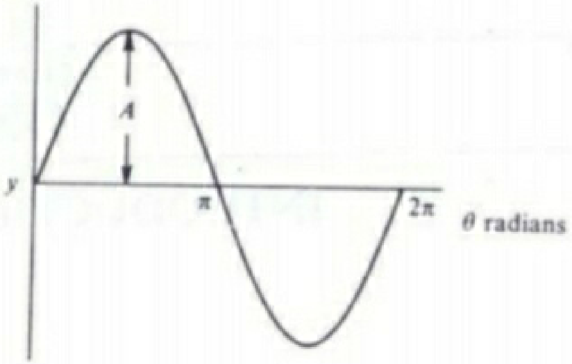

Figure 1.1 The curve of $y = A \sin \theta$.

Fig. 1.2. A point P travels with uniform angular velocity ω 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:

$$y = A \sin \omega t = A \sin 2\pi \nu t \tag{1.1}$$

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

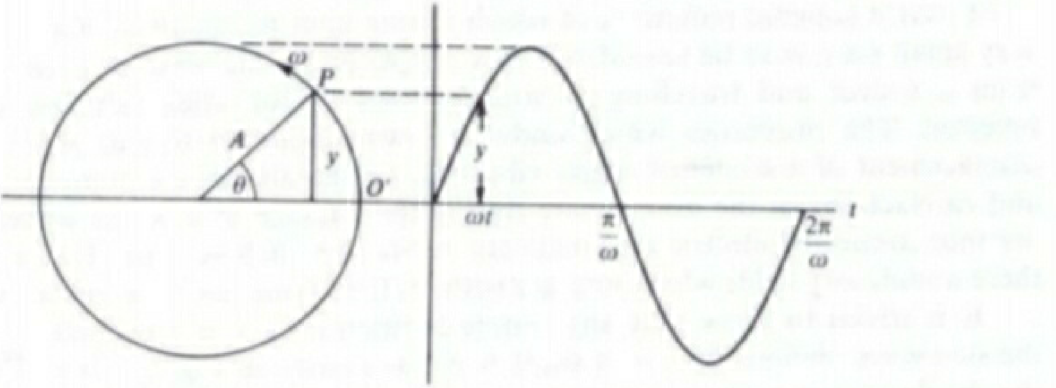

Figure 1.2 The description of a sine curve in terms of the circular motion of a point P at a uniform angular velocity of ω rad s^{-1}.

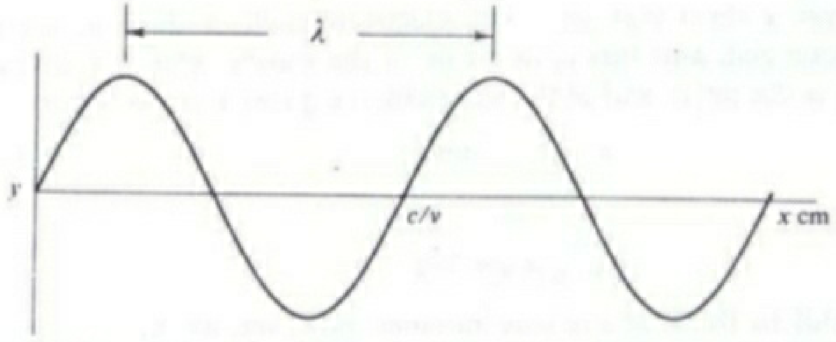

Figure 1.3 The concept of a travelling wave with a wavelength λ.

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

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

so we have:

$$y = A \sin \frac{2\pi x}{\lambda} \tag{1.4}$$

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

$$1\ \mu\text{m} = 10^{-6}\ \text{m} \tag{1.5}$$

In the visible and ultra-violet region, λ is still often expressed in Ångstrom units (Å) where $1\ \text{Å} = 10^{-10}$ m, although the proper SI unit for this region is the nanometre:

$$1\ \text{nm} = 10^{-9}\ \text{m} = 10\ \text{Å} \tag{1.6}$$

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*:

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

and hence

$$y = A \sin 2\pi\bar{\nu}x \tag{1.8}$$

It is more useful to think of the wavenumber, however, as the number of compete waves or cycles contained in each centimetre length of radiation. Since the formal definition is based on the centimetre rather than the metre, the wavenumber is, of course, a non-SI unit; it is, however, so convenient a unit for the discussion of infra-red spectra that—like the Ångstrom—it will be many years before it falls into disuse.

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, 3×10^{10} cm s^{-1}); the velocity in SI units is, of course, 3×10^8 m 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

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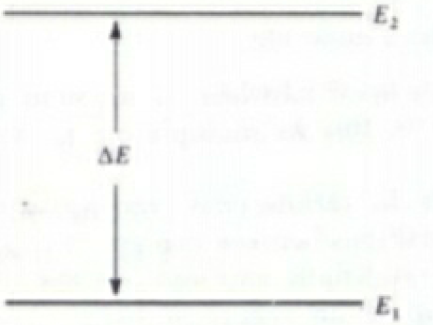
one level to another only by a sudden jump involving a finite amount of energy.

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.,

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

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:

$$h = 6{\cdot}63 \times 10^{-34} \text{ joules s molecule}^{-1}$$

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 $N = 6{\cdot}02 \times 10^{23}$.

However, the spectroscopist measures the various characteristics of the absorbed or emitted radiation during transitions between energy states and he often, rather loosely, uses frequency, wavelength, and wavenumber as if they were energy units. Thus in referring to 'an energy of 10 cm^{-1}' he 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: 3×10^6–3×10^{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).

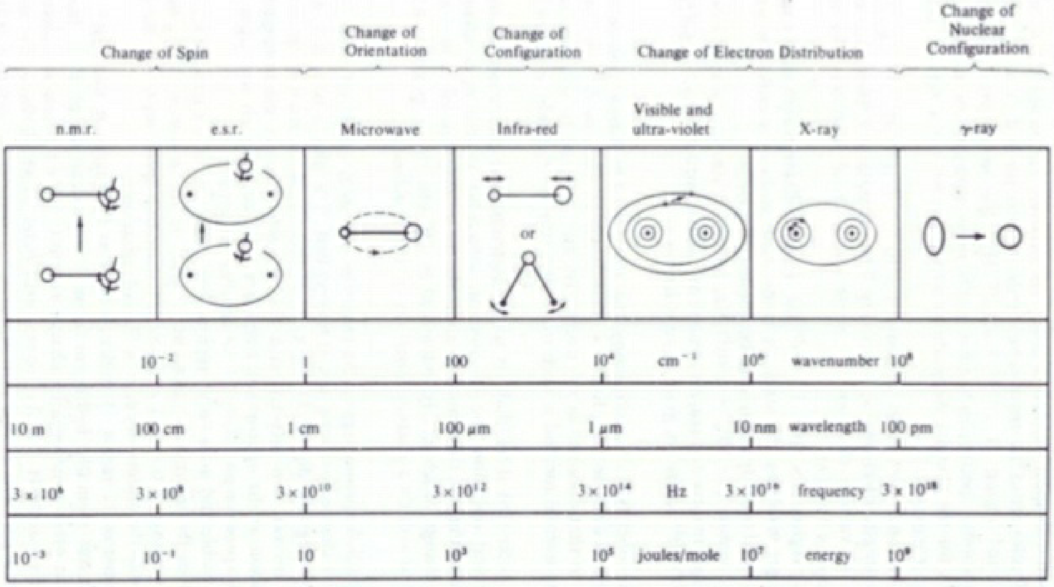


Figure 1.4 The regions of the electromagnetic spectrum.

2. Microwave region: 3×10^{10}–3×10^{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: 3×10^{12}–3×10^{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: 3×10^{14}–3×10^{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: 3×10^{16}–3×10^{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).
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 8).

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 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.
3. 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

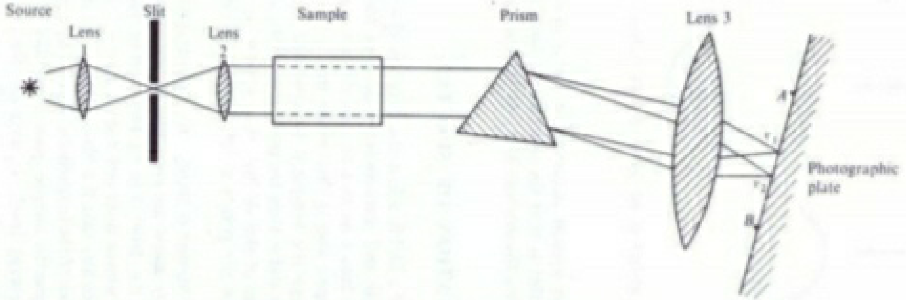


Figure 1.9 Schematic diagram of a spectrometer suitable for operation in the visible region.

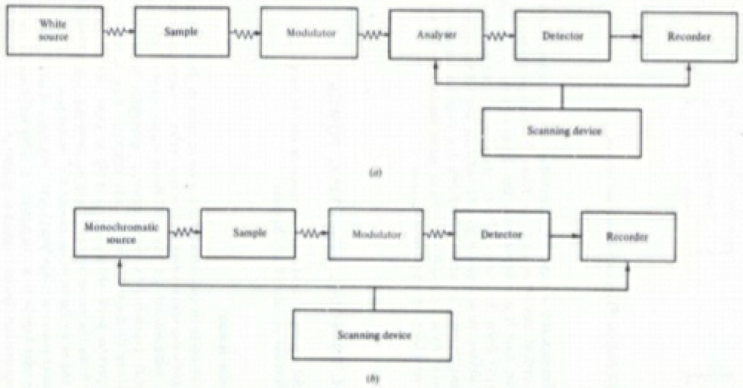


Figure 1.15 Block diagram of a typical absorption spectrometer for use in (*a*) the infra-red, visible, and ultra-violet regions where a 'white' source is available, and (*b*) the microwave and radiofrequency regions where the source can be tuned over a considerable range of frequencies.

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② Quantum mechanical to the rotation molecular (linear)

Rotational linear momentum

$P = m_1 v_1 r_1 + m_2 v_2 r_2$ — ①

momentum in linear particles

$P = \Sigma m_i v_i r_i = (m_i v_i) r_i$ — ②

multiply equation 2 by $(\frac{r_i}{r_i})$, so we conclude

$P = m_i r_i^2 (\frac{v_i}{r_i})$ — ③

$\because \omega = \frac{v_i}{r_i}$, $I = m_i r_i^2$

$\therefore P = I\omega$ — ④

momentum in quantum mechanics is

$P = M_J \hbar$ — ⑤ wher M_J

$P = \sqrt{J(J+1)}\, \hbar$ — ⑥

But the kinetic energy of the particles

$E_k = \frac{1}{2} m v^2$ — ⑦

Rotation energy level according to quantum mechanic

$E = \frac{1}{2} I \omega^2$ — ⑧ multiply by (I) and dividing (I)

$E = \frac{I\omega^2}{2} = \frac{(I\omega)^2}{2I} = \frac{P^2}{2I} = \frac{P^2}{2\mu r^2}$ — ⑨

we substitute 6 in 9

$E_J = \frac{J(J+1)}{2I} \hbar^2 = \frac{h^2}{8\pi^2 I} J(J+1)$ — ⑩

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:

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

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) expresses 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:

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \qquad (J = 0, 1, 2, \ldots) \tag{2.11}$$

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:

$$\varepsilon_J = BJ(J+1) \text{ cm}^{-1} \qquad (J = 0, 1, 2, \ldots) \tag{2.12}$$

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

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

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.

From Eq. (2.12) we can show the allowed energy levels diagrammatically as in Fig. 2.2. Plainly for $J = 0$ we have $\varepsilon_J = 0$ and we would say that the molecule is not rotating at all. For $J = 1$, the rotational energy is $\varepsilon_1 = 2B$ 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.

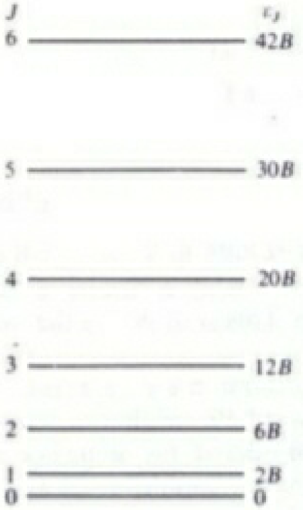

Fig. 2.2

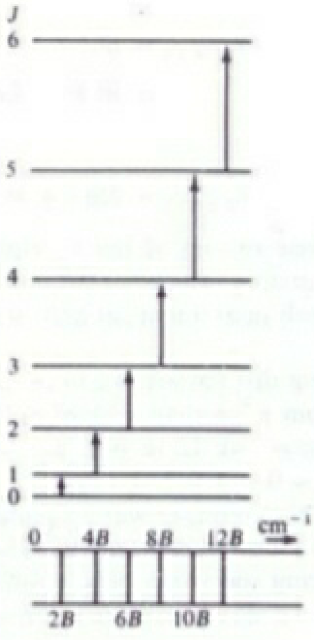

Fig. 2.3

Figure 2.2 The allowed rotational energy levels of a rigid diatomic molecule.

