Core Elective III: Spectroscopy

3.9. NATURE OF ELECTROMAGNETIC RADIATIONS

WAVE THEORY OF RADIATIONS

Light is an important form of energy. According to Newton's corpuscular theory it was considered as a stream of particles called corpuscles of light. This theory could successfully explain phenomena of reflection and refraction but failed to explain phenomena of diffraction and interference. Therefore, corpuscular theory was discarded and it was replaced by Maxwell's wave theory of light. According to this theory, light is transmitted in the form of electromagnetic waves. These waves are associated with oscillating electric field and magnetic field.

These two fields are perpendicular to each other and also to the direction of propagation as shown in Fig. 3.15.
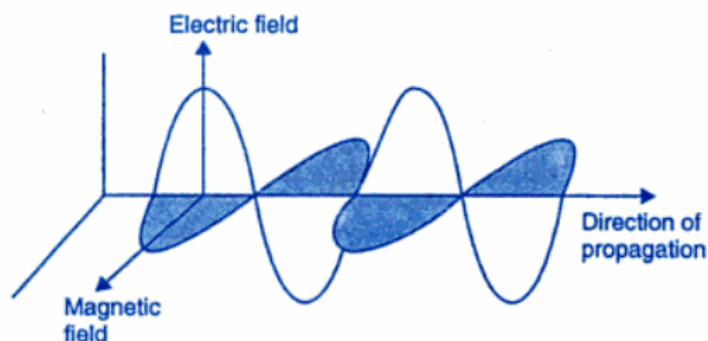

Fig. 3.15. Electromagnetic wave.

In order to characterise these waves following parameters are used :

1. Wavelength. *It may be defined as the distance between two neighbouring crests or troughs of the wave as* shown in Fig. 3.16. It is represented by Greek letter λ (*lambda*) and is generally measured in Angstrom units (Å) or nanometers (nm).

$$1\ \text{Å} = 10^{-10}\ \text{m}$$

$$1\ \text{nm} = 10^{-9}\ \text{m}.$$

In addition, the following units are also sometimes used.

$$\text{picometer, pm} = 10^{-12}\ \text{m}$$

$$\text{microns, } \mu = 10^{-6}\ \text{m}$$

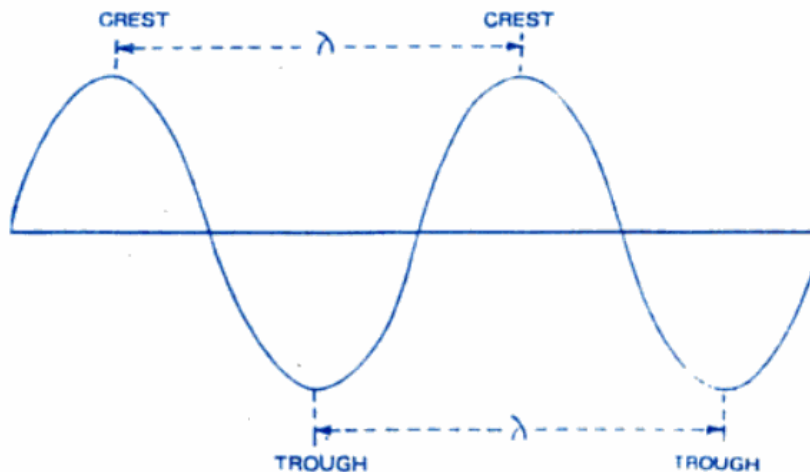$$\text{millimicron, m}\mu = 10^{-9}\ \text{m}$$

Fig. 3.16. Propagation of wave motion.

2. Frequency. *It may be defined as the number of waves which pass through a particular point in one second.* It is represented by Greek letter ν *(nu)*. Its units are :

Cycles per second *(cps)* or **Hertz** *(Hz).*

$$1\,cps = 1\,Hz$$
$$1\,kHz = 10^3\,Hz$$
$$1\,MHz = 10^6\,Hz.$$

3. Velocity. *The distance travelled by a wave in one second is called velocity of the wave.* It is denoted by letter *c*. The frequency (ν) and wavelength (λ) are related to velocity (*c*) by the following relation :

$$c = \nu\lambda \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

Velocity of all electromagnetic radiations in space or in vacuum is same and is equal to $3 \times 10^8\ m/sec$ *or* $3 \times 10^{10}\ cm/sec.$

4. Wave number. *It may be defined as the number of wavelengths per unit length. It is equal to the inverse of wavelength.* It is denoted by $\bar{\nu}$. Its unit is the reciprocal of wavelength unit. It is generally expressed as cm^{-1} or m^{-1}.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}\ .$$

5. Amplitude. *It is the height of a crest or depth of a trough of a wave.* It is generally expressed by the letter '*a*'. The amplitude of a wave determines the intensity of radiation.

