which involve $\Delta \rightleftharpoons \Lambda$ interconversions with no exchange, a topologically equivalent mechanism is one in which when the bis chelate complex is viewed along the C_3 axis of the octahedral framework the six ligating nuclei[36] of the upper and lower triangular faces move toward each other along arcs somewhat parallel to the C_3 axis. The transition state has an hexagonal planar geometry analogous to the one proposed for the digonal twist, noting however that the latter leads to retention of configuration. Continued motion of the ligators about the six arcs leads to the enantiomer. Such a sterically crowded transition state would make this type of mechanism energetically unfavorable also, making it doubtful that the corresponding averaging sets A_8' and A_6'' (or A_4''') would ever be operative, that is, enantiomerization without exchange of terminal groups in *cis*-$M(AA)_2XY$ and *cis*-$M(AB)_2X_2$ systems. In case (2) above, averaging set A_5' may be obtained by pseudorotation of the appropriate TBP-axial transition state, while A_6' and A_7' may by produced by pseudorotation of certain TBP-equatorial intermediates (cf. Table III of ref 6); this pathway is probably of lower energy than the digonal twist(s). Analogous considerations may lead to the discovery of similar, yet energetically more reasonable, pathways.

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(36) Here the two chelate rings would have to span both the upper and lower faces.

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An All-Orders Crystal Field Perturbation Treatment of d–d Optical Activity in Trigonal Transition Metal Complexes

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The crystal field, one-electron perturbation model of d–d optical activity in trigonal transition metal complexes is extended to all orders in the first two noncubic terms of the crystal field interaction operator. As model systems we consider six-coordinate transition metal complexes of nearly octahedral (O_h) but exactly trigonal-dihedral (D_3) symmetry. The crystal field potential at the metal ion is assumed to be octahedral to zeroth order in the perturbation treatment, and the nonoctahedral components of the complete crystal field potential are treated as small perturbations. Chromophoric basis states are constructed from metal 3d, 4p, and 4f orbitals. The perturbation treatment of the chromophoric wave functions is carried to all orders by diagonalizing the Hamiltonian matrix formed by the cubic basis states of the metal ion chromophore and the Hamiltonian operator $\hat{H}$ (trigonal) = $\hat{H}$ (cubic) + $\hat{H}$ (noncubic). The eigenvectors of the diagonalized Hamiltonian are then used to calculate rotatory strengths and from the eigenvalues trigonal splitting energies are obtained. This work is an extension of previous applications of the crystal field, one-electron model of d–d optical activity in which the perturbation treatment was carried only to first or second order in the chiral parts of the crystal field potential.

I. Introduction

Transition metal complexes of trigonal-dihedral (D_3) symmetry have played a central role as model systems in both experimental and theoretical investigations of natural optical activity in coordination compounds. A variety of theoretical models have been proposed for relating the optical activity associated with the d–d transitions in these systems to specific stereochemical and electronic structural features. Most of the proposed models are based on an independent-systems representation of the metal complexes. In this representation the central metal ion is treated as a symmetric chromophoric subsystem which is perturbed by the chiral Coulombic fields created by the ligand environment (comprised of atomic and molecular fragments or subsystems).[1–4] Molecular orbital models have also been applied to the d–d optical activity of chiral transition metal complexes.[5–8] In these models, d–d rotatory strengths are calculated directly from wave functions generated for the entire metal complex. In this case the wave functions reflect the chirality of the complex directly and will lead to nonvanishing values for the rotatory strength quantities $R_{i\to j} = \mathrm{Im}\langle\psi_i|\hat{\mu}|\psi_j\rangle\cdot\langle\psi_j|\hat{\mathbf{m}}|\psi_i\rangle$. The angular overlap model has also been used to calculate the d–d optical activity of dissymmetric tris-bidentate metal complexes.[9] Although this approach appears to have considerable merit for representing the essential aspects of the optical activity problem, a detailed account of its applications has not yet been given.

The simplest independent-systems model proposed for d–d optical activity in transition metal complexes is the so-called "ionic" or static coupling (SC) model. This model was first proposed by Moffitt[10] and it is an adaptation of the crystal field (CF) model of d–d spectroscopic properties and the "one-electron" theory of molecular optical activity.[11,12] In this model the chromophoric d electrons are presumed to be localized on the metal ion and interactions between these chromophoric electrons and the ligand environment are represented by a crystal field type expansion. That is, the ligand environment is represented by an array of point charges or static charge distributions. In the spirit of the crystal field model and the "one-electron" (or static coupling) theory of molecular optical activity, the chromophore–ligand interactions serve to mix, scramble, or split the eigenstates of the isolated or unperturbed chromophoric unit (the metal ion in the present case).