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

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:

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

and, therefore,

$$\bar{\nu}_{J=0 \to J=1} = 2B \quad \text{cm}^{-1} \tag{2.14}$$

In other words, an absorption line will appear at $2B$ 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:

$$\begin{aligned}\bar{\nu}_{J=1 \to J=2} &= \varepsilon_{J=2} - \varepsilon_{J=1} \\ &= 6B - 2B = 4B \quad \text{cm}^{-1}\end{aligned} \tag{2.15}$$

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

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

or

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

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \ldots,\ \text{cm}^{-1}$, 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 $J = 0 \to J = 2 \to J = 4 \ldots$. 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:

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

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

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

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

$$N_J/N_0 = \exp(-E_J/kT) = \exp\{-BhcJ(J+1)/kT\} \tag{2.18}$$

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 $B = 2$ cm^{-1}, and room temperature (say $T = 300$ K), the relative population in the $J = 1$ state is:

$$\frac{N_1}{N_0} = \exp\left\{-\frac{2 \times 6{\cdot}63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1{\cdot}38 \times 10^{-23} \times 300}\right\}$$
$$= \exp(-0{\cdot}019) \approx 0{\cdot}98$$

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:

$$E = \tfrac{1}{2}I\omega^2 \qquad \mathbf{P} = I\omega$$

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

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

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

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

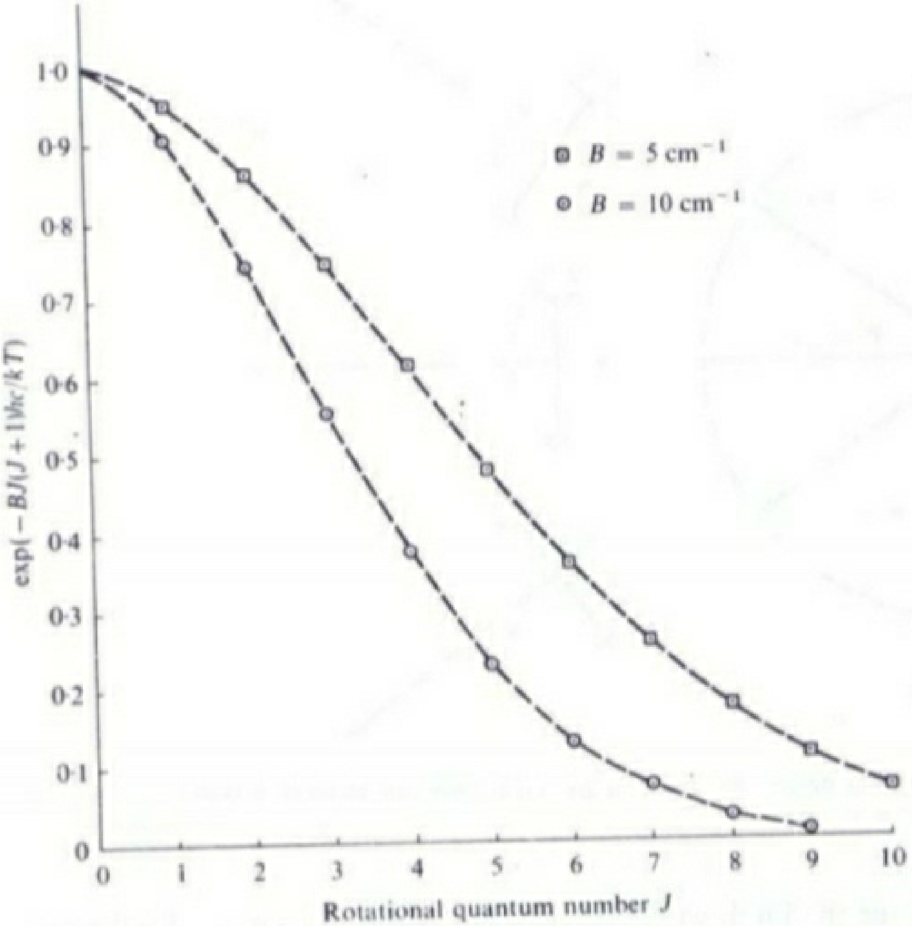

Figure 2.4 The Boltzmann populations of the rotational energy levels of Fig. 2.2. The diagram has been drawn taking values of $B = 5$ and $10\ \text{cm}^{-1}$ and $T = 300$ K in Eq. (2.18).

and hence

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

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

Throughout the above derivation **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.'

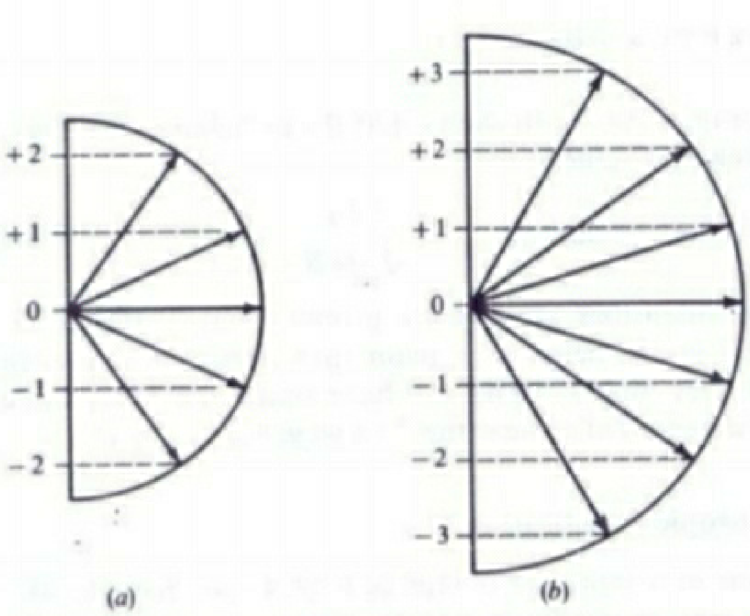

Figure 2.6 The five and seven degenerate rotational orientations for a molecule with $J = 2$ and $J = 3$ respectively.

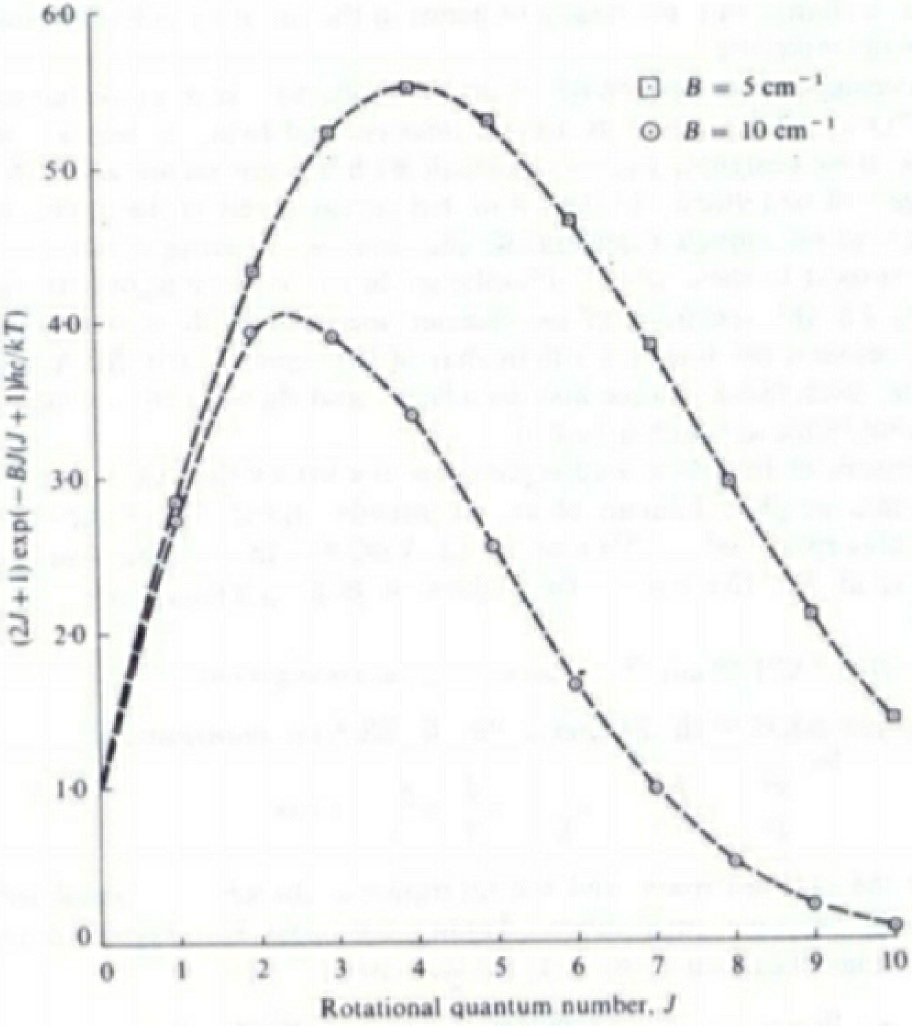

Figure 2.7 The total relative populations, including degeneracy, of the rotational energy levels of a diatomic molecule. The diagram has been drawn for the same conditions as Fig. 2.4.

diminishes. Differentiation of Eq. (2.20) shows that the population is a maximum at the nearest integral J value to:

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

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 $^{12}C^{16}O$ to $^{13}C^{16}O$ there is a mass increase and hence a decrease in the B value. If we designate the ^{13}C molecule 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 $^{12}C^{16}O$ to be at $3{\cdot}842\,35$ cm^{-1}, while that of $^{13}C^{16}O$ was at $3{\cdot}673\,37$ cm^{-1}. The values of B determined from these figures are:

$$B = 1{\cdot}921\,18\ \text{cm}^{-1} \qquad \text{and} \qquad B' = 1{\cdot}836\,69\ \text{cm}^{-1}$$

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

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I'c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1{\cdot}046$$

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:

$$\frac{\mu'}{\mu} = 1{\cdot}046 = \frac{15{\cdot}9994m'}{15{\cdot}9994 + m'} \times \frac{12 + 15{\cdot}9994}{12 \times 15{\cdot}9994}$$

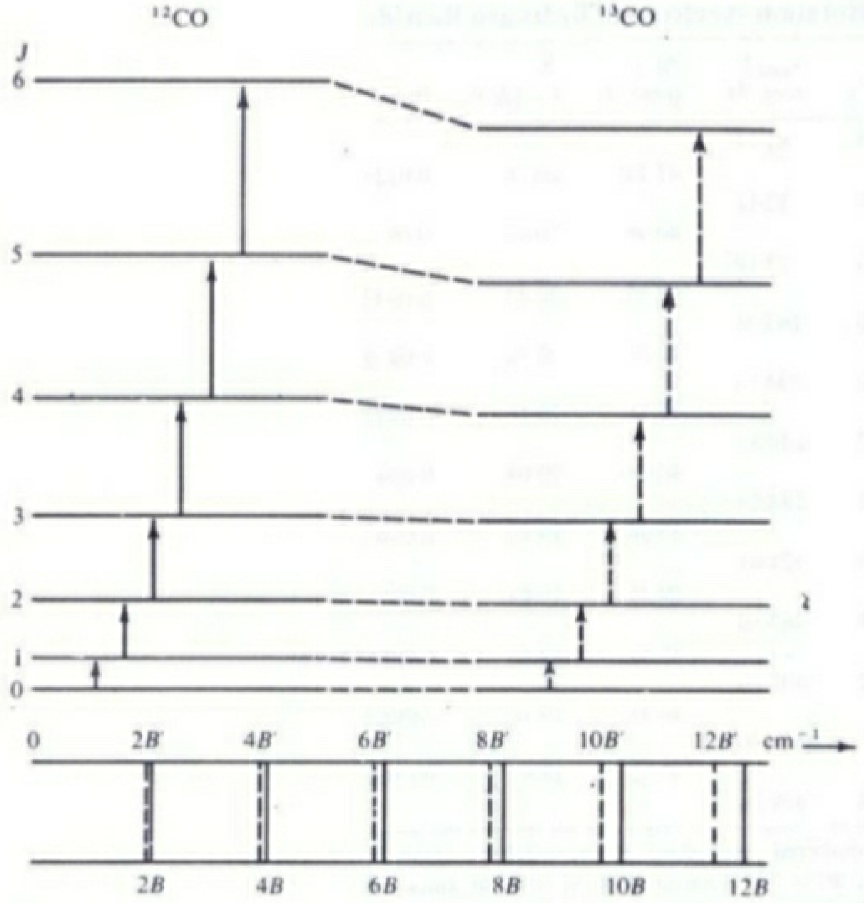

Figure 2.8 The effect of isotopic substitution on the energy levels and hence rotational spectrum of a diatomic molecule such as carbon monoxide.

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 $^{13}C^{16}O$ 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 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:

$$k = 4\pi^2\bar{\omega}^2c^2\mu \tag{2.22}$$

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:

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

or

$$B \propto 1/r^2 \tag{2.23}$$

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:

$$\langle r\rangle_{\text{av.}} = \frac{0{\cdot}09 + 0{\cdot}11}{2} = 0{\cdot}1 = r_e$$

but

$$\left\langle\frac{1}{r^2}\right\rangle_{\text{av.}} = \frac{(1/0{\cdot}09)^2 + (1/0{\cdot}11)^2}{2} = 103{\cdot}05\ \mathrm{nm}^2$$

and therefore $\langle r\rangle_{\text{av.}} = \sqrt{1/103{\cdot}5} = 0{\cdot}0985$ nm. The difference, though small, is not negligible compared with the precision with which B can be measured spectroscopically. And 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:

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

or

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

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

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

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:

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \cdots \text{ cm}^{-1} \qquad (2.26)$$

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

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

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:

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

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:

$$\bar{\nu}_J = 41{\cdot}122(J+1) - 8{\cdot}52 \times 10^{-3}(J+1)^3 \text{ cm}^{-1} \tag{2.29}$$

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

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16{\cdot}33 \times 10^6 \text{ (cm}^{-1})^2$$

i.e.,

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

lows the usual pattern: source, monochromator, beam direction, sample, and detector. We shall discuss each in turn.

1. *The source and monochromator.* The usual source in this region is the klystron valve which, since it emits radiation of only a very narrow frequency range, is called 'monochromatic' and acts as its own monochromator. The actual emission frequency is variable electronically and hence a spectrum may be scanned over a limited range of frequencies using a single klystron.

   One slight disadvantage of this source is that the total energy radiated is very small—of the order of milliwatts only. However, since all this is concentrated into a narrow frequency band a sharply tuned detector can be sufficiently activated to produce a strong signal.
2. *Beam direction.* This is achieved by the use of 'waveguides'—hollow tubes of copper or silver, usually of rectangular cross-section—inside which the radiation is confined. The waveguides may be gently tapered or bent to allow focusing and directing of the radiation. Atmospheric absorption of the beam is considerable, so the system must be efficiently evacuated.
3. *Sample and sample space.* In almost all microwave studies so far the sample has been gaseous. However, pressures of 0·01 mmHg are sufficient to give a reasonable absorption spectrum, so many substances which are usually thought of as solid or liquid may be examined provided their vapour pressures are above this value. The sample is retained by very thin mica windows in a piece of evacuated waveguide.
4. *Detector.* It is possible to use an ordinary superheterodyne radio receiver as detector, provided this may be tuned to the appropriate high frequency; however, a simple crystal detector is found to be more sensitive and easier to use. This detects the radiation focused upon it by the waveguide, and the signal it gives is amplified electronically for display on an oscilloscope, or for permanent record on paper.

2.5.2 The Stark Effect

We cannot leave the subject of microwave spectroscopy without a brief description of the Stark effect and its applications. A more detailed discussion is to be found in the books by Kroto and by Townes and Schawlow mentioned in the bibliography.

