P.G. Sem. III

Core course X.

Rotational Spectroscopy.

Unit I: The rotation of molecules

~~Classification~~

The rotation of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendi-cular directions through the centre of gravity — the principal axes of rotation. Thus a body has three principal moment of inertia, one about each axis, usually designated as I_A, I_B and I

classification of molecules into the principal rotational classes →.

The rotation of any three -dimensional body is conveniently described in terms of rotations about three principal axes of inertia which are mutually at right angles and pass through the centre of gravity of the body. Thus the body has three principal 'moment of inertia' — one about each axis, conveniently designated I_A, I_B and in order of increasing magnitude. ($I_A < I_B < I_C$). On the basis of P.I. molecules may be classified into four groups according to their shapes.

(i) Linear molecules :→

Example → CO_2, HCN, C_2H_2, HCl, Cl–C≡C–H, OCS etc

These, as the name implies, are the molecules in which all the atoms are arranged in a straight line. Three directions of rotations (the principal axis of rotation) may be taken as

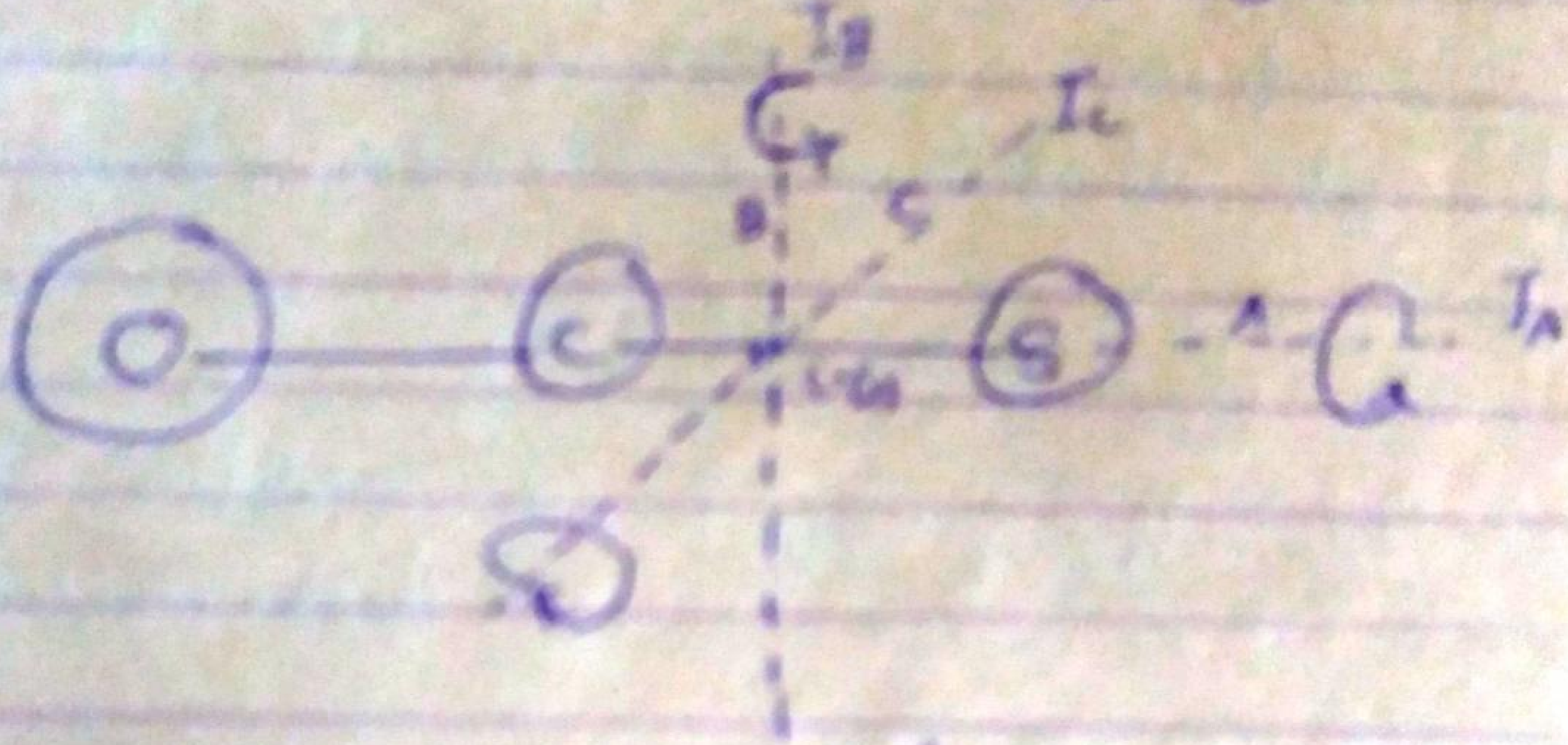
(a) about the bond axis or the molecular axis 'A',

