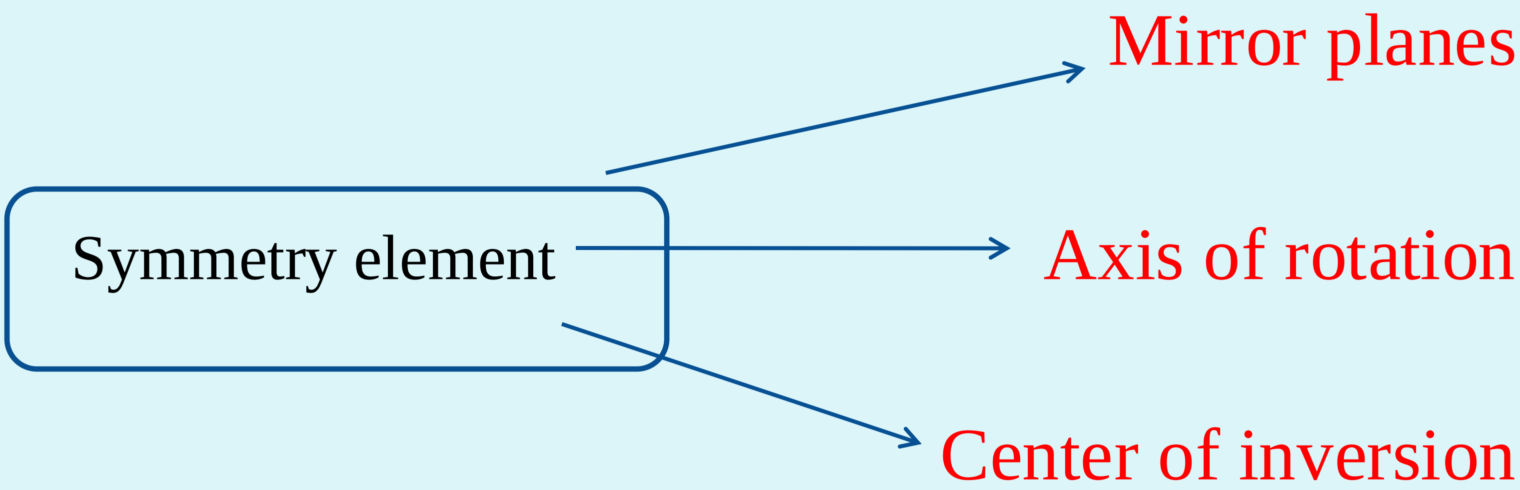
Symmetry and Group Theory

⇒ The symmetry properties of molecules and how can be used to predict vibrational spectra, hybridization, optical activity.

Point groups: Molecule with similar symmetry are put into the same point group.

A point group contains all objects that have the same symmetry.

Symmetry Element



Symmetry Element

Element	Symmetry operation	Symbol
-n-fold axis or (axis of rotation)	Rotation by 360/n	C_n
-	Identity	E
Mirror plane	Reflection	σ
Center of inversion	Inversion	i
-n-fold axis of improper rotation or (improper rotation axis)	Rotation by 360/n followed by reflection perpendicular to the axis of rotation د	S_n

Identity, E

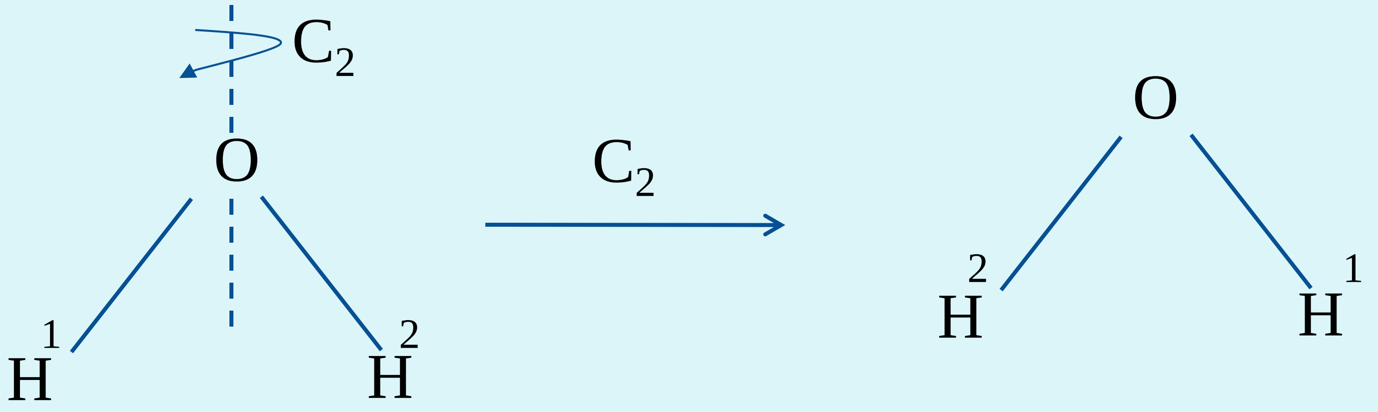
All molecules have identity. This operation leaves the entire molecule unchanged.

Ex.: Tetrahedral carbon with four different group (CHFBrCl) has only identity and No other symmetry element.

