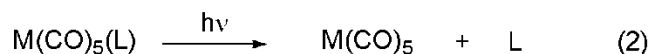


## Problem Set 4

Ch153a – Winter 2025

Due: 7 February 2025

- (10 points) Consider the  $C_{4v}$  complex  $W(CO)_5L$ , where L is an uncharged ligand.
  - Draw the molecular structure of the complex with L aligned along the Cartesian z axis.
  - Construct an MO diagram for  $W(CO)_5L$  using the following orbitals: 5 W 5d, one W 6s, three W 6p, five CO  $\sigma$ , ten CO  $\pi^*$ , and one L  $\sigma$ . Give the electronic configuration and term symbol for the ground electronic state.
  - Identify the spin-allowed ligand-field electronic transitions; determine term symbols for the excited states; and predict the relative energy ordering for these states.
  - The UV-visible absorption spectrum of  $W(CO)_5(\text{pyridine})$  features bands with peaks at 440 ( $\epsilon = 627 \text{ M}^{-1}\text{cm}^{-1}$ ) and 380 nm ( $\epsilon = 6904 \text{ M}^{-1}\text{cm}^{-1}$ ). Propose electronic transition assignments for these bands.
  - UV-visible irradiation of  $W(CO)_5(\text{pyridine})$  results either in loss of CO (reaction 1) or loss of L (reaction 2). The quantum yields for these two processes have been found to be wavelength dependent, as shown in the table on the following page. Using the MO diagram derived above, suggest an interpretation for the observed photochemistry.
  - The product of reaction 1 reacts with excess L to form  $M(CO)_4(L)_2$ . Based on the interpretation you gave in part (e), do you expect the *cis* or *trans* isomer to form preferentially? Explain.



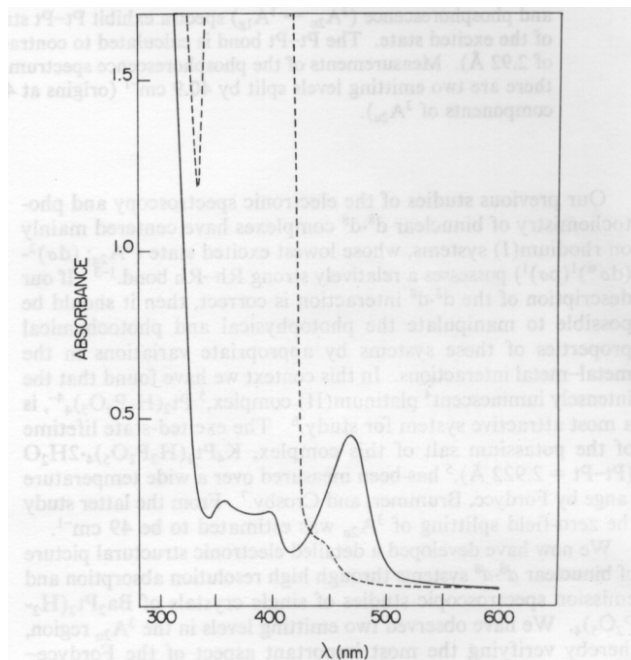
**Table: Wavelength Dependence for Processes 1 and 2 for  $W(CO)_5(\text{pyridine})$**

Irradiation, $\lambda$ /nm	$\Phi_{\text{eq 1}}$	$\Phi_{\text{eq 2}}$
436	0.00	0.63
366	0.01	0.50
313	0.03	0.38
254	~0.04	0.34

- (5 points) A persistent question in complexes of metals coordinated to Lewis-acidic ligands is the relative  $\pi$ -accepting strength of CO and  $\text{PF}_3$  ligands. Explore the literature to find a series of complexes and associated *experimental* data that provide insight(s) into this question (computational studies, as always, will not suffice). On the basis of this literature, explain why you believe CO or  $\text{PF}_3$  is the better  $\pi$ -acceptor.

