Inorganic Chemistry

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Unit- 3 Symmetry and Molecular point Group

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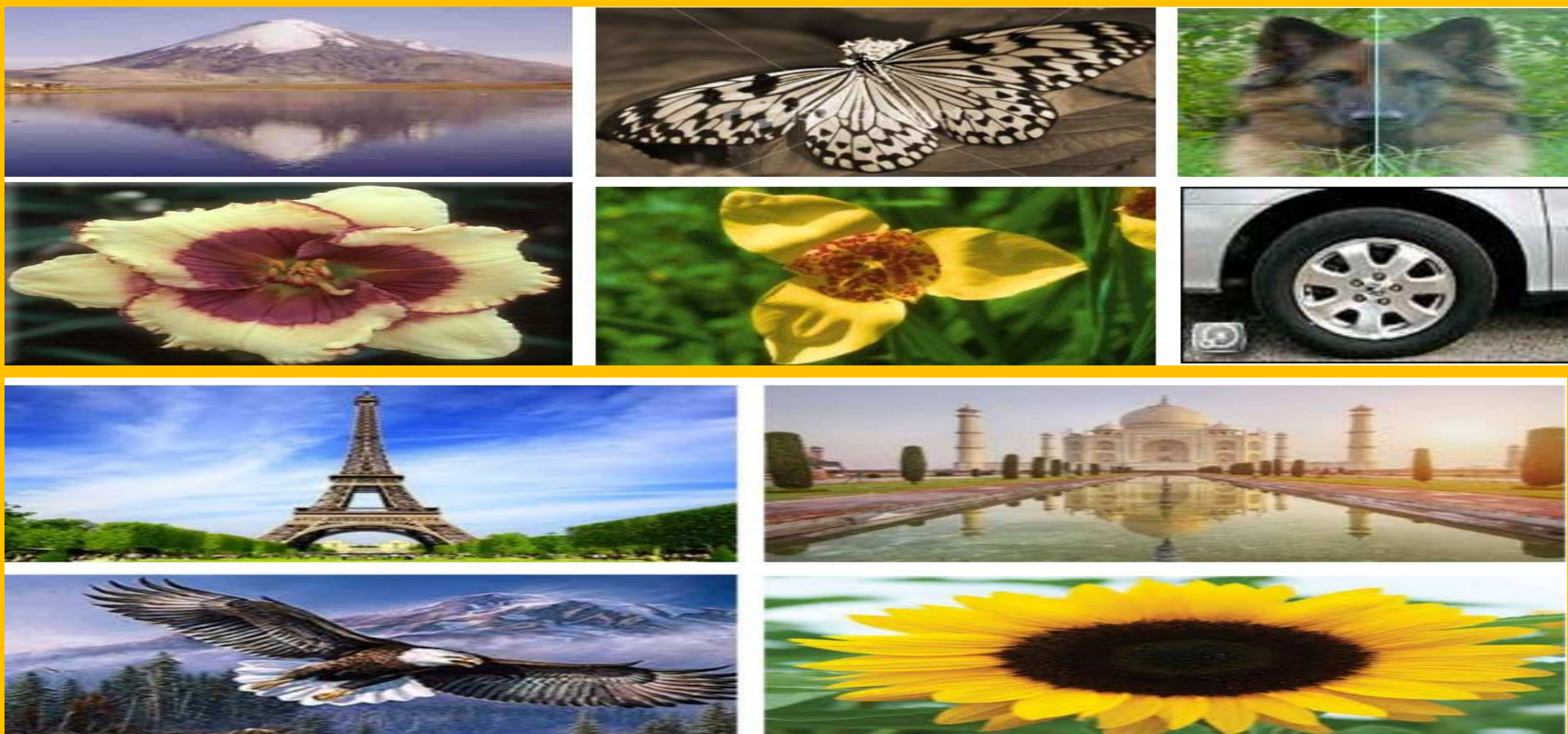
❖ *INTRODUCTION:*

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 (Fig. 1.1). 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

The term **symmetry** is derived from the Greek word "**symmetria**" which means "measured together"

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.



❖*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 (C_n 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 (--C_{n-}):**

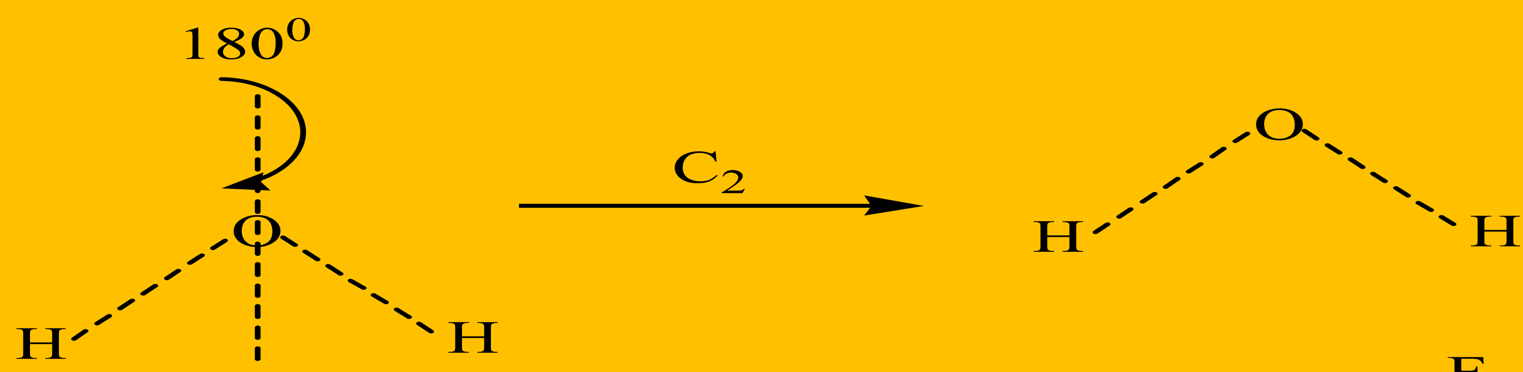
The symmetry element in which the molecule can represent the identical image after rotation of molecule by 360^0 /n with respect to any imaginary axis called as axis of symmetry or rotational axis.

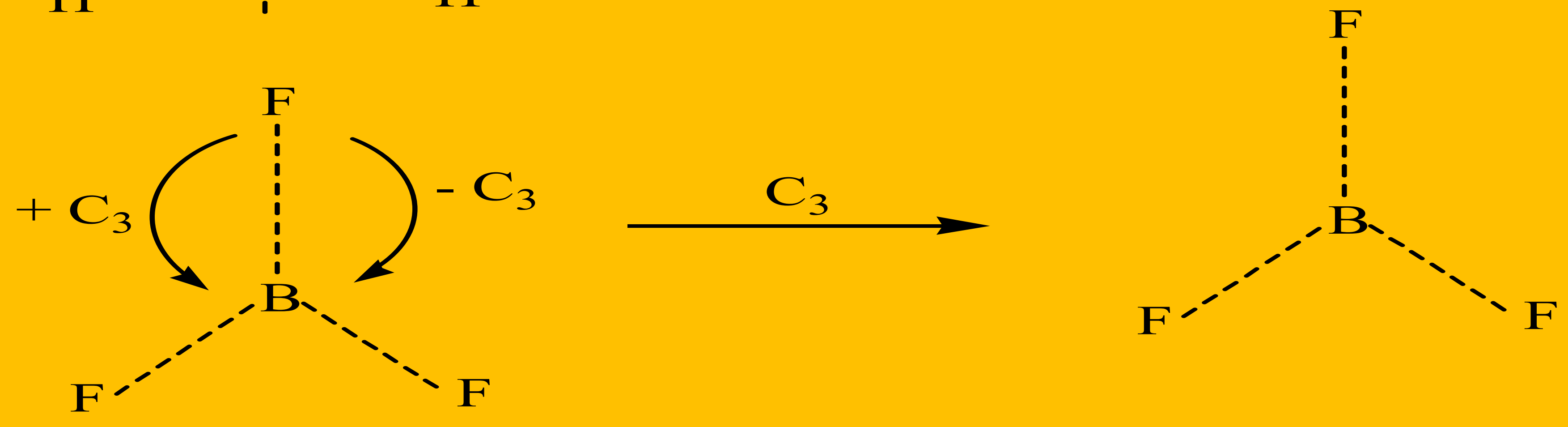
$$\mathbf{n = 360/\theta}$$

Where n is always an integer. This axis defined is an n-fold rotation axis, **Cn.**

•In water there is a C_2 axis so we can perform a 2-fold (180°) rotation to get the identical arrangement of atoms (Fig. 1)

•In BF_3 there is a C_3 axis so we can perform 3-fold (120°) rotations to get identical arrangement of atoms (Fig. 2)





1. Rotations are considered positive in the counter-clockwise direction.
2. Each possible rotation operation is assigned using a superscript integer m of the form C_n^m.
3. The rotation C_n^n is equivalent to the identity operation (nothing is moved).

✓**Classification of axis of symmetry:**

Many molecules have more than one C_n axis, so 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 z-axis 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.