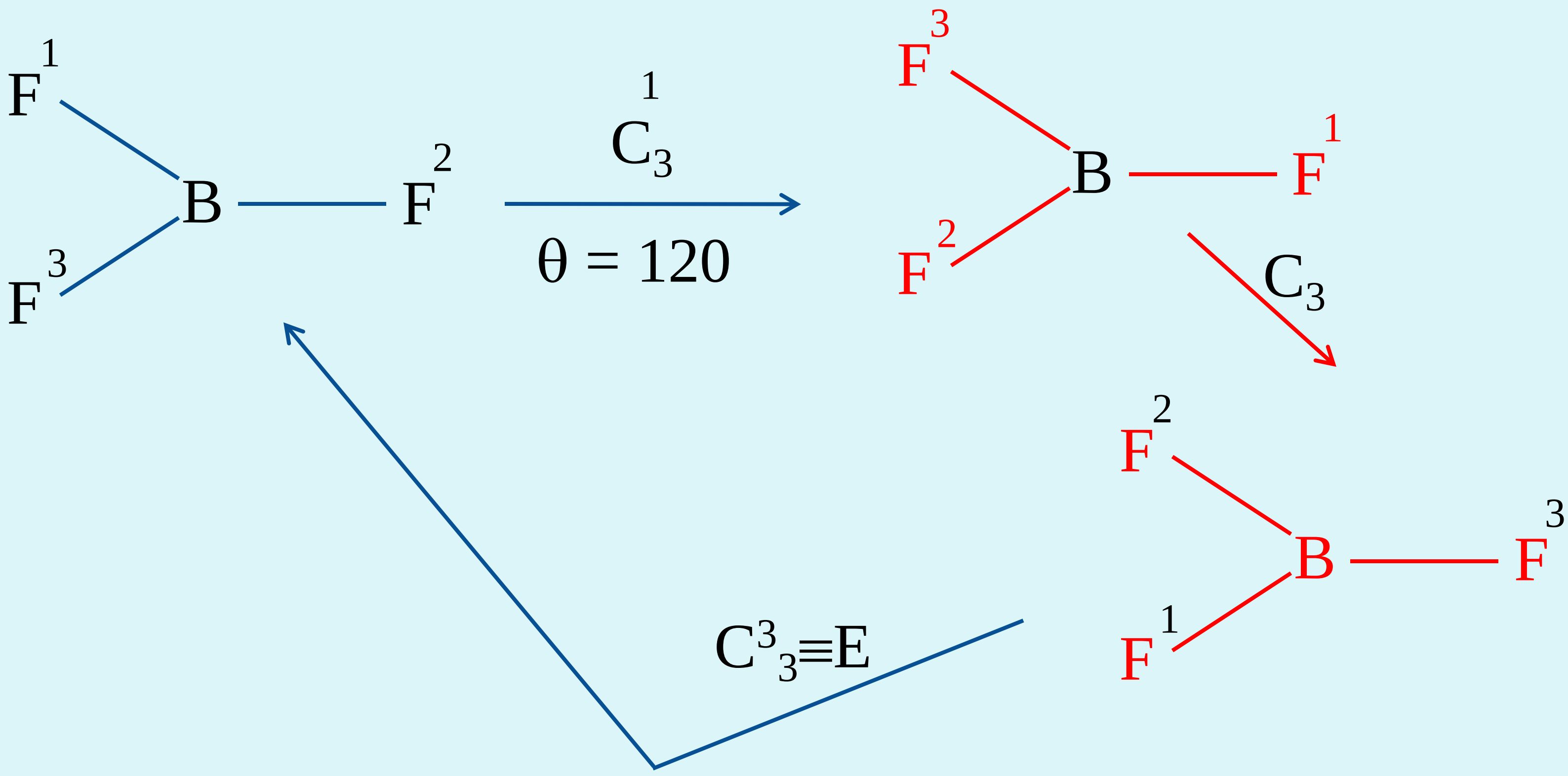
n-fold rotation

Ex: (1) H_2O has C_2

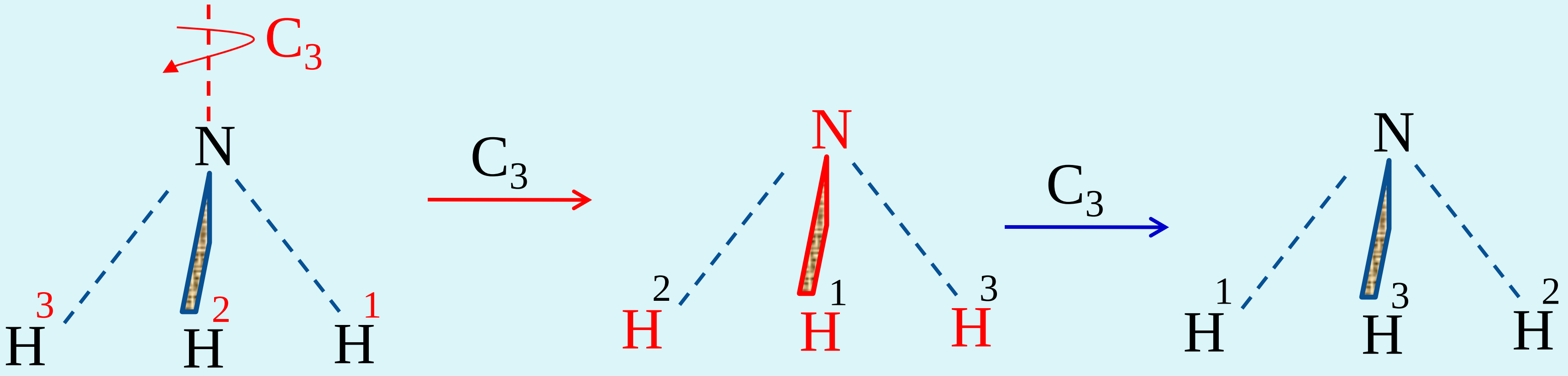
$\theta = 180$ angle of rotation



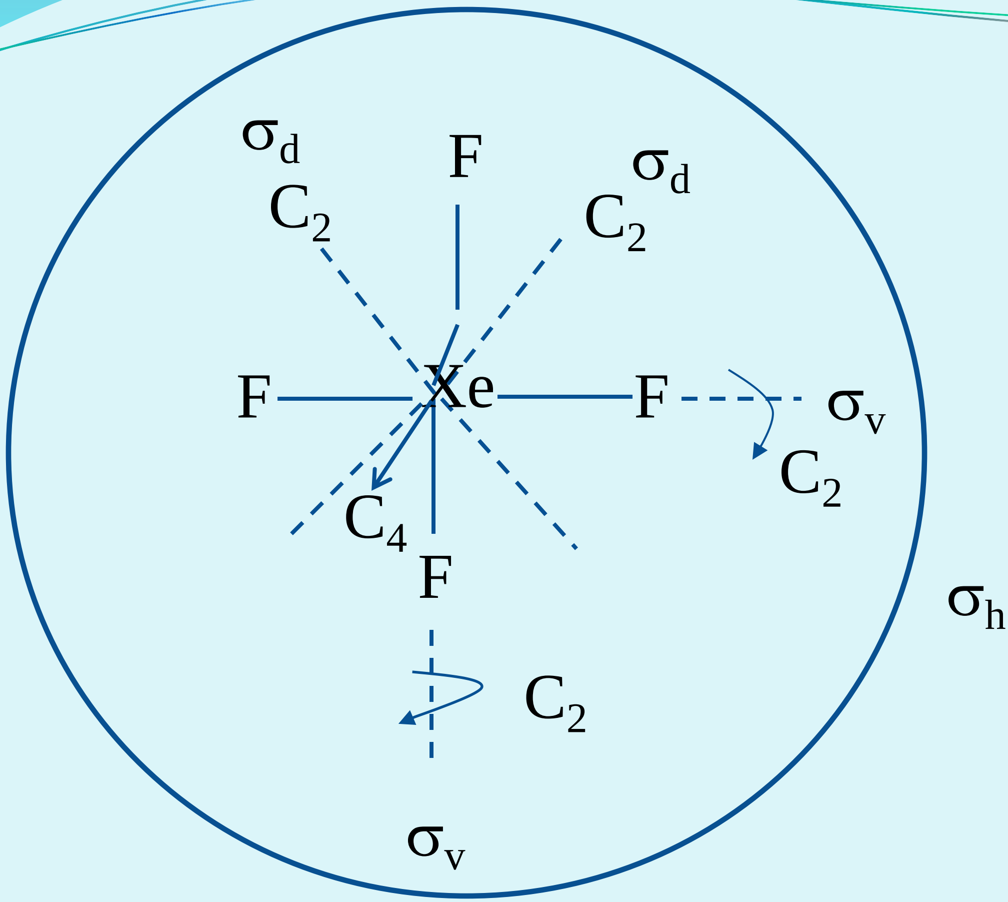
Ex: (2)



Ex: (3) Ammonia



