

---

## UNIT 3 ROTATIONAL SPECTRA

---

### Structure

- 3.1 Introduction
  - Objectives
- 3.2 Molecular Motion and Energy
- 3.3 Rotational Spectrum of a Rigid Diatomic Molecule
- 3.4 Applications of Study of Rotational Spectra
- 3.5 Non-Rigid Rotors
- 3.6 Rotational Spectra of Polyatomic Molecules
- 3.7 Population of Rotational Energy Levels and the Intensities of Spectral Lines
- 3.8 Summary
- 3.9 Terminal Questions
- 3.10 Answers

---

### 3.1 INTRODUCTION

---

From this unit onwards we shall study the interaction of electromagnetic radiation with an assembly of molecules rather than atoms, as has been done in the first unit of this Block. This interaction will result in the so called molecular spectra of compounds. Just like we extracted information about the structure of atoms from the atomic spectra, we shall try to find out what information can be obtained from the molecular spectrum regarding the structure and the behaviour of a molecule.

It will be seen that absorption or emission of electromagnetic radiation in different regions, corresponding to different amounts of energy, would cause various types of changes in the molecule. Thus, the spectra in each region would give a definite and specific piece of information about the molecule. For instance, when the molecule is subjected to radiations in the microwave region, we get information about the rotational properties of the molecule which in turn gives the values of molecular parameters like bond length.

On the other hand, molecular spectrum in the infrared region is related to the vibrational properties of the molecule. About vibrational spectra, you will study in Units 4 and 5 of Block 2. Since each region of spectrum requires a separate source of characteristic radiation, sample preparation and recording technique, you will study about them separately in Unit 9 of Block 3.

In this unit, we will start our discussion with the concept of motion leading to the idea of moment of inertia associated with a rotating body. On the basis of the moment of inertia, molecules will be classified as linear, symmetric top, asymmetric top and spherical top molecules. We will then explain the rotational spectra of rigid linear molecules in detail. We will also see what happens when a molecule is not rigid? We will explain briefly the rotational spectra of simple polyatomic molecules and intensity of spectral lines.

### Objectives

After studying this unit, you should be able to:

- define the moment of inertia,
- discuss the rotational spectra of rigid linear diatomic and triatomic molecules,
- give applications of study of rotational spectra,

- explain the effect of isotopic substitution and non-rigidity on the rotational spectra of a molecule,
- classify various molecules according to their values of moment of inertia,
- discuss the rotational spectra of simple polyatomic molecules, and
- relate the intensity of spectral lines with the population of a rotational level.

### 3.2 MOLECULAR MOTION AND ENERGY

The understanding of molecular motions help in the interpretation of molecular spectra. When we talk about molecular motions, there are various possibilities. When we want to specify the position of a body in space, we have to specify the **number of degrees of freedom** it possesses. The number of degrees of freedom is related to the number of independent coordinates required to specify the position of the body in space. For example, for a single particle we need three Cartesian coordinates  $x, y$  and  $z$  to specify its position. Hence, it is said to have three degrees of freedom. Thus, for a molecule having  $N$  atoms, the total number of degrees of freedom is  $3N$ .

For a single particle, only one type of motion is possible which is called **translational motion**. Hence, we can say that a single particle possesses three degrees of translational freedom.

But what about translational motion of molecules? A molecule contains two or more than two atoms. Since the atoms in a molecule are joined together, the molecule as a whole will show translatory motion and the atoms will not move independently. The translational motion of a molecule can be described in terms of the **centre of mass**. The centre of mass is the point where the whole mass can be considered to be concentrated. Thus, we can specify three coordinates for the centre of mass and say that it has three degrees of freedom, similar to a single particle. The translational motion of centre of mass of a molecule (non-linear) is shown in Fig. 3.1.

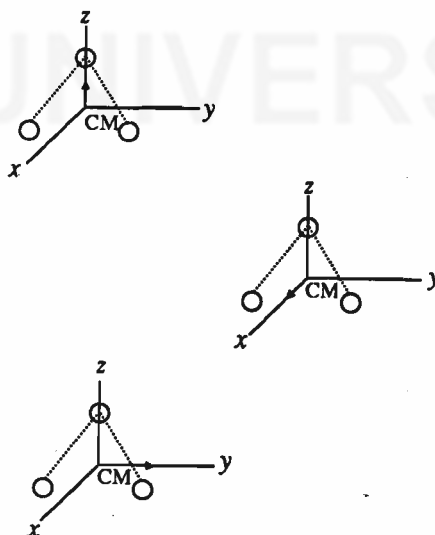


Fig. 3.1: Translational motion of centre of mass of a nonlinear molecule.

A molecule can store energy by way of molecular motions.

For a polyatomic molecule having  $N$  atoms,  $(3N - 3)$  degrees of freedom still remain. These can be attributed to internal motions such as rotation and vibrations.

Let us now know more about rotational motion. The simplest case of rotation is that of a particle about a fixed point, as shown in Fig. 3.2.

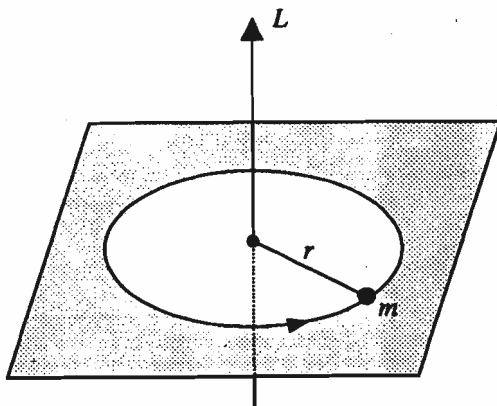


Fig. 3.2: Rotation of a particle about a fixed point.

The rotational kinetic energy of this particle having mass  $m$  and velocity  $v$  can be expressed as

$$E_k = \frac{1}{2} mv^2 = \frac{p^2}{2m} \text{ where } p = mv \text{ is the momentum of the particle} \quad \dots (3.1)$$

The velocity of this particle could be expressed as the distance travelled by it divided by the time taken. For one revolution, we can say that

$$v = \frac{\text{distance}}{\text{time}} = \frac{2\pi r}{t} \quad \dots (3.2)$$

where  $t$  is the time taken for one revolution and is also known as *period*.

$$\text{Also } t = \frac{1}{\text{frequency } (f)} \quad \dots (3.3)$$

Substituting the value of  $t$  from Eq. 3.3 into Eq. 3.2, we get

$$v = 2\pi r f \quad \dots (3.4)$$

Replacing  $v$  in Eq. 3.1 by its value from Eq. 3.4, we can write

$$E_k = \frac{1}{2} m (2\pi r f)^2 \quad \dots (3.5)$$

The terms in the above equation can be rearranged as given below:

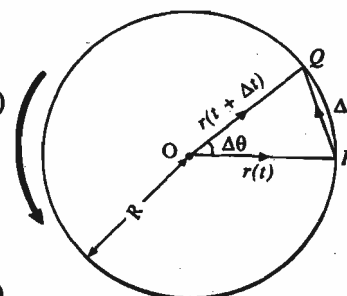
$$E_k = \frac{1}{2} m r^2 (2\pi f)^2 \quad \dots (3.6)$$

The quantity  $m r^2$  of the above equation is called the **moment of inertia** and is represented by  $I$ . The term  $2\pi f$  is known as the **angular velocity** and is denoted by  $\omega$ .

Thus, we can rewrite Eq. 3.6 as

$$E_k = 1/2 I \omega^2 \quad \dots (3.7)$$

On comparing Eqs. 3.1 and 3.7, we can say that in the equation for rotational motion (i.e., Eq. 3.7), moment of inertia is the equivalent of mass as used in Eq. 3.1. Also in Eq. 3.7, angular velocity ( $\omega$ ) is used in place of linear velocity ( $v$ ) used in Eq. 3.1.