Experimentally the Stark effect requires the placing of an electric field, either perpendicular or parallel to the direction of the radiation beam, across the sample. Practically it is simpler to have a perpendicular field. We shall consider three advantages of this field.

1. A molecule exhibiting a rotational spectrum must have an electric dipole moment, and so its rotational energy levels will be perturbed by the

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CHAPTER

THREE

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

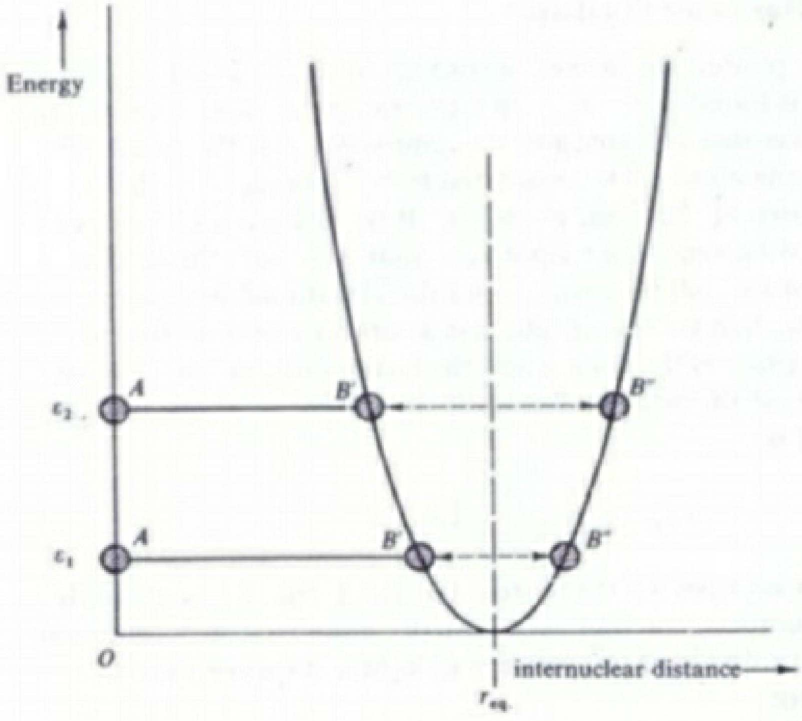

Figure 3.1 Parabolic curve of energy plotted against the extension or compression of a spring obeying Hooke's law.

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

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

$$f = -k(r - r_{eq.}) \tag{3.1}$$

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

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

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 according to Eq. (3.2). The zero of curve and equation is found at $r = r_{\text{eq.}}$, and any energy in excess of this, for example, ε_1, arises because of extension or compression of the bond. The figure shows that if one atom (A) is considered to be stationary on the $r = 0$ axis, the other will oscillate between B' and B''. If the energy is increased to ε_2 the oscillation will become more vigorous—that is to say, the degree of compression or extension will be greater—but the vibrational frequency will not change. An elastic bond, like a spring, has a certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion. Classically it is easy to show that the oscillation frequency is:

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

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:

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

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

$$E_v = (v + \tfrac{1}{2})h\omega_{\text{osc.}} \quad \text{joules} \qquad (v = 0, 1, 2, \ldots) \tag{3.5}$$

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

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

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

$$E_0 = \tfrac{1}{2}h\omega_{\text{osc.}} \quad \text{joules} \qquad [\omega_{\text{osc.}} \text{ in Hz}]$$

or

$$\varepsilon_0 = \tfrac{1}{2}\bar{\omega}_{\text{osc.}} \quad \text{cm}^{-1} \qquad [\bar{\omega}_{\text{osc.}} \text{ in cm}^{-1}] \tag{3.7}$$

The implication is that the diatomic molecule (and, indeed, *any* molecule) can never have zero vibrational energy; the atoms can never be completely

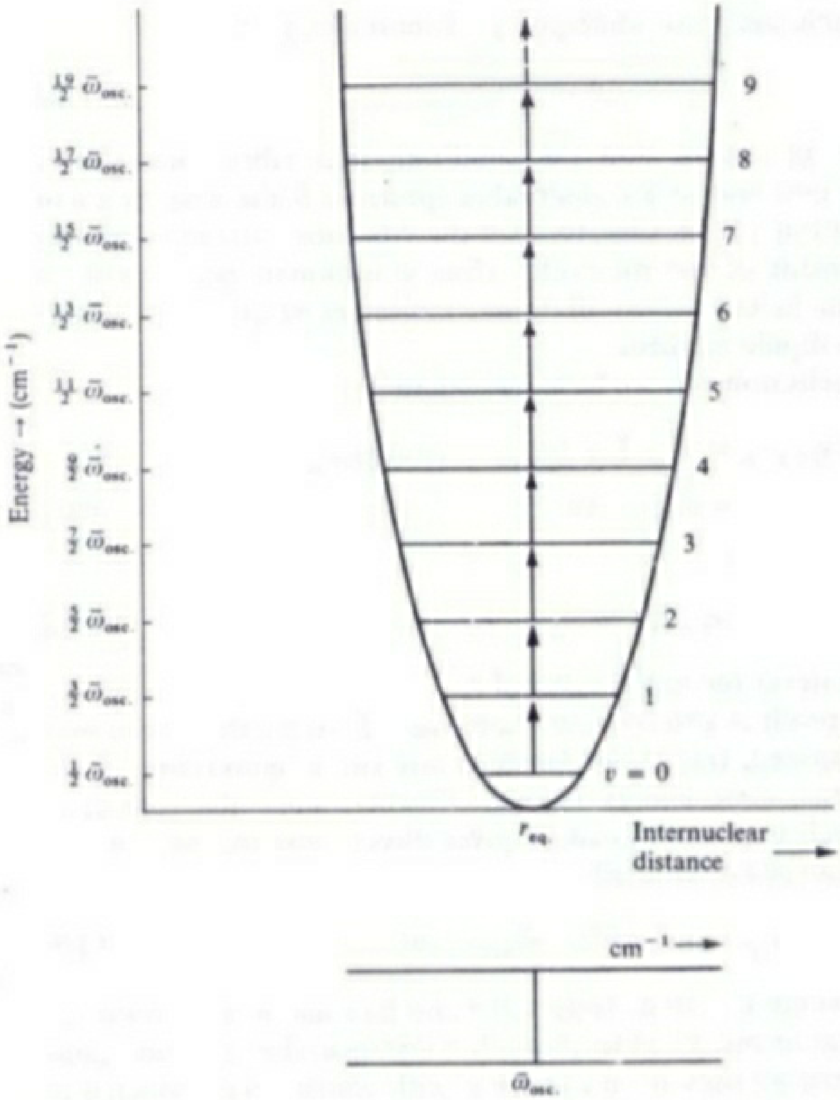

Figure 3.2 The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion.

at rest relative to each other. The quantity $\frac{1}{2}h\omega_{osc.}$ joules or $\frac{1}{2}\bar{\omega}_{osc.}$ cm^{-1} is known as the zero-point energy; it depends only on the classical vibration frequency and hence (Eq. (3.3) or (3.4)) on the strength of the chemical bond and the atomic masses.

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

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

$$\Delta v = \pm 1 \tag{3.8}$$

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.

Applying the selection rule we have immediately:

$$\begin{aligned}\varepsilon_{v+1 \to v} &= (v + 1 + \tfrac{1}{2})\bar{\omega}_{\text{osc.}} - (v + \tfrac{1}{2})\bar{\omega}_{\text{osc.}} \\ &= \bar{\omega}_{\text{osc.}} \quad \text{cm}^{-1}\end{aligned} \tag{3.9a}$$

for emission and

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

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

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

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.

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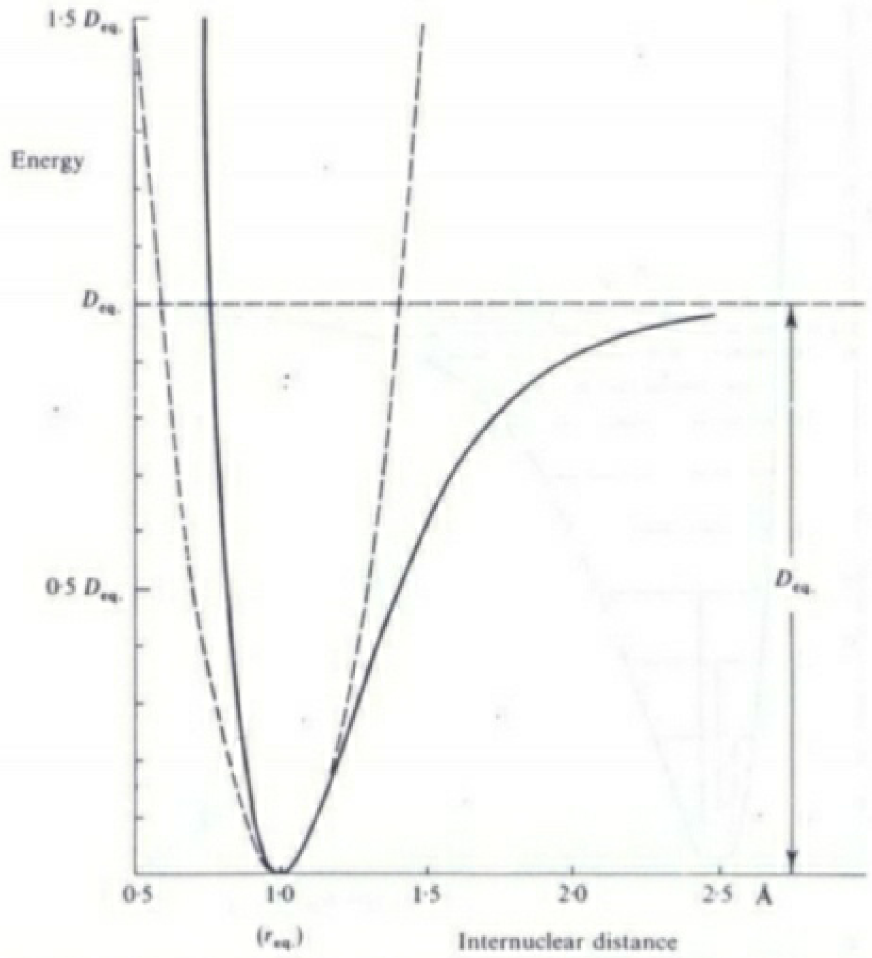

Figure 3.3 The Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

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

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

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

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

$$\varepsilon_v = (v + \tfrac{1}{2})\bar{\omega}_e - (v + \tfrac{1}{2})^2\bar{\omega}_e x_e \quad \text{cm}^{-1} \qquad (v = 0, 1, 2, \ldots) \qquad (3.12)$$

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

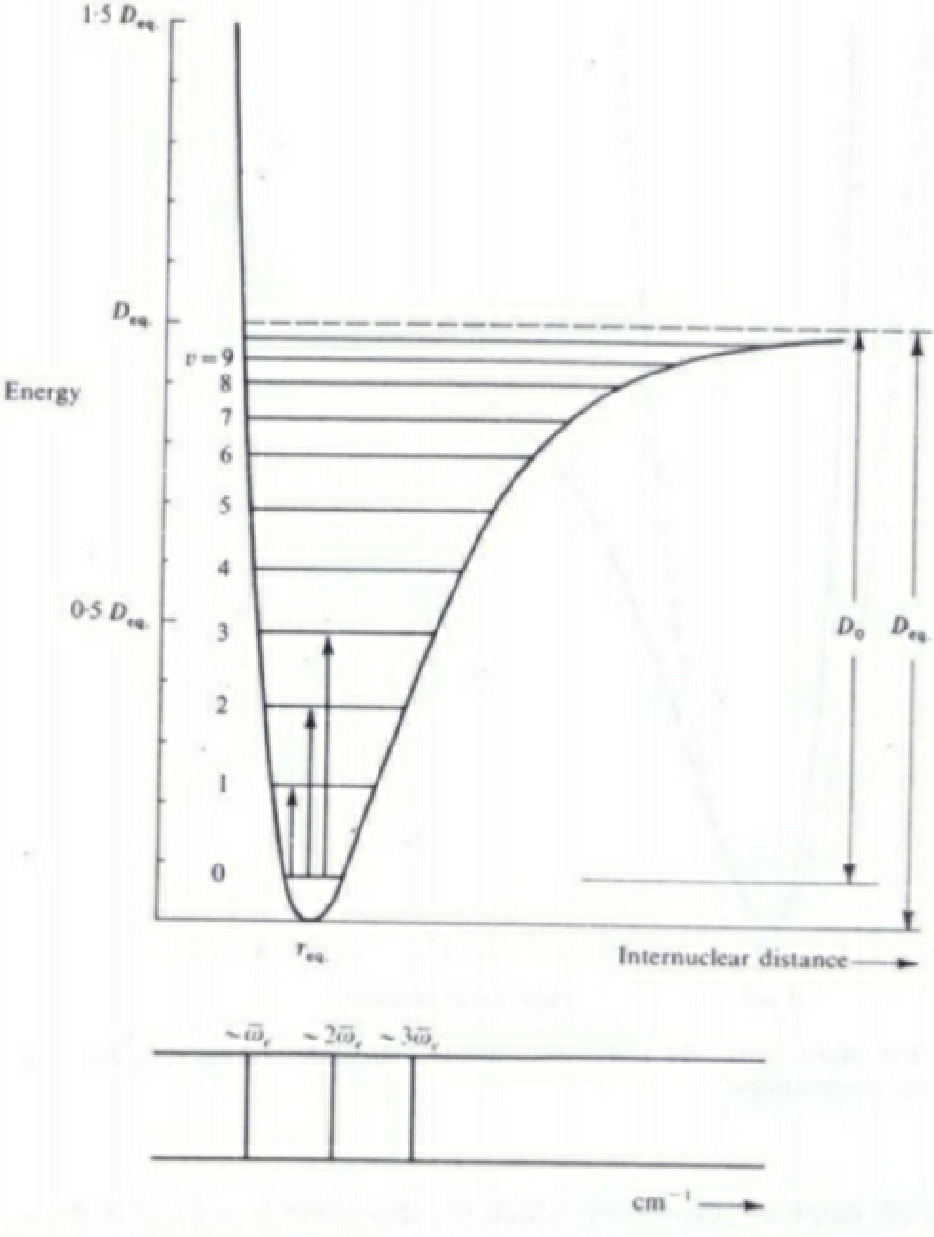

Figure 3.4 The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

($\approx +0{\cdot}01$), so that the vibrational levels crowd more closely together with increasing v. Some of these levels are sketched in Fig. 3.4.

