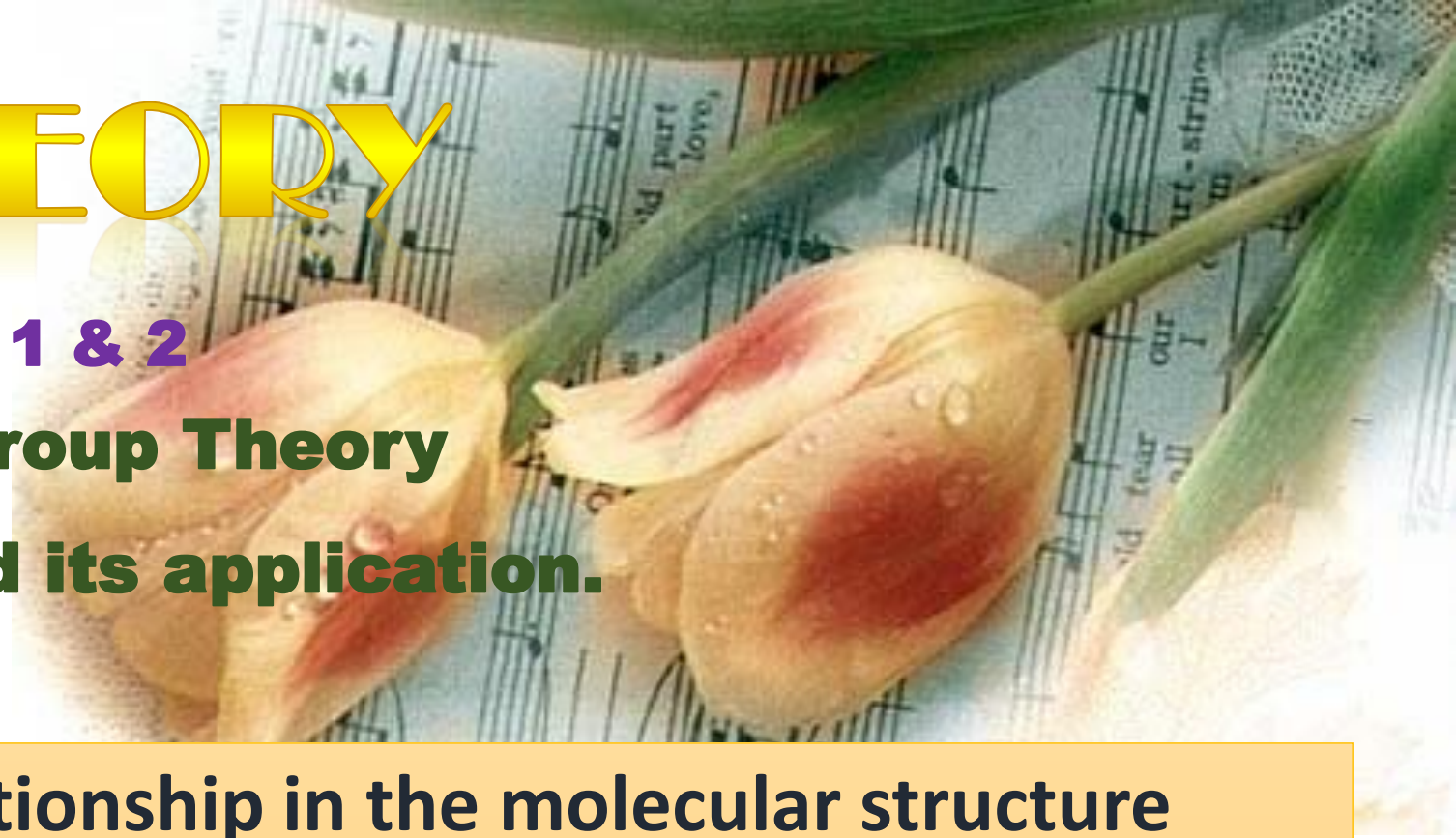
GROUP THEORY



Paper: CHNN 404 Unit 1 & 2

Unit 1 : Symmetry and Group Theory

Unit 2 : Group theory and its application.

The symmetry relationship in the molecular structure understand by the basis for mathematical theory is called

Group Theory. = Algebra of Geometry

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Course: CHNN – 404 (Core compulsory)

Symmetry, Group Theory & Spectroscopy

UNIT-01 Symmetry & Group Theory 16 Hrs

- Outline of symmetry elements and symmetry operation
- Schonflies method for determining the point group of the molecules.
- Multiplication of symmetry operation and multiplication table for C_2v, C_3v, C_{2h}.
- Equivalent symmetry elements, similarity transformation and conjugacy of symmetry operation within the point group
- Matrics: Characteristics, types of matrices(common & special), and Algebra of matrices(Particularly Multiplication)
  Use of Matrix and matrix representation of symmetry Elements and Their point groups(using various Vectors: position vector, translation vector, base vector)
- Γ_{3N} Representation :For H_2O,NH_3,BF_3,$PtCl_4$,PCl_5,SF_6,$POCl_3$,CCl_4,Cis &Trans N_2F_4, $XeOF_4$
- Reducible and Irreducible Representation& charactor Table
- Characteristics of Irreducible Representation: The great orthogonality theorem
- Construction of Character Table For C_3v using properties of irreducible Representation
- Direct product and its utility.

UNIT 02 : Group theory and its applications **16 Hrs**

- Character table and their presentation
- Reduction formula for reducible representation of any matrix presentation of particular point groups
- Application of symmetry to hybrid orbital, molecular orbital
- Hybridisation schemes for sigma-orbitals (for AB_3 : planar triangle, trigonal pyramidal e.g. BF_3 & NH_3 , AB_4 : tetrahedral and square planar molecules e.g. CH_4 & $[PtCl_4]^{-2}$, AB_5 : trigonal bipyramidal & square pyramidal e.g. PCl_5 & IF_5 and AB_6 : octahedral e.g. SF_6 and pi-orbital for AB_3 (e.g. BF_3) AB_6 (e.g. SF_6)
- Application of symmetry to molecular vibrations, interpretation of IR & Raman activity. (spectral data)

MATHEMATICAL REQUIREMENTS FOR A GROUP THEORY

The S.E. of molecule Collect correctly by physical inspection but it is necessary to check whether they from complete set.

A complete set of S.E. should satisfy the following four criteria which is define a mathematical group.

1. **Closure rule**
2. **Associative Rule**
3. **Identity rule**
4. **Inverse rule**

There are four rules are required for mathematical group.

1. Closure rule.:

The product of any two element and the square of any element in a group is also an element of in the same group.

- **A.B = C or A^2 = C; where A, B and C are same group elements.**

- **A.B = C and B.A = C** , then A and B are commute.
- **A.B = C and B.A = D** , then A and B are not commute.

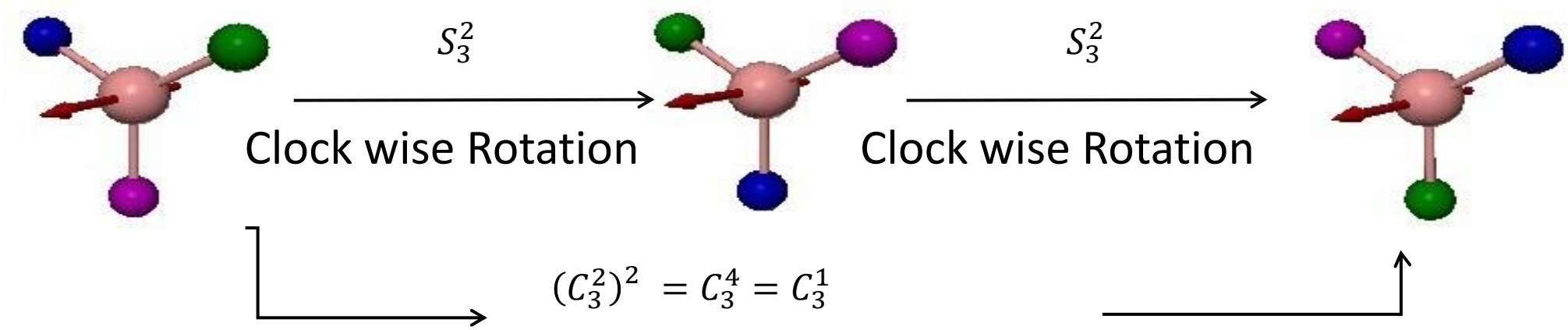
- All element of any group are commute with each other, then such a group is called **" Abelian or Cyclic Group".**

- **Abelian or Cyclic Groups: C_2; S_2; C_2h; C_2v; D_2; D_2h**

Square of element

Element	Square of element
σ	$\sigma^2 = E$
i	$i^2 = E$
C_n^m	$(C_n^m)^2 = C_n^{2m}$
S_n^m	$(S_n^m)^2 = S_n^{2m} = C_n^{2m} \cdot \sigma^{2m} = C_n^{2m}$

$(S_3^2)^2=(C_3^4 = C_3^1)$



2. Associative Rule.: *All the symmetry elements must obey the associative law of multiplication.*

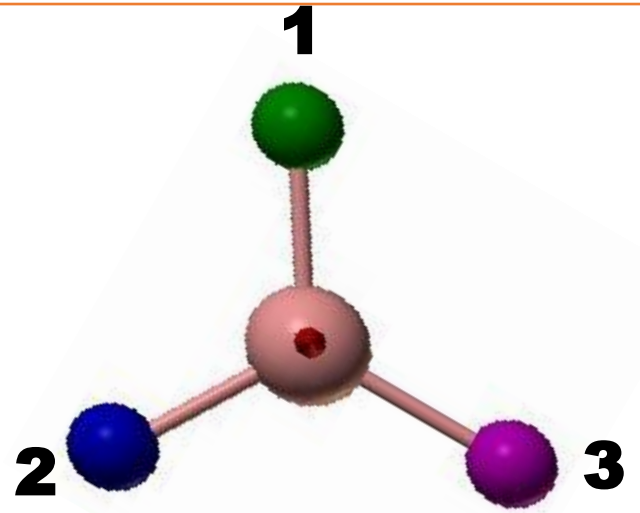
- (AB)C=A(BC) OR A(CB)D =(AB)(CD);
- where A, B and C and D are same group elements.

In NH_3 six elements are present, they are obey the associative law.

$$C_{3v} \Rightarrow C_3^1 \cdot C_3^2 \cdot \sigma_v^1 \cdot \sigma_v^2 \cdot \sigma_v^3$$

Associative law ; (AB)C=A(BC) [Antilock wise rotation]

$$(C_3^1 \cdot C_3^2)\sigma v^1 = C_3^1(C_3^2 \cdot \sigma v^1)$$
$$(C_3^3)\sigma v^1 = C_3^1(\sigma v^2)$$
$$\sigma v^1 = \sigma v^1$$



3. Identity rule.:

There should be atleast one E element in the group which when combined with all other elements must leave them unchanged.

- A.E=A, where A is any element of any group.

4. Inverse rule.:

Each element has a reciprocal (inverse), which is also an element of the same group. And the combination of element and the reciprocal of such element is always E.

- Inverse of Element A is A^{-1} =B where A and B are same group elements.
- **Hear A. A^{-1} = E**

S.E.	n	m	Inverse of S.E.	Multiplication S.E. × Inverse of S.E. = E
σ			σ	$\sigma \cdot \sigma = E$
i			i	$i \cdot i = E$
C_n^m	Even or Odd	Even or Odd	C_n^{n-m}	$C_n^m \cdot C_n^{n-m} = C_n^{m+n-m} = C_n^n = E$
S_n^m	Even	Even or Odd	S_n^{n-m}	$S_n^m \cdot S_n^{n-m} = S_n^{m+n-m} = S_n^n = E$
	Odd	Even	C_n^{n-m}	$S_n^m \cdot C_n^{n-m} = C_n^m \cdot \sigma^m C_n^{n-m} = C_n^{m+n-m}\sigma^m = E$
	Odd	Odd	S_n^{2n-m}	$S_n^m \cdot S_n^{2n-m} = S_n^{m+2n-m} = S_n^{2n} = C_n^{2n}\sigma^{2n} = E$

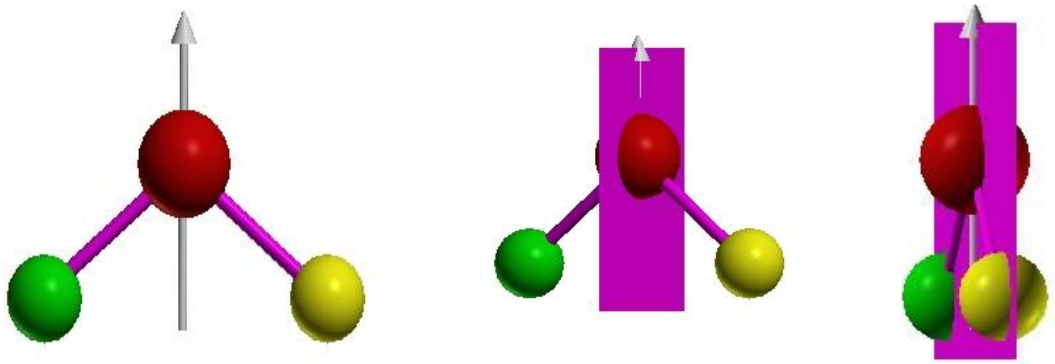
Group Multiplication Table (GMT)

All the algebraic properties of a group can be complied in the from of table called GMT.

Condition:

1. Every ele. of the group occurs once and only once in any raw or column of GMT.
2. First a raw a column consisting of the all ele. of group, E must always be first in raw and column.
3. The order of multiplication must be by either row into column or column in to raw.
4. Multiplication for non cyclic group [Column *raw (anti clock wise)].
5. The product ele. at the cross junction in the body of table.

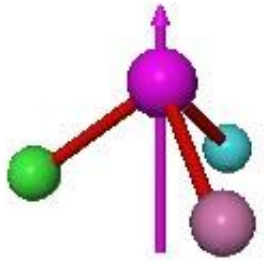
GMT for C_{2v}; C_{3v} and C_{2h} Point Group.

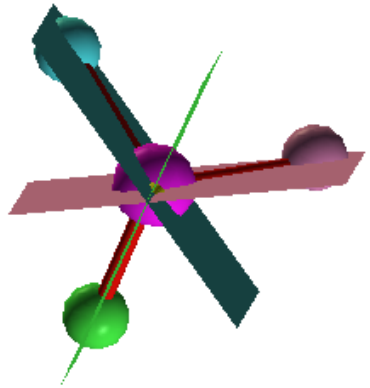


Group Multiplication Table for C_{2v}

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

GMT for C_{2v}; C_{3v} and C_{2h} Point Group.

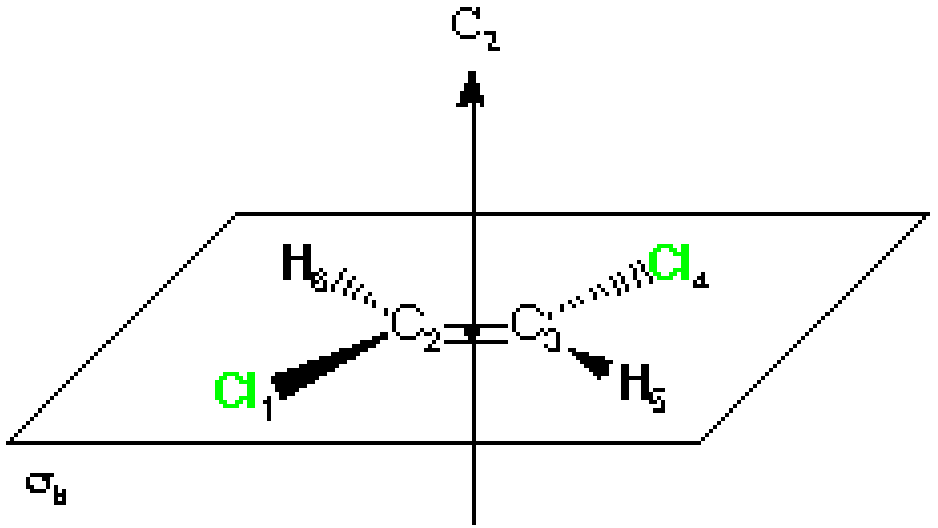




C_3v	**E**	**C^1_3**	**C^2_3**	**σv1**	**σv2**	**σv3**
E	E	C^1_3	C^2_3	σv1	σv2	σv3
C^1_3	C^1_3	C^2_3	E	σv3	σv1	σv2
C^2_3	C^2_3	E	C^1_3	σv2	σv3	σv1
σv1	σv1	σv2	σv3	E	C^1_3	C^2_3
σv2	σv2	σv3	σv1	C^2_3	E	C^1_3
σv3	σv3	σv1	σv2	C^1_3	C^2_3	E

GMT for C_{2v}; C_{3v} and C_{2h} Point Group.

C_{2h}	E	$C_{2(z)}$	σ_{xy}	i
E	E	$C_{2(z)}$	σ_{xy}	i
$C_{2(z)}$	$C_{2(z)}$	E	i	σ_{xy}
σ_{xy}	σ_{xy}	i	E	$C_{2(z)}$
i	i	σ_{xy}	$C_{2(z)}$	E



Isomorphic Group :

There are two or more groups have same GMT (No of Element , No of Column and Raw are Same) and algebraic structure are said to be isomorphic group.

$C_{2h} \approx C_{2v} \approx D_2$

$C_n \approx S_n$ — n-even

$C_{nv} \approx D_n$

$D_{2n} \approx D_{nd}$ — n-any value (even or odd)

$D_{nh} \approx D_{nd}$

$C_{nh} \approx C_{2n}$ — n-Odd

$C_2 \approx C_s \approx C_i$

$D_2 \approx C_{2h}$

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

D_2	E	$C_{2(z)}$	$C_{2(x)}$	$C_{2(y)}$
E	E	$C_{2(z)}$	$C_{2(x)}$	$C_{2(y)}$
$C_{2(z)}$	$C_{2(z)}$	E	$C_{2(y)}$	$C_{2(x)}$
$C_{2(x)}$	$C_{2(x)}$	$C_{2(y)}$	E	$C_{2(z)}$
$C_{2(y)}$	$C_{2(y)}$	$C_{2(x)}$	$C_{2(z)}$	E

C_{2h}	E	$C_{2(z)}$	σ_{xy}	i
E	E	$C_{2(z)}$	σ_{xy}	i
$C_{2(z)}$	$C_{2(z)}$	E	i	σ_{xy}
σ_{xy}	σ_{xy}	i	E	$C_{2(z)}$
i	i	σ_{xy}	$C_{2(z)}$	E

Group Generating element.