ELECTROMAGNETIC SPECTRUM

The different electromagnetic radiations have different wavelengths. The visible light in the presence of which our eye can see contains radiations having wavelengths between 3800 Å —7600 Å. Different colours in the visible light correspond to radiations of different wavelengths. In addition to visible light there are so many other electromagnetic radiations, such as X-rays, ultraviolet rays, infra-red rays, microwaves and radiowaves.

Arrangement of all the electromagnetic radiations in the increasing order of their wavelengths or decreasing order of their frequencies is called electromagnetic spectrum.

Different regions of electromagnetic spectrum are identified by different names. Complete electromagnetic spectrum is shown in Fig. 3.17.
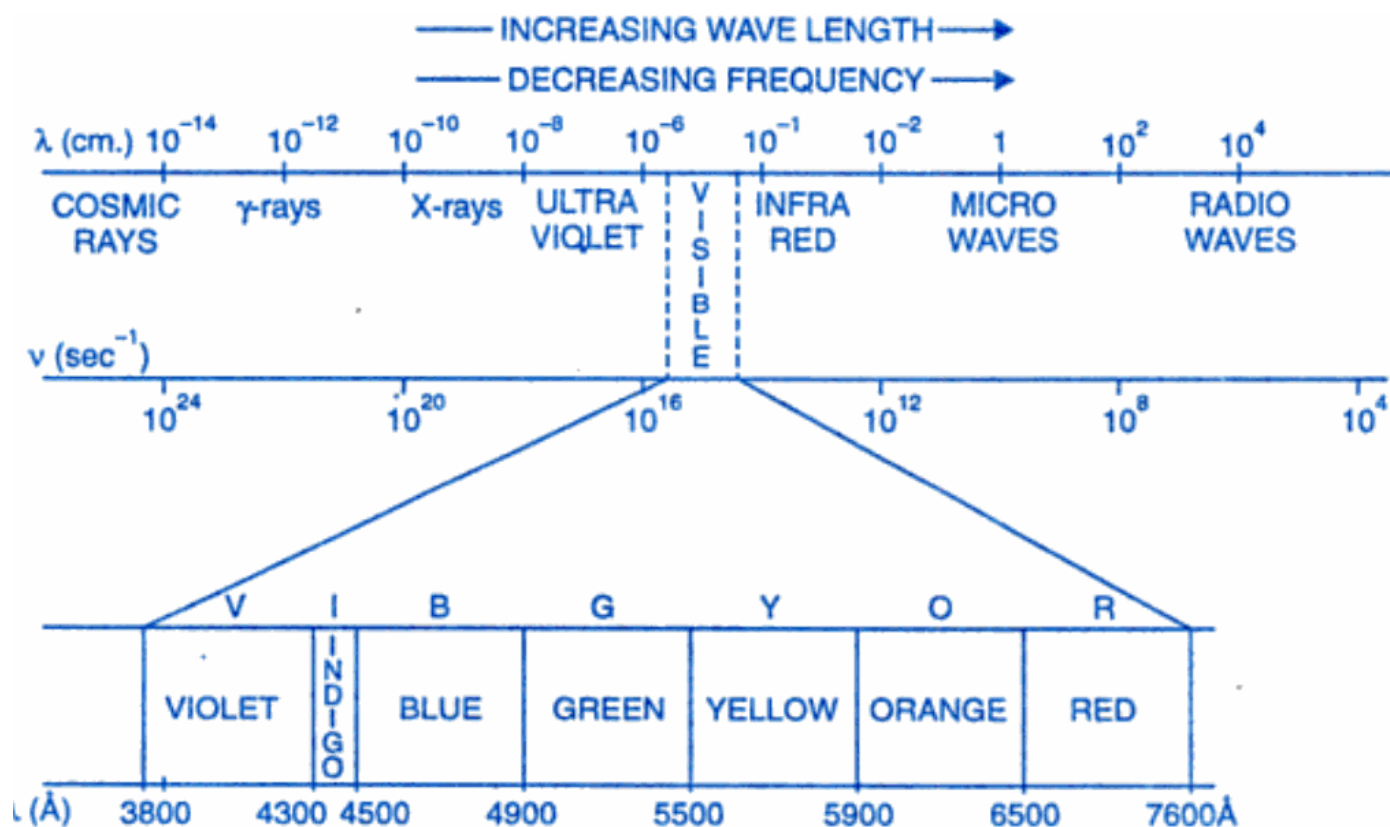
The various types of electromagnetic radiations have different energies and are being used for different purposes as listed below in Table 3.3.

