* Classification of Poly atomic molecule :—

The rotation of a three dimensional body is resolved in to rotational components about three mutually perpendicular directions through the centre of gravity i.e. the principal axis of rotation. Thus a body has three moments of inertia. I_A, I_B & I_C. The three directions of rotations are—

1. About the bond axis—
2. End-over-end rotation in the plane of paper—
3. End-over-end rotation at right angle to the plane—

Molecules are classified in to groups a/c to the relative values of the three moments of inertia which depend upon the shape of the molecule.

I_c = about c-axis → about which the moment of inertia has maximum value.

I_a = about a-axis → about which the moment of inertia has minimum value.

(1). Linear Molecules:—

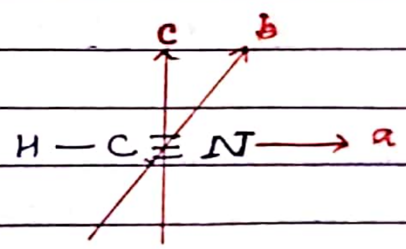
$I_c = I_b > I_a = 0$

$I_c = I_b$

$I_b > I_a$

$I_a = 0$

eg— HCN



b and c may be in any direction which is perpendicular to the inter nuclear axis. Considering the nuclei as point masses on the 'a' axis, I_a must be zero. Since all r_i are zero.

Examples — H–Cl, OCS etc.

(2). Symmetric tops or symmetric rotors :–

(1) $I_c > I_b = I_a$ (oblate symmetric tops)

eg – C_6H_6, CH_3F etc.

(2). $I_c = I_b > I_a \neq 0$ (Prolate symmetric rotor)

eg – CH_3I.

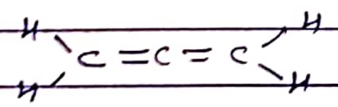
Heavy Iodine nucleus makes no contribution to I_a. So having small value.

A symmetric rotor must have a C_n axis with $n \geq 2$ or an S_4-axis.

CH_3I — C_3 axis

C_6H_6 — C_6 axis

Allene — S_4 axis



(3). Spherical rotors OR tops :–

All three moments of inertia are equal. i.e.

$I_a = I_b = I_c$

eg – CH_4, SF_6 molecules belonging to T_d OR O_h point groups are spherical rotors.

(4). Assymmetric top molecules:-

Majority of molecules belonging to this class -
where, $I_a \neq I_b \neq I_c$

eg:-
acrolein, Perazine etc.

* Linear Molecules:-

characteristics:-

(1). Isotopic substitution does not lead to a dipole moment. as well as inter nuclear distance.
Let us an example of CO_2.

$^{16}O = C = {}^{16}O$ & $^{16}O = C = {}^{18}O$

Thus these two are microwave -inactive.

On the other hand another example is taken -

O —— C —— S

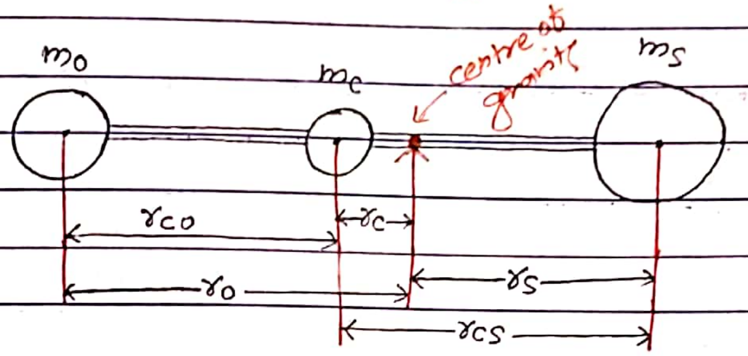
This molecule possess a dipole moment because the inter nuclear distance of OC is different from CS. Hence $\mu > 0$.
So, This molecule is microwave active.

(2). End-over-end rotation in polyatomic molecules is higher than that of diatomic molecules. So, moment of inertia is higher & hence B is smaller for polyatomic molecules. So, rotational lines are closely spaced in poly atomic linear molecules than in diatomic molecules.

(3). Problem:- How we get the moment of inertia OR Inter nuclear distance between CO & CS in OCS molecule by the help of microwave analysis?

