

(परीक्षाशी द्वारा भरा जाए)

(To be filled by the Candidate)

First Periodical Test, July-December, 2021

परीक्षा का नाम (Name of Examination)..... First Periodical Test, July-

December, 2021.....

अनुमतिग्राहक अंकों गों(In figures) 2141991

अनुमतिग्राहक(शब्दों गों)(Roll No. in Words) Twenty one lakh forty one thousand
nine hundred and ~~ninety~~ one

नामांकन संख्या (Enrollment No.)

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विषय(Subject) CHEMISTRY

प्रश्न पत्र कोड सहित (Paper withCode). Inorganic Chemistry (CHEM 405)

परीक्षा दिन और दिनांक (Day and Date of Examination). 6th SEPTEMBER 2021

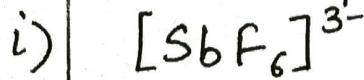
MONDAY

Total Number of Pages excluding this page _____ 24 _____

Question	1	2	3	4	5	6
Write NA for questions not attempted			NA		NA	

Signature of the Student

Q1a) Predict the shape of following molecules on the basis of VSEPR Theory.



$$VE = \frac{1}{2} [v + m - c + a]$$

v = valence electron on central atom

m = no. of monovalent atom

c = cation charge

a = anion charge

$$VE = \frac{1}{2} [5 + 6 - 0 + 3]$$

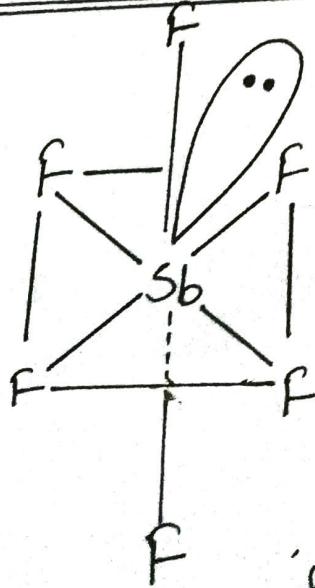
$$VE = \frac{1}{2} \times 14$$

VE = 7 e⁻ pairs

6 bp + 1 lp

Hybridisation - sp^3d^3

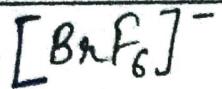
Shape - Distorted Octahedral



Distorted Octahedral
(Monocapped Octahedron)

Normally, sp^3d^3 shows pentagonal bipyramidal since the size of the central atom is larger and the surrounding atoms are smaller so the shape is distorted octahedral.

ii)



$$VE = \frac{1}{2}(v+m-c+a)$$

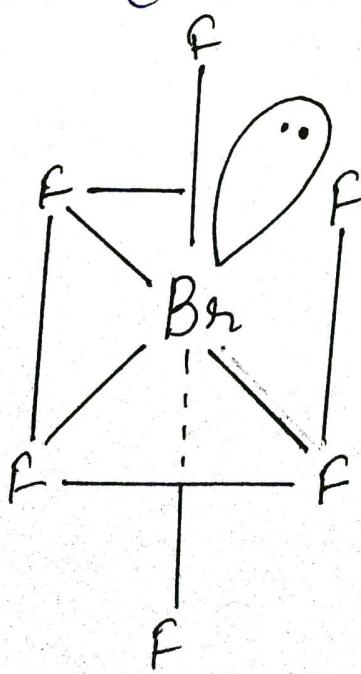
$$VE = \frac{1}{2} \times [7+6-0+1]$$

$$VE = \frac{1}{2} \times 14 = 7 e^- \text{ pairs}$$

$\rightarrow 6 bp + 1 lp$

Shape - Distorted Octahedral
(Monocapped Octahedron)

Since, the size of the central atom Bromine is larger and the size of the surrounding atom is much smaller so lone pair orbital ~~can get~~ occupy space as the fluorine atoms are smaller and result into Distorted Octahedral Geometry.
(Monocapped Octahedron).



