

* Difference between the levels:-

(i) $E_j = 0 \rightarrow J = 1$

$$\begin{aligned} &= B \times 1(1+1) \text{ cm}^{-1} - B \times 0(0+1) \text{ cm}^{-1} \\ &= 2B \text{ cm}^{-1} - 0 \\ &= 2B \text{ cm}^{-1} \end{aligned}$$

(ii) $E_j = 1 \rightarrow E_j = 2$

$$= 4B \text{ cm}^{-1}$$

(iii) $E_j = 2 \rightarrow E_j = 3$

$$= 6B \text{ cm}^{-1}$$

(iv) $E_j = 3 \rightarrow E_j = 4$

$$= 8B \text{ cm}^{-1}$$

(v) $E_j = 4 \rightarrow E_j = 5$

$$= 10B \text{ cm}^{-1}$$

(vi) $E_j = 5 \rightarrow E_j = 6$

$$= 12B \text{ cm}^{-1}$$

(vii) $E_j = 6 \rightarrow E_j = 7$

$$= 14B \text{ cm}^{-1}$$

Thus,

In general to raise the molecule from the state J to $J+1$, we would have —

$$E_j \rightarrow E_{j+1}$$

$$= B(J+1)(J+2) - BJ(J+1) \text{ cm}^{-1}$$

$$= B \left\{ (J^2 + 2J + J + 2) \right\} - BJ^2 - BJ$$

$$= B \left[\cancel{J^2} + 2J + \cancel{J} + 2 - \cancel{J^2} - \cancel{J} \right]$$

$$= B[2J+2] \text{ cm}^{-1}$$

$$\text{i.e. } E_j \rightarrow E_{j+1}$$

$$= 2B(J+1) \text{ cm}^{-1}$$

where, $J = 0, 1, 2, 3, 4$.

1st method

Problem :-

(i) The 1st line in the rotation spectrum of the CO is 3.84235 cm^{-1} .

Calculate —

(i) Bond distance of CO.

(ii) Reduced mass of CO.

(iii) Moment of inertia of CO.

Soln :-

$$E_j = 0 \rightarrow E_j = 1 = 3.84235 \text{ cm}^{-1}$$

$$\text{i.e. } 2B = 3.84235 \text{ cm}^{-1}$$

$$B = 1.921175 \text{ cm}^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} \text{ cm}^{-1} = \frac{6.624 \times 10^{-34} \text{ J sec}}{8 \times 3.14 \times 3.14 \times 1.921175 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm sec}^{-1}}$$

$$= 1.4570782 \times 10^{-46} \text{ J sec}^2$$

$$I = 1.4570782 \times 10^{-46} \text{ kg m}^2 \quad | \quad 1 \text{ J} = \text{kg m}^2 \text{ sec}^{-2}$$

$$M = \frac{12 \times 16}{12 + 16} \text{ amu}$$

$$= 6.85 \text{ amu} = 6.85 \times 1.67 \times 10^{-27} \text{ kg} = 1.14395 \times 10^{-26} \text{ kg}$$

$$(\text{amu} = 1.67 \times 10^{-27} \text{ kg})$$

$$I = Mr^2$$

$$r = \sqrt{\frac{I}{M}} = \sqrt{\frac{1.4570782 \times 10^{-46} \text{ kg m}^2}{1.14395 \times 10^{-26} \text{ kg}}}$$

$$r = \sqrt{\frac{1.4570 \times 10^{-20} \text{ m}^2}{1.14395}}$$

$$r = \sqrt{1.2737127 \times 10^{-20} \text{ m}^2}$$

$$r = 1.12 \times 10^{-10} \text{ m}$$

$$r = 1.12 \text{ \AA}$$

$$r = 0.112 \text{ nm}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ nm} = 10^9 \text{ m}$$

$$1 \text{ erg} = 9 \times 10^8 \text{ cm}^2 \text{ sec}^{-2} \quad | \quad 1 \text{ J} = \text{kg m}^2 \text{ sec}^{-2}$$

* Relative intensities of spectral lines:

we have $2J \rightarrow J+1 = 2B(J+1) \text{ cm}^{-1}$.

The relative intensities of spectral line depends upon -

(i) Transition probability -

(ii) Relative population of energy levels -

(i) Transition probability -

The transition probability of spectral line depends upon the relative probabilities of transition between the various energy levels. For instance, a molecule have more or less chance of making the transitions. viz $J=0 \rightarrow J=1$ and $J=1 \rightarrow J=2$. This calculation shows that a changes of -

$\Delta J = \pm 1$. is almost the same in all successive energy levels. Hence, Transition probability is governed by Selection rules.

(ii) Relative population of Energy levels :-

The relative population of energy level is governed by Boltzmann distribution law.

A/c to this -

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp \left(-\frac{\Delta E}{kT} \right)$$

where, $\Delta E = E_{\text{upper}} - E_{\text{lower}}$

T. = temperature in Kelvin scale

k = universal constant.

We know that -

The lowest rotational energy level is zero.

since $J=0$.