Example: In BF_3 molecule three fold rotation axis (C_3) and two fold rotational axis (C_2) are present. The three fold axis is coincident with the perpendicular to the plane and the rotation angle is $=120^0$. After two C_3 operations molecule comes into identity operation. Three-fold axis have higher order than two fold axis, therefore C_3 is the principal axis of BF_3 molecule **Figure 2 and Figure 3**.

In Benzene there is six fold axes of symmetry C_6 as principal axes and it has six axes of two fold symmetry three passing through centre of Benzene and two opposite carbon atoms and three passing through centre of symmetry and centre of two opposite edges **Figure 4**. In NH_3 molecule only three-fold axis of symmetry **Figure 5** and in water only two fold symmetry is present **Figure 6**.

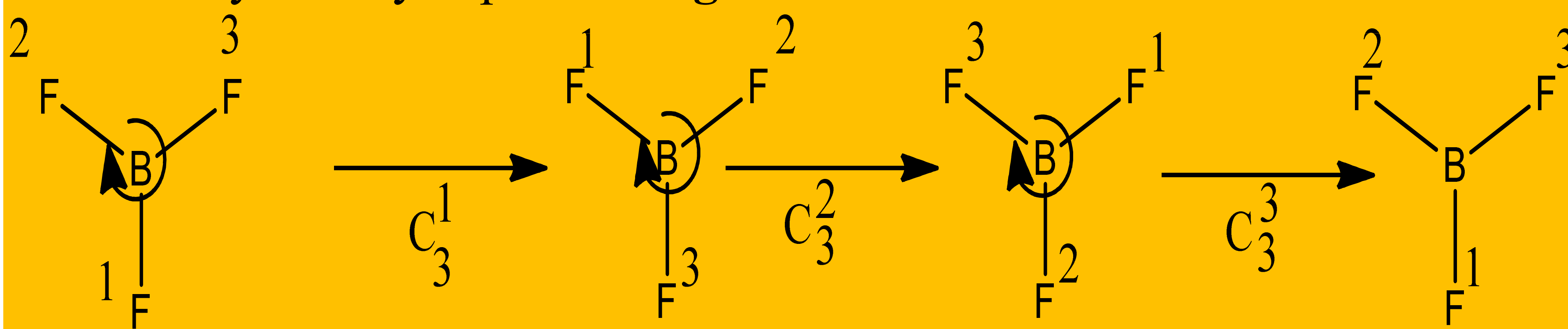
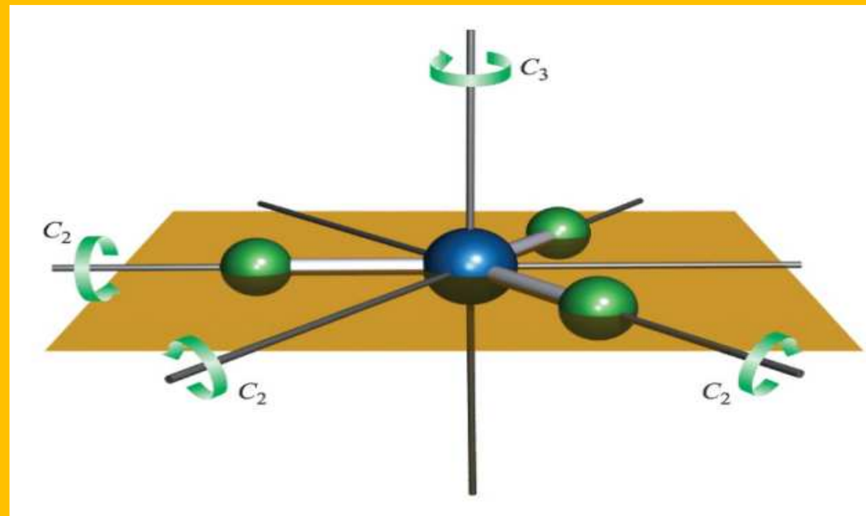


Figure- 2

$C_3^1 = 120^o$, $C_3^2 = 240^o$, $C_3^3 = E = 360^o$



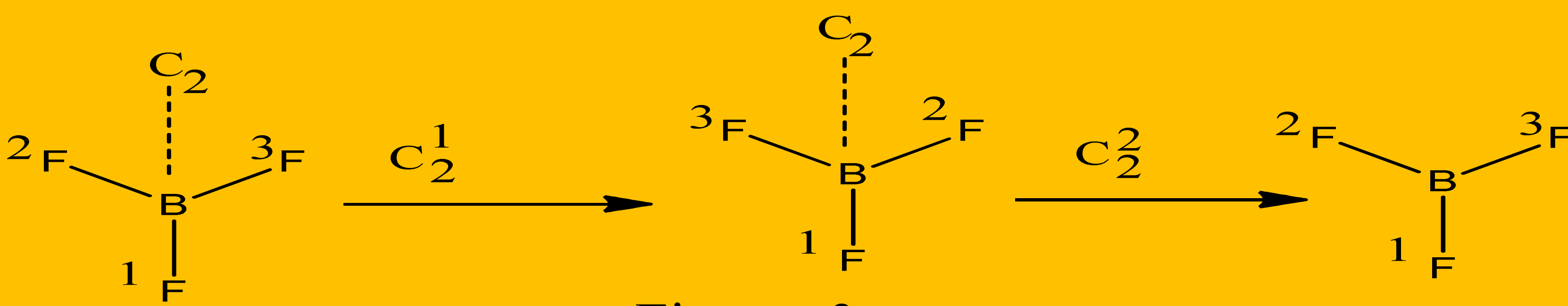


Figure- 3

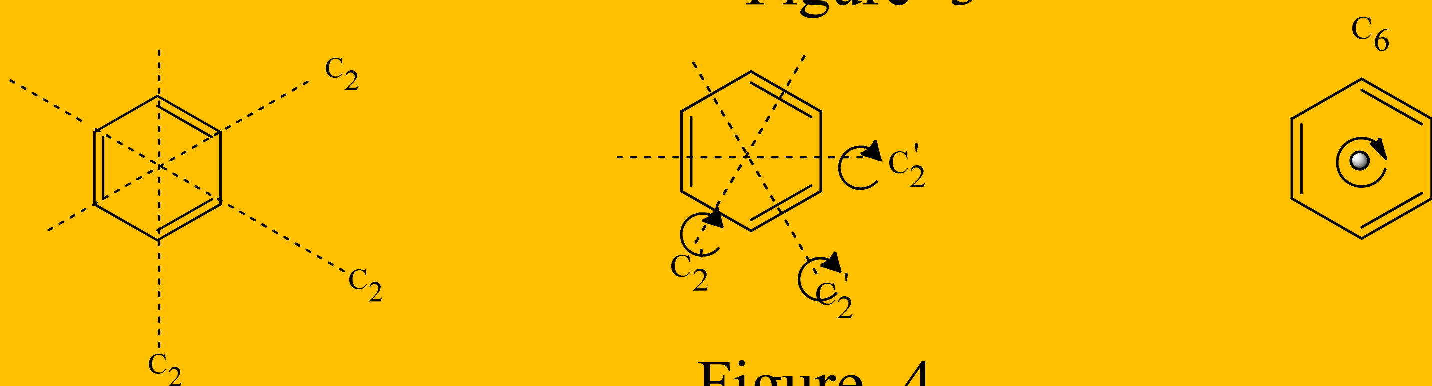


Figure- 4

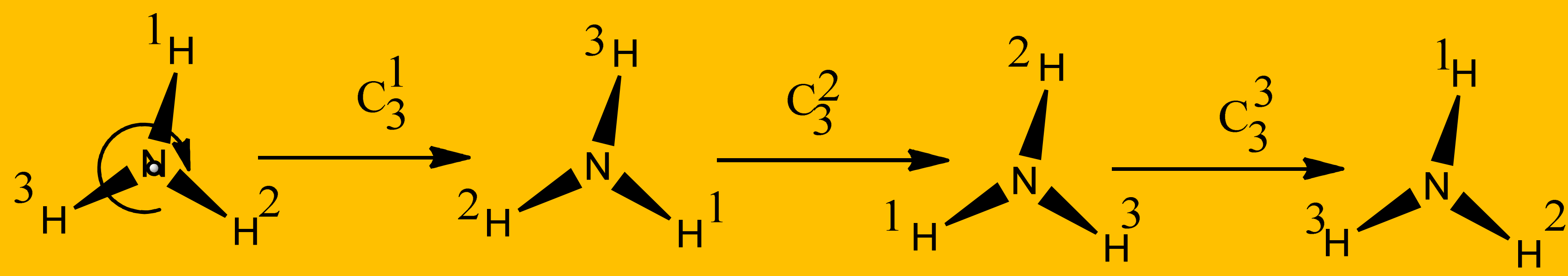


Figure- 5

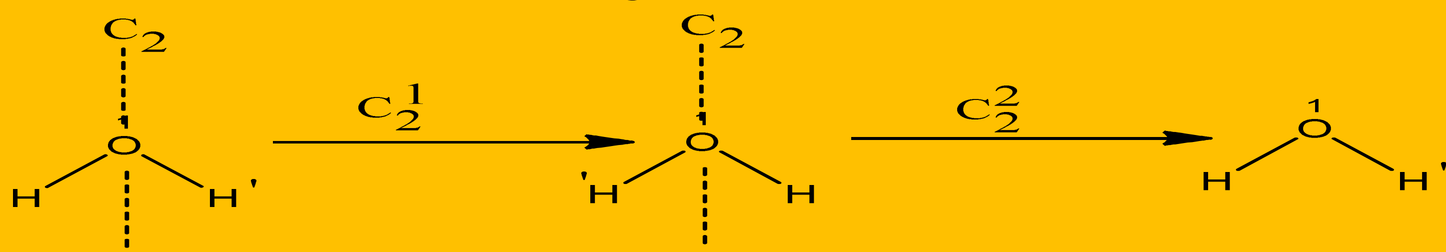


Figure- 6

➢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 BF_3 molecule C_3 axis is principal axis and C_2 axis is secondary axis. In ethane molecule $C\text{-}_2'$ is the principal axis and C_2 is subsidiary axis. In NH_3 molecule three-fold of axis present that is principal axis, here subsidiary axis is absent.