For circular motion if a particle P traverses an angle  $\Delta\theta$  in time  $\Delta t$ , the arc PQ represented as  $\Delta s$  is given by the following relation:

$$r \cdot \Delta\theta = \Delta s$$

Dividing by  $\Delta t$  on both the sides, we get

$$r \cdot \frac{\Delta\theta}{\Delta t} = \frac{\Delta s}{\Delta t}$$

When  $\Delta t \rightarrow 0$ , we can write

$$r \cdot \lim_{\Delta t \rightarrow 0} \frac{\Delta\theta}{\Delta t} = \lim_{\Delta t \rightarrow 0} \frac{\Delta s}{\Delta t}$$

$$r \cdot \frac{d\theta}{dt} = \frac{ds}{dt}$$

or  $r\omega = v$  where  $\omega$  is the angular velocity and  $v$  is the linear velocity. The angular velocity,  $\omega$  is defined as the number of radians of angle swept in unit time.

It is given by  $\frac{d\theta}{dt}$ , where  $d\theta$  is the angle traversed in  $dt$  time. It is expressed in terms of radians  $\text{sec}^{-1}$ .

### 3.3 ROTATIONAL SPECTRUM OF A RIGID DIATOMIC MOLECULE

Let us now apply the above ideas to the rotation of a diatomic molecule. We will first assume that this diatomic molecule is a **rigid body**. This means that the distance between the atoms, i.e. the bond length *does not* change during the rotation. In other

words, vibrational movement is not taking place during rotation. We are also assuming that the centre of mass of the molecule is fixed. Hence, there is no translational motion of the molecule. No real molecule can be called an ideally rigid body. But many molecules may be considered as rigid because their vibrational motion is small. Let us now focus our attention on Fig. 3.3 which depicts the rotation of a rigid diatomic molecule.

Note that the axis about which the rotation takes place, is perpendicular to the axis of symmetry of the molecule.

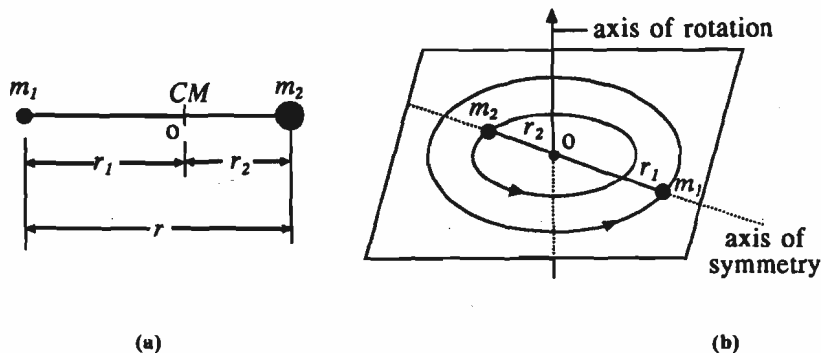


Fig. 3.3:(a) A rigid diatomic molecule.  
(b) Rotation of a rigid diatomic molecule.

When such a molecule rotates, it rotates about an axis passing through its centre of mass (CM). The centre of mass is shown by the point O. For a system, the centre of mass is such a point for which the following condition is satisfied:

$$m_1 r_1 = m_2 r_2 \quad \dots (3.8)$$

We can rearrange Eq. 3.8 as follows

$$\frac{r_1}{r_2} = \frac{m_2}{m_1} \quad \dots (3.9)$$

Using the characteristics of proportions, Eq.3.9 can be written as

$$\frac{r_1}{(r_1 + r_2)} = \frac{m_2}{(m_1 + m_2)} \quad \dots (3.10)$$

or 
$$r_1 = \frac{m_2 (r_1 + r_2)}{(m_1 + m_2)} \quad \dots (3.11)$$

We also know that the bond length or the distance between two atoms,  $r$ , is equal to the sum of  $r_1$  and  $r_2$ . Thus, we can write

$$r = r_1 + r_2 \quad \dots (3.12)$$

Substituting  $r = r_1 + r_2$  from Eq. 3.12 into Eq.3.11, we get

$$r_1 = \frac{m_2}{(m_1 + m_2)} \cdot r \quad \dots (3.13)$$

On similar lines, we can get

$$r_2 = \frac{m_1}{(m_1 + m_2)} \cdot r \quad \dots (3.14)$$

by starting from Eq.3.8 and rearranging it as

$$\frac{r_2}{r_1} = \frac{m_1}{m_2} \quad \dots (3.15)$$

Why do not you try Terminal Question 1 and check it.

Let us now write the energy of this system using Eq.3.7.

$$E_k = 1/2 I \omega^2 \quad \dots (3.7)$$

You can imagine this molecule as a two particle system (Compare Figs. 3.2 and 3.3). Here, you can see that two particles (atoms having masses  $m_1$  and  $m_2$ ) are rotating about the point o. Thus, the rotational kinetic energy,  $E_k$  of this system will be the sum of the  $E_k$  values of both the particles. So, we can write

$$E_k = \frac{1}{2} m_1 r_1^2 \omega_1^2 + \frac{1}{2} m_2 r_2^2 \omega_2^2 \quad \dots (3.16)$$

The angular velocities of the two masses  $m_1$  and  $m_2$  will be equal because of the rigidity of the molecule. Hence,

$$\omega_1 = \omega_2 \quad \dots (3.17)$$

Let this angular velocity be  $\omega$ . So, we can rewrite Eq.3.16 as

$$\begin{aligned} E_k &= \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2 \\ &= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2 = \frac{1}{2} I \omega^2 \end{aligned} \quad \dots (3.18)$$

where  $I$  is the moment of inertia of the diatomic molecule.

The terms  $r_1$  and  $r_2$  can be eliminated from Eq. 3.18 by using the values of  $r_1$  and  $r_2$  from Eqs. 3.13 and 3.14, respectively, as given below:

$$\begin{aligned} E_k &= \frac{1}{2} \left[ m_1 \left( \frac{m_2 r}{m_1 + m_2} \right)^2 + m_2 \left( \frac{m_1 r}{m_1 + m_2} \right)^2 \right] \omega^2 \\ &= \frac{1}{2} \left[ \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2} \right] \omega^2 \\ &= \frac{1}{2} \frac{m_1 m_2 r^2}{(m_1 + m_2)^2} [m_2 + m_1] \omega^2 \\ &= \frac{1}{2} \frac{m_1 m_2 r^2 \omega^2}{(m_1 + m_2)} \end{aligned} \quad \dots (3.19)$$

Remember that we have earlier defined  $I$  as  $mr^2$ .

Comparing Eq. 3.19 with Eq. 3.18, we can say that

$$E_k = \frac{1}{2} \frac{m_1 m_2 r^2 \omega^2}{(m_1 + m_2)} = \frac{1}{2} I \omega^2 \quad \dots (3.20)$$

$$\text{Thus, } I = \frac{m_1 m_2}{(m_1 + m_2)} r^2 \quad \dots (3.21)$$

Here,  $\frac{m_1 m_2}{(m_1 + m_2)}$  can be denoted by  $\mu$  which is known as the reduced mass.

Thus, we can write

$$I = \mu r^2 \quad \dots (3.22)$$

Note that the moment of inertia for the single particle was expressed as  $I = mr^2$  and for a diatomic molecule (two particle system) it is expressed as  $I = m_1 r_1^2 + m_2 r_2^2$ . We can extend this argument and generalise it for polyatomic molecules as follows. For a polyatomic molecule, the moment of inertia about a particular axis is given by the sum of moments due to various nuclei about that axis i.e.,  $I = \sum_i m_i r_i^2$  where  $r_i$  is the perpendicular distance of the nucleus of mass  $m_i$  from the axis.

Thus, the idea of using reduced mass is to mathematically simplify the rotation of a two-particle system into that of a one-particle problem. In other words, we have replaced the two masses  $m_1$  and  $m_2$  by a single mass  $\mu$ . You must have also realised that similarly we have also replaced the two distances  $r_1$  and  $r_2$  by  $r$ .

At this stage, we have come to a point where we can deal with the rotation of a diatomic molecule having masses  $m_1$  and  $m_2$  in terms of the rotation of a single particle of mass  $\mu$  having a distance  $r$  from the origin.

