Unit 3

Group Theory:

Symmetry elements and symmetry operations:

Symmetry elements:

A symmetry element is defined as a molecular entity (or geometrical entity) such as an imaginary line, an imaginary plane or an imaginary point with respect to which one or more symmetry operations may be carried out.

Symmetry operations:

* A symmetry operation in general is defined as a movement of a molecule, such that it brings the molecule into an equivalent configuration. Such a configuration is indistinguishable from the original one.

List of symmetry elements and symmetry operations:

S.No	Symmetry element	Symmetry operation	Symbol
1	Proper axis of symmetry	Rotation about an axis	C_n
2	Plane of symmetry	Reflection about a plane	σ
3	Center of symmetry	Inversion through the centre	i
4	Improper axis of symmetry	Rotation about an axis followed by reflection about a plane perpendicular to the rotation axis	S_n
5	Identity element	Leaving the molecule as such	E or I

1) Identity element:

This symmetry element is present in all molecule. The corresponding symmetry operation is called identity operation. Identity operation is really not an operation at all. It means that leave the molecule as such (i.e., doing nothing). It (both symmetry element and symmetry operation) is denoted by the symbol I or E. This symmetry element is introduced in group theory in order to fulfill the mathematical completeness of a group.

Identity element → E

Identity operation → E

2) Proper axis of symmetry:

* The proper axis of symmetry is an imaginary line about which rotation through a given angle brings the object or molecule into an equivalent configuration.

* It is designated as C_n (n-fold axis of symmetry), where n is called the order of the rotation axis and C - stands for cyclic.

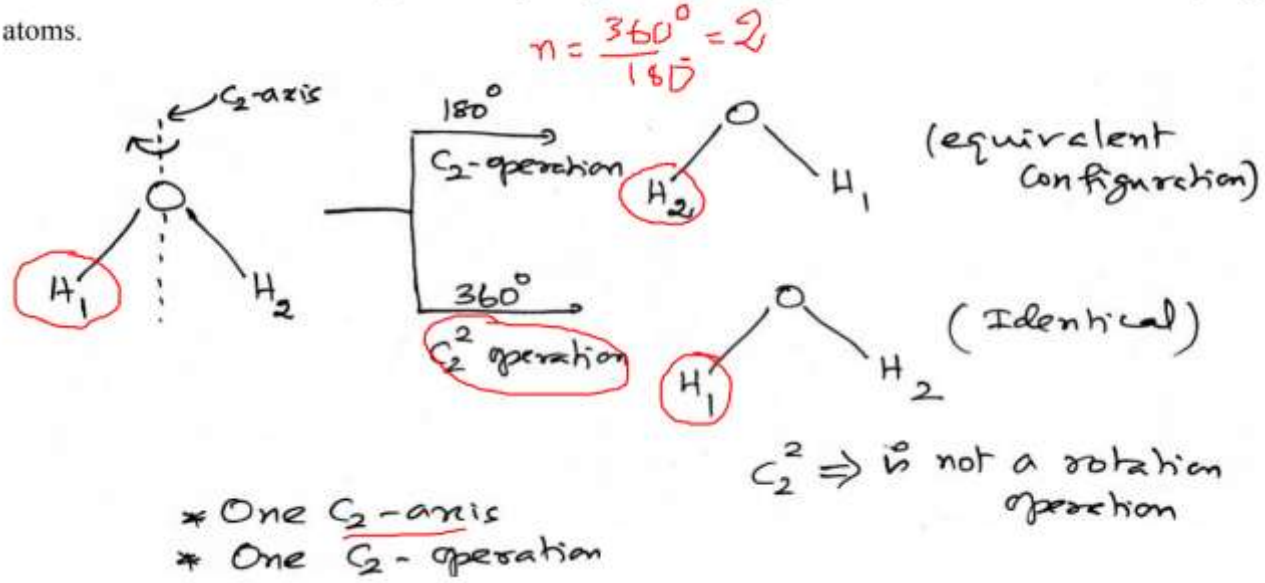
$n = \frac{360^\circ}{\theta}$

* A rotation of 360°/n yields a new orientation of the molecule. The new orientation must be indistinguishable from the original configuration.

