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The Influence of Vibronic Interactions on the Chiroptical Spectra of Dissymmetric Pseudo Tetragonal Metal Complexes

Frederick S. Richardson, Gary Hilmes, Jacqueline J. Jenkins
Department of Chemistry, University of Virginia at Charlottesville

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The influence of vibronic interactions on the chiroptical spectra associated with a threesome of nearly degenerate electronic excited states in a dissymmetric molecular system is examined on a formal theoretical model. The model considers two vibrational modes to be effective in promoting pseudo Jahn-Teller (PJT) type interactions between the three closely spaced electronic excited states. Formal expressions are developed for the rotatory strengths of individual vibronic levels derived from the coupled electronic states. Two mode (vibrational)-three state (electronic) vibronic Hamiltonians are constructed (basis set size, 63-108, depending upon interaction parameters used) and diagonalized for a large number of different parameter sets representative of various vibronic coupling strengths, electronic energy level spacings, oscillator (vibrational mode) frequencies, and electronic rotatory strengths. Diagonalization of these vibronic Hamiltonians yields vibronic wave functions and energies which are then used to calculate "rotatory strength spectra" for the model system. The calculated results demonstrate the profound influence which vibronic interactions of the PJT type may have on the sign patterns and intensity distributions within the rotatory strength spectrum associated with a set of nearly degenerate electronic states. The implication of these results for the interpretation of circular dichroism spectra of chiral transition metal complexes with pseudo tetragonal symmetry are discussed.

Key words: Metal complexes – Chiroptical spectra, influence of vibronic interactions on ~

1. Introduction

The use of chiroptical properties to probe the stereochemical and electronic features of dissymmetric transition metal complexes has recieved a great deal of attention over the past fifteen years. The circular dichroism (CD) spectra of metal complexes representing many structural classes (classified with respect to coordination number, the size, number, and distribution of chelate rings, donor atom type, and number of donor sites per ligand molecule) have been reported and spectra-structure relationships have been proposed for a number of these systems. Although the CD associated with the pure ligand-ligand transitions as well as the ligand-metal charge transfer (CT) transitions have been studied for many metal complexes, it is generally the CD spectra associated with the metal ion *d-d* or ligand-field transitions which are used as diagnostic probes of structure or structural changes.

The spectra-structure relationships commonly employed in interpreting the CD of transition metal complexes require the assignment of the observed CD bands to specific electronic *d-d* transitions on the metal ion. Having identified a specific CD band or set of bands with a specific electronic transition or set of transitions, one may then apply rules which relate the sign and, sometimes, the magnitude of the observed CD to specific structural features of the complex. These rules may be based entirely on correlations between empirically derived spectroscopic and structural data, or on theoretical models which relate the fundamental stereochemical and electronic structural properties of the system to the spectroscopic observables via quantum mechanical representations. In most instances, the theoretical models offered as bases fpr the observed spectra-structure relationships either have neglected the influence of vibronic interactions or have treated vibronic interactions in a heuristic or qualitative way. In some cases, "vibronic effects" have been invoked in a purely *ad hoc* way to "explain" apparent anomalies in the observed CD spectra.

Vibronic interactions play a particularly important role in determining the spectroscopic properties of *d-d* transitions in transition metal complexes which are nearly centrosymmetric. In these systems, the non-centrosymmetric components of the ligand field are generally small and are relatively ineffective in mixing the gerade *d-d* states with ungerade states which will lead to observable absorption intensity in electric dipole radiation. In most cases, the mechanism by which the ligand-field transitions gain intensity is through vibronically induced mixing with ungerade states. Generally the gerade ligand-field states and the ungerade states with which they can mix via a vibronic mechanism are sufficiently separated in energy that the vibronic coupling energy can be assumed small compared to the energy separation. Under these conditions the socalled Herzberg-Teller (H-T) vibronic coupling theory can be applied to obtain a reasonably reliable representation of the vibronically-induced intensity mechanism. The adiabatic approximation is assumed in the H-T theory so that electronic motion is fully correlated to instantaneous nuclear positions.

When the ratio of vibronic coupling energy to energy separation between two interacting electronic states is greater than or approaches unity, the adiabatic approximation is no longer valid and the H-T theory is not applicable. Under these circumstances, the nuclear motion is modified by electronic motions leading to a deformation of the potential energy surface associated with the coupling mode (*s*). In this case a non-adiabatic representation is required. Manifestations of this kind of vibronic coupling are the Jahn-Teller (JT) and pseudo Jahn-Teller (PJT) effects arising, respectively, in the presence of degenerate and nearly degenerate electronic states [1].

Weigang and coworkers [2] have worked out in some detail the influence of H-T type vibronic coupling on the chiroptical properties of optically active molecules. Recently, we have been concerned with the consequences of JT and PJT effects on the chiroptical properties of optically active systems having degenerate or nearly degenerate electronic states [3–5]. The work described herein is related to the latter problem in pseudo-tetragonal metal complexes.

It is quite common in metal complexes of pseudo-tetragonal symmetry to find several *d-d* states which lie within 1000–4000 cm^{-1} of each other in energy. Furthermore, the vibrational modes localized in the ML_4 or ML_6 clusters of such systems ($M =$ metal ion and $L =$ donor atom of ligand) are generally expected to be quite effective in promoting mixing among these nearly degenerate or closely spaced electronic states. In the present study we consider a model having just C_2 symmetry in which there are three closely spaced *d-d* electronic states, two of which are nontotally symmetric with respect to the C_2 operation (symmetry type B) and one of which is totally symmetric (symmetry type A) with respect to the C_2 operation. The A and B states are assumed to couple through two different vibrational modes, each of which is nontotally symmetric. We shall assume that transitions from the ground state to each of the three excited states are inherently optically active, gaining their rotatory strengths from the dissymmetric components of the ligand field. In our model system, only vibronic interactions between the three closely spaced electronic excited states are considered and the *net* rotatory strength associated with transitions to these three states is assumed to be invariant to vibronic coupling. The only consequences of the vibronic interactions, then, are redistributions of rotatory strength of CD intensity among the vibronic levels derived from the three interacting electronic states, and alterations in the vibronic energy level spectrum. Since the net or total rotatory strength associated with the three electronic excited states remains unaffected by the vibronic interactions introduced in our model, the total integrated area of the associated CD bands must also be invariant to the vibronic interactions. However, the shapes and profiles of the CD bands are very sensitive to the strength and nature of the vibronic interactions and in the presence of strong vibronic couplings it becomes impossible to interpret the CD spectrum in terms of individual bands originating with transitions to specific electronic states. In these cases, spectra-structure relationships requiring assignments of CD bands to specific electronic transitions can not be used.