Let us now reconsider Eq.3.18 which says

$$E_k = \frac{1}{2} I \omega^2$$

This equation is alright as per the classical mechanics approach. But when we apply quantum mechanical approach to the molecule, certain restrictions appear on the rotational energy.

Eq. 3.18 can be expressed in terms of angular momentum  $L$  which can be defined as

$$L = I \omega \quad \dots (3.23)$$

Substituting  $L$  for  $I \omega$  in Eq.3.18, we get

$$E_k = \frac{1}{2} \frac{L^2}{I} \quad \dots (3.24)$$

Since the angular momentum is quantised, it can be expressed in terms of the rotational quantum number,  $J$ , as given below:

$$L = \sqrt{J(J+1)} \cdot \frac{h}{2\pi} = \sqrt{J(J+1)} \hbar \quad \dots (3.25)$$

where  $J$  can take values 0, 1, 2, 3...

Substituting the above value of  $L$  in Eq.3.24, we get

$$E_k = \frac{1}{2} \cdot \frac{J(J+1)\hbar^2}{I} = \frac{J(J+1)\hbar^2}{2I} \quad \dots (3.26)$$

The above equation gives the rotational energy of a molecule. The energy can also be expressed in terms of wave number,  $\bar{\nu}$ . The energies as expressed in terms of  $\bar{\nu}$  are referred to as term values and are denoted by  $F(J)$ . The SI unit of a term value is  $m^{-1}$  but they are usually expressed in  $cm^{-1}$ .

Thus, 
$$\bar{\nu} = F(J) = \frac{E_k}{hc} = \frac{J(J+1)\hbar^2}{8\pi^2 I \cdot hc} = \frac{J(J+1)h}{8\pi^2 Ic} \quad \dots (3.27)$$

The term  $\frac{h}{8\pi^2 Ic}$  can be represented by a constant  $B$  which is known as rotational constant. Hence, Eq.3.27 can be written as

$$\bar{\nu} = BJ(J+1)$$

Thus, when  $J = 1, \bar{\nu} = 2B \text{ cm}^{-1}$

$$J = 2, \bar{\nu} = 6B \text{ cm}^{-1}$$

$$J = 3, \bar{\nu} = 12B \text{ cm}^{-1}$$

and so on.

Do not confuse the  $L$  used in Eq. 3.24 with that used in unit 1. Here,  $L$  represents the angular momentum of the molecule undergoing end to end rotation about the centre of mass whereas in unit 1, it was used to denote the angular momentum of the electron in an atom.

The restriction on the value of  $J$  comes from quantum mechanics.

We have used  $\hbar = \frac{h}{2\pi}$  in Eq.3.27.

The corresponding energy levels are depicted in Fig. 3.4

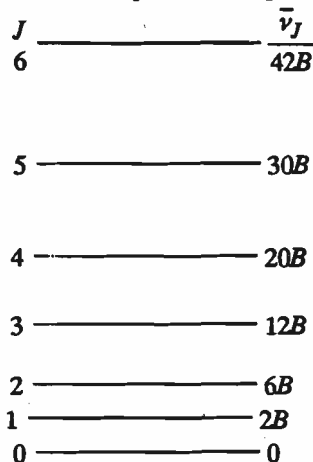


Fig. 3.4: Rotational levels of a rigid diatomic molecule.

But we are more interested in knowing the difference between these energy levels so that we can know the radiation of what frequency or wavenumber is absorbed or emitted when a molecule changes from one rotational level to the other. Thus, we can write the difference between two rotational levels as follows.

$$\begin{aligned} \Delta E &= E_{k_{J'}} - E_{k_J} && \text{where } J' \text{ is the final rotational level and } J \\ & && \text{is the initial rotational level.} \\ &= \frac{J'(J'+1)h^2}{2I} - \frac{J(J+1)h^2}{2I} \\ &= \frac{h^2}{2I} [J'(J'+1) - J(J+1)] && \dots (3.28) \end{aligned}$$

The  $\bar{\nu}$  for the above energy change can be given as follows:

$$\nu_{J'-J} = B [J'(J'+1) - J(J+1)] \quad \dots (3.29)$$

From Fig. 3.4, we can see that the *energy difference* between the successive energy levels is  $2B, 4B, 6B, 8B, 10B$  and so on. The spectral lines originating from these transitions will appear as shown in Fig. 3.5.

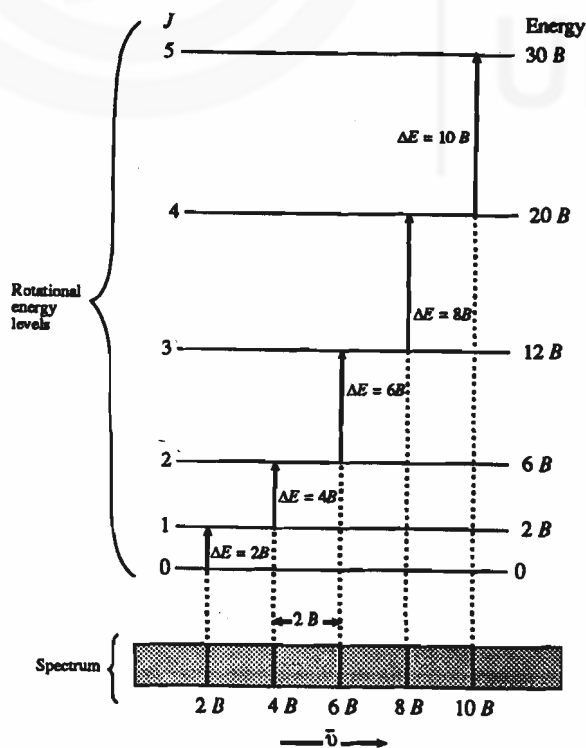


Fig. 3.5: The transitions between the various rotational levels and spectral lines arising from these transitions.

If you carefully see Fig. 3.5, we will notice that these spectral lines are equally spaced and there is a constant difference of  $2B$  between the successive lines.

For a molecule to show rotational spectrum, the following requirements should be met.

- i) The first condition which a molecule should satisfy for showing rotational spectra is that it should possess a permanent dipole moment. This is because a rotating dipole produces an oscillating electric field which interacts with the oscillating field of the radiation.
- ii) There is a further restriction on rotational transitions for molecules having permanent dipole moment. The selection rule for linear molecule is  $\Delta J = \pm 1$ . So transitions could be from rotational levels having  $J = 0 \rightarrow J = 1$ ;  $J = 1 \rightarrow J = 2$ ;  $J = 2 \rightarrow J = 3$ ;  $J = 3 \rightarrow J = 4$  and so on and in the reverse order also.

Another factor which governs the intensity of rotational lines is the population of the initial or ground state. You will study about this in Sec. 3.7.

### The Condition for the Occurrence of Pure Rotation Spectra

In the Appendix of Unit 2, we have mentioned the applications of character tables. One of the applications lies in determining whether a spectral transition could occur from an energy state  $a$  to the energy state  $b$ . For such a transition to occur, at least one of the components of the transition dipole moment,  $\mu$ , which is equal to  $\int \psi_b \mathbf{M} \psi_a$ , must have a non-zero value. You may be aware that  $\psi_b$  and  $\psi_a$  refer to the wave functions of the energy states,  $b$  and  $a$ , whereas  $\mathbf{M}$  is the dipole moment operator. In case of pure rotation spectra, it means that at least one of the three components of transition dipole moment,  $\mu_x, \mu_y$  or  $\mu_z$  in  $x, y$  and  $z$  directions must have a non zero value in order that the molecule absorbs in the microwave region.  $\mu_x, \mu_y$  and  $\mu_z$  are related to  $M_x, M_y$  and  $M_z$  which are the components of the dipole moment operator  $\mathbf{M}$  as given below:

$$\mu_x = \int \psi_b M_x \psi_a d\tau \quad \dots (A.1)$$

$$\mu_y = \int \psi_b M_y \psi_a d\tau \quad \dots (A.2)$$

$$\mu_z = \int \psi_b M_z \psi_a d\tau \quad \dots (A.3)$$

Note that  $\mu$  (bold type) stands for transition dipole moment whereas  $\mu$  (Roman type) refers to the permanent dipole moment. Also  $\mu_x, \mu_y$  and  $\mu_z$  are the components of transition dipole moment in  $x, y$  and  $z$  directions.

