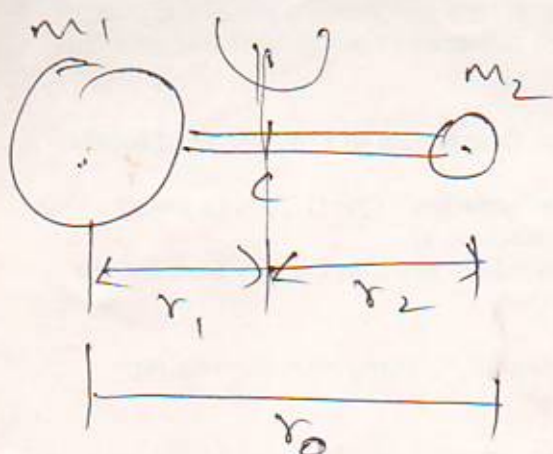


Rotational Spectra.

⑥

The rigid diatomic molecule.



$$r_0 = r_1 + r_2$$

Molecule rotates about an axis passing through C .

C is the centre of mass defined by the balancing equation,
 $m_1 r_1 = m_2 r_2$

The moment of inertia about C is

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

$$= m_1 r_1 r_1 + m_2 r_2 r_2$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 (m_1 + m_2)$$

~~$(r_0 = r_1 + r_2) \therefore m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$~~

~~$r_2 = (r_0 - r_1)$~~

~~$r_1 = \frac{m_2 r_0}{m_1 + m_2}$~~

~~$r_2 = \frac{m_1 r_0}{m_1 + m_2}$~~

~~$r_1 = \frac{m_2 r_2}{m_1} = \frac{m_2 (r_0 - r_1)}{m_1}$~~

$m_1 r_1 = m_2 r_0 - m_2 r_1$

$r_1 = \frac{m_2 r_0 - m_2 r_1}{m_1}$

~~$2 \frac{m_2 m_1 r_0}{m_1 + m_2}$~~

$$m_1 r_1 + m_2 r_1 = m_2 (r_0 - r_1) + m_2 r_1$$

$$(m_1 + m_2) r_1 = m_2 r_0 - m_2 r_1 + m_2 r_1$$

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

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

$$\therefore I = r_1 r_2 (m_1 + m_2) = \left(\frac{m_2 r_0}{m_1 + m_2} \right) \left(\frac{m_1 r_0}{m_1 + m_2} \right) (m_1 + m_2)$$

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

where $\mu = \frac{(m_1 m_2)}{(m_1 + m_2)}$

The allowed rotational energy levels are (by using Schrodinger's eqn)

$$E_j = \frac{h^2}{8\pi^2 I} J(J+1) \text{ (Joules)}$$

where $J = 0, 1, 2, 3, \dots$

called rotational quantum no.

The difference in rotational energy levels will be ΔE . The corresponding

frequency $\nu = \frac{\Delta E}{h}$ hertz.

or wave no. $\bar{\nu} = \frac{\Delta E}{hc} \text{ (cm}^{-1}\text{)}$

In terms of wave no, the energy is

$$E_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) (\text{cm}^{-1})$$

$$J = 0, 1, 2, 3, \dots$$

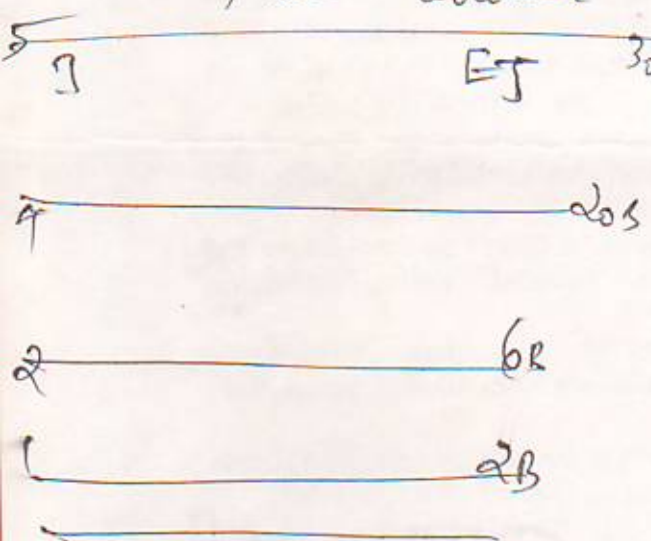
↳ can be written as

$$E_J = B J(J+1) \text{ cm}^{-1}$$

↳ rotational constant

$$B = \frac{h}{8\pi^2 I c}$$

The allowed rotational energy levels are



The difference in energy

Imagine a molecule to be in the $J=0$ state (ground rotational state) (no rotation occurs)

