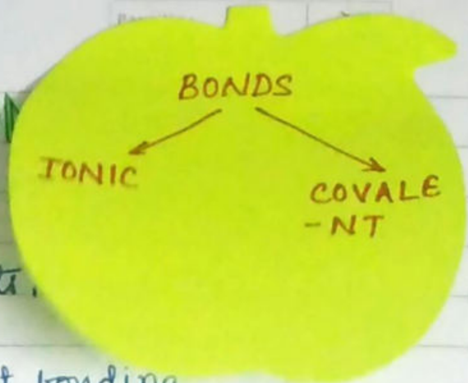
19-01-2021

CHEMICAL BON[D]



Topics to be covered
- Type of bonding (ionic & covalent)
- Lattices, unit cells, symmetry elements.
- Lattices & molecules
- Shape and geometry - (VBT) - in covalent bonding
- Hybridisation
- MOT
- Band theory for conductors, insulators, semiconductors
- Types of semi-conductors
- Defects in lattices (solids)

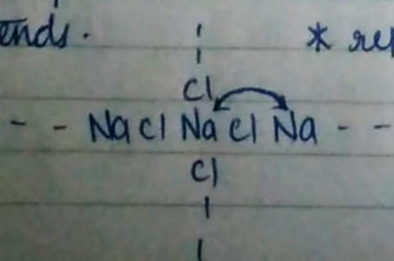
Ionic bond

There is no sharp boundary b/w ionic bond & covalent bond.
But division has been done to define properties of lattices.
ionic solid :- experimentally
- high mpt.
- lattice geometry with unit cell (particular)
- brittleness — explains formula as well
- solid structure
- conduct electricity in aqueous state
- solubility in polar solvents

★ DIAMOND (covalent bond - weaker bond) but extremely hard substance, but doesn't dissolve in water.

To understand better let's go with bonding styles.
why ionic solids are soluble in polar solvents?
Because atoms of ionic solids are charged spheres.
These charged spheres are bonded but in solvent their bonding extends.

★ repetition of similar atom in 3-D space.



18-01-2021

CHEMICAL BONDING

Topics to be covered

- Type of bonding (ionic & covalent)
- Lattices, unit cells, symmetry elements, symmetry
- Lattices & molecules
- Shape and geometry - (VBT) - in covalent bonding
- Hybridisation
- MOT
- Band theory for conductors, insulators, semiconductors
- Types of semi-conductors
- Defects in lattices (solids)

Ionic bond

Each Na^+ is being surrounded by $6 Cl^-$ in 3D space.
This is made of lattice (3-D). In this lattice if we choose atoms to define geometry (like cube, hexagon etc) & geometry means regularity. Ionic solids are crystalline in nature. It is difficult to differentiate Na & Na^+ from each other by using modern day machines. But we can justify by dissolving it in water. Water being a polar solvent has potential to overcome electrostatic force of attraction b/w Na^+ & Cl^- because it introduces hydration energy as water molecules will get inculcated into lattice energy then,

Hydration energy > lattice energy (NaCl dissolves)

Hence, we can say that they are made up of cations & anions.

- All hard substances / substances with high mpt are not made up of cations & anions.

- Brittle (not malleable & ductile) - pressure applied on solid, distortion of lattice (Na^+ atoms come close to Na^+ & Cl^- to Cl^- atoms & same charge repel each other) so they break apart.

Silver, Gold, Iron (hard) but not brittle - so no ionic bonds.

CONDITION TO FORM IONIC BOND

- low ionisation energy of cation
- high electron enthalpy of anions
- high lattice energy of solids

STRUCTURAL ASPECT OF IONIC SOLIDS

These lattices follow symmetry. Nature also follows symmetry. (unsymmetrical obj. shows optical isomerism).

Unit cell of NaCl has been described by X-Ray diffraction method. (cubic structure)

Cl^- at corners & face centered

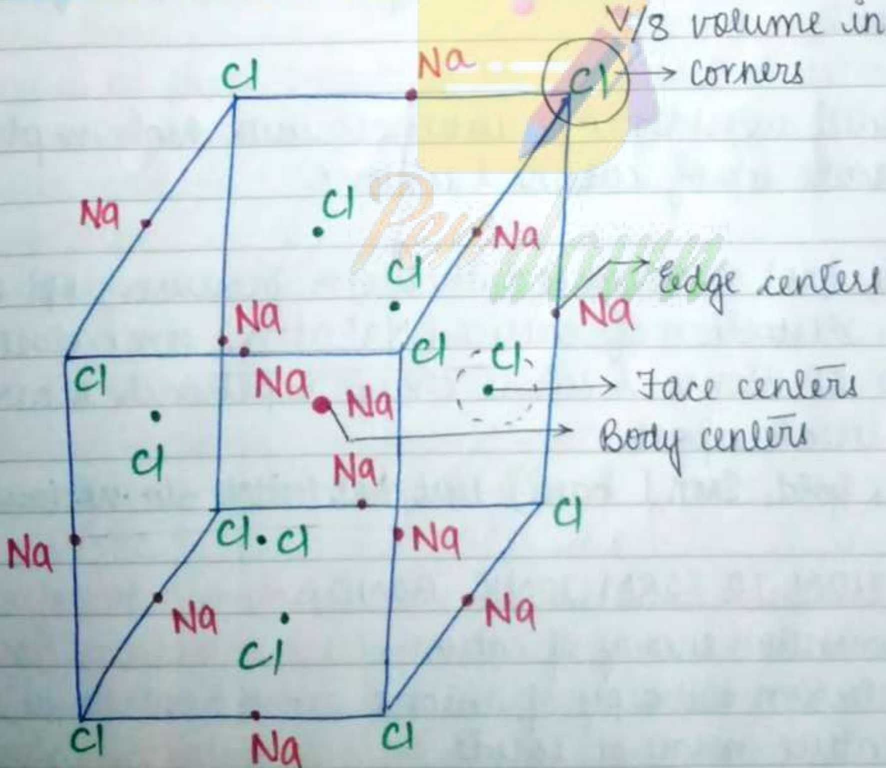
Na^+ at body center & edge center

- If we proceed by closest packing approach then in NaCl Cl^- atom are in cubic closest packing. i.e. ABC type.
- unit cell - cubic
- Voids are created - tetrahedral & Octahedral

In NaCl, Na^+ atoms are in octahedral voids.

NO. OF OCTAHEDRAL VOIDS = NO. OF SPHERES TAKING PART IN PACKING

- Tetrahedral voids in NaCl are vacant.



corner = $\frac{1}{8}$ contri. = $\frac{1}{8} \times 8 = 1$

face = $\frac{1}{2}$ contri = $\frac{1}{2} \times 6 = 3$

$\overline{\quad 4\,Cl^- \quad}$

edge = $\frac{1}{4} \times 12 = 3$

body center = 1

$\overline{\quad\quad}$
$4Na^+$

$4Na^+$ & $4Cl^-$ atoms – in a cell (unit)
This unit cell is present everywhere hence sharp mpt.

If we crystalline NaCl from water [sulphurated solⁿ → crystals of NaCl] then we will see NaCl is externally also cubic
But if we crystalline NaCl from ethanol then crystals won't be cubic but octahedral but unit cell (structure) remains same.

* Unit cell will be same but external geometry differs.
Similarity – symmetry elements
what is symmetry & what are symmetry elements?
If a body can have show/display more than one similar orientations upon application of the operation of the symmetry elements it is said to contain symmetry
There are 3 symmetry elements

- ~~Axis of symmetry~~ – line passing through body center.
After rotating the body by a fixed angle ~~through~~ along the axis it will have fixed orientation (same).

For eg. ①
① C ↻ $180°$
$O=C=O$ symbol of axis is C_2.
② ↻ $180°$

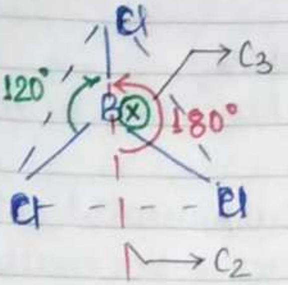
$C_{②}$
↳ means $\frac{360}{180} = 2$

if $90°$ then C_4. $\left[\frac{360}{90} = 4\right]$

C_1 axis always present in every molecules i.e. 360° rotation. $C_1 \rightarrow$ Identity element of symmetry

