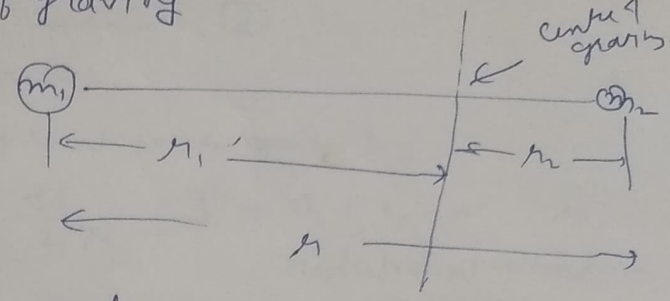
Rotational (microwave) spectra of Diatomic molecules :—

Consider a diatomic molecule in which m_1 & m_2 are the masses of two atoms & R is the eqbm bond length, rotating about an axis passing through centre of gravity

The centre of gravity of a diatomic molecule is the point which satisfies the following condition:



$$m_1 r_1 = m_2 r_2 \quad \text{—— (1)}$$

The moment of Inertia I of a molecule is defined as:

$$I = \sum_i m_i r_i^2 \quad \text{—— (2)}$$

where r_i is the distance of i^{th} ~~mol~~ particle of mass m_i from the centre of gravity. Since a diatomic molecule has two atoms we have.

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{—— (3)}$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad [\text{from eqn (1)}]$$

$$I = r_1 r_2 (m_1 + m_2) \quad \text{—— (4)}$$

also from fig $R = r_1 + r_2$

from eqn. (1) $m_1 r_1 = m_2 r_2 = m_2 (R - r_1)$

~~$r_1 = m_2$~~ $m_1 r_1 = m_2 R - m_2 r_1$

or $(m_1 + m_2) r_1 = m_2 R$

or $r_1 = \dfrac{m_2 R}{m_1 + m_2} \quad \text{—— (5)}$

also from (1)

$$m_1 r_1 = m_2 r_2$$

$$m_1 (R - r_2) = m_2 r_2$$

$$m_1 R - m_1 r_2 = m_2 r_2$$

$$\text{or } r_2 = \frac{m_1 R}{m_1 + m_2} \quad \text{—— (6)}$$

Put the values of r_1 & r_2 in eq. (4)

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

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

or $I = \mu r^2$ — (1)

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is called reduced mass of molecule.

Now by definition angular momentum of rotating molecule is given by $L = I\omega$ — (2)

where ω = angular velocity

But angular momentum is quantized & given by

$L = \sqrt{J(J+1)}\,\frac{h}{2\pi}$ $J = 0, 1, 2, \ldots$ is rotational quantum number.

the energy of ~~rigid~~ rotating molecule is given by

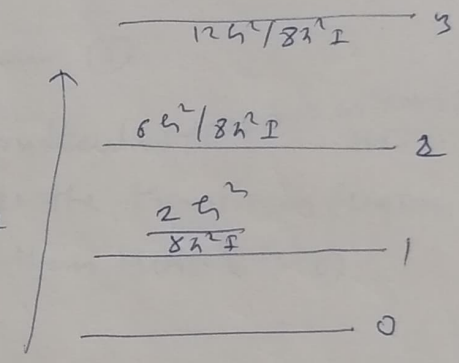
$$E = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

$$\therefore E = \frac{1}{2I} J(J+1)\frac{h^2}{4\pi^2}$$

$$\boxed{E = \frac{h^2}{8\pi^2 I} J(J+1)}$$ where $J = 0, 1, 2, 3 \ldots$

or $\boxed{E = \frac{h^2}{2I} J(J+1)}$

Evidently the spacing b/w the energy level increases as J increases



Rotational Selection rules:- According to the selection rules the transition take place only b/w those rotational energy levels for which

$$\Delta J = \pm 1$$

i.e. the change in rotational quantum number is unity

The transition $\Delta J = +1$ corresponds to absorption & $\Delta J = -1$ corresponds to emission. In other words, a transition can take place from a particular rotational level to just the next higher or just lower rotational level. All these transitions can take place with equal probability whereas all other transitions are forbidden.

