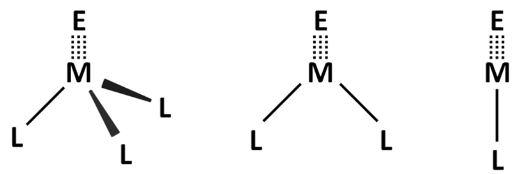
Problem Set 5

Ch 153a – Winter 2021

Due: 5 February, 2021

1) As discussed in class, the oxo wall for tetrahedral MO_4^{n-} and tetragonal (C_{4v}) OML_5 complexes lies between groups 8 and 9 in the transition series elements. Consider the metal-ligand multiply bonded complex geometries shown to the right. Assume that E atoms have two filled $p\pi$ and one filled $p\sigma$ donor orbital, and that each L ligand has one filled $p\sigma$ donor orbital.



C_{3v} C_{2v} $C_{\infty v}$

   a) For each of the three complex geometries, develop a molecular orbital bonding model using five metal *d* orbitals, and the ligand orbitals described above.

   b) For each of the three complex geometries, determine the location of the multiply-bonded-ligand wall. Explain your reasoning.

   c) For each of the three complex geometries, determine the M-E bond order for every d^n configuration from n = 0 to the maximum value of n that is consistent with your positioning of the wall.

2) The $Ru(bpy)_3^{2+}$ ion (bpy = 2,2′-bipyridine) has a luminescent MLCT excited state ($*Ru(bpy)_3^{2+}$) that decays with a time constant of about 600 ns in aqueous solution. The energy difference between the minimum of the ground-state potential energy surface and that of $*Ru(bpy)_3^{2+}$ is approximately 2.0 eV.

   The $Ru(bpy)_3^{2+}$ ion also can undergo one-electron oxidation and reduction reactions. The relevant reduction potentials are:

   $E°(Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+})$ = 1.25 V *vs.* NHE

   $E°(Ru(bpy)_3^{2+}/Ru(bpy)_3^{+})$ = −1.25 V *vs.* NHE

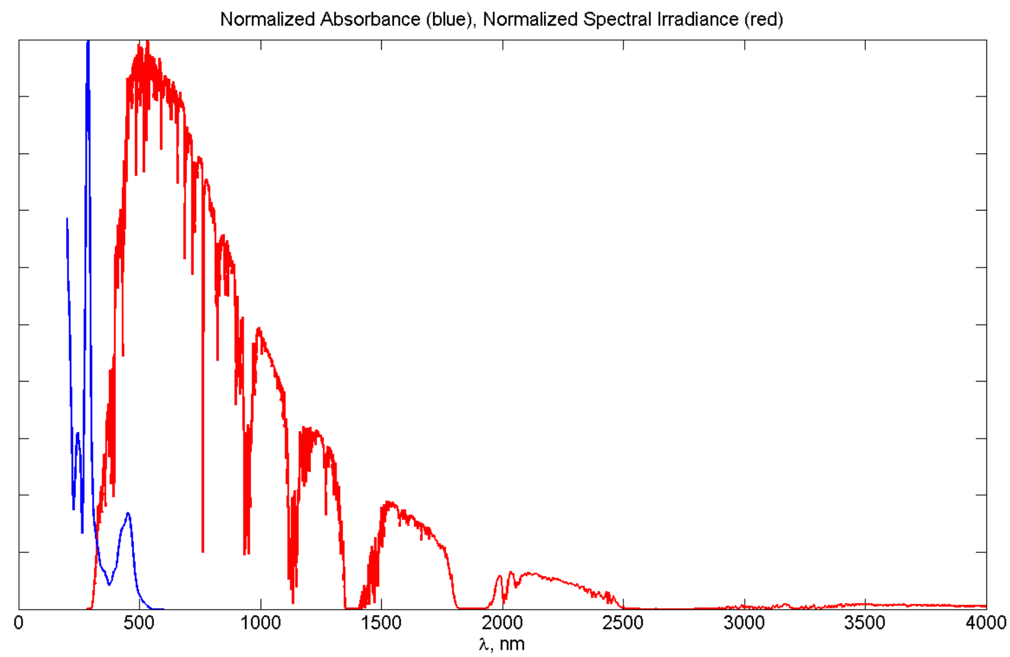
   a) What is the standard free-energy change for the reaction between $Ru(bpy)_3^{+}$ and $Ru(bpy)_3^{3+}$.

   b) Estimate the formal potential for the $*Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+}$ half reaction.

   c) Estimate the formal potential for the $Ru(bpy)_3^{3+} + e^- \rightarrow *Ru(bpy)_3^{2+}$ half reaction.

   d) Do you expect anything unusual to occur when $Ru(bpy)_3^{+}$ reacts with $Ru(bpy)_3^{3+}$?

3) The spectrum of solar energy striking the earth and the absorbance spectrum of $Ru(bpy)_3^{2+}$ are shown below. Excel spreadsheets of these two spectra are available on the Ch153a website. The units of spectral irradiance are: W m^{-2} nm^{-1}. The $Ru(bpy)_3^{2+}$ spectrum is given in molar absorbance units: M^{-1} cm^{-1}.



a) Make an overlay plot of the solar spectrum in which one plot has units of J s^{-1} m^{-2} nm^{-1}, and the other has units of photons s^{-1} m^{-2} nm^{-1}. Normalize both plots so that the peak in each spectrum is equal to one.

b) If photon energies of at least 1.23 eV are required to split water into H_2 and O_2, what fraction of the solar energy incident on the earth can be used to drive this reaction? What fraction of the photons incident on the earth can be used?

c) Assume that the solar flux is incident on a 10^{-4} M solution of $Ru(bpy)_3^{2+}$. The cross-sectional area of the solution is 1 cm^2 and the path length of the solution is 1 cm. What fraction of the energy incident on the solution is absorbed by the $Ru(bpy)_3^{2+}$ ions? What fraction of the incident photons are absorbed by the $Ru(bpy)_3^{2+}$ ions? For a sample of the same size, plot the fractions of incident energy and incident photons absorbed as functions of $Ru(bpy)_3^{2+}$ concentration between 10^{-4} and 10^{-3} M.