(iii) $[SbCl_6]^{3-}$

$$VE = \frac{1}{2} [v+m-c+a]$$

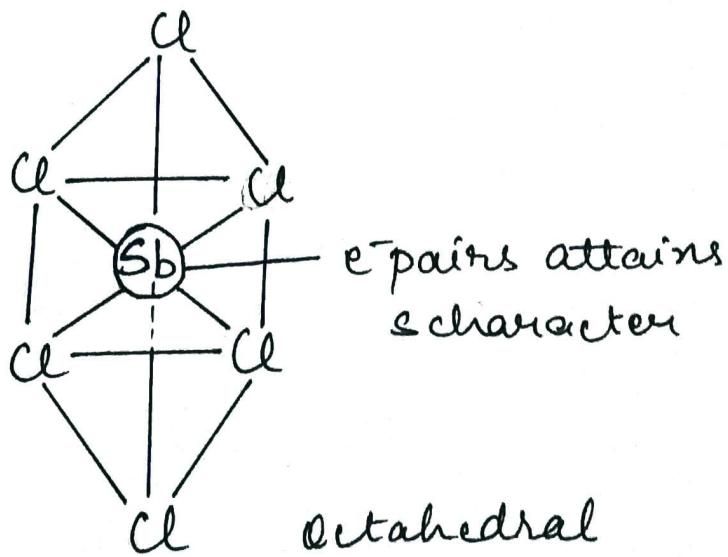
$$VE = \frac{1}{2} [5+6-0+3]$$

$$VE = \frac{1}{2} \times 14 = 7 e^- \text{ pairs}$$

$\rightarrow 6 bp + 1 lp$

Shape - Octahedral

as lone pair attains s character
and become inactive.

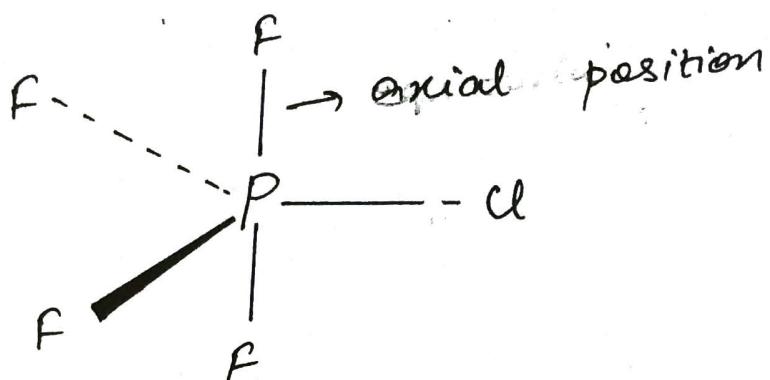


Here the size difference in the surrounding atom and the central atom is less so the lone pair attains s character and becomes inactive, so the shape of $[SbCl_6]^{3-}$ is octahedral.

Vivek

b) Suggest the structures for PF_4Cl , PF_3Cl_2 , PF_2Cl_3 , PF_4CH_3 , $\text{PF}_3(\text{CH}_3)_2$ and $\text{PF}_2(\text{CH}_3)_3$ and justify your answer.

(1) PF_4Cl

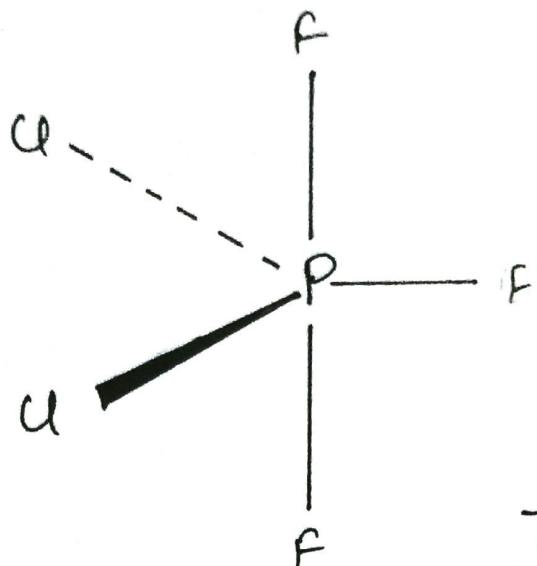


from Bent's Rule, we know that the more electronegative atoms tend to occupy orbital with less s-character. Here, Fluorine is more electronegative. Axial orbitals have zero s-character so, fluorine wants to occupy axial orbitals.

The lone pair tends to occupy equatorial position since the equatorial position has more s-character.

Aakriti

(ii) PF_3Cl_2



Trigonal Bipyramidal

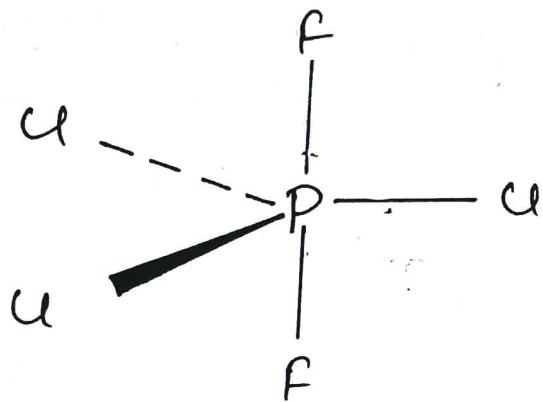
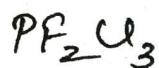
According to Bent's Rule,

The fluorine atom is more electronegative and it occupies the axial position (less s-character)
chlorine being less electronegative will occupy the equatorial position (with more s-character) (33%)

In PF_3Cl_2 , two chlorine atoms take up the planar position.