Table 3.3. Some Applications of Electromagnetic Waves

Name (Hz)	Frequency	Wavelength (m)	Uses
Gamma rays	10^{20} to 10^{21}	10^{-12}	Cancer treatment
X rays	10^{17} to 10^{19}	10^{-10}	Medical "pictures", materials testing
Ultraviolet	10^{15} to 10^{16}	10^{-7}	Germicidal lamps
Visible	10^{13} to 10^{14}	10^{-6}	Illumination
Infrared	10^{12} to 10^{13}	10^{-4}	Heating
Microwave	10^{9} to 10^{11}	10^{-2}	Cooking, radar
Radio frequency	10^{5} to 10^{8}	10^{2}	Signal transmission

SOLVED PROBLEMS BASED ON RELATIONS $c = \nu\lambda$ AND $\nu = c\bar{\nu}$

Example 3.3. *Calculate frequency and wave number of a radiation having wavelength 600 nm.*

Solution. Wavelength of the radiation $\lambda = 600$ nm

$$= 600 \times 10^{-9} \text{ m} = 6 \times 10^{-7} \text{ m}$$

Velocity of radiation, $c = 3 \times 10^8$ m/s

$$c = \nu\lambda$$

Frequency $\qquad \nu = \dfrac{c}{\lambda} = \dfrac{3 \times 10^8 \text{ ms}^{-1}}{6 \times 10^{-7} \text{ m}} = 5 \times 10^{14} \text{ s}^{-1}.$

Wave number $\qquad \bar{\nu} = \dfrac{1}{\lambda} = \dfrac{1}{6 \times 10^{-7} \text{ m}} = 1.67 \times 10^6 \text{ m}^{-1}.$

Example 3.4. *A visible radiation has frequency 6×10^{14} cycle/sec. Find out the wavelength of the radiation in nanometers.*

Solution. Frequency of the radiation $\nu = 6 \times 10^{14}$ cycle/sec

Velocity of the radiation $\qquad c = 3 \times 10^8$ m/s

$$c = \nu\lambda$$

$\therefore \qquad \lambda = \dfrac{c}{\nu} = \dfrac{3 \times 10^8 \text{ ms}^{-1}}{6 \times 10^{14} \text{ s}^{-1}} = 5 \times 10^{-7} \text{ m} = 5 \times 10^{-7} \times 10^9 = 500 \text{ nm.}$

Example 3.5. *The wave number of a beam of light is 400 cm^{-1}. What is the wavelength of the light in nanometers ? Also find out frequency of the light.*

Solution. *Calculation of wavelength*

$$\bar{\nu} = 400 \text{ cm}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

or $\qquad \lambda = \dfrac{1}{\bar{\nu}} = \dfrac{1}{400} \text{ cm} = 2.5 \times 10^{-3} \text{ cm} = 2.5 \times 10^{-3} \times 10^7 \text{ nm} = 2.5 \times 10^4 \text{ nm.}$

Calculation of Frequency

$$c = \nu\lambda$$

$$\nu = \frac{c}{\lambda} = c\bar{\nu} = 3 \times 10^{10} \text{ cm s}^{-1} \times 400 \text{ cm} = 1.2 \times 10^{13} \text{ s}^{-1}.$$

Example 3.7. *Calculate the wavelength, frequency and wave number of a light whose period is 2.0×10^{-10} s.*