(b) end-over-end rotation in the plane of paper and perpendicular to the ~~axis~~ 'A' molecular axis 'A',

(c) end-over-end rotation at right angles to the plane i.e perpendicular to the both axes.

All the axes passing through the centre of gravity of the molecule.

For example — OCS



The principal axis of rotation is taken as A, B and C. and MI corresponding to these axes is I_A, I_B and
Here,

$I_A = 0$. since the nuclei on axis 'A' have practically all of the mass of the molecule.

$I_B = I_C$, It is also self evident that the moment of ~~inertia about~~ end-over-end rotation about the axes B, and C are the same

So that $I_B = I_C$.

∴ Thus for linear molecule we have

$I_B = I_C$ and $I_A = 0$

The rotational spectra of this molecule is similar to that for ~~for~~ diatomic molecule And,

$E = \bar{B} hc J(J+1)$

$\Delta \bar{\nu} = 2\bar{B}$ (modified by distortion const.)

2.) Symmetric tops molecules →

Example → NH_3, BF_3, C_6H_6
$CHCl_3$, CH_3Cl, BCl_3
CH_3F etc.

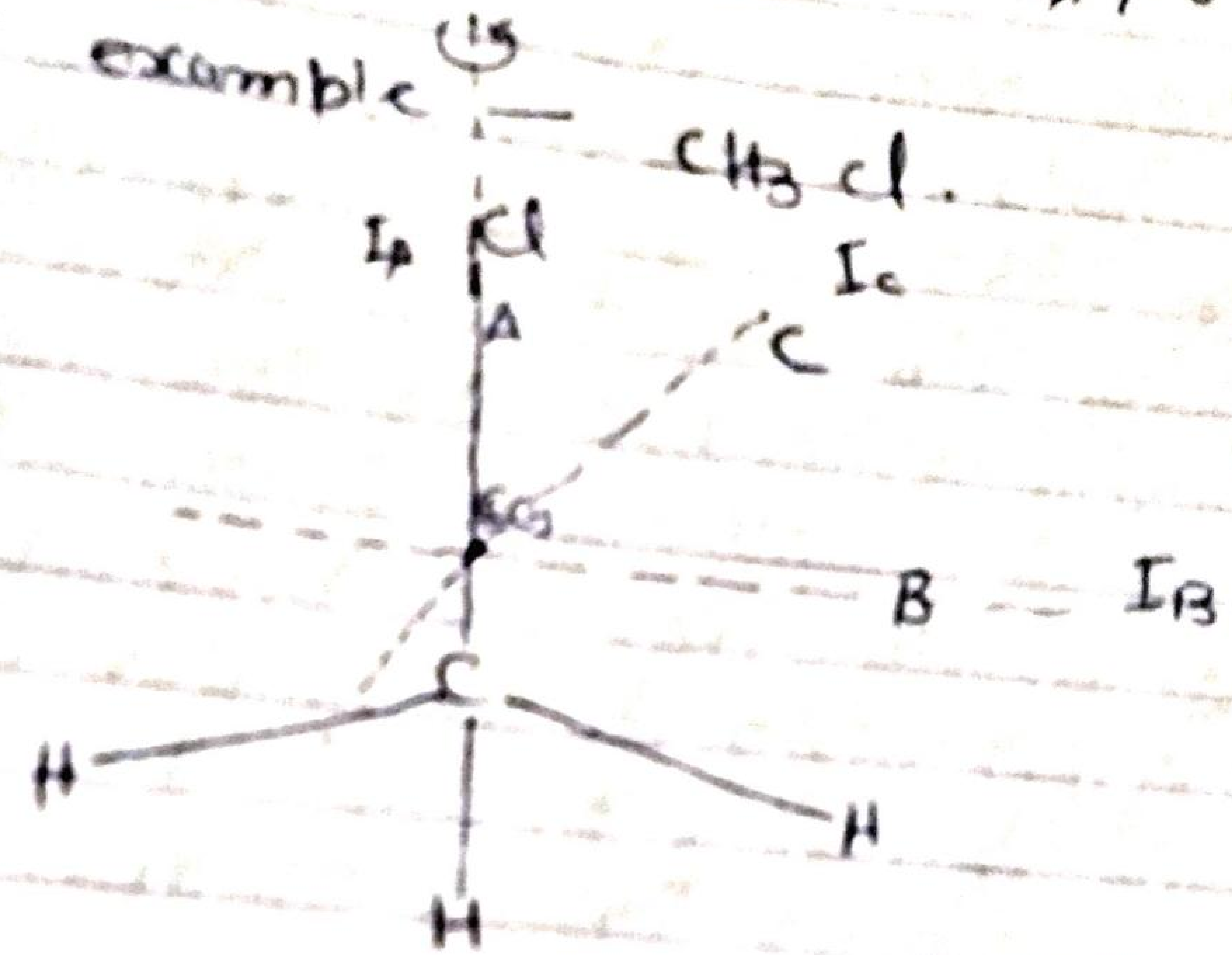
A symm. tops molecule has ~~three~~ three non-zero moments of inertia two of which are equal. i.e.,