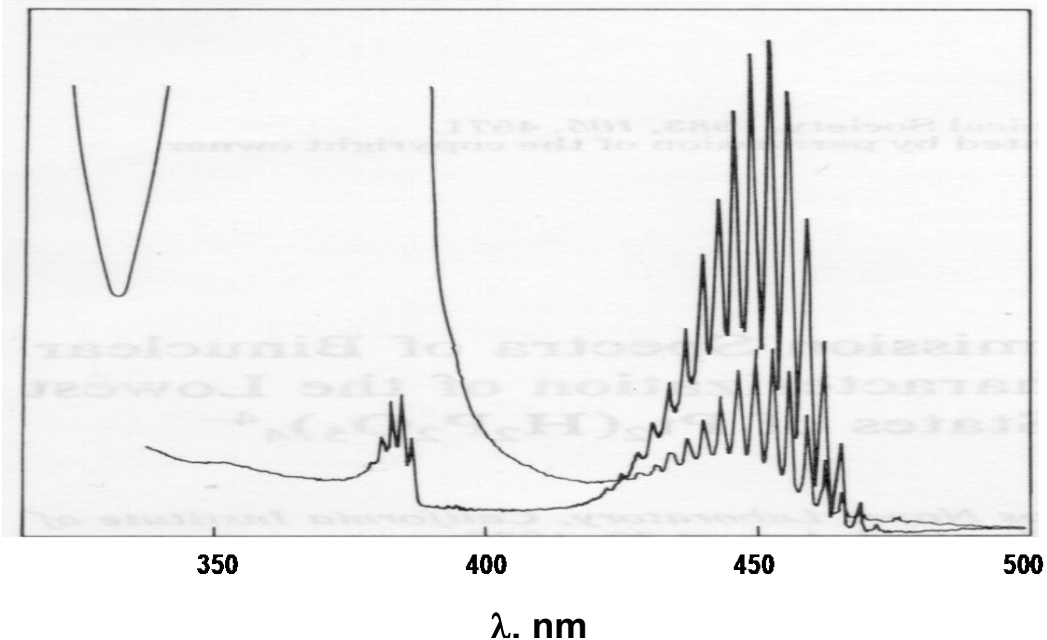
3. (10 points) The room-temperature absorption spectrum of a single crystal of  $\text{K}_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4 \cdot 2\text{H}_2\text{O}$  ( $\text{K}_4\text{Pt-POP}$ ) is shown to the right.  $\text{Pt-POP}^{4-}$  also is luminescent, displaying intense green phosphorescence with a maximum near 500 nm.

At cryogenic temperatures, the absorption spectrum of the  $\text{Ba}^{2+}$  salt of  $\text{Pt-POP}^{4-}$  develops rich vibrational fine structure in the lowest energy absorption band (below). The vibrational fine structure is associated with an excited-state distortion along the Pt-Pt stretching coordinate. The vibronic peak positions for the lowest energy absorption band are given in the table on the following page.



**Figure 2.** Absorption spectrum of a single crystal of  $\text{K}_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4 \cdot 2\text{H}_2\text{O}$  at 300 K. Solid line: electric dipole perpendicular to the crystallographic  $c$  axis. Dashed line: parallel to the  $c$  axis and the Pt-Pt axis.

**Figure 1.** Absorption spectrum along two extinction directions of the same face of a single crystal of  $\text{Ba}_2\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4$  at 5 K. The orientation of the metal-metal direction is not known in this salt.