Solution. Frequency (v) of wave is inverse of period

$$\therefore \quad v = \frac{1}{2.0 \times 10^{-10} \text{ s}} = 5 \times 10^9 \text{ s}^{-1}$$

$$c = v\lambda$$

$$\therefore \quad \lambda = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{5 \times 10^9 \text{ s}^{-1}} = 6 \times 10^{-2} \text{ m}$$

Wave number $\quad \bar{v} = \frac{1}{\lambda} = \frac{1}{6 \times 10^{-2} \text{ m}} = 16.66 \text{ m}^{-1}.$

Example 3.6. *A radiostation is broadcasting programmes at 100 MHz frequency. If the distance between the radiostation and the receiver set is 300 km, how long would it take the signal to reach the set from the radiostation ? Also calculate wavelength and wavenumber of these radiowaves.*

Solution. All electromagnetic waves travel in vacuum or in air with the same speed of 3×10^8 m s^{-1}.

$$\text{Time taken} = \frac{\text{Distance}}{\text{Speed}} = \frac{300 \times 1000 \text{ m}}{3 \times 10^8 \text{ ms}^{-1}} = 1 \times 10^{-3} \text{ s.}$$

Calculation of wavelength (λ)

$$c = v\lambda$$

$$\lambda = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{100 \times 10^6 \text{ s}^{-1}} = 3 \text{ m.}$$

Calculation of wave number ($\bar{v}$)

$$\bar{v} = \frac{1}{\lambda} = \frac{1}{3m} = 0.33 \text{ m}^{-1}.$$

Microwave Spectroscopy

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).

The microwave region. A molecule such as hydrogen chloride, HCl, in which one atom (the hydrogen) carries a permanent net positive charge and the other a net negative charge, is said to have a permanent electric dipole moment. H_2 or Cl_2, on the other hand, in which there is no such charge separation, have a zero dipole. If we consider the rotation of HCl (Fig. 1.5, where we notice that if only a pure rotation takes place, the centre of gravity of the molecule must not move), we see that the plus and minus charges change places periodically, and the component dipole moment in a given direction (say upwards in the plane of the paper) fluctuates regularly. This fluctuation is plotted in the lower half of Fig. 1.5, and it is seen to be exactly similar in form to the fluctuating electric field of radiation (cf. Fig. 1.2). Thus interaction can occur, energy can be absorbed or emitted, and the rotation gives rise to a spectrum. All molecules having a permanent moment are said to be 'microwave active'. If there is no dipole, as in H_2 or Cl_2, no interaction can take place and the molecule is 'microwave inactive'. This imposes a limitation on the applicability of microwave spectro--scopy.
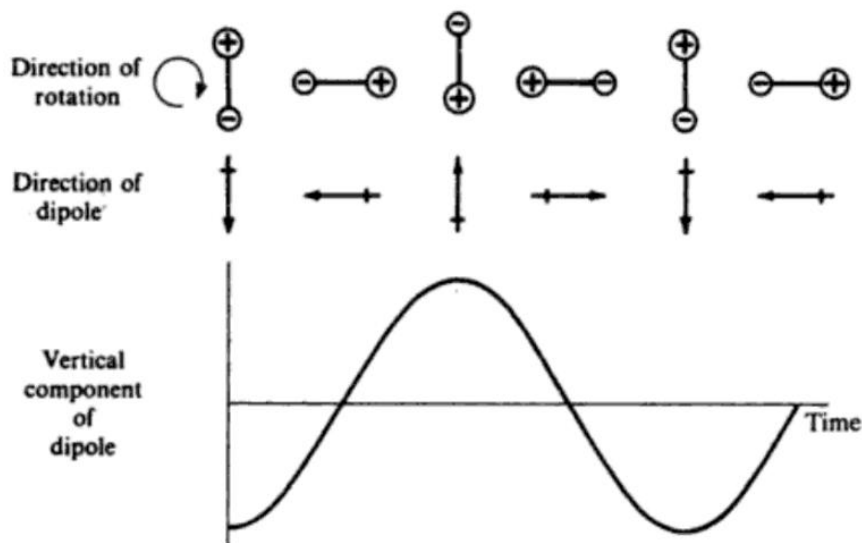

Figure 1.5 The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction.

