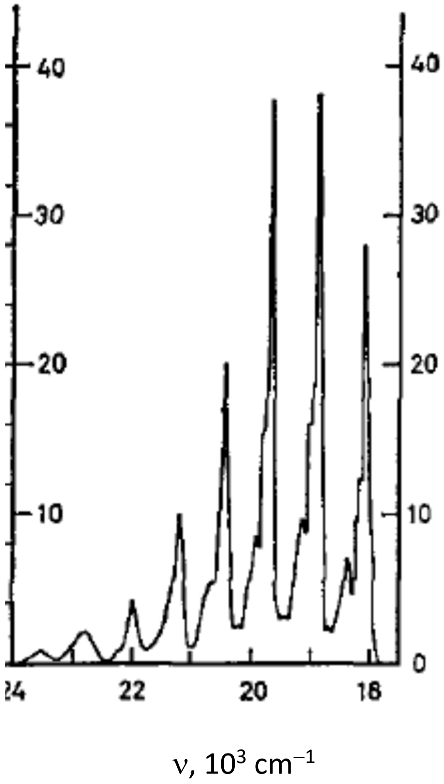
Problem Set 4
Ch 153a – Winter 2021
Due: 29 January, 2021

1) The 4K single crystal polarized absorption spectrum of $KMnO_4$ doped into a $KClO_4$ lattice and a table of peak positions are shown below.

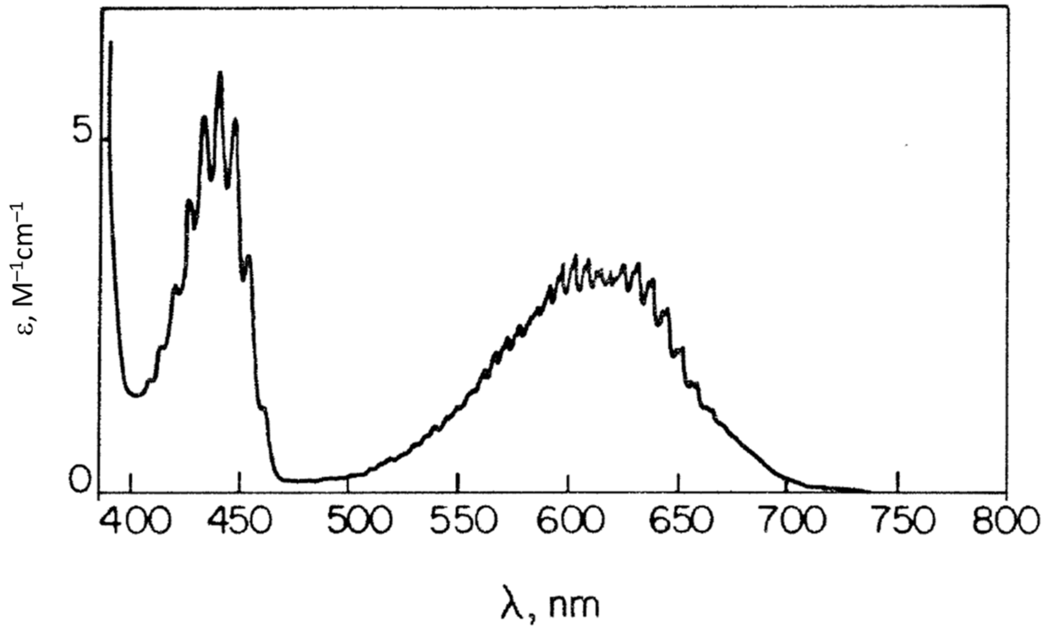
Peak Position (cm^{-1})	Relative Intensity
18,072	74
18,842	100
19,602	96
20,380	59
21,145	27
21,915	10



   a) Perform a Franck-Condon analysis of the vibrational fine structure in the absorption band.
   b) What S_{HR}-value gives the best fit to the observed spectrum?
   c) If the force constant for the distorting mode is 5.91 mdyne/Å, give the magnitude of the distortion in the normal mode (ΔQ).
   d) 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.

