UNIT-II : Molecular Spectra

Introduction :

The atomic spectra, which is the spectra emitted by atoms (when the emitting substance is in atomic state) due to energy changes in their electronic system There is another class of spectra, called the molecular spectra, which is the spectra emitted by molecules (when the emitting substance is in molecular sp state) containing two or more atoms. Molecular spectra is also known as Band Spectra, because the component lines of spectra were found indistingui- shable, which appeared merged together into strips of shaded intensity. Thus under low dispersion, molecular spectra appear as continuous bands. usually a band has a sharp intense edge on one side called 'band head', which gradually decreases in intensity toward the other side. Thus the continuous spectrum appears to be divided into several bands.

With High resolving power instruments, the band spectra is found to have threefold struct:

(i) Each band is composed of a Large no. of lines which are crowded together at the Long wavelength side, called 'band head'. The lines become more widely separated & weaker as they recede from the band head.

(ii) Several bands follow one another in regular sequence constituting a group of bands.

(iii) Different group of bands are quite close, and because of their regular arrangement, they form a band system.

Types of molecular spectra :-

Band spectra produced by molecules are found to occur in different spectral regions. Accordingly, molecular spectra is divided into three spectral ranges corresponding to the different type of transitions bet^n molecular energy states.

(i) Pure Rotational Spectra :

Molecular energy states arising from the rotation of a molecule as a whole are separated by quite small energy interval ($\approx 10^{-3}$ ev). spectra arising from transitions bet^n these states are observed in absorption in the far infra red region ($10^2 \mu$ to $10^3 \mu$ where $1\mu = 10^{-6}$ m $= 10^4 A^\circ$) or in the microwave region ($10^3 \mu - 10^4 \mu$)

Only those molecules which have permanent electric dipole moment can give rise to a pure rotational spectra. Thus pure rotational spectra are observed only for the Heteronuclear diatomic molecule such as HCl, HBr, HF etc. Homonuclear diatomic molecule such as H_2, O_2, N_2 etc do not exhibit pure rotational spectra.

(ii) vibrational - rotational spectra :

Rotation-vibration bands arise from the vibration of the atoms inside the molecule, upon which are suspended the rotational motion of molecules. The spectra so obtained are observed in absorption in the near infrared region (1μ to $10^2 \mu$). They are observed, like pure rotational spectra, only for the Heteronuclear

molecule like HCl, HBr, HF etc. The Homonuclear diatomic molecules like H_2, O_2, N_2 etc do not produce vibrational - rotational spectra.

(ii) Electronic Spectra :

The most complex molecular spectra is the electronic spectra, which is observed, both in emission and absorption in the visible and ultraviolet regions (μ to $100 A°$). All diatomic molecules, Homonuclear as well as Heteronuclear, exhibit electronic spectra. Thus Homonuclear molecule, such as H_2, O_2, N_2 etc which give neither rotational nor vibrational - rotational spectra, because they do not have permanent dipole moment, give electronic spectra.

The molecular & electronic spectra involves a change in all the three electronic, vibrational and rotational energies of the molecule. The electronic transition occurs due to the change in electronic energy. The change in electronic energy is accompanied by a change in vibrational energy, which gives rise to vibrational transitions forming a group of various bands. The change in vibrational energy in turn is accompanied by changes in rotational energy of the molecule giving rise to rotational transitions forming a series of lines in each band. Thus, the bands of electronic spectra show a fine structure.

When two atoms are brought together, following situation occurs :

(i) No bond is formed :

According to Pauli's exclusion principle, no two electrons can occupy the same quantum state. When the electronic structures of the atoms forming bond overlap and if their quantum states are same then the electrons are pushed to higher energy state. We know that with the higher energy, the system becomes unstable and bond (molecule) is not formed.

(ii) An ionic bond :

Ionic bonding between two atoms occurs when one or more electrons from one atom are transferred to other atom. This results in the formation of positive and negative ions which strongly attract each other to form a stable system (molecule). The bonding is called as ionic bond.

e.g. In NaCl molecule, Na^+ and Cl^- ions formed by transfer of one electron from Cl-atom to Cl-atom attract each other.

The condition for stable molecule of NaCl to be formed is that the total energy of the system of two ions be less than the total energy of a system of two atoms of the same elements.