No. of C_2 axis = ∞

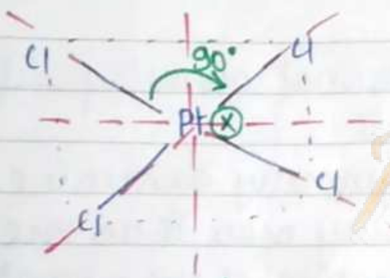
which axis is passing through -θ

② 

sp^2 hybridised trigonal planar

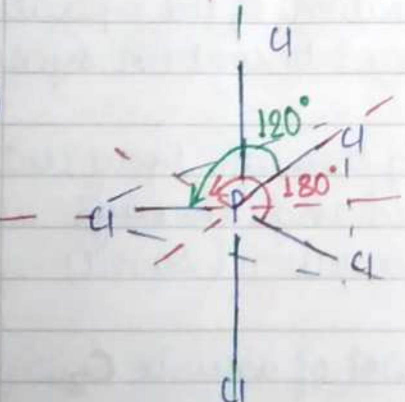
C_2 axis is $\perp^r$ to C_3

3 C_2 axis in BCl_3 & 1 C_3 axis & 1 C_1 axis as well.

③ 

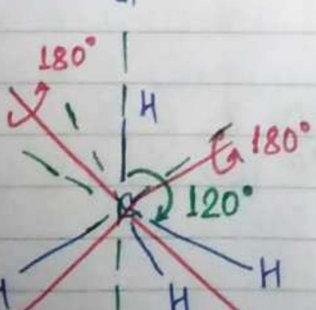
1 C_4 axis, 4 C_2 axis } $\perp^r$

1 C_1 axis

④ 

1 C_3 axis, 3 C_2 axis } $\perp^r$

1 C_1 axis

⑤ 

tetrahedral

4 C_3 axis

1 C_1 axis

2 C_2 axis

No. of C_2 axis $= \infty$

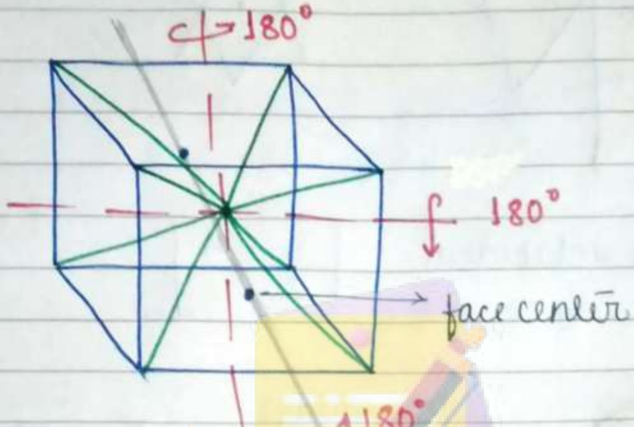
which axis is passing through $-O=C=O-$ $= C_\infty = \frac{360}{0}$

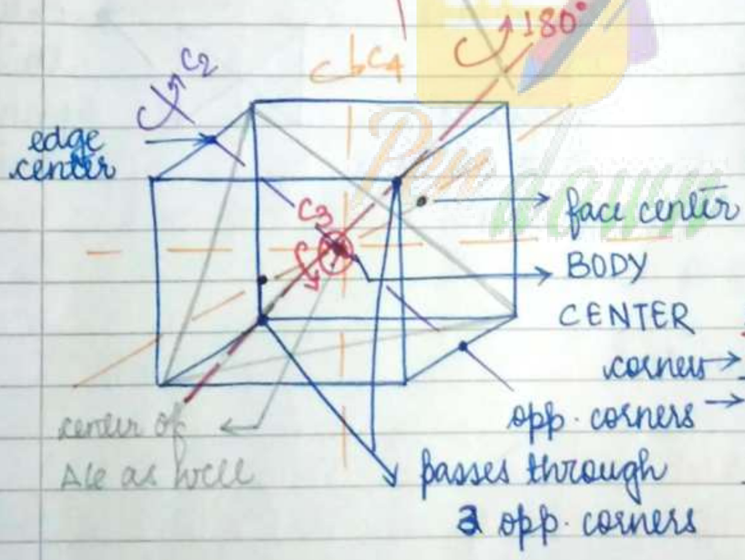
25-01-2021

No bond is 100% ionic or 100% covalent.

25-01-2021 Symmetry is also followed by molecules formed by covalent bonds.

HOW TO VISUALISE C_2 axis in CH_4.





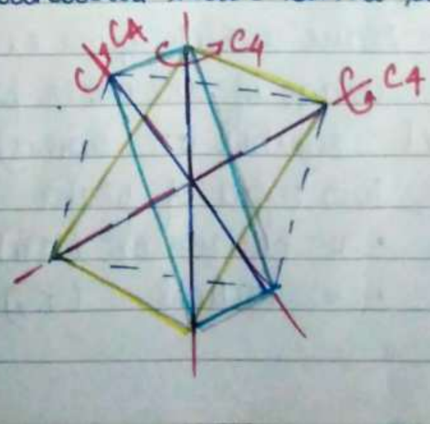
line of symmetry in a cube

3 C_4 axis

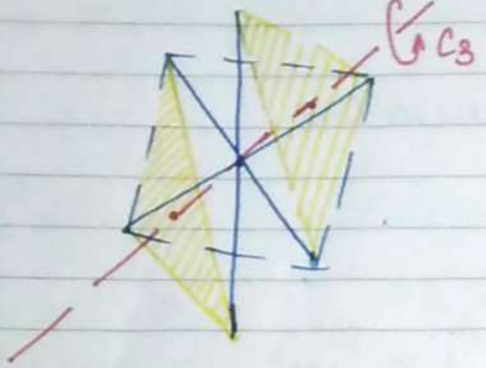
corners → $\frac{8}{2}$ = 4 C_3 axis

$\frac{12}{2}$ = 6 C_2 axis

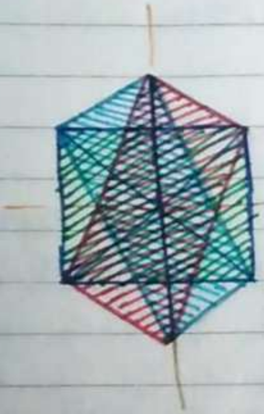
★ cube & octahedral have same aspects on symmetry