$I_A > I_B = I_C$ or $I_A < I_B = I_C$

For Symmetric tops

$$I_B = I_C \neq I_A \quad \text{and} \quad I_A \neq 0$$

For example — CH_3Cl.



It is umbrella shaped with the three hydrogen atoms ~~bed~~ bonded tetrahedrally to the carbon atom, as shown in figure. ~~As in the case of linear molecule~~ The principal axes of inertia are the C–Cl bond axis A, on which the CG lies, and two mutually perpendicular axes B and C in a plane perpendicular ~~to~~ to the axis A. As in the case of linear molecules, the end-over end rotation in, and out of the plane of paper are still identical and we have $I_B = I_C$. The M.I. about the C—Cl bond axis (chosen as the main principal axis since C–G lie along it) is now not negligible, however, because it involves the rotation of three comparatively massive H-atoms off this axis. Such a molecule spinning about this axis resembles a spinning top, and hence the name of 'Symmetric top' for the group. ~~There are two~~ we have then;

$$\text{Symmetric tops}; \; I_B = I_C \neq I_A$$

$$I_A \neq 0$$

There are two subdivisions of this class —

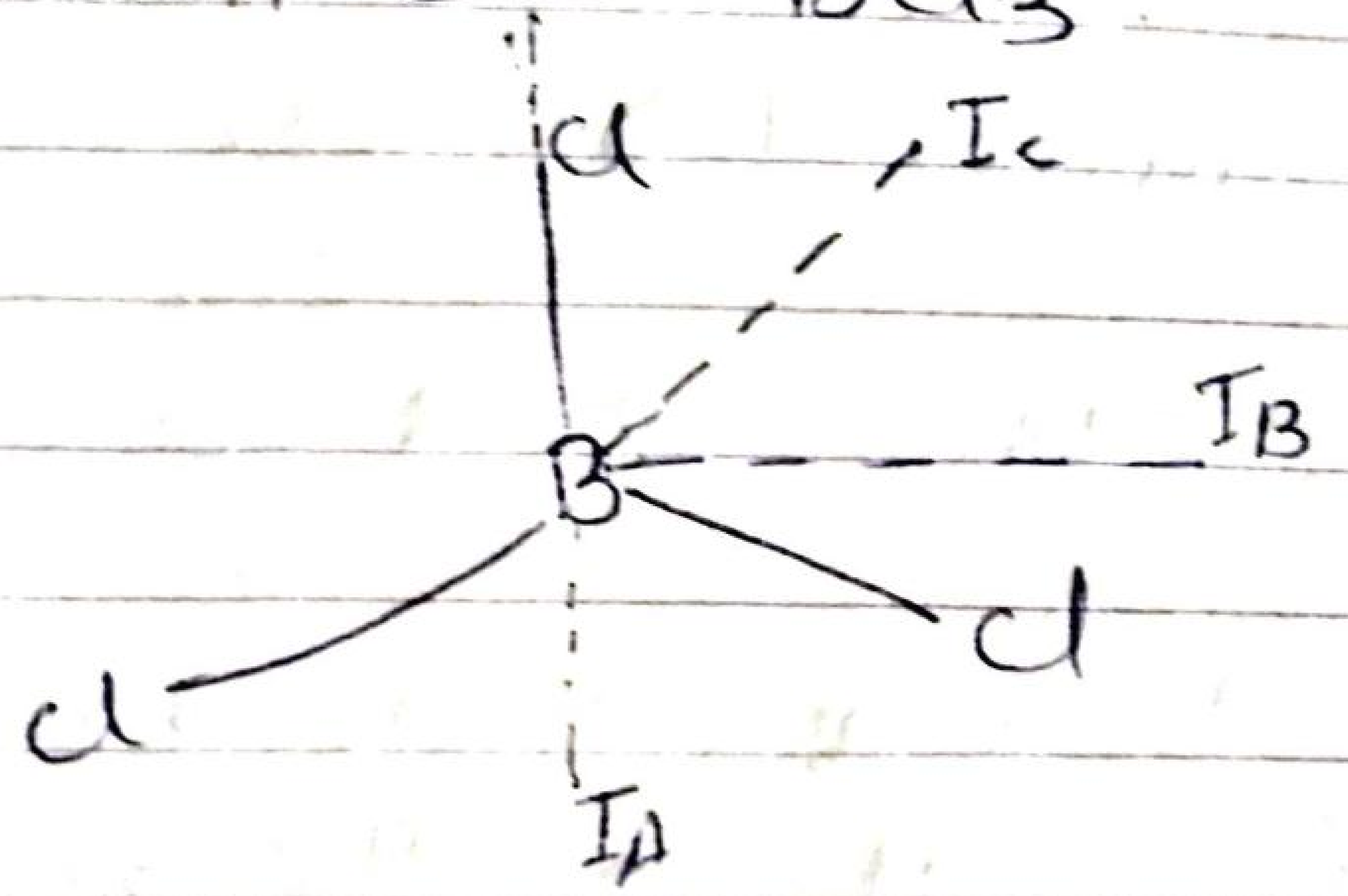
(a) Prolate symmetric top →
If $I_A < I_B = I_C$ as in the above example CH_3Cl, the molecule is called Prolate ...

Symmetric top.

(b) Oblate Symmetric top —

If $I_A > I_B = I_C$, it is refered to as Oblate Symm. top molecule.