In the more general application of the independent-systems model, one must consider dynamical coupling (DC) between the chromophoric electrons and the ligand groups as well as static coupling (SC).[1–3] Whereas the SC arises from electrostatic interactions between "static" charge distributions in the ligand environment and the chromophoric electrons (treated dynamically), the DC arises from electrostatic interactions between "dynamical" charge distributions in the ligand environment and the chromophoric electrons. That is, the DC takes into account the correlated (or coupled) motions of the ligand-localized electrons and metal-localized electrons. Recent work of Mason and co-workers has demonstrated the importance of DC in the independent-systems treatment of d–d optical activity in trigonal transition metal complexes.[13,14]

In the present study we extend the crystal field, one-electron model (SC) of d–d optical activity in trigonal metal complexes to all orders in the first two noncubic terms of the crystal field expansion. To zeroth order the systems are assumed to have exactly octahedral (O_h) symmetry and the zeroth order crystal field terms are, therefore, the cubic (O_h) terms. The first two (lowest order) noncubic terms appearing in the trigonal crystal field expansion are retained and treated as perturbations on the zeroth-order cubic eigenstates of the metal ion chromophore. The perturbation treatment of the chromophoric wave functions is then carried to all orders by diagonalizing the Hamiltonian matrix formed by the cubic basis states of the metal ion chromophore and the Hamiltonian operator $\hat{H}$(trigonal) = $\hat{H}$(cubic) + $\hat{H}$(noncubic). The eigenvectors of the diagonalized Hamiltonian $\hat{H}$(trigonal) are then used to calculate rotatory strengths.

In previous examinations of the crystal field, one-electron model of d–d optical activity in trigonal metal complexes considerable attention has been given the detailed nature of the chiral part of the crystal field potential and the relative merits of admitting d–p vs. d–f interactions into the model to provide an electric dipole mechanism for the ligand field transitions of the metal ion. If the perturbation treatment is carried to first order in the noncubic (trigonal) parts of the crystal field interaction potential, then the d–d transitions can acquire a *net* rotatory strength only if the crystal field expansion is carried to terms of degree $l = 9$. That is, the first term in the crystal field expansion, which is totally symmetric in O_h and in D_3 and which leads to a nonvanishing *net* d–d rotatory strength, transforms as $Y_{l=9}{}^m$. This potential term is of ninth order with respect to electron coordinates and it can mix the 3d orbitals ($l = 2$) only with orbitals of very large angular momentum and high energy at the metal ion ($l = 7$, 9, 11). It will not promote d–p or d–f mixing. The Cartesian coordinate form of this potential (in a real tetragonal-coordinate basis) is given by $xyz(x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$. This is often referred to as the octahedral sector or regional rule for six-coordinate metal complexes.[1,2,4,7,15–17]

If the crystal field, one-electron treatment is carried to second order in perturbation theory, the d–d transitions can acquire *net* rotatory strength from second-order terms involving the simultaneous action of two noncubic crystal field interaction terms of relatively low order, one of which is gerade in O_h ($l = 2$) and one of which is ungerade in O_h ($l = 3$).[1,16] The ungerade term can promote both d–p and d–f mixing, and the gerade term can scramble the d orbitals. This second-order perturbation treatment leads to "mixed" sector rules for near-cubic six-coordinate complexes.[4]

Despite the rather obvious fact that the octahedral pseudoscalar potential which gives rise to *net* d–d rotatory strength in the first-order crystal field, one-electron treatment is physically unrealistic (due to its extremely sharp r^{-19} distance dependence and the necessity for introducing metal orbitals of $l \geq 7$), a considerable number of spectra–structure correlations have been based on its resultant sector rule.[17] The leading crystal field terms responsible for *net* d–d rotatory strength in the second-order perturbation treatment are somewhat more realistic physically (given the validity of the crystal field model itself). It is rather easy to show that if the crystal field, one-electron model is carried to third order in perturbation theory, then the lowest order ungerade term appearing in the trigonal (D_3) crystal field expansion ($l = 3$) will lead to a nonvanishing *net* d–d rotatory strength. In a Cartesian trigonal-coordinate framework (the z axis coincident with the C_3 axis and the x axis coincident with one of the dihedral C_2 axes), this potential has the Cartesian form $y(3x^2 - y^2)$. In a Cartesian tetragonal-coordinate framework for a six-coordinate near-octahedral system, this potential assumes the form $(x - y)(y - z)(z - x)$.

The purpose of the work presented here was to extend the "ionic" or crystal field, one-electron model to "all orders" in the leading noncubic terms of the trigonal crystal field interaction potential. This is essentially a variation method in which the basis set is restricted to 3d, 4p, and 4f metal orbitals and the noncubic crystal field interaction potential includes only the $Y_2{}^0$ and $(Y_3{}^{-3} - Y_3{}^3)$ trigonally symmetric terms. The "perturbed" wave functions are obtained by diagonalizing the trigonal Hamiltonian matrix and these wave functions are then used to calculate the rotatory strengths associated with trigonally perturbed d–d transitions.

II. Model

A. Basis Orbitals. We choose as our one-electron basis set 3d, 4p, and 4f orbitals located on the central metal ion. For the 3d orbitals, we use the trigonal orbitals defined by Moffitt[10]

Table I. d–d Interaction Matrix:[a] $\langle \hat{V}_g \rangle_{dd}$

	t_0	t_+	t_-	e_+	e_-
t_0	2	0	0	0	0
t_+	0	-1	0	$-(2^{1/2})$	0
t_-	0	0	-1	0	$-(2^{1/2})$
e_+	0	$-(2^{1/2})$	0	0	0
e_-	0	0	$-(2^{1/2})$	0	0

[a] In units of $(5/196\pi)^{1/2}A_2{}^0\langle R_d|r^2|R_d\rangle = (5/196\pi)^{1/2}A_2{}^0\langle r^2\rangle_{dd}$.