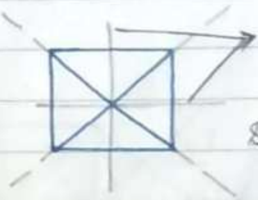
In octahedral there are 3 C_4 axis. Any 2 trans bonds/ line passing through them in octahedral forms C_4 axis.



4 C_3 axis in octahedral. $\left[\frac{8}{2} = 4\right]$



each square only 2
3 squares =
$3 \times 2 = 6$ C_2 axis



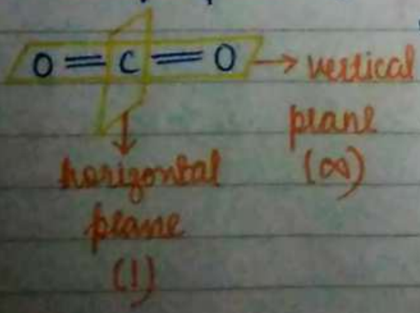
only this symmetry axis.

Why diagonal axes are being ignored?
Intermingled squares
$2C_4 \longrightarrow 1C_2$
so, if diagonal is considered then it will give repetitions of parts.

6 C_2 axis in octahedral

The plane $\perp^r$ to highest order axis is called horizontal axis (only for linear molecules).

- Plane of symmetry : Plane which gives exactly the mirror image of the other projected part. symbol σ (sigma)

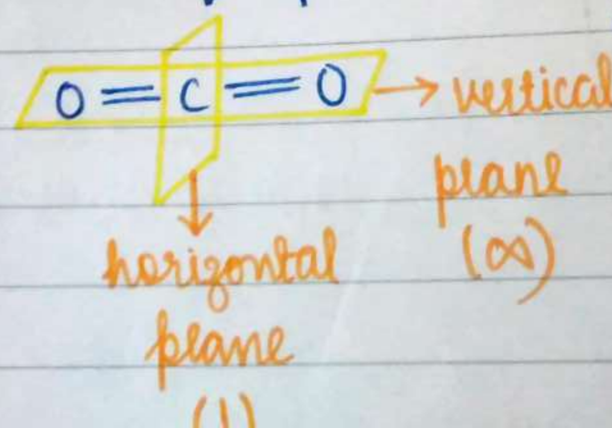
(1) 

Two types of plane of symmetry.
- σ horizontal (σ_H)
- σ vertical (σ_V)

6 C_2 axis in octahedral

The plane ⊥ᵣ to highest order axis is called horizontal axis (only for linear molecules).

- Plane of symmetry : Plane which gives exactly the mirror image of the other projected part. symbol σ (sigma)

(1) 

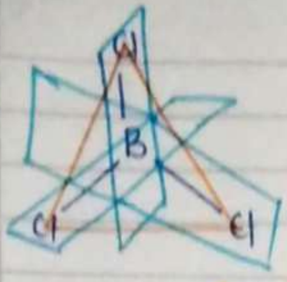
Two types of plane of symmetry.

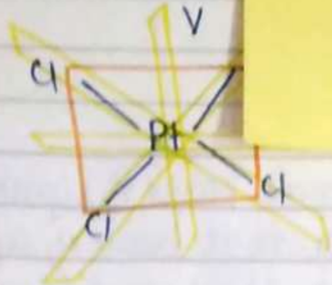
- σ horizontal (σ_H)
- σ vertical (σ_V)

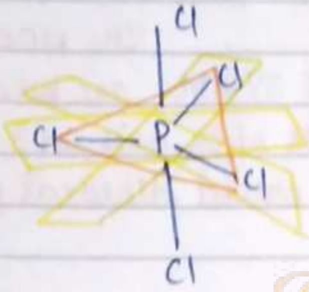
In cube there are two types of plane of symmetry –

(A) Rectangular plane of symm.
(mid. of two opp. faces)

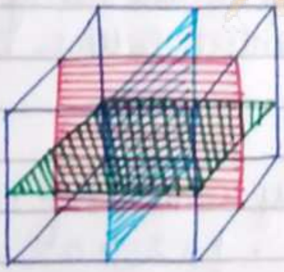
(B) diagonal plane of symm.
(two opp. edges)

(2) 

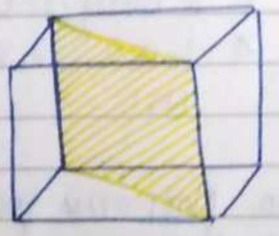
(3) 

