

Problem Set 5

Ch153a – Winter 2026

Due: 13 February 2026

1. (10 points) The strong-field energy expressions for states associated with the $(t_{2g})^6$, $(t_{2g})^5(e_g)^1$, $(t_{2g})^3(e_g)^2$, and $(t_{2g})^3(e_g)^3$ configurations are given below.

$$(t_{2g})^6$$

$${}^1A_{1g}: E = -12\Delta_o/5 + 15A - 30B + 15C$$

$$(t_{2g})^5(e_g)^1$$

$${}^3T_{1g}: E = -7\Delta_o/5 + 15A - 30B + 12C$$

$${}^3T_{2g}: E = -7\Delta_o/5 + 15A - 22B + 12C$$

$${}^1T_{1g}: E = -7\Delta_o/5 + 15A - 30B + 14C$$

$${}^1T_{2g}: E = -7\Delta_o/5 + 15A - 14B + 14C$$

$$(t_{2g})^4(e_g)^2$$

$${}^5T_{2g}: E = -2\Delta_o/5 + 15A - 35B + 7C$$

$$(t_{2g})^3(e_g)^3$$

$${}^5E_g: E = 3\Delta_o/5 + 15A - 35B + 7C$$

Turner and Schultz examined the spectra of $\text{Fe}(\text{tacn})_2^{2+}$ (*Inorg. Chem.* **2001**, 40, 5296-5298) and found absorption bands indicative of both the high-spin and low-spin species.

- Determine Δ_o for high-spin and low-spin states of $\text{Fe}(\text{tacn})_2^{2+}$ from the spectra in the Turner/Schultz paper (assume $C/B = 4$).
- Explain the result in terms of the d^6 Tanabe-Sugano diagram on the following page.
- Estimate the energy of the low-spin \rightarrow high-spin absorption maximum in the low-spin complex, and that of the high-spin \rightarrow low-spin absorption maximum in the high-spin complex.

