Rotational Spectra of Diatomic molecules

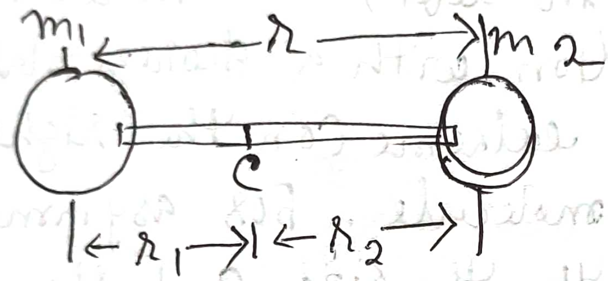

Figure A rigid diatomic molecule treated as two masses m_1 and m_2, joined by a rigid bar of length $r_0 = r_1 + r_2$

A rotating diatomic molecule may be treated as a rigid rotator with a fixed internuclear distance. The rotational energy of a rigid diatomic molecule is quantized and its value is

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

where J is the rotational quantum number having integral values 0, 1, 2 ... and I is the moment of Interita of a molecule, defined as

$$I = \mu r^2$$

where, μ is the reduced mass defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Now equtioon ① can be written as in wavenumber (cm^{-1})

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

$$F(J) = BJ(J+1)\ cm^{-1} \quad \text{where } B = \frac{h}{8\pi^2 Ic}$$

$$J = (0, 1, 2 \ldots)$$

where c is the velocity of light is expressed in $cm\,s^{-1}$.

B is a constant and is known as rotational constant. B is always expressed in units of cm^{-1}.

F(J) is called rotational term.

Rotational selection rule

From quantum mechanical studies it was found that a pure rotational spectrum would be observed only in molecules which possess a permanant dipole moment. That is, the molecule mu[st] be polar in order to produce a rotational spectrum. Since homonuclear diatomic molecules, such as H_2, O[$_2$] [e]tc. possess no dipole moment, they donot show pure rotational spectra.

Selection rule for rotational transitions

$$\boxed{\Delta J = \pm 1}$$

The transition $\Delta J = +1$ corresponds to absorption and the transition $\Delta J = -1$ corresponds to emission.

Transition from J to J+1 level

$$F(J+1) - F(J) = [B(J+1)(J+2) - B(J+1)]$$

$$\bar{\nu}_{(J \to J+1)} = 2B(J+1) \quad \text{——— (1)}$$

$\bar{\nu}_{(J \to J+1)}$ is the difference in wave numbers of the two states and $J = 0, 1, 2$.

2B, 4B, 6B, 8B etc.

Thus the difference (spacing) between two adjacent lines will be 2B.

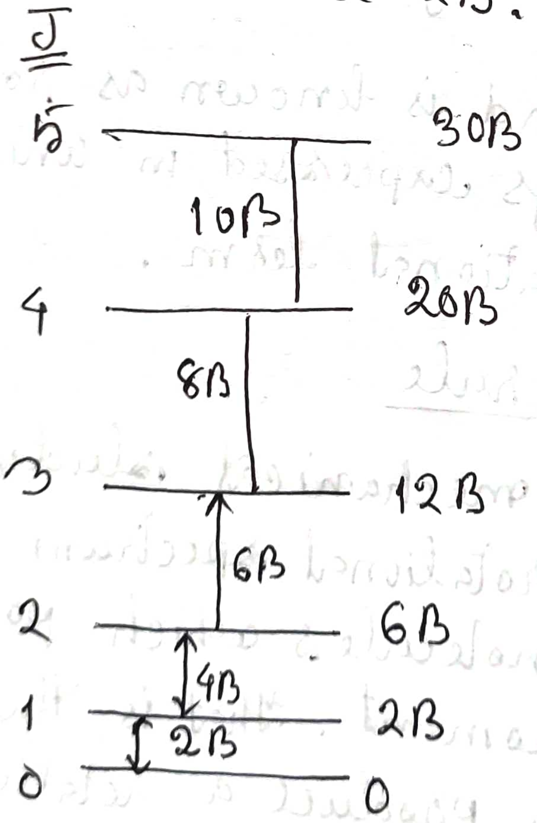

Fig:

Determination of Inter nuclear Distance

The analysis of rotational spectra can give accurate values for the moment of inertia and hence the inter-nuclear distance

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

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

$$\Rightarrow \mu r^2 = \frac{h}{8\pi^2 B c}$$

$$\boxed{r = \left[\frac{h}{8\pi^2 B c \mu}\right]^{1/2}}$$

Q. Calculate the reduced mass and the moment of inertia of $D^{35}Cl$ molecule using the inter-nuclear distance of 0.1275 nm (Given $^{35}Cl = 34.97\mu$ and that of $D = 2.014\mu$)

Ans Reduced mass $= \frac{m_D m_{cl}}{[m_D + m_{cl}]}$

$$= \frac{[2.014 \times 10^{-3}\ kg\ mol^{-1}]\ [34.97 \times 10^{-3}\ kg\ mol^{-1}]}{(2.014 + 34.97) \times 10^{-3}\ kg\ mol^{-1}\ (6.02 \times 10^{23}\ mol^{-1})}$$

$$= 3.162 \times 10^{-27}\ kg$$

Moment of inertia $I = \mu r^2$

$$= [3.162 \times 10^{-27}\ kg]\ [0.1275 \times 10^{-9}\ m]^2$$

$$= 5.141 \times 10^{-47}\ kg\ m^2$$

Q. The rotational spectrum of HCl molecules shows that the rotational lines are equally separated by 20.70 cm^{-1}. Calculate the internuclear bond length.

Since $2B = 20.70\ cm^{-1}$

$B = 10.35\ cm^{-1} = 10.35 \times 10^{2}\ m^{-1}$

Reduced mass $\mu = \frac{m_H\, m_{Cl}}{[m_H + m_{Cl}]}$

$m = \frac{\text{at mass}}{\text{avd no}}$ in kg

$= \frac{[1.0\ gm\ mol^{-1}][35.46\ gm\ mol^{-1}]}{[1+35.46]\ gm\ mol^{-1}\ [6.023 \times 10^{23}\ mol^{-1}]}$

$= \frac{[1 \times 10^{-3}\ kg\ mol^{-1}][35.46 \times 10^{-3}\ kg\ mol^{-1}]}{[1+35.46] \times 10^{-3}\ kg\ mol^{-1}]\ [6.023 \times 10^{23}\ mol^{-1}]}$

$= 1.627 \times 10^{-27}\ kg$

$$r = \left[\frac{6.627 \times 10^{-34}\ Js}{8\pi^2 (1.627 \times 10^{-27}\ kg)(3.0 \times 10^{8}\ ms^{-1})(10.35 \times 10^{2}\ m^{-1})} \right]^{1/2}$$

$= 0.129 \times 10^{-9}\ m = 0.129\ nm$