THE UNIVERSITY OF WESTERN ONTARIO
LONDON   CANADA

Final Examination-2008

CHEMISTRY 734b

Instructions: You have one week to complete this exam. The latest I will accept the exam is 5pm Monday April 21, 2008. While you are **not** allowed to consult with anyone including the course instructor, you are free to use your notes or any other references on Group Theory. Show **all** your work for full marks. Each problem has the same weight.

1.) a) Construct a group multiplication table for the six functions below that form a group under the operation of substitution of one function into another:

$f_1(x) = x$;
$f_2(x) = 1-x$;
$f_3(x) = (x-1)/x$;
$f_4(x) = 1/x$;
$f_5(x) = 1/(1-x)$;
$f_6(x) = x/(x-1)$

 (For example, $f_3 f_4$ in the table would be defined as the substitution of f_3 into f_4; that is $1/(x-1)/x = x/(x-1) = f_6$).

b) Find the identity element of the group.

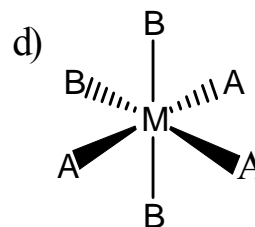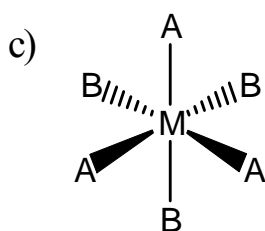c) Find the inverse of each group element.

d) Divide all the elements into classes.

2.) a) Determine the point groups of the following MA_4B_2, MA_3B_3, and $MA_2B_2C_2$ octahedral complexes. Explain fully how you arrived at your assignments.

a)

b)

c)

d)

e)

f)

g)

h)

i)
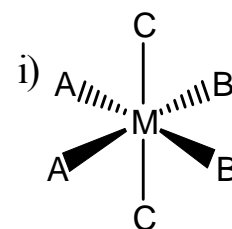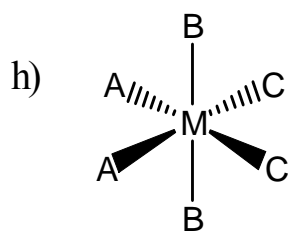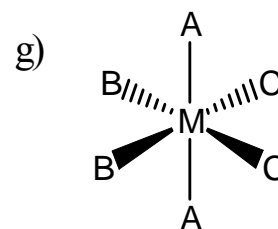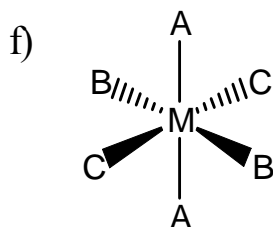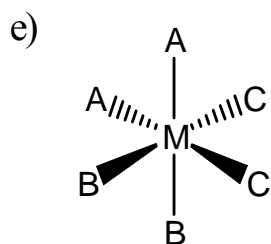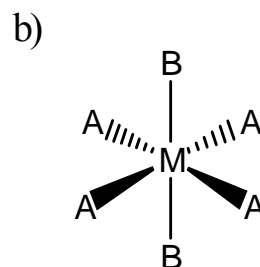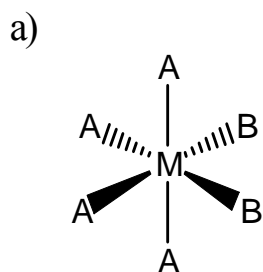
b) Determine the point groups of the following $M(AA)B_2C_2$ and $M(AB)C_2D_2$, and $M(AB)C_2BD$ octahedral complexes. Explain fully how you arrived at your assignments. The ligands connected by a line are bidentate ligands.

a)

B
B⧸⧸⧸ M ⧹⧹⧹ A
C   A
C

b)

B
C⧸⧸⧸ M ⧹⧹⧹ A
C   A
B

c)

C
B⧸⧸⧸ M ⧹⧹⧹ A
B   A
C

d)

C
A⧸⧸⧸ M ⧹⧹⧹ C
B   D
D

e)

A
A⧸⧸⧸ M ⧹⧹⧹ D
B   C
D

f)

C
A⧸⧸⧸ M ⧹⧹⧹ B
B   D
C

g)

