Chem 65.354* February 15, 2002

Total Marks:50

12

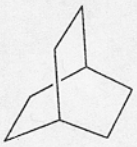
1. (a)Determine the symmetry point group of :

A)

PF_4Cl

Axial chlorine

B)

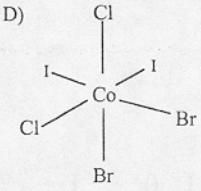


ignore hydrogens

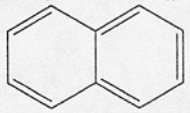
C)

Planar

D)



E)



Planar

(b) Are any of these molecules optically active?

5

2. Determine the reducible representation of molecular motion for square pyramidal:

$[FeCl_4Br]^{2-}$ C_{4v} E $2C_4$ C_2 $2\sigma_v$ $2\sigma_d$

12

3. For the molecule CH_2Cl_2, the following reducible representation for molecular motion was determined,

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
	15	-1	3	3

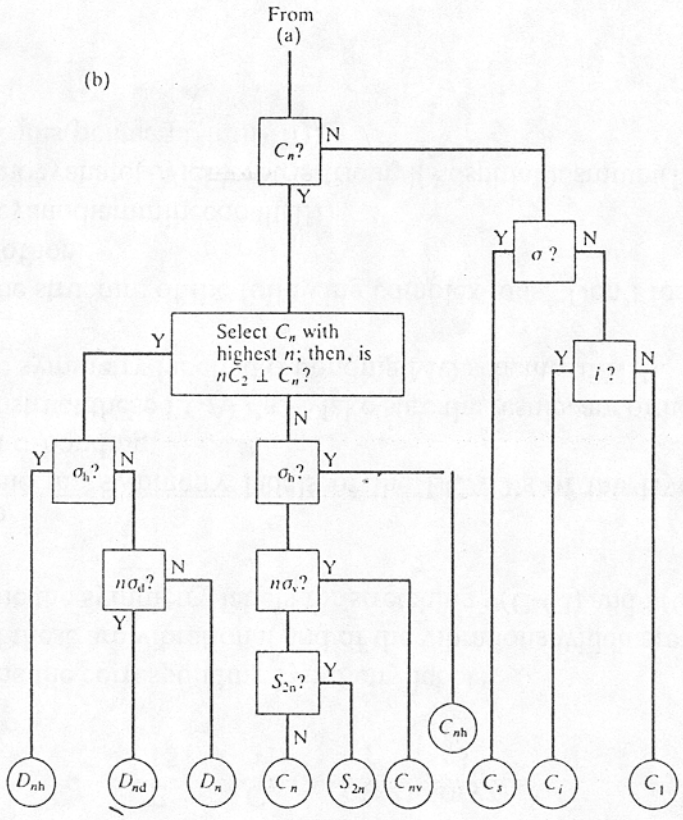
a) Determine the corresponding symmetry labels
b)Which of these are vibrational and of the vibrations which are Raman and/or IR active?
c) Determine the symmetry labels for stretching ν(C-Cl) and ν(C-H).

15

4. For NH_3,
a) Determine the symmetry labels of the LCAO's of the Hydrogen s-orbitals that are involved in σ-bonding.
b) Now construct these LCAO's. Make sure the results are orthogonal and normalized.
c) Draw the symmetry labelled σ bonding MO scheme of NH_3.

6

5. Draw the structure of the following complex ions. Don't forget to indicate the total charge of ion.
a) *cis*-tetracyanodiamminecobalt(III)
b) *mer*-trithiocyanato(-*N*)chlorotris(triethylphosphine)osmium(III)
c) (μ-chloro)bis(pentaaquairon(III))



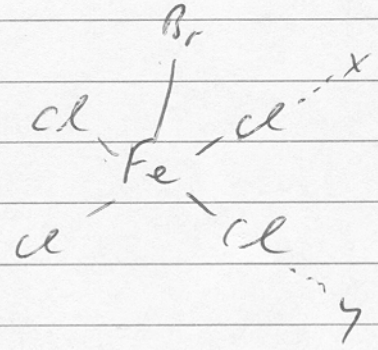
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

1. (a) C_{3v} (b) D_{3h} (c) D_{2h} (d) C_i

(e) D_{2d}

↑ OPTICALLY ACTIVE

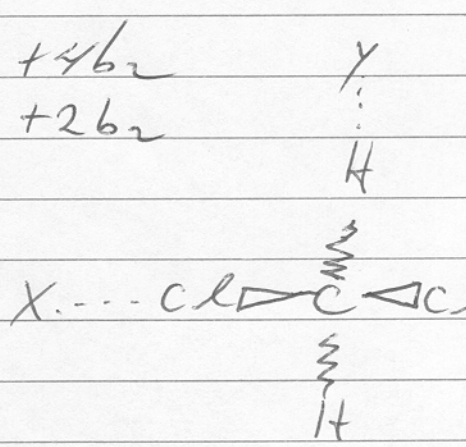
2.