Let the incident radiation is absorbed and the molecule goes to $J=1$ state

$$E_{J=1} - E_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

$$\bar{\nu}_{1-0} = 2B \text{ cm}^{-1}$$

Left the molecules goes to $J=2$ state ⁽⁴⁾
to $J=1$ state

$$\begin{aligned} \bar{\nu}_{J=1 \rightarrow J=2} &= E_{J=2} - E_{J=1} \\ &= 6B - 2B = 4B \text{ cm}^{-1} \end{aligned}$$

In general, to raise the molecule from
 J state to $J+1$,

$$\begin{aligned} \bar{\nu}_{J \rightarrow J+1} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[J^2 + 3J + 2 - (J^2 + J)] \\ &= B(2J + 2) \\ &= 2B(J+1) \text{ cm}^{-1} \end{aligned}$$

The selection rule can be written
as $\Delta J = \pm 1$

Ans The first line ($J=0$) the rotational spectrum
of CO is 3.842 cm^{-1}

$$\bar{\nu}_{0 \rightarrow 1} = 3.842 = 2B(0+1) = 2B$$

$$\therefore B = 1.921$$

$$\begin{aligned} \therefore I &= \frac{h}{8\pi^2 Bc}, & I_{CO} &= \frac{6.626 \times 10^{-34}}{8\pi^2 \times 3 \times 10^{10} \times B} \\ &= 14.569 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

the masses of C, O are 19.921×10^{-27} , 26.561×10^{-27} (5)

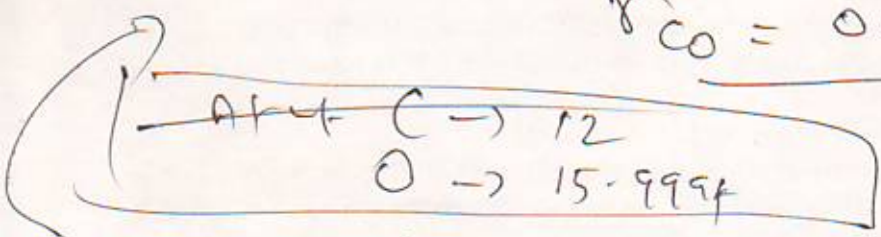
\therefore the reduced mass μ

$$= \frac{19.921 \times 26.561 \times 10^{-54}}{46.483 \times 10^{-27}} = 11.323 \times 10^{-27} \text{ kg}$$

$\mu r^2 = I$

$\therefore r^2 = \frac{I}{\mu} = 1.2799 \times 10^{-20} \text{ m}^2$

$r_{CO} = 0.1131 \text{ nm}$



1.673×10^{-27} (abs. mass of H atom with at wt 1.008)

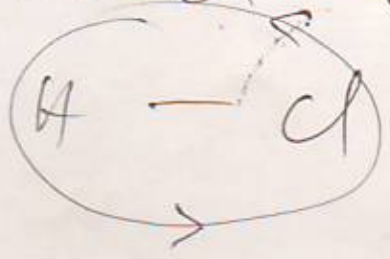
$$\frac{1.673 \times 10^{-27}}{1.008}$$

① Linear molecule \rightarrow HCl \rightarrow H — Cl
Rotation \rightarrow O — C — O