(4) 

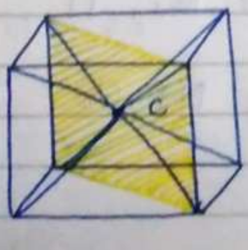
$1\sigma H$
$3\sigma V$

(5) 

$\frac{\text{6 faces}}{\text{2 opp. faces}}$ = 3 rectangular plane of symmetry

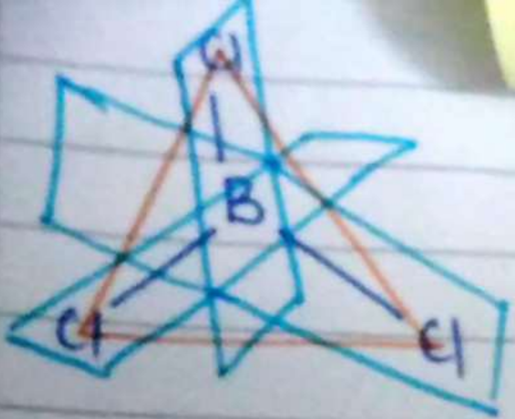


$\frac{\text{12 sides}}{\text{2 opp. sides}}$ = 6 diagonal plane of symmetry

(6) 

all 6 diagonal plane of symmetry will act as mirror plane of symmetry in tetrahedron (regular). By regular we mean achiral C and all are same func. groups at corners of tetrahedron.

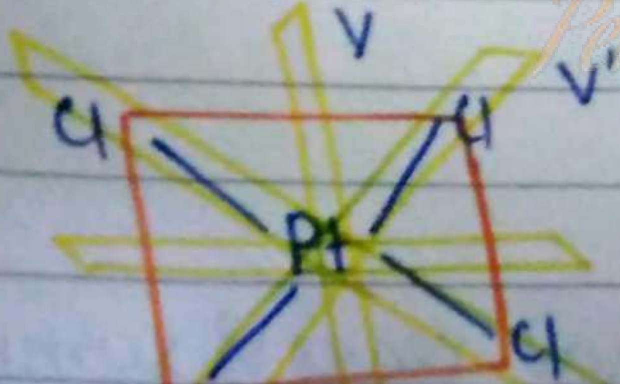
②



$1\sigma_H$

$3\sigma_v$

③



$1\sigma_H$

$4\sigma_v\ (2\sigma_v + 2\sigma_{v'})$

(7)

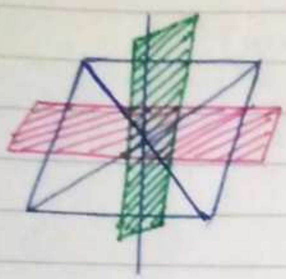
3- square plane of symmetry

$3\sigma - H$

why asymmetrical object rotate plane polarized light?

symmetry → mirror images superimposable

unsymmetry → non-superimposable mirror images



Ignoring diagonal plane of symmetry there are 6σ dihedral plane of symmetry or $6\sigma d$ → dihedral/ lihedral (dividing the face)

TOTAL → 9 PLANE OF SYMM.

The planes which are present in middle of C_2 axis in 3-D molecules are called dihedral planes.

C_n → proper axis of symm.

S_n → improper axis of symm.

Que If in a NaCl unit cell structure the atoms line along one C_4, one C_3 and C_2 axis are removed in entire lattice then what will be new formula for NaCl?