Table II. d–p Interaction Matrix:[a] $\langle \hat{V}_u \rangle_{dp}$

	p_{+1}	p_0	p_{-1}
t_0	0	0	0
t_+	$-(2^{1/2})i$	0	0
t_-	0	0	$-(2^{1/2})i$
e_+	i	0	0
e_-	0	0	i

[a] In units of $(3/56\pi)^{1/2}A_3{}^3\langle R_p|r^3|R_d\rangle = (3/56\pi)^{1/2}A_3{}^3\langle r^3\rangle_{pd}$.

Table III. d–f Interaction Matrix:[a] $\langle \hat{V}_u \rangle_{df}$

	f_{+3}	f_{+2}	f_{+1}	f_0	f_{-1}	f_{-2}	f_{-3}
t_0	$75^{1/2}$	0	0	0	0	0	$-(75^{1/2})$
t_+	0	0	$20^{1/2}i$	0	0	5	0
t_-	0	5	0	0	$20^{1/2}i$	0	0
e_+	0	0	$-(10^{1/2})i$	0	0	$50^{1/2}$	0
e_-	0	$50^{1/2}$	0	0	$-(10^{1/2})i$	0	0

[a] In units of $(1/756\pi)^{1/2}A_3{}^3\langle R_f|r^3|R_d\rangle = (1/756\pi)^{1/2}A_3{}^3\langle r^3\rangle_{fd}$.

Table IV. p–p Interaction Matrix:[a] $\langle \hat{V}_g \rangle_{pp}$

	p_{+1}	p_0	p_{-1}
p_{+1}	-1	0	0
p_0	0	1	0
p_{-1}	0	0	-1

[a] In units of $(1/20\pi)^{1/2}A_2{}^0\langle R_p|r^2|R_p\rangle = (1/20\pi)^{1/2}A_2{}^0\langle r^2\rangle_{pp}$.

Table V. p–f Interaction Matrix:[a] $\langle \hat{V}_g \rangle_{pf}$

	f_{+3}	f_{+2}	f_{+1}	f_0	f_{-1}	f_{-2}	f_{-3}
p_{+1}	0	0	$2^{1/2}$	0	0	0	0
p_0	0	0	0	$3^{1/2}$	0	0	0
p_{-1}	0	0	0	0	$2^{1/2}$	0	0

[a] In units of $(9/140\pi)^{1/2}A_2{}^0\langle R_p|r^2|R_f\rangle = (9/140\pi)^{1/2}A_2{}^0\langle r^2\rangle_{pf}$.

Table VI. f–f Interaction Matrix:[a] $\langle \hat{V}_g \rangle_{ff}$

	f_{+3}	f_{+2}	f_{+1}	f_0	f_{-1}	f_{-2}	f_{-3}
f_{+3}	-5	0	0	0	0	0	0
f_{+2}	0	0	0	0	0	0	0
f_{+1}	0	0	3	0	0	0	0
f_0	0	0	0	4	0	0	0
f_{-1}	0	0	0	0	3	0	0
f_{-2}	0	0	0	0	0	0	0
f_{-3}	0	0	0	0	0	0	-5

[a] In units of $(1/180\pi)^{1/2}A_2{}^0\langle R_f|r^2|R_f\rangle = (1/180\pi)^{1/2}A_2{}^0\langle r^2\rangle_{ff}$.

Table VII. Magnetic Dipole Transition Matrix:[a] $\langle \hat{\mathbf{m}} \rangle_{dd}$

	t_0	t_+	t_-	e_+	e_-
t_0	0	$-l_+$	l_-	$-(2^{1/2})l_+$	$2^{1/2}l_-$
t_+	$-l_-$	$-(2^{1/2})k$	0	$2k$	$i(2^{1/2})l_+$
t_-	l_+	0	$2^{1/2}k$	$i(2^{1/2})l_-$	$-2k$
e_+	$-(2^{1/2})l_-$	$2k$	$-i(2^{1/2})l_+$	0	0
e_-	$2^{1/2}l_+$	$-i(2^{1/2})l_-$	$-2k$	0	0

[a] In units of $2^{-1/2}(e\hbar/2mc)$. $l_+ = (\mathbf{i} + i\mathbf{j})$, $\mathbf{k} = \mathbf{k}$, $l_- = (\mathbf{i} - i\mathbf{j})$, $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ = unit vectors in x, y, z directions.