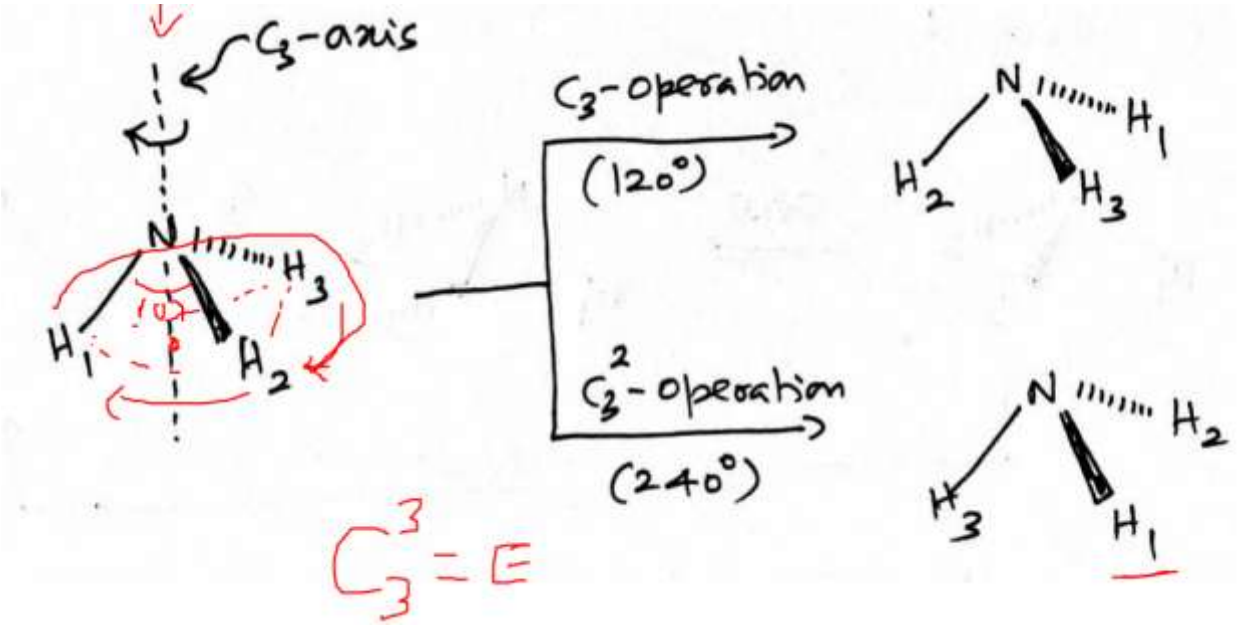
The possible number of rotation operations on a C_n axis is n-1.

Example :1 Water molecule

Water molecule has only one axis passing through oxygen atom and in between the two hydrogen atoms.



Example :2 Ammonia molecule



* If a molecule possesses single axis of symmetry, then this axis is considered as the principal axis.

* If a molecule possesses more than one Cn axes of different order, then the axis of highest order (n) is considered as the principal axis.

3) Plane of symmetry:

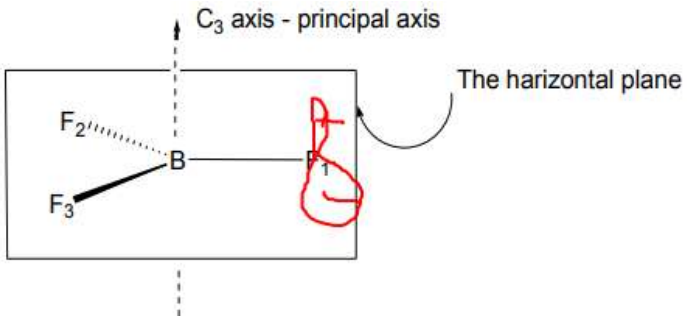
* Plane of symmetry is an imaginary plane which divides a molecule into two equal halves and the reflection about the plane produces an equivalent configuration.

* It is designated by the symbol '**σ**'.

* The reflection plane can be classified into three types based on their relationship with the principal axis.

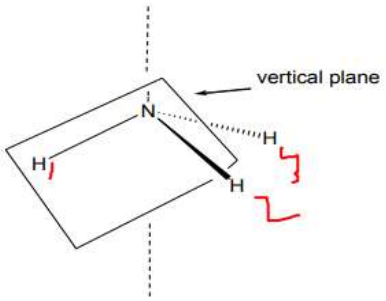
a) The horizontal plane (σ_h):

* The horizontal plane is one which lies perpendicular to the principal axis.



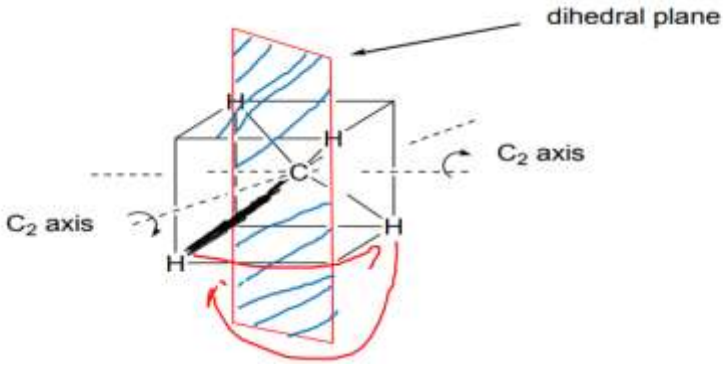
b) The vertical plane (σ_v):

* The vertical plane is one which contains the principal axis.