In the entire list of symmetry elements of P.G., a small No. of ele. Will be very important to define the P.G., are Called 'Group Generating elements'

For example, consider D3h point group which is contains the following 12 elements.[BF_3]

$$D_3h: E, C_3^1, C_3^2, 3C_2^1, 3\sigma_v, \sigma_h, S_3^1, S_3^5$$

The group generating elements are only three elements.

$$C_3^1, 3C_2^1, \sigma_h$$

Point Group	Group generating elements
C_1	C_1
C_s	σ
C_i	i
C_n	C_n^1
C_{nv}	C_n^1, σ_v
C_{nh}	C_n^1, σ_h
D_n	C_n^1, C_2^*
D_{nd}	C_n^1, C_2^*, σ_d
D_{nh}	C_n^1, C_2^*, σ_h
S_n (n = even)	S_n^1
$C_{\infty v}$	C_∞, σ_v
$D_{\infty h}$	$C_\infty, C_2^*, \sigma_h$

SUBGROUPS

There are always smaller groups in larger groups,
Subgroup is a group of symmetry elements of main group.

They are two types-
(i) Trivial subgroup, in which there is only one element E (h =1)
(ii) Non-trivial type of subgroups, in which element E is invariably present (h>=2.)

- A subgroup, which is a part of the group, satisfies all the rules of a full group.
- If the order of the subgroup is '*g*', and that of the full group is '*h*'.

  Then, $h/g=k$ where, K is integral.

Point Group	Sub groups	Symmetric Elements	m
C_2v	E, C_2, $2\sigma_v$		
	C_s	E, σ_v	2
	C_2	E, C_2	2
C_3v	E, C_3^1, C_3^2, $3\sigma_v$		
	C_s	E, σ_v	2
	C_3	E, C_3^1, C_3^2	3
C_4v	E, C_4^1, C_4^2, C_4^3, $4\sigma_v$		
	C_s	E, σ_v	2
	C_2	E, C_4^2	2
	C_4	E, C_4^1, C_4^2, C_4^3,	4
	C_2v	E, C_4^2, $2\sigma_v$	4

All the subgroups satisfies all the rules of a full group.
All the rules are write in GMT.

However, subgroup differ from their full group in one aspect.

The elements of a full group need not necessarily commute with each other, but the elements of a sub group do necessarily commute. E.g. all sub groups are always Cyclic or Abelian group.

(ii) Consider D_{3h} point group as a second example:

It has the following elements:

$$D_{3h} \rightarrow E, C_3^1, C_3^2, C_2, C_2', C_2'', \sigma_v, \sigma_v', \sigma_v'', \sigma_h, S_3^1, S_3^5$$

The subgroups can be written as

$C_1 \rightarrow E$ (cyclic) (g = 1)

$C_2 \rightarrow E, C_2$ (cyclic) (g = 2)

$C_2' \rightarrow E, C_2'$ (cyclic) (g = 2)

$C_2'' \rightarrow E, C_2''$ (cyclic) (g = 2)

$C_s^h \rightarrow E, \sigma_h$ (cyclic) (g = 2)

$C_s \rightarrow E, \sigma_v$ (cyclic) (g = 2)

$C_s' \rightarrow E, \sigma_v'$ (cyclic) (g = 2)

$C_s'' \rightarrow E, \sigma_v''$ (cyclic) (g = 2)

$C_3 \rightarrow E, C_3^1, C_3^2$ (cyclic) (g = 3)

$C_{3h} \rightarrow E, C_3^1, C_3^2, \sigma_h, S_3^1, S_3^5$ (g = 6)

$C_{3v} \rightarrow E, C_3^1, C_3^2, \sigma_v, \sigma_v', \sigma_v''$ (g = 6)

$D_3 \rightarrow E, C_3^1, C_3^2, C_2, C_2', C_2''$ (g = 6)

Classes of group.

How it is possible to select sets of S.E. constituting of group. There is way to sorting S.E. of a group in to class.

A set of elements which are conjugate to one another is called class of group.

What is conjugation ?

If A, B and X are same group elements. Than,

$$X^{-1} \times A \times X = B \qquad \text{OR} \qquad X^{-1} \times B \times X = A,$$

so that A and B are conjugated to one another.

Types of Conjugation:

1. Every ele. is conjugate with itself. [$X^{-1} \times A \times X=A$] is called Self conjugation.

2. If A and B conjugate with one another.[$X^{-1} \times A \times X=B$ OR $X^{-1} \times B \times X=A$,] is called Mutual conjugation

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

   $X^{-1} \times A \times X=B$ OR $X^{-1} \times A \times X=C$, $X^{-1} \times B \times X=C$ OR $X^{-1} \times C \times X=B$, is called Associative conjugation.

An example of C3V group, and work out the similarity transform of each the six ele. with every other.

$$C_3v: E \cdot C_3^1 \cdot C_3^2 \cdot \sigma_v \cdot \sigma_v' \cdot \sigma_v''$$

E	E	**E**	**=E**
C^2_3	E	**C^1_3**	**=E**
C^1_3	E	**C^2_3**	**=E**
σv	E	**σv**	**=E**
σv'	E	**σv'**	**=E**
σv''	E	**σv''**	**=E**

Self conjugation

E	**C^1_3**	**E**	**= C^1_3**
C^2_3	**C^1_3**	**C^1_3**	**= C^1_3**
C^1_3	**C^1_3**	**C^2_3**	**= C^1_3**
σv	**C^1_3**	**σv**	**= C^2_3**
σv'	**C^1_3**	**σv'**	**= C^2_3**
σv''	**C^1_3**	**σv''**	**= C^2_3**

E	**C^2_3**	**E**	**= C^2_3**
C^2_3	**C^2_3**	**C^1_3**	**= C^2_3**
C^1_3	**C^2_3**	**C^2_3**	**= C^2_3**
σv	**C^2_3**	**σv**	**= C^1_3**
σv'	**C^2_3**	**σv'**	**= C^1_3**
σv''	**C^2_3**	**σv''**	**= C^1_3**

Mutual conjugation

$C_3v: E \cdot C_3^1 \cdot C_3^2 \cdot \sigma_v \cdot \sigma_v' \cdot \sigma_v''$

E	σv	E	= σv
C^2_3	σv	C^1_3	=σv’
C^1_3	σv	C^2_3	= σv”
σv	σv	σv	= σv
σv’	σv	σv’	=σv”
σv”	σv	σv”	= σv’

E	σv’	E	= σv’
C^2_3	σv’	C^1_3	=σv
C^1_3	σv’	C^2_3	= σv”
σv	σv’	σv	= σv”
σv’	σv’	σv’	=σv’
σv”	σv’	σv”	= σv

E	σv”	E	= σv”
C^2_3	σv”	C^1_3	=σv’
C^1_3	σv”	C^2_3	= σv
σv	σv”	σv	= σv’
σv’	σv”	σv’	=σv
σv”	σv”	σv”	= σv”

Mutual conjugation

There are three class of C_{3v} P.G. $C_3v: E \cdot 2C_3 \cdot 3\sigma_v$

An important note on Classes:

✓ **In all Abelian P.G. each element is in a class by itself., e.g. the number of element (order of group=h) is equal to the number of Class.**

Abelian or Cyclic Groups: C_2; S_2; C_2h; C_2v; D_2; D_2h.

✓ **In non Ablelian group the number of classes is always less than the order of group=h.**

Sr. No.	Point Group	Symmetric Elements	h	k
1	C_1	E	1	1
2	Cs	E, σ	2	2
3	Ci	E, i	2	2
4	C_2v	E, C_2, $2\sigma_v$	4	4
5	C_3v	E, C_3^1, C_3^2, $3\sigma_v$	6	3
6	C_4v	E, C_4^1, C_4^2, C_4^3, $4\sigma_v$	8	5
7	C_5v	E, C_5^1, C_5^2, C_5^3, C_5^4, $5\sigma_v$	10	4
8	C_6v	E, C_6^1, C_6^2, C_6^3, C_6^4, C_6^5, $6\sigma_v$	12	6
9	C_2h	E, C_2, σ_h, i	4	4
10	C_3h	E, C_3^1, C_3^2, σ_h, S_3^1, S_3^5	6	6
11	C_4h	E, C_4^1, C_4^2, C_4^3, σ_h, S_4^1, S_4^3, i	8	8
12	C_5h	E, C_5^1, C_5^2, C_5^3, C_5^4, σ_h, S_5^1, S_5^3, S_5^7, S_5^9	10	10

Some hints on classes:

(i) E is always in a class by itself, i. e., E is transformed into itself by all the elements of the group.

(ii) Inversion element, i, is in a class by itself.

(iii) All C_n^m axes are in a class.

(iv) Similar C_2s are in one class.

(v) S_n^m axes like C_n^m are in a class. If there are two or many such types, they are placed in as many classes.

(vi) Similar vertical planes (σ_v) and similar dihedral planes (σ_d) are in separate classes.

(vii) Horizontal plane is a special plane (σ_h) and is always placed in a different class from other planes.

C_{2v} (2*mm*)	E	C_2	$\sigma_v(xz)$	σ'_v (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_{3v} (3*m*)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, 2xy)(xz, yz)$

C_{4v} (4*mm*)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	R_z	
E_1	2	2 cos 72°	2 cos 144°	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	2 cos 144°	2 cos 72°	0		$(x^2 - y^2, 2xy)$

C_{6v} (6*mm*)	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1		

Matrix Methods in Symmetry and Group Theory

Type of Matrix: (No of Raw × No of Column) =($m \times n$)

1. Rectangular matrix

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{bmatrix} (2 \times 3)$$

2. Square matrix

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ a & b & c \end{bmatrix} (3 \times 3)$$

3. Raw matrix

$$[1 \quad 2 \quad 3](1 \times 3)$$

4. Column matrix

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix} (3 \times 1)$$

5. Null OR Zero matrix

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} (3 \times 3)$$

6. Diagonal matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 5 & 0 \\ 0 & 0 & c \end{bmatrix} (3 \times 3)$$

7. Scalar matrix

$$\begin{bmatrix} 5 & 0 & 0 \\ 0 & 5 & 0 \\ 0 & 0 & 5 \end{bmatrix} (3 \times 3)$$

8. Identity matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} (3 \times 3)$$

Character of matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 5 & 0 \\ 0 & 0 & c \end{bmatrix} (3 \times 3)$$

It is the sum of the diagonal elements of a square matrix

$$\chi(chi) = 1 + 5 + c$$

Matrix Mathematics

1. Addition and subtraction of matrix: Simply addition or subtraction of two equal type matrix

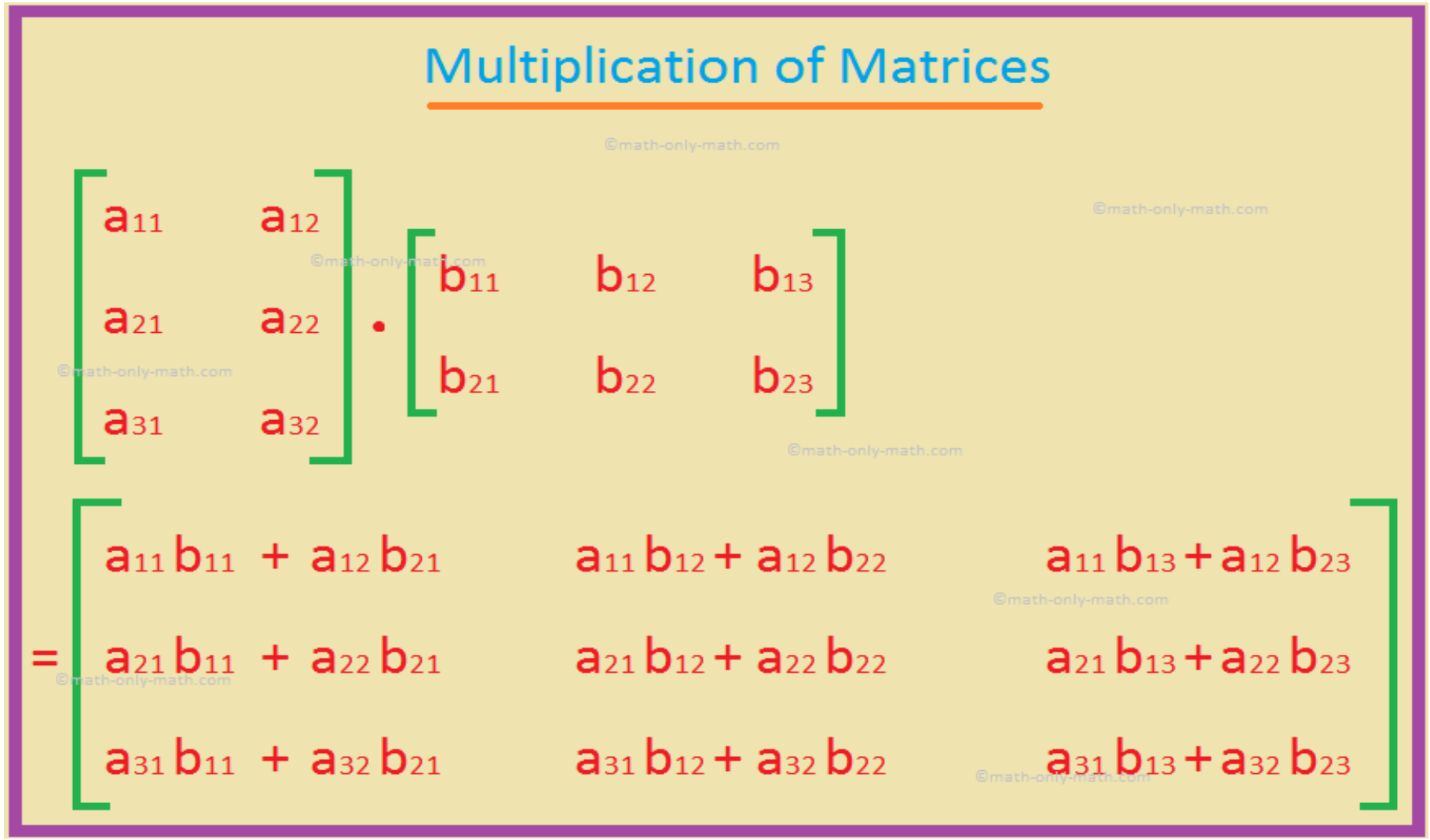
$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \pm \begin{bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{bmatrix} = \begin{bmatrix} 1 \pm a & 2 \pm b & 3 \pm c \\ 4 \pm d & 5 \pm e & 6 \pm f \\ 7 \pm g & 8 \pm h & 9 \pm i \end{bmatrix}$$

$\ldots\ldots(3 \times 3) \ldots \quad (3 \times 3) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3 \times 3)$

Matrix Mathematics

2. Matrix multiplication:

Two matrix $(m_1 \times n_1)$ and $(m_2 \times n_2)$, when $n_1 = m_2$ than the resultant matrix is $(m_1 \times n_2)$



$$M=\begin{bmatrix} 2 & 3 \\ 2 & 1 \\ 5 & 3 \end{bmatrix} \quad N=\begin{bmatrix} 5 & 3 & 2 \\ 2 & 1 & 4 \end{bmatrix}$$

M is of dimension 3×2, N is of dimension 2×3

$$M\times N=\begin{vmatrix} 2*5+3*2 & 2*3+3*1 & 2*2+3*4 \\ 2*5+1*2 & 2*3+1*1 & 2*2+1*4 \\ 5*5+3*2 & 5*3+3*1 & 5*2+3*4 \end{vmatrix}$$

$$M\times N=\begin{vmatrix} 16 & 9 & 16 \\ 12 & 7 & 8 \\ 31 & 18 & 22 \end{vmatrix}$$

$\chi(chi) = 16 + 7 + 22$=45

Commute Matrix

The A and B matrix are square and same type (order) matrix,
Multiplication of matrix are

$$AB \neq BA$$
$$but$$
$$\chi(AB) = \chi(BA)$$

The character of multiplication matrix are equal than A and B matrix are Commute Matrix.

$$A = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} (2 \times 2) \qquad B = \begin{bmatrix} 1 & 1 \\ 2 & 1 \end{bmatrix} (2 \times 2)$$

$$A \times B = \begin{bmatrix} 1+4 & 1+2 \\ 3+8 & 3+4 \end{bmatrix} = \begin{bmatrix} 5 & 3 \\ 11 & 7 \end{bmatrix} \ldots \chi(AB) = 5 + 7 = 12$$

$$B \times A = \begin{bmatrix} 1+3 & 2+4 \\ 2+3 & 4+4 \end{bmatrix} = \begin{bmatrix} 4 & 6 \\ 5 & 8 \end{bmatrix} \ldots \chi(AB) = 4 + 8 = 12$$

Matrix representation of symmetry elements

Matrix for E (identity):

Consider 'P' point on space, coordinates of point P is (X,Y,Z).

$$[X, Y, Z] \xrightarrow[opatation]{Identity} [X', Y', Z']$$

Initial
(Before operation)

Final
(After operation)

Relation of initial and final coordinates represented by mathematical equation.

$$X = X'$$
$$Y = Y'$$
$$Z = Z'$$

OR

$$X = 1X' + 0Y' + 0Z'$$
$$Y = 0X' + 1Y' + 0Z'$$
$$Z = 0X' + 0Y' + 1Z'$$

Representation equations by matrix method.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

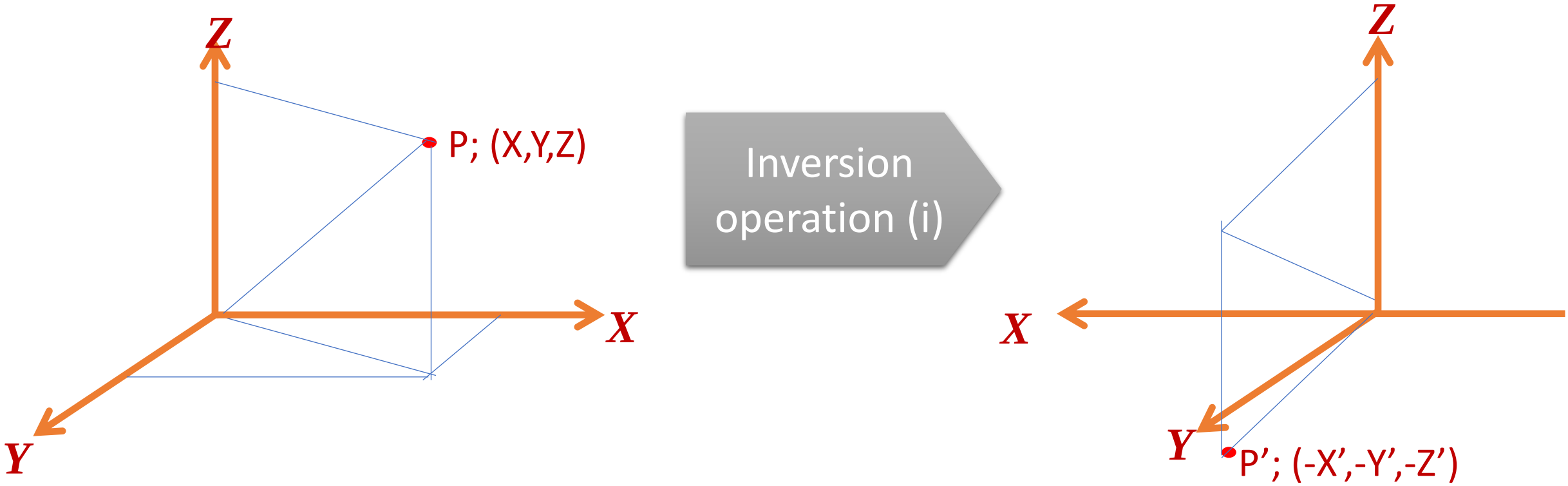
Matrix Representation for E.

