P-VIII
Part III
Group-C

Give an account of Rotational spectra of a diatomic molecule.

Let us consider a rotation in diatomic molecule regarded as a rigid rotator. The two atoms A and B are at a distance r as shown in fig-①:

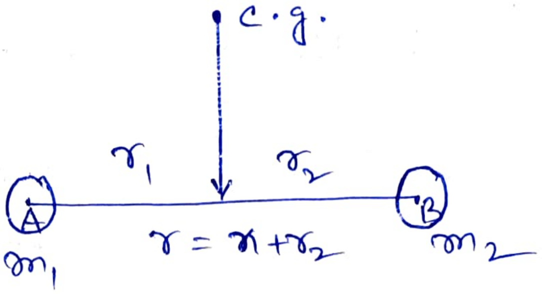

Fig-①

If r_1 ad r_2 be the distance of the two atoms from the centre of gravity (c.g) of the system, then the moment of inertia of the system is given by.

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \text{①}$$

we Know that about the c.g.,

$$m_1 r_1 = m_2 r_2$$

$$\text{or, } m_1 r_1 = m_2 (r - r_1) \qquad [\because r = r_1 + r_2]$$

$$\therefore r_1 = \frac{m_2 r}{m_1 + m_2} \qquad \text{②}$$

similarly, $$r_2 = \frac{m_1 r}{m_1 + m_2} \qquad \text{③}$$

$$\therefore \quad I = m_1\left(\frac{m_2 r}{m_1+m_2}\right)^2 + m_2\left(\frac{m_1 r}{m_1+m_2}\right)^2$$

$$\text{or,} \quad I = \left(\frac{m_1 m_2}{m_1+m_2}\right) r^2$$

$$= \mu r^2 \quad \text{———} \quad ④$$

Where, $\mu = \frac{m_1 m_2}{m_1+m_2}$ is called the reduced mass of the system.

The K.E. of rotation is

$$E_r = \frac{1}{2} I \omega^2 \quad \text{———} \quad ⑤$$

Where ω is the agular velocity of the system. Since the molecule is rigid, the P.E is zero. i.e, $V \simeq 0$. The quantised energy levels of rotation are obtained by solving the schroodinger equation

$$\nabla^2 \psi + \frac{8\pi^2 \mu E}{h^2} \cdot \psi = 0 \quad \text{———} \quad ⑥$$

The approopriate and acceptable solution of this equation yields that,

$$E = \frac{h^2}{8\pi^2 I} \cdot J(J+1) \quad \text{———} \quad ⑦$$

Where, J is the rotational quantum number having integral values 0, 1, 2, 3, - -

For a given species of molecules, $\frac{h}{8\pi^2 I}$ is a Constant and is called the Rotational constant.

Let us put $\frac{h}{8\pi^2 I} = B$.

$$\therefore E = Bh \cdot j(j+1) \quad \text{------} \quad (8)$$

The difference in energy between two rotational levels j and j'.

$$\Delta E = Bh\, j(j+1) - Bh\, j'(j'+1) \quad \text{------} \quad (9)$$

There are two restriction in such rotational transitions.

1) According to electrodynamic considerations, the absorption or emission of a radiation in rotational levels would occur only if a change in dipole moment of the molecule is associated with it. This means that the molecule must be polar in order to produce a rotational spectrum. Homopolar molecules like H_2, N_2, Cl_2 - - - etc have no rotational band. This restriction also applies to vibrational quantum level changes.

2) The transition in rotational engy is limited to adjacent levels, i.e;

$$\Delta j = \pm 1.$$

Since, $j - j' = 1$ eqn. (9) takes the form

$$\Delta E = Bhj(j+1) - Bh(j-1)j = 2Bhj \quad \text{------} \quad (10).$$

where higher quantum level $J = 1, 2, 3$; J cannot be zero. For in that case J' becomes negative.

$$\therefore \Delta E = h\nu, \quad \therefore \nu = 2BJ \quad \text{(11)}$$

putting $J = 1, 2, 3, \ldots$, the frequencies of the lines in rotational band are -

$\nu_{1 \to 0} = 2B$

$\nu_{2 \to 1} = 4B$

$\nu_{3 \to 2} = 6B$

$\nu_{4 \to 3} = 8B$, etc.

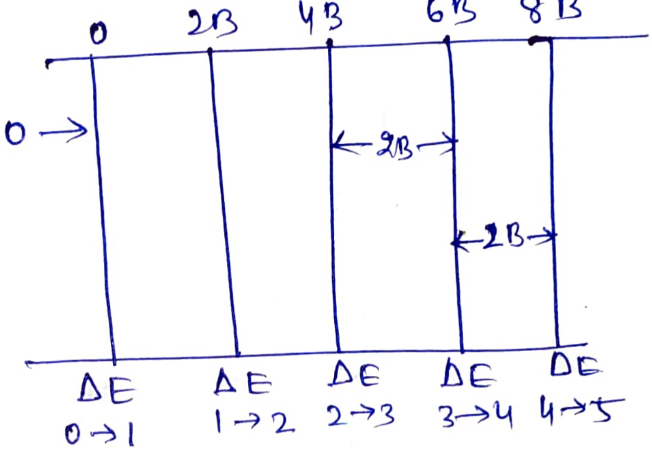

Fig (2)

The spectral lines are thus equispaced, the spacings $\Delta\nu = 2B$. The difference in wave number $\Delta\bar{\nu} = \frac{\Delta\nu}{c} = \frac{2B}{c}$.

The equidistant lines, as shown in fig (2), have been experimentally confirmed and the magnitude of B ascertained.

A higher quantum levels of rotation when the rotational energy is quite large the rigid character of the rotator is affected and there is tendency for the band to stretch the engy of rotation is then expressed as,

$$E_r = BhJ(J+1) - DhJ^2(J+1)^2 \quad \text{(12)}$$

Where, D is a small constant of the order of 10^{-4}. The spectral lines will not then be exactly equiditant especially at higher levels.