Theory of Optical Activity in the Ligand-Field Transitions of Chiral Transition Metal Complexes

FREDERICK S. RICHARDSON

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received August 24, 1978

Contents

I. Introduction

The optical activity of chiral transition metal complexes has occupied the attention of coordination chemists and theoretical spectroscopists for many years. The optical rotatory properties of coordination compounds have played a prominent and venerable role in the development of inorganic stereochemical analysis and structure elucidation, and experimental and theoretical research in this area has been particularly intense over the past 20 years. The first observation of circular dichroism (CD) in the visible absorption bands of transition metal complexes was reported by Cotton in 1895.[1] Over the period 1911–1919, Werner[2] resolved into optical isomers a wide range of bis- and tris-chelated complexes containing achiral ligands and transition metal ions from each of the three transition metal series of the periodic table. This work established the octahedral structure of hexacoordinated complexes and posed the problems of molecular stereochemistry and absolute configuration of metal coordination compounds. The optical rotatory properties of the Werner complexes were the subject of considerable study in the 1930's, most notably by Jaeger,[3] Mathieu,[4] and Kuhn.[5-7] The first purely theoretical examination of the origins of optical activity in chiral transition metal complexes was made by Kuhn and Bein.[5,6] Their treatment of these systems was based on the general coupled-oscillator model of molecular optical activity proposed earlier by Kuhn.[8-10] This model was purely classical, and it was used to relate the absolute configuration to the sign and the form of the visible Cotton effects observed for tris-chelated complexes.

The first definitive determination of the absolute configuration of a chiral metal complex was made by Saito and co-workers[11] in 1955, using the anomalous X-ray scattering method. Saito and co-workers[11] found that the tris(ethylenediamine)cobalt(III) isomer which is dextrorotatory at the sodium D-line, (+)-$[Co(en)_3]^{3+}$, has the Λ configuration.[12] This finding was contrary to the configurational assignment predicted according to the Kuhn and Bein coupled-oscillator model for tris-chelated complexes.[5,6]

Moffitt[13] introduced the first quantum mechanical theory of optical activity in chiral transition metal complexes. He adopted a crystal-field model on which to represent the spectroscopic states of the metal ion d electrons, and used the "one-electron" theory of molecular optical activity proposed by Condon, Altar, and Eyring[14] to develop expressions for the rotatory strengths of the metal d–d transitions. Moffitt applied his theory specifically to tris-chelated complexes of Co(III) and Cr(III) which have exact trigonal dihedral (D_3) symmetry. An error in sign in the d–d transition matrix of the angular momentum operator led Moffitt to incorrect conclusions regarding the optical rotatory properties of these systems, and Sugano[15] subsequently demonstrated that Moffitt's model could not account for the *net* optical activity observed for the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition in trigonal dihedral complexes of Co(III) and for the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition in Cr(III) complexes of trigonal dihedral symmetry. However, the general aspects of Moffitt's model remained intact, and his work provided an important stimulus for much of the subsequent theoretical effort in this area.

The availability of improved optical rotatory dispersion (ORD) and circular dichroism (CD) instrumentation in the early 1960's signaled a great resurgence in the study of molecular optical activity and in the use of optical rotatory properties as probes of molecular stereochemistry and electronic structure. Biopolymer systems, organic carbonyl compounds, and chiral transition metal complexes received, perhaps, the most experimental and theoretical attention during this time. The rather highly developed state of ligand-field theory, in its applications to sorting out the optical spectra associated with the d–d transitions of transition metal complexes, was especially important to providing a theoretical framework (albeit, approximate) within which d–d optical activity could be interpreted or rationalized. Spectra–structure relationships were, and remain, somewhat less well defined for chiral transition metal complexes than for the $n \rightarrow \pi^*$ optical activity of carbonyl compounds (for example), but they are sufficiently good to provide valuable working hypotheses and guidelines for researchers in the field.

Developments in the theory of optical activity of chiral transition metal complexes have been enormously aided by the very large quantity of experimental data reported over the past 15 years on a wide variety of metal complex structural types (classified with respect to metal ion, ligand donor atoms, ligand chelation, chelate bridging groups and side chains, and general symmetry characteristics). Furthermore, the dramatic increase in the number of metal complexes whose detailed structural features have been elucidated by single-crystal X-ray diffraction techniques has been important to developing reliable spectra–

0009-2665/79/0779-0017$05.00/0
© 1979 American Chemical Society

structure correlations.[16] Finally, improvements and refinements in the quantum mechanical descriptions of d–d spectroscopic states have, over the past 15 years, led to some refinement in the d–d optical activity models developed subsequent to Moffitt's simple crystal-field model.[13]

The plan for this paper is to briefly review and describe the major developments in the theory of optical activity of chiral transition metal complexes, to discuss in some detail the models and theories of current interest, to survey the spectra–structure relationships associated with the chiroptical properties of chiral transition metal complexes, to discuss special effects arising, for example, from vibronic interactions, solvent perturbations, and crystalline environments, and, finally, to assess the current status and future prospects of the field. The focus will be on the d–d or so-called ligand-field transitions of the metal complexes, and only indirect references will be made to the optical activity associated with the ligand–ligand and metal–ligand charge-transfer transitions.

