CHEM 5620, Physical Methods in Chemistry
Spring 2003, Dr. Omary
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Homework set #1 *General introduction to physical methods; Electronic absorption spectroscopy*
Due in class Wednesday, February 5.

(1) Suggest a suitable technique(s) to solve the following research problems:

a)Obtain an accurate molecular structure of a crystalline solid compound:

b) Obtain structural information for a thin film:

c)Obtain detailed structural information for a solid that could not be obtained as single crystals:

d) Characterize electronic transitions between frontier or valence MOs of a coordination compound:

e)Obtain an accurate MO diagram describing the electronic structure of a simple gas phase molecule:

f) Describe the electronic structure of a transition metal complex in the solid state:

g) Obtain the molecular weight of a polymer:

h) Obtain information about the oxidation state and local environment of a solid containing ^{57}Fe:

i) Obtain detailed structural information about a diamagnetic organic compound in solution:

j) Test whether a free radical forms and can be trapped at low temperature in an organic reaction:

k) Obtain information about bond lengths and angles in the gas phase for a simple molecule:

l) Characterize the functional groups present in an unknown compound:

m) Selectively characterize electronic transitions involving a chiral moiety in a compound:

(2) Answer the following questions using information in the article: Mason, W. R., III.; Gray, H. B. "Electronic structures of square-planar complexes" *J. Am. Chem. Soc.* **1968**, *90*, 5721.

a) Fill the following table referring to the MO diagram in Figure 2. Include the spin multiplicity in the notation you use for the term symbols of ? $_e^{gr}$ and ? $_e^{ex}$.

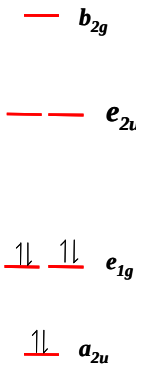
Transition	? $_e^{gr}$	? $_e^{ex}$	***Spin allowed?***	***Laporte allowed?***	***Expected ? ($M^{-1}cm^{-1}$)***
$b_{2g}(xy)$? $b_{1g}(x^2-y^2)$					
$b_{2g}(xy)$? $a_{2u}(?^*)$					
$b_{2g}(xy)$? $e_u(?^*)$					

b) Assign the various absorption peaks shown in the dashed curve in Figure 4 representing the spectrum at 77 K. In answering this question, write (i) the energy, (ii) orbitals involved in the transition (in terms of Figure 2), and (iii) classification of the transition (e.g., spin-allowed MLCT; spin-forbidden d-d).

c) Explain why don't we see LMCT transitions for the tetracyano complexes while we saw such transitions for the tetrachloro complexes. (**Hint:** refer to Figures 1 and 2.)

(3) The complex $[Cr(en)_3]^{3+}$ has a D_3 symmetry and a $^4A_2$ ground state. Evaluate whether electronic transitions to the following excited states are spin- or Laporte-allowed. Show your work and conclude, for Laporte-allowed transitions, whether they are polarized and if so in which direction. The required excited states are: $^4A_1$, $^2A_1$, $^4A_2$, $^2A_2$, ^4E, and ^2E.

(4) The figure below shows a qualitative MO diagram for the ? orbitals of benzene (D_{6h}). Fill the adjacent table. Include the spin multiplicity in the notation you use for the term symbols of $?_e^{gr}$ and $?_e^{ex}$.



Transition	$?_e^{gr}$	$?_e^{ex}$	*Spin allowed?*	*Laporte allowed?*	*Expected ?*
e_{1g}? e_{2u}					
e_{1g}? b_{2g}					
a_{2u}? e_{2u}					
a_{2u}? e_{2u}					

(5) The figure below shows a qualitative MO diagram for formaldehyde $H_2C=O$ (C_{2v}). Fill the adjacent table. Conclude the term symbols of ? $_e^{gr}$ and ? $_e^{ex}$ based on the C_{2v} notation of the orbitals instead of the standard ?, ?, and n notation. Show your work and conclude, for Laporte-allowed transitions, whether they are polarized and if so in which direction (use either Method 1 or 2).

— ***a*** $_1$ (C-O ? ?)

— ***b*** $_1$ (C-O ? ?)

↑↓ ***b*** $_2$ (lone pair, n_b)

↑↓ ***a*** $_1$ (lone pair, n_a)

↑↓ ***b*** $_1$ (C-O ? bond)

↑↓ ***a*** $_1$ (C-O ? bond)

Transition	? $_e^{gr}$	? $_e^{ex}$	*Spin allowed?*	*Laporte allowed?*
n_b? ?*				
n_b? ?*				
?? ??				
?? ??				

(6) Answer the following regarding f-f transitions in a centrosymmetric octahedral (O_h) complex. Explain.

a. Are they allowed via an electric-dipole mechanism? (Show your work).

b. Are they allowed via a magnetic-dipole mechanism? (Show your work).

c. Why is it more reasonable to use the extinction coefficients ($?_{max}$) to characterize resolved f-f transitions while it is better to use oscillator strengths (*f*) for resolved d-d transitions?

d. Give a few reasons that may explain the experimental observation of spin-allowed and spin-forbidden f-f transitions although they are usually Laporte-forbidden.