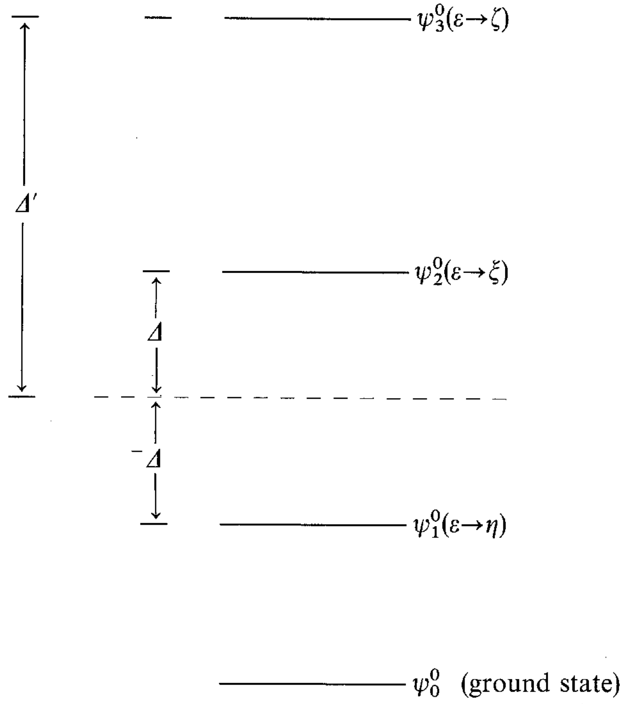
2. Theory

2.1. Basic Model

As a model system we consider a transition metal complex which has near tetragonal (D_{4h}) or digonal dihedral (D_2) symmetry but whose actual symmetry is just C_2. We shall assume that the ξ, η, and ζ *d*-orbitals of the metal ion all lie within an energy interval of $\sim 4000\,\mathrm{cm}^{-1}$ in the complex, and that the ε *d*-orbital lies highest in energy while the θ *d*-orbital lies lowest. Restricting our attention to d^9 and low-spin d^8 systems, the *d-d* transitions of interest will be: $\theta \rightarrow \varepsilon$, $\xi \rightarrow \varepsilon$, $\eta \rightarrow \varepsilon$, and $\zeta \rightarrow \varepsilon$. The symmetries of the respective *d*-orbitals in the D_{4h}, D_2, and C_2 point groups are:

	ε	θ	ξ	η	ζ
D_{4h}	B_{1g}	A_{1g}	E_g	E_g	B_{2g}
D_2	A	A	B_2	B_3	B_1
C_2	A	A	B	B	A

Given the near degeneracy of the ξ, η, and ζ levels in our model system, we shall assume that the states formed by the $\xi \rightarrow \varepsilon$, $\eta \rightarrow \varepsilon$, and $\zeta \rightarrow \varepsilon$ excitations are nearly degenerate and subject to strong PJT interactions. The electronic energy levels of interest in our study, then, are the following:



In this diagram the energy zero is chosen midway between the $\psi_1^0(\varepsilon\rightarrow\eta)$ and $\psi_2^0(\varepsilon\rightarrow\xi)$ excited states. The wave functions ψ_0^0, ψ_1^0, ψ_2^0, and ψ_3^0 are assumed to be solutions to the Schroedinger equation,

$$\mathscr{h}_e^0\psi_i^0=E_i^0\psi_i^0 \tag{1}$$

where $\mathscr{h}_e^0$ is that part of the full electronic Hamiltonian which reflects the D_2 symmetry of the model system with the nuclei clamped in the equilibrium configuration of the ground electronic state. The wave functions ψ_i^0, then, may be classified according to their transformation properties under the symmetry operations of the D_2 point group.

The complete vibrational-electronic (vibronic) Hamiltonian of the system may be written as,

$$\mathscr{H}(r,Q)=\mathscr{H}_e(r,Q)+\mathscr{T}_n(Q) \tag{2}$$

where $\mathscr{T}_n(Q)$ is the kinetic energy operator for nuclear vibrational motion, $\{r\}$ represents the collection of electron coordinates, $\{Q\}$ represents the collection of nuclear displacement coordinates (measured from the ground state equilibrium configuration), and

$$\mathscr{H}_e(r,Q)=\mathscr{T}_e(r)+V(r,Q) \tag{3}$$

where $\mathscr{T}_e(r)$ is the kinetic energy operator for electrons. The electronic Hamiltonian $\mathscr{H}_e(r, Q)$ reflects the true symmetry (C_2) of the model system. Assuming displacements from the equilibrium geometry, $\{Q\}=0$, are small, the electronic Hamiltonian $\mathscr{H}_e(r, Q)$ may be expanded in a series about $\{Q\}=0$,

$$\mathscr{H}_e(r, Q)=\mathscr{H}_e^0+\sum_a V_a'Q_a+\frac{1}{2}\sum_a\sum_b V_{ab}''Q_aQ_b+\dots \tag{4}$$

where $V_a'=[\partial V(r, Q)/\partial Q_a]_0$, $V_{ab}''=[\partial^2 V(r, Q)/\partial Q_a\partial Q_b]_0$, and a and b label normal coordinates of the system. The term $\mathscr{H}_e^0$ is defined by,

$$\begin{aligned}\mathscr{H}_e^0&=\mathscr{T}_e(r)+V_d^0(D_2)+V_c^0(C_2)\\&=\hbar_e^0+V_c^0\end{aligned} \tag{5}$$

where V_c^0 is that part of the ligand field interaction potential not included in $\hbar_e^0$. $\mathscr{H}_e^0$ has C_2 symmetry, whereas $\hbar_e^0$ has D_2 symmetry. Both $V_d^0(D_2)$ and $V_c^0(C_2)$ are evaluated with the nuclei at their equilibrium positions, $\{Q\}=0$.

We shall assume that two vibrational modes are responsible for PJT interactions within the manifold of states ψ_1^0, ψ_2^0, and ψ_3^0. We shall label these modes as Q_η and Q_ξ. Both of these vibrational modes are nontotally symmetric (B symmetry) in the C_2 point group of the molecular system and they have E_g parentage in the tetragonal D_{4h} point group. The Q_η mode is effective in coupling ψ_2^0 and ψ_3^0, and the Q_ξ mode is effective in coupling ψ_1^0 and ψ_3^0. Considering only linear terms in the expansion of $\mathscr{H}_e(r, Q)$, we may write:

$$\mathscr{H}_e(r, Q)=\mathscr{H}_e^0+V_\eta'Q_\eta+V_\xi'Q_\xi\,. \tag{6}$$

Utilizing Eqs. (5) and (6) we may rewrite $\mathscr{H}_e(r, Q)$ as,

$$\mathscr{H}_e(r, Q)=\hbar_e^0+V_\eta'Q_\eta+V_\xi'Q_\xi+V_c^0\,. \tag{7}$$

In our model we choose the eigenfunctions of $\hbar_e^0$ as zero-order basis functions and treat the terms, $V_\eta'Q_\eta+V_\xi'Q_\xi+V_c^0$, as a perturbation on these functions. We neglect perturbations on the ground state ψ_0^0, and consider only interactions among the three nearly degenerate states ψ_1^0, ψ_2^0, and ψ_3^0. The term V_c^0 will mix ψ_1^0 and ψ_2^0.