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

Character of E matrix $\chi(E) = 1 + 1 + 1 = 3$

2. Matrix for *i* (inversion center):

Consider 'P' point on space, coordinates of point 'P' is (X,Y,Z).



$$[X, Y, Z] \xrightarrow[opatation]{Inversion} [-1X', -1Y', -1Z']$$

Initial
(Before operation)

Final
(After operation)

Mathematics Relation of initial and final coordinates by mathematical equation

$$X = -1X'$$
$$Y = -1Y'$$
$$Z = -1Z'$$

$$X = -1X' + 0Y' + 0Z'$$
$$Y = 0X' - 1Y' + 0Z'$$
$$Z = 0X' + 0Y' - 1Z'$$

Representation equations by matrix method.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

Matrix Representation for *i*.

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

Character of *i* matrix

$$\chi(i) = -1 - 1 - 1 = -3$$

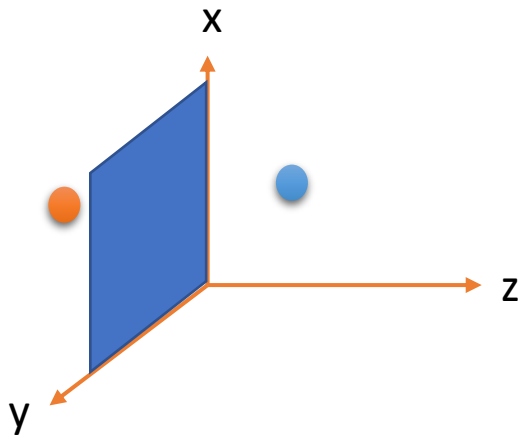
3 . Matrix for σ (plane of symmetry):

Consider 'P' point on space, coordinates of point 'P' is (X,Y,Z).

$$[X, Y, Z] \xrightarrow[\sigma_{xy}]{\text{Reflection}} [0X', 0Y', -1Z']$$

Initial
(Before operation)

Final
(After operation)



$$X = 1X' + 0Y' + 0Z'$$
$$Y = 0X' + 1Y' + 0Z'$$
$$Z = 0X' + 0Y' - 1Z'$$

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

Character of σ matrix

$$\chi(\sigma_{xy}) = 1 + 1 - 1 = 1$$

$$X = -1X' + 0Y' + 0Z'$$
$$Y = 0X' + 1Y' + 0Z'$$
$$Z = 0X' + 0Y' + 1Z'$$

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi(\sigma_{yz}) = 1$$

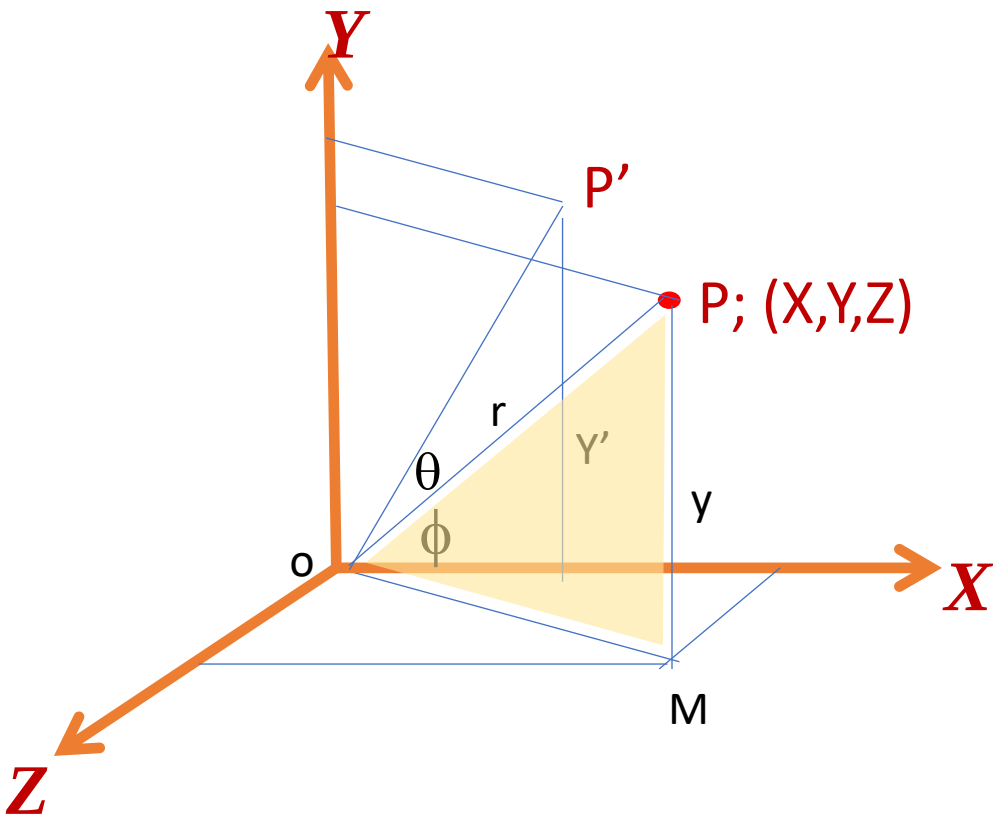
$$X = 1X' + 0Y' + 0Z'$$
$$Y = 0X' - 1Y' + 0Z'$$
$$Z = 0X' + 0Y' + 1Z'$$

$$\sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi(\sigma_{xz}) = 1$$

4 . Matrix for Cn (Rotational axis):

Consider ‘P’ point on space, coordinates of point ‘P’ is (X,Y,Z).

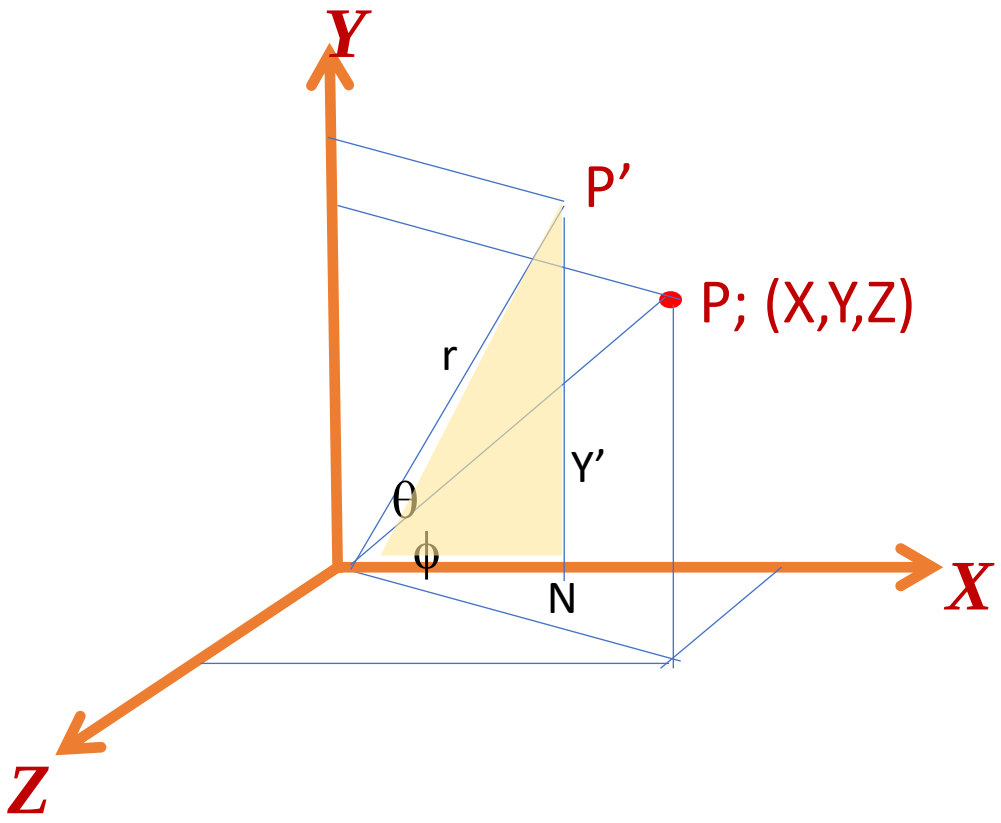
$$[X,Y,Z] \underset{anticlock(\theta)}{\overset{C_{n(Z)}}{\longrightarrow}} [X',Y',Z']$$



$$z' = 0X + 0Y + 1Z$$

$$\sin\phi = \frac{y}{r} \Rightarrow y = r \cdot \sin\phi$$

$$\cos\phi = \frac{x}{r} \Rightarrow x = r \cdot \cos\phi$$



$$\sin(\phi+\theta)=\frac{y'}{r}\Rightarrow y'=r\cdot\sin(\phi+\theta)$$

$$y'=r\cdot\sin\theta\cos\phi+r\cdot\cos\theta\sin\phi$$

$$\boxed{y'=x\sin\theta+y\cos\theta}$$

$$\cos(\phi+\theta)=\frac{x'}{r}\Rightarrow x'=r\cdot\cos(\phi+\theta)$$

$$x'=r\cdot\cos\theta\cos\phi-r\cdot\sin\theta\sin\phi$$

$$\boxed{x'=x\cos\theta-y\sin\theta}$$

$$\sin\phi=\frac{y}{r}\Rightarrow y=r\cdot\sin\phi$$

$$\cos\phi=\frac{x}{r}\Rightarrow x=r\cdot\cos\phi$$

$$x' = x\cos\theta - y\sin\theta + 0z$$

$$y' = x\sin\theta + y\cos\theta + 0z$$

$$z' = 0X + 0Y + 1Z$$

$$C_{n(Z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\chi\left(C_{n(Z)}\right) = 2\cos\theta + 1$$

Clockwise Rotation

$$C_{n(Z)} = \begin{bmatrix} \cos(-\theta) & -\sin(-\theta) & 0 \\ \sin(-\theta) & \cos(-\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$cos(-\theta) = cos\theta$ &
$sin(-\theta) = -sin\theta$

$$C_{n(X)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix}$$

$$C_{n(Y)} = \begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix}$$

5 . Matrix for *Sn* (Improper rotational axis):

Improper rotational = Rotation + reflection

(perpendicular plane to the rotational axis)

$$S_{n(z)} = C_{n(z)} \times \sigma_{xy}$$

$$S_{n(x)} = C_{n(x)} \times \sigma_{yz}$$

$$S_{n(y)} = C_{n(y)} \times \sigma_{xz}$$

$$S_{n(Z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S_{n(Z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\chi(S_{n(Z)}) = 2\cos\theta - 1$$

$$S_{n(X)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix} \times \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix}$$

$$S_{n(Y)} = \begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & -1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix}$$

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_{n(z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad S_{n(z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

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

Character of Symmetry element					
S.E.	*E*	*Cn*	σ	*Sn*	*i*
χ	*3*	$2\cos\theta+1$	*1*	$2\cos\theta-1$	*-3*

θ	0/360 1	30	45 8	60 6	90 4	120 3	180 2
Sin θ	0	½	$1/\sqrt{2}$	$\sqrt{3}/2$	1	$\sqrt{3}/2$	0
Cos θ	1	$\sqrt{3}/2$	$1/\sqrt{2}$	½	0	-½	-1

Matrix representation of point groups or molecules

$$C_{2v} \Rightarrow E; C_{2(z)}; \sigma_{(xy)}; \sigma_{(yz)}$$

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

$$C_{2(z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos(180) & -\sin(180) & 0 \\ \sin(180) & \cos(180) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character of Symmetry element				
C_{2v}	E	Cn	σxy	σyz
χ	3	2cosθ+1	1	1
χ	**3**	**-1**	**1**	**1**

Characteristics of Matrix representation of P.G.

- Matrix representation OR Character can be obtain for any group and Molecules which is called Character Representation of group.
- This character representation are equal to all the molecules having same P.G.

C_2v : H2O; Pyridine,

- This character is equal to the total character of Translation vector character.

$$\chi_{(R)} = \tau_{(T)} = \tau_{(x)} + \tau_{(y)} + \tau_{(z)}$$

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

Note:
x,y is indicate the R is obtained through x & y T.V. (double)

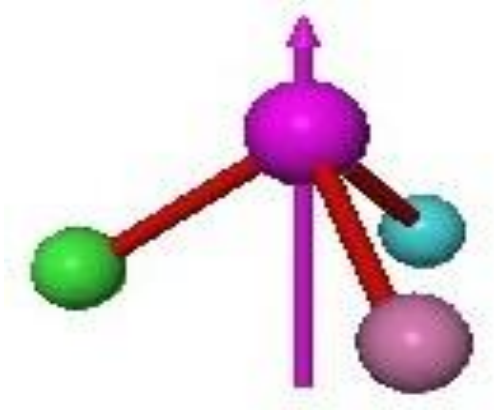
(x,y) is indicate R. obtained through both (x,y) T.V. (single)

C_{2v}	E	Cn	σxy	σyz
B1 = $\tau_{(x)}$	1	-1	1	-1
B2 = $\tau_{(y)}$	1	-1	-1	1
A1 = $\tau_{(z)}$	1	1	1	1
$\chi_{(R)} = \tau_{(T)}$	**3**	**-1**	**1**	**1**

Matrix representation of point groups C_3v

$$C_{3v} \Rightarrow E; C^1_{3(z)}; C^2_{3(z)}; \sigma^1_v(\sigma_{xz}); \sigma^2_v; \sigma^3_v$$

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



$$C^1_{3(z)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos(120) & -\sin(120) & 0 \\ \sin(120) & \cos(120) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C^2_{3(z)} = inverse \cdot of \cdot C^1_{3(z)} = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma^1{}_v = \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma^2{}_v = \sigma_{xz} \times C_3^1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma^3{}_v = \sigma_{xz} \times C_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character of Symmetry element			
C_{3v}	E	$2C_3$	$3\sigma v$
χ	3	$2\cos\theta+1$	1
χ	3	0	1

Table 2.17 Character table for point group C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$	Basis components		
A_1	1	1	1	z		x^2+y^2,z^2
A_2	1	1	−1		R_z	
E	2	−1	0	(x,y)	(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$

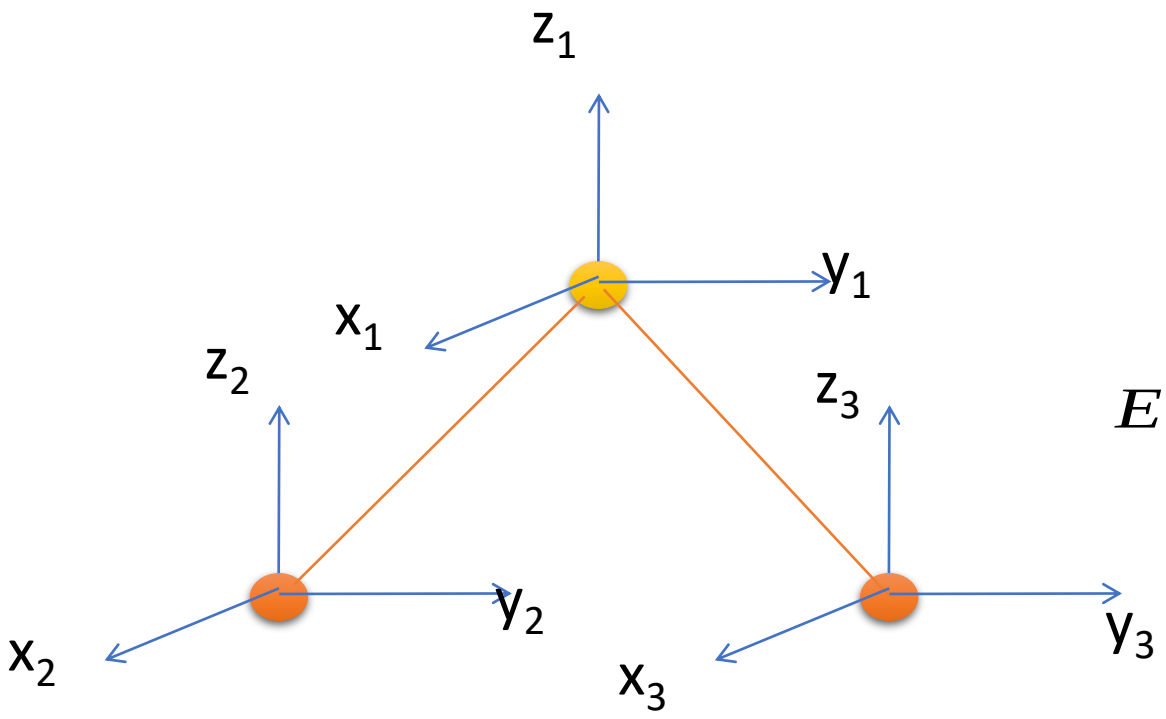
Character of Symmetry element for NH3			
C_{3v}	E	$2C_3$	$3\sigma v$
E = $\tau_{(x,y)}$	2	-1	0
A1 = $\tau_{(z)}$	1	1	1
$\tau_{(T)}$	3	0	1

Total Representation of Group (τ_{3N})

Total representation is define as representation obtain through Translation(τ_T), Rotational (τ_R) and Vibrational ($\tau_{Vib.}$).

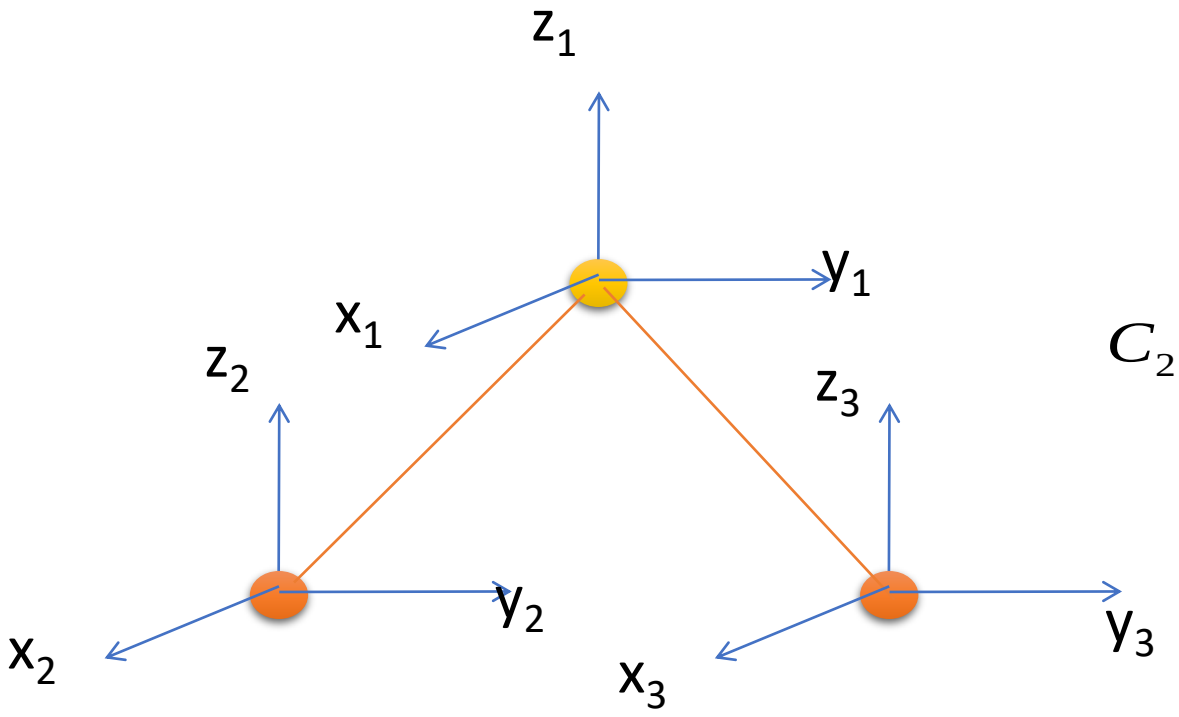
The Total number of Modes(Degrees of freedom) = τ_{3N} = 3N = ($\tau_T + \tau_R + \tau_{Vib.}$)

Where N is no. of atom in Mole.



