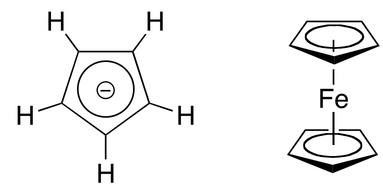
Recommended reading: 4.7, **14**
Ch 102 Problem Set 4
Due: Tuesday, April 26, before class

Problem 1 (20 points)

The cyclopentadienyl anion (Cp^-) is a common ligand in organometallic compounds. One of the classic cyclopentadienyl compounds is the 'sandwich' complex, ferrocene ($FeCp_2$, shown below), a common electrochemical reference compound ($\varepsilon_{Fe(II)/Fe(III)}$=0.641 V vs. normal hydrogen electrode).



Cyclopentadienyl anion   Ferrocene

The aromatic π-system in Cp is of interest because it allows for interaction with metal orbitals. For this problem, use the $\boldsymbol{D_{5h}}$ character table included in the handout you received in class.

a) Using the 5 carbon $2p_z$ orbitals (z is perpendicular to the plane of Cp) as a basis set, determine the reducible representation.

b) Reduce the representation to a sum of irreproducible representations.

c) Sketch the 5 SALCs, label with Mulliken symbols, and draw a partial MO diagram comprising of the π-system of Cp. Indicate all nodes. Note: clearly define your axes. Include a drawing of the atomic orbitals that these SALCs resemble (from the character table).

e) Using the $\boldsymbol{C_{5v}}$ point group instead of $\boldsymbol{D_{5h}}$, what are the irreducible representations that make up the 5 C $2p_z$ basis set? (you don't have to show any derivation, just provide the Mulliken symbols under $\boldsymbol{C_{5v}}$)

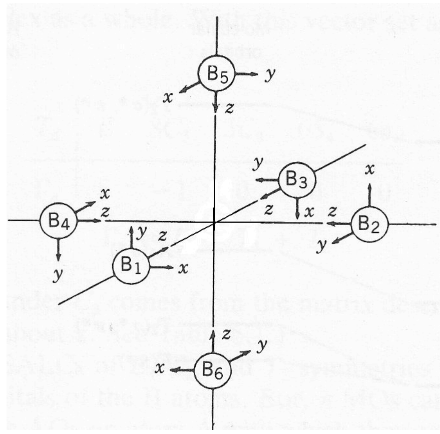
f) For candy (no points): Attach a picture of the HOMO as computed with the provided software.

Problem 2 (20 points)

On page 365 of your textbook you will find a discussion of the octahedral $[B_6H_6]^{2-}$ cluster. In this discussion the bonding of the cluster is simplified by only considering the frontier orbitals. Each B-H fragment has only three frontier orbitals, which are shown in the top right figure.

These frontier orbitals can be combined to form the molecular orbital (MO) diagram of the $[B_6H_6]^{2-}$ cluster. Part of this MO is shown and includes molecular orbitals of three symmetries (a_{1g}, t_{1u}, and t_{2g}).

For this problem we will treat the radial frontier orbital separately from the two tangential frontier orbitals. An easy way to do this is to use the axis system shown below, in which each boron has its own x, y, and z axis. The z axis corresponds to the radial orbitals, the x and y axes correspond to the tangential orbitals.



a) Using only the 6 boron p_z orbitals as a basis set, generate a reducible representation Γ_{6Bz}.

b) Reduce the Γ_{6Bz} representation to the irreducible representations for the bonding framework including only the radial orbitals. You can do this either by inspection or mathematically. No symmetry adapted linear combinations (SALCs) need to be sketched or MO diagram derived.

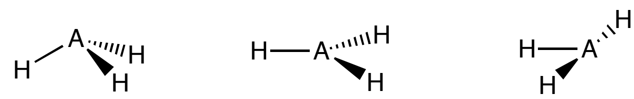
c) Using the 12 boron p_x and p_y orbitals together as a basis set, generate a reducible representation Γ_{12Bxy}.

d) Reduce the Γ_{12Bxy} representation to the irreducible representations for the bonding framework including only the tangential orbitals. You can do this either by inspection or mathematically. No SALCs need to be sketched or MO diagram derived.