Also  $M_x, M_y$  and  $M_z$  are related to the permanent dipole moment,  $\mu$ , of a rotor and the polar coordinates,  $\theta$  and  $\phi$ , as per Eqs. A.4 to A.6. For understanding the resolution of the dipole moment operator  $\mathbf{M}$  in terms of  $M_x, M_y$  and  $M_z$  as per Eqs. A.4 to A.6 and Fig. A.1, you are advised to go through Eq. 2.54 of Unit 2 of CHE-01 ('Atoms and Molecules' Course) where the relationship between the spherical polar coordinates and the cartesian coordinates is given.

$$M_x = \mu \sin \theta \cos \phi \quad \dots (A.4)$$

$$M_y = \mu \sin \theta \sin \phi \quad \dots (A.5)$$

$$M_z = \mu \cos \theta \quad \dots (A.6)$$

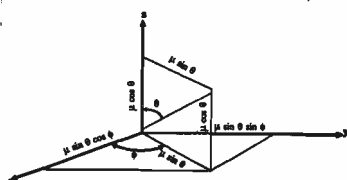


Fig. A.1: Transformation of cartesian to spherical polar coordinates.

If a molecule lacks permanent dipole moment (i.e.,  $\mu = 0$ ), then  $M_x, M_y$  and  $M_z$  and hence,  $\mu_x, \mu_y$  and  $\mu_z$  are zero as per Eqs. A.1 to A.6. For a molecule having zero dipole moment, all the three components of transition dipole moment are thus equal to zero. As a result of this, a molecule with zero dipole moment cannot give rise to pure rotation spectra. In other words, for a molecule to absorb in the microwave region, it must have permanent dipole moment. In sub-Sec. 2.10, of the last unit, we have mentioned that only molecules belonging to the groups  $C_n$  ( $C_1$  and  $C_2$ ) and  $C_{nv}$  ( $C_{2v}, C_{3v}, \dots, C_{\infty v}$ ) and  $C_s$  may have permanent dipole moment. Now you can understand as to why  $\text{HBr}$ ,  $\text{CO}$  and  $\text{OCS}$  (all of  $C_{\infty v}$  point group) can exhibit pure rotation spectra but  $\text{H}_2$  and  $\text{CO}_2$  of  $D_{\infty h}$  point group) cannot.



## SAQ 1

What is the effect of decrease in the moment of inertia on the energy of the rotational level?

## SAQ 2

What is the necessary condition for a molecule to show rotational spectrum?

## 3.4 APPLICATIONS OF STUDY OF ROTATIONAL SPECTRA

### (i) Determination of moment of inertia and bond length

From the last section, you know about the relationship between the energy (or wavenumber) of radiation absorbed or emitted, required for the change of rotational level and the moment of inertia. You can now think of the reverse process of what we have learnt above. If we determine the frequency of radiation absorbed or emitted required for the change of a particular rotational level, we can relate it to the value of  $B$ , the rotational constant. Once  $B$  is determined, we can calculate the moment of

inertia using the expression  $B = \frac{h}{8\pi^2 Ic}$ . The value of moment of inertia so obtained

can be used to give the value of  $r$ , the bond length if we know the reduced mass of the system. One such example is illustrated below:

The transition from  $J = 0$  to  $J' = 1$  for HCl takes place at  $\bar{\nu} = 21.18 \text{ cm}^{-1}$ . What is the bond length of  $^1\text{H}^{35}\text{Cl}$ ?

Let us follow the steps we have listed above.

$$\bar{\nu}_{J=0 \rightarrow J'=1} = 21.18 \text{ cm}^{-1}$$

Thus,  $\bar{\nu} = 2B \text{ cm}^{-1}$  (from Eq. 3.29)

So, 
$$B = \frac{\bar{\nu}}{2} = \frac{21.18}{2} = 10.59 \text{ cm}^{-1}$$

$$= 10.59 \times 10^2 \text{ m}^{-1}$$

Also, 
$$I = \frac{h}{8\pi^2 Bc}$$

So, 
$$I = \frac{6.626 \times 10^{-34} \text{ Js}}{8 \times (3.14)^2 \times 10.59 \times 10^2 \text{ m}^{-1} \times 2.998 \times 10^8 \text{ m s}^{-1}}$$

$$= 0.2646 \times 10^{-46} \text{ kg m}^2$$

Now  $I = \mu r^2$

To know  $r$ , from the above equation, we have to first calculate  $\mu$  as shown below:

The value of rotational constant,  $B$  of some molecules as obtained from their rotational spectrum is given below:

Molecule	$B/\text{cm}^{-1}$
CO	1.93128
HF	20.90
HBr	8.4648
HCl	10.59
HI	6.426
KCl	0.1286
NaCl	0.2180
NO	1.70

$$\begin{aligned}\mu &= \frac{m_{\text{Cl}} \cdot m_{\text{H}}}{m_{\text{Cl}} + m_{\text{H}}} \\ &= \frac{(35.45)(1.008)}{(35.45 + 1.008)} \times \frac{10^{-3}}{6.022 \times 10^{23}} \\ &= 1.627 \times 10^{-27} \text{ kg}\end{aligned}$$

Thus,

$$\begin{aligned}r &= \frac{I}{\mu} \\ r &= \frac{0.2646 \times 10^{-46} \text{ kg m}^2}{1.627 \times 10^{-27} \text{ kg}} \\ r &= \sqrt{\frac{0.2646 \times 10^{-46} \text{ m}^2}{1.627 \times 10^{-27}}} \\ &= 1.275 \times 10^{-10} \text{ m} \\ r &= 127.5 \text{ pm}\end{aligned}$$

(ii) Another application of the study of rotational spectra is in the determination of the mass of a particular isotope or isotopic abundance of a particular isotope.

You know that isotopes differ from each other in atomic mass. If we consider a particular molecule and another substituted molecule having an isotope of a particular atom substituted, there will be a difference in the masses of these two molecules. For example, if we consider  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ , there is an increase in the mass of  $^{13}\text{C}^{16}\text{O}$  as compared to  $^{12}\text{C}^{16}\text{O}$ . Then, the reduced mass of the molecule having higher mass isotope, i.e.  $^{13}\text{C}^{16}\text{O}$  in this case, is more than the  $^{12}\text{C}^{16}\text{O}$ . This would lead to a higher value of  $I$  for  $^{13}\text{C}^{16}\text{O}$  which in turn indicates a lower value for rotational constant,  $B$  for this molecule. The experimental values of rotational constants of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  are as given below:

$$\text{Rotational constant for } ^{12}\text{C}^{16}\text{O} = B = 1.92118 \text{ cm}^{-1}$$

$$\text{Rotational constant for } ^{13}\text{C}^{16}\text{O} = B' = 1.83669 \text{ cm}^{-1}$$

If we carefully examine the expression  $B = \frac{h}{8\pi^2 Ic}$ , we conclude that the terms  $h, \pi, c$  are all constant and  $B$  is inversely proportional to  $I$ . Thus, we can write

$$\begin{aligned}\frac{B}{B'} &= \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I' c}{h} && \text{(here } I \text{ and } I' \text{ represent the moment of inertia} \\ & && \text{for } ^{12}\text{C}^{16}\text{O} \text{ and } ^{13}\text{C}^{16}\text{O}, \text{ respectively.)} \\ &= \frac{I'}{I}\end{aligned}$$

$$\text{And } I' = \mu' r^2 \text{ and } I = \mu r^2$$

$$\text{Thus, } \frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046 \quad \dots (3.30)$$

(the bond length  $r$  of the molecule does not change on isotopic substitution)

From the above equation, we know the ratio of  $\mu'$  to  $\mu$ . Thus, if we know  $\mu$ , we can calculate  $\mu'$ .

