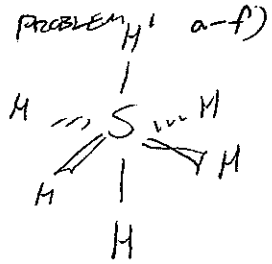
PROBLEM a-f)



$\underline{O_h}$ BASIS SET: $S : s, p \overset{\text{FROM TABLE}}{\Rightarrow} A_{1g} + T_{1u}$

$6H : 6s$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
Γ_{HisA}	6	0	0	2	2	0	0	0	4	2

$$a_{A_{1g}} = \frac{1}{48}(6\cdot1\cdot1 + 0 + 0 + 2\cdot1\cdot6 + 2\cdot1\cdot3 + 0 + 0 + 0 + 4\cdot1\cdot3 + 2\cdot1\cdot6)$$

$$= \frac{1}{48}(6 + 12 + 6 + 12 + 12)$$

$$= 1$$

$$a_{E_g} = \frac{1}{48}(6\cdot2\cdot1 + 0 + 0 + 0 + 2\cdot2\cdot3 + 0 + 0 + 0 + 4\cdot2\cdot3 + 0)$$

$$= \frac{1}{48}(12 + 12 + 24)$$

$$= 1$$

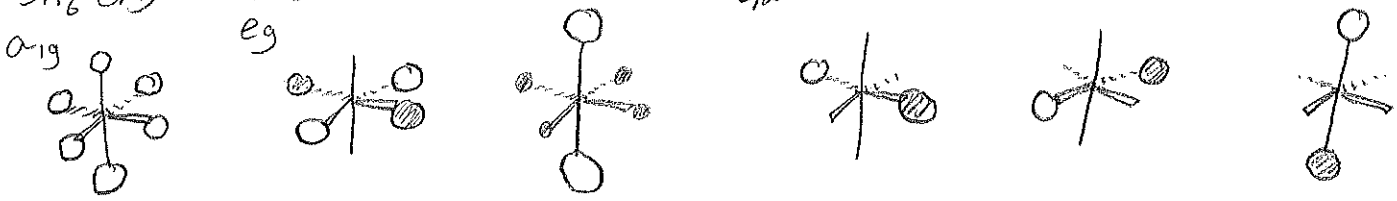
$$a_{T_{1u}} = \frac{1}{48}(6\cdot3\cdot1 + 0 + 0 + 2\cdot1\cdot6 + 2\cdot-1\cdot3 + 0 + 0 + 0 + 4\cdot1\cdot3 + 2\cdot1\cdot6)$$