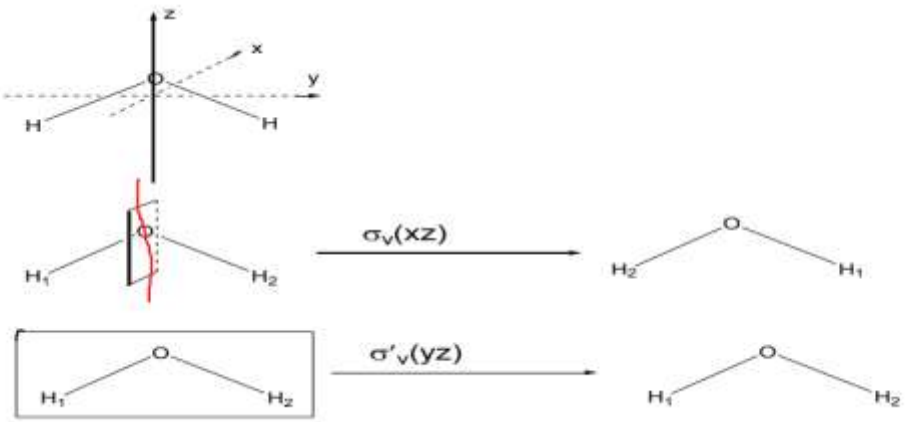
c) The dihedral plane (σ_d):

* The dihedral plane is one which contains the principal axis and also bisects the angle formed between two adjacent equivalent C2 axes.



Example : 1 Water molecule

* It has two vertical planes of symmetry. One of the planes passing through all the atoms called $\sigma_v(yz)$ and the other pass through oxygen and bisect the angle formed by the two bonds called $\sigma'_v(xz)$.



Example :2 Ammonia molecule

* It has three vertical planes of symmetry. Each of these planes pass through a N-H bond and also present in between other two hydrogen atoms.

Similarly, two more vertical planes also present in the molecule as shown below:

4) Center of symmetry:

* Draw a line from any point to the center of the molecule and produce it an equal distance in the opposite side, if it comes to an equivalent point, then the molecule said to possess centre of symmetry

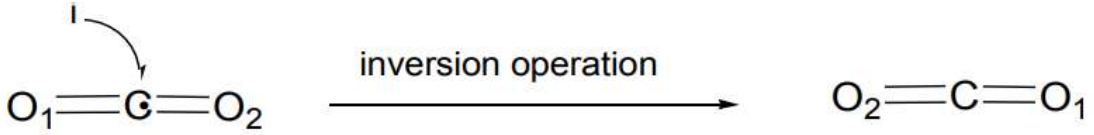
* The center of this molecule is called the center of symmetry. It is denoted by the symbol 'i'.

* Only one inversion operation can be performed on a molecule about the center point. The symmetry operation of inversion is also denoted by ' i '.

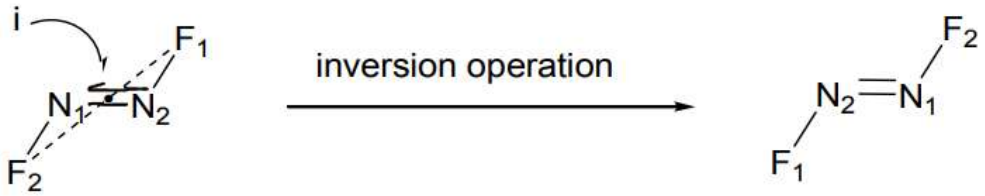
* A molecule cannot have dipole moment if it has the symmetry element ' i '.

Examples:

1) CO_2 :



2) trans - N_2F_2:



5) Improper axis of symmetry (or) Alternate axis of symmetry:

* If rotation of a molecule through an angle θ about an axis, followed by **reflection through a plane perpendicular to that axis**, yields an indistinguishable configuration, then the axis is an n-fold rotation – reflection axis, also called an n-fold improper rotation axis.

* The symmetry operation "improper rotation" is denoted by the symbol S_n and it is expressed mathematically as

$$S_n = \sigma \cdot C_n. \quad \text{(rotation followed by reflection)}$$

* An S_n axis generates 'n' operations when 'n' is even and '2n' operations when 'n' is odd i.e., The symmetry operations of S_n axis (if 'n' is even) are $S_n^1, S_n^2, \ldots, S_n^n = E$ similarly the symmetry operations of S_n axis (if 'n' is odd) are $S_n^1, S_n^2, \ldots, S_n^{2n} = E$.