At small separation, the energy of the system $(Na^+ + Cl^-)$ is less than that of (Na + Cl) system and eventually at this separation, stable NaCl molecule is formed. The situation is represented as,

$$Na + Cl \rightarrow Na^+ + Cl^- + 0.4 \text{ eV}$$
$$\leftarrow \infty \rightarrow \qquad \leftarrow 8 \text{ A}° \rightarrow \qquad \text{(separation)}$$
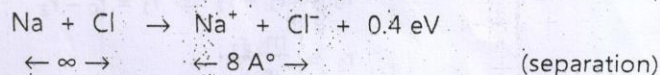
(iii) A covalent bond :

A covalent bond is formed when one or more pairs of electrons are shared by two atoms. The circulating electrons spend more time in between atoms resulting in the production of attractive forces. The resulting charge distribution can be interpreted as sharing of electrons by both atoms. e.g. In H_2 molecule, one electron from both H atoms are shared to form stable molecule.

3.2 ROTATIONAL ENERGY LEVELS AND ROTATIONAL SPECTRA

The molecular energy states (levels) arising due to rotation of molecule are quantized. That means they have fixed values depending on the shape and size of the molecule. The molecules may be diatomic or polyatomic. The diatomic molecules are always linear molecules, however, the polyatomic molecules may be linear or non-linear. The non-linear

molecules have symmetric top or asymmetric top symmetry. For simplicity, here we discuss the case of linear rigid diatomic molecule also called as rigid rotator.

Let the two atoms with masses m_1 and m_2 respectively are joined by a rigid rod (the bond) whose length is $r_0 = r_1 + r_2$ as shown in Fig. 3.1. The molecule rotates about the centre of gravity C and perpendicular to the line joining the two atoms.
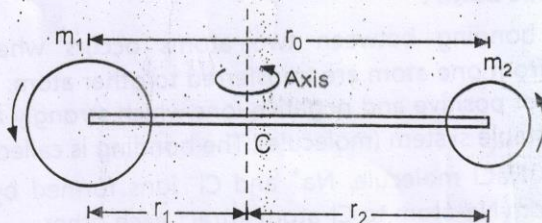
Fig. 3.1 : Rotation of a diatomic molecule

The moment of inertia of molecule is

$$I = m_1 r_1^2 + m_2 r_2^2$$

But

$$m_1 r_1 = m_2 r_2$$

and

$$r_0 = r_1 + r_2 \Rightarrow r_1 = r_0 - r_2$$

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

$$= \frac{m_1 (r_0 - r_2)}{m_2} = \frac{m_1}{m_2} r_0 - \frac{m_1}{m_2} r_2$$

$$\therefore \quad r_2 + \frac{m_1}{m_2} r_2 = \frac{m_1}{m_2} r_0$$

$$\therefore \quad r_2 \left(1 + \frac{m_1}{m_2}\right) = \frac{m_1}{m_2} r_0$$

$$\therefore \quad r_2 \left(\frac{m_1 + m_2}{m_2}\right) = \frac{m_1}{m_2} r_0$$

$$\therefore \quad r_2 = \frac{m_1 r_0}{(m_1 + m_2)}$$

Similarly, r_1 can be calculated as

$$r_1 = \frac{m_2 r_0}{(m_1 + m_2)}$$

Therefore I becomes

$$I = m_1 \left[\left(\frac{m_2}{m_1 + m_2} \right) r_0 \right]^2 + m_2 \left[\left(\frac{m_1}{m_1 + m_2} \right) r_0 \right]^2$$

$$= \frac{m_1 m_2^2 + m_2 m_1^2}{(m_1 + m_2)^2} r_0^2 = \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} \cdot r_0^2$$

$$= \frac{m_1 m_2}{(m_1 + m_2)} r_0^2$$

$$\therefore \quad I = \mu r_0^2$$

where, $\mu = \dfrac{m_1 m_2}{(m_1 + m_2)}$ is called reduced mass.

The rotational motion of molecule is quantized.

i.e. angular momentum $L = I\omega$ is quantized.

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

where $J = 0, 1, 2, \ldots$ is called rotational quantum number.

The rotational kinetic energy is given by,

$$E_J = \frac{1}{2} I\omega^2 = \frac{1}{2} \frac{I^2 \omega^2}{I} = \frac{1}{2} \frac{L^2}{I}$$

$$= \frac{J(J+1) h^2}{8\pi^2 I} \qquad \ldots \left(L = \sqrt{J(J+1)} \cdot \frac{h}{2\pi} \right)$$

Thus E_J is proportional to $J(J+1)$.

Since E_J is of the order of thermal energy (kT) at room temperature, molecules are excited in rotational states. This energy is about few eV, which is of the order of bond (or dissociation) energy. Hence during excitation of these energy states, the molecule dissociates and therefore these states cannot be excited. So only significant rotations are allowed. i.e. about axis passing through C.M. and perpendicular to the axis of symmetry (line joining the two atoms).