2.2. *Vibronic Wave Functions*

The vibronic wave functions for our three-state model system may be expressed as:

$$\begin{aligned}\Phi_n=&\,\psi_1^0\sum_v^N\sum_\nu^N A_{nv\nu}\chi_v(\eta)\chi_\nu(\xi)+\psi_2^0\sum_v^N\sum_\nu^N B_{nv\nu}\chi_v(\eta)\chi_\nu(\xi)\\&+\psi_3^0\sum_v^N\sum_\nu^N C_{nv\nu}\chi_v(\eta)\chi_\nu(\xi)\end{aligned} \tag{8}$$

where,

ψ_1^0, ψ_2^0, ψ_3^0 = zeroth-order electronic wave functions,

$\chi_v(\eta)$ = wave function for perturbing mode Q_η,

$\chi_\nu(\xi)$ = wave function for perturbing mode Q_ξ,

v, ν = vibrational quantum numbers,

n = vibronic quantum number.

These vibronic wave functions are found as eigenfunctions of the Hamiltonian:

$$\mathscr{H} = \mathscr{h}_e^0 + \mathscr{h}_\eta^0 + \mathscr{h}_\xi^0 + V_\eta' Q_\eta + V_\xi' Q_\xi + V_c^0 \tag{9}$$

where $\mathscr{h}_\eta^0$ and $\mathscr{h}_\xi^0$ are harmonic oscillator Hamiltonians for modes Q_η and Q_ξ. The Hamiltonian, $\mathscr{h}^0 = \mathscr{h}_e^0 + \mathscr{h}_\eta^0 + \mathscr{h}_\xi^0$, is diagonal in the basis $\psi_i^0 \chi_v(\eta)\chi_\nu(\xi)$, where $i = 1, 2$, or 3, whereas the interaction operators, $V_\eta' Q_\eta + V_\xi' Q_\xi + V_c^0$, are entirely off-diagonal in this basis.

To obtain the coefficients $A_{nv\nu}$, $B_{nv\nu}$, and $C_{nv\nu}$ in Eq. (8) and thereby determine the vibronic wave functions Φ_n, we diagonalize the Hamiltonian matrix formed from the basis set $\psi_i^0 (i = 1, 2, \text{ or } 3)\ \chi_v(\eta)\chi_\nu(\xi)$ and the Hamiltonian operator given in Eq. (9). The diagonal elements of this matrix may be expressed as:

$$\begin{aligned} H_{ii} &= \langle \chi_v(\eta)\chi_\nu(\xi) | E_i^0 + \mathscr{h}_\eta^0 + \mathscr{h}_\xi^0 | \chi_{v'}(\eta)\chi_{\nu'}(\xi) \rangle \\ &= \left[E_i^0 + \left(V + \frac{1}{2} \right) \hbar\omega(\eta) + \left(\nu + \frac{1}{2} \right) \hbar\omega(\xi) \right] \delta_{vv'} \delta_{\nu\nu'} \end{aligned} \tag{10}$$

where $\omega(\eta)$ and $\omega(\xi)$ are the natural oscillator frequencies of vibrational modes Q_η and Q_ξ in electronic state i. As was noted in the previous section, we set $E_1^0 = -\Delta$, $E_2^0 = \Delta$, and $E_3^0 = \Delta'$. The off-diagonal elements of the Hamiltonian matrix are given by:

$$\begin{aligned} H_{ij} &= \langle \chi_v(\eta)\chi_\nu(\xi) | \alpha_{ij} Q_\eta + \beta_{ij} Q_\xi + \gamma_{ij} | \chi_{v'}(\eta)\chi_{\nu'}(\xi) \rangle \\ &= \alpha_{ij} \langle \chi_v(\eta) | Q_\eta | \chi_{v'}(\eta) \rangle \delta_{\nu\nu'} + \beta_{ij} \langle \chi_\nu(\xi) | Q_\xi | \chi_{\nu'}(\xi) \rangle \delta_{vv'} \\ &\quad + \gamma_{ij} \delta_{vv'} \delta_{\nu\nu'}\,, \end{aligned} \tag{11}$$

where,

$$\begin{aligned} \alpha_{ij} &= \langle \psi_i^0 | V_\eta' | \psi_j^0 \rangle \\ \beta_{ij} &= \langle \psi_i^0 | V_\xi' | \psi_j^0 \rangle \\ \gamma_{ij} &= \langle \psi_i^0 | V_c^0 | \psi_j^0 \rangle\,. \end{aligned}$$

Furthermore, we note that:

$$\langle \chi_v(\eta) | Q_\eta | \chi_{v'}(\eta) \rangle = [(v+1)/2]^{1/2}\,, \quad v' = v + 1 \tag{12a}$$

$$= (v/2)^{1/2}\,, \quad v' = v - 1\,, \tag{12b}$$

$$= 0\,, \quad v' \neq v \pm 1\,, \tag{12c}$$

$$\langle \chi_\nu(\xi) | Q_\xi | \chi_{\nu'}(\xi) \rangle = [(\nu+1)/2]^{1/2}\,, \quad \nu' = \nu + 1\,, \tag{13a}$$

$$= (\nu/2)^{1/2}\,, \quad \nu' = \nu - 1\,, \tag{13b}$$

$$= 0\,, \quad \nu' \neq \nu \pm 1\,. \tag{13c}$$

If Q_η and Q_ξ are expressed as dimensionless quantities [as implied by Eqs. (12) and (13)], then α_{ij} and β_{ij} are expressed in energy units. By symmetry we note that $\alpha_{12} = \alpha_{13} = 0$, $\beta_{12} = \beta_{23} = 0$, and $\gamma_{13} = \gamma_{23} = 0$. The only nonvanishing interaction matrix elements between electronic states are: $\alpha_{23} = \alpha$, $\beta_{13} = \beta$, and $\gamma_{12} = \gamma$.

According to Eqs. (10) and (11) and the inherent symmetry constraints, the input parameters required to set up and diagonalize the vibronic Hamiltonian are summarized as follows: $E_1^0 = -\Delta$, $E_2^0 = \Delta$, $E_3^0 = \Delta'$, $\omega(\eta)$, $\omega(\xi)$, α, β, and γ.

Diagonalization of the vibronic Hamiltonian gives us both the energies and the wave functions (8) of the vibronic states derived from the couplet ψ_1^0, ψ_2^0, and ψ_3^0 electronic states.

