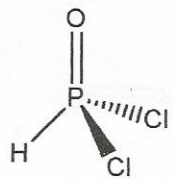


Chemistry 6011 (Fall 2013)
Advanced Inorganic Chemistry I: From Atoms to Coordination Compounds
Problem Set #2

Chapter 4-

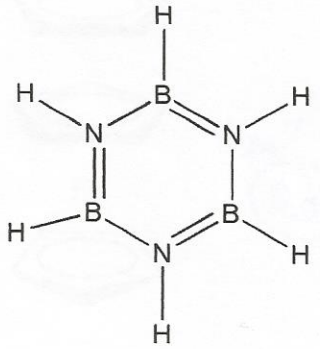
1. Assign the following molecules to their appropriate point groups.



C_{∞} ? no C_n ? no σ ? Yes C_s



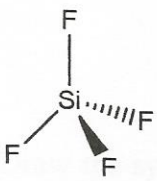
C_{∞} ? no C_n ? yes $\rightarrow C_2$
 $2C_2 \perp C_2$? no S_4 ? no σ_h ? no $2\sigma_v$? Yes C_{2v}



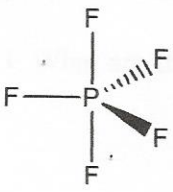
C_{∞} ? no C_n ? yes $\rightarrow C_3$
 $3C_2 \perp C_3$? No S_4 ? No σ_h ? Yes
As drawn, not delocalized. C_{3h}



C_{∞} ? no C_n ? no σ ? no i ? no C_1

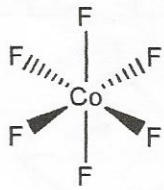


C_{∞} ? no C_n ? yes $\rightarrow C_3 \rightarrow 4C_3$ i ? no 6σ ? yes T_d

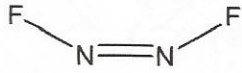


C_{∞} ? no C_n ? yes $\rightarrow C_3 \rightarrow C_3$
 $3C_2 \perp C_3$? Yes σ_h ? yes D_{3h}

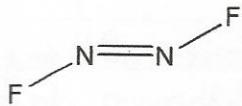
(2)



C_{∞} ? no C_n ? Yes $\rightarrow C_4$ $3C_4$? Yes i ? Yes
 (O_h)



C_{∞} ? no C_n ? Yes $\rightarrow C_2$ $3C_2 \perp C_2$? no S_4 ? No
 σ_h ? ~~Yes~~ No $2\sigma_v$? Yes
 (C_{2v})



C_{∞} ? no C_n ? Yes $\rightarrow C_2$ $2C_2 \perp C_2$? no S_4 ? no σ_h ? yes
 (C_{2h})



Fe

C_{∞} ? no C_n ? Yes $\rightarrow C_5$ $5C_2 \perp C_5$? Yes σ_h ? Yes (D_{5h})

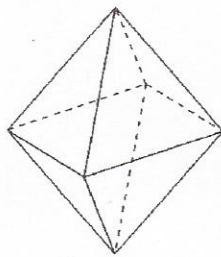


Fe

C_{∞} ? no C_n ? Yes $\rightarrow C_5$ $5C_2 \perp C_5$? Yes σ_h ? no $5\sigma_v$? Yes
 (D_{5d})

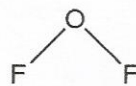


2. Find and draw all of the symmetry elements in an octahedron.



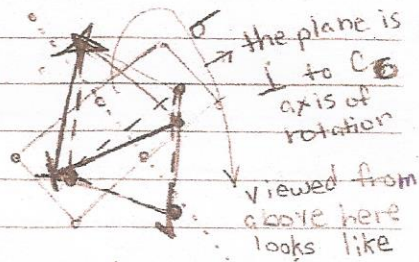
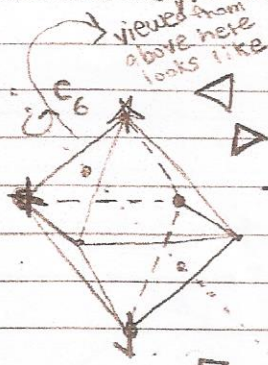
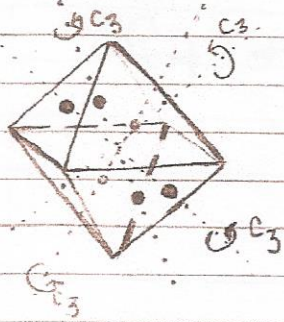
Draw the symmetry elements. You can redraw the molecule a few times so that it is easy to see your elements. Also give one example of each type of symmetry element.

3. What are the symmetries of the normal modes of vibration of these molecules?



Find and draw all of the symmetry elements in an octahedron.

$4 C_3 + 4 S_6$

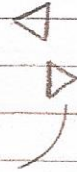


the plane is \perp to C_6 axis of rotation

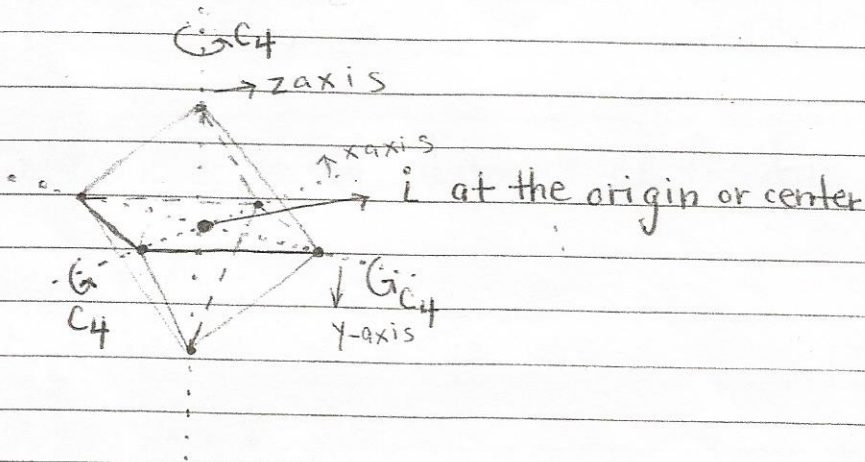
viewed from above here looks like

reflect through get what looks from above like

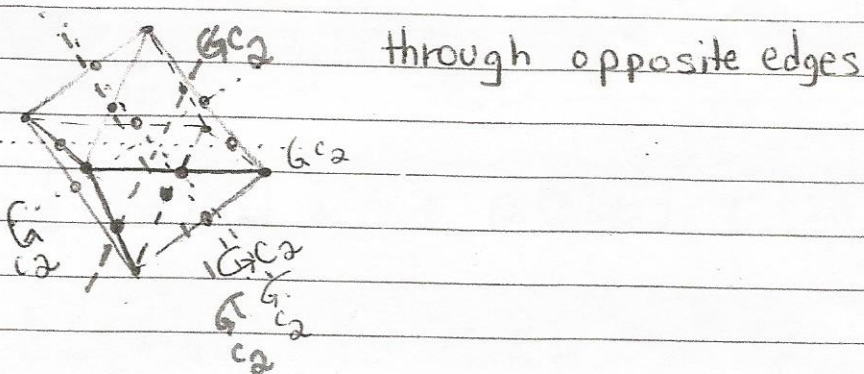
$4 C_3 + 4 S_6$ exist through opposite faces. I will show an example of S_6 .



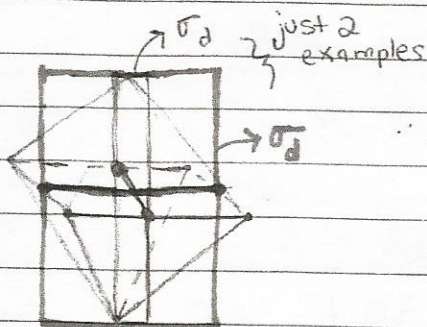
$3C_4 + i$



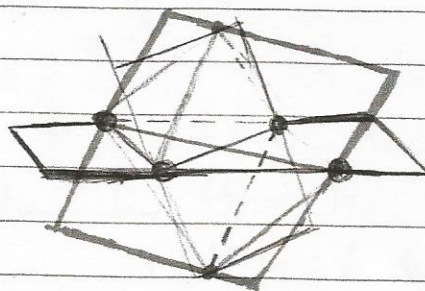
$6C_2$



$6\sigma_d$

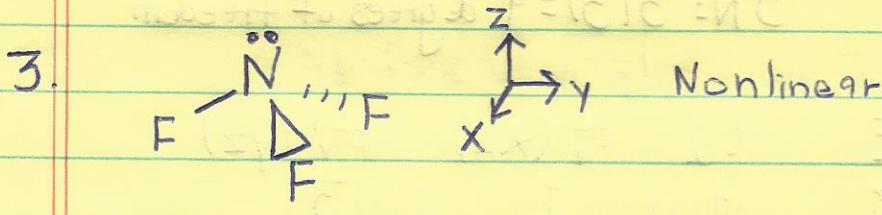


$3\sigma_h$



through opposite edges
like the C_2

through $xy, xz, + yz$ planes



$3N = 3(4) = 12$ total degrees of freedom.

