

Ch153a

Winter 2020

Due Monday, 9 March, 2020, 5:00 PM

Problem Set 9

1. 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 (bottom of the page). 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.

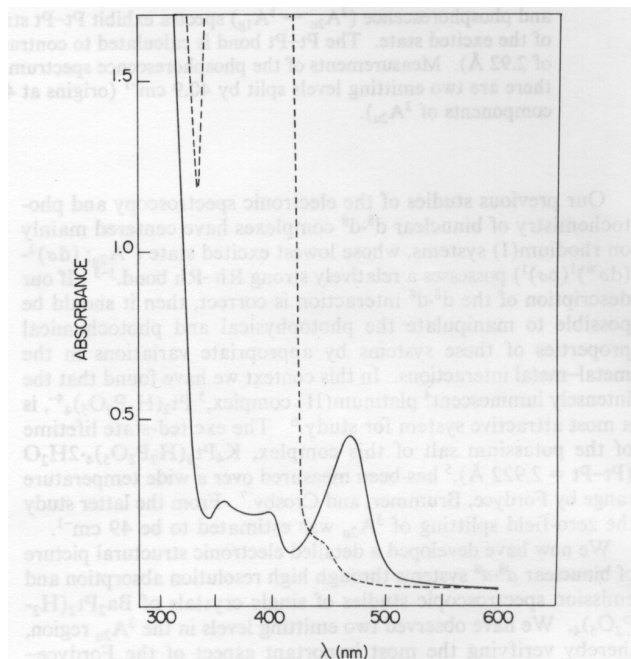
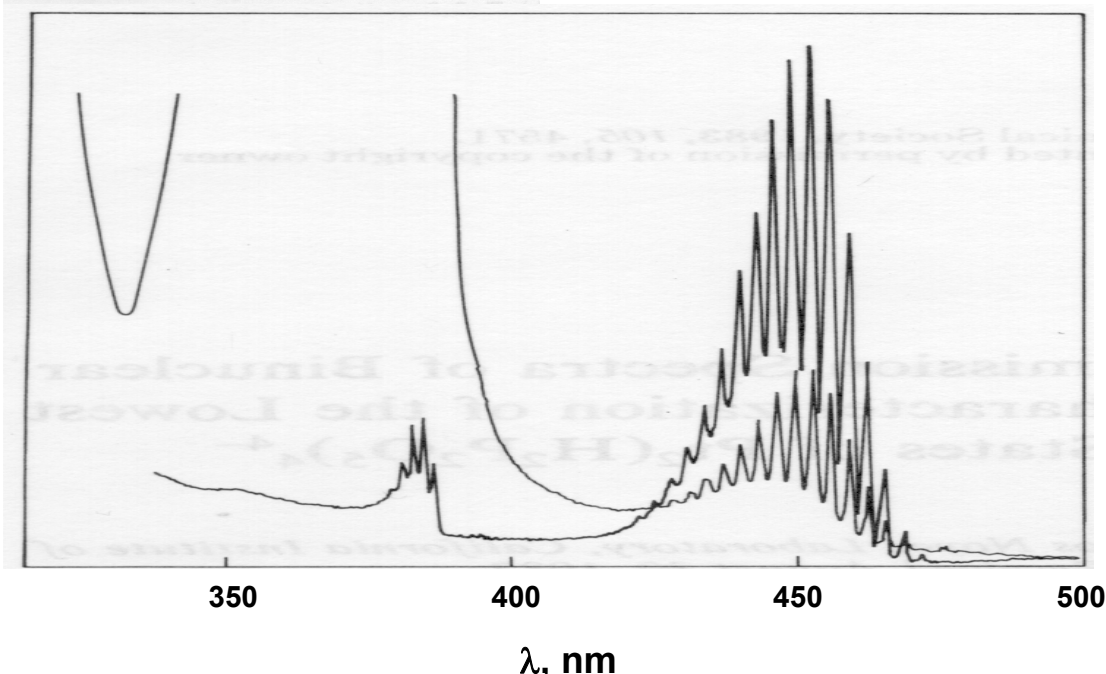


Figure 2. Absorption spectrum of a single crystal of $\text{K}_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4 \cdot 2\text{H}_2\text{O}$ at 300 K. Solid line: electric dipole perpendicular to the crystallographic c axis. Dashed line: parallel to the c axis and the Pt-Pt axis.

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.



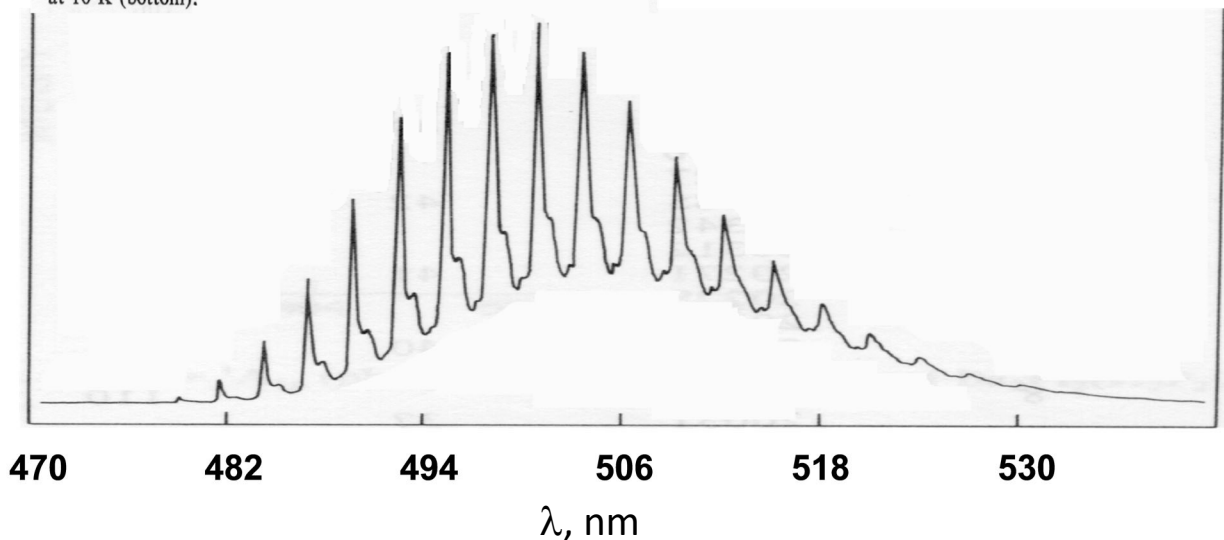
- What is the vibrational frequency of the distorting mode in the excited state?
- What value of the Huang-Rhys parameter (S_{HR}) gives the best fit to the lowest energy absorption band?
- If the force constant for the Pt-Pt stretching mode is 1.0 mdyne/Å, what is the magnitude of the distortion along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

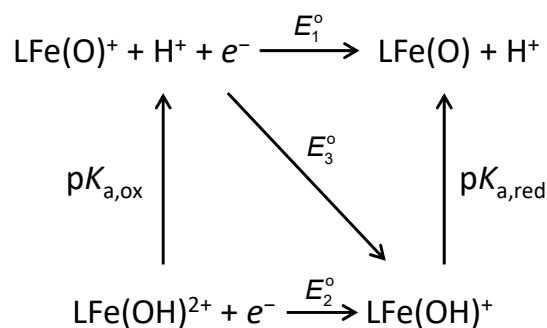


- d. What is the vibrational frequency of the distorting mode in the ground state?
- e. What value of the Huang-Rhys parameter (S_{HR}) gives the best fit to the phosphorescence band?
- f. On the basis of your fit to the phosphorescence spectrum, what is the magnitude of the distortion along the Pt-Pt 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

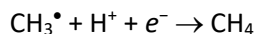
v	λ , nm
0	476.5
1	479.0
2	481.6
3	484.2
4	486.8
5	489.5
6	492.3
7	495.1
8	497.8
9	500.6
10	503.3
11	506.1
12	509.1
13	512.0
14	515.0
15	517.9
16	520.9
17	523.9
18	526.9
19	530.1
20	533.3
21	536.5

2. Consider an iron-oxo complex $\text{LFe}(\text{O})^+$ (where L is a dianionic ligand) that undergoes electron and proton transfer reactions as described by the diagram on the right. Assume that the potentials are defined with respect to the reference electrode potential E_{ref}° .



- a. Express $\Delta E^{\circ} \equiv E_1^{\circ} - E_2^{\circ}$ as a function of $\text{p}K_{a,red}$ and $\text{p}K_{a,ox}$.
- b. Express E_3° as a function of E_1° and $\text{p}K_{a,red}$.
- c. Express E_3° as a function of E_2° and $\text{p}K_{a,ox}$.

3. The pK_a values for alkanes are generally assumed to be ~ 50 .
- a. Use the value obtained for $E^\circ(\text{CH}_3^{\bullet}/^-)$ in Problem Set 8 to estimate the standard potential for the following half-reaction:



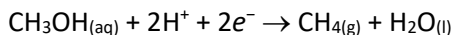
- b. For the $\text{LFe}(\text{O})^+$ complex of problem 2, assume that $E_1^\circ = 1.0 \text{ V}$ vs NHE, and $pK_{a,\text{red}} = 10$. Calculate the value of E_3° .
- c. On the basis of your answers to (a) and (b), would the following reaction be spontaneous?
- $$\text{LFe}(\text{O})^+ + \text{CH}_4 \rightarrow \text{LFe}(\text{OH})^+ + \text{CH}_3^{\bullet}$$
- d. If the reaction in part c is not spontaneous, what would the C-H BDE have to be in order for the following reaction to be spontaneous (assume the alkane $pK_a = 50$):



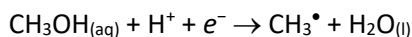
4. The standard free energies of formation of $\text{CH}_3\text{OH}_{(\text{aq})}$, $\text{H}_{2(\text{g})}$, $\text{CH}_{4(\text{g})}$ and $\text{H}_2\text{O}_{(\text{l})}$ are given in the Table.

	$\Delta G_f^\circ \text{ (kcal mol}^{-1}\text{)}$
$\text{CH}_3\text{OH}_{(\text{aq})}$	-41.7
$\text{H}_{2(\text{g})}$	0
$\text{CH}_{4(\text{g})}$	-12.1
$\text{H}_2\text{O}_{(\text{l})}$	-56.7

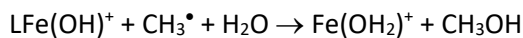
- a. Use the data in the Table to define the standard reduction potential for the following half reaction:



- b. Use your results from 3a and 4a to estimate the standard reduction potential for the following half reaction:



- c. Consider the following reaction:



In order for this reaction to be spontaneous, what standard potential is required for the following half-reaction:

