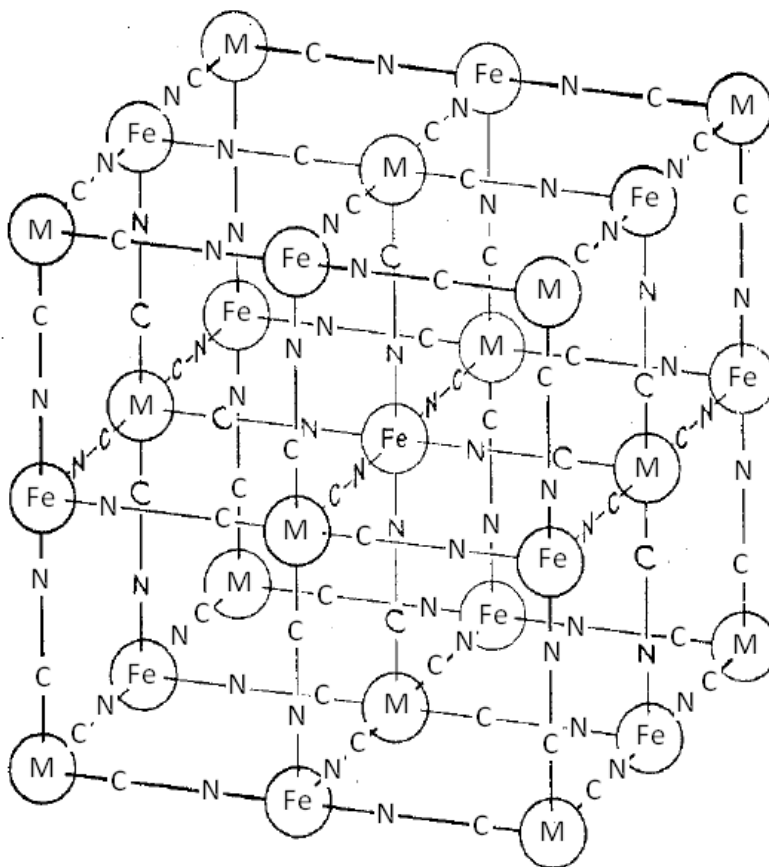


**Problem Set 5**

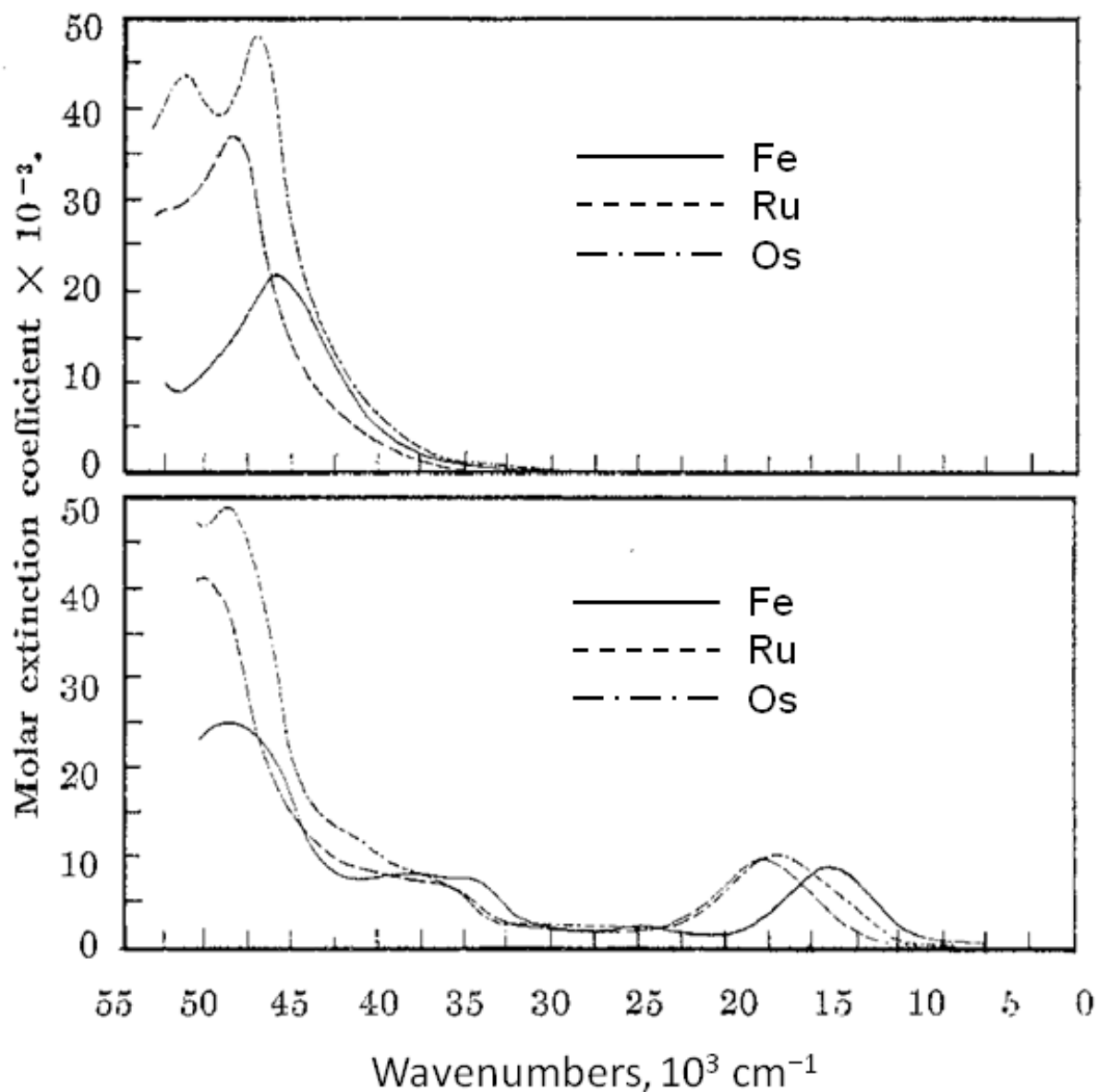
**Ch 153a – Winter 2025**

**Due: 14 February 2025**

1. (5 points) The three ferric hexacyanometallates, Prussian blue, ruthenium purple, and osmium purple ( $\text{Fe}_4[\text{M}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ ,  $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) are prepared by mixing solutions of the corresponding hexacyanometallates with a ferric perchlorate solution. The general structure of the three compounds is shown below.



The absorption spectra (next page) of the hexacyano-metallates are shown in the upper panel, and the spectra of the ferric-hexacyano-metallates appear in the lower panel.



Propose assignments for the absorption bands in the ferric-hexacyano-metallates spectra. Explain your reasoning.

- (15 points) The intensity of an intervalence charge transfer (IVCT) absorption band is related to the strength of the electronic coupling between the electron donor and acceptor. In this problem, you will derive the following expression for the square of the transition moment integral ( $|\bar{\mu}_{12}|^2$ ) for IVCT absorption:

$$|\bar{\mu}_{12}|^2 = \frac{H_{DA}^2 (ed_{DA})^2}{(hc\tilde{\nu}_{\max})^2},$$

where  $H_{DA}$  is an electronic coupling matrix element,  $e$  (esu = statC = erg<sup>1/2</sup> cm<sup>1/2</sup>) is the unit electronic charge,  $d_{DA}$  is the donor-acceptor distance,  $h$  (erg – sec) is Planck's constant,  $c$  (cm sec<sup>-1</sup>) is the speed of light, and  $\tilde{\nu}_{\max}$  (cm<sup>-1</sup>) is the frequency in wavenumbers of the IVCT absorbance maximum.

Assume that you have an electron donor in close proximity to an electron acceptor ( $D|A$ ). We will consider just the ground state ( $D|A$ ) and a charge-transfer excited state ( $D^+|A^-$ ). We can define zero-order wavefunctions for the two states:

$$\Psi_g = \phi_D(r_1)\Theta_{D^+}(r_2 \cdots r_m)\Theta_A(r_{m+1} \cdots r_n) = \phi_D \Theta_{D^+} \Theta_A$$

$$\Psi_e = \phi_{A^-}(r_1)\Theta_{D^+}(r_2 \cdots r_m)\Theta_A(r_{m+1} \cdots r_n) = \phi_{A^-} \Theta_{D^+} \Theta_A$$

