CHEM 5620, Physical Methods in Chemistry; Spring 2003, Dr. Omary
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Homework set #2 *Circular Dichroism, Luminescence Spectroscopy, Electrochemical Methods, and Vibrational Spectroscopy (Infrared and Raman).* ***Due in class Monday, March 3.***

(1) For the compound $Ni(bpy)_2Cl_2$ (where bpy = 2,2'-bipyridine):

a) Explain why the *cis*-isomer is CD-active while the *trans*-isomer isn't (base your answer on the point group for each).

b) For the *cis*-isomer, evaluate whether an electronic transition to each of the following excited states is CD-active or not: ^1A, ^1B. Determine the polarization for CD-active transitions.

(2) The two luminescence bands for $*Hg_2$ (335 nm) and $*Hg_3$ (485 nm) are shown in the handout distributed in class from *J. Phys. Chem.* **1977**, *68*, 5656-5666. Answer the following questions given that λ_{abs}=253.7 nm:

a) Calculate the Stokes' shift for each band.

b) Calculate the FWHM value for each band.

c) Comment on the magnitudes of the values calculated in parts a and b above in terms of excited-state distortion.

d) Justify the dissimilarity in the luminescence properties of mercury vapor versus those of typical organic compounds such as anthracene in the following aspects:

i. Lifetimes: μs for mercury vapor; ns for anthracene.

ii. Structureless emissions for mercury vapor; emissions showing resolved vibronic bands for anthracene.

iii. Phosphorescence mechanism may involve direct excitation to the triplet for mercury while it occurs exclusively through intersystem crossing for anthracene.

(3) Draw the electronic configuration for a neutral molecule whose ground singlet state has non-degenerate HOMO and LUMO after the following processes take place (ignore the spin state):

a) Nothing

b) One-electron oxidation

c) One-electron reduction

d) Lowest-energy absorption to form an exciton (*A)

e) One-electron oxidation of *A

f) One-electron reduction of *A

(4) For SO_2, determine the number of vibrational modes, draw them, and determine whether each is infrared-active.

(5)Use group theory to deduce the irreducible representations for the vibrational modes of the sulfate ion (SO_4^{2-}) and determine the number of IR and Raman bands.

(6) For carbon tetrachloride, the lowest-energy Raman-active vibrational mode occurs at 218 cm^{-1}. Calculate the following for this mode assuming that the 1064 nm line of a Nd/YAG laser was used in the Raman experiment:

(a) The absolute wavenumber and wavelength of the Stokes line.

(b) The absolute wavenumber and wavelength of the anti-Stokes line.

(c) The relative Raman intensity of the anti-Stoke/Stokes lines at 298 K.