Only C_3

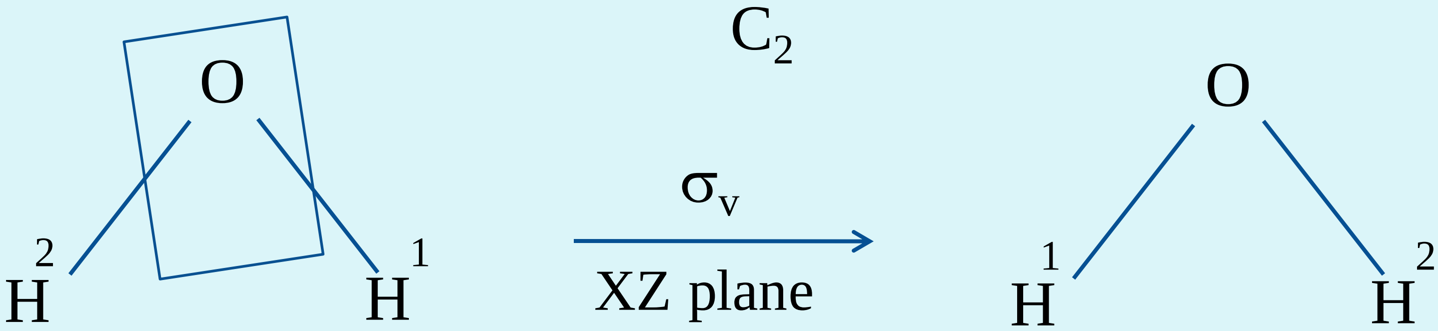


Square planar

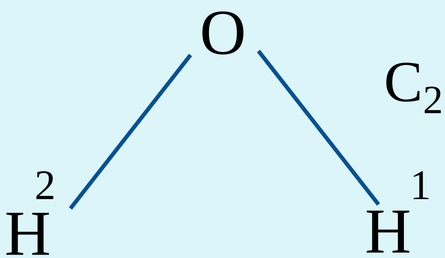
$C_4 \perp 4C_2$, $2\sigma_v$, $2\sigma_d$, σ_h
$+ S_4$

Mirror plane ⇒ Reflection of molecules

Ex:

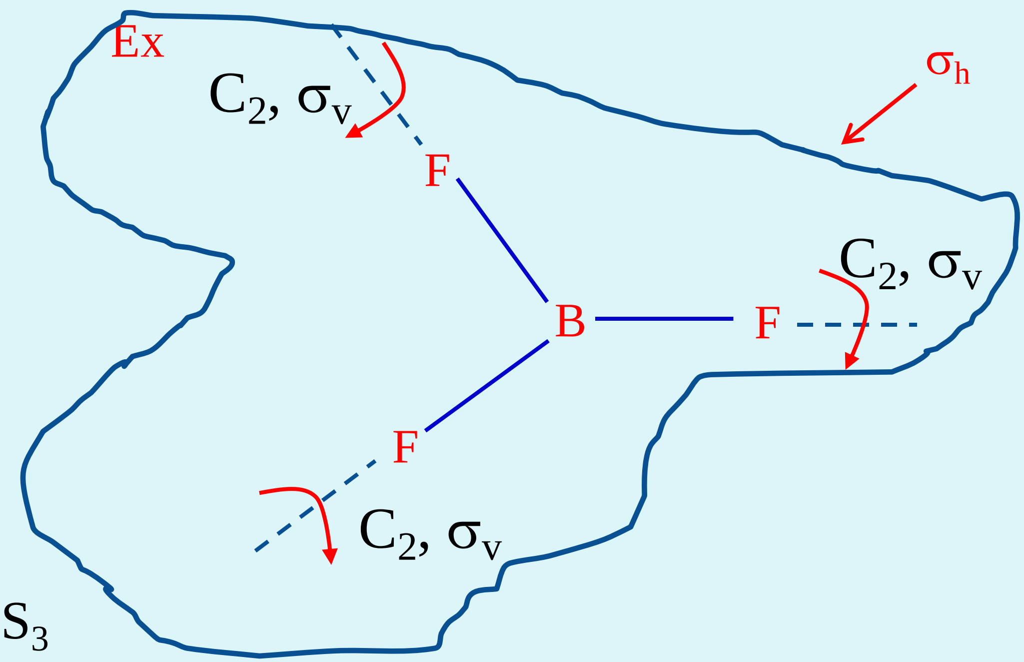


Vertical plane σ_v



C_2, 2 σ_v

Mirror plane



Horizontal plane symmetry

$(C_3 \perp 3C_2 + \sigma_h + 3\sigma_v) + S_3$

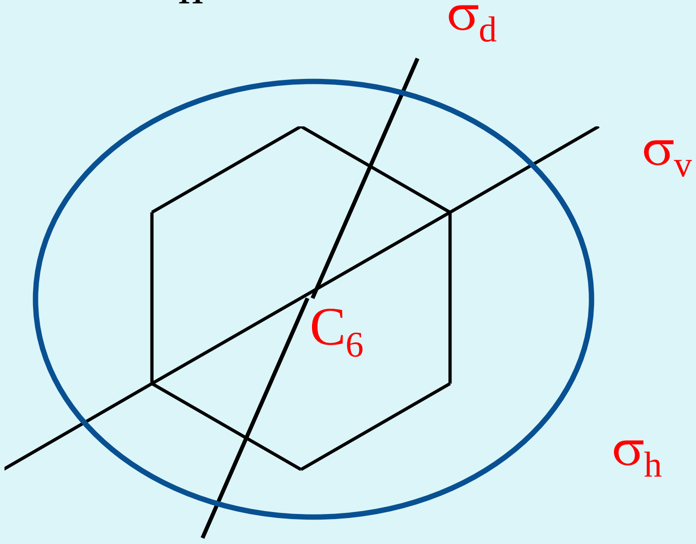
Ex.: Benzene

The benzene ring has C6 axis which is the principle axis of rotation.

- has σ_v, σ_d

- has horizontal plane σ_h

[The plane that bisect the bonds are called dihedral plane]