Va:

(iii)



Trigonal Bipyramidal

This structure can also be explained on the basis of Bent's rule.

Fluorine being the more electronegative atom occupy the axial position as axial position has zero s-character whereas chlorine being less electronegative occupy the equatorial positions as lone pair tend to occupy more s-character orbitals.

$$sp^3d = sp^2 + pd$$

(equatorial) (0 s-character)
(axial position)

$$\% \text{ s character} = \cos \theta = \frac{s}{s-1}$$

$$\theta = 120^\circ \text{ (for equatorial)}$$

$$\cos 120^\circ = \frac{s}{s-1}$$

$$-\frac{1}{2} = \frac{s}{s-1} \Rightarrow 2s = 1 - s \Rightarrow 3s = 1$$

$$\Rightarrow s = \frac{1}{3} = 33\%$$

for axial position

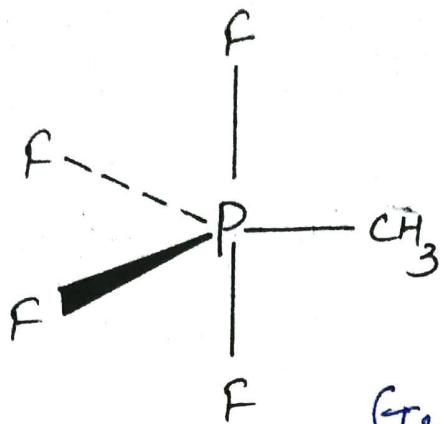
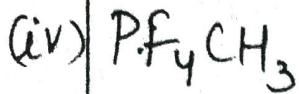
$$\cos \theta = s/s - 1$$

$$\theta = 90^\circ$$

$$\cos 90^\circ = s/s - 1$$

$$0 = s/s - 1$$

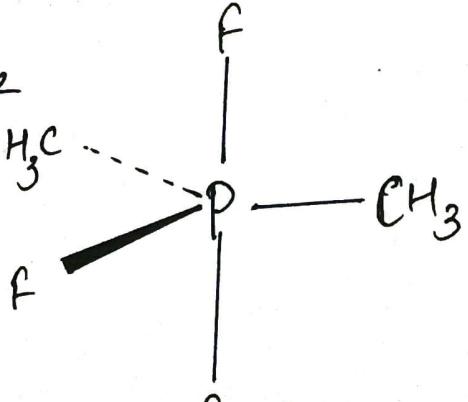
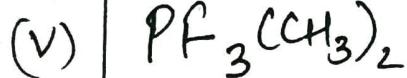
$$s = 0\%$$



(Trigonal Bipyramidal)

from Bent's Rule, we know that

The more electronegative atoms tend to occupy orbital with less s-character. Here, fluorine is more electronegative axial orbitals have zero s-character so, fluorine will occupy axial orbitals. Since, there is one CH_3 molecule so their one pair position of CH_3 will not affect much.

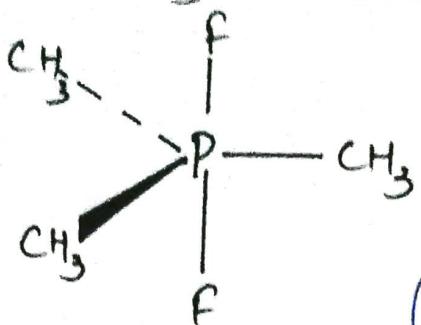


(Trigonal Bipyramidal)

The more the electronegative atom, tend to occupy orbital with less s-character.

Here fluorine is more electronegative and will occupy axial orbitals having less s-character. CH_3 being less electronegative will occupy equatorial position.

[Signature]

(vi) $\text{PF}_2(\text{CH}_3)_2$ 

(Trigonal Bipyramidal)

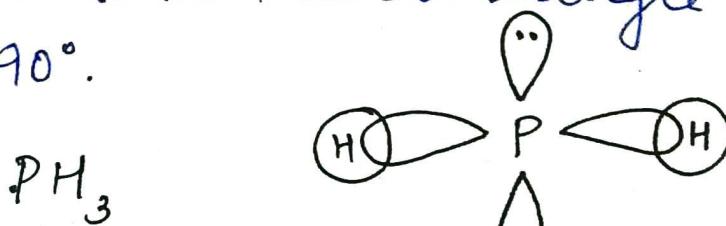
In this also, the structure is explained by Bent's Rule.

The more electronegative atom tends to occupy the orbital with less s-character so fluorine being the more electronegative atom occupies the axial orbital (0 s-character). As shown in the calculation before. the CH_3 being the less electronegative atom occupies the equatorial position (33% s-character). As shown in the calculation before.