By removing 1 C_4

2 atoms of Cl^- are removed

$\frac{1}{2} \times 4 = 2$

By removing 1 C_3

2 atoms of Cl^- are removed

$\frac{1}{8} \times 6 = 0.75$

2.75 atoms of Cl^-

By removing 1 C_2

- $\frac{1}{4} \times 2 \Rightarrow 0.5$ removal
- 1 body center removed

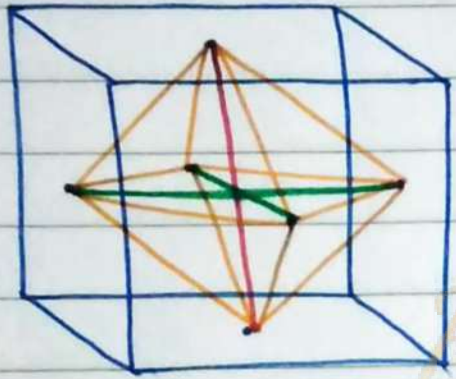
$4 - 1 - 0.5 = 2.5$ atoms of Na^+

So, NaCl new formula

$\Rightarrow Na_{2.5}Cl_{2.75}$

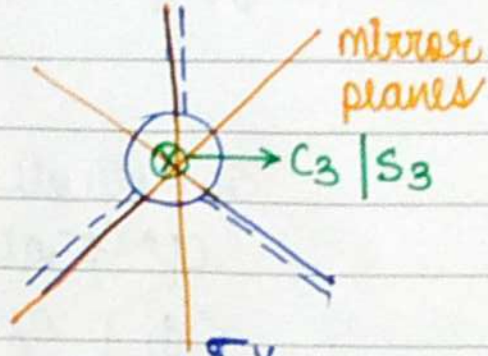
$\Rightarrow Na_{10}Cl_{11}$

OCTAHEDRAL IN A CUBE

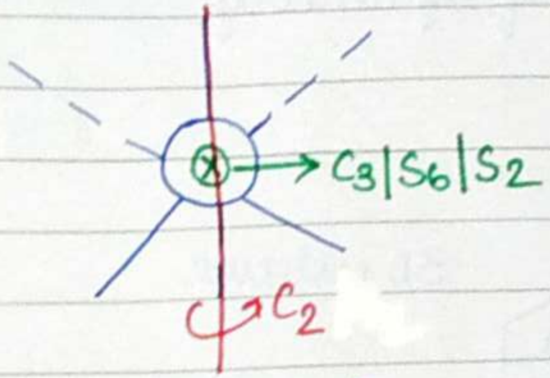


Que Eclipsed ethane, staggered ethane & ethane random find symmetry elements types and no.

Que Eclipsed ethane, staggered ethane & ethane random find symmetry elements types and no.



eclipsed

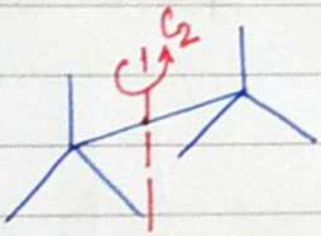


staggered

(vertically) σ - H mirror plane b/w (C-C)

- no. of mirror planes = 3 (⊥ to C-H bond)

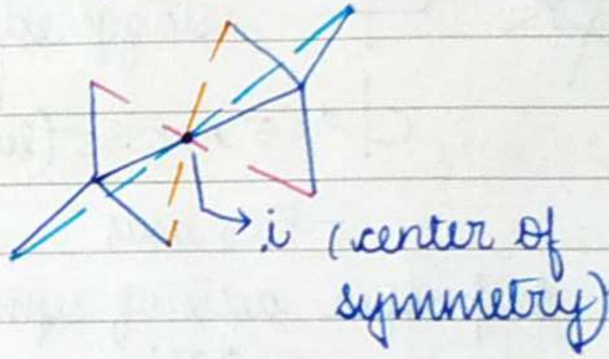
- 1 - C_3 axis (highest order axis)



- 3 C_2 axis (along C-H bonds)

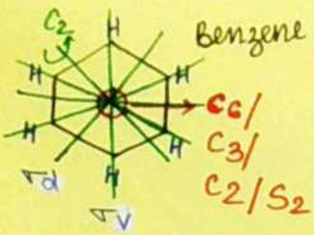
- no center of symmetry

- no mirror plane (σ_H)
- no. of mirror planes = 3 σ_v



- 3 C_2 axis
- 1 S_6 axis
- 1 C_3 axis
- 1 S_2 axis

01-02-2021



- $1C_6$
- σ_H
- $3\sigma_v$
- $3\sigma_d \rightarrow$ dihedral
- center of symmetry also exists

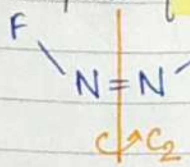
Which all ... ems.

(a) F N=N ...

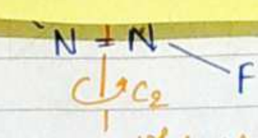
(cis)

(b) eclipsed ...

(a)



(b)



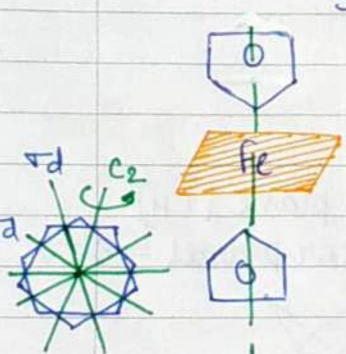
$\perp^r$ to plane of paper

- σ_H plane
- no center of symmetry

- σ_H plane
- center of symm.

