Private Madam

unit-one

Symetry and Group theory in chemistry

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unit-one Symetry & group theory
(Analytical)

Introduction :

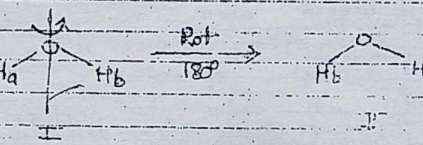
Symmetry is a very fascinating phenomenon in nature which come from the Greek word syn-metron i.e to measure together Mathematical study of symmetry is called Group theory

Symmetry :

Any molecule or object is said to be symmetrical if it can take one or more equivalent configuration by performing some geometrical manipulation on it.

e.g. H_2O molecule.

In H_2O molecule rotation by 180° about an axis passing through Oxygen atom results on equivalent configuration hence H_2O molecule is said to be symmetrical



I II

I & II are equivalent but not identical to understand symmetry concept one should familier with

(1) symmetry element (2) symmetry operation

① **symmetry elements:-**

A symmetry element is a geometrical entity such as a line or a plane or a point about which an operation of rotation or reflection or inversion is performed.

② **symmetry Operation:-**

A symmetry operation is a movement of the molecule such that the resulting configuration of the molecule is indistinguishable from the original OR It is a geometrical manipulation when performed in a molecule always result an equivalent configuration. The molecule may assume an equivalent configuration or an identical configuration.

e.g. In H_2O molecule rotation by 180° about an axis passing through the oxygen atom results an equivalent configuration hence it is said to be symmetry operation.

In order to perform a symmetry operation molecule one should familiar with the following

① The shape of the molecule should be know

② All the atoms in molecule assume to face state

③ The centre of gravity or centre of the molecule should remain unchanged.

④ Folding of the molecule in a proper orientation is also important.

There are five types of symmetry elements corresponding to symmetry operations.

symmetry elements and symmetry operations.

Sr No.	symmetry elements	symmetry operations
1.	Proper axis of rotation (Cn)	Rotation by an angle (2π/n) about the axis.
2.	plane of symmetry (σ)	One or more reflection in a plane
3.	Improper axis of rotation or rotation-reflection axis (Sn)	Rotation about the axis followed by reflection in a plane ⊥ar to the rotation axis.
4.	Centre of symmetry or inversion center (i)	Inversion of all atoms through the centre of symmetry
5.	Identity element (E)	This operation leaves the molecule unchanged

1 Proper axis of rotation (C_n)

It is an axis passing through the molecule about which rotation operation is carried out result in an equivalent configuration. It is represented by C_n

n = order of rotation

$n = \frac{360}{\theta}$, θ = Angle of rotation / symmetry angle

when $\theta = 180^\circ$

$n = \frac{360}{180} = 2$ i.e $n=2$ C_2

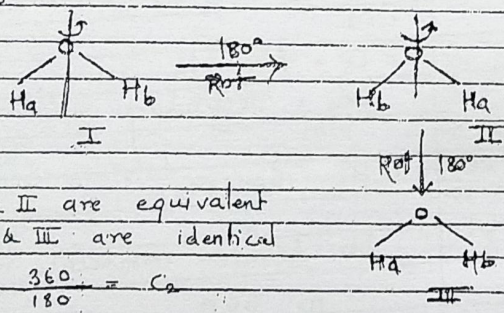
$\theta = 120^\circ$ $n=3$ i.e C_3

$\theta = 90^\circ$ $n=4$ i.e C_4

$\theta = 72^\circ$ $n=5$ i.e C_5

$\theta = 60^\circ$ $n=6$ i.e C_6

① e.g H_2O molecule



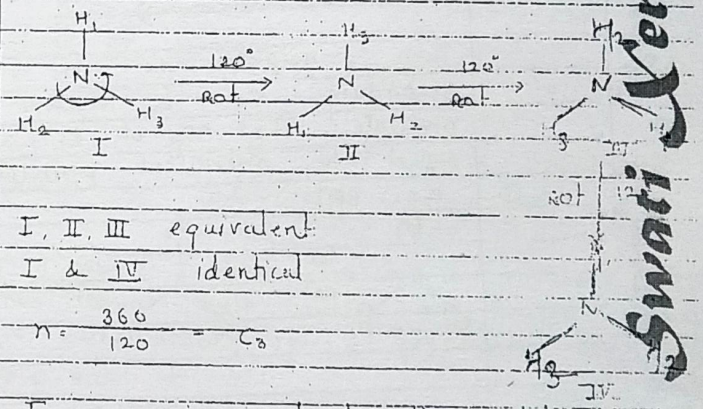
I & II are equivalent

I & III are identical

$n = \frac{360}{180} = C_2$

In H_2O molecule the rotation axis passing through oxygen atom rotation about this axis is 180° results an equivalent configuration hence water is said to have C_2 rotation axis or two fold rotational axis. In order to get identical molecule or configuration it should be rotated twice about the same axis

② eg NH_3



I, II, III equivalent

I & IV identical

$n = \frac{360}{120} = C_3$

In ammonia molecule the rotation axis is passing through Nitrogen atom rotation by 120° about this axis results an equivalent configuration. Hence NH_3 molecule said to have C_3 or 3 fold rotational axis.

... operation दिशा को ध्यान में रखते हुए.

(C_n) C_n

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Type of rotational axis

① Principal axis

② simple or secondary axis.

① Principal axis :-

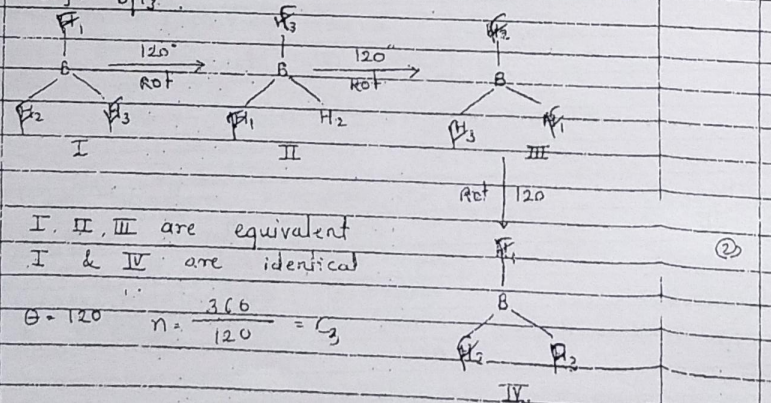
The highest fold rotational axis said to be principal axis. C_n

n = order of rotation.