Table VIII. d–p Electric Dipole Transition Matrix:[a] $\langle \hat{\boldsymbol{\mu}} \rangle_{pd}$

	t_0	t_+	t_-	e_+	e_-
p_{+1}	$2^{-1/2}l_-$	$-k$	$-i(2^{1/2})l_+$	$-(2^{1/2})k$	il_+
p_0	$2k$	$2^{-1/2}l_+$	$2^{-1/2}l_-$	l_+	l_-
p_{-1}	$-(2^{-1/2})l_+$	$-i(2^{1/2})l_-$	k	il_-	$2^{1/2}k$

[a] In units of $(1/15)^{1/2}e\langle R_p|r|R_d\rangle = (1/15)^{1/2}e\langle r\rangle_{pd}$.

and by Piper and Karipedes[18]

$$t_+ = -(1/3)^{1/2}d_{+1} - i(2/3)^{1/2}d_{-2}$$

$$t_- = (1/3)^{1/2}d_{-1} + i(2/3)^{1/2}d_{+2}$$

$$t_0 = d_0$$

$$e_+ = -(2/3)^{1/2}d_{+1} + i(1/3)^{1/2}d_{-2}$$

$$e_- = (2/3)^{1/2}d_{-1} - i(1/3)^{1/2}d_{+2}$$

where the orbitals d_m are those prescribed by Condon and Shortley.[19] These orbitals form both trigonal (D_3) and octahedral (O_h) bases. In the O_h point group, the orbital set (t_0, t_+, t_-) transforms as t_{2g}, and the orbital set (e_+, e_-) transforms as e_g. In the D_3 point group, t_0 transforms as a_1 and the orbitals e_+, e_-, t_+, and t_- transform as e.

B. Crystal Field Potential. The noncubic part of the crystal field interaction potential is restricted to just the two leading terms of the general expansion. This interaction potential is expressed as

$$\begin{aligned} V &= eA_2{}^0r^2Y_2{}^0 + eA_3{}^3r^3(1/2)^{1/2}(Y_3{}^{-3} - Y_3{}^3) \\ &= V_g + V_u \end{aligned} \tag{1}$$

where the functions $Y_l{}^m$ are spherical harmonics normalized to unity and are dependent upon electron angular coordinates, r is the electron radial coordinate, and $A_2{}^0$ and $A_3{}^3$ are crystal field parameters dependent upon the charges and positions of perturber sites in the ligand environment. The gerade term, V_g, transforms as a_1 in D_3 and as t_{2g} in O_h. The ungerade term, V_u, transforms as a_1 in D_3 and as t_{2u} in O_h. The interaction potential, V_u, is the one employed by Moffitt[10] and by Piper and Karipedes[18] in their initial applications of the ionic model to the problem of d–d optical activity in trigonal-dihedral transition metal complexes.

C. Interaction Matrix Elements. The interaction potential, V (eq 1), induces interactions between the 3d, 4p, and 4f basis orbitals defined in section IIA. The resultant interaction matrix elements are given in Tables I (d–d), II (d–p), III (d–f), IV (p–p), V (p–f), and VI (f–f).

D. Perturbed Wave Functions. The perturbed wave functions are obtained in our model by diagonalizing the Hamiltonian matrix (15 × 15) constructed from the basis orbitals given in section IIA and the Hamiltonian operator defined by $\hat{H} = \hat{H}^\circ + \hat{V}$, where $\hat{H}^\circ$ is the Hamiltonian operator for the chromophoric electrons moving in a cubic (octahedral) ligand field and $\hat{V}$ is the interaction potential defined in eq 1. The Hamiltonian matrix is diagonal in $\hat{H}^\circ$ and has both diagonal and off-diagonal elements in $\hat{V}$. The five lowest eigenvalues and eigenvectors of the Hamiltonian matrix yield the energies and wave functions of the trigonally perturbed "d" orbital set.

E. Electric and Magnetic Dipole Transition Moments. To compute rotatory strengths, $R_{ij} = \mathrm{Im}\langle\psi_i|\hat{\boldsymbol{\mu}}|\psi_j\rangle\cdot\langle\psi_j|\hat{\mathbf{m}}|\psi_i\rangle$, it is necessary to have the electric and magnetic dipole transition integrals between the 3d, 4p, and 4f orbitals in our model. The wave functions ψ_i and ψ_j are expressed as linear combinations of these orbitals, and $\langle\psi_i|\hat{\boldsymbol{\mu}}|\psi_j\rangle$ and $\langle\psi_j|\hat{\mathbf{m}}|\psi_i\rangle$ reduce to weighted sums of $\langle d_m|\hat{\boldsymbol{\mu}}|p_m\rangle$, $\langle d_m|\hat{\boldsymbol{\mu}}|f_m\rangle$, $\langle d_m|\hat{\mathbf{m}}|d_m\rangle$, $\langle p_m|\hat{\mathbf{m}}|p_m\rangle$, and $\langle f_m|\hat{\mathbf{m}}|f_m\rangle$. The relevant $\langle d_m|\hat{\boldsymbol{\mu}}|p_m\rangle$, $\langle d_m|\hat{\boldsymbol{\mu}}|f_m\rangle$, and $\langle d_m|\hat{\mathbf{m}}|d_m\rangle$ matrix elements are listed in Tables VII–IX.