THE ROTATION OF MOLECULES

The rotation of a three-dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity—the principal axes of rotation. Thus a body has three principal *moments of inertia*, one about each axis, usually designated I_A, I_B, and I_C.

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

$$H—Cl$$

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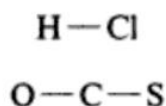
The three directions of rotation may be taken as (*a*) about the bond axis, (*b*) end-over-end rotation in the plane of the paper, and (*c*) end-over-end rotation at right angles to the plane. It is self-evident that the moments of (*b*) and (*c*) are the same (that is $I_B = I_C$) while that of (*a*)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

Thus for linear molecules we have:

$$I_B = I_C \qquad I_A = 0 \tag{2.1}$$

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

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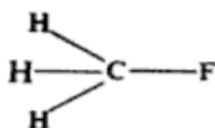
As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper are still identical and we have $I_B = I_C$. The moment of inertia about the C—F bond axis (chosen as the main rotational axis since the centre of gravity lies along it) is now not negligible, however,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

$$\text{Symmetric tops: } I_B = I_C \neq I_A \qquad I_A \neq 0 \tag{2.2}$$

There are two subdivisions of this class which we may mention: if, as in methyl fluoride above, $I_B = I_C > I_A$, then the molecule is called a *prolate* symmetric top; whereas if $I_B = I_C < I_A$, it is referred to as *oblate*.

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

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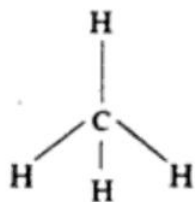
$$\text{Spherical tops: } I_A = I_B = I_C \qquad (2.3)$$

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

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

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

Simple examples are water H_2O and vinyl chloride $CH_2{=}CHCl$.
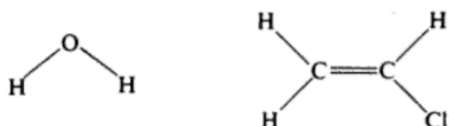
2.3 DIATOMIC MOLECULES

2.3.1 The Rigid Diatomic Molecule

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

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

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

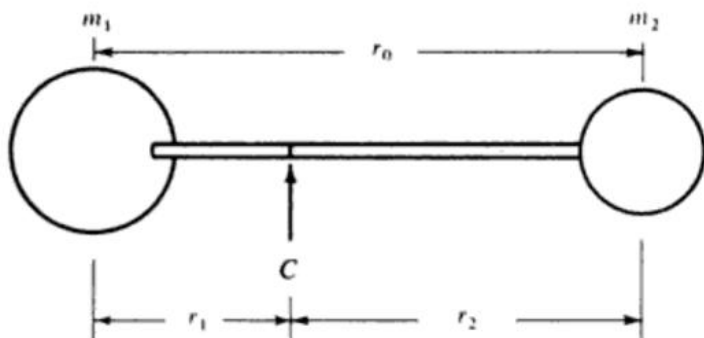$$m_1 r_1 = m_2 r_2 \qquad (2.6)$$

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

The moment of inertia about C is defined by:

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

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

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

Therefore,

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

Replacing (2.8) in (2.7):

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \tag{2.9}$$

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

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

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

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.

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Equation (2.10) expressed the allowed energies in joules; we, however, are interested in differences between these energies, or, more particularly, in the corresponding frequency, $v = \Delta E/h$ Hz, or wavenumber, $\bar{v} = \Delta E/hc$ 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:

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

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:

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

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

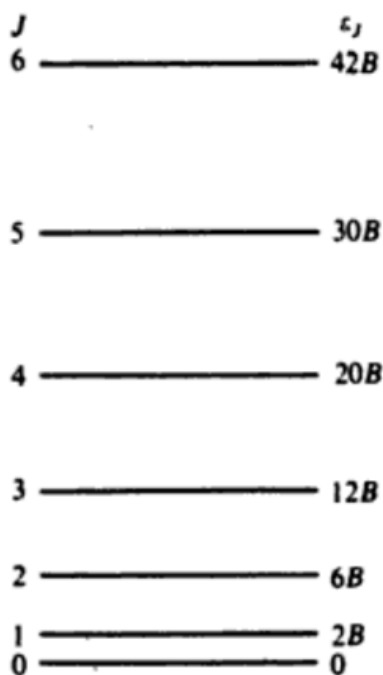$$B = \frac{h}{8\pi^2 I_{BC}} \quad \text{cm}^{-1} \tag{2.13}$$