II. Background Review

As was mentioned in the Introduction, Kuhn and Bein[5,6] proposed the first theoretical model for the optical activity of chiral transition metal complexes. Selecting the tris complexes, $Co(en)_3^{3+}$ and $Co(ox)_3^{3-}$, as model systems, Kuhn and Bein[5,6] postulated that electronic transitions localized on the metal ion gained optical activity by coupling with electric dipole oscillators localized on the three bidentate ligands. More specifically, they represented the optical electron on the metal ion as a three-dimensional isotropic harmonic oscillator with a characteristic frequency (say, ν_M) and the ligands by three linear oscillators of frequency ν_L ($\nu_L > \nu_M$) directed along the edges of the octahedron spanned by the chelate rings. On this model, the spatial arrangement of the three ligand oscillators is dissymmetric (chiral) and their *coupled* motions give rise to a dissymmetric force field. If the metal ion (three-dimensional) oscillator is, in turn, coupled to the ligand oscillators via this dissymmetric force field, then optical activity will be observed at the frequencies of the perturbed metal oscillator (i.e., in the metal ion absorption bands near ν_M), as well as at the frequencies of the perturbed ligand oscillators (i.e., in the ligand absorption bands near ν_L). In the Kuhn and Bein model, the metal ion oscillator represented *linear* displacements of the optical electron and the metal–ligand coupling mechanism was assumed, therefore, to be electric dipole–electric dipole. This model was entirely classical in its details and did not take into account the detailed nature of the electronic transitions responsible for the visible absorption bands of the metal complexes. Subsequent characterization of these transitions as essentially parity-forbidden d–d excitations pointed to the necessity of treating the optical electrons as *circular*, rather than *linear*, oscillators. In quantum mechanical language, the d–d transitions may be characterized in general as having substantial magnetic dipole character and only very weak electric dipole character.

Moffitt[13] introduced the first theory of optical activity in transition metal complexes based on quantum mechanical principles. This theory was introduced in 1956 and it made use of the Rosenfeld expression for electronic rotatory strengths,[17] the "one-electron" theory of molecular optical activity as proposed by Condon, Altar, and Eyring,[14] and the crystal-field theory of transition metal ion d–d absorption spectra.[18] The central problem was to calculate the rotatory strength, R_{ij}, associated with a specific d–d transition, $i \rightarrow j$, of the transition metal complex. The Rosenfeld expression for rotatory strength is given by

$$R_{ij} = \mathrm{Im}\langle\psi_i|\hat{\mu}|\psi_j\rangle \cdot \langle\psi_j|\hat{m}|\psi_i\rangle \qquad (1)$$

where $\hat{\mu}$ is the electric dipole operator, $\hat{m}$ is the magnetic dipole operator, and $\mathrm{Im}(A + iB) = B$. Considering only hexacoordinate, tris-chelated complexes of exact trigonal dihedral (D_3) symmetry, Moffitt adopted a crystal-field perturbation model in which, to zeroth order, the d electrons of the metal ion were subjected to a crystal-field potential of exact octahedral (O_h) symmetry. The magnetic dipole transition moments of eq 1 were then calculated using the d-electron eigenstates of the zeroth-order (octahedral) crystal-field Hamiltonian. Using first-order perturbation theory, he then introduced the ungerade components of the trigonal dihedral (D_3) crystal field and permitted mixing of the metal ion d and p orbitals. This admixture of metal ion d and p orbitals resulted in nonvanishing values for the electric dipole transition moments (calculated to first order) of eq 1. The d–d optical activity was assumed to arise, then, from (dissymmetric) crystal-field-induced mixing of the metal ion d and p orbitals.

Moffitt applied his model to tris-chelated complexes of Co(III) and Cr(III) and predicted strong optical activity within the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of Co(III) and within the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of Cr(III). These transitions are both magnetic dipole allowed under octahedral (O_h) selection rules. The magnetic dipole forbidden transitions, $^1A_{1g} \rightarrow {}^1T_{2g}$ for Co(III) and $^4A_{2g} \rightarrow {}^4T_{1g}$ for Cr(III), were predicted to be optically inactive within the approximations of the Moffitt model. These predictions were in good qualitative agreement with experimental observation since the magnetic dipole allowed transitions (referring to selection rules based on the octahedral parentage of the ground and excited states) do, in fact, exhibit substantially stronger optical activity than do the magnetic dipole forbidden transitions in the tris(oxalato) and tris(ethylenediamine) complexes of Cr(III) and Co(III). However, Moffitt's predictions were based on calculations which included an error in sign in the d–d transition matrix of the angular momentum operator (and, consequently, the magnetic dipole operator). Sugano[15] showed that when this error is corrected, Moffitt's model leads to zero *net* rotatory strength within the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions of Co(III) and Cr(III), respectively. Sugano[15] further showed that in order for Moffitt's model to yield a *net* rotatory strength in these transitions, the crystal-field expansion would have to include at least one ungerade term with $\ell \geq 9$. More specifically, the chiral (D_3) trigonal crystal-field perturbation potential must include at least one term which transforms as the pseudoscalar A_{1u} irreducible representation of the O_h point group. The lowest order term transforming as A_{1u} in O_h has $\ell = 9$. In his calculations, Moffitt truncated the (D_3) trigonal crystal-field expansion after the leading ungerade term ($\ell = 3$) which transforms as T_{2u} in the O_h point group. Sugano's conclusions were based on the uniquely deduced arguments of group theory and therefore depended on the physical model only insofar as the zeroth-order basis states of the perturbation model were taken to be eigenstates of an octahedral (O_h) crystal-field Hamiltonian. A crystal-field potential term with $\ell = 9$ can mix d orbitals ($\ell = 2$) only with metal orbitals of azimuthal quantum numbers $\ell = 7, 9$, or 11, a most unrealistic condition. Moffitt's ungerade trigonal potential ($\ell = 3$) can mix the metal d orbitals with p and f orbitals, but to first-order the rotatory strengths associated with the two trigonal (D_3) components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of Co(III) will be equal in magnitude and opposite in sign. The *net* $^1A_{1g} \rightarrow {}^1T_{1g}$ rotatory strength will, therefore, vanish. The same result is obtained for the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of Cr(III).