$$= \frac{1}{48}(18 + 12 - 6 + 12 + 12)$$

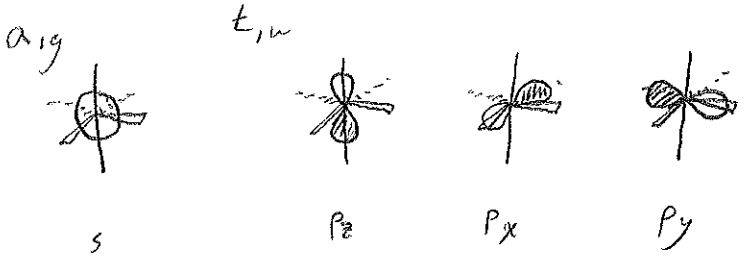
$$= 1$$

$$\Gamma_{HisA} = A_{1g} + E_g + T_{1u}$$

SH_6 (A) SALCs

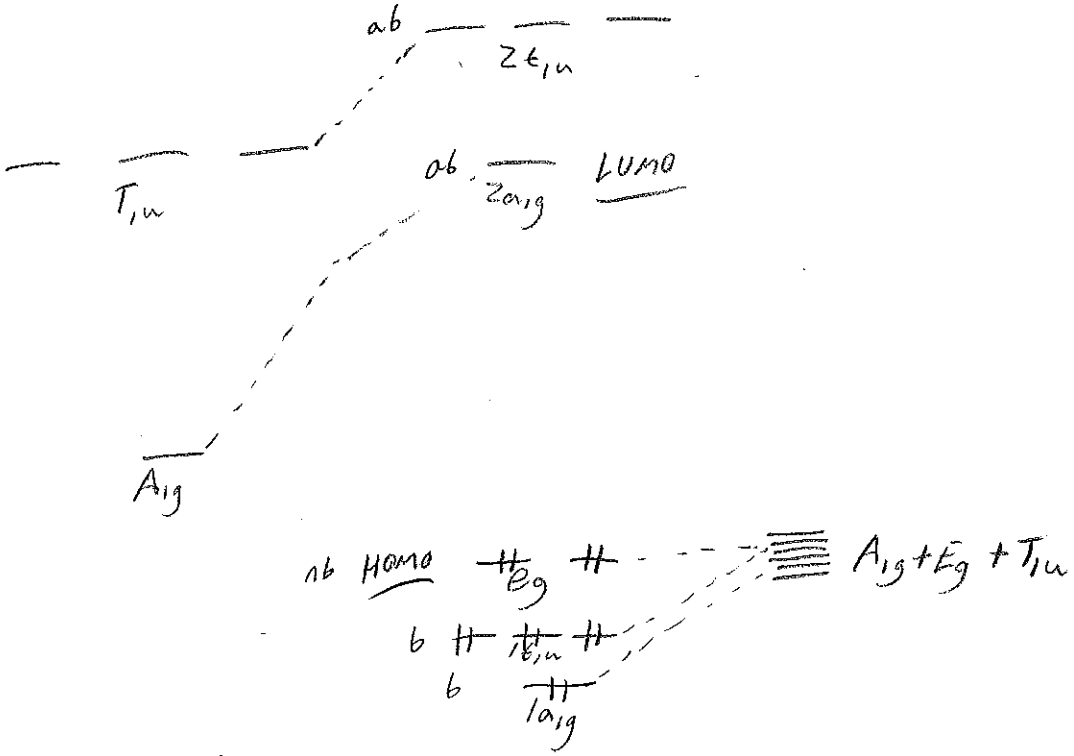


5 VALENCE ORBITALS



A MO:

S SH_6 6H



b = BONDING
nb = NON BONDING
ab = ANTIBONDING

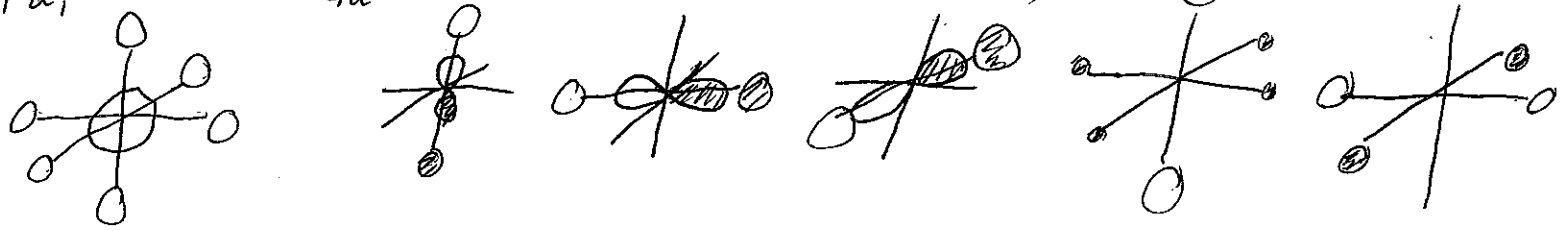
PES: 3 PEAKS

BO: $\frac{8}{2} = 4$

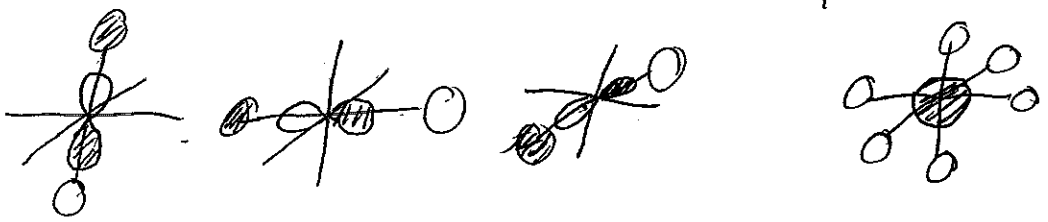
DIAMAGNETIC

SH_6 (A) MOs

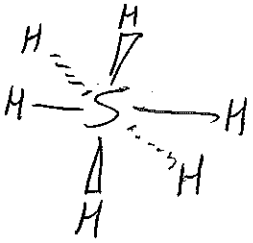
$1a_1$ $1t_{1u}$ e_g



$2t_{1u}$ $2a_1$



B



D_{3h} BASIS SET S: 3S, 3P $\Rightarrow E' + A_2'' + A_1'$

6H: 6s

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0
$\Gamma_{6H's B}$	6	0	0	0	0	2

