

Problem Set 7

Ch 153a – Winter 2021

Due: 19 February, 2021

- 1) Consider a binuclear metal complex constructed from two square-planar ML_4 fragments where the L ligands are σ -donors. There are two limiting conformations in the resulting M_2L_8 complex: in one the ligands are eclipsed and in the other they are staggered.

 - a) Draw the two conformations of the binuclear metal complex and assign each to a symmetry point group.
 - b) Construct an MO diagram for the *eclipsed* conformation using the following orbitals: five M d orbitals and four L σ orbitals. Assume that M-L σ -bonding is quite strong.
 - c) Assume that ML_4 has a d^4 electron configuration, that each ligand L contributes two σ electrons, and that the corresponding M_2L_8 complex is in the eclipsed conformation.
 - i. Give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.
 - ii. Identify the spin-allowed electronic transitions involving the d -orbitals, determine the term symbols for the excited states.
 - iii. Predict the lowest-energy electric-dipole-allowed transition. Also, predict the polarization of light that will induce the transition.
- 2) The absorption spectrum of $Mn_2(CO)_{10}$ exhibits an intense absorption band at $30,000\text{ cm}^{-1}$, and a lower-energy feature at $27,000\text{ cm}^{-1}$. The $30,000\text{-cm}^{-1}$ absorption band is polarized parallel to the Mn-Mn axis, and the $27,000\text{ cm}^{-1}$ band is polarized perpendicular to this axis. Propose assignments for these bands based on an MO diagram for binuclear M_2L_{10} d^7 - d^7 complexes. For simplicity, assume that M_2L_{10} is in the eclipsed conformation.

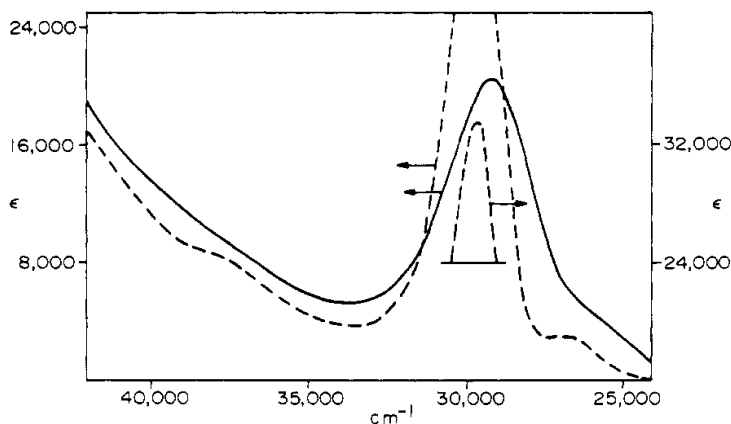


Figure 2. Electronic spectra of $Mn_2(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

- 3) 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. Pt-POP^{4-} also is luminescent, displaying intense green phosphorescence with a maximum near 500 nm.

At cryogenic temperatures, the absorption spectrum of the Ba^{2+} salt of 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.

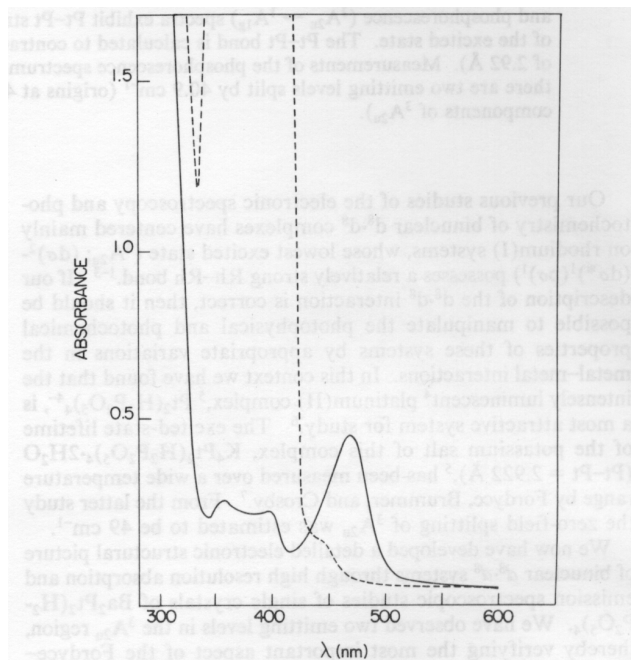
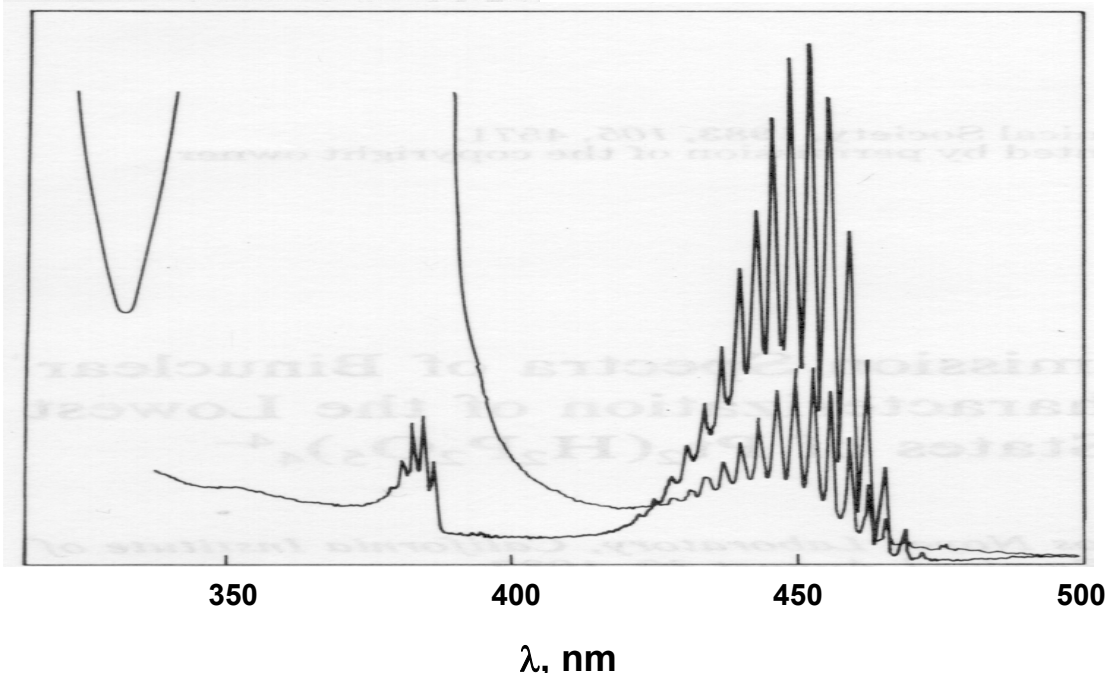