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

Total Representation of Group (τ_{3N})



$$C_{2(z)} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

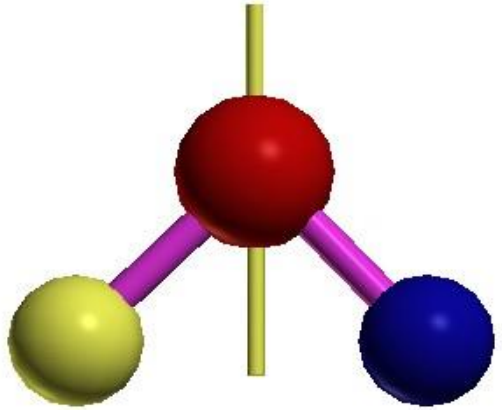
Total Representation of Group (τ_{3N})

Γ_{3N} Representation :For H_2O,NH_3,BF_3,$PtCl_4$,PCl_5,SF_6,$POCl_3$,CCl_4,Cis &Trans N_2F_4, $XeOF_4$

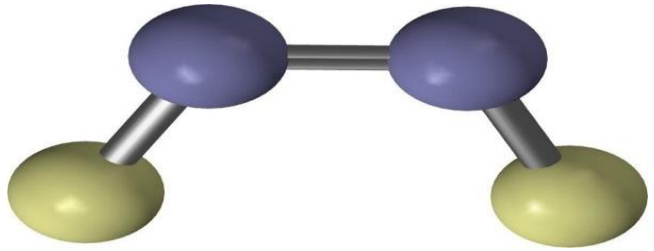
- An alternative simple method for Total Representation.
- τ_T are equal for all mole. having same P.G. but τ_{3N} are not equal for any mole. It is depends on number of atoms in mole.

$$\tau_{3N} = \tau_T \times NUSA$$

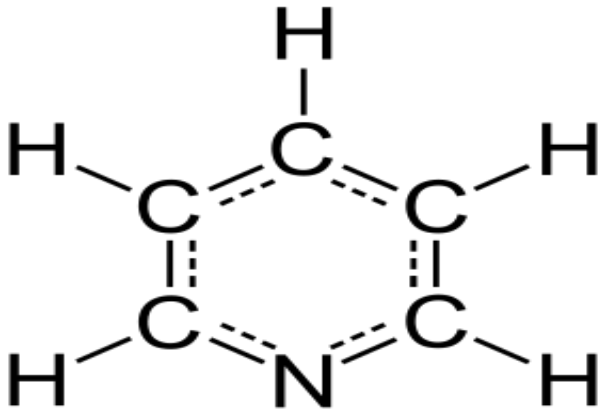
NUSA= number of un-sifted atom after operation.



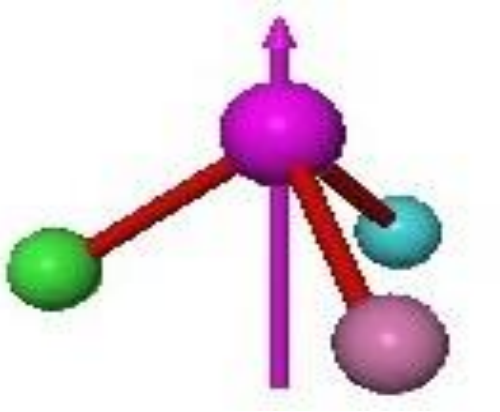
τ_{3N} Representation for H2O mole.				
C_{2v}	E	C2	σxy	σyz
τ_T	3	-1	1	1
NUSA	3	1	1	3
τ_{3N}	9	-1	1	3

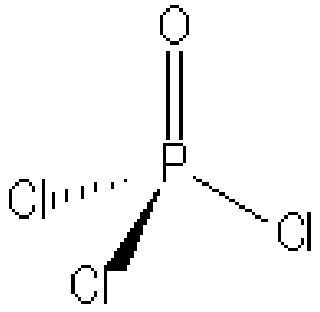


τ_{3N} Representation for cis N2F2 mole.				
C_{2v}	E	C2	σxy	σyz
τ_T	3	-1	1	1
NUSA	4	0	0	4
(Rr)=τ_{3N}	**12**	**0**	**0**	**4**

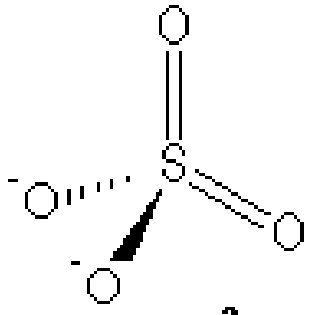


τ_{3N} Representation for pyridine mole.				
C_{2v}	E	C2	σxy	σyz
τ_T	3	-1	1	1
NUSA	11	3	3	11
(Rr)=τ_{3N}	**33**	**-3**	**3**	**11**





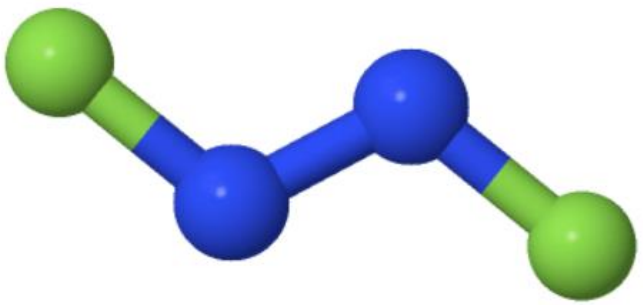
$POCl_3$



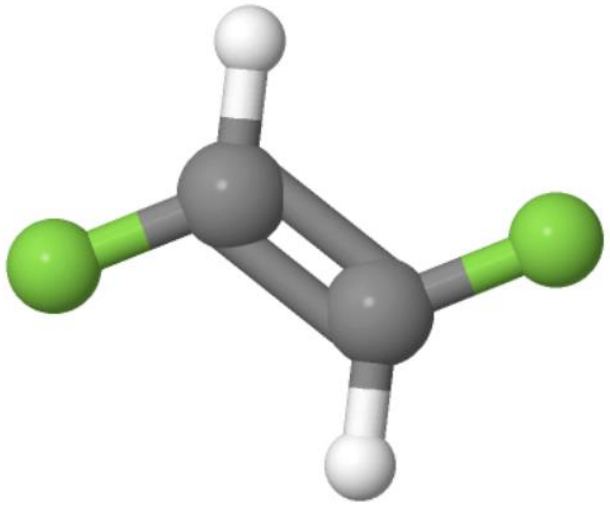
SO_4^{2-}

τ_{3N} Representation for Ammoniya mole.			
C_{3v}	E	$2C_3$	$3\sigma v$
τ_T	3	0	1
NUSA	4	1	2
$(Rr)=\tau_{3N}$	**12**	**0**	**2**

τ_{3N} Representation for POCl3 mole.			
C_{3v}	E	$2C_3$	$3\sigma v$
τ_T	3	0	1
NUSA	5	2	3
$(Rr)=\tau_{3N}$	**15**	**0**	**3**

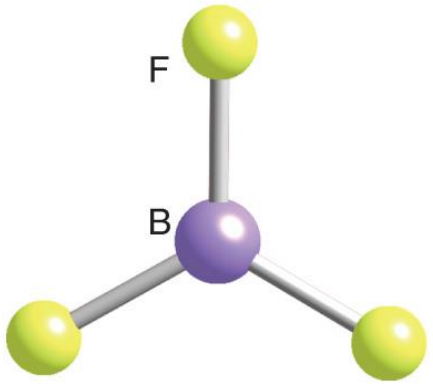


τ_{3N} Representation for H2O2(Pln) mole.				
C_{2h}	E	C2	σh	i
τ_T	3	-1	1	3
NUSA	4	0	4	0
(Rr)=τ_{3N}	**12**	**0**	**4**	**0**



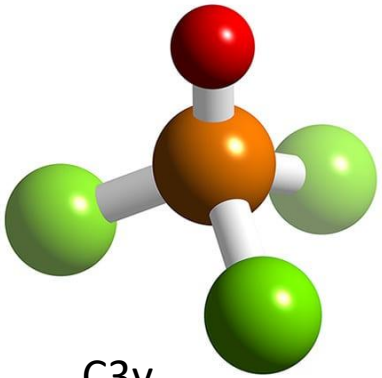
1,2-difluoroethylene (trans)

τ_{3N} Representation for FHC=CHF mole.				
C_{2h}	E	C2	σh	i
τ_T	3	-1	1	3
NUSA	6	0	6	0
(Rr)=τ_{3N}	**18**	**0**	**6**	**0**

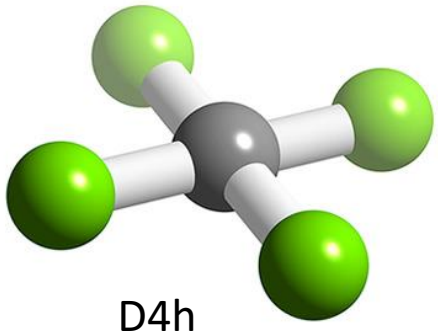


D_3h	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
τ_T	3	0	1	3	0	1
NUSA	**4**	**1**	**2**	**0**	**1**	**2**
τ_{3N}	12	0	2	0	0	2

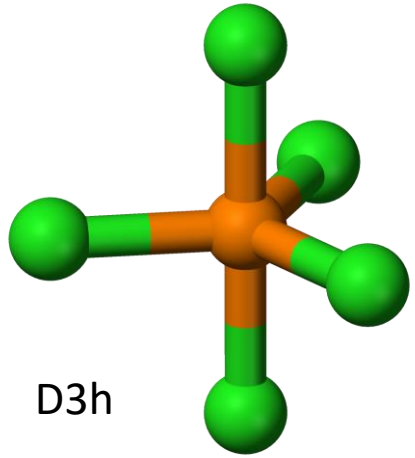
Γ_{3N} Representation :For H_2O,NH_3,BF_3,$PtCl_4$,PCl_5,SF_6,$POCl_3$,CCl_4,Cis &Trans N_2F_4, $XeOF_4$



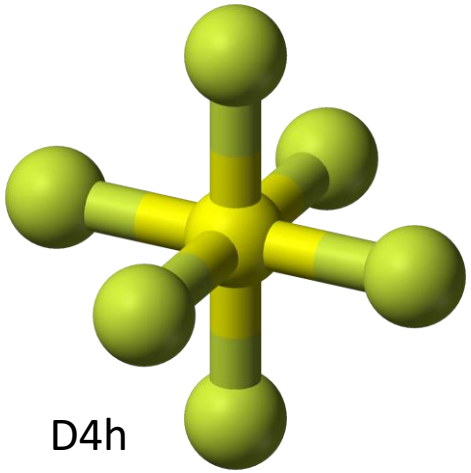
C3v



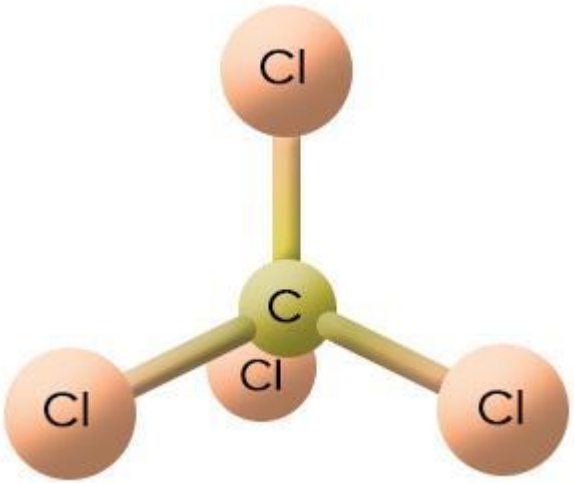
D4h



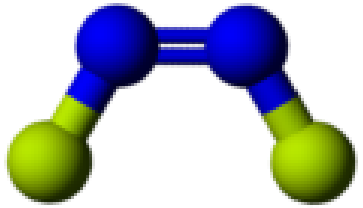
D3h



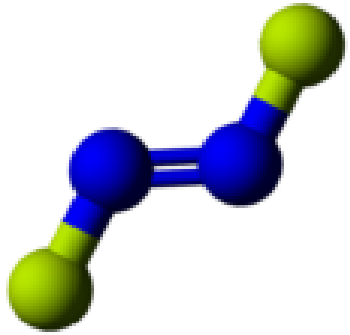
D4h



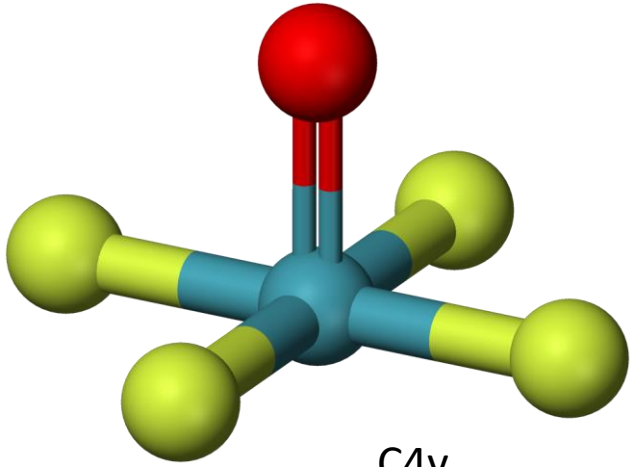
Td



C2v



C2h



C4v

Reducible and Irreducible representation.

- The various types of matrix representation are obtained for any group or mole.
- τ_{3N} of any mole. Give full matrix, no. of Colum and raw increases when the number of atoms are increase in mole.
- The full matrix is divided in small or block matrix, the big matrix is called reducible and small/ block matrix are called Irreducible matrix.
- The matrix can not divisible in block is called irreducible matrix and its character is called irreducible representation. (Irs)

$$C^{1}{}_{3(z)} = \left[\begin{array}{cc|c} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ \hline 0 & 0 & 1 \end{array}\right]$$

$$T_1 = \left[-1/2\right]$$

$$T_2 = \left[-1/2\right]$$

$$T_3 = [1]$$

irreducible representation. (Irs)

Simple method to determination of Irreducible representation from reducible representation.

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R) \cdot \chi_{IR(R)} \cdot \chi_{RR(R)}\right]$$

$n(\tau i)$ = the number of Irs.
h = order of group
n(R) = no. symmetry element in class.
$\chi_{IR}(R)$ = character of irreducible representation.(from C. Table)
$\chi_{RR}(R)$ = character of reducible representation.

τ_{3N} Representation for H2O mole.

C_{2v}	E	Cn	σxy	σyz
τ_{3N}	9	-1	1	3

Obtained IRs using above equation are (Mulliken Symbol)

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

τ_{3N} Representation for H2O mole.

C_{2v}	E	Cn	σxy	σyz
τ_{3N}	9	-1	1	3

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R) \cdot \chi_{IR(R)} \cdot \chi_{RR(R)}\right]$$

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

No. of

$$A_1 = \frac{1}{4}[(1)(9)(\quad) + (1)(-1)(\quad) + (1)(1)(\quad) + (1)(3)(\quad)]$$

$$A_2 = \frac{1}{4}[(1)(9)(\quad) + (1)(-1)(\quad) + (1)(1)(\quad) + (1)(3)(\quad)]$$

$$B_1 = \frac{1}{4}[(1)(9)(\quad) + (1)(-1)(\quad) + (1)(1)(\quad) + (1)(3)(\quad)]$$

$$B_2 = \frac{1}{4}[(1)(9)(\quad) + (1)(-1)(\quad) + (1)(1)(\quad) + (1)(3)(\quad)]$$

- The sum of Character of the IRs is equal to the Character of RRs.(τ_{3N})
- The total number of IRs are equal to the 3N

(N= no. of atoms in mole.)

In H_2O mole. $3 \times 3 = 9$

$$3A_1 + A_2 + 2B_1 + 3B_2 = 9$$

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

IRs of τ_{3N} for H2O mole.

C_{2v}	E	Cn	σxy	σyz
$3A_1$	3	3	3	3
A_2	1	1	-1	-1
$2B_1$	2	-2	2	-2
$3B_2$	3	-3	-3	3
τ_{3N}	9	-1	1	3

Properties of irreducible representations:

- ✓There are many number of RRs for a P.G., but there are finite number of IRs.
- ✓The nature and numbers of IRs are characteristics of a P.G.
- ✓The IRs are same for different types of mole. Having same P.G.
- ✓The number of IRs is change with the change P.G. of mole.
- ✓The two IRs are not identical in any P.G.
- ✓Dimensionality may be same, but the IRs differ from each other in the nature of character.

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

Rule :-1. Number of IRs

- The number of IRs are equal to the number of class of the P.G.
  (The IRs are indicated by Mulliken symbols in C.T.)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

Rule :-2. Dimensionality of Irs.

The sum of the squares of character of the dimensional of each of the IRs of any element of a group is equal to the order of the group h

$$\sum n(R) \cdot \chi^2(IRs) = h$$

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

Rule :-3. Characters of Irs.

The sum of the squares of the characters under any IRs is equal to the order of the group h

$$\sum_{IRs} n(R) \cdot \chi_R{}^2(IRs) = h$$

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

The character of IRs for S.E. in same class are equal.

Rule :-4. Orthogonallity rule:

The sum of the products of characters under any two IRs representations is equal to zero.

$$\sum n(R) \cdot \chi_i(IRs)\chi_j(IRs) = 0$$

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

STRUCTURE OF CHARACTER TABLES- its consists of six areas

Point Group (I)	S.E. in Class (II)		
IRs in Symbol (III)	Characters (IV)	Translation and rotational functions. (V)	Vector of d-orbital. (VI)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

Area (I) : This space in the table is used for writing Point Group.

Area (II) : All S.E. grouped into Class have been placed in this area.

Area (III) : The IRs of particular P.G. are indicated by Mulliken symbol in this area.

Area (IV) : This part of C.T. is congaing the Characters, which are the magic numbers defining the structural and spectral properties of Mole.

Area (V) : This area containing Translation and Rotational function.

x, y and z represented the translation and p-orbital vector.

Rx, Ry, Rz represented the Rotational vector.

This part introduce the IR activity of mole.