$$\text{Hence } \mu' = 1.046 \mu \quad \dots (3.31)$$

We know that atomic mass of  $^{16}\text{O} = 15.9994$  and that of  $^{12}\text{C} = 12.00$

$$\text{So, } \mu' = \frac{15.9994 m_{^{13}\text{C}}}{15.9994 + m_{^{13}\text{C}}} \quad \dots (3.32)$$

and

$$\mu = \frac{12 \times 15.9994}{12 + 15.9994} \quad \dots (3.33)$$

Expressing the Eq. 3.31 in terms of atomic masses as expressed in Eq. 3.32 and 3.33, we get

$$\frac{15.9994 m_{^{13}\text{C}}}{15.9994 + m_{^{13}\text{C}}} = 1.046 \times \frac{12 \times 15.9994}{12 + 15.9994}$$

On solving the above equation, we obtain the value of  $m_{^{13}\text{C}} = 13.0007$  which is the precise value of mass of  $^{13}\text{C}$  isotope and is in agreement with the value obtained by other methods. Before we close our discussion on the determination of atomic mass of an isotope, we would also like to focus your attention on the appearance of the rotational spectra after isotopic substitution. You have studied above in case of  $^{13}\text{C}^{16}\text{O}$  that substitution of a heavier isotope leads to a decrease in the value of rotational constant. Since the value of  $B$  is related to the spacing of spectral lines in the rotational spectrum, a lower value of  $B'$  indicates smaller separation between the rotational levels and also in spectral lines. This is shown in Fig. 3.6.

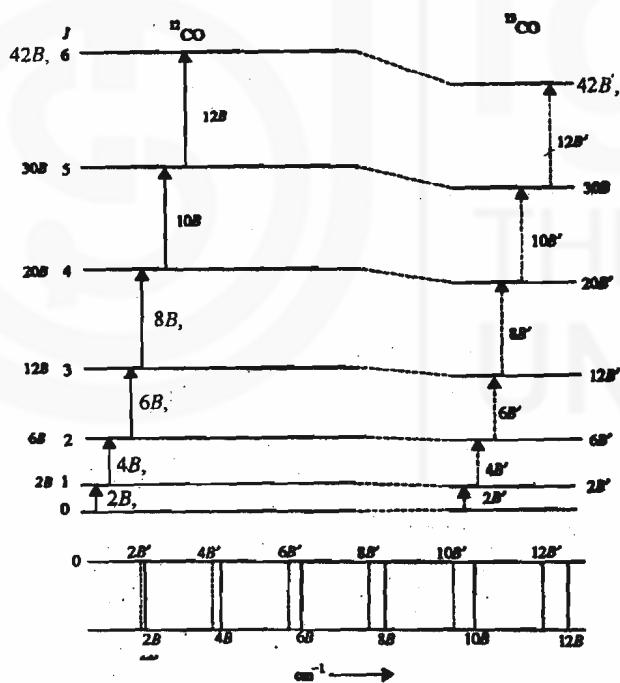


Fig. 3.6: Decrease in spacing between rotational levels and spectral lines due to isotopic substitution.

Till now we based our discussions on the rigid diatomic molecules. In the next section, you will study what happens when we are dealing with a non-rigid molecule. Before going to the next section, answer SAQ 3 given below to check your understanding about the above section.

### SAQ 3

From the rotational spectra of  $^{14}\text{NO}$  and  $^{15}\text{NO}$ , it was found that  $\frac{B}{B'} = 1.0361$  where  $B$  and  $B'$  are rotational constants for  $^{14}\text{NO}$  and  $^{15}\text{NO}$ , respectively. Calculate the atomic mass of  $^{15}\text{N}$  if the masses of  $^{14}\text{N}$  and  $\text{O}$  are 14.004 and 15.9994, respectively.

### 3.5 NON-RIGID ROTORS

The rigid rotors we considered before present an ideal case and actually when a molecule rotates, its atoms experience a centrifugal force. Since the bonds are elastic to some extent, when a non-rigid molecule rotates, the centrifugal force leads to the stretching of the bonds. This stretching leads to an increase in the bond length and hence an increase in the moment of inertia. As a result of this, there is a decrease in the separation between the rotational energy levels and also in the spectral lines. see Figs. 3.7 and 3.8.

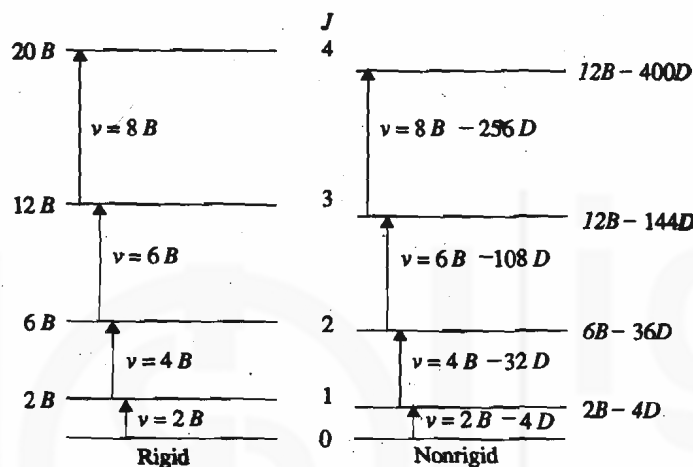


Fig. 3.7: Effect of centrifugal distortion on the energy levels of a diatomic rotor.

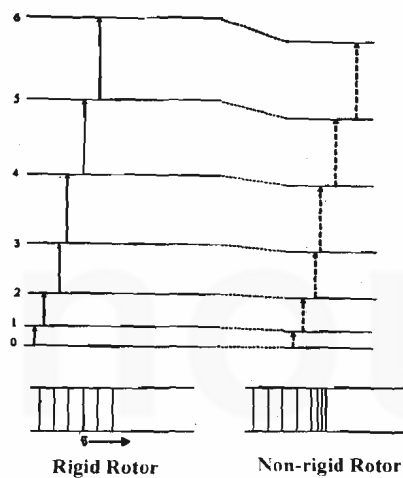


Fig. 3.8: Energy level diagram for the rigid and non-rigid rotors. The spectral lines arising from the transitions are indicated below the energy level diagrams.

This effect is taken care of if we write the  $\nu$  as given below:

$$\bar{\nu} = B J (J + 1) - D J^2 (J + 1)^2 \quad \dots (3.34)$$

where  $D$  is the centrifugal distortion constant and is given by the following equation.

$$D = \frac{4 B^3}{\omega^2} \quad \dots (3.35)$$

The value of  $D$  is obtained from the spectral results and is always very much less than  $B$ . The spectra of non-rigid molecules will show a decrease in the spacing between rotational levels and in spectral lines similar to the one shown in Fig. 3.6 but here the decrease will be comparatively much smaller.

In the next section, you will study about the rotational spectra of polyatomic molecules.

### 3.6 ROTATIONAL SPECTRA OF POLYATOMIC MOLECULES

Till now, we focussed our attention on the simple case of linear diatomic molecules. The rotation of a polyatomic molecule is quite complex as compared to the diatomic molecules considered above. The rotation of a polyatomic molecule could be simplified and understood in a better way if we consider components of the rotation about the three principal axes. Thus, a three dimensional molecule will have three moments of inertia about the three axes ( $x, y, z$ ). You may remember that in the previous case of a diatomic molecule, we considered the rotation about an axis perpendicular to the axis of symmetry of the molecule. But actually, the rotation of the diatomic molecule could be about all the three axes ( $x, y$  and  $z$ ) as shown below:

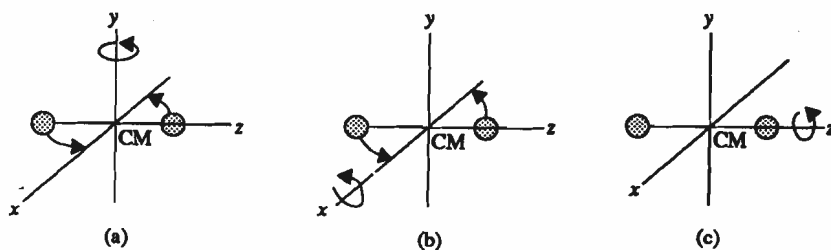


Fig. 3.9 : Rotation of a diatomic molecule about centre of mass:  
(a) about x axis (b) about y axis (c) about z axis.