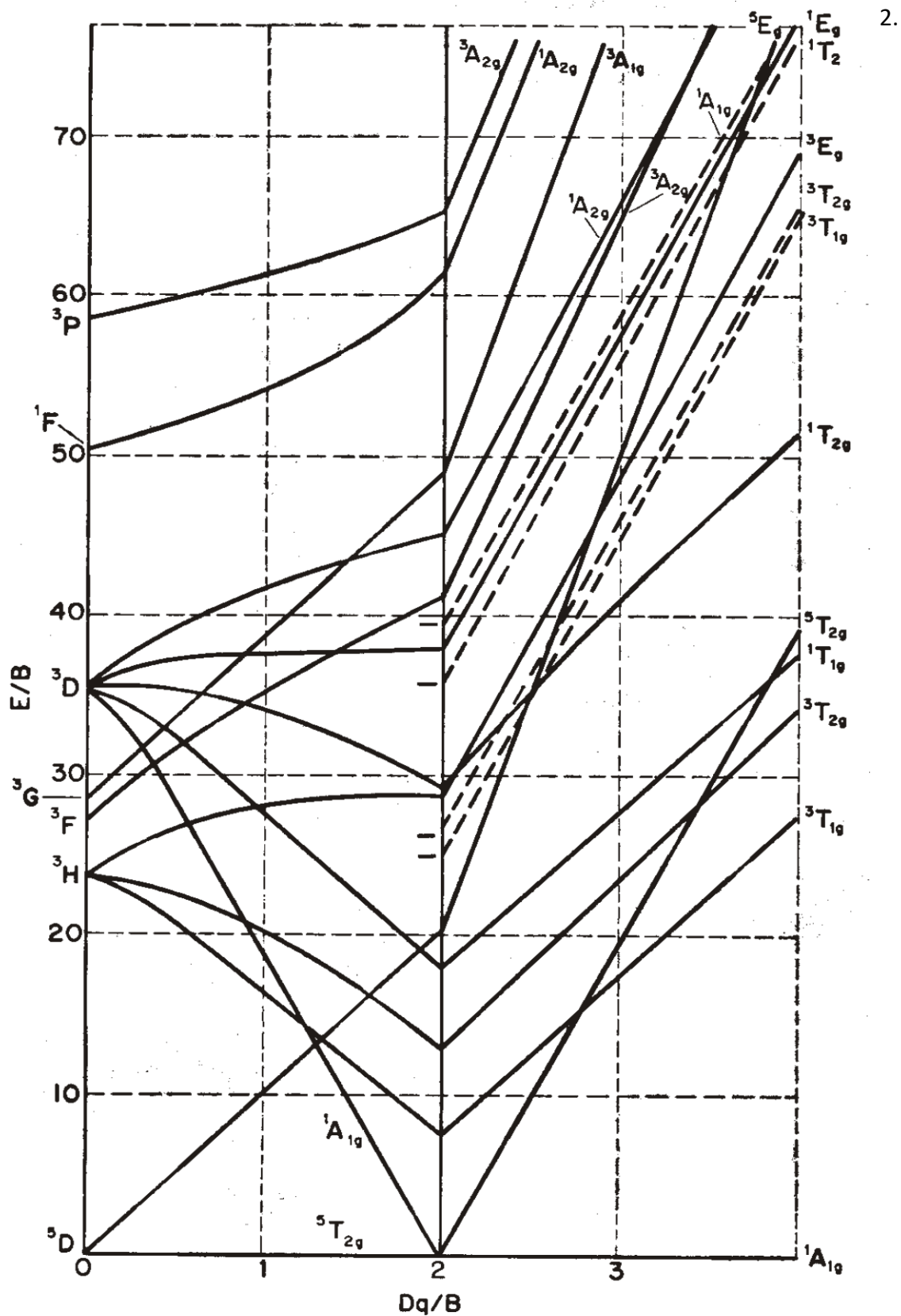


FIG. 7.13 The energy diagram for d^6 .

2. (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 σ , ten CO π^* , and one L σ . 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 below. 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.

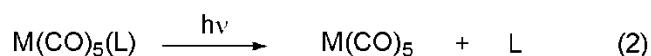


Table: Wavelength Dependence for Processes 1 and 2 for $W(CO)_5(\text{pyridine})$

Irradiation, λ /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

3. (20 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. 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.

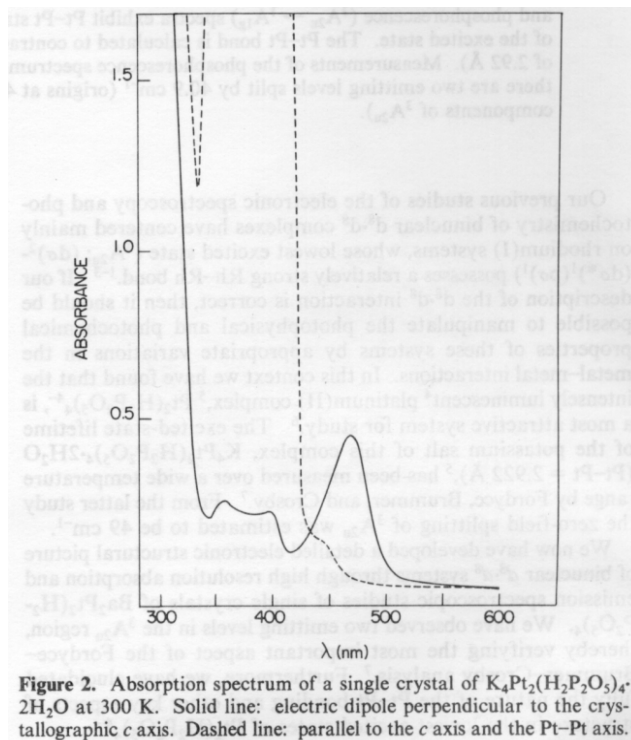
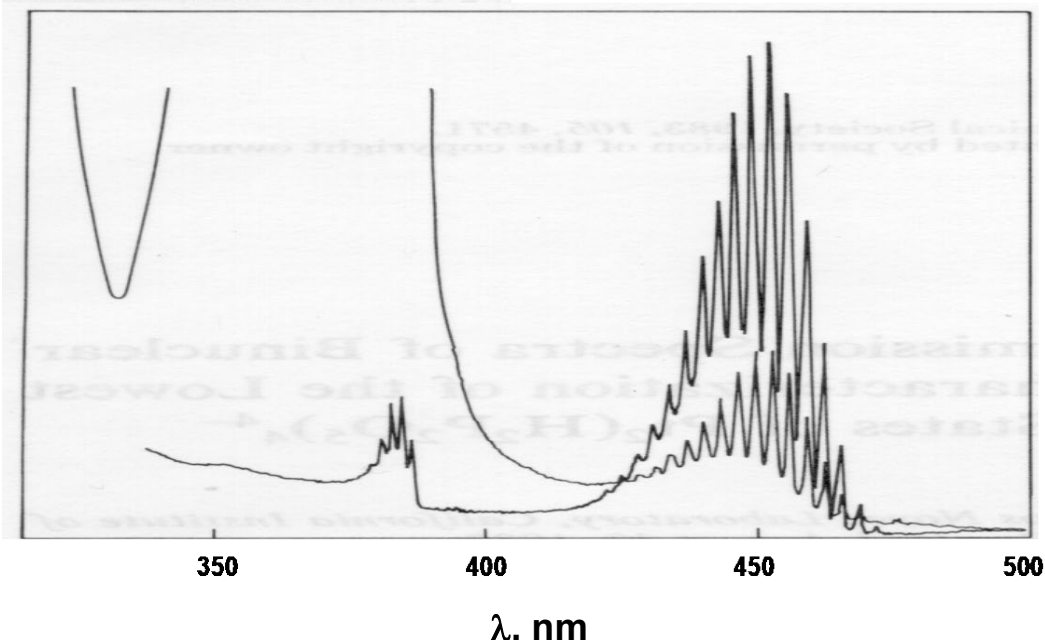