(b)

3D molecule



- no. of mirror planes = $5\sigma_d$

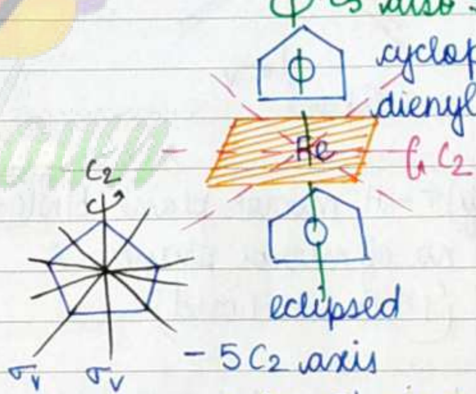
staggered

C_5 not S_5 (but S_{10})

$-5C_2$ axis

3D molecule

C_5 also S_5



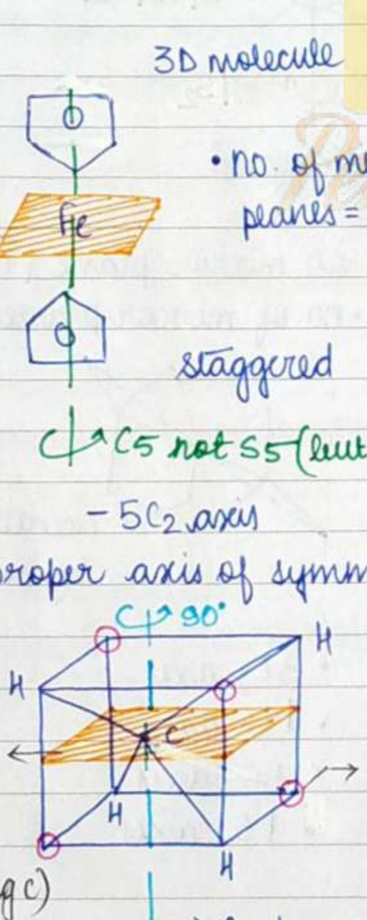
cyclopenta dienyl rings

eclipsed

$-5C_2$ axis

- no. of mirror planes = $5\sigma_v + 1\sigma_H$

- Improper axis of symmetry (S_n)

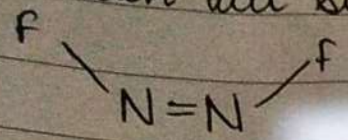
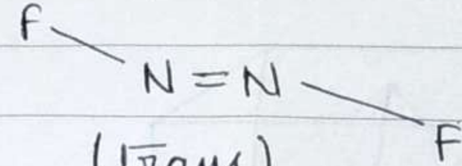


mirror plane (containing c)

$\rightarrow$ new positions of H after rotation by 90°

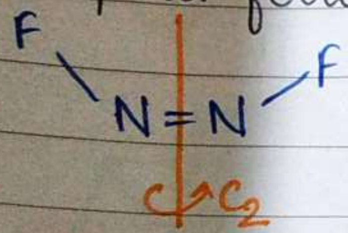
$\rightarrow C_4$ for cube but not for tetrahedral (T_d)

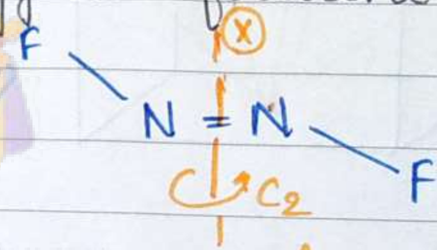
Which all symmetry axes are present in these forms.

(a)  and (b) 

(cis) (trans)

(b) eclipsed ferrocene and staggered ferrocene

(a) 

(b) 

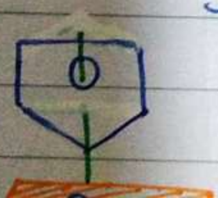
$\perp^{r}$ to plane of paper

- σ_H plane
- no center of symmetry

- σ_H plane
- center of symm.

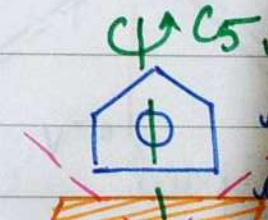
(b)

3D molecule



- no. of mirror

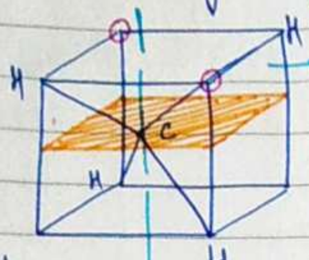
3D molecule



cyclopenta dienyl rings

After rotating only half of cube

3- S_4 for tetrahedral
3 - S_4 for cube
0 - C_4 for tetrahedral
3 - C_4 for cube



→ only upper half is rotated by 90°.

Upper half & lower half are mirror images.

S_4 for tetrahedral

$S_n = C_n + \sigma_h$ → then apply horizontal operation (inserting plane mirror containing c)

↓

apply C_2, C_3 or C_4 operation

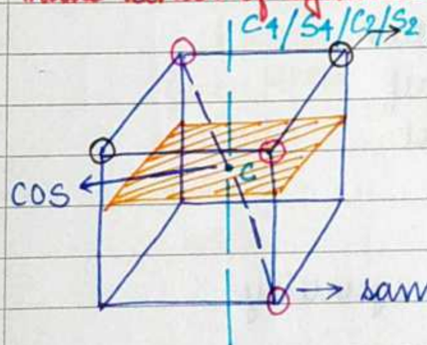
In NaCl structure
it has S_4 as well as C_4.