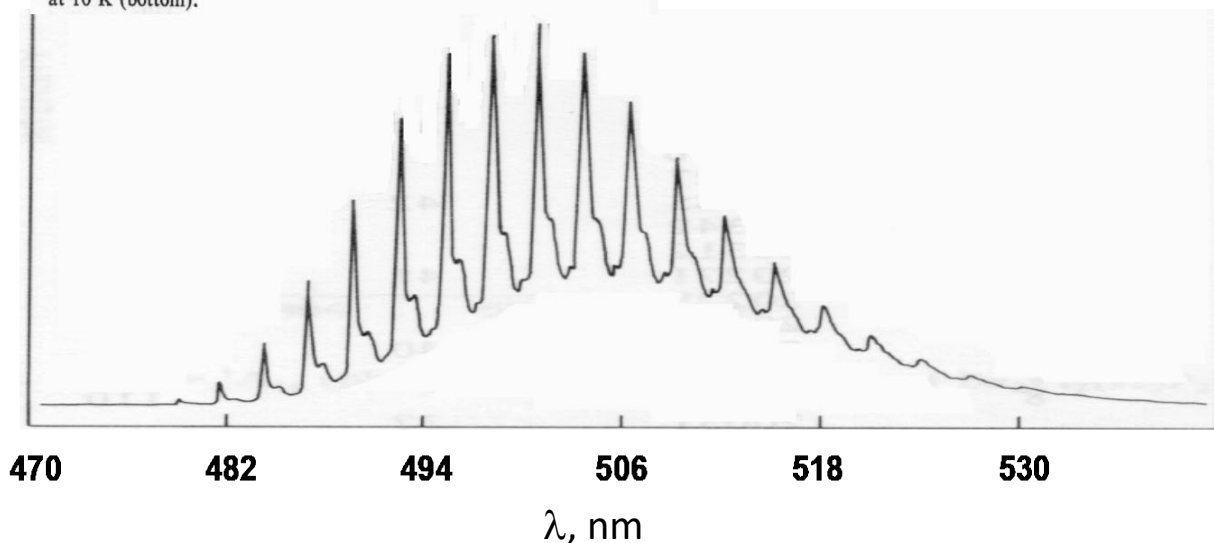


- What is the vibrational frequency of the distorting mode in the excited state?
- What value of the Huang-Rhys parameter ( $S_{HR}$ ) gives the best fit to the lowest energy absorption band?
- If the force constant for the Pt-Pt stretching mode is  $1.0 \text{ mdyne/\AA}$ , what is the magnitude of the distortion along the Pt-Pt coordinate in the excited state?

**Ba<sub>2</sub>Pt-POP Absorption**

v	$\lambda$ , nm
0	476.0
1	472.5
2	469.1
3	465.7
4	462.4
5	459.2
6	456.1
7	452.9
8	449.8
9	446.7
10	443.5
11	440.4
12	437.4
13	434.4
14	431.5
15	428.7
16	425.8
17	423.2
18	420.3
19	417.5

Figure 5.  ${}^3A_{2u} \rightarrow {}^1A_{1g}$  (phosphorescence) spectrum of  $Ba_2Pt_2(H_2P_2O_5)_4$  at 10 K (bottom).



The phosphorescence spectrum of crystalline  $Ba_2Pt$ -POP at 10 K also displays rich fine structure in the Pt-Pt vibrational mode (above). The vibronic peak positions for the phosphorescence band are given in the table on the following page.

- d. What is the vibrational frequency of the distorting mode in the ground state?
- e. What value of the Huang-Rhys parameter ( $S_{HR}$ ) gives the best fit to the phosphorescence band?
- f. On the basis of your fit to the phosphorescence spectrum, what is the magnitude of the distortion along the Pt-Pt coordinate in the excited state? How does this value compare to that extracted from the fit to the absorption spectrum?
- g. The Pt-Pt distance in the ground state of  $Pt\text{-POP}^{4-}$  is 2.92 Å. On the basis of the structured absorption and phosphorescence band profiles, what do you estimate for the Pt-Pt distance in the excited state?

**$Ba_2Pt$ -POP  
Phosphorescence**

v	$\lambda, \text{nm}$
0	476.5
1	479.0
2	481.6
3	484.2
4	486.8
5	489.5
6	492.3
7	495.1
8	497.8
9	500.6
10	503.3
11	506.1
12	509.1
13	512.0
14	515.0
15	517.9
16	520.9
17	523.9
18	526.9
19	530.1
20	533.3
21	536.5