- c) The bond angle PH_3 is approximately equal to 90° . Comment.

This can be explained through Drago's Rule.

- If the central atom is in third row or below in the periodic table, the lone pair will occupy stereochemically inactive s orbital and the bonding will be through p-orbitals
- If the electronegativity of surrounding atom is ≤ 2.5 the bond angle will be nearly 90° .



In PH_3 , no hybridization will take place. simple overlapping will take place. pure p-orbitals are involved in bond formation.

In PH_3 3p orbitals of phosphorus overlap with 1s orbital of H.

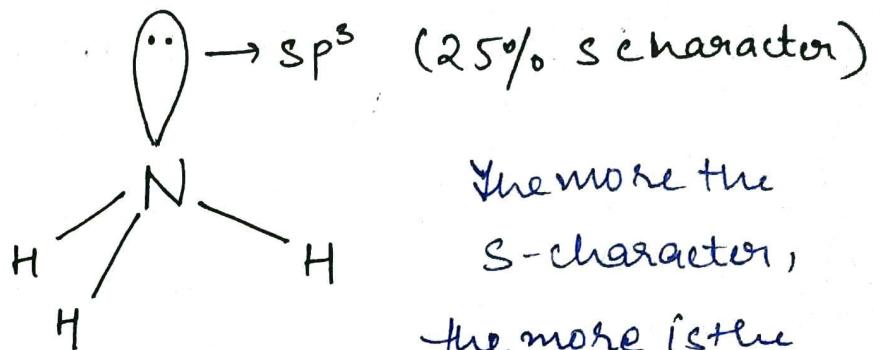
This molecule follows Drago's Rule, as the electronegativity of Hydrogen is less than 2.5, so its bond angle will be nearly 90° .

d) Why NH_3 is more basic than NF_3 ?

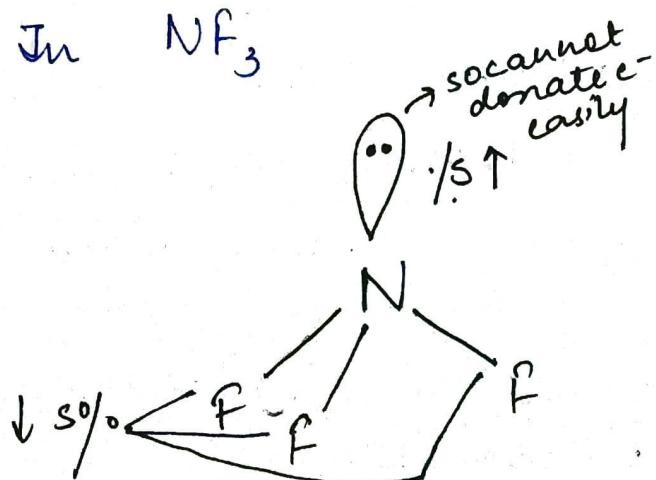
NH_3 is more basic than NF_3 , this can be explained with the help of Bent's Rule.

According to the Bent's Rule, the electronegative atom tends to move towards the orbital having less s-character.

In NH_3



In NF_3



The surrounding atoms here is fluorine, the electronegativity of fluorine

In NF_3 , the surrounding atoms here are fluorine not hydrogen and the electronegativity of fluorine is much higher than hydrogen.

So, fluorine will reduce the s-character of its orbital by 25% (Bent's Rule).

So, the percent s-character reduces in its orbitals but due to this percent s-character increases at the lone pair orbital. So, the binding capability of lone pair orbital will increase and it will not be able to donate electrons easily. So, it is a weaker base.

Basicity is dependent on the tendency to donate e^- pairs.

NH_3 will donate e^- pair more easily as hydrogen is the less electronegative atom but NF_3 cannot donate e^- pair easily as fluorine is the more electronegative atom and it will tend to occupy the orbitals with less s-character due to which its strength reduces and is less basic.

So, this is why NH_3 is more basic than NF_3 .

e) The different hybridization exhibited by the molecules with steric number 5.

Steric Number = 5

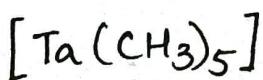
These molecules having steric number 5 possess sp^3d hybridization

sp^3d involves $\begin{cases} S + 3p + dz \rightarrow \text{Trigonal bipyramidal} \\ S + 3p + dx^2 - y^2 \rightarrow \text{square pyramidal} \end{cases}$

no. of repulsions in square pyramidal geometry is less because the no. of planar orbitals are higher.

[And the more the no. of orbitals higher, the less is the repulsion]

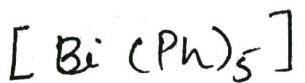
$\overrightarrow{p^2d^3}$ $\overrightarrow{sp^2d^2}$ In this s-orbital is inactive or inert result in square pyramidal geometry.



