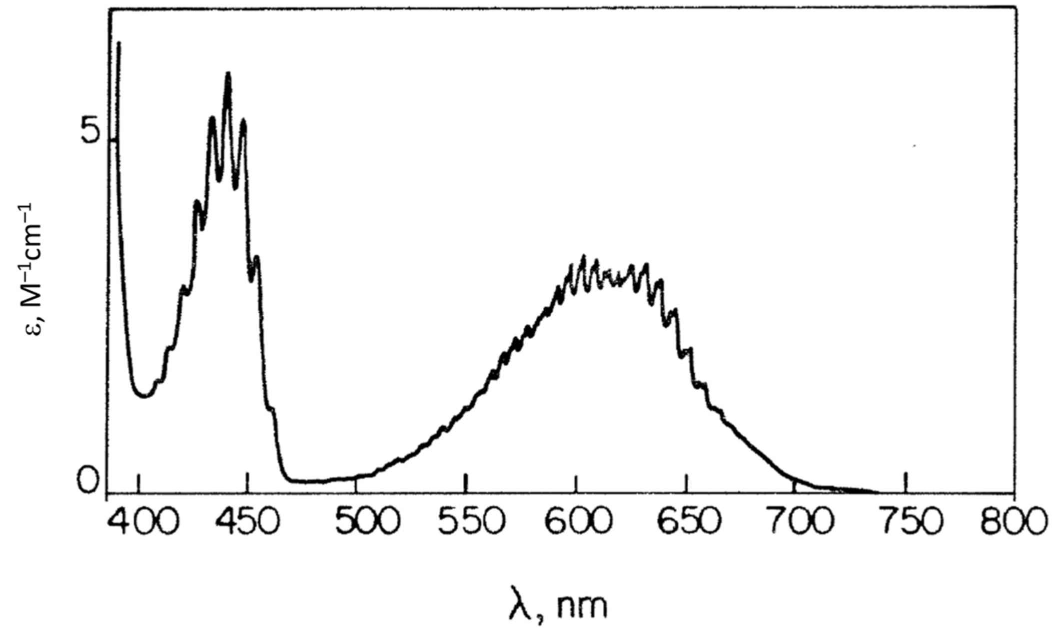
Problem Set 3
Ch 153a – Winter 2022
Due 21 January, 2022

1) The 4K single crystal polarized electronic absorption spectrum of the tetragonal molybdenyl ion in (Ph$_4$As)[MoOCl$_4$] is shown below.
   a) Construct an MO diagram for [MoOCl$_4$]$^-$ using the following orbitals: five Mo 4*d* orbitals, four Cl$^-$ σ orbitals, eight Cl$^-$ π orbitals and the oxo $\sigma + 2\pi$ orbitals. Give the term symbol for the ground electronic state.
   b) On the basis of your MO diagram, assign the two absorption bands with maxima at $\sim$640 nm and $\sim$430 nm to specific electronic transitions (give the electronic configurations and term symbols for both excited states).
2) The [MoOCl$_4$]$^-$ ion has 12 normal modes of vibration with the following symmetries and frequencies (ν refers to a stretching mode; π and δ refer to deformation or bending modes):

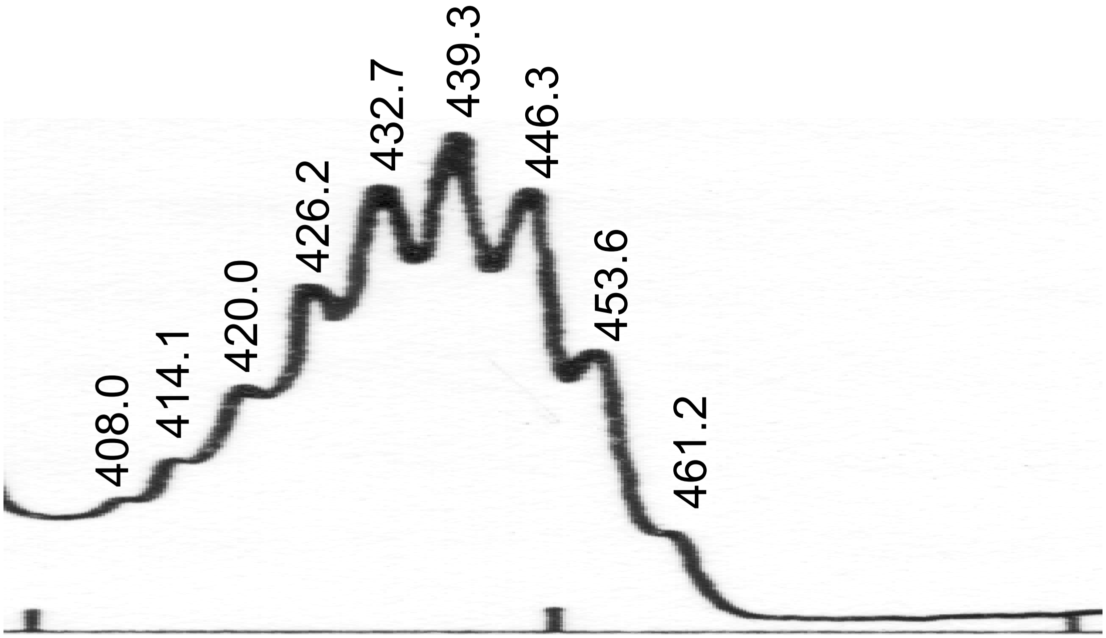
	vibration	cm^{-1}
a$_1$:	ν(Mo-O)	1008
a$_1$:	ν(Mo-Cl)	354
a$_1$:	π(Mo-Cl)	184
b$_1$:	ν(Mo-Cl)	327
b$_1$:	π(Mo-Cl)	158
b$_2$:	δ(Mo-Cl)	167
e:	ν(Mo-Cl)	364
e:	δ(O-Mo-Cl)	240
e:	δ(Cl-Mo-Cl)	114