Point group? C_{3v}

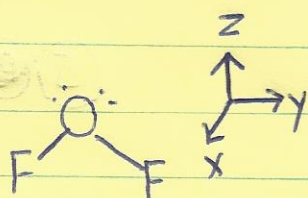
C_{3v}	E	$2C_3$	σ_v
Unshifted atoms	4	1	2
Contributions	3	0	1
per atom			
Γ_{total}	12	0	2

$A_1 = \frac{1}{6} [12(1)(1) + 0 + 2(3)(1)] = \frac{1}{6} (18) = 3$

$A_2 = \frac{1}{6} [12(1)(1) + 0 + 2(3)(-1)] = \frac{6}{6} = 1$

$E = \frac{1}{6} [12(1)(2) + 0 + 2(3)(0)] = \frac{24}{6} = 4$

$\Gamma_{total} = 3 \overset{1D \text{ rep.}}{\widetilde{A}_1} + \overset{1D \text{ rep.}}{\widetilde{A}_2} + 4 \overset{2D \text{ rep.}}{\widetilde{E}} \Rightarrow 12$ degrees of freedom
 $\Gamma_{trans} = A_1 + E$ (from x, y, z in character table)
 $\Gamma_{rot} = A_2 + E$ (from R_x, R_y, R_z in table)
 $\Gamma_{vib} = 2A_1 + 2E$ ($3N - 6 = 6$ degrees of freedom)
 6 normal modes



C_{2v}

(4)

(8)

$3N = 3(3) = 9$ degrees of freedom

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
U.A.	3	1	1	3
Cont. per atom.	3	-1	1	1
	9	-1	1	3

$A_1: \frac{1}{4} [9(1)(1) + -1(1)(1) + 1(1)(1) + 3(1)(1)] = \frac{12}{4} = 3$

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

$B_1: \frac{1}{4} [9(1)(1) + -1(1)(-1) + 1(1)(1) + 3(1)(-1)] = \frac{8}{4} = 2$

$B_2: \frac{1}{4} [9(1)(1) + -1(1)(-1) + 1(1)(-1) + 3(1)(1)] = \frac{12}{4} = 3$

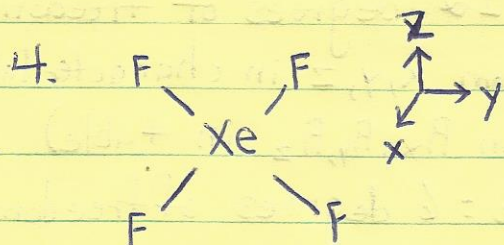
$\Gamma_{total} = 3A_1 + 1A_2 + 2B_1 + 3B_2$

$-\Gamma_{trans} = A_1 + B_1 + B_2$

$-\Gamma_{rot} = A_2 + B_1 + B_2$

$\Gamma_{vib} = 2A_1 + B_2$ Three degrees of freedom

$3N - 6 = 3$



Point group? D_{4h}

$3N - 6 = 15 - 6 = 9$

Because it has five atoms, we expect 9 vibrational modes, four of which will be stretching modes (because there are 4 bonds) and five of which will be bending modes.

3(5) = 15 degrees of freedom

	E	2C ₄	C ₂	2C' ₂	2C'' ₂	i	2S ₄	σ _h	2σ _v	2σ _v
U.A.	5	1	1	3	1	1	1	5	3	1
C/A	3	1	-1	-1	-1	-3	-1	1	1	1

A_{1g}: $\frac{16}{16} = 1$

A_{2u} = 2

A_{2g}: $\frac{16}{16} = 1$

B_{1u} = 0

B_{1g}: $\frac{16}{16} = 1$

B_{2u} = 1

E_u = 3

B_{2g}: $\frac{16}{16} = 1$

E_g: $\frac{16}{16} = 1$

A_{1u} = 0

$$\Gamma_{\text{rot}} = 1A_{1g} + 1A_{2g} + 1B_{1g} + 1B_{2g} + 1E_g + 2A_{2u} + 1B_{2u} + 3E_u$$

$$- \Gamma_{\text{trans}} = \dots A_{2u} \dots$$

$$- \Gamma_{\text{rot}} = \dots + E_g \dots + E_u$$

$$\Gamma_{\text{vib}} = 1A_{1g} + 1B_{1g} + 1B_{2g} + 1A_{2u} + 1B_{2u} + 2E_u$$

9 vibrations

$A_{2u} + E_u$: IR active; transforms like x, y, z

$A_{1g}, B_{1g} + B_{2g}$: Raman active; transform like quadratic functions of x, y, + z + linear combinations of them

B_{2u} : Neither IR nor Raman

Since this molecule has i , the IR + Raman active modes would be different.

5.

P: $1s^2 2s^2 2p^6 3s^2 3p^3$ $n=3$; has d-orbitals

Point group: D_{3h}

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{total}	5	2	1	3	0	3

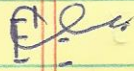


$A_1' = 2$



$A_2' = 0$

$E' = 1$



$A_1'' = 0$

$A_2'' = 1$

$E'' = 0$

$\Gamma_{red} = 2A_1' + E' + A_2''$

A_1' orbitals: s, dz^2

E' orbitals: $p_x, p_y, d_{x^2-y^2}, d_{xy}$

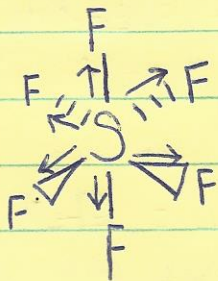
A_2'' : p_z

Possible combinations:

$s, dz^2, p_x, p_y, p_z \quad dsp^3$

$s, dz^2, d_{x^2-y^2}, d_{xy}, p_z \quad d^3sp$

5 atomic orbitals \rightarrow 5 hybrid orbitals



Si: $[Ne]3s^2 3p^4$ has d-orbitals

Point group: O_h

	E	8 C ₃	6 C ₂	6 C ₄	3 C ₂	i	6 S ₄	8 S ₆	3 σ _h	6 σ _v
Γ _T	6	0	0	2	2	0	0	0	4	2

A_{1g} = 1 E_u = 0 Γ_{red} = A_{1g} + E_g + T_{1u}

A_{2g} = 0 T_{1u} = 1 A_{1g} orbitals: s

E_g = 1 T_{2u} = 0 E_g " : d_{z²}, d_{x²-y²} } d² sp³
 T_{1g} = 0 T_{1u} " : p_x, p_y, p_z } only possible combination

T_{2g} = 0

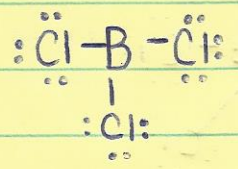
A_{1u} = 0

A_{2u} = 0

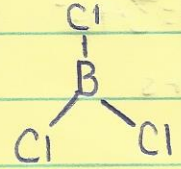
Chapter 3 and Valence Bond Theory

1) a. BCl_3

B Cl_3
 $3 + 3(7) = 24e^-$
 12 pairs



Geometry: trigonal planar



b. BeH_2

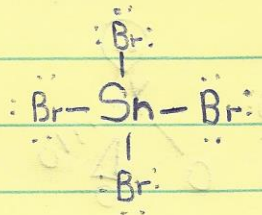
$2 + 2(1) = 4e^-$
 2 pairs

Geometry: linear

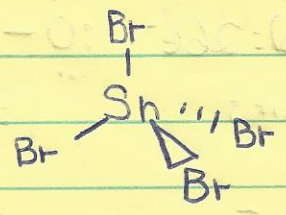


c. $SnBr_4$

$4 + 4(7) = 32e^-$
 16 pairs

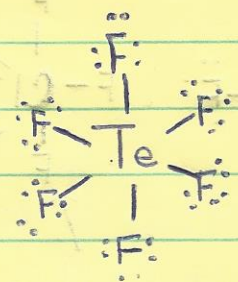


Geometry: tetrahedral

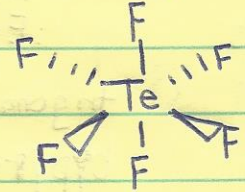


d. TeF_6

$6 + 6(7) = 48e^-$
 24 pairs

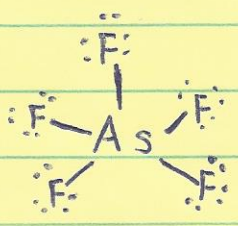


Geometry: Octahedral

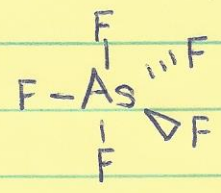


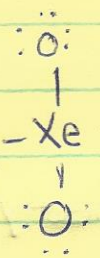
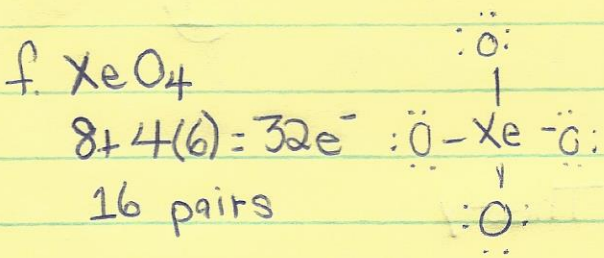
e. AsF_5

$5 + 5(7) = 40e^-$
 $\Rightarrow 20$ pairs

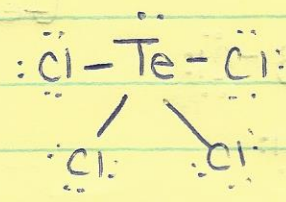
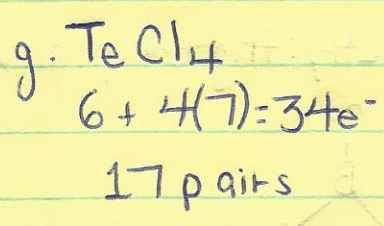


Geometry: trigonal bipyramidal

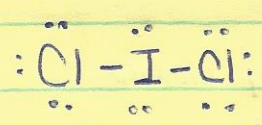
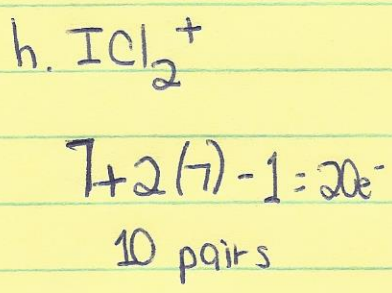
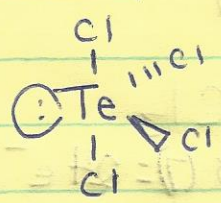