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

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

$$\varepsilon_v = \bar{\omega}_e\{1 - x_e(v + \tfrac{1}{2})\}(v + \tfrac{1}{2}) \tag{3.13}$$

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

$$\bar{\omega}_{\text{osc.}} = \bar{\omega}_e\{1 - x_e(v + \tfrac{1}{2})\} \tag{3.14}$$

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), $\varepsilon = 0$) 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:

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

and

$$\varepsilon_0 = \tfrac{1}{2}\bar{\omega}_e(1 - \tfrac{1}{2}x_e) \quad \text{cm}^{-1}$$

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:

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

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

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left\{-\frac{6{\cdot}63 \times 10^{-34} \times 3 \times 10^{10} \times 10^3}{1{\cdot}38 \times 10^{-23} \times 300}\right\}$$

$$\approx \exp(-4{\cdot}8) \approx 0{\cdot}008.$$

In other words, the population of the $v = 1$ state is nearly 0·01 or some one per cent of the ground state population. Thus, to a very good approximation, we may ignore all transitions originating at $v = 1$ or more and restrict ourselves to the three transitions:

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

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{v=1} - \varepsilon_{v=0}\\ &= (1+\tfrac{1}{2})\bar{\omega}_e - x_e(1+\tfrac{1}{2})^2\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\bar{\omega}_e\}\\ &= \bar{\omega}_e(1-2x_e) \quad \mathrm{cm}^{-1} \qquad (3.15a)\end{aligned}$$

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

$$\begin{aligned}\Delta\varepsilon &= (2+\tfrac{1}{2})\bar{\omega}_e - x_e(2+\tfrac{1}{2})^2\bar{\omega}_e - \{\tfrac{1}{2}\bar{\omega}_e - (\tfrac{1}{2})^2 x_e\bar{\omega}_e\}\\ &= 2\bar{\omega}_e(1-3x_e) \quad \mathrm{cm}^{-1} \qquad (3.15b)\end{aligned}$$

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

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

These three transitions are shown in Fig. 3.4. To a good approximation, since $x_e \approx 0{\cdot}01$, 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)):

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

and we find $\bar{\omega}_e = 2990$ cm^{-1}, $x_e = 0{\cdot}0174$. 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 $\bar{\omega}_e$:

$$\begin{aligned}k &= 4\pi^2\bar{\omega}_e^2c^2\mu \quad \mathrm{N\ m^{-1}}\\ &= 516\ \mathrm{N\ m^{-1}}\end{aligned}$$

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

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Molecular spectroscopy

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

Molecule	Vibration (cm^{-1})	Anharmonicity constant, x_e	Force constant ($N\ m^{-1}$)	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.

Although we have ignored transitions from $v = 1$ to higher states, we should note that, if the temperature is raised or if the vibration has a particularly low frequency, the population of the $v = 1$ state may become appreciable. Thus at, say, 600 K (i.e., about 300°C) $N_{v=1}/N_{v=0}$ becomes exp $(-2·4)$ or about 0·09, and transitions from $v = 1$ to $v = 2$ will be some 10 per cent the intensity of those from $v = 0$ to $v = 1$. A similar increase in the excited state population would arise if the vibrational frequency were 500 cm^{-1} instead of 1000 cm^{-1}. We may calculate the wavenumber of this transition as:

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

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

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

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

3.2 THE DIATOMIC VIBRATING-ROTATOR

We saw in Chapter 2 that a typical diatomic molecule has rotational energy separations of 1–10 cm^{-1}, while in the preceding section we found that the vibrational energy separations of HCl were nearly 3000 cm^{-1}. Since the energies of the two motions are so different we may, as a first approximation, consider that a diatomic molecule can execute rotations and vibrations quite independently. This, which we shall call the Born–Oppenheimer approximation (although, cf. Eq. (6·1), this strictly includes electronic energies), is tantamount to assuming that the combined rotational–vibrational energy is simply the sum of the separate energies:

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

$$\varepsilon_{\text{total}} = \varepsilon_{\text{rot.}} + \varepsilon_{\text{vib.}} \quad (\text{cm}^{-1}) \tag{3.16}$$

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

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

$$\begin{aligned} \varepsilon_{J,v} &= \varepsilon_J + \varepsilon_v \\ &= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \ldots \\ &\qquad + (v+\tfrac{1}{2})\bar{\omega}_e - x_e(v+\tfrac{1}{2})^2\bar{\omega}_e \quad \text{cm}^{-1} \end{aligned} \tag{3.17}$$

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

$$\varepsilon_{\text{total}} = \varepsilon_{J,v} = BJ(J+1) + (v+\tfrac{1}{2})\bar{\omega}_e - x_e(v+\tfrac{1}{2})^2\bar{\omega}_e \tag{3.18}$$

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

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

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

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

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

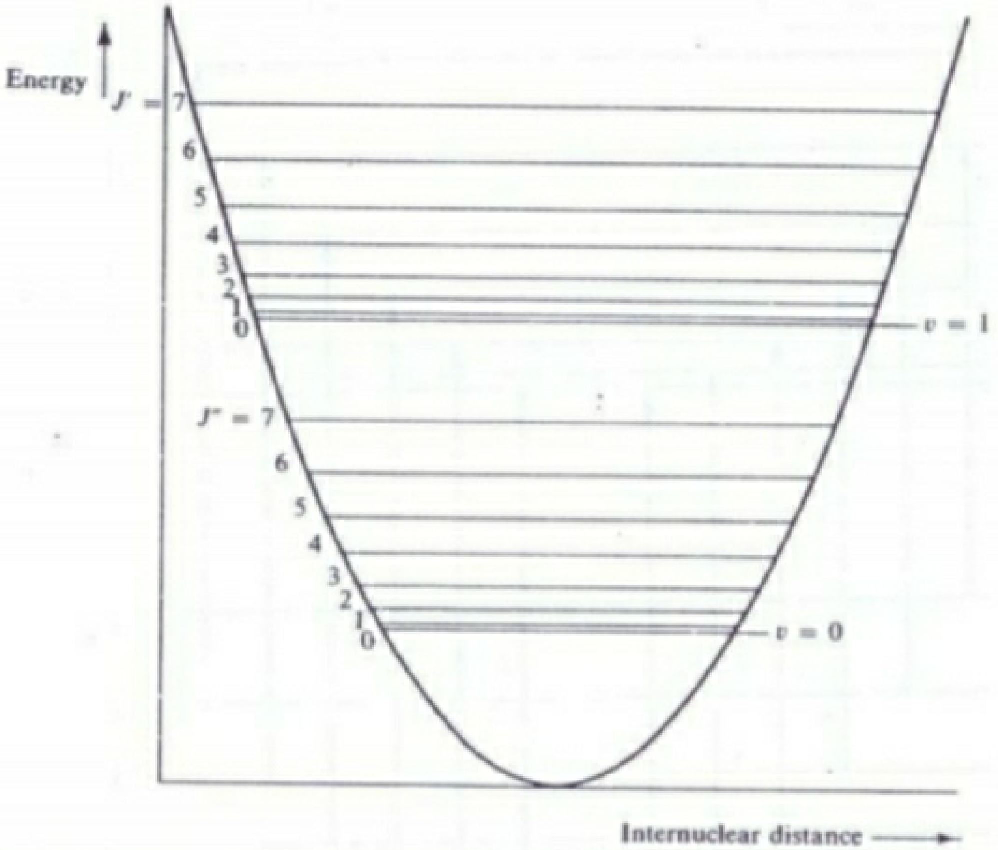

Figure 3.5 The rotational energy levels for two different vibrational states of a diatomic molecule.

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:

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

where, for brevity, we write $\bar{\omega}_o$ 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.

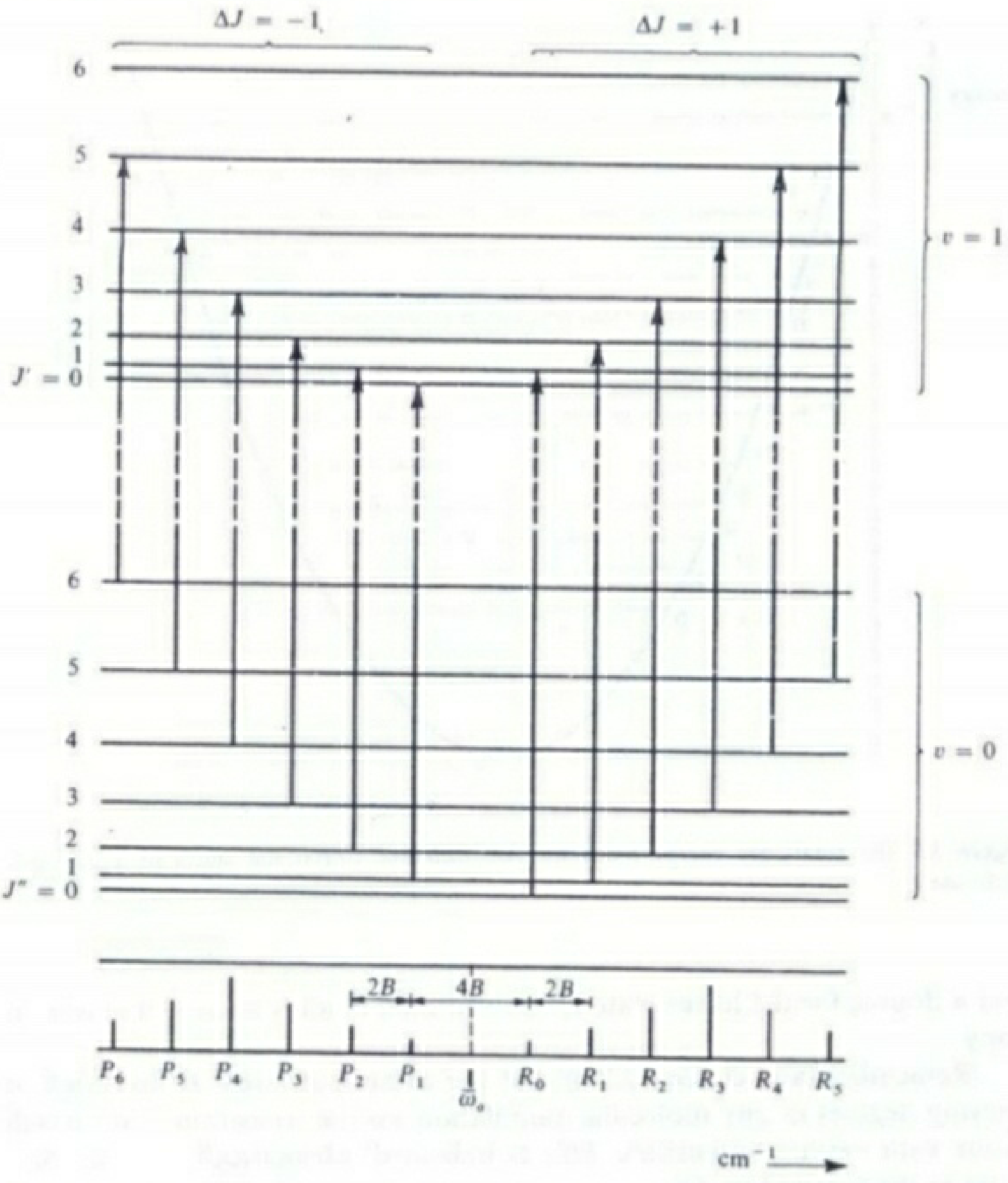

Figure 3.6 Some transitions between the rotational–vibrational energy levels of a diatomic molecule together with the spectrum arising from them.

Now we can have:

1. $\Delta J = +1$, i.e., $J' = J'' + 1$ or $J' - J'' = +1$; hence

$$\Delta \varepsilon_{J,v} = \bar{\omega}_o + 2B(J'' + 1)\ \text{cm}^{-1} \qquad J'' = 0, 1, 2, \ldots \tag{3.20a}$$

2. $\Delta J = -1$, i.e., $J'' = J' + 1$ or $J' - J'' = -1$; and

$$\Delta \varepsilon_{J,v} = \bar{\omega}_o - 2B(J' + 1)\ \text{cm}^{-1} \qquad J' = 0, 1, 2, \ldots \tag{3.20b}$$

3.4 BREAKDOWN OF THE BORN–OPPENHEIMER APPROXIMATION: THE INTERACTION OF ROTATIONS AND VIBRATIONS

So far we have assumed that vibration and rotation can proceed quite independently of each other. A molecule vibrates some 10^3 times during the course of a single rotation, however, so it is evident that the bond length (and hence the moment of inertia and B constant) also changes continually during the rotation. If the vibration is simple harmonic the mean bond length will be the same as the equilibrium bond length and it will not vary with vibrational energy; this is seen in Fig. 3.1. However, the rotational constant B depends on $1/r^2$ and, as shown by an example in Sec. 2.3.4, the average value of this quantity is not the same as $1/r_{\text{eq.}}^2$ where $r_{\text{eq.}}$ is the equilibrium length. Further an increase in the vibrational energy is accompanied by an increase in the vibrational amplitude and hence the value of B will depend on the v quantum number.

In the case of anharmonic vibrations the situation is rather more complex. Now an increase in vibrational energy will lead to an increase in the average bond length—this is perhaps most evident from Fig. 3.4. The rotational constant then varies even more with vibrational energy.

In general, it is plain that, since $r_{\text{av.}}$ *increases* with the vibrational energy, B is *smaller* in the upper vibrational state than in the lower. In fact an equation of the form:

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) \qquad (3.22)$$

gives, to a high degree of approximation, the value of B_v, the rotational constant in vibrational level v, in terms of the equilibrium value B_e and α, a small positive constant for each molecule.