2.3. Rotatory Strengths

We shall be interested in the rotatory strengths associated with transitions from the ground electronic state ψ_0^0 to the vibronic levels Φ_n derived from the coupled threesome of electronic states, ψ_1^2, ψ_2^0, and ψ_3^0. These rotatory strengths may be expressed as,

$$R_{0\to n}=\mathrm{Im}(\boldsymbol{P}_n\cdot\boldsymbol{M}_n) \tag{14}$$

where,

$$\boldsymbol{P}_n=\langle\psi_0^0\chi_0'(\eta)\chi_0'(\xi)|\hat{\boldsymbol{\mu}}|\Phi_n\rangle\,, \tag{15}$$

$$\boldsymbol{M}_n=\langle\Phi_n|\hat{\boldsymbol{m}}|\psi_0^0\chi_0'(\eta)\chi_0'(\xi)\rangle\,. \tag{16}$$

In Eqs. (15) and (16), $\chi_0'(\eta)$ and $\chi_0'(\xi)$ are ground state oscillator functions for the Q_η and Q_ξ modes, respectively, in the ground electronic state, $\hat{\boldsymbol{\mu}}$ is the electric dipole moment operator, and $\hat{\boldsymbol{m}}$ is the magnetic dipole moment operator. Both $\hat{\boldsymbol{\mu}}$ and $\hat{\boldsymbol{m}}$ are pure electronic operators. Using the explicit form of Φ_n from Eq. (8), we may rewrite Eqs. (15) and (16) as follows:

$$\boldsymbol{P}_n=\sum_v^N\sum_\nu^N S_{ov}(\eta)S_{o\nu}(\xi)[\boldsymbol{P}_1^e A_{nv\nu}+\boldsymbol{P}_2^e B_{nv\nu}+\boldsymbol{P}_3^e C_{nv\nu}]\,, \tag{17}$$

$$\boldsymbol{M}_n=\sum_v^N\sum_\nu^N S_{ov}(\eta)S_{o\nu}(\xi)[\boldsymbol{M}_1^e A_{nv\nu}+\boldsymbol{M}_2^e B_{nv\nu}+\boldsymbol{M}_3^e C_{nv\nu}]\,, \tag{18}$$

where,

$$\boldsymbol{P}_i^e=\langle\psi_0^0|\hat{\boldsymbol{\mu}}|\psi_i^0\rangle\,,\qquad i=1,2,\mathit{or}\ 3$$

$$\boldsymbol{M}_i^e=\langle\psi_i^0|\hat{\boldsymbol{m}}|\psi_0^0\rangle\,,\qquad i=1,2,\mathit{or}\ 3$$

$$S_{ov}(\eta)=\langle\chi_0'(\eta)|\chi_v(\eta)\rangle$$

$$S_{o\nu}(\xi)=\langle\chi_0'(\xi)|\chi_\nu(\xi)\rangle\,.$$

The Franck-Condon overlaps integrals, $S_{ov}(\eta)$ and $S_{o\nu}(\xi)$, may be evaluated from,

v even

$$S_{ov}(\eta)=\left\{\frac{4\omega(\eta)\omega'(\eta)}{[\omega(\eta)+\omega'(\eta)]^2}\right\}^{1/4}\left[\frac{\omega'(\eta)-\omega(\eta)}{\omega'(\eta)+\omega(\eta)}\right]^{v/2}\frac{(-1)^{v/2}(v!)^{1/2}}{2^{v/2}(v/2)!}\,, \tag{19a}$$

$$v\ \text{odd},\quad S_{ov}(\eta)=0, \tag{19b}$$

ν even,

$$S_{o\nu}(\xi)=\left\{\frac{4\omega(\xi)\omega'(\xi)}{[\omega(\xi)+\omega'(\xi)]^2}\right\}^{1/4}\left[\frac{\omega'(\xi)-\omega(\xi)}{\omega'(\xi)+\omega(\xi)}\right]^{\nu/2}\frac{(-1)^{\nu/2}(\nu!)^{1/2}}{2^{\nu/2}(\nu/2)!}\,, \tag{20a}$$

$$\nu\ \text{odd},\quad S_{o\nu}(\xi)=0, \tag{20b}$$

where $\omega'(\eta)$ and $\omega'(\xi)$ are oscillator frequencies in the ground electronic state and $\omega(\eta)$ and $\omega(\xi)$ are excited state oscillator frequencies. Note that if $\omega'(\eta)=\omega(\eta)$ and $\omega'(\xi)=\omega(\xi)$, then $S_{o\upsilon}(\eta)=0$ for $\upsilon\neq0$ and $S_{o\nu}(\xi)=0$ for $\nu\neq0$.

The vibronic dipole and rotatory strengths expressions are summarized by,

$$D_n=|P_n(x)|^2+|P_n(y)|^2+|P_n(z)|^2\,, \tag{21}$$

$$R_n=\mathrm{Im}[P_n(x)M_n(x)+P_n(y)M_n(y)+P_n(z)M_n(z)]\,. \tag{22}$$

To calculate D_n and R_n, one requires $\omega(\eta)$, $\omega'(\eta)$, $\omega(\xi)$, $\omega'(\xi)$, $\boldsymbol{P}^e_1$, $\boldsymbol{P}^e_2$, $\boldsymbol{P}^e_3$, $\boldsymbol{M}^e_1$, $\boldsymbol{M}^e_2$, and $\boldsymbol{M}^e_3$ as well as the set of coefficients $\{A_{n\upsilon\nu}, B_{n\upsilon\nu}, C_{n\upsilon\nu}\}$.

3. Calculations

To investigate the possible influence of vibronic interactions of the PJT type on the chiroptical observables of our model system, we carried out a large number of calculations based on the theoretical model described in Section 2. The input parameters for these calculations were the following: (*a*) electronic state energies, $E^0_1=-E^0_2=-\Delta$ and $E^0_3=\Delta'$; (*b*) vibronic coupling parameters, α and β; (*c*) low-symmetry ligand field potential energy parameter, γ; (*d*) oscillator frequencies, $\omega(\eta)$, $\omega'(\eta)$, $\omega(\xi)$, and $\omega'(\xi)$; and, (*e*) the electronic transition moments, $\boldsymbol{P}^e_1$, $\boldsymbol{P}^e_2$, $\boldsymbol{P}^e_3$, $\boldsymbol{M}^e_1$, $\boldsymbol{M}^e_2$, and $\boldsymbol{M}^e_3$. We shall find it convenient to express Δ, Δ', α, β, and γ in units of $(1/2)\hbar[\omega(\eta)+\omega(\xi)]$, in which case we denote them by $\bar{\Delta}$, $\bar{\Delta}'$, $\bar{\alpha}$, $\bar{\beta}$, and $\bar{\gamma}$. We shall also express $\omega'(\eta)$ in units of $\omega(\eta)$ and $\omega'(\xi)$ in units of $\omega(\xi)$. The electronic dipole transition moments are expressed in arbitrary units as are the vibronic dipole strengths and rotatory strengths.

The "output" of our calculations are: (*a*) vibronic wave functions expressed in the $\psi^0_i(i=1, 2, \text{or } 3)\ \chi_\upsilon(\eta)\chi_\nu(\xi)$ basis; (*b*) vibronic energy levels; (*c*) cartesian components of the vibronic electric and magnetic dipole transition integrals; (*d*) vibronic rotatory strengths and $\sum_n R_n$; (*e*) vibronic dipole strengths and $\sum_n D_n$; and, (*f*) "smoothed" rotatory strength spectra calculated from,

$$\varrho(\omega)=\frac{1}{\lambda}\sum_n R_n\exp[-(\omega-\omega_n)^2/\lambda^2] \tag{23}$$

where λ = bandwidth parameter, ω_n = eigenfrequency of n^{th} vibronic level, R_n = rotatory strength of the n^{th} vibronic level, and ω is a frequency variable. (Note that $\hbar\omega_n$ is measured from $E^0_1+\Delta$ or $E^0_2-\Delta$.) Assuming a Gaussian shape for each vibronic band, the function $\varrho(\omega)$ can be used to simulate (rather crudely) the CD spectrum associated with transitions to the manifold of vibronic states $\{\Phi_n\}$.

In our calculations, $\bar{\Delta}$ was varied from 0 to 2, $\bar{\Delta}'$ was varied from 0 to 15, $\bar{\alpha}$ and $\bar{\beta}$ were varied from 0 to 10 (individually), and $\bar{\gamma}$ was varied from 0 to 5. The ratios, $\omega'(\xi)/\omega(\xi)$ and $\omega'(\eta)/\omega(\eta)$, were varied from 2 to 1 (individually).

The magnetic dipole transition moments, $\boldsymbol{M}^e_1$, $\boldsymbol{M}^e_2$, and $\boldsymbol{M}^e_3$, were not varied. The relative values chosen for them were those expected if the $\psi^0_0\rightarrow\psi^0_1$, $\psi^0_0\rightarrow\psi^0_2$, and $\psi^0_0\rightarrow\psi^0_3$ electronic transitions were pure *d-d* transitions between a d_ε orbital and the d_η, d_ξ, and d_ζ orbitals, respectively. That is, we used the following values: $i\boldsymbol{M}^e_1=\boldsymbol{j}$; $i\boldsymbol{M}^e_2=\boldsymbol{i}$; $i\boldsymbol{M}^e_3=-2\boldsymbol{k}$ where $i=(-1)^{1/2}$, and $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in the x, y, and z directions, respectively. The electric dipole transition moments,

$\boldsymbol{P}^e_1$, $\boldsymbol{P}^e_2$, and $\boldsymbol{P}^e_3$, were treated as variables in our calculations. Both their signs and relative magnitudes were varied.

The electronic rotatory strengths, $R^e_1 = \mathrm{Im}(\boldsymbol{P}^e_1 \cdot \boldsymbol{M}^e_1)$, $R^e_2 = \mathrm{Im}(\boldsymbol{P}^e_2 \cdot \boldsymbol{M}^e_2)$, and $R^e_3 = \mathrm{Im}(\boldsymbol{P}^e_3 \cdot \boldsymbol{M}^e_3)$, are treated as variable parameters in our calculations. The total (or net) rotatory strength associated with transitions to the three coupled states, ψ^0_1, ψ^0_2, and ψ^0_3, is invariant to the interaction parameters of our model (α, β, and γ) and is equal to,

$$R(\mathrm{total}) = \textstyle\sum_n R_n = R^e_1 + R^e_2 + R^e_3\,. \tag{24}$$

The vibronic (α and β) and static (γ) interactions merely lead to redistributions of rotatory strength among the various substates of the (ψ^0_1, ψ^0_2, ψ^0_3) manifold. They do not introduce any new soures of chirality into the system.

Basis sets for the expansions of the vibronic wave functions (8) ranged in size from 63 ($v + \nu = 0, 1, 2, \ldots, 5$) to 108 ($v + \nu = 0, 1, 2, \ldots, 7$). Adequacy of basis size was tested according to the following criteria: (1) stability of eigenvalues and of eigenvector matrices; (2) convergence of $R(\mathrm{total}) = \sum_n R_n$ to the sum ($R^e_1 + R^e_2 + R^e_3$).

All calculations were performed on a CDC 6400 computing system.

4. Results

The results presented here were chosen to be illustrative of the model and its application to the interpretation of CD spectra. They are representative of the computed data, but are not complete (that is, results from just a few of the parameter sets actually studied are presented).

Rotatory strength spectra for a number of different parameter sets are displayed in Figs. 1–7. The energy scale in each of these figures is expressed in units of

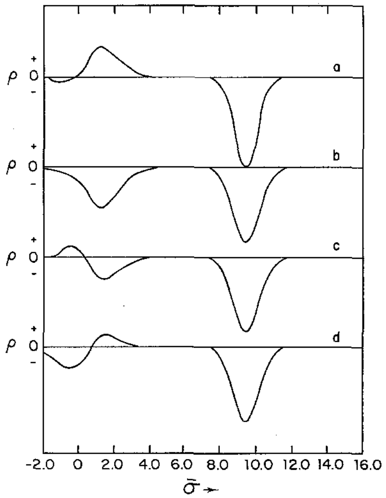


Fig. 1. Rotatory strength spectra for $\bar{\alpha} = \bar{\beta} = 3.0$, $\bar{\gamma} = 0.5$, $\bar{\Delta} = 0.50$, $\bar{\Delta}' = 7.5$, $\lambda = \hbar\omega(\xi) = \hbar\omega(\eta) = 350\ \mathrm{cm}^{-1}$, $\hbar\omega'(\xi) = \hbar\omega'(\eta) = 400\ \mathrm{cm}^{-1}$. ($R^e_1$, R^e_2, R^e_3): a. (−0.5, 1.5, −2.0); b. (0.5, −1.5, −2.0); c. (1.0, −1.0, −2.0); d. (−1.0, 1.0, −2.0)

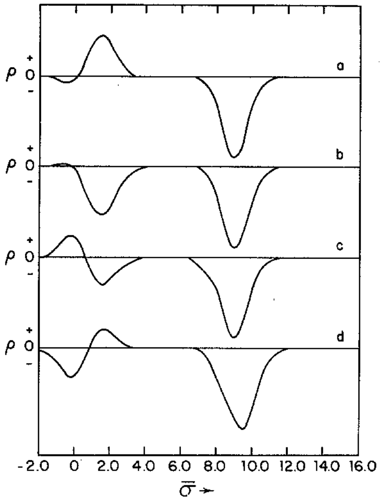


Fig. 2. Rotatory strength spectra for $\bar{\alpha}=\bar{\beta}=2.0$, $\bar{\gamma}=0.5$, $\bar{\Delta}=0.5$, $\bar{\Delta}'=7.5$, $\lambda=\hbar\omega(\xi)=\hbar\omega(\eta)=350\ \text{cm}^{-1}$, $\hbar\omega'(\xi)=\hbar\omega'(\eta)=400\ \text{cm}^{-1}$. (R_1^e, R_2^e, R_3^e): a. $(-0.5, 1.5, -2.0)$; b. $(0.5, -1.5, -2.0)$; c. $(1.0, -1.0, -2.0)$; d. $(-1.0, 1.0, -2.0)$

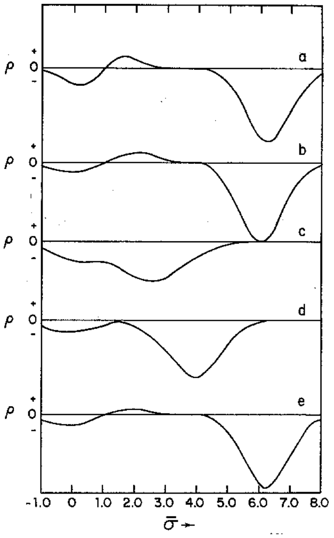


Fig. 3. Rotatory strength spectra for $\bar{\Delta}=0.25$, $\lambda=\hbar\omega(\xi)=\hbar\omega(\eta)=350\ \text{cm}^{-1}$, $\hbar\omega'(\xi)=\hbar\omega'(\eta)=400\ \text{cm}^{-1}$, $(R_1^e, R_2^e, R_3^e)=(-1.0, 1.0, -2.0)$

	$\bar{\Delta}'$	$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$
a.	5.0	1.0	1.0	0.1
b.	5.0	0.1	0.1	1.0
c.	1.0	1.0	1.0	1.0
d.	2.5	1.0	1.0	1.0
e.	5.0	1.0	1.0	1.0

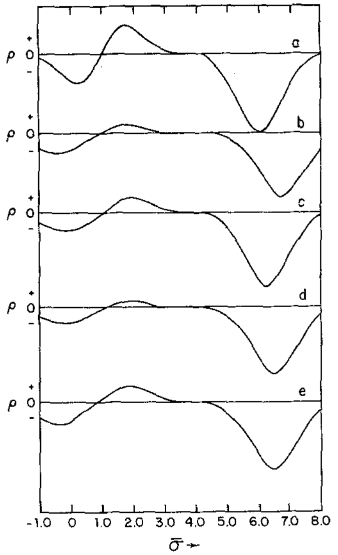


Fig. 4. Rotatory strength spectra for $\bar{\Delta} = 0.50$, $\lambda = \hbar\omega(\xi) = \hbar\omega(\eta) = 350\ \text{cm}^{-1}$, $\hbar\omega'(\xi) = \hbar\omega'(\eta) = 400\ \text{cm}^{-1}$, $(R_1^e, R_2^e, R_3^e) = (-1.0, 1.0, -2.0)$

	$\bar{\Delta}'$	$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$
a.	5.0	0.1	0.1	0
b.	5.0	2.0	2.0	1.0
c.	5.0	1.0	1.0	1.0
d.	5.0	1.0	2.0	1.0
e.	5.0	2.0	1.0	1.0

$\frac{1}{2}[\hbar\omega(\xi) + \hbar\omega(\eta)]$, and the zero point on each energy scale is at $E_1^0 + \Delta$. In calculating these spectra the bandwidth parameter, λ, was set equal to 350 cm^{-1} in each case. This value is of the order of a vibrational quantum in our model system, and leads to rather broad, smoothed-out resultant spectra for rotatory strength. These spectra are most appropriately compared with CD spectra obtained on solution samples at room temperature. The units of rotatory strength used in Figs. 1–7 are arbitrary; however, the algebraic sum of band areas in each spectrum is determined entirely by the set of parameters (R_1^e, R_2^e, R_3^e). That is the quantity, $\sum_n R_n = R(\text{total})$, is invariant to all parameters in our model except the set (R_1^e, R_2^e, R_3^e).

All the spectra shown in Figs. 1–7 were calculated assuming that the system was initially in the ground vibrational level of the ground electronic state (that is, "hot band" contributions were eliminated).

The eigenvalues, symmetries, and dipole strengths computed for the lower vibronic levels of our model system using various parameter sets are listed in Tables 1–3. The symmetry designations refer to the transformation properties of the vibronic wave functions with respect to 180° rotation about the single C_2 axis of the model system. The eigenvalues are measured from the reference energy, $E_1^0 + \Delta$, and the dipole strengths are defined in the footnote to Table 1. Except where $\bar{\Delta}'$ is less than ~2.0–2.5, the lower 10–13 vibronic levels (that is, the ones

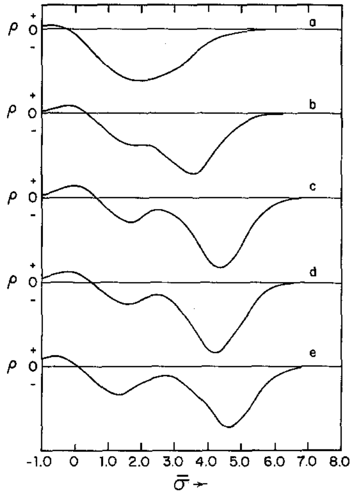


Fig. 5. Rotatory strength spectra for $\bar{\Delta}=0.25$, $\bar{\beta}=1.0$, $\bar{\gamma}=0.5$, $\lambda=\hbar\omega(\xi)=350\ \text{cm}^{-1}$, $\hbar\omega'(\xi)=400\ \text{cm}^{-1}$, $(R_1^{\xi}, R_2^{\xi}, R_3^{\xi})=(1.0, -1.0, -2.0)$

	$\bar{\Delta}'$	$\hbar\omega(\eta)$	$\hbar\omega'(\eta)$	$\bar{\alpha}$
a.	1.0	350 cm^{-1}	400 cm^{-1}	1.0
b.	2.0	350	400	1.0
c.	3.0	350	400	1.0
d.	3.0	250	300	1.0
e.	3.0	250	300	2.0

included in Tables 1–3) only span that part of the energy spectrum close to the unperturbed electronic states ψ_1^0 and ψ_2^0. However, the evidence for significant mixing of ψ_3^0 into the lower vibronic levels is apparent from the dipole strength which is computed for many of the low-lying vibronic states of A symmetry. Transitions from the lowest vibrational level of the ground electronic state to vibronic states of A symmetry are z-polarized and those to vibronic states of B symmetry are x, y-polarized.

5. Discussion

The results displayed in Tables 1–3 and in Figs. 1–7 demonstrate the profound influence which vibronic coupling can have on the distributions of dipole strength and rotatory strength among the vibronic levels associated with three nearly degenerate electronic excited states of a chiral molecular system. The results given in Tables 1–3 reveal the sensitivity of vibronic level spacings and vibronic level orderings (with respect to symmetry type, A or B) to the relative magnitudes of the coupling parameters, $\bar{\alpha}$, $\bar{\beta}$, and $\bar{\gamma}$, and to the splitting parameters, $\bar{\Delta}$ and $\bar{\Delta}'$. These vibronic level spacing are seldom apparent from absorption or CD measurements on solution samples, and the polarizations (or symmetry types) of the various vibronic transitions can only be determined from polarized single-crystal spectral measurements. Note, however, that if high-resolution, polarized absorption

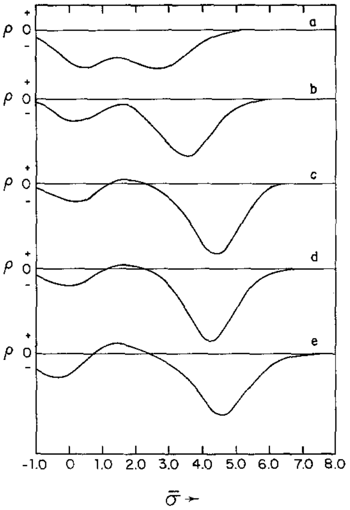


Fig. 6. Rotatory strength spectra for $\bar{\Delta}=0.25$, $\bar{\beta}=1.0$, $\bar{\gamma}=0.5$, $\lambda=\hbar\omega(\xi)=350\,\mathrm{cm}^{-1}$, $\hbar\omega'(\xi)=400\,\mathrm{cm}^{-1}$, $(R_1^e, R_2^e, R_3^e)=(-1.0, 1.0, -2.0)$

	$\bar{\Delta}'$	$\hbar\omega(\eta)$	$\hbar\omega'(\eta)$	$\bar{\alpha}$
a.	1.0	350 cm^{-1}	400 cm^{-1}	1.0
b.	2.0	350	400	1.0
c.	3.0	350	400	1.0
d.	3.0	250	300	1.0
e.	3.0	250	300	2.0

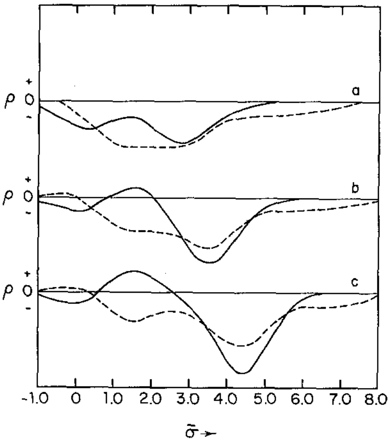


Fig. 7. Rotatory strength spectra for $\bar{\Delta}=0.25$, $\bar{\alpha}=\bar{\beta}=1.0$, $\bar{\gamma}=0.50$, $\lambda=\hbar\omega(\xi)=\hbar\omega(\eta)=350\,\mathrm{cm}^{-1}$, $\hbar\omega'(\xi)=\hbar\omega'(\eta)=400\,\mathrm{cm}^{-1}$. Solid line spectra $(R_1^e, R_2^e, R_3^e)=(-1.0, 1.5, -2.0)$; broken line spectra, $(R_1^e, R_2^e, R_3^e)=(1.0, -1.5, -2.0)$. $\bar{\Delta}'=1.0$(a), 2.0(b), and 3.0(c)

Table 1. Eigenvalues, symmetries, and dipole strengths computed for lower vibronic levels.[a] $\bar{\Delta}=0.5$, $\bar{\Delta}'=5.0$, $\hbar\omega(\xi)=\hbar\omega(\eta)=350\ \text{cm}^{-1}$

	$\bar{\alpha}=2.0, \bar{\beta}=2.0, \bar{\gamma}=1.0$			$\bar{\alpha}=2.0, \bar{\beta}=1.0, \bar{\gamma}=1.0$			$\bar{\alpha}=1.0, \bar{\beta}=2.0, \bar{\gamma}=1.0$			$\bar{\alpha}=1.0, \bar{\beta}=1.0, \bar{\gamma}=1.0$		
n	*Sym.*	$E(\text{cm}^{-1})$	D	*Sym.*	$E(\text{cm}^{-1})$	D	*Sym.*	$E(\text{cm}^{-1})$	D		$E(\text{cm}^{-1})$	D
1	B	-223	0.266	B	-174	0.293	B	-115	0.318	B	-78	0.329
2	A	-108	0.017	A	-153	0.015	A	121	0.013	A	253	0.007
3	A	129	0	B	214	0.032	A	274	0	A	321	0
4	B	136	0.051	A	217	0	B	348	0.029	B	589	0
5	B	202	0.024	B	369	0.007	B	490	0.014	B	639	0.018
6	A	412	0.010	A	509	0.003	A	624	0	B	719	0.001
7	B	478	0	B	611	0	B	663	0.001	B	813	0.307
8	A	487	0.001	A	622	0.001	A	708	0.005	A	933	0
9	A	518	0	A	764	0.001	B	740	0.252	A	974	0
10	B	606	0.129	B	775	0.279	A	860	0.002	A	1011	0.003

[a] Dipole strengths expressed in relative units assuming that:

$$\textstyle\sum_n D_n = 1 = D_1^e + D_2^e + D_3^e \quad \text{and} \quad D_1^e = D_2^e = D_3^e$$

where $D_1^e = |\langle\psi_0^0|\hat{\mu}|\psi_1^0\rangle|^2 =$ dipole strength for electronic transition $\psi_0^0 \to \psi_1^0$. The summation $\sum_n$ extends over all vibronic levels derived from PJT coupling within the $(\psi_1^0, \psi_2^0, \psi_3^0)$ set of electronic states via the Q_η and Q_ξ vibrational modes of our model system. The ten vibronic levels listed above correspond to only the lowest energy vibronic states.

