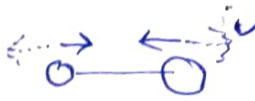
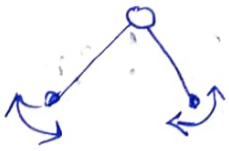
Lec 11

Molecular spectra

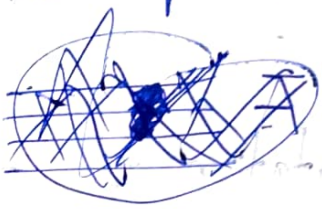
In case of molecules, (1) the vibration





Gives rise to

→ Vibrational energy which is also quantized (Quantum Mechanics)



$\updownarrow \Delta E = \frac{hc}{\lambda}$

$\lambda \sim$ Infra-red order of ~~$\lambda \sim 1\,\mu m$~~

~~$100\,\mu m \leq \lambda \leq 1\,\mu m$~~

$1\,\mu m \lesssim \lambda \lesssim 100\,\mu m$

(2) the rotation gives rise to rotational energy which is also quantized (Quantum Mechanics)

The separations are of the order corresponding to microwave

$\sim 100\,\mu m < \lambda < \sim 1\,cm$

Molecular spectroscopy

MICROWAVE SPECTROSCOPY

$100\,\mu m \lesssim \lambda \lesssim 1\,cm$

Deals with rotation of molecules

Rotation of three-dimensional body is quite complex. ⟹ Described by three principal axes of rotation

⇓

three principal moments of inertia

I_A, I_B, I_C

Different cases

1. Linear molecules :

Atoms are arranged in a straight line

Eg: H — Cl Hydrogen chloride

O — C — S Carbon oxysulphide

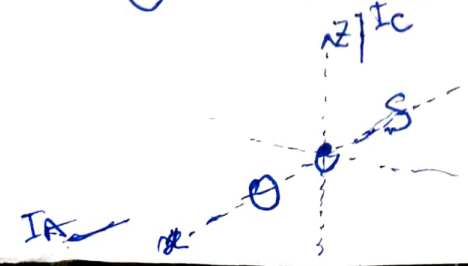


Fig 1

Three directions of rotation maybe taken as

(a) about the bond axis [x-axis in fig 1]

(b) end-over-end rotation in x-y plane

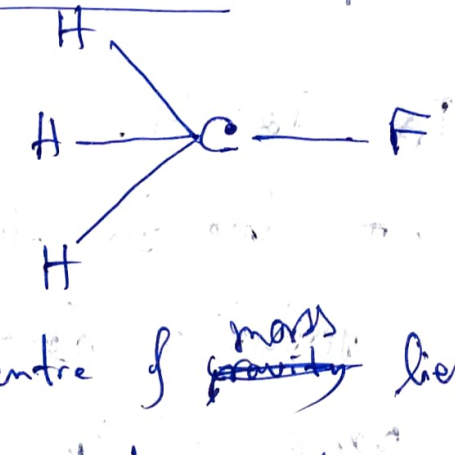
(c) end-over-end rotation in x-z plane.

Moment of inertia for (b) & (c) are same (See the symmetry) $\Rightarrow I_B = I_C$

For linear molecule $I_A = 0$

2. Symmetric tops

(i) prolate



methyl fluoride

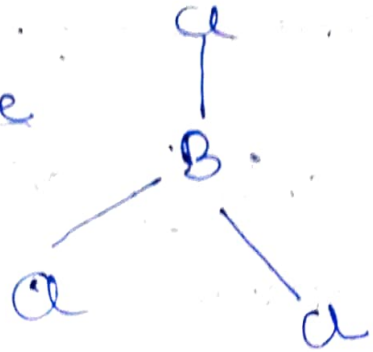
tetrahedral

The centre of ~~gravity~~ mass lies along C-F bond, we take this as main axis (A)

However $I_A \neq 0$ because of massives hydrogens rotates being away from centre of mass.

$\therefore$ $I_B = I_C \neq I_A$ $\quad I_A \neq 0$

(ii) Oblate

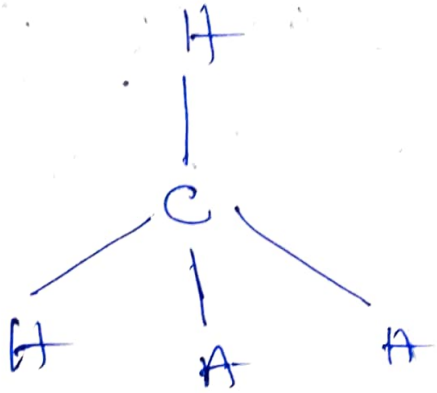


(planar)

