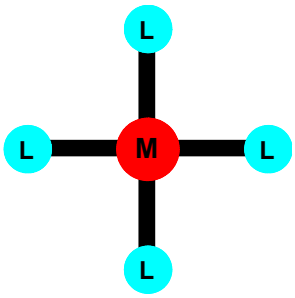
Problem Set 5
Ch 153a – Winter 2022
Due: 4 February, 2022

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 cm^{-1}, and a lower-energy feature at 27,000 cm^{-1}. The 30,000-cm^{-1} absorption band is polarized parallel to the Mn-Mn axis, and the 27,000 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.

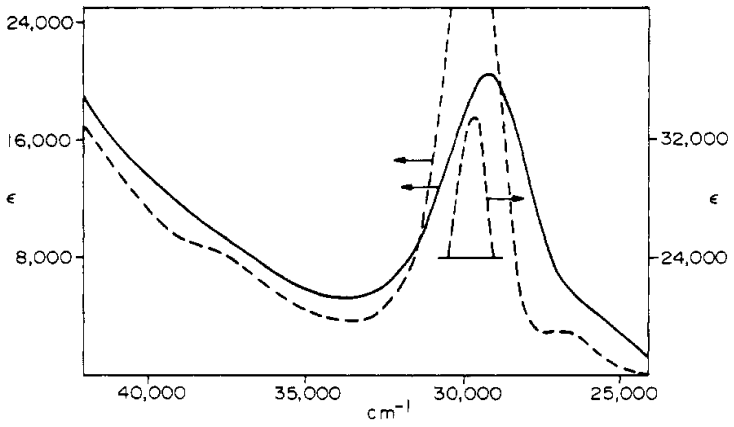


Figure 2. Electronic spectra of $Mn_2(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

3) The room-temperature absorption spectrum of a single crystal of $K_4Pt_2(H_2P_2O_5)_4 \bullet 2H_2O$ (K_4Pt-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.

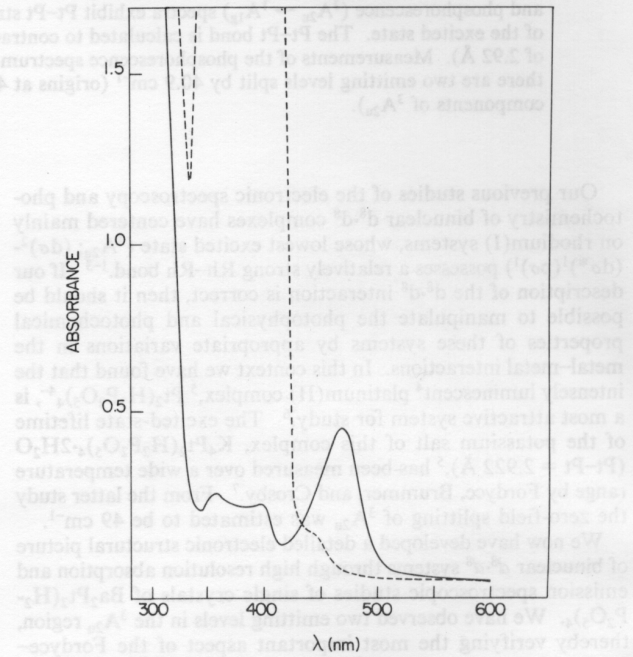
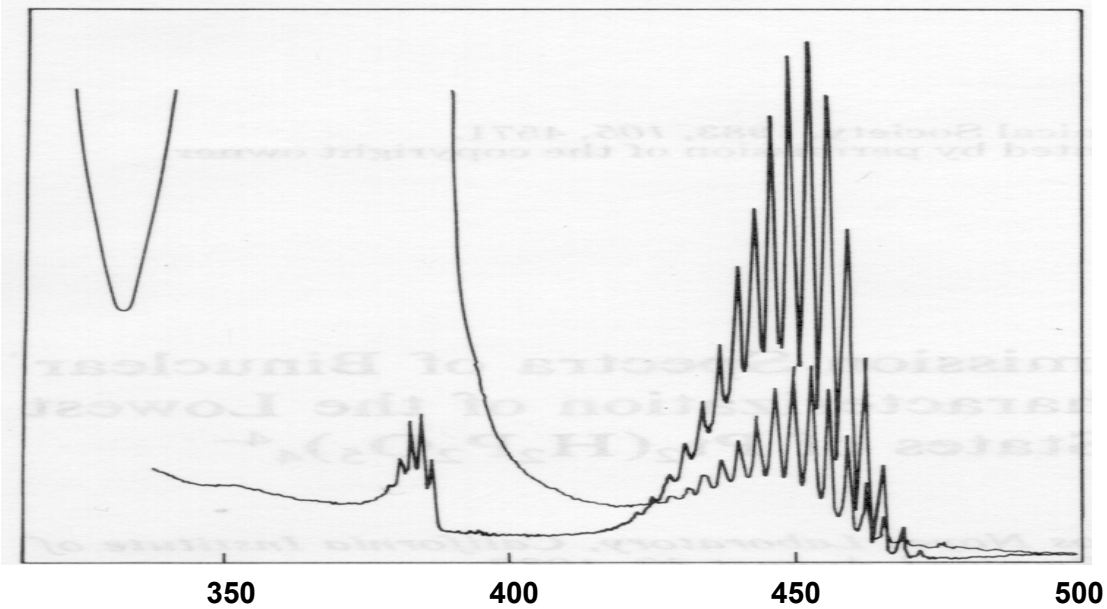


