MOLECULAR SYMMETRY

Dr. G L Jadav
Assistant Professor (Chemistry)









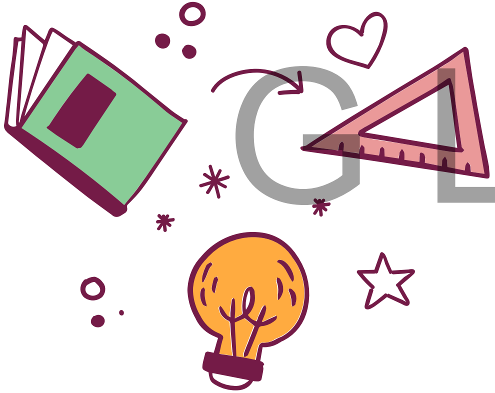
Whoa!

WHAT IS SYMMETRY AND WHY IT IS IMPORTANT

“ I can’t define symmetry but I know it when I see it”

—Unkown

Sym-metros



The word Symmetry comes
Greek words: sym meaning
metros meaning Measure. I.
Measure

- That which has symmetry si
  measurements
- Symmetry is an important component of Art and what we as humans call beauty.
- Human Beings are programmed to look for symmetry. Babies quickly recognize the bilateral symmetry of a mothers face.

Use of SYMMETRY

1

Detect whether a molecular structure will be optical active or have dipole moments

2

Predict and understand whether a molecular structure will be IR or Raman Spectroscopy active

3

Form molecular orbitals

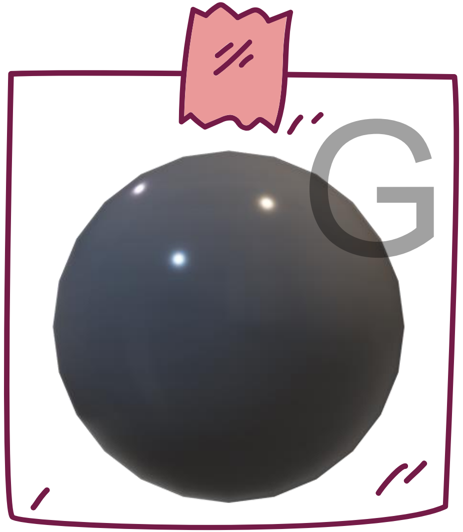
4

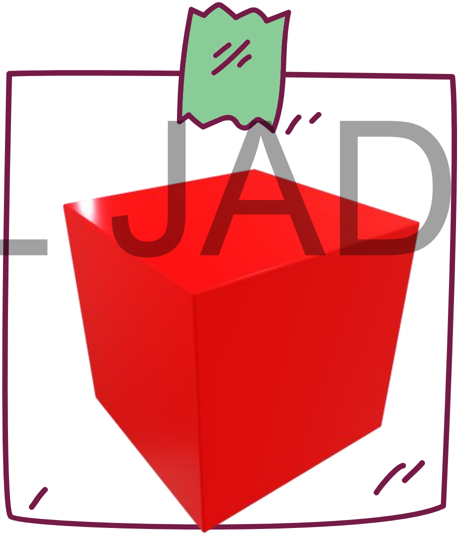
Predict and understand which molecular orbital transitions will be UV visible active

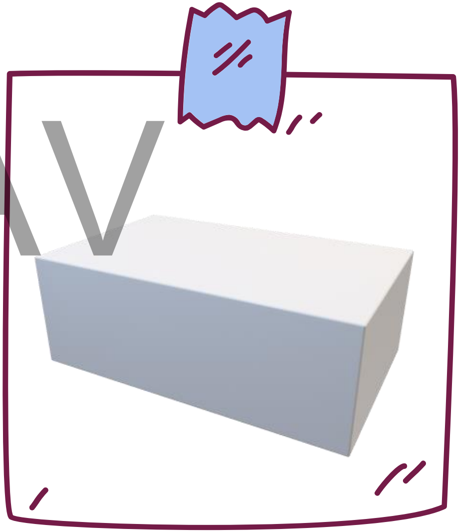
In Chemistry SYMMETRY is a powerful mathematical tool for understanding structure and properties of molecules

How do we determine Molecular Symmetry? Sometimes the answer can be obtained simply.

What has a higher relative symmetry, a sphere, a cube or a parallelbiped (rectangular box)?

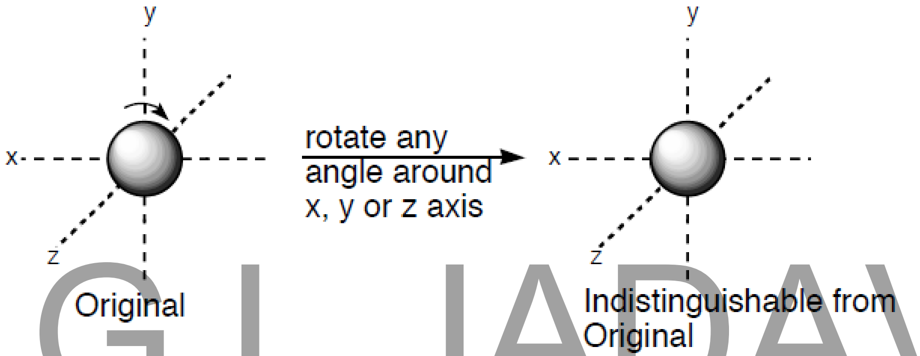




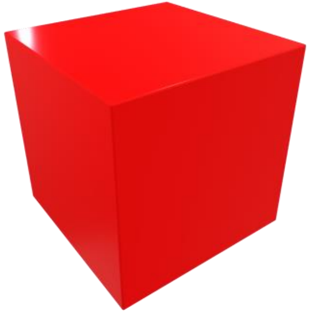


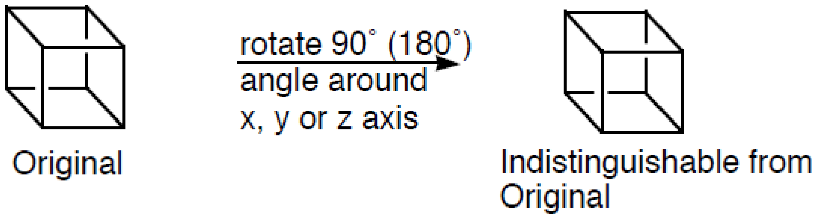
COMPARISON OF RELATIVE SYMMETRY

SPHERE



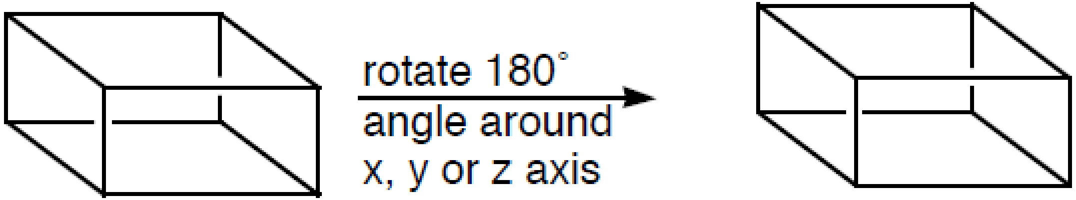
CUBE



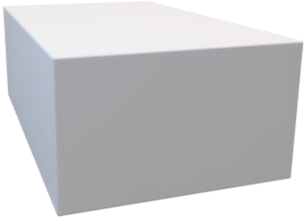


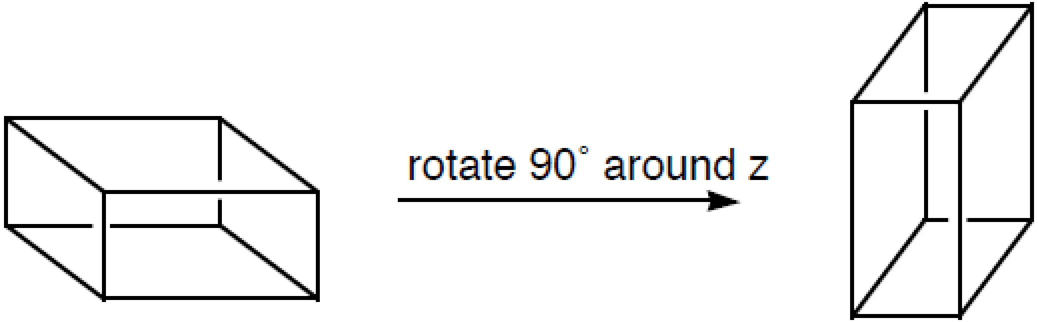
BUT ANGLES OTHER THAN 90° RESULTS IN DISTINGUISHABLE REPRESENTATIONS

PARALLELBIPED



BUT ANGLES OF 90° RESULTS IN DISTINGUISHABLE REPRESENTATIONS





IMPORTANT TERMS

SYMMETRY

Invariance to transformation (Object appears unchanged)

SYMMETRY ELEMENT

Operation that transforms an object

SYMMETRY ELEMENT

Feature that permits transformation

Point group

Collection
Symmetry elements
operations

1
IDENTITY

Doing nothing

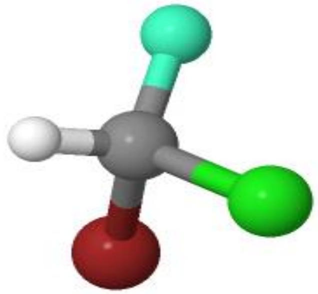
IDENTITY – E

- No operation or operation bringing back original molecule
- eg. H_2O on $360°$ rotation
- All molecules have identical structure called identity
- $C_n^n = E$, $\sigma^2 = E$, $i^2 = E$, $S_n^k = E$ (k even), $S_n^{2k} = E$ (k odd)

The Identity Operation (E)

- The identity operation is the simplest of all -- do nothing! It may seem pointless to have a symmetry operation that consists of doing nothing, but it is very important. All objects (and therefore all molecules) at the very least have the identity element. There are many molecules that have no other symmetry.
- the following molecule contain no other symmetry other than identity:

- CHFClBr



Proper Axis of symmetry C_n

Rotation about axis

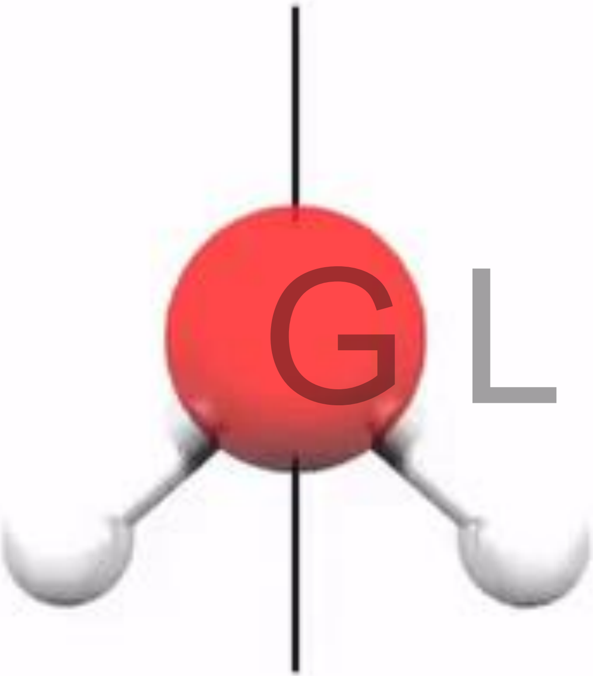
Proper axis of symmetry Cn

The rotation operations (both proper and improper) occur with respect to line called an axis of rotation.

$n = 360°/\theta$

θ = minimum angle of rotation to get equivalent orientation

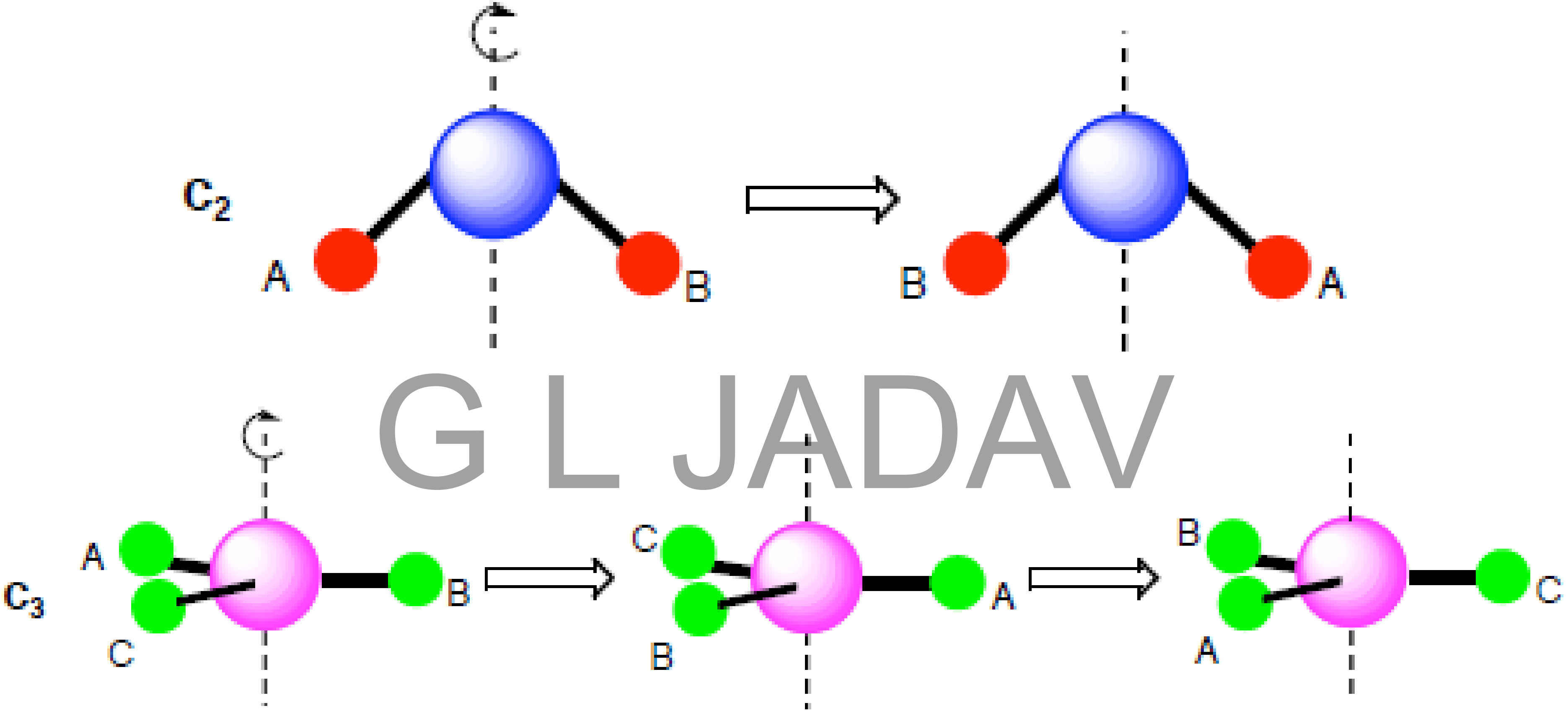
- If the resulting configuration is indistinguishable from the original, we say there exists an *n*-fold proper rotation axis (or C_n axis) in the molecule.