➢ **Plane of symmetry:**

Plane of symmetry have generate only one operation, on repeating the reflection operation molecule comes into initial structure that is $\sigma^2 = E$. The imaginary plane bisects the molecule into two halves which are mirror image to each other.

$\sigma^n = E$ (if n is even)

$\sigma^n = \sigma$ (if n is odd)

The molecules possessing only plane of symmetry but no rotation axis other than C_1 (=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 C_s.

Rotational axis along with plane, the planes can be classified into three types.

•Vertical Plane (σv: σ ‖ principal axis)

•Horizontal plane (σh : σ ⊥ principal axis)

•Dihedral plane (σd bisect plane with respect to two C_2 axis)

(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 σ_v, 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).

(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 H_2O have $\sigma v_{(yz)}$ and $\sigma v_{(xz)}$ C plane, in $\sigma v_{(xz)}$ all the atoms of H and O are bisect in the same plane and in $\sigma v_{(yz)}$, two hydrogen atoms are reflected to each other.

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) shown in **figure:7, and 8.**

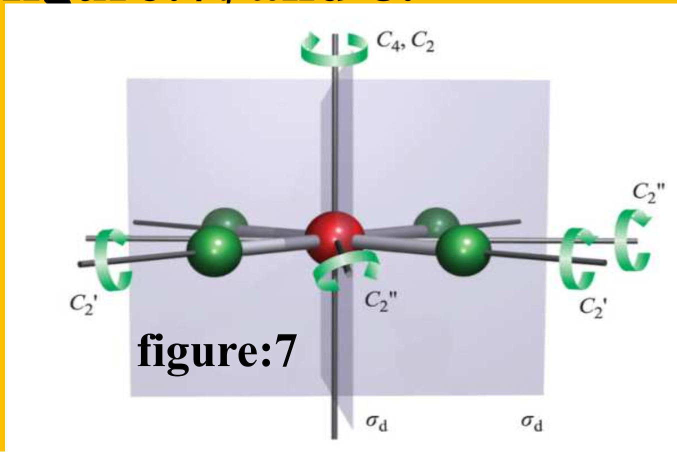


figure:7

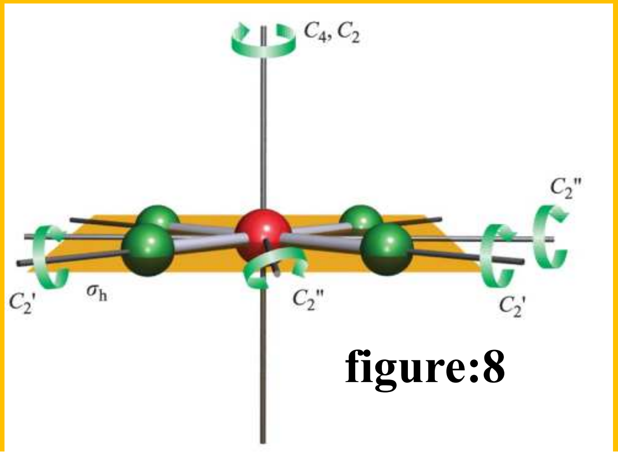


figure:8

(c) Dihedral plane:

The plane passing through the principal axis but passing between two subsidiary axis is called dihedral plane and denoted by σd.

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.

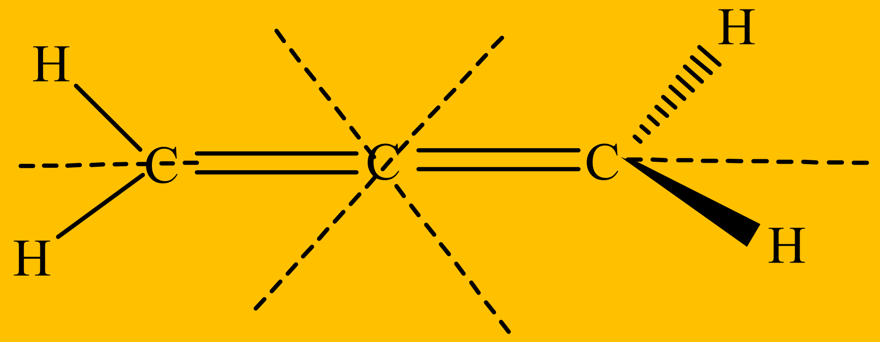


Figure: 9

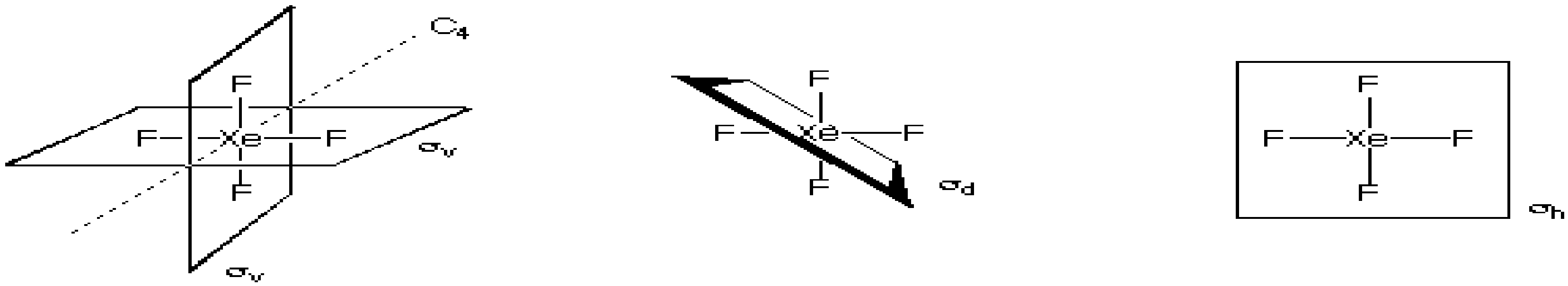


Figure: 10

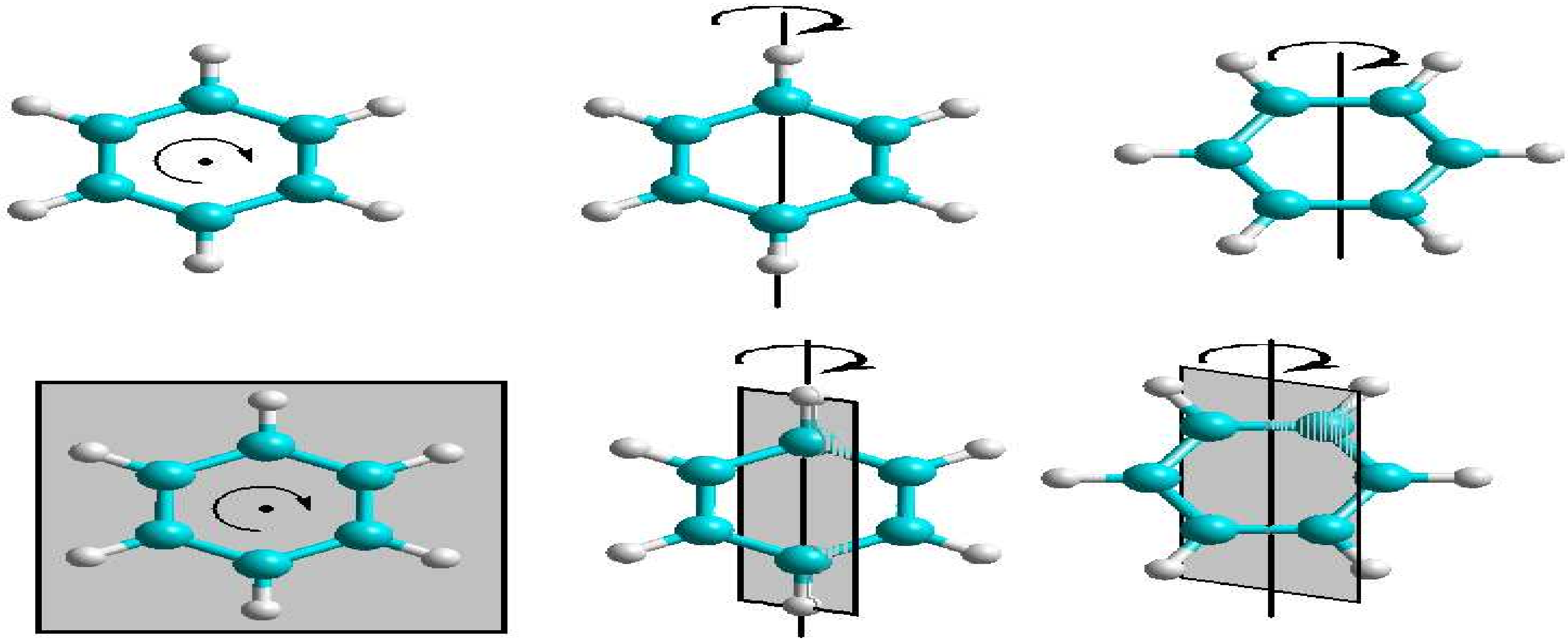


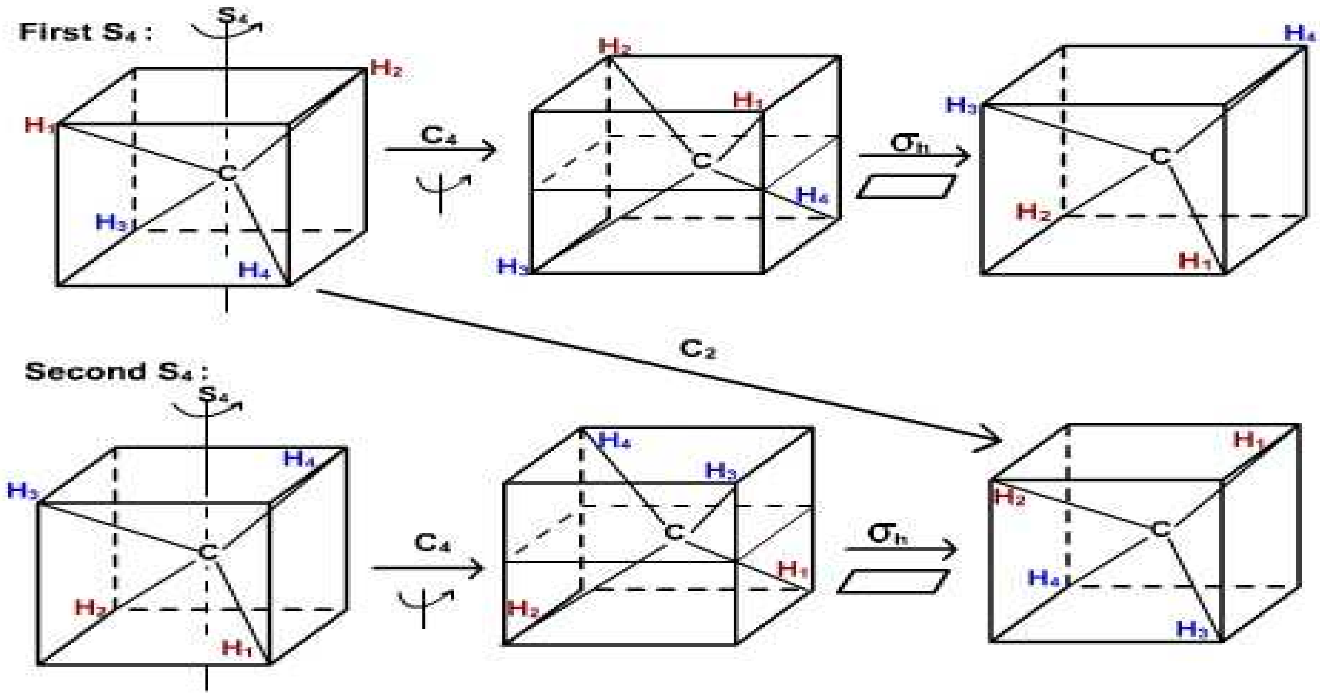
Figure: 11 Rotational axes and mirror planes in Benzene

➢ Improper axis of symmetry (S_n):

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.

$\mathbf{S_n = C_n \perp \sigma_n}$

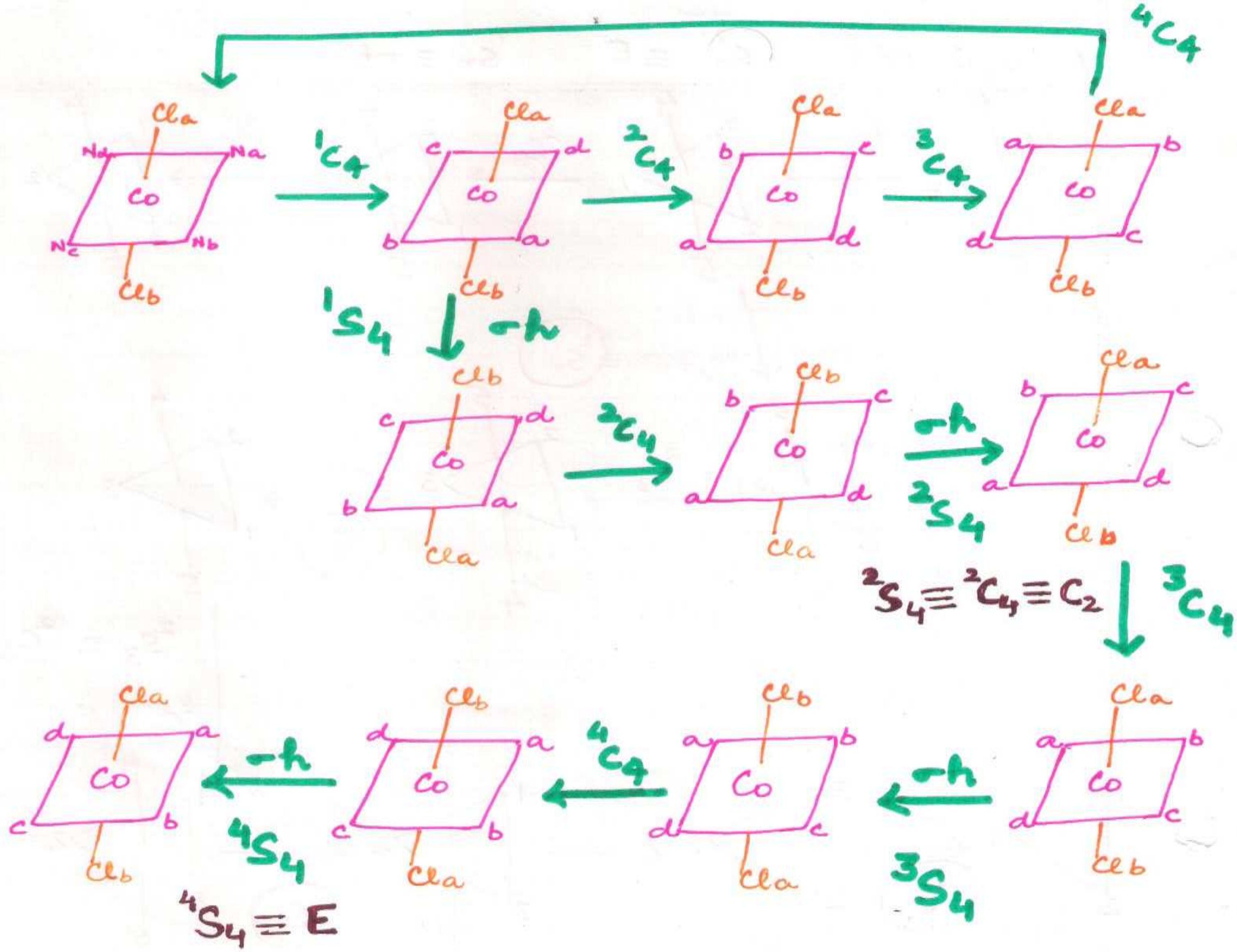
Example: In CH_4 has tetrahedral geometry. If we place a tetrahedral in a cube then the four atom touches the four corners of cubical box. CH_4 having S_4 it doesn't mean that C_4 symmetry is present.