Let the moments of inertia for the above rotations be represented by  $I_B$ ,  $I_C$  and  $I_A$ , respectively. Since the rotations as shown in part (a) and (b) are equivalent, we can say  $I_B = I_A$ . In part (c), the moment of inertia about the bond axis ( $y$ -axis) has a very small value as compared to  $I_B$  and  $I_C$  and we can use an approximation that  $I_A = 0$ . The small value of  $I_A$  could be attributed due to the differences in the masses and the radii of the nucleus and the electrons.

You know that most of the mass of the molecule is concentrated in the nuclei of its atoms in a very small space. But the electrons having very less mass occupy relatively large space. Therefore, the electrons contribute a major share to the moment of inertia along the axis of symmetry because only they will be contributing to the motion. The total moment of inertia (both due to electrons and nucleus) is very small. Since the energy of the rotational levels is proportional to  $\frac{1}{I}$ , the energy of the rotational levels corresponding to rotation about the symmetry axis (Fig. 3.9(c)) will be very-very high as compared to that of the rotational levels for rotations shown in Figs. 3.9(a) and (b). Thus, these rotational levels will not contribute to the rotational spectra and the value of moment of inertia used in Eq. 3.26 could be either of  $I_B$  or  $I_C$  because both of them are equal.

With this background in our mind, let us shift our attention to polyatomic molecules. Polyatomic molecules can be classified into various groups according to their values of moments of inertia along the three principal axes. Such a classification is given below in Table 3.1.

Table 3.1 : Various Classes of Polyatomic Molecules.

Moments of Inertia	Type of Rotor	Examples	Rotational Constant
$I_B = I_C, I_A = 0$	Linear	CO, HCl, OCS	$A = \alpha, B = C$
$I_B = I_C = I_A$	Spherical top	CH <sub>4</sub> , SF <sub>6</sub>	$A = B = C$
$I_A < I_B = I_C$	Prolate	CH <sub>3</sub> F, CH <sub>3</sub> Cl	$A > B = C$
	Oblate		
$I_A > I_B = I_C$		BCl <sub>3</sub> , C <sub>6</sub> H <sub>6</sub>	$A = B > C$
$I_A \neq I_B \neq I_C$	Asymmetric top	CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O	$A \neq B \neq C$

About the linear systems, you have already studied in detail for diatomic molecules. Similarly, we can treat linear triatomic and other linear polyatomic molecules.

Let us study the case of a triatomic molecule OCS. Here also we will assume that it is a rigid molecule. If you see the structure of OCS shown in Fig. 3.10, you can find that there are two bond lengths, C–O and C–S. But we have one value for the moment of inertia which cannot give two values of bond distances. This problem can be solved by using isotopic substitution as follows.

Note that the moment of inertia about the molecular axis is zero and the moment of inertia about the other two axes perpendicular to the molecular axis are identical. Hence, only one numerical value of  $I$  occurs for a linear molecule and the energy is defined by only one quantum number,  $J$ .

In case of polyatomic molecules when the rotation in three dimensions is possible, kinetic energy of rotation ( $E_k$ ) can be given as

$$E_k = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \quad \dots (3.36)$$

Similar to Eq. 3.24, we can write

$$E_k = \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C} \quad \dots (3.37)$$

where  $L_A = I_A \omega_A$

$$L_B = I_B \omega_B$$

$$L_C = I_C \omega_C$$

Here, the magnitude of total angular momentum is given as follows:

$$L^2 = L_A^2 + L_B^2 + L_C^2$$

Thus for linear molecules where  $I_A = 0$ , Eq. 3.37 becomes as follows:

$$E_k = \frac{(L_A^2 + L_B^2)}{2I_A} = \frac{L^2}{2I_A}$$

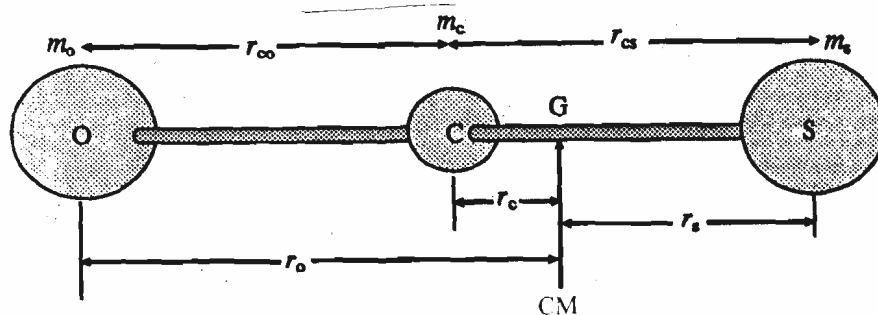


Fig. 3.10: OCS molecule.

Let the masses of O, C and S be represented by  $m_o$ ,  $m_c$  and  $m_s$ , respectively. Also let the distances of the atoms O, C and S from the centre of mass (G) be represented as  $r_o$ ,  $r_c$  and  $r_s$ , respectively. The centre of mass (G) will be such that

$$m_o r_o + m_c r_c = m_s r_s \quad \dots (3.38)$$

The moment of inertia of this system ( $I$ ) is given by the following equation.

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \quad \dots (3.39)$$

We can express  $r_o$  and  $r_s$  by the following expressions (see Fig. 3.10).

$$r_o = r_{co} + r_c \quad \dots (3.40)$$

and  $r_s = r_{cs} - r_c \quad \dots (3.41)$

We can substitute the above values of  $r_o$  and  $r_s$  from Eqs. 3.40 and 3.41 into Eq. 3.38 to yield the following expression.

$$m_o (r_{co} + r_c) + m_c r_c = m_s (r_{cs} - r_c)$$

or  $m_o r_{co} + m_o r_c + m_c r_c = m_s r_{cs} - m_s r_c$

Bringing all the terms containing  $r_c$  on one side, we can write

$$m_o r_c + m_c r_c + m_s r_c = m_s r_{cs} - m_o r_{co}$$

$$r_c (m_o + m_c + m_s) = m_s r_{cs} - m_o r_{co}$$

If we represent  $m_o + m_c + m_s$ , the total mass by  $M$ , the above equation becomes as given below

$$r_c M = m_s r_{cs} - m_o r_{co} \quad \dots (3.42)$$

Similarly, we can express Eq. 3.39 for  $I$  in terms of  $r_o$  and  $r_s$  as given below:

$$\begin{aligned} I &= m_o (r_{co} + r_c)^2 + m_c r_c^2 + m_s (r_{cs} - r_c)^2 \\ &= m_o r_{co}^2 + m_o r_c^2 + 2m_o r_{co} r_c + m_c r_c^2 + m_s r_{cs}^2 + m_s r_c^2 - 2m_s r_{cs} r_c - \end{aligned}$$

Rearranging, we get

$$I = m_o r_c^2 + m_c r_c^2 + m_s r_c^2 + 2r_c (m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \quad \dots (3.43)$$

$$I = M r_c^2 + 2r_c (m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \quad \dots (3.44)$$

Substituting value of  $r_c$  from Eq. 3.42 into the above equation, we get

$$\begin{aligned}
 I &= M \left( \frac{m_s r_{cs} - m_o r_{co}}{M} \right)^2 + 2 \left( \frac{m_s r_{cs} - m_o r_{co}}{M} \right) \cdot (m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \\
 &= M \left( \frac{m_s r_{cs} - m_o r_{co}}{M} \right)^2 - \frac{2(m_o r_{co} - m_s r_{cs})^2}{M} + m_o r_{co}^2 + m_s r_{cs}^2 \\
 &= m_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o r_{co} - m_s r_{cs})^2}{M} \quad \dots (3.45)
 \end{aligned}$$

Eq. 3.45 can be simplified to the following expression.

$$I = \frac{1}{M} \left[ m_o m_c r_{co}^2 + m_c m_s r_{cs}^2 + m_o m_s (r_{co} + r_{cs})^2 \right]$$

Eq. 3.45 is the one on which we will further focus our discussion. It contains the two unknown distances  $r_{co}$  and  $r_{cs}$ . Suppose we carry out an isotopic substitution in the molecule. i.e., we substitute  $^{18}\text{O}$  in place of  $^{16}\text{O}$  and then record the rotational spectra. The equation for moment of inertia ( $I'$ ) of this new molecule thus becomes as given below:

You may remember that bond distances do not change when isotopic substitution is carried out.

$$I' = m_o' r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o' r_{co} - m_s r_{cs})^2}{M'} \quad \dots (3.46)$$

where  $m_o'$  represents the mass of the isotope of oxygen. Now, we have two equations [Eqs. 3.45 and 3.46] and we can evaluate two unknowns  $r_{co}$  and  $r_{cs}$  provided we know the other parameters in these equations.