Hamer[19] extended Sugano's analysis[15] of Moffitt's one-electron crystal-field perturbation model to show that for any metal complex assumed to be centrosymmetric to zeroth order, a first-order *net* d–d rotatory strength is generated only by a ligand-field potential possessing at least one component which transforms under the pseudoscalar irreducible representation of the point group of the zeroth-order complex.

Despite the initial failure of the one-electron crystal-field model (often referred to as the "ionic" model) to account for the *net* optical activity observed in the d–d transitions of tris-chelated Cr(III) and Co(III) complexes, the elegance and simplicity of this model inspired numerous additional efforts to adapt its basic physical and symmetry-determined features to the problem at hand.[20-31] Poulet[20] modified Moffitt's treatment of tris-chelated Co(III) and Cr(III) complexes by allowing some trigonal splitting to occur within the triply degenerate octahedral excited states. It was postulated that a gerade component of the D_3 crystal-field potential lifted the degeneracy of the zeroth-order octahedral states and, as in Moffitt's treatment,[13] the lowest order ($\ell = 3$) ungerade component of the D_3 potential induced the optical activity. This, of course, resulted in a predicted CD spectrum for the Cr(III) $^4A_{2g} \rightarrow {}^4T_{2g}$ transition with two closely spaced components of identical intensities and opposite signs. The *net* CD intensity was calculated to be zero (as required by Sugano's analysis). Piper and Karipedes[21] extended Moffitt's treatment to include 3d, 4p, and 4f orbitals in the zeroth-order metal orbital basis set for calculations on tris-chelated Co(III) and Cr(III) complexes. Restricting their perturbation treatment to first order in the $\ell = 3$ component of the D_3 crystal field, they too found the *net* d–d rotatory strength to be zero.

The first extension of Moffitt's ionic model which led to a nonvanishing *net* d–d rotatory strength for tris-chelated transition metal complexes was reported by Sugano and Shinada.[22,32] In their physical model, Sugano and Shinada[22,32] represented the ligand environment by two sets of point–dipoles located on the ligand atoms coordinated directly to the metal ion. One set produced a trigonal (D_3) potential of odd (ungerade) parity (and with $\ell = 3$ transformation properties), and the other set produced a trigonal (D_3) potential of even (gerade) parity (and with $\ell = 2$ transformation properties). The gerade potential is effective in mixing the metal d orbitals among themselves and in lifting the degeneracy of the (D_3) trigonal components of the octahedral (zeroth-order) parent states. The ungerade potential is effective in mixing zeroth-order octahedral states of opposite parities (or in promoting d–p and d–f orbital mixing on the metal ion). The gerade and ungerade perturbation potentials employed by Sugano and Shinada[22,32] transformed as T_{2g} and T_{2u}, respectively, under the symmetry operations of the O_h point group. The direct product representation spanned by products of the ungerade (T_{2u}) and gerade (T_{2g}) potentials includes in it one component which transforms as the pseudoscalar A_{1u} irreducible representation of the O_h point group. Carrying out their perturbation calculations to second-order in the rotatory strength, Sugano and Shinada[22,32] found that the *net* second-order rotatory strength contributions were nonvanishing and that the signs of these contributions were dependent upon the sign of the trigonal splitting parameter (as determined by the gerade perturbation potential) and upon the detailed nature of the ungerade perturbation potential. The dominance of one trigonal field component rotatory strength over the other was predicted to be entirely determined by the sign and magnitude of the trigonal field splitting parameter.