So, if No molecule is present in this state (i.e.

lowest energy level then the number in any higher state is given by -

$$\frac{N_J}{N_0} = \exp\left(-E_J/kT\right)$$

$$= \exp\left[-\frac{Bhc J(J+1)}{kT}\right]$$

where, $c = 3 \times 10^{10} \text{ cm sec}^{-1}$ $h = 6.634 \times 10^{-34} \text{ J sec.}$

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

$$T = 300 \text{ K}$$

$$J = 1.$$

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

$$= \exp(-0.019)$$

$$\boxed{\frac{N_1}{N_0} \approx 0.98.}$$

~~The~~

2nd
method

Q. The first line in the rotation spectrum of the CO is 3.84235 cm^{-1}

- calculate — (i) bond distance (r)
(ii) reduced mass (μ)
(iii) moment of inertia (I)

Soln —

$$E_j = 0 \rightarrow E_j = 2 = 3.84235 \text{ cm}^{-1}$$

$$2B = 3.84235 \text{ cm}^{-1}$$

$$B = 1.921175 \text{ cm}^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.624 \times 10^{-27} \text{ erg sec}}{8 \times 3.14 \times 3.14 \times 1.921175 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm}^{-1} \text{ sec}^{-1}}$$

$$= \frac{6.624 \times 10^{-27} \text{ erg sec}^2}{454.60842 \times 10^{10}}$$

$$= \frac{6.624 \times 10^{-37} \text{ erg sec}^2}{454.60842}$$

$$= \frac{6.624 \times 10^{-39} \text{ erg sec}^2}{4.5460}$$

$$I = 1.4571051 \times 10^{-39} \text{ erg sec}^2$$

$$1 \text{ erg} = \text{gm cm}^2 \text{ sec}^{-2}$$

$$I = 1.4571051 \times 10^{-39} \text{ gm cm}^2 \text{ sec}^2 \text{ sec}^2$$

$$I = 1.4571051 \times 10^{-39} \text{ gm cm}^2$$

$$\mu = \frac{12 \times 16}{12+16} \text{ amu} = \frac{192}{28} \text{ amu} = 6.857 \text{ amu}$$

$$1 \text{ amu} = 1.67 \times 10^{-27} \text{ kg} = 1.67 \times 10^{-24} \text{ gm} = 685 \times 1.67 \times 10^{-24} \text{ gm}$$
$$= 1.14395 \times 10^{-23} \text{ gm}$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.4571051 \times 10^{-39} \text{ gm cm}^2}{1.14395 \times 10^{-23} \text{ gm}}}$$

$$r = 1.12 \text{ \AA} \quad [1 \text{ \AA} = 10^{-8} \text{ cm}]$$

$$r = 0.112 \text{ nm} \quad [1 \text{ nm} = 10^{-7} \text{ cm}]$$

$$= \sqrt{\frac{1.4571051 \times 10^{-39} \text{ gm cm}^2}{1.14395}}$$

$$r = \sqrt{1.2737489 \times 10^{-16} \text{ cm}^2}$$

$$r = 1.12 \times 10^{-8} \text{ cm}$$

Q. The HCl molecule in the gaseous state shows pure rotational line. Its following frequency (cm^{-1}) 20.7, 41.5, 62.0, 83.0 & 103.8. Assign these lines to the rotational transitions -

$J \rightarrow J+1$ from the absorption spectrum calculate the bond distance of HCl - ?

<u>Soln</u>	$J=0 \rightarrow J=1$	20.7 cm^{-1}	$\Delta J = J_2 - J_1 = 41.5 - 20.7 = 20.8 \text{ cm}^{-1}$
	$J=1 \rightarrow J=2$	41.5 cm^{-1}	$\Delta J = J_3 - J_2 = 62.0 - 41.5 = 20.5 \text{ cm}^{-1}$
	$J=2 \rightarrow J=3$	62.0 cm^{-1}	$\Delta J = J_4 - J_3 = 83.0 - 62.0 = 21 \text{ cm}^{-1}$
	$J=3 \rightarrow J=4$	83.0 cm^{-1}	$\Delta J = J_5 - J_4 = 103.8 - 83.0 = 20.8 \text{ cm}^{-1}$
	$J=4 \rightarrow J=5$	103.8 cm^{-1}	

$$\text{Average spacing} = \frac{20.8 + 20.5 + 21 + 20.8}{4} \text{ cm}^{-1}$$

$$= 20.775 \text{ cm}^{-1}$$

$$2B = 20.775 \text{ cm}^{-1}$$

$$B = 10.38 \text{ cm}^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.624 \times 10^{-34} \text{ J sec}}{8 \times 3.14 \times 3.14 \times 10.38 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm}^{-1} \text{ sec}^{-1}}$$

$$I = 2.698 \times 10^{-47} \text{ J sec}^2$$

$$I = 2.698 \times 10^{-47} \text{ kg m}^2$$

$$\mu = \frac{35.5 \times 1}{35.5 + 1} \text{ amu}$$

$$= \frac{35.5}{36.5} \text{ amu}$$

$$= 0.972 \text{ amu}$$

$$= 0.972 \times 1.67 \times 10^{-27} \text{ kg}$$

$$\mu = 1.624 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2 = \frac{2.698 \times 10^{-47} \text{ kg m}^2}{1.624 \times 10^{-27} \text{ kg}}$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.698 \times 10^{-47} \text{ kg m}^2}{1.624 \times 10^{-27} \text{ kg}}}$$

$$r = 1.29 \text{ \AA}$$

$$r = 0.129 \text{ nm}$$

$$r = \sqrt{1.659 \times 10^{-20} \text{ m}^2} = 1.29 \times 10^{-10} \text{ m}$$

$$r = 1.29 \times 10^{-10} \text{ m}$$