Next category of molecules is that of spherical top. These molecules have all the three moments of inertia as identical. As far as the value of rotational energy is concerned, it can be obtained by using any one of the above values of moment of inertia. These molecules behave similar to linear molecules as far as their rotation is concerned. The same equation as obtained for linear molecules can be applied to give the value of  $E_r$  or  $B$ . But because these molecules, being symmetric in nature, do not possess any dipole moment; Thus, these molecules do not show pure rotational spectra.

We will next consider symmetric top molecules. You are aware that in these molecules, two moments of inertia are equal but the third one is different. When this third moment of inertia is less than the other two equal moments of inertia, the molecules are known as prolate molecules. On the other hand, when the third moment of inertia is greater than the other two moments of inertia, then the molecules are known to be of oblate type. Both these type of molecules are shown below in Fig. 3.11.

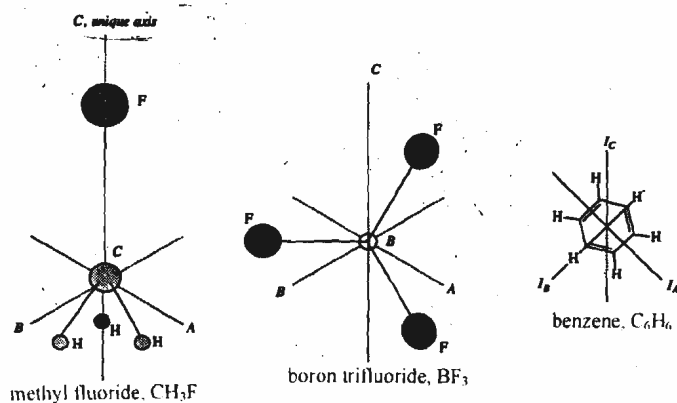


Fig. 3.11: Prolate and oblate symmetric molecules.

Again, in these molecules first we consider that the molecules are rigid and derive the energy expression by solving the Schrödinger equation. The following equation is obtained by using the above method.

**Basic Concepts and Rotational Spectra**

$$\bar{\nu}_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2 \text{ cm}^{-1} \quad \dots (3.47)$$

We will not go into the details of arriving at Eq. 3.47. It is valid for prolate molecules.

where,  $B = \frac{h}{8\pi^2 I_B c}$

For oblate molecules,

$$A = \frac{h}{8\pi^2 I_C c}$$

$$\bar{\nu} = BJ(J+1) - (B-C)K^2 \text{ cm}^{-1}$$

Unique axis is also known as Top axis.

Here,  $J$  is the total angular momentum and  $K$  is the component of angular momentum about the *unique axis*. The unique axis along the C-X bond of  $\text{CH}_3\text{X}$  molecule is shown in Fig.3.11. Obviously the values of  $K$  will be smaller than or equal to  $J$ . Thus,  $K$  can take the following values.

$$K = J, J-1, J-2, \dots, 0, \dots, (J-1), -J \quad \dots (3.48)$$

So,  $K$  can take  $2J + 1$  values.

From the above equation, you can see that  $K$  can have negative values as well. The +ve and -ve values are associated with the clockwise and anticlockwise rotation about the symmetry axis. When  $K = 0$ , it means that there is no rotation about the symmetry axis or unique axis.

Eq. 3.50 permits determination of only one rotational constant.

Hence the complete geometry of a symmetric top molecule cannot be determined by using this single value of  $B$  obtained from spectra.

In such a case, isotopic substitution is used in structure determination.

Thus, centrifugal distortion leads to a slight separation of the components of  $J$ .

Eq. 3.47 shows that the rotational energy depends upon the  $K^2$  terms. So the anticlockwise or clockwise rotation (i.e., the +ve and -ve values of  $K$ ) will have same value for  $K^2$  or energy. Thus, the levels corresponding to  $+K$  and  $-K$  will be degenerate.

The selection rules for the rotation of such molecules are

$$\Delta J = \pm 1 \text{ and } \Delta K = 0 \quad \dots (3.49)$$

The selection rule of  $\Delta K$  comes from the fact that there is no dipole moment about the symmetry axis (rotation about which is represented by  $K$ ), hence electromagnetic radiation cannot interact with the rotation about this axis. Hence, it is expressed as  $\Delta K = 0$ .

If we apply the above selection rules to Eq. 3.47, we get

$$\begin{aligned} \bar{\nu}_{(J+1,K)} - \bar{\nu}_{(J,K)} &= [B(J+1)(J+2) + (A-B)K^2] - [BJ(J+1) + (A-B)K^2] \\ &= 2B(J+1) \text{ cm}^{-1} \end{aligned} \quad \dots (3.50)$$

where  $J = 0, 1, 2, \dots$

You can see that  $K$  is not reflected in the final equation for rotation and Eq. 3.50 is similar to expression for  $\bar{\nu}$  obtained for the rotation of linear molecules.

Similar to the case of linear molecules, the centrifugal distortions due to non-rigid nature of real molecules are taken care of by incorporating an additional term in the energy expression as given below in Eq. 3.51:

$$\begin{aligned} \bar{\nu}_{(J,K)} &= BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{J,K} J(J+1)K^2 - D_K K^4 \text{ cm}^{-1} \\ \bar{\nu}_{(J+1,K)} - \bar{\nu}_{(J,K)} &= 2B(J+1) - 4D_J(J+1)^3 - 2D_{J,K}(J+1)K^2 \text{ cm}^{-1} \end{aligned} \quad \dots (3.51)$$

Thus, we could take the case of symmetric top molecules to be similar to that of linear molecules. The same procedure can be used for calculating  $B$  and  $I$  and bond lengths for symmetric top-molecules as done earlier for linear molecules. But here, there will



be a difference in the observed spectrum for symmetric top molecules as far as the splitting of rotational lines is concerned. Since each value of  $J$  is associated with  $2J + 1$  values of  $K$  and the levels corresponding to  $+K$  and  $-K$  being degenerate. This leads to the fact that the spectral line associated with a particular level will be split into  $J + 1$  components. Thus, the following splitting pattern will be observed.

when,	$J$	$K$	$\bar{\nu}$ (from Eq. 3.51)
	1	0	$4B - 32D_J$
		$\pm 1$	$4B - 32D_J - 4D_{J,K}$
		0	$6B - 108D_J$
	2	$\pm 1$	$6B - 108D_J - 6D_{J,K}$
		$\pm 2$	$6B - 108D_J - 24D_{J,K}$

Thus, the spectrum obtained will look like as shown below in Fig. 3.12.