Sugano and Shinada's extension[22,32] of the one-electron crystal-field model to second order in the rotatory strength quantities was successful in accounting for the *net* d–d rotatory strengths observed for tris-chelated metal complexes, and it also accounted for the nonzero (but small) optical activity observed in the regions of magnetic dipole forbidden transitions such as the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition of Co(III) complexes and the $^4A_{2g} \rightarrow {}^4T_{1g}$ transition of Cr(III) complexes. The latter feature of Sugano and Shinada's treatment originated with interactions (and mixings) between different d–d excited states under the influence of the gerade trigonal potential. The *simultaneous* consideration of the lowest order gerade *and* ungerade components of the trigonal perturbation potential required only d–d and d–p metal orbital mixings to achieve *net* optical activity, and avoided the need for including $\ell \geq 7$ metal orbitals in the zeroth-order basis set as was required by the original Moffitt model. The representation of the ligand environment by sets of point–dipoles located on the donor atoms of the ligands provided only a crude physical approximation to the real structural features of the complexes, but it remained within the spirit of applied crystal-field theory.

Richardson and co-workers[24-28,30,31] have carried out perhaps the most extensive theoretical investigations on the one-electron crystal-field model of optical activity in chiral transition metal complexes. These investigations have included studies of a wide variety of structural types, of various sources of dissymmetry in the ligand environment (e.g., configurational, conformational, and vicinal), and of the convergent nature of the perturbation and crystal-field expansions employed in the model. In this work, a pure crystal-field representation of the ligand environment was employed in which all atoms or groups (molecular fragments) of the ligands were treated as point charge distributions. The signs and magnitudes of the (partial) charges assigned to each perturber site in the ligand environment were assumed to be derivable from local bond moments and formal charges (of ionized groups) characteristic of the ligand ground-state charge distributions. Each term in the crystal-field perturbation potential expansion was taken as a sum over all ligand perturber sites in the complex. This latter feature of the model permitted a partitioning of effects attributable to *configurational* dissymmetry (reflecting the distribution of chelate rings about the metal ion), *conformational* dissymmetry (reflecting conformational features and preferences within chelate rings), the presence of asymmetrically substituted sites in the ligands, and local (dissymmetric) distortions within the metal–donor atom cluster of the complex.

In most (but not all) cases examined by Richardson and co-workers, a centrosymmetric microsymmetry was assumed to zeroth order for the metal–donor atom chromophoric cluster, and rotatory strength expressions were developed to second order in a chiral perturbation potential. The chiral perturbation potential was chosen such that only the metal d, p, and f orbitals were required in constructing the zeroth-order basis states of the perturbation model. The principal focus of these studies was on how the *net* CD intensity might be expected to distribute itself among the various d–d transitions of a given metal complex, and on how the sign and intensity observables of a given CD spectrum may be related to specific stereochemical and electronic structural features of a metal complex. The latter problem was addressed through the formulation of detailed "sector" or "regional" rules for metal complex CD spectra.

Sector (or regional) rules in chiroptical spectroscopy are used to correlate the sign and, in some cases, the intensity observables of a CD spectrum with the *relative* positions or spatial arrangements of the chromophoric and extrachromophoric atoms (or groups) of a chiral molecular system. They are useful, therefore, in deducing stereochemical information concerning optically active systems. In most applications to simple optically active organic compounds, sector rules are applied to just one electronic transition at a time (e.g., the $n \rightarrow \pi^*$ transition of chiral carbonyl compounds in the famous octant rule[33]) and are based on simple *pairwise* (chromophore–perturber) interaction mechanisms.[34] For transition metal complexes, however, Richardson[24-27] proposed that the most appropriate (and reliable) sector rules be based on the *net* optical activity associated with all the d–d transitions in a given complex (that is, the algebraic sum of all d–d CD intensities), and that the sector rules must include consideration of *three-way* interactions involving the metal ion (chromophore) and two different ligand perturber groups. The latter emphasis of three-way interactions (leading to so-called "mixed" sector rules) is a consequence of the second-order nature of the perturbation model employed by Richardson, and the necessity for considering *total* or *net* d–d optical activity (rather than the optical activity of individual d–d transitions) arises from the assumed strong coupling (and intensity borrowing) between the relatively closely spaced d–d transitions of most metal complexes. Detailed accounts of how Richardson's sector rules may be applied to the prediction and interpretation of metal complex CD spectra have been given,[24-27,35] and some use of them has been reported in the experimental literature. The general validity of the sector rules proposed by Richardson rests on the validity of the one-electron crystal-field model from which they were derived. Although the symmetry-determined aspects of this model are straightforward and valid, its completeness and its reliability in modeling the optical activity of transition metal complexes remain in question.

Strickland and Richardson[28] employed the one-electron crystal-field perturbation model in performing detailed calculations on the d–d optical activity of Ni(II) in crystalline $NiSO_4 \cdot 6H_2O$, and Richardson and Hilmes[30] performed similar calculations on the d–d optical activity of Cu(II) in crystalline $ZnSeO_4 \cdot 6H_2O$. The site symmetry at the metal ion in both of these systems is C_2, while the microsymmetry of the MO_6 clusters is very nearly octahedral (O_h). Second-order perturbation theory was used in each case to calculate the d–d rotatory strengths. In the case of Cu(II) in $ZnSeO_4 \cdot 6H_2O$, vibronic interactions of the pseudo-Jahn–Teller type were also taken into account in calculating the d–d CD spectrum.[30] Kato[36] has performed a theoretical analysis of the d–d optical activity observed for a series of divalent transition metal ions doped into single crystals of $ZnSeO_4 \cdot 6H_2O$. Her analysis was based on Sugano and Shinada's[22,32] model for d–d optical activity and included consideration of Cu(II), Ni(II), Co(II), Fe(II), and Mn(II).

