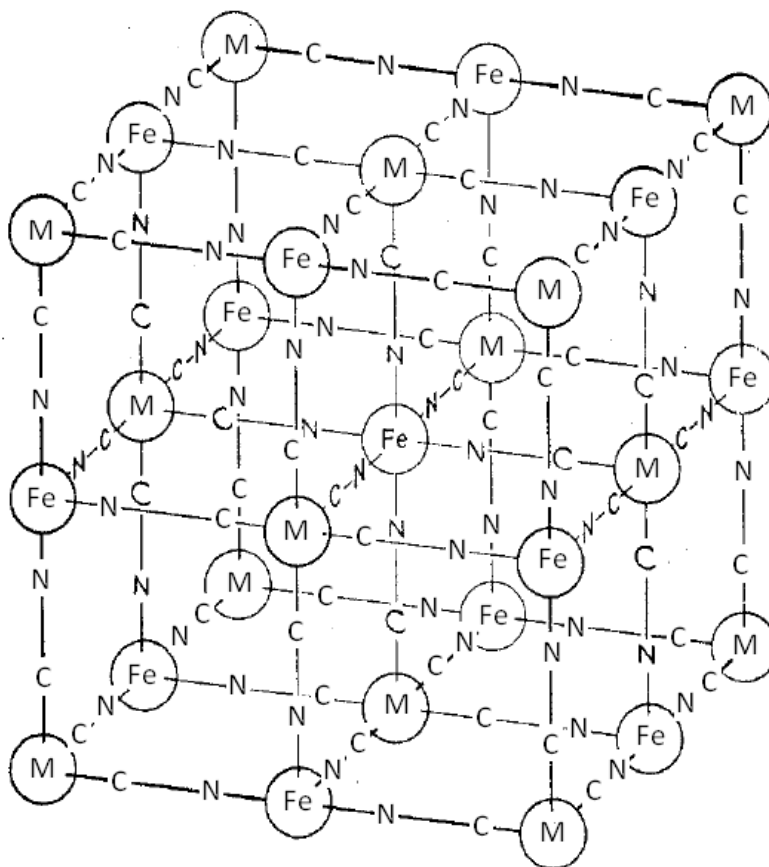**Problem Set 8**

**Ch 153a – Winter 2021**

Due: 26 February, 2021

1) The three ferric hexacyanometallates, Prussian blue, ruthenium purple, and osmium purple ($Fe_4[M(CN)_6]_3 \bullet xH_2O$, M = Fe, Ru, 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.
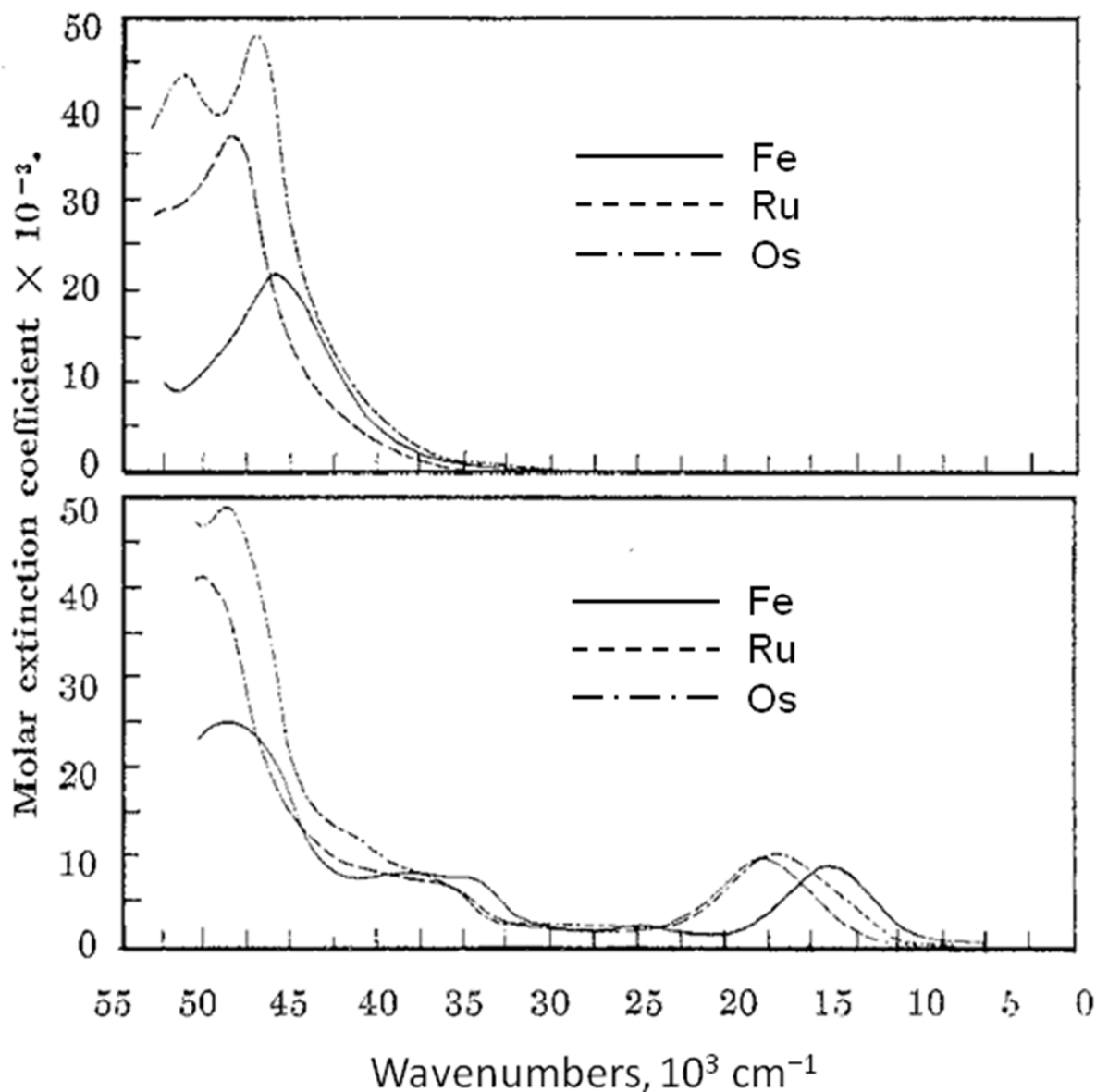
Propose assignments for the absorption bands in the ferric-hexacyano-metallates spectra. Explain your reasoning.

2) 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 ($|\vec{\mu}_{12}|^2$) for IVCT absorption:

$$|\vec{\mu}_{12}|^2 = \frac{H_{DA}^2(er_{DA})^2}{(hc\tilde{v}_{max})^2},$$

where H_{DA} is an electronic coupling matrix element, $e(esu = statC = erg^{1/2}\ cm^{1/2})$ is the unit electronic charge, r_{DA} is the donor-acceptor distance, $h(erg-sec))$ is Planck's constant, $c(cm\ sec^{-1})$ is the speed of light, and $\tilde{v}_{max}(cm^{-1})$ is the frequency 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 ϕ_D is the HOMO on D; ϕ_{A^-} is the LUMO on A; Θ_{D^+} describes the core electrons on D^+; and Θ_A is the function for the core electrons on A. We assume that ψ_g and ψ_e are real, normalized,

$$\int \psi_g\psi_g d\tau = \int \psi_e\psi_e d\tau = 1,$$

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:

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

a) Derive an expression for $\vec{\mu}_{GE}$ as a function of e, α, β, 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 ϕ_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 ϕ_{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 $H = H_o + H_1$, and the following equations are assumed to be valid:

$$H_o \psi_g = \varepsilon_g \psi_g ; \qquad H_o \psi_e = \varepsilon_e \psi_e ;$$

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

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

Substitute for H, Ψ_G, and E_G in the Schrödinger equation, left-multiply by ψ_e, then integrate over all space to obtain an expression for α 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, Ψ_E, and E_E in the Schrödinger equation, left-multiply by ψ_g, then integrate over all space to obtain an expression for β in terms of E_E, E_G, and H_{DA}.

d) Substitute your expressions for α and β into your result from part (a). Compare this result to the expression for $|\vec{\mu}_{12}|^2$ given above. Explain what assumptions and/or approximations are necessary to make your expression for $|\vec{\mu}_{GE}|^2$ match that for $|\vec{\mu}_{12}|^2$. Can you provide justifications for these assumptions and/or approximations?