Consider, $\qquad E_J = \dfrac{J(J+1) h^2}{8\pi^2 I}$

$$E_J = J(J+1) \cdot \frac{h^2}{8\pi^2 I} = J(J+1) \cdot B$$

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

For $J = 0$, $E_J = 0$

For $J = 1$, $E_J = 2B$

For $J = 2$, $E_J = 6B$

For $J = n$, $E_J = n(n + 1) B$

$J = 3$ ——————————— $E = 12 B$

$J = 2$ ——————————— $E = 6 B$

$J = 1$ ——————————— $E = 2 B$

$J = 0$ ——————————— $E = 0 B$

Fig. 3.2 : Rotational energy levels

Rotational spectra :

Here we need to consider differences between the rotational energy levels in order to discuss the spectrum. The transitions among the rotational levels give rise to rotational spectra.

Rotational transitions are governed by the selection rule,

$$\Delta J = \pm 1$$

i.e. J changes by only one unit.

Generally rotational spectra are obtained in absorption. Therefore, if we represent initial and final states by J and $(J + 1)$ respectively, then change in energy is,

$$\Delta E_{(J \to J + 1)} = \frac{h^2}{8\pi^2 I} [(J + 1)(J + 2) - J(J + 1)]$$

$$= \frac{h^2}{8\pi^2 I} (J + 1) [J + 2 - J]$$

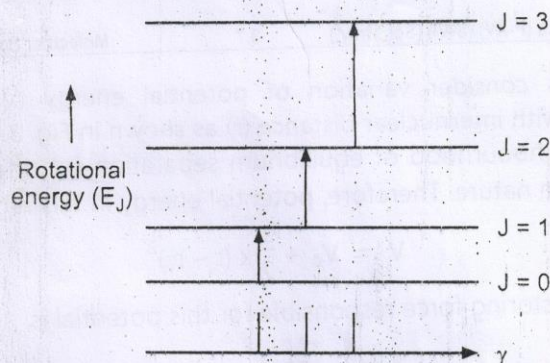$$\Delta E_{(J \to J + 1)} = \frac{h^2}{4\pi^2 I} (J + 1) \qquad \qquad \dots (3.1)$$

This energy difference is given out as radiation of frequency (υ) such that

$$\upsilon = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I} (J + 1) \quad \text{(in cm}^{-1}) \qquad \dots (3.2)$$

Fig. 3.3 : Rotational energy levels and spectrum

Thus rotational spectrum consists of equispaced lines as shown in Fig. 3.3. Since energy differences are very small, pure rotational spectrum occurs in microwave region. The polar molecules such as CO, HCl give rise to rotational spectra. The measurement of frequencies or difference in frequency of the rotational spectral lines provided a method of estimating moment of inertia and thereby bond length (R) can be calculated.

3.3 VIBRATIONAL ENERGY LEVELS AND VIBRATIONAL SPECTRA
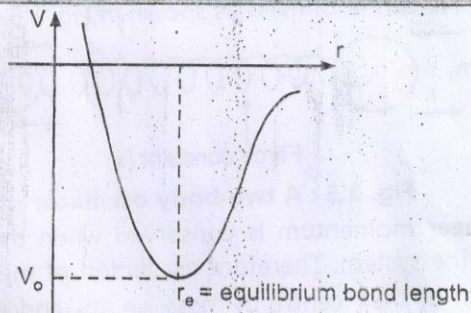
Fig. 3.4 : Potential energy curve of a diatomic molecule

In the study of rotational spectra, we deal with the diatomic rigid rotator possessing rotational motion. In fact the atoms in a molecule do not remain in fixed relative positions but vibrate (oscillate) about some mean position i.e. molecule can oscillate as well as rotate.

The vibrations of molecule may be harmonic or anharmonic; depending on which the spacing between the energy levels also changes. For simplicity here we consider the simple harmonic oscillations of a diatomic molecule.

Let us consider variation of potential energy (V) of a diatomic molecule with internuclear distance (r) as shown in Fig. 3.4.

In neighbourhood of equilibrium separation (r_e), the curve is almost parabolic in nature. Therefore, potential energy in this region is,

$$V = V_0 + \frac{1}{2} k (r - r_e)^2 \qquad \ldots (3.3)$$

∴ Restoring force responsible for this potential is,

$$F = -\frac{dV}{dR}$$
$$= -k (r - r_e) \qquad \ldots (3.4)$$

where F is the restoring force of harmonic oscillator and k is the spring constant.

