UNIT 4 GROUP THEORY AND ITS APPLICATIONS

LESSON STRUCTURE

4.1 Introduction

The concept of symmetry and group theory are important in chemistry to study the structure of molecules. The measurement of crystal structures, infra–red spectra, ultra–violet spectra, dipole moments and optical activities, all these are properties which depend on molecular symmetry. The term symmetry is synonymous to beauty. The nature has made most of its creation symmetrical i.e., the sun planets animals and plants. symmetry is present in geometrical figures, crystalline solids and molecule. Entities which possess more element of symmetry are more symmetrical. The square is said to be more symmetrical than the

rectangle due to fact that all sides of a square are equal whereas in a rectangle opposite sides are equal. One can quantitatively say that square is more symmetrical due to the presence of larger number of symmetry elements and symmetry operations in it.

4.2 Symmetry Elements and Symmetry Operations

Symmetry operations is a movement of the molecule such that the resulting configuration of the molecule is in distinguishable from the original. In another way we can define a symmetry operation is to say that its effect is to take the body into an equivalent configuration or an identical configuration.

A *symmetry element* is a geometrical entity such as a line, a plane or a point with respect to which one or more symmetry operations may be carried out.

A symmetry elements and symmetry operations are closely inter related. The symmetry operation should be performed with the molecule. There should be atleast one point in the molecule which is unaffected by all the symmetry operations. All the symmetry elements intersect at this point. Thus there is no translational motion of the molecule during the course of a symmetry operation.

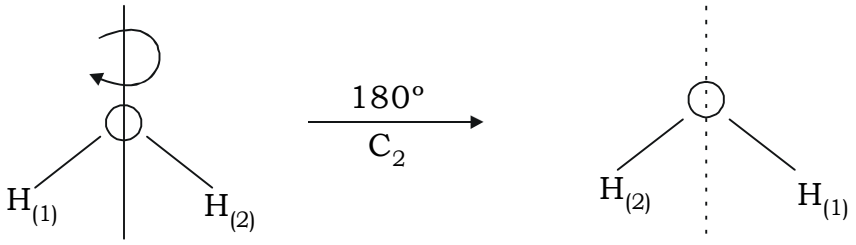
The followings are the symmetry elements and symmetry operations used in the molecular symmetry with their symbol.

	Symmetry Element	**Symmetry Operation**	**Symbol**
1.	Identity	To leave the molecule uncharged	E
2.	Axis of symmetry	Rotation by angle $\theta = \left(\frac{2\pi}{n}\right)$ about the axis	C_n
3.	Plane of Symmetry	Reflection in a plane	σ
4.	Centre of Symmetry	Inversion of all atoms through the centre	i
5.	Improper axis of Symmetry	Rotation about the axis followed by reflection in a plane perpendicular to the rotational axis	S_n

1. **Identity**—An identity operation results in the production of an orientation which is identical to the original orientation. This is the operation of doing nothing (leaving the molecule unchanged). The operation results not only in the production of an equivalent orientation but in a identical one. The identity operation is really not an operation at all but its is a mathematical requirements.

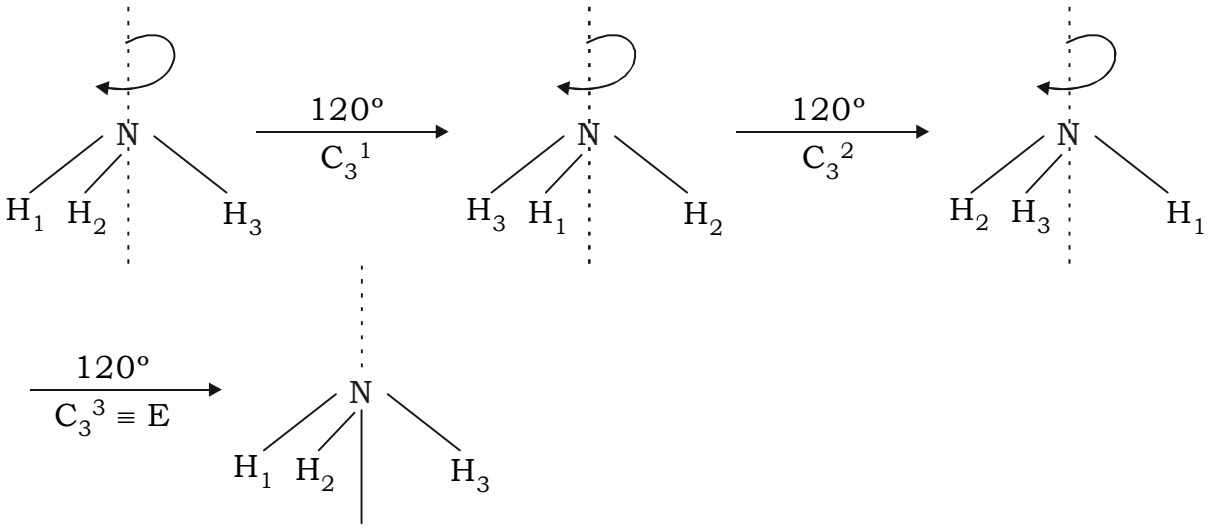
2. **Axis of Symmetry**—This is defined as an axis around which the rotation of the molecule (we may choose clockwise rotation as +ve and counter clock–wise rotation as –ve) by an angle $\theta = \frac{2\pi}{n}$ gives an equivalent configuration, where n is the order of the axis. The order of axis may be two fold (C_2), three fold (C_3), four fold (C_4) etc. If there are axes of different order in a molecule, the axis with the highest order is referred to as principle axis of rotation.

In water (H_2O) molecule C_2 (two fold) axis of rotation is present became equivalent configuration is obtained by rotation through 180°.



A two-fold axis of rotation

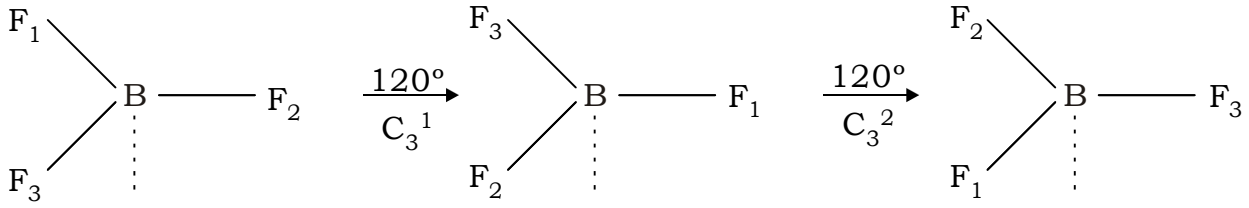
In ammonia (NH_3) molecule has a C_3 axis passing through nitrogen atom. The identical configuration is obtained by rotating the molecule through 120°.



Three fold axis of rotation

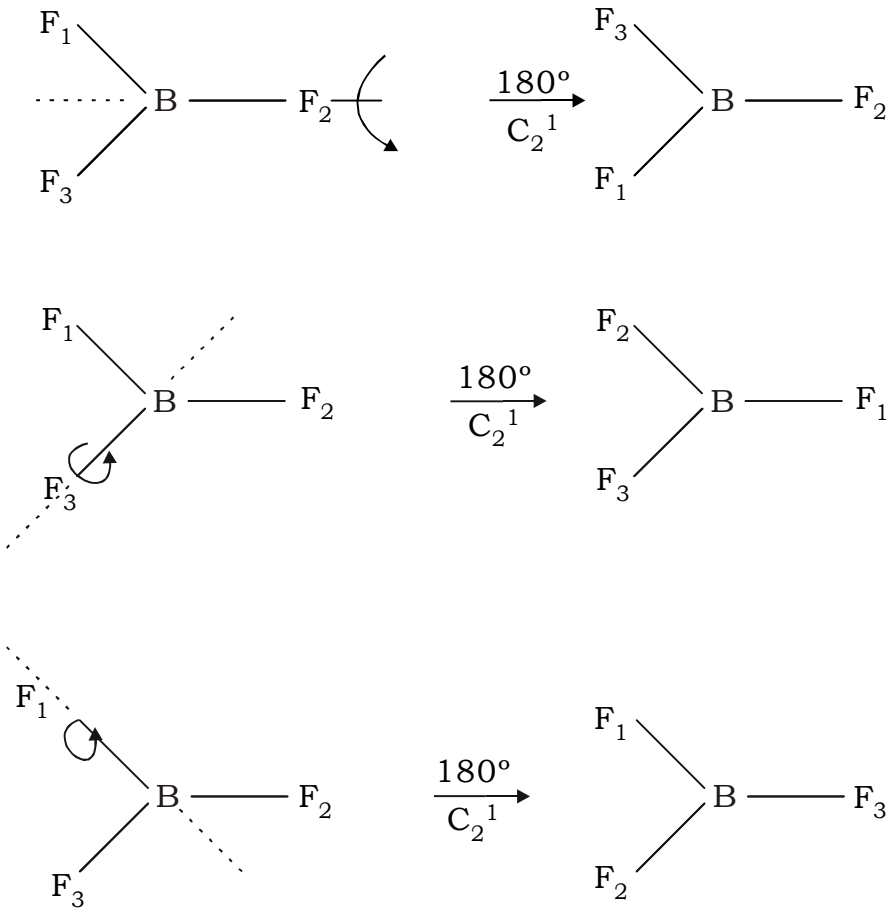
C_3^1 means one time rotation by an angle 120°, C_3^2 means two time rotation by an angle 120° while C_3^3 is the identity (After C_3^3 original configuration is obtained).

BF_3 molecule (AB_3 type planar molecule) possess a three fold (C_3) axis of rotation passing through B–atom and is perpendicular to the plane of molecule.



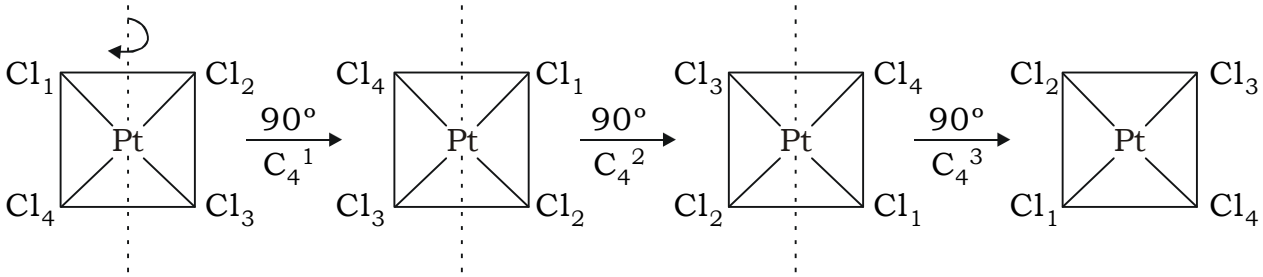
Three fold anix of rotation

In addition to C_3, this type of molecules possess three more two–fold (C_2) axes which are perpendicular to the C_3 axis, passing through boron and each of the fluorine atoms. There axes are in the plane of the molecule.