The deficiencies of the one-electron crystal-field perturbation model in properly representing the physical aspects of the ligand environment and its interactions with the metal ion are readily apparent and widely recognized. However, the more subtle problems with this model such as dealing with the proper convergence criteria for the perturbation potential expansion and the order to which the perturbation calculation (of rotatory strengths) should be carried are not so widely appreciated. For six-coordinate metal complexes of near octahedral (O_h) microsymmetry, it seems clear that a first-order treatment of the model is inappropriate owing to the rather "unphysical" requirements of including metal orbitals of $\ell \geq 7$ angular momentum in the zeroth-order basis set and of using a perturbation potential of extremely short distance dependence (R^{-10}). As shown by Sugano and Shinada[22,32] and by Richardson,[24] a second-order treatment will generate *net* d–d optical activity when the metal orbital basis set is restricted to d, p, and f orbitals and the perturbation potential is limited to just two low-order terms, a gerade term with $\ell = 2$ and an ungerade term with $\ell = 3$. Richardson[31] has also pointed out that if the model is carried to third order (in the rotatory strengths), a single ungerade term of $\ell = 3$ in the perturbation potential will lead to *net* d–d optical activity. Recently, Hilmes and Richardson[31] reported calculations of d–d optical activity in trigonal dihedral (D_3) complexes based on the one-electron crystal-field ("ionic") perturbation model carried to "all-orders" in the leading noncubic (trigonal) terms of the crystal-field interaction potential. This was essentially a variational calculation in which the metal orbital basis set was restricted to 3d, 4p, and 4f orbitals, and the crystal-field perturbation potential was restricted to the $Y_2{}^0$ and $(Y_3{}^{-3} - Y_3{}^3)$ trigonally symmetric terms. The "perturbed" wave functions were obtained by diagonalizing the trigonal Hamiltonian matrix, and these wave functions were then used to calculate the rotatory strengths associated with trigonally perturbed d–d transitions.

The "ionic" or one-electron crystal-field model of d–d optical activity has had a very strong and useful influence on the interpretation and understanding of the 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 can be discussed and has served as a point of departure for more refined theoretical treatments. However, it seems clear at this point that the ionic model has little, if any, quantitative usefulness and that many of the qualitative deductions drawn from it should be considered with some circumspection. It has provided valuable working hypotheses for experimentalists in the field, and its formalism has been important in analyzing the symmetry-determined aspects of d–d optical activity in a wide range of metal complex structural types. The shortcomings of the 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 ligand field. Modifications of the basic model to include consideration of an "extended" chromophoric unit comprised of the metal ion and the ligand donor atoms, and the inclusion of ungerade metal–ligand charge-transfer states in the zeroth-order basis set,[37] improve the physical representation of the problem but do not enhance its quantitative utility.

The successes and failures of the various applications of the ionic model to correlating CD spectral observables to absolute configuration will not be reviewed here. Such correlations are related more directly to how the crystal-field potential constants are calculated and defined than to the general, formalistic aspects of the model. As is true in most applications of crystal-field theory to the absorption spectra of metal complexes, the proper methods for evaluating these potential constants remain ambiguous. Mason has commented upon this problem in a previous review article.[35]

In 1963, Bürer[38] suggested a ligand-field approach to the problem of calculating d–d rotatory strengths in tris-chelated complexes of the type studied by Moffitt[13] and by Piper and Karipedes.[21] In this approach it was presumed that explicit consideration of metal–ligand bonding (or antibonding) would lead to a trigonal potential of a sign opposite to that used by Piper and Karipedes[21] in their crystal-field treatment, and would also yield a trigonal splitting energy with a sign opposite that assumed in the crystal-field calculation. Bürer never reported rotatory strength calculations based on his proposed ligand-field model and this approach has not been pursued further.

The first theoretical studies of optical activity in transition metal complexes to employ a molecular orbital representation of the spectroscopic states were reported by Liehr[39,40] and by Karipedes and Piper.[41] In the latter study, the molecular orbitals were constructed in the LCAO (linear combination of atomic orbitals) approximation, the ligand orbital basis set was restricted to the 2s and 2pσ atomic orbitals on the ligand donor atoms, and only the 3d and 4p orbitals of the metal ion were included. Metal–ligand π-bonding was neglected. Optical activity was generated by chiral distortions within the metal–donor atom cluster of the complex. Dissymmetry in the nondonor atom parts of the ligand environment was presumed to contribute only *indirectly* to the d–d metal ion optical activity through ligand-induced distortions of the metal–donor atom cluster away from an achiral microsymmetry. Karipedes and Piper[41] applied their molecular orbital model to the tris(ethylenediamine) and tris(oxalato) complexes of Co(III) and Cr(III) and made correlations between the signs of the various CD bands associated with metal ion d–d transitions and specific structural distortions within the metal–donor atom chromophoric cluster. However, since precise relationships between these distortions in the ML_6 cluster and the distribution and structural features of the chelate rings could not be formulated generally or unambiguously, assignments of absolute configuration based on this model remained tentative. The Karipedes and Piper[41] molecular orbital model leads to the prediction that two complexes (of a given metal ion) with *different* absolute configurations will exhibit identically signed rotatory strengths (and CD bands) if the chelate rings in the two systems induce similar (chiral) distortions within the ML_6 cluster. This result follows from the neglect of direct interactions between the nondonor atoms of the chelate systems and the chromophoric electrons of the metal ion. The nondonor atoms and groups in the ligand environment merely serve to "mechanically" distort the ML_6 cluster.