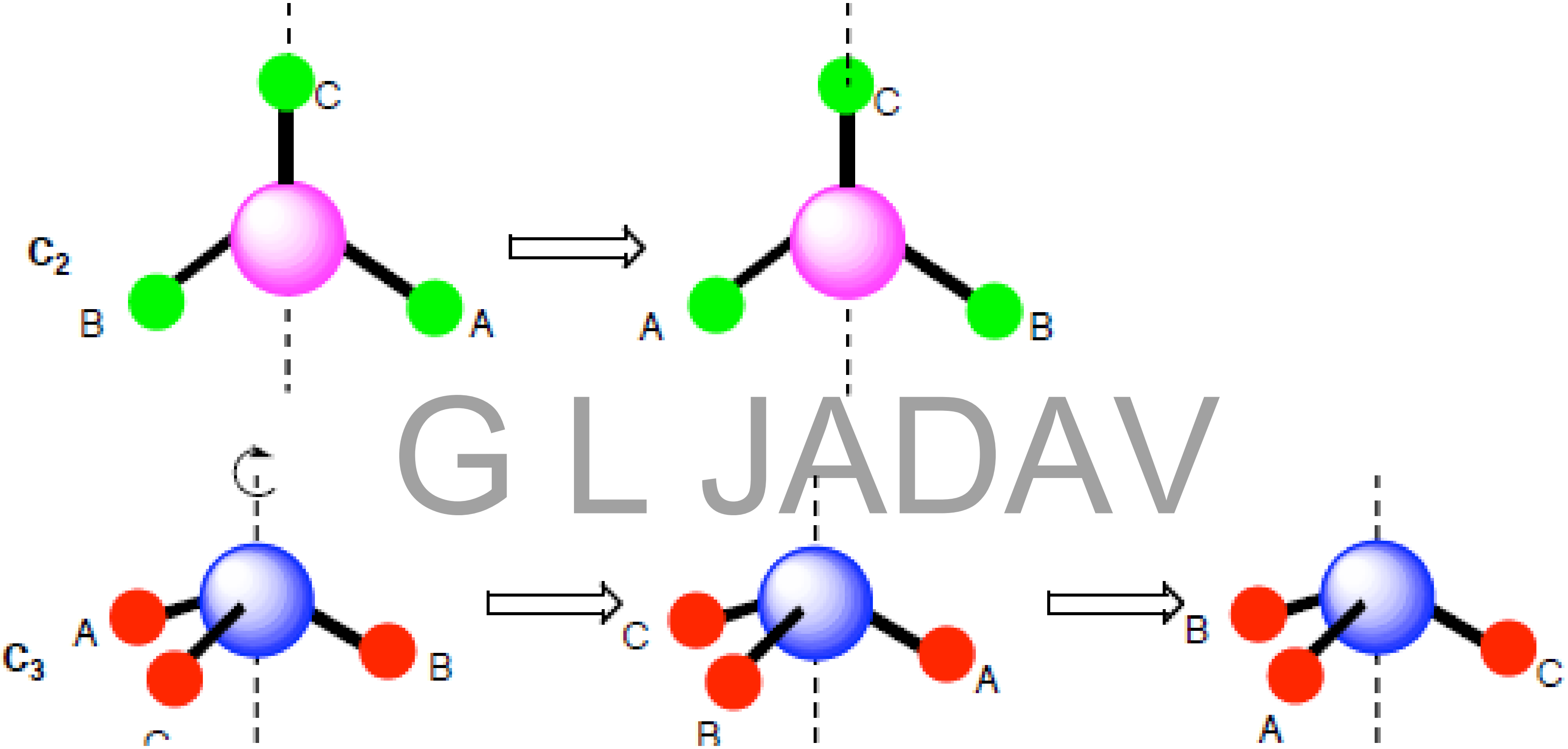
- In symmetry
- Rotation -> anti clockwise = C_n^k
- IF clockwise = C_n^{-k}

Each of the following molecules contains one or more proper axis:

- The water molecule contains a C2 axis
- Ethane contains both C2 and C3 axes



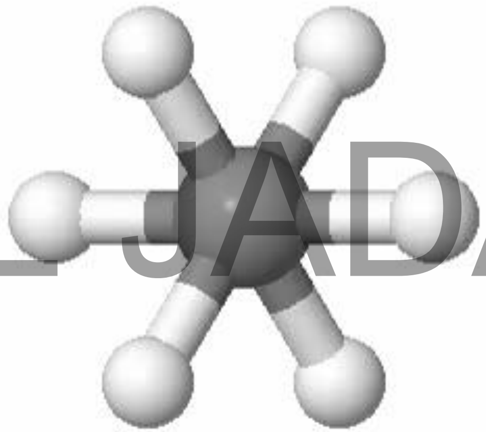
Axis of symmetry



Axis of symmetry

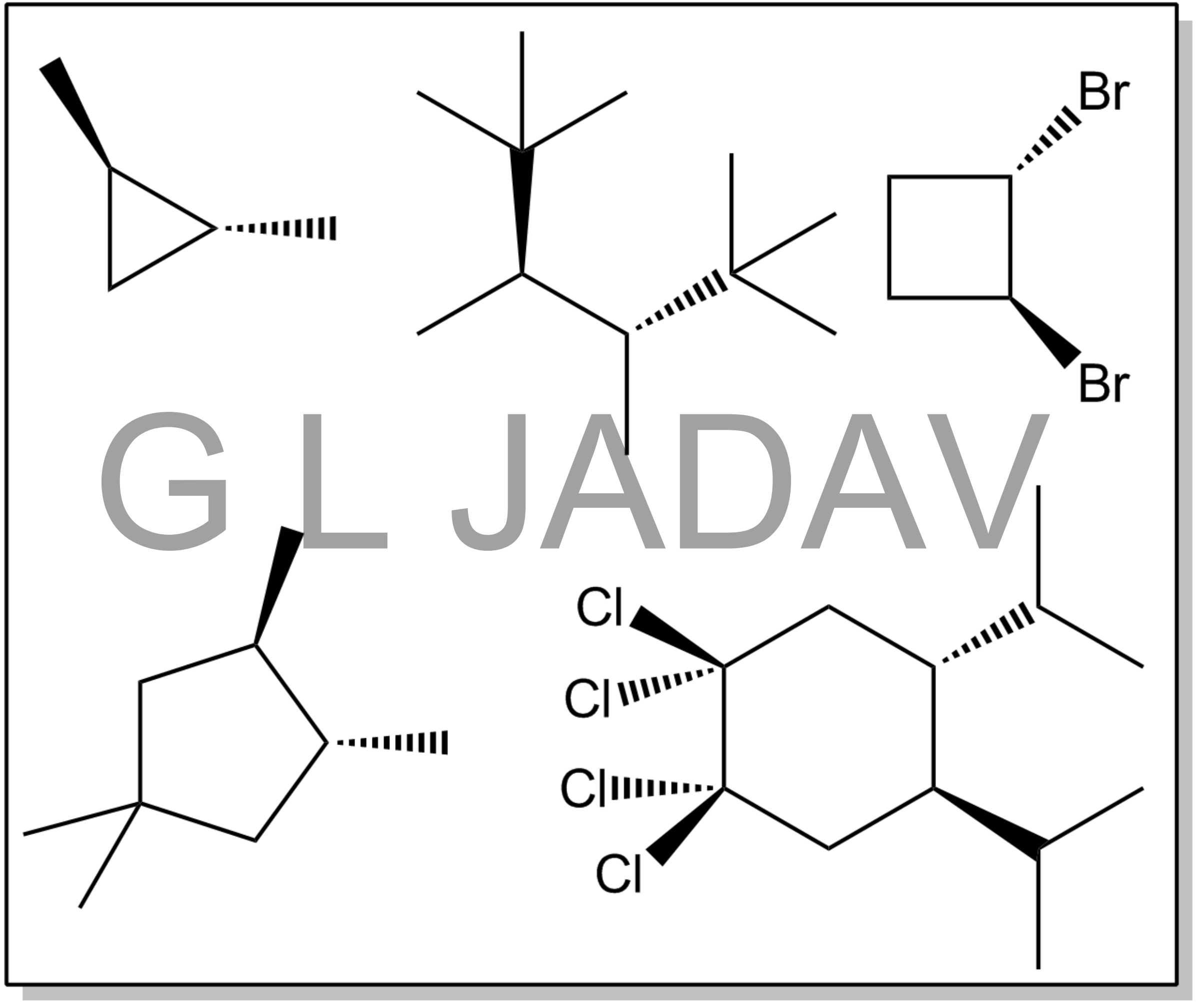
White Board

G L JADAV



- $[Ni(CN)_4]^{-2}$
- $[Pt(Cl)_4]^{-2}$
- Four fold axis of symmetry passing through Ni and Pt and Perpendicular to Plane
- Angle of rotation = 90° and C_4
- Benzene
- C_6 θ = 60, One C_6 and two C_2

G L JADAV


Br
Br
Cl
Cl
Cl
Cl

Selection of Principle axis

1

Axis with highest fold symmetry

BF_3

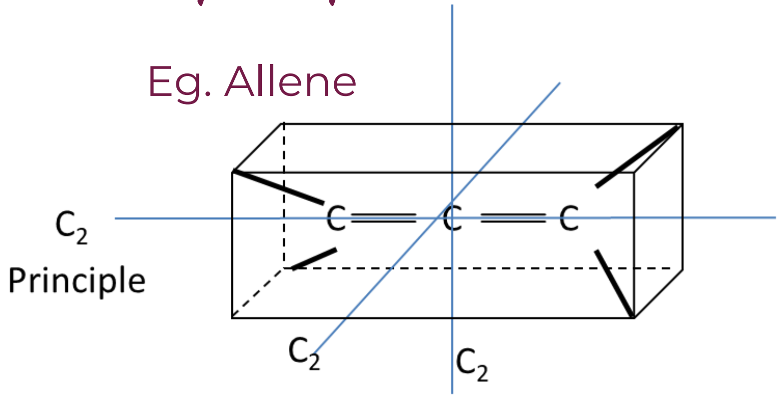
3 two fold & 1 three fold

Thus 3 fold axis C3 is principle axis

2

More than one axis of same order then axis passing through maximum number of atoms is principal axis

Eg. Allene



Some important points

A

C_∞ axis

Infinite fold symmetry

e.g. HCl, H_2 any rotation equivalent orientation

B

$C_2 \rightarrow C_2'$, $\theta = 180$,

$C_2^2 = E = 360$ (original)

One operation

C

Possible no. of symmetry operation

C_n axis is n-1, nth is the original

D

$C_3 \rightarrow C_3'$ (120),

C_3^2 (240), C_3^3 (360) (orig.)