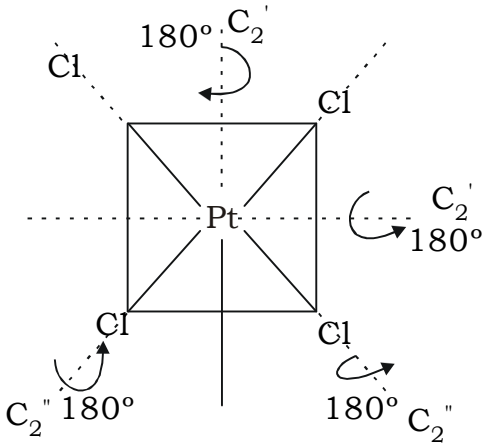


Two fold anis of rotation

Like these square planare AB_4 molecule e.g., $[PtCl_4]^{2-}$ has four fold symmetry i.e., C_4^1, C_4^2, Cu^3, $2C_2'$, $2C_2''$, C_2'''.



Four fold axis of rotation



Cyclopentadienyl anion $C_2H^-_5$ has four five fold axis of rotation i.e., C_5^1, C_5^2, C_5^3, C_5^4 and five two fold axis of rotation ($5C_2$).

3. **Plane of Symmetry**—It is defined as an imaginary plane that bisects molecule in such a way that the two parts are morror images of each ohter. It should be noted that the operation of reflection gives a configuration equivalent to the original one. If the operation is carried out twice on the molecules, we get the original configuration ($\sigma.\sigma = \sigma^2 = E$).

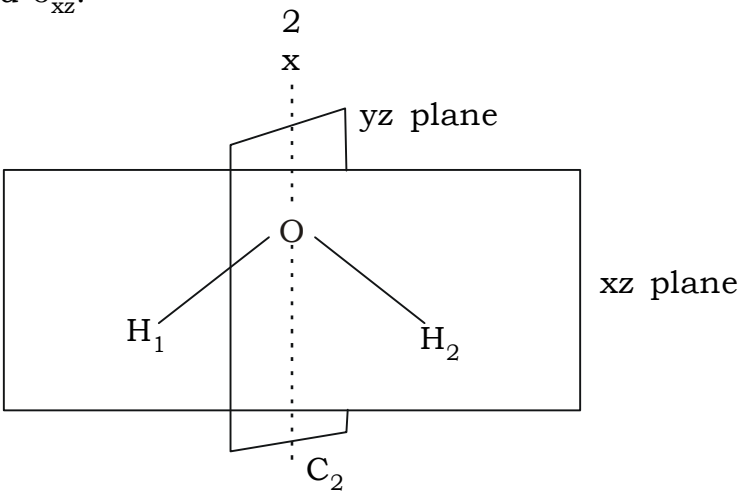
The plane of symmetry can be classified into three types :

(a) Vertical plane (σ_v) : The plane passing through the principle axis and one of the subsidiary axis (if present) is called vertical plane.

(b) Horizontal plane (σ_h) : The plane which is perpendicular to the principle axis is called horizontal plane.

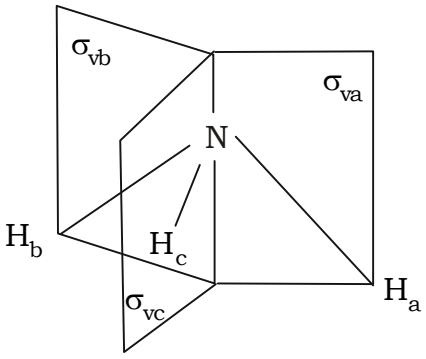
(c) Dihedral plane (σ_d) : The plane passing through the principle axis but bisecting an angle between two subsidiary axis (C_2) is called dihedral plane.

Water molecule has two symmetry planes i.e., σ_{xz} σ_{xz}. One is passing through oxygen atom and bisecting the angle ∠HOH i.e., yz plane called as σ_{yz}. The other plane of symmetry is passing through oxygen atom and two H–atoms. This is an xz plane and is called σ_{xz}.

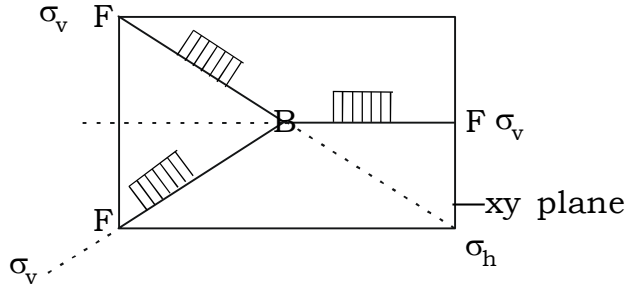


Plane of symmetry is H_2O molecule

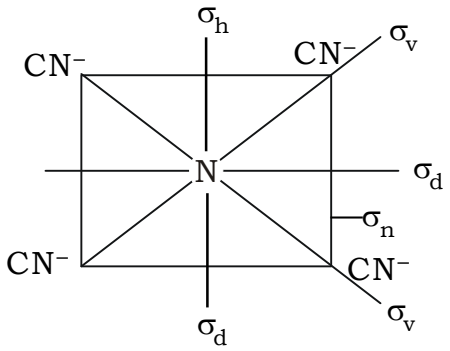
Ammonia molecule has three symmetry plane i.e., $3\sigma_v$. All there planes are passing through rotational axis. N–atom and one H–atom.



In case of BF_3 (triangular planar) molecule, there are three σ_v plane, each passing through the principal axis (C_3) and one of the C_2 i.e., through B–atom and one of the fluorine atom and bisecting the angle between other two F–atoms. BF_3 is planar molecule and hence plane of molecule is also a plane of symmetry. This is perpendicular to the principal axis and is denoted by σ_h.

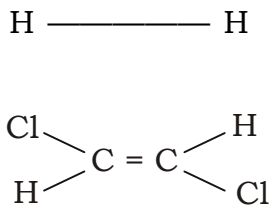


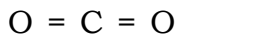
In case of square planar $[Ni(CN)_4]^{2-}$, there are four σ_v plane and one σ_h plane. Two σ_v plane passes through C_4–axis Ni(II) ion and two CN^- ion at opposite corners. To σ plane passes through Cu–axis, Ni(II) ion and between two CN– and is called σ_d. The molecular plane passing through Ni(h) ion and four CN^- is σ_h.

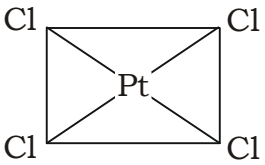


In hexagonal planar benzene molecule, six σ_v and one σ_h are present.

4. **Centre of invertion (*i*)**—If a point exists in the centre of a molecule such that identical atoms are found on either side at equal distances from it, the central point is called the centre of inversion. All homonuclear diatomic molecule possess the centre of symmetry. e.g., Cl_2, H_2, Br_2 etc. CO_2, C_2H_2 ethylene *trans* dichloroethane, benzene, $[PtCl_4]^{--}$, $[Ni(CN)_4]^{--}$ etc. have a centre of symmetry.







5. **Improper axis of symmetry or Rotational–reflectional axis of symmetry (S_n)**—This operation in combination of a rotation (C_n) with a reflection (σ) in a plane perpendicular to the rotational axis. After this composite operation, it leaves the molecule in an indistinguishable configuration.

$$S_n = C_n.\sigma_h$$

If any molecule contains Cn and σ_h operations, then it is generally contains S_n.

$$S_2 = C_2.\sigma_h = i$$

S_2 is *i* became after the rotation by 180° and then reflection perpendicular to C_2 produce *i*.

$$S_3 = C_3.\sigma_h$$

BCl_3 contains S_3. BCl_3 molecule after C_3 and then $\sigma_h \perp C_3$ produce indistinguishable configuration.

As C_n generates n operations i.e., C_n^1, C_n^2, C_n^3, ... C_n^4(=E), S_n also generates n such operations when n is even but generates $2n$ when n is odd.

If n = even

i.e., $n = 3$

$$S_3^1 = C_3^1.\sigma_h^1 = C_3.\sigma_h$$

$$S_3^2 = C_3^2.\sigma_h^2 = C_3^2.E = C_3^2$$

$$S_3^3 = C_3^3.\sigma_h^3 = E.\sigma_h^2.\sigma_h = E.E.\sigma_n = \sigma_n$$

$$S_3^4 = C_3^4.\sigma_h^4 = C_3^3.C_3^1.\sigma_h^2.\sigma_h^2 = E.C_3^1.E.E = C_3^1$$

$$S_3^5 = C_3^5.\sigma_h^5 = C_3^3.C_3^2.\sigma_h^2.\sigma_h^2.\sigma_h = E.C_3^2.E.E.\sigma_h = C_3^2.\sigma_h$$

$$S_3^6 = C_3^6.\sigma_h^6 = C_3^3.C_3^3.\sigma_h^2.\sigma_h^2.\sigma_h^2 = E.E.E.E.E.= E$$

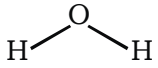
Hence S_3 generate two S_3^1 and S_3^5.

Like this S_4 generates two S_4^1 and S_4^3.

Writing all symmetry operations in a molecule.

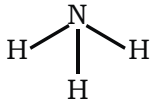
Examples :

(i) H_2O



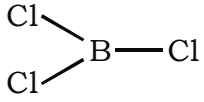
E, $C_{2(2)}$, σ_{xz}, σ_{yz}

(ii) NH_3

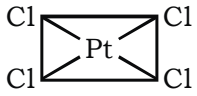


$E, C_3^1, C_3^2, \sigma_a, \sigma_b, \sigma_c$

(iii) BCl_3

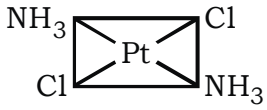


$$E, C_3^1, C_3^2, 3C_2, 3\sigma_v, \sigma_h, S_3^1, S_3^5 = 12$$

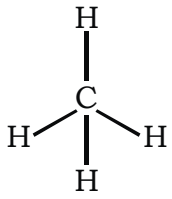
(iv) $[PtCl_4]^{--}$ 

$E, C_4^1, C_4^2, C_4^3, 2C_2', 2C_2'', 4\sigma_v, \sigma_h, S_4^1, S_4^3, i = 14$

(v) [Pt $(NH_3)_2Cl_2$] (*Trans* dichloro diamine Pt (11))



E, C_{21}, $2C_2$, $2\sigma_v$, σ_h, i = 8

(vi) CH4 

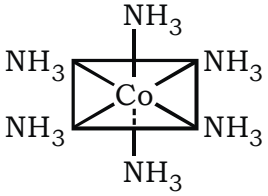
$E, 8C_3, 3C_2, 6S_4, 6\sigma_d = 24$

(vii) H_2 H—H

$E, C_\infty, \infty C_2, \infty\sigma_v, \sigma_h$

(viii) HCl H—Cl

$E, C_\infty, \infty\sigma_v$

(ix) $[Co(NH_3)_6]^{3+}$ 

$E, 6C_4, 3C_2, 8C_3, 6C_2', 6S_4, 8S_6, 6\sigma_v, 3\sigma_h, i = 48$

4.3 Group and its Characteristics

A group is a collection of elements that are interrelated according to certain rule. We shall be concerned with the groups formed by the sets of symmetry

operations that may be carried out on molecules or crystals. The followings are the requirements for a mathematical group.

