

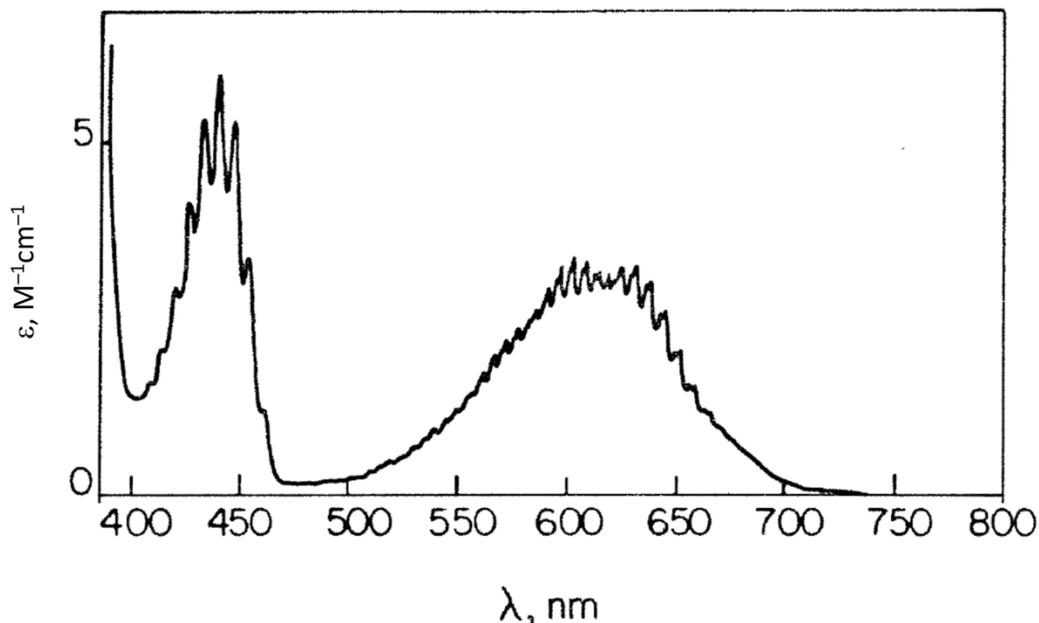
Problem Set 4

Ch153a – Winter 2024

Due: 29 January 2024

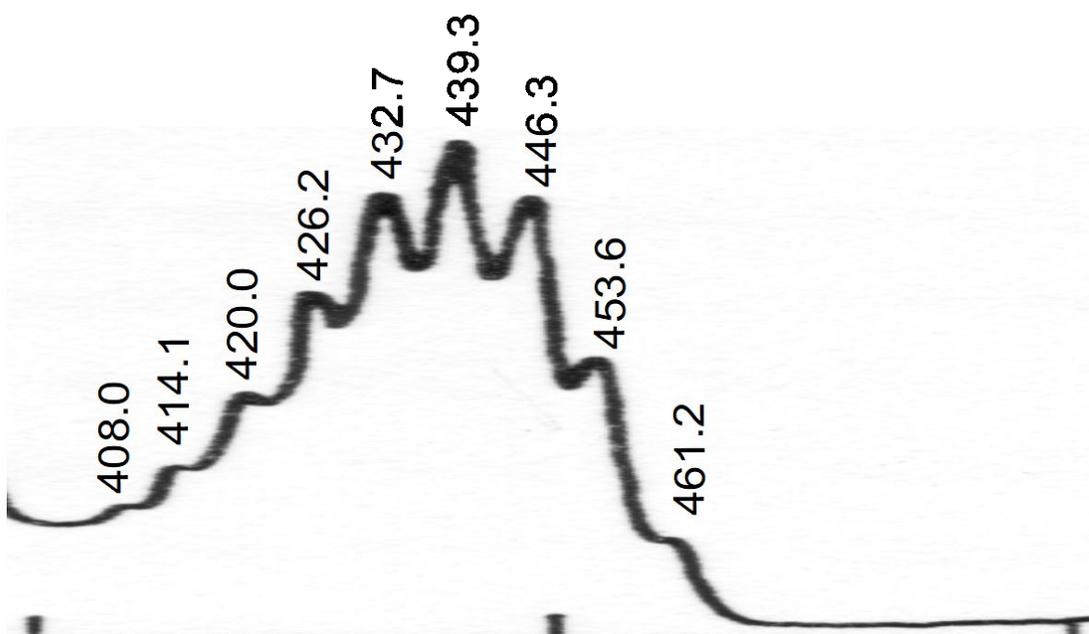
- The 4K single crystal polarized electronic absorption spectrum of the tetragonal molybdenyl ion in $(\text{Ph}_4\text{As})[\text{MoOCl}_4]$ is shown below.
 - Construct an MO diagram for $[\text{MoOCl}_4]^-$ using the following orbitals: five Mo 4d orbitals, four Cl^- σ orbitals, eight Cl^- π orbitals and the oxo $\sigma + 2\pi$ orbitals. Give the term symbol for the ground electronic state.
 - 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 term symbols for both excited states).
- The $[\text{MoOCl}_4]^-$ 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 :	$\nu(\text{Mo-O})$	1008
a_1 :	$\nu(\text{Mo-Cl})$	354
a_1 :	$\pi(\text{Mo-Cl})$	184
b_1 :	$\nu(\text{Mo-Cl})$	327
b_1 :	$\pi(\text{Mo-Cl})$	158
b_2 :	$\delta(\text{Mo-Cl})$	167
e:	$\nu(\text{Mo-Cl})$	364
e:	$\delta(\text{O-Mo-Cl})$	240
e:	$\delta(\text{Cl-Mo-Cl})$	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	

- 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?
- 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/\AA , 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. a. Construct an MO diagram for $\text{Cr}(\text{CO})_6$, using the five 3d orbitals, one 4s orbital, three 4p orbitals, a set of 6 $\sigma(\text{CO})$ orbitals, a set of 12 $\pi(\text{CO})$ orbitals, and a set of 12 $\pi^*(\text{CO})$ orbitals (assume O_h symmetry).
- b. Identify the states and associated one-electron transitions for all of the ligand-field excitations in $\text{Cr}(\text{CO})_6$.
- c. Identify the states and associated one-electron transitions for all of the allowed MLCT excitations in $\text{Cr}(\text{CO})_6$.
- d. The d^6 hexacarbonyl complexes of V, Cr, and Mn exhibit the intense absorption bands listed in the table below. Propose assignments for these features. Explain your reasoning.

	$\tilde{\nu}_1, \text{ cm}^{-1} (\epsilon, \text{ M}^{-1}\text{cm}^{-1})$	$\tilde{\nu}_2, \text{ cm}^{-1} (\epsilon, \text{ M}^{-1}\text{cm}^{-1})$
$\text{V}(\text{CO})_6^-$	28,400 (6,240)	37,550 (60,900)
$\text{Cr}(\text{CO})_6$	35,700 (13,100)	43,600 (85,100)
$\text{Mn}(\text{CO})_6^+$	44,500 (16,000)	49,900 (27,000)