Center of symmetry / Point of symmetry / Point of inversion :-

(i) → center of symmetry

$i = S_2$ axis $= C_2$ axis $+ \sigma_H$

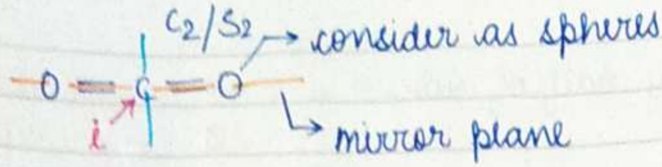
It is the point in the body through which you move in one direction to get some atom & exactly in the opposite direction to get same atom, then that molecule is said to said to have center of symmetry.



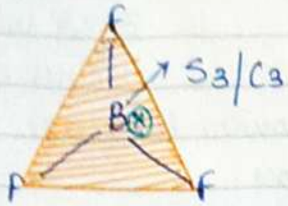
→ new positions after C_2.

→ same atom we will get.

(i)



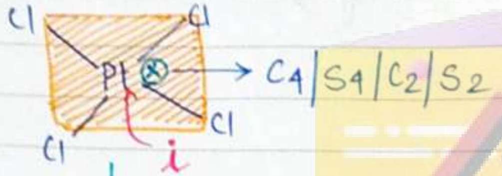
(ii)



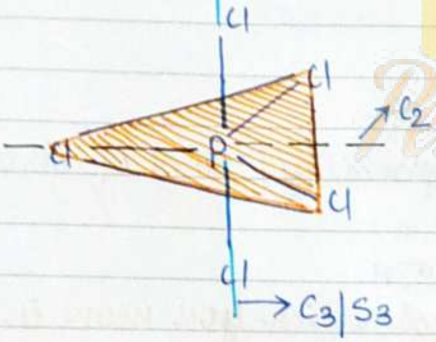
NO S_2 axis (after mirror (σ) plane we won't get mirror images)

NO i

(iii)

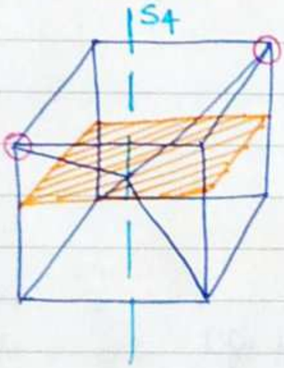


(iv)



NO S_2 axis

(v) tetrahedron

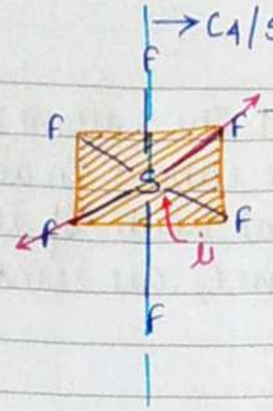


after C_2 operation in upper half the two H got cancelled.

NO S_2 axis

So, NO center of symmetry

(vi)

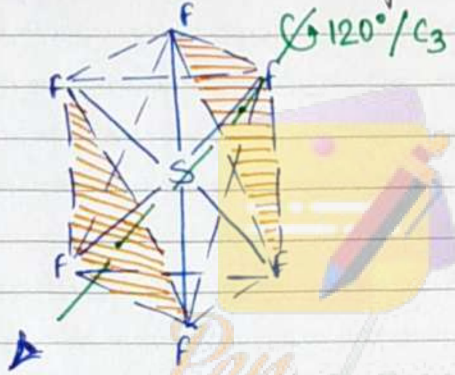


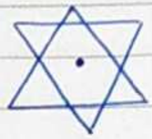
$3 = C_4/S_4$

BUT WE CAN'T SAY THERE ARE $3 S_2$ as center of symmetry is only 1.

So $1 S_2$

Does octahedral contains any other S axis other than S_4 and S_2?





If upper Δle is rotated by 60° then they will superimpose.

(a) Is C_3 in S_3 or not? NO

(b) Are there any other S axes? $S_6 = C_6 + \sigma_H$

$4C_3$ and $4S_6$ are present in octahedral.

In crystallography

the structure of unit cell (NaCl) symmetry is represented by this $Fm\bar{3}m$ or O_h → O stands for octahedral (in ethanol soln)

F ↓ face centered cube (in water)

m ↓ mirror planes

$\bar{3}$ → C_3 axis of symm.

m → 2 type of mirror planes

Page No.:
Date:

Que. In zinc blende structure (ZnS) [cubic] cell. The S atoms are present at corners & face centers of the cube & Zn atoms are present in $\frac{1}{2}$ alternate tetrahedral voids. If the atoms lying along one C_4, one C_3 & one C_2 are removed. Find new formula of ZnS.