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_{mol}	18	2	-2	4	2

3. (a) $\Gamma_{mol} = 5a_1 + 2a_2 + 4b_1 + 4b_2$

$\Gamma_{VIB} = 4a_1 + a_2 + 2b_1 + 2b_2$



FOR ν(C-Cl)

	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_{C-Cl}	2	0	2	0

$\Gamma_{C-Cl} = a_1 + b_1$

FOR ν(C-H)

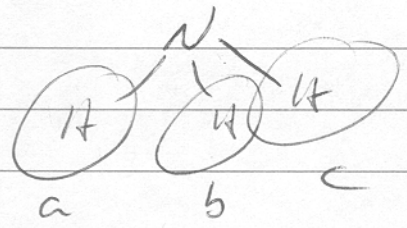
	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_{C-H}	2	0	2	2

$\Gamma_{C-H} = a_1 + b_2$

IR ACTIVE ~~VIBRATIONS~~ VIB ARE a_1, b_1 AND b_2

RAMAN ACTIVE VIB ARE a_1, a_2, b_1 AND b_2

4.



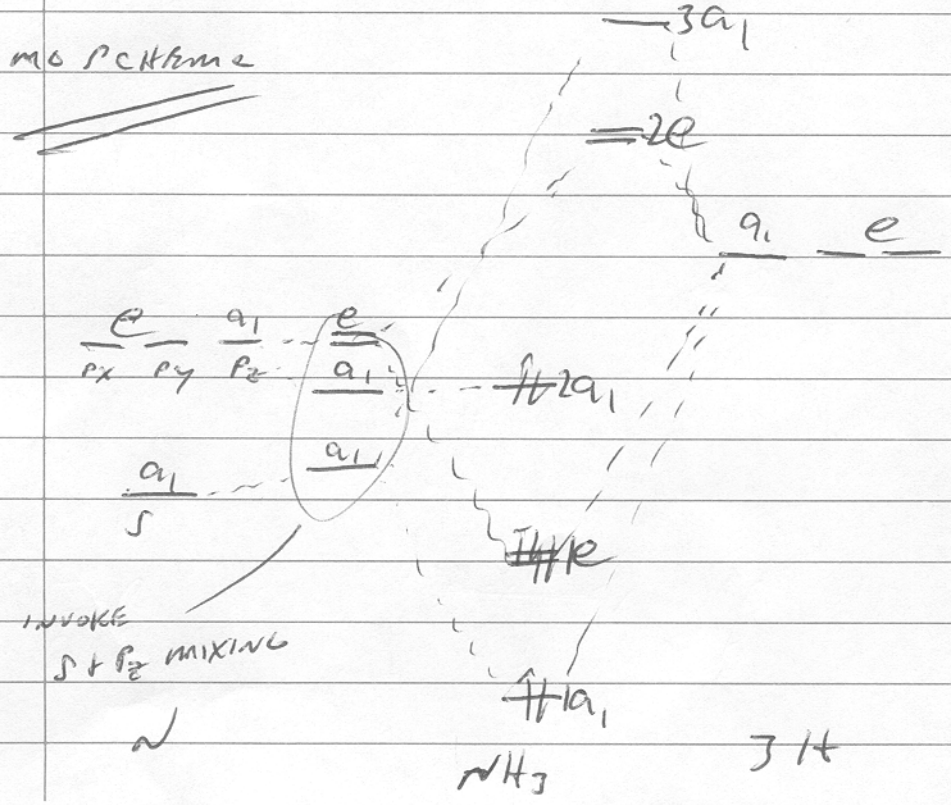
C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{LCAO}	3	0	1