Two operations

Lets revise

Order of axis :-

n = 360 / θ ,

number of equivalent structure including original

Principal Axis :- highest order

Subsidiary axis :- All other axis other than principle

e.g. BF_3, $C_3 - 3C_2$

NH_3- $1C_3$

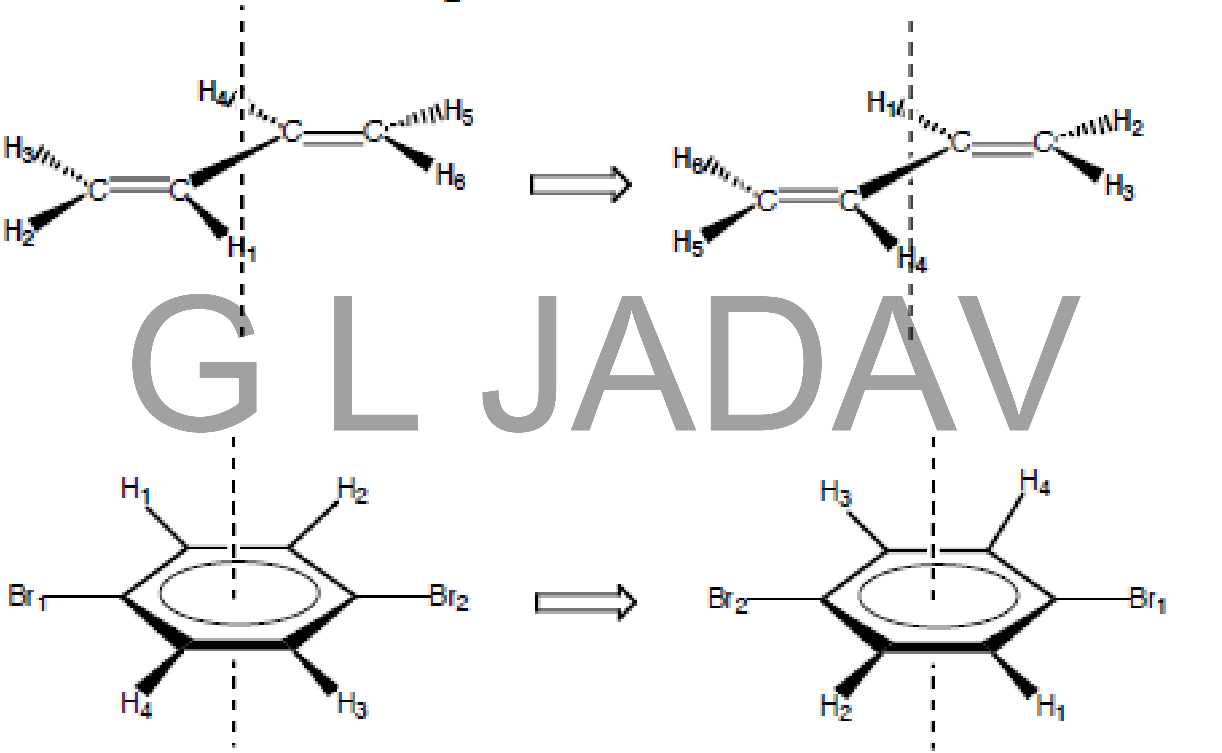
CCl_4, $4C_3 - 3C_2$

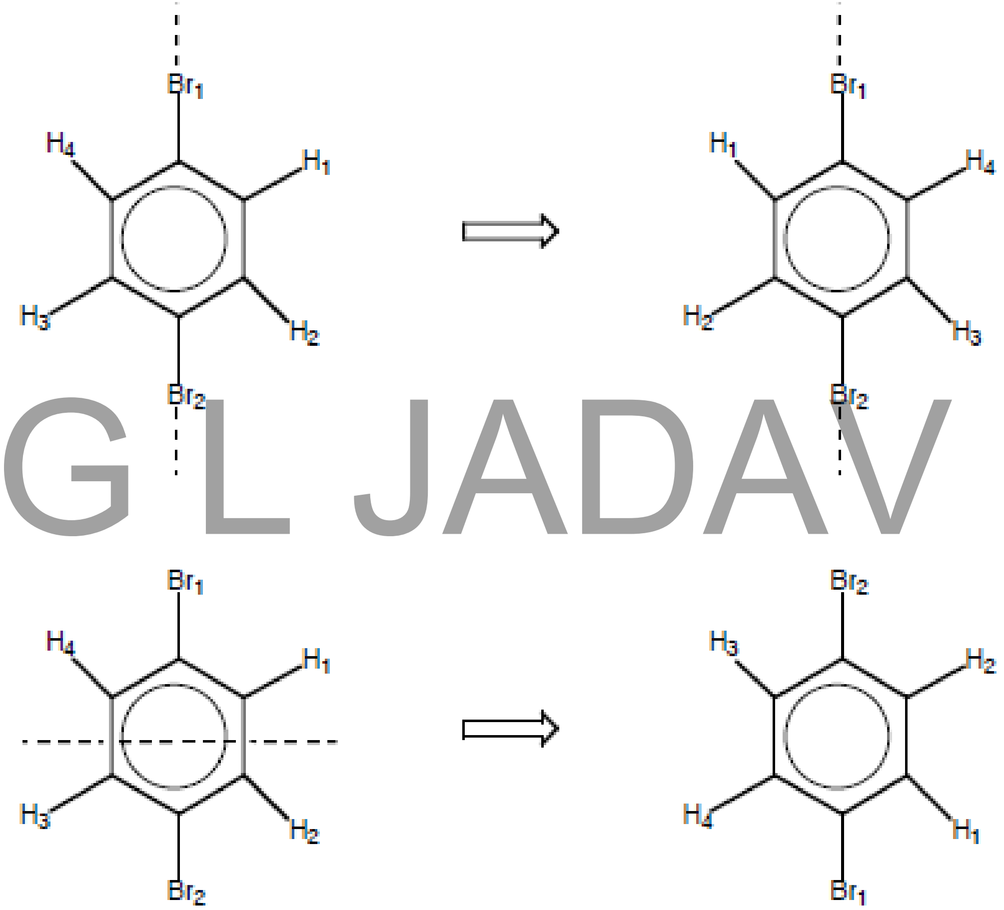
PCl_5, $1C_3 - 3C_2$

N_2O- Nitrous oxide

$N \equiv N \rightarrow O$ Laughing gas

C_2 Rotational Axes

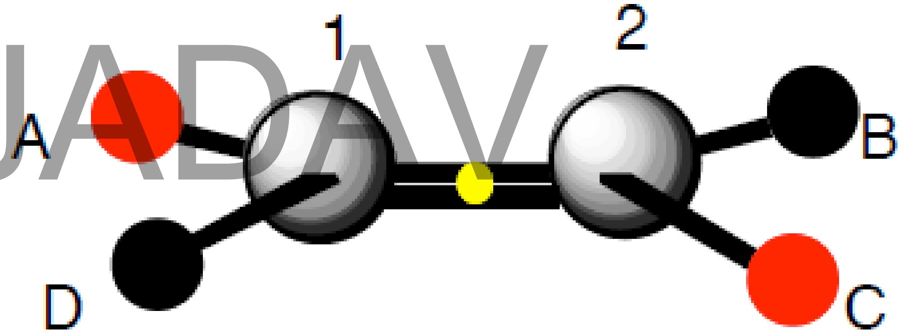



Br1
H4
H1
H3
H2
Br2
Br1
H1
H4
H2
H3
Br2
Br1
H4
H1
H3
H2
Br2
Br2
H3
H2
H4
H1
Br1

CENTER OF INVERSION (i) / Inversion Center

You Can Use Some Graphs

Inverts all atoms through the center of the object. Extended equally opposite side



Center of inversion

Denoted by i

Reflection

Center

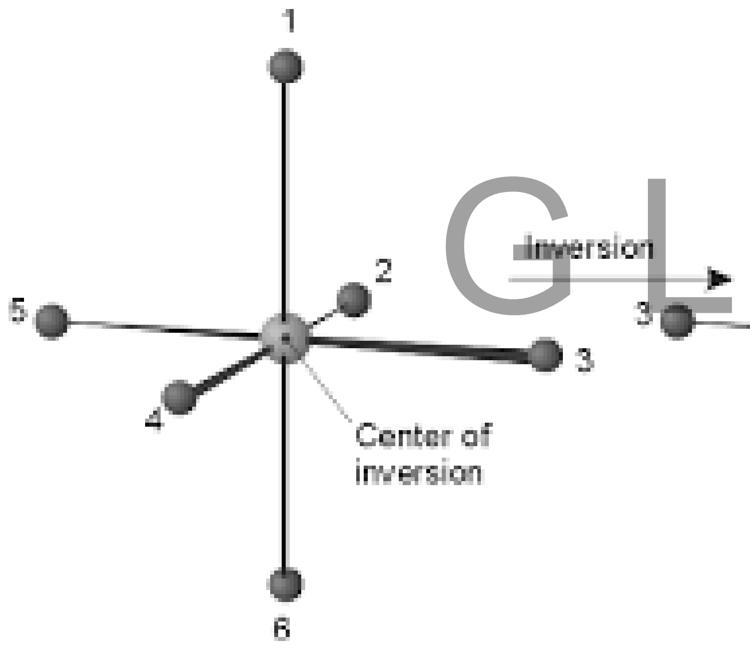
Equivalent atom

Inversion operation

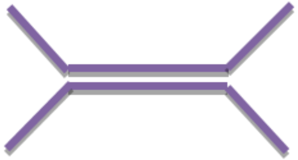
Only one center of symmetry in one molecule

$i^2 = E$, one i,

2nd i will give E, original orientation

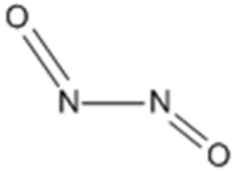


XeF_4 

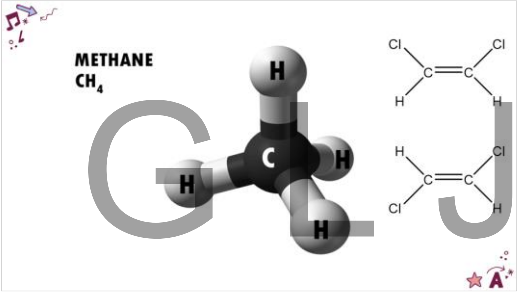
C_2H_4 

CO_2

$_1O{=}{=}C{=}{=}O_2$

N_2O_2 

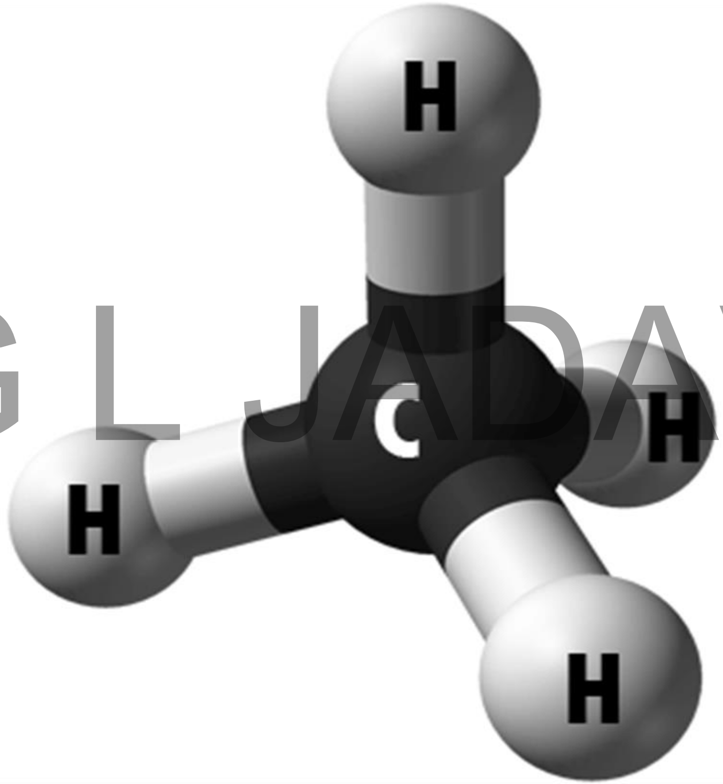
Center of Symmetry in Methane

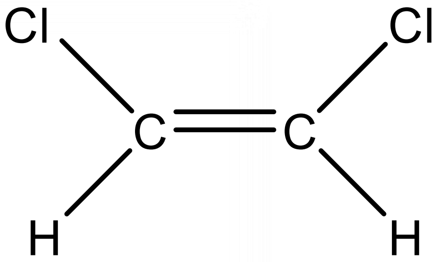


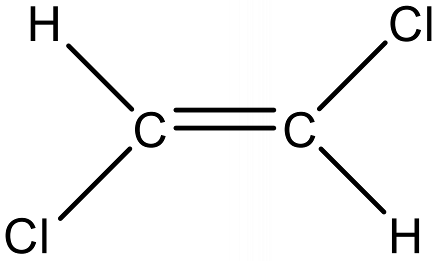
Tetrahedral Structure
No Center of Symmetry
Present
In
Methane Molecule

METHANE

CH_4



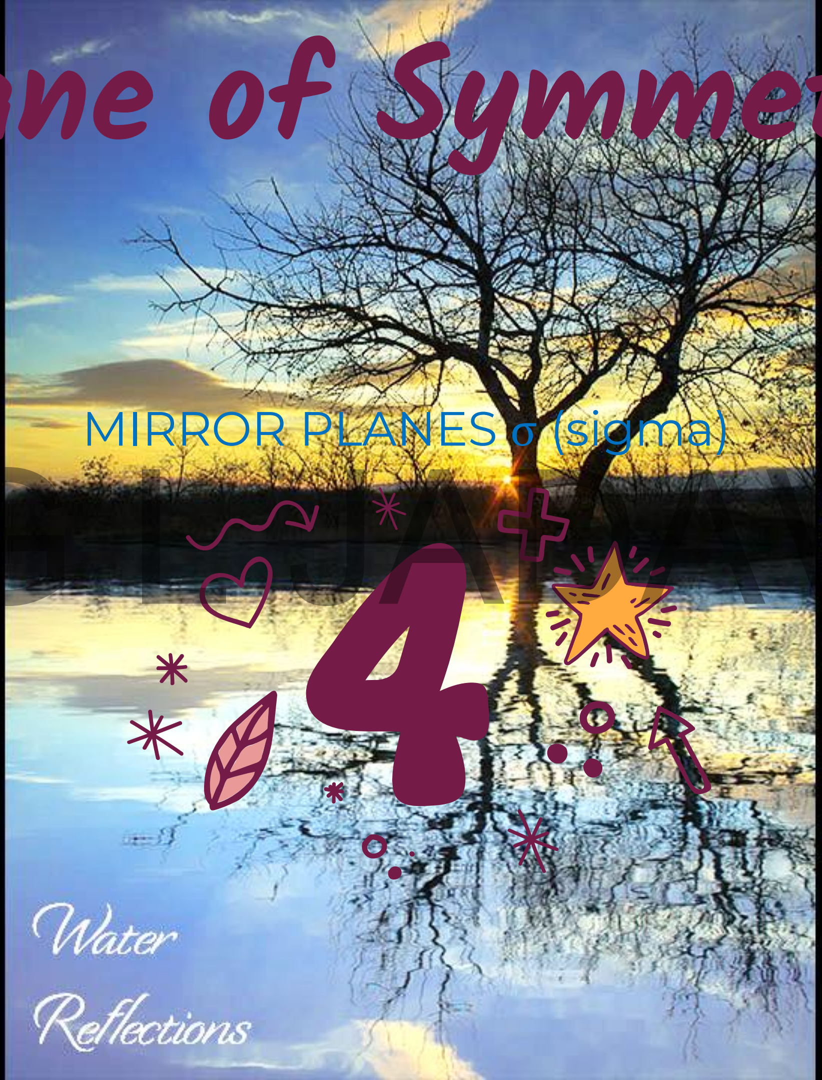




Plane of Symmetry

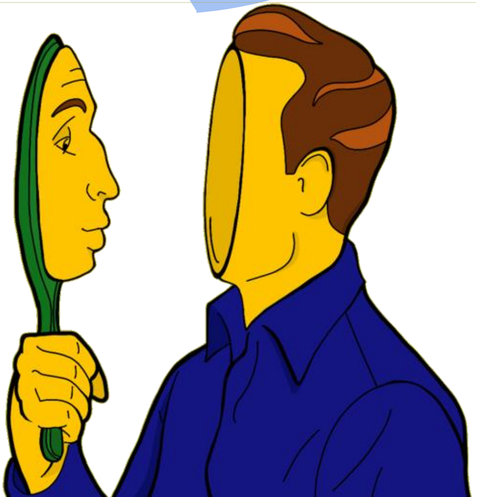
MIRROR PLANES σ (sigma)

4



"An imaginary plane which divides the molecules in two equal parts and if these two parts are mirror image of each other such imaginary plane is called as Plane of Symmetry"

—*Plane of Symmetry*



- Reflection of object through a mirror plane: Objects in the plane are reflected onto themselves, objects on either side of the plane are reflected to opposite side.