Table 2. Eigenvalues, symmetries, and dipole strengths computed for lower vibronic levels[a]. $\bar{\alpha}=\bar{\beta}=1.0$, $\bar{\gamma}=0.5$, $\hbar\omega(\xi)=\hbar\omega(\eta)=350\ \text{cm}^{-1}$

	$\bar{\Delta}=0.25, \bar{\Delta}'=1.0$			$\bar{\Delta}=0.25, \bar{\Delta}'=2.0$			$\bar{\Delta}=0.25, \bar{\Delta}'=3.0$			$\bar{\Delta}=0.25, \bar{\Delta}'=5.0$		
n	*Sym.*	$E(\text{cm}^{-1})$	D	*Sym.*	$E(\text{cm}^{-1})$	D	*Sym.*	$E(\text{cm}^{-1})$	D	*Sym.*	$E(\text{cm}^{-1})$	D
1	B	81	0.293	B	110	0.313	B	126	0.321	B	257	0.327
2	A	241	0.088	A	344	0.042	A	403	0.023	B	467	0.324
3	B	421	0.179	A	497	0	A	518	0	A	569	0.011
4	A	456	0	B	504	0.252	B	545	0.291	A	650	0
5	B	546	0.023	B	643	0.008	B	712	0.003	A	789	0.006
6	A	599	0.054	A	725	0.036	B	805	0.026	A	872	0
7	B	706	0.105	B	761	0.055	A	805	0.022	B	897	0.001
8	B	818	0	B	877	0	B	907	0	B	954	0.003
9	A	827	0.032	A	897	0	A	939	0	B	1038	0
10	A	829	0	A	958	0.006	A	1037	0.001	B	1121	0

[a] See footnote to Table 1 for definition of dipole strength.

Table 3. Eigenvalues, symmetries, and dipole strengths computed for lower vibronic levels[a]. $\bar{\Lambda}=0.25$, $\bar{\Lambda}'=5.0$, $\hbar\omega(\xi)=\hbar\omega(\eta)=350\ \text{cm}^{-1}$, $\bar{\gamma}=1.0$

Weak coupling case ($\bar{\alpha}=\bar{\beta}=0.1$)				Intermediate coupling case ($\bar{\alpha}=\bar{\beta}=1.0$)			
n	*Sym.*	$E(\text{cm}^{-1})$	*D*	*n*	*Sym.*	$E(\text{cm}^{-1})$	*D*
1	B	-12.6	0.332	1	B	-43.3	0.329
2	A	386.7	0	2	A	285.9	0.007
3	A	387.4	0	3	A	354.9	0
4	B	786.0	0.001	4	B	621.8	0
5	B	786.7	0	5	B	665.7	0.042
6	B	787.4	0.001	6	B	752.8	0.001
7	B	811.9	0.332	7	B	785.4	0.283
8	A	1185.4	0	8	A	964.5	0
9	A	1186.0	0	9	A	1001.6	0
10	A	1186.7	0	10	A	1018.4	0.006
11	A	1187.4	0	11	A	1131.5	0.006
12	A	1210.8	0	12	A	1150.8	0
13	A	1211.9	0	13	A	1188.6	0

[a] See footnote to Table 1 for definition of dipole strength.

spectra could be obtained on our model system, and if $\bar{\Lambda}=0.5$, $\bar{\Lambda}'=5.0$, $\bar{\gamma}=1.0$, and $\hbar\omega(\xi)=\hbar\omega(\eta)=350\ \text{cm}^{-1}$ (see Table 1), the frequency intervals between the lowest energy vibronic transition of A symmetry and that of B symmetry are computed to be:

	$\bar{\alpha}=\bar{\beta}=2.0$	$\bar{\alpha}=\bar{\beta}=1.0$	$\bar{\alpha}=2.0, \bar{\beta}=1.0$	$\bar{\alpha}=1.0, \bar{\beta}=2.0$
$\delta(\text{cm}^{-1})=$	115	331	21	236

The results presented in Tables 1–3 also show apparently irregular energy spacings of the vibronic levels. That is, the spacings are not, in general, equal to single quanta of the Q_η or Q_ξ vibrational modes. The computed spacings are strongly dependent upon the relative values $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}$, $\bar{\Lambda}$, and $\bar{\Lambda}'$.

The "rotatory strength spectra" shown in Figs. 1–7 suggest that considerable caution must be exercised in applying spectra-structure relationships to systems similar to our model system in the absence of a detailed vibronic analysis of the results. Most spectra (CD)-structure relationships proposed for chiral systems require assignments of bands or other features in the CD spectra to specific electronic transitions. These relationships generally correlate the sign and magnitudes of the rotatory strength of a specific electronic transition to specific stereochemical features of the system. It is assumed that the electronic rotatory strength can be determined by assigning a particular CD band to the diagnostic transition and then relating the area under this band to the electronic rotatory strength according to:

$$R_h = \text{constant} \times \int \Delta\varepsilon(v) dv/v$$

where the integration extends over the frequency interval spanned by the assigned CD band. Our calculated results show that when three electronic excited states lie within ~4000 cm^{-1} of each other and are subject to moderately strong vibronic coupling via a PJT type mechanism, it is no longer possible to talk about pure electronic states or to make spectral assignments based on the assumption of pure electronic states. Instead, one must consider vibronic states of "mixed" electronic parentage insofar as the nearly degenerate pure electronic states are thoroughly scrambled (or mixed) by the vibronic perturbation. Distinct band systems and spectral features may still appear in the CD spectra, but these cannot be assigned to transitions to specific electronic states.

The existence of two or three closely spaced electronic excited states which are subject to strong vibronic interactions is quite common in transition metal complexes of pseudo tetragonal symmetry. CD spectra obtained on solution samples of such systems are generally much too broad for detailed vibronic analysis. In this case, the total or net rotatory strength associated with the manifold of vibronic levels derived from the coupled electronic states is the most suitable chiroptical parameter to use in making spectra (CD)-structure correlations. R(net) is invariant to the PJT type vibronic interactions which couple the nearly degenerate electronic states. Its sign and magnitude are determined entirely by stereochemical and other structure features of the chiral system. Whereas the splittings and sign patterns observed in the CD spectra may reflect PJT vibronic coupling characteristics more strongly than they reflect the detailed stereochemical features of the dissymmetric ligand environment, the total integrated band area of the CD spectrum in the region spanned by the vibronic levels of the coupled electronic states depends entirely on structural features and is independent of the PJT vibronic parameters.

In our model, R(total) or R(net) is determined by $R(\text{total}) = R_1^e + R_2^e + R_3^e$. We did not calculate R_1^e, R_2^e, and R_3^e for specific systems; instead, we introduced these electronic rotatory strengths as parameters. To calculate R_1^e, R_2^e, and R_3^e requires a specific model for the electronic structural details of the system as well as for the origins of the optical activity of the system. Calculations of the electronic rotatory strengths associated with the *d-d* transitions of metal complexes have been the subject of numerous previous studies [6, 7]. The values we chose in this study for (R_1^e, R_2^e, R_3^e) are representative of the values expected for *d-d* transitions in pseudo tetragonal complexes comprised of various classes of chiral bidentate or terdentate ligands. The primary objectives of the present study were to calculate the vibronic wave functions and energy levels derived from PJT interactions between the electronic states ψ_1^0, ψ_2^0, and ψ_3^0, to examine how the total electronic rotatory strength, $(R_1^e + R_2^e + R_3^e)$, distributes among the vibronic levels, and to predict the resulting low-resolution CD spectra.

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Prof. Dr. F. S. Richardson
Department of Chemistry
University of Virginia
Charlottesville, Virginia 22901, USA