MoOCl$_4^-$ Vibronic Peak Maxima	
λ /nm	λ /nm
652.0	461.2
645.2	453.6
638.4	446.3
631.8	439.3
625.5	432.7
619.3	426.2
615.6	420.0
609.5	414.1
603.5	408.0
597.5	
591.7	
586.3	
583.3	
577.7	
572.3	
567.0	
562.0	
557.0	

a) On the basis of your assignment of the lower energy electronic absorption band, in which vibrational mode(s) would you expect to see fine structure? Can you explain the fine structure that appears in the lower energy band?

b) An enlarged view of the second band appears on the following page. Examine the vibrational fine structure in this band and assign it to a ground-state vibrational mode. Discuss whether a distortion in this mode is consistent with the assignment of the electronic transition.



c) Perform a Franck-Condon analysis of the vibrational fine structure of the higher energy absorption band. What S-value give the best fit to the observed spectrum? If the force constant for the distorting mode is 1.91 mdyne/Å, give the magnitude of the distortion in the normal mode (ΔQ). Use group theory to define the normal mode in terms of bond stretching coordinates to estimate the magnitude of the distortion in the individual bonds.

3) Construct a diagram illustrating the dependence of electrode potentials (*vs.* NHE) on pH (Pourbaix diagram) for the following redox couples:

   a. $O_2 + e^- + H^+ \rightarrow HO_2^\bullet$

   b. $HO_2^\bullet + e^- + H^+ \rightarrow H_2O_2$

   c. $H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$

   d. $HO^\bullet + e^- + H^+ \rightarrow H_2O$

   e. $O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$

   f. $H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

   g. $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

   In constructing your diagram, use the following standard potentials:

$O_2 + e^- \rightarrow O_2^{\bullet -}$	$E^\circ = -0.35$ V *vs.* NHE
$HO_2^\bullet + e^- \rightarrow HO_2^-$	$E^\circ = 0.76$ V *vs.* NHE
$H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$	$E^\circ = 0.80$ V *vs.* NHE
$HO^\bullet + e^- + H^+ \rightarrow H_2O$	$E^\circ = 2.72$ V *vs.* NHE;

and the following pK_a values:

$HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+$ pK_a = 4.8

$H_2O_2 \rightarrow HO_2^- + H^+$ pK_a = 11.62

$HO^{\bullet} \rightarrow O^{\bullet-} + H^+$ pK_a = 11.7

$H_2O \rightarrow HO^- + H^+$ pK_a = 14.0

The standard state for potentials is 25 °C, concentrations of 1 molal (1 *m*), partial gas pressures of 100 kPa, and the activity of water is taken to be unity. For the purposes of your diagram, assume the following conditions:

$pO_2 = 100$ kPa

$[HO_2^{\bullet}] + [O_2^{\bullet-}] = 1\ m$

$[H_2O_2] + [HO_2^-] = 1\ m$

$[HO^{\bullet}] + [O^{\bullet-}] = 1\ m$

Your plot should span the range from pH 0 to pH 14.

4) Using the data from your Pourbaix diagram give the electrode potentials for the redox couples *a-g* at the following pH values:

   a. pH 0 b. pH 7 c. pH 14

5) Using the data from your Pourbaix diagram determine the standard free energy change for the following reaction:

$$2HO^{\bullet} \rightleftharpoons H_2O_2$$