Types of Plane of Symmetry

σ_v

Vertical, parallel to principle axis

σ_h

Horizontal, perpendicular to principle axis Cn (with largest n)

σ_d

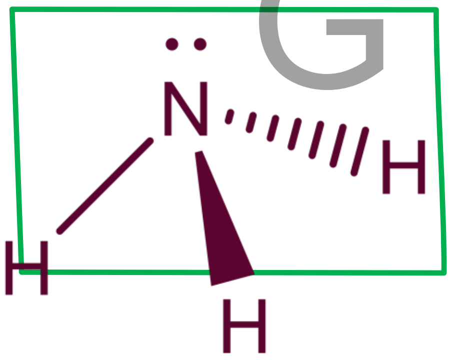
Dihedral, same plane as v but related by half a rotation of the principle axis

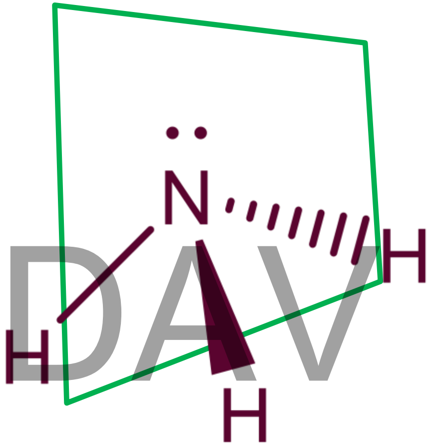
Vertical Plane of Symmetry σ_v

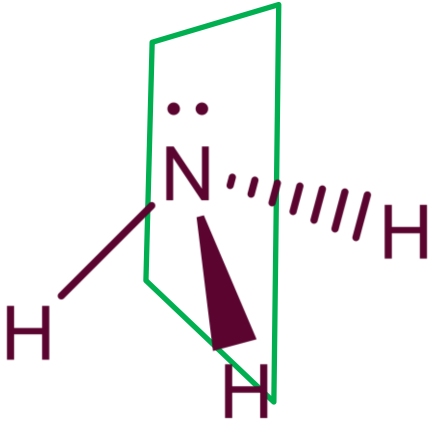
Plane passing through principal axis

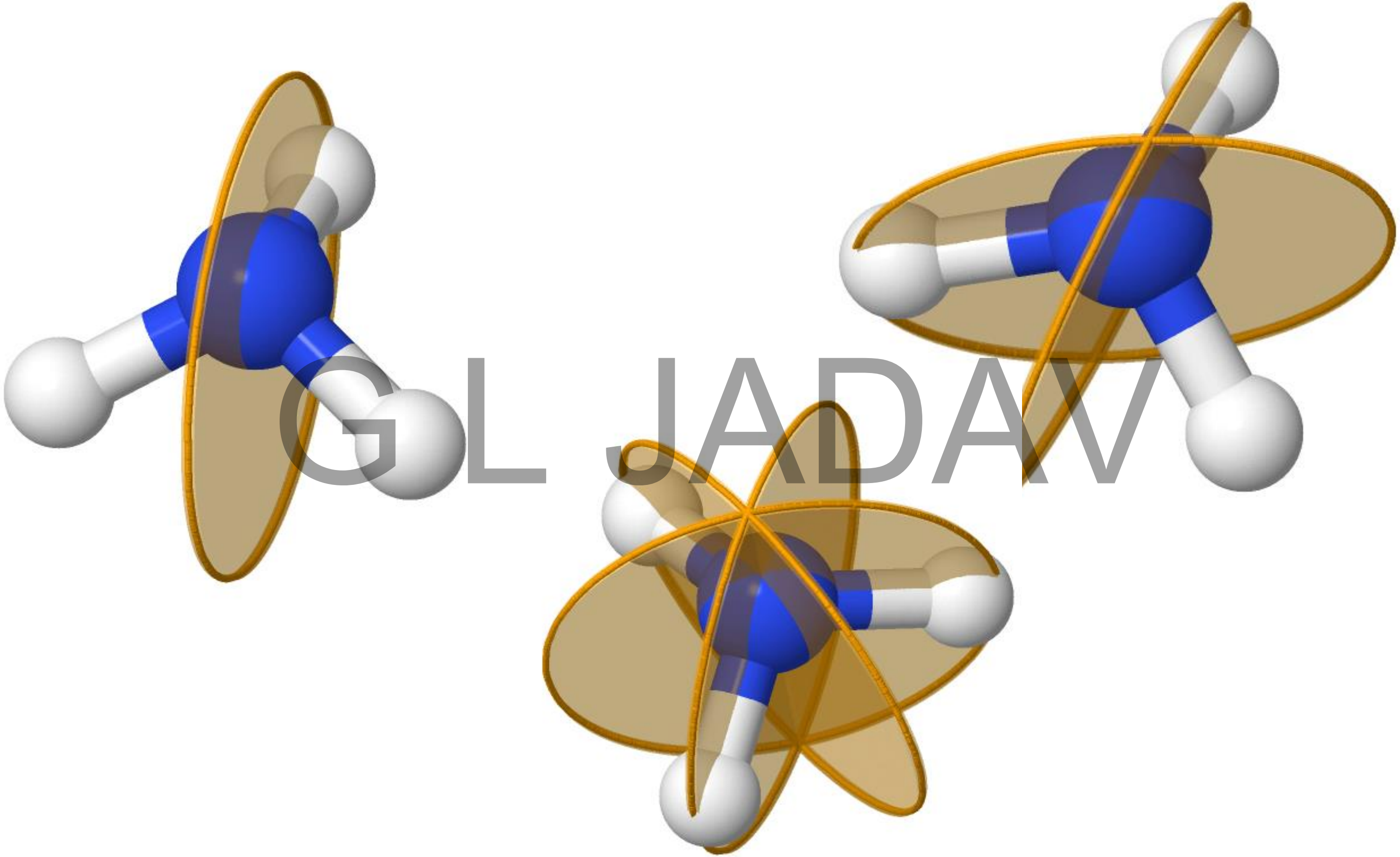
Eg. Ammonia

NH_3

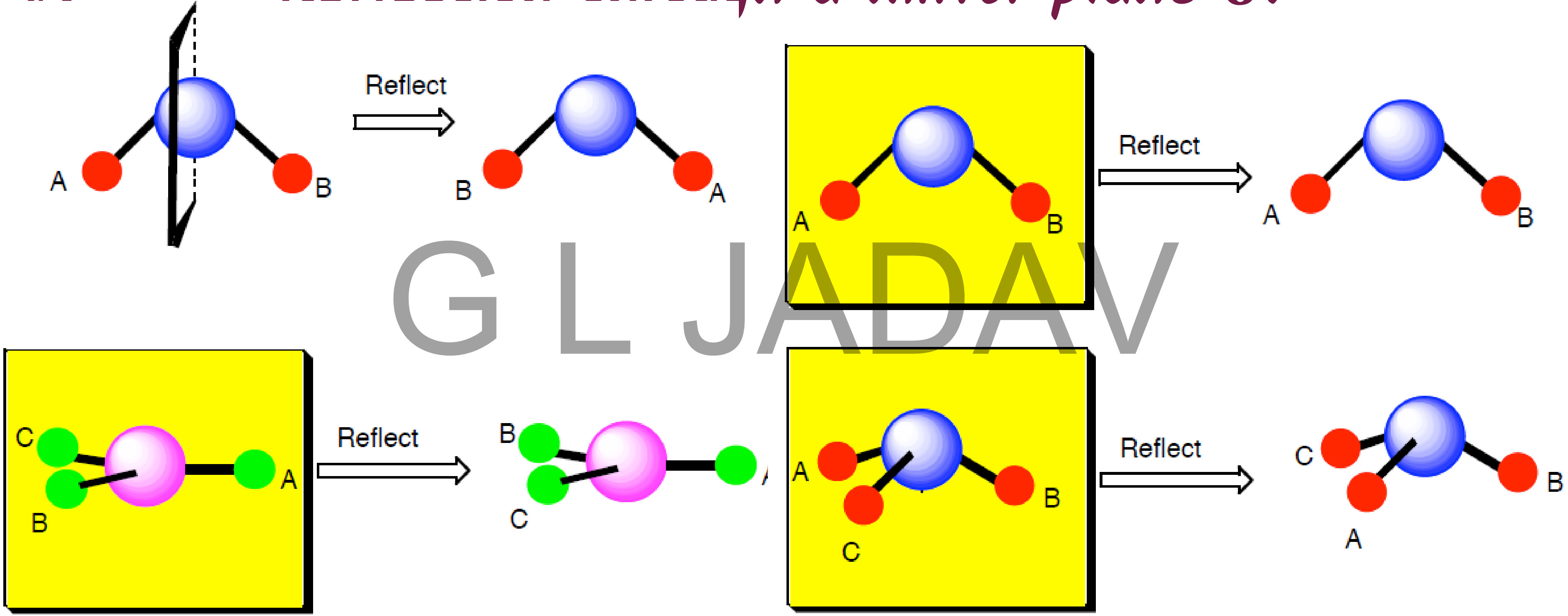






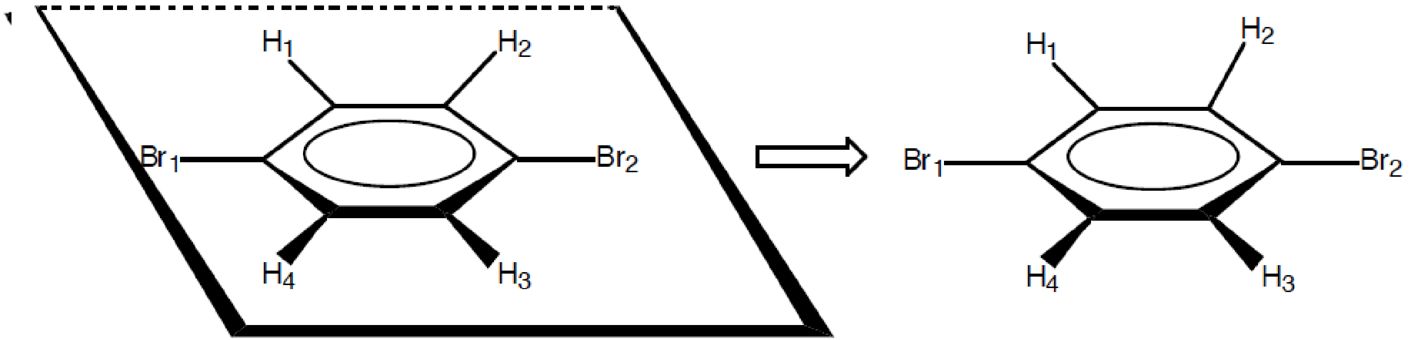


Reflection through a mirror plane σv



Horizontal Plane of Symmetry σ_h

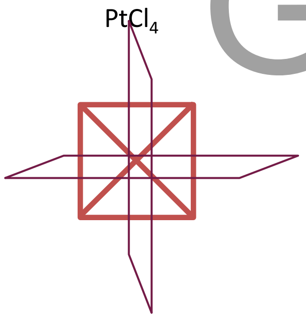
- Plane perpendicular to principal axis
- Only one σ_h but more σ_v
- σ_h present i.e. σ_v present
- σ_v present σ_h may be / may not be present
- σ_v and σ_h are always perpendicular

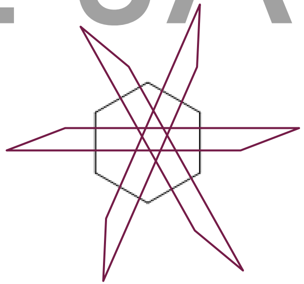


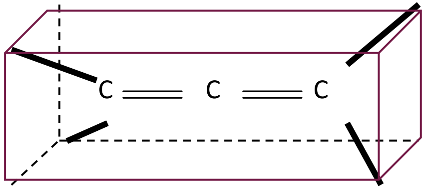
Dihedral plane/diagonal plane of symmetry

σ_d

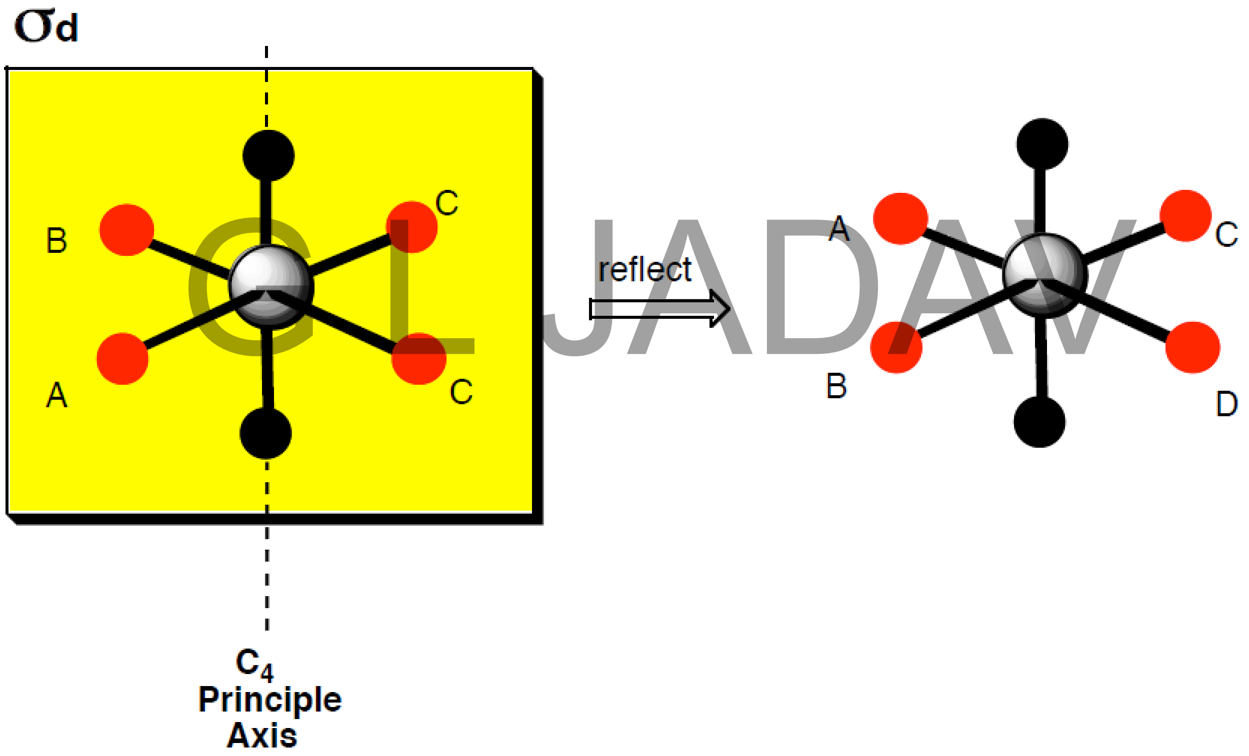
- Includes principal axis, bisects two C_2 and passes through minimum number of atoms
- σ_d always perpendicular to σ_h