The function  $\phi_D$  is the HOMO on  $D$ ;  $\phi_{A^-}$  is the LUMO on  $A$ ;  $\Theta_{D^+}$  describes the core electrons on  $D^+$ ; and  $\Theta_A$  is the function for the core electrons on  $A$ . We assume that  $\Psi_g$  and

$$\int \Psi_g \Psi_g d\tau = \int \Psi_e \Psi_e d\tau = 1,$$

$\Psi_e$  are real, normalized,

and orthogonal,

$$\int \Psi_g \Psi_e d\tau = 0.$$

If  $D$  and  $A$  interact weakly with one another, the wave functions will be perturbed slightly:

$$\Psi_G = \Psi_g + \alpha\Psi_e$$

$$\Psi_E = \Psi_e + \beta\Psi_g$$

The transition moment integral for the  $G \rightarrow E$  excitation is given by:

$$\bar{\mu}_{GE} = \int \Psi_G (-e \sum_{i=1}^n \vec{r}_i) \Psi_E d\tau$$

- a. Derive an expression for  $\bar{\mu}_{GE}$  as a function of  $e$ ,  $\alpha$ ,  $\beta$ , the average positions of electrons in orbitals 2 through  $n$  ( $\langle \vec{r}_i \rangle$ ,  $i = 2 \cdots n$ ), the average position of an electron in  $\phi_D$  ( $\langle \vec{r}_D \rangle = \int \phi_D \vec{r}_1 \phi_D d\vec{r}_1$ ), the average position of an electron in  $\phi_{A^-}$  ( $\langle \vec{r}_{A^-} \rangle = \int \phi_{A^-} \vec{r}_1 \phi_{A^-} d\vec{r}_1$ ), and  $\langle \vec{r}_{DA^-} \rangle = \int \phi_D \vec{r}_1 \phi_{A^-} d\vec{r}_1$ .

- b. The Hamiltonian for the perturbed system is  $H = H_0 + H_1$ , and the following equations are assumed to be valid:

$$H_0 \psi_g = \varepsilon_g \psi_g; \quad H_0 \psi_e = \varepsilon_e \psi_e;$$

$$H \Psi_G = E_G \Psi_G; \quad E_G = \varepsilon_g + \varepsilon'_g \approx \varepsilon_g + \int \psi_g H_1 \psi_g d\tau$$

$$H \Psi_E = E_E \Psi_E; \quad E_E = \varepsilon_e + \varepsilon'_e \approx \varepsilon_e + \int \psi_e H_1 \psi_e d\tau$$

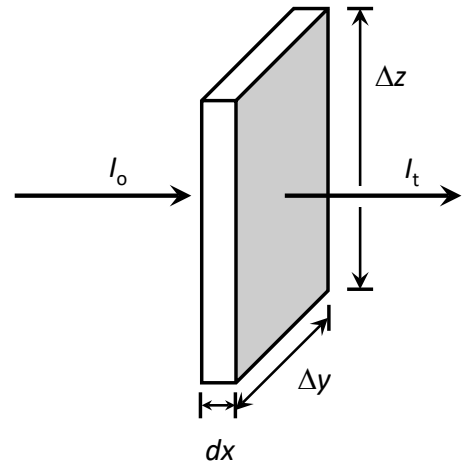
Substitute for  $H$ ,  $\Psi_G$ , and  $E_G$  in the Schrödinger equation, left-multiply by  $\psi_e$ , then integrate over all space to obtain an expression for  $\alpha$  in terms of  $E_E$ ,  $E_G$ , and

$$H_{DA} \equiv \int \psi_g H_1 \psi_e d\tau = \int \psi_e H_1 \psi_g d\tau.$$

- c. Substitute for  $H$ ,  $\Psi_E$ , and  $E_E$  in the Schrödinger equation, left-multiply by  $\psi_g$ , then integrate over all space to obtain an expression for  $\beta$  in terms of  $E_E$ ,  $E_G$ , and  $H_{DA}$ .
- d. Substitute your expressions for  $\alpha$  and  $\beta$  into your result from part (a). Compare this result to the expression for  $|\bar{\mu}_{12}|^2$  given above. Explain what assumptions and/or approximations are necessary to make your expression for  $|\bar{\mu}_{GE}|^2$  match that for  $|\bar{\mu}_{12}|^2$ . Can you provide justifications for these assumptions and/or approximations?