Therefore the frequency (v_0) of oscillation of mass connected to a spring of force constant (k) is,

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

But diatomic molecule is a two body oscillator i.e. two masses m_1 and m_2 attached to the ends of a spring constant (k) and oscillating back and forth relative to the centre of mass as shown in Fig. 3.5.

Force constant (k)
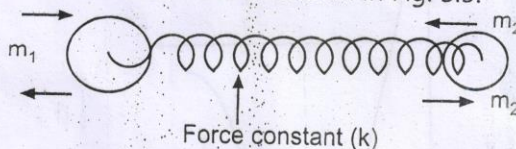
Fig. 3.5 : A two body oscillator

The total linear momentum is conserved when there is no external force acting on the system. Therefore oscillation of m_1 and m_2 does not affect the motion of their centre of mass. i.e. m_1 and m_2 simultaneously reach the extreme positions. The frequency of oscillation (v_0) of such a two body oscillator is expressed in terms of reduced mass,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{as}$$

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \qquad \ldots (3.5)$$

According to quantum mechanics, the vibrational energy (E_v) is also quantized, such that,

$$E_v = \left(V + \frac{1}{2}\right) h v_0 \qquad \ldots (3.6)$$

where, V = 0, 1, 2, ... is vibrational quantum number.

The lowest energy state with $V = 0$, also possess a finite energy $\frac{1}{2} h\upsilon_0$, called zero point energy.

$$\therefore \quad E_v = \left(V + \frac{1}{2}\right) \cdot \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \qquad \ldots (3.7)$$

$$\ldots \text{(from equations 3.5 and 3.6)}$$

Equation (3.7) gives vibrational energy levels.

The vibrational energy is of the order of 0.1 eV which is generally, larger than the thermal energy ($kT = 2.6 \times 10^{-2}$ eV) and hence molecules are mostly found in lowest energy state ($V = 0$).

Vibrational spectra :

The vibrational energy levels are given by

$$E_v = \left(V + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

It is seen that, the vibrational energy levels are equispaced.

Since $\qquad E_v \propto \left(V + \frac{1}{2}\right)$

However at higher V-values, the harmonic oscillator approximation is not valid as the shape of potential energy curve deviates from parabolic nature.

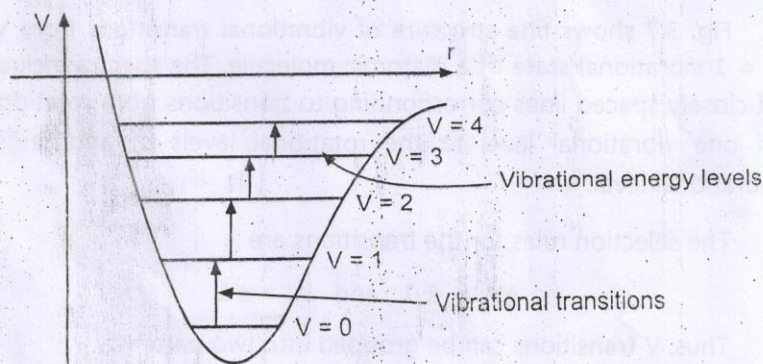Therefore, the spacing between energy levels goes on decreasing with increase in V as shown in Fig. 3.6.

Fig. 3.6 : Vibrational transitions for harmonic oscillator

The selection rule for vibrational transitions are

$$\Delta V = \pm 1$$

The vibrational spectra are known only in absorption in the infra-red region. Electromagnetic radiations can induce transitions among the vibrational energy levels when electric field interact with dipole moment. Pure vibrational spectra observed only in liquids whose molecules possess electric dipole moment. The homonuclear diatomic molecules like H_2, N_2 and O_2 that possess zero dipole moment will not interact with the radiation. On the other hand, molecules like HF, HCl, HBr, HCN have dipole moment, hence exhibit vibrational spectra.

3.4 VIBRATION ROTATION SPECTRA

It is observed that some diatomic molecules possess different rotational and vibrational energies. Therefore from first observation, we may consider that a diatomic molecule can execute rotations and vibrations independently. Thus neglecting the interaction between rotational and vibrational motions, let total energy of a molecule may be given by.

$$E_{total} = E_{vib} + E_{rot}$$

$$E_{V, J} = E_V + E_J$$

$$E = \left(V + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} + J(J+1)\frac{h^2}{8\pi^2 I}$$

Fig. 3.7 shows fine structure of vibrational transitions from $V = 0$ to $V = 1$ vibrational state of a diatomic molecule. The spectra includes a set of closely spaced lines corresponding to transitions from rotational levels of one vibrational level to the rotational levels of another adjacent vibrational level.
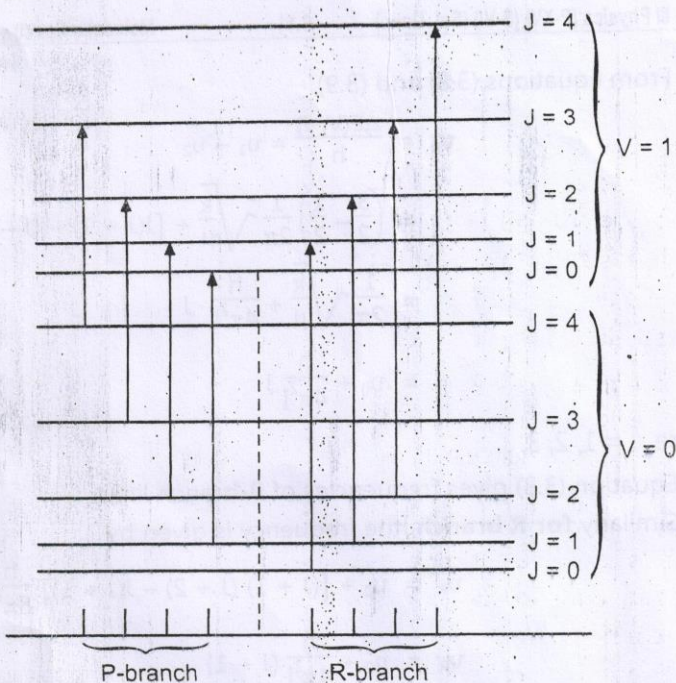
The selection rules for the transitions are

$$\Delta V = \pm 1 \quad \text{and} \quad \Delta J = \pm 1$$

Thus, V transitions can be grouped into two parts viz.

(1) $\Delta V = +1$ and $\Delta J = -1$ called P-branch.

(2) $\Delta V = +1$ and $\Delta J = +1$ called R-branch.

**Fig. 3.7 : Vibrational-rotational transitions
(fine structure of vibrational spectra)**

Let us calculate the frequency of spectra lines in P and R branch.

In P branch :

Since, transitions are $V = 0 \to 1$ and $J \to J - 1$, the corresponding frequencies are

$$\upsilon_1 = \frac{E}{h} = \left(1 + \frac{1}{2}\right) \cdot \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} + (J - 1)J \cdot \frac{h}{8\pi^2 I}$$

$$= \frac{3}{2} \cdot \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} + (J + 1)J \cdot \frac{h}{8\pi^2 I}$$

... (For $V = 1$ and $J \to J + 1$) ... (3.8)

Similarly for $V = 0$ and $J \to (J - 1)$,

$$\upsilon_2 = -\frac{1}{2}\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} + J(J - 1) \cdot \frac{h}{8\pi^2 I}$$

... (3.9)

From equations (3.8) and (3.9),

$$v_P = \frac{\Delta E(V, J)}{h} = v_1 - v_2$$

$$= \left(\frac{3}{2} - \frac{1}{2}\right)\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} + \left[J(J+1) - (J-1)J\right]\frac{h}{8\pi^2 I}$$

$$= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} + \frac{h}{4\pi^2 I} \cdot J$$

$$= v_0 + \frac{h}{4\pi^2 I}J \qquad \qquad \ldots (3.10)$$

where $J = 1, 2, 3, \ldots$

Equation (3.8) gives frequencies of P-branch lines.

Similarly **for R branch**, the frequency is given by

$$v_R = v_0 + \left[(J+1)(J+2) - J(J+1)\right]\frac{h}{8\pi^2 I}$$

$$v_R = v_0 + \frac{h}{4\pi^2 I}(J+1) \qquad \qquad \ldots (3.11)$$

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

Since $\Delta J = 0$ is forbidden transition, there is no line corresponding to frequency $v = v_0$, called band origin. The spacing between P and R branch is $\frac{h}{4\pi^2 I}$.

Thus, study of vibration-rotation spectra in infra-red region provides a method to estimate moment of inertia (I) of the molecule and hence bond length R if reduced mass of a molecule is known.

3.5 ELECTRONIC SPECTRA OF A DIATOMIC MOLECULE

A electronic transition is the result of change in electronic energy. A small change in electronic energy results in large change in vibrational energy and a small change in vibrational energy results in large change in rotational energy of the molecule.

The total energy of a molecule for certain configuration is, approximately given as

$$E = E_e + E_V + E_J \qquad (\because E_e > E_V > E_J) \ldots (3.12)$$

where E_e — electronic energy

               E_V — vibrational energy

and E_J — rotational energy.