# Molecular Spectra

The spectrum emitted by a substance when it is in the molecular state is called Molecular spectrum or band spectrum. The spectrum of Molecules gives information about its properties & structure. Just like on atom, a molecule possesses definite energy levels. The energy of a diatomic molecule is due to

1) The electronic configuration of the electrons in the molecule [ electronic energy $E_e$]
2) The rotation of the molecule as a whole about the centre of mass [ rotational energy $E_r$].
3) The vibration of the atoms about the equm position ( vibration energy $E_v$]

There are assumed to be independent of each other which is not strictly true. The total energy of a molecule is given by

$$E = E_e + E_v + E_r$$

Molecules possess different degrees of freedom like vibrational & rotational degree of freedom. When a molecule undergoes a transition from one energy level to another energy level there will be changes in their rotational, vibrational energies in addition to the changes in the electronic energies as in the case of an atom. Hence the spectrum emitted by a molecule is more complicated than atomic spectra.

As the transition can take place from any of these levels subject to the spectrum rules there will be a large no of closely spaced lines,

giving rise to band instead of discreate lines 5

If $(E_e)_2$, $(E_v)_2$ & $(E_{ri})_2$ are the electronic vibrational & rotational energies in the excited state. respectively & corresponding energies in the ground state are $(E_e)_1$, $(E_v)_1$ & $(E_{ri})_1$, due to the transition from level 2 to 1 give a quantum of radiation $h\vartheta$ given by

$$h\vartheta = [(E_e)_2 + (E_v)_2 + (E_{ri})_2] - [(E_e)_1 + (E_v)_1 + (E_{ri})_1]$$

$$h\vartheta = \Delta E_e + \Delta E_v + \Delta E_r$$

Usually $\Delta E_e$, $\Delta E_v$ & $\Delta E_{ri}$ are of order of 1ev, 0.01ev, 0.005ev respectively & these energies correspond to visible, infrared & microwave region.

Hence molecular spectra is of three types

1) **Pure rotational Spectra :—**

A transition can take place b/w any of these levels, according to the selection rules If the molecule remains in its ground state level of electronic & vibrational energies & if it suffers transitions b/w different rotational energies, the resulting spectrum is called pure rotational spectrum.

These are observed in the microwave & far infrared regions.

2) **Vibrational rotational Spectra :—**

If the molecule remains in its ground state level of electronic energy & if transitions occur b/w the different vibrational & rotational energies, the resulting spectrum is the vibrational

rotational spectrum:

These are observed in the near infrared region

## ) Electronic Spectrum :—

If transitions occur b/w different electronic - vibrational - rotational energy levels, the resulting spectrum is the electronic spectrum
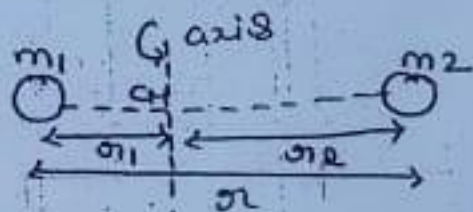
These are observed in visible & ultraviolet regions

Pure- rotational spectrum of a molecule
[ The rigid diatomic molecule ]

A diatomic molecule is considered as a rigid body & its shape is determined by the eqm position of the nuclei. Let $m_1$ & $m_2$ be the masses of the atoms & $r$ is the distance b/w them.



The diatomic molecule can rotate about its Centre of mass (CM). If $r_1$ & $r_2$ are the distance of $m_1$ & $m_2$ from the CM then the moment of inertia of the molecule about the axis through the CM & $\perp^r$ to the line joining the atoms is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad —— ①$$

From the law of moments

$$m_1 r_1 = m_2 r_2 \quad —— ②$$
$$r = r_1 + r_2 \quad —— ③$$

Hence $r_1 = \dfrac{m_2 r_2}{m_1} = r - r_2$

$$r = \dfrac{m_2}{m_1} r_2 + r_2$$

$$\therefore \quad r_2 = \dfrac{m_1 r}{m_1 + m_2}$$

$^{\text{ll}^{ly}}$ $r_1 = \dfrac{m_2 r}{m_1 + m_2}$ $\qquad r_2 = \dfrac{m_1 r}{m_1 + m_2}$

Substituting these values in eqn ①

$$I = \dfrac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \dfrac{m_2 m_1^2 r^2}{(m_1 + m_2)^2}$$

$$= \dfrac{m_1 m_2}{(m_1 + m_2)^2} (m_2 + m_1) r^2$$

$$I = \dfrac{m_1 m_2}{(m_1 + m_2)} \times r^2$$

$$I = \mu r^2$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass

The K.E of rotation of the molecule is

$$E_r = \tfrac{1}{2} I \omega^2$$

Since the angular momentum $L = I\omega$

$$E_r = \dfrac{L^2}{2I}$$

$$E_r = \dfrac{L^2}{2\mu r^2}$$

Since the angular momentum is quantised

$$L = \sqrt{l(l+1)}\, \hbar \quad \text{where } l = 0, 1, 2, 3 \cdots \text{etc}$$

$$E_r = \dfrac{\hbar^2}{2I} l(l+1)$$

: Selection rule

Rotational transitions occur only in molecules that are permanent electric dipole moment. Thus molecule such as HCl & CO will have rotational spectrum, while $Ne_2O_2$ will not have rotational spectrum. The selection rule for the $\Delta l = \pm 1$ or $[\Delta J = \pm 1]$