3. (15 points) Consider a collimated beam of light impinging on an absorbing sample of thickness  $dx$  and cross-sectional area  $\Delta y \Delta z$ , as shown to the right. Assume that that incident beam has spectral irradiance  $I_o(\tilde{\nu}) \left( \frac{\text{erg}}{\text{sec cm}^2 \text{ cm}^{-1}} \right)$ . Throughout this problem we will use cgs and esu units, and express light frequency in terms of wavenumbers,

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{v(\text{sec}^{-1})}{c \left( \frac{\text{cm}}{\text{sec}} \right)}.$$



The rate per wavenumber interval at which molecules in the sample volume are excited is given by:

$$\frac{dn_e}{dt} \left( \frac{\text{molecules}}{\text{cm}^3} \frac{1}{\text{sec}} \frac{1}{\text{cm}^{-1}} \right) = n_g \left( \frac{\text{molecules}}{\text{cm}^3} \right) \times \rho(\tilde{\nu}) \left( \frac{\text{erg}}{\text{cm}^3} \frac{1}{\text{cm}^{-1}} \right) \times B_{ge} \left( \frac{\text{cm}^3}{\text{erg}} \frac{1}{\text{sec}} \text{cm}^{-1} \right) \times g(\tilde{\nu}) \left( \frac{1}{\text{cm}^{-1}} \right)$$

where  $n_g$  is the concentration of molecules in the ground state;  $\rho(\tilde{\nu})$  is the radiant energy density per wavenumber interval;  $B_{ge}$  is the Einstein coefficient for induced  $g \rightarrow e$  absorption; and  $g(\tilde{\nu})$  is an absorption band shape function obeying the normalization condition:  $\int_{-\infty}^{+\infty} g(\tilde{\nu}) d\tilde{\nu} = 1$ .

- a. Derive an expression for  $\frac{dI(\tilde{\nu})}{dx} \left( \frac{\text{erg}}{\text{sec}} \frac{1}{\text{cm}^2} \frac{1}{\text{cm}^{-1}} \frac{1}{\text{cm}} \right)$  in terms of  $n_g$ ,  $\rho(\tilde{\nu})$ ,  $\tilde{\nu}$ ,  $B_{ge}$ ,  $g(\tilde{\nu})$ ,

Planck's constant ( $h(\text{erg} - \text{sec})$ ), and the speed of light,  $c$ . Demonstrate that your result has the proper units.

- b. Beer's law can be derived from the following differential equation,

$-\frac{dI(\tilde{\nu})}{dx} = \alpha(\tilde{\nu})N_g I(\tilde{\nu})$ , where  $N_g$  is the **molar** concentration of ground-state molecules and  $\alpha(\tilde{\nu})$  is a molar absorption coefficient. You are probably more familiar with Beer's

law in the following form:  $Abs = -\log_{10} \left( \frac{I_t(\tilde{\nu})}{I_o(\tilde{\nu})} \right) = \epsilon(\tilde{\nu})N_g \Delta x$ . Derive an expression

relating  $\alpha(\tilde{\nu})$  to  $\epsilon(\tilde{\nu}) \left( \frac{\text{liter}}{\text{mole}} \frac{1}{\text{cm}} \right)$ .

- c. Use the results from parts (a) and (b), and the relationship between the spectral irradiance and the energy density,  $I(\tilde{\nu}) = c \rho(\tilde{\nu})$ , to derive an expression for  $\frac{\epsilon(\tilde{\nu})}{\tilde{\nu}}$  as a function of Avogadro's number ( $N_A \left( \frac{\text{molecules}}{\text{mole}} \right)$ ),  $h$ ,  $B_{ge}$ , and  $g(\tilde{\nu})$ .