Sol:-

***. Bond length of OCS molecule:-**



r_O, r_C & r_S represents the distance of respective atoms from centre of gravity.

Consideration of moments gives:-

$$m_O r_O + m_C r_C = m_S r_S \quad \text{———} \quad (1)$$

The moment of Inertia is given by-

$$I = m_O r_O^2 + m_C r_C^2 + m_S r_S^2 \quad \text{———} \quad (2).$$

Here,

$$\left.\begin{aligned} r_O &= r_{CO} + r_C \\ \& \quad r_S &= r_{CS} - r_C \end{aligned}\right\} \quad \text{———} \quad (3).$$

Putting the value of equation-(3) in equation-(1) we get-

$$m_O(r_{CO} + r_C) + m_C r_C = m_S(r_{CS} - r_C)$$

or $m_O r_{CO} + m_O r_C + m_C r_C = m_S r_{CS} - m_S r_C$

or $m_O r_C + m_C r_C + m_S r_C = m_S r_{CS} - m_O r_{CO}$

or $(m_O + m_C + m_S) r_C = m_S r_{CS} - m_O r_{CO}$

or $M r_C = m_S r_{CS} - m_O r_{CO}$ ——— (4)

$$r_C = \frac{m_S r_{CS} - m_O r_{CO}}{M} \quad \text{———} \quad (5)$$

where $M = (m_o + m_c + m_s)$.

From equation — (2) we calculate moment of Inertia -

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2$$

$$\approx I = m_o (r_{co} + r_c)^2 + m_c r_c^2 + m_s (r_{cs} - r_c)^2$$

$$= m_o (r_{co}^2 + r_c^2 + 2 r_{co} r_c) + m_c r_c^2 + m_s (r_{cs}^2 + r_c^2 - 2 r_{cs} r_c)$$

$$= m_o r_{co}^2 + m_o r_c^2 + 2 m_o r_{co} r_c + m_c r_c^2 + m_s r_{cs}^2 + m_s r_c^2 - 2 m_s r_{cs} r_c$$

$$= m_o r_{co}^2 + m_s r_{cs}^2 + (m_o r_c^2 + m_s r_c^2 + m_c r_c^2) + (2 m_o r_{co} r_c - 2 m_s r_{cs} r_c)$$

$$= m_o r_{co}^2 + m_s r_{cs}^2 + r_c^2 (m_o + m_c + m_s) + 2 r_c (m_o r_{co} - m_s r_{cs})$$

$$I = m_o r_{co}^2 + m_s r_{cs}^2 + r_c^2 M + 2 r_c (m_o r_{co} - m_s r_{cs}) \quad \text{—— (6)}$$

on putting the value of r_c in equation — (6) from equation — (5) we get -

$$I = m_o r_{co}^2 + m_s r_{cs}^2 + \frac{(m_s r_{cs} - m_o r_{co})^2}{M^2} \times M$$

$$+ 2 \left\{ \frac{m_s r_{cs} - m_o r_{co}}{M} \right\} (m_o r_{co} - m_s r_{cs})$$

$$= m_o r_{co}^2 + m_s r_{cs}^2 + \frac{(m_s r_{cs} - m_o r_{co})^2}{M}$$

$$- \frac{2 (m_s r_{cs} - m_o r_{co})^2}{M}$$

$$= m_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_s r_{cs} - m_o r_{co})^2}{M} \quad \text{—— (7)}$$

From eqⁿ – (7) r_{co} & r_{cs} are not known. In order to determine their value a similar expression for the moment of Inertia I' of another isotopic speises $O^{16}\ C^{12}\ S^{34}$ is obtained.

i.e. $$I' = m_o r_{co}^2 + m_s' r_{cs}^2 - \frac{(m_s' r_{cs} - m_o r_{co})^2}{M} \quad \text{—— (8)}$$

Similarly, taking $O^{18}\ C^{12}\ S^{32}$. we obtained moment of inertia as –

$$I'' = m_o' r_{co}^2 + m_s r_{cs}^2 - \frac{(m_s r_{cs} - m_o' r_{co})^2}{M} \quad \text{—— (9)}$$

with these three values of I, I' & I'' we can show for two bond lengths that is present in r_{co} & r_{cs}.