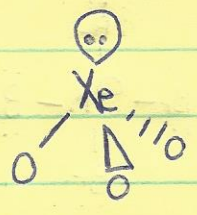
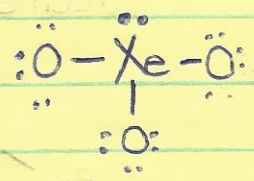
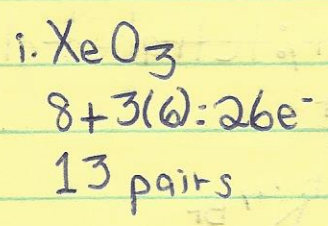
Geometry: tetrahedral



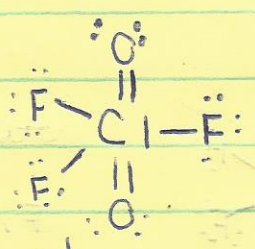
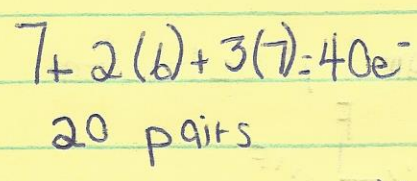
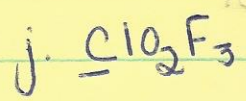
Geometry: See-saw



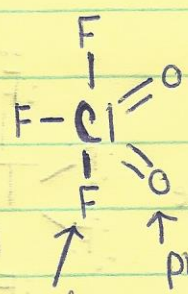
Geometry: bent



Geometry: Pyramidal



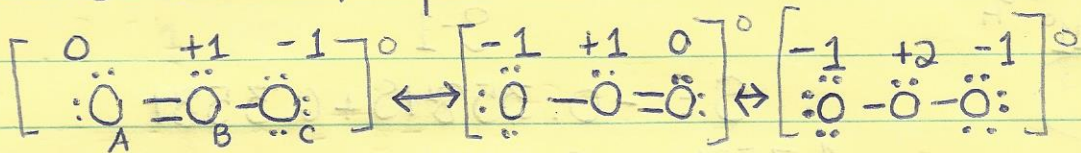
trigonal bipyramidal



prefer equatorial
Prefers axial

2) O_3

$6 \times 3 = 18e^- \Rightarrow 9 \text{ pairs}$



Formal charge

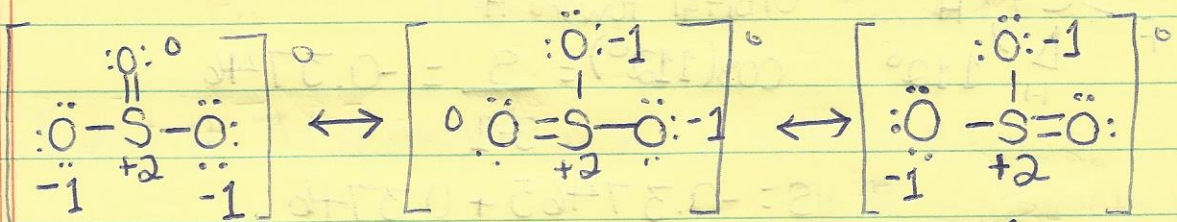
A: $6 - 4 - 2 = 0$

B: $6 - 2 - 3 = +1$

C: $6 - 6 - 1 = -1$

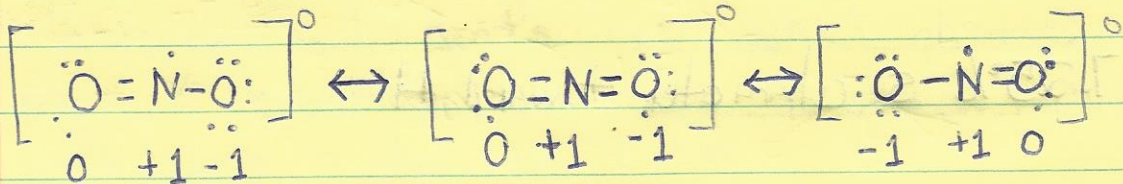
SO_3

$6 + 3(6) = 24e^- \Rightarrow 12 \text{ pairs}$



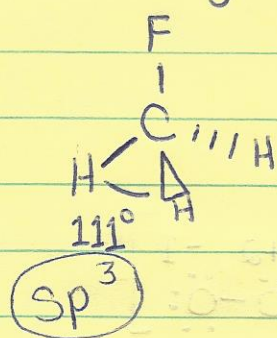
NO_2

$5 + 2(6) = 17e^-$



3) 9. CH_3F

(4)