(a) Closure (b) Identity

(c) Inverse (d) Association

(a) **Closure**—The product of any two elements in the group and the square of each element must be an element in the group.

The product of any element A and B produce C. C must be element of the group.

$A.B = C$

$A^2 = D$

$B^2 = E$

C, D and E must be element of the group.

The order of combination is very important as AB is not necessarity equal to BA.

If AB = BA, the members A and B are said to commutative.

and if AB ≠ BA, the members A & B are not commutative. The members of the group which are commutative form *Abelian group.*

(b) **Identity**—One element of the group must commute with all other elements and leave them unchanged. This element is called identity and represented as E.

Identity must be present in a group.

$E.A = A.E = A$

$E.B = B.E = B$

A and B are elements of the group.

(c) **Inverse**—Every member of the group must have its inverse as an member of the group.

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

(d) **Association**—Multiplication must be associative.

$A(B.C) = (A.B).C$

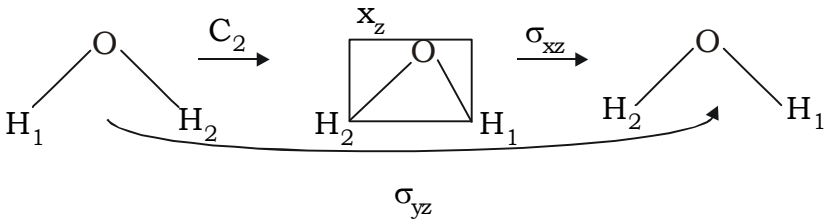
Symmetry elements of a molecule constitute a group.

4.4 Product of Symmetry Operations

The set of symmetry operations of water molecule represents a group. The

total symmetry operations of water molecule are E, C_2, σ_{xz}, σ_{yz}. There four symmetry operations follow the all requirement of a mathematical group.

Rule (a) : C_2, $\sigma_{xz} = \sigma_{yz}$



$C_2.C_2 = E$

Rule (b) : $C_2.E = C_2$

$\sigma_x^z . E = \sigma_x^z$

Rule (c) : $C_2.C_2^{-1} = E$

$\sigma_x^z . s_{xz}^{-1} = E$

Rule (d) : $C2.(\sigma_{xz}.\sigma_{yz}) = (C_2.\sigma_{xz}).\sigma_{yz}$

$\Rightarrow \quad C_2.C_2 = \sigma_{y_z}.\sigma_{yz}$

$\Rightarrow \quad E = E$

There rules may also be verified using the multiplication table.

Multiplication Table for symmetry operations of water molecule i.e., for C_{2v} point group.

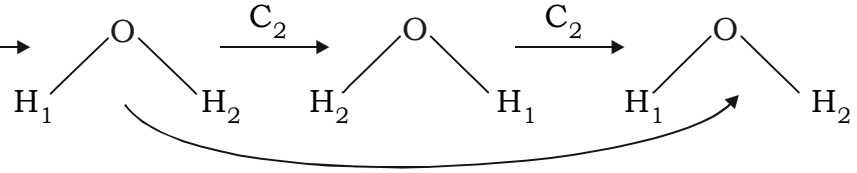
Symmetry Operations				
H_2O (C_{2v})	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{xz}	σ_{yz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

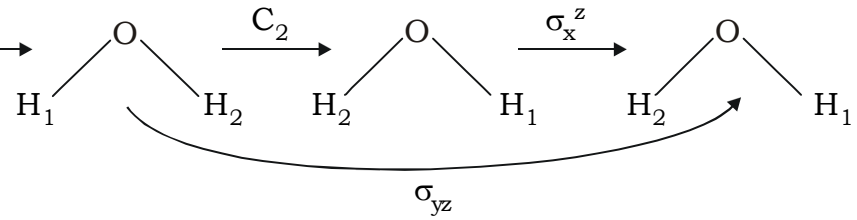
These are illustrated as :

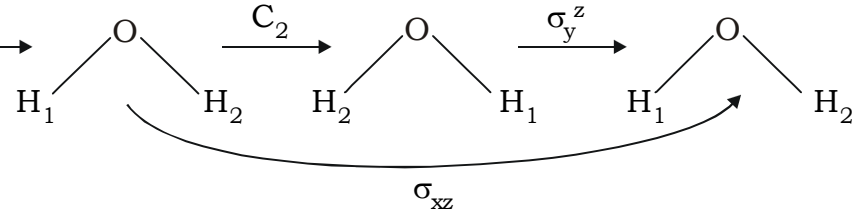
$C_2.E = E.C_2 = C_2$

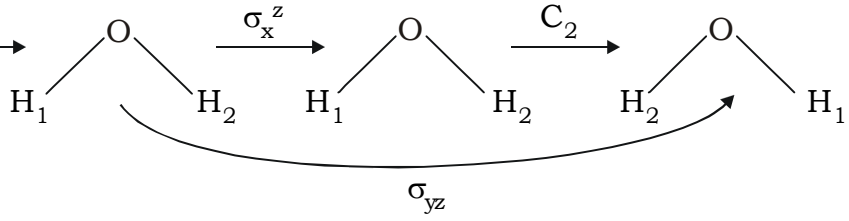
$\sigma_x^z.E = E.\sigma_x^z = \sigma_x^z$

$\sigma_y^z = E.\sigma_y^z = \sigma_y^z$

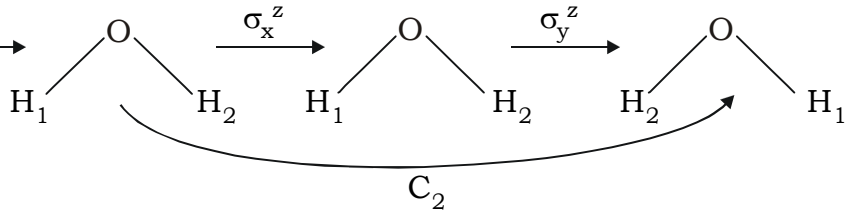
$C_2 \cdot C_2 = E$ 

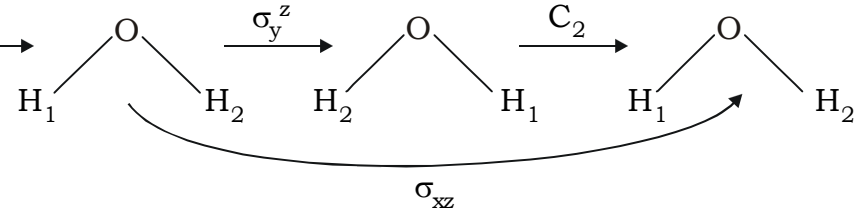
$C_2\ \sigma_{xz} = \sigma_{yz}$ 

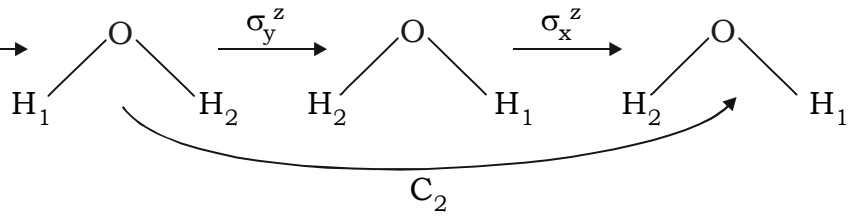
$C_2.\sigma_y^z = \sigma_x^z$ 

$\sigma_x^z.C_2 = \sigma_y^z$ 

$\sigma_x^z.\sigma_x^z = E$

$\sigma_{xz}.\sigma_{yz} = C_2$ 

$\sigma_{yz}.C_2 = \sigma_{xz}$ 

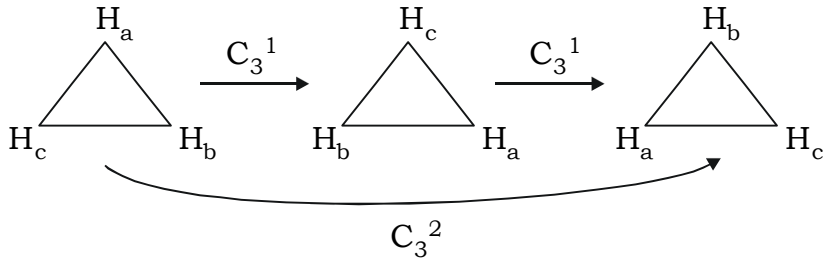
$\sigma_{yz}.\sigma_{xz} = C_2$ 

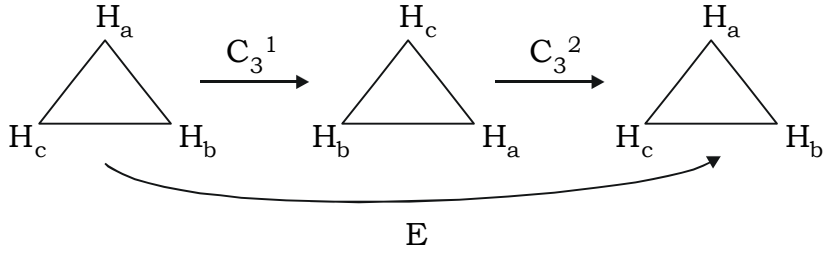
$\sigma_y^z.\sigma_x^z = E$

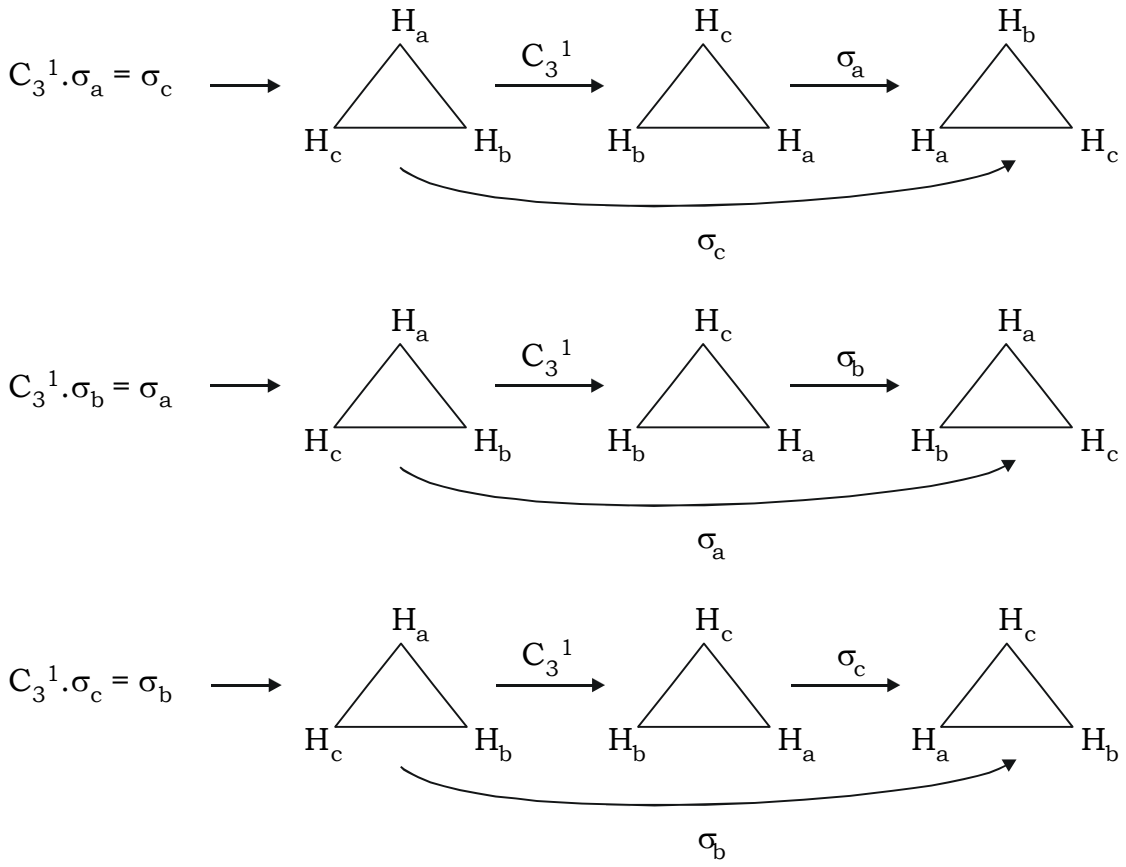
Multiplication Table for Symmetry Operations of NH_3 molecule i.e., for C_{3v} Point Group.

Symmetry operations						
NH_3 (C_{3v})	E	C_3^1	C_3^2	σ_a	σ_b	σ_c
E	E	C_3^1	C_3^2	σ_a	σ_b	σ_c
C_3^1	C_3^1	C_3^2	E	σ_c	σ_a	σ_b
C_3^2	C_3^2	E	C_3^1	σ_b	σ_c	σ_a
σ_a	σ_a	σ_c	σ_b	E_3^1	C_3^1	C_3^2
σ_b	σ_b	σ_a	σ_c	C_3^2	E	C_3^1
σ_c	σ_c	σ_b	σ_a	C_3^1	C_3^2	E

Some of them are illustrated as :

$C_3^1.C_3^1 = C_3^2$ 

$C_3^1.C_3^2 = E$ 



4.5 Sub Groups, Classes, Similarity Transformation and Conjugate

Order of a group : The no. of elements in a group is called its order and is represented as h. In a molecular point group, order is the no. of symmetry operations possible. In water molecule (C_{2v} point group), the total no. of symmetry operations are four and hence order is four. In ammonia molecule (C_{3v} point group), the total no. of symmetry operations are sin and hence order is sinx.

Sub group : Smaller groups that may be found within a larger group are called subgroups. The elements of a subgrup should obey the following conditions :

(i) The elements of sub groups must obey all the conditions of a group.

(ii) If g is the order of the group and s is the order of the sub group, the g/s is a natural number.

In water molecule, the followings are the subgroups :

(i) E

(ii) E, C_2^1

(iii) E, σ_{xz}

(iv) E, σ_{yz}

In ammonia molecule the symmetry operations E, C_3^1, C_3^2 constitute a subgroup of order 3.

Classes, Similarity Transformation and Conjugate : There is another way in which the elements of a group may be separated into smaller sets and such sets are called classes. Before defining a class, we should know about similarity transformation.

If *A* and *X* are two elements of a group, then $X^{-1}AX$ will be equal to some element of the group, say B. We have

$$X^{-1}AX = B$$

Here element B is the similarity transform of A by X. A & B are also called as conjugate. The followings are the properties of conjugate.

(i) Every element is conjugate with itself

$$A = X^{-1}AX$$

(ii) If A is conjugate with B, then B is conjugate with A.

$$A = X^{-1}BX$$

$$B = Y^{-1}AY$$

Y be the another element of the group.

(iii) If A is conjugate with B and C, then B and C are conjugate with each other.

A complete set of element that are conjugate to one another is called a class of the group.

For NH_3 molecule (C_{3v} point group), operations C_3^1 & C_3^2 and σ_a, σ_b, σ_c are similar. According to similarity transformation rule.

$$A = \sigma_a^{-1}.C_3^1.\sigma_a = \sigma_a.\sigma_c = C_3^2$$

(See Multiplication Table)

Here $B = C_3^1$, $x = \sigma_a$, $x^{-1} = \sigma_a^{-1}$

Taking B = C_3^1 and any operation *x* of the C_{3v} group and see that according to similarity transparent leads, to either C_3^2 or C_3^1 and hence we say that C_3^1 and C_3^2 are similar and belongs to same class.

Like this σ_a, σ_b and σ_c belongs to some class in C_{3v} point group.

Following one the classes for the point group given

$$C_{2v} - E,\ C_2,\ \sigma_{xz},\ \sigma_{yz} = 4 \text{ classes}$$

$C_{2h} - E,\ C_2,\ \sigma_h,\ i = 4$ classes

$D_{3h} - E, C_3^1.C_3^2, C_2, C_2', C_2'', \sigma_n, S_3^1, S_3^5, \sigma_v, \sigma_v^{\ 1}, \sigma_v$

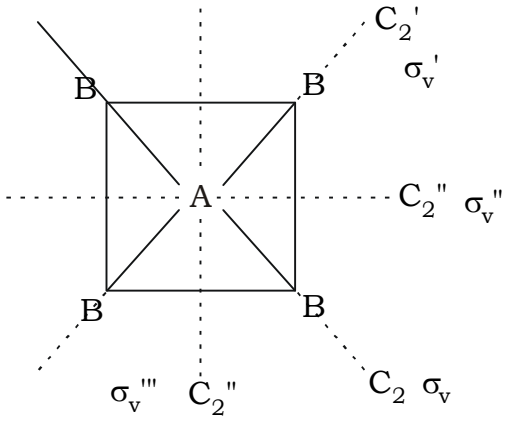
or, $E, 2C_3, 3C_2,\ \sigma_h,\ 2S_3,\ 3\sigma_v = 6$ classes

4.6 Equivalent Atoms and Equivalent Symmetry Elements

Equivalent atoms in a molecule are those that may be inchanged with one another by symmetry operations. Equivalent atoms must be of the same chemical species. All hydrogen atoms in methane, ethane, benzene are equivalent. All fluorine atoms in SF_6, all nitrogen and hydrogen atoms in $[Co(NH_3)_6]^{++}$ are equivalent. All fluorine atoms in PF_5 are not equivalent became apical and equitorial fluorine atoms are not interchanged by the symmetry operations.

A symmetry element *P* if charged into element *Q* by an operation generated by a third element *X* and *Q* interchanged back into *P* by X^{-1}, then *P* and *Q* elements are equivalent. If *P* can be interchanged into still a third element *R* and *Q* may also be changed into *R*. The three elements *P*, *Q* and *R* form an equivalent set. Any set of symmetry elements that can be transformed into each and every other member of the set by application of some symmetry operation is said to be a set of equivalent symmetry elements.

In a square planar AB_4 molecule there are four two fold axes in the molecular plane. It is easy to say that C_2 may be interchanged into C_2' and vice versa while C_2'' may be interchanged into C_2''' and vice versa by rotations about the four fold (C_4) axis and by reflections in the symmetry planes. But there is no way for interchanging C_2 or C_2' into C_2'' or C_2''' or vice–versa. Hence, C_2 & C_2' form one set of equivalent symmetry axes and C_2'' & C_2''' are another equivalent symmetry axes. Similarily, two plane σ_v & σ_v' are equivalent symmetry planes while σ_v'' & σ_v''' are another equivalent symmetry planes.



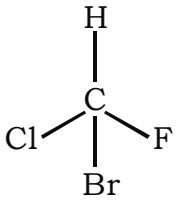
4.7 PointGroups and Classifications

Molecule may be of high symmetry or may be of low symmetry. Symmetry of the molecule can be judged using the symmetry elements and symmetry operations present in them. All the symmetry operations present in a molecule form a group. A molecular group is called as a point group. The symmetry group or a point group of a molecule is denoted by a specific symbol. This symbol was introduced by Schoenflies. Several molecules have the same set of operations and hence, belong to the same point group but different set of operations belong to the different point group.

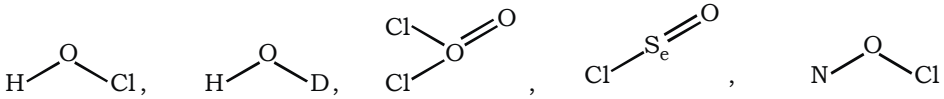
Classification : Molecules are classified into different groups.

Type 1 : Molecules with low symmetry.

(i) **Point group C_1**—Molecule having no other symmetry elements except identity (E) belong to this group. This group has a onefold proper axis of rotation (C_1) and includes all molecule possessing one assymetric atom.

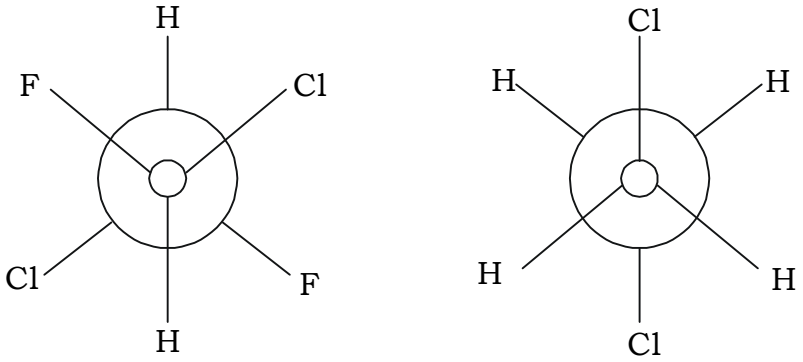


(ii) **Point group C_s**—This group has only two elements of symmetry i.e., E (identity) and σ (plane of symmetry) e.g.,



(iii) **Point group C_i**—This group has only two elements of symmetry i.e., E and i (point of symmetry)

i.e., 1, 2–dichloro dibromoethane



(iv) Point group C_n – This group has only a n–fold proper rotational axis e.g., 1, 2–Dichloroethane–point group C_2, 1, 3–Dichloroallene – point group C_3.

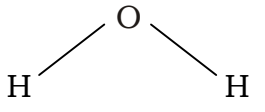
Type–2 : Molecules with intermediate symmetry.

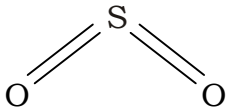
Characteristic for this type of symmetry group is the presence of rotational axis (C_n) along with plane of symmetry (σ), subsidiary rotational axis (C_2), point of symmetry (i).

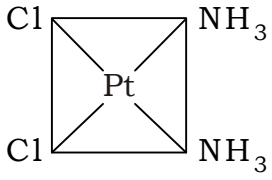
(i) **Point group C_{nv}**—The assocation of a rotational axis (C_n) with *n* vertical reflection planes ($n\sigma_v$) generates C_{nv} point group. There are so many molecules which have C_{nv} point group.

(a) C_{2v} – contains E, C_2 and $2\sigma_v$

e.g., H_2O, SO_2, CH_2Cl_2, ClF_3, SO_2Cl_2, $SiCl_2Br_2$, $BClF_2$, C_6H_5X, $C_6H_4X_2$(0$_2$ & m), *Cis*–$[Pt(NH_3)_4Cl_2]^{--}$, *Cis*–$[Pt(NH_3)_2Cl_2]$, *Cis*–H_2O_2.

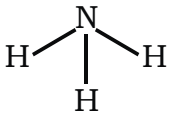






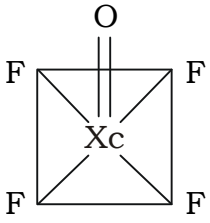
(b) C_{3v} – Contains E, $2C_3$ and $3\sigma_v$

e.g., NH_3, PH_3, PCl_3, $CHCl_3$, $POCl_3$, CH_3Cl



(c) C_{4v} – Contains E, $3C_4$ and $4\sigma_v$

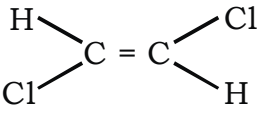
e.g., $[Co(NH_3)_4ClH_2O]^+$, SF_5Cl (octahedral), $XeOF_4$, ClF_5



(ii) Point group C_{nh} – A rotational axis C_n, σ_h perpendicular to C_n gives rise to C_{nh} group. Here Sn ($C_n.\sigma^h$) also be present.

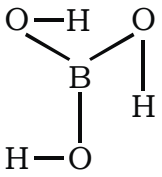
(a) C_{2h} – Contains E, C_2, σ_h, S_2 (≡ i)

e.g., *Trans*–H_2O_2, *Trans*–2–butene, *Trans*–CHCl = CHCl, *Trans*–N_2F_2



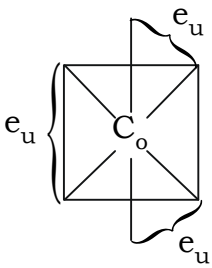
(b) C_{3h} – Contains E, $2C_3$, σ_h, $2S_3$

e.g., H_3BO_3 (Planar)



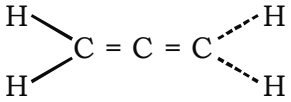
(iii) **Point group D_n**—A D_n group is generated by high order rotational axis C_n ($n = \geq 2$) and nC_2 axes pependicular to it. This group has only a few molecular species.

(a) D_3 – e.g., $[Co(en)_3]^{+++}$, Gauche conformation of ethane.



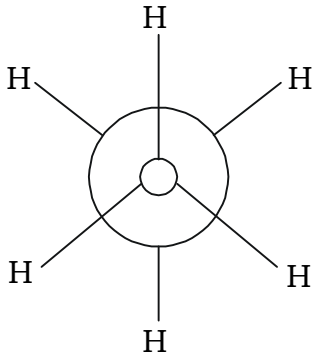
(iv) **Point group D_{nd}**—The D_{nd} groups are generated by the association of the D_n ($C_n + nC_2$) elements with n dihedral planes ($n\sigma_d$).

(a) D_{2d} – Contains E, $3C_2$ (mutually perpendicular), S_4 e.g., Allene, cyclooctatetroene.



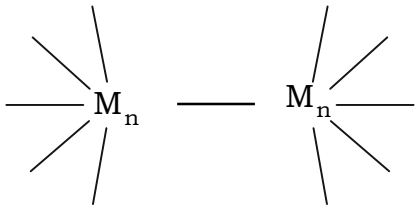
(b) D_{3d} – Contains E, $2C_3$, $3C_2$, S_6, i, $3\sigma_d$

e.g., staggered ethane, cyclohexane



(c) D_{5d} – Contains E, $4C_5$, $5C_2$, $5\sigma_d$

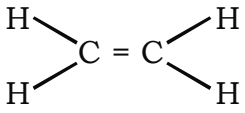
e.g., $Mn_2(Co)_{10}$, staggered ferrocene



(v) Point group D_{nh} – The D_{nh} groups are generated by the association of D_n (C_n + nC_2) with σ_n and improper axes also.

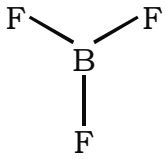
(a) D_{2h} – Contains E, C_2, $2C_2$, $2\sigma_v$, σ_n, i

e.g., C_2H_4, N_2O_4 (planar), $C_2O_4^{--}$, $Pt(NH_3)_2Cl_2$ *trans*, *para*–$C_6H_4X_2$, Naphthalene.



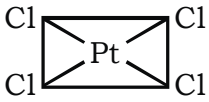
(b) D_{3h} – Contains E, $2C_3$, $3C_2$, $3\sigma_v$, σ_h, $2S_3$

e.g., BF_3, PF_5, PCl_5, SO_3, BCl_3, CO_3^{--}, NO_3^-, C_2H_6 (eclipsed), planar–tribromobenzene.



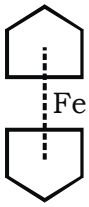
(c) D_{4h} – E, $3C_4$, $4C_2$, $4\sigma_v$, σ_h, i, $2S_4$

e.g., $[PtCl_4]^{--}$, $[Ni(CN)_4]^{--}$, trans–SF_4Cl_2, *trans* MA_4B_2 coplanar cyclobutane.



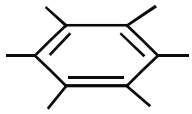
(d) D_{5h} – E, $4C_5$, $5C_2$, $5\sigma_v$, σ_h, $2S_5$

e.g., cyclopentane, eclipsed ferrocene



(e) D_{6h} – E, $5C_6$, $6C_2$, $6\sigma_v$, σ_h, $2S_6$, i

e.g., Benzene, Eclipsed C_v $(C_6H_6)_2$

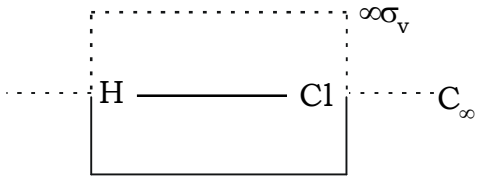


Type – 3 : Molecules of high symmetry.

[A] Linear Molecules :

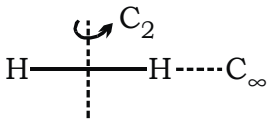
(i) Point group $C_{\infty v}$ – The linear molecules have infinite rotational axis (C_∞') and infinite no. of vertical plane ($\infty\sigma_v$) $C_{\infty v}$ – E, C_∞, $\infty\sigma_v$

e.g., HCl, HCN, CO, OC, HBr, NO



(ii) $D_{\infty h}$ – Contains E, C_∞, ∞C_2, $\infty\sigma_v$, σ_h, i

e.g., H_2, Br_2, Cl_2, CH ≡ CH, CO_2, $BeCl_2$, XeF_2



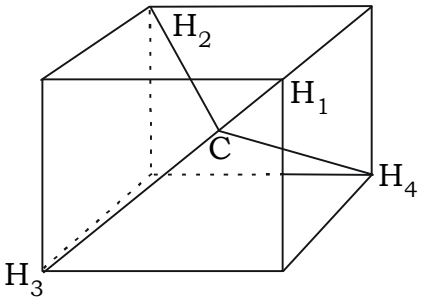
[B] Molecules having regular geometric bodies i.e., tetrahedral octahedral, icosahedron

(i) Point group T_d : Regular tetrahedra molecules have T_d point group.

e.g., CH_4, CCl_4, $Ni(Co)_4$, $SiCl_4$, $[Zn(CN)_4]^{2-}$

Total symmetry operations in T_d – E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$ = 24

Symmetry operations are illustrated as follows :



(a) There are four axes of three fold symmetry each passing through C–atom and one H–atom. i.e., $4C_3^1$, $4C_3^2$.

(b) There are three axes of two fold symmetry each passing through centres of opposite edges. i.e., H_1, H_2 and H_3H_4, H_2H_3 and H_1H_4 H_2H_4 and H_1H_3.

(c) Each of the C_2 axis is also S_4 and S_4 is S_4^1, $2S_4^2$ hence $6S_4$ are present.

(d) There are sin planes of symmetry each passing through one edge and centre of opposite edges.

(ii) Point group Oh – Regular octahedral molecules have Oh point group.

e.g., SF_6, $[PtCl_6]^{-\ -}$, $[Co(NH_3)_6]^{+++}$, octahedral complex of MA_6 Total symmetry operations in Oh – E, $6C_4$, $3C_2(C_4^2)$, $8C_3$, $6C_2$, $6S_4$, $8S_6$, $6\sigma_v$, $3\sigma_h$, i = 48

(iii) Point group I_n – Regular icosahedral molecule have I_n point group.

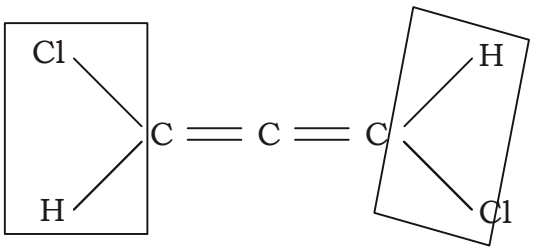
e.g., Dodecaborane $(B_{12}H_{12})^{2-}$, $[Mo(CN)_8]^{4-}$

Total symmetry operations – E, $24C_5$, $24S_{10}$, $20C_3$, $20S_6$, $15C_2$, 15σ, i = 120.

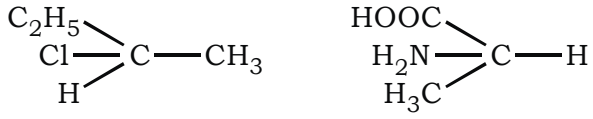
4.8 Optical Activity and Dipole Moments

Optical activity : The mirror image of a molecule cannot be superimposed on the original, then the molecule is optically active. In case, it can be superimposed, the molecule is optically in active. A knowledge of the point group symmetry of a molecule can be used to find whether the molecule is optically active or not. A molecule will be optically active if it does not possess the S_n axis of any order. This means that the molecules should not have the reflections plane (S_1 axis), the inversion centre (S_2 axis) and any improper axis of order n. A molecule without a S_n axis is optically active.

The molecule may possess a C_n axis or many C_n axes. Such a molecule is said to be dissymmetric 1, 3–dichloroallene is the example of dissymmetric molecules and is optically active.



A molecules with an assymmetric centre may also be optically active. Sec butyl chloride and α–methylaminoacetic acid are examples of molecules possessing the assymmetric centre.



Dipole moment : Dipole moment is related to the magnitude of the charge multiplied by the distance between the centres. the use of symmetry elements can tell us whether a molecule has dipole moment or not. A molecular possesses dipole moment if it belongs to C_n, C_s, C_{nv}, $C_{\infty v}$. The dipole moment is along the C_n axis in the C_n and C_{nv} groups. In C_s groups the moment lies in the reflectional plane. If there is a plane of symmetry σ, the dipole moment must lie in this plane and for several σ, the dipole moment must lie along their interaction. In case of NH_3, the dipole moment lies along C_3 axis which is also the intersection of three symmetry plane.

A molecule containing a centre of symmetry (i) can not have a dipole moment, since inversion centre reverses the direction of any vector. Molecules with many C_2 axes also possess zero dipole moment. Since they have symmetry operations which turn them upside down.

4.9 Representation of Groups

Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinate x, y and z of an atom into a set of new coordinates x′, y′ and z′. The two sets of coordinates of the atom can be related by a set of equations. This set of equations may also be formulated in matrix notation. Thus each symmetry operation can be represented by a specific matrix. A knowledge of the matrices of the various operations in a molecule will be useful to solve structural problems in chemistry.

This chapter will begin with an account of matrix essential to an understanding the discussion of representation of groups.

A matrix is a rectangular array of numbers or symbol for numbers.

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \text{ or } \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

Any element of the matrix can be represented by a_{ij}, where i denotes the rows (horizontal set) and j denote the columns (vertical sets). The order or dimension of a matrix is defined by the number of rows and columns. When the number of rows equal the number of columns, the matrix is called as square matrix. The elements a_{ij} of a square matrix for which $i = j$ (i.e., a_{11}, a_{22}, a_{33} etc) are called the diagonal elements, and the other elements are called off–diagonals, when all of the off–diagonal elements of a matrix are zero, the matrix is called as diagonal matrix. The sum of the diagonal elements of a square matrix is called the trace or character of the matrix and is represented by symbol χ(chi).

Diagonal matrix $\begin{bmatrix} 3 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ character of this matrix is 8.

Unit matrix $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ character of this matrix is 3.

Matrices may be added, subtracted, multiplied or divided by using the appropriate rules of matrix algebra. In order to add subtract two matrices, both matrices must be of the same dimension, i.e., same no. of rows and columns. For multiplication, column of A must be equal to row of B.

Representation of Groups—Each symmetry operation in a point group can be represented by a number or more generally, by a matrix of number. The matrices for the different symmetry operation can be obtained by considering the effect of there operations on the components of a two–dimensional vector. The results can then be entended to three dimensions.

Matrix for the identity operation (E)—By identity operation, the components x, y and z of a vector remain unchanged. The equations which represent the effect of identity operation on the vector r are given as :

$$E.x = 1.x + 0.y + 0.z$$

$$E.y = 0.x + 1.y + 0.z$$

$$E.z = 0.x + 0.y + 1.z$$

In matrix form these equations become

$$E\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Hence matrix for identity operation E is :

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

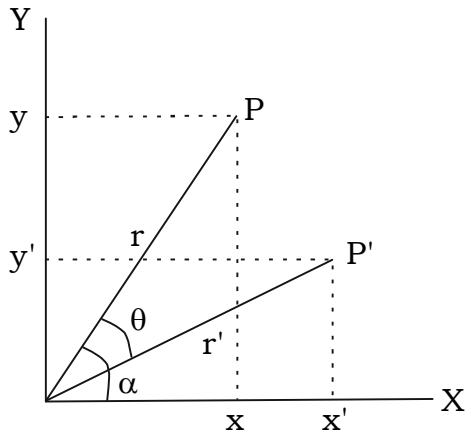
Matrix for rotation operations—The z coordinate will be unchanged by any rotation about the z–axis. Thus, the matrix we seek must be in part,

$$\begin{bmatrix} & & 0 \\ & & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The finding the four missing elements can then be solved as a two–dimensional problem in the xy plane.

Consider the vector r in the two–dimensional coordinate system as given below. The vector r can be expressed as a column matrix r.

$$r = \begin{bmatrix} x \\ y \end{bmatrix}$$



x and y are the components of the vector r. The vector r be rotated clockwise through an angle θ such that the components of the vector becomes x' and y. The resulting vector r'.

$$r' = \begin{bmatrix} x' \\ y \end{bmatrix} = C_n . r$$

$$x' = r\cos(\alpha - \theta)$$

$$= r(\cos\alpha . \cos\theta + \sin\alpha . \sin\theta)$$

$$= r\cos\alpha . \cos\theta + r\sin\alpha . \sin\theta$$

$$x' = x\cos\theta + y\sin\theta \qquad \ldots (i)$$

and

$$y' = r\sin(\alpha - \theta)$$

$$= r\sin\alpha . \cos\theta - r\cos\alpha . \sin\theta$$

$$= y\cos\theta - x\sin\theta$$

$$y' = y\cos\theta - x\sin\theta \qquad \ldots (ii)$$

These equations (i) & (ii) are represented in the matrix form as follows :

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix}$$

This eq^n. is just like

$$r' = C_n . r$$

$$\therefore \quad C_n = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

C_n represents the matrix for rotation operation. In three dimension the matrix $C_n(z)$ become

$$C_n(z) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Matrix for reflection operation :

Consider the vector *r* with the components *x* and *y*. By reflection across the yz plane, the components x and y becomes *x′* and *y′*. *x′* and *y′* are related as

$$x' = -1x + 0y$$

$$y' = 0x + 1y$$

Matrix for this is

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix}$$

The reflection operation σ_{yz} is expressed as

$$r' = \sigma_{yz}$$

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$$

In three dimension

$$\sigma_{y_2} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Like this $\sigma_{x_z} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Matrix for inversion operation (*i*) :

The *x*, *y* and *z* component of a vector *r* are transformed into their respective negative by the inversion operation.

$$i.x = -1x + 0y + 0z$$

$$i.y = 0x - 1y + 0z$$

$$i.z = 0x + 0y \times 0z$$

$$\therefore \quad i \times \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

The matrix for inversion operation is

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Matrix for improper rotation (S_n) :

Improper rotational axis will be obtained by rotation axis multiplied by σ_n

$S_n = C_n, \sigma_{xy}(\sigma_h)$

Matrix of $C_n X$ matrix of σ_{xy}

$$S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

The character of the matrices corresponding to the symmetry operations are as follows :

Symmetry operation	**Character of the matrix**
Identity (E)	3
Proper rotation (C_n)	$2 \cos\theta + 1$
Reflection (σ)	1
Inversion (i)	–3
Improper rotation (S_n)	$2 \cos\theta - 1$

4.10 Reducible and Irreducible Representation

The character of the identity operation is the dimension of a representation. Above representation is a three dimensional representation.

A representation of higher dimension which can be reduced tp representation of lower dimension is called reducible representation. Those representation which cannot be further reduced to representation of lower dimension are called irreducible representation. In group theory, one is interested in knowing the number of irreducible representation in a group.

Representation of higher dimension may be reduced to matrices of smaller dimension by a process of similarity transformation. If A is a big matrix and is to be reduced to B, a matrix of smaller dimension. We choose a matrix X and evaluate $X^{-1}AX$ which gives us B.

i.e., $X^{-1}AX = B$

A, B and X matrices are of the same dimensions.

$$\text{If } A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \xrightarrow[\text{transformation}\ [X^{-1}AX]]{\text{Similarity}} \begin{bmatrix} b_{11} & b_{12} & 0 \\ b_{21} & b_{22} & 0 \\ 0 & 0 & b_{33} \end{bmatrix}$$

A matrix A of 3×3 dimension has been converted to two matrices one of 2×2 and the other 1×1 dimension. This similarity transformation block diagonalises the original matrix to matrices of reduced order in block form. We know transformation matrices are operators of the class to which they belong. A matrix X does not reduce B further ($X^{-1}BX = B$), then we say that the dimension is irreducible and its matrices can not be further reduced to lower dimension.

Irreducible representations which are of prime significance in dealing with the problems associated with molecular geometry. It is also noted that there will be as many irreducible representations for any point group as there are classes of symmetry operations for that group. Thus in C_{2v}, there are four classes and four irreducible one dimensional representation and in C_{3v}, three classes and hence three irreducible representation.

4.11 The Great Orthogonality Theorem and its Consequences

The orthogonality theorem is concerned with elements of matrices constituting irreducible representation of a point group. The great orthogonality theorem in mathematical form is as follows :

$$\sum_{R}\left[\Gamma_i(R)_{mn}\right]\left[\Gamma_j(R)_{m'n'}\right] = \frac{h}{\sqrt{l_i\, l_j}}\,\delta_{ij}\;\delta_{mm'}\;\delta_{nn'}$$

$\Gamma_i(R)_{mn}$ is denoted for the element in the *m*th row and the *n*th column of the matrix corresponding to an operation *R* in the *i*th irreducible representation. It is necessary to take the complex conjugate (denoted by *) of one factor on the left–hand side whenever imaginary or complex numbers are involved. The complex conjugate of the element in the *m*′th row and *n*′th column of a matrix in the *j*th irreducible representation is denoted by $\left[\Gamma_j(R)_{m'n'}\right]^*$ l_i and l_j are the dimension of the *i*th and *j*th irreducible representation. *h* is the order (total number of symmetry operations) of the point group δ_{ij}, $\delta_{mm'}$, $\delta_{nn'}$ denote the kronecker delta symbol.

For simplicity we can omit the explict designation of complex conjugate. Then simple equations can be represented as :

$$\sum_{R}\left[\Gamma_i(R)_{mn}\right]\left[\Gamma_j(R)_{mn}\right] = 0 \text{ if } i \neq j$$

Elements of corresponding matrices of different irreducible representation are orthogonal.

$$\sum_{R}\left[\Gamma_i(R)_{mn}\right]\left[\Gamma_i(R)_{m'n'}\right] = 0 \text{ if } m \neq m' \text{ and } n \neq n'$$

Elements of different set of the matrices of the same irreducible representation are orthogonal

$$\sum_{R}\left[\Gamma_i(R)_{mn}\right]\left[\Gamma_i(R)_{m'n'}\right] = \frac{h}{l_i}$$

Elements in the *m*th ros and *n*th column of a matrix for operation *R* in the *i*th irreducible representation. The square of the length of any such vector equals $\frac{h}{l}$.

Consequences of orthogonality theorem (Properties of irreducible representation) :

The properties of irreducible representation is essential to construct the character talls of a point group. The following fine rules are given below about the irreducible representation.

(i) The number of irreducible representation of a group is equal to the number of classes in the group.

(ii) The sum of the square of the dimension of the irreducible representation of a group is equal to the order of the group.

$$\sum l_i^{\,2} = l_1^2 + l_2^2 + l_3^2 + \ldots\ldots\ldots = h$$

Since χ_i(E), the character of the representation of identity operation (E) in the *i*th irreducible representation is equal to the order of representation. We can also write :

$$\sum_i \left[\chi_i(E)\right]^2 = h$$

(iii) The sum of the square of the character of any irreducible representation is equal to *h*.

$$\sum_R \left[\chi_i(R)\right]^2 = h$$

(iv) The characters of two different irreducible representations of the same group are orthogonal to each other.

$$\sum_R \chi_i(R).\chi_j(R) = 0 \qquad \text{when } i \neq j$$

(v) The character of all matrices belonging to operations in the same class are identical.

By using these rules we can construct character table of different point group.

4.12 Character Table

A more compact and self–explanatory representation table of a point group is said as 'character table'. The character tables of molecular point groups are important from the point of view of their application to chemical problems. The character of reducible and irreducible representation of symmetry operation of a point group are arranged in the character table and are used for understanding the various problems like atomic orbitals, hybrid orbitals, molecular orbitals in polyatomic molecules, crystal field theory of complex compounds, electronic and vibrational spectra of molecules.

Symbol for irreducible representation :

The symbol for the irreducible representation was given by Mulliken and hence called as Mulliken symbol. The rules are as follows :

(i) All unidimentional representations are represented either by A or B, two dimensional representations are represented by E and three dimensional representations are represented by T.

(ii) One dimensional representations which are symmetrical with respect to the principal axis (i.e., character of C_n operation is +1) are designated as *A* while those antisymmetric in this respect (i.e., character of C_n operation–1) are designated as *B*.

(iii) Those irreducible representations which are symmetrical with respect to the subsidiary axis, or in its absence to σ_v plane, subscript 1, (i.e., A_1, B_1, E_1, T_1) is used and for antisymmetric subscript 2 (i.e., B_1, A_2, E_2, T_2) is used.

(iv) Primes and double primes are attached to all *A*, *B*, *E* or *T* to indicate the symmetric and antisymmetric with respect to σ_h. *A′* or *E′* appears forth σ_h having +1 and *A″* or *E″* appear for the σ_h having –1.

(v) Subscript *g* and *u* are used to indicate the symmetric and antisymmetric to the inversion. If the point group has no centre of symmetric, *g* or *u* are not used. Term *g* stands for gerade (centro symmetric) and *u* stands for ungerage (non–centro symmetric)

Construction of character table for C_{2v} point group :

There are total of four symmetric operations C_{2v} point group i.e., E, $C_{2(2)}$, σ_{xz}, σ_{yz}

(i) There operations belong to four different classes hence there are four irreducible representations. Let be $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$.

(iii) It is also requires that the sum of the square of the dimensions of these representations equal h (order of the group) i.e., 4. Hence each representation must be unidimensional so that

$$1^2 + 1^2 + 1^2 + 1^2 = 4$$

Because the character of identity operation is equal to the dimension of the representation and hence *E* must be equal to one (1) in all of them.

	E	$C_{2(2)}$	σ_{xz}	σ_{yz}
Γ_1	1			
Γ_2	1			
Γ_3	1			
Γ_4	1			

(iii) The sum of the square of the character of an irreducible representation must be equal to 4 as

$$\sum_{R}\left[\chi_i(R)\right]^2 = 4$$

i.e. $1^2 + 1^2 + 1^2 + 1^2 = 4$

	E	$C_{2(2)}$	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1			
Γ_3	1			
Γ_4	1			

(iv) The sum of the square of the character of other irreducible representation must be equal to four and the character must also be orthogonal. Hence character must include two +1 & two –1.

Therefore, we will have

	E	$C_{2(2)}$	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	–1	–1	1
Γ_3	1	–1	1	–1
Γ_4	1	1	–1	–1

All there representation are also orthogonal to one another taking $\Gamma_2.\Gamma_3$, we have

$$(1)(1) + (-1)(-1) + (-1)(1) + (1)(-1) = 0$$

The complete character table for the point group C_{2v} is as follows :

C_{2v}	E	$C_{2(2)}$	σ_{x_2}	σ_{y_2}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_2	xy
B_1	1	–1	1	–1	x, R_y	x_z
B_2	1	–1	–1	1	y, R_x	y_z
I	II				III	IV

In the upper left corner is the schonflies notation for the group and the upper row of the table are listed the symmetry operations grouped into classes.

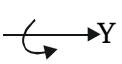
Area I : Area I represents the symbol for the irreducible represnetation according to the Mulliken. All these irreducible representation are of unidimensional and hence *A* or *B* symbol be used. Because upper two irreducible representations are symmetrical with respect to the principal axis and hence *A*'s are written and lower two representation are anti symmetrical with respect to the principal axis and hence *B*'sare written. Subscript 1 or 2 are written for the symmetrical and antisymmetrical respectively with respect to $\sigma_{xz.}$

Area II : Area II of the character table are the characters of the irreducible representation of the point group C_{2v}.

Area III : Area III represents the Cartesian coordinates or rotational axis corresponding to irreducible representation. In order to assign the Cartesian coordinate or rotational axis, we must perform the operations on them and enquire the character.

Consider a vector along *z*–axis. The operations E, $C_{2(2)}$, σ_{xz}, σ_{yz} do not change the direction of the head of the vector. Hence its character are 1, 1, 1, 1. Thus the vector *z* transforms under the symmetry operations into A_1. Similarly *X* and *Y* vector transform into B_1 and B_2 representation.

Rotational axis R_x, R_y and R_z represent rotation about *x*, *y* and *z*–axis. To understand the transformation by rotational axis, we should mark a curved arrow and symmetry operation is performed. If the direction of the head of the arrow does not change due to operation, the character is +1 and –1 for the change of head of arrow :

		E	C_2	σ_{xz}	σ_{yz}	Transformation into
R_z 	R_z	1	1	–1	–1	A_2
R_y 	R_y	1	–1	1	–1	B_1
R_y 	R_x	1	1	–1	1	B_z

Area IV : Area IV represnets squares binary products to the irreducible representation. For assignment of the square and binary products of the vectors, the characters are squared or direct products are obtained. x^2, y^2 and z^2 belongs to A_1 irreducible representation. The product of character of *X* & *Y* belongs to A_2,

product of X & Z belongs to B_1 and product of Y & Z belongs to B_2 representations.

Construction of character table for C_{3v} point group :

(i) There are total of six symmetry operations present in C_{3v} point group i.e., $E, C_3^1, C_2^2, \sigma_a, \sigma_b, \sigma_c$. These operations are divided into the three classes are hence there are $E, 2C_2, 3\sigma_v$ three irreducible representations. Let it be Γ_1, Γ_2 and Γ_3.

(ii) The sum of the square of the dimensions (character of the identity operation) should be equal to 6

$$\sum l_i^2 = l_1^2 + l_2^2 + l_3^2 = 6$$

The only value of the l_i that with satisfy this requirement and 1, 1, and 2.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1		
Γ_2	1		
Γ_3	2		

(iii) Every point group possesses one representation which is totally symmetric. In this representation, all the operations have the character value one(1). Thus we have

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1

It can be seen that the summation of the square, of the character of the operations is equal to 6.

$$1^2 + 2 \times 1^2 + 3 \times 1^2 = 6$$

(iv) Γ_2 (second irreducible representation) must be orthogonal to Γ_1. since $\chi_2(E)$ must always be positive and hence Γ_2 must consist of three +1 and three –1. This is only possible if Γ_2 has 1, 1 and –1.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	–1

(v) One third representation will be of two dimensions and hence $\chi_3(E)$ is 2. In order to find out the values of $\chi_3(C_1)$ and $\chi_3(\sigma_v)$ we make the use of the orthogonality relationship. Γ_1 & Γ_3 are orthogonal to each other and Γ_2 & Γ_3 are also.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	–1
Γ_3	2	$\chi_3(C_3)$	$\chi_3(\sigma_v)$

$$\sum_R \chi_1(R).\chi_3(R) = (1).(2) + 2(1).\chi_3(C_2) + 3.(1)\chi_3(\sigma_v) = 0 \quad \ldots \text{(i)}$$

and $$\sum_R \chi_2(R).\chi_3(R) = (1).(2) + 2(1).\chi_3(C_3) + 3.(-1)\chi_3(\sigma_v) = 0 \quad \ldots \text{(ii)}$$

Solving eqn. (i) & (ii),

$$2\chi_3(C_3) + 3\chi_3(\sigma_v) = -2 \quad \ldots \text{(iii)}$$

$$2\chi_3(C_3) - 3\chi_3(\sigma_v) = -2 \quad \ldots \text{(iv)}$$

Both equations are added

$$4\chi_3(C_3) = -4$$

$$\therefore \quad \chi_3(C_3) = -1$$

This value is substituted in equation (iii)

$$2(-1) + 3\chi_3(\sigma_v) = -2$$

$$3\chi_3(\sigma_v) = 0$$

$$\therefore \quad \chi_3(\sigma_v) = 0$$

Thus the complete set of character of irreducible representation of C_{3v} point group is :

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	–1
Γ_3	2	–1	0

The complete character table for the point group C_{3v} is as follows :

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	R_2	
E	2	–1	0	(x, y) (R_x, R_y)	$(x_2 - y_2, xy)$ (xz, yz)
I		II		III	IV

In the upper left corner in the schonflies notation for the group and the upper row of the table are listed the symmetry operations grouped into the classes.

Area I represents the symbol for the irreducible representations according to the Mulliken. This is why these symbols ar called as Mulliken symbol.

Because first two irreducible representations are uni dimensional and hence *A* or *B* are used. The character of principal axis of rotation for both the representations are symmetrical and hence *A* is used. Subscript 1 is written for the symmetrical character (+1) of operation σ_v which subscript 2 is written for the unsymmetrical character (–1) of operation σ_v. The symbol *E* show the two dimensional representation.

Area II—In area II of the table are the characters of the irreducible representation of the point group.

Area III—Area III gives the transformation properties of cartesian coordinates *x*, *y*, *z* and rotations about *x*, *y* and *z* axes. i.e., R_x, R_y and R_z.

The vector along *z*–axis remains unchanged with respect to *E*, C_3 and σ_v operations. The matrices and character for the transformation of coordinate *z* by these operations are :

	E	C_3	σ_v
Matrices	[1]	[1]	[1]
Character	1	1	1

This set of characters corresponds to the A_1 representation and hence *z* transforms or the A_1 represntation. This is why *z* is written in the A_1 representation.

The matrices and character for the transformation of coordinates x and y by the operators E, C_3 and σ_v are :

	E	C_3	σ_v
Matrices	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$
Character	[2]	[–1]	[0]

This set belongs to the E representation. It is important that x and y are inseparable in this respect.

Transformation properties of R_x, R_y and R_z – The rotation axis R_z can be shown as an arrow around z–axis. On performing E or C_2, the direction of the head of the arrow remains same (character = +1). However, on performing σ_v, the direction of the head of the arrow changes (character = –1). Thus its character is 1, 1, –1 and belongs to representation A_2. This is why R_2 is written for A_2 representation. R_x and R_y form a two dimensional representation and belongs to E.

Area IV – In this area of the table, squares and binary products of coordinate according to their transformation properties are described. The squares of the vectors ($x^2 - y^2$) and z^2 belong to A1. $x^2 - y^2$ and xy takes together and xz, yz taken together belong to E.

4.13 Direct Products and Reduction Formula

Reduction formula – Relationship between reducible representation and irreducible representation.

The relationship that exist between the two q of prime importance because this can readily tell us the number of time the jth irreducible representation occurs in the reducible representation when we know the character of each representation.

The reducible representation can be split into irreducible representation with the help of similarity transformation method. The irreducible representation appear as block–factored matrices along the diagonal. Using the principle that the character of a matrix is unaltered by any similarity transformation, we can write

$$X(R) = \sum_j n_j X_j(R)$$

Where $X(R)$ is the character of the matrix corresponding to an operation R in the reducible representation. n_j refers to the number of times the block consistituting the irreducible representation repeats itself in the diagonal $X_j(R)$ refers to the character of the matrix for the operation R in the jth irreducible representation. The relation between $X(R)$ and $X_j(R)$ can be obtained by the following formula called as reduction formula.

$$\eta_j = \frac{1}{h}\sum_R X(R).n.X_j(R)$$

h = order of the group, n = no. of operations of that type.

Using the characters of irreducible representation of point group C_{3v}, the no. of times each irreducible representation ocuurs in the following two reducible representation can be calculated as follows :

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	Irreducible representation
A_2	1	1	–1	
E	2	–1	0	
Γ_a	5	2	–1	Reducible representation
Γ_b	7	2	–3	

Using the reduction formula

$$\eta_j = \frac{1}{h}\sum_R X(R).n.X_j(R)$$

For Γ_a reducible representation :

$$\Gamma_1 = n_1 = \frac{1}{6}\,[1(1)(5) + 2(1)(2) + 3(1)(-1)] = 1$$

$$\Gamma_2 = n_2 = \frac{1}{6}\,[1(1)(5) + 2(1)(2) + 3(-1)(-1)] = 2$$

$$\Gamma_3 = n_3 = \frac{1}{6}\,[1(2)(5) + 2(-1)(2) + 3(0)(-1)] = 1$$

$$\Gamma_a = \Gamma_1 + 2\,\Gamma_2 + \Gamma_3$$

In the Γ_a reducible representation, there are four irreducible representation i.e., one Γ_1, two Γ_2 and one Γ_3. If we add all the character of all operations of all irreducible representations, we find the character of reducible representation as follows :

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	–1
Γ_2	1	1	–1
Γ_3	2	–1	0
Γ_4	5	2	–1

For Γ_b reducible representation

$$\Gamma_1 = n_1 = \frac{1}{6}\,[1(1)(7) + 2(1)(1) + 3(1)(-3) = 0$$

$$\Gamma_2 = n_2 = \frac{1}{6}\,[1(1)(7) + 2(1)(1) + 3(-1)(-3) = 3$$

$$\Gamma_3 = n_3 = \frac{1}{6}\,[1(2)(7) + 2(-1)(1) + 3(0)(-3) = 2$$

Thus $\Gamma_b = 3\Gamma_2 + 2\Gamma_3$

In the Γ_b representation, there are five irreducible representation i.e., three Γ_2 and two Γ_3. This can be verified by the following table.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_2	1	1	–1
Γ_2	1	1	–1
Γ_2	1	1	–1
Γ_3	2	–1	0
Γ_3	2	–1	0
Γ_b	7	1	–3

Directi products :

Suppose ϕ_i and ϕ_j are the two wave functions which are bases for representations of a group. The product of these functions can also forms a basis for representation of the group. This representation is called the direct product representation. The direct product representation can also be obtained for products of three, four or more functions. An important rate concerning the characters of operations in the direct product is stated as :

The characters of the representation of a direct product are equal to the products of the characters of the representations based on the individual sets of functions.

If $X_A(R)$ and $X_B(R)$ denote the characters for operation R in the representations A and B, then the character for operation R in the direct product represent is given by :

$$X_{AB}(R) = X_A(R).X_B(R)$$

Where $X_{AB}(R)$ denotes the character of operation R in the direct product representation AB. The direct product representation of the irreducible representations of a group can be obtained using the character table for the group.

The direct products of some irreducible representations of point group D_{3h} are as follows :

D_{3h}	E	$2C_3$	$3C_2$	σ_n	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0

The direct product $A_1'.A_2'$ is given by :

$$A_1'.A_2' = 1\times1 \;\; 1\times1 \;\; 1\times(-1) \;\; 1\times1 \;\; 1\times1 \;\; 1\times-1$$

$$A_1'.A_2' = \;\; 1 \quad\; 1 \quad\; -1 \quad\; 1 \quad\; 1 \quad\; -1 \;\; = A_2'$$

Similarily,

$$A_1'.E' = E'$$

$$E' .A_1'' = E''$$

$$A_2' .E' = E'$$

$$E'^2 = 4\ 1\ 0\ 4\ 1\ 0$$

$$= A_1^1 + A_2^1 + E^1$$

The product representations $A_1'.E_1'$ $E'.A_z''$ and $A_2'E'$ are irreducible representation. The direct product representation E'^2 is reducible.

The representation of a direct products. Γ_{AB}, will contain the totally symmetric representation only if the irreducible representation Γ_A is equal to the irreducible representation Γ_B.

4.14 Summary

The crystal structure, infrared spectra, ultra–violet spetra, dipole moments optical activities all there are properties which depends on molecular symmetry. Symmetry is present in geometrical figures, crystalline solids and molecules C_n (axis of symmetry), σ (plane of symmetry), i (centre of symmetry) and S_n (improper axis of symmetry) are the element of symmetry. The symmetry operations are rotation about axis, reflection in a plane, inversion about point and rotation–reflection or reflection–rotation, we have to know about the total symmetry operations present in a certain molecules. All the symmetry operations present in a molecule form a group. Groups have four requirements i.e., closure, identity, inverse and assiciation. There requirements are judged by the multiplication table, subgroup is the smaller group within a group which also obey all the requirements of group. Classes of operations, similarity transformation, conjugate have very important points of group theory. Point group of a molecule is determined using the total symmety operations present in that molecule. Point group of molecule is just abbreviation of total symmetry operations of a molecule. Optical activity and dipole moment may also be determined using the point group of the molecule.

Symmetry elements in a point group may also be represented by matrix representations may be reducible or irreducible. Great orthogonality theorem in concerned with the irreducible representation of a point group. This theorem is useful for the construction of character table. Character table is self explanatory and is used to solve the problem of chemical importance.

4.15 Questions for Exercise

1. Explain elements of symmetry and symmetry operations.
2. Write all the symmetry operations in the following molecules.

   H_2O, NH_3, BF_3, PCl_5, SF_6, CH_4, $Ni(Co)_4$, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6, H_2 HCl, CO_2, SO_2, CO_3^{--}, NO_3^{-}, *cis*–$[Co(NH_3)_4Cl_2]^+$, *trans*–$[Co(NH_3)_4Cl_2]^+$, $[Co(NH_3)_5Cl]^{++}$, $[Pt(NH_3)_4]^{++}$, Cl_2, CH_2Cl_2 (*trans*), $[Co(NH_3)_6]^{+++}$, $[Fe(CN)_6]^{----}$.
3. What are the requirements of a mathematical groups ? Explain with examples.
4. Explain subgroup, class, conjugate, similarity transformation with examples.
5. Write multiplication table for point group C_{2v} and C_{3v}.
6. Write the two examples of the following point group.

   C_{3v}, C_{2h}, C_{3h}, D_{3h}, D_{2h}, C_i, C_s, D_n, D_{2d}, D_{6h}, *Td*, *Oh*, $C_{\infty v}$, $D_{\infty v}$, C_i.
7. Write the point group of the following molecules written in question (2).
8. Explain abelian groups I_s C_{2v} point group form an abelian group ?
9. Deduce the matrix representation for the identity rotational operation, reflectional operation, rotational–reflectional operation and inversion.
10. Explain reducible and irreducible reprsentations. Write the Great orthogonality theorem and its consequences.
11. Construct the character table for the point group C_{2v} and C_{3v}.
12. How the irreducible representation are symbolised? Write the reduction formula and explain with examples ?
13. Explain why the following molecules posses zero dipole moment :
    (a) CO_2
    (b) staggered form of ethane
    (c) Methane.
14. Write the order of C_{3v} point group. Is any subgroup present in the multiplication table for C_{3v} point group.
15. Write the direct product representation with examples.

4.16 Suggested Readings

1. F. Albert Cotton : Chemical applications of group theory John Wiley & Sons (Asia) Pte ltd.
2. R. K. Prasad : Quantum Chemistry, Wiley Eastern Limited
3. F. A. Cotton and G. Wilkinson : Advanced Inorganic Chemistry, Wiley Eastern Limited.
4. J. E. Huheey : Inorganic Chemistry, Harper International II Edition.
5. Gurdeep Raj : Advanced Inorganic Chemistry vol. II, Goel Publishing House, Merrut.

V