Chem 224 Exam I
October 26, 2004   8 Questions 6 Pages   200 points

Name:_____

(10 pts) 1) Tell whether the following is a valid mathematical groups or not. **List the conditions for a group that are satisfied and those that are not** if your answer is no.

a) The set of symmetry operations $\{E, C_4(z), C_2(z), C_4^3(z), \sigma_h\}$.

(40 pts) 2) Give the point groups for the following molecules:

a) *cis*-$Mo(CO)_4Cl_2$

b) *trans*- $Mo(CO)_4Cl_2$

c) *fac*-$Mo(CO)_3Cl_3$

d) *fac*-$Mo(CO)_3Cl_3$

(10 pts) 3) Express the following direct product as a sum of irreducible representations.

E_{1g} x E_{1g} in the point group D_{6h}.

(40 pts) 4) Sketch the sigma bonding part of the MO diagram for $CFCl_3$, a CFC found in the atmosphere that contributes to both global warming and ozone depletion. On carbon consider the valence s and p orbitals and for the halogens consider each to have a generic sigma orbital pointing toward carbon. For partial credit answer in the following stages.

a) To what irreducible representations do the carbon orbitals belong?

b) Give the irreducible representation for the fluorine sigma orbital, and the representations for the chlorine sigma orbitals.

c) Sketch the MO diagram and fill with the proper number of sigma bonding electrons.

(30 pts) 5) The photoelectron spectra of bicyclo[2.2.2]octane, quinuclidine, and DABCO are shown in the order top → bottom in the panel below. Explain why one low energy ionization is seen in quinuclidine at 8 eV, but DABCO shows two at 7.8 and 9.8 eV. Explain in terms of molecular orbital theory and symmetry.

(30 pts) 6) What are the symmetries of vibrations that can be seen in the infra-red spectrum of a D_{6h} molecule? What are the symmetries of vibrations that can be seen in the Raman spectrum? In any molecule that has inversion symmetry, what do you think is generally true about the information obtained from the infra-red and the Raman spectra.

a) Infra-red allowed –

b) Raman allowed –

c) For any molecule with inversion symmetry we can conclude that (you finish the sentence)

(20 pts) 7) How would the irreducible representations from the D_{4h} point group correlate to those in its subgroup C_{4v}? Complete the correlation table below:

D_{4h}   **C_{vv}**

A_{1g}

A_{2g}

B_{1g}

B_{2g}

E_g

A_{1u}

A_{2u}

B_{1u}

B_{2u}

E_u

(20 pts) 8) Give the irreducible representations of the following pi orbitals of the allyl cation in its proper point group. (Hint, calculate the character for how each orbital transforms as a whole under the symmetry operations)