Orbital toward H:

$$\cos(111^\circ) = \frac{S}{S-1} = -0.3584$$

$$S = -0.3584S + 0.3584$$

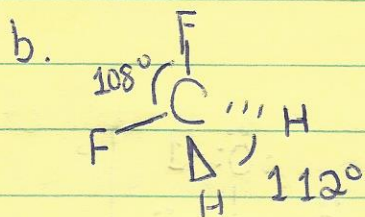
$$1.3584S = 0.3584$$

$$S = \frac{0.3584}{1.3584} = 0.2638 \Rightarrow 26.4\%$$

$$S \text{ character}$$

Orbital toward F:

$$3(0.2638) + x = 1 \quad x = 0.2085 \Rightarrow 20.9\% S$$



Orbital toward H:

$$\cos(112^\circ) = \frac{S}{S-1} = -0.3746$$

$$S = -0.3746S + 0.3746$$

$$1.3746S = 0.3746$$

$$S = \frac{0.3746}{1.3746} = 0.2725$$

$$S \text{ character}$$

27.25% S character toward H

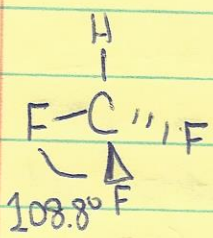
Orbital toward F: $\cos(108^\circ) = \frac{S}{S-1} = -0.3090$

$$S = -0.3090S + 0.3090$$

$$1.3090 s = 0.3090$$

$$s = \frac{0.3090}{1.3090} = 0.2361 \quad 23.6\% \text{ s character toward F}$$

c. CHF_3



Orbital toward F:

$$\cos(108.8^\circ) = \frac{s}{s-1} = -0.3222$$

$$s = -0.3222s + 0.3222$$

$$1.3222s = 0.3222$$

$$s = \frac{0.3222}{1.3222} = 0.2437 \quad 24.4\% \text{ s character toward F}$$

$$\text{Toward H: } 3(0.2437) + x = 1 \quad x = 0.2689$$

26.9% s character toward H

d. In general, the hybrid orbitals toward F have less s character than do the hybrid orbitals toward H. This is consistent with Bent's rule, which observes that more χ substituents are going to bind to hybrid orbitals with less s character.

4) Phosphorus will be more χ when binding through its equatorial hybrid orbitals, because those orbitals have s character. The more s character a hybrid orbital has, the more closely the e^- are held to the nucleus.

5) The addition of some d character will lower the X. Sulfur would be more X if sp³.

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

σ_{C-O}

σ_{C-O}

σ_{C-O}

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

σ_{C-O}

σ_{C-O}

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

σ_{C-O}

σ_{C-O}

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

σ_{C-O}

In general, the higher the electronegativity of the atom, the more s character is in the orbital.

Carbon is more electronegative than hydrogen, so it has more s character in its orbitals.

Consistent with this, the C-H bond is shorter than the C-C bond.

When a carbon atom is bonded to a more electronegative atom, the C-X bond is shorter.

With less s character, the orbital is larger and the bond is longer.

$\sigma_{C-O} = \sigma_{C-O} + \sigma_{C-O}$

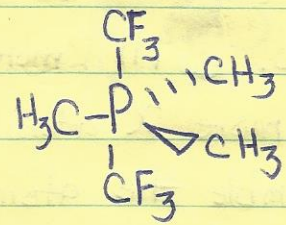
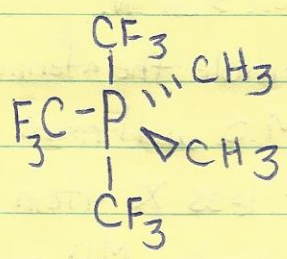
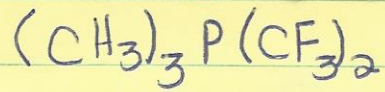
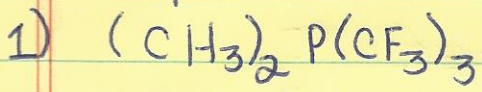
Phosphorus will have more s character in its orbitals.

Equation applied to the C-H bond, because these orbitals are s character.

The more s character, the more electronegative the atom is.

To make a bond, the orbitals must overlap.