Example — BCl_3

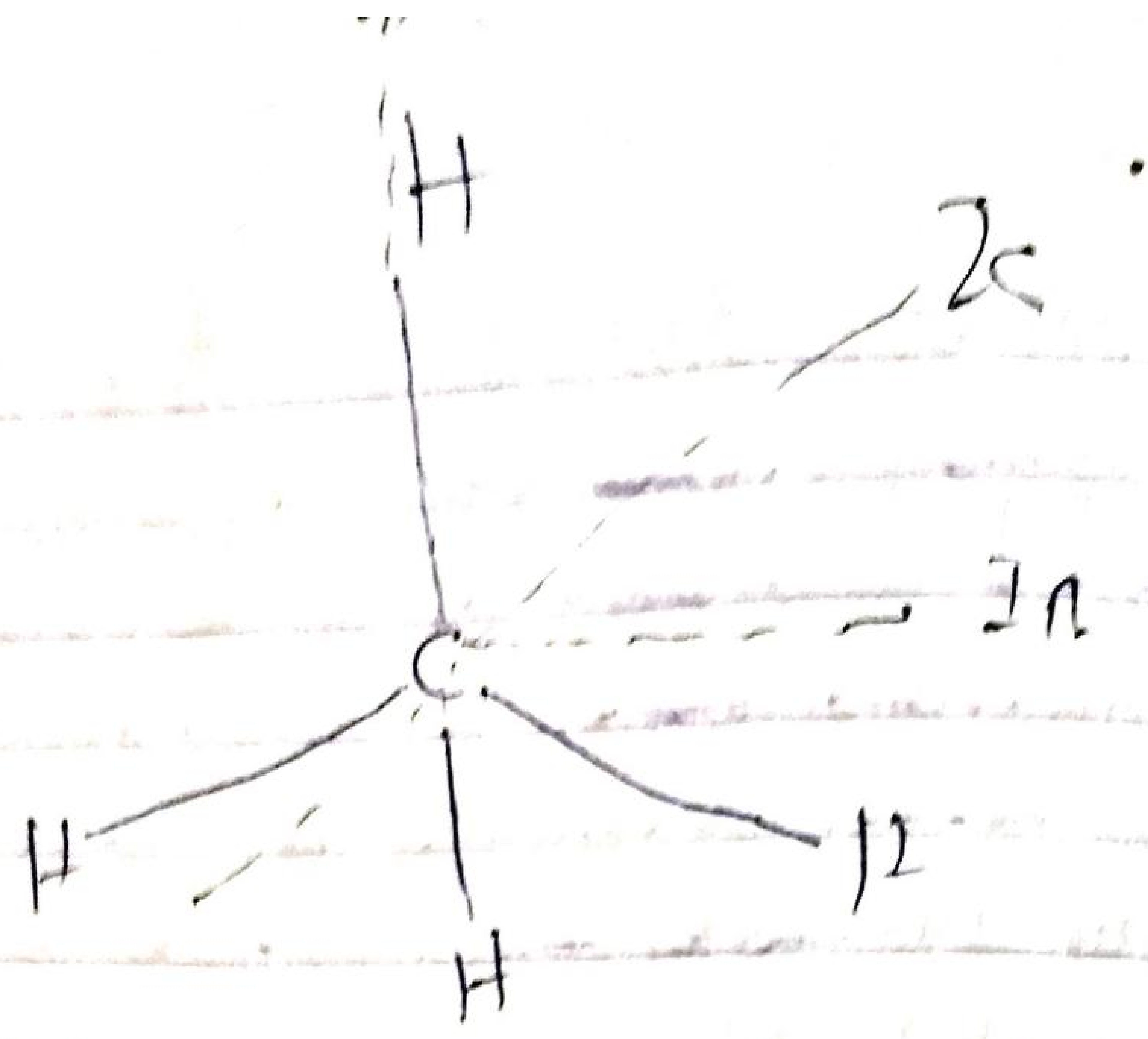


BCl_3 is planar and Symmetrical molecule. In this case

$$I_A = 2 I_B = 2 I_C$$

(3) Spherical tops molecules →

When a molecule has all three principal moment of inertia identical, it is called a Spherical top. A simple example is the tetrahedral molecule methane CH_4.



Spherical tops ;

$$I_A = I_B = I_C$$

If magnetic moment (μ) = 0 hence it is MW inactive.

Example – CH_4, SF_6 etc.