Figure 2. Absorption spectrum of a single crystal of $K_4Pt_2(H_2P_2O_5)_4 \cdot 2H_2O$ at 300 K. Solid line: electric dipole perpendicular to the crystallographic *c* axis. Dashed line: parallel to the *c* axis and the Pt–Pt axis.

Figure 1. Absorption spectrum along two extinction directions of the same face of a single crystal of $Ba_2Pt_2(H_2P_2O_5)_4$ at 5 K. The orientation of the metal–metal direction is not known in this salt.



a) What is the vibrational frequency of the distorting mode in the excited state?

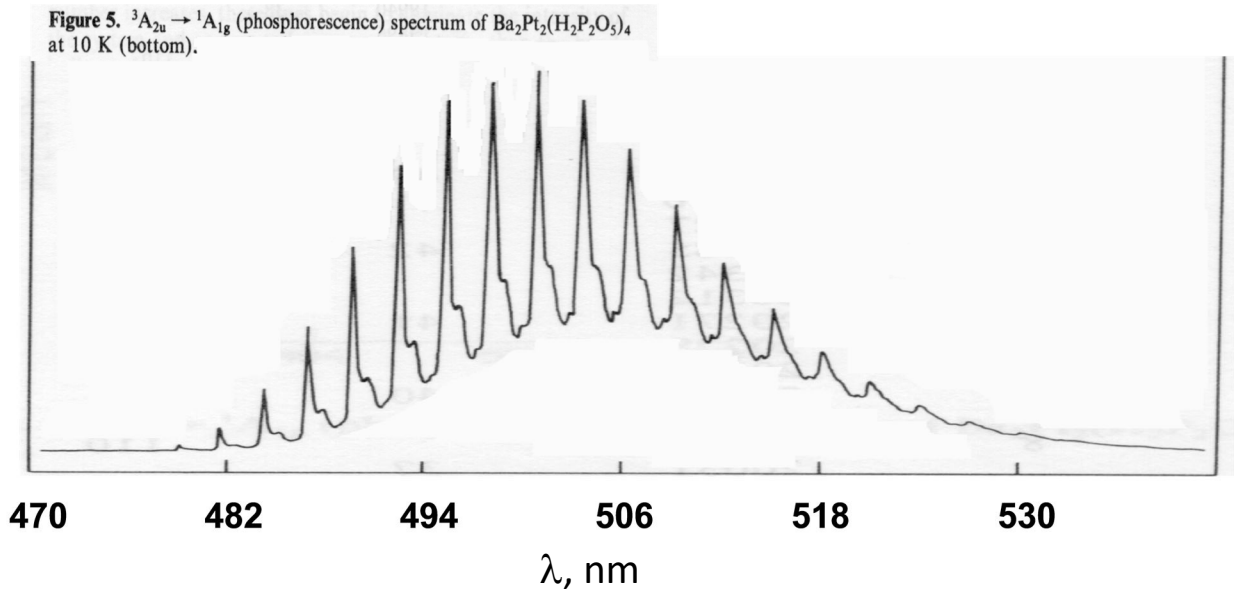
b) What value of the Huang-Rhys parameter (S_{HR}) gives the best fit to the lowest energy absorption band?

c) If the force constant for the Pt-Pt stretching mode is 1.0 mdyne/Å, what is the magnitude of the distortion along the Pt-Pt coordinate in the excited state?

Ba_2Pt-POP Absorption

v	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 Ba_2Pt-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.



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?

Ba_2Pt-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