III. Calculations

To carry out calculations based on the model described in sections I and II the following parameters are required: (a) *radial integrals* $\langle r\rangle_{dp}$, $\langle r\rangle_{df}$, $\langle r^2\rangle_{dd}$, $\langle r^2\rangle_{pp}$, $\langle r^2\rangle_{ff}$, $\langle r^2\rangle_{pf}$, $\langle r^3\rangle_{dp}$,

Table IX. d-f Electric Dipole Transition Matrix:[a] $\langle\hat{\mu}\rangle_{fd}$

	t_0	t_+	t_-	e_+	e_-
f_{+3}	0	$i((5/2)^{1/2})l_-$	0	0	$-i(5^{1/2})l_-$
f_{+2}	$(10/3)^{1/2}l_-$	$-i((5/3)^{1/2})k$	0	$(5/3)^{1/2}l_-$	$i((10/3)^{1/2})k$
f_{+1}	$-((16/3)^{1/2})k$	$-i((1/6)^{1/2})l_+$	$-(3^{1/2})l_-$	$-((8/3)^{1/2})k$	$i((1/3)^{1/2})l_+$
f_0	$-l_+$	$-l_-$	3k	$-(2^{-1/2})l_+$	$-(2^{-1/2})l_+$
f_{-1}	$-i((1/6)^{1/2})l_-$	$(16/3)^{1/2}k$	$3^{1/2}l_+$	$i((1/3)^{1/2})l_-$	$(8/3)^{1/2}k$
f_{-2}	$i((5/3)^{1/2})k$	$(10/3)^{1/2}l_+$	0	$-i((10/3)^{1/2})k$	$(5/3)^{1/2}l_+$
f_{-3}	$i((5/2)^{1/2})l_+$	0	0	$-i(5^{1/2})l_+$	0

[a] In units of $(1/35)^{1/2}e\langle R_f|r|R_d\rangle = (1/35)^{1/2}e\langle r\rangle_{fd}$.

$\langle r^3\rangle_{df}$; (b) *zeroth-order energies* for 3d, 4p, and 4f metal orbitals; (c) *crystal field parameters* A_2^0 and A_3^3. Various sets of radial integrals were used in our calculations but the results appeared to be *qualitatively* insensitive to the values chosen. The results presented here were calculated using the following values for the radial integrals: $\langle r\rangle_{dp} = 1.79$ au, $\langle r\rangle_{df} = 2.40$ au, $\langle r^2\rangle_{dd} = 1.90$ au, $\langle r^2\rangle_{pp} = 2.73$ au, $\langle r^2\rangle_{ff} = 3.00$ au, $\langle r^3\rangle_{dp} = 4.74$ au, and $\langle r^3\rangle_{df} = 12.83$ au (where au = atomic unit = 0.529 Å).

Various sets of zeroth-order orbital energies were employed in our calculations and again the results appeared to be qualitatively insensitive to the values chosen. For the results presented here we chose ϵ_t (the energy of the t_0, t_+, and t_- orbitals in an octahedral ligand field) = 0 and ϵ_e (the energy of the e_+ and e_- orbitals in an octahedral ligand field) = 0.10 au (21 947 cm^{-1}). The energy of the 4p orbitals was chosen to be $\epsilon_p = 0.25$ au (54 868 cm^{-1}). The 4f orbitals were assumed to be degenerate to zeroth order (in the octahedral ligand field) and their energy was taken as $\epsilon_f = 0.30$ au (65 842 cm^{-1}).

The crystal field parameters A_2^0 and A_3^3 were treated as independent variables in our calculations and we computed d–d rotatory strengths as functions of them. In the "ionic" model it is these parameters which carry the magnitude and "sense" of chirality or dissymmetry in the ligand environment. The A_2^0 term accompanies an axially symmetric (about the C_3 axis of the trigonal system) polar crystal field perturbation of the metal ion and by itself (i.e., with $A_3^3 = 0$) cannot produce optical activity since it preserves the inversion center of the system. The A_2^0 term will, of course, lead to an energy splitting between the t_0 and t_+, t_- orbitals. The A_3^3 term accompanies a chiral crystal field perturbation of the metal ion and it can produce optical activity in the d–d transitions. The sign of the A_3^3 term reflects the chiral "sense" of the perturbation—oppositely signed A_3^3 terms arising from enantiomeric crystal field potentials.

The values of A_2^0 and A_3^3 used in the present study were chosen to span a physically reasonable range. Again we point out that the crystal field, one-electron (or ionic) model is somewhat artificial on purely physical grounds and that the radial integrals, crystal field parameters, and orbital energies which enter into it must be chosen somewhat arbitrarily. However, this model does preserve the essential symmetry-determined aspects of the optical activity problem and its simplicity has made it both attractive and useful to workers in the field.

Following Karipedes and Piper[18] we shall label the "perturbed" d orbitals as τ_0, τ_+, τ_-, η_+, and η_- which are related to the unperturbed orbitals t_0, t_+, t_-, e_+, and e_-, respectively. The eigenvalues and wave functions for the (τ_0, τ_+, τ_-, η_+, η_-) set are obtained by diagonalizing the Hamiltonian matrix as discussed in section II. The eigenvalues are labeled E_0^τ for τ_0, $E_\pm^\tau$ for the degenerate set (τ_+, τ_-), and $E_\pm^\eta$ for the degenerate set (η_+, η_-). The energy difference ($E_0^\tau - E_\pm^\tau$) is referred to as the trigonal splitting energy δ. In the present study we were principally interested in calculating the rotatory strengths associated with transitions from the (τ_0, τ_+, τ_-) set of orbitals to the (η_+, η_-) set of orbitals. By symmetry, the following relationships obtain for the rotatory strengths of these transitions

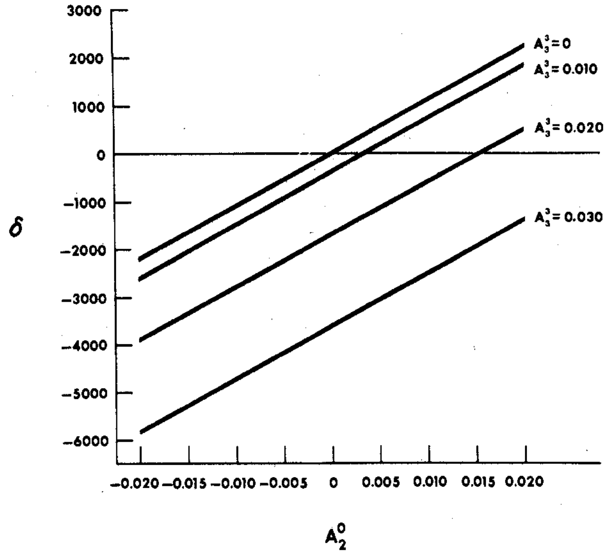

Figure 1. Trigonal splitting energy, δ (cm^{-1}), plotted vs. A_2^0 for selected fixed values of A_3^3. A_2^0 and A_3^3 are expressed in atomic units.

$$R(\tau_0 \rightarrow \eta_+) = \mathrm{Im}\langle\tau_0|\hat{\mu}|\eta_+\rangle\cdot\langle\eta_+|\hat{m}|\tau_0\rangle = R(\tau_0 \rightarrow \eta_-) = R_e'$$

$$R(\tau_+ \rightarrow \eta_+) = \mathrm{Im}\langle\tau_+|\hat{\mu}|\eta_+\rangle\cdot\langle\eta_+|\hat{m}|\tau_+\rangle = R(\tau_- \rightarrow \eta_-) = R_a$$

$$R(\tau_+ \rightarrow \eta_-) = \mathrm{Im}\langle\tau_+|\hat{\mu}|\eta_-\rangle\cdot\langle\eta_-|\hat{m}|\tau_+\rangle = R(\tau_- \rightarrow \eta_+) = R_e''$$

Only three independent one-electron rotatory strengths are required then to characterize the rotatory strengths associated with all of the (τ_0, τ_+, τ_-) → (η_+, η_-) transitions. Note that the $\tau_\pm \rightarrow \eta_\pm$ transitions are a_1 polarized (in D_3), whereas the $\tau_0 \rightarrow \eta_\pm$ and $\tau_\pm \rightarrow \eta_\mp$ transitions are e polarized (in D_3). The general d–d rotatory strength matrix may be written as

	η_+	η_-
τ_0	R_e'	R_e'
τ_+	R_a	R_e''
τ_-	R_e''	R_a

We define R(net), the net or total d–d rotatory strength, according to $R(\text{net}) = 2R_e' + 2R_e'' + 2R_a$. We also define a ratio quantity, $\rho = (R_e' + R_e'')/R_a$, which reflects how the total d–d rotatory strength is distributed between the e-polarized and a_1-polarized trigonal transitions.

IV. Results

The computed results of primary interest are (a) trigonal splitting energy $\delta = (E_0^\tau - E_\pm^\tau)$, (b) rotatory strengths R_a, R_e', and R_e'', (c) net rotatory strength $R(\text{net}) = 2(R_a + R_e' + R_e'')$, and (d) the ratio $\rho = (R_e' + R_e'')/R_a$. These properties were calculated for a large number of different parameter sets—radial integrals, zeroth-order orbital energies, and crystal field interaction terms (A_2^0 and A_3^3). Although the *quantitative* nature of the results was found to depend upon all three types of input parameters, the *qualitative* nature of the results was found to be relatively insensitive to the choice

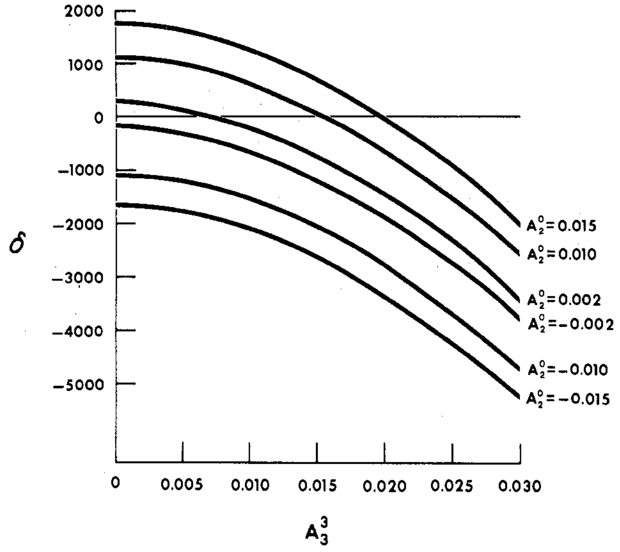

Figure 2. Trigonal splitting energy, δ (cm^{-1}), plotted vs. A_3^3 for selected fixed values of A_2^0. A_2^0 and A_3^3 are expressed in atomic units.