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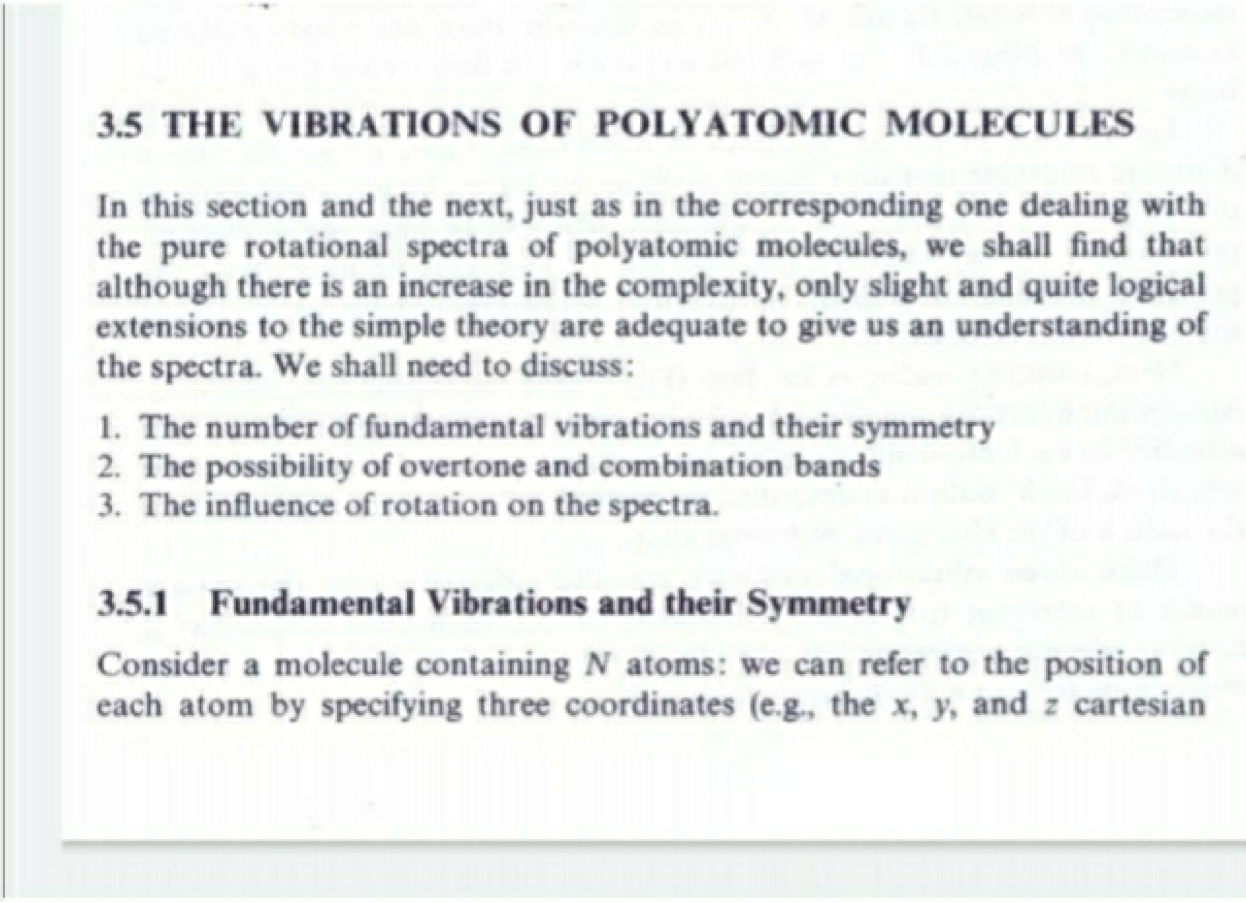


3.5 THE VIBRATIONS OF POLYATOMIC MOLECULES

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

1. The number of fundamental vibrations and their symmetry
2. The possibility of overtone and combination bands
3. The influence of rotation on the spectra.

3.5.1 Fundamental Vibrations and their Symmetry

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

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

$$\text{Non-linear:} \quad 3N - 6 \text{ fundamental vibrations} \qquad (3.24a)$$

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

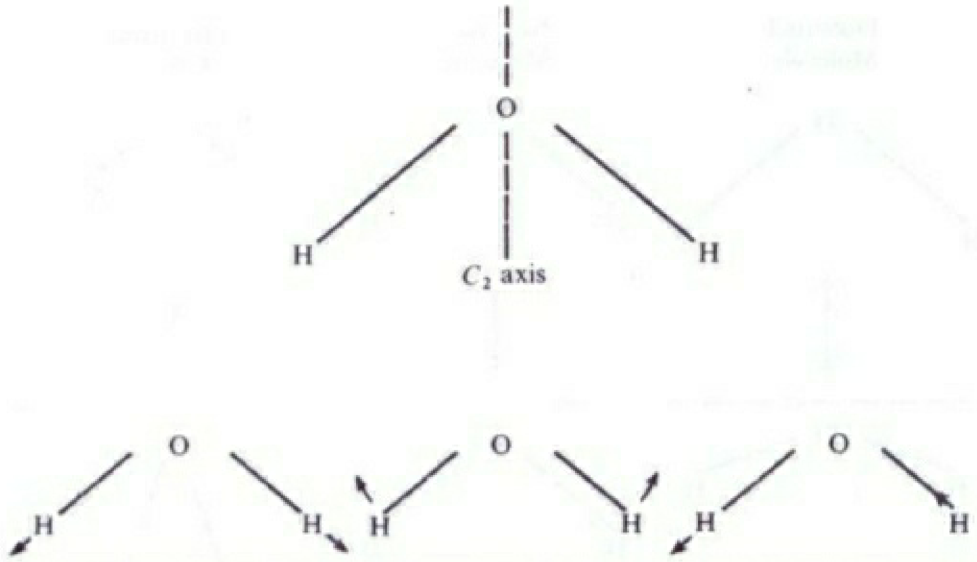
$$\text{Linear:} \quad 3N - 5 \text{ fundamental vibrations} \qquad (3.24b)$$

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

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

Next, consider water, H_2O. This (Fig. 3.9) is non-linear and triatomic. Also in the figure are the $3N - 6 = 3$ allowed vibrational modes, the arrows attached to each atom showing the direction of its motion during half of the vibration. Each motion is described as stretching or bending depending on the nature of the change in molecular shape.

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



(*a*) symmetric stretching
$3651{\cdot}7\ \text{cm}^{-1}$
ν_1, parallel (‖)

(*b*) symmetric bending
$1595{\cdot}0\ \text{cm}^{-1}$
ν_2, parallel (‖)

(*c*) antisymmetric stretch
$3755{\cdot}8\ \text{cm}^{-1}$
ν_3, perpendicular (⊥)

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

Further each motion of Fig. 3.9 is labelled either symmetric or antisymmetric. It is not necessary here to go far into the matter of general molecular symmetry since other excellent texts already exist for the interested student, but we can see quite readily that the water molecule contains some elements of symmetry. In particular consider the dashed line at the top of Fig. 3.9 which bisects the HOH angle; if we rotate the molecule about this axis by 180° its final appearance is identical with the initial one. This axis is thus referred to as a C_2 axis since twice in every complete revolution the molecule presents an identical aspect to an observer. This particular molecule has only the one rotational symmetry axis, and it is conventional to refer the molecular vibrations to this axis. Thus consider the first vibration, Fig. 3.9(*a*). If we rotate the *vibrating* molecule by 180° the vibration is quite unchanged in character—we call this a symmetric vibration. The bending vibration, ν_2, is also symmetric. Rotation of the stretching motion of Fig. 3.9(*c*) about the C_2 axis, however, produces a vibration which is in antiphase with the original and so this motion is described as the antisymmetric stretching mode.

In order to be infra-red active, as we have seen, there must be a dipole change during the vibration and this change may take place either along the line of the symmetry axis (parallel to it, or ‖) or at right angles to the line (perpendicular, ⊥). Figure 3.10 shows the nature of the dipole changes for the three vibrations of water, and justifies the labels parallel or perpen-

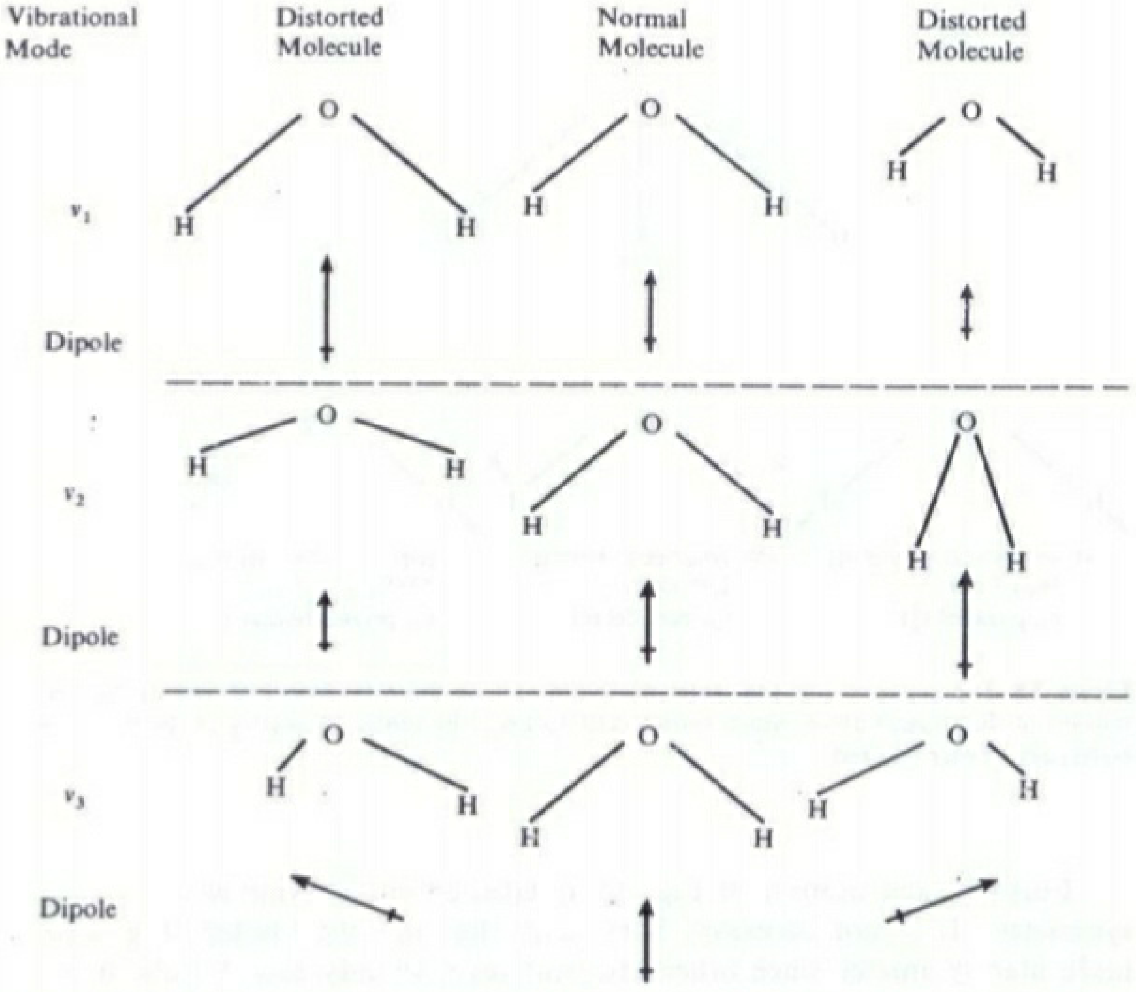
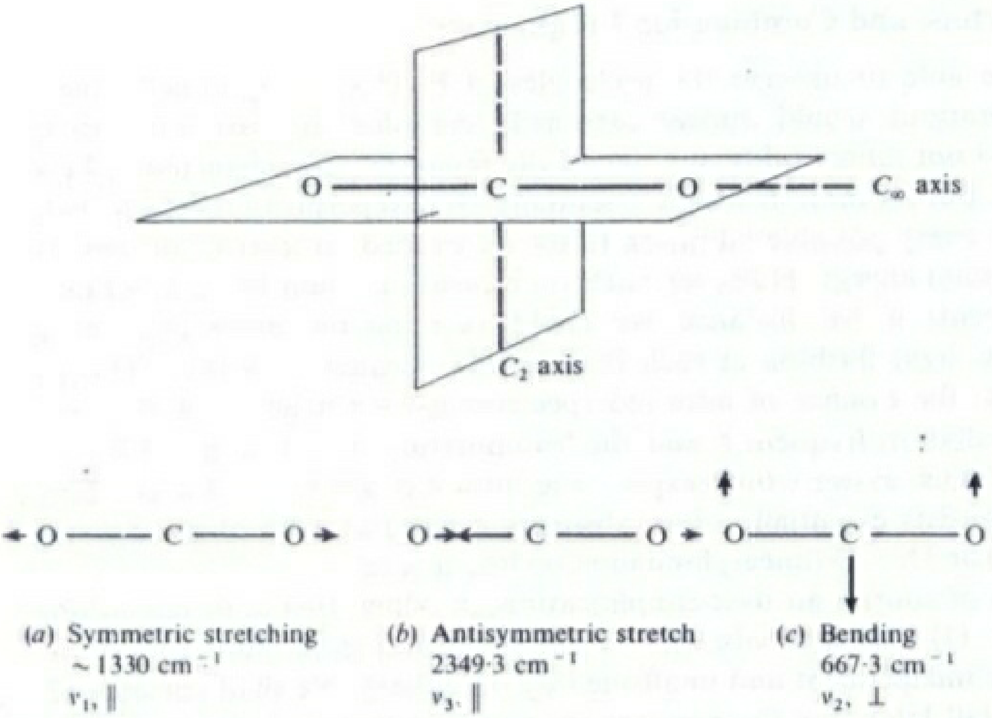


Figure 3.10 The change in the electric dipole moment produced by each vibration of the water molecule. This is seen to occur either along (‖) or across (⊥), the symmetry axis. The amplitudes are greatly exaggerated for clarity.

dicular attached to them in Fig. 3.9. We shall see later that the distinction is important when considering the influence of *rotation* on the spectrum.

Finally the vibrations are labelled in Fig. 3.9 as ν_1, ν_2, and ν_3. By convention it is usual to label vibrations in decreasing frequency within their symmetry type. Thus the symmetric vibrations of H_2O are labelled ν_1 for the highest fully symmetric frequency (3651·7 cm^{-1}), and ν_2 for the next highest (1595·0 cm^{-1}); the antisymmetric vibration at 3755·8 cm^{-1} is then labelled ν_3.

Our final example is of the linear triatomic molecule CO_2, for which the normal vibrations are shown in Fig. 3.11. For this molecule there are two different sets of symmetry axes. There is an infinite number of twofold axes (C_2) passing through the carbon atom at right angles to the bond direction, and there is an ∞-fold axis (C_∞) passing through the bond axis



(*a*) Symmetric stretching
~1330 cm^{-1}
ν_1, ∥

(*b*) Antisymmetric stretch
2349·3 cm^{-1}
ν_3, ∥

(*c*) Bending
667·3 cm^{-1}
ν_2, ⊥

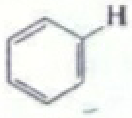
Figure 3.11 The symmetry and fundamental vibrations of the carbon dioxide molecule.