Liehr constructed molecular orbital models for the optical activity of six-coordinate complexes of trigonal dihedral symmetry[39] and four-coordinate complexes of digonal dihedral symmetry.[40] The essential feature of Liehr's models is a "significant angle of mismatch" between the directions of maximum charge density for the metal d orbitals and the donor orbitals of the ligand atoms. In the trigonal dihedral (six-coordinate) systems, the ligand donor atoms were assumed to be situated at the vertices of a regular octahedron, but the donor atom σ orbitals were taken to be "canted" with respect to the metal-donor atom internuclear axis. This angle of cant (denoted α by Liehr[39]) was assumed to reflect the detailed structural features of the chelate rings, and all the dissymmetry in the ligand environment was assumed to be communicated to the metal ion via this deviation of each primary metal-donor atom linkage from axial symmetry (about the M-L internuclear axis). In this treatment the rotatory strengths turn out to be proportional to sin α. Liehr's model for digonal dihedral (four-coordinate) systems depended similarly on distortions within M-L σ bonds of the complex.

Liehr did not carry out detailed calculations based on his models, and the conceptual basis of his work is not easily transformed into working hypotheses which can be tested by experiment. Piper and Karipedes[42] calculated the d-d dipole strengths of the $Cu(en)_3^{3+}$ system using Liehr's bent-bond model and concluded that it underestimates the electric dipole transition integrals by at least an order of magnitude.

In 1973, Strickland and Richardson[43] reported molecular orbital calculations on the d-d rotatory strengths of trigonally distorted six-coordinate complexes of Co(III) and Cr(III) with nitrogen and oxygen donor atoms. The electronic states of spectroscopic interest were constructed from molecular orbitals calculated on a modified Wolfsberg-Helmholz model. Calculations were carried out on ML_6 clusters (M = metal atom, L = donor or ligator atom) in which either the nuclear geometry of the ML_6 system had trigonal dihedral (D_3) symmetry or the donor orbitals of the ligand atoms (L) were trigonally disposed about the metal atom. That is, chirality was introduced into the ML_6 cluster either by a Piper representation (trigonal nuclear geometry)[41] or by a Liehr representation (ligand donor orbitals canted from the M-L axes in an octahedral ML_6 cluster).[39,40] Additional calculations were carried out in which *both* a trigonally distorted ML_6 cluster and (dissymmetrically) canted donor orbitals were present simultaneously. Trigonal distortion parameters for donor atom displacements (from octahedral geometry) and for donor orbital directions (with respect to the M-L axes) were varied to simulate the various structural features known to occur in a variety of tris-chelated complexes of Co(III) and Cr(III). The atomic orbital basis set used in the molecular orbital calculations consisted of the 4s, 4p, and double-ζ 3d metal orbitals and the 2s and 2p orbitals on each ligand atom (either oxygen or nitrogen). M-L σ and π interactions were treated separately in the molecular orbital parameterization scheme.

The results reported by Strickland and Richardson[43] suggest that neither the Piper model[41] nor the Liehr model[39] provides an adequate representation of the source of d-d optical activity in trigonal dihedral metal complexes. However, the more refined and comprehensive molecular orbital model employed by Strickland and Richardson[43] did prove to be useful in deducing *qualitative* information about the sensitivity of d-d rotatory strengths to various kinds of distortions within the ML_6 cluster of these systems. Furthermore, since the computational parameters of the model were defined to reflect specific structural features of the ligand environment, rather specific spectra-structure correlations could be deduced from the calculated results.

In 1974, Evans, Schreiner, and Hauser[44] reported molecular orbital calculations on the d-d optical activity of the tris(ethylenediamine) complexes of Co(III) and Cr(III). The level of approximation and general features of the molecular orbital model employed in this study[44] were similar (but not identical) to those of Strickland and Richardson's model.[43] However, whereas Strickland and Richardson[43] considered only distorted ML_6 clusters, Evans, Schreiner, and Hauser (ESH)[44] included all atoms (M, C, N, and H) in their calculations. ESH used structure parameters derived from the X-ray crystallographic study of D-$Co(en)_3Br_3 \cdot H_2O$ reported by Nakatsu.[45] The only structure variations considered in the ESH study were "lel" → "ob" geometry changes within the metal-ethylenediamine chelate rings. ESH did, however, thoroughly investigate the sensitivity of their rotatory strength calculations to various computational features of their molecular orbital model and to various operator representations of the rotatory strength quantity. They also carried out comparative rotatory strength calculations using *complete* multicenter operator matrices (angular momentum, dipole velocity, and dipole length) and successively approximate ones. The ESH calculations proved successful in relating the absolute configurations of $Co(en)_3^{3+}$ and $Cr(en)_3^{3+}$ to the natural CD observed for the magnetic dipole allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions in the Co(III) and Cr(III) complexes, respectively. Furthermore, the calculations correctly accounted for the relative signs of the trigonal components of the rotatory strengths (associated with the magnetic dipole allowed transitions), as well as the *net* $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ rotatory strengths. The model also showed sensitivity of d-d rotatory strength to ligand (chelate ring) conformation.