① $H \uparrow \text{Cl} \rightarrow m r^2 \rightarrow I_C$

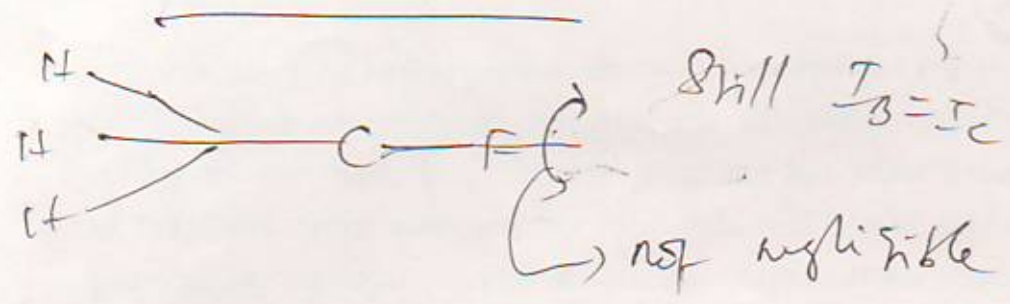
② $H - \text{Cl} \rightarrow I_A$

③ $H - \text{Cl} \rightarrow I_B$ $I_A \approx 0$



$I_B = I_C$

Q Symmetric tops.

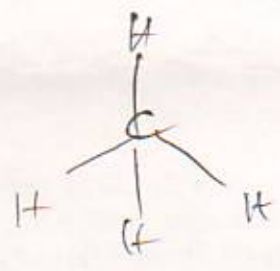


This is called symmetric top

$$I_B = I_C \neq I_A$$

$$I_A \neq 0$$

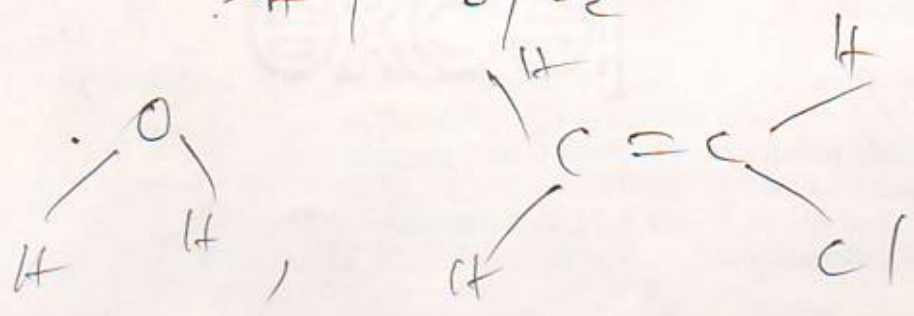
Q Spherical tops



$$I_A = I_B = I_C$$

Q Asymmetric tops.

$$I_A \neq I_B \neq I_C$$



Intensity of Spectral line

All the rotational spectral lines will not have equal intensities. This is due to the different populations of molecules in different levels. The first factor governing the population of the energy levels is Boltzmann distribution.

The lowest rotational energy level is $J=0$. Suppose there are N_0 molecules in the lower state, the no. of molecules in any higher state N_J is given by