$2\ S_4 = 1\ C_2$

Figure: 12

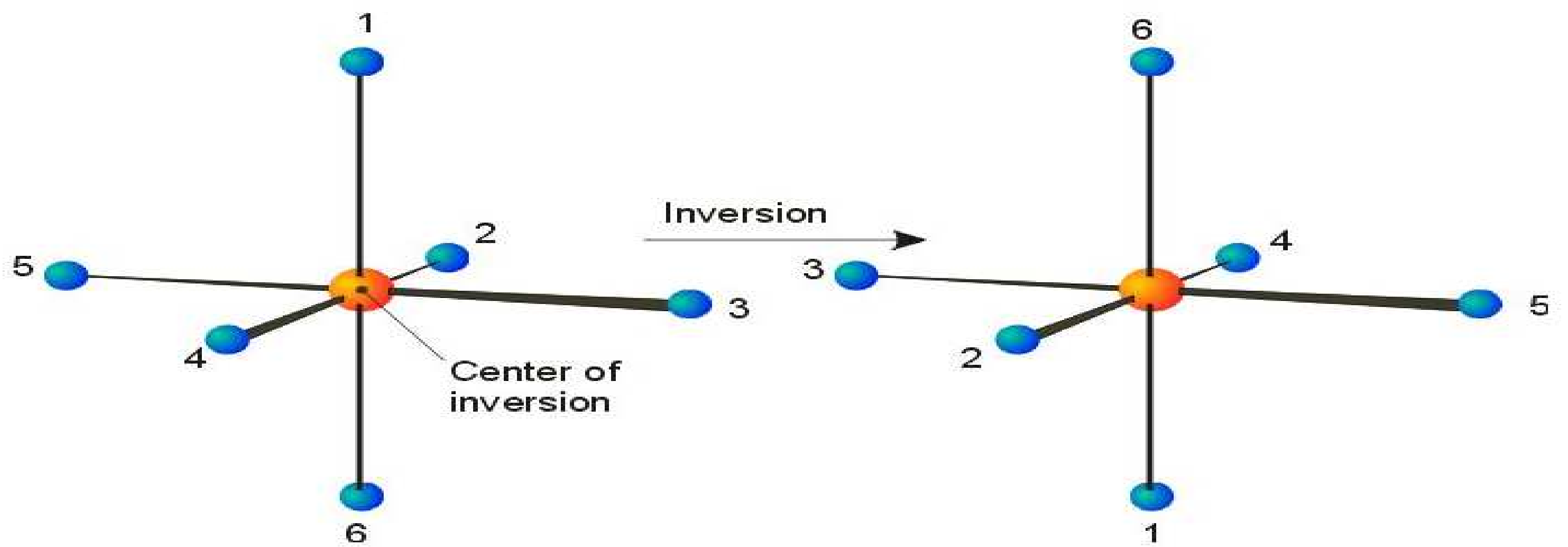
IMPROPER AXIS IN OCTAHEADRAL STRUCTURE   Sn = 4   even



Order of improper rotation is even $S_n^n \equiv E$

➢ **Point of symmetry:**

It is a point within the molecule through which all the atoms can inverted within a point. The element corresponds to this operation is a center of symmetry. This is designated by i. In this operation, every part of the object is reflected through the inversion center, which must be at the center of mass of the object



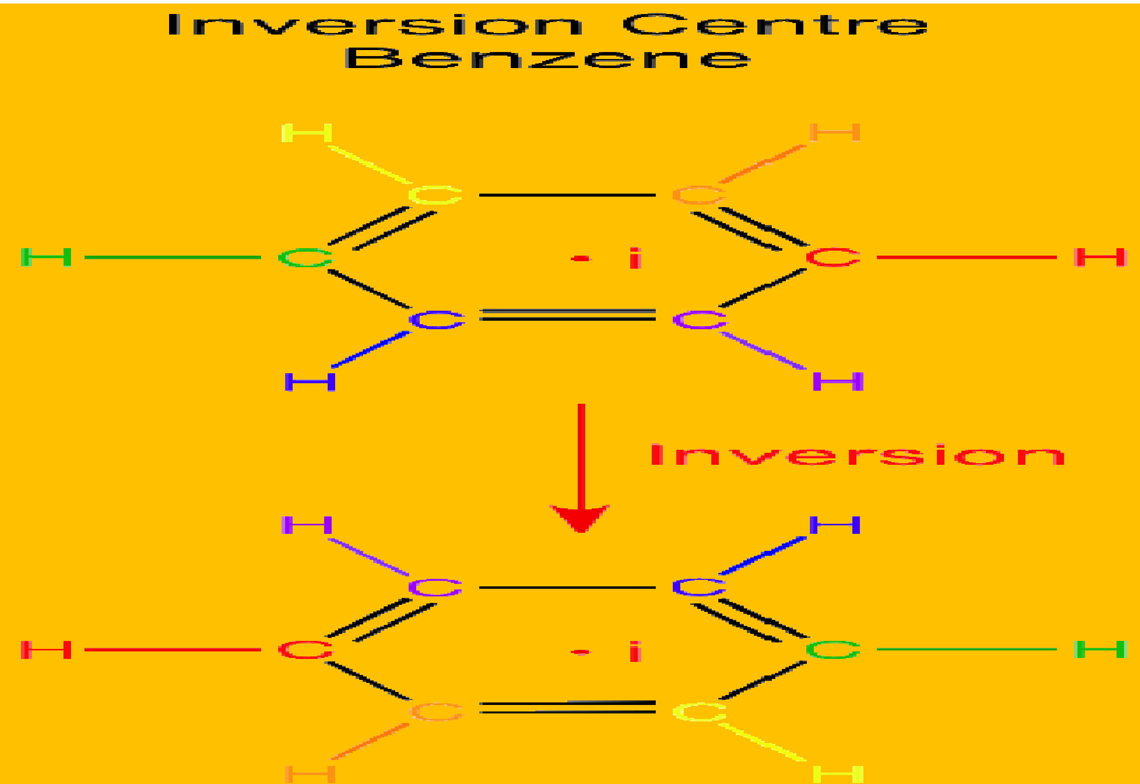

Inversion Centre
Benzene
H
H
H
C
C
H
C
i
C
C
C
H
H
Inversion
H
H
H
C
C
H
C
i
C
C
C
H
H

Figure: 13

➢Identity Operation:

This operation gives no change in the molecule. It is included mathematical completeness. An identity operation is characteristic of every molecule, even if it has no other symmetry.

Difference between

➢ symmetry operation and symmetry element:

S.N.	Symmetry operation	Symmetry element
1.	No change	Identity
2.	Rotation by 360/θ about an axis of symmetry (n)	A n-fold axis of rotation
3.	The reflection in any plane of symmetry parallel w.r.t. to principle axis of symmetry (σv).	A plane of symmetry containing the principle axis of symmetry (σv)

4.	The reflection of plane of symmetry perpendicular to the principle axis of symmetry (σh).	A plane of symmetry perpendicular to the principle axis of symmetry.
5.	Reflection of a plane of symmetry containing parallel w.r.t. principle axis of symmetry and bisecting between two C_2 axes of symmetry (σd).	A plane of symmetry containing the principle axes of symmetry and bisecting angle between two C_2 of symmetry (σd).
6.	Rotation by 360/θ about axis followed by reflection in a plane perpendicular to that axis (S_n)	The n fold alternating axis (S_n).

➢ *COMPLETE SET OF SYMMETRY OPERATIONS AS MATHEMATICAL GROUP:*

Group was defined by Arthor and Cayley in 1854. “Groups are a collection or set of element and obey the certain rules. It should denote number, matrix, vector, symmetry operation, element, addition-matrix and multiplication etc. are called group.”

There are four postulate of the group:

1.The product (multiplication of any two elements) in the group and the square of each element must be an element in the group.

Example: In H_2O, element of symmetry C_2 (z), E, σv_{xz}, σv_{yz} are present.

$\mathbf{C_2.C_2= E}$

Since the product of $C_2.C_2$= E which is the element present in group.

$\mathbf{C_2.\ \sigma v_{xy}= C_2}$

In this, the product of $C_2 . \sigma v_{xy} = C_2$, which is also present in the group.

The product multiplication of elements means combination of elements of the group. The square of an element means multiplication an element with itself.

The product of two group of elements A and B of the group can be AB or BA these type of groups are known as Abelian group.

Case1- A.B=B.A

$C_2.E=E.C_2$

Case 2 - $\mathbf{A.B \neq B.A}$

$$C_3^1 . \sigma v \neq \sigma v . C_3^1$$

Quite often the product A.B may give the element C, the group where B.A may give another element D of the same group.

2.There is one element in each mathematical group which must commute (A.B=B.A) with all other elements of the group and leave them unchanged such element is known as identity element and this operation is called identity operation.

A.E = E.A = A

Example: In H_2O

$C_2.E = E.C_2 = C_2$

Example: In NH_3

$C_3.E = E.C_3 = C_3$

3. The element of mathematical group obeys the associative law of multiplication.

A.B (C.D.E) = A (B.C) (D.E) = (A.B) (C.D). E

Each element of mathematical group must have a reciprocal which is also an element of the group. When an element is multiplied by its reciprocal we get identity.