2) The 4K single crystal polarized electronic absorption spectrum of the tetragonal molybdenyl ion in $(Ph_4As)[MoOCl_4]$ is shown on the following page.
   a) Draw the molecular structure of the $[MoOCl_4]^-$ ion, determine the oxidation state of the Mo center and its d-electron count.
   b) 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.
   c) On the basis of your MO diagram, assign the two absorption bands with maxima at ~640 nm and ~430 nm to specific electronic transitions (give the electronic configurations and state designations for both excited states).

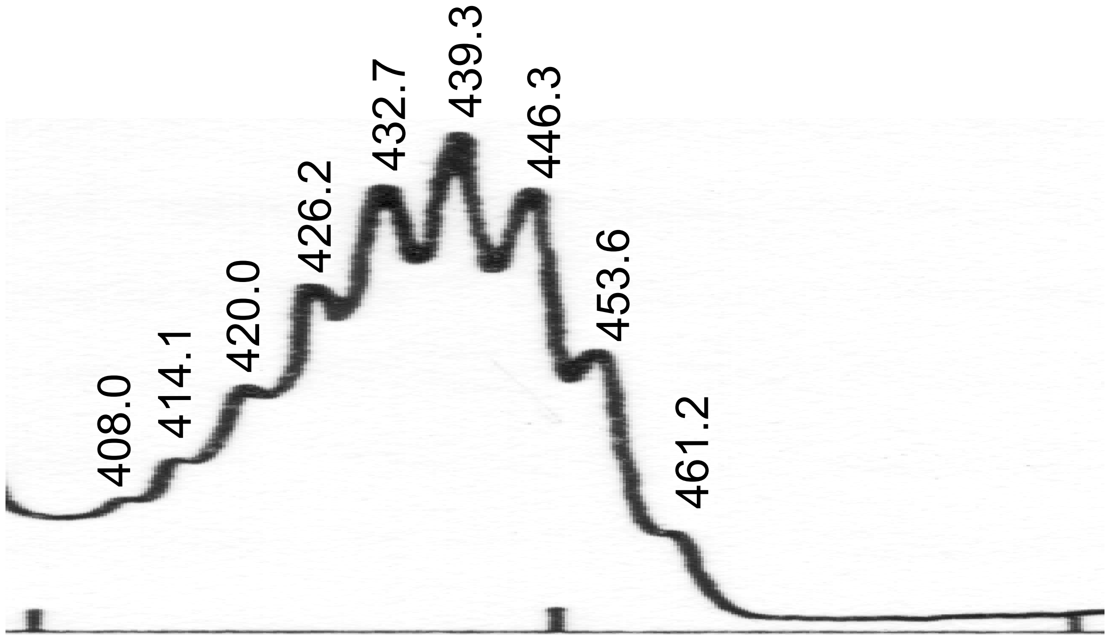
3) The $[MoOCl_4]^-$ ion has 12 normal modes of vibration with the following symmetries and frequencies (ν refers to a stretching mode; π and δ refer to deformation or bending modes):



vibration	cm^{-1}
a1: ν(Mo-O)	1008
a1: ν(Mo-Cl)	354
a1: π(Mo-Cl)	184
b1: ν(Mo-Cl)	327
b1: π(Mo-Cl)	158
b2: δ(Mo-Cl)	167
e: ν(Mo-Cl)	364
e: δ(O-Mo-Cl)	240
e: δ(Cl-Mo-Cl)	114

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.

4) Low-spin d^6 metal hexacarbonyl compounds exhibit two intense ($\varepsilon > 10^4$ M^{-1} cm^{-1}) absorption bands in the ultraviolet region of the spectrum; peak positions are listed in the following table.

Compound	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$	$V(CO)_6^-$	$Mn(CO)_6^+$	$Re(CO)_6^+$
$\nu_{1,max}$ (cm^{-1})	35,700	34,600	34,650	28,400	44,500	44,500
$\nu_{2,max}$ (cm^{-1})	43,600	42,800	43,750	37,550	49,900	51,200

a) Construct an MO diagram for d^6 metal hexacarbonyl compounds assuming O_h symmetry using: five metal *nd* orbitals; one metal (*n*+1)*s* orbital; three (*n*+1)*p* orbitals; six CO σ orbitals; twelve CO π orbitals; and twelve CO π^* orbitals. Give the electronic configuration and term symbol for the ground electronic state.

b) Propose assignments for the two intense ultraviolet absorption bands in each compound. Identify the one-electron transitions giving rise to the bands and the term symbols for the resulting excited states.