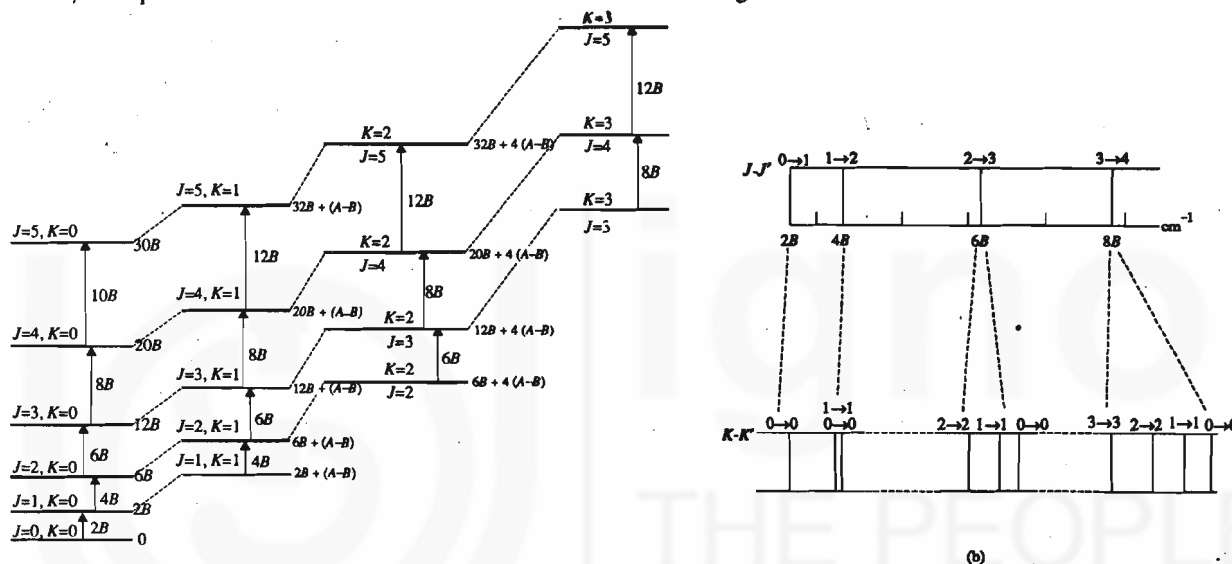


Fig. 3.12: (a) Rotational energy levels of prolate symmetric top molecules.  
(b) Splitting of rotational spectral lines for symmetric top molecules.

Remember that no such splitting was observed for linear molecules. In other words, by studying the spectra, you can know whether a certain molecule is of linear type or of symmetrical top type.

The analysis of rotational spectra of last class of molecules, i.e., **Asymmetric top** molecules is quite complex and a general expression for energy cannot be written for them. Each molecule of this class requires individual treatment. In this course, we will not go into the details of analysis of rotational spectra for this kind of molecules.

Note that in case of symmetric top molecules, each lines is really a superposition of  $(J + 1)$  lines.

In the next section, you will study about the intensity of spectral lines.

### 3.7 POPULATION OF ROTATIONAL ENERGY LEVELS AND THE INTENSITIES OF SPECTRAL LINES

According to the selection rule, all those transitions where  $\Delta J = \pm 1$  are possible. It has been shown by calculations that the probability of all such transitions is the same. However, this does not mean that all the transitions will have the same intensity. Although the chances of a molecule going from  $J = 0$  to  $J = 1$  is the same as  $J = 2$  to  $J = 3$ , yet the intensity of the two lines may differ. This is so because the total number of molecules initially present in  $J = 0$  will be different from the molecules present in  $J = 2$ . The larger the number of molecules present in a particular state, the

larger will be the chances of transitions to the next state and hence greater will be the intensity.

The population of the energy state depends on (1) Boltzmann distribution and (2) the degeneracy of the state.

Boltzmann distribution can be expressed as,

$$\frac{N_J}{N_0} = e^{-\Delta E_J / kT} \quad \dots (3.52)$$

where,  $N_J$  = number of molecules in any state

$N_0$  = number of molecules in the lowest level, i.e.,

$J = 0$

$E_J$  = energy difference between the two states

$k$  = Boltzmann constant

$T$  = temperature in Kelvin

Eq. 3.52 can be rewritten as,

$$\frac{N_J}{N_0} = e^{+BhcJ(J+1)/kT} \quad \dots (3.53)$$

One thing is clear from Eqs. 3.52 and 3.53 that the population of different states keeps on decreasing in an exponential manner as we keep on increasing the  $J$  value.

However, there is another factor—the degeneracy of the state which will affect the population. We shall not discuss the origin and number of such degenerate states, except to emphasise that degeneracy of a state increases the population of a particular energy state.

The net result of the two factors is that the population rises to a maximum and then decreases as  $J$  value increases. The band with maximum intensity is given by,

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad \dots (3.54)$$

#### SAQ 4

Calculate the relative population of first two rotational energy levels for HCl at 300K. Use  $B = 10.49 \text{ cm}^{-1}$

.....  
 .....

---

### 3.8 SUMMARY

---

In this unit, you learnt about various types of energies associated with different kind of molecular motions. Rotational motion was the one in which were interested in. In this context, the terms moment of inertia and angular velocity were explained. Then, the rotation of a rigid diatomic molecule was discussed in detail. The energy levels associated with such molecules were considered which in turn were related to the observed rotational spectra.

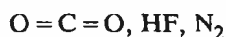
The applications of rotational spectra study were highlighted. The case of non-rigid molecules was also explained. This was followed by the discussion of rotational spectra

of polyatomic molecules. In this class, linear, spherical and symmetric top molecules were discussed.

Lastly, the relationship between the intensity of rotational spectral lines with population of rotational levels was described.

### 3.9 TERMINAL QUESTIONS

- Using  $m_1 r_1 = m_2 r_2$ , derive  $r_2 = \frac{m_1 r}{(m_1 + m_2)}$ .
- Calculate the energy in terms of  $\bar{\nu}$  of the energy level corresponding to  $J = 7$ .
- What is the selection rule for a rigid diatomic molecule to show rotational spectrum?
- Which of the following molecules will show rotational spectra?



- If the rotational constant for  $\text{H}^{35}\text{Cl}$  is  $10.59 \text{ cm}^{-1}$ , what is the value of rotational constant for  $^2\text{D}^{35}\text{Cl}$ ?

Use mass of  $^{35}\text{Cl} = 58.06 \times 10^{-27} \text{ kg}$

mass of  $^2\text{D} = 3.344 \times 10^{-27} \text{ kg}$

mass of  $^1\text{H} = 1.673 \times 10^{-27} \text{ kg}$

### 3.10 ANSWERS

- From Eq. 3.26, a decrease in moment of inertia will lead to an increase in the energy of the rotational level.
- It should possess a permanent dipole moment.

$$3. \quad \frac{B}{B'} = \frac{\mu'}{\mu} = 1.0361$$

$$\mu' = 1.0361 \times \mu$$

$$\frac{^{15}\text{N} \times 15.9994}{^{15}\text{N} + 15.9994} = \frac{1.0361 (14.004 \times 15.9994)}{14.004 + 15.9994}$$

$$^{15}\text{N} = 14.98257$$

$$4. \quad \frac{hcB}{kT} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})(10.4 \text{ cm}^{-1})(10^2 \text{ m}^{-1})}{(1.3806 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}$$

$$= 5.007 \times 10^{-2}$$

$$\text{For } J=0, \frac{N_J}{N_0} = 1$$

$$\text{For } J=1, \frac{N_J}{N_0} = e^{-2(5.007 \times 10^{-2})}$$

### Terminal Questions

1.  $m_1 r_1 = m_2 r_2$

$$\frac{r_2}{r_1} = \frac{m_1}{m_2}$$

From the characteristics of proportions,

$$\frac{r_2}{r_1 + r_2} = \frac{m_1}{m_1 + m_2}$$

$$r_2 = \frac{m_1 (r_1 + r_2)}{(m_1 + m_2)}$$

$$= \frac{m_1 r}{(m_1 + m_2)}$$

2.  $= BJ(J + 1)$   
 $= B \times 7(7 + 1)$   
 $= B \times 7 \times 8$   
 $= 56B$

3.  $\Delta J = \pm 1$

4. HF

5.  $5.446 \text{ cm}^{-1}$



## Further Reading

1. **J.R.Dyer, Application of Absorption Spectroscopy of Organic Compounds, Eastern Economy Edition, Prentice-Hall of India Pvt.Ltd.**
2. **D.H.Williams and Ian Fleming, Spectroscopic Methods in Organic Chemistry. Tata Mc Graw Hill Publishing Co. Ltd. 4thEd.**
3. **C.N Banwell, Fundamentals of Molecular Spectroscopy, 3rd Ed, Tata McGraw Hill Publishing Co. Ltd.**



NOTES