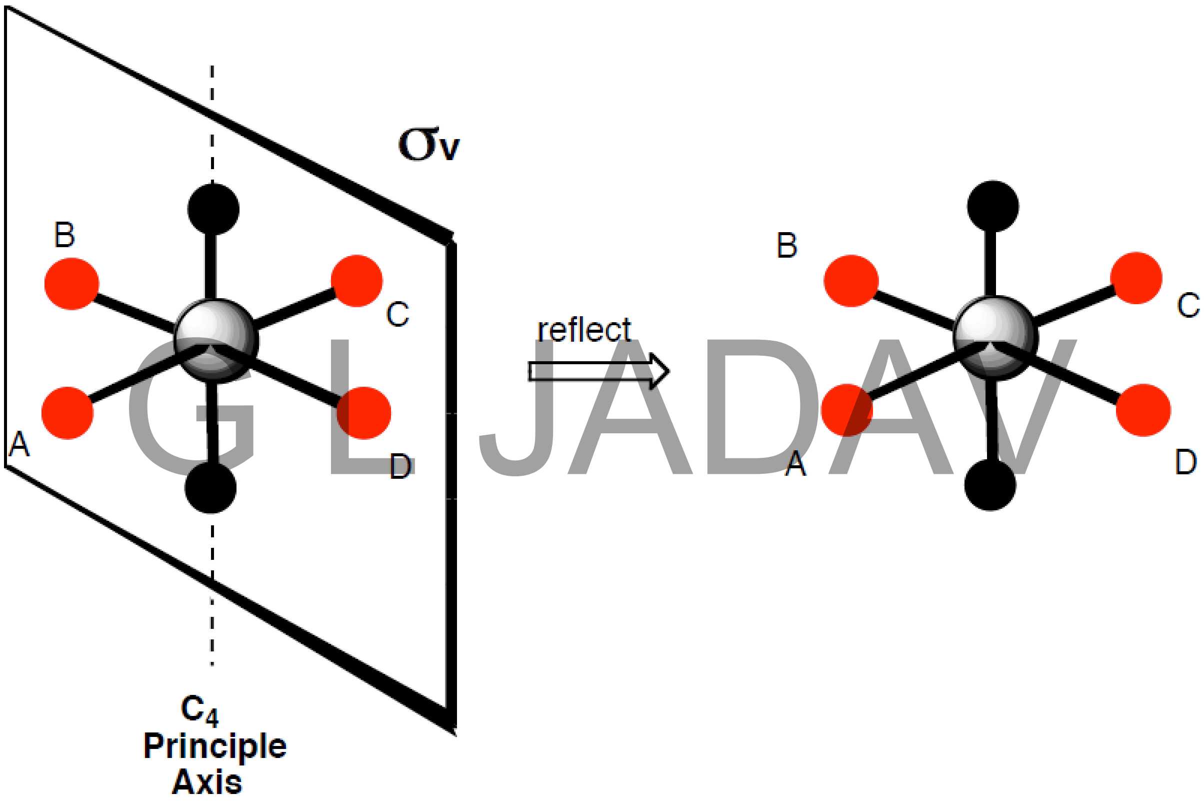






Dihedral vs. Vertical Mirror Planes Rule of Thumb




σv
B
C
A
D
C4
Principle
Axis
reflect
B
C
A
D

Difference

σ_v

- Vertical plane of symmetry
- Includes principal axis

- More than one σ_v
- Square planner
- $4\sigma_v$ but $2\ \sigma_d$
- Thus, $2\sigma_v$

σ_h

- Horizontal plane of symmetry
- perpendicular to C_n
- Only one σ_h
- σ_h always perpendicular
- to σ_v & σ_d

σ_d

- Diagonal plane of symmetry
- Consist C_n and bisects $2\ C_2$
- More than one
- σ_d present σ_h may/ may not be present

SOME EXAMPLES

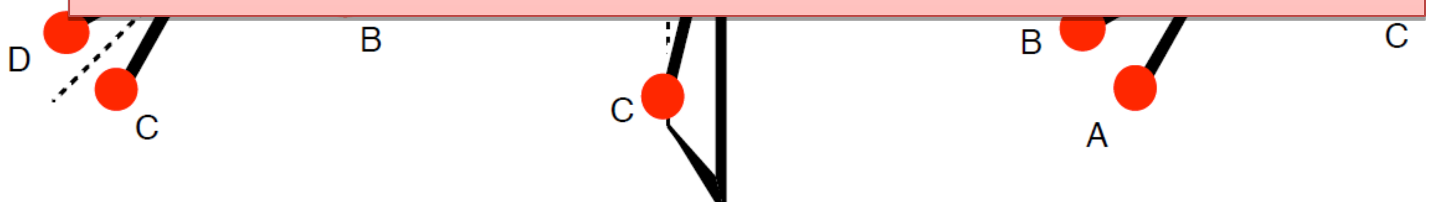
- H_2O C_2
- $PtCl_4^{-2}$ $1C_4$ $4C_2$
- $PtCl_6$ $3C_4$ $4C_3$ $6C_2$
- $NOCl$ $C_1 = E$
- $C_2H_2Cl_2$ (trans)
- C_2Cl_4
- $XeOF_4$

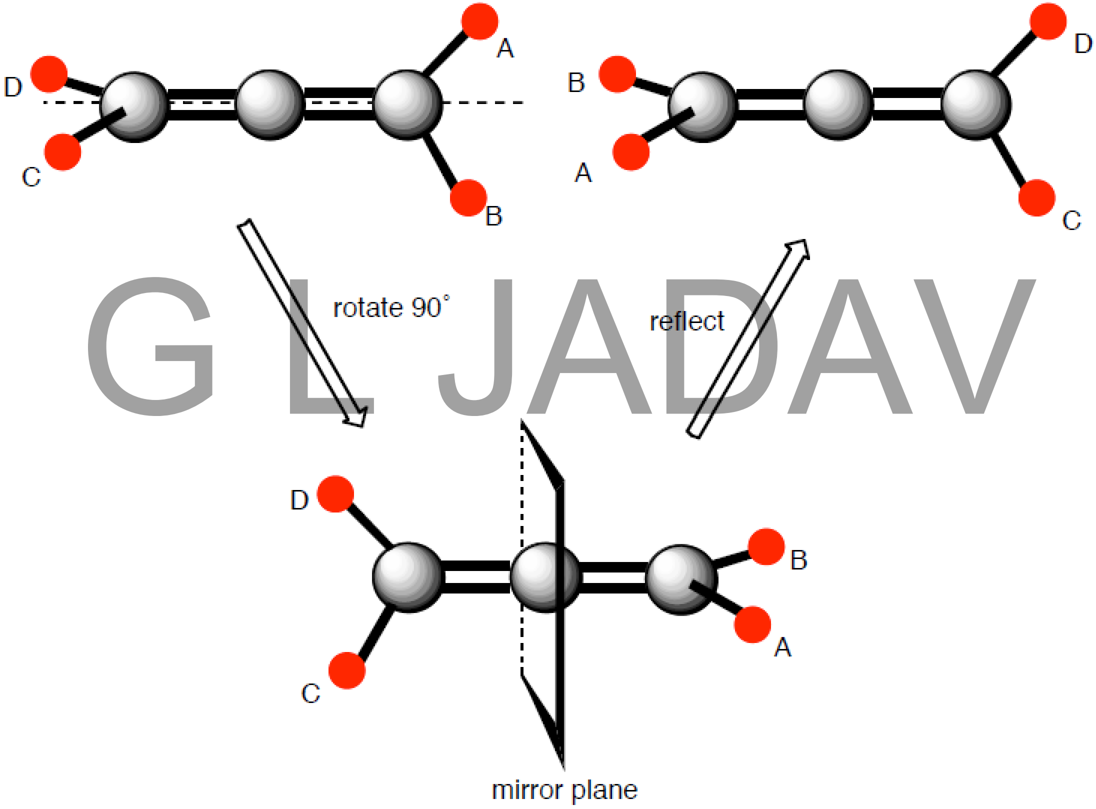
IMPROPER ROTATION AXIS – S_n

- Two step operation
- Rotate 360°/n followed by reflection in a mirror plane perpendicular to axis of rotation. All Planar Molecules have S_n

Rotation - Reflection (Improper Rotation) Axis, S_n

It is an imaginary axis through which if a species/molecule is rotated about certain degree followed by a reflection through a plan perpendicular to rotation axis giving an equivalent configuration to original.

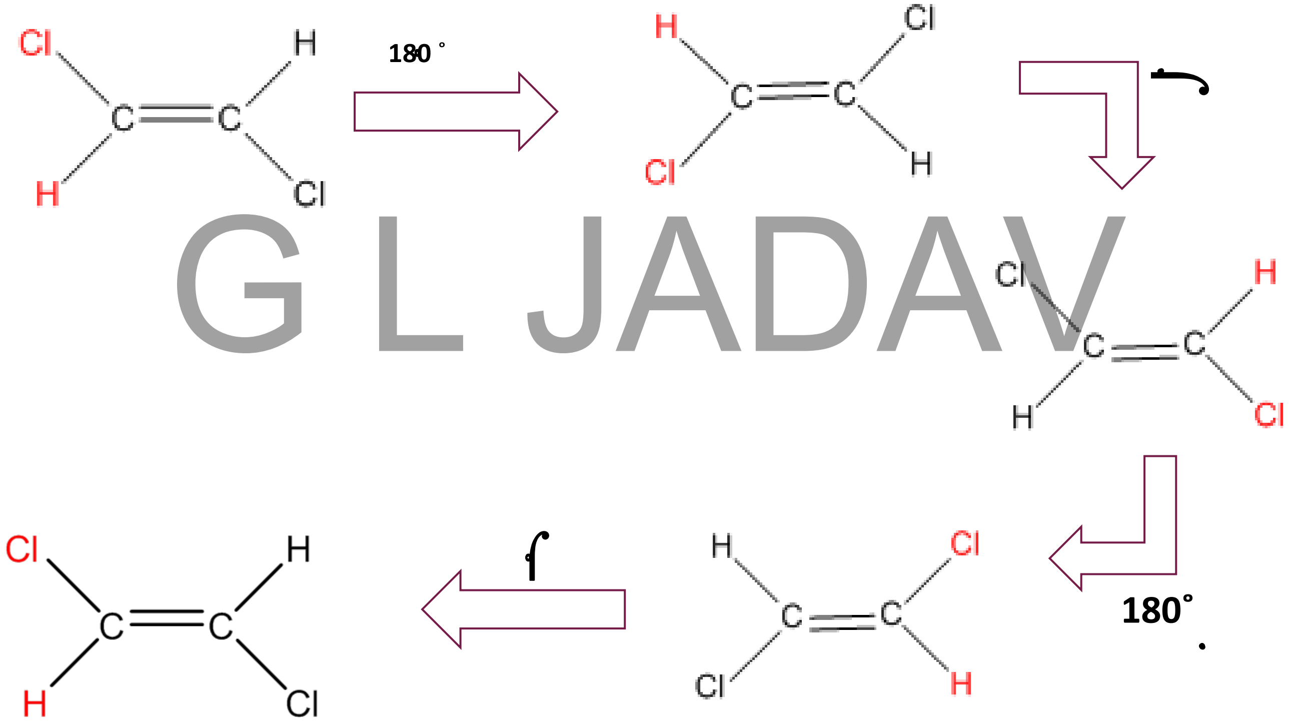



D
C
A
B
B
A
D
C
rotate 90°
reflect
D
C
B
A
mirror plane

- S_n^k
- $n = 360 / \theta$,
- n= order of axis(improper axis)
- K= distinct operations
- e.g. S6, follows 6 distinct operations
- $S_6^1, S_6^2, S_6^3, S_6^4, S_6^5, S_6^6$

- $C_n^n = E$,
  - But $S_n^{2n} = E$, n = odd
  - $S_n^n = E$, n=even
- Axis is of odd no. $C_n^n = E$, but $S_n^n = \sigma_h$ not E

Trans dichloroethylene $C_2H_2Cl_2$

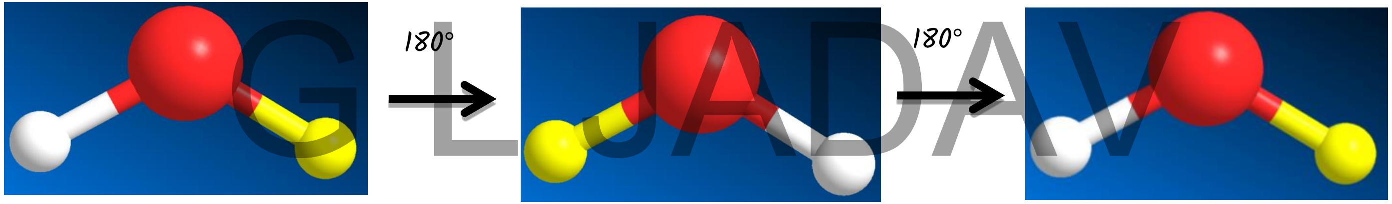


C_n	S_n
C_n proper axis of rotation	S_n Shoenflie symbol of improper axis of rotation
Imaginary axis Rotation θ° To get equivalent orientation	Anticlock wise rotation followed by reflection (perpendicular plane) Equivalent orientation
Order of rotation No. of rotation $n = \dfrac{360}{\theta}$	Degree of rotation decides order of improper rotation
$C_n^n = E$	$S_n^k = E$, k is even $S_n^{2k} = E$, k is odd