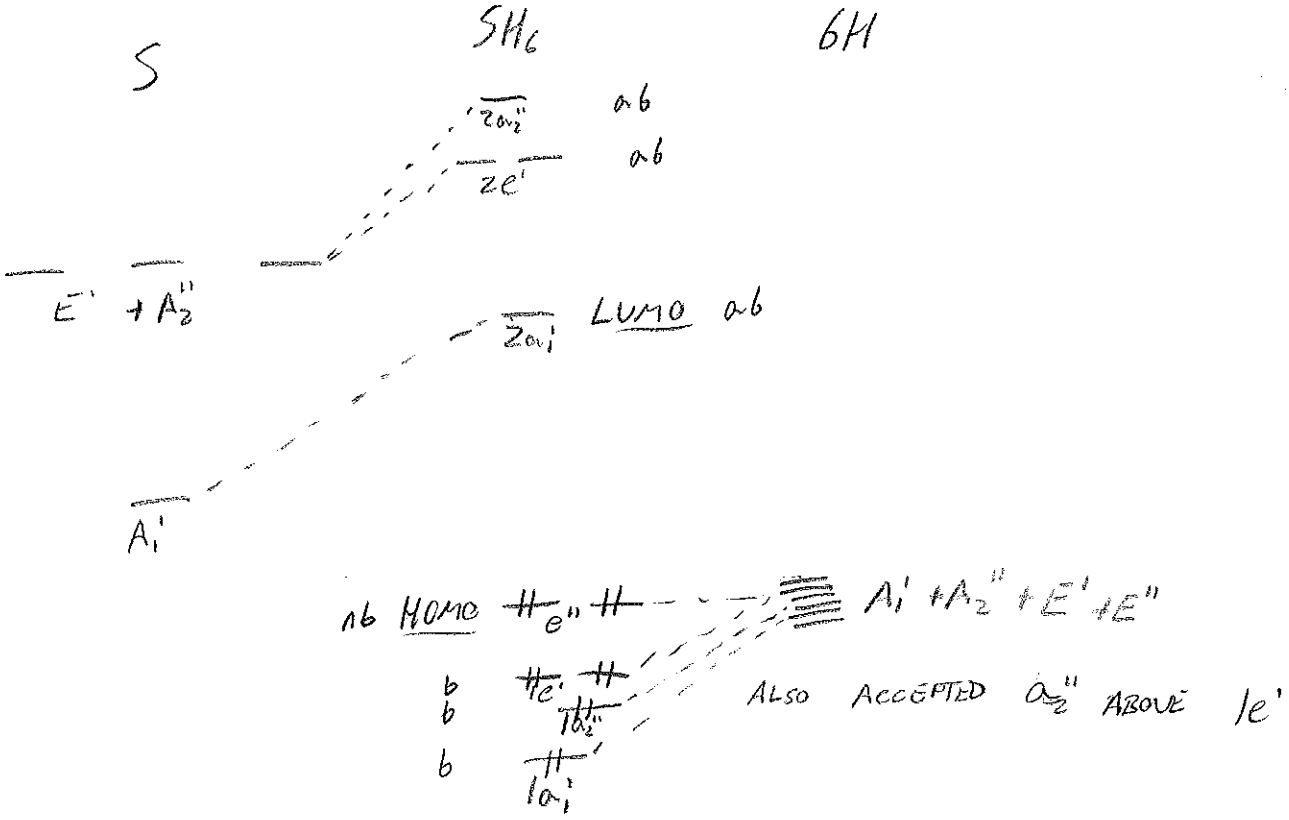
$$a_{A_1'} = \frac{1}{12}(6\cdot1\cdot1 + 0+0+0+0+2\cdot1\cdot3)$$
$$= \frac{1}{12}(6+6)$$
$$= 1$$

$$a_{E'} = \frac{1}{12}(6\cdot2\cdot1 + 0+0+0+0+2\cdot0\cdot3)$$
$$= 1$$

$$a_{E''} = \frac{1}{12}(6\cdot 2\cdot 1 + 0 + 0 + 0 + 0 + 0) = 1$$

$$a_{A_2''} = \frac{1}{12}(6\cdot 1\cdot 1 + 0 + 0 + 0 + 0 + 2\cdot 1\cdot 3) = 1$$

$$\Gamma_{6H_{1s}} = A_1' + A_2'' + E' + E''$$

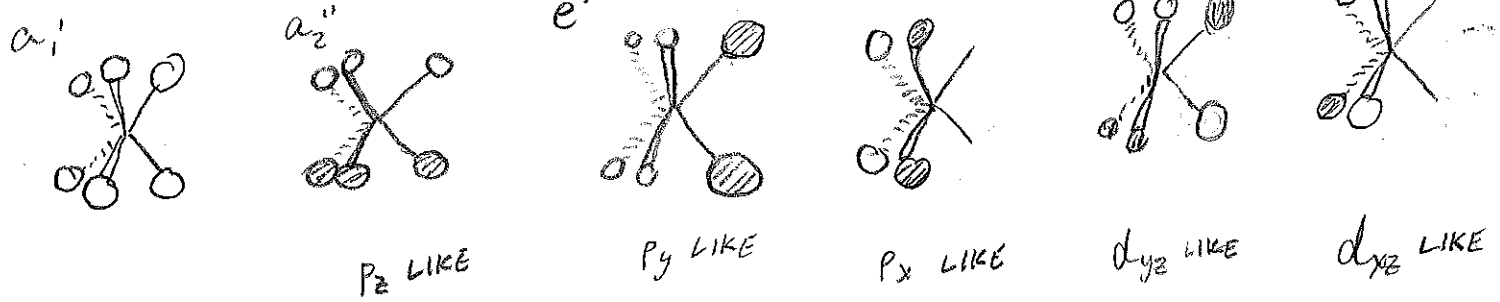


PES : 4 PEAKS

BO : $\frac{8}{2} = 4$

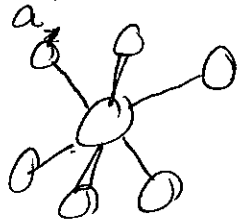
DIAMAGNETIC

SH_6 (CB) SALCS

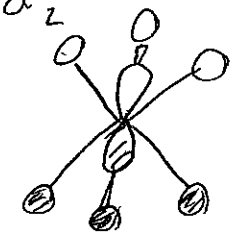


SH_6 (D3) MOs

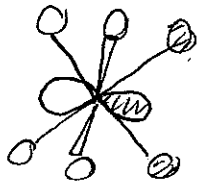
$1a_1'$

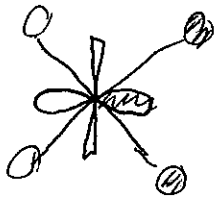


$1a_2''$

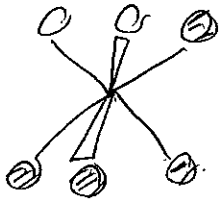


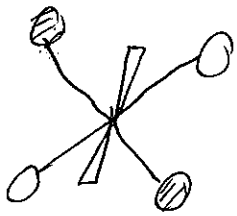
$1e'$



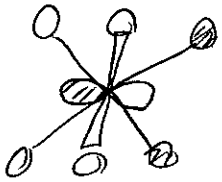


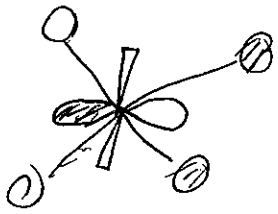
e''



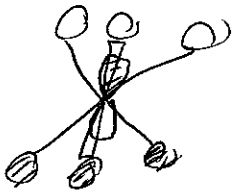


$2e'$

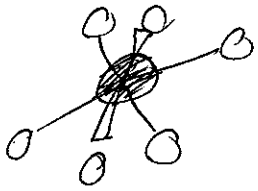




$2a_2''$



$2a_1'$



9) $A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$

TRANSLATION: T_{1u}

ROTATION: T_{1g}

NORMAL VIBRATION: $A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$

h) IR SPECTRUM: 2 PEAKS ($2\ T_{1u}$)

RAMAN SPECTRUM: 3 PEAKS ($A_{1g} + E_g + T_{2g}$)

i)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_{S-H}	6	0	0	2	2	0	0	0	4	2	$= A_{1g} + E_g + T_{1u}$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ_{S-H}	6	0	0	0	0	2	$= A_1' + E' + A_2'' + E''$

For corresponding vibrational stretching modes, please see last page.

j) ISOMER A: 1 IR S-H STRETCHES (T_{1u})

2 RAMAN S-H STRETCHES ($A_{1g} + E_g$)

ISOMER B: 2 IR S-H STRETCHES ($E' + A_2''$)

3 RAMAN S-H STRETCHES ($A_1' + E'' + E'$)

2 PART 1

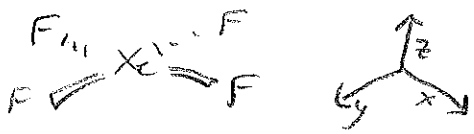
a)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_{6B_z}	6	0	0	2	2	0	0	0	4	2	$= A_{1g} + E_g + T_{1u}$

b)

$\Gamma_{B_{x,y}}$	12	0	0	0	-4	0	0	0	0	0	$= T_{1g} + T_{2g} + T_{1u} + T_{2u}$

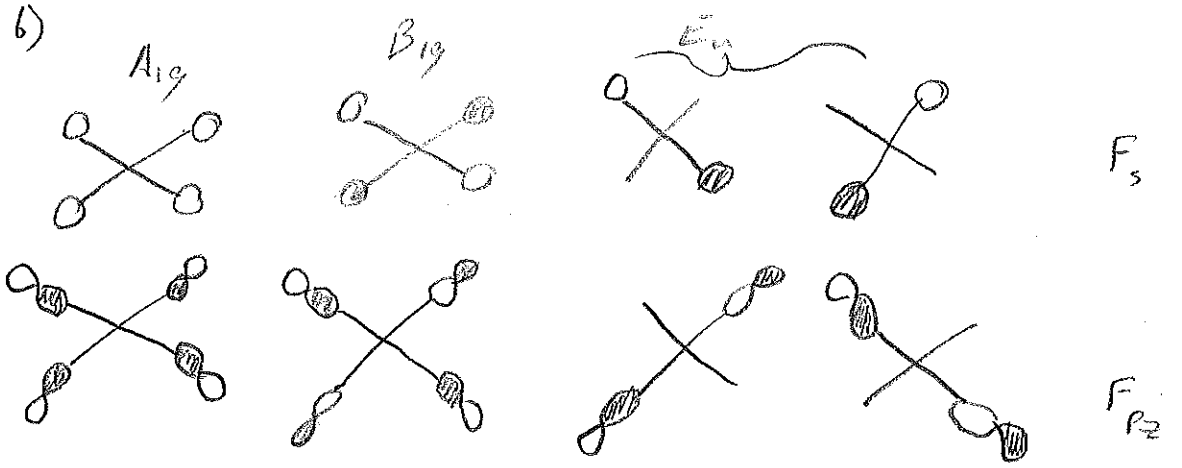
2 PART II

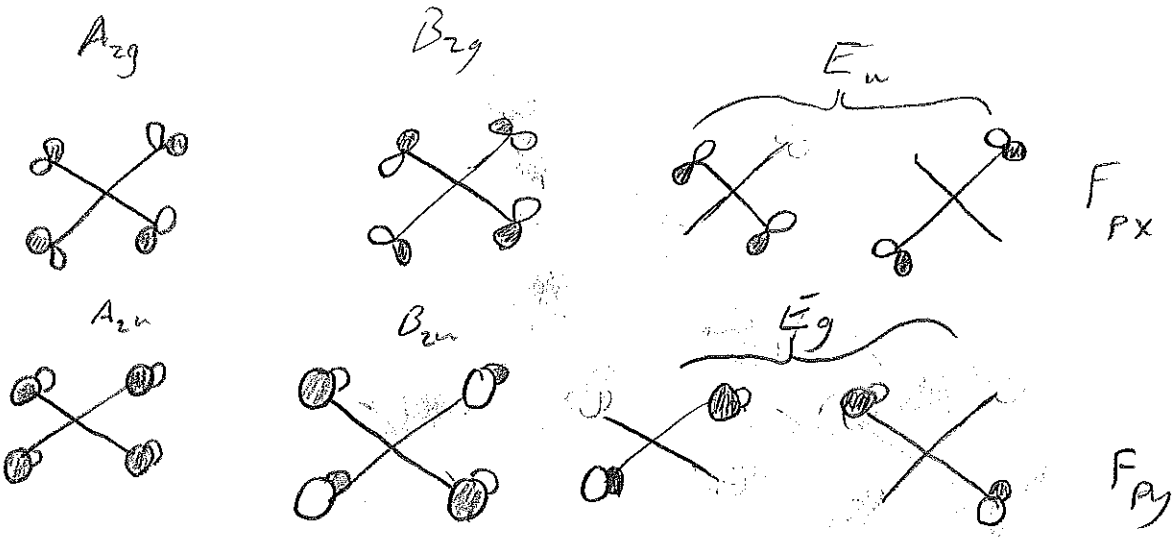


a)