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

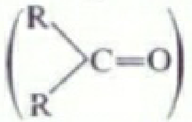
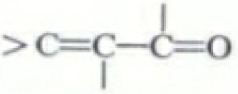
For linear triatomic molecules, $3N - 5 = 4$, and we would expect four vibrational modes instead of the three shown in Fig. 3.11. However, consideration shows that ν_2 in fact consists of *two* vibrations—one in the plane of the paper as drawn, and the other in which the oxygen atoms move simultaneously into and out of the plane. The two sorts of motion are, of course, identical in all respects except direction and are termed *degenerate*; they must, nevertheless, be considered as separate motions, and it is always in the degeneracy of a bending mode that the extra vibration of a linear molecule over a non-linear one is to be found.

It might be thought that ν_2 of H_2O (Fig. 3.9(*b*)) could occur by the hydrogens moving simultaneously in and out of the plane of the paper. Such a motion is not a vibration, however, but a *rotation*. As the molecule approaches linearity this rotation degenerates into a vibration, and the molecule loses one degree of rotational freedom in exchange for one of vibration.

Table 3.4 Characteristic stretching frequencies of some molecular groups

Group	Approximate frequency (cm^{-1})	Group	Approximate frequency (cm^{-1})
$-\mathrm{OH}$	3600	$>\mathrm{C=O}$	1750–1600
$-\mathrm{NH_2}$	3400	$>\mathrm{C=C}<$	1650
$\equiv\mathrm{CH}$	3300	$>\mathrm{C=N}\diagdown$	1600
	3060	$\geqslant\mathrm{C-C}\leqslant$ $\geqslant\mathrm{C-N}<$ $\geqslant\mathrm{C-O}\diagdown$	1200–1000
$=\mathrm{CH_2}$	3030		
		$>\mathrm{C=S}$	1100
$-\mathrm{CH_3}$	2970 (asym. stretch)		
	2870 (sym. stretch)	$\geqslant\mathrm{C-F}$	1050
	1460 (asym. deform.)		
	1375 (sym. deform.)	$\geqslant\mathrm{C-Cl}$	725
$-\mathrm{CH_2}-$	2930 (asym. stretch)	$\geqslant\mathrm{C-Br}$	650
	2860 (sym. stretch)		
	1470 (deformation)	$\geqslant\mathrm{C-I}$	550
$-\mathrm{SH}$	2580		
$-\mathrm{C\equiv N}$	2250		
$-\mathrm{C\equiv C}-$	2220		

replaced by sulphur; the question might be asked: is the molecule $CH_3CO.SH$, or $CH_3CS.OH$? The infra-red spectrum gives a very clear answer. It shows a very sharp absorption at about 1730 cm^{-1}, and one at about 2600 cm^{-1}, and these are consistent with the presence of $>C{=}O$ and $-SH$ groups, respectively (cf. Table 3.4). Also there is little or no absorption at 1100 cm^{-1} (apart from the general background caused by the skeletal vibrations), thus indicating the absence of $>C{=}S$.

The idea of group vibrations also covers the motions of isolated features of a molecule which have frequencies not too near those of the skeletal vibrations. Thus isolated multiple bonds (for example, $>C{=}C<$ or $-C{\equiv}C-$) have frequencies which are highly characteristic. When, however, two such groups which, in isolation, have comparable frequencies, occur together in a molecule, resonance occurs and the group frequencies may be shifted considerably from the expected value. Thus the isolated carbonyl in a ketone  and the $>C{=}C<$ double bond, have group frequencies of 1715 and 1650 cm^{-1} respectively; however, when the grouping  $>C{=}\underset{|}{C}-\overset{|}{C}{=}O$ occurs, their separate frequencies are shifted to 1675 and about 1600 cm^{-1} respectively and the intensity of the $>C{=}C<$ absorption increases to become comparable with that of the inherently strong $>C{=}O$ band (cf. Fermi resonance, p. 97). Closer coupling of the two groups, as in the ketene radical, $>C{=}C{=}O$, gives rise to absorptions at about 2100 and 1100 cm^{-1}, which are very far removed from the 'characteristic' frequencies of the separate groups.

Shifts in group frequencies can arise in other ways too, particularly as the result of interactions between different molecules. Thus the $-OH$ stretching frequency of alcohols is very dependent on the degree of hydrogen bonding, which lengthens and weakens the $-OH$ bond, and hence lowers its vibrational frequency. If the hydrogen bond is formed between the $-OH$ and, say, a carbonyl group, then the latter frequency is also lowered, although to a less extent than the $-OH$, since hydrogen bonding weakens the $>C{=}O$ linkage also. However, shifts in group frequency position caused by resonance or intermolecular effects are in themselves highly characteristic and very useful for diagnostic purposes.

In a similar way a change of physical state may cause a shift in the frequency of a vibration, particularly if the molecule is rather polar. In general the more condensed phase gives a lower frequency: $\nu_{\text{gas}} > \nu_{\text{liquid}} \approx \nu_{\text{solution}} > \nu_{\text{solid}}$. Thus in the relatively polar molecule HCl there is a shift of some 100 cm^{-1} in passing from vapour to liquid and a further decrease of 20 cm^{-1} on solidification. Non-polar CO_2, on the other hand, shows negligible shifts in its symmetric vibrations (Fig. 3.11(*a*) and (*b*)) but a lowering of some 60 cm^{-1} in ν_3 on solidification.

CHAPTER

SIX

ELECTRONIC SPECTROSCOPY OF MOLECULES

In the first section of this chapter we shall discuss, in some detail, the electronic spectra of diatomic molecules. We shall find that the overall appearance of such spectra can be considered without assuming any knowledge of molecular structure, without reference to any particular electronic transition, and indeed, with little more than a formal understanding of the nature of electronic transitions within molecules. In Sec. 6.2 we shall summarize modern ideas of molecular structure and show how these lead to a classification of electronic states analogous to the classification of atomic states discussed in the previous chapter. Section 6.3 will extend the ideas of Secs 6.1 and 6.2 to polyatomic molecules and Sec. 6.4 will deal briefly with experimental techniques.

6.1 ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

6.1.1 The Born–Oppenheimer Approximation

As a first approach to the electronic spectra of diatomic molecules we may use the Born–Oppenheimer approximation previously mentioned in Sec. 3.2; in the present context this may be written:

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} \tag{6.1}$$

which implies that the electronic, vibrational, and rotational energies of a molecule are completely independent of each other. We shall see later to what extent this approximation is invalid. A change in the total energy of a molecule may then be written:

$$\Delta E_{\text{total}} = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}} \quad \text{J}$$

or

$$\Delta \varepsilon_{\text{total}} = \Delta \varepsilon_{\text{elec.}} + \Delta \varepsilon_{\text{vib.}} + \Delta \varepsilon_{\text{rot.}} \quad \text{cm}^{-1} \tag{6.2}$$

The approximate orders of magnitude of these changes are:

$$\Delta \varepsilon_{\text{elec.}} \approx \Delta \varepsilon_{\text{vib.}} \times 10^3 \approx \Delta \varepsilon_{\text{rot.}} \times 10^6 \tag{6.3}$$

and so we see that vibrational changes will produce a 'coarse structure' and rotational changes a 'fine structure' on the spectra of electronic transitions. We should also note that whereas pure rotation spectra (Chapter 2) are shown only by molecules possessing a permanent electric dipole moment, and vibrational spectra (Chapter 3) require a change of dipole during the motion, electronic spectra are given by *all* molecules since changes in the electron distribution in a molecule are always accompanied by a dipole change. This means that homonuclear molecules (for example, H_2 or N_2), which show no rotation or vibration–rotation spectra, *do* give an electronic spectrum and show vibrational and rotational structure in their spectra from which rotational constants and bond vibration frequencies may be derived.

Initially we shall ignore rotational fine structure and discuss the appearance of the vibrational coarse structure of spectra.

6.1.2 Vibrational Coarse Structure: Progressions

Ignoring rotational changes means that we rewrite Eq. (6.1) as

$$E_{\text{total}} = E_{\text{elec.}} + E_{\text{vib.}} \quad \text{J}$$

or

$$\varepsilon_{\text{total}} = \varepsilon_{\text{elec.}} + \varepsilon_{\text{vib.}} \quad \text{cm}^{-1} \tag{6.4}$$

From Eq. (3.12) we can write immediately:

$$\varepsilon_{\text{total}} = \varepsilon_{\text{elec.}} + (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \quad \text{cm}^{-1} \qquad (v = 0, 1, 2, \ldots) \tag{6.5}$$

The energy levels of this equation are shown in Fig. 6.1 for two arbitrary values of $\varepsilon_{\text{elec.}}$. As in previous chapters the lower states are distinguished by a *double* prime (v'', $\varepsilon''_{\text{elec.}}$), while the upper states carry only a *single* prime (v', $\varepsilon'_{\text{elec.}}$). Note that such a diagram cannot show correctly the relative separations between levels of different $\varepsilon_{\text{elec.}}$, on the one hand, and those with different v' or v'' on the other (cf. Eq. (6.3)), but that the spacing between the upper vibrational levels is deliberately shown to be rather smaller than that between the lower; this is the normal situation since an excited electronic state usually corresponds to a weaker bond in the molecule and hence a smaller vibrational wavenumber $\bar{\omega}_e$.

There is essentially no selection rule for v when a molecule undergoes an electronic transition, i.e., every transition $v'' \rightarrow v'$ has some probability, and a great many spectral lines would, therefore, be expected. However, the situation is considerably simplified if the *absorption* spectrum is considered from the electronic ground state. In this case, as we have seen in Sec. 3.1.3, virtually all the molecules exist in the lowest vibrational state, that is, $v'' = 0$, and so the only transitions to be observed with appreciable intensity are those indicated in Fig. 6.1. These are conventionally labelled according to their (v', v'') numbers (note: upper state *first*), that is, (0, 0), (1, 0), (2, 0), etc. Such a set of transitions is called a *band* since, under low resolution, each line of the set appears somewhat broad and diffuse, and is more particularly called a v' *progression*, since the value of v' increases by unity for each line in the set. The diagram shows that the lines in a band crowd together more closely at high frequencies; this is a direct consequence of the anharmonicity of the upper state vibration which causes the excited vibrational levels to converge.

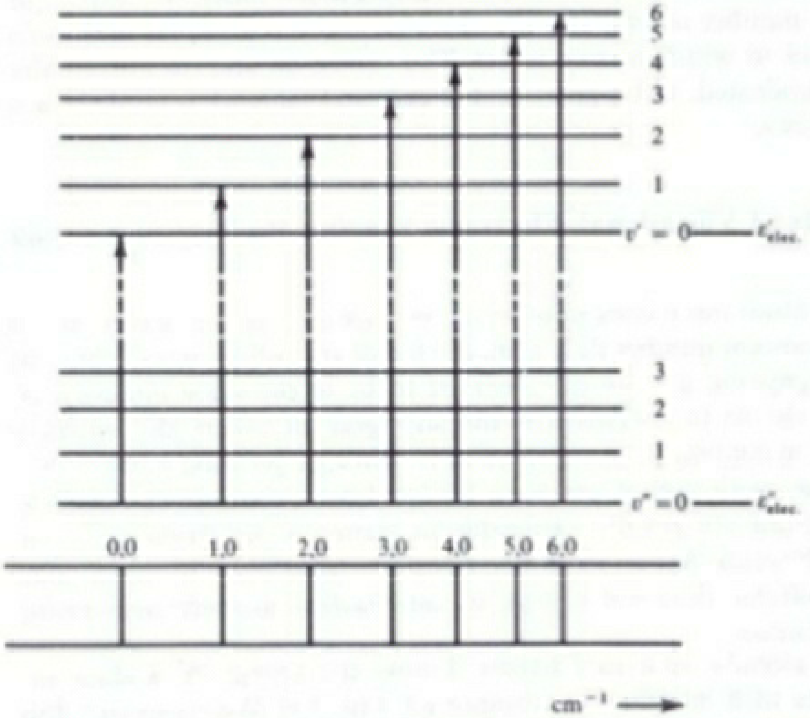


Figure 6.1 The vibrational 'coarse' structure of the band formed during electronic absorption from the ground ($v'' = 0$) state to a higher state.