From the above it is evident that only those transition per permitted in which there is an increased or decreased by unity in the rotational quantum no. It means that $J = 0 \to J = 2 \to J = 4$ are not possible. These transitions are spectroscopically forbidden.

## Vibrational Spectrum

In each electronic state a molecule can have a no of vibrational sublevels. The atoms in a diatomic molecule vibrate back & forth. According to quantum mechanics the vibrational energy levels for a diatomic molecule are given by

$$E = (n + 1/2) h \gamma_0$$

where $n = 1, 2, 3$ etc. (quantized energies of a harmonic oscillator)

Therefore $E_v = (n + 1/2) \hbar \omega_0$ where $\omega_0 = 2\pi \gamma_0$

The energy levels are equally spaced & the zero point energy is given by $1/2 \hbar \omega_0$. The energy difference b/w adjacent levels $n$ & $(n+1)$ is $\Delta E_v = \hbar \gamma_0$

According to Bohr's freqn condition the freqn of the emitted or absorbed radiation is $\gamma_0 = \frac{\Delta E_v}{\hbar}$. This means that the only allowed vibrational transitions are b/w neighbouring energy levels & the selection rule is $\Delta n = \pm 1$
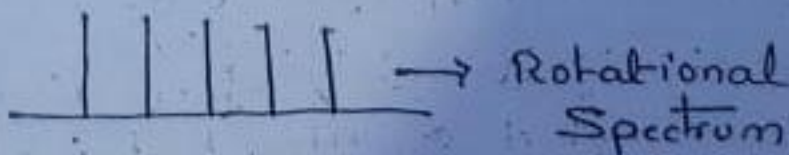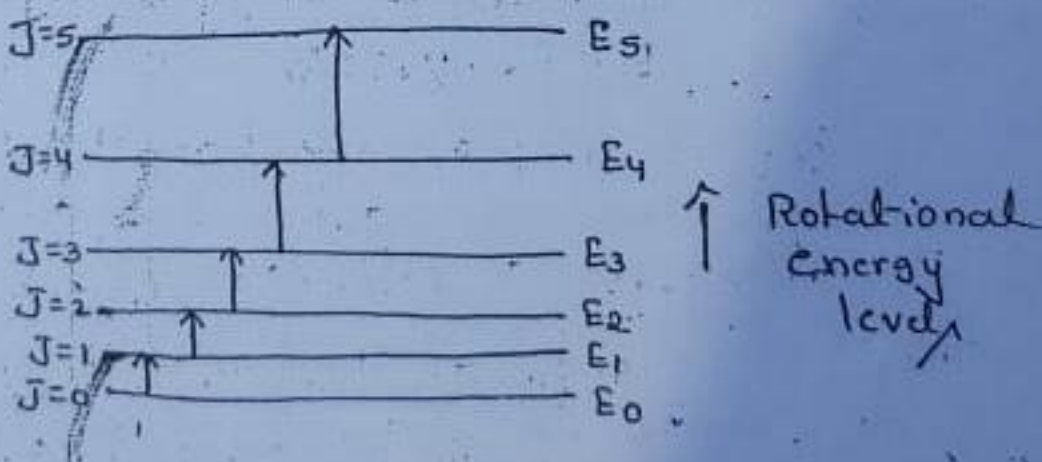
The rotational energy levels of the molecules ⑥ are found by using the selection rule $\Delta l = \pm 1$. For two successive energy levels corresponding to $l$ to $(l+1)$, the energy difference