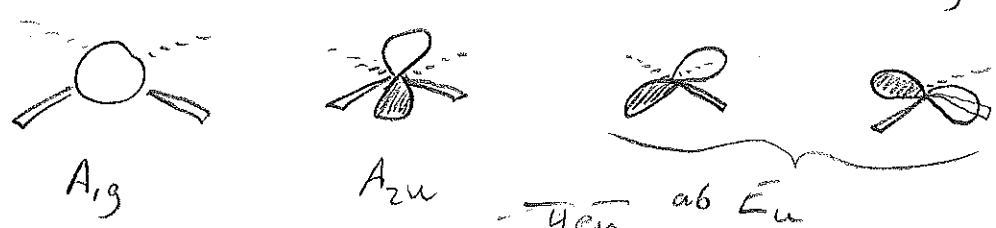
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ_{F_s}	4	0	0	2	0	0	0	4	2	0	$= A_{1g} + B_{1g} + E_u$
$\Gamma_{F_{Pz}}$	4	0	0	2	0	0	0	4	2	0	$= A_{1g} + B_{1g} + E_u$
$\Gamma_{F_{Px}}$	4	0	0	-2	0	0	0	4	-2	0	$= E_u + B_{2g} + A_{2g}$
$\Gamma_{F_{Py}}$	4	0	0	-2	0	0	0	-4	2	0	$= A_{2u} + B_{2u} + E_g$

b)



