## Chemistry 213a

Advanced Ligand Field Theory

## Problem Sets

A. Weak Crystal Fields
B. Strong Crystal Fields
C. Intermediate Crystal Fields; Tanabe-Sugano Diagrams
D. Introduction to Electronic Spectra

## Texts

Ballhausen, C.J. Introduction to Ligand Field Theory; McGraw-Hill, 1962.
Figgis, B.N. Introduction to Ligand Fields; Wiley, 1966.
Figgis, B.N. and Hitchman, M.A. Ligand Field Theory and Its Applications; Wiley, 2000.
Griffith, J.S. The Theory of Transition Metal Ions; Cambridge University Press, 1961.

Additional references have been placed on permanent reserve in the Millikan Library on the eighth floor.

## Introduction

The four accompanying problem sets will illustrate the development of crystal field theory for the $d^{3}$ electronic configuration in an octahedral ligand environment. In principle, once the calculations are understood for this case, they can be applied readily to other configurations.

The theory of atomic spectroscopy provides the starting point for the crystal field formalism. For a many-electron ion or atom, the Hamiltonian has the form:

$$
\hat{H}=\frac{\hbar^{2}}{2 m} \sum_{i} \nabla_{i}^{2}-\sum_{i} \frac{Z e^{2}}{r_{i j}}+\sum_{i>j} \frac{e^{2}}{r_{i j}}+\sum_{i} \xi_{i}\left(r_{i}\right) l_{i} s_{i}
$$

Here, the potential function takes into account interelectron repulsion and spin-orbit coupling in the last two terms, respectively. For simplicity, the spin-orbit contribution will be ignored initially and considered later in the second half of this course (Ch 213b).

The total energy of a $d^{n}$ term is given by the sum of its own electrostatic energy and its energy in the field of the core electrons. For our purposes, the core energy can be neglected since, to a first approximation, the core energy should be the same for all $d^{3}$ configurations and will vanish when energy differences between terms are considered.

Upon complex formation, the Hamiltonian for the free ion will change to include the interactions between the electrons and the ligand field, $V_{i}$, present in the complex. The strength of the ligand field relative to other electronic forces present will vary from one complex to another, allowing three principle cases to be identified:

$$
\begin{aligned}
& V_{i}<\sum_{i>j} \frac{e^{2}}{r_{i j}} \\
& V_{i}=\sum_{i>j} \frac{e^{2}}{r_{i j}} \\
& V_{i}>\sum_{i>j} \frac{e^{2}}{r_{i j}}
\end{aligned}
$$

These three cases correspond to weak, intermediate, and strong crystal fields, respectively. The approach for determining the nature of the electronic structure of a metal complex is first to find the relative energies for the electronic terms of the system in each of these regimes and second construct a correlation diagram that illustrates the change in relative term energies as the crystal field varies from weak to strong (relative to the interelectron repulsion energy). The metal complex is then positioned on this diagram.

The ligand field formalism follows a first-order perturbation treatment. In the weak-field case, the crystal field is considered small compared to interelectron repulsions, while in the strong-field case, the interelectron repulsions are considered small compared to the crystal field. For each case, wavefunctions will be constructed and diagonalized with respect to both energy operators to yield energies for all the electronic terms in the complex. In addition to the ligand field strength, the symmetry of the complex will affect the splitting of the terms. Therefore, group theory will play a critical role in simplifying calculations.

Problem sets A and B will outline the procedure for determining energy expressions for a $d^{3}$ ion in the limiting cases of weak and strong octahedral fields. In problem set $\mathbf{C}$, the case of intermediate ligand fields will be treated from both weak and strong-field perspectives. These two approaches will be shown to yield identical results and used to construct a simplified Tanabe-Sugano diagram. Finally, problem set D will introduce some practical applications of ligand field theory to the electronic spectra of metal complexes.

A partial list of references is included in this package. Several of the more useful texts can be found on the Ch 213 reserve shelf in the Millikan Library. You are encouraged to explore any sources (including scientific journals) that may be helpful to you.

## A. Weak Crystal Fields

Reading: Ballhausen (Intro. to LFT) Chapters 1-3, 4a-d, g; Gerloch and Slade (Ligand Field Parameters) Chapter 2; Weissbluth (Atoms and Molecules) Chapters 1 and 11; Figgis (Intro. to $L F)$ Chapters 1-4.

1. a.) Briefly explain the terms orbital, term, state, and level.
b.) Using a microstate table, find all of the terms for the $d^{3}$ configuration and determine the ground state.
c.) Using group theory, show how each term splits in the presence of a weak cubic field.
2. Find the following wavefunctions by using the raising and lowering operators described in Ballhausen: $\quad \Psi\left(3,2, \frac{3}{2}, \frac{1}{2}\right), \Psi\left(4,2, \frac{1}{2}, \frac{1}{2}\right), \Psi\left(5,2, \frac{1}{2}, \frac{1}{2}\right), \Psi\left(3,2, \frac{1}{2}, \frac{1}{2}\right)$
3. a.) Set up the equations to find the two wavefunctions for the state $\Psi\left(2,2, \frac{1}{2}, \frac{1}{2}\right)$. Do you see a problem? Do the two wavefunctions exist independently? Are they degenerate? Explain.
b.) Detail a variational method for finding these wavefunctions.
c.) Using a less rigorous approach, solve your equations in part a.) to find two wavefunctions for the ${ }^{2} D$ term. (Hint: arbitrarily set the coefficient of $\left(2^{-}, 1^{+},-1^{+}\right)$equal to zero for one wavefunction.) How do these functions relate to your results from part b.)?
4. Determine the energies of all the terms except ${ }^{2} D$ and ${ }^{2} P$. For the quartet terms, use the method described on page 23 of Ballhausen. Express your answers in terms of both SlaterCondon parameters and Racah parameters.
5. a.) Derive an expression for the energies of the ${ }^{2} D$ terms in terms of two arbitrary, normalized, and orthogonal wavefunctions $\psi_{\mathrm{a}}$ and $\psi_{\mathrm{b}}$ where:

$$
\Psi\left({ }^{2} \mathrm{D}\right)=\mathrm{a} \psi_{\mathrm{a}}\left(2,2, \frac{1}{2}, \frac{1}{2}\right)+\mathrm{b} \psi_{\mathrm{b}}\left(2,2, \frac{1}{2}, \frac{1}{2}\right)
$$

b.) Discuss this result in terms of the diagonal sum rule.
c.) Find the mean energy of the terms. Part of this expression is needed in the next problem.

Express your answer in terms of both Slater-Condon parameters and Racah parameters.
6. Determine the energy of the ${ }^{2} P$ term.
7. Determine the crystal field energies of all the quartet terms.
8. a.) How would you go about finding the energies of the two ${ }^{2} D$ terms?
b.) Find the energies of the wavefunctions that you derived in problem 3c. Solve for the energies of the two ${ }^{2} D$ terms.
9. Using the operator equivalent method, determine how the weak-field energies of the $O_{h}$ states arising from the ${ }^{2} F$ and ${ }^{4} F$ terms are related. Use this information to determine the ligand field energies of the doublet term. (Refer to Griffith, Theory of Transition Metal Ions, page 38 and Ballhausen, Intro. to LFT, page 84.)
10. Like many functions, the crystal field operator can be expanded in terms of a complete set of basis functions. We can write the expansion using the basis functions for an electron on the central metal ion.

$$
\begin{equation*}
V=\sum_{k} \sum_{q} C_{k}^{q} R_{k}(r) Y_{k}^{q}(\theta, \phi) \tag{1}
\end{equation*}
$$

Here $R_{k}$ and $Y_{k}^{q}$ are the radial and spherical harmonic functions, respectively, and $\mathrm{C}_{\mathrm{k}}^{q}$ are the expansion coefficients.
a.) Starting with equation (1) show that the crystal field operator for an octahedral complex can be written as:

$$
\begin{equation*}
V_{O_{h}}=Y_{4}^{0}+\sqrt{\frac{5}{14}}\left(Y_{4}^{4}+Y_{4}^{4-}\right) \tag{2}
\end{equation*}
$$

In the point charge model for the crystal field (i.e., no mixing of ligand and metal orbitals) the crystal field operator is given by:

$$
\begin{equation*}
V_{O_{h}}=\sum_{k=0}^{\infty} \sum_{q=-k}^{k} \frac{4 \pi}{2 k+1} \sum_{i} Z e Y_{k}^{q^{*}}\left(\Theta_{i}, \phi_{i}\right) \frac{r^{k}}{r^{k+1}} Y_{k}^{q}\left(\Theta_{i}, \phi_{i}\right) \tag{3}
\end{equation*}
$$

Here, $i$ refers to the point charges and $j$ to an individual electron.
b.) Compare equations (1) and (3). What wavefunctions in (3) correspond to the expansion coefficients in equation (1)? Comment on the physical information about the ligand field contained in the radial and spherical components of the expansion coefficients.
c.) Without determining coefficients, what are the expressions analogous to (2) for $V_{D_{4 n}}$ and $V_{C_{3 v}}$ ? In the latter case, the field does not possess a center of symmetry. What complications with this introduce?

## Strong Crystal Fields

Reading: Ballhausen (Intro to LFT) Chapter $4 \mathrm{e}, \mathrm{h}$, i; Figgis (Intro to $L F$ ) Chapter 7; Griffith (Theory of Transition Metal Ions) Chapter 9.

These are the five steps used to determine how the octahedral ligand field perturbs the free ion in the strong-field approximation:

1. Determine the splitting of the $d$ levels by the crystal field;
2. Determine the possible electronic configurations and associated terms;
3. Determine the wavefunctions for each term of each configuration;
4. Evaluate the interelectronic repulsion energies within each term;
5. Add on the crystal field stabilization energy (CFSE).

The following problems will illustrate various aspects of this general process. The strong-field case is somewhat more difficult computationally because it involves the use of the interelectron repulsion operator on the strong-field functions. Fortunately, most of the mechanics has been worked out by Griffith and are tabulated. It is important that you become familiar with these tables.

1. a.) Enumerate the strong-field configurations that exist for the $d^{3}$ case and compute the degeneracy of each.
b.) Determine the energies of the $e_{g}$ and $t_{2 g}$ levels. Write down the secular determinant in block diagonal form for the $d$ electrons quantized about the three-fold axis in an
octahedral field. Solve and then explain how you determine which energy corresponds to which level.
c.) Neglecting electron-electron repulsion, calculate the appropriate energies for each configuration using an additive procedure. Draw a splitting diagram summarizing these results.
2. This problem deals with the determination of the strong-field terms arising from the $\left(t_{2 g}\right)^{3}$ configuration. Decompose the direct product $T_{2 g} \otimes T_{2 g} \otimes T_{2 g}$ into its components. It is known that the only terms that come out of this configuration are: ${ }^{4} A_{2 g},{ }^{2} E_{g},{ }^{2} T_{1 g}$, and ${ }^{2} T_{2 g}$. Explain what happened to the remaining terms.
3. Determine the effect of the Coulombic repulsions of the electrons on the lowest energy level found in Problem 1. Use the following procedure:
a.) Write down the wavefunctions for the $\left(t_{2 g}\right)^{3}$ configuration using the notation of Griffith (e.g., $M_{\mathrm{S}}=\frac{3}{2}$ and $M_{\mathrm{S}}=0, \phi_{1}=\left(\zeta^{+}, \eta^{+}, \xi^{+}\right)$). What is the degeneracy of this configuration?
b.) Apply the electron repulsion operator to each ket yielding a $20 \times 20$ secular determinant. Refer to Griffith (Theory of Transition Metal Ions), Table A26, for the evaluation of the matrix elements.
c.) Regroup the matrix into block diagonal form and solve for the energies using the following simplifying substitutions:

$$
\alpha=3 A+5 C ; \quad \beta=-3 B-C ; \quad \gamma=3 A-9 B+2 C
$$

Express your final answers in terms of both Slater-Condon parameters and Racah parameters. Compare your energies with those of Griffith in Table A28.
d.) In Table A24 of Griffith, half of the strong-field wavefunctions are missing. Provide the remaining functions.
4. In the previous problem you found the energies of all the terms arising from the $\left(t_{2 g}\right)^{3}$ configuration, but you were not able specify the terms associated with each energy.

Generally, this can be accomplished by constructing wavefunctions for each term according to symmetry and subsequently solving for their energies.

The process of bringing up six identical ligands to a central metal ion results in a reduction of symmetry from spherical to octahedral. Sometimes, reductions in symmetry can be used to our advantage computationally by lifting degeneracies and simplifying wavefunctions. In this problem, descent in symmetry from $O_{h}$ to $D_{4 h}$ will be used to find the energies of the terms arising from the $\left(t_{2 g}\right)^{3}$ configuration.
a.) Determine how each $d$ orbital transforms in $D_{4 h}$ by filling in the following table:

| $D_{4 \mathrm{~h}}$ | $\hat{\mathrm{E}}$ | $\hat{C}_{4}$ | $\hat{\mathrm{C}}_{2}$ | $\hat{\mathrm{C}}_{2}^{\prime}$ | $\hat{\mathrm{C}}_{2}^{\prime \prime}$ |
| :---: | :--- | :--- | :--- | :--- | :--- |
| xy |  |  |  |  |  |
| xz |  |  |  |  |  |
| yz |  |  |  |  |  |
| $\mathrm{z}^{2}$ |  |  |  |  |  |
| $\mathrm{x}^{2}-\mathrm{y}^{2}$ |  |  |  |  |  |

b.) The ${ }^{4} A_{2 g}$ is the only quartet term found for the $\left(t_{2 g}\right)^{3}$ configuration. Write a wavefunction for this term and verify that it transforms as $B_{1 g}$ in the lower symmetry point group. Evaluate the repulsion energy using this wavefunction (see Ballhausen page 76).
c.) Now write down all the possible combinations of spatial functions ((xy), (xz), (yz), ( $z^{2}$ ), and $\left.\left(\mathrm{x}^{2}-\mathrm{y}^{2}\right)\right)$ and spin functions (+,-) for this configuration and determine how they transform in $D_{4 h}$ using the table in part a). Take combinations where appropriate.
d.) Calculate energies for each term arising from this configuration. Express your answers in terms of Slater-Condon parameters and Racah parameters. Comment on any degeneracies. Compare your energies with those found in problem 3.
e.) After adding in the ligand field energies found in problem 1, draw a splitting diagram summarizing your results.
5. A useful analogy between $p$ and $t_{2}$ electrons exists according to the following relations:

$$
\begin{aligned}
\left(p_{-1}\right) & =\left(d_{-1}\right) \\
\left(p_{0}\right)=\left(d_{0}\right) & =\left(d_{2}-d_{-2}\right) \\
\left(p_{1}\right) & =\left(d_{1}\right)
\end{aligned}
$$

Use this concept to find the energies of all the terms arising from the $\left(t_{2 g}\right)^{3}$ strong-field configuration. Compare your answers to those found in Problem 3.

# Problem Set C. Intermediate Fields; Tanabe-Sugano Diagrams 

## Reading: Ballhausen (Intro to LFT) Chapter 4 f; Figgis (Intro to LF) Chapter 7.

Neither the weak-field nor the strong-field limit is physically realistic. In general, complexes will fall in the so-called intermediate region, in which terms of the same symmetry will mix via configuration interaction. In calculating the term energies in this region, two approaches are possible:
a. In the weak-field approach, the interelectron repulsions are considered first and the intermediate-field levels are found by perturbing the free ion levels.
b. In the strong-field approach the ligand field levels are found and then perturbed by the interelectron repulsions to find the intermediate-field levels.

1. Using the weak-field basis functions, derive expressions for the energies of all the quartet terms for all values of $D q$. Here you must consider the interaction of the two $T_{l g}$ terms.
2. Repeat Problem 1 using the strong-field basis functions. (Hint: use the descent in symmetry method.)
3. Show that the energy relations found in problems 1 and 2 are equal.
4. Determine the limiting weak-field and strong-field energies and compare with the results found in sets A and B. Draw a correlation diagram illustrating the progression from weak to strong fields. Observe the non-crossing rule.
5. To facilitate comparisons, express the energies of the quartet terms in terms of $D q$ and the Racah parameters. Then shift the energy scale so that the energy of the ground state is zero.

Plot a simplified Tanabe-Sugano diagram for $0<D q / B<6$ for the quartet terms. Give energy expressions for all curves and indicate limiting energies.
6. Treating the $d^{7}$ configuration as three holes repeat Problem 2. This situation will be complicated by spin crossover at some point. Assume a $C / B$ ratio of 4.5 and find the value of $\mathrm{Dq} / B$ at which the ground state changes from ${ }^{4} T_{1 \mathrm{~g}}$ to ${ }^{2} E_{\mathrm{g}}$ (neglect configuration interactions with other $E$ terms). Plot a simplified Tanabe-Sugano diagram for $0<\mathrm{Dq} / B<6$ for the quartet and ${ }^{2} E_{\mathrm{g}}$ terms.
7. The relation $D q\left(T_{d}\right)=-\frac{4}{9} D q\left(O_{h}\right)$ is quite useful and will be proved in Ch 213 c . Thus, the magnitude of $D q$ changes on going from tetrahedral to octahedral symmetry. The sign change is also very important. Ignoring $D q$ magnitudes Tanabe-Sugano diagrams for $d^{n}$ ions in octahedral fields are qualitatively similar to those for $d^{(10-n)}$ ions in tetrahedral symmetry. Plot simplified Tanabe-Sugano diagrams for:
a.) a $d^{3}$ ion in a $T_{d}$ field
b.) a $d^{7}$ ion in a $T_{d}$ field.
8. Consider the $d^{l}$ through $d^{9}$ configurations:
a.) Discuss the terms spin-free, spin-paired, high-spin, and low-spin with respect to Tanabe-Sugano diagrams for ions having these configurations. What are the ground states of these configurations? Provide examples where possible.
b.) Draw Orgel diagrams for each configuration. Compare the relative advantages of Orgel and Tanabe-Sugano diagrams.
c.) When dealing with atomic spectra, the assignment of ground state terms is dictated by Hund's Rules. Are these always applicable to the full set of $5 d$ orbitals? Explain.

## Problem Set D. Introductin to Electronic Spectra

Reading: Ballhausen (Intro to LFT) Chapters 4j, 5, 7b; Figgis (Intro to $L F$ ) Chapter 9; Flint in Adv. IR Raman Spectr. 1976, 2, 53-79.

1. The following transitions could occur in an octahedral $d^{3}$ complex:
a. ${ }^{4} A_{2 g} \rightarrow{ }^{4} T_{2 u}$
b. ${ }^{4} A_{2 g} \rightarrow{ }^{4} T_{2 g}$
c. ${ }^{4} A_{2 g} \rightarrow{ }^{4} T_{1 u}$
d. ${ }^{4} A_{2 g} \rightarrow{ }^{2} E_{g}$
e. ${ }^{4} A_{2 g} \rightarrow{ }^{2} T_{2 u}$
a.) Which of these are formally forbidden and why? Make an order of magnitude estimate of the extinction coefficient and oscillator strength of each transition. Propose mechanisms by which each transition could gain intensity.
b.) Determine the symmetries of the normal modes of vibration of an octahedral complex. Use these to justify intensity gains in the transitions of part a.) via vibronic interactions based on these modes.
2. Absorption spectra of $\mathrm{Cr}(\mathrm{III})$ complexes are readily analyzed using the ligand field theory derived in parts A-C.
a.) Summarize the atomic selection rules. The absorption of a free $\mathrm{Cr}(\mathrm{III})$ ion shows a weak band at about $14,000 \mathrm{~cm}^{-1}$. Explain.
b.) The electronic spectra of four $\mathrm{Cr}(\mathrm{III})$ complexes, $\mathrm{CrL}_{6}{ }^{\mathrm{n}-}$, are summarized in the table on the next page. Assign the bands (assuming they are all allowed transitions). Estimate $D q$ and $B$ values from a Tanabe-Sugano diagram. Use these values to calculate the positions of each band for each of the complexes. Draw an energy level diagram showing the levels for all four compounds. On the basis of these results, order the ligands in the table in the spectrochemical series and the nephelauxetic series.

| L |
| :---: |


| $\mathrm{H}_{2} \mathrm{O}$ | 17,400 | 24,500 | 38,000 |
| :---: | :---: | :---: | :---: |
| $\mathrm{~F}^{-}$ | 14,900 | 22,700 | 34,400 |
| Urea | 16,150 | 22,600 | 34,400 |
| $\mathrm{CN}^{-}$ | 26,600 | 32,500 | $?$ |

c.) Read the paper by Krause, Trabjerg, and Ballhausen (Chem. Phys. Lett. 1969, 3, 297299) and comment critically on the significance of this two photon experiment.
d.) Read the paper by Witzke (Theoret. Chim. Acta. 1971, 20, 171-185). This is typical of efforts aimed at parameterizing $d$ - $d$ spectra. Summarize the conclusions and general methodology.
e.) The absorption spectra of $\mathrm{Cr}(\mathrm{en}) 3^{3+}(-)$ and of the cis and trans isomers of $\mathrm{Cr}(\mathrm{en})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}{ }^{3+}$ are shown on the next page. Assign the observed bands and identify which spectra correspond to the cis and trans isomers. Explain.

3. a.) Briefly discuss the stability of octahedral low- and high-spin $d^{7}$ complexes.
b.) In both cases in a.) a distortion from $O_{\mathrm{h}}$ symmetry is predicted. Explain. What geometries might you expect and how will the ground states be split? Comment on the relative magnitudes of the splitting.
c.) Shown below are absorption spectra for $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ and $\mathrm{CoCl}_{4}{ }^{2-}$ in aqueous solution. Identify which spectrum belongs to which compound. Explain.

d.) The absorption spectra for two crystals of $\mathrm{KCoF}_{3}$ of different thickness at approximately 150 K are shown below. What are the advantages of working at low-temperature and using crystalline samples to study the spectroscopy of metal complexes?


Assuming the two most intense features in this spectrum correspond to spin-allowed transitions, assign these bands. Identify any other spin-allowed feature(s) and comment on their intensity. Assuming the weak feature at $\sim 10,000 \mathrm{~cm}^{-1}$ is the lowest energy $E_{g}$ term, determine values for $D q, B$, and $C$. Comment on these results. Comment on any
remaining features in the spectrum. Why does the broad spin-allowed band around $19,200 \mathrm{~cm}^{-1}$ appear structured?
4. The visible spectrum of $\mathrm{VCl}_{6}^{4-}$ is strongly temperature dependent (see below). The positions of the peak maxima at 77 K are $7,200 \mathrm{~cm}^{-1}, 11,700 \mathrm{~cm}^{-1}$, and $19,100 \mathrm{~cm}^{-1}$.

a.) Assign the bands in this spectrum.
b.) Account for the temperature dependence of this spectrum.
5. a.) Read Steinfeld, J.I. Molecules and Radiation: An Introduction to Modern Spectroscopy; MIT Press, 1985, 2nd Edition, Chapter 1.
b.) The ability to predict the relative intensities of electronic transitions available to molecular system often proves to be a useful tool when assigning an absorption spectrum. Selection rules derived from quantum mechanical arguments provide a means of doing just that. However, it is important to remember that selection rules for a particular molecule in question are only as reliable as the wavefunctions and approximations used to derive them. This problem will deal with the derivation of selection rules for a hydrogen atom in a beam of plane polarized light. The methodology used here can be extended to molecular systems as well.

A development of the equations describing the interaction of an atomic or molecular system with the time-dependent electric and magnetic fields of an incident light beam usually begins with Fermi's golden rule:

$$
\begin{equation*}
\left.\left.P_{o j}=\frac{2 \pi}{\hbar^{2}}|\langle j| \hat{G}| o\right\rangle\right\rangle^{2} \boldsymbol{\varphi}_{o j} \tag{1}
\end{equation*}
$$

(Those not familiar with this relation should consult Saxon's Elementary Quantum Mechanics $2^{\text {nd }}$ Edition,(1968), p. 208). By solving Maxwell's equations along with the classical Hamiltonian for a charged particle moving in an electric and magnetic field it may be shown that the time-dependent perturbation found in equation (1) can be written as:

$$
\begin{equation*}
\hat{G}=\sum_{\eta} \frac{i \hbar Q_{\eta}}{M_{\eta} c} \vec{A}_{\eta} \cdot \nabla_{\eta} \tag{2}
\end{equation*}
$$

where $\vec{A}_{\eta}$ is the vector potential produced by the time-dependent fields found in the incident radiation. (See for example Bohm, D. Quantum Theory; Prentice-Hall, 1951, pp. 321-322, 433-437).

$$
\begin{equation*}
\overrightarrow{A_{\eta}}=A(\boldsymbol{\omega}) \vec{u} \exp \left(i \frac{\boldsymbol{\omega}}{c} \vec{k} \cdot \vec{r}\right)+A(\boldsymbol{\omega}) \vec{u} \exp \left(-i \frac{\omega}{c} \vec{k} \cdot \vec{r}\right) \tag{3}
\end{equation*}
$$

Here $\vec{k}$ is the wave vector pointing in the direction of the propagation of the light wave and $\vec{u}$ is the unit vector pointing in the direction of the oscillating electric field. If the wavefunctions $j$ and $o$ are taken to be Born-Oppenheimer functions, then the sum over nuclear coordinates in equation (2) reduces to a sum over electronic coordinates multiplied by some Frank-Condon factors. Using this idea and these equations we have:

$$
\begin{equation*}
\left.P_{o j}=\frac{2 \pi}{\hbar^{2}}\left|\langle\tilde{j}| \sum_{n} A_{\omega} \vec{u} \exp \left(i \frac{\boldsymbol{\omega}}{c} \vec{k} \cdot \vec{r}\right) \cdot \nabla_{n}\right| \tilde{o}\right\rangle\left.\right|^{2} \boldsymbol{\varphi}_{o j} \tag{4}
\end{equation*}
$$

Here the index $n$ runs over all electronic coordinates. Using equation (4) as a starting point derive selection rules for electric dipole, magnetic dipole, and electric quadrupole allowed electronic transitions of the form $(n, l, m) \rightarrow(n, \tilde{l}, \tilde{m})$ in a hydrogen atom for light traveling in the $z$ direction and polarized in the $x$ direction. Start by expanding the exponential in equation (4) as a series keeping the first two terms. The following commutation relations will help you:

$$
\begin{align*}
& (H, x)=\frac{-\hbar^{2}}{m} \frac{\partial}{\partial x}  \tag{5}\\
& (H, x z)=\frac{-\hbar^{2}}{m}\left(x \frac{\partial}{\partial z}+z \frac{\partial}{\partial x}\right) \tag{6}
\end{align*}
$$

6. The Fe atom in the protein rubredoxin is thought to reside in a roughly tetrahedral environment consisting of four mercaptide $S$ atoms. The UV/Vis spectra of ferric and ferrous rubredoxin are dominated by charge transfer bands. The $d-d$ bands were located in the near IR by Eaton and Lovenberg (JACS 1970, 92, 7195-7198). Read this paper and answer the following questions:
a.) Briefly describe why circular dichroism is as useful as absorption spectroscopy in locating the ligand field bands in this case (see Drago p. 123). Explain the assignment of the band at $6250 \mathrm{~cm}^{-1}$.
b.) The authors state that the other spectral data indicate that the Fe site symmetry may be less than $T_{d}$. Assuming a distortion leading to $D_{2 d}$ symmetry can occur, how will the $d$ orbitals split in this lower symmetry environment? How many excited states would you expect? A transition has been detected in Mossbauer experiments that does not
correspond to an iron nuclear spin flip $\left(850 \mathrm{~cm}^{-1}\right)$. Which symmetry do you think is present in this protein? Explain.
7. The first two spin-allowed $d$ - $d$ transitions in three octahedral $d^{6}$ low-spin cobalt(III) complexes have been reported at the following positions:

| complex | $\mathrm{V}_{1}\left(\mathrm{~cm}^{-1}\right)$ | $\mathrm{V}_{2}\left(\mathrm{~cm}^{-1}\right)$ |
| :---: | :---: | :---: |
| $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ | 17,000 | 25,000 |
| $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ | 21,000 | 29,000 |
| $\mathrm{Co}(\mathrm{CN}) 6^{3-}$ | 32,100 | 38,500 |

Using the appropriate Tanabe-Sugano diagram in Figgis, predict the following transitions:

$$
{ }^{1} A_{l g} \rightarrow{ }^{3} A_{l g} ;{ }^{1} A_{l g} \rightarrow{ }^{3} T_{2 g} ;{ }^{1} A_{l g} \rightarrow{ }^{5} T_{2 g}
$$

Careful examination of a 3 mm thick single crystal of $\mathrm{K}_{3} \mathrm{Co}(\mathrm{CN})_{6}$ reveals a band at $26,000 \mathrm{~cm}^{-1}, \varepsilon=0.25$. Assign this band and obtain a value for $C$ which fixes the $C / B$ ratio for low-spin $\mathrm{Co}(\mathrm{III})$. Recalculate the positions of the three spin-forbidden transitions mentioned above for all three complexes. Would you expect to be able to observe more than one of these transitions? Appropriate strong-field energy expressions may be found in Table A29 of Griffith (ignore configuration interactions). Finally draw an energy level diagram illustrating how the three configurations $\left(t_{2 g}{ }^{6} ; t_{2 g}{ }^{5} e_{g} ; t_{2 g}{ }^{4} e_{g}{ }^{2}\right)$ split into their ligand field states for hexacyanocobaltate and draw the transitions corresponding to the bands discussed above.
8. Gillespite is a rare silicate mineral which has figured prominently in the development of mineral spectroscopy. Read the paper by Burns, Clark and Stone (Inorg. Chem. 1966, 5, 1268-1272) and answer the following questions:
a.) Derive all of the possible spin-allowed electronic transitions from the ground state.
b.) Assume it is reasonable to consider only the local environment of the iron site and determine the symmetries of the $\mathrm{FeO}_{4}$ vibrations. Do you think this assumption reasonable?
c.) Derive the assignments and polarizations which are reported in Table II of the paper.
9. In addition to an absorption spectrum, the emission spectrum of a metal complex yields useful information about transitions between ground states and low-lying excited states. Emission from a transition metal complex with an unfilled $d$ shell generally occurs from the lowest electronic excited state in the molecule or from those states that can achieve a significant Boltzmann population relative to the lowest excited state. In problem 2 of this set, the absorption spectra of $\mathrm{Cr}(\mathrm{III})$ complexes were discussed. In this problem the absorption and emission behavior of octahedral $\mathrm{Cr}(\mathrm{III})$ complexes will be linked together by potential energy surface considerations. Background material may be found in N.J. Turro Modern Molecular Photochemistry, pp. 52-96.
a.) Excitation from the ${ }^{4} A_{2 g}$ ground state into one of the spin-allowed ${ }^{4} T_{\mathrm{ng}}$ excited states is followed by rapid internal conversion and vibrational relaxation into the zeroth vibrational level of the ${ }^{4} T_{2 \mathrm{~g}}$ term. From this point, two main photophysical processes occur, namely fluorescence or intersystem crossing (ISC) into the ${ }^{2} E_{\mathrm{g}}$ term from which phosphorescence is observed. This emission is not Stokes shifted; it overlaps the very weak corresponding absorption band. This leads to an unusual situation in that the fluorescence is found to the red of the phosphorescence. The situation is illustrated in the following Jablonski diagram:


Typical spectra are shown on the next page.


Absorption (-, 298 K ) and emission $(--, 77 \mathrm{~K})$ spectra of $\left[\mathrm{Cr}(\text { urea })_{6}\right]^{3+}$

Construct qualitative plots of energy vs. Q (a totally symmetric nuclear coordinate) in which the intersections, energy gaps and widths of the PE surfaces for the ${ }^{4} A_{2 g},{ }^{4} T_{2 g},{ }^{2} E_{g}$, and ${ }^{4} T_{1 g}$ terms are illustrated. Keeping in mind that each $D q / B$ value in a Tanabe-Sugano diagram corresponds to a different set of nuclear coordinates, provide plots for three
cases: (a) $D q / B<2.1$; (b) $D q / B=2.1$; (c) $D q / B>2.1$. Use the appropriate TanabeSugano diagram in Figgis.
b.) The luminescence behavior of some $O_{h} \mathrm{Cr}(\mathrm{III})$ complexes is tabulated below (energy in $\mathrm{cm}^{-1}$ ). Discuss the data with regard to the spectrochemical series and your plots in part a).

| $\overline{\mathrm{v}}_{\text {max }}\left({ }^{4} A_{2 \mathrm{~g}} \rightarrow{ }^{4} T_{2 \mathrm{~g}}\right)$ | $\bar{v}_{\text {max }}\left({ }^{4} A_{2 \mathrm{~g}} \rightarrow{ }^{2} E_{2 \mathrm{~g}}\right)$ | $\underline{\bar{v}_{0-0}(\text { phos })}$ | $\overline{\mathrm{v}}_{\text {max }} \text { (fluor ) }$ |
| :---: | :---: | :---: | :---: |
| 13,060 | 14,480 | -- | 11,600 |
| 14,900 | 15,700 | -- | 12,830 |
| 16,150 | 14,350 | 14,240 | 12,550 |
| 20,800 | ? | 13,420 | -- |
| 17,500 | 14,350 | 14,390 | -- |
| 21,550 | 15,300 | 15,120 | -- |
| 23,800 | 13,700 | 13,720 | -- |
| 26,600 | 12,470 | 12,430 | -- |

c.) Read the paper by Kenney, Clymire and Agnew (J. Am. Chem. Soc. 1995, 117, 16451646), and summarize the interpretation of the spectrum reported in Figure 1. Draw an energy level diagram as a function of pressure illustrating this situation.
10. Substitution reactions of low-spin Co(III) complexes generally proceed very slowly. $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ is a striking exception. Taube and coworkers suggested that the high-spin term ${ }^{5} T_{2 g}$ should be substitution labile and thermally accessible. In order to ascertain whether this is reasonable, the energy gap between the ${ }^{l} A_{1 g}$ and ${ }^{5} T_{2 g}$ must be determined (see the potential energy surfaces below).


Potential energy surfaces of Co (III).
a.) What is the problem with using straightforward ligand field analysis to find this energy difference? What is the verticle transition energy in terms of ligand field parameters ( $\mathrm{E}_{\mathrm{FC}}$ )?
b.) Experimentally observed splittings in the electronic origin of the ${ }^{3} T_{1 g}$ may be used to estimate the position of the ${ }^{5} T_{2 \mathrm{~g}}$ potential energy surface (Wilson and Solomon JACS 1980, 102, 4084-4095). The position of this surface may also be found using the following equation:

$$
\left[\frac{\text { slope }{ }^{5} T_{2 \mathrm{~g}}}{\text { slope }{ }^{3} T_{1 \mathrm{~g}}}\right]^{2}=\frac{\mathrm{S}_{a_{1 \mathrm{~g}}}\left({ }^{5} T_{2 \mathrm{~g}}\right)}{\mathrm{S}_{a_{1 \mathrm{~g}}}\left({ }^{3} T_{1 \mathrm{~g}}\right)}
$$

where slope is the slope of the curve on the Tanabe Sugano diagram and the quantity S is the Huang-Rhys factor for the normal coordinate of $a_{1 \mathrm{~g}}$ symmetry in the indicated state.

$$
\mathrm{S}=\frac{\mathrm{K}(\Delta \mathrm{Q})^{2}}{2 \hbar \omega}
$$

The Tanabe-Sugano slope of the quintet term is twice that of the triplet term. It is then assumed that the force constant for the ${ }^{5} T_{2 \mathrm{~g}}$ totally symmetric vibration is $\mathrm{K}^{*}=\alpha \mathrm{K}$ where K is the ground state value and $\alpha$ varies from 0 to 1 . Locating the quintet surface now reduces to a problem in analytical geometry.

$$
\begin{aligned}
& \mathrm{E}\left({ }^{1} A_{1 g}\right)=\frac{1}{2} \mathrm{KQ}^{2} \\
& \mathrm{E}\left({ }^{5} T_{2 g}\right)=\mathrm{E}_{0}+\frac{1}{2} \mathrm{~K}^{*}\left(\mathrm{Q}-\mathrm{Q}_{0}\right)^{2}
\end{aligned}
$$

E $\mathrm{E}_{\mathrm{FC}}$ for the ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{5} T_{2 \mathrm{~g}}$ is just $\mathrm{E}\left({ }^{5} T_{2 \mathrm{~g}}\right)$ evaluated at $\mathrm{Q}=0$. Substituting into the expression for $\mathrm{E}_{\mathrm{FC}}$ the parameters $\mathrm{Dq}, B$ and $C$, what is the separation of the minima of the ground state and the first quintet state potential energy surfaces? Let $\hbar \omega=357 \mathrm{~cm}^{-1}$. The reflectance spectrum of $\mathrm{CsCo}\left(\mathrm{SO}_{4}\right)_{2} \cdot 12 \mathrm{H}_{2} \mathrm{O}$ yields $\mathrm{Dq}=2080 \mathrm{~cm}^{-1}, B=513 \mathrm{~cm}^{-1}$, and $C$ $=4250 \mathrm{~cm}^{-1} . \quad \mathrm{S}_{a_{1 \mathrm{lg}}}\left({ }^{3} T_{\mathrm{lg}}\right)$ can be assumed to be 2.5 from Solomon's work. Using this experimental data, calculate the energy gap $\mathrm{E}_{0}$. Estimate the activation energy for the spin crossover process in $\mathrm{kcal} /$ mole.
11. From analysis of the emission spectrum of $\mathrm{K}_{3} \mathrm{Co}(\mathrm{CN})_{6}$, Hipps and Crosby concluded that the maximum of the ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{3} T_{1 \mathrm{~g}}$ transition in absorption to be at $20,300 \mathrm{~cm}^{-1}$. The emission peak at $14,000 \mathrm{~cm}^{-1}$ was attributed to the ${ }^{3} T_{1 \mathrm{~g}} \rightarrow{ }^{1} A_{1 \mathrm{~g}}$ transition.

a.) Is the predicted $20,300 \mathrm{~cm}^{-1}$ band consistent with the expected reduction in the Racah parameter $C$ from the free ion value of $5120 \mathrm{~cm}^{-1}$ ? Explain. If not, at approximately what energy would you expect this transition?
b.) IR studies indicate that the $a_{1}(\mathrm{Co}-\mathrm{C})$ stretch occurs at $414 \mathrm{~cm}^{-1}$. Discuss the above spectrum in this context.
c.) Discuss the significance of the ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{3} T_{1 \mathrm{~g}}$ transition with regard to molecular geometry and ligand field parameters $\mathrm{Dq}, B$ and $C$.
d.) The absorption spectrum of an excited state offers an interesting view of the energy level pattern of a molecule. The hexacyanocobaltate ion gives rise to a structured $d-d$ transient absorption spectrum obtained directly after laser excitation of the ground state system. The spectrum is shown on the next page. From Griffith table A25, determine the energies of the relevant excited states. Draw an energy level diagram illustrating these levels and the impact of configuration interaction on their energies. Interpret the spectrum.

12. The previous problem dealt with the structured emission spectrum of hexacyanocobaltate. Luminescence spectra are appropriate for investigation of vibrational progressions in electronic transitions, since they can be measured with high sensitivity. The Frank-Condon principle may be used to evaluate the change in molecular geometry which accompanies an electronic transition. Such a vibronic intensity analysis yields important information such as the excited-state geometry and excited-state force constants. In this problem you will carry out a FC analysis of the hexacyanocobaltate emission spectrum.
a.) Background material:

1. C. J. Ballhausen Molecular Electronic Structures of Transition Metal Complexes, sec. 4.7.
2. S. E. Schwartz J. Chem. Ed. 1973, 50, 608-610.
3. G. Herzberg Spectra of Diatomic Molecules, chap. 4.
4. M.A. Hitchman Trans. Met. Chem. 1985, 9, 1.
b.) The theory outlined below derives from work of Ansbacher (Z. Naturforsh. 1959, 14a, 889) and Henderson and co-workers (J. Chem. Phys. 1964, 41, 580).

The vibronic emission intensities are given by:

$$
\mathrm{I}_{v, \mathrm{v}^{*}}=\left.\frac{64}{3} \frac{\pi^{4}}{h^{4}} \mathrm{cN}_{v} \mathrm{E}_{v, \mathrm{v}^{*}}^{4} \mathrm{R}_{\mathrm{e}}^{2}\left\langle\psi_{\mathrm{v}}\right| \psi_{v^{*}}\right|^{2}
$$

Here $\mathrm{E}_{v, v^{*}}$ is the energy of the electronic transition between vibrational states with the quantum numbers $v$ and $v^{*}$ for the excited and ground vibrational states respectively. $\mathrm{R}_{\mathrm{e}}$ is the average value of the electronic transition dipole moment, and the integrals are the Frank-Condon overlap integrals hereafter called $\mathrm{R}_{v, v^{*}}$, and N is the number of molecules in the initial state. In practice the relative intensities can be related via the following equation.

$$
\frac{\mathrm{I}_{0, \mathrm{n}}}{\mathrm{I}_{0,0}}=\left[\frac{\mathrm{E}_{0, \mathrm{n}}}{\mathrm{E}_{0,0}}\right]^{4}\left[\frac{\mathrm{R}_{0, \mathrm{n}}}{\mathrm{R}_{0,0}}\right]^{2}
$$

The frequency dependence for emission is given by:

$$
E_{0, n}=E_{0,0}-n h \nu_{0}
$$

where $\mathrm{E}_{0,0}$ is the energy of the electronic transition between the lowest vibrational states of the excited and ground electronic states, and $v_{0}$ is the eigenfrequency of the oscillator in the electronic ground state. The most useful relations for the vibration overlap integrals are given by:

$$
R_{0,0}=\frac{2 \delta}{\sqrt{1+\delta^{2}}} \exp \left(-\frac{\rho^{2}}{2}\right)
$$

$$
\begin{gathered}
\mathrm{R}_{0, \mathrm{n}+1}=\frac{-2 \mathrm{D} \delta \mathrm{R}_{0, \mathrm{n}}-\sqrt{2 \mathrm{n}}\left(\delta^{2}-1\right) \mathrm{R}_{0, \mathrm{n}-1}}{\left(1+\delta^{2}\right) \cdot \sqrt{2(\mathrm{n}+1)}} \\
\delta=\left(\frac{v_{0}}{v_{0}^{*}}\right) \\
\mathrm{D}=\mathrm{C} \Delta \mathrm{~S} \cdot \sqrt{\mu v_{0}^{*}} \\
\rho=\frac{\mathrm{D}}{\sqrt{1+\delta^{2}}}
\end{gathered}
$$

When the displacement $\Delta \mathrm{S}$ of the minimum of the PE surface of the excited state along the stretching coordinate $S$ is expressed in angstroms, the vibrational energy in wavenumbers and the masses of the ligands in amu, the constant C takes on the value 0.1722 .

The distortions calculated from FC analysis are distortions in the normal coordinate whose vibrations comprise the progression in the spectrum. For the totally symmetric stretch in an octahedral complex, the change in each metal ligand bond length is $\frac{1}{\sqrt{6}} \Delta \mathrm{~S}$. $\Delta \mathrm{S}$ is normally determined by calculating the vibronic band shape for different values of $\Delta \mathrm{S}$ and seeing which value most satisfactorily reproduces the observed spectrum.
c) The energy of the vibronic peaks are given below:
$\mathrm{E}_{0, \mathrm{n}}\left(\mathrm{cm}^{-1}\right)$

16,650
16,244
15,857

15,439
15,048
14,660
14,267
13,852
13,462

The origin for this progression is located at $17,020 \mathrm{~cm}^{-1}$. You may assume $\frac{v_{0}}{v_{0}^{*}}=0.65$.
Calculate the vibronic intensity distribution and plot the intensities for the following values of $\Delta \mathrm{S}$ : (a) 0.05 , (b) 0.3 and (c) $0.5 \AA$. It may be useful to write a simple computer program to do these calculations. From a comparison of these distributions and the known spectrum determine the distortion of the metal ligand bonds in the excited state.
d) What does this distortion imply with respect to excited state substitution reactions of these kinds of complexes? You have fit the spectrum using the symmetric stretching mode; what other mode would you expect to be involved?
e) Recall the feature around $26,000 \mathrm{~cm}^{-1}$ observed in the absorption spectrum of a thick crystal of $\mathrm{K}_{3} \mathrm{Co}(\mathrm{CN})_{6}$ (problem 7). Estimate a value for the $\mathrm{E}_{0,0}$ of the emission band.

How does this change your result found in c)? Comment on any changes in the quality of fit.
13. This problem deals with the absorption spectrum of the square planar complex $\mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-}$.
a.) The solution spectrum is composed mainly of charge transfer transitions and has been interpreted by Gray and Ballhausen (JACS 1963, 85, 260-264) using an MO scheme that predicts the same ordering of terms as does the ligand field theory for a strong tetragonal field.


What happens to this ordering if a weak ligand field treatment is used? Draw diagrams illustrating the effect of weak and strong tetragonal distortions on the energy levels and terms. The $d$ - $d$ transitions and proposed assignments for a single crystal of $\mathrm{BaNi}(\mathrm{CN})_{4} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ are given below.

| $\mathrm{v} \mathrm{cm}^{-1}$ | $\varepsilon$ | Assignment |  |
| :---: | :---: | :---: | :---: |
| 22,400 | 2 | ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{1} A_{2 \mathrm{~g}}$ | $b_{2 \mathrm{~g}} \rightarrow b_{1 \mathrm{~g}}$ |
| 24,000 | 50 | ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{1} B_{1 \mathrm{~g}}$ | $a_{1 \mathrm{~g}} \rightarrow b_{1 \mathrm{~g}}$ |
| 27,000 | 100 | ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{1} E_{\mathrm{g}}$ | $e_{\mathrm{g}} \rightarrow b_{1 \mathrm{~g}}$ |

b.) Determine the symmetries of the normal vibrations in the $\mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-}$ unit. Determine the selection rules for the $d-d$ transitions in the $\sigma$ and $\pi$ polarizations.
c.) The square planar anions in crystals of tetracyanonickelate salts typically stack to form a nearly linear chain of nickel atoms. This allows for the determination of the absorption spectrum of the crystal perpendicular and parallel to the stacking axis. The band at $23,000 \mathrm{~cm}^{-1}$ is observed only in the $\pi$ polarization. This indicates that the $D_{4 \mathrm{~h}}$ selection rules deduced in part c) may not be appropriate. Read the paper by Ballhausen, Bjerrum, Dingle, Eriks and Hare (Inorg. Chem. 1965, 4, 514-518). Here cogent arguments are advanced to the effect that the $D_{4 \mathrm{~h}}$ excited states ${ }^{1} B_{2 \mathrm{~g}}$ and ${ }^{1} E_{\mathrm{g}}$ are unstable with respect to distortion to the $D_{2 \mathrm{~d}}$ states ${ }^{1} B_{2}$ and ${ }^{1} E_{1}$, in $D_{4 \mathrm{~h}}$ symmetry. The $B_{2 \mathrm{u}}$ vibration will transform a $D_{4 \mathrm{~h}}$ molecule into a $D_{2 \mathrm{~d}}$ molecule. The $23,000 \mathrm{~cm}^{-1}$ must therefore terminate in a ${ }^{1} B_{1 \mathrm{~g}} \otimes$ ? excited state. Fill in the ? and explain your answer. Work out selection rules for the ${ }^{1} A_{1 \mathrm{~g}} \rightarrow{ }^{1} B_{2}$ and ${ }^{1} A_{1 g} \rightarrow{ }^{1} E$ transitions. Observe the symmetry change. Finally draw qualitative PE curves for the ${ }^{1} A_{1 \mathrm{~g}},{ }^{1} A_{2 \mathrm{~g}},{ }^{1} B_{2}$, and ${ }^{1} E$ terms on a plot of energy vs. Q. Given the appearance of the $27,000 \mathrm{~cm}^{-1}$ band, is this assignment convincing?
d) From the band width at half max. and the band extinction coefficient one finds an oscillator strength of $5 \times 10^{-6}$ for the transition at $22,400 \mathrm{~cm}^{-1}$. Based on the assignment given in part a), is this transition allowed by a magnetic dipole mechanism?
e) The band at $22,400 \mathrm{~cm}^{-1}$ is only present in the spectrum of the barium salt and absent in spectra of the strontium and calcium salts. It has been proposed that this feature may arise from a spin-forbidden $d$ - $d$ transition. Does this explanation seem plausible? The band at $22,400 \mathrm{~cm}^{-1}$ is temperature dependent, red-shifting $\left(\sim 300 \mathrm{~cm}^{-1}\right)$ and broadening with decreasing temperature from 295 to 80 K . When crystals are doped with
$\operatorname{Pt}(\mathrm{CN})_{4}{ }^{2-}$ anions, the band also red-shifts $\left(\sim 500 \mathrm{~cm}^{-1}\right)$ and broadens. Below $90 \%$ nickel, the feature is no longer resolved. Given the structural data summarized below, propose an alternative assignment for this transition. (Hint: consider the report by Miskowski and coworkers (Inorg. Chem. 1994, 2799).)

| Crystal | $\mathrm{Ni} \cdots \mathrm{Ni}$ Distance | C-Ni..NNi-C Torsion |
| :---: | :---: | :---: |
| $\mathrm{SrNi}(\mathrm{CN})_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ | 3.64 Å | 0 |
| $\mathrm{CaNi}(\mathrm{CN})_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ | 3.39 Å | 27 |
| $\mathrm{BaNi}(\mathrm{CN})_{4} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ | 3.36 Å | 45 |

