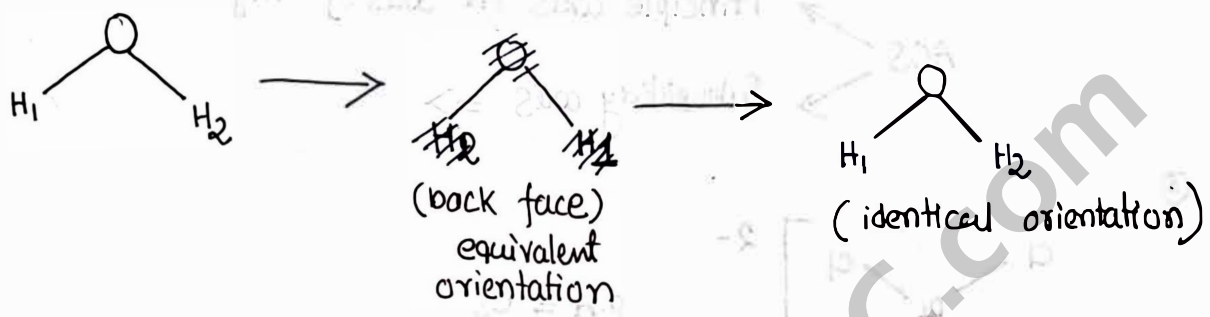
-: Group Theory :-

mathematical Study of Symmetry.

- Conformation / orientation :-
  - → equivalent
  - → identical orientation



- Symmetry element :-

Any geomatric entity like ....

Symmetry operation on Axis, plane, point,

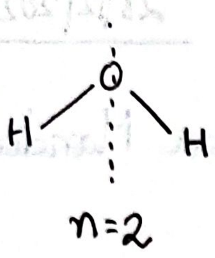
1. Axis of Symmetry (AOS)
2. plane of Symmetry (POS)
3. center of Symmetry (COS)
4. Improper axis of Symmetry (IAOS)

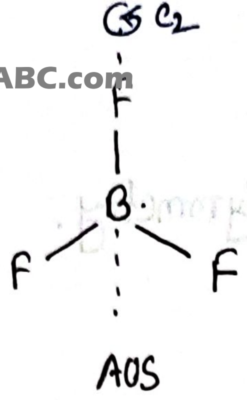
Symmetry operations
→ rotation
→ reflection
→ inversion.

AOS :- any imaginery axis which is passed through the molecule Symetrically an rotn around which gives an equivalent orientation.

$$\boxed{n = \frac{360°}{\theta}}$$

@mundal





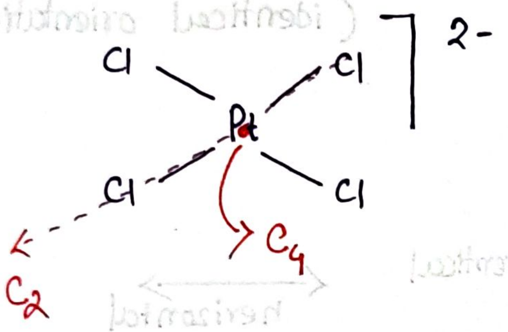
C_3 = principle axis

$3C_2$ = Subsidiary axis

∴ maximum No. of n = P.A

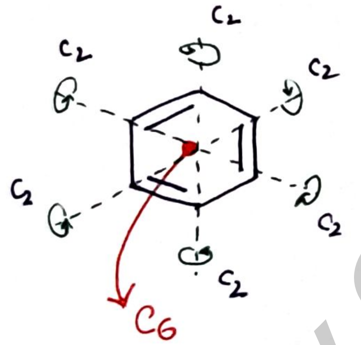
AOS → Principle axis ⇒ axis of Highest order

AOS → Subsidiary axis ⇒



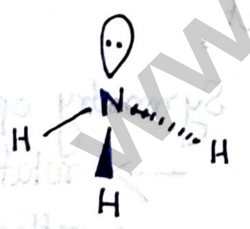
P.A = C_4

S.A = $4C_2$



P.A = C_6

S.A = $6C_2$



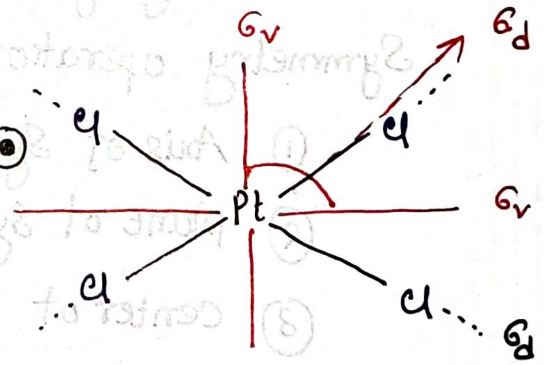
P.A = C_3

no S.A.

Cn → nC_2

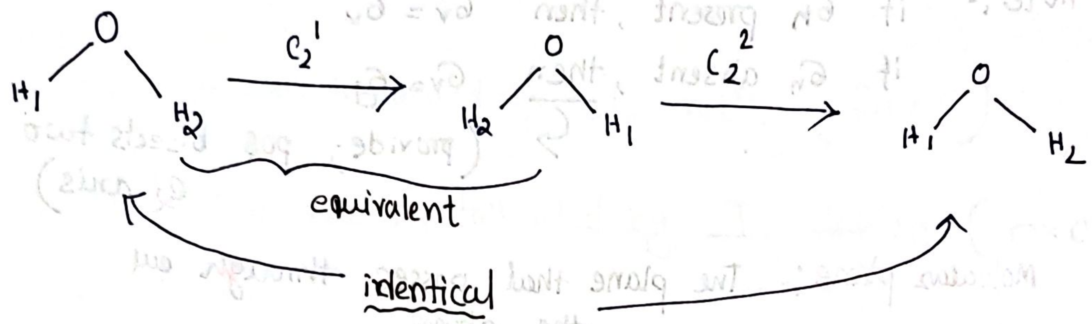
Cn → no C_2

principle axis

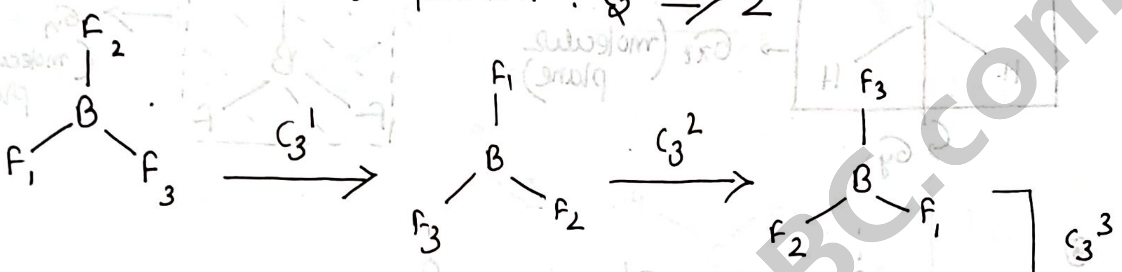


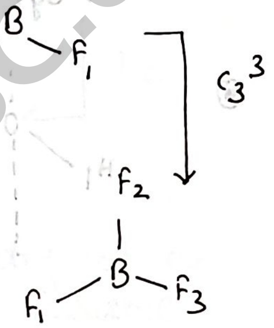
vartical plane passing through max[m] no. of atoms is called σd.

No. of operations :



∴ No. of operation : $C_2 \Rightarrow 2$





∴ No. of operation $C_3 = 3$

No. of operation $C_n = n$

$$\boxed{C_n^n = E}$$

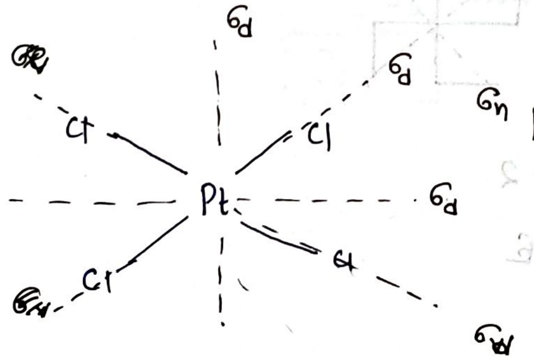
Plane of Symmetry :-

Vertical POS (σ_v) — parallel to P.A

Horizontal (POS) (σ_h) — perpendicular to P.A

Dihedral POS (σ_d) ⇒ the vertical plane that bisects the angle between two C_2 axis, (when σ_h is absent)

molecular plane — σ_v, σ_h



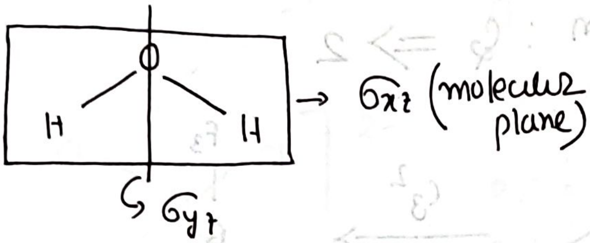
σ_h present

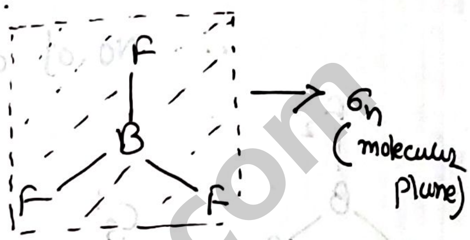
C_4	⇒	C_n
$4C_2$		$4C_2$
$4\sigma_v$		$2\sigma_v$
σ_h		$2\sigma_d$
		$\cancel{\sigma_h}$

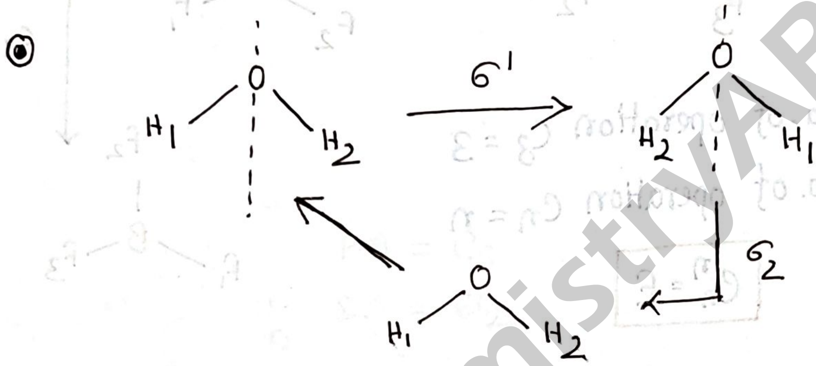
এক্ষেত্রে σ_h absent হলে ২টি σ_v গুলো হবে σ_d লেখা হত ।

Note :- if σ_h present , then $\sigma_v = \sigma_v$
if σ_h absent , then $\sigma_v = \sigma_d$
(provide; pos bisects two C_2 axis)

Molecular plane :- The plane that passes through all the atoms.



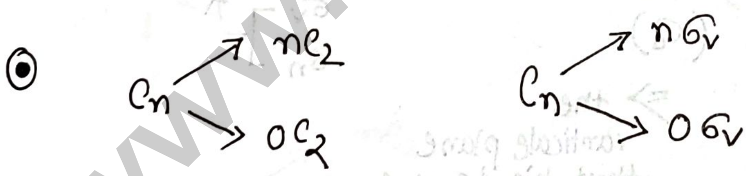




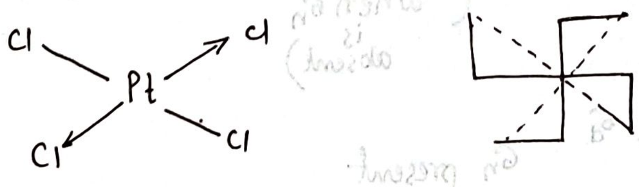
No. of operations = 2

$C_n^n = E$

$\sigma^2 = E$



Center of Symmetry :- (i)



No. of operation = 2

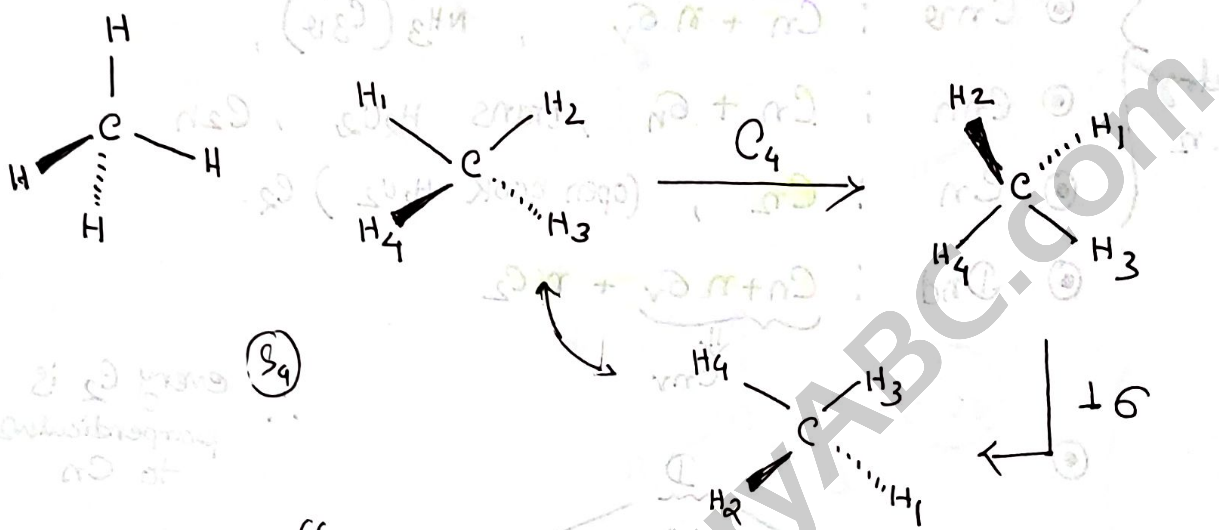
$i^2 = E$

 www.ChemistryABC.com

Improper axis of Symmetry: (Rota-Reflection Axis) => S_n

S_n → σ followed by ⊥ rot^n. ($C_n \times \sigma$)

S_n → rotation followed by ⊥ reflection ($\sigma \times C_n$)



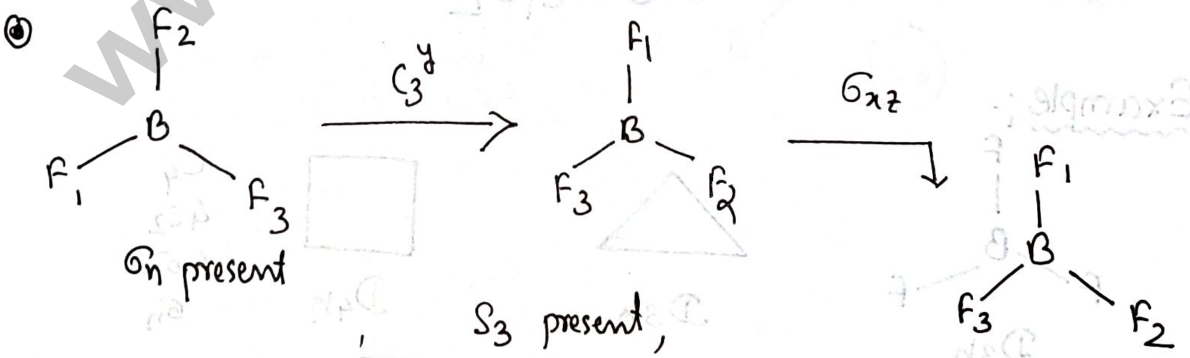
66

For improper axis of symmetry of a molecule there are no boundation for a prescence of proper axis of symmetry".

C_n (principle axis) → no S_n

C_n → S_n (if σ_h present)

C_n → S_{2n} (if σ_h absent)



, S_3 present,

$\boxed{S_2 = i}$

identity = E

www.ChemistryABC.com

point group :-

the collection of all the symmetry elements present in a molecule can be represented by a single term. called point group.

Symmetry no. n

- C_{nv} : $C_n + n\sigma_v$, NH_3 (C_{3v}) ;
- C_{nh} : $C_n + \sigma_h$, trans H_2O_2 , C_{2h}
- C_n : C_n , (open book H_2O_2) C_2.
- D_{nd} : $\underbrace{C_n + n\sigma_v}_{\Downarrow\ C_{nv}} + nC_2$

∴ every C_2 is parperdicular to C_n

- D

$$D \rightarrow D_n,\ D_{nd},\ D_{nh}$$

$D_n = C_n + nC_2$

$D_{nd} = C_n + nC_2 + n\sigma_v$

$D_{nh} = C_n + nC_2 + n\sigma_v + \sigma_h$

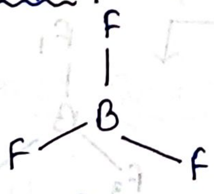
$\cancel{C_n + nC_2 + \sigma_h}$ → σ_v আসবে

- $C_s = E + \sigma$ ← molecular plane

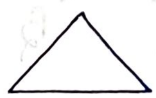
HOCl

- $C_i = E + i$
- $C_1 = E$

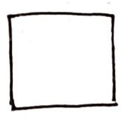
Example :-



D_{3h},

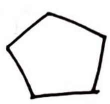


D_{3h}

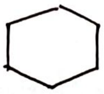


D_{4h}

C_4
$4C_2$
$4\sigma_v$
σ_h



D_{5h}



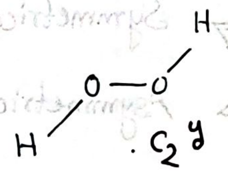
D_{6h},

@mandal

 (point gr does not change on rotation of molecule) www.ChemistryABC.com

- H_2O_2 → cis, trans, open-book

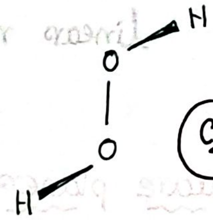
C_{2v}



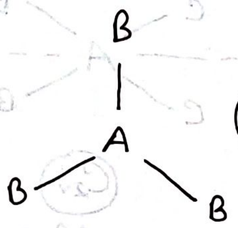
C_2 y

σ_h

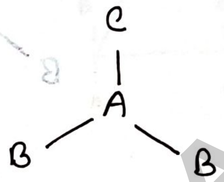
C_{2h}



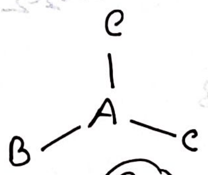
C_2

- 

D_{3h}

- 

C_{2v}

- 

C_{2v}

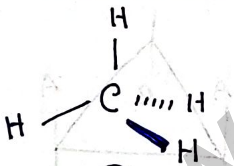
- 

C_s

E + σ

trigonal planes

- Tetrahedral :-

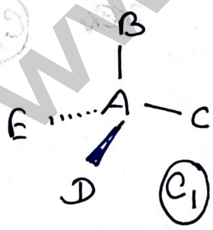


Td

C_{3v}

C_{2v}

like H_2O



C_1

- linear molecule :-

----B—A—B----

C_∞

∞C_2

∞C_v

σ_h

$D_{\infty h}$

 www.ChemistryABC.com

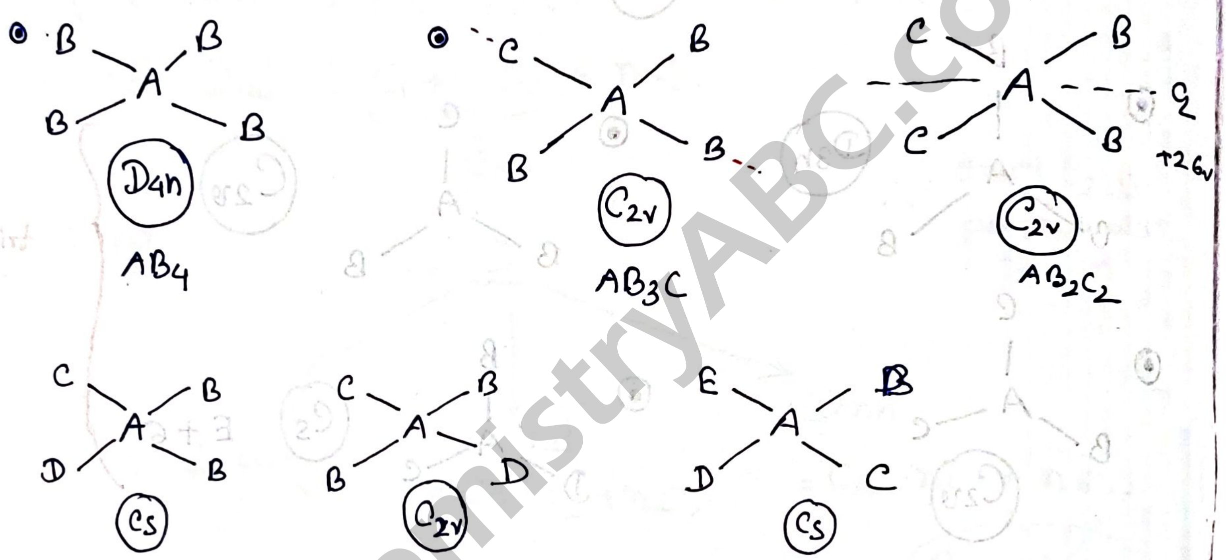
$---A — B---$ C_∞

$H — Cl$ ∞C_v $\Rightarrow$ $C_{\infty v}$

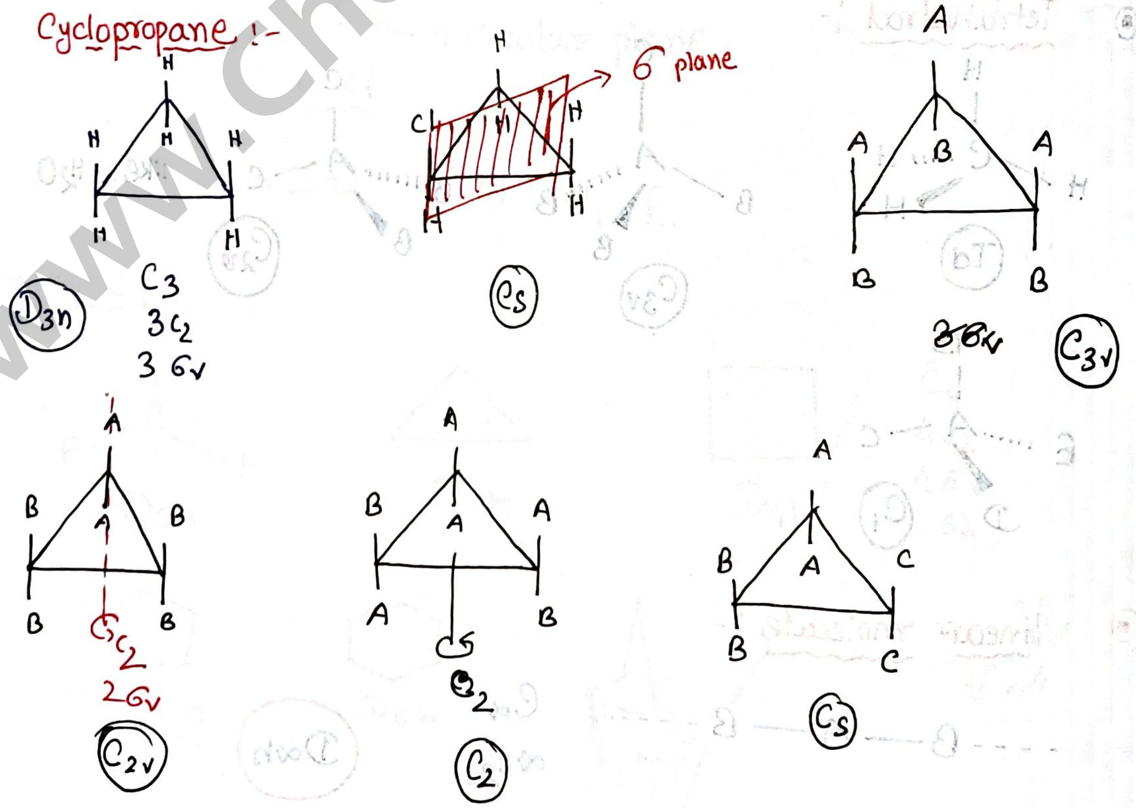
linear molecules → Symmetrical ⇒ $D_{\infty h}$, CO_2

linear molecules → Asymmetrical ⇒ $C_{\infty v}$, HCl

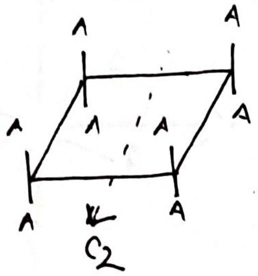
◉ Square planer :-



◉ Cyclopropane :-

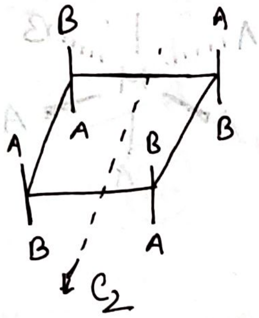


Cyclobutane:-

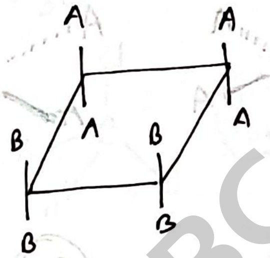


C_4
$4C_2$
$4\sigma_v$
σ_h

D_{4h}

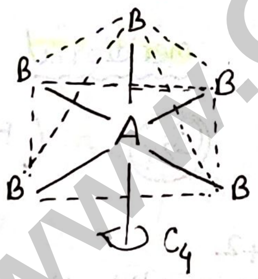


C_2
$+2\sigma_v$
σ_h not present here.
so, $\sigma_v = \sigma_d$
$\therefore C_2 + 2C_2 + 2\sigma_d$
$\Rightarrow D_{2d}$



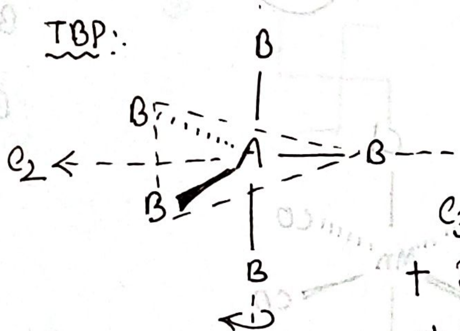
C_2
$2\sigma_v$
C_{2v}

Square pyramidal:-

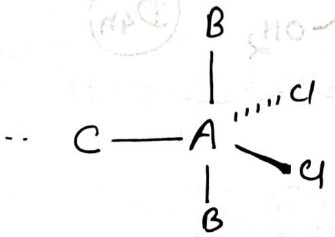


C_4
$4\sigma_v$
σ_h (x)
C_{4v}

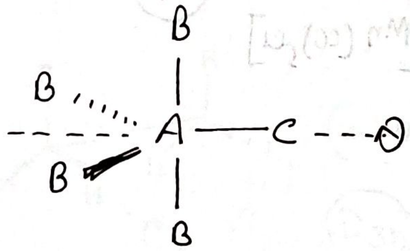
TBP:-



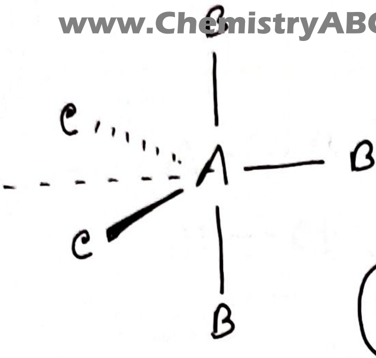
C_3
$+ 3C_2$
$+ 3\sigma_v$
$+ \sigma_h$
D_{3h}



C_3
$+3C_2$
$+3\sigma_v$
$+\sigma_h$
D_{3h}



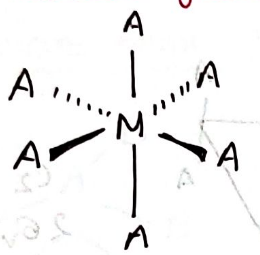
C_2
$2\sigma_v$
σ_h (x) answ
C_{2v}



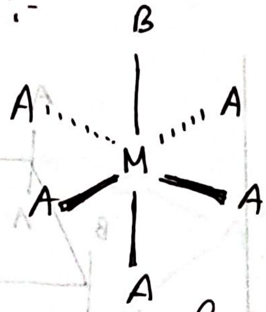
C_2
$+ 2\sigma_v$
$\sigma_h(x)$

C_{2v}

- octahedral geometry :-

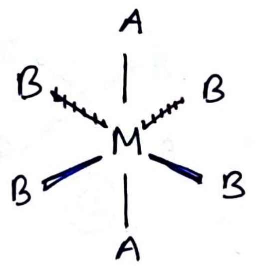


O_h



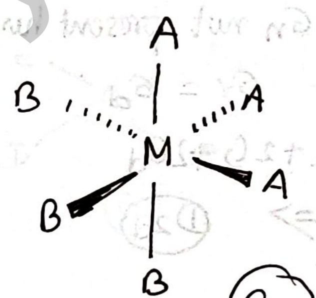
C_{4v}

C_4
$4\sigma_v$
$\sigma_h X$



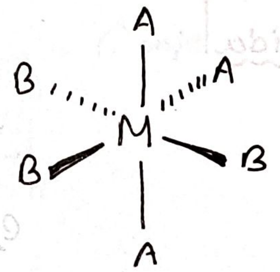
C_4
$+ 4C_2$
$+ 4\sigma_v$
$+ \sigma_h$

D_{4h}



C_{3v}

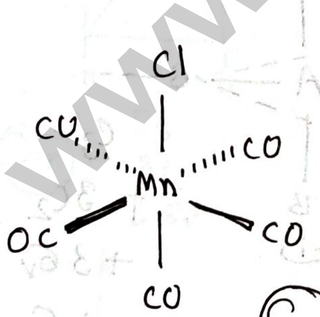
facial isomers (ammonia facial)



meridional

C_{2v}

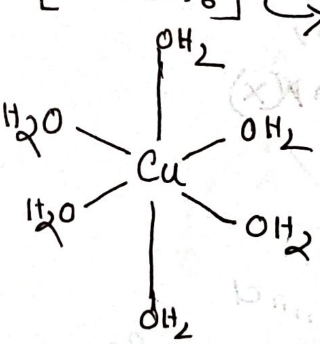
($H_2O \rightarrow$ meri



C_{4v}

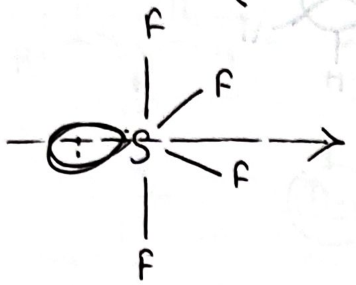
$[Mn(CO)_5Cl]$

$[Cu(H_2O)_6]^{+2} \rightarrow$ distortion oh due to JTD.



D_{4h}

- SF_4 :- (geometry TBP, shape = sea, saw)



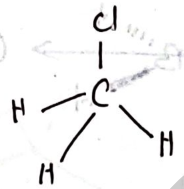
C_2
$2\sigma_v$
C_{2v}

(remember?)

- BH_2Cl

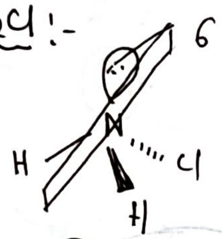
C_{2v}

- CH_3Cl



C_{3v}

- NH_2Cl :-

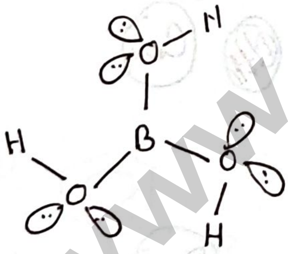


C_s

- HOCl :

C_s

- H_3BO_3 :

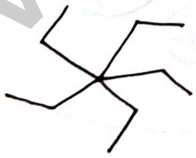


C_3
σ_h
C_{3h}

-

C_4
σ_h
C_{4h}

-

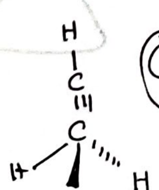


C_5
σ_h
C_{5h}

- $H-C\equiv C-H$ $D_{\infty h}$

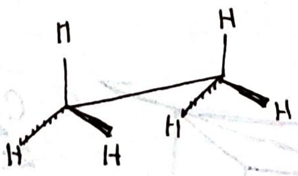
- $H-C\equiv C-CH_3$

|||



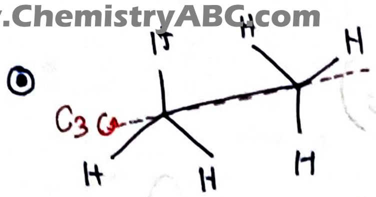
C_{3v}

-

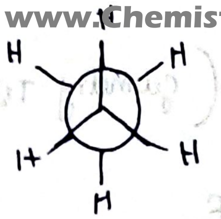


(eclipsed ethane.)

C_3
$3C_2$
$3\sigma_v$
$+\sigma_h$
D_{3h}



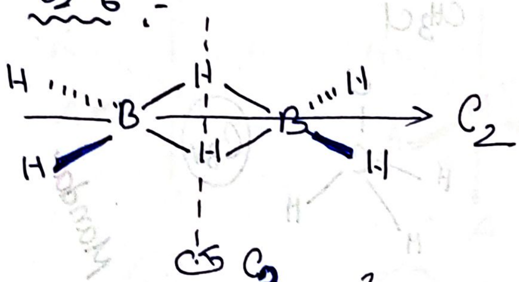
Staggered



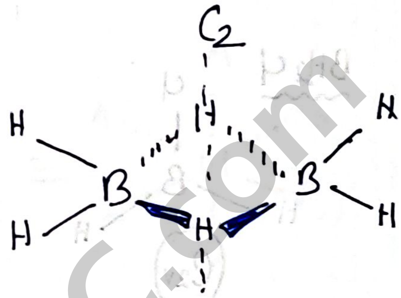
C_3
$3C_2$
$3\sigma_v$ $\sigma_v = \sigma_d$
σ_h absent

D_{3d}

- B_2H_6 :-



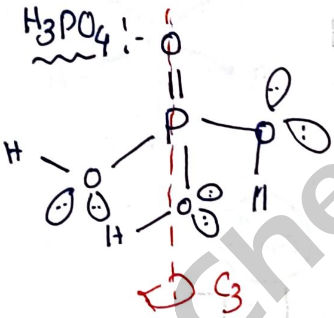
=



C_2
$2C_2$
$2\sigma_v$

D_{2h}

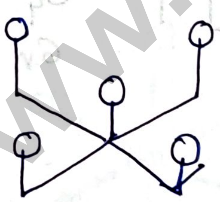
- H_3PO_4 :-



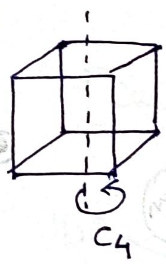
C_3

C_s

$C_{\infty v}$

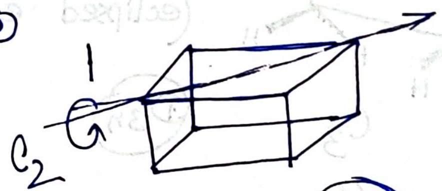


C_4
$4\sigma_v$
C_{4v}



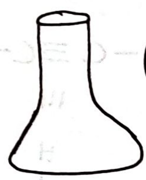
C_4
$4C_2$
$4\sigma_v$
σ_h

D_{4h}

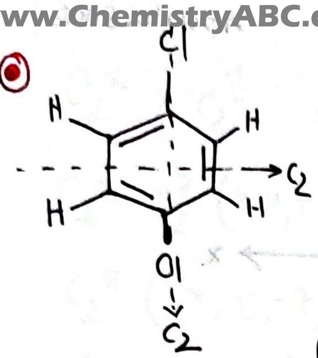


C_2
$2C_2$
$2\sigma_v$
σ_h

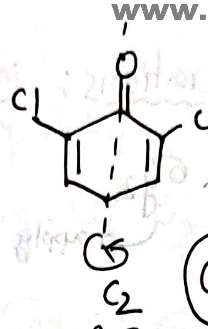
D_{2h}



$C_{\infty v}$

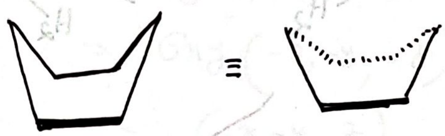


C_2
$2C_2$
$2\sigma_v$
σ_h
D_{2h}

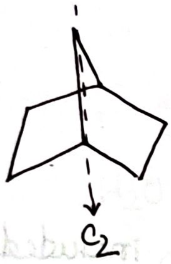


C_2
$2\sigma_v$
C_{2v}

C_2
$2\sigma_v$
C_{2v}

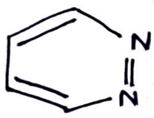


C_{2v}

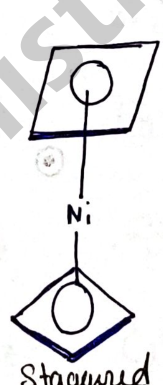


C_2
$2\sigma_v$
C_{2v}

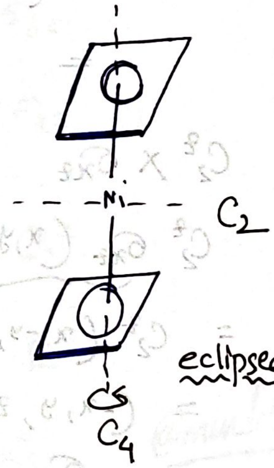
C_3
$3\sigma_v$
$3C_2$
σ_h
D_{3h}



C_2
$2\sigma_v$
σ_h absent
C_{2v}

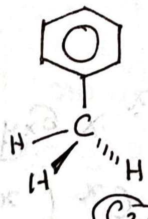


Staggered
D_{4d}

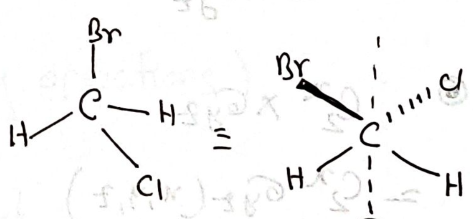


C_4
$4C_2$
$4\sigma_v$
σ_h
eclipsed
D_{4h}

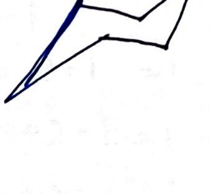
C_2
$2\sigma_v$
C_{2v}



C_{3v}



C_s



D3d

Symmetry operations : Multiplication :-

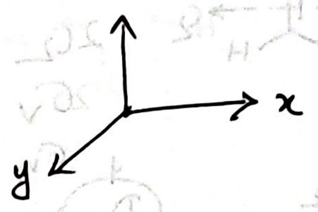
H_2O

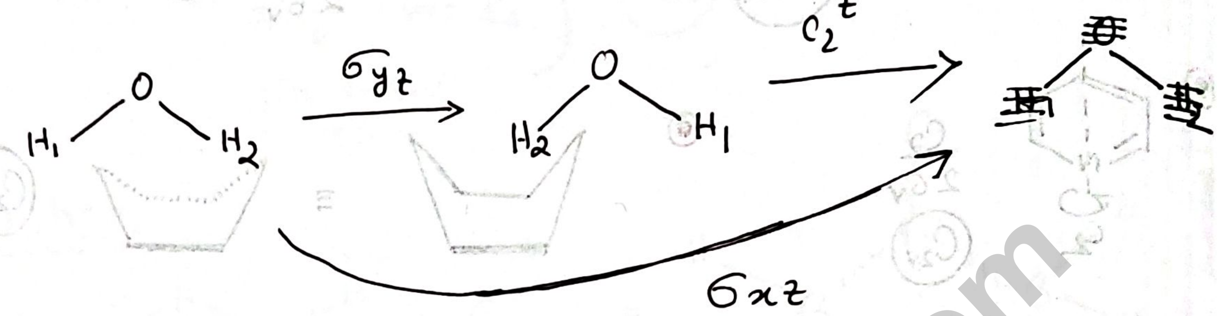
$C_2^z \times \sigma_{yz}$ → apply first (σ_{yz})

apply 2nd (C_2^z)

$\Downarrow$

$C_2(z)$





$$\boxed{C_2^z \times \sigma_{yz} = \sigma_{xz}}$$

- $C_2^z \times \sigma_{yz}\,(x, y, z)$

  $C_2^z\,(-x, y, z)$

  $(x, -y, z)$

  $= \sigma_{xz}$

$\sigma \Rightarrow$ 2 axis included.

$C_2 \rightarrow$ only 1 axis involved.

- $C_2^z \times \sigma_{xz}$

  $C_2^z\,\underbrace{\sigma_{xz}\,(x, y, z)}$

  $= C_2^z\,(x, -y, z)$

  $= (-x, y, z)$

  $= \sigma_{yz}$

- $\sigma_{yz} \times \sigma_{xz}$

  $\sigma_{yz}\,\sigma_{xz}\,(x\,y\,z)$

  $\sigma_{yz}\,(x, -y, z)$

  $(-x, -y, z)$

  $= C_2^z$

- $C_2^x \times \sigma_{yz}$

  $= C_2^x\,\sigma_{yz}(x, y, z)$

  $= C_2^x\,(-x, y, z)$

  $= (-x, -y, -z)$

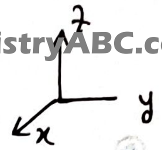
  $\Rightarrow i$

- $C_2^x \times \sigma_{xy}\,(x, y, z)$

  $C_2^x\,(x, y, -z)$

  $\Rightarrow (x, -y, z)$

  $\Rightarrow \sigma_{xz}$



- $C_2^x \times C_2^y$

$C_2^x \; C_2^y \, (x, y, z)$

$C_2^x \, (-x, y, -z)$

$(-x, -y, z)$

$= C_2^z$

- $\sigma_{xy} \times S_4^z$

$\sigma_{xy} \cdot C_4^z \; \sigma_{xy}$ → perpendicular to C_n

$= \sigma_{xy} \, C_4^z \, \sigma_{xy} \, (x y z)$

$= \sigma_{xy} \, C_4^z \, (x, y, -z)$

$= \sigma_{xy} \, (-x, -y, -z)$

$= (-x, -y, z)$

$= \sigma_{xy} \, C_4^z$

C_{nh}
n = even,
i always present

Group Multiplication table :-

H_2O, C_{2v}

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
E	E	C_2^z	σ_{xz}	σ_{yz}
C_2^z	C_2^z	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2^z
σ_{yz}	σ_{yz}	σ_{xz}	C_2^z	E

@mundel.

Order of the point gr :-

(total no. of symmetry operations)

No. of operation

C_n $\quad n-1+1=n$
σ $\quad 1+1=2$
i $\quad 1+1=2$

E বাদ দিয়ে

1 = for E

- $H-O-H$

$E = 1$

$C_2 = 2-1 = 1$

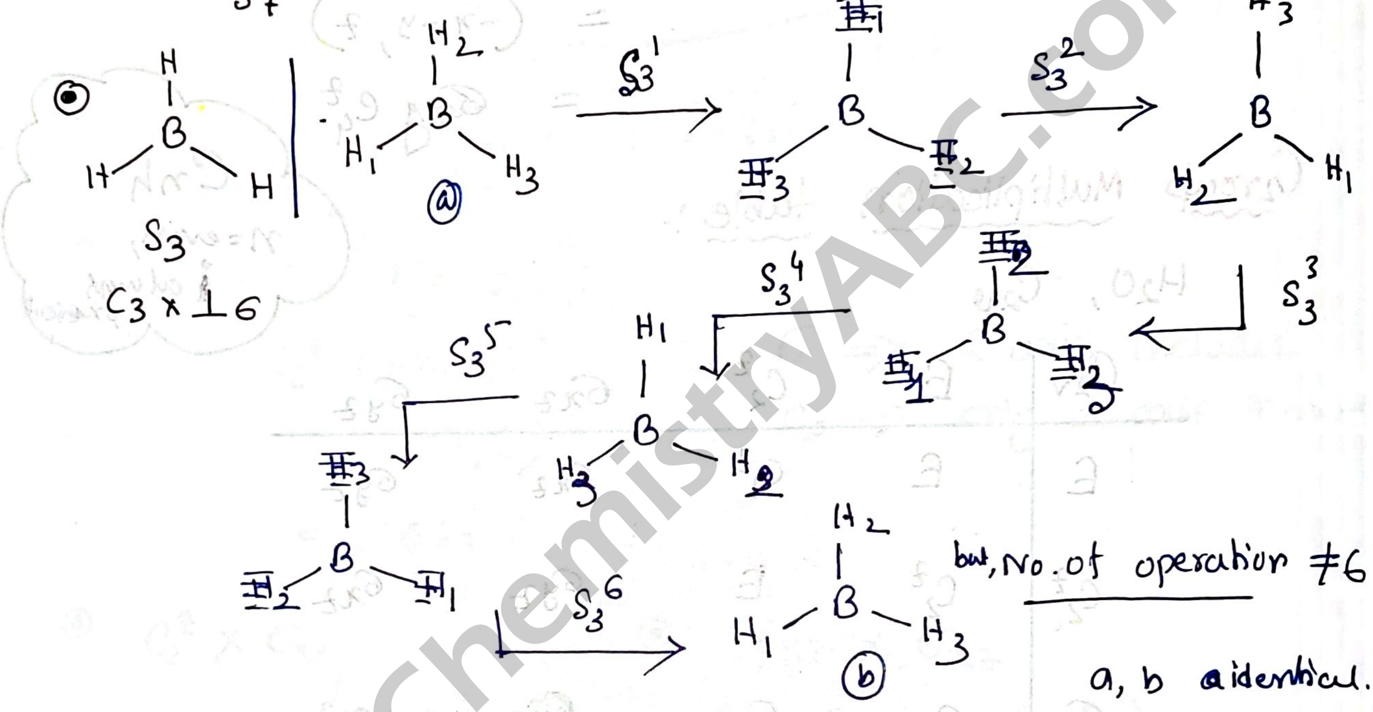
$\sigma_{xz} = 2-1 = 1$

$\sigma_{yz} = 2-1 = 1$

(1 minus করা হচ্ছে কারণ E = 1 করা আছে)

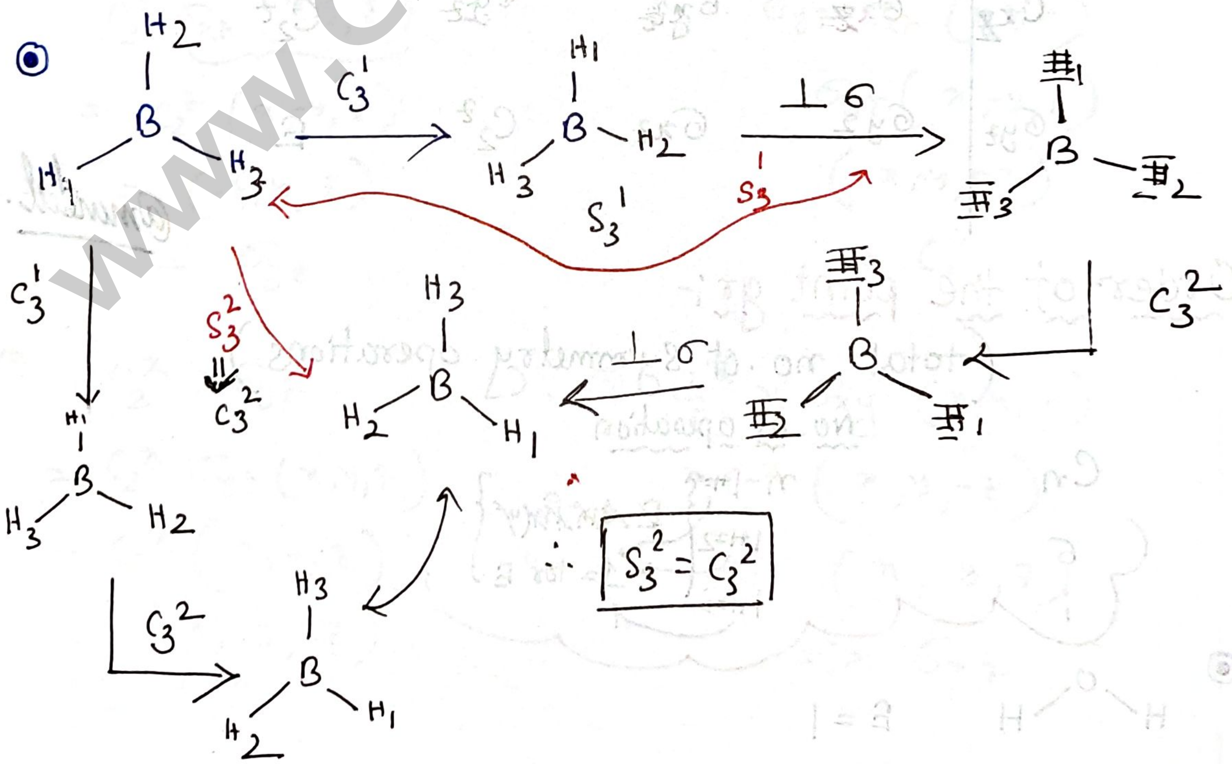
total order = 4

- S_1
- S_2
- S_3
- S_4
- S_5
- S_6
- S_7



but, No. of operation $\neq 6$

a, b identical.



$\therefore \boxed{S_3^2 = C_3^2}$

• S_3,

$6 \times 6 = E$

$C_n \times C_n = E$

$S_3^1 = C_3^1 \times \sigma^1 = S_3^1$

$S_3^2 = C_3^2 \times \sigma^2 = C_3^2 = C$

$S_3^3 = C_3^3 \times \sigma^3 = C_1^1 \times \sigma = \sigma$

$S_3^4 = C_3^4 \times \sigma^4 = C_{3 \times E}^{4-3} = C_3^1 \times E = C_3^1$

$S_3^5 = C_3^5 \times \sigma^5 = C_3^2 \times \sigma = S_3^2$

$S_3^6 = C_3^6 \times \sigma^6 = C_3^3 \times E = C_1^1 \times E = E$

$\sigma^{odd} = \sigma$

$\sigma^{even} = E$

$C_{\cancel{3}}^{\cancel{3}} = C_1^1$

S_a^b $b<a$ if not then $b \Rightarrow b-a$

No. of operation $S_3 = 2 \; (S_3^1, S_3^2)$

Similar for S_5 $S_5 = 4 \; (S_5^1, S_5^2, S_5^3, S_5^4)$

$S_7 = 6 \; (S_7^1, S_7^2, S_7^3, S_7^4, S_7^5, S_7^6)$

∴ if n = odd,
then S_n will have $(n-1)$ no. of operations

• $S_1^1 = C_1^1 \times \sigma^1 = E \times \sigma^1 = \sigma$

$S_1^2 = C_1^2 \times \sigma^2 = C_1 \times E = E$

$\boxed{S_1 = \sigma}$

• S_2,

$S_2^1 = C_2^? \sigma_{xy}^1 = i$

$S_2^2 = C_2^2 \times \sigma^2 = C_1^1 \times E = E \times E = E$

∴ $\boxed{S_2 = i}$

•

- $S_4 = 2$,

$$S_4^1 = C_4^1 \times \sigma^1 = S_4^1$$
$$S_4^2 = C_4^2 \times \sigma^2 = C_2^1 \times E = C_2^1$$
$$S_4^3 = C_4^3 \times \sigma^3 = C_4^3 \times \sigma = S_4^3$$
$$S_4^4 = C_4^4 \times \sigma^4 = C_1^1 \times E = E \times E = E$$

- S_6,

$\Downarrow$

2 rotations,

$$S_6^1 = C_6^1 \times \sigma^1 = S_6^1$$
$$S_6^2 = C_6^2 \times \sigma^2 = C_3^1 \times E = C_3^1$$
$$S_6^3 = C_6^3 \times \sigma^3 = C_2^1 \times \sigma = S_2^1 = S_2 = i$$
$$S_6^4 = C_6^4 \times \sigma^4 = C_3^2 \times E = C_3^2$$
$$S_6^6 = C_6^6 \times \sigma^6 = C_1^1 \times E = E \times E = E$$
$$S_6^5 = C_6^5 \times \sigma_6^5 = C_6^5 \times \sigma = S_6^5$$

- C_{3v} :

$E = 1$
$C_3 = 2 - 1 = 2$
$3\sigma_v = 3(2-1) = 3$

order = 6

- $PtCl_4^{2-}$:

E	1
C_4	4 − 1
$4C_2$	4(2−1)
$4\sigma_v$	4(2−1)
$1\sigma_h$	1(2−1)
S_4	2
i	2 − 1 = 1

order = 16

order :

	order
C_{nv}	$= 2n$
C_{nh}	$= 2n$
C_n	$= n$
D_{nh}	$= 4n$
D_{nd}	$= 4n$
C_1	$= 1$
C_s	$= 2$
C_i	$= 2$
D_n	$= 2n$

- $T_d = 24$ (order)

$= 1E + 8C_3 + 3C_2 + 6S_4 + 6\sigma_d$

no. of operation

- $O_h = 48$
- $I_h = 120$

$E = 1$

$4C_3 = 4(2) = 8$

$3C_2 = 3(1) = 3$

$3S_4 = 3(2) = 6$

$6\sigma_d = 6(1) = 6$

$\overline{\quad 24}$

Matrix representation of Symmetry elements :-

1E, 4C3, 3C2, 6S4, 6σd

- $E\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{vmatrix} 1x + 0y + 0.z \\ 0x + 1.y + 0.z \\ 0x + 0.y + 1.z \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}\begin{bmatrix} x \\ y \\ z \end{bmatrix}$

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

Character or trace = Sum of elements of main diagonal.

$$E = 1+1+1$$
$$= 3$$

Character of identity is called dimension.

$$\chi_E = 1 \longrightarrow 1D$$
$$2 \longrightarrow 2D$$
$$3 \longrightarrow 3D$$

- $C_2^z\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix} = \begin{bmatrix} -x + 0.y + 0.z \\ 0x + (-y) + 0.z \\ 0x + 0.y + 1z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} x \\ y \\ z \end{bmatrix}$

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

$$\chi_{C_2} = -1 - 1 + 1$$
$$= -1$$

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

$$\chi_{C_2^x} = 1 + (-1) + (-1)$$
$$= -1$$

$$\sigma_{xz} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix} = \begin{bmatrix} 1x + 0\cdot y + 0z \\ 0x - 1y + 0\cdot z \\ 0x + 0\cdot y + 1z \end{bmatrix}$$

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

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

$$\therefore \chi_{\sigma_{xz}} = 1 - 1 + 1 = 1$$

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

$$\chi_{yz} = -1 + (1) + 1$$
$$= 1$$

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

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

$$\chi_i = -1 + (-1) + (-1)$$
$$= -3$$

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

axis of Symmetry

$n = \frac{360}{2} = 180^\circ$

$C_2 = \begin{bmatrix} \cos 180^\circ & \sin 180^\circ & 0 \\ -\sin 180^\circ & \cos 180^\circ & 0 \\ 0 & 0 & 1 \end{bmatrix}$

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

$\chi_{C_2} = -1$

- $\boxed{\chi_{C_n} = 2\cos\theta + 1}$

sin | All
tan | cos

- $C_3 = 2\cos 120^\circ + 1$
$= 2(-\frac{1}{2}) + 1$
$= -1 + 1$
$= 0$

$\cos(90^\circ + 30^\circ)$
$= -\sin 30^\circ$
$= -$

$\chi_{C_4} = 2\cos 90^\circ + 1$
$= 0 + 1$

$\boxed{\chi_{C_4} = 1}$

- Improper AOS :-

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

$\boxed{\chi_{S_n} = 2\cos\theta - 1}$

$\therefore S_2 = \begin{bmatrix} \cos 180^\circ & \sin 180^\circ & 0 \\ -\sin 180^\circ & \cos 180^\circ & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = i$

● (x, y, z)

i) rotation along z axis

ii) reflection in yz plane

⇒ find matrix representation 2 step formation.

$$\Rightarrow \quad C_2^z \begin{bmatrix} \cancel{x} \\ \cancel{y} \\ \cancel{z} \end{bmatrix} = \begin{bmatrix} \cancel{-x} \\ \cancel{-y} \\ \cancel{z} \end{bmatrix}$$

$$\sigma_{yz} C_2^z (x, y, z)$$

$$\sigma_{yz} (-x, -y, z)$$

$$(x, -y, z)$$

$$= \sigma_{yz}$$

$$\sigma_{yz} = \begin{bmatrix} 1.x & +0.y & +0.z \\ 0 & -1.y & +0.z \\ 0 & +0.y & +1.y \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 1 & +1 \end{bmatrix}$$

● Representation of a group:-

→ Irreducible representation

⇒ (can't be reduced to representation of lower dimension).

Reducible representation

(which can be reduced to lower dimension)

How to derive reducible representation ?

⇒ Can be derived with respect to some basis

① 3N coordinate.

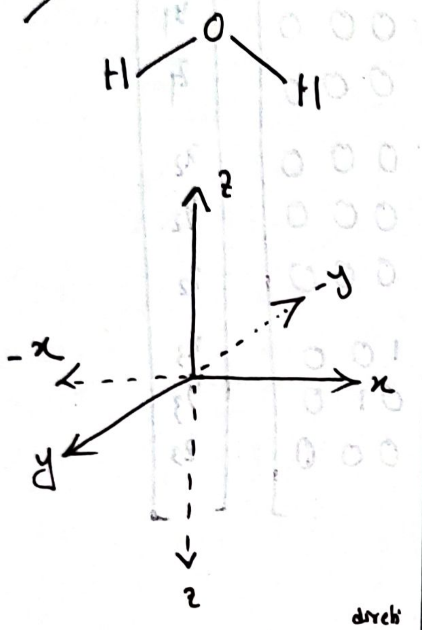
② (x, y, z) axis

③ bond angles.

④ bond length

⊙ Derivation of Reducible representation on the basis of (x, y, z) axis :-

⇒



Effect on	E	C_2^z	σ_{xz}	σ_{yz}
x axis	1	−1	1	−1
y axis	1	−1	−1	1
z axis	1	+1	1	1
	3	−1	1	1

⇒ no change in direction = +1

⇒ change in direction = −1

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
R·R	3	−1	1	1

Bethe notation

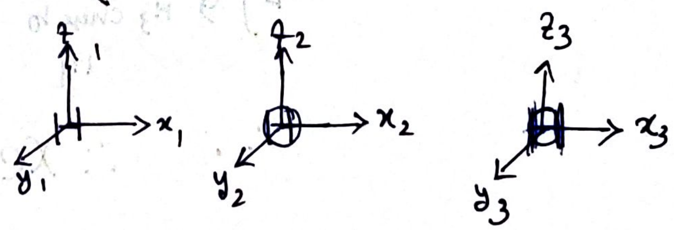
Dimension of R·R = 3

⊙ Derivation of R.R on the basis of 3N coordinates :-

⇒ N = no. of atoms.

3N = 3×3 = 9 = Coordinate System.

↳ (3 coordinate of each atom)



$$E\begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{array}{c} \begin{array}{ccccccccc} x_1 & y_1 & z_1 & x_2 & y_2 & z_2 & x_3 & y_3 & z_3 \end{array} \\ \begin{bmatrix} 1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{bmatrix} \end{array} \begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix}$$

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

$$E = 1+1+1+1+1+1+1+1+1$$
$$= 9$$

$$C_2^z\begin{bmatrix} x_1\\ y_1\\ z_1\\ x_2\\ y_2\\ z_2\\ x_3\\ y_3\\ z_3 \end{bmatrix} = \begin{bmatrix} -x_3\\ -y_3\\ z_3\\ -x_2\\ -y_2\\ z_2\\ -x_1\\ -y_1\\ z_1 \end{bmatrix}$$

} change place, H_1 change to H_3

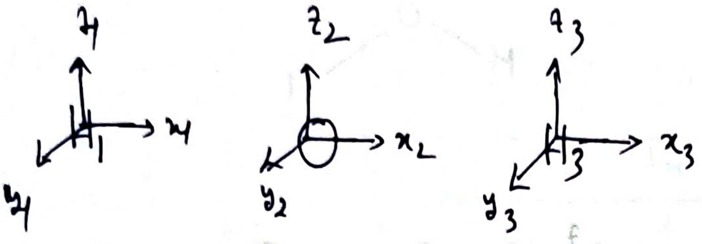
} oxygen does not change place

} H_3 change to H_1

$$= \begin{array}{c} \begin{array}{ccccccccc} x_1 & y_1 & z_1 & x_2 & y_2 & z_2 & x_3 & y_3 & z_3 \end{array} \\ \begin{bmatrix} 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&-1&0\\ 0&0&0&0&0&0&0&0&1\\ 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&-1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ -1&0&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0 \end{bmatrix} \end{array}$$

$$\therefore \chi_{C_2} = -1-1+1$$
$$= -1$$

⊙

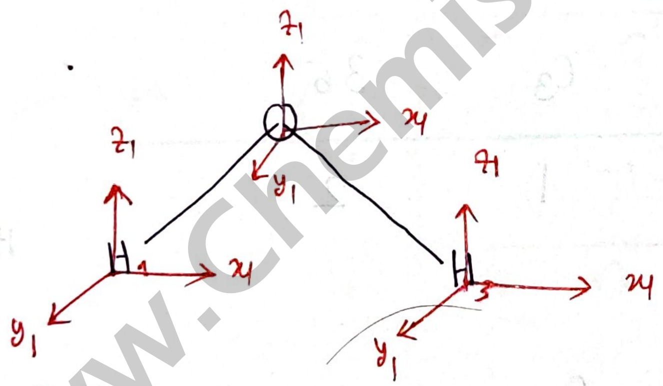


$$\sigma_{xz} = \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} x_1 \\ -y_1 \\ z_1 \\ x_2 \\ -y_2 \\ z_2 \\ x_3 \\ -y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{bmatrix}$$

$$\chi_{\sigma_{xz}} = 1 + \cancel{(-1)} + \cancel{1} + 1 + \cancel{(-1)} + \cancel{1} + 1 + \cancel{(-1)} + \cancel{1}$$

$$\boxed{\chi_{\sigma_{xz}} = 3}$$

⊙

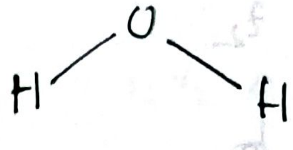


$$\sigma_{yz} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} -x_3 \\ y_3 \\ z_3 \\ -x_2 \\ y_2 \\ z_2 \\ -x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

$$\chi_{\sigma_{yz}} = 1$$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{R.R}$	9	−1	3	1

(3N coordinate)



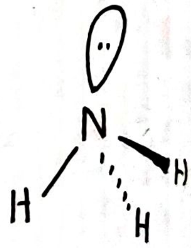
⊙ Short - method :-

H_2O

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
No. of un shifted atom	3	1	3	1
χ (w.r.t to xyz)	3	−1	1	1
R.R (3N coordinate)	9	−1	3	1

NH_3

C_{3v}	E	C_3	$3\sigma_v$
NUSA	4	1	2
χ (w.r.t to xyz)	3	0	1
R.R (3N)	12	0	2

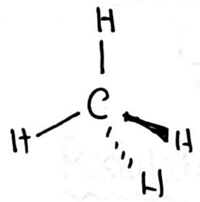


C_3: $2\cos\theta + 1 = 0$

⊙ CH_4 :-

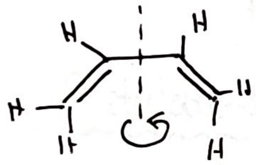
T_d	E	C_3	C_2	S_4	σ_d
NUSA	5	2	1	1	3
χ (w.r.t xyz)	3	0	-1	-1	1
	15	0	-1	-1	3

rememb



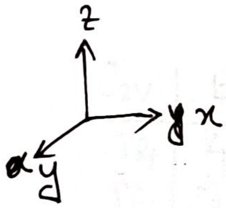
$\Gamma_{R.R}$ (3N coordinate system).

⊙



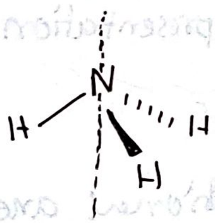
C_{2v}

rememb



C_{2v}	E	C_2^z	σ_{yz}	σ_{xz}
NUSA	10	0	0	10
χ	3	-1	1	1
$\Gamma_{R.R}$ (3N)	30	0	0	10

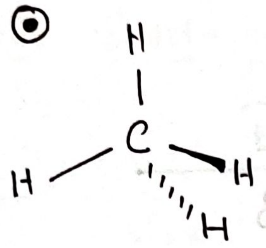
⊙ Derivation w.r.t bond vectors :-



for all molecules ⟹

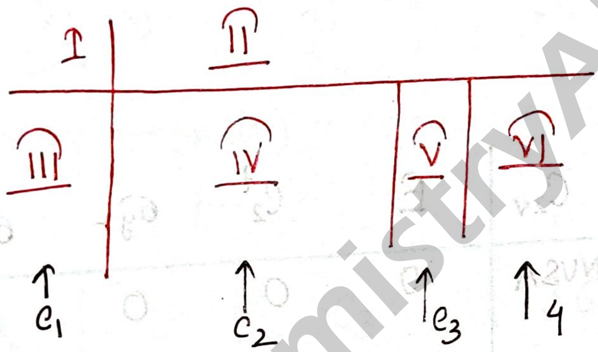
C_{3v}	E	C_3	$3\sigma_v$
NUSA (bond vector)	4	1	2
Contribution for bond vectors	1	1	1
$\Gamma_{R.R}$ (bond vector)	4	1	2

(1 for all molecu)



T_d	E	C_3	C_2	S_4	σ_d
NUSA bond vector	4	1	0	0	2
χ	1	1	1	1	1
R.R (basis of bond vector)	4	1	0	0	2

Character table :



part-1 :- Schoenflies notation of point gr.
e.g : for H_2O . C_{2v}

Part-II :- contains symmetry elements of the point gr along with their classes
C_{2v} : $E + C_2 + \sigma_{xz} + \sigma_{yz}$

part III :- Mulliken notation for irreducible representation.

part-IV :- characters of I.R.

part-V :- translational properties of translational axes (x, y, z) and rotational axes (R_x, R_y, R_z)

Part: VI :- transformation properties of quadratic functions of x, y, z $(x^2, y^2, z^2, xy, yz, xz, x^2+y^2 \ldots + \ldots)$

C_{2v}	E C_2 σ_{xz} σ_{yz}		
IR_1 IR_2 IR_3 ⋮	Character of I.R	x, y, z (R_x, R_y, R_z)	quadratic functions.

Part-IV of Character table:-

↳ By Grater orthogonality theorem (GOT).

Postulate 1 :-

No. of IRs = no. of classes of the gr.

for H_2O molecules class = 4

Postulate-2 :-

Sum of Square of dimantion of all IRs = order of gr.

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
IR_1	k_1	l_1	m_1	n_1
IR_2	k_2	l_2	m_2	n_2
IR_3	k_3	l_3	m_3	n_3
IR_4	k_4	l_4	m_4	n_4

$k_1^2+k_2^2+k_3^2+k_4^2 = 4$

Dimention Can't be -ve or zero.

$k_1 = k_2 = k_3 = k_4 = 1$

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

postulate-3 :-

Sum of Square of characters of any IR = order of the gr.

$IR_1 : k_1^2+l_1^2+m_1^2+n_1^2 = 4 \quad \therefore \quad 1^2+l_1^2+m_1^2+n_1^2 = 4$

$IR_2 : k_2^2+l_2^2+m_2^2+n_2^2 = 4 \qquad 1^2+1^2+1^2+1^2 = 4$

$IR_3 : k_3^2+l_3^2+m_3^2+n_3^2 = 4$

$IR_4 : k_4^2+l_4^2+m_4^2+n_4^2 = 4$

Postulate ~~of~~ 4 :-

All the IRs are orthogonal to each other.
(Any two IRs of a group are orthogonal to each other).

$IR_1 \times IR_2 = 0$

$IR_2 \times IR_3 = 0$

$IR_3 \times IR_4 = 0$

⋮

$IR_1 \times IR_2 = 0$

$1\times1 + 1\times l_2 + 1\times m_2 + 1\times n_2 = 0$

$1 + l_2 + m_2 + n_2 = 0$

let, $l_2 = 1$

$m_2 = n_2 = -1$

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

$IR_1 \times IR_3 = 0$

$1\times1 + 1\times l_3 + 1\times m_3 + 1\times n_3 = 0$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
IR_1	1	1	1	1
IR_2	1	1	-1	-1
IR_3	1	-1	-1	1
IR_4	1	-1	1	-1

Part-III :-

Mulliken notation of IR

Rule-1 :-

if IR is 1D → A (if IR is Symmetric to principle axis)
→ B (if IR is assymetric to principle axis)

IR → 1D → (+P) → Symmetric to P.A
→ (−P) → AntiSymmetric to P.A

if IR is 2D , 3D
↓ ↓
E T

rule-2 :- Subscript 1 or 2 :

Symmetric wrt Subsidiary axis (+) ⟶ 1

Asymmetric w.r.t Subsidary axis (−) ⟶ 2

if Subsidiary axis is absent, go as per molecule plane
Molecular plane (always passes through all the atoms of a molecule)

Molecular plane (+, Symmetric) $\longrightarrow$ 1
(−, Asymmetric) $\longrightarrow$ 2

Rule: 3 :- for Subscript g or u :-
if IR is Symmetric w.r.t inversion center $\Rightarrow$ g
IR is Asymmetric w.r.t inversion center $\Rightarrow$ u

Rule: 4 :- for Superscript ′ and ″
if IR is Symmetric w.r.t σ_h ($\perp$ plane to P.A) = ′
if IR is Asymmetric w.r.t = σ_h = ″

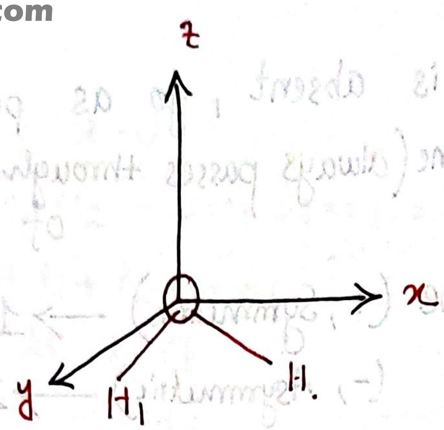
here not molecular plane, only σ_h,

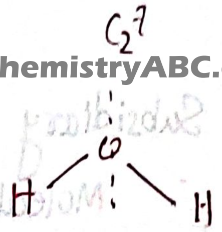
Example :-

	E	C_n	nC_2	i	σ_h
A''_{2u}	1	1	−1	−1	−1

Part - V and VI :-

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	Z	X^2, Y^2, Z^2
A_2	1	1	−1	−1	R_z	XY
B_1	1	−1	1	−1	X, R_y	XZ
B_2	1	−1	−1	1	Y, R_x	YZ





Z

	E	C_2^z	σ_{xz}	σ
Z axis	1	1	1	
X axis	1	-1	1	-
Y axis	1	-1	-1	1

E, C_2, σ_{xz}, σ_{yz} - এই গুলো operate করলে, x, y, z axis - এর কী change করছে, তার মেমোরি হচ্ছে।

(X.X করলে 1, 1, 1, 1 আসবে তাই, X^2 লেখা হচ্ছে)

C_{2v}						
	1	1	1	1	Z	X^2, Y^2, Z^2
	1	1	-1	-1	R_z	XY
	1	-1	1	-1	X, R_Y	XZ
	1	-1	-1	1	Y, R_X	YZ

$Z = (1, 1, 1, 1)$

$X = (1, -1, 1, -1)$

$Y = (1, -1, -1, 1)$

$X = 1 \quad -1 \quad 1 \quad -1$

$X = 1 \quad -1 \quad 1 \quad -1$

$1 \quad 1 \quad 1 \quad 1$

C_{3v} Character Table :

C_{3v}	E	$2C_3$	$3\sigma_v$
IR_1	K_1	l_1	m_1
IR_2	K_2	l_2	m_2
IR_3	K_3	l_3	m_3

①

② $K_1^2 + K_2^2 + K_3^2 = 6$

$1^2 + 1^2 + 2$

(3) $1^2 + 2l_1^2 + 3m_1^2 = 6$

(don't forget these Coefficient)

$1^2 + 2(1)^2 + 3(1)^2 = 6$

$l_1 = m_1 = 1$

(4) $IR_1 \times IR_2 = 0$

$\cancel{1 \times 1 + 2 \times 1 \times l_2 + 3 \times 1 \times m_2 = 0}$

$1 \times 1 + (2) \times 1 \times l_2 + (3) \times 1 \times m_2 = 0$

(don't forget these Coefficiens)

$1 + 2l_2 + 3m_2 = 0$

$l_2 = 1$

$m_2 = -1$

$1 + 2l_2 + 3m_2 = 0$

Similarly, $IR_1 \times IR_3 = 0$

$1 \times 2 + 2 \times 1 \times l_3 + 3 \times 1 \times m_3 = 0$

$2 + 2l_3 + 3m_3 = 0$

$l_3 = -1$

$m_3 = 0$

C_{3v}	E	$2C_3$	$3\sigma_v$
IR_1	1	1	1
IR_2	1	1	-1
IR_3	2	-1	0

remain

Class 6(3):

Reduction of Reducible representation into irreversible representation:

$$\boxed{\eta_{I.R} = \frac{1}{h} \sum x_i y_i z_i}$$

h = order

X = character of reducible representation.

Y = character of I.R

Z = coefficient of symmetry elements in character table.

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
$\Gamma_{R.R}$	9	−1	3	1

→ basis of 3N coordinates.

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{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

$$\therefore \eta_{A_1} = \frac{1}{4}\left(X_1Y_1Z_1 + X_2Y_2Z_2 + X_3Y_3Z_3 + X_4Y_4Z_4\right)$$

$$= \frac{1}{4}\left(9\times1\times1 + (-1)(1)(1) + 3\times(1)(1) + 1(1)(1)\right)$$

$$= 3$$

$$\therefore \eta_{A_2} = \frac{1}{4}\left(9\times1\times1 + (-1)1\times(1) + 3(-1)(1) + 1(-1)1\right)$$

$$= 1$$

$$\therefore \eta_{B_1} = \frac{1}{4}\left(9\times1\times1 + (-1)(-1)1 + 3(1)(1) + (1)(-1)(1)\right)$$
$$= 3$$

$$\therefore \eta_{B_2} = \frac{1}{4}\left(9\times1\times1 + (-1)(-1)\times1 + 3(-1)(1) + 1(1)(1)\right)$$
$$= 2$$

$$\therefore \boxed{R.R = \underbrace{3A_1 + A_2 + 3B_1 + 2B_2}_{D.R}}$$

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
A_1	3	3	3	3
A_2	1	1	-1	-1
B_1	3	-3	3	-3
B_2	2	-2	-2	2
	9	-1	3	1

⊙ Reduced C_{3v} point group:-

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

$D.R = \cancel{6}\ \cancel{30}\ 6 \quad 3 \quad 0$

$$\therefore \eta_{A_1} = \frac{1}{6}\left[6\times1\times1 + 3(1)(2) + 0(1)(3)\right]$$
$$= 2$$

$$\eta_{A_2} = \frac{1}{6}\left[6\times1\times1 + 3\times(1)(2) + 0(-1)(3)\right]$$
$$= 2$$

$$\eta_{E} = \frac{1}{6}\left[6\times(2)\times1 + 3(-1)\times2 + 0(0)3\right]$$
$$= 1$$

$$\therefore R.R = 2\eta_{A_1} + 2\eta_{A_2} + \eta_{E}$$

Applications of group theory :-

① IR of IR | Raman active modes and normal modes of vibration

⇒ B N coordinate system (As a Basis)

Based as used to derive reducible representation.

- parallel and perpendicular vibration :-

parallel vibration : Symmetric to principle axis.

perpendicular vibration ; asymmetric to principle axis.

- out of plane : Asymmetric w.r.t σ_h

in plane vibration ; Symmetric w.r.t σ_h

- Consider the H_2O molecule and find its normal modes of vibration and classify them. IR, active, Raman Active, IR and Rama both active, parallel and perpendicular active mode of vibration.

⇒

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy,
B_1	1	-1	1	-1	x, R_y	xz,
B_2	1	-1	-1	1	y, R_x	yz

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
R.R.	9	-1	3	1

① Reduce R·R into R·R :.

$$3A_1 + A_2 + 3B_1 + 2B_2$$

⊙ Translational modes: (x, y, z axis)

$\therefore (A_1 + B_1 + B_2)$

⊙ Rotational modes (R_x, R_y, R_z axis).

$(A_2 + B_1 + B_2)$

⊙ vibrational modes = (Total modes) − (T + R)

$= 3A_1 + A_2 + 3B_1 + 2B_2$
$- A_1 - B_1 - B_2$
$- A_2 - B_1 - B_2$

$= 2A_1 + B_1$

⊙ vibrational modes : $2A_1 + B_1$:-

IR active modes of vibration (transformation according x, y, z axis)

Raman Active modes of vibration (quadratic functions, $x^2, y^2, z^2, xy, x^2+y^2$)

IR and Raman Both active.

@mandal 12.02.2021

$\therefore$ IR active :- $2A_1 + B_1$

Raman active :- $2A_1 + B_1$

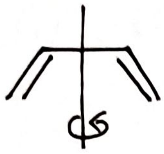
IR active and Raman active : (Same Common (υ 2(∞ ∞))

$2A_1 + B_1$

⊙ parallel vibration :- (+P) $= 2A_1$

perpendicular vibration: (−P) $= B_1$

⊙ cis -1,3- butadiene. :



C_{2v} point gr.

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

$\Gamma_{R \cdot R} = 30 \quad 0 \quad 10 \quad 0$

$\eta_{A_1} = \frac{1}{4}\left(30 \times 1 \times 1 + 10(1)(1)\right) = 10$

$\eta_{A_2} = \frac{1}{4}\left(30 \times 1 \times 1 + 10(-1)(1)\right) = 5$

$\eta_{B_1} = \frac{1}{4}\left(30 \times 1 \times 1 + 10(1)(1)\right) = 10$

$\eta_{B_2} = \frac{1}{4}\left(30 \times 1 \times 1 + (10)(-1)1\right) = 5$

$R \cdot R = 10A_1 + 5A_2 + 10B_1 + 5B_2$
Total modes.

∴ Translational modes : $A_1 + B_1 + B_2$
rotational modes : $A_2 + B_1 + B_2$

∴ vibrational modes :- $10A_1 + 5A_2 + 10B_1 + 5B_2 - A_1 - A_2 - 2B_1 - 2B_2$

$\Rightarrow \underline{9A_1 + 4A_2 + 8B_1 + 3B_2}$

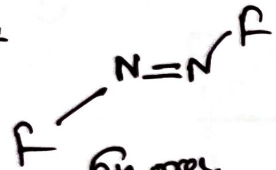
∴ IR active :- $9A_1 + 8B_1 + 3B_2$
Raman active : $9A_1 + 4A_2 + 8B_1 + 3B_2$
IR active and Raman active : $9A_1 + 8B_1 + 3B_2$

⊙ ∥ vibration : $9A_1 + 4B_2\, 4A_2$
⊥ vibration : $8B_1 + 3B_2$

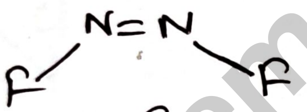
σ_v molecular plane.

	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

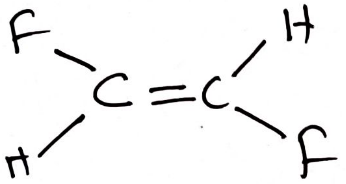
*



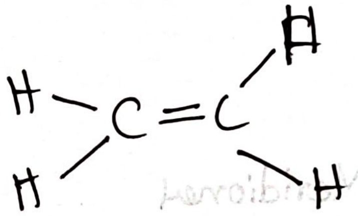
σ_h pres



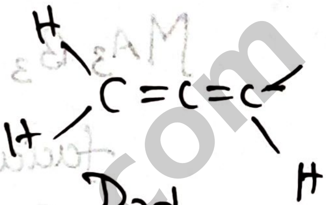
σ_v present.



C_{2h}



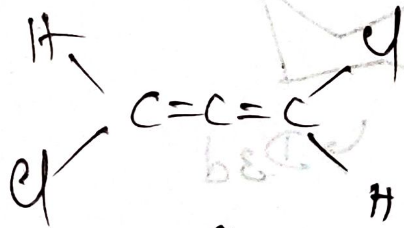
D_{2h}.



D_{2d}.

B_2H_6 : D_{2h}.

remen



C_2