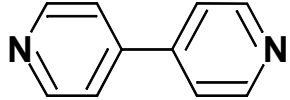
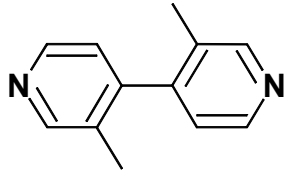
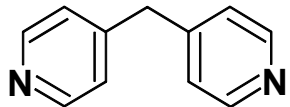


Chemistry 153a
Winter 2019
Due 1 March, 2019

Problem Set 8

1. Intervalence charge transfer absorption bands have been observed in a large number of complexes of the type: $[(\text{NH}_3)_5\text{RuL-LRu}(\text{NH}_3)_5]^{5+}$; data for three of these are given in the following table.

L-L	$r, \text{Å}$	Abs _{max} , nm	$\epsilon_{\text{max}}, \text{M}^{-1}\text{cm}^{-1}$
	11.3	1030	920
	11.3	890	165
	10.5	810	30

For each complex, use the results from problem set 7 to determine the value of H_{AB} and λ , and predict the full-width at half-maximum of the intervalence band. Offer explanations for any trends that you observe in these parameters.

2. The intervalence charge transfer absorption bands of six complexes of the type $[(\text{CN})_5\text{M}_a\text{CNM}_b(\text{NH}_3)_5]^{1-}$ ($M_a = \text{Fe, Ru, Os}$; $M_b = \text{Ru, Os}$) are shown in the figure on the following page. The M_a - M_b distances in these ions are about 5 Å.
- a) Stark spectroscopy can be used to estimate the change in dipole moment ($\Delta\mu_{12}$) associated with an electronic absorption band (Table). If it is assumed that a single electron is associated with the transition, then it is possible to use $\Delta\mu_{12}$ to calculate the effective (adiabatic) charge transfer distance (R_{12}). Calculate the effective charge transfer distances for the six ions. How do these compare to the M_a - M_b ; offer an explanation for any differences.

Complex	$ \Delta\mu_{12} \text{ (D)}$	$\mu_{12} \text{ (eÅ)}$
1	11.5	0.77
2	13.4	0.63
3	16.8	0.42
4	12.5	0.44
5	13.4	0.42
6	14.9	0.40