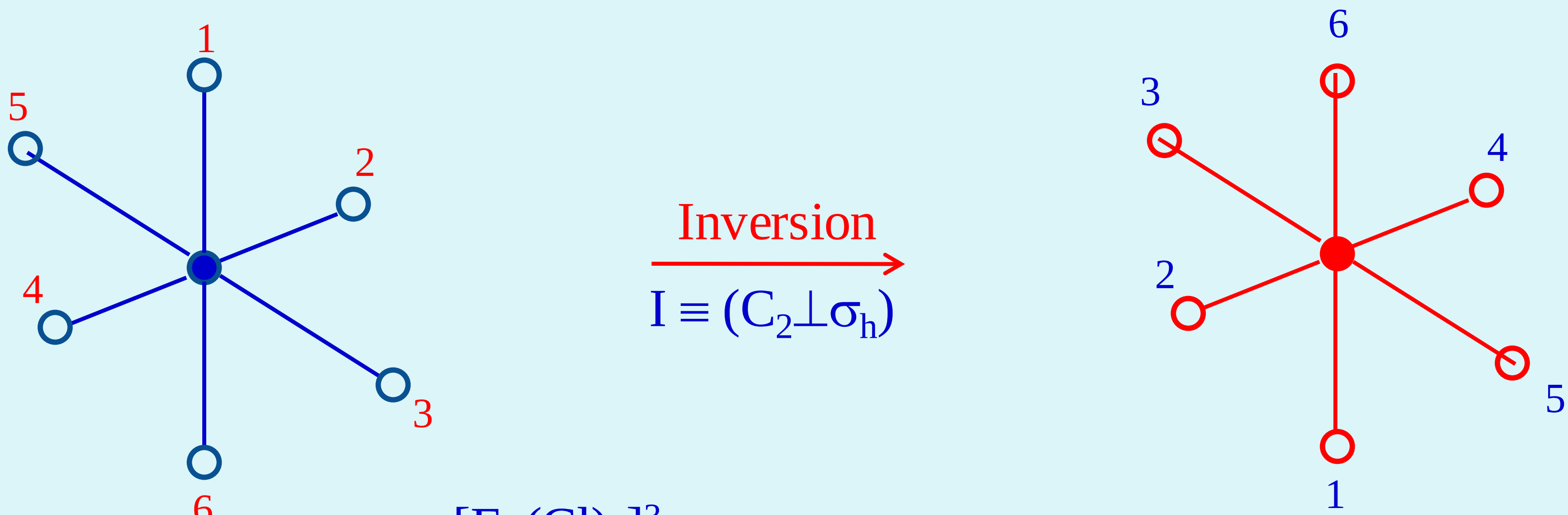


]The vertical plane σv, through carbon atom, and include C_6 axis

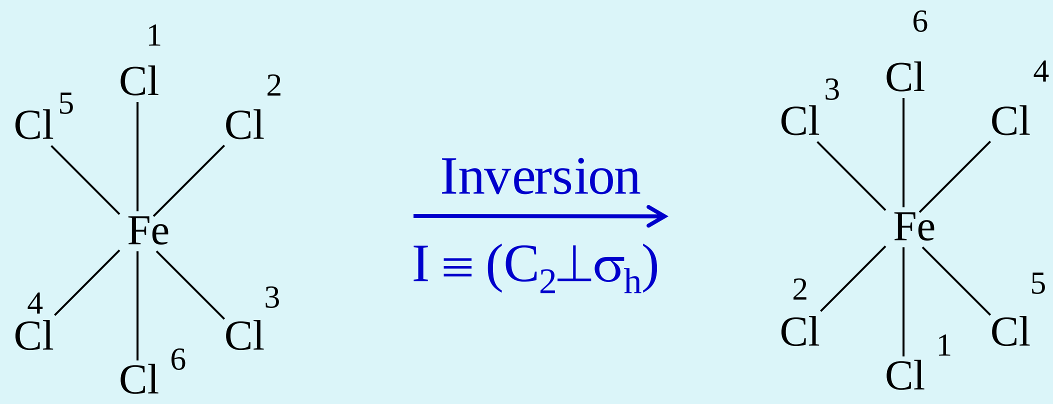
[horizontal plane rependicular to C_6 axis called σ_h]

(i) Inversion

The inversion operation projects each atom through the center of inversion, and across to the other side of the molecules



$[Fe(Cl)_6]^{3-}$



Improper axis of rotation

$S_1 \Rightarrow S_1$ axis doesn't exist it is the same as mirror plane.

$S_2 \Rightarrow S_2$ axis is center of inversion.

Improper rotation (Sn): is rotation followed by reflection in the plane perpendicular to the axis of rotation.

Point group:

Molecules with the same symmetry elements are placed into point group.

Types of point groups

1- C1 point group:

Molecules with no symmetry element.

Ex.: CH Br F Cl

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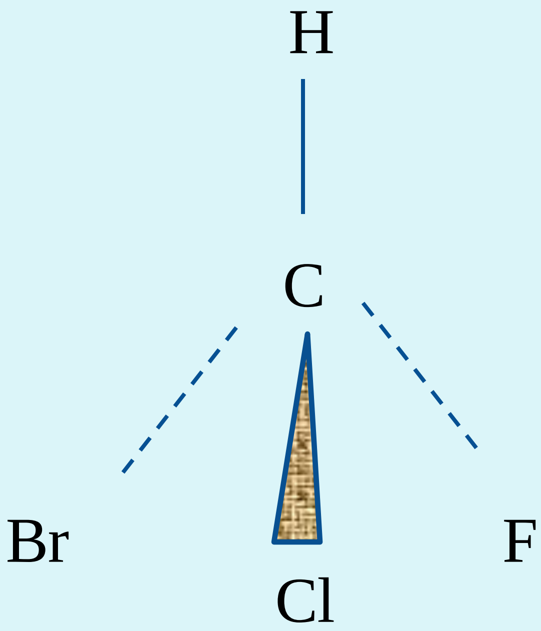
1- C1 point group:

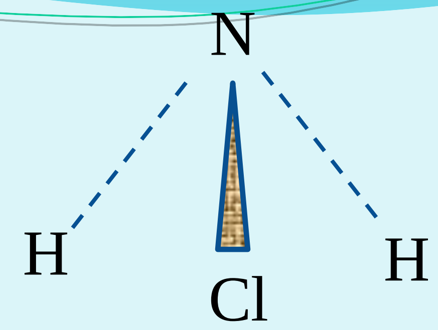
- Molecules with no symmetry element.
- Ex.: CH Br F Cl



2- Cs-point group:

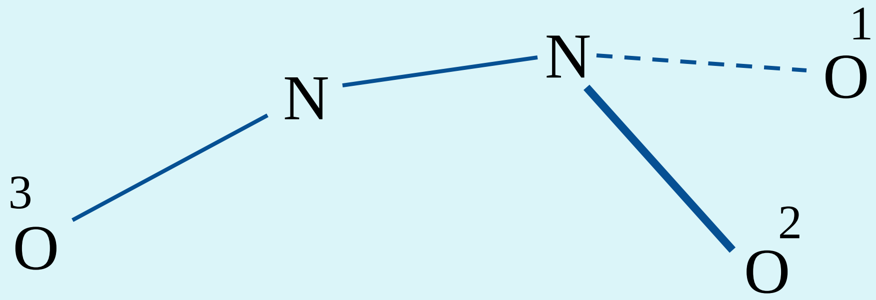
Molecules with only σ (plane).

Ex1: NH_2Cl



σv only

Ex2: N_2O_3



containPlane

3- Ci-point group:

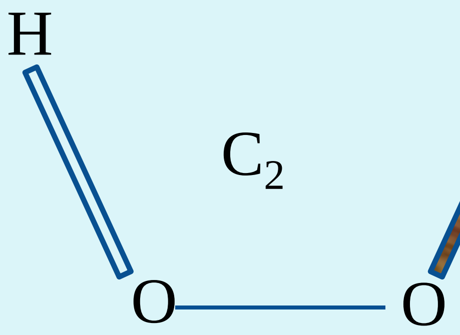
Molecules with only E & i.

