**Types of molecules exhibiting rotational spectra :-** For observing the pure rotational spectrum of a molecule the molecule must possess permanent dipole moment so that it can interact with electromagnetic radiation & absorb or emit a photon. Thus pure rotational spectrum is given by polar molecules. Consequently homonuclear diatomic molecule (like $H_2$, $N_2$, $O_2$ etc) & symmetrical linear molecule like $CO_2$ or $C_6H_6$ do not give rotational spectra. Thus polar molecules like $H_2O$, NO, $N_2O$, $C_6H_5Cl$ give pure rotation spectra.

**NOTE :-** heteronuclear diatomic molecules like NO, CO, CN etc. always give pure rotational spectra as they have permanent dipole moment.

**Application of Microwave spectroscopy :-** By determining the frequency separation $\Delta\bar{\nu}$, it is possible to calculate the moment of inertia $I$ of molecule using $\bar{B} = \frac{h}{8\pi^2 I c}$. Then knowing the masses of atoms present in diatomic molecule, it is possible to calculate distance b/w the atoms $r_0$ (i.e. internuclear distance or bond length)

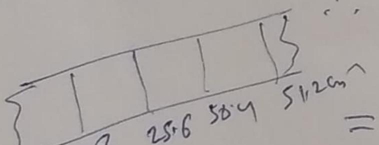
**Num :-** The microwave spectrum of HI consists of equally spaced lines with $\Delta\bar{\nu} = 12.8\ cm^{-1}$. What is
a) moment of inertia & b) the internuclear distance?

Sol$^n$

$$\Delta\bar{\nu} = 12.8\ cm^{-1} = 12.8 \times 100\ m^{-1} = 1280\ m^{-1}$$

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

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




$$= \frac{6.626 \times 10^{-34}}{4 \times (3.14)^2 \times 3 \times 10^8 \times 1280} = \frac{6.626 \times 10^{-34}}{151443.46 \times 10^8}$$

$$= \frac{6.626 \times 10^{-34}}{1.51 \times 10^{13}} = 4.388 \times 10^{-47}\ kg\ m^2$$

Now $m_H = 1\ g\ mol^{-1} = 1 \times 1.67 \times 10^{-27}\ kg$

$m_I = 126.9\ g\ mol^{-1} = 126.9 \times 1.67 \times 10^{-27}\ kg$

since $I = \mu r_0^2$ $\qquad \mu = \frac{m_H m_I}{m_H + m_I}$

$$\mu = \left(\frac{1 \times 126.9}{1 + 126.9}\right) \times 1.67 \times 10^{-27}\ kg$$

$$= \frac{126.9}{127.9} \times 1.67 \times 10^{-27}\ kg$$

$$= 1.66 \times 10^{-27}\ kg$$

$$\therefore \quad r^2 = \frac{I}{\mu} = \frac{4.388 \times 10^{-47}\ kg\,m^2}{1.66 \times 10^{-27}\ kg}$$

$$r^2 = 2.643 \times 10^{-20}\ m^2$$

$$r = 1.62 \times 10^{-10}\ m = 0.162\ nm$$

Num :- The Internuclear distance (i.e. bond length) of carbon monoxide molecule is 1.13 Å. Calculate the energy (in joules & eV) & angular velocity of this molecule in the first excited rotational level. The atomic masses are $^{12}C = 1.99 \times 10^{-26}$ kg & $^{16}O = 2.66 \times 10^{-26}$ kg

Sol :-

$$r = 1.13\,\text{Å} = 1.13 \times 10^{-10}\ m$$

$$\mu = \frac{m_c m_o}{m_c + m_o} = \frac{1.99 \times 10^{-26} \times 2.66 \times 10^{-26}}{(1.99 + 2.66) \times 10^{-26}}\ kg$$

$$= \frac{5.293}{4.65} \times 10^{-26} = 1.14 \times 10^{-26}\ kg$$

$$\therefore \quad I = \mu r^2 = 1.14 \times 10^{-26}\ kg \times (1.13 \times 10^{-10}\ m)^2$$

$$= 1.46 \times 10^{-46}\ kg\,m^2$$

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

for the first excited rotation level $J = 1$

$$\therefore \quad E = \frac{(6.626 \times 10^{-34})^2}{8 \times (3.14)^2 \times 1.46 \times 10^{-46}} (1)\cancel{(1+1)}$$

$$= \frac{(6.626 \times 10^{-34})^2}{5.758 \times 10^{-45}} = 7.625 \times 10^{-68} \times 10^{45}$$

$$= 7.625 \times 10^{-23}\ J$$

since $1\ eV = 1.61 \times 10^{-19}\ J$

$$\therefore \quad E = \frac{7.625 \times 10^{-23}}{1.61 \times 10^{-19}}\ eV = 4.74 \times 10^{-4}\ eV$$