boron trichloride

$I_A = 2I_B = 2I_C$

3. Spherical tops



Methane

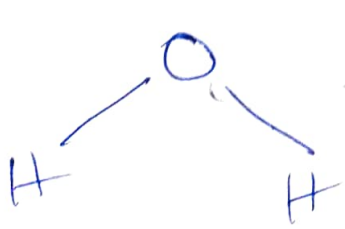
$I_A = I_B = I_C$

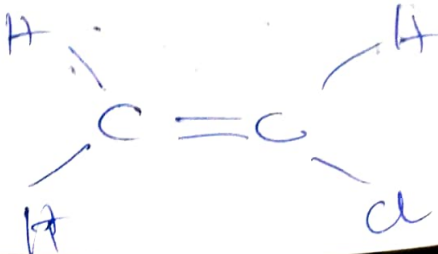
No dipole ment due to their symmetry ⇒ rotation alone can't produce dipole change ⇒ No rotational spectra

4. Asymmetric tops

$I_A \neq I_B \neq I_C$

water



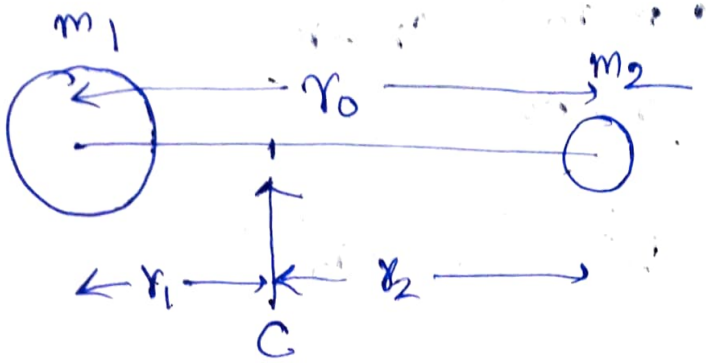


Vinyl chloride

Rotational spectra for diatomic molecules

↓ rigid

r_0 is fixed.



C denote center of mass.

$r_0 = r_1 + r_2$

Consider end-over-end rotation about point C

$$m_1 r_1 = m_2 r_2$$

The moment of inertia about C,

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

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

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

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

$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$

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

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

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

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

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2 \rightarrow = \mu r_0^2$$

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

Quantum Mechanics calculation can show that rotational energy levels for rigid diatomic molecule

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \qquad J = 0, 1, 2, \ldots$$

J rotational quantum number.

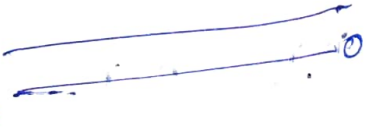
~~Name number~~ ~~$E = h\nu$~~ Energy in unit of ~~hc~~

$J = 0$ $E_0 = 0$

$J = 1$ $E_1 = \frac{h^2}{8\pi^2 I} 2$

$J = 2$ $E_2 = \frac{h^2}{8\pi^2 I} 6$

$J = 3$ $E_3 = \frac{h^2}{8\pi^2 I} 12$



$0 \rightarrow 1$ transition by absorbing radiation.

the wave number of the radiation should be

$$\bar{\nu}_{0\to1} = \frac{E_1 - E_0}{hc} = \frac{h}{8\pi^2 I c} 2 = 2B$$

$$B \equiv \frac{h}{8\pi^2 I c}$$ called rotational constant.

$$\bar{\nu}_{1-2} = \frac{E_2 - E_1}{hc} = B\left[2(2+1) - 1(1+1)\right]$$

$$= 4B$$

$$\bar{\nu}_{J \to J+1} = B\left[(J+1)(J+1+1) - J(J+1)\right]$$

$$= B\left[J^2 + 3J + 2 - J^2 - J\right]$$

$$= 2B(J+1)$$

Selection rule $\Delta J = \pm 1$

Another important fact

The molecule must be heteronuclear.

For homonuclear, there will be no dipole component change during rotation $\Rightarrow$ no interaction with radiation.

H.W. The 1st line in rotation spectra of CO is 3.84235 cm^{-1} Find out the moment of inertia.

$$\bar{\nu}_{0\to 1} = 2B = 2\times\frac{h}{8\pi^2 I c}$$

$$I_{CO} = \frac{h}{8\pi^2 c\,\bar{\nu}_{0\to 1}} = 1.456\times 10^{-46}\ kg\,m^2$$

Knowing the relative atomic weights

$$C = 12.0000$$

$$O = 15.9994$$

$$\mu \simeq \frac{12\times 15.9994}{12+15.9994}\times 1.6734\times 10^{-27}\ kg$$

$$\simeq 1.1\times 10^{-26}\ kg$$

$$r_0^2 = \frac{I_{CO}}{\mu} \quad \therefore r_0 = r_{CO} = 0.1131\ nm$$

(bond length)