EXAMPLES

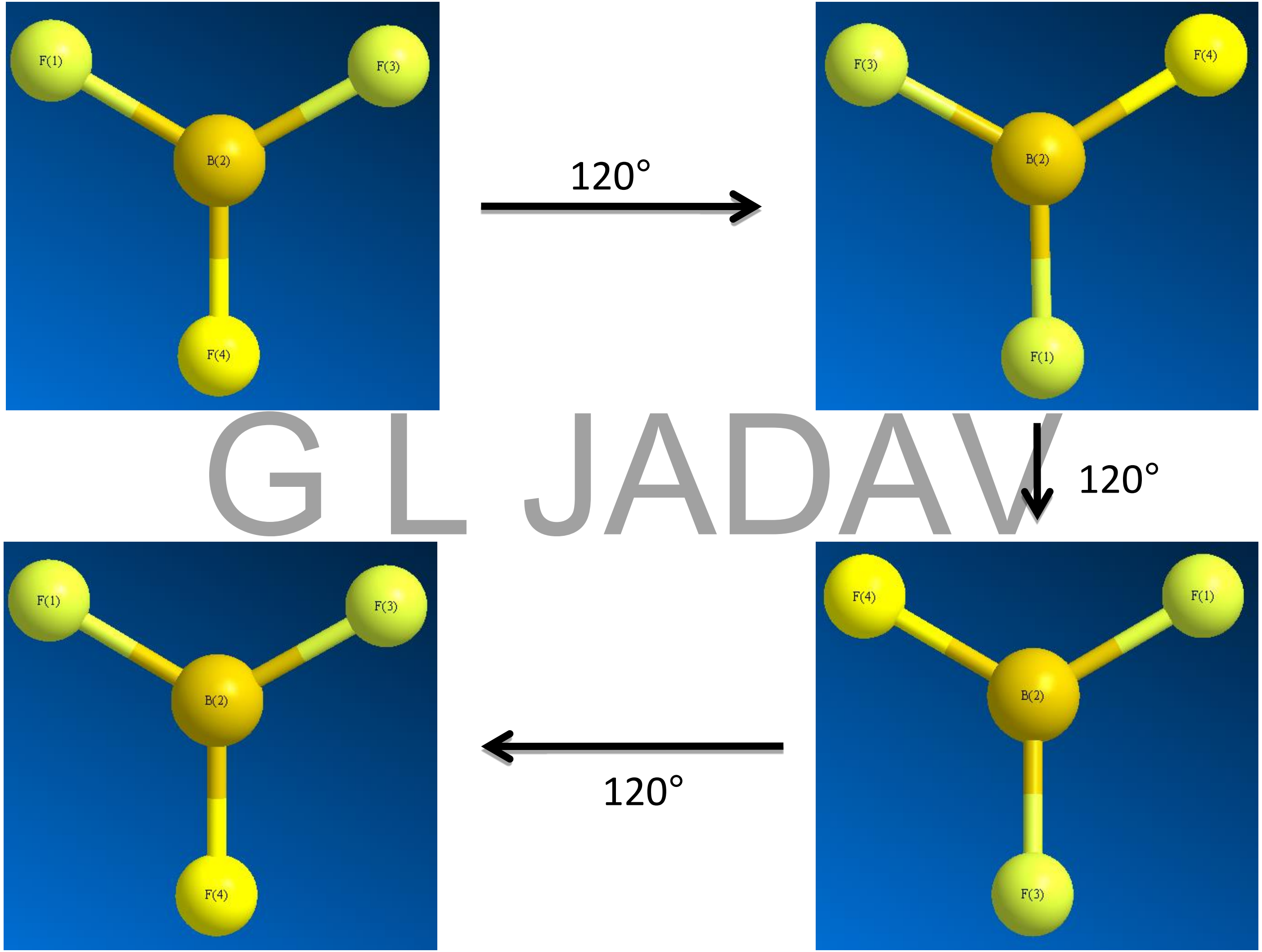
- $C_2^2 = E$

H_2O n=2 $n = \frac{360}{\theta} = 180$

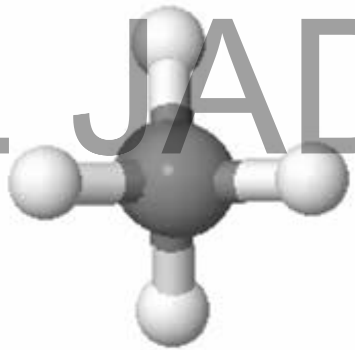


- $C_3^3 = E$

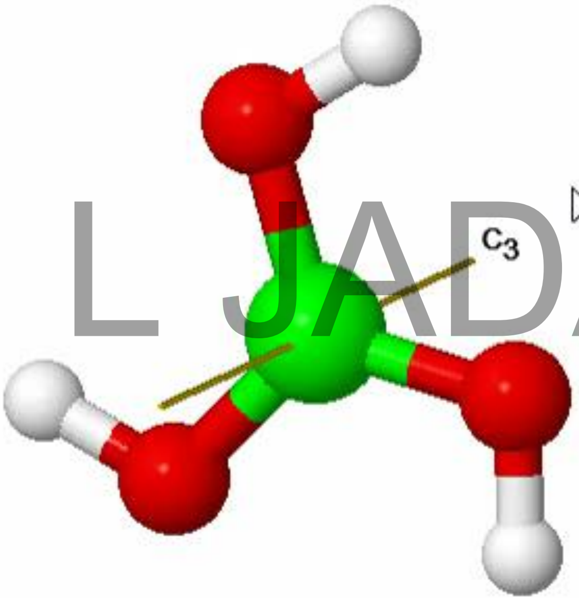
BF_3 n=3 $n = \frac{360}{\theta} = 120$


F(1)
F(3)
B(2)
F(4)
120°
F(3)
F(4)
B(2)
F(1)
120°
F(4)
F(1)
B(2)
F(3)
120°
F(1)
F(3)
B(2)
F(4)

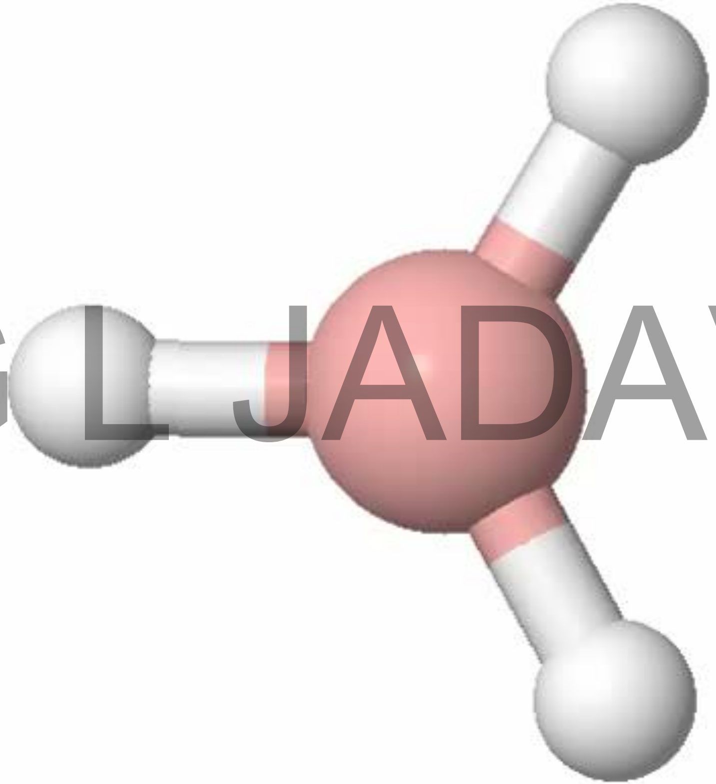
ALLENE



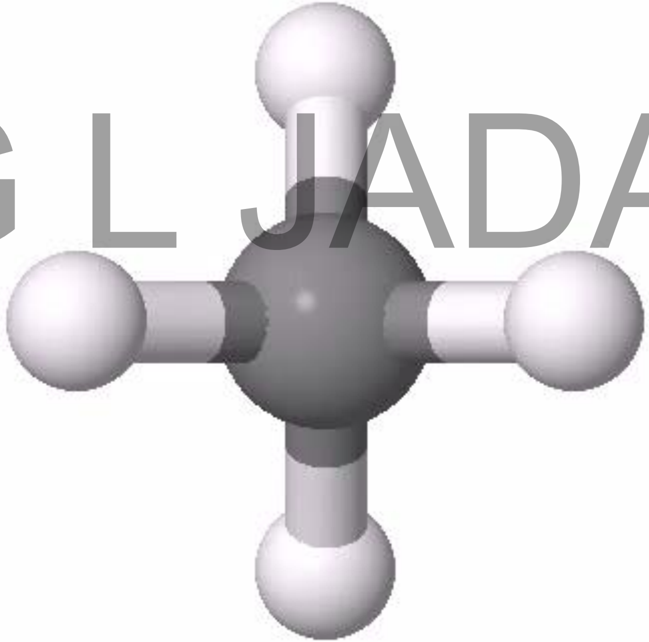
BORIC ACID , $B(OH)_3$



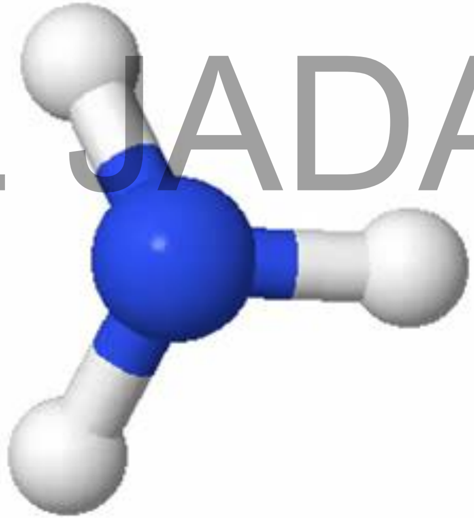
BF_3



METHANE



AMMONIA



Point Group

POINT GROUP

- Collection of specific symmetry elements and operations for a certain molecular structure
- ***A Group is a collection of elements that are interrelated according to certain rules.***
- In order for any set of elements to form a group, the following conditions or rules must be satisfied:

1. Law of Identity

One element in the group must commute with all other and leave them unchanged.

i.e. the group must include the identity E

$$X\ E = X$$

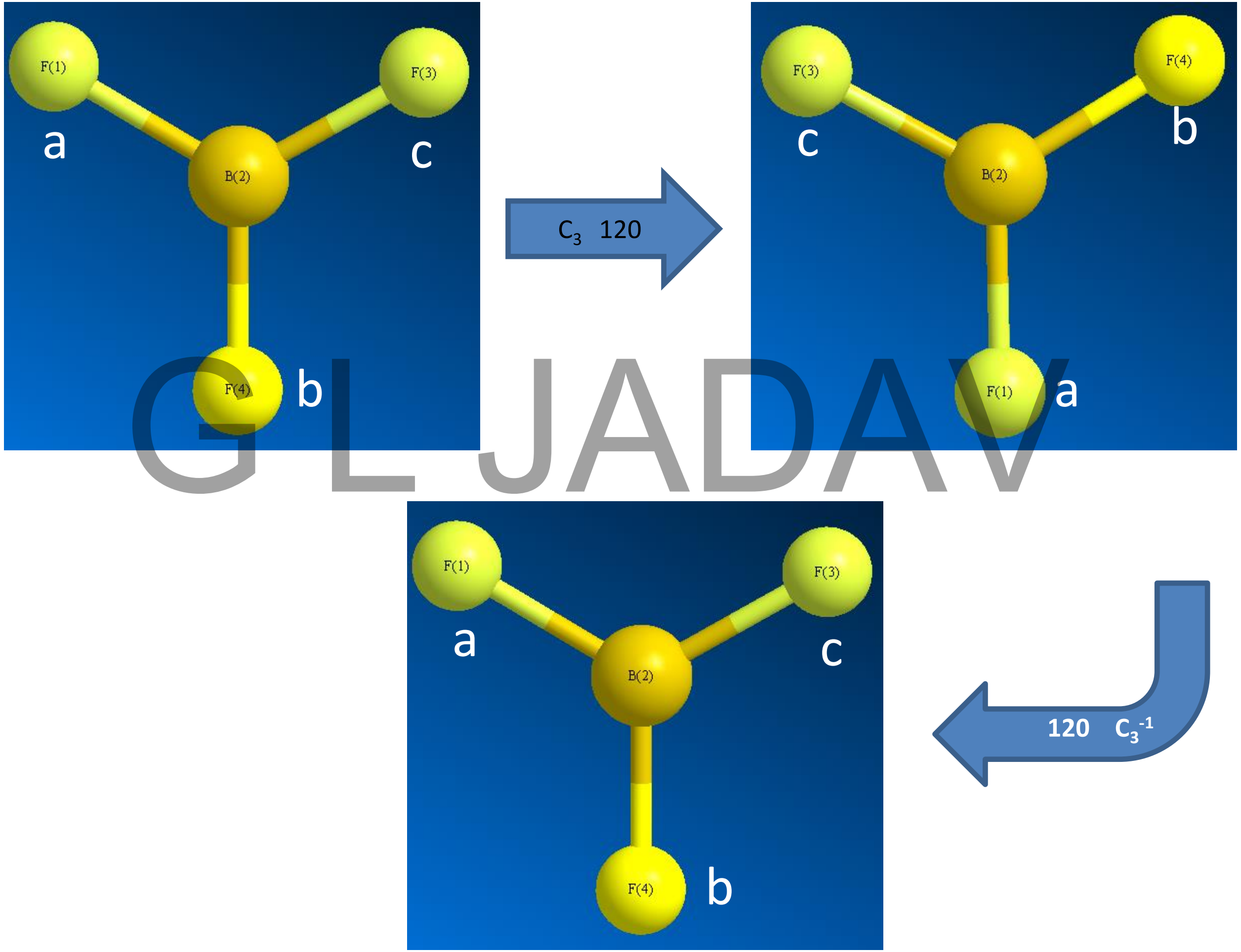
2. Law of inverse (Reciprocality)

Every element must have reciprocal, which is also an element of the Group.