D
A⧸⧸⧸ M ⧹⧹⧹ C
B   C
D
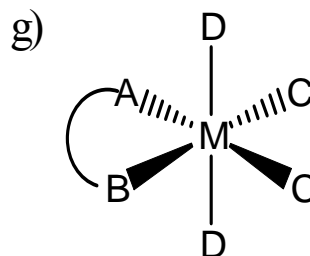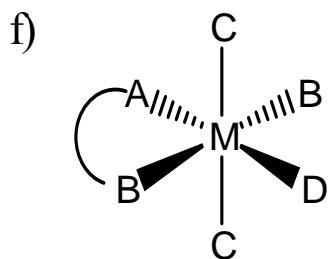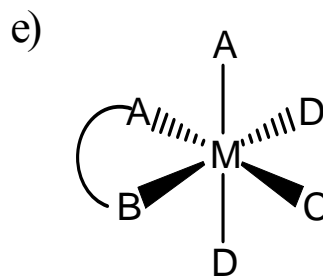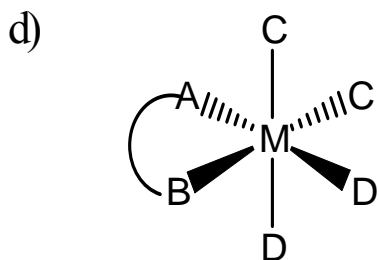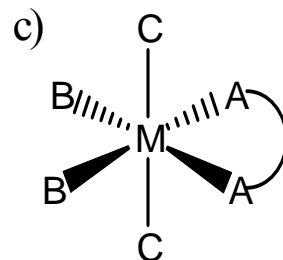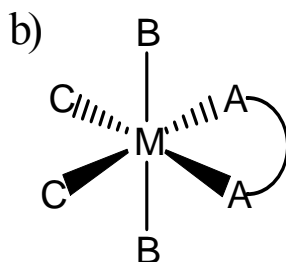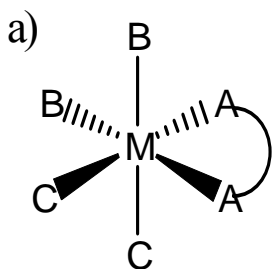
3.) Cyclopropane, C_3H_6, is remarkably stable despite its extreme ring strain. A delocalized MO model suggests the ring is stabilized by pπ-bonding, a result hardly expected for an alkane.

The entire catalogue of MOs for cyclopropane can be deduced by considering three kinds of interactions:
1) hydrogen 1s with carbon 2s and in-plane 2p interactions leading to σ_{C-H}-MOs of all types.
2.) in plane C 2p interactions leading to σ_{C-C} bonding and antibonding MOs, and
3.) out of plane C 2p interactions leading to π_{C-C} bonding and antibonding MOs.

a) The most effective σ_{C-H} interactions are formed between the 6 H 1s orbitals and the 3 C 2s orbitals. Determine the symmetries of the MOs formed from the three C 2S orbitals. Then determine the symmetries of the MOs formed from the 6 H 1s orbitals. By matching symmetries, give the Mulliken designations and possible bonding types for MO that can be formed from C2s with H 1s interactions.
Sketch the MOs using projection operators.

b) Less effective σ_{C-H} interactions can be formed between the H 1s orbitals and the in-plane C 2p orbitals shown with the following orientations:
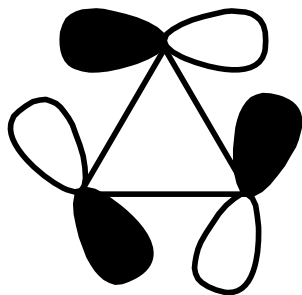
Determine the MOs that can be formed from these three C 2p orbitals. By matching symmetries with H 1s MOs previously determined, give their Mulliken designations and possible bonding types for all MOs that can be formed. Sketch the MOs using projection operators.

c) Ring sigma bonding results from in-plane C 2p orbitals with the following orientations:
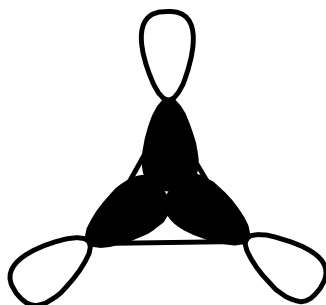
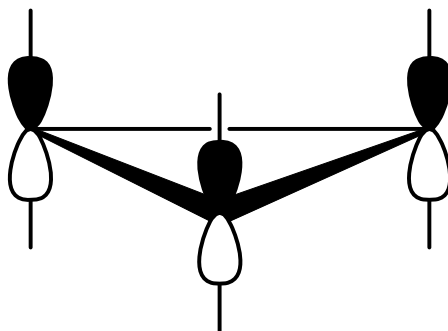Determine the symmetries of the MOs formed from these three C 2p orbitals and give their Mulliken labels. Indicate the possible bonding type of MOs that can be formed. Sketch the MOs using projection operators.

d) Ring π-interactions result from out-of-plane C 2p orbitals with the following orientations (the lines are there to guide the eyes only):