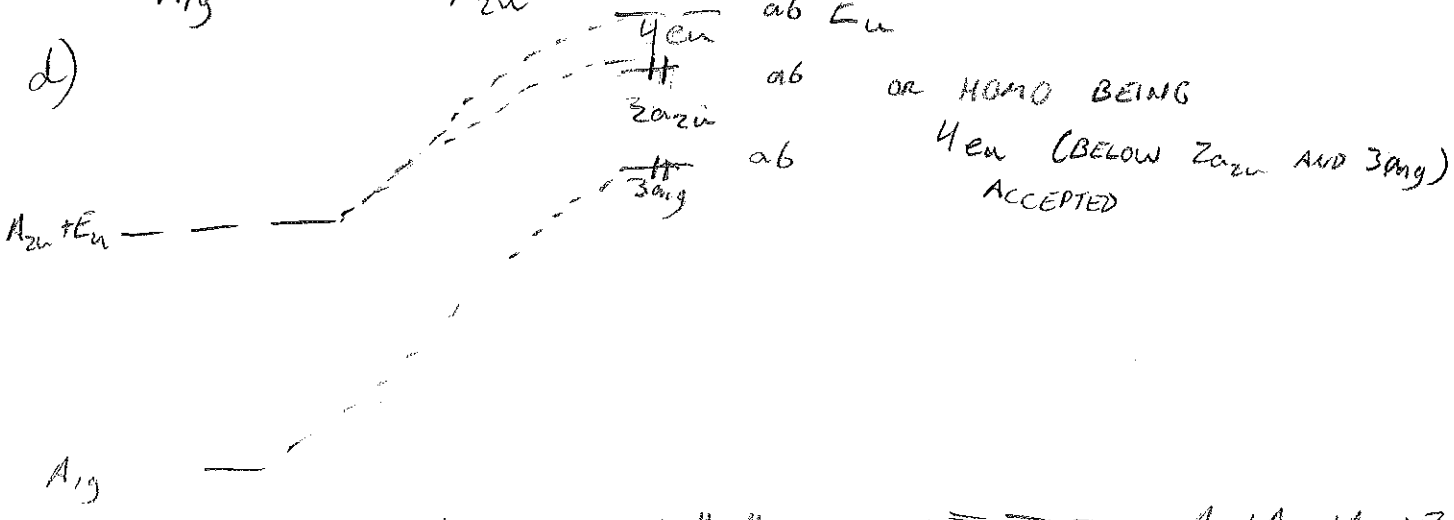


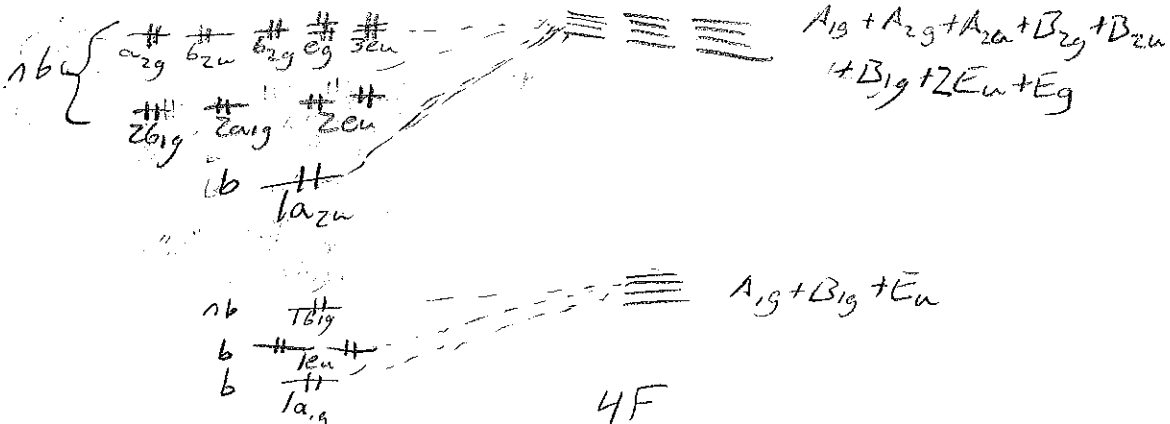
c)



A_{1g} A_{2u} E_u

d)



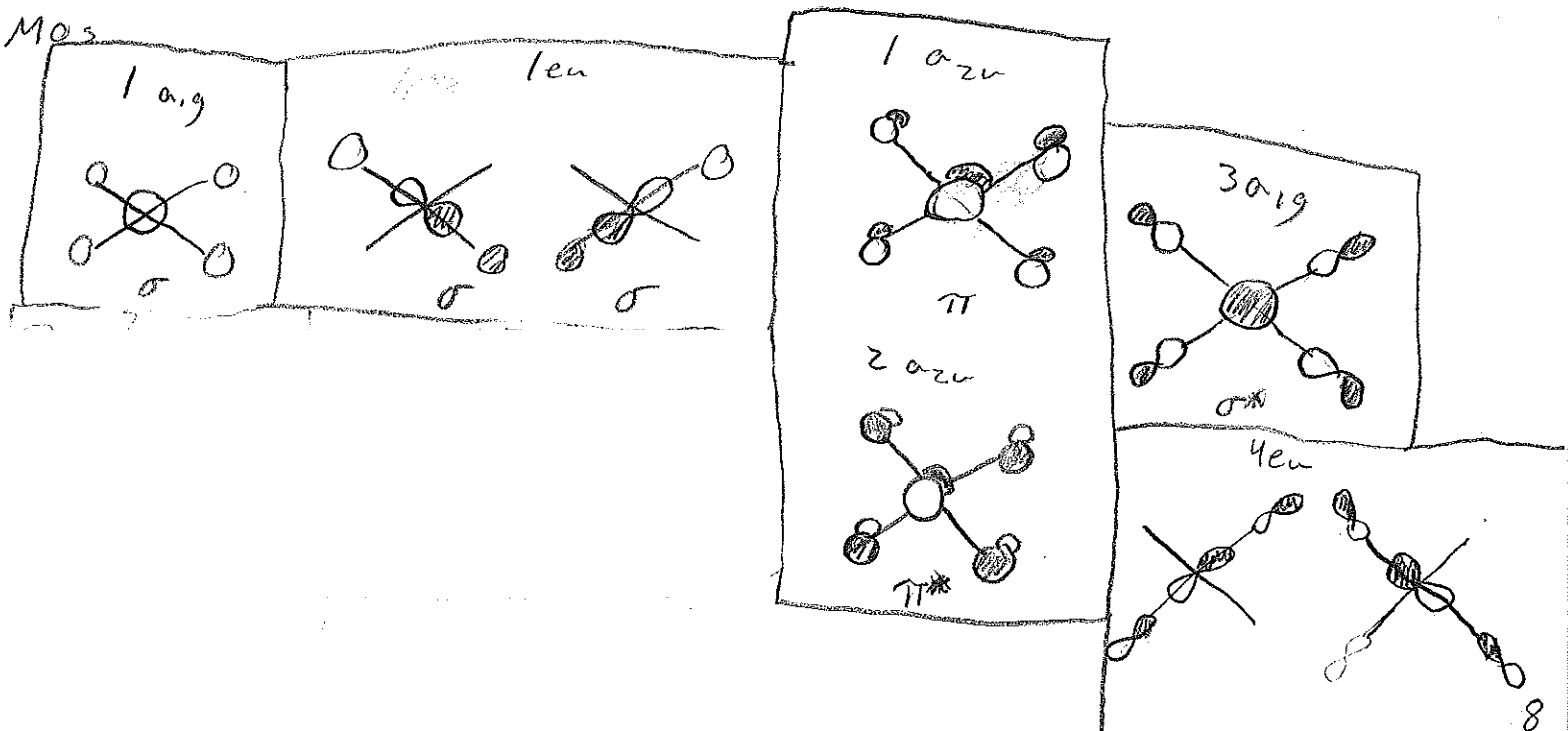


Xe

4F

XeF_4;