Chapter 5

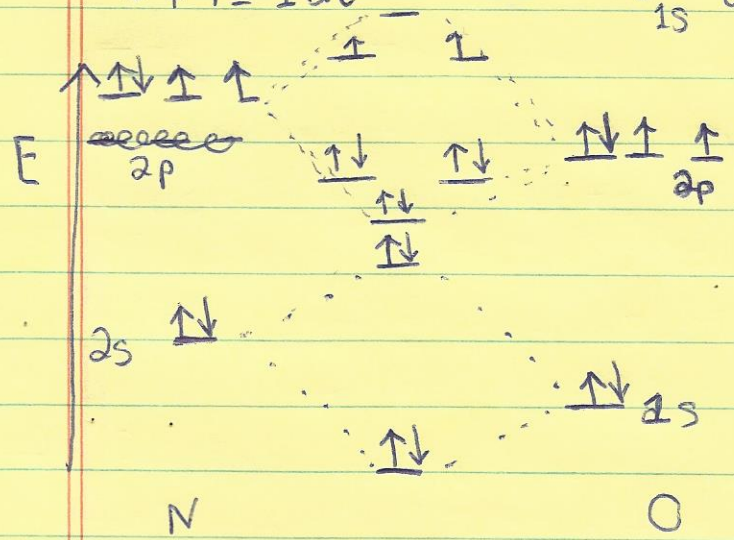


CF_3 is more χ than CH_3 , so it is more likely to bind to orbitals on P that have less s character so that the competition for e^- s is minimized. The CF_3 groups will occupy the axial positions. The barrier to pseudorotation will be fairly great because the CF_3 's will not "care" to occupy the equatorial ~~sites~~ sites. Those sites have more s character on the P hybrids.



$5 + 7 = 12e^-$

$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 \pi_{2p_x}^2 \pi_{2p_y}^2 \pi_{2p_x}^{*1} \pi_{2p_y}^{*1}$



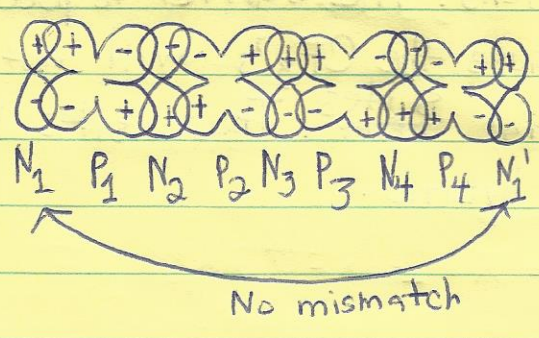
9. Bond order = $\frac{1}{2} (8 - 4) = 2$

b. B.O. = 2.5 will be shorter for NO.

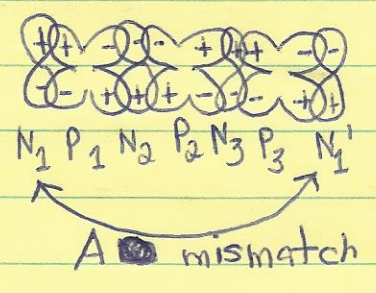
c. 2 unpaired e⁻ for NO⁻.

d. The unpaired e⁻ will be concentrated more on N. Bonding M.O. will more closely resemble the atomic orbitals of more X atom. Antibonding M.O. will more closely resemble the atomic orbitals of less X atom. The unpaired e⁻ are ~~in~~ in antibonding M.O. and will be thus more concentrated on N.

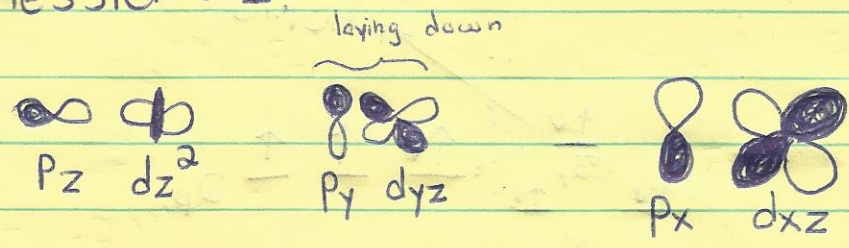
3. (PNCl₂)₄



(PNCl₂)₃



4) Miessler 5.1



5.2.