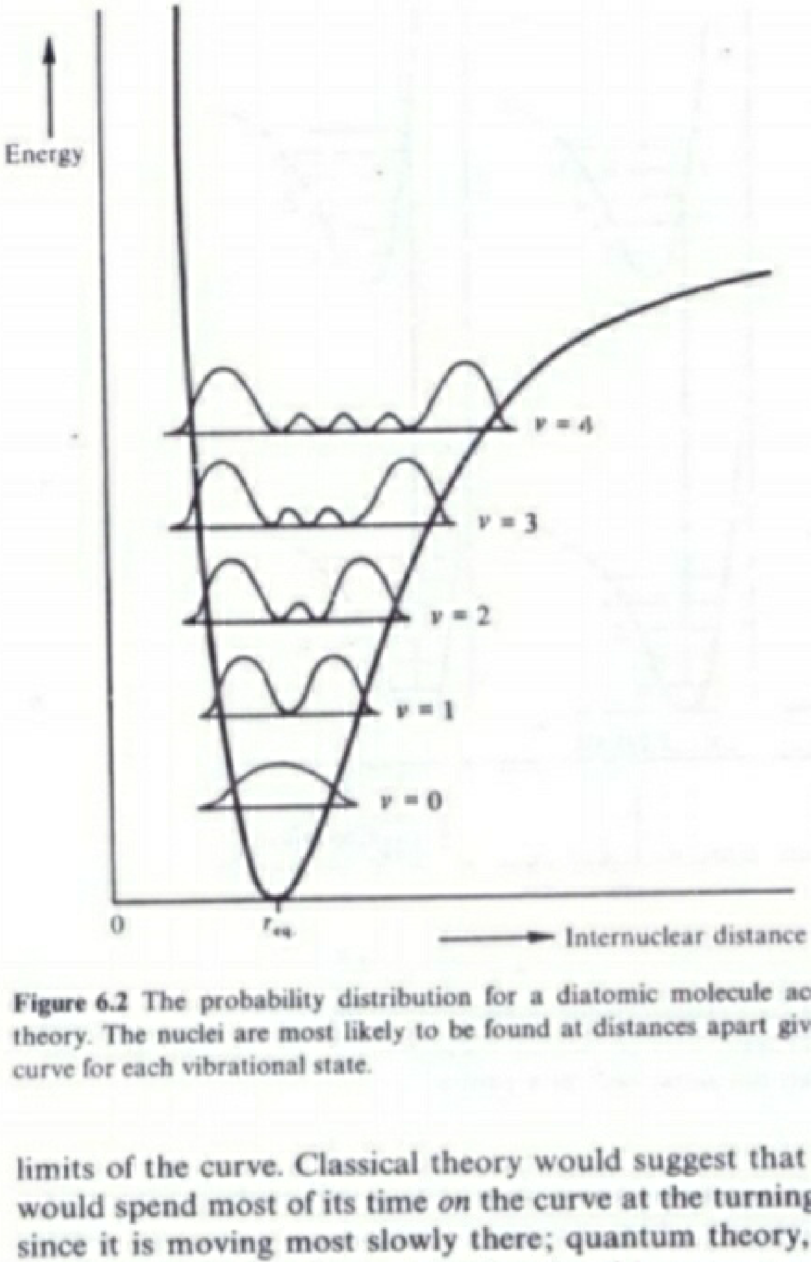


Figure 6.2 The probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.

limits of the curve. Classical theory would suggest that the oscillating atom would spend most of its time *on* the curve at the turning point of its motion, since it is moving most slowly there; quantum theory, while agreeing with this view for high values of the vibrational quantum number, shows that for $v = 0$ the atom is most likely to be found at the *centre* of its motion, i.e., at the equilibrium internuclear distance $r_{eq.}$. For $v = 1, 2, 3, \ldots$ the most probable positions steadily approach the extremities until, for high v, the quantal and classical pictures merge. This behaviour is shown in Fig. 6.2 where we plot the probability distribution in each vibrational state against internuclear distance. Those who have studied quantum mechanics will realize that Fig. 6.2 shows the variation of ψ^2 with internuclear distance, where ψ is the vibrational wave function.

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in

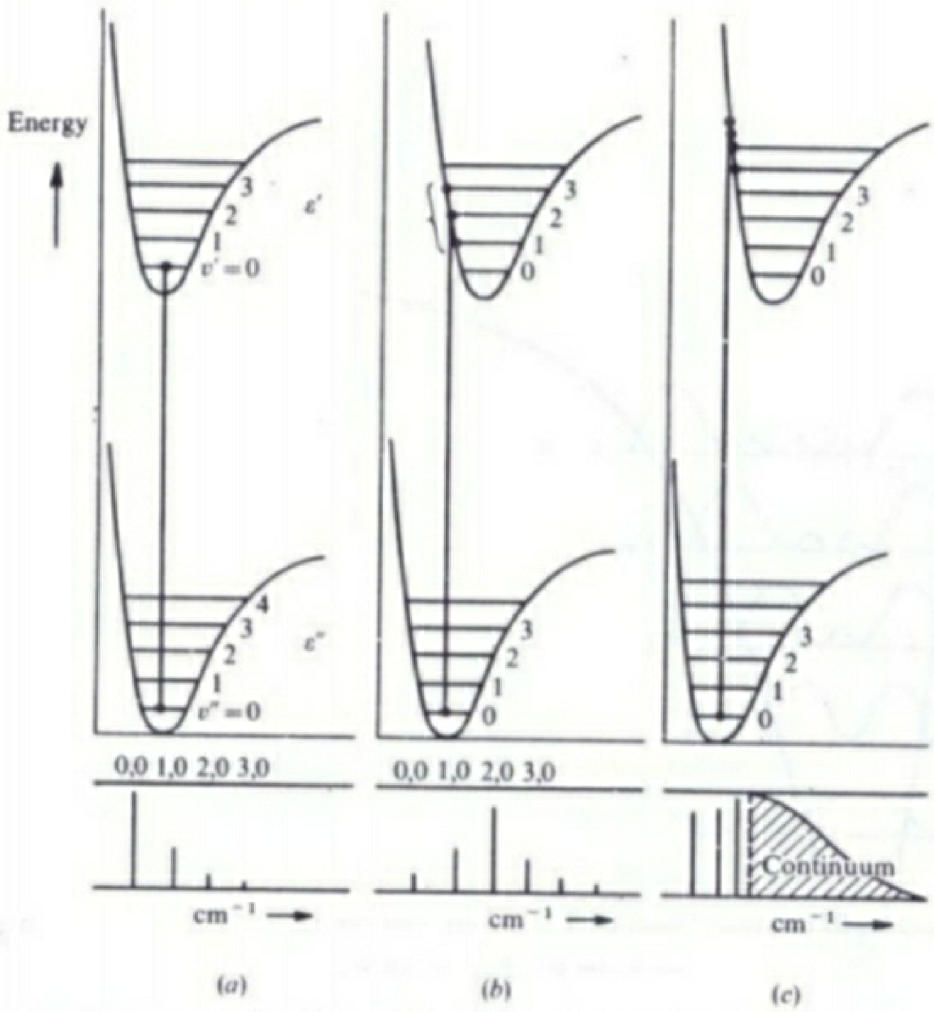


Figure 6.3 The operation of the Franck–Condon principle for (*a*) internuclear distances equal in upper and lower states, (*b*) upper-state internuclear distance a little greater than that in the lower state, and (*c*) upper-state distance considerably greater.

outline to that of the ground electronic state. There will probably (but not necessarily) be differences in such parameters as vibrational frequency, equilibrium internuclear distance, or dissocation energy between the two states, but this simply means that we should consider each excited molecule as a new, but rather similar, molecule with a different, but also rather similar, Morse curve.

Figure 6.3 shows three possibilities. In (*a*) we show the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Franck–Condon principle suggests that a transition occurs *vertically* on this diagram, since the internuclear distance does not change, and so if we consider the molecule to be initially in the ground state both electronically (ε'') and vibrationally ($v''=0$), then the most probable transition is that indicated by the vertical line in Fig. 6.3(*a*). Thus the strongest spectral line of the $v''=0$ progression will be the (0, 0). However, the quantum theory may take up any value of kinetic energy, the transitions are not quantized and a continuum results. This is shown at the foot of the figure. We consider the phenomenon of dissociation more fully in the next section.

The situation is rather more complex for emission spectra and for absorption from an excited vibrational state, for now transitions take place from *both ends* of the vibrational limits with equal probability; hence each progression will show two maxima which will coincide only if the equilibrium separations are the same in both states.

6.1.4 Dissociation Energy and Dissociation Products

Figure 6.4(*a*) and (*b*) shows two of the ways in which electronic excitation can lead to dissociation (a third way called *predissociation*, will be considered in Sec. 6.1.7). Part (*a*) of the figure represents the case, previously discussed, where the equilibrium nuclear separation in the upper state is considerably greater than that in the lower. The dashed line limits of the Morse curves represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being D''_0 and D'_0 from the $v = 0$ state in each case. We see that the total energy of the dissociation products (i.e., atoms) from the upper state is greater by an amount called $E_{\text{ex.}}$ than that of the products of dissociation in the lower state. This energy is the *excitation energy* of one (or rarely both) of the atoms produced on dissociation.

We saw in the previous section that the spectrum of this system consists of some vibrational transitions (quantized) followed by a continuum (non-quantized transitions) representing dissociation. The lower wavenumber

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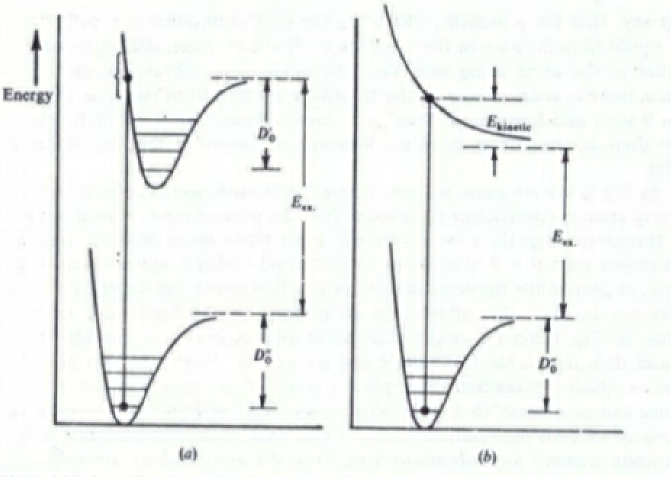

Figure 6.4 Illustrating dissociation by excitation into (*a*) a stable upper state, and (*b*) a continuous upper state.

limit of this continuum must represent just sufficient energy to cause dissociation and no more (i.e., the dissociation products separate with virtually zero kinetic energy) and thus we have

$$\bar{\nu}_{\text{(continuum limit)}} = D''_0 + E_{\text{ex.}} \quad \text{cm}^{-1} \tag{6.7}$$

and we see that we can measure D''_0, the dissociation energy, if we know $E_{\text{ex.}}$, the excitation energy of the products, whatever they may be. Now, although the excitation energy of atoms to various electronic states is readily measurable by atomic spectroscopy (cf. Chapter 5), the precise *state* of dissociation products is not always obvious. There are several ways in which the total energy $D''_0 + E_{\text{ex.}}$ may be separated into its components, however; here we shall mention just two.

Firstly, thermochemical studies often lead to an approximate value of D''_0 and hence, since $D''_0 + E_{\text{ex.}}$ is accurately measurable spectroscopically, a rough value for $E_{\text{ex.}}$ is obtained. When the spectrum of the atomic products is studied, it usually happens that only one value of excitation energy corresponds at all well with $E_{\text{ex.}}$. Thus the state of the products is known, $E_{\text{ex.}}$ measured accurately, and a precise value of D''_0 deduced.

Secondly, if more than one spectroscopic dissociation limit is found, corresponding to dissociation into two or more different states of products with different excitation energies, the separations between the excitation energies are often found to correspond closely with the separations between is studied, it usually happens that only one value of excitation energy corresponds at all well with $E_{ex.}$. Thus the state of the products is known, $E_{ex.}$ measured accurately, and a precise value of D_0^c deduced.

Secondly, if more than one spectroscopic dissociation limit is found, corresponding to dissociation into two or more different states of products with different excitation energies, the separations between the excitation energies are often found to correspond closely with the separations between

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designate l values of 0, 1, 2, ... However, it will be remembered that in order to discuss the components of **l** we required to invoke some reference direction called the z direction; in a diatomic molecule a reference direction is already quite obviously specified—the inernuclear axis, or bond—and it would be perverse (not to say *wrong*) to discuss the components of **l** along any other direction. Furthermore, a force-field exists along this direction due to the presence of two nuclear charges; therefore different **l** components are not degenerate but represent *different energies*.

The axial component of orbital angular momentum is of more importance in molecules than the momentum itself and for this reason it is given the special symbol λ. Formally $\lambda \equiv |l_z|$, so that λ takes *positive* integral values or is zero, and we designate the λ state of an electron in a molecule by using the small Greek letters corresponding to the $s, p, d, \ldots$ of atomic nomenclature. Thus we have, for

$$l_z = 0, \pm 1, \pm 2, \pm 3, \ldots$$

$$\lambda = 0, 1, 2, 3, \ldots$$

and the symbols are $\quad \sigma, \pi, \delta, \phi, \ldots$

Since λ has positive values only, each λ state with $\lambda > 0$ is *doubly degenerate*, because it corresponds to l_z being both positive and negative. The significance of λ is that the *axial component of orbital angular momentum* $= \lambda h/2\pi$ or *λ units*.

The total orbital angular momentum of several electrons in a molecule can be discussed, as for atoms, in terms of the quantum number $L = \Sigma l$, $\Sigma l - 1$, etc., with $\mathbf{L} = \sqrt{L(L+1)}h/2\pi$, but again the axial component, denoted by Λ, is of greatest significance. Since, by definition, all individual λ_i lie along the internuclear axis, their summation is particularly simple. We have

$$\Lambda = |\Sigma \lambda_i| \tag{6.29}$$

and states are designated by capital Greek letters Σ, Π, Δ, etc., for $\Lambda = 0, 1, 2, \ldots$. We must take into account, when using Eq. (6.29), that the individual λ_i may have the same or opposite directions and all possible combinations which give a positive Λ should be considered. Thus for a π and a δ electron ($\lambda_1 = 1$, $\lambda_2 = 2$) we could have $\Lambda = 1$ or 3 (but not -1), that is, a Π or a Φ state.

Electron *spin* momentum, on the other hand, is not greatly affected by the electric field of the two nuclei—we say the spin–axial coupling is weak, whereas the orbital–axial coupling is usually strong. Normally, therefore, we use the same notation for electronic spin in molecules as in atoms; the total spin momentum **S** is given by $\sqrt{S(S+1)}$ where the total spin quantum number S is:

$$S = \Sigma S_i, \Sigma S_i - 1, \Sigma S_i - 2, \ldots, \tfrac{1}{2} \text{ or } 0 \tag{6.30}$$

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[illegible] Thus 286 nm, for example, is equivalent to 100 kcals ($\approx$ 420 kJ)—enough energy, incidentally, to initiate many interesting reactions; compounds should not, therefore, be left in the ultraviolet beam any longer than is necessary.

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1–3. The Absorption Laws

Two empirical laws have been formulated about the absorption intensity. *Lambert's law* states that the fraction of the incident light absorbed is independent of the intensity of the source. *Beer's law* states that the absorption is proportional to the number of absorbing molecules. From these laws, the remaining variables give the equation 1–2.

$$\log_{10}\frac{I_0}{I} = \varepsilon . l . c \qquad (1\text{–}2)$$

I_0 and I are the intensities of the incident and transmitted light respectively, l is the path length of the absorbing solution in centimetres, and c is the concentration in moles/litre. $\text{Log}_{10}\,(I_0/I)$ is called the absorbance or optical density; ε is known as the molar extinction coefficient and has units of 1000 cm.^{2}/mole but the units are, by convention, never expressed.