E.C. (Ta): $[Xe] 4f^{14} 5d^3 6s^2$

The d-orbital is part of valence shell.
→ It may be more effective in bond formation process.

This in fact results in sp^2d^2 hybridization and square pyramidal geometry.



- If ligand is softer (e.g. Ph) then it tries to occupy and tries to remain there in planar position.
- If the absence of significant repulsion, then the contribution of d-orbital increases. Then the resulting geometry will be square pyramidal and the molecule will be sp^2d^2 hybridized.



Steric No. 5, hybridisation sp^3d

Molecular formula

AB_5

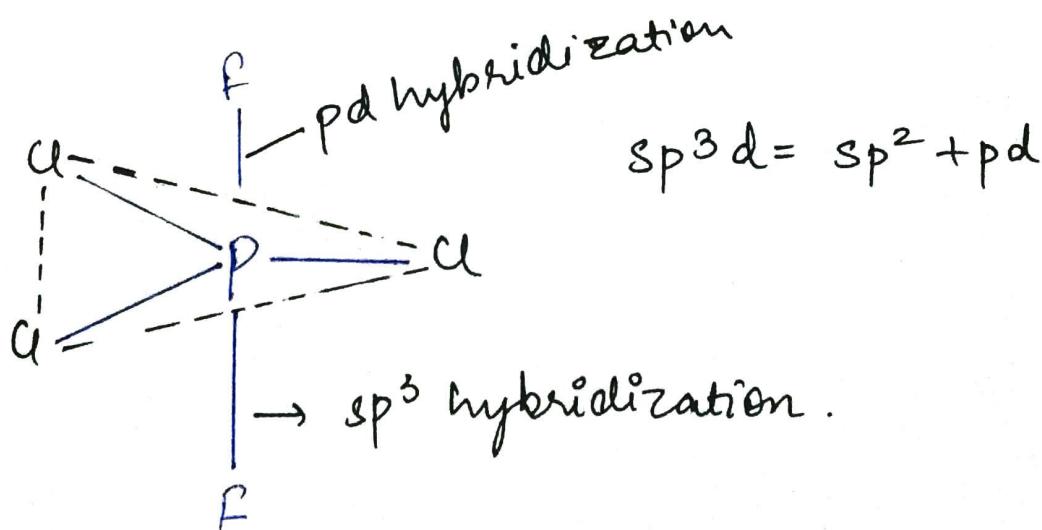
No. of B.P. = 5

No. of L.P. = 0

Shape of the molecule

- Trigonal Bipyramidal

E.g. PCl_5 , SbF_5 , PCl_3F_2



PCl_3F_2

AB₄E

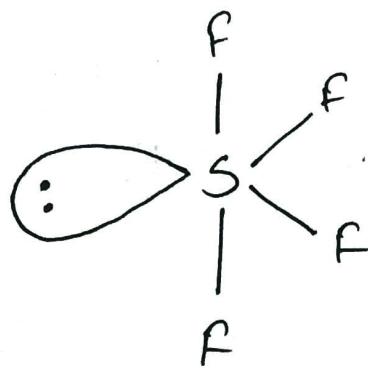
Hybridisation - sp^3d

$$\text{No. of B.P} = 4$$

$$\text{No. of L.P} = 1$$

Shape of the molecule - See-saw

E.g. SF_4, SF_2Cl_2



SF_4

$$VE = \frac{1}{2}(6+4)$$
$$= 10/2 = 5$$

4 bp and 1 lp

~~Nitin~~

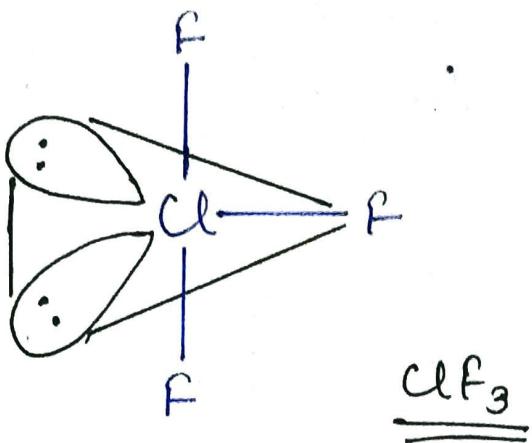
AB_3E_2

No. of B.P. = 3

No. of L.P. = 2

Shape of the molecule - T-shape

E.g. ClF_3 ; BrF_3



AB_2E_3

No. of B.P. = 2

No. of L.P. = 3

Shape - linear geometry

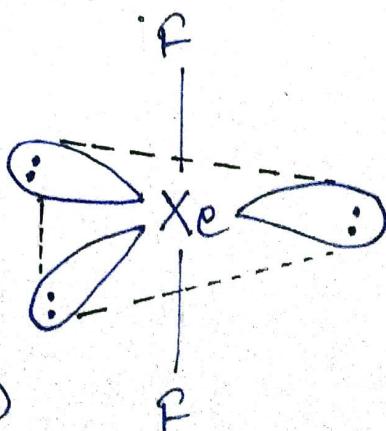
E.g. XeF_2 , ICl_2

F

Xe

F

linear (shape)