② simple or secondary axis :-

The axis other than principal axis are said to be secondary axis & always exist in multiple. The no. of C_2 axis always equal to order of principle axis (nC_2)

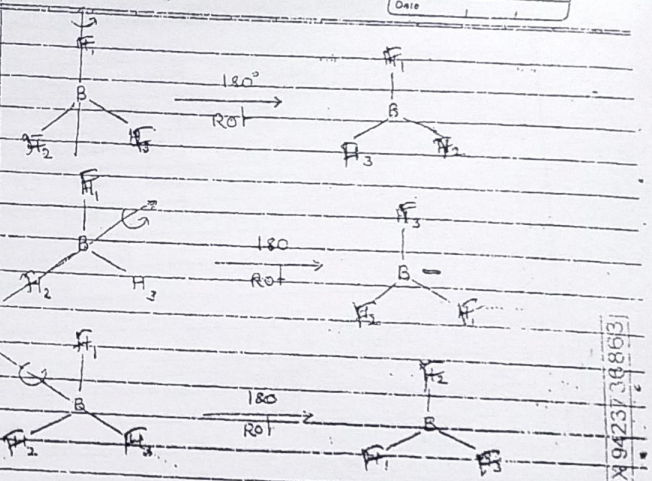
① e.g. BF_3



I, II, III are equivalent

I & IV are identical

$\theta = 120 \quad n = \frac{360}{120} = C_3$



In above ① $\theta = 180° \quad \therefore n = \frac{360}{180} = C_2$

In BF_3 molecule there are three C_2 i.e. $3C_2$ these are called secondary axis

C_3 = Principle axis

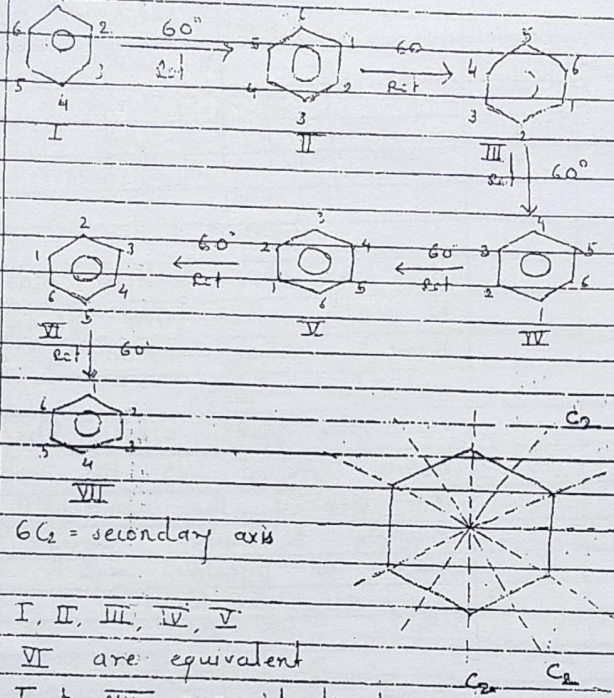
$3C_2$ = secondary axis

② C_6H_6 Benzene

In Benzene molecule $\theta = 60°$

$n = \frac{360}{60} = C_6$

C_6 = Principal axis



$6C_2$ = secondary axis

I, II, III, IV, V are equivalent

VI are equivalent

I & VII are identical

C_6 axis of symmetry is a principal axis in benzene. beside this there are six axis of two fold symmetry three passing through centre of benzene & two opposite carbon atoms and three passing through the centers of symmetry & center of two opposite edge.

In all linear molecule C_∞ the molecul axis is considered as C_∞ fold rotation axis since rotation by any fraction of angle results an equivalent configuration In this molecule the angle of rotation $\theta = 0$

$$n = \frac{360^\circ}{0} = \infty \quad i.e\ C_\infty$$

e.g CO_2, H_2, HCl.

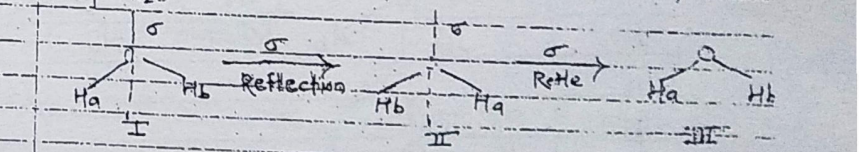
② **Plane of symmetry (σ)**

A molecule is said to be have plane of symmetry if reflection through that plane always results an equivalent configuration

OR

A plane which bisects a molecule two equal half which are mirror image to each other. It is represented by σ

e.g H_2O



I & II are equivalent

I & III are identical

In H_2O molecule the plane is passing through the oxygen atom remains same while the hydrogen atom get exchanged Thus H_2O molecule said to be have plane of symmetry.

Types of plane :-

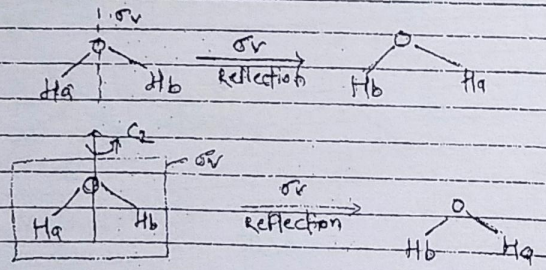
There are three types of plane

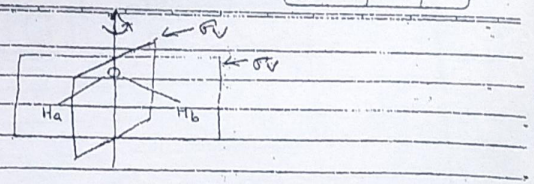
① Vertical plane (σ_v)
② Horizontal plane (σ_h)
③ Dihedral plane (σ_d)

① Vertical plane (σ_v)

The plane which is passing through C_n axis and one of secondary axis if present is said to be vertical plane. It is represented by. σ_v

① e.g. H_2O molecule

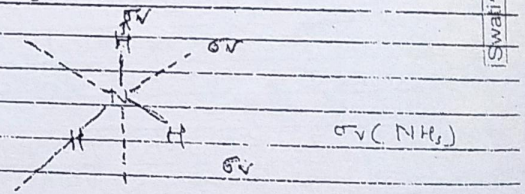




H_2O has two vertical planes perpendicular to each other one plane is passing through oxygen atom & another is molecular plane.

The plane which bisects all the atoms present in the molecule In general the vertical plane exist multiple & always equal to n i.e order of principal axis

② e.g. NH_3 Ammonia

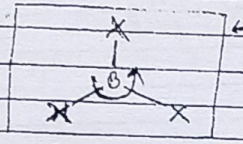


Ammonia has three vertical plane each vertical plane is passing through C_3 axis i.e each passing through one of the H atom & N atom hence there are three horizontal vertical plane i.e $3\sigma_v$

② Horizontal plane (σ_h)

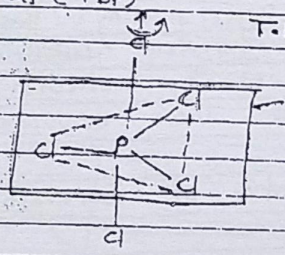
The plane which is perpendicular to C_n i.e principal axis is said to be horizontal plane. It is represented by σ_h

① e.g. BX_3 molecule



In BX_3 molecule the molecular plane is considered as horizontal plane since it is perpendicular to C_3 principle axis.

② eg. PCl_5 (TBP)

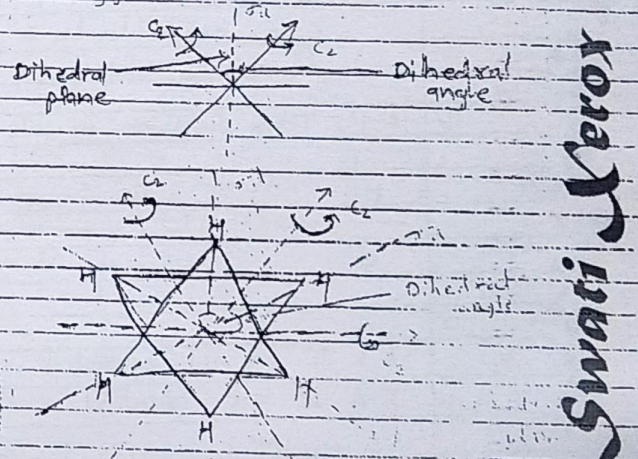


In PCl_5 plane which is passing through equitorial atoms and a central atom is considered as horizontal plane since it is perpendicular to C_3 principle axis.

③ Dihedral plane (σ_d)

The angle between two consecutive C_2 is known as dihedral angle. The plane which bisects the dihedral angle is called dihedral plane. It is represented by σ_d

e.g staggered ethane



3 σ_d (C_2H_6)

④ Improper axis of Symmetry (S_n)

It is an axis passing through the molecule about which rotation followed by reflection perpendicular to rotation

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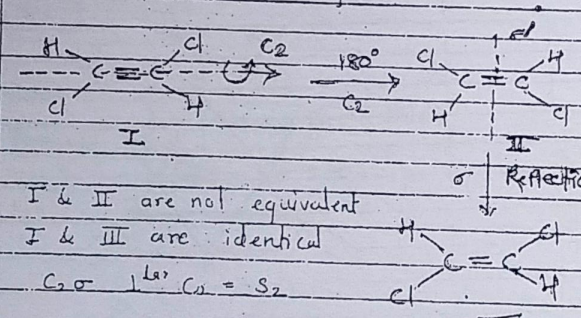
or reflection followed by rotation perpendicular to the reflection.
It is represented by S_n. S_n is product element which can be generated by doing combined operation. This operation results an equivalent configuration.

$C_3\sigma$ Perpendicular to $C_3 = S_3$
$C_2\sigma$ perpendicular to $C_2 = S_2$
$C_n\sigma$ $\perp^{ar}$ to $C_n = S_n$

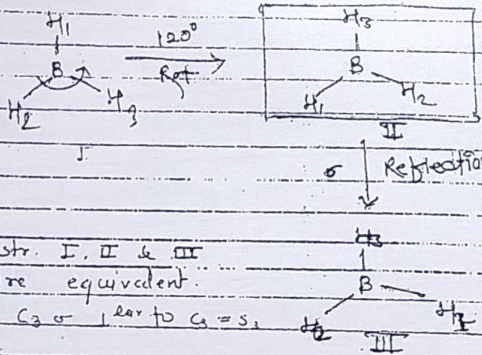
① e.g. Trans dichloro ethylene



I & II are not equivalent
I & III are identical
$C_2\sigma \perp^{ar} C_2 = S_2$

In trans dichloro ethylene rotation by 180° about an axis passing through two carbon atoms will not result equivalent configuration while C_2 rotation followed by reflection $\perp^{ar}$ to C_2 rotation result on equivalent configuration hence it having S_2 improper axis.

② e.g. BH_3 molecule



str. I, II & III are equivalent.
$C_3\sigma \perp^{ar}$ to $C_3 = S_3$

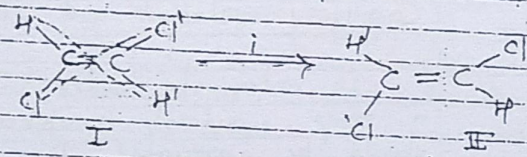
In BH_3 molecule rotation by 120° about an axis passing through B atom results an equivalent configuration while rotation followed by reflection $\perp^{ar}$ to rotation also results same equivalent configuration.

4) Centre of Inversion :-

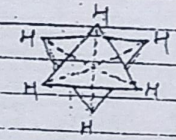
A molecule said to have centre of inversion if all the straight line passing through centre of the molecule meet similar atoms at equal distance from the centre OR.
It is a point lie at exactly center of the molecule about which all the atoms present in the molecule are inverted.

to result equivalent configuration
It is represented by (i) two consecutive inversion always result identical configuration.

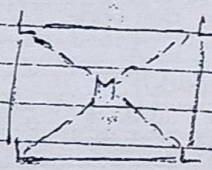
e.g trans dichloroethylene.



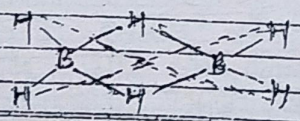
I & II are equivalent
I & III are identical



staggered ethane have center of inversion



square plane have i



Diborane have i

1) Identity Element :-

Identity obtained by 360° or 0° rotation All molecule possess an identity element. It is an operation when performed in molecule results in an identical configuration.

The identical configuration can be visualise into two way

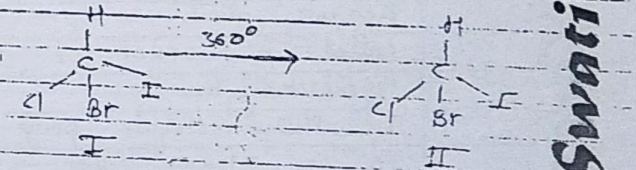
① Rotation by 360° about an axis

② Do not do anything to molecule i.e 0° rotation.

Thus it is unique element exist in molecule

If it represented by E

e.g.



I & II are identical

Group :

A group is a collection of elements which are interrelated according to certain rules

OR

A group is a collection of elements having certain properties in common which enables a wide variety of algebric manipulations to be carried out on the collection It should denote numbers, matrices vectors and symmetry operations

Order of Group :

The total no. of symmetry elements which is present in a group called as order of group. It is represented by h

In H_2O molecule point group is C_{2v} in C_{2v} group order is 4 & in C_{2v} point group order is 6.

Sub-group :-

A subsent of element of a group forming a group of smaller order is referred to as a sub-group.

OR

smaller groups which may be found within a larger group are called sub-group

e.g In C_{2v} group there is E, C_2, σ_v are smaller groups.

Conjugacy relation and classes :

In order to understand classes in a group, similarity transformations of elemen should be apreciated. The group having element X, A & B the following reldn may hold good.

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

X^{-1} = Reciprocal of x in such a case B is said to be a similarity transform of A by X or A & B are conjugate.

Conjugate elements having following properties

① Every element is conjugate to itself i.e

$$[X^{-1}][A][X] = A$$

where X is identity

② If A is conjugate with B, B must be conjugate with A.

i.e if $[X^{-1}][A][X] = B$ therefore $B = Y^{-1} A Y$

Y is another element of the group.

③ If A is conjugated with B & C then B & C are conjugate with each other.

$[X^{-1}][A][X] = B$ $\therefore B = [Y^{-1}][A][Y]$

If $C = [Z^{-1}][A][Z]$

Class : A set of elements in a group which are conjugate to one another is said to form a class.

Let us perform the similarity transformation of the C_2 operation of H_2O molecule with all the other operations

$E^{-1} C_2 E = C_2$ $\quad \sigma_v^{-1} C_2 \sigma_v = C_2$

$(\sigma_{v'})^{-1} C_2 \sigma_{v'} = C_2$ $\quad (C_2)^{-1} C_2 C_2 = C_2$

Relation between orders of a Finite Group and its subgroup

Group containing finite number of elements is referred to as finite group whereas the infinite number of elements constitute infinite group ($h=\infty$). Consider finite group of order $h=4$ i.e $1, -1, i, -i$. The combining rule being algebric multiplication $= i\sqrt{-1}$. The identity element is 1 and the inverse of 1 is -1 of i is $-i$ and of -1 is 1 etc. Note that the group $(1, -1)$ is a part of larger group $1, -1, i, -i$. Thus $1, -1$ is said to be a subgroup of the group $1, -1, i, -i$. The order of the group is an integral multiple of its subgroup.

However, $i, -i$ is not a group since there is no identity element and the ring closure does not not hold

Point symmetry group

All the symmetry operations in a molecule can be combined to form molecular group. This p group is called the point group

OR

The collection of all the symmetry elements at a single point i.e exactly at the centre of molecule is known as point group or point symmetry

Order of a point group is represented by h where h= no. of symmetry elements present in the molecule

The molecular point groups are represented by the Schoenflies symbols

Schoenflies symbols :-

Each molecular point group is identified by a symbol known as schoenflies notation that consists of a capital letter and a subscript. These are

C	simple rotation axis
D	n fold rotation axis perpendicular to principal axis
T	symmetry based on tetrahedron
O	symmetry based on octahedron
I	symmetry based on icosahedron
S	Only plane of symmetry
i	only centre of symmetry
n	only n fold rotation axis
nV	Vertical symmetry plane or that contain principal rotation axis
nh	Horizontal symmetry plane or perpendicular to principal rotation axis
nd	Dihedral symmetry plane or perpendicular to principal rotation axis

molecules can be divided into

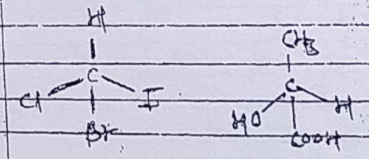
Molecules

① molecules of low symmetry (containing less no of symm. element)	② molecules of high symmetry (contains more no. of symm. element)	③ molecules with special symmetry (Easily identified geometry)
C_1, C_i, C_s	C_n, C_{nv}, C_{nh}, D_n D_{nh}, D_{nd} S_n etc	C_∞ $D_{\infty h}$ O_h I_h

① Molecules of zero symmetry :

① C_1 : Molecule with only C_1 rotation of element comes under C_1 point group order of group $h = 1$ i.e E or C_1

e.g All asymmetric molecule are the best example of point group C_1



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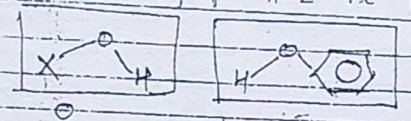
② C_s point group : Molecule with only a plane of symmetry comes under C_s point group

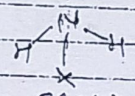
Order of group $h = 2$ i.e E & σ

eg



$\sigma(COFBrCl)$

σC

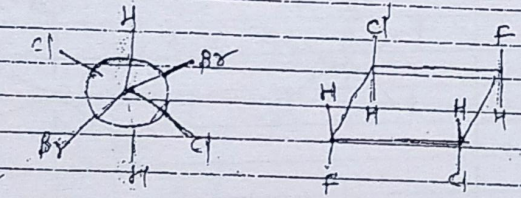


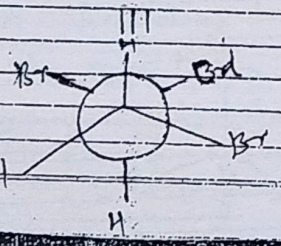
$\sigma(CNX)$

③ C_i point group : molecules with only centre of inversion comes under C_i point group

order of group $h = 2$ i.e E, i

These molecules are very rare.





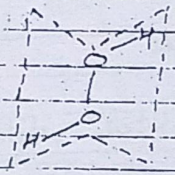
⑩ Molecules of high symmetry :

A] C_n point group :- It is a pure rotational group molecule with only C_n rotation or order of group $h = n$

B] C_2 point group : $C_2 = 180°$ rotation axis

$h = 2$ i.e E, C_2

eg



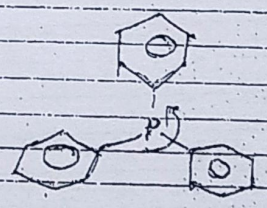
← open book shape

H_2O_2

⑪ C_3 point group

$h = 3$ i.e E, C_3, C_3^2 $C_3 = 120°$ rotation

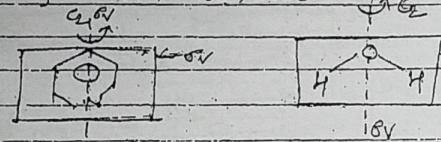
eg NPh_3, ePh_3, $AsPh_3$



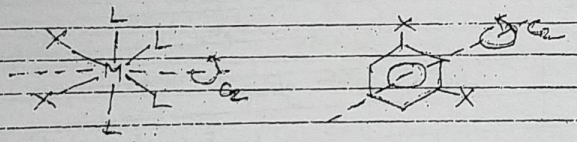
(b) C_{nv} point group : It contains C_n element & number of vertical plane order of group i.e. $h = 2n$

(i) C_{2v} $h=4$ i.e $E, C_2, 2\sigma_v$

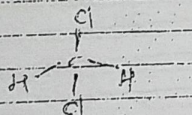
e.g H_2O, H_2S; NO_2



(ii) cis disubstituted octahedral complexes



(iii) disubstituted tetrahedral complex

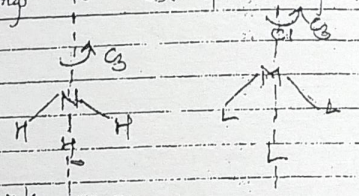


(ii) C_{3v} point groups

$h = 6$ i.e. E, C_3^1, C_3^2 $3\sigma_v$

e.g. All pyramidal molecules i.e trigonal pyramidal molecule

In NH_3 molecule C_3 axis as a principle rotational axis & $3\sigma_v$ planes. Therefore it belong to C_{3v} point group



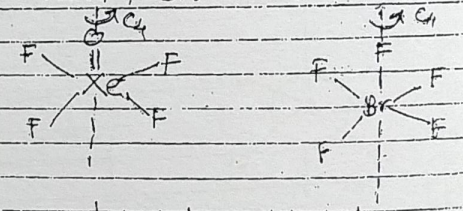
(iii) C_4V Point group

It contains C_4 axis as the rotational axis

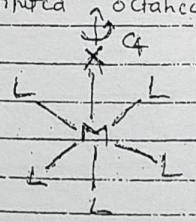
$h = 8$ i.e $E\ C_4^1\ C_4^2\ C_4^3\ 4\sigma_v$

e.g All square pyramidal molecule are of C_{4v} point group

$XeOF_4$, IF_5, SbF_5, BrF_5 etc.



monosubstituted octahedral ML_5X



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(c) C_{nh} point group

This point group contain C_n rotational axis horizontal plane & S_n element order of group $h = 2n$

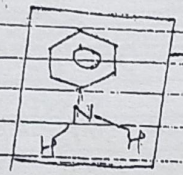
If n is even this point group necessarily contain center of inversion (i)

C_h point group:

order of group $h = 2$ i.e E, σ_h

It contains only plane of symmetry

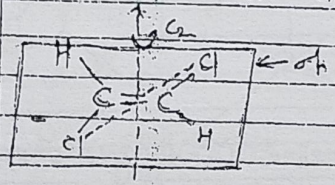
e.g Aniline



② C_{2h} point group:

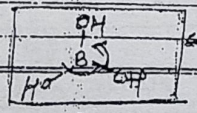
$h = 4$ i.e. E C_2 σ_h S_2 (i)

e.g Trans dichloro ethylene



③ C_{3h} point group:

$h = 6$ i.e. E, C_3^1, C_3^2 σ_h S_3^1 S_3^2

e.g 

σ_h $B(OH)_3$ Boric acid

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(d) D_n Point group

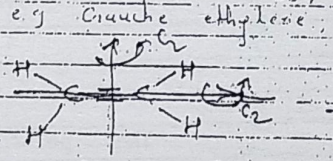
It is also a pure rotation point group This point group consists of a C_n element, n number of C_2 & perpendicular to C_n $h = 2n$ element

All Gauche molecules comes under D_n point group

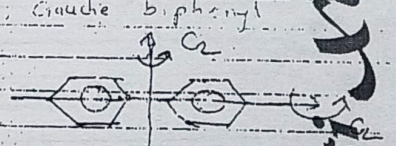
① D_2 point group:

In this point group $h = 4$ element i.e E C_2^1 $2C_2$

e.g Gauche ethylene, Gauche biphenyl



Gauche ethylene



Gauche biphenyl

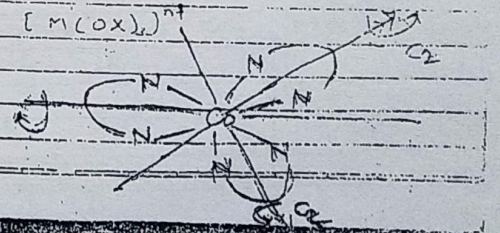
② D_3 point group

In this point group $h = 6$ i.e E, C_3^1 C_3^2 $3C_2$

e.g All tris symmetric bidentate metal complexes

$[M(en)_3]^{n+}$ $[M(ox)_3]^{n+}$

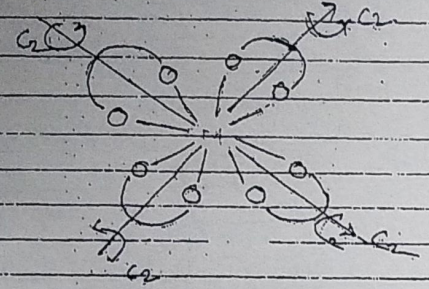
$[Co(en)_3]^{3+}$



(3) D_4 point group

h=8 E i.e E, C_4^1, C_4^2, C_4^3, $4C_2$

ex: Tetra symmetric bidentate compler



E) Dnh point group:

This point group contain C_n rotational axis, n number of C_2 perpendicular to C_n, n no. of vertical plane horizontal plane & S_n improper axis. If n is even this point group is necessary contain center of inversion (i)

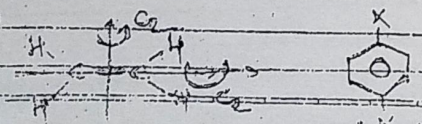
h=4n element

i.e C_n nC_2 $1\sigma_h$ C_n, $n\sigma_v$ σ_h, S_n

(1) Dnh point group:

h=8 element i.e E, C_2, $2C_4$, $2\sigma_v$, σ_h, S_2

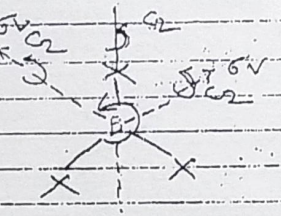
e.g. C_2H_4



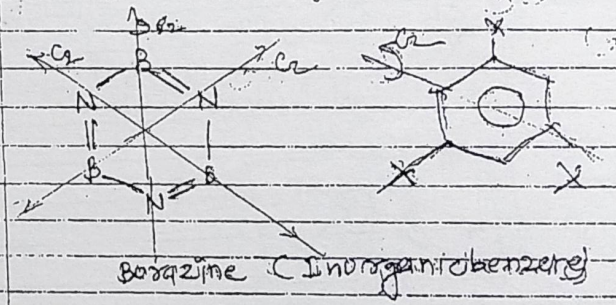
(2) D3h point group

h=12 i e E C_3^1 C_3^2 $3C_2$ $3\sigma_v$ σ_h S_3^1 S_3^2

e.g. All eclipsed molecules comes under Dnh point group. All trigonal planar molecule comes under D3h point group e.g. BX_3, CO_3^{2-}, NO_3^-



All trigonal bipyramidal molecule are comes under this point group e.g PCl_5

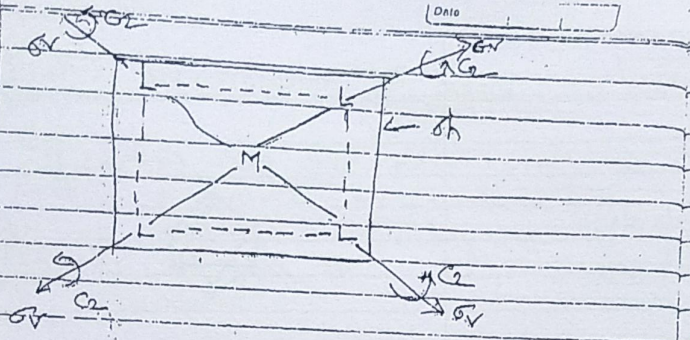


Borazine (Inorganic benzene)

(4) D4h point group:

h=16 i.e E, C_4^1, C_4^2 C_4^3, $4C_2$, $4\sigma_v$, σ_h S_4^1, S_4^3, i

e.g. All square planar molecule comes under D4h point group



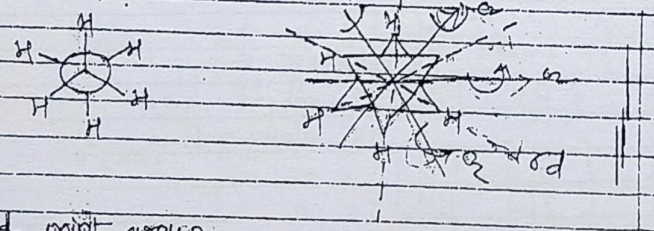
F) Dnd point group:

All staggered molecule comes under Dnd point group. h = 4n

① D3d point group

h = 12 i.e E, C_3^1, C_3^2, 3C_2, 3rd, S_6^1, S_6^5, i

e.g staggered ethane



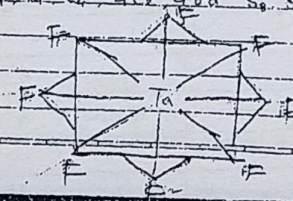
② D4d point group

h = 16 i.e E, C_4^1, C_4^2, C_4^3, 4C_2, 4rd, S_8^1, S_8^3, S_8^5, S_8^7

e.g TaF_5

Tantalum

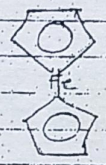
At. no. 73



③ D5d point group

h = 20 i.e E, C_5^1, C_5^2, C_5^3, C_5^4, 5C_2, 5rd, S_{10}^1, S_{10}^3, S_{10}^7, S_{10}^9, i

e.g staggered ferrocene

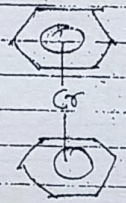


staggered ferrocene

④ D6d point group

h = 24 i.e E, C_6^1, C_6^2, C_6^3, C_6^4, C_6^5, 6C_2, 6rd, S_{12}^1, S_{12}^3, S_{12}^5, S_{12}^7, S_{12}^9, S_{12}^{11}, S_{12}^{11}

e.g staggered dibenzene chromium



⑤ Molecules of special symmetry

molecules which have easily identified geometry comes under the locate of special symmetry

$C_{\infty v}$, $D_{\infty h}$, Td, Oh, Ih, Kh

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$C_{\infty v}$ point group:

h = ∞ i.e C_∞, $\infty\sigma_v$

e.g All non centrosymmetric linear molecule

HCl, HBr, CO, NO, HCN H–C≡C–H

X=C=S, X=C=O etc

$D_{\infty h}$ point group

h = ∞ i.e E C_∞, ∞C_2, $\perp$ to C_∞, $\infty\sigma_v$, σ_h

e.g All centrosymmetric linear molecules

Homoatomic molecules

H_2, O_2, N_2, Cl_2, CO_2, S=C=S, N_3

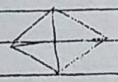
Td point group:

All tetrahedral molecule not comes under this point group

h = 24 i.e E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$

It must be a pure tetrahedral

e.g CCl_4, NH_4^+, BH_4^-, SO_4^{2-}, PO_4^{3-}, FeO_4^{2-}



Oh point group

h = 48 i.e E $6C_4$, $3C_2$, $8C_3$, $6C_2$, $6S_4$, $8S_6$, $6\sigma_d$, $3\sigma_h$, i

Those molecule with 48 symmetry element comes under Oh point group

e.g SF_6, PF_6^- $[Fe(CN)_6]^{4-}$

6 corners
8 faces
12 edges

Ih point group

h = 120

All icosahedral or Dodecahedral

E, 24S_5, 20C_3, 15C_2, 24S_{10}, 20S_6, 15σ_d, i

12: corners
20: triangle faces
30: edges

e.g $B_{12}H_{12}^{2-}$ C_{60} fullerene C_{80} fullerene C_{240} fullerene

Kh point group:

Sphere group

All atoms h = ∞

* Matrix representation of groups

A matrix is a rectangular array of numbers or symbols for numbers. The set of matrices corresponding to the symmetry operations of a group is called its representation

Matrix representation of symmetry operation

① Matrix for the identity operation

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

② Reflection operations :- Principal Cartesian plane is (xy, xz or yz)

$$\sigma(xy) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$

$$\sigma(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$$\sigma(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

OR

$$\sigma = \begin{bmatrix} \cos 2\beta & \sin 2\beta & 0 \\ \sin 2\beta & -\cos 2\beta & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

③ Inversion operation

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

④ Rotation

$$C_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ or } \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

⑤ Improper rotation

$S_n = C_n \times \sigma(xy)$ for xy plane

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

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

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

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

① Matrix representation of symmetry operations of the point group C_{2h}

	E	C_2	σ_h	i
Point group Γ =	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

② Matrix representation of symmetry operation in C_{2v} group.

	E	C_2	σ_v	
Γ =	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

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

③ Matrix Representation of symmetry operations in C_{3v} group.

E $\quad$ C_3^1 $\theta = 120°$ $\quad$ C_3^2 $\theta = 240$

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

σ_1 $\theta = 0°$ $\quad$ σ_2 $\theta = -60$ $\quad$ σ_3 $\theta = 60°$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Representation for C_{2v} point group

For C_{2v} point groups possible symmetry operations are E, C_2, $\sigma_v(xz)$ & $\sigma_v(yz)$ combination of E with single column matrix leaving it unchanged as below

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

Matrix representation for C_2 operations can similarly carried out

$$C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

similarly for $\sigma_v(xz)$ operation

$$\sigma_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

similarly for $\sigma_v(yz)$ operation

$$\sigma_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

The combination of two operation of H_2O molecule can shown combination of matrices i.e.

Swati Xerox

$$C_2 \times \sigma_v(xz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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

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

$C_2 \times \sigma_v(xz) = \sigma_v(yz)$

Multiplication table of H_2O i.e C_{2v} point group is as follow

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
E	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
C_2	C_2	E	$\sigma_v(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	E	C_2
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	C_2	E

In case of character table

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
E	1	1	1	1
C_2	1	1	−1	−1
$\sigma_v(xz)$	1	−1	1	−1
$\sigma_v(yz)$	1	−1	−1	1

Representation of character

Representation is divided into two main types

1. Reducible representation
2. Irreducible representation

1. Reducible Representation

Representation of higher dimension which can be reduced into representation of lower dimension known as reducible representation for given molecule there can be an number of reducible representation Reducible representation can be understand by considering symmetry transformation consider representation having matrices A, B, C, D by applying similarity transformation for each matrix representation

$$[X^{-1}] A [X] = A'$$

$$[X^{-1}] \begin{bmatrix} A_1 & & \\ & A_2 & \\ & & A_3 \end{bmatrix} [X] = \begin{bmatrix} A_1' & & \\ & A_2' & \\ & & A_3' \end{bmatrix}$$

Block factorised 'A'

$$[X^{-1}] \begin{bmatrix} B_1 & & \\ & B_2 & \\ & & B_3 \end{bmatrix} [X] = \begin{bmatrix} B_1' & & \\ & B_2' & \\ & & B_3' \end{bmatrix}$$

Block factorised 'B' matrix

$$[X^{-1}]\begin{bmatrix} C_1 & & \\ & C_2 & \\ & & C_3 \end{bmatrix}[X] = \begin{bmatrix} C_1' & & \\ & C_2' & \\ & & C_3' \end{bmatrix}$$

Block factorised 'C' matrix.

$$[X^{-1}]\begin{bmatrix} D_1 & & \\ & D_2 & \\ & & D_3 \end{bmatrix}[X] = \begin{bmatrix} D_1' & & \\ & D_2' & \\ & & D_3' \end{bmatrix}$$

Block factorised 'D' matrix

$[B][C] = D$

$[B_1][C_1] = D_1$

$[B_2'][C_2] = D_2$

$[B_3'][C_3] = D_1'$

It shows that for given molecule there can be only number of reducible representation

(1) Irreducible representation :

Representation which can not be reduced into other lower representation is known as irreducible representation.

For given point group a final number of irreducible representation only possible

Type of groups :

* (1) Abelian group :

A abelian group is one in which all the element commute with each other (The element which follow the commutative law of multiplication)

e.g. A, B, C are the elements of a group

$A \cdot B = C$

$B \cdot A = C$,

Then A & B element said to be commutative to each other.

e.g. C_{2v} point group

In C_{2v}, $h = 4$ i.e $E, C_2, \sigma_v, \sigma_v'$

$E \times C_2 = C_2$

$C_2 \times E = C_2$

$\sigma_v \times \sigma_v' = C_2$

$\sigma_v' \times \sigma_v = C_2$

$C_2 \times \sigma_v = \sigma_v'$

$\sigma_v \times C_2 = \sigma_v'$

$\sigma_v' \times \sigma_v' = E$

$\sigma_v \times \sigma_v = E$ e.g. H_2O

* (2) Non abelian groups :

Non abelian group is one in which the element may not commute to each other. The element may not follow the commutative law of multiplication.

e.g. A, B, C, D are the elements in a group

$A \cdot B = C$

$B \cdot A = D$

$\therefore$ A, B said to be non commutative

e.g. C_{3v} point group

In C_{3v}, $h = 6$ i.e E, C_3^1, C_3^2, σ_v, σ_v', σ_v''

$C_3^1 \cdot C_3^2 = C_3^3 = E$

$C_3^{2'} \cdot C_3^1 = C_3^3 = E$

$C_3^1 \cdot \sigma_v = \sigma_v'$

$\sigma_v \cdot C_3^1 = \sigma_v''$

e.g. NH_3

③ Isomorphic Groups:

If two groups have the same order and if the forms of their multiplication tables are the same, the groups are said to be isomorphic and thus simplifies the construction of character tables.

Following point groups are isomorphic

$C_{nv} \sim D_n$, $C_n \sim S_n$ (n even), $C_{nh} \sim C_{2n}$ (n odd)

$D_{2nd} \sim D_{nd}$, $D_{nh} \sim D_{nd}$ (n odd),

$O \sim T_d$.

e.g. C_{3v} and D_3 have the same character table, although their symmetry operations are different.

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* Great orthogonality Theorem (GOT)

The relationship between the elements of unitary matrices to form group representation is given by Great orthogonality Theorem. As the name indicates the the theorem shows orthogonal relationships that exist betⁿ the matrix elements of the different representations of a group.

Mathematically it is stated as

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'} \quad \text{①}$$

h = order of the group

l_i & l_j = Dimension of two irreducible representations of the group

R = various symmetry operations of the group

m and n represents m^{th} row & n^{th} column of the matrix

* represents the complex conjugate

δ is Kronecker delta $\delta_{ij} = 0$ if $j \neq i$ and $\delta_{ij} = 1$ if $i = j$

Each element is normalized & orthogonal to the other element in the matrix

The character of the i^{th} representation of operation R, is just the sum of

The diagonal elements of the matrix representing R.

The equation ① can be put in three simpler equation

1) If $i \neq j$, $\sigma_{ij} = 0$ and $m = m'$ and $n = n'$. Then

$$\sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{mn} = 0$$

or $\sum_R \chi_i(R) \chi_j(R) = 0$

Elements corresponding to matrices of different irreducible representation are orthogonal.

② If $m \neq m'$ and $n \neq n'$ $\sigma_{mm'} = 0$ & $\sigma_{nn'} = 0$ then

$$\sum_R \Gamma_i(R)_{mm'} \Gamma_j(R)_{nn'} = 0$$

Elements of the different sets of the matrices of the same IR_i are orthogonal

③ If $i = j$, $m = m'$ and $n = n'$ $\sigma_{ij} = 1$. $\sigma_{mn} = 1$ Then

$$\sum_R \Gamma_i(R)_{mn} \Gamma_j(R)^*_{mn} = \frac{h}{l_i} \delta_{ij}$$

where h = order of group
l_i = dimensional length

Importance of Great Orthogonality Theorem

Following rules can be derived from GOT for irreducible representations of a group

① The number of irreducible representation in a group is equal to number of classes of operations of groups.

② The sum of the squares of the dimensions of the irreducible representations is equal to the order of the point group.

$$\sum_i l_i^2 = l_1^2 + l_2^2 + l_3^2 + \cdots = h$$

where the summation is taken overall the representations Γ_i. since the dimension of an IR is equal to the character of its identity operation E, so that sum of the squares of the character of E of IR_i of group is equal to the order of group

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

③ The sum of the squares of the characters of an irreducible representation is equal to the order of the group.

$$\sum_i [\chi_i(R)]^2 = h$$

④ The characters of the same each other irreducible rep table form o

$$\sum_i [\chi_i(R$$

⑤ The characte same class or reducible

④ The characters of the irreducible representations of the same group are orthogonal to each other. i.e. the columns of the irreducible representations in the character table form orthogonal vectors.

$$\Sigma [\chi_i(R)\chi_j(R)] = 0$$

⑤ The characters of the elements of the same class of an irreducible representation or reducible representation are same

Notations for irreducible representations OR Mulliken symbols

① Dimensions of the irreducible representations

If the dimension of the irreducible representation is unidimensional term A or B is used i.e

- A or B ⟶ one dimensional
- E ⟶ two dimensional
- T ⟶ Three dimensional
- G ⟶ four dimensional

② Symmetry with respect to principle axis

If the one dimensional irreducible representation is symmetrical with respect to principle axis C_n (i.e the character for C_n operation is +1) term A is used. one dimensional representation unsymmetrical with respect to principle axis (character of is -1) term -1 is used i.e

C_n { symmetrical ⟶ A (+1)
unsymmetrical ⟶ B (-1)

③ Symmetry with respect to at subsidiary axis:

If the (IR) irreducible representation symmetrical with respect to the subsidiary axis subscripts A_1, B_1, E_1 & T_1 are used & if it is unsymmetrical subscripts A_2, B_2, E_2 & T_2 are used.

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subsidary axis { symmetrical → A_1, B_1, E_1, T_1 ; unsymmetrical → A_2, B_2, E_2, T_2

(b) Symbol for centre of symmetry

If there is center of symmetry in the molecule subscript 'g' is used for symmetry and 'u' is used for antisymmetry. i.e

i { symmetry → g ; antisymmetry → u }

(c) For a symbol with a prime (') character +1 must appear for σh and for symbol with double prime (") character −1 is used for σh i.e

σh { single prime (') → +1 ; double prime (") → −1 }

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

In C_{2v} point group there are four operations of four different classes E, C_2, $\sigma_v(xz)$ & $\sigma_v(yz)$

① In C_{2v} point there are four classes of operations, there are four irreducible representations i.e $\Gamma_1, \Gamma_2, \Gamma_3$ & Γ_4 .....

② The sum of squares of dimension of irreducible representations should be equal to 4. Hence each representation must be unidimensional i.e

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

since, dimensions of representation is equal to the character of identity the operation of irreducible representation E must be equal to 1 in all of them.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Γ_1	1			
Γ_2	1			
Γ_3	1			
Γ_4	1			

③ The sum of squares of the characters of an irreducible representation must be equal to 4. for one of the irreducible.

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representation (Γ_1) all characters must be equal to 1 i.e

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Γ_1	1	1	1	1

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

④ In case of other irreducible representation also the sum of squares of characters equal to 4 and characters must be orthogonal. Thus the character must be two +1 and two −1

The irreducible representation with their characters shown as follows

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Γ_1	1	1	1	1
Γ_2	1	1	−1	−1
Γ_3	1	−1	1	−1
Γ_4	1	−1	−1	1

⑤ Γ_1 is one dimensional symmetrical to the principle axis and the vertical plane $\sigma_v(xz)$ Hence symbol is A_1

Γ_2 is unidimensional but unsymmetrical to $\sigma_v(xz)$ Hence symbol is A_2

Γ_3 is unidimensional unsymmetrical with respect to principle axis but symmetrical with respect to $\sigma_v(xz)$ Hence symbol is B_1

Γ_4 is unidimensional unsymmetrical to the principle axis and also unsymmetrical to $\sigma_v(xz)$ Hence symbol is B_2

Therefore the complete character table for C_{2v} point group is

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

Construction of Character Table for C_{3v} point group elements [E, C_3, σ_v]

There In C_{3v} point group h = 6 but the classes of operations are three therefore in C_{3v} three irreducible representations are present. i.e Γ_1, Γ_2 & Γ_3

① The sum of squares of the dimension should be equal to the 6. since the dimension has be an integer, there should be two one dimensional & one two dimensional.

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

(3) i.e $1^2 + 1^2 + 2^2 = 6$

(2) It can be seen that the summation of squares of characters of operation is equal to 6

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	1	1	1

i.e $1\times(1)^2 + 2\times(1)^2 + 3\times(1)^2 = 6$

(1) The characters of Γ_1 & Γ_2 are orthogonal Hence the characters C_3 & σ_v for Γ_2

$1\times1 + 2\times1\times C_3 + 3\times1\cdot\sigma_v = 0$

when $C_3 = 1$ & $\sigma_v = -1$ eqⁿ is correct

i.e $1 + 2 - 3 = 0$

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

The characters of Γ_3 are orthogonal to Γ_1 & Γ_2

∴ orthogonality theorem betⁿ Γ_1 & Γ_3

let $C_3 = 0$, $\sigma_v = 1$

$1\cdot1\cdot2 + 2\cdot1\cdot C_3 + 3\cdot1\cdot\sigma_v = 0$ — (1)

$\simeq 2 \simeq 0$

∴ Orthogonality theorem betⁿ Γ_2 & Γ_3

$1\cdot1\cdot2 + 2\cdot1\cdot C_3 + 3\cdot(-1)\cdot\sigma_v = 0$ — (2)

$\simeq 2 \simeq 0$

$\sigma_v = 0$ & $C_3 = -1$

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

- Γ_1 is one dimensional, symmetrical to principle axis & to the vertical plane hence symbol A_1 is assigned.
- Γ_2 is one dimensional & symmetrical to principle axis but unsymmetrical with respect to vertical plane so symbol A_2 is used
- Γ_3 is two dimensional so symbol E is used

therefore complete character table for C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

* Construction of character table for C_{1h} point group

In C_{1h} point group there are two different classes i.e h = 2 which are E, σ_h

① since there are ~~four~~ two classes of operations there are two (2) irreducible representations.
i.e Γ_1 & Γ_2

② The sum of squares of dimensions of irreducible representation should be equal to 2 Hence each representation must be unidimensional
i.e $1^2 + 1^2 = 2$

C_{1h}	E	σ_h
Γ_1	1	
Γ_2	1	

③ The sum of squares of the characters of an irreducible representation must be equal to 2.

C_{1h}	E	σ_h
Γ_1	1	1
Γ_2	1	

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

④ characters of irreducible representations of a group are orthogonal to the each other.

$\therefore 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot \sigma_h = 0$

$1 + \sigma_h = 0$

$\therefore \sigma_h = -1$

C_{1h}	E	σ_h
Γ_1	1	1
Γ_2	1	-1

Γ_1 is unidimensional & symmetrical with respect to σ_h therefore A' is used
Γ_2 is unidimensional & unsymmetrical with respect to σ_h therefore A'' is used

C_{1h}	E	σ_h
A'	1	1
A''	1	-1

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* Character tables and their use

For a point group whenever the symmetry elements and the irreducible representation are arranged along with their characters in the form of table, containing rows & columns is known as character table It consist of four columns.

Character tables of molecular point groups are extremely important for their applications in solving chemical problems related to molecular spectroscopy.

Character tables find their extensive use in

1. symmetry properties of orbitals
2. Hückel molecular orbital theory
3. Electronic transitions
4. Infrared & Raman active vibrations
5. structure elucidation of molecules

* Applications of group theory

1. Group theory is an extremely useful tool to predict the probability of transitions in atomic & molecular spectroscopy
2. It helps in the classification of the normal vibration according to the irreducible representations of the point group of molecules.
3. It aid in qualitatively finding out the infrared & Raman spectral activity of the fundamental as well as the overtone combinations bands
4. Group theory can be applied in the construction of hybrid orbitals & symmetry adapted linear combination of atomic orbitals in MOT.
5. Group theory helps in determining optical activity and polarity of molecules, classification of elementary particals into fermions & bosons and simplifying the secular equation, which is a special feature of the quantum mechanical calculations in both VBT and MOT.