Chemistry 410A **Exam 5** **Fall 2011**

Solutions

1. **40 points.**

   (a) Evaluate $b_g \otimes a_u$ in the point group C_{2h}. $\boxed{B_u.}$

   (b) Is the transition from a_{2u} to a_{1u} in ethane (point group D_{3d}) allowed:

   i. by electric dipole selection rules? $\boxed{\text{no}}$

   ii. by Raman selection rules? $\boxed{\text{no}}$

   Solution: The direct product $a_{2u} \otimes a_{1u} = A_{2g}$, which does not correspond to any of the first- or second-order cartesian functions.

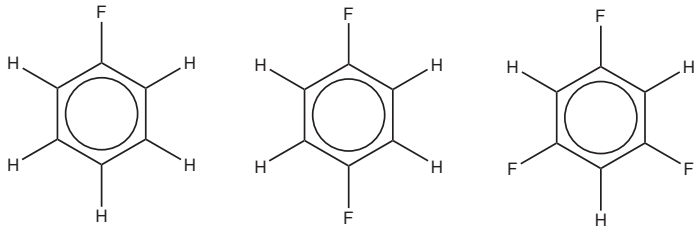
   (c) What is the symmetry representation for the C—C σ-bonding orbital in ethane? **Solution:** The C—C σ-bond occupies the region along the axis of symmetry between the two carbons, and is symmetric under all the opertaions of the point group, so its representation is $\Gamma_{\text{tot sym}} = \boxed{a_{1g}.}$

   (d) Assume that Li_2^+ follows the line for N_2 in the correlation diagram.

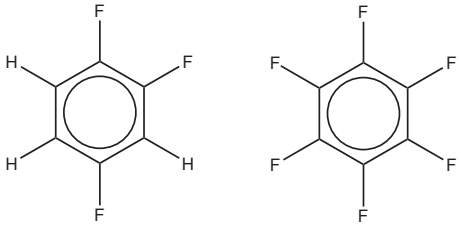
   i. Write the MO configuration for the ground state of Li_2^+. **Solution:** Li_2^+ has 5 electrons, and the MO configuration is $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^1.}$

   ii. Write the term symbol for the ground state of Li_2^+. **Solution:** There is one unopaired electron, for a tiotal spin opf $S = 1/2$, so $2S + 1 = 2$. The overall symmetry is the symmetry of the unpaired electron MO: $\boxed{^2\Sigma_g^+.}$

2. List all the point groups possible for the fluorobenzenes, C_6H_5F, $C_6H_4F_2$, $C_6H_3F_3$, $C_6H_2F_4$, C_6HF_5, and C_6F_6. **Solution:** There are five distinct possibilities. Other substitutions fall into one of these five point groups:

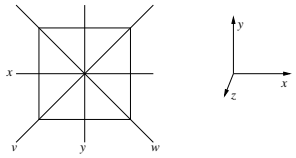


C_{2v} D_{2h} D_{3h}



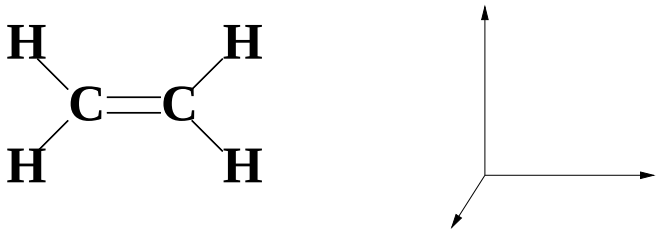
C_s D_{6h}

3. One corner of a multiplication table for the group D_{4h} is left blank below. For convenience, we have labeled the four dihedral $\hat{C}_2$ rotation axes by v, w, x, and y, as shown. Fill in the missing entries. (You may choose any direction of rotation, but be consistent.)



D_{4h}	$\hat{E}$	$\hat{C}_4(z)$	$\hat{C}_2(w)$	$\hat{I}$
$\hat{E}$	$\hat{E}$	$\hat{C}_4(z)$	$\hat{C}_2(w)$	$\hat{I}$
$\hat{C}_4(z)$	$\hat{C}_4(z)$	$\hat{C}_2(z)$	$\hat{C}_2(x)$	$\hat{S}_4^3(z)$
$\hat{C}_2(w)$	$\hat{C}_2(w)$	$\hat{C}_2(y)$	$\hat{E}$	$\hat{\sigma}_{vz}$
$\hat{I}$	$\hat{I}$	$\hat{S}_4^3(z)$	$\hat{\sigma}_{vz}$	$\hat{E}$

4. The *complete* MO configuration of ethene is $1a_g^2 1b_{3u}^2 2a_g^2 3a_g^2 2b_{3u}^2 1b_{1u}^2 1b_{2g}^2 1b_{2u}^2$.



(a) Label the coordinate axes x, y, and z above, based on the representations used in this MO configuration.

(b) Identify each of the MO's with one of the following groups of electrons: (A) C—H σ-bond electrons, (B) C—C π-bond electrons, (C) $1s$ core electrons, (D) C—C σ-bond electrons.

Solution: The point group is D_{2h}. There are two b_{3u} orbitals, one for the $1s_\mathrm{A} - 1s_\mathrm{B}$ core orbital and another for one of the C—H σ-bond MOs. The b_{3u} representation is symmetric with respect to $\hat{C}_2(x)$, so the x axis must be the axis containing the two carbon atoms. The b_{2g} must correspond to the C—H σ-bond MOs that is symmetric for rotation in the molecular plane, $\hat{C}_2(y)$, but antisymmetric under the other rotations, so the molecular plane is the xz plane. The two lowest energy MO's must be for the $1s$ core electrons, The π-bonding MO is unique, in that it is the only orbital that will be antisymmetric with respect to reflection through the plane of the molecule, $\hat{sigma}_{xz}$, so that representation is the $1b_{2u}$.

$1a_g^2$ [C]
$1b_{3u}^2$ [C]
$2a_g^2$ [D] or [A]
$3a_g^2$ [A] or [D]
$2b_{3u}^2$ [A]
$1b_{1u}^2$ [A]
$1b_{2g}^2$ [A]
$1b_{2u}^2$ [B]