Geometry -
Trigonal
Bipyramidal
(includes sp³d shape)

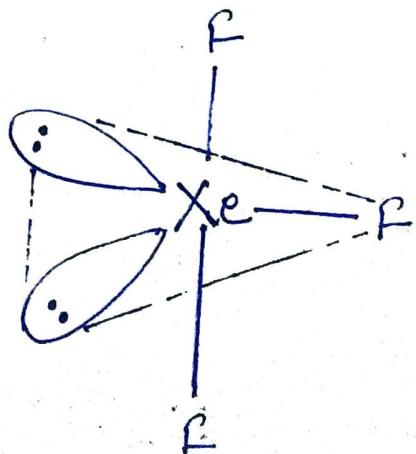
XeF_2

Q2(a)

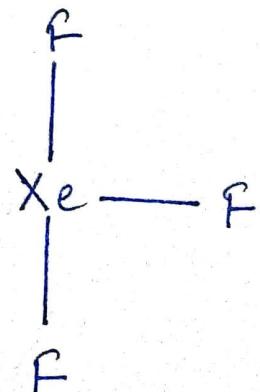
SN: Steric Number

COMPOUND	FORMULA TYPE	SN	GEOMETRY	BOND ANGLE (°)
AlCl_4^-	AX_4	4	Tetrahedral	109.5°
XeF_3^+	AX_3E_2	5	^{shape} T-shaped	<90°
PCl_6^-	AX_6	6	Octahedral	90°

In XeF_3^+ → Geometry is Trigonal Bipyramidal and Shape of the molecule is T-shaped.
coz ge when there are lone pairs
Geometry ≠ Shape



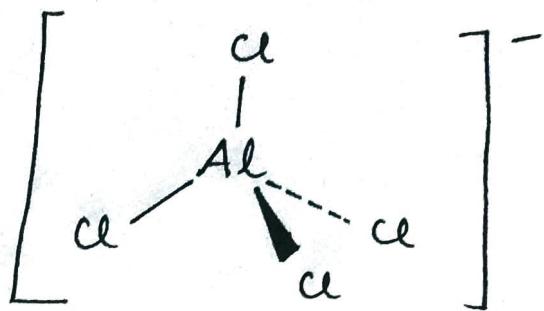
Trigonal
Bipyramidal
(Geometry)



(T-shaped)
(shape)

Aakriti

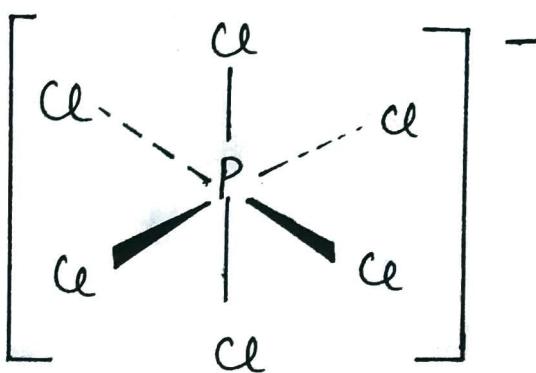
AlCl_4^-



$[\text{AX}_4]$

Steric no. 4

PCl_6^-



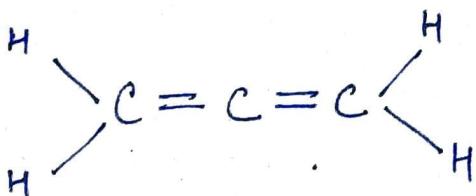
$[\text{AX}_6]$

Steric no. 6

Rishabh

Q4. Use the flow chart to find point group of the following molecules -

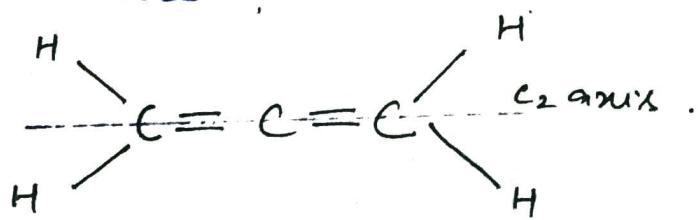
a) Allene



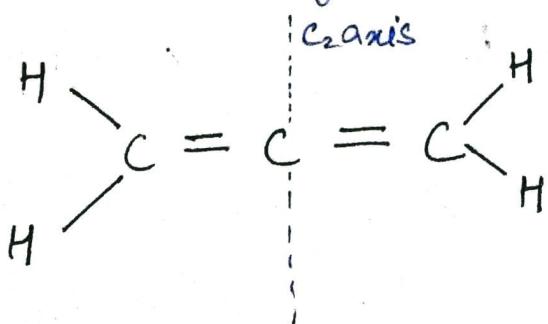
Allene has 2π -bond perpendicular to each other.