Area (VI) : This area containing following symbols which are represented vector of d-orbital.

xy, yz, zx, $x^2 - y^2$, z^2

This part is introduced the Raman activity of mole.

Mulliken symbol for IRs .

1. Character of E (identity) represented A, B, & E Mulliken symbol.

χ(E)	Symbol
1	A OR B
2	E
3	T OR F
4	G

Character of Cn is Represented

χ(Cn)	Symbol
+1 (Sy)	A
-1 (USy)	B

2. Subscripts rule.

(i) Subscripts 1 and 2 used with A, B, E….. Character of C_2 (S. R. Axis perpendicular to P. R. A.) is represented 1 & 2 subscript with symbols.

$\chi(C_2)$	Symbol
+1	A_1 , B_1 , E_1
-1	A_2 , B_2 , E_2

When S.R.A. are not present then use character of σv.

$\chi(\sigma v)$	Symbol
+1	A_1 , B_1 , E_1
-1	A_2 , B_2 , E_2

(ii) Subscripts ‘u’ and ‘g’ used with A, B, E….. Character of ‘*i*’ (inversion center) is represented ‘u’ & ’g’ subscript with symbols.

$\chi(i)$	Symbol
+1	A_u , B_u , E_u
-1	A_g , B_g , E_g

3. Superscripts rule.

(i) Superscripts single prime(‘) and double prime(‘’) used with A, B, E…..
Character of ‘σh ’ (horizontal plane) is represented (’) & (‘’) superscript with symbols.

χ(σh)	Symbol
+1	A’ : B’ : E’
-1	A’’ : B’’ : E’’

(ii) Many P.G. containing both S.E. σh and i (inversion center) then use both subscript (u and g) and superscript (‘ and ‘’)

χ(i)	χ(σh)	Symbol
+1	+1	A’u : B’u : E’u
-1	-1	A’’g : B’’ g: E’’g

4. Multi dimensional representations.

Σ,π,Δ,ϕ symbols are used for higher symmetry of mole. Which is very difficult to introduce the symmetry of molecules.

$D_{\infty h}$	E	$2C_\infty^\phi$	…	$\infty\sigma_v$	i	$2S_\infty^\phi$	…	∞C_2		
Σ_g^+	1	1	…	1	1	1	…	1		x^2+y^2, z^2
Σ_g^-	1	1	…	–1	1	1	…	–1	R_z	
Π_g	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0		$(x^2-y^2, 2xy)$
…	…	…	…	…	…	…	…	…		
Σ_u^+	1	1	…	1	–1	–1	…	–1	z	
Σ_u^-	1	1	…	–1	–1	–1	…	1		
Π_u	2	$2\cos\phi$	…	0	–2	$2\cos\phi$	…	0	(x,y)	
Δ_u	2	$2\cos 2\phi$	…	0	–2	$-2\cos 2\phi$	…	0		
…	…	…	…	…	…	…	…	…		

Constriction of Character Table for C_3v P.G. using properties of IRs

$$C_{3v} \Rightarrow E; C_{3(z)}^{1}; C_{3(z)}^{2}; \sigma_v^1(\sigma_{xz}); \sigma_v^2; \sigma_v^3$$

$$C_{3v} \Rightarrow E; 2C_3^1; 3\sigma_v$$

Order of the C3v P.G. = 6
Class of the C3v P.G. = 3

STEP:-1,

The number of irreducible representations is equal to the number of classes in the group.

In this P.G. there are three class the IRs are τ_1 , τ_2, τ_3

C_3v	E	$2C_3$	$3\sigma_v$
τ_1			
τ_2			
τ_3			

STEP:-2,

For any P.G., character of any one IRs are identical for all symmetry element.

C_3v	E	$2C_3$	$3\sigma_v$
τ_1	1	1	1
τ_2	x		
τ_3	y		

STEP:-3,

Character of E for all IRs are symmetrical.

For E, The sum of the squares of the dimensions of the characters of Irs is equal to the order of the group h.

$$\sum n(R)\cdot \chi^2(IRs) = h$$

$$\left[1(1)^2 + 1(x)^2 + 1(y)^2\right] = 6$$

Take x=1 and y=2, for solve this equation

C_3v	E	$2C_3$	$3\sigma_v$
τ_1	1	1	1
τ_2	1		
τ_3	2		

STEP:-4,

The sum of the squares of the characters under any Irs is equal to the order of the group h.

The characters of all operations in the same class are equal in each given irreducible (or reducible) representation.

$$\sum_{IRs} n(R)\cdot \chi_R{}^2(IRs) = h$$

C_3v	E	$2C_3$	$3\sigma_v$
τ_1	1	1	1
τ_2	1	X	Y
τ_3	2		

$$\left[1(1)^2 + 2(1)^2 + 3(1)^2\right] = 6$$

$$\left[1(1)^2 + 2(x)^2 + 3(y)^2\right] = 6$$

Where x=1 or -1 and y=1 or -1

STEP:-4, Orthogonallity rule

The sum of the products of characters under any two Irs representations is equal to zero.

$$\sum n(R)\cdot \chi_i(IRs)\chi_j(IRs) = 0$$

$$[1(1)(1) + 2(1)(x) + 3(1)(y)] = 0$$

Where x=1 and y= -1

$$\sum n(R)\cdot \chi_i(IRs)\chi_j(IRs) = 0$$

C_3v	E	$2C_3$	$3\sigma_v$
τ_1	1	1	1
τ_2	1	1	-1
τ_3	2	x	y

$$\tau_2 \times \tau_3 = [1(1)(2)+2(1)(x)+3(-1)(y)] = 0$$

$$2+2x-3y=0$$

$$2x-3y=-2$$

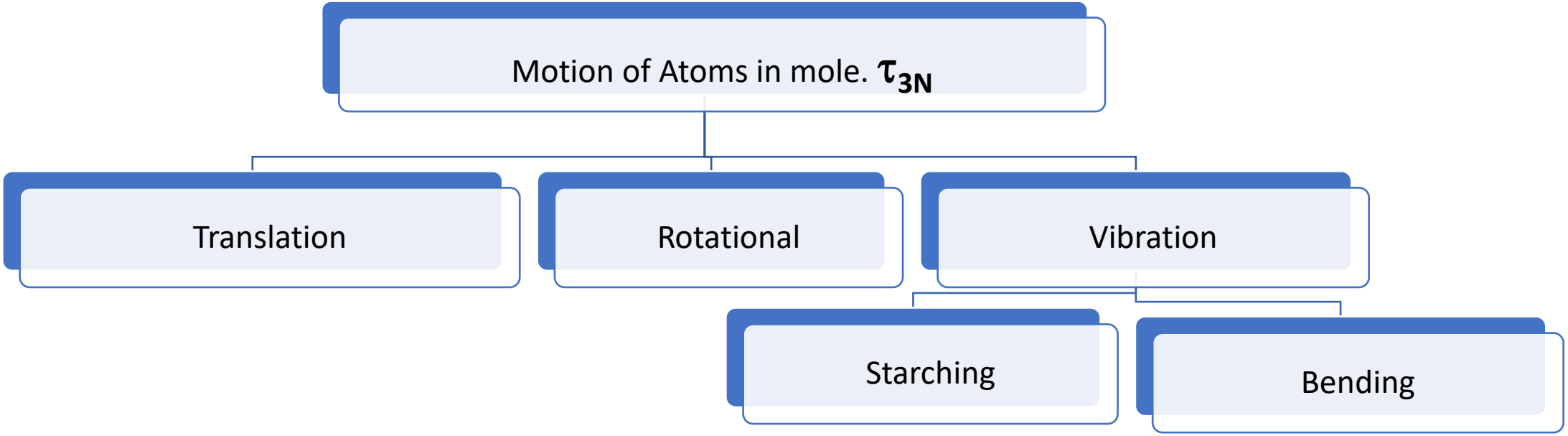
$$\tau_1 \times \tau_3 = [1(1)(2)+2(1)(x)+3(1)(y)] = 0 \qquad 2+2x+3y=0 \qquad 2x+3y=-2$$

Solving both equation, we get x= -1, and y=0

Mulliken Sym.	C_3v	E	$2C_3$	$3\sigma_v$
A_1	τ_1	1	1	1
A_2	τ_2	1	1	-1
E	τ_3	2	-1	0

SYMMETRY OF NORMAL MODES OF MOLECULES

Application of symmetry to molecular vibrations, interpretation of IR and Raman activity.



The Total number of Modes(Degrees of freedom) = $\tau_{3N} = 3N = (\tau_T + \tau_R + \tau_{Vib.})$

Where N is no. of atom in Mole.

Molecule	Translation modes (τ_T)	Rotational modes (τ_R)	Vibrational modes(τ_{Vib})		
			Starching	Bending	Total
Linear	3	2	N-1	2N-4	3N-5
Non-linear	3	3	N-1	2N-5	3N-6

There are two convenient method for determine the normal modes of mole.

1. Cartesian coordinate method.

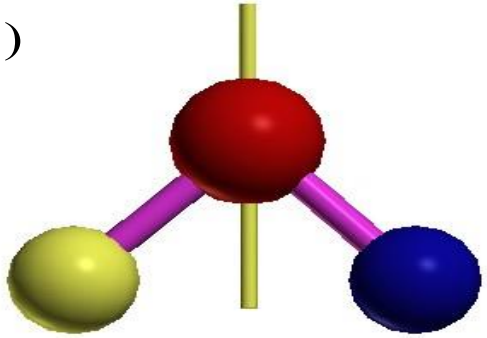
2. Internal coordinate method.

These method deal how the **symmetry of normal modes arising** and their **IR and Raman spectral activity.**

SYMMETRY OF NORMAL MODES OF H_2O MOLEC ULES

1. Cartesian coordinate Method.

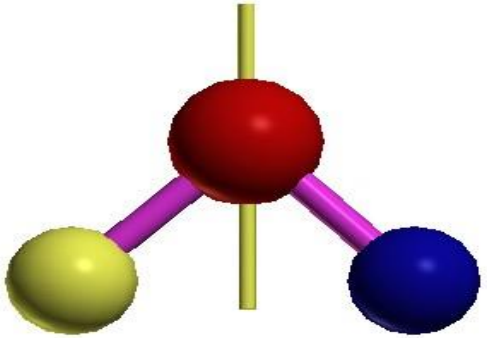
1. P.G. and Symmetry elements = $C_{2v} \Rightarrow E; C_{2(z)}; \sigma_{(xy)}; \sigma_{(yz)}$
2. Number of atoms (N)= 3
3. Order of Group = 4
4. Class of Group =4
5. Modes in Molecules (degree of freedom)



Molecule (H2O)	Translation modes (τ_T)	Rotational modes (τ_R)	Vibrational modes(τ_{Vib})		
			Starching	Bending	Total
Non-linear	3	3	N-1	2N-5	3N-6
3N=9	3	3	2	1	3

SYMMETRY OF NORMAL MODES OF H_2O MOLEC ULES

6. Γ_{3N} Representation = Total modes



C_{2v}	E	C2	σxy	σyz	Number of Modes
$\chi = \Gamma_T$	3	-1	1	1	A1+B1+B2 = 3
NUSA	3	1	1	3	
Γ_{3N}	9	-1	1	3	3A1+A2+2B1+3B2 = 9

Total number of modes can be obtained using Standard Reduction formula.

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R) \cdot \chi_{IR(R)} \cdot \chi_{RR(R)}\right]$$

7. Translation modes Γ_T And Rotational modes Γ_R Obtain from Character Table.

Γ_T = A1+B1+B2 = 3 (using x, y and z symbol.)

Γ_R = A2+B1+B2 = 3 (using Rx, Ry and Rz symbol)

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

8. Vibrational modes modes Γ_{Vib} Obtain through

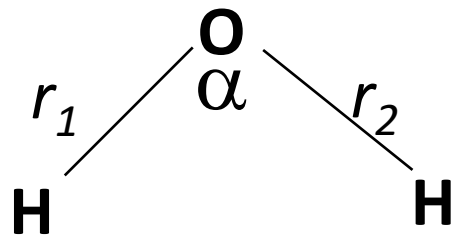
$\Gamma_{3N} = \Gamma_T + \Gamma_R + \Gamma_{Vib.}$ $\Gamma_{Vib.} = \Gamma_{3N} - (\Gamma_T + \Gamma_R)$

$\Gamma_{Vib.}$ =3A1+A2+2B1+3B2-(A1+B1+B2 + A2+B1+B2)

$\Gamma_{Vib.}$ =2A1+B2 = 3

2. Internal Coordinate Method.

1. Consideration of bond vector and bond angle vector for mole.
   Number of bond vector = 2 (O-H bond)= r1 and r2
   Number of bond angle = 1 (H-O-H) = α
   Total number of internal coordinates = 3



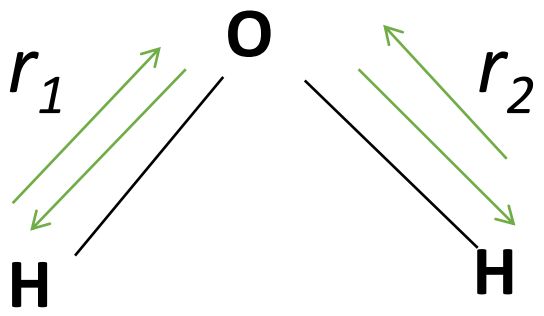
2. Workout symmetry operation on mole. In terms of above Internal modes and determine the character.

C_{2v}	E	Cn	σxy	σyz	Number of Modes
$\Gamma_{Stre.} = \Gamma_{r1+}\Gamma_{r2}$	2	0	0	2	A1+B2 = 2
$\Gamma_{bend.} = \Gamma_{\alpha}$	1	1	1	1	A1 = 1
$\Gamma_{vib.}$	3	1	1	3	2A1 + B2 = 3

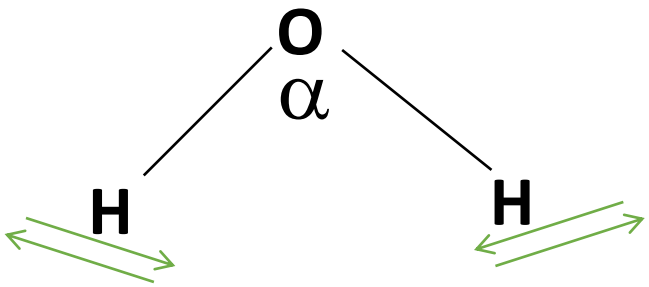
Note: when position of vector is change then character is = 0
when change of direction of vector then character is = -1
when nothing change in position and direction then character is = 1

3. Assignment of Normal Vibrational modes.

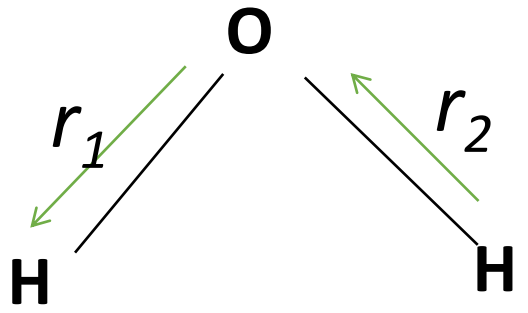
the corresponding normal modes for mole are given following fig.



Symmetrical stretching
A1 (υ1)



Symmetrical bending
A1 (υ3)



Unsymmetrical stretching
B2 (υ2)

4. **IR and Raman spectral activity.**

The IR frequency associated to the vibrational mode are define as

IRs is correlated with the x, y, z then IRs is IR active.

IRs is correlated with the xy,yz,zx,x2-y2 and z2 then IRs is Raman active.

5. Determination of IR Frequency

$$\nu_{stre.} \succ \nu_{bend.}$$

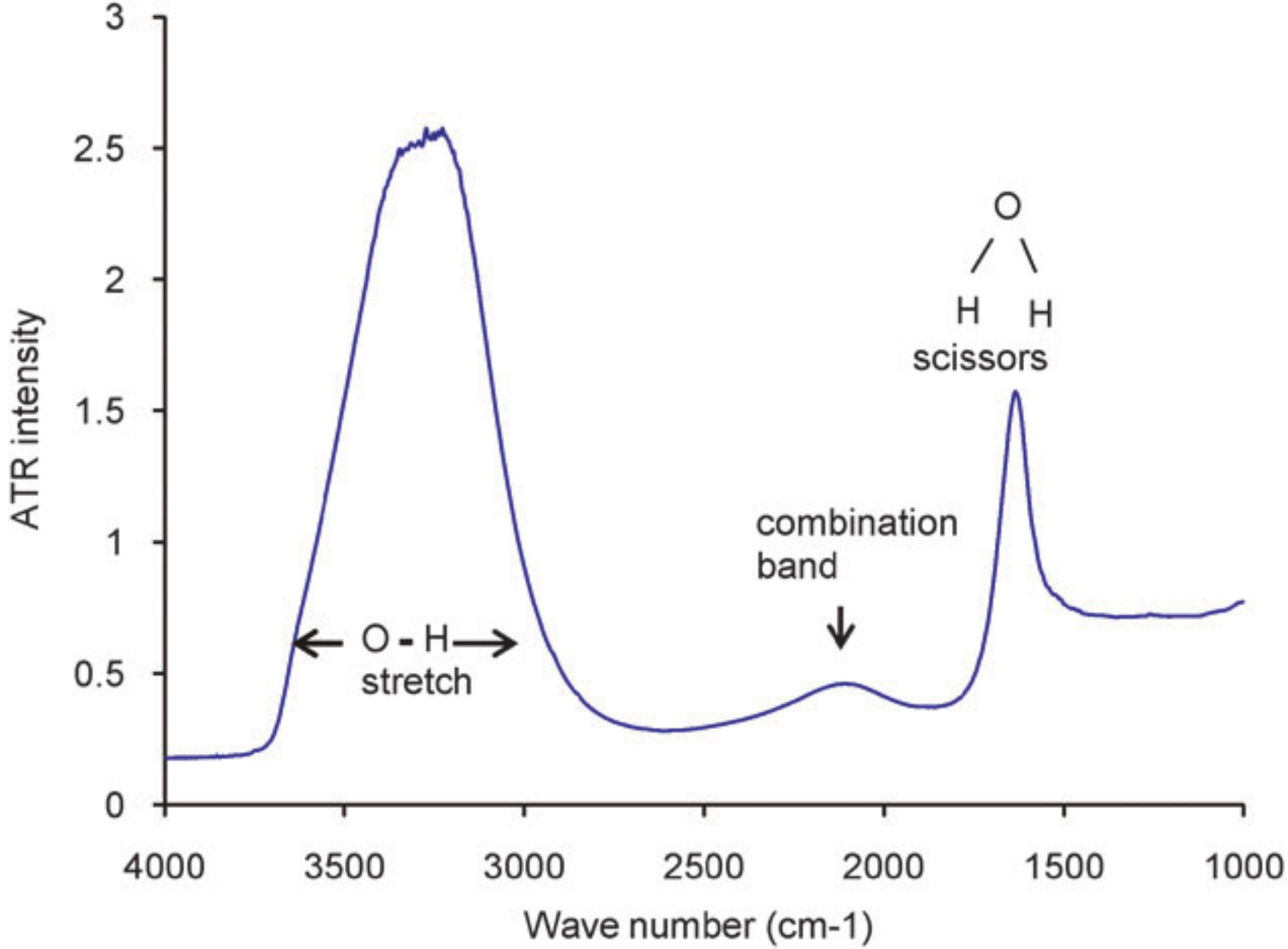
$$\nu_{unsym.} \succ \nu_{sy.}$$

$$\nu_{in.plane.} \succ \nu_{OOP.}$$

$$\nu_{DB} \succ \nu_{SB}$$

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

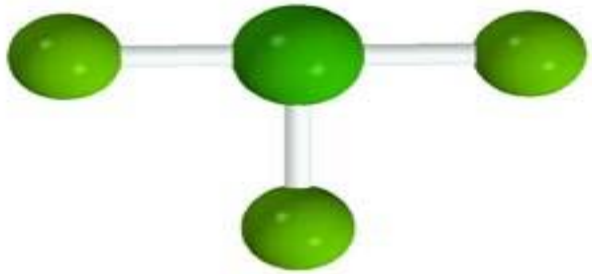
Vibrational mode (Mulliken sym.)	Stretching Or Bending	Symmetry of Mode	IR Active	Raman Active	IR frequency (cm^{-1})
A1	Stretching	Symmetrical	Yes	Yes	$\upsilon_1 = 3642$
B2	Stretching	unsymmetrical	Yes	Yes	$\upsilon_2 = 3756$
A1	Bending	Symmetrical	Yes	Yes	$\upsilon_3 = 1595$