- d. The semi-classical formulation of the Franck-Condon principle for transitions from a harmonic ground-state surface to a harmonic excited state surface predicts a band shape of the form:

$$\frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} = \left( \frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} \right)_{\text{max}} \exp \left( -\frac{(hc\tilde{\nu} - \lambda - E_{00})^2}{4\lambda RT} \right)$$

where  $\lambda(\text{erg})$  is the reorganization energy,  $E_{00}(\text{erg})$  is the energy difference between the minima of the two harmonic surfaces,  $R \left( \frac{\text{erg}}{\text{K}} \right)$  is the gas constant, and  $T(\text{K})$  is the

absolute temperature. If the band shape is narrow relative to  $\tilde{\nu}_{ge}$ , then

$$\left(\frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}}\right)_{\max} \approx \frac{\varepsilon_{\max}}{\tilde{\nu}_{\max}}. \text{ Use this approximation, the result from part (c), and the } g(\tilde{\nu})$$

normalization condition to derive an expression for  $\varepsilon_{\max}$  as a function of  $N_A$ ,  $h$ ,  $B_{ge}$ ,  $c$ ,  $\lambda$ ,  $R$ ,  $T$ , and  $\tilde{\nu}_{\max}$ . Your expression should not contain any explicit dependence on  $\tilde{\nu}$  or  $g(\tilde{\nu})$ .

- e. Use the semi-classical band shape function to derive an expression for  $\Delta\tilde{\nu}_{1/2}$ , the full width of the band at half-maximum, as a function of  $h$ ,  $c$ ,  $\lambda$ ,  $R$ , and  $T$ .
- f. A Golden-Rule treatment of the  $g \rightarrow e$  radiative transition probability defines  $B_{ge}$  in terms of the transition moment integral,  $\mu_{12}$ :

$$B_{ge} = \frac{8\pi^3 |\mu_{12}|^2}{3h^2 c}$$

Demonstrate that this expression gives the same units for  $B_{ge}$  as those above. Use this expression and the results from parts (d) and (e) to express  $\varepsilon_{\max}$  as a function of  $h$ ,  $c$ ,  $N_A$ ,  $\mu_{12}$ ,  $\tilde{\nu}_{\max}$ , and  $\Delta\tilde{\nu}_{1/2}$ .

- g. In Problem 2 you showed that a perturbation theory treatment of (intervalence) charge-transfer absorption predicts that  $\mu_{12}$  will depend on the electronic coupling matrix element between donor and acceptor ( $H_{DA}(\text{erg})$ ), the distance between donor and acceptor ( $d_{DA}(\text{cm})$ ), and  $\tilde{\nu}_{\max}$ , according to the expression:

$$|\bar{\mu}_{12}|^2 = \frac{H_{DA}^2 (ed_{DA})^2}{(hc\tilde{\nu}_{\max})^2},$$

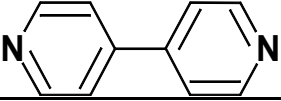
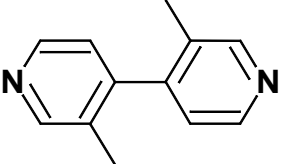
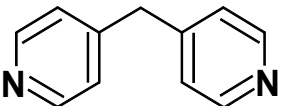
where  $e$  ( $\text{esu} = \text{statC} = \text{erg}^{1/2} \text{cm}^{1/2}$ ) is the unit electronic charge. Use this definition to derive an expression for  $\varepsilon_{\max}$  as a function of  $N_A$ ,  $h$ ,  $c$ ,  $e$ ,  $d_{DA}$ ,  $H_{DA}$ ,  $\Delta\tilde{\nu}_{1/2}$ , and  $\tilde{\nu}_{\max}$ .

- h. Evaluate the constants in your expression to derive the following result:

$$\varepsilon_{\max} = \frac{2.35 \times 10^3 H_{DA}^2 d_{DA}^2}{\Delta\tilde{\nu}_{1/2} \tilde{\nu}_{\max}}$$

where  $d_{DA}$  is expressed in  $\text{\AA}$  units, and  $H_{DA}$ ,  $\tilde{\nu}_{\max}$ , and  $\Delta\tilde{\nu}_{1/2}$  are expressed in  $\text{cm}^{-1}$  units.

4. (5 points) 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	$r, \text{Å}$	$\text{Abs}_{\text{max}}, \text{nm}$	$\epsilon_{\text{max}}, \text{M}^{-1}\text{cm}^{-1}$
	11.3	1030	920
	11.3	890	165
	10.5	810	30

For each complex, use the results from problem 3 to determine the value of  $H_{\text{DA}}$  and  $\lambda$ , and predict the full-width at half-maximum of the intervalence band. Offer explanations for any trends that you observe in these parameters.