It has $3 C_2$ axes

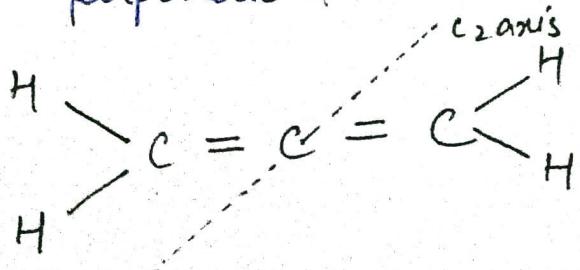
- a) passes through the three carbon atoms of the allene



- b) passes through central carbon of allene



- c) Passes through central carbon of allene perpendicular to earlier axis.

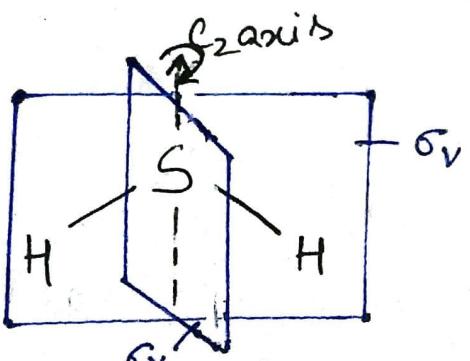


KV

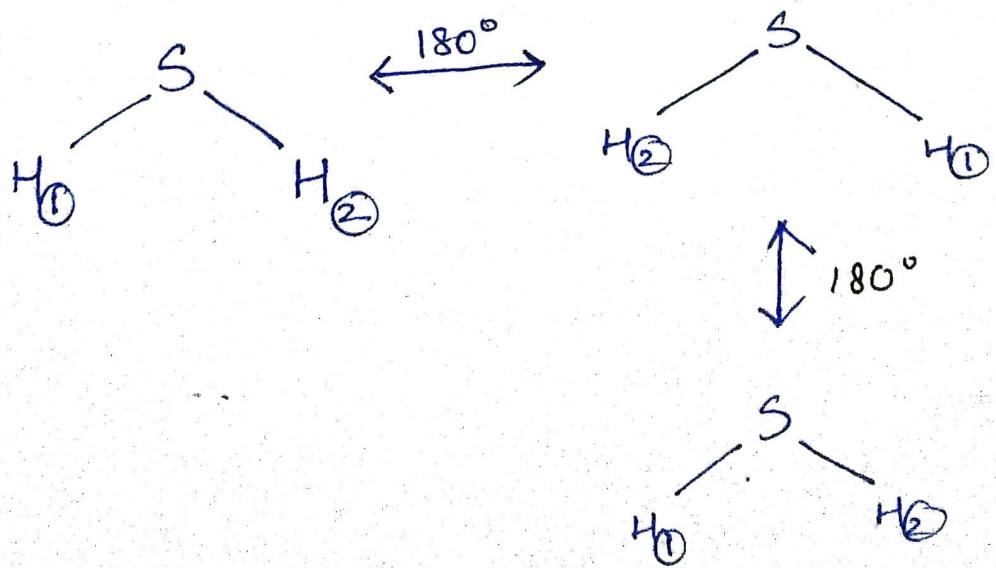
3. It has one improper axis (S_4), it passes through three carbon atoms of the allene and plane is perpendicular to tw's ($S_n = Cn \perp \sigma$)
 The rotation of 90° and then reflection through plane gives indistinguishable allene. (i.e. S_4)

- (4) It has two σ_d planes (dihedral planes)
 (5) The point group of allene is D_{2d}