36e⁻



#2 f)

IR PEAKS: 141.8 cm^{-1}
240.0 cm^{-1}
522.1 cm^{-1}

VALUES DEPENDED ON BASIS SET / FUNCTIONAL

RAMAN PEAKS: 187.4 cm^{-1}
426.9 cm^{-1}
446.0 cm^{-1}

STRETCHING MODES FOR RAMAN PEAK AT 446 cm^{-1}, 426.9 cm^{-1}
IR PEAK AT 522.1 cm^{-1}

#3

a) 20 - A_{1g} 21 - E_u 22 - E_u 23 - B_{1g} 24 - A_{1g}

25 - A_{2u} 26 - A_{1g} 27 - E_u 28 - E_u 29 - A_{2u}

30 - B_{2g} 31 - E_g 32 - E_g 33 - B_{1g} 34 - E_u

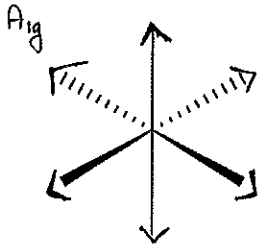
35 - E_u 36 - B_{2u} 37 - A_{2g} 38 - A_{2u} 39 - A_{1g}

40 - E_u 41 - E_u 42 - E_g 43 - E_g 44 - A_{1g}

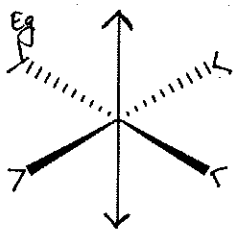
b) FLUORINE IS MORE ELECTRONEGATIVE THAN CHLORINE, SO ITS ORBITALS ARE LOWER IN ENERGY. F-BASED MOs ARE THEREFORE LOWER IN ENERGY THAN Cl BASED MOs

c) 33 - B_1
40 - E

Problem 1-i) Vibrational stretching modes



IR: inactive
Raman: active



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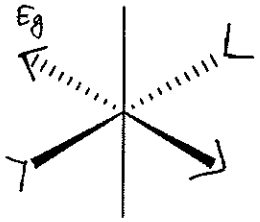

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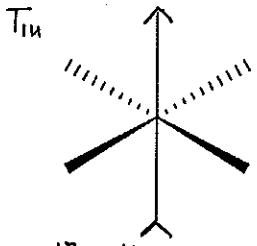

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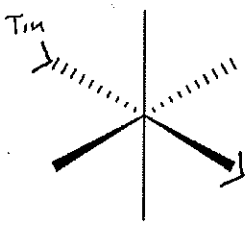

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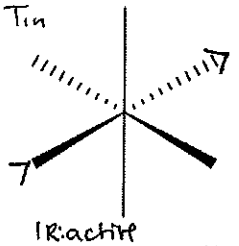

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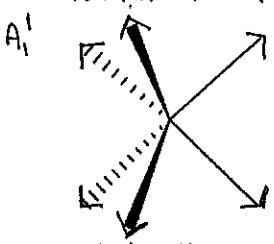

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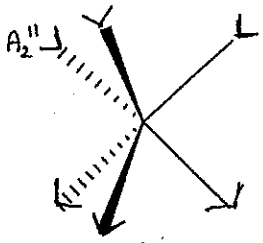

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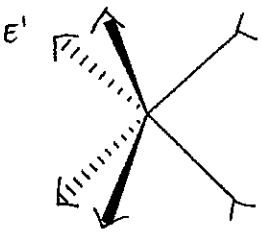

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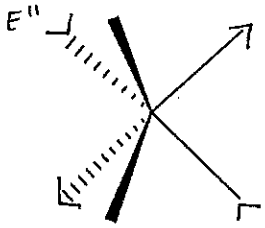

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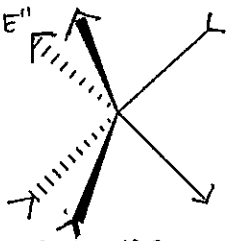

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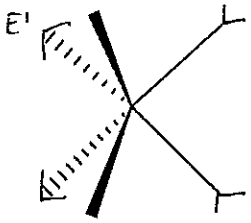

IR: active
Raman: active