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

$$\therefore \quad \omega = \sqrt{\frac{2E}{I}} = \sqrt{\frac{2 \times 7.625 \times 10^{-23}}{1.46 \times 10^{-46}}}$$

$$= \sqrt{\frac{1.52 \times 10^{-22}}{1.46 \times 10^{-46}}} = \sqrt{1.04 \times 10^{24}}\ rad\ s^{-1}$$

$$= 1.01 \times 10^{12}\ rad\ s^{-1}$$

(8)

Num :- The pure rotational (microwave) spectrum of gaseous molecule CN consists of a series of equally spaced lines separated by 3.7978 $cm^{-1}$. Calculate internuclear distance of the molecule. The molar masses are $^{12}C = 12.011$ & $^{14}N = 14.007$ g $mol^{-1}$

Sol :- given $\Delta\bar{\nu} = 2\bar{B} = 3.7978\ cm^{-1} = 3.7978 \times 100\ m^{-1}$

$= 379.78\ m^{-1}$

$\therefore \bar{B} = \frac{379.78}{2} m^{-1} = 189.89\ m^{-1}$

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

or $I = \frac{h}{8\pi^2 c \bar{B}} = \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 3 \times 10^8 \times 189.89}$

$= \frac{6.626 \times 10^{-34}}{4.493 \times 10^{12}} = 1.475 \times 10^{-46}\ kg\,m^2$

$\mu = \frac{m_c m_N}{m_c + m_N} = \frac{12.011 \times 14.007}{12.011 + 14.007}$ g $mol^{-1}$

$= \frac{168.238}{26.018} = 6.466$ g $mol^{-1}$

$= \frac{6.466 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.074 \times 10^{-23}$ g

$= 1.074 \times 10^{-26}$ kg

since $I = \mu r^2 \therefore r = \sqrt{\frac{I}{\mu}}$

$r = \sqrt{\frac{1.475 \times 10^{-46}}{1.074 \times 10^{-26}}} = \sqrt{1.373 \times 10^{-20}}$

$= 1.17 \times 10^{-10}$ m

$= 0.117$ nm

Num :- The pure rotational spectrum of $H^{35}Cl$ gas consists of series of equally spaced lines separated by 20.80 $cm^{-1}$. Calculate internuclear distance of molecule.

Sol :- here $\Delta\bar{\nu} = 2\bar{B} = 20.80\ cm^{-1} = 20.80 \times 100\ m^{-1}$

$2\bar{B} = 2080\ m^{-1}$

$\therefore \bar{B} = \frac{2080}{2} = 1040\ m^{-1}$

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

$$\therefore I = \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 3 \times 10^8 \times 1040}$$

$$= \frac{6.626 \times 10^{-34}}{2.46 \times 10^{13}} = 2.693 \times 10^{-47}\ kg\,m^2$$

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1.0)(35.0)}{(1+35.0)}\ g\,mol^{-1}$$

$$= 0.9722\ g\,mol^{-1} = \frac{0.9722\ g\,mol^{-1}}{6.022 \times 10^{23}\ mol^{-1}}$$

$$= 0.1614 \times 10^{-23}\ g = 1.614 \times 10^{-27}\ kg$$

since $I = \mu r^2$ $\quad r = \sqrt{\frac{I}{\mu}}$

$$r = \sqrt{\frac{2.693 \times 10^{-47}}{1.614 \times 10^{-27}}} = \sqrt{1.668 \times 10^{-20}}$$

$$= 1.29 \times 10^{-10}\ m = 0.129\ nm$$

$$129 \times 10^{-12}\ m = 129\ pm$$

Limitation of Rotational Spectra to structure Determination:-

The studies of Rotational spectra should be made on the substance in gaseous state since in such a state rotation is free. The molecules ~~as stated~~ which possess permanent dipole moment can only be studied. Homonuclear diatomic molecules like $H_2$, $Cl_2$, $N_2$, $O_2$ etc. & linear polyatomic molecules like $CO_2$, $SO_2$ etc. do not show rotational spectra. Since polyatomic linear molecule have several Internuclear distances these quantities cannot be determined from their single values of moment of Inertia.

→ Another statement of numerical :-

Num:- The lines in the far IR spectrum of HCl are positioned at the following wave numbers:

| Line No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $\bar{\nu}_{rot}$ ($cm^{-1}$) | 85.384 | 106.730 | 128.076 | 149.422 | 170.768 | 192.114 |

Find the average value of moment of Inertia & bond length of HCl.