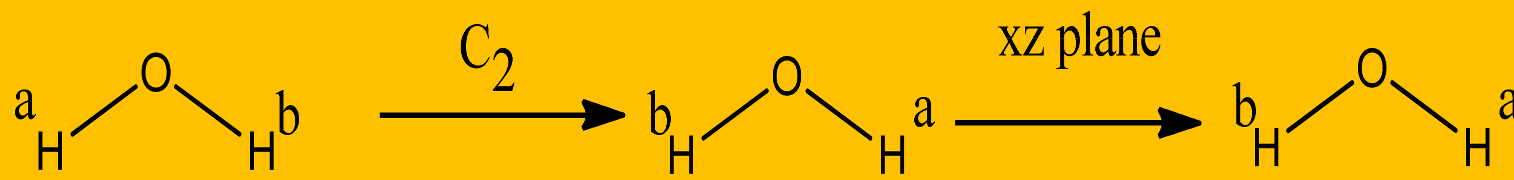
$A.A^{-1} = A^{-1}.A = E$

Type of group:

a. Abelian group

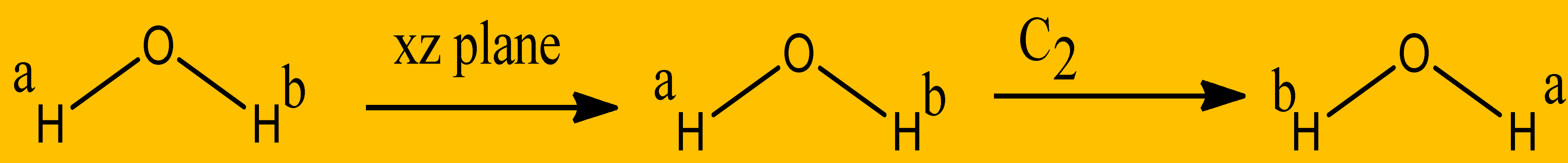
b. Non-abelian

a. Abelian group: "The groups in which all elements commute to each other are called Abelian group."



$$\begin{bmatrix} +x \\ +y \\ +z \end{bmatrix} \qquad \begin{bmatrix} -x \\ -y \\ +z \end{bmatrix} \qquad \begin{bmatrix} +x \\ -y \\ +z \end{bmatrix}$$

(Matrix of plane of symmetry)



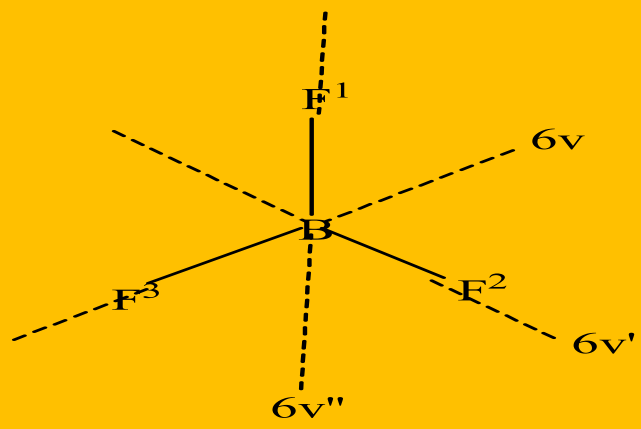
$$\begin{bmatrix} +x \\ +y \\ +z \end{bmatrix} \qquad \begin{bmatrix} +x \\ -y \\ +z \end{bmatrix} \qquad \begin{bmatrix} -x \\ +y \\ +z \end{bmatrix}$$

(Matrix of plane of symmetry)

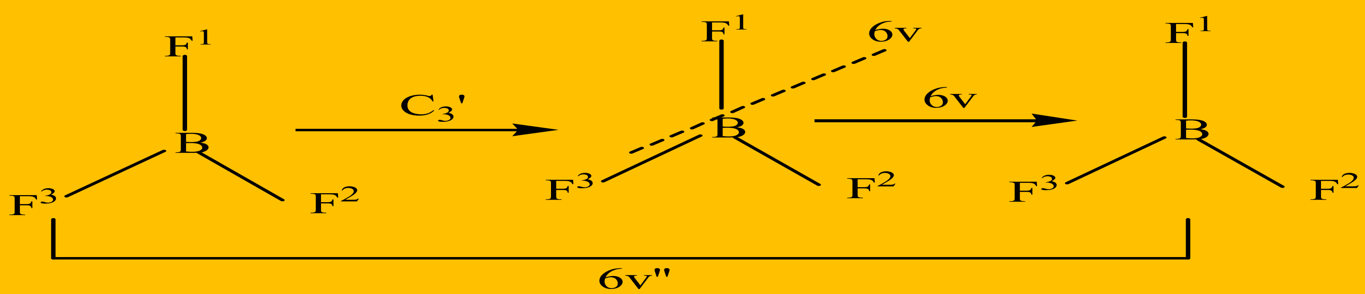
Non-Abelian Group: “If all the elements do not commute to each other known as Non-abelian group. Shown below figure:

? 6v+

1. BF_3- Element of symmetry - $^2C_3$,$3C_2$ 6v, $6v^1$, 6v'',6h for C_3', 6v = 6v , C_3' = ?

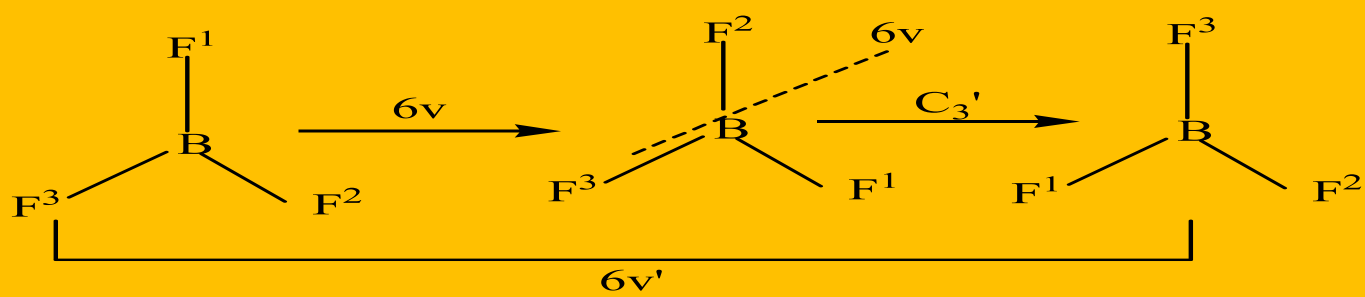


(a) For C_3'. 6v = ?



C_3. 6v = 6v''

(b) For 6v. C_3'. = ?



Since,

$$\left.\begin{array}{r} C_3' \cdot 6v = 6v'' \\ 6v.\ C_3' = 6v' \end{array}\right\}\text{Non- abilian group}$$

❖***GENERATOR:***

For arriving at the point group of a molecule we need to have knowledge of the generator of the symmetry operation. Generator can be defined as: "The minimum number of symmetry operation combined to each other be give the product of the group is known as **point group.**"

Classification of point group:

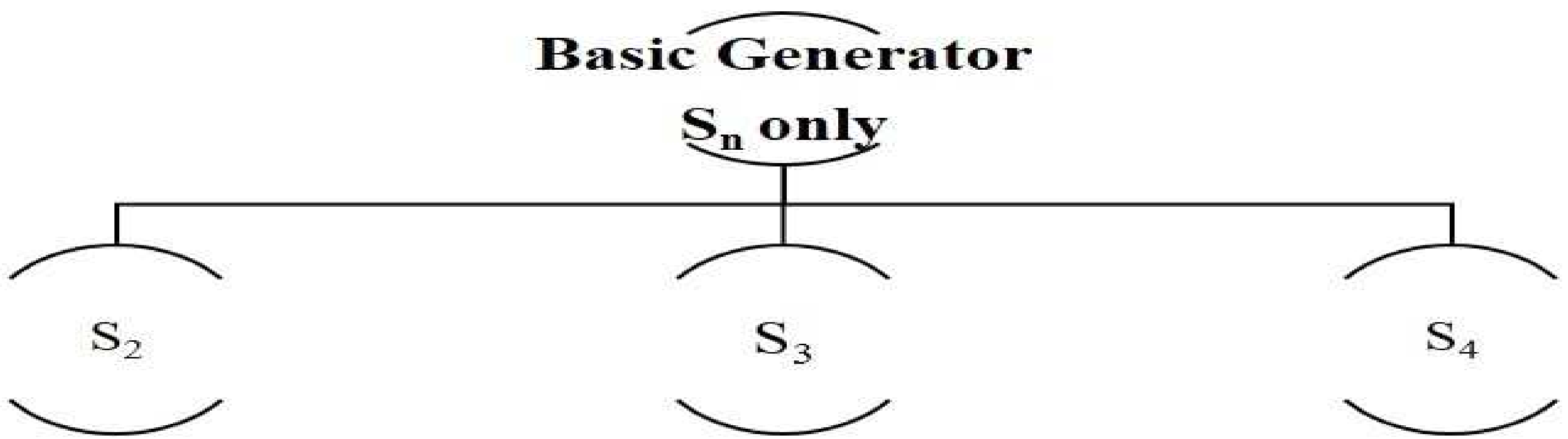
1) Non-axial point group

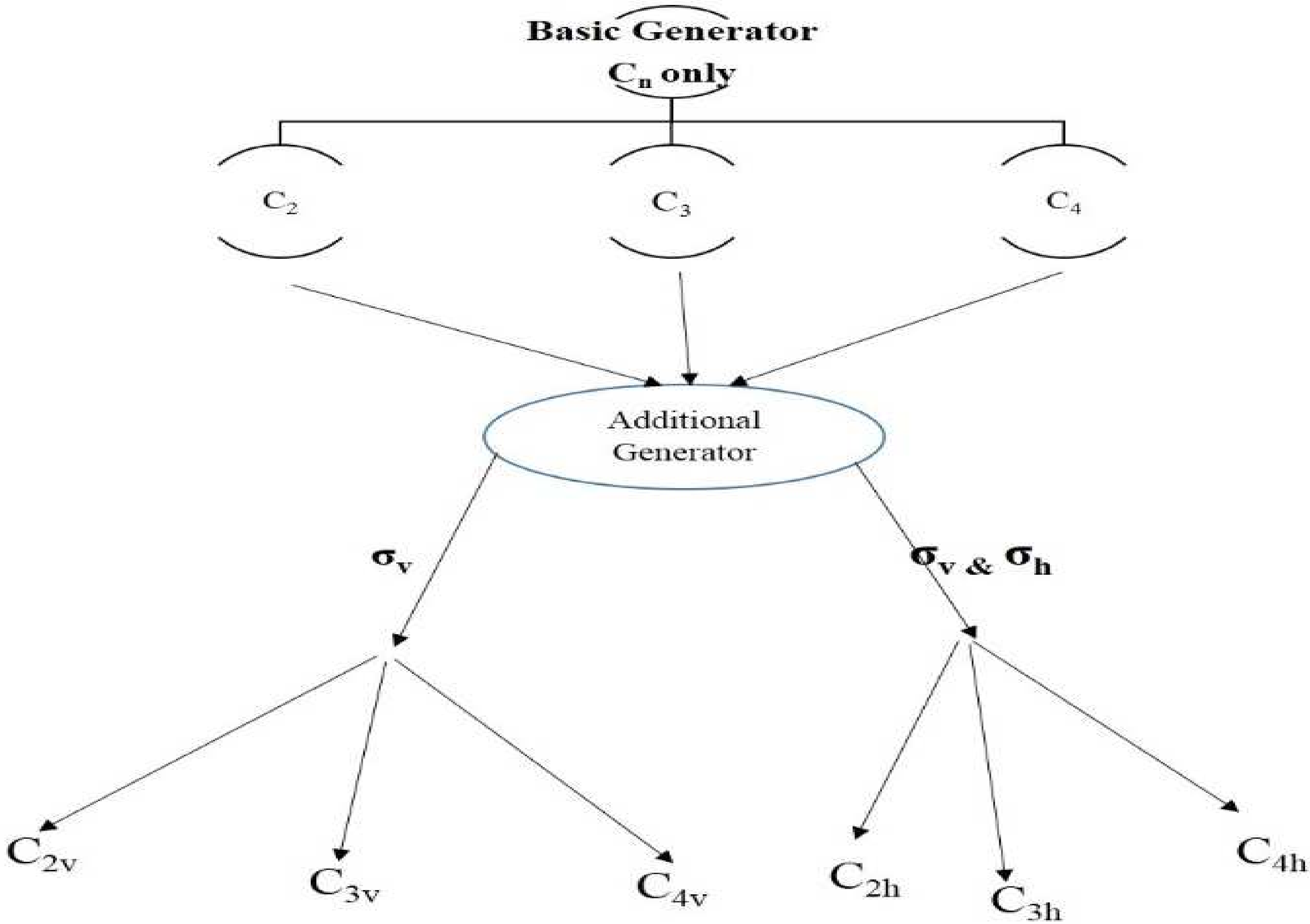
2) Axial point group

1. Non-axial point group:

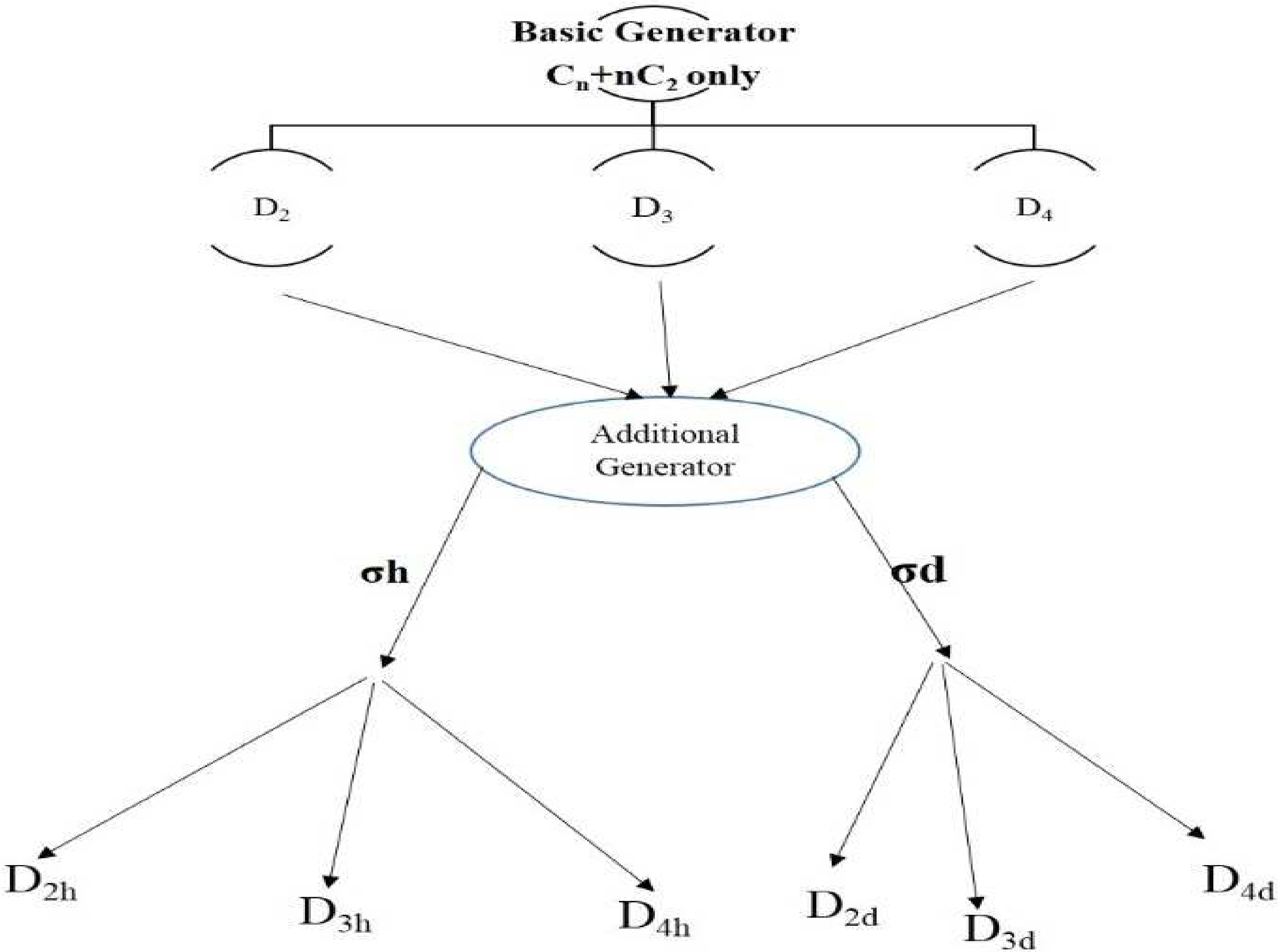
No axis of symmetry present in this type of point group.
If only identity (E) present as generator. Only C_1(n=360/360) or e operator is possible so that the point group is C_{-1}.
Only plane of symmetry is present in a group, the point group is C_s.
If only point of symmetry present the point group is C_i

(b) Axial point group: Basic generator as well as additional generators are present in the molecule those are called axial group.



