Group Theory in chemistry

1.1 **INTRODUCTION** Symmetry is a phenomenon of geometrical property of the world in which we live. In nature many type of flowers and plants, snowflakes, insects, certain fruits vegetables and various microscopic organism exhibit characteristic symmetry . Symmetry concepts are extremely useful in Chemistry. On the basis of symmetry we can predict infrared spectra, type of orbital used in bonding, predict the optical activity and interpret electronic spectra and study of molecular properties. Symmetry helps us understand molecular structure, some chemical properties, and characteristics of physical properties (spectroscopy) – used with group theory to predict vibrational spectra for the identification of molecular shape, and as a tool for understanding electronic structure and bonding.

A group consists of a set of symmetry elements (and associated symmetry operations) that completely describe the symmetry of an object. Point groups have symmetry about a single point at the center of mass of the system.

1.2 ELEMENT OF SYMMETRY Symmetry elements are geometric entities as point, line, plane of molecule about which a symmetry operations as rotations, reflections, inversions and improper rotations can be performed. In a point group, all symmetry elements must pass through the center of mass (the point). A symmetry operation is the action that produces an object identical (i.e. position indistinguishable from the original position) to the initial object (even though atoms and bonds may have been moved. In generally we can say that the element of symmetry is geometrical tools of symmetry or entity of symmetry tools i.e. point, line, plane in the molecule. The actual reflection, rotation or inversion is called the symmetry operation. A molecule possesses a symmetrical element, which is unchanged in appearance after applying the symmetry operation, correspond to the element. The element of symmetry divided into five operations.

1. Identity symmetry (E)

2. Axis of symmetry (Cn where n=360/angle of rotation in θ)

3. Plane of symmetry (σ)

4. Improper axis of symmetry (Sn and then ⊥ Cn)

5. Point of symmetry

(i) Identity (E): The operation, which brings back the molecule to the original orientation, is called identity operation. It is represented as E from the German word Einhert meaning unity. The identity operation in effect means doing nothing on the molecule and hence does not seen to be of much consequence but it is important lies in considering the molecule as a group. Each molecule has this type of symmetry.

Axis of symmetry (Cn): The symmetry element in which the molecule can represent the identical image after rotation of molecule by 360 0 /n with respect to any imaginary axis called as axis of symmetry or rotational axis. n= - Where n is always an integer. This axis defined is an n-fold rotation axis, Cn. - In water there is a C2 axis so we can perform a 2-fold (180°) rotation to get the identical arrangement of atoms In BF3 there is a C3 axis so we can perform 3-fold (120°) rotations to get identical arrangement of atoms.

- Rotations are considered positive in the counter-clockwise direction. - Each possible rotation operation is assigned using a superscript integer m of the form Cn m. - The rotation Cn n is equivalent to the identity operation (nothing is moved) Classification of axis of symmetry Many molecules have more than one Cn axis It can be divided into two different types: a) Principal axis of symmetry b) Secondary/ subsidiary axis of symmetry (a) Principal axis of symmetry The Principal axis in an object is the highest order rotation axis i.e. having largest value of n. It is usually easy to identify the principle axis and this is typically assigned to the zaxis if we are using Cartesian coordinates.If there are more than one axis of same order ,then the axis passing through maximum number of atoms is called Principle axis.

(b) Subsidiary or secondary axes of Symmetry: Lower fold of rotation axis (lower order of axis of symmetry) is the secondary or subsidiary axis of the molecule. Example: In BF3 molecule C3 axis is principal axis and C2 axis is secondary axis. In ethane molecule C2 ′ is the principal axis and C2 is subsidiary axis. In NH3 molecule threefold of axis present that is principal axis, here subsidiary axis is absent.

1.1.3 Plane of symmetry: Plane of symmetry have generate only one operation, on repeating the reflection operation molecule comes into initial structure that is σ2 = E. The imaginary plane bisects the molecule into two halves which are mirror image to each other. σn = E (if n is even) σn = σ (if n is odd) The molecules possessing only plane of symmetry but no rotation axis other than C1 (=E), there can be no definition vertical and horizontal planes and the symbol for this plane is simply σ. The point group for this type of molecule is Cs. Rotational axis along with plane, the planes can be classified into three types. a) Vertical Plane (σv: σ ‖ principal axis) b) Horizontal plane (σh : σ ⊥ principal axis) c) Dihedral plane (σd bisect plane with respect to two C2 axis)

1.1.4 (a) Vertical plane: The plane of operation undergoes parallel with respect to principal axis is vertical plane of symmetry and denoted by σv. The subscript "v" in σv, indicates a vertical plane of symmetry. This indicates that the mirror plane passing through the principle axis and one of the subsidiary axis (if present).

1.1.3 (b) Horizontal plane: The plane reflection is perpendicular with respect to principal axis is called horizontal plane and denoted by σh. Example: In bent molecule of H2O have σv(yz) and σv(xz) C plane, in σv(xz) all the atoms of H and O are bisect in the same plane and in σv(yz), two hydrogen atoms are reflected to each other. Example: In pyramidal NH3 molecule, three plane of reflections are present. Which are parallel with respect to C3 principal axis, i.e. there are three vertical planes are present. Example: In trigonal planar BF_3 molecule have three reflection of plane which are parallel with respect to three fold (C_3) axis. One reflection of plane which is perpendicular with respect to principal axis. Example: In square planar complex $[PtCl_4]^{-2}$ have a horizontal plane, two vertical plane and two dihedral plane (which bisect the two C_2 axis).

Dihedral plane: The plane passing through the principal axis but passing between two subsidiary axis is called dihedral plane and denoted by σ_d. Example: In allene compound there are two C_2 axis which are different type one of them have three atoms are passed though the axis and principle axis. There are two dihedral angle which are bisecting to two C_2 axis.

Improper axis of symmetry (Sn): An improper rotation operation is one that comprises of a proper rotation operation around an axis followed by reflection through a plane perpendicular to it. It is denoted by S_n. n order of rotational axis. It can be also defined as, imaginary axis passing through molecule rotation in which perpendicular reflection to give equivalent orientation. $S_n = C_n \perp \sigma_n$ Example: In CH_4 has tetrahedral geometry. If we place a tetrahedral in a cube then the four atom touches the four corners of cubical box. CH_4 having S_4 it doesn't mean that C_4 symmetry is present.