Figure 1. Absorption spectrum along two extinction directions of the same face of a single crystal of $\text{Ba}_2\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4$ at 5 K. The orientation of the metal-metal direction is not known in this salt.

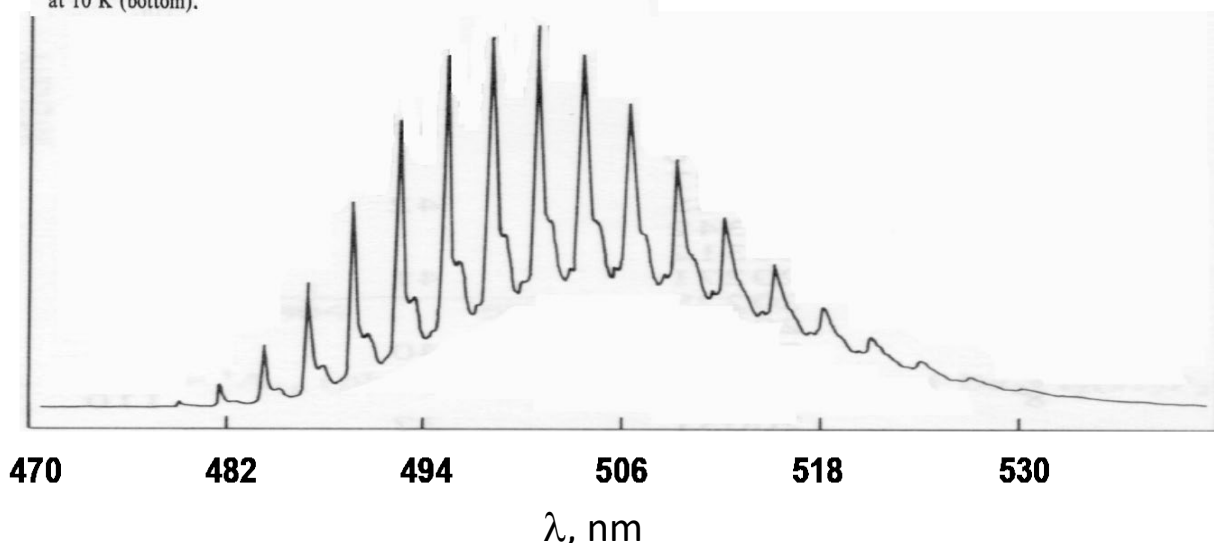


- What is the vibrational frequency of the distorting mode in the excited state?
- What value of the Huang-Rhys parameter (S_{HR}) gives the best fit to the lowest energy absorption band?
- If the force constant for the Pt-Pt stretching mode is 1.0 mdyne/\AA , what is the magnitude of the distortion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

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

ν	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