$$\frac{N_J}{N_0} = \exp(-E_J/k_B T)$$

$$= \exp\left(-\left[-BhcJ(J+1)/k_B T\right]\right)$$

Let $B = 2 \text{ cm}^{-1}$

At RT, $T = 300\text{k}$

The population in $J=1$ state is

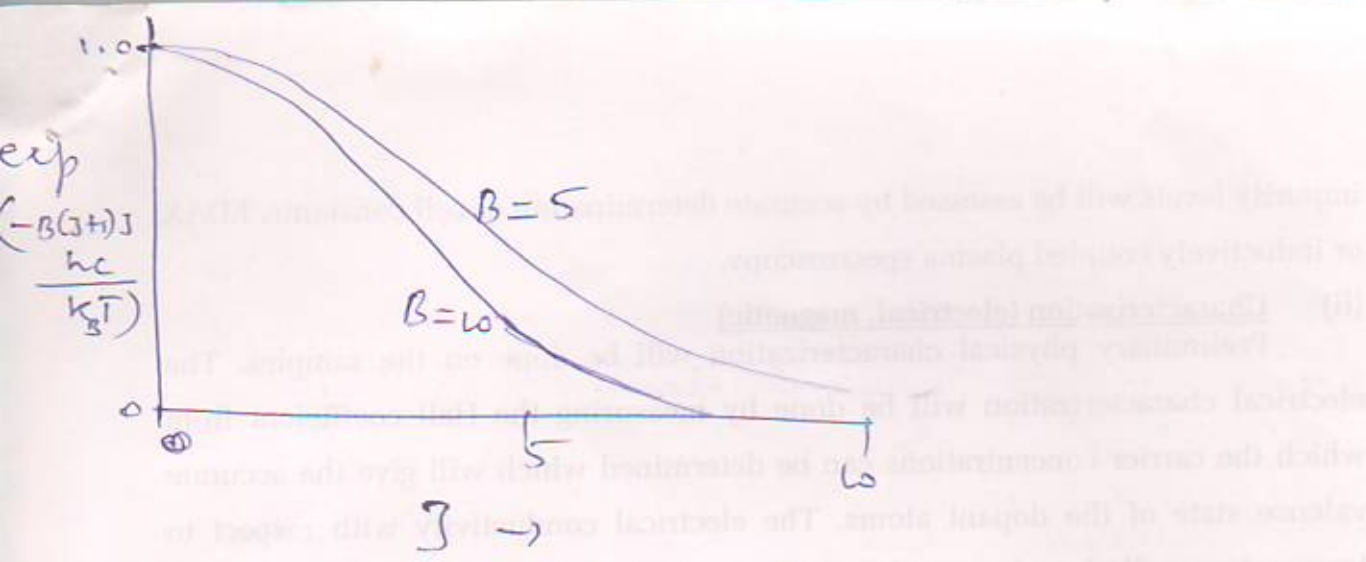
$$\frac{N_1}{N_0} = \exp\left(\frac{-2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right)$$

$$= \exp(-0.019) \approx 0.98$$

$N_1 = 0.98 N_0$

When B increases, $\frac{N_J}{N_0}$ decreases rapidly with T .

Qa



The Second factor ~~for the~~ which influences the intensity is the degeneracy in the energy states.

~~Degeneracy~~ Degeneracy is the existence of 2 or more energy states having the same energy.

In diatomic molecules degeneracy can be approached in terms of angular momentum.

The energy $E = \frac{1}{2} I \omega^2$

(momentum) $\vec{p} = I \omega$, rotational frequency

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

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

$2 I E = I^2 \omega^2$

$\sqrt{2 I E} = I \omega = \vec{p}$
 $\therefore \vec{p} = \sqrt{2 I E}$

$$2EI$$

$$\text{But } E = \frac{h^2}{8\pi^2 I} J(J+1)$$

3 a

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

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

$$P = \sqrt{2EI}$$

$$P^2 = 2EI$$

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

$$\vec{P} = \left(\frac{h}{4\pi} \right) \sqrt{J(J+1)}$$

↳ Fundamental unit of

$$\vec{P} = \sqrt{J(J+1)} \text{ angular momentum units}$$

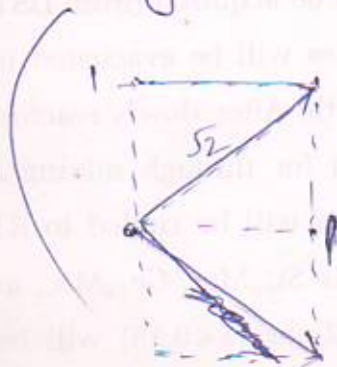
$P \rightarrow$ quantized

$\vec{P} \rightarrow$ vector

when $J=1$,

$$\vec{P} = \sqrt{1 \times 2} \text{ units} = \sqrt{2} = 1.414$$

Along a reference direction, \vec{P} can have only 3 values, with length 1.414



(If side is 1 unit, diagonal is $\sqrt{2}$ units)

Thus if $J=1$, the level is 3 fold degenerate
 for $J=2$, $\vec{P} = \sqrt{2 \times 3} = \sqrt{6}$

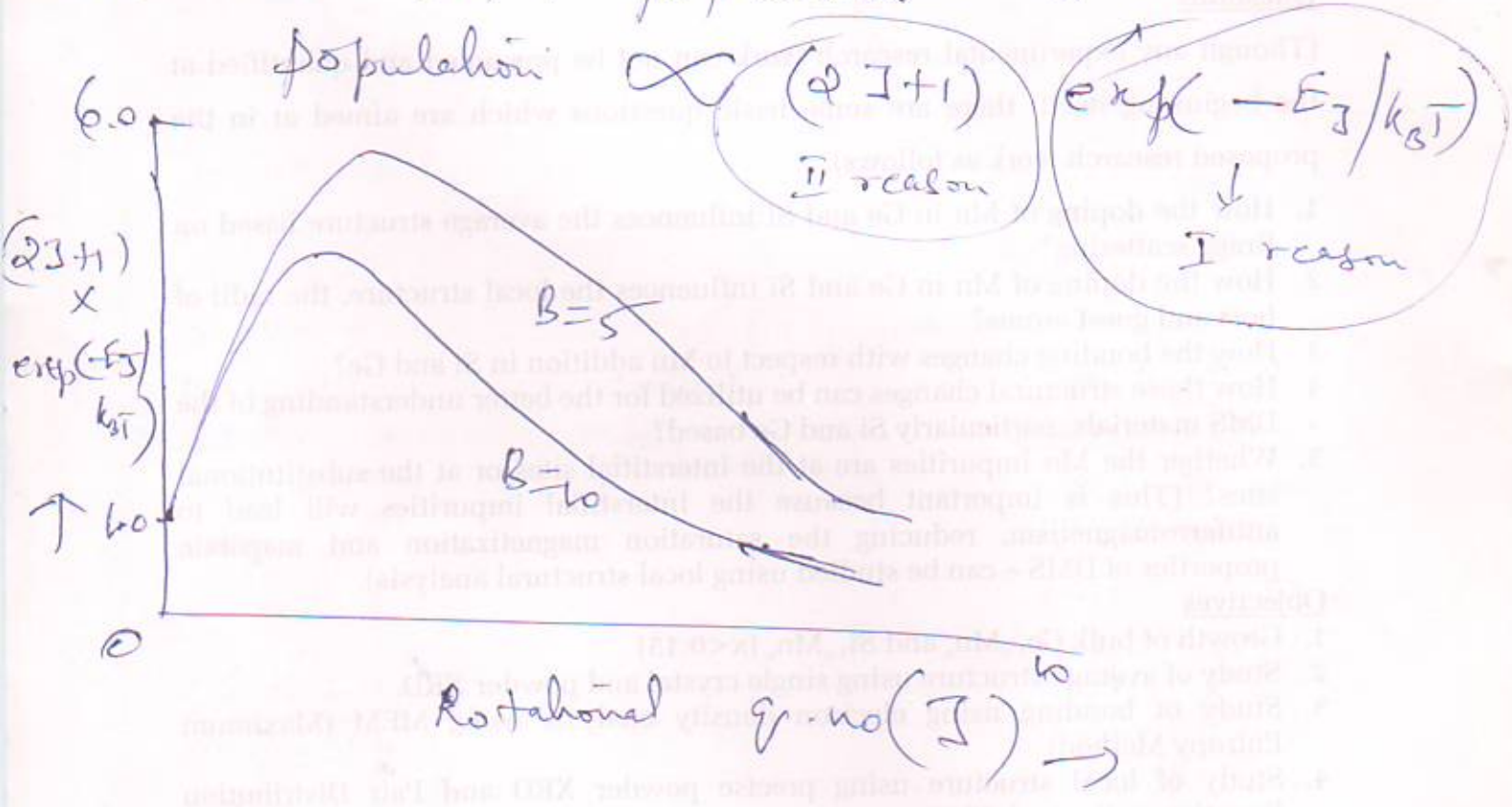
reference direction

(4) a

For $J=2$, the level is 5 fold degenerate.
In general, the energy levels are
 $(2J+1)$ fold degenerate.

The no. of degenerate levels
increases with J .

Thus the total population is



1.5. This is a very important and interesting topic. It will be covered in detail for this purpose. The next growth technique will be used using a high temperature furnace. Appropriate amounts of the elemental samples will be weighed accurately using the electronic balance to be accurate and the amount shown will be added with concentrations ranging from 0.01 to 0.1 mol % These samples will be loaded in