4- Molecules with only C_n n > 1

Cn-point group

Ex: H_2O_2 & N_2O_2 & N_2H_2

These molecules have book structure (not planar)



H_2O_2

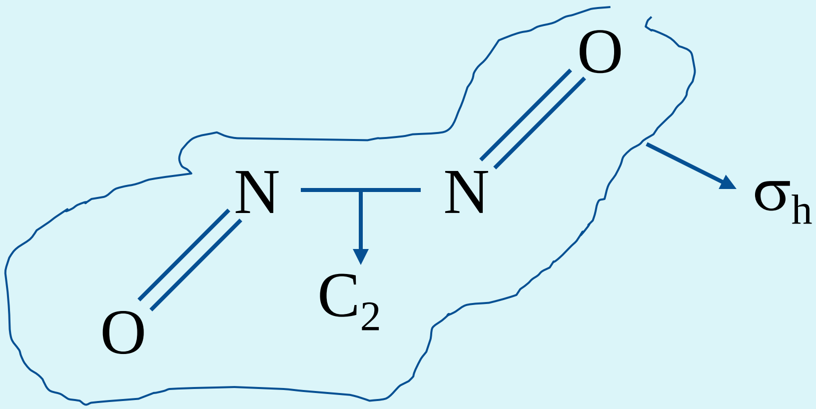
C2-point group

5- Molecules with $C_n + \sigma_h$

belong to Cnh – point group

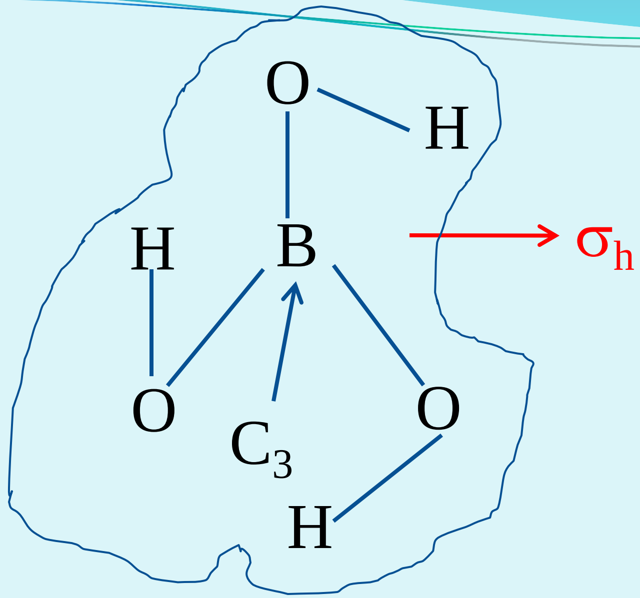
Ex: H_2O_2, N_2O_2 in planar structure

C2h



i, S_2, $C_2 \perp \sigma_h$

Ex: $B(OH)_3$

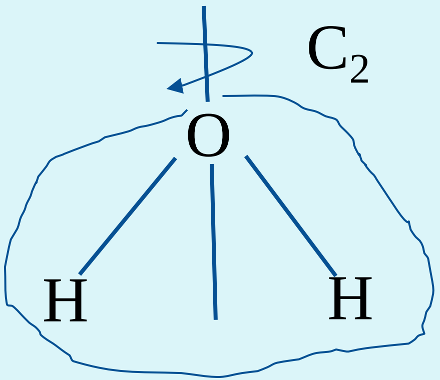


These molecule have C_3 and no C_2 due to (O-H bond)

- All atom are in σ_h

C3h

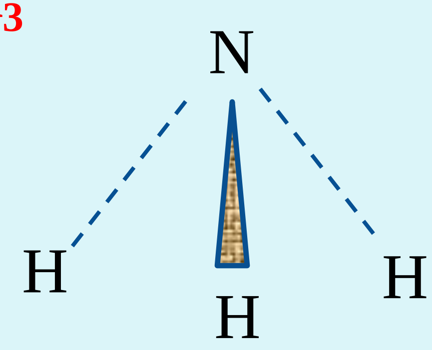
6) Molecules with only (C_n + n σ_v) belong to C_nv

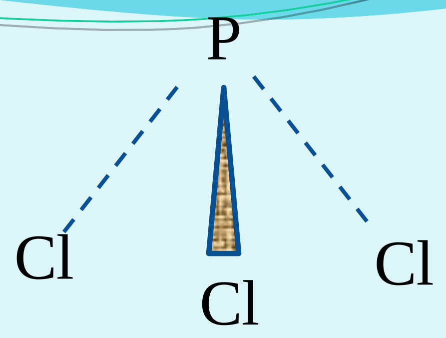


$C_2 + 2\sigma_v$

C_2V – point group

Ex2: NH_3, PCl_3

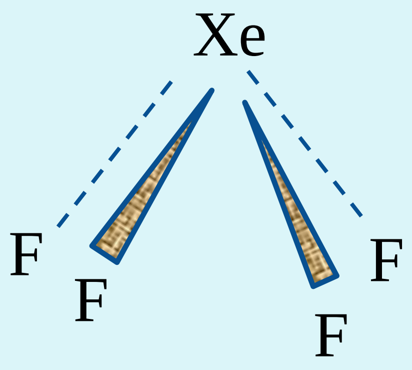




C_3 and 3 σ_v

C_{3V}-point group

Ex3: XeF_4 square pyramide

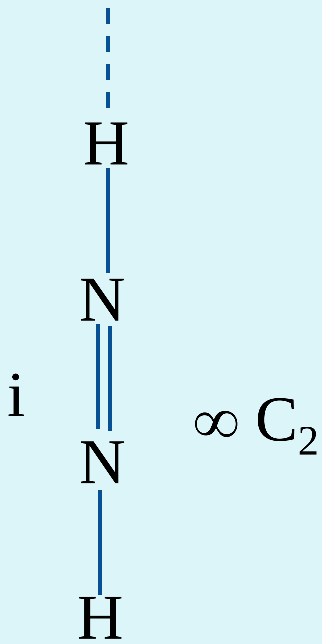


C_4, 4 σ_v

C_{4v}

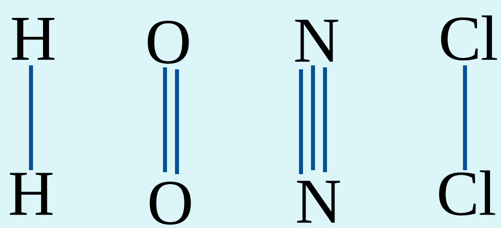
7) Molecules with $C_n \perp nC_2$ belong to D_n if then are σ_h it become dnh point group

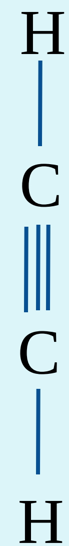
Ex: Linear molecules



$$C\infty \perp \infty C_2 + \sigma_h$$
$$\infty \sigma_v + \infty S_2 + i$$

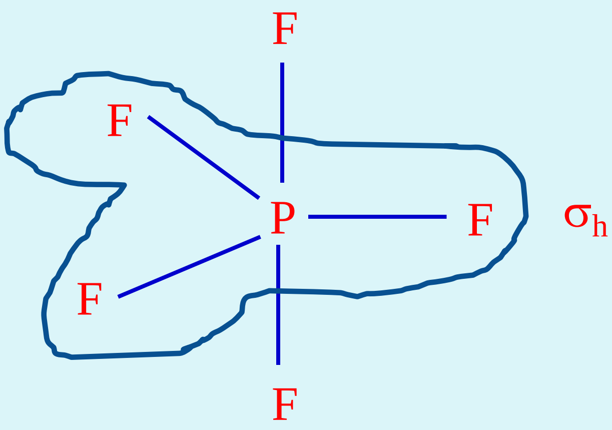
$D\infty h$





The same

Ex: PFs trigonal bipyramide

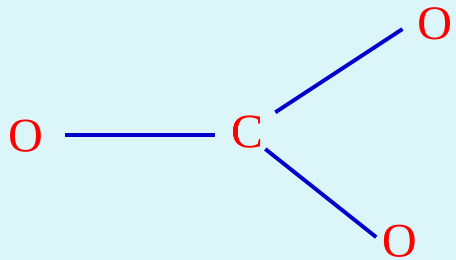


$C_3 \perp 3C_2\ \sigma_h$

$S_3 + 3\sigma_v$

D3h

Ex: Co_3^{2-}



$C_3 \perp 3C_2$

$+ \sigma_h$

D3h

Ex: Benzene

$C_6 \perp 6C_2\ + \sigma_h \equiv D6h$

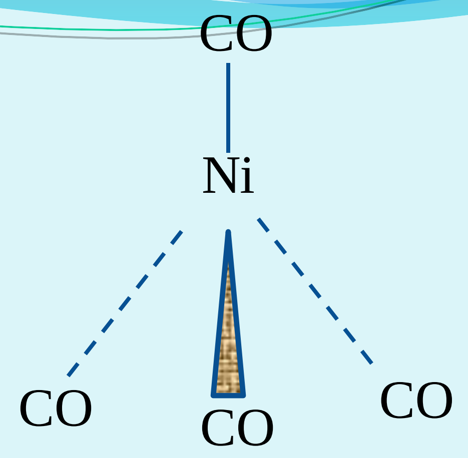
8- Special groups

(a) Octahedral $[M(L)_6]$

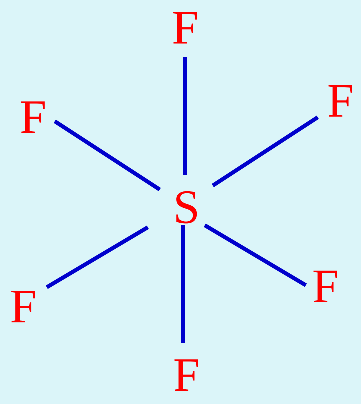
Oh P.G

(b) tetrahedral →

$[CH_4, SO_4^{-2}]$



Td.P.G.

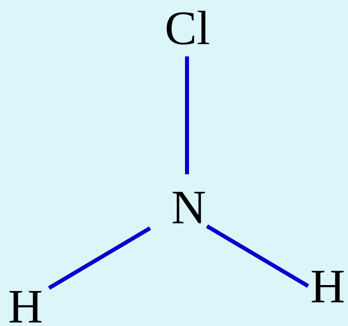


Oh

Q: Determine all symmetry elements and point group for each possible structure

NH_2Cl, N_2O_3, N_2O_2, N_2O_5 WF_5

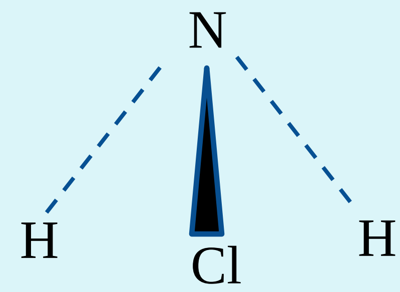
Answer: [1]



Planar

$C_2 + \sigma_v + \sigma_v'$

C_{2v} point group



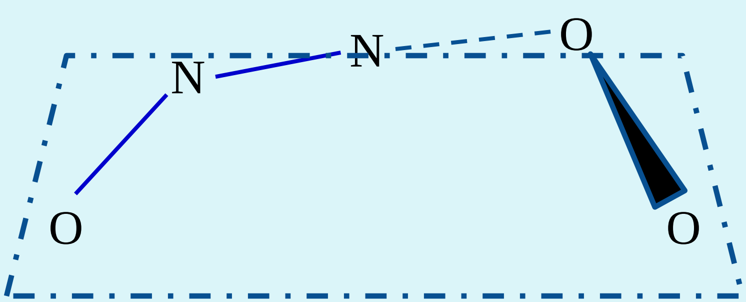
Trigonal pyramid

σ_v only

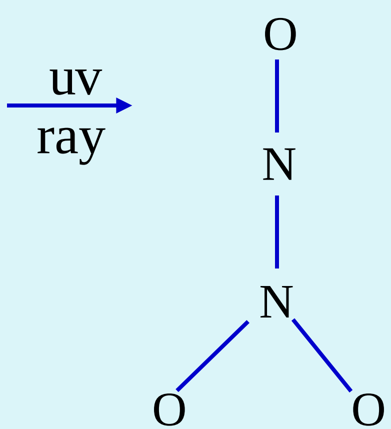
Cs point group

[2]