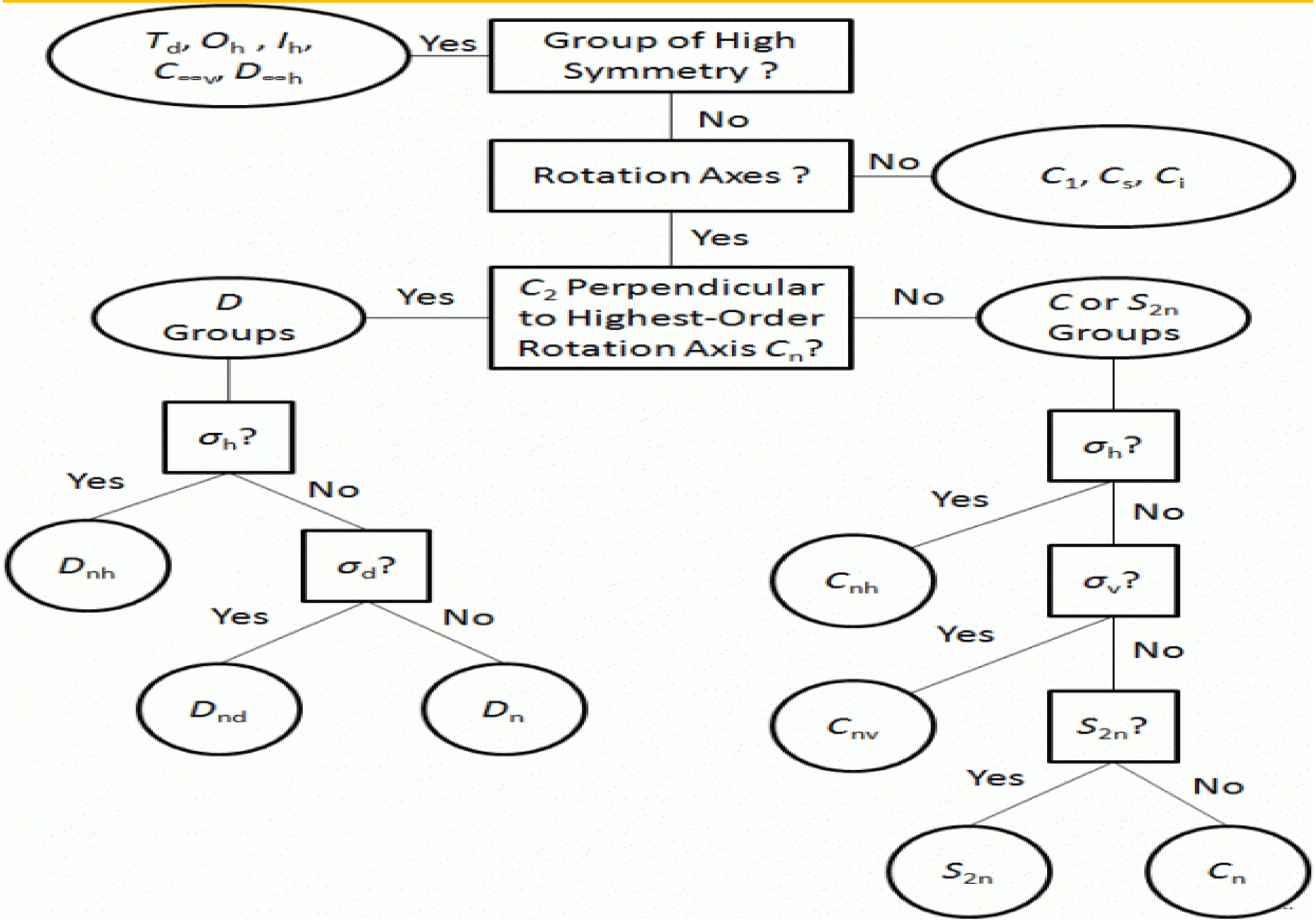


Basic Generator
C_n only
C_2
C_3
C_4
Additional Generator
σ_v
σ_v & σ_h
C_{2v}
C_{3v}
C_{4v}
C_{2h}
C_{3h}
C_{4h}



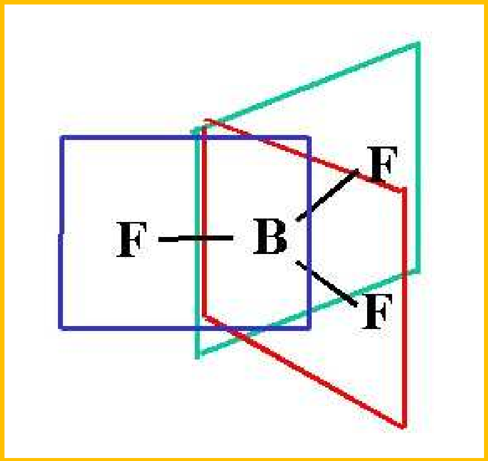
Basic Generator
C_n+nC_2 only
D_2
D_3
D_4
Additional Generator
σh
σd
D_{2h}
D_{3h}
D_{4h}
D_{2d}
D_{3d}
D_{4d}

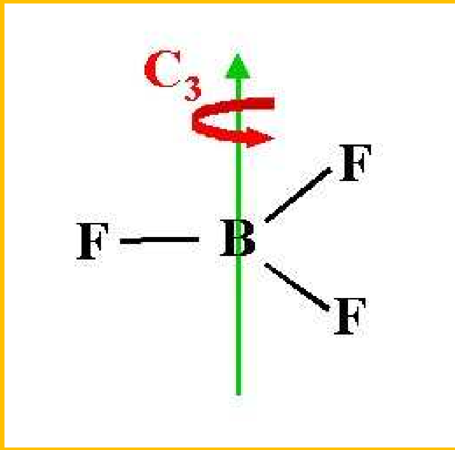
Figure: 2.4 Flow chart for point group determination



➢*Some Examples of various point groups of compounds:*

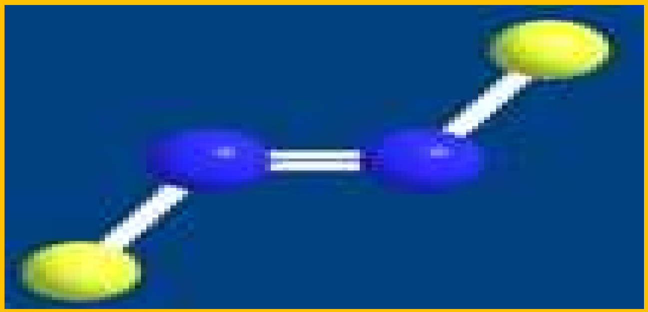
1. BF_3 molecules the point group is D_{3h}



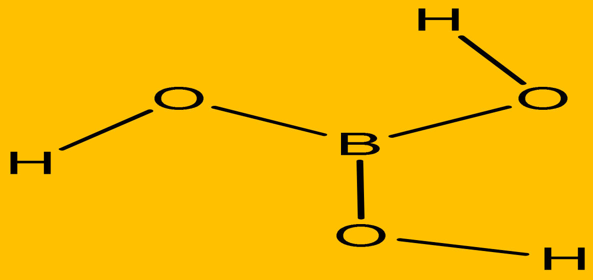


D3h

2. Cnh Point Groups :

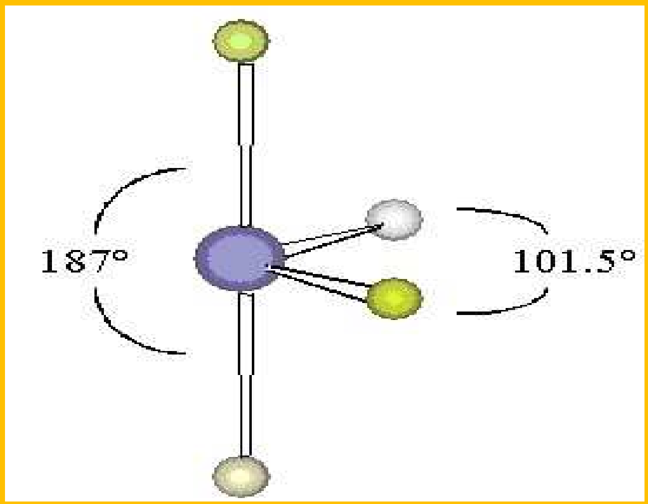


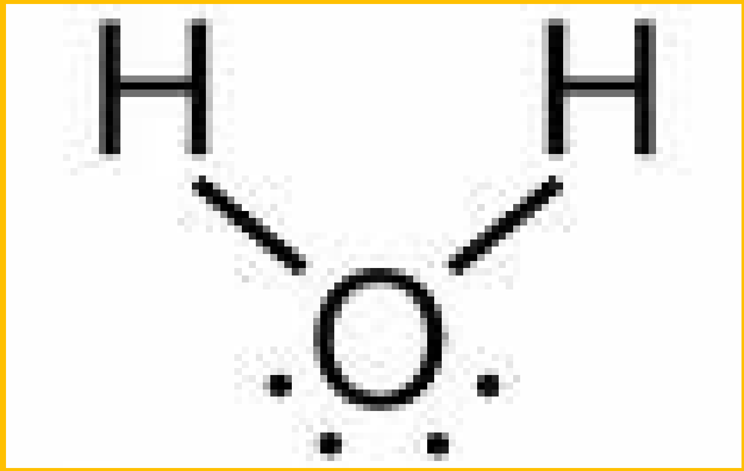
(N2F2)
C2h



$B(OH)_3$
C3h

***3. Cnv** Point Groups AX_2 bent type molecule. If a mirror plane contains the rotational axis, the group is called a Cnv group.*

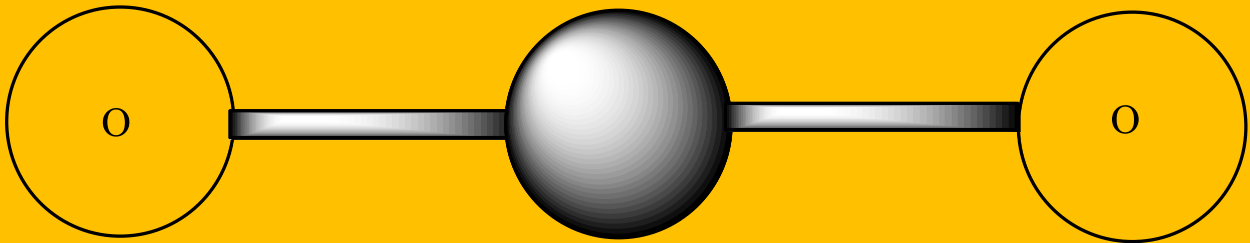




SF4

C2v

3. D_{nh} type point group, in CO_2 :



There are an infinite number of possible C_n axes and σ_v mirror planes in addition to the σ_h.

Point groups with their characteristic symmetery

Point Group	Characteristic symmetry operations
C_1	E
C_i	i
C_s	σ
C_n	C_n
C_{nv}	C_n , n σ_v
C_{nh}	C_n , σ_h (S_n , i for even n)
D_n	C_n , n perpendicular C_2's, no σ's
D_{nd}	C_n , n perpendicular C_2's, n σ_d ,S_{2n}, i for odd n.
D_{nh}	C_n , n perpendicular C_2's, σ_h,S_n, (i, $n/2$ σ_d 's, $n/2$ σ_v's for even n)
S_n	S_n only, n is even. Possible i, $C_{n/2}$
$D_{\infty h}$	Linear, i
$C_{\infty v}$	Linear, no i
T_d	Tetrahedral
O_h	Octahedral
K_h	Sphere

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THANK YOU