Symmetry in Chemistry - Group Theory

Group Theory is one of the most powerful mathematical tools used in Quantum Chemistry and Spectroscopy. It allows the user to predict, interpret, rationalize, and often simplify complex theory and data.

At its heart is the fact that the **Set of Operations** associated with the **Symmetry Elements** of a molecule constitute a mathematical set called a **Group**. This allows the application of the mathematical theorems associated with such groups to the **Symmetry Operations**.

All **Symmetry Operations** associated with isolated molecules can be characterized as Rotations:

> (a) **Proper Rotations**: C_n^k ; k = 1,......, n
> When k = n, C_n^k = E, the Identity Operation
> n indicates a rotation of 360/n where n = 1,....

> (b) **Improper Rotations**: S_n^k , k = 1,....., n
> When k = 1, n = 1 $S_n^k = \sigma$, Reflection Operation
> When k = 1, n = 2 S_n^k = i , Inversion Operation

In general practice we distinguish **Five** types of operation:

> (i) **E**, Identity Operation
> (ii) $\mathbf{C_n^k}$, Proper Rotation about an axis
> (iii) **σ**, Reflection through a plane
> (iv) **i**, Inversion through a center
> (v) $\mathbf{S_n^k}$, Rotation about an an axis followed by reflection through a plane perpendicular to that axis.

Each of these **Symmetry Operations** is associated with a Symmetry Element which is a point, a line, or a plane about which the operation is performed such that the molecule's orientation and position before and after the operation are indistinguishable.

The **Symmetry Elements** associated with a molecule are:

> (i) A **Proper Axis of Rotation:** $\mathbf{C_n}$ where n = 1,....
> This implies n-fold rotational symmetry about the axis.

(ii) A **Plane of Reflection: σ**
This implies bilateral symmetry about the plane.
These planes are further classified as:

σ_h - Horizontal Plane which is perpendicular to the Principal Axis of Rotation (i.e. Axis with highest value of n). If no principal axis exists σ_h is defined as the molecular plane.

σ_v or σ_d - Vertical Plane which contains the Principal Axis of Rotation and is perpendicular to a σ_h plane, if it exists. When both σ_v and σ_d planes are present, the σ_v planes contain the greater number of atoms, the σ_d planes contain bond angle bisectors. If only one type of vertical plane is present, σ_v or σ_d may be used depending on the total symmetry of the molecule.

(iii) A **Center of Inversion - i**
This is a central point through which all C_n and s elements must pass. If no such common point exists there is no center of symmetry.

(iv) **Improper Axis: S_n**
This is made up of two parts: C_n and σ_h both of which may or may not be true symmetry elements of the molecule. If both the C_n and the σ_h are present then S_n must also exist.
The following relations are helpful in this regard:
(a) If n is even, $S_n^n = E$
(b) If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
(c) If m is even, $S_n^m = C_n^m$ when m < n
$S_n^m = C_n^{m-n}$ when m > n
(d) If S_n with even n exists then $C_{n/2}$ exists.
(e) If S_n with odd n exists then both C_n and s perpendicular to C_n exist.

The key to applying **Group Theory** is to be able to identify the **"Point Group"** of the molecule i.e. its characteristic set of **Symmetry Operations**. The possible **Symmetry Operations** associated with a molecule are determined by the **Symmetry Elements** possessed by that molecule. Therefore the first step in applying Group Theory to molecular properties is to identify the complete set of Symmetry Elements possessed by the molecule. This requires the individual to visually identify the elements of symmetry in a 3-dimensional object. Experience

has shown that this is often the most difficult step for a beginner.

Molecules can be categorized as:

(i) **Linear**
(ii) **Planar**
(iii) **Non-Planar**

Knowing the Symmetry Elements of the molecule we can now use the following flow chart to determine the molecular point group.