$$\Gamma_{LCAO} = a_1 + e$$

$$\psi_{a_1} = \frac{1}{\sqrt{3}}(\phi_a + \phi_b + \phi_c)$$

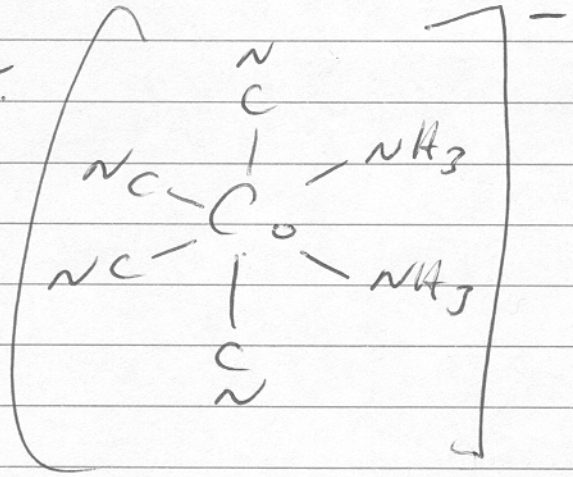
$$\psi_e = \frac{1}{\sqrt{6}}(2\phi_a - \phi_b - \phi_c)$$

$$\psi_e = \frac{1}{\sqrt{2}}(\phi_b - \phi_c)$$

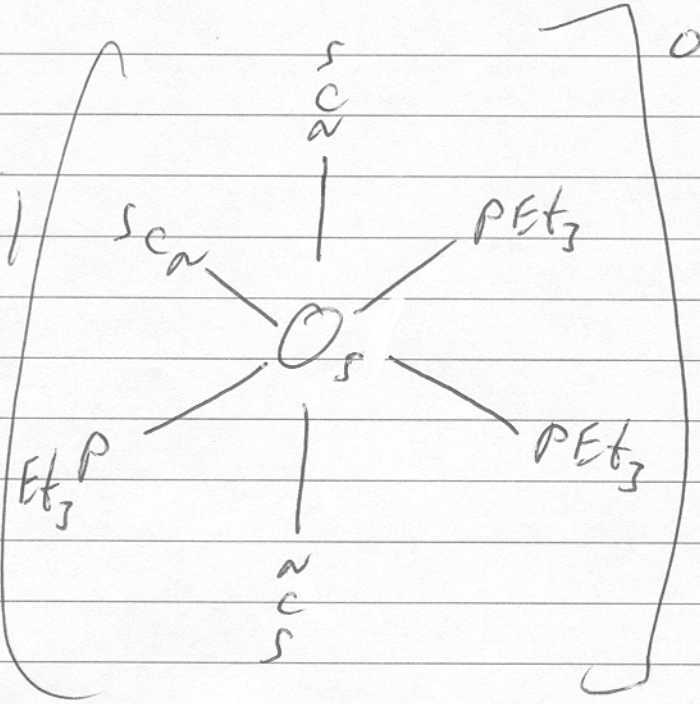


5.

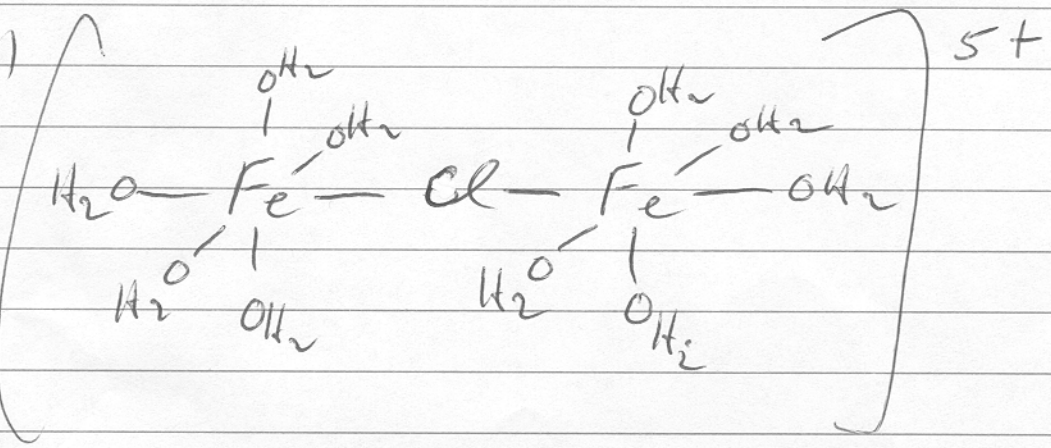
(a)


NC
NC
NC
NC
Co
NH3
NH3
−

(b)


SCN
SCN
PEt3
Et3P
PEt3
Os
NCS
0

(c)


H2O
OH2
OH2
Fe
Cl
Fe
OH2
OH2
OH2
H2O
H2O
OH2
5+