Rotational Spectra of the diatomic molecules :-

Since we know that the rotational energy is given by

$$E_R = \frac{h^2}{8\pi^2 I} J(J+1), \quad J = 0, 1, 2, \cdots \quad \text{—(1)}$$

Since $E = h\nu \therefore \nu = \frac{E}{h}$

$$\therefore \nu = \frac{h}{8\pi^2 I} J(J+1), \quad J = 0, 1, 2 \cdots \quad \text{— (2)}$$

also $\nu = c/\lambda$ & $\lambda = \frac{1}{\bar{\nu}}$

$\therefore \nu = c\bar{\nu}$ or $\bar{\nu} = \frac{\nu}{c}$

$\therefore$ In terms of wave number eqn. (2) reduces to

$$\bar{\nu} = \frac{h}{8\pi^2 I c} J(J+1)$$

or $\bar{\nu} = \bar{B} J(J+1), \quad J = 0, 1, 2 \cdots \quad \text{— (3)}$

where $B = \frac{h}{8\pi^2 I c}$ is called rotational constant

or $\nu = B J(J+1), \quad J = 0, 1, 2, \cdots \quad (2)$

where $B = \frac{h}{8\pi^2 I}$ (Hz) — (3)

is called the rotational constant of molecule expressed in terms of Hz.

It is also common practice to express the transition frequency in terms of wave number (cm^{-1}) rather than Hertz (Hz)

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$\therefore$ eqn. (2) reduces to

$$\bar{\nu} = \frac{h}{8\pi^2 I c} J(J+1)$$

or $\bar{\nu} = \bar{B} J(J+1), \quad J = 0, 1, 2, \cdots \quad (4)$

where $\bar{B} = \frac{h}{8\pi^2 I c}$ (cm^{-1}) — (5)

is called rotational constant expressed in terms of wave numbers.

Now putting $J = 0, 1, 2, 3, \cdots$ in eqn. (4) the wave number of different rotational level will ~~begin by~~

$0, 2\bar{B}, 6\bar{B}, 12\bar{B}, 20\bar{B} \cdots$ & so on

When a transition takes place from a lower rotational level with rotational quantum number J to a higher rotational

level with rotational quantum number J', the energy absorbed will be given by:

$$\Delta E_R = E_{J'} - E_J$$

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

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

However according to rotational selection rules, only those rotational transitions are allowed for which $\Delta J = \pm 1$ i.e. only those transitions are allowed in which the rotational quantum number changes by unity. The + sign refers to absorption & − sign to emission of radiation. Microwave spectra are usually observed as absorption spectra so the operative part of selection rule is $\Delta J = +1$, For transition taking place from J to $J+1$ then the above eqn. becomes

$$\Delta E_1 = \frac{h^2}{8\pi^2 I} [(J+1)(J+2) - J(J+1)]$$

$$\Delta E_1 = \frac{h^2}{8\pi^2 I} 2(J+1) \quad \text{—— (6)}$$

~~$\Delta E_1 = 2B(J+1)$ —— (7)~~

in terms of frequency

$$\Delta E = h\nu \quad \text{or} \quad \bar{\nu} = \frac{\Delta E_1}{h}$$

$$\therefore \Delta\bar{\nu} = \frac{h}{8\pi^2 I} \cdot 2(J+1)$$

$$\Delta\nu = 2B(J+1) \quad \text{—— (7)}$$

In term of wave number $\nu = c/\lambda$ or $\nu = c\bar{\nu}$

$$\text{or } \Delta\bar{\nu} = \frac{\Delta\nu}{c}$$

$$\therefore \Delta\bar{\nu} = \frac{h}{8\pi^2 I c} \cdot 2(J+1)$$

$$\text{or } \Delta\bar{\nu} = 2\bar{B}(J+1) \quad \text{—— (8)}$$

Now $\bar{\nu}(J \to J')$ =

Now by putting $J = 0, 1, 2, 3$ etc. (i.e. from transition $J=0$ to $J'=1$, $J=1$ to $J'=2$ etc.) or in general from J to $J+1$ involving absorption of energy the wave

number of line obtained will be

$\bar{\nu}_{(0\to1)} = 2\bar{B}$, $\bar{\nu}_{(1\to2)} = 4\bar{B}$, $\bar{\nu}_{(2\to3)} = 6\bar{B}$

$\bar{\nu}_{(3\to4)} = 8\bar{B}$ etc.

Thus we find the most important feature of the pure rotational spectrum is that every two successive lines have a constant difference with separation $2B_{(Hz)}$ called frequency separation (or $2\bar{B}_{(cm^{-1})}$ called wave number separation)

Thus the various lines of in rotational spectra will be equally spaced.

Thus the separation b/w any two successive lines will have the difference in wave number given by

$$\Delta\bar{\nu} = 2\bar{B} = \frac{h}{4\pi^2 I c}$$

The following figure show the energy level & absorption transition of a rigid rotator. The absorption transition occurs b/w adjacent levels & so the absorption spectrum shown below the energy levels consists of a series of equally spaced lines.