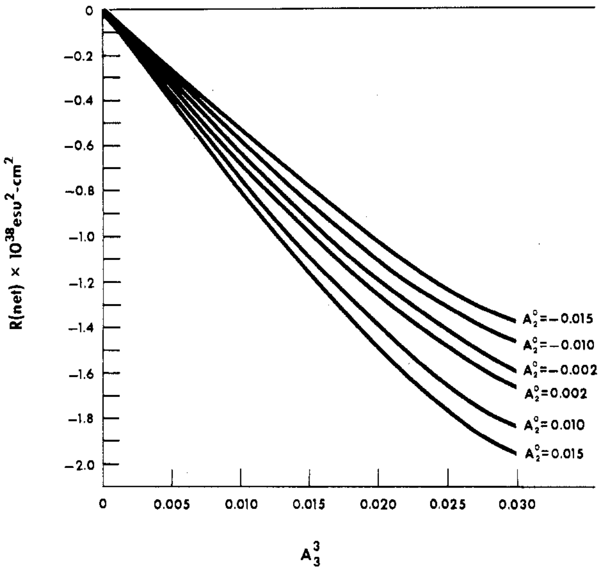

Figure 3. Net d-d rotatory strength, R(net), plotted vs. A_3^3 for selected fixed values of A_2^0. A_2^0 and A_3^3 are expressed in atomic units.

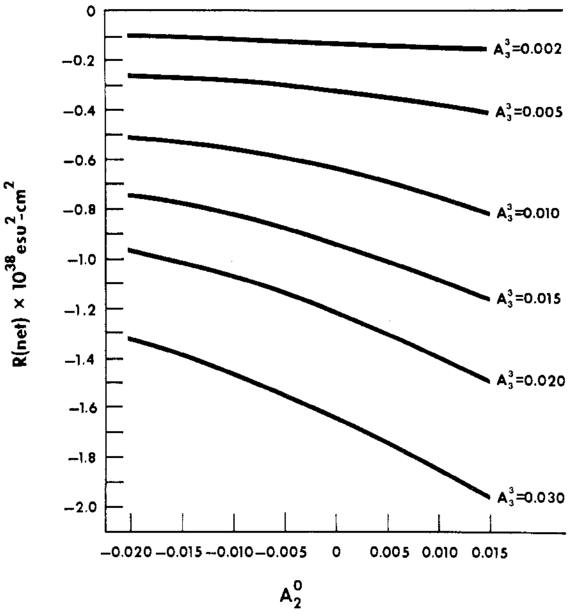

Figure 4. Net d-d rotatory strength, R(net), plotted vs. A_2^0 for selected fixed values of A_3^3. A_2^0 and A_3^3 are expressed in atomic units.

Table X. Computed Values of R_e', R_e'', R_a, and ρ[a]

	A_3^3, au					
	0.002	0.005	0.010	0.015	0.020	0.030
			A_2^0 = 0.002 au			
R_e'	−0.24	−0.62	−1.20	−1.72	−2.18	−2.90
R_e''	0.70	1.76	3.46	5.04	6.46	8.76
R_a	−1.84	−4.60	−9.02	−13.12	−16.80	−22.76
$\|\rho\|$	0.25	0.25	0.25	0.25	0.25	0.26
			A_2^0 = −0.002 au			
R_e'	−0.24	−0.56	−1.12	−1.62	−2.06	−2.74
R_e''	0.66	1.66	3.26	4.76	6.12	8.36
R_a	−1.76	−4.36	−8.56	−12.46	−16.00	−21.76
$\|\rho\|$	0.25	0.25	0.25	0.25	0.25	0.26
			A_2^0 = 0.010 au			
R_e'	−0.28	−0.70	−1.38	−1.98	−2.48	−3.24
R_e''	0.80	1.98	3.88	5.62	7.18	9.62
R_a	−2.06	−5.12	−10.04	−14.56	−18.56	−24.86
$\|\rho\|$	0.25	0.25	0.25	0.25	0.25	0.25
			A_2^0 = −0.010 au			
R_e'	−0.20	−0.50	−0.96	−1.40	−1.80	−2.44
R_e''	0.60	1.48	2.90	4.26	5.50	7.60
R_a	−1.58	−3.92	−7.70	−11.26	−14.50	−19.88
$\|\rho\|$	0.25	0.25	0.25	0.25	0.25	0.26
			A_2^0 = 0.015 au			
R_e'	−0.32	−0.78	−1.52	−2.16	−2.70	−3.48
R_e''	0.86	2.14	4.18	6.04	7.66	10.18
R_a	−2.22	−5.50	−10.76	−15.56	−19.76	−26.30
$\|\rho\|$	0.25	0.25	0.25	0.25	0.25	0.25
			A_2^0 = −0.015 au			
R_e'	−0.18	−0.46	−0.88	−1.30	−1.66	−2.26
R_e''	0.56	1.36	2.70	3.96	5.12	7.14
R_a	−1.48	−3.66	−7.22	−10.56	−13.62	−18.76
$\|\rho\|$	0.25	0.25	0.25	0.25	0.26	0.26

[a] R_e', R_e'', and R_a are expressed in 10^{-39} esu^2 cm^2 units.

of radial integrals and orbital energies. We present here only representative results obtained for various sets of crystal field interaction parameters A_2^0 and A_3^3. In obtaining these results the radial integrals and orbital energies listed in section III (Calculations) were used.