1–4. Measurement of the Spectrum

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used

The ultraviolet or visible spectrum is usually taken on a very dilute solution. An appropriate quantity of the compound (often about 1 mg. when the compound has a molecular weight of 100 to 200) is weighed accurately, dissolved in the solvent of choice (see below) and made up to, for instance, 100 ml. A portion of this is transferred to a silica cell. The cell is so made that the beam of light passes through a 1 cm. thickness (the value l in equation 1–2) of solution. A matched cell containing pure solvent is also prepared, and each cell is placed in the appropriate place in the spectrometer. This is so arranged that two equal beams of ultraviolet or visible light are passed, one through the solution of the sample, one through the pure solvent. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. In most spectrometers there are two sources, one of 'white' ultraviolet and one of white visible light, which have to be changed when a complete scan is required. Usually either the visible or ultraviolet alone is sufficient for the purpose in hand. The spectrum is plotted automatically on most machines as a $\log_{10}\,(I_0/I)$ ordinate

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and λ abscissa. For publication and comparisons these are often converted to an ε versus λ or log ε versus λ plot. The unit of λ is almost always nm. Strictly speaking the intensity of a transition is better measured by the area under the absorption peak (when plotted as ε versus frequency) than by the intensity of the maximum of the peak. For several reasons, most particularly convenience and the difficulty of dealing with overlapping bands, the latter procedure is adopted in everyday use. Spectra are quoted, therefore, in terms of λ_{max}, the wavelength of the absorption peak, and ε_{max}, the intensity of the absorption peak as defined by equation 1–2.

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1–5. Vibrational Fine Structure

The excitation of electrons is accompanied by changes in the vibrational and rotational quantum numbers so that what would otherwise be an absorption *line* becomes a broad peak containing vibrational and rotational fine structure. Due to interactions of solute with solvent molecules this is usually blurred out, and a smooth curve is observed. In the vapour phase, in non-polar solvents, and with certain peaks (e.g., benzene with the 260 nm band), the vibrational fine structure is sometimes observed.

1–6. Choice of Solvent

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The solvent most commonly used is 95 per cent ethanol (commercial absolute ethanol contains residual benzene which absorbs in the ultraviolet). It is cheap, a good solvent and transparent down

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Table 1–1

Some Solvents used in Ultraviolet Spectroscopy

Solvent	Minimum wavelength for 1 cm. cell, nm
Acetonitrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
* Ethanol	204
Ether	215
Methylene dichloride	220
Chloroform	237
Carbon tetrachloride	257

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to about 210 nm. Fine structure, if desired, may be revealed by using cyclohexane or other hydrocarbon solvents which, being less polar, have least interaction with the absorbing molecules. Table 1–1 gives a list of common solvents and the minimum wavelength from which they may be used in 1 cm. cells.

The effect of solvent polarity on the position of maxima is discussed in section 1–9.

1–7. Selection Rules and Intensity

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The irradiation of organic compounds may or may not give rise to excitation of electrons from one orbital (usually a lone-pair or bonding orbital) to another orbital (usually a non-bonding or antibonding orbital). It can be shown that:

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$$\varepsilon = 0{\cdot}87 \times 10^{20}\, P.\mathbf{a} \rightarrow \quad (1\text{–}3)$$

مساحة الهدف النظام الممتص

where P is called the transition probability (with values from 0 to 1) and **a** is the target area of the absorbing system; the absorbing system is usually called a chromophore. With common chromophores of the order of 10 Å long, a transition of unit probability will have an ε value of 10^5. This is close to the highest observed values, though—with unusually long chromophores— values in excess of this have been measured. In practice, a chromophore giving rise to absorption by a fully allowed transition will have ε values greater than about 10,000, while those with low transition probabilities will have ε values below 1000. The important point is that, in general, *the longer a particular kind of chromophore, the more intense the absorption.*

There are many factors which affect the transition probability of any particular transition. In the first place there are rules about which transitions are allowed and which are forbidden. These are complicated because they are a function of the symmetry and multiplicity both of the ground state and excited state orbitals concerned. The spectra of chromophores, with $\varepsilon_{\max}$ less than about 10,000, are the result of 'forbidden' transitions. Two very important and 'forbidden' transitions are observed: (*a*) the $n \rightarrow \pi^*$ band near 300 nm of ketones, with ε values of the order of 10 to 100, and (*b*) the benzene 260 nm band and its equivalent in more complicated systems, with ε values from 100 upwards. Both occur because the symmetry which makes absorption strictly forbidden is broken up by molecular vibrations and—in the latter case—by substitution.

4 Both types are discussed further under the sections on ketones and aromatic systems.

In this and the following discussions a very simplified theoretical picture is given; there is considerable danger in being satisfied with so little in so well developed a subject. The books by Jaffé and Orchin and by Murrell, listed in the bibliography, give excellent accounts of the state of the art.

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الامتصاص في موضوع النقاش (تحت البحث)

1–8. Chromophores

The word chromophore is used to describe the system containing the electrons responsible for the absorption in question. Most of the simple unconjugated chromophores described in Table 1–2 below give rise to such high-energy, and therefore such short-wavelength absorption, that they are of little use.

Table 1–2

The Absorption of Simple Unconjugated Chromophores

Chromophore	Transition notation†	λ_{max} in nm
σ-Bonded electrons		
$>C-C<$ and $>C-H$	$\sigma \rightarrow \sigma^*$	~150
Lone-pair electrons		
$-\ddot{O}-$	$n \rightarrow \sigma^*$	~185
$-\ddot{N}<$	$n \rightarrow \sigma^*$	~195
$-\ddot{S}-$	$n \rightarrow \sigma^*$	~195
$>C=\ddot{O}$	$n \rightarrow \pi^*$	~300
$>C=\ddot{O}$	$n \rightarrow \sigma^*$	~190
π-bonded electrons		
$>C=C<$ (isolated)	$\pi \rightarrow \pi^*$	~190

† There are many other notations used

One of the few useful simple unconjugated chromophores is the very weak forbidden $n \rightarrow \pi^*$ transition of ketones mentioned earlier which appears in the 300 nm region and is of particular importance in connection with optical rotatory dispersion. This band is due to the excitation of one of the lone pair of electrons (designated n) on the oxygen atom to the lowest anti-bonding orbital (designated π^*)

5

NMR spectra

3. Nuclear Magnetic Resonance Spectra

3–1. Note

Many of the NMR spectra illustrated in this chapter are reproduced from the Varian NMR catalogues, volumes 1 and 2, with the permission of Varian Associates to whom we express our most sincere thanks. Each spectrum is referenced in terms of its catalogue number. These spectra have been determined in dilute solution (*ca.* 7 per cent) in $CDCl_3$ and at 60 MHz.

3–2. Nuclear Spin and the Spectrometer

The NMR phenomenon (first observed in 1946) is observable because certain nuclei behave like tiny spinning bar magnets. Most important among such nuclei are ^{1}H, ^{13}C, ^{19}F and ^{31}P, all having nuclear spin values of $\frac{1}{2}$. Certain other nuclei which are important in organic chemistry have a nuclear spin value of zero and therefore give no nuclear resonance signals; these include ^{12}C and ^{16}O.

If a proton is placed in a uniform magnetic field, it may take up one of two orientations with respect to the field; these may be considered to be: a low-energy orientation in which the nuclear magnet is aligned with the field, and a high-energy orientation in which it is aligned against the field. The transition between these two energy states can be brought about by the absorption of a quantum of suitable electromagnetic radiation of energy $h\nu$. It turns out that if we employ field strengths of the order of 10,000 gauss, the energy required to flip the nuclear magnet is supplied

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by the radiofrequency range of the electromagnetic spectrum (in practice around 10 to 100 MHz).

The simple outline given in the previous paragraph indicates that to observe nuclear magnetic resonance signals for protons, we will require:

(*i*) a radio-frequency transmitter
(*ii*) a homogeneous magnetic field
(*iii*) a radio-frequency receiver

It will be seen in section 3–3 that since different protons in an organic molecule have varying electronic environments, the precise value of the magnetic field required to bring any one into resonance at constant frequency will vary slightly from proton to proton. Thus if we operate the NMR spectrometer at a fixed frequency, a fourth requirement in the instrument will be a unit to sweep the magnetic field over a small range. A schematic diagram showing the relationship between these basic components and the sample is given in Fig. 3–1.

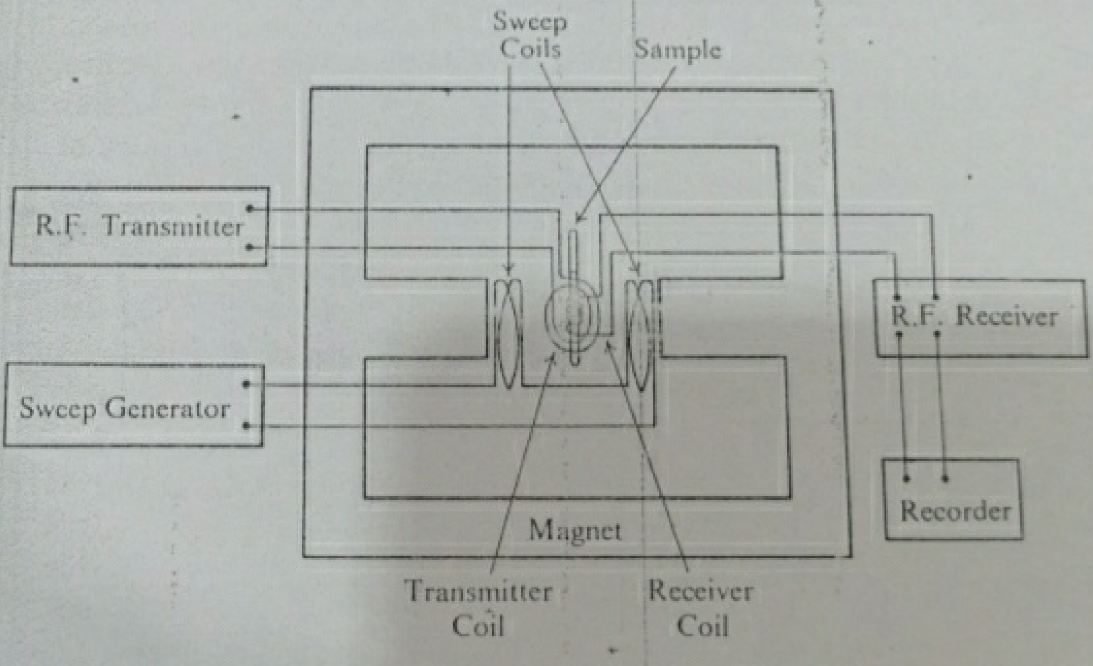

Fig. 3–1

In practice, the field sweep required to bring protons occurring in the vast majority of chemical environments into resonance is only ten parts in a million. This fact places stringent requirements on the homogeneity of the magnetic field employed in NMR experiments. These requirements may be met in part by designing the magnet with a much smaller air gap between the poles than has in fact been shown in the diagram (Fig. 3–1). Moreover, by spinning the solution of the sample about the vertical axis of the sample tube, field inhomogeneities perpendicular to the direction of spinning can be averaged out.

In practice, the most difficult part in obtaining a good NMR spectrum lies in obtaining a homogeneous field in the region of the sample. Once this has been achieved, the remaining operations are relatively simple. The sample (as little as 1 mg. in the case of some modern instruments, but preferably about 10–30 mg.) is dissolved in the solvent (most frequently about 0·5–1·0 ml. of carbon tetrachloride or deuterochloroform ($CDCl_3$)) and the resulting solution transferred to the sample tube; which, having an internal diameter of about 4 mm., will be filled to a depth of approximately 3–7 cm. A few per cent of a reference substance (tetramethylsilane, see section 3–3) is then added to the solution, the sample tube is placed between the poles of the magnet, and the spectrum may be scanned and recorded by a conventional chart and pen-and-ink recorder within a few minutes.

If the available sample size is a few hundred microgrammes, then the signal response will only be of the same order of magnitude as the 'noise' inherently associated with the instrument. The spectrum must then be scanned many times and the information from each scan stored in a computer of average transients (CAT). Noise, being of random nature, will be averaged out, while the signals associated with the sample will add up. In this way, repeated scanning can lead to a good spectrum from a very small amount of material.

So far, we have referred only to spectra recorded by continuously sweeping the field at constant frequency. A serious disadvantage of this approach [resulting in so-called continuous wave (cw) spectra] is that only a very small portion of the spectrum is being excited at any given time. Thus, the signal/noise (S/N) ratio which is attainable in a given time is adversely affected, and this situation is particularly undesirable if we are dealing with a nucleus where sensitivity is a problem. Such is the case for ^{13}C, where the low natural abundance (1·1 per cent) and magnetogyric ratio render the sensitivity about 10^{-4} of that observed for ^{1}H. For such nuclei, or indeed when sample size is a problem (e.g., 0·1–1 mg. for ^{1}H spectra), Fourier transform techniques can advantageously be employed. The radio frequency is applied at one end of the spectrum as a short, powerful pulse and this behaves like a spread of frequencies. If Δ Hz is the entire range of chemical shifts to be recorded in the spectrum, then the pulse length (t_p sec.) must be chosen such that

$$t_p \ll \tfrac{1}{4}\Delta$$

Pulse lengths for ^{13}C spectra are of the order of μsecs.

All nuclei in the spectrum can be excited by a single pulse and, as they decay back to their equilibrium state, the receiver coils of the spectrometer record a decay of magnetization which takes the form of a complex series of sine waves decaying exponentially in time. This information is related to the normal NMR spectrum *via* a Fourier transform which can conveniently be carried out by an on-line computer. Many thousands of pulsed spectra (each *spectrum* being recorded in seconds) can be accumulated before the Fourier transform operation is carried out, and the result is a dramatic improvement in S/N for a given expenditure of time.

Pulsed spectra and Fourier transform techniques are most commonly used to obtain ^{13}C spectra (section 3–13). Unless otherwise stated the spectra reproduced in this chapter are obtained by continuous wave techniques.

3–3. Chemical Shift

The frequency (ν) at which any proton will resonate in the NMR spectrum is given by equation 3–1, in which H is the local field experienced by the proton and γ is a constant known as the magnetogyric ratio.

$$\nu = \frac{\gamma H}{2\pi} \tag{3–1}$$

The local field (H) experienced by the proton will not correspond to the applied magnetic field (H_0) since the nucleus will in general be shielded by the electrons surrounding it. The extent of this shielding may be represented in terms of a shielding parameter (σ), defined such that the local field (H) is given by equation 3–2.

$$H = H_0(1-\sigma), \tag{3–2}$$

therefore

$$\nu = \frac{\gamma H_0(1-\sigma)}{2\pi} \tag{3–3}$$

Equation 3–3 follows and hence it may be seen that protons with