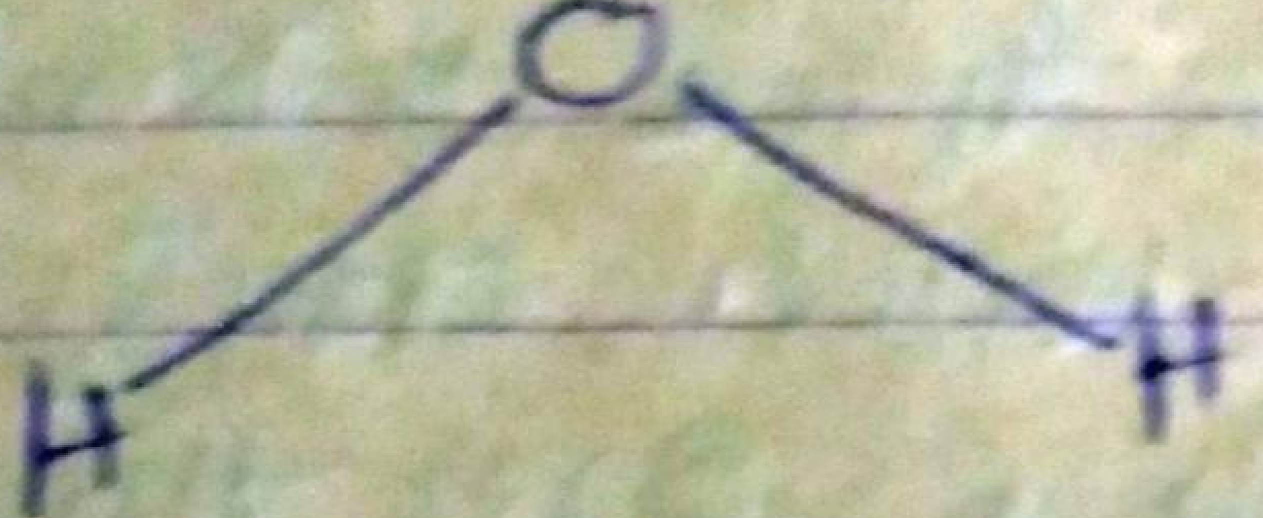
(4) Asymmetric tops :—

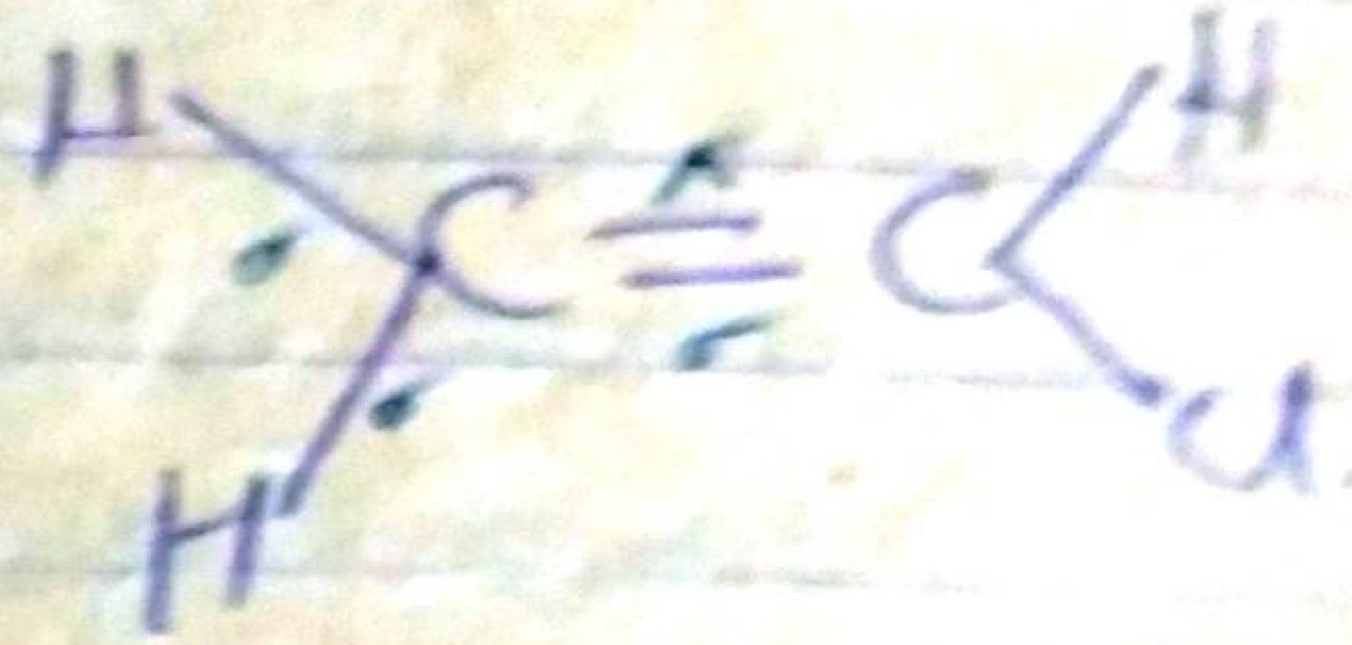
When all the three principal moments of inertia are different the molecule is called an assymmetric top i.e,

$$I_A \neq I_B \neq I_C$$

The majority of substances belonging to this group.

example → H_2O, CH_3OH, vinyl chloride ($CH_2=CHCl$) etc.





An asymmetric top molecule has invariably dipole moment. Selection rule are only appropriate. Effects of centrifugal distortion are large. The rotational spectrum rich in line and complex. It is difficult to determine anything.