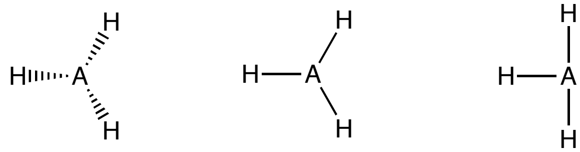
For a good final check on your work, look at the partial MO diagram on page 365 and confirm that your irreducible representations include those shown. The electronic structure of $[B_6H_6]^{2-}$ was computed and the file is available on the class website, if you are interested in viewing the MOs (not necessary for the solution).

Problem 3 (15 points)

Consider the three geometries shown below (**a**, **b**, and **c**) for AH_3. Draw Walsh diagrams for the distortion of **a** to **b** and **a** to **c**. These diagrams should include the full MO diagrams of **a**, **b**, and **c** including MO drawings and labels in the corresponding point group. Clearly correlate the molecular orbitals in **a** with the ones in **b** and **c**, respectively. Based on these diagrams determine which geometry is favored for BeH_3^-, NH_3, and ClH_3, respectively. Explain.



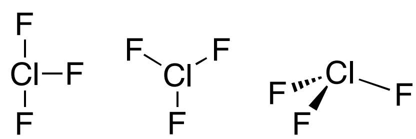
b **a** **c**



Problem 4 (25 points)

Part A

Chlorine trifluoride (ClF_3) is a fluorinating agent that has seen some employment in the processing of spent uranium fuel from nuclear power plants. ClF_3 is used to convert uranium metal to uranium hexafluoride (UF_6), which can then be stored in metal drums. For ClF_3, three distinct geometries can be proposed – t-shaped (**1**), trigonal planar (**2**), and trigonal pyramidal (**3**).

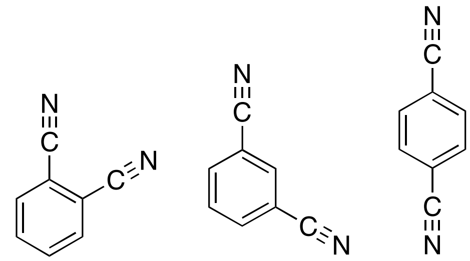


1 **2** **3**

a) Assign point groups to compounds **1**-**3**.
b) Determine the reducible representations for the degrees of freedom of each geometry, and reduce them to their irreducible representations. Determine the irreducible representations corresponding to translations, rotations, stretching modes, and bending modes.
c) How many peaks do you expect in the ^{19}F NMR, IR and Raman spectra for each of the above geometries (assuming the geometries are "frozen")? Which single spectroscopic technique (from the ones above) can distinguish between the three isomers?
d) Using VSEPR, predict the geometry of ClF_3.
e) Draw and label with Mulliken symbols the vibrations for the geometry predicted in part d).
f) Using the provided software build compound **1**, and compute its vibrational spectra. What are the computed Cl-F stretching frequencies (in cm^{-1}) in the IR and Raman spectra for each compound? Include a printout of the IR and Raman spectra.

Part B

Organic nitriles (i.e. compound displaying carbon-nitrogen triple bonds) have characteristic vibronic absorptions around 2200-2300 cm^{-1} due to the C-N stretches. Shown below are three isomers of dicyanobenzene – *ortho*-dicyanobenzene (**1**), *meta*-dicyanobenzene (**2**), and *para*-dicyanobenzene (**3**).



1 2 3

a) Assign a point group to each of the above species.
b) For each compound, determine the number of IR and Raman peaks expected for C-N stretches. You don't need to analyze all degrees of freedom – focus on the C-N stretches.
c) Which isomer(s) may be identified unambiguously using vibrational spectroscopy?

Problem 5 (20 points)

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, Lewis dot structures, symmetry, MO theory, vibrational spectroscopy, etc.) and some application of the provided software (since MO theory and vibrational spectroscopy were covered in class, you are now expected to include some molecular orbital pictures / MO diagram analysis / IR/Raman analysis).