3) 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 $I_o(\tilde{v}) \left(\dfrac{erg}{sec} \dfrac{1}{cm^2} \dfrac{1}{cm^{-1}} \right)$. Throughout this problem we will use cgs and esu units, and express light frequency in terms of wavenumbers, $\tilde{v}(cm^{-1}) = \dfrac{v(sec^{-1})}{c\left(\dfrac{cm}{sec}\right)}$.
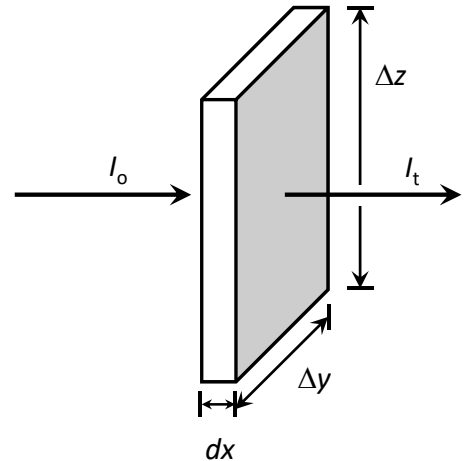
The rate per wavenumber interval at which excited molecules in the sample volume are produced is given by:

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

where n_g is the concentration of molecules in the ground state; $\rho(\tilde{v})$ is the radiant energy density per wavenumber interval; B_{ge} is the Einstein coefficient for induced

$g{\rightarrow}e$ absorption; and $g(\tilde{v})$ is an absorption bandshape function obeying the normalization condition: $\int_{-\infty}^{+\infty}g(\tilde{v})d\tilde{v}=1$.

a) Derive an expression for $\dfrac{dI(\tilde{v})}{dx}\left(\dfrac{erg}{sec\ cm^2}\dfrac{1}{cm^{-1}}\dfrac{1}{cm}\right)$ in terms of n_g, $\rho(\tilde{v})$, $\tilde{v}$, B_{ge}, $g(\tilde{v})$, Planck's constant ($h(erg-sec)$), 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, $-\dfrac{dI(\tilde{v})}{dx}=\alpha(\tilde{v})N_g I(\tilde{v})$, where N_g is the **molar** concentration of ground-state molecules and $\alpha(\tilde{v})$ is a molar absorption coefficient. You are probably more familiar with Beer's law in the following form: $Abs = -\log_{10}\left(\dfrac{I_t(\tilde{v})}{I_o(\tilde{v})}\right)=\varepsilon(\tilde{v})N_g\Delta x$.

Derive an expression relating $\alpha(\tilde{v})$ to $\varepsilon(\tilde{v})\left(\dfrac{liter}{mole}\dfrac{1}{cm}\right)$.

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

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:

$$\dfrac{\varepsilon(\tilde{v})}{\tilde{v}}=\left(\dfrac{\varepsilon(\tilde{v})}{\tilde{v}}\right)_{max}\exp\left(-\dfrac{(hc\tilde{v}-\lambda-E_{00})^2}{4\lambda RT}\right)$$

where $\lambda(erg)$ is the reorganization energy, $E_{00}(erg)$ is the energy difference between the minima of the two harmonic surfaces, $R\left(\dfrac{erg}{K}\right)$ is the gas constant, and $T(K)$ is the absolute temperature. If the bandshape is narrow relative to $\tilde{v}_{ge}$, then $\left(\dfrac{\varepsilon(\tilde{v})}{\tilde{v}}\right)_{max}\approx\dfrac{\varepsilon_{max}}{\tilde{v}_{max}}$. Use this approximation, the result from part (c), and the $g(\tilde{v})$ normalization condition to derive an expression for ε_{max} as a function of N_A, h, B_{ge}, c, λ, R, T, and $\tilde{v}_{max}$. Your expression should not contain any explicit dependence on $\tilde{v}$ or $g(\tilde{v})$.

e) Use the semi-classical bandshape function to derive an expression for $\Delta\tilde{\nu}_{\frac{1}{2}}$, the full width of the band at half-maximum, as a function of h, c, λ, 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, μ_{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 ε_{max} as a function of h, c, N_A, μ_{12}, $\tilde{\nu}_{max}$, and $\Delta\tilde{\nu}_{\frac{1}{2}}$.

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

$$|\mu_{12}|^2 = \frac{H_{DA}^2 (er_{DA})^2}{(hc\tilde{\nu}_{max})^2}$$

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

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

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

where r_{DA} is expressed in Å units, and H_{DA}, $\tilde{\nu}_{max}$, and $\Delta\tilde{\nu}_{\frac{1}{2}}$ are expressed in cm^{-1} units.