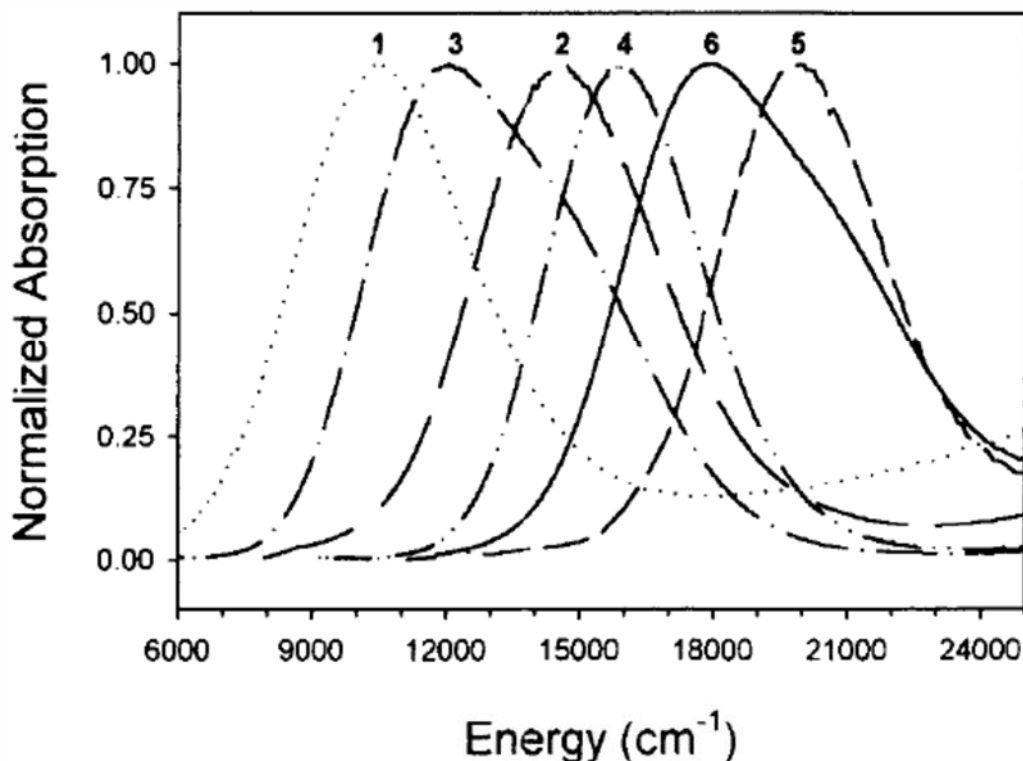


Figure 1. Room-temperature absorption spectra (normalized) showing MM'CT bands of compounds **1**–**6** in unbuffered water as solvent. **1** = $(\text{CN})_5\text{Fe}^{\text{II}}\text{CNRu}^{\text{III}}(\text{NH}_3)_5^{1-}$, **2** = $(\text{CN})_5\text{Ru}^{\text{II}}\text{CNRu}^{\text{III}}(\text{NH}_3)_5^{1-}$, **3** = $(\text{CN})_5\text{Os}^{\text{II}}\text{CNRu}^{\text{III}}(\text{NH}_3)_5^{1-}$, **4** = $(\text{CN})_5\text{Fe}^{\text{II}}\text{CNOs}^{\text{III}}(\text{NH}_3)_5^{1-}$, **5** = $(\text{CN})_5\text{Ru}^{\text{II}}\text{CNOs}^{\text{III}}(\text{NH}_3)_5^{1-}$, **6** = $(\text{CN})_5\text{Os}^{\text{II}}\text{CNOs}^{\text{III}}(\text{NH}_3)_5^{1-}$.

- b) The diabatic charge transfer distance is the electron-transfer distance that would be obtained under the hypothetical condition of zero electronic coupling ($H_{ab} = 0$). This distance can be estimated from $\Delta\mu_{12}$ and the transition moment (μ_{12}) of the absorption band according to the following equation:

$$\Delta\mu_{ab} = eR_{ab} = \left[(\Delta\mu_{12})^2 + 4(\mu_{12})^2 \right]^{\frac{1}{2}}$$

Calculate the diabatic charge transfer distances for the six ions.

- c) The degree of delocalization in a mixed valence complex can be described by the coefficient c_b^2 : a value of 0 corresponds to complete localization; a value of 0.5 corresponds to full delocalization. This quantity can be determined from the following expression:

$$c_b^2 = \frac{1}{2} \left[1 - \left(\frac{\Delta\mu_{12}^2}{\Delta\mu_{12}^2 + 4\mu_{12}^2} \right)^{\frac{1}{2}} \right] = \frac{1}{2} \left[1 - \frac{\Delta\mu_{12}}{\Delta\mu_{ab}} \right]$$

Determine the values of c_b^2 for the six ions.

d) The value of H_{ab} can be estimated from the following equation: $H_{ab} = \frac{\mu_{12} \tilde{\nu}_{\max}}{eR_{ab}}$

Estimate values of H_{ab} for the six ions.

- e) Estimate values of the reorganization energies from the room temperature absorption spectra of the six ions.
- f) Estimate values of ΔE for the six ions. Compare these values to literature values for the reduction potentials of suitable model complexes.

3. Wolfram's red salt, $[\text{Pt}^{\text{II}}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{Pt}^{\text{IV}}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$, consists of linear chains of halogen bridged alternating Pt(II) and Pt(IV) subunits. Wolfram's red salt has the following properties: the Cl atom is displaced 0.44 Å from the midpoint between the two Pt atoms; an intense absorption band is observed at ~480 nm, polarized parallel to the Pt-Pt axis; resonance Raman spectra with excitation into this band exhibit strong enhancement of a Pt-Cl stretching mode; a luminescence band maximizing at 1080 nm. Spectra are reproduced below and on the following page.

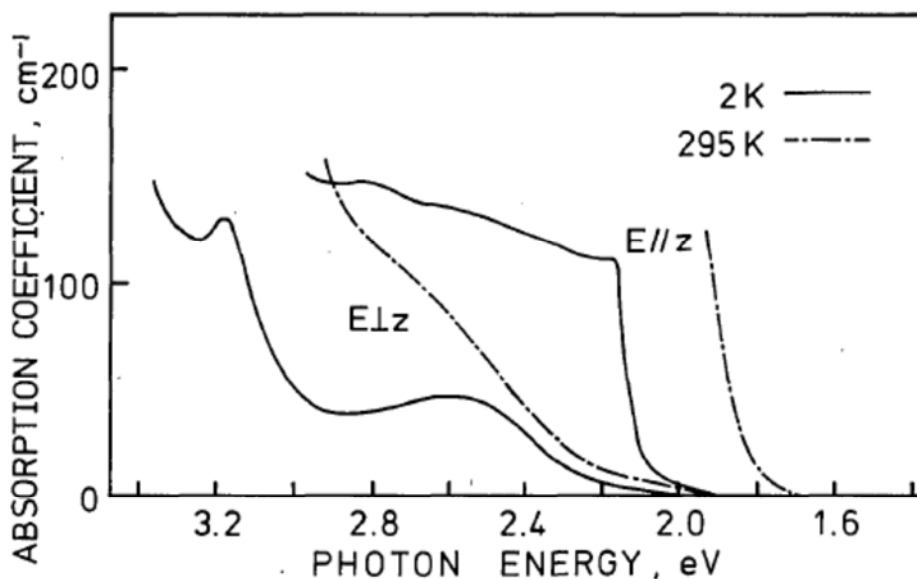


Fig. 2. Absorption spectra at RT and 2 K for $E//z$ ($E//(001)$) and $E_{\perp}z$ ($E//(110)$).

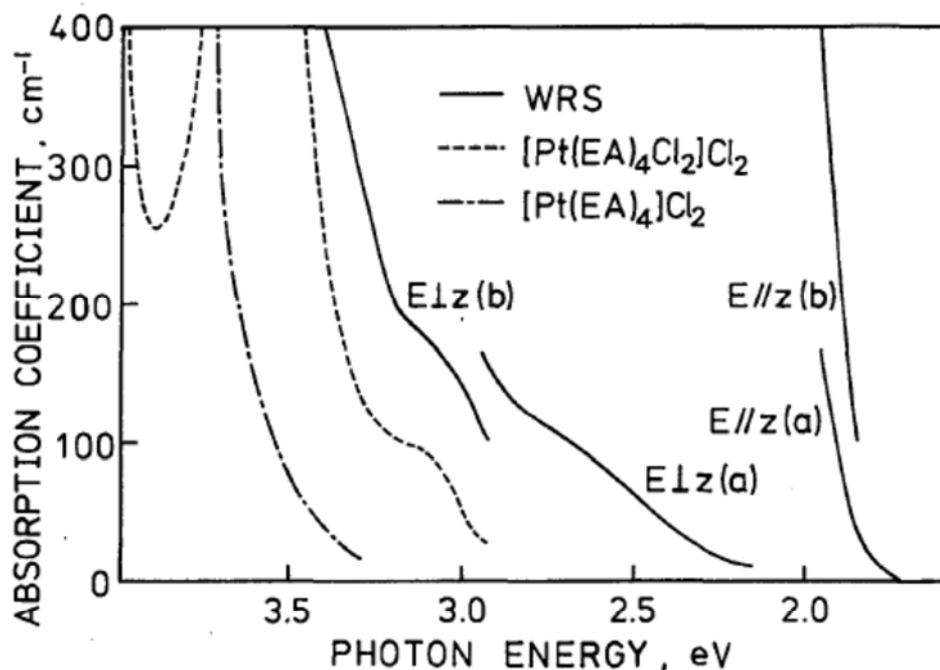


Fig. 11. Absorption spectra of Wolfram's red salt (— (a) and (b)) and its constituent radicals [Pt(EA)₄Cl₂]Cl₂ (----) and [Pt(EA)₄]Cl₂ (-·-), respectively, at RT. Curves (a) are the same spectra

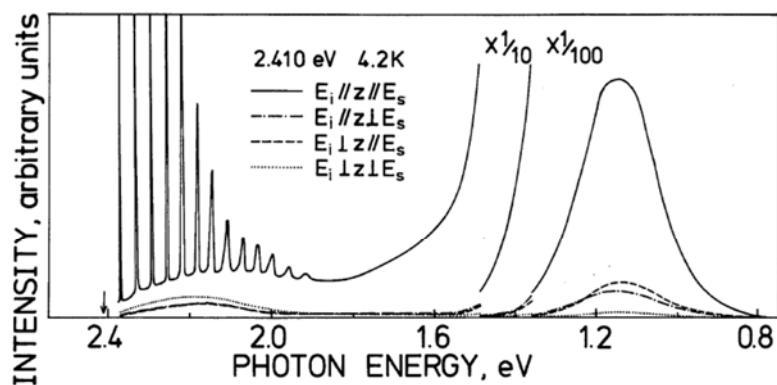


Fig. 5. Resonance Raman and luminescence spectra for 2.410 eV excitation (indicated by an arrow) at 4.2 K for E_i//z//E_s, E_i//z⊥E_s, E_i⊥z//E_s and E_i⊥z⊥E_s.

Develop a molecular orbital diagram for Wolfram's red salt and propose an assignment for the 480 nm absorption band. What structural distortion do you expect to accompany population of this excited state?

4. The Ti(III) oxidation state is rare in terrestrial minerals due to the comparatively highly oxidizing environment on Earth. Trivalent titanium does occur in extraterrestrial materials; one example is a titanium pyroxene found in the Allende meteorite. The empirical formula for this mineral is $\text{Ca}_{1.01}\text{Mg}_{0.38}(\text{Ti}^{3+})_{0.34}(\text{Ti}^{4+})_{0.14}\text{Al}_{0.87}\text{Si}_{1.26}\text{O}_6$. The crystal structure reveals that this mineral contains chains of edge-shared distorted octahedra with $\text{Ti}^{3+/4+}$ ions at the center. The Ti-Ti distance is 3.15 Å. The polarized single-crystal absorption spectra of the Ti^{3+} - Ti^{4+} pyroxene from the Allende meteorite at different pressures are shown below (α and β refer to two different polarization directions).

Propose assignments for the absorption bands at 14,000, 16,000, and 20,000 cm^{-1} (1 bar). On the basis of your assignments, offer explanations for the pressure dependent behavior of the three bands.