Cs



σ_v only



$C_2 + \sigma_v + \sigma_v'$

C_{2v}

[3] N_2O_2

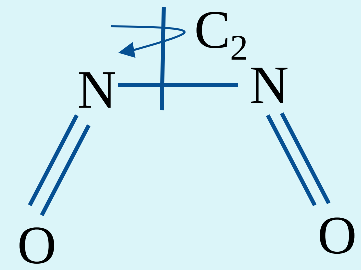
(i) Linear st

$C\infty + \infty\sigma_v$

$S_2\ \sigma_h,\ \infty\sigma_v$

$\equiv D\infty h$

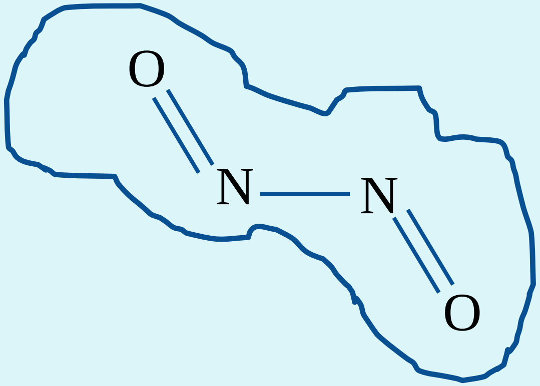
(ii) Non Linear st



$C_2,\ \sigma_v$

C_2v

(ii) Planar trans

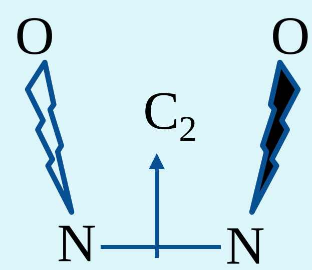


σ_h

C2 + S2, I + σ_h

C_2h

(iv) Book st

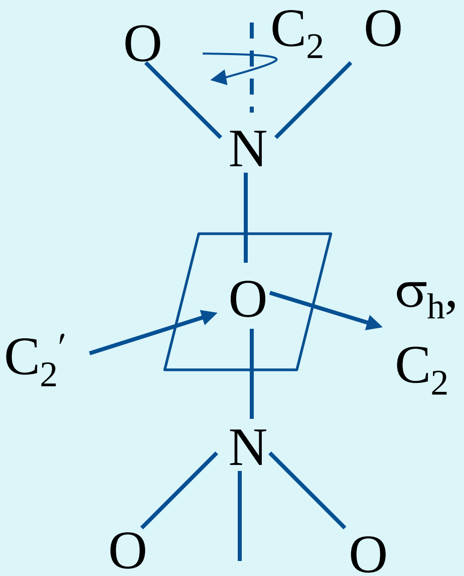


C_2 only

C_2 point group

[4] N_2O_5

(1) Two possible

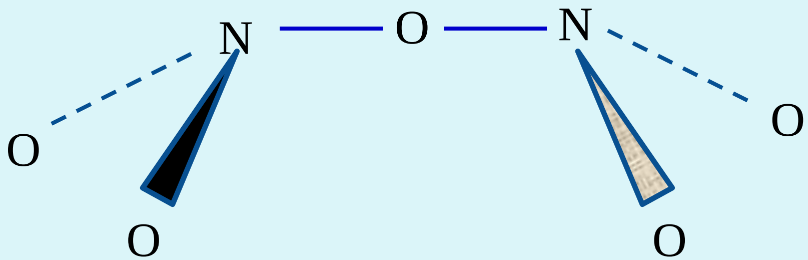


$C_2 \perp 2C_2' + \sigma_h, 2\sigma_v$

$3S_2 + I$

D_2h

(2) Donky st



$C_2, 2\sigma_v$

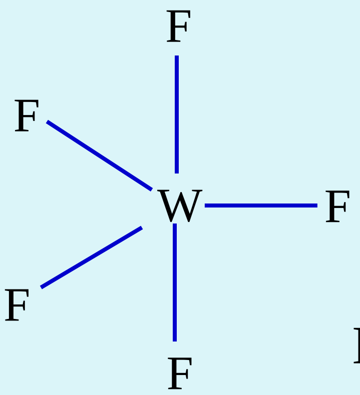
C_2v

(v) WF_5

(a) Trigonal bipyramid

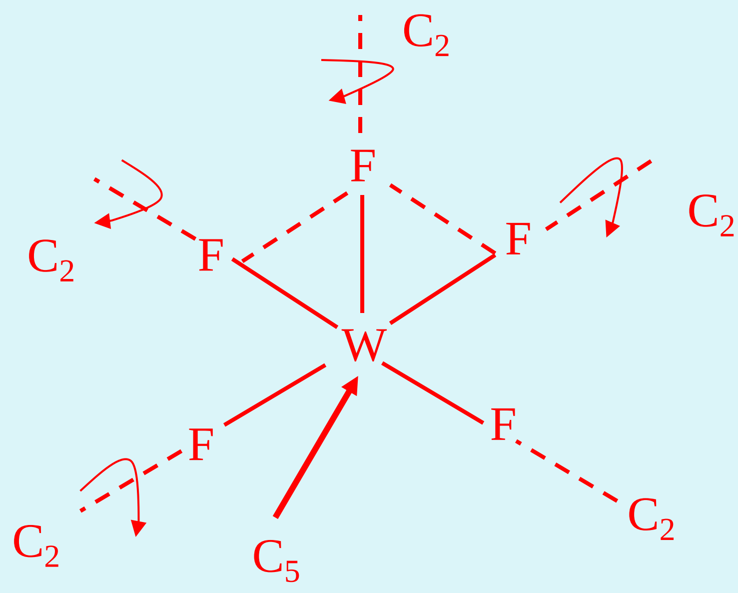
$3\sigma_v$ + $C_3 \perp 3C_2 + \sigma_h$

S_3



D_3h

(B) Pentagon



$C_5 \perp 5C_2 + S_5$

$5\sigma_v$, σ_h

D5h