a. Li_2 B.O. = 1.0 → shorter bond

Li_2^+ B.O. = 0.5

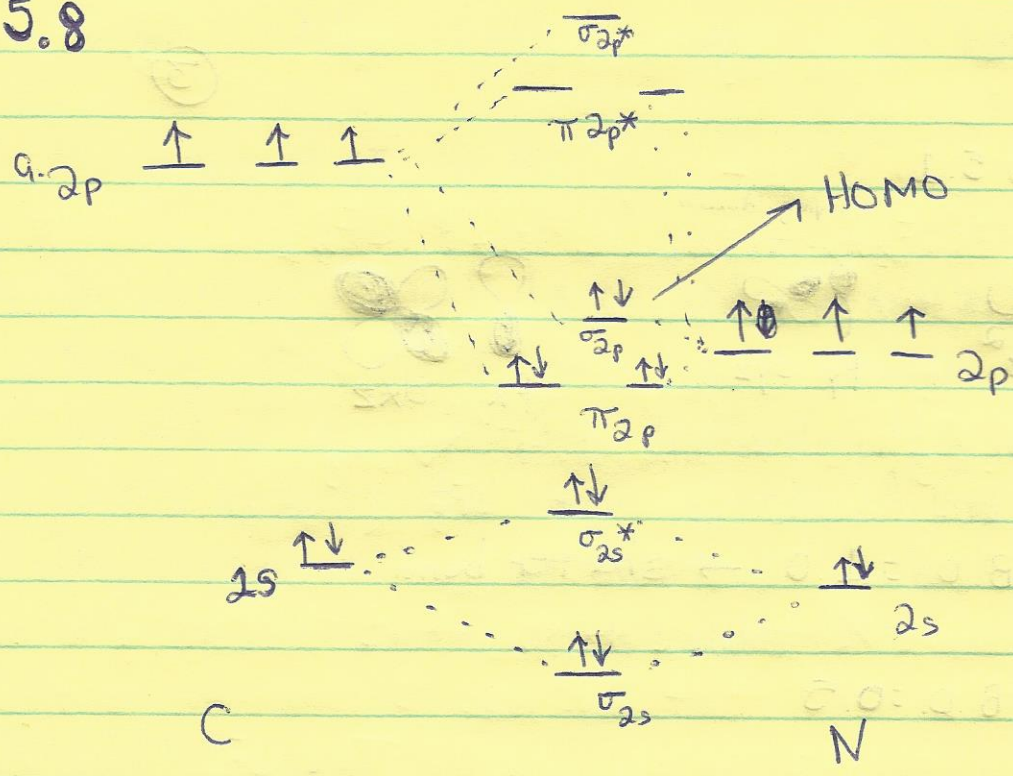
b. F_2 B.O. = 1.0

F_2^+ B.O. = 1.5 → shorter bond

c.	Bonding electrons	Antibonding electrons	Bond order
He_2^+	2	1	0.5
HHe^+	2	0	1
H_2^+	1	0	0.5

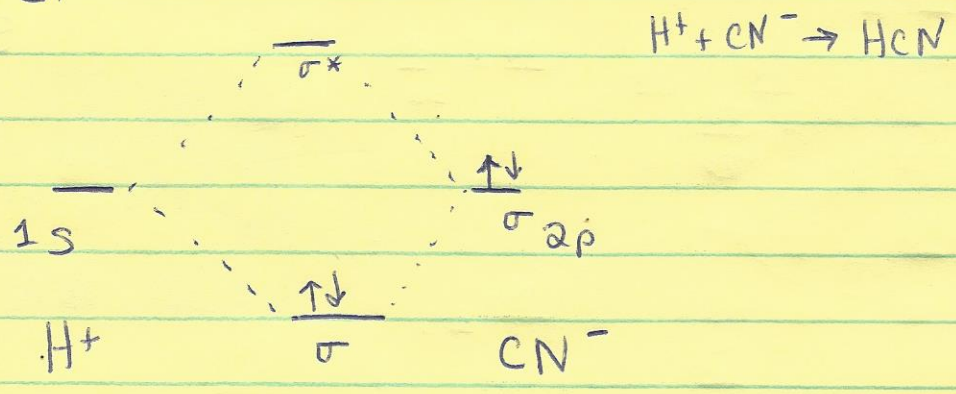
↓
Shortest bond

5.8



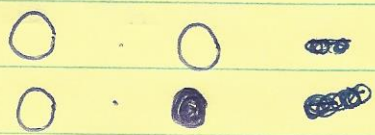
b. $B.O. = \frac{1}{2} [8 - 2] = 3$

c. The HOMO is the σ_{2p} orbital, which can interact with the $1s$ of the H^+ , as in the diagram at right. The bonding orbital has an energy near that of the π orbitals; the antibonding orbital becomes the highest energy orbital.

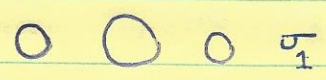


5.14) CH₂

a. The group orbitals on hydrogen are



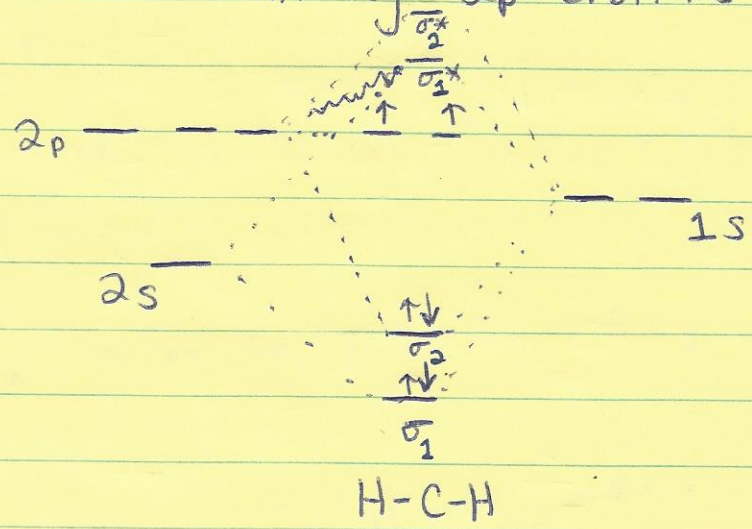
The first group orbital interacts with the 2s orbital on carbon.



And the second group orbital interacts with a 2p orbital on carbon.



Carbon's remaining 2p orbitals are nonbonding.



b. Linear CH₂ is a paramagnetic diradical, with one e⁻ in each of the p_x and p_y orbitals of carbon.