3
2.5
2
1.5
1
0.5
0
ATR intensity
4000
3500
3000
2500
2000
1500
1000
Wave number (cm-1)
O - H
stretch
combination
band
O
H H
scissors

SYMMETRY OF NORMAL MODES OF ClF_3 (T-Shaped) MOLEC ULES

1. Cartesian coordinate Method.

1. P.G. and Symmetry elements = $C_{2v} \Rightarrow E; C_{2(z)}; \sigma_{(xy)}; \sigma_{(yz)}$
2. Number of atoms= (N)=4
3. Order of Group = 4
4. Class of Group =4
5. Modes in Molecules (degree of freedom)

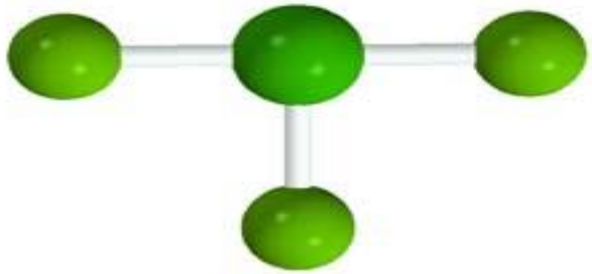


Molecule (ClF3)	Translation modes (τ_T)	Rotational modes (τ_R)	Vibrational modes(τ_{Vib})		
			Starching	Bending	Total
Non-linear	3	3	N-1	2N-5	3N-6
3N=12	3	3	3	3	6

SYMMETRY OF NORMAL MODES OF ClF_3 (T-Shaped) MOLEC ULES

6. Γ_{3N} Representation = total modes

$$C_{2v} \Rightarrow E; C_{2(z)}; \sigma_{(xy)}; \sigma_{(yz)}$$



C_{2v}	E	Cn	σxy	σyz	Number of Modes
$\chi = \Gamma_T$	3	-1	1	1	A1+B1+B2 = 3
NUSA	4	2	2	4	
Γ_{3N}	12	-2	2	4	4A1+A2+3B1+4B2 = 12

Total number of modes can be obtained using Standard Reduction formula.

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R) \cdot \chi_{IR(R)} \cdot \chi_{RR(R)}\right]$$

7. Translation modes Γ_T And Rotational modes Γ_R Obtain from Character Table.

Γ_T = A1+B1+B2 = 3 (using x, y and z symbol.)

Γ_R = A2+B1+B2 = 3 (using Rx, Ry and Rz symbol)

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

8. Vibretional modes modes Γ_{Vib} Obtain through

$\Gamma_{3N} = \Gamma_T + \Gamma_R + \Gamma_{Vib.}$ $\Gamma_{Vib.} = \Gamma_{3N} - (\Gamma_T + \Gamma_R)$

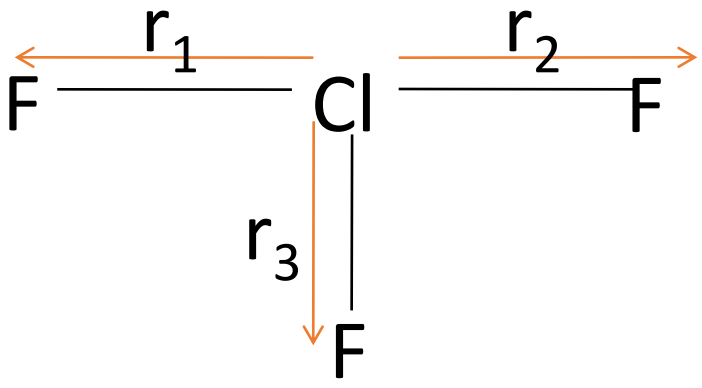
$\Gamma_{Vib.}$ = 4A1+A2+3B1+4B2 -(A1+B1+B2 + A2+B1+B2)

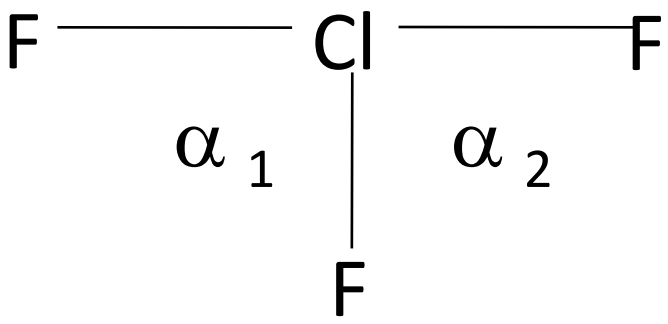
$\Gamma_{Vib.}$ =3A1+B1+2B2 = 6

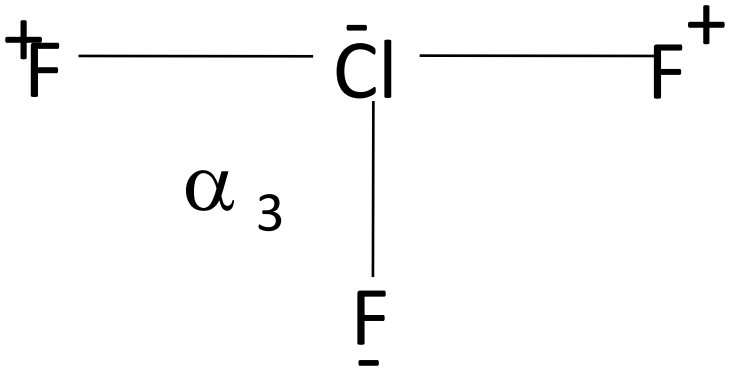
2. Internal Coordinate Method.

1. Consideration of bond vector and bond angle vector for mole.
   Number of bond vector = 3 (O-H bond)= r1 ; r2 and r3
   Number of bond angle = 3 [α1 ; α2 (in plane) and α3 (out of plane)]

   Total number of internal coordinates = 6

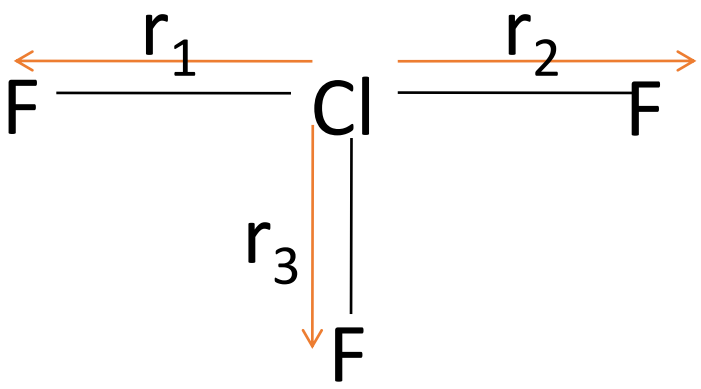


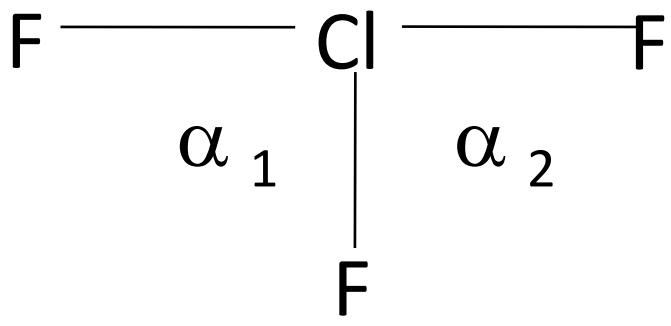


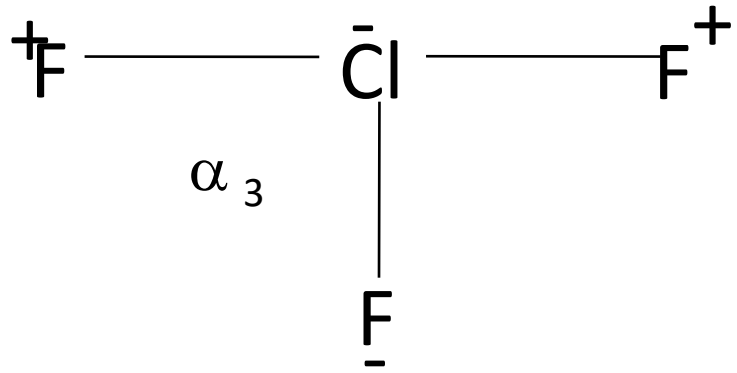


2. Workout symmetry operation on mole. In terms of above Internal modes and determine the character.

C_{2v}	E	Cn	σxy	σyz	Number of Modes
$\Gamma_{Stre.} = \Gamma_{r1}+\Gamma_{r2}+\Gamma_{r3}$	3	1	1	3	2A1+B2 = 3
$\Gamma_{bend.} = \Gamma_{\alpha1}+\Gamma_{\alpha2}$	2	0	0	2	A1 +B2= 2
$\Gamma_{bend.} = \Gamma_{\alpha3}(OOP)$	1	-1	1	-1	B1=1
$\Gamma_{vib.}$	6	0	2	4	3A1+B1+2B2 = 6







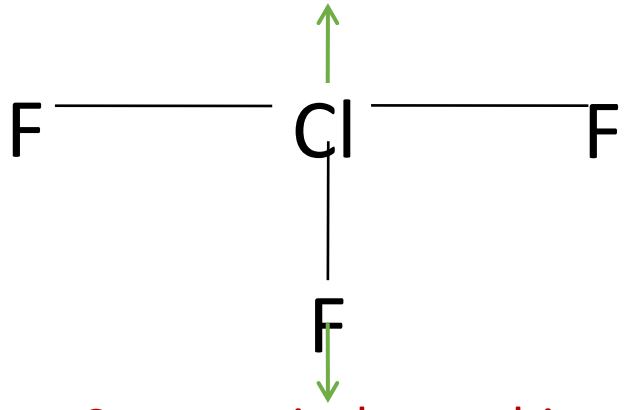
Note: when position of vector is change then character is = 0

when change of direction of vector then character is = -1

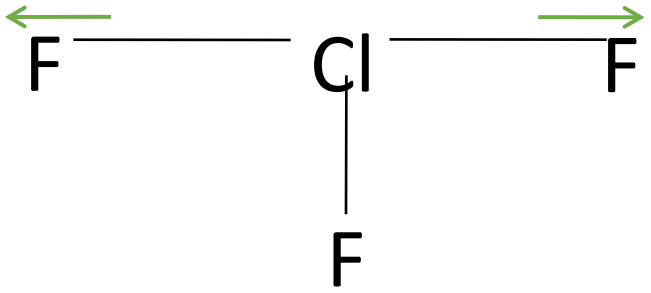
when nothing change in position and direction then character is = 1

3. Assignment of Normal Vibrational modes.

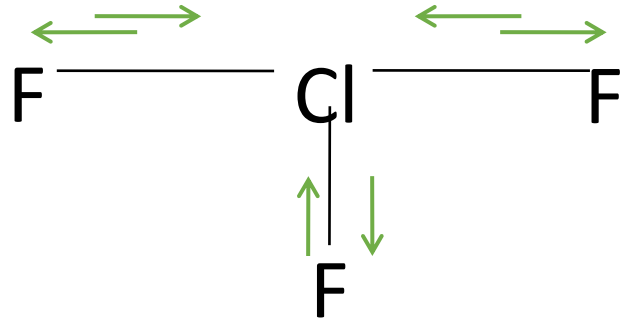
The corresponding normal modes for mole are given following fig.



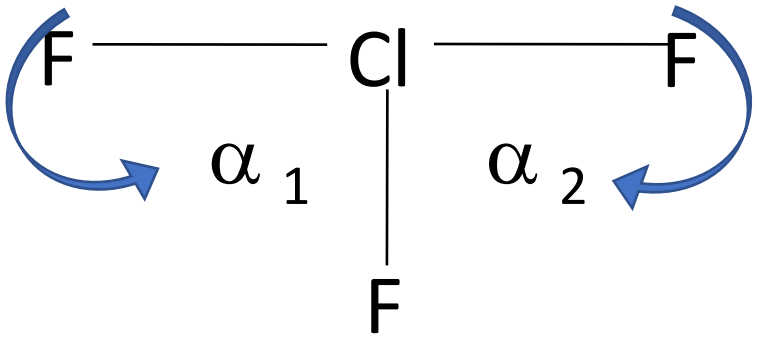
Symmetrical stretching
A1 (υ_1)



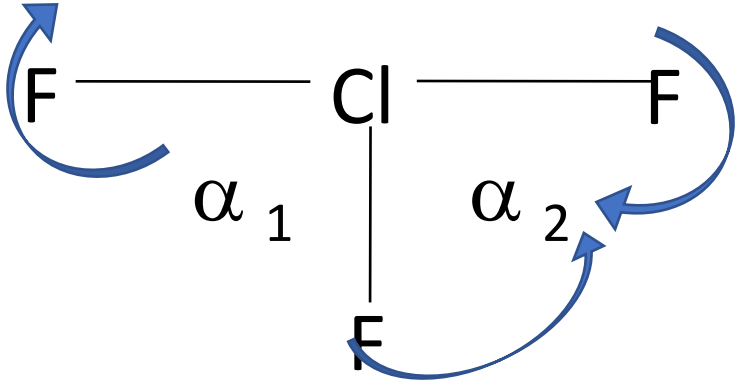
Symmetrical stretching
A1 (υ_2)



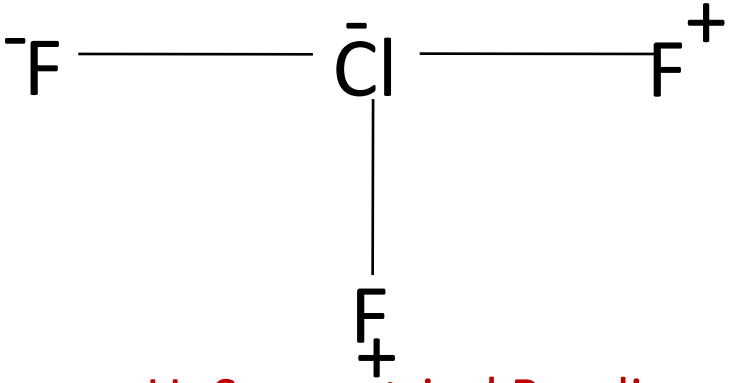
Unsymmetrical stretching
B2 (υ_3)



Symmetrical Bending
A1 (υ_4)



UnSymmetrical Bending
B2 (υ_5)



UnSymmetrical Bending
(OOP) B2 (υ_6)

4. **IR and Raman spectral activity.**

The IR frequency associated to the vibrational mode are define as

IRs is correlated with the x, y, z then IRs is IR active.

IRs is correlated with the xy,yz,zx,x2-y2 and z2 then IRs is Raman active.

$$\nu_{stre.} \succ \nu_{bend.}$$

$$\nu_{unsym.} \succ \nu_{sy.}$$

$$\nu_{in.plane.} \succ \nu_{OOP.}$$

$$\nu_{DB} \succ \nu_{SB}$$

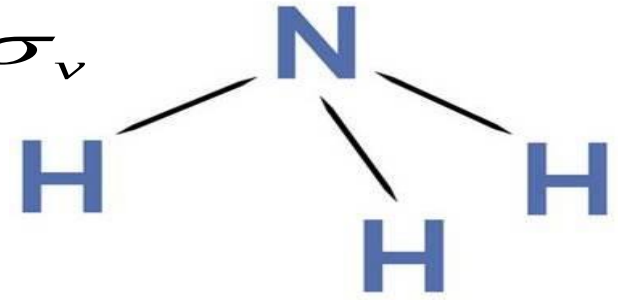
5. Determination of IR Frequency

Vibrational mode (Mulliken sym.)	Stretching Or Bending	Symmetry of Mode	IR Active	Raman Active	IR frequency (cm^{-1})
A1	Stretching	Symmetrical	Yes	Yes	$\upsilon_1 = 603$
A1	Stretching	Symmetrical	Yes	Yes	$\upsilon_2 = 528$
B2	Stretching	unsymmetrical	Yes	Yes	$\upsilon_3 = 752$
A1	Bending	Symmetrical	Yes	Yes	$\upsilon_4 = 326$
B2	Bending	unsymmetrical	Yes	Yes	$\upsilon_5 = 434$
B1	Bending(oop)	unsymmetrical	Yes	Yes	$\upsilon_6 = 364$

SYMMETRY OF NORMAL MODES OF NH_3 MOLEC ULES

1. Cartesian coordinate Method.

1. P.G. and Symmetry elements = $C_{3v} \Rightarrow E; 2C_3^1; 3\sigma_v$
2. Number of atoms= 4
3. Order of Group = 6
4. Class of Group =3
5. Total number of modes (Nonlinear Mole.) = 3N= 3(4)=12



Molecule (H2O)	Translation modes (τ_T)	Rotational modes (τ_R)	Vibrational modes(τ_{Vib})		
			Starching	Bending	Total
Non-linear	3	3	N-1	2N-5	3N-6
3N=12	3	3	3	3	6

C_3v	E	$2C_3$	$3\sigma_v$	Number of Modes
$\chi = \Gamma_T$	3	0	1	A1+E = 3
NUSA	4	1	2	
Γ_{3N}	12	0	2	3A1+A2+4E *(doublet)* = 12

Total number of modes can be obtained using Standard Reduction formula.

$$\mathbf{n(\tau_i) = \frac{1}{h}\left[\sum_i n(R) \cdot \chi_{IR(R)} \cdot \chi_{RR(R)}\right]}$$

8. Translation modes Γ_T And Rotational modes Γ_R Obtain from Character Table.

Γ_T = A1+E (*d*) = 3 (using x, y and z symbol.)