If R is a reciprocal of the element S then R . S = E

Eg. $C_3^{-1} \times C_3^{1} = E$

BF_3


F(1)
F(3)
a
c
B(2)
F(4)
b
C_3 120
F(3)
F(4)
c
b
B(2)
F(1)
a
F(1)
F(3)
a
c
B(2)
F(4)
b
120 C_3^{-1}

3. Law of Closure

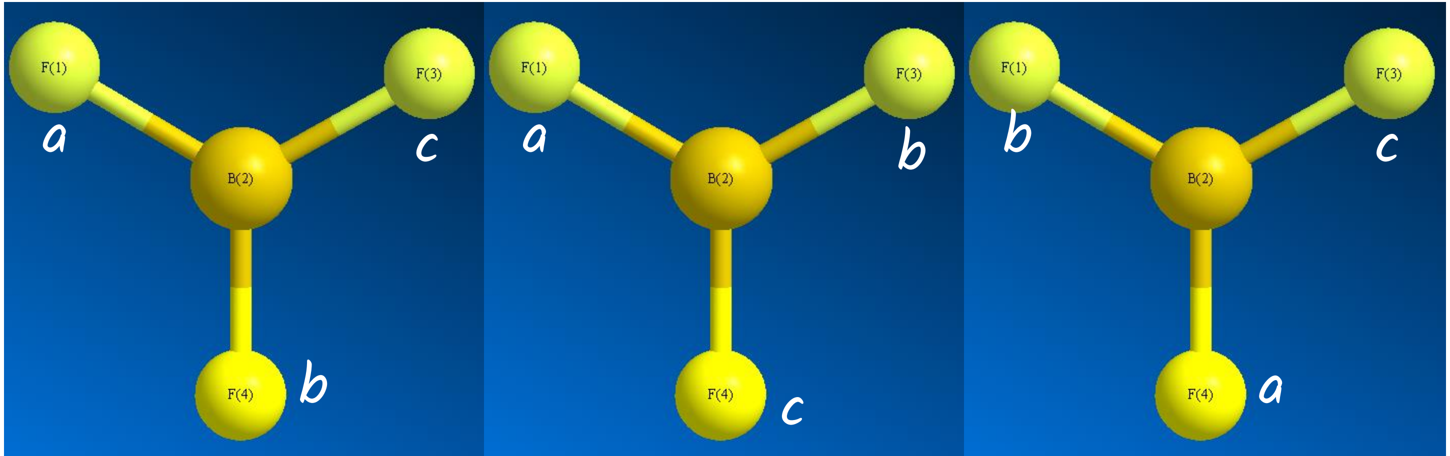
The combination of two elements in the group must give an element of the group.

$A \times B = C$ (B operation First)

BF_3 $A = C_3$ $B = \sigma_{Va}$ Then $C = ?$

$C_3 \times \sigma_{Va} = \sigma_{Vc}$

Must be an element of group



4. Law of multiplication (Commutative Law)

For any point group if A and B are the possible symmetry operations and if $A \times B = B \times A$, it means it obeys the law of multiplication.

Commutative Law:

In algebra, $X \times Y = Y \times X$

$6 \times 3 = 3 \times 6$

A B or B A

But in group theory, the commutative law does not in general hold.

A B may be equal to C But, B A = D, and $C \neq D$

- There are some groups in which combination is commutative and such groups are called Abelian Groups
- Non – Commutative -> Non Abelian group

❖ $A \times B = B \times A$ -> Abelian

❖ $A \times B \neq B \times A$ -> Non Abelian

- H_2O: $A \times B = C_2 \times \sigma_v$

- $B \times A = \sigma_v \times C_2$

5. LAW OF ASSOCIATION

- The association law of multiplication must hold (obey).
- If A, B, C are possible symmetry elements

– $A\,(B\,C) = (A\,B)\,C$

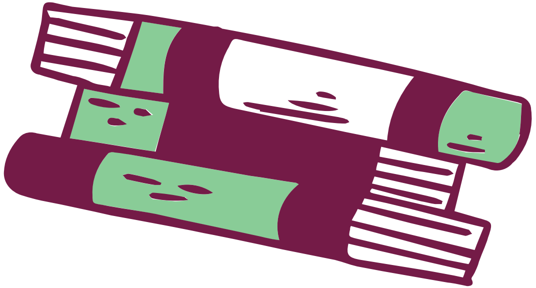
- $B\,C = S$ $\qquad$ $A\,S$
- $A\,B = R$ $\qquad$ $R\,C$

Same obeys association law

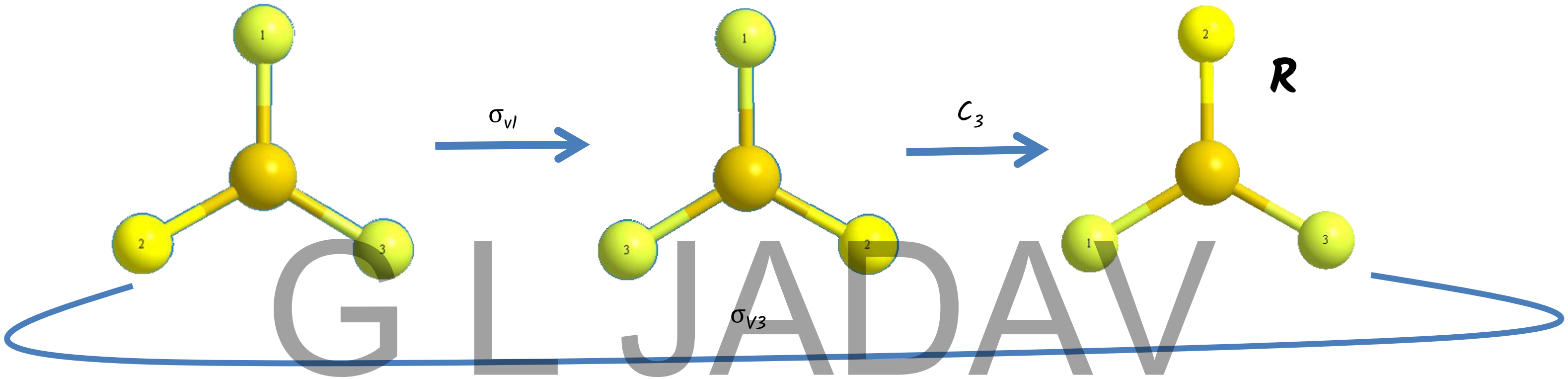
- Prove that:

– $(A\,B)\,C = A\,(B\,C)$

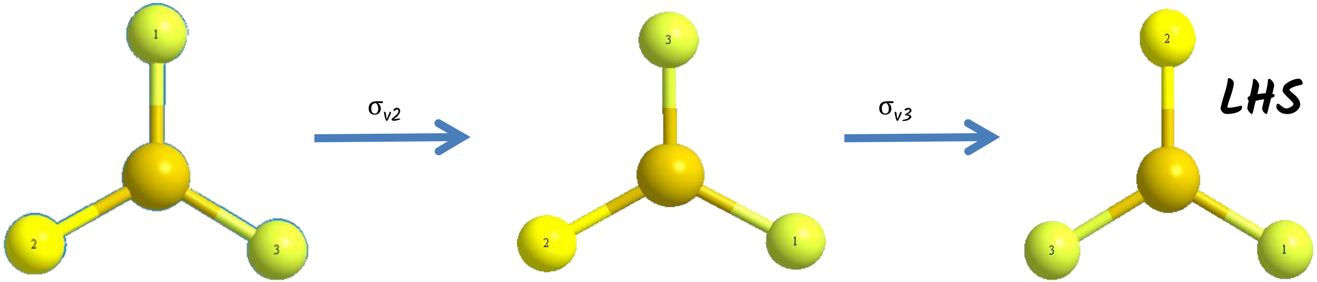
- Eg. BF_3
- $A = C_3 \quad B = \sigma_1 \qquad C = \sigma_2$



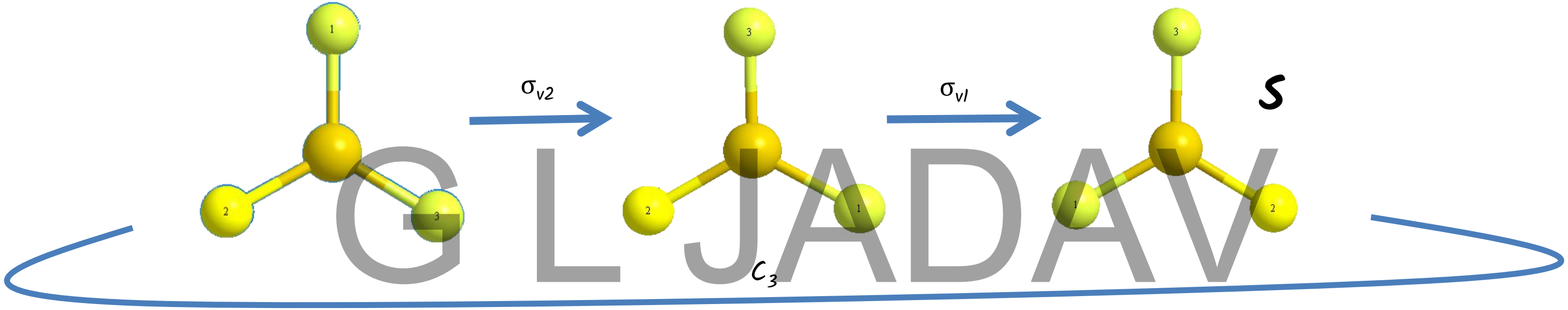
- $A \times B = R$
- $R = \sigma_{V3}$



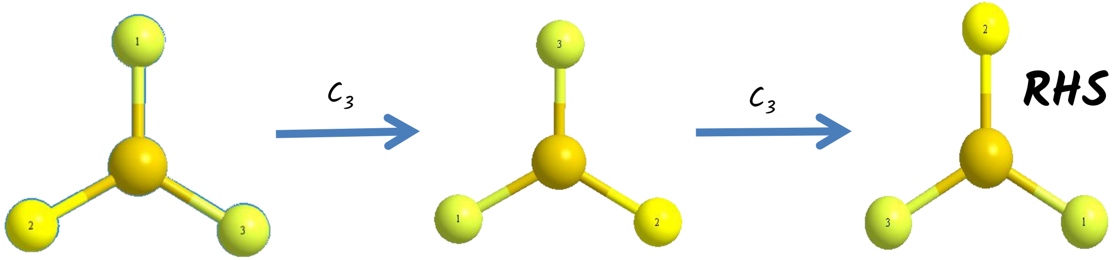
$R \times C = \sigma_3 \times \sigma_2$



- $RHS = A\,(B\,C)$
  - First B C operation than A operation
  - In B C first C operation Than B operation
  - $C_3\,(\sigma_{v1}$ x $\sigma_{v2})$



$S \times A = C_3 \times C_3 = C_3^2$

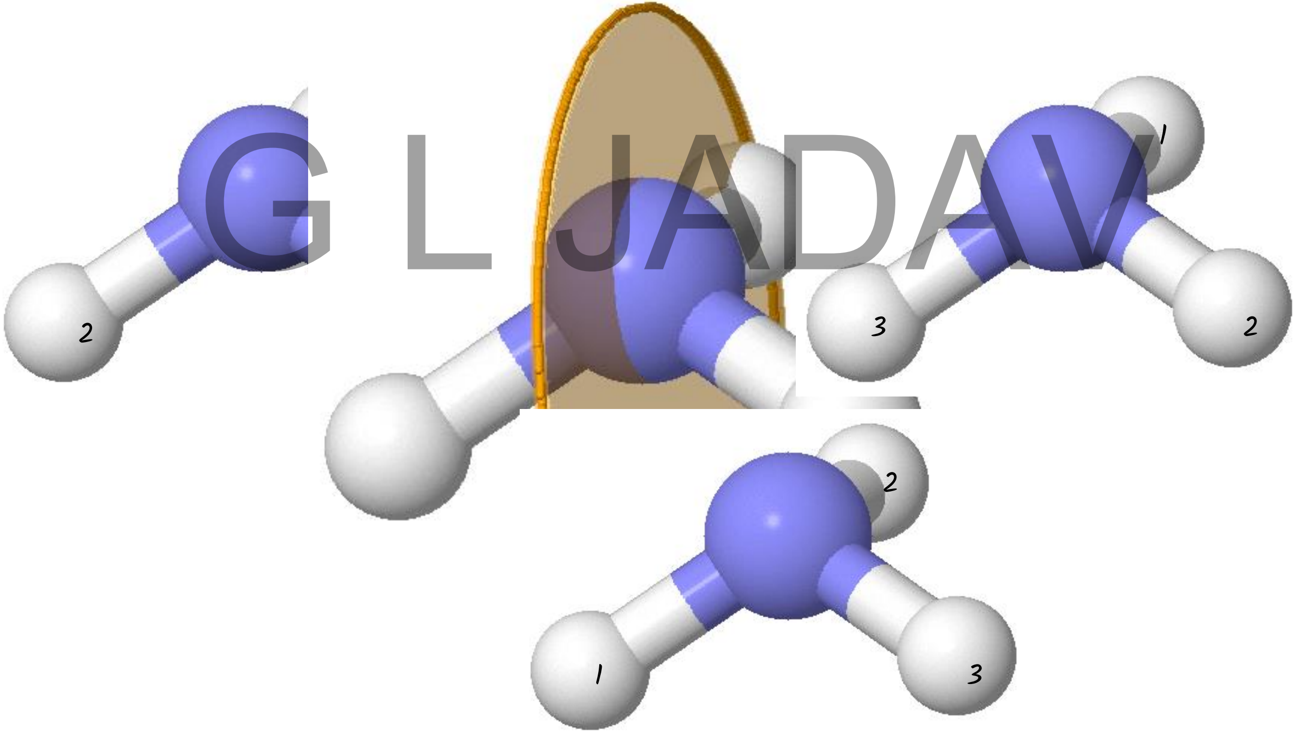


Thus LHS = RHS, in BF3 the law of association Obeys

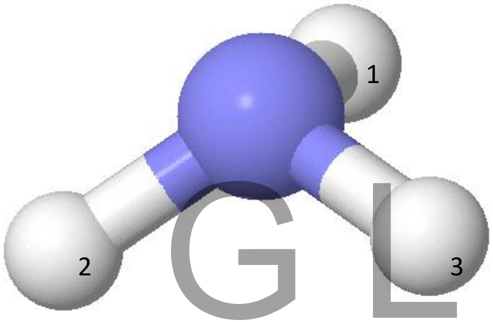
Prove that : in NH_3

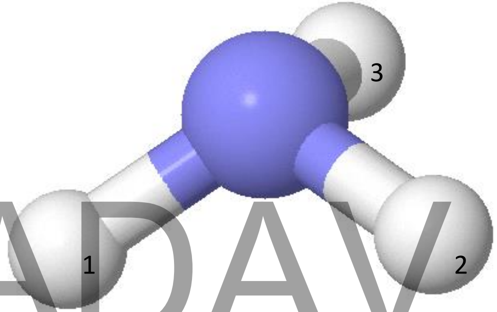
$C_3 \times \sigma_{v1} \neq \sigma_{v1} \times C_3$