Determine the symmetries of the MOs formed from these three C 2p orbitals and give their Mulliken labels. Indicate the possible bonding type of MOs that can be formed. Sketch the MOs using projection operators.
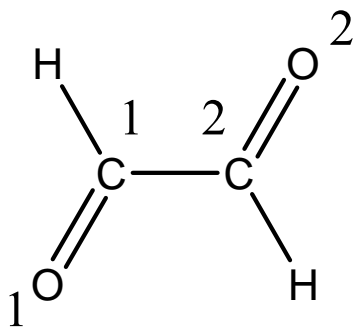
e) Draw an MO diagram. Ignoring the C 1s electrons, cyclopropane has 18 electrons. On the basis of the work done above what is the electronic configuration of the cyclopropane ground state?

4.) Consider the *trans*-configuration of planar glyoxal:

a) Determine the point group of the molecule.

b) Using 2 pure in-plane p-orbitals on the two oxygen atoms (labeled 1 and 2 in the figure) show that the two resultant non-bonding orbitals, {n}, on the O-atoms transform as $\Gamma_n = a_g \oplus b_u$. For this problem assume that the energy of the b_u orbital lies lower than a_g.

c) Using pure out-of-plane p-orbitals on the oxygen atoms and the carbon atoms (also numbered 1 and 2 in the figure), derive the character representation for each individual p-orbital; that is $\Gamma(p(O_1))$; $\Gamma(p(C_1))$; $\Gamma(p(C_2))$; $\Gamma(p(O_2))$, and reduce the resultant direct sum $\Gamma(p(O_1)) \oplus \Gamma(p(C_1)) \oplus \Gamma(p(C_2)) \oplus \Gamma(p(O_2))$ which is the representation for the resultant π-orbitals.

d) ***Without*** using projection operators draw the four resultant π-orbitals (in terms of the out-of-plane p-orbitals) showing the nodal structure. Assign the Mulliken symbols and energy order the π-orbitals on the basis of the number of nodal planes.

e) Assume there are 4 non-bonding electrons and 4 π-electrons in the π-system, what are the possible n → π^* transitions (give states and spin multiplicities)? Which transitions are allowed and/or forbidden?

f) Do a normal mode analysis for *trans*-glyoxal. Indicate which modes are IR and Raman active. Can any of these modes make any forbidden electronic transition of *trans*-glyoxal possible through vibronic coupling?

5.) Show that all the planar C_nH_n hydrocarbons have just a single IR active C-H stretching mode.

$C_3H_3{}^+$

$C_4H_4{}^+$

$C_2{}'', \sigma_d \qquad C_2{}', \sigma_v$

$C_5H_5{}^-$

C_6H_6

$C_2{}'', \sigma_d$

$C_2{}', \sigma_v$
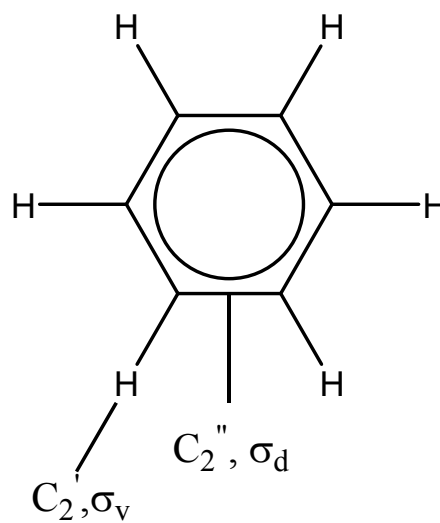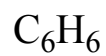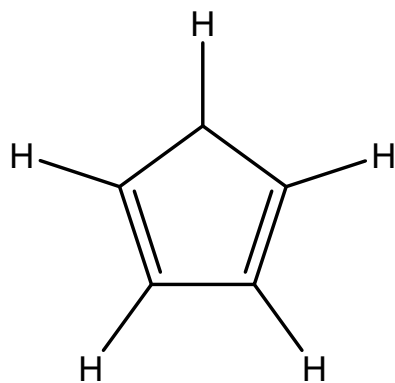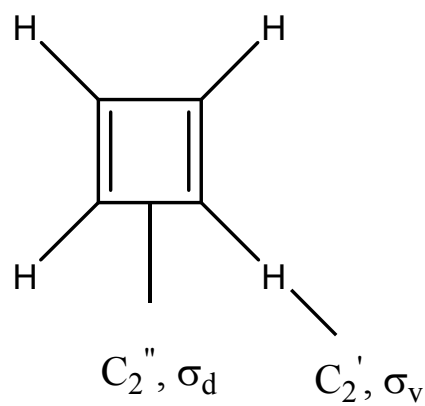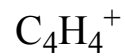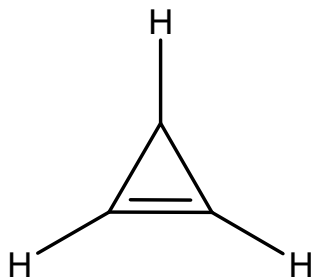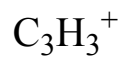
6.) Consider 3 hypothetical particles with each the following orbital (ℓ) and spin angular (s) momenta:
$\ell_1 = 1$, $s_1 = 1$; $\ell_2 = 1$, $s_2 = 1$; $\ell_3 = 2$, $s_3 = 1$.
a) Determine all the resultant Russell-Saunders terms and their parities in the form $^{2S+1}L_J$. Be sure to indicate how many of each state there are.
b) Determine all the resultant j-j coupling terms and their parities. Be sure to indicate how many of each state there are.