(b) H_2S



- There are one C_2 axis \rightarrow principle axis

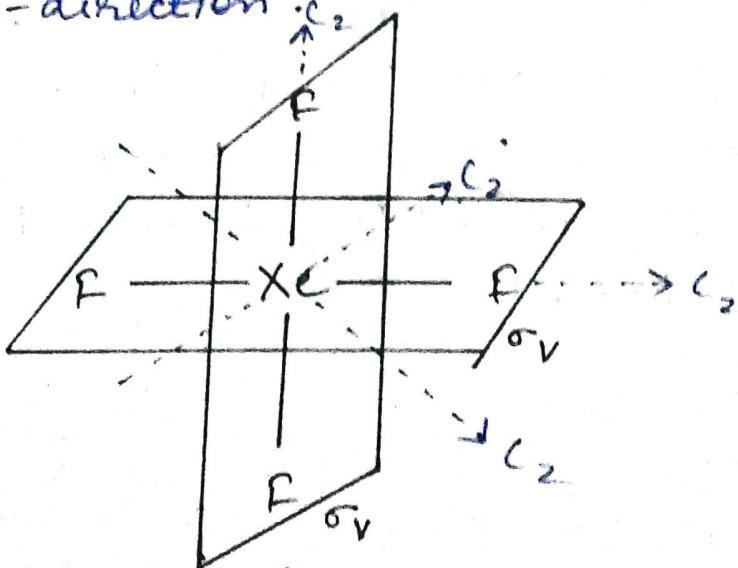


Later.

- It contains 2 vertical mirror planes that include the axis is called vertical mirror plane (σ_v) but no σ_h mirror planes.
- The point group of H_2S is C_{2v} .

③ XeF_4

- It has four different C_2 axes.
- A C_4 axis cut off the page is called the principle axis's because it has largest n.
- By convention, the principle axis is in the z-direction.



- It contains 1 σ_h plane.

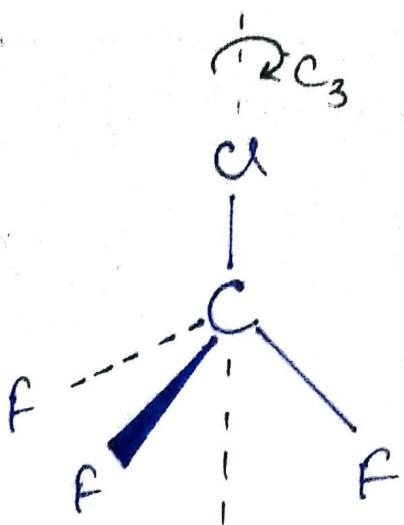
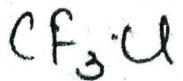
The point group of XeF_4 is D_{4h} .

- It has two σ_v planes.

- It has two σ_d planes.

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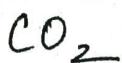
(4)



- CF_3Cl has the symmetry elements E , C_3 , σ_v
- CF_3Cl belongs to the C_{3v} point group.
- It has the symmetry element E , a C_3 axis and three σ_v planes.
- The molecule can be rotated 120° left or right and get a new configuration that is indistinguishable from the original

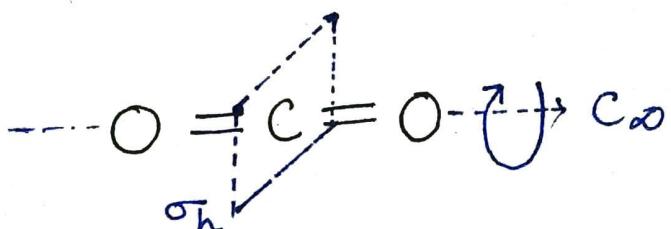
Sachet

③



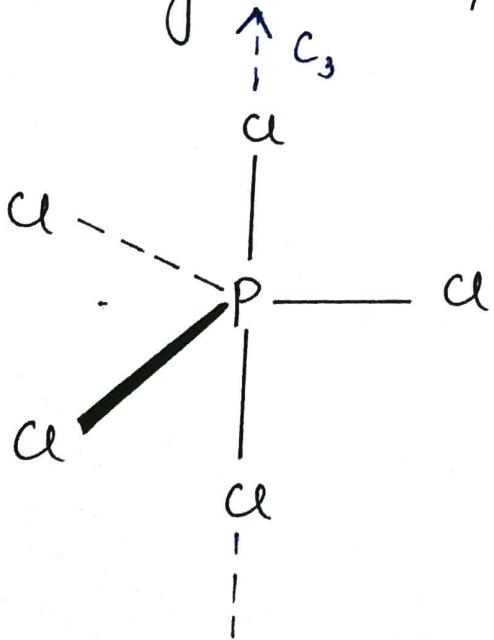
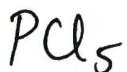
CO_2 molecule is linear, and has a center of inversion.

$\text{C}\infty \rightarrow$ principle rotational axis



$\rightarrow \text{CO}_2$ belongs to $D\infty h$ point group.

⑥



- PCl_5 contains a C_3 principle rotation axis and 3 C_2 axis (perpendicular axis)
- It contains a σ_h plane perpendicular to the C_3 axis.
- It contains three σ_v planes.
- There are two improper axis of rotation ($2S_3$)
- The point group of PCl_5 is D_{3h} .