Γ_R = A2+E (*d*) = 3 (using Rx, Ry and Rz symbol)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

9. Vibrational modes modes Γ_{Vib} Obtain through

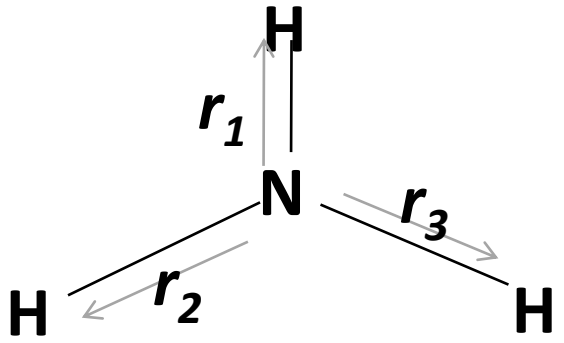
$\Gamma_{3N} = \Gamma_T + \Gamma_R + \Gamma_{Vib.}$ $\Gamma_{Vib.} = \Gamma_{3N} - (\Gamma_T + \Gamma_R)$

$\Gamma_{Vib.}$ = 3A1+A2+4E -(A1+E + A2+E)

$\Gamma_{Vib.}$ =2A1+2E(*d*) = 6

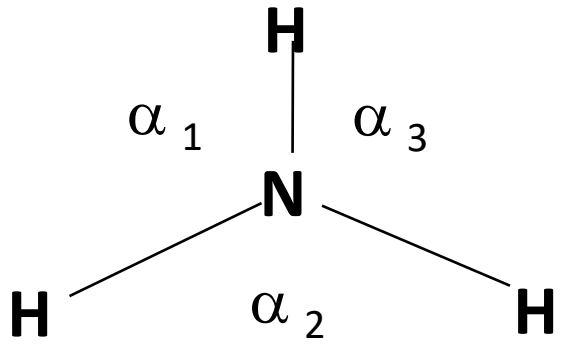
2. Internal Coordinate Method.

1. Consideration of bond vector and bond angle vector for mole.
   Number of bond vector = 3 (N-H bond)= r1 ; r2 and r3
   Number of bond angle = 3 [α1 ; α2 ; α3]
   Total number of internal coordinates = 6



2. Workout symmetry operation on mole. In terms of above Internal modes and determine the character.

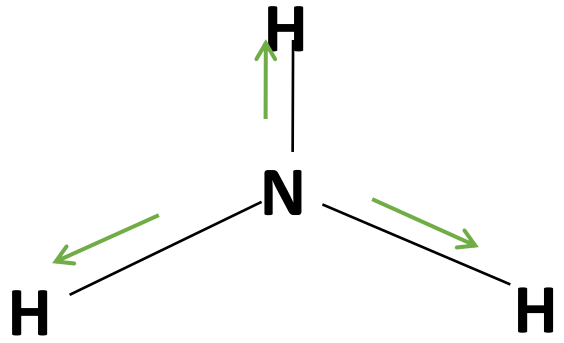
C_3v	E	$2C_3$	$3\sigma_v$	Number of Modes
$\Gamma_{Stre.} = \Gamma_{r1}+\Gamma_{r2}+\Gamma_{r3}$	3	0	1	A1+E (*d*) = 3
$\Gamma_{bend.} = \Gamma_{\alpha1}+\Gamma_{\alpha2}+\Gamma_{\alpha3}$	3	0	1	A1+E (*d*) = 3
$\Gamma_{vib.}$	6	0	2	2A1+2E = 6



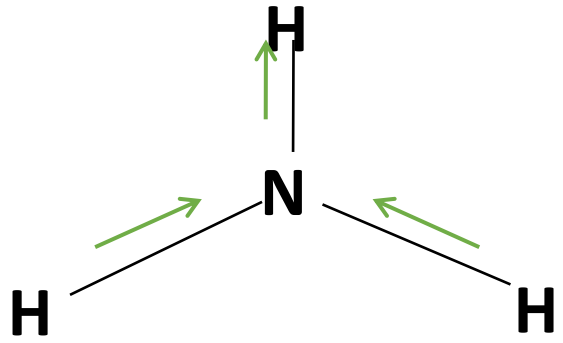
Note: when position of vector is change then character is = 0
when change of direction of vector then character is = -1
when nothing change in position and direction then character is = 1

3. Assignment of Normal Vibrational modes.

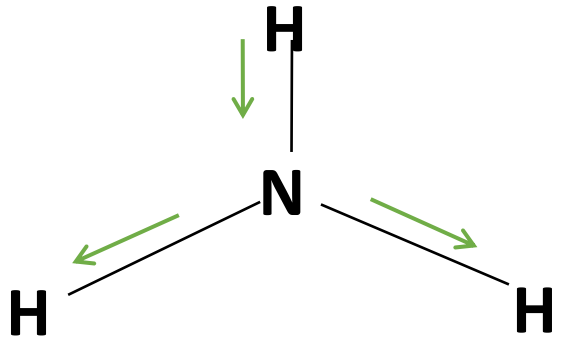
The corresponding normal modes for mole are given following fig.



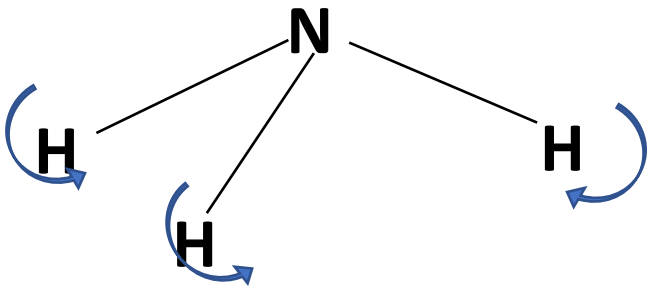
Symmetrical stretching
A1 (υ_1)



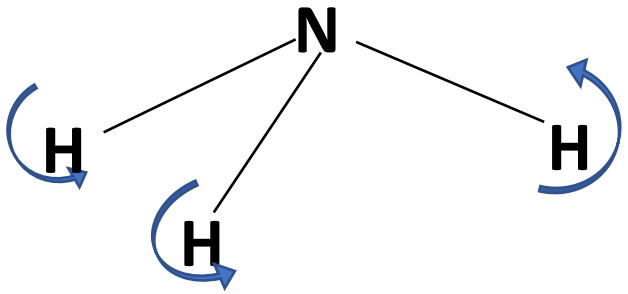
Unsymmetrical stretching
E (d) (υ_2)



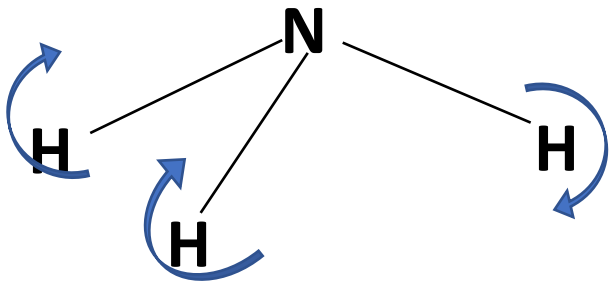
Unsymmetrical stretching
E (d) (υ_2)



Symmetrical Bending
A1 (υ_3)



UnSymmetrical Bending
E *d*(υ_4)



UnSymmetrical Bending
E *d*(υ_4)

4. IR and Raman spectral activity.

The IR frequency associated to the vibrational mode are define as

IRs is correlated with the x, y, z then IRs is IR active.

IRs is correlated with the xy,yz,zx,x2-y2 and z2 then IRs is Raman active.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

$$\nu_{stre.} \succ \nu_{bend.}$$

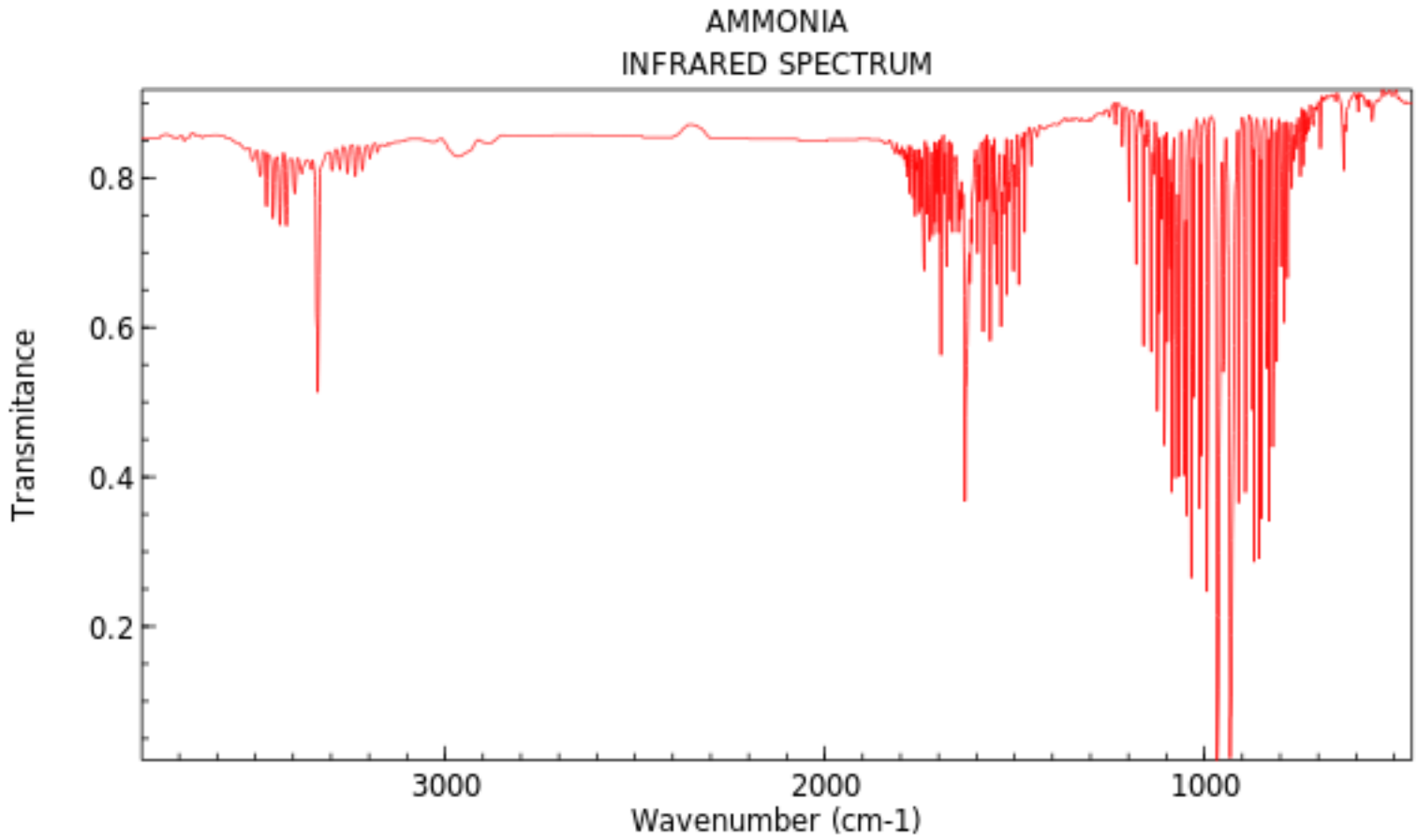
$$\nu_{unsym.} \succ \nu_{sy.}$$

$$\nu_{in.plane.} \succ \nu_{OOP.}$$

$$\nu_{DB} \succ \nu_{SB}$$

5. Determination of IR Frequency

Vibrational mode (Mulliken sym.)	Stretching Or Bending	Symmetry of Mode	IR Active	Raman Active	IR frequency (cm^{-1})
A1	Stretching	Symmetrical	Yes	Yes	3534 cm υ_1
E	Stretching (d)	unsymmetrical	Yes	Yes	3464 cm $\upsilon_{2\,(d)}$
A1	Bending	Symmetrical	Yes	Yes	1139 cm υ_3
E	Bending (d)	unsymmetrical	Yes	Yes	1765 cm $\upsilon_{4\,(d)}$



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Application of Group Theory
Determination of Hybridization of molecules.

Hybridization schemes for sigma-orbitals :

AB_3: planar triangle (BF3) and trigonal pyramidal (NH3)
AB_4: Tetrahedral (CH4) and Planar (PtCl4)
AB_5: Trigonal bipyramidal (PCl5) and square pyramidal (IF5)
AB_6: Octahedral (SF6)

Hybridization schemes for pi-orbitals :

AB_3 : planar triangle (BF3)
AB_6 : Octahedral (SF6)

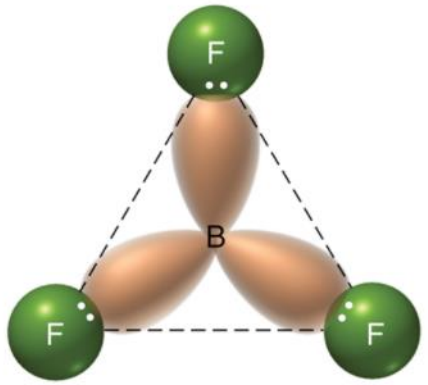
Hybridization schemes for sigma-orbitals :AB_3: planar triangle (BF_3)

$B_{(z=5)}: 1s^2, 2s^2, 2p^1$ $\quad B^*_{(z=5)}:$ 

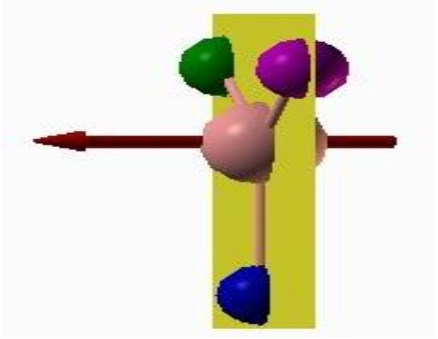
Reducible Representation of the Sigma bonding(Sigma Orbitals)

Decide the number of sigma bond unchanged during operation.

D_3h	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{RR}	3	0	1	3	0	1



D_{3h}	E	$2\,C_3$	$3\,C_2'$	σ_h	$2\,S_3$	$3\,\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)



$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R)\cdot\chi_{IR(R)}\cdot\chi_{RR(R)}\right]$$

$\Gamma_{\text{hybrid orbitals}}$: A'_1 (s) + E'(d) [*total 3 H.Os are participate to make sigma bond*]

A'_1 : Represent Hybrid orbitals of 'S' and dz2

E' : Represent Hybrid orbitals are Px; Py and dx2-y2; dxy

Possible set of Hybridization (1) SP2 (2) Sd2 (3)dP2 (4) d3

Borane atom has only 'p' orbitals so the hybridization in BF3 is Sp2

D_{3h}	E	2 C_3	3 C_2'	σ_h	2 S_3	3 σ_v		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Hybridization schemes for sigma-orbitals :AB_3: Pyramidal (NH_3)

$N_{(z=7)}: 1s^2, 2s^2, 2p^3$

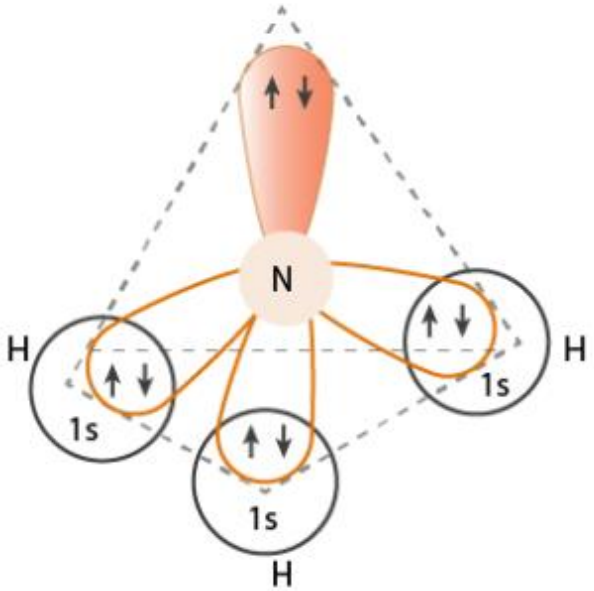
$N_{(z=7)}$: 

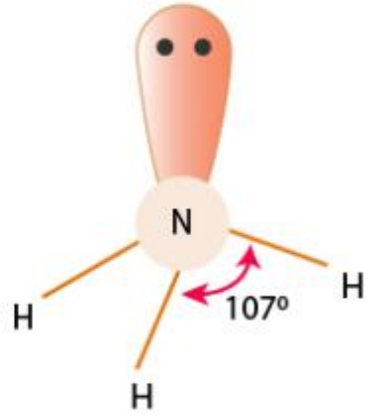
Decide the number of sigma bond unchanged during operation.

Reducible Representation of the Sigma bonding(Sigma Orbitals)

C_3v	E	$2C_3$	$3\sigma_v$
Γ_{RR}	4	1	2

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, y$





$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R)\cdot\chi_{IR(R)}\cdot\chi_{RR(R)}\right]$$

$\Gamma_{\text{hybrid orbitals}}$: $2A_1$ (s) + E (d) [*total 4 H.Os are participate to make sigma bond*]

A_1 : Represent Hybrid orbitals of 'S' and Pz and dz2

E : Represent Hybrid orbitals are (Px; Py) and (dx2-y2; dxy) and (dyz; dzx)

Possible set of Hybridization (1) SP3 (2) Sdp2 (3)pdP2 or dp3 (4) sd3 (5) spd2

Nitrogen atom has only 'p' orbitals so the hybridization in NH3 is Sp3

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

Hybridization schemes for sigma-orbitals :AB_4: Tetrahedral (CH4)

$C_{(z=6)}: 1s^2, 2s^2, 2p^2$

$C^*_{(z=6)}$: 

Decide the number of sigma bond unchanged during operation.