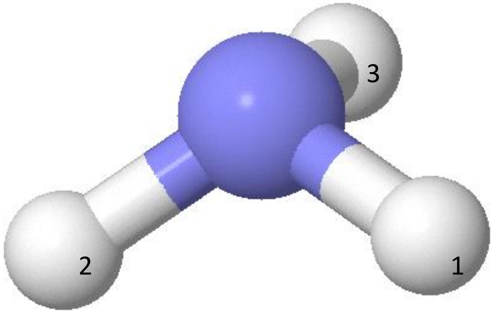
- NH_3 is non planner, 1 C_3 and 3 σ_v



$$RHS = \sigma_{v'} \times C_3$$







C_n^k find n and k, for 1140° rotation

- How to find θ (minimum angle of rotation)?
- 360 x 3 = 1080
- Thus θ = 1140 – 1080 = 60
- n = 360 / θ = 360 /60 = 6
- $C_n = C_6$
- Now, k

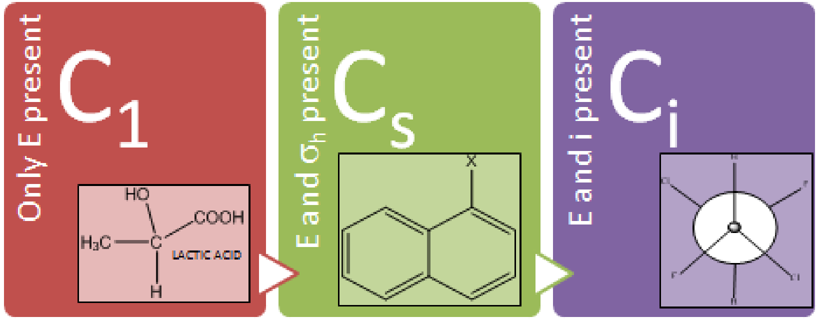
$$K = \frac{totalangleofrotation}{minimumangleofrotation} = \frac{1140}{60} = 19$$

- n= 6 and k = 19
- $C_n^k = C_6^{19}$

Rules for the determination of point group

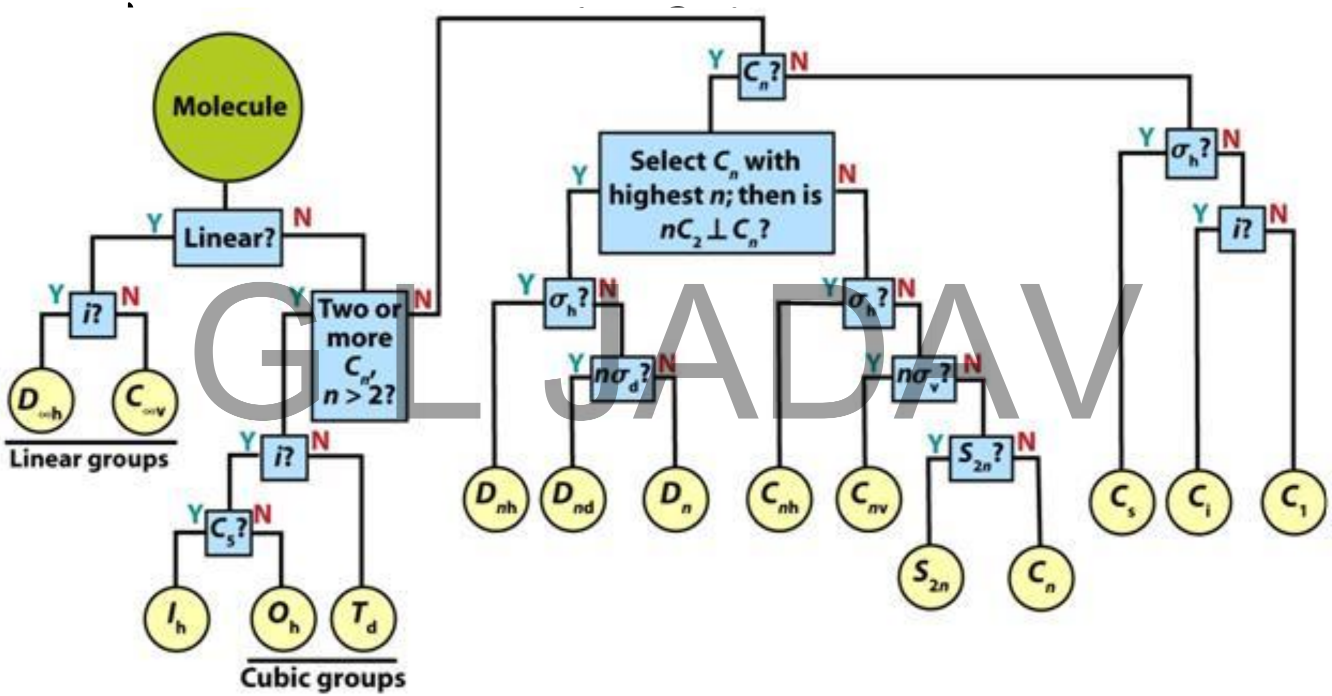
1. Check the presence of principle rotational axis
   - If absent P.G. C_1 C_s or C_i which depends on the presence of i and σ_h

If C_n absent



2. If principle rotational axis present P.G. C_n
3. Check presence of C_2 axis
   - If $nC_2 \perp C_n$ then D_n
4. Presence of symmetrical plane σ_v $n\sigma_h$ $n\sigma_d$
   I. If only n σ_v , C_{nv}
   II. n σ_v, σ_h, PG C_{nh}
   III. σ_d present then always $nC_2 \perp C_n$, PG. D_{nd}
   IV. $nC_2 \perp C_n$, σ_d absent , σ_h present, PG. D_{nh}
   V. If molecule possess specific shape PG will be special
      I. Tetrahedral shape = Td
      II. Octahedral shape = Oh
5. If molecule is linear check center of symmetry
   - Inversion present = $C_{\infty n}$
   - Inversion Absent = $C_{\infty v}$

- *Molecules that only have Cn proper axis of rotation with (n-1) distinct symmetry*



MULTIPLICATION TABLE

- C_2v

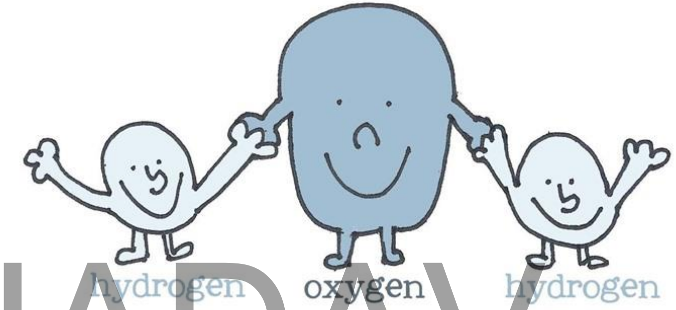
❖ H_2O

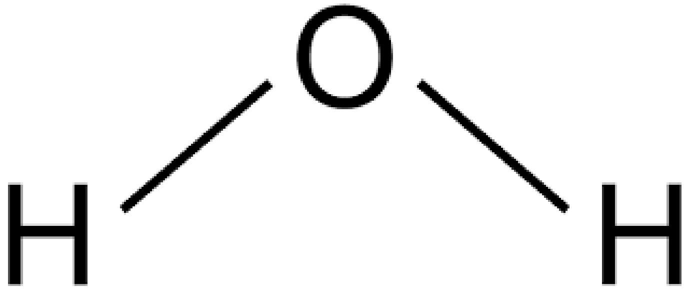
E

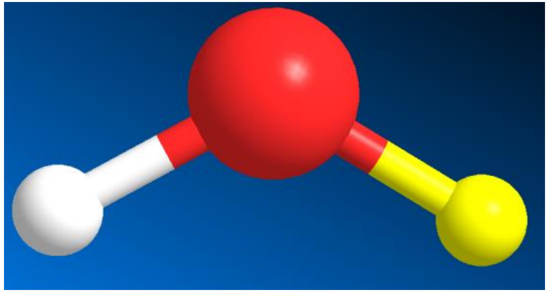
C_2

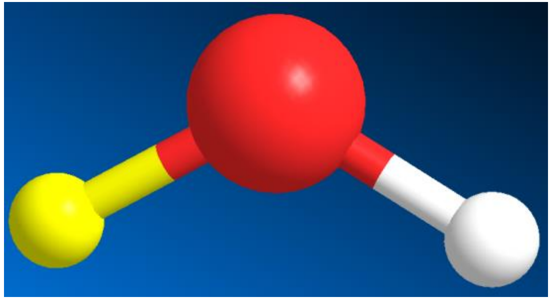
σ_{v1}

σ_{v2}









C_2V	E	C_2	σ_{V1}	σ_{V2}
E	E	C_2	σ_{V1}	σ_{V2}
C_2	C_2	E	σ_{V2}	σ_{V1}
σ_{V1}	σ_{V1}	σ_{V2}	E	C_2
σ_{V2}	σ_{V2}	σ_{V1}	C_2	E

C_2V	E	C_2	σ_{V1}	σ_{V2}
E	E	C_2	σ_{VI}	σ_{V2}
C_2	C_2	E	σ_{V2}	σ_{VI}
σ_{V1}	σ_{VI}	σ_{V2}	E	C_2
σ_{V2}	σ_{V2}	σ_{VI}	C_2	E

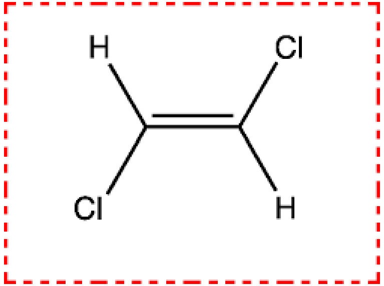
G L JADAV

MULTIPLICATION TABLE

- C_2h

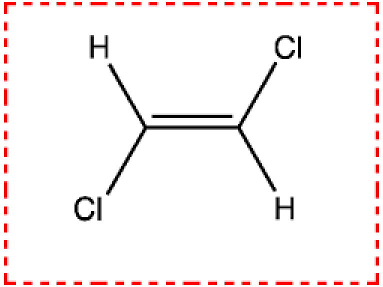
❖ Trans dichloro ethylene

E
C_2
σ_h
i



C_2h	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

C_2V	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E



G L JADAV

MULTIPLICATION TABLE

- C_3v

❖ NH_3

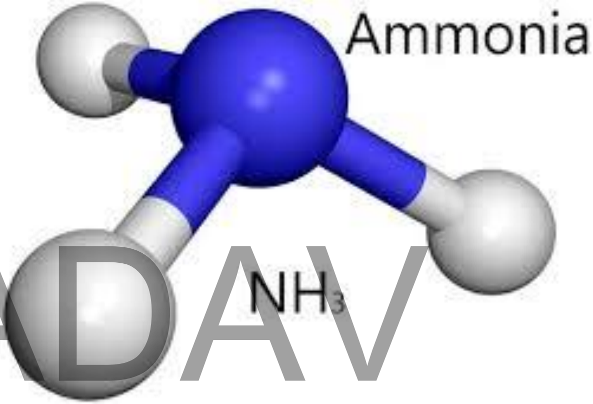
E

C_3

σ_{v1}

σ_{v2}

σ_{v3}



C_3V	E	C_3	C_3^{-1}	σ_{V1}	σ_{V2}	σ_{V3}
E	E	C_3	C_3^{-1}	σ_{V1}	σ_{V2}	σ_{V3}
C_3	C_3	C_3^{-1}	E	σ_{V3}	σ_{V1}	σ_{V2}
C_3^{-1}	C_3^{-1}	E	C_3	σ_{V2}	σ_{V3}	σ_{V1}
σ_{V1}	σ_{V1}	σ_{V2}	σ_{V3}	E	C_3	C_3^{-1}
σ_{V2}	σ_{V2}	σ_{V3}	σ_{V1}	C_3^{-1}	E	C_3
σ_{V3}	σ_{V3}	σ_{V1}	σ_{V2}	C_3	C_3^{-1}	E

C_3V	E	C_3	C_3^{-1}	σ_{V1}	σ_{V2}	σ_{V3}
E	E	C_3	C_3^{-1}	σ_{V1}	σ_{V2}	σ_{V3}
C_3	C_3	C_3^{-1}	E	σ_{V3}	σ_{V1}	σ_{V2}
C_3^{-1}	C_3^{-1}	E	C_3	σ_{V2}	σ_{V3}	σ_{V1}
σ_{V1}	σ_{V1}	σ_{V2}	σ_{V3}	E	C_3	C_3^{-1}
σ_{V2}	σ_{V2}	σ_{V3}	σ_{V1}	C_3^{-1}	E	C_3
σ_{V3}	σ_{V3}	σ_{V1}	σ_{V2}	C_3	C_3^{-1}	E

G L JADAV