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

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

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

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

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

or

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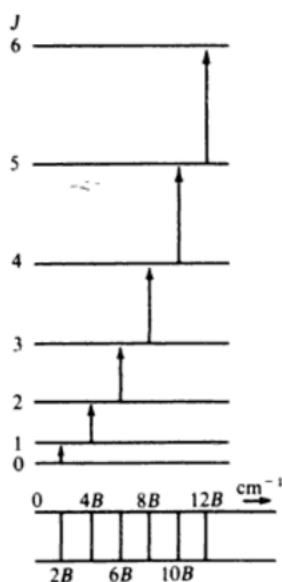

Figure 2.3 Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

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

Selection rule:

In deriving this pattern we have made the assumption that a transition can occur from a particular level only to its immediate neighbour, either above or below: we have not, for instance, considered the sequence of transitions $J = 0 \rightarrow J = 2 \rightarrow J = 4$ ... 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:

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

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 $3.842\,35\,cm^{-1}$, while that of $^{13}C^{16}O$ was at $3.673\,37\,cm^{-1}$. The values of B determined from these figures are:

$$B = 1.921\,18\,\text{cm}^{-1} \quad \text{and} \quad B' = 1.836\,69\,\text{cm}^{-1}$$

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

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I'c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$
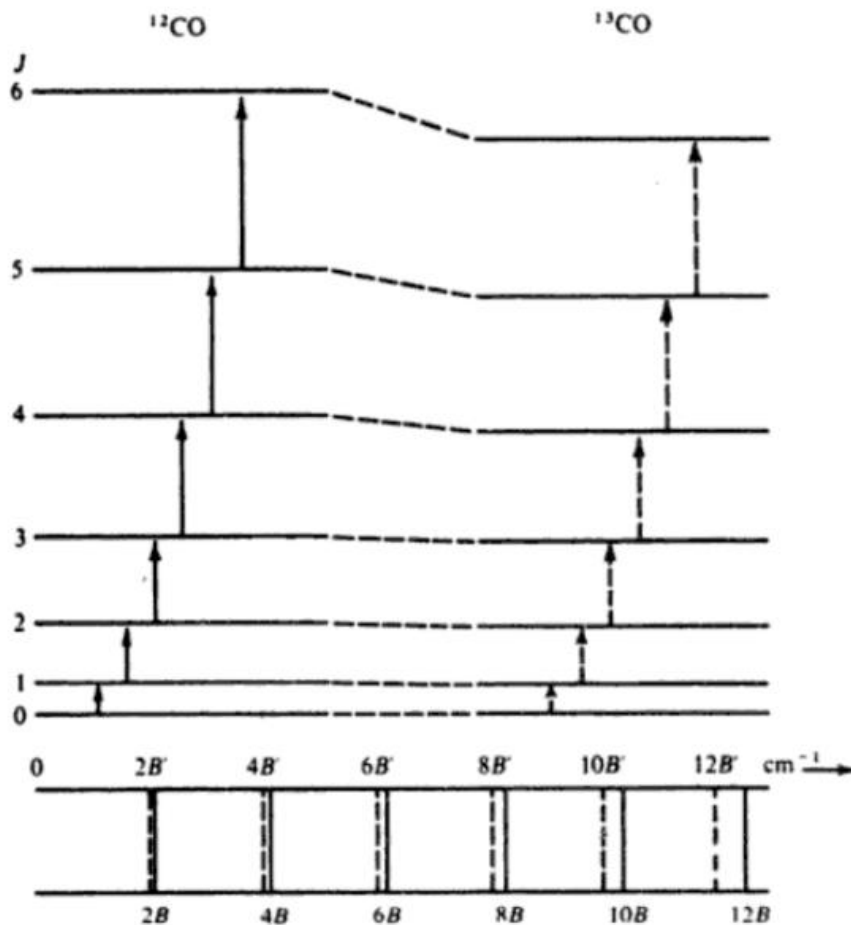
where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00, we have:

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

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