Richardson and co-workers[46,47] have reported additional "all-atom" molecular orbital calculations of d-d rotatory strengths for a number of four-coordinate and six-coordinate Cu(II) complexes of variable ligand type and coordination geometry. These calculations were based on a modified Wolfsberg-Helmholz molecular orbital model, and they included consideration of all atoms in the metal complex system. The rotatory strengths associated with ligand-to-metal charge-transfer transitions and with ligand-ligand transitions were also calculated and reported in these studies.[46,47]

Schäffer[48] reported a theoretical analysis of optical activity in chiral transition metal complexes based essentially on the angular overlap model[49,50] of metal-ligand interactions. This model focused primarily on chiral distortions within the metal-donor atom cluster of tris-chelated and cis-bis-chelated complexes of d^3 and low-spin d^6 transition metal ions.

Perhaps the most generally applicable and useful theoretical treatments of d-d optical activity in transition metal complexes are those based on the so-called independent systems/perturbation (ISP) model as developed by Mason and co-workers[29,35,51-53] and by Richardson and co-workers.[25,54] The basic concepts of this model derive primarily from the work of Tinoco[55] (on polymer systems) and of Höhn and Weigang[56] (on small organic molecules). According to this model, the metal complex is partitioned into a chromophoric unit (either the metal ion or the metal-donor atom cluster) and a set of extrachromophoric perturber atoms (or groups) situated in the ligand environment. To zeroth-order in the perturbation representation, the chromophoric and extrachromophoric groups are treated as noninteracting (independent) subsystems. Interactions between the subsystems are then treated by first- or second-order perturbation techniques. The interaction potential is generally expressed in terms of electrostatic interactions between nonoverlapping charge distributions localized on the various subsystems, and is commonly represented by a bicentric electrostatic multipolar expansion. This model subsumes the crystal-field representation of metal complexes insofar as it includes all interactions arising from point-charge distributions in the ligand environment interacting with the various multipolar components of metal localized charge distributions and transition densities. This aspect of the ISP model leads to the so-called static-coupling (SC) interaction terms in the final spectroscopic expressions which arise from ligand ground state point-charge interactions with multipolar components of the metal ion (or chromophoric) electronic transition densities. The d-d optical activity generated in the one-electron crystal-field (or "ionic") model described previously can be associated entirely with this static-coupling mechanism.

In addition to the SC interaction terms, the general ISP model also includes so-called dynamic-coupling (DC) interaction terms arising from multipole–multipole interactions between transition densities located on the various subsystems of the metal complex. The DC terms arise from the correlated (or "complementary") motions of electrons on different subsystems undergoing (virtual) transitions induced by the electrostatic interaction potential operating between the subsystems. In most applications of the ISP model reported to date,[25,29,35,51-54] expansions of the extra-chromophoric (perturber) group charge distributions have been truncated after the (electric) dipolar term and only the multipole (metal)–dipole (ligand) DC terms have been retained. To first order in perturbation theory, these multipole (metal)–dipole (ligand) DC terms lead to rotatory strength expressions (for the metal ion d-d transitions) which depend upon ligand (perturber) group polarizabilities (and polarizability anisotropies), perturber group positions relative to the metal ion, and multipolar transition matrix elements characteristic of the metal ion chromophoric electrons.

Sector rules based on the DC mechanism for generating d–d optical activity within the ISP model have been worked out and proposed by Mason[29,35] and by Richardson.[25,54] In general, these sector rules are different (qualitatively *and* quantitatively) from those based on the SC mechanism leading to considerable ambiguity in the use of sector rules for sorting out spectra–structure correlations in metal complex CD spectra. Calculations and spectral interpretations based solely on the DC aspects of the ISP model have enjoyed considerable success as reported in several recent studies,[51-54] and it would appear that the DC mechanism is perhaps dominant over the SC mechanism in complexes possessing no charged groups.

Although the ISP model neglects all exchange interactions between the chromophoric and extrachromophoric subsystems of the complex, this neglect is not so serious when the chromophoric subsystem is defined to include the metal ion *and* the ligand donor atoms. However, consideration remains restricted to through-space vs. through-bond interactions, and thus the physical representation of the model must be considered highly approximate.

Very recently, Schipper[57] has reported a theory of d–d optical activity based on what he calls the associate-induced circular dichroism (AICD) theory. This theory is based essentially on the general ISP model carried to second order in perturbation theory. The derived rotatory strength expressions include SC, DC, and "mixed" SC/DC contributions, and the theory was applied in a general way to a wide variety of metal complex types.