7.) a) The tetrahedral permanganate ion MnO_4^- has the ground state configuration:

$(1e)^4(1t_2)^6(2t_2)^6(t_1)^6$ and the next lowest MO is an antibonding $3t_2$ orbital. Determine the symmetries of the states that correspond to the excited state configurations:
... $(2t_2)^6(t_1)^5(3t_2)^1$ and ...$(2t_2)^5(t_1)^6(3t_2)^1$. Find which E1, M1 and two-photon allowed transitions from the ground state are symmetry- and spin allowed. State the polarization of the allowed E1 transitions. (*Note: Γ for two-photon operator transforms as the components of $\vec{r} \otimes \vec{r}$*).

b) In a crystal of $KClO_4$ containing some MnO_4^- substituting for ClO_4^-, the symmetry at an impurity anion site is reduced to C_{2v}. Use correlation tables to describe what splittings and relabeling of states that occur in the ground state of MnO_4^- and the excited states to which E1 transitions are allowed in the free ion when the symmetry is lowered from T_d to C_{2v}. State which E1 transitions are allowed now, and what their polarizations are.

8.) a) Classify the terms of a $3d^1 4p^1$ configuration in an intermediate D_{4h}, D_{2d} and C_{2v} crystal field.

b) Consider an atom M, having a p^2 configuration. How do the p-orbitals transform in O_h symmetry? If **strong** field ligands are brought up to M to form an O_h environment what is the resultant electronic configuration of the molecule?

b) Deduce the Mulliken symbols for the resultant states of the molecule (including parity). For this problem establish the spin multiplicities by Bethe's method of descending symmetry.

9.) Consider the following ring closing reaction of 2,4,6-octatriene:
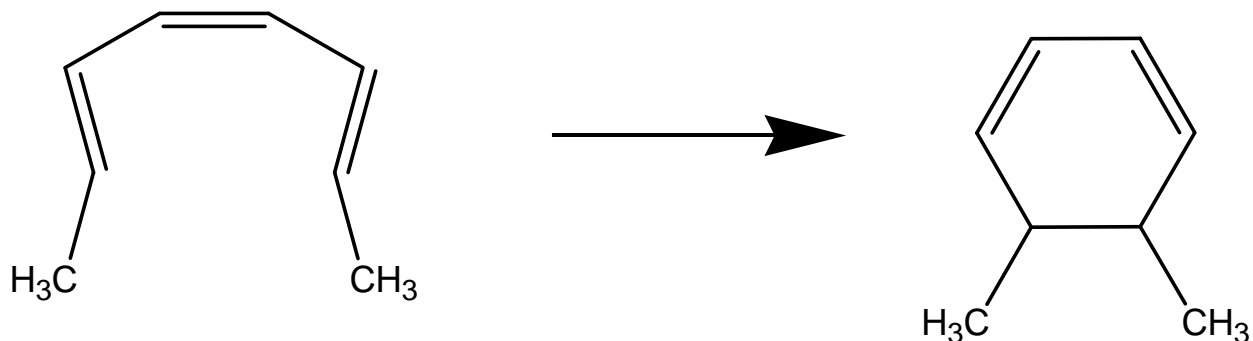
a) Find the irreducible representations of the MOs of the 2,4,6-octatriene reactant, and use projection operators to find the normalized wave functions, and sketch them. In addition find their Hückel energies in zero-overlap approximations.

b) Based on your results in part a) argue if thermally the ring will close in a conrotatry or disrotatory fashion and whether the two methyl groups are *cis* or *trans* with respect to the formed sigma bond.

c) Based on your results in part a) argue if photochemically the ring will close in a conrotatry or disrotatory fashion and whether the two methyl groups are *cis* or *trans* with respect to the formed sigma bond.