$$\Delta E_{sr} = \frac{\hbar^2}{2I}(l+1)(l+2) - \frac{\hbar^2}{2I}l(l+1)$$

$$= \frac{\hbar^2}{2I}(l+1)(l+2-l)$$

$$= \frac{\hbar^2}{I}(l+1)$$

The freqn associated with the transitions b/w these adjacent states are

$$\vartheta = \frac{\Delta E_{sr}}{h} \quad [\text{Bohr's freqn Condition}]$$

$$= \frac{\hbar}{2\pi I}(l+1)$$

Thus the spectrum of a rigid molecule consists of equally spaced lines



Pure rotational spectra fall in the microwave region or far infrared regions of the spectrum with freqn of the $10^{12}$ Hz or energies of $10^{-4}$ ev.
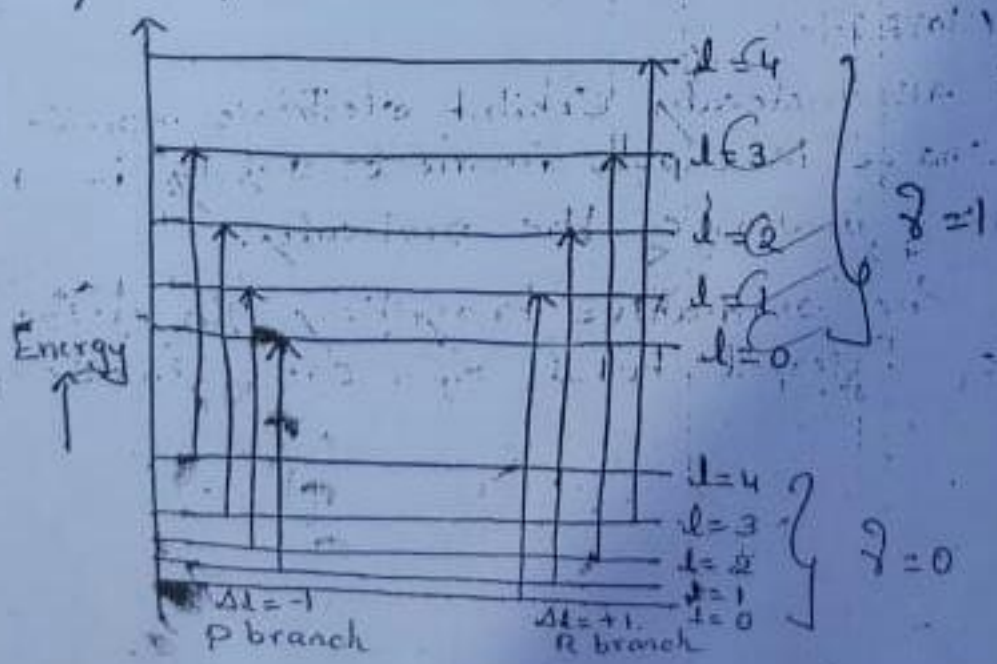
tation-vibration spectrum of a molecule ⑦

The molecular energy due to both rotation & vibration is obtained by combining the above two cases

$$E_{vr} = \frac{\hbar^2}{2I} l(l+1) + (n+\frac{1}{2})\hbar\omega_0 \qquad E_{va} = \frac{\hbar^2}{2I} l(l+1) +$$

The vibrational energy is much greater than the rotational energy. Thus to each vibrational level there correspond several rotational levels. The selection rules are $\Delta n = \pm 1$ & $\Delta l = \pm 1$. The transition corresponding to $l = 0 \to l = 1$ fall into two categories, namely i) the p branch & ii) R branch.

The first one is the result of the transition from $l$ to $(l-1)$ i.e $\Delta l = -1$ while the second results due to the transition from $l$ to $(l+1)$. The spacing b/w the lines in both the P & R branch is $\Delta \nu = \frac{\hbar}{2\alpha I}$ $\Delta \nu = \frac{\hbar}{2\pi I}$

This again gives a method of measuring the moment of inertia I, the length of the chemical bond gives a method of measuring the moment of inertia I, the length of the chemical bond & force constant. Some of the transition in the rotation vibration is as shown in fig.



Energy

$l=4$
$l=3$
$l=2$
$l=1$
$l=0$
$\}\ l=1$

$l=4$
$l=3$
$l=2$
$l=1$
$l=0$
$\}\ l=0$

$\Delta l = -1$
P branch

$\Delta l = +1$
R branch

# Electronic Spectra

A given molecule have several electronic configurations of stationary states. Each of the state will have its own energy. The energy required to excite the electronic motion in molecules is of the order of 10eV (same as in atoms). When transition occurs from one state to another, the resulting spectrum usually in visible or ultraviolet-region.

The total molecular energy is $E = E_e + E_r + E_v$. When an electronic transition occurs, all the three energies may change & hence the change in energy is given by

$$\Delta E = \Delta E_e + \Delta E_r + \Delta E_v$$

$\Delta E_e$, $\Delta E_r$ & $\Delta E_v$ are the changes in the electronic, rotational & vibrational energy levels. The frequency of the radiation, according to Bohr's frequency condition is

$$\bar{\nu} = \frac{\Delta E}{h} = \frac{\Delta E_e}{h} + \frac{\Delta E_v}{h} + \frac{\Delta E_r}{h}$$

$$= \bar{\nu}_e + \bar{\nu}_v + \bar{\nu}_r$$

The frequency $\bar{\nu}_e$ is the largest & the electronic spectra consists of a series of bands.

NOTE :-

1) All molecules exhibit electronic spectra bcoz a change in dipole moment results in the electronic configuration of the molecules.

2) The radiative transitions b/w electronic states of different total spin are forbidden.