This review article is focused primarily on the various *formal* and *computational* theoretical models proposed for explaining or interpreting the optical activity associated with the ligand-field (d–d) transitions of chiral transition metal complexes. The numerous empirical and semiempirical spectra–structure relationships and rules developed for this purpose lie outside the scope of this article. Most of the semiempirical spectra–structure relationships developed for d–d optical activity are based on (or are related to) at least one of the theoretical models discussed so far. However, by necessity, the semiempirically based relationships are generally more flexible and are designed to accommodate a number of "special cases" or "exceptions". It appears that none of the purely theoretically models proposed to date is sufficiently general or complete to be applicable to all d–d transitions in all the various classes of chiral transition metal complexes. This is particularly true in those cases where vibronic coupling effects, solvent perturbations, and spin–orbit coupling are expected to be especially strong. In all the theoretical models discussed up to this point, these effects have been ignored.

Concern about the possible influence of vibronic interactions upon the CD spectra of metal complexes was first expressed by Denning.[58] Denning[58] proposed that the $^1T_{1g}$ excited state of $Co(en)_3{}^{3+}$ undergoes a strong (tetragonal) Jahn–Teller distortion via coupling to an e_g vibrational mode of the CoN_6 cluster. This strong tetragonal Jahn–Teller (JT) distortion was then presumed to be effective in "quenching" the crystal-field-induced trigonal splitting of the $^1T_{1g}$ state (a manifestation of the so-called Ham effect[59]) in $Co(en)_3{}^{3+}$. Denning[58] further suggested that the two CD bands observed in the $^1A_{1g} \rightarrow {}^1T_{1g}$ region arose from two different JT vibronic states derived from $^1T_{1g}$–e_g coupling, rather than from the two trigonal components (^1E and $^1A_2$) of the $^1T_{1g}$ electronic state. The influence of Jahn–Teller and pseudo-Jahn-Teller (PJT) interactions upon the CD spectra of d–d transitions has been studied in considerable detail (theoretically) by Richardson and co-workers.[24,30,60-63] These studies included consideration of metal complexes belonging to trigonally symmetric structural classes[24,61] as well as metal complexes of pseudo-tetragonal try symmetry.[30,60,62,63] The main conclusion of these studies was that whereas vibronic interactions of the JT and PJT types (*within* the manifold of d–d excited states) will not, in general, alter the *net* d–d rotatory strength for a given system, they can play a dominant role in determining how CD intensity is distributed throughout the d–d transition region. These studies thus pointed to an additional reason why only *net* d–d CD intensity (or rotatory strength) can be safely used in making spectra–structure correlations. In the presence of strong JT or PJT interactions among the d–d states, it becomes impossible (or meaningless) to assign specific features in the CD spectra to specific d–d electronic transitions. The individual CD bands, in such cases, will generally reflect "mixed" electronic parentage.

Vibronically induced coupling of the d–d spectroscopic states to odd-parity (ungerade) electronic states of metal complexes plays a significant (and sometimes dominant) role in determining the observed dipole strengths and absorption intensities of d–d transitions. The possible influence of these vibronic interactions upon d–d rotatory strengths has been considered qualitatively by Harding[64] using the vibronic coupling formalism of Weigang and co-workers.[65-68]

Hilmes, Caliga, and Richardson[63] investigated the influence of (simultaneous) spin–orbit and vibronic interactions upon the chiroptical properties of nearly degenerate d–d transitions in metal complexes of pseudo-tetragonal symmetry. A model system was considered in which three nearly degenerate d–d excited states are coupled via both spin–orbit and vibronic interactions. Vibronic interactions among the three nearly degenerate d–d electronic states were assumed to arise from a PJT coupling mechanism involving three different vibrational modes of the undistorted metal complex system. The model adopted was *conservative* with respect to the total (or *net*) rotatory strength associated with transitions to the vibronic sublevels of the three perturbed d–d excited states. The vibronic rotatory strengths and simulated CD spectra calculated in this study[63] again demonstrated the extreme sensitivity of d–d CD intensity distributions to vibronic and spin–orbit coupling *within* the manifold of d–d excited states.

The (essential) role of spin–orbit coupling in generating optical activity in the spin-forbidden d–d transitions of chiral transition metal complexes has been studied by a number of workers.[69-74] Most of the experimental data reported to date on CD within spin-forbidden transitions have been acquired on Co(III) and Cr(III) complexes. As might be expected for metal ions belonging to the first row of the transition metal series, the $\Delta S = 0$ spin selection rule remains rather strong (owing to relatively small spin–orbit coupling constants), and the CD intensities observed for the spin-forbidden transitions are generally found to be several orders of magnitude weaker than those observed for the corresponding spin-allowed transitions. One might expect stronger spin-forbidden optical activity in complexes involving metal ions belonging to the second and third rows of the transition metal series (where the spin–orbit coupling constants are larger). All the theoretical work reported to date on spin–orbit induced optical activity in spin-forbidden transitions has been based on perturbation models involving single-center (metal atom) spin–orbit interactions. The possible influence of metal–ligand bonding effects has been ignored.

Solvent perturbations on the d–d optical activity of chiral