Figure 2. Absorption spectrum of a single crystal of $\text{K}_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4 \cdot 2\text{H}_2\text{O}$ at 300 K. Solid line: electric dipole perpendicular to the crystallographic c axis. Dashed line: parallel to the c axis and the Pt-Pt axis.

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.



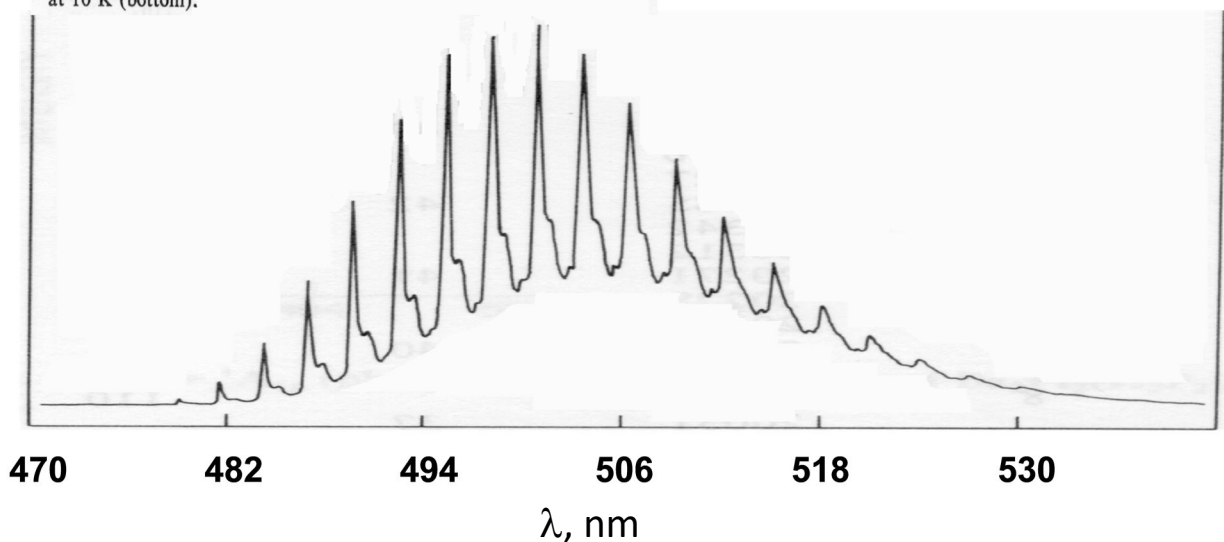
- What is the vibrational frequency of the distorting mode in the excited state?
- What value of the Huang-Rhys parameter (S_{HR}) gives the best fit to the lowest energy absorption band?
- If the force constant for the Pt-Pt stretching mode is $1.0 \text{ mdyne}/\text{\AA}$, what is the magnitude of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

Ba₂Pt-POP Absorption

ν	λ , 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

The phosphorescence spectrum of crystalline Ba₂Pt-POP at 10 K also displays rich fine structure in the Pt-Pt vibrational mode (below). The vibronic peak positions for the phosphorescence band are given in the table on the following page.

Figure 5. $^3A_{2u} \rightarrow ^1A_{1g}$ (phosphorescence) spectrum of Ba₂Pt₂(H₂P₂O₅)₄ at 10 K (bottom).



- 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 $Pt-POP^{4-}$ 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?

Ba₂Pt-POP
Phosphorescence

v	λ , 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