In Figure 1 δ (calculated) is plotted as a function of A_2^0 for five different values of A_3^3. We note that within the approximations of our model δ is a linear function of the polar crystal field distortion parameter A_2^0 (for the fixed values of A_3^3 shown in Figure 1). In Figure 2, δ (calculated) is plotted as a function of A_3^3 for various fixed values of A_2^0. The dependence of R(net) on A_3^3 (for fixed values of A_2^0) is shown in Figure 3, and the dependence of R(net) on A_2^0 (for fixed values of A_3^3) is shown in Figure 4. Only positive values of A_3^3 were chosen in computing the results shown in Figures 3 and 4; negative values of A_3^3 would simply change the sign of R(net). The sign of R(net) is entirely determined by the sign of A_3^3.

Computed values of R_e', R_e'', R_a, and ρ are displayed in Table X for selected sets of the crystal field parameters (A_2^0, A_3^3). Perhaps the most remarkable features of these data are the near constancy of the ratio $\rho = (R_e' + R_e'')/R_a$ and the observation that this ratio is always computed to be <1. The results given in Table I were computed using the radial integrals and zeroth-order orbital energies listed in section III and assuming 3d–4p–4f interactions. The absolute value of ρ is somewhat sensitive to the choice of radial integrals and orbital energies and to whether 3d–4p, 3d–4f, or 3d–4p–4f basis sets are employed. However, the near invariance of ρ to (A_2^0, A_3^3) parameter sets held for all of our calculations, and ρ was computed to be <1 for all values of input parameters which we used.

The data presented in Figures 1–4 and in Table X were obtained from calculations in which metal ion orbital basis sets included 3d, 4p, and 4f orbitals. We also performed calculations in which only 3d–4p and 3d–4f orbital basis sets were employed. The *qualitative* aspects of our computed results were not essentially different for these three basis sets, although the absolute values of R_e', R_e'', and R_a were about an order of magnitude larger for the 4d–4p basis set vs. the 3d–4f basis set (given the orbital energies and radial integral values listed in section III).

V. Discussion

The principal purpose of this study was to extend the crystal field, one-electron model of d–d optical activity in trigonal-dihedral (D_3) metal complexes to all orders in the first two noncubic terms of the crystal field potential energy operator and to examine the d–d rotatory strengths computed from such a model. The crystal field, one-electron model was first applied to the d–d optical activity of such systems by Moffitt,[10] and several subsequent studies[1–4,15,16,18,20–22] were devoted to the refinement and use of the basic Moffitt treatment. Despite the obvious crudity of this model with respect to the physical representation of metal–ligand interactions, its simplicity and essential correctness in representing the symmetry-related aspects of the problem make it particularly attractive for developing spectra–structure relationships (such as, for example, sector or regional rules).

In previous applications of the crystal field, one-electron model, the crystal field perturbation of the chromophoric d electrons of the metal ion was carried to either first or second order in the noncubic terms of the crystal field Hamiltonian operator. The first-order treatments lead to the so-called "octahedral sector rule" for d–d optical activity in trigonal six-coordinate transition metal complexes, and the second-order treatments lead to so-called "mixed sector rules". Since it is by no means clear that the perturbation treatment should yield convergent results at or after a specified perturbation order, it seemed in order to examine the results obtained with the basic model when the perturbation treatment was carried to "all orders". This is what was done in the present study. This approach does not, of course, improve upon the basic physical limitations of the crystal field, one-electron model (which are substantial), but it *does* permit a more complete assessment of the reliability and validity of the model in its application to d–d optical activity.

The most troublesome results obtained in the present study with regard to the use of the crystal field, one-electron model in interpreting experimental chiroptical data are the apparent constancy of ρ with respect to A_2^0 and A_3^3 values (varied over "physically reasonable" ranges) and the finding that ρ is always <1. These computed results are in apparent conflict with experimental data.[1,20] Experimentally it has been found that ($R_e' + R_e''$) is generally larger in magnitude than R_a for trigonal metal complexes and that the ratio $(R_e' + R_e'')/R_a$ is somewhat sensitive to the detailed structural (stereochemical) features of the ligand environment. Since, in the crystal field model, A_2^0 and A_3^3 are meant to reflect these structural features, one might expect $\rho = R_e' + R_e'')/R_a$ to vary with A_2^0 and A_3^3.

The "ionic" or crystal field, one-electron model of d–d optical activity has had a very strong and useful influence on the interpretation of chiroptical spectra associated with dissymmetric transition metal complexes. Whatever the merits or otherwise of this very simple model, it has provided a convenient focus from which many aspects of the problem could be discussed and a point of departure for more refined theoretical treatments. However, the results obtained in the present study as well as those reported in several other recent studies strongly suggest that the ionic model has very little, if any, quantitative usefulness and that even purely *qualitative* deductions drawn from it should be considered with great circumspection (and some skepticism). The shortcomings of this model lie deeper than truncation of the perturbation treatment after first or second order and inclusion or exclusion of higher order terms (large values of l) in the expansion of the chiral parts of the crystal field. If a one-electron, static coupling model is adopted, it would seem essential to include among the chromophoric basis states charge-transfer excitations involving both metal orbitals and donor atom orbitals. Recent studies by Mason and co-workers[13,14] indicate that, even when the ligands contain only saturated groups, a dynamical coupling model appears to provide a fully satisfactory description of d–d optical activity in trigonal metal complexes.

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