Reducible Representation of the Sigma bonding(Sigma Orbitals)

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_v$
Γ_{RR}	4	1	0	0	2

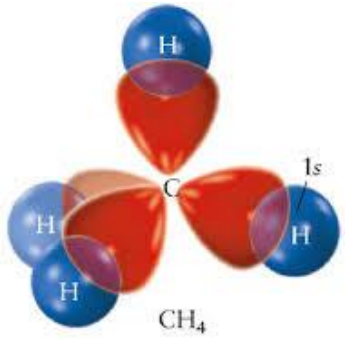
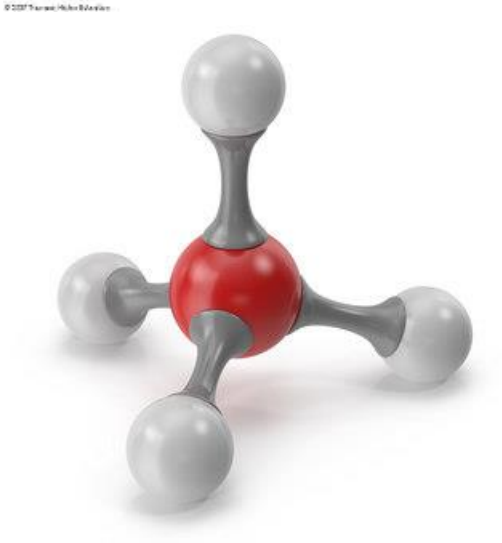


Table 1: Character table for T_d point group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)



$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R)\cdot\chi_{IR(R)}\cdot\chi_{RR(R)}\right]$$

$\Gamma_{\text{hybrid orbitals}}$: A_1 (s) + T_2 (t) [*total 4 H.Os are participate to make sigma bond*]

A_1 : Represent Hybrid orbitals is 'S'

T_2 : Represent Hybrid orbitals are (Px; Py; pz) and (dxy;dyz; dzx)

Possible set of Hybridization (1) SP3 (2) Sd3

Carbone atom has only 'p' orbitals so the hybridization in CH4 is Sp3

Table 1: Character table for T_d point group

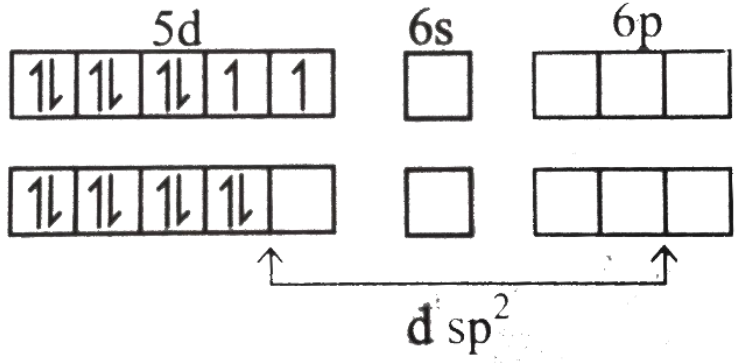
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)

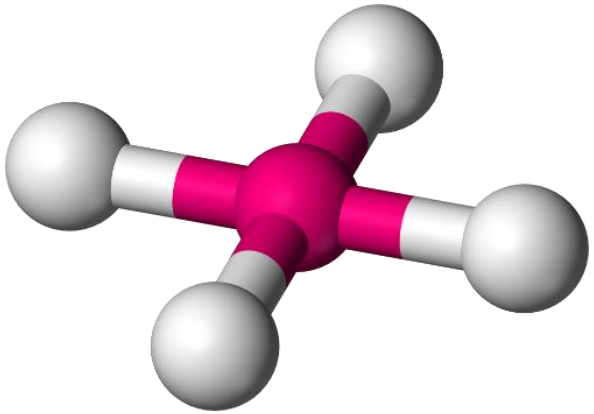
Hybridization schemes for sigma-orbitals :AB_4: Square planer (PtCl4)

$Pt\ (Z = 78) \Rightarrow 5d^8\ 6s^2,\ Pt^{2+} \Rightarrow 5d^8.$

$Pt^{+2}\ (5d^8\ 6s^0\ 6p^0)$

$[PtCl_4]^{2-}$





	4	0	0	2	0	0	0	4	2	0		
D_{4h}	**E**	**$2C_4$**	**C_2**	**$2C_2'$**	**$2C_2''$**	***i***	**$2S_4$**	**σ_h**	**$2\sigma_v$**	**$2\sigma_d$**		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R) \cdot \chi_{IR(R)} \cdot \chi_{RR(R)}\right]$$

$\Gamma_{\text{hybrid orbitals}}$: A_{1g} (s) +B_{1g} (s) + E_u (d) [*total 4 H.Os are participate to make sigma bond*]

A_{1g} : Represent Hybrid orbitals is 'S' and dz2

B_{1g} : Represent Hybrid orbitals is dx2-y2

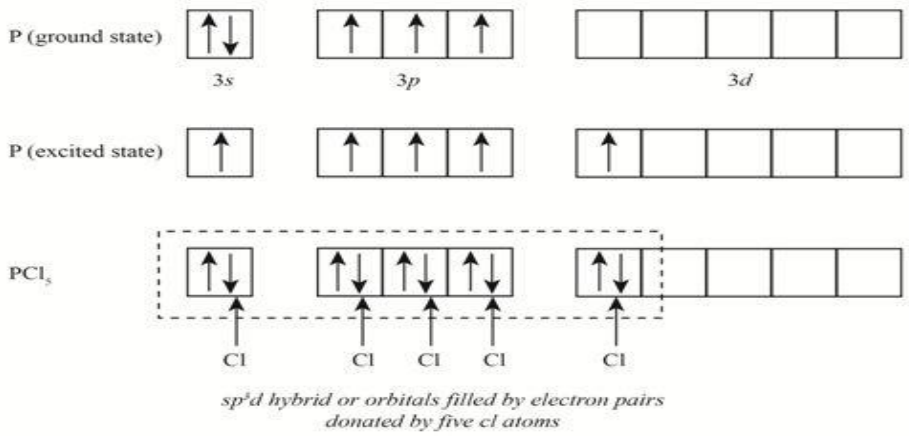
E_u : Represent Hybrid orbitals are (Px; Py)

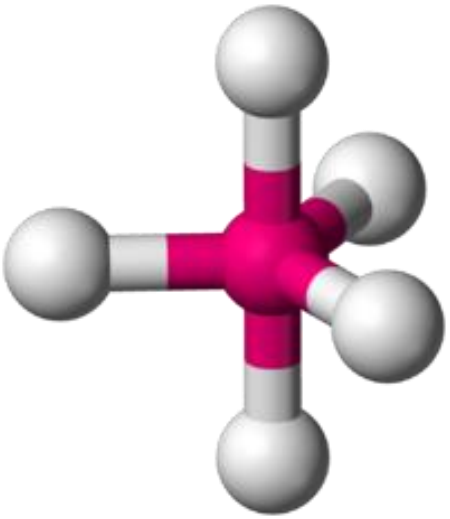
Possible set of Hybridization (1) SdP2 OR dsp2 (2) d2p2

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Hybridization schemes for sigma-orbitals :AB_5: Trigonal pyramidal (PCl5)

P(z=15)





	5	2	1	3	0	3	D_3h	
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R)\cdot\chi_{IR(R)}\cdot\chi_{RR(R)}\right]$$

$\Gamma_{\text{hybrid orbitals}}$: $2A'_1$ (s) $+A''_2$ (s) + E' (d) [*total 5 H.Os are participate to make sigma bond*]

A'_1 : Represent Hybrid orbitals is 'S' and dz2

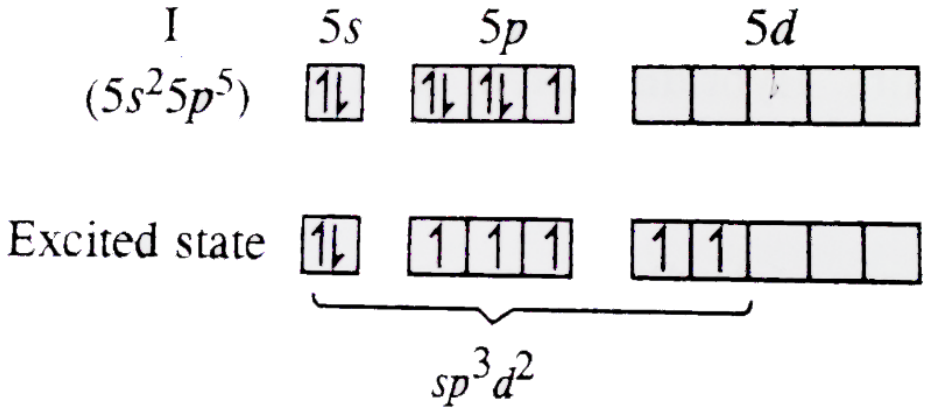
A''_2 : Represent Hybrid orbitals is Pz

E' : Represent Hybrid orbitals are (Px; Py) and(dx2-y2, dxz)

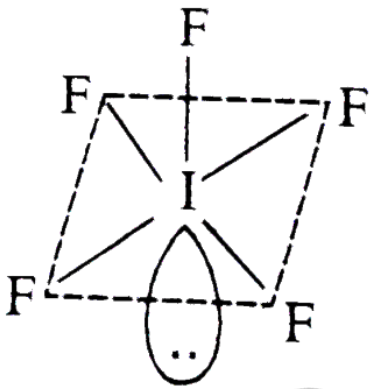
Possible set of Hybridization (1) SdP3 OR sp3d (2) sd3p

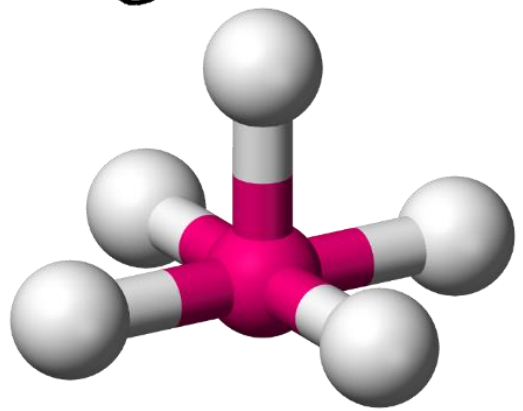
Hybridization schemes for sigma-orbitals :AB_5: Squar pyramidal (IF5)

I(z=15)



	6	2	2	4	2	C4v	
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x,y)(R_x,R_y)$	(xz,yz)





$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R)\cdot\chi_{IR(R)}\cdot\chi_{RR(R)}\right]$$

$\Gamma_{\text{hybrid orbitals}}$: $3A_1$ (s) +B_1 (s) + E (d) [*total 6 H.Os are participate to make sigma bond*]

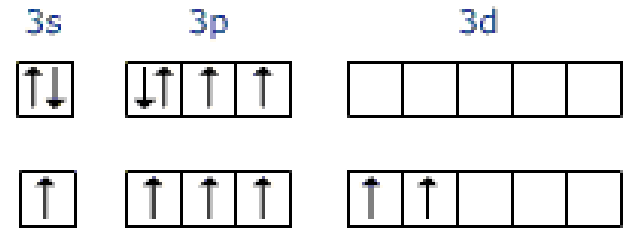
$3A_1$: Represent Hybrid orbitals is 'S' , Pz and dz2

B_1 : Represent Hybrid orbitals is dx2-y2

E : Represent Hybrid orbitals are (Px; Py) and(dxy, dyz)

Possible set of Hybridization (1) Spddp2 OR sp3d2 (2) spddd2 OR spd4

Hybridization schemes for sigma-orbitals :AB_6: Octrahedral (SF6)



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Irreducible components
Γ_π	6	0	0	2	2	0	0	0	4	2	$a_{1g} + e_g + t_{1u}$

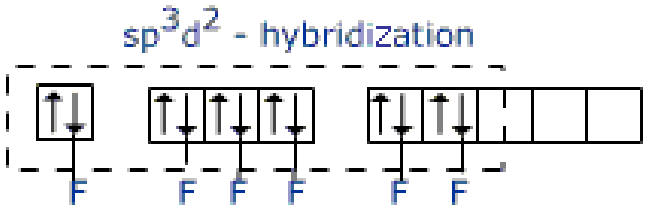
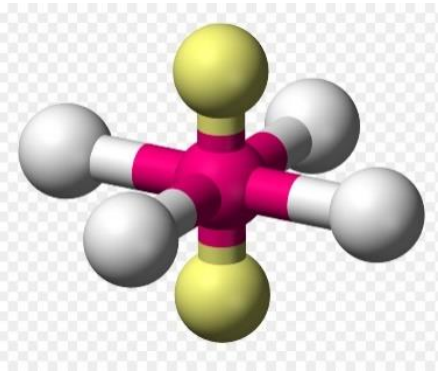


Table 2: Character table for O_h point group

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

$$n(\tau_i) = \frac{1}{h}\left[\sum_i n(R)\cdot\chi_{IR(R)}\cdot\chi_{RR(R)}\right]$$



$\Gamma_{\text{hybrid orbitals}}$: A_{1g} (s) +T_{1u} (t) + Eg (d) [*total 6 H.Os are participate to make sigma bond*]

A_{1g} : Represent Hybrid orbitals is 'S'

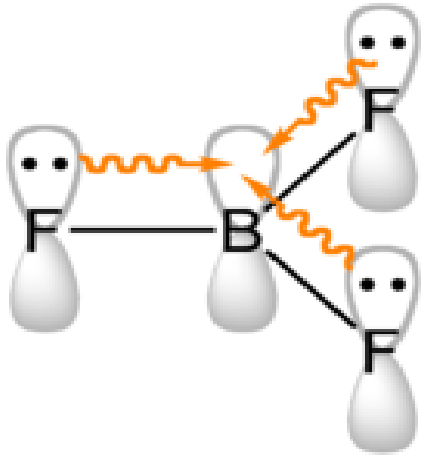
T_{1u} : Represent Hybrid orbitals is Px,Py,Pz

E_g : Represent Hybrid orbitals are (dx2-y2, dz2)

Possible set of Hybridization (1) Sp3d2

Hybridization schemes for pi-orbitals :

AB_3 : planar triangle (BF3)



$\Gamma_{\text{Pi -orbitals}}$: A_2"(s) +E" (d)

[*total 3 H.Os are participate to make Pi bond*]

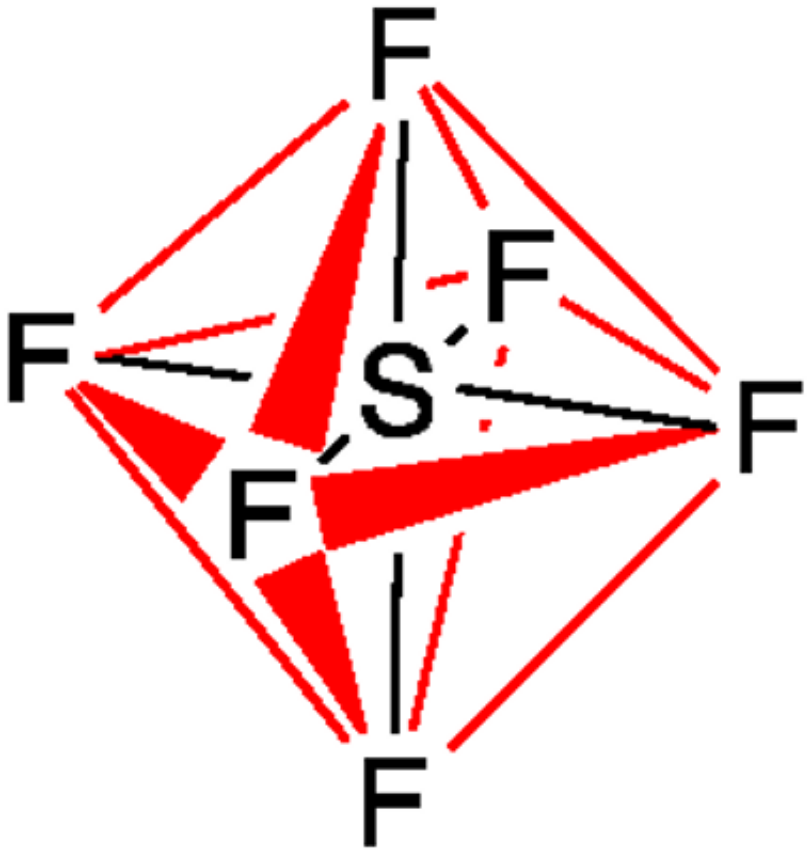
$A"_2$: Represent H.O is Pz

E" : Represent H.O are dxy & dyz

D_3h	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{RR}	3	0	-1	-3	0	1

D_{3h}	E	$2\,C_3$	$3\,C_2'$	σ_h	$2\,S_3$	$3\,\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Hybridization schemes for pi-orbitals : AB_6 : Octahedral (SF6)



$\Gamma_{\text{Pi -orbitals}}$: $T_{1g}(t) + T_{2g}(t) + T_{1u}(t) + T_{2u}(t)$

[*total 12 H.Os are participate to make Pi bond*]

Oh	E	8C3	6C2	6C4	3C2	i	6S4	8S6	3σh	6σd
Γ_{Pi}	12	0	0	0	-4	0	0	0	0	0

$\Gamma_{\text{Pi -orbitals}}$: $T_{1g}(t) + T_{2g}(t) + T_{1u}(t) + T_{2u}(t)$

[*total 12 H.Os are participate to make Pi bond*]

Table 2: Character table for O_h point group

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Direct Product

C_{4v} (4mm)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	−1	1	1	−1
B_2	1	−1	1	−1	1
E	2	0	−2	0	0

XeOF4

1. The direct product of any representation with the totally symmetric (A1) is the representation itself.

A1 × A2 = A2 A1 × B2 = B2 A1 × E = E

C4v	E	2C4	C2	2σv’	2σv’’
A1	1	1	1	1	1
A2	1	1	1	-1	-1
A2	1	1	1	-1	-1

2. The direct product of non -degenerate representation (A,B) is a non- degenerate representation also.

B1 × B2 = A2 B1 × A2 = B2 B2 × A2 = B1

C4v	E	2C4	C2	2σv’	2σv’’
B1	1	-1	1	1	-1
B2	1	-1	1	-1	1
A2	1	1	1	-1	-1

C_{4v} $(4mm)$	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	−1	1	1	−1
B_2	1	−1	1	−1	1
E	2	0	−2	0	0

3. The direct product of non -degenerate representation (A,B) and degenerate (E,T) representation is a degenerate representation.

$B1 \times E = E$ $A2 \times E = E$

C4v	E	2C4	C2	2σv'	2σv''
B1	1	-1	1	1	-1
E	2	0	-2	0	0
E	2	0	-2	0	0

4. The direct product of non- degenerate representation (A,B) with itself is a totally symmetric representation.

$B1 \times B1 = A1$ $B2 \times B2 = A1$ $A2 \times A2 = A1$

C4v	E	2C4	C2	2σv'	2σv''
B1	1	-1	1	1	-1
B1	1	-1	1	1	-1
Γ red	1	1	1	1	1

5. The direct product of degenerate representation (E,T) is a reducible representation.

$E \times E = \Gamma$ reducible

C4v	E	2C4	C2	2σv'	2σv''
E	2	0	-2	0	0
E	2	0	-2	0	0
Γ red	4	0	4	0	0

Using reduction formula, Γ red = A1+A2+B1+B2

Direct Product table for XeOF4 (C4v Point Group)

C4v	A1	A2	B1	B2	E
A1	A1	A2	B1	B2	E
A2	A2	A1	B2	B1	E
B1	B1	B2	A1	A2	E
B2	B2	B1	A2	A1	E
E	E	E	E	E	A1+A2+B1+B2

Hint for Direct Products:

$A \times A = A$ $B \times B = A$ $A \times B = B$	$1 \times 1 = 1$ $2 \times 2 = 1$ $1 \times 2 = 2$
$g \times g = g$ $u \times u = g$ $g \times u = u$	$' \times ' = '$ $'' \times '' = '$ $' \times '' = ''$

Direct Products 2

For C_2, C_3, C_6, D_3, D_6, C_{2v}, C_{3v}, C_{6v}, C_{2h}, C_{3h}, C_{6h}, D_{3h}, D_{6h}, D_{3d}, S_6

	A_1	A_2	B_1	B_2	E_1	E_2
A_1	A_1	A_2	B_1	B_2	E_1	E_2
A_2		A_1	B_2	B_1	E_1	E_2
B_1			A_1	A_2	E_2	E_1
B_2				A_1	E_2	E_1
E_1					$A_1 + [A_2] + E_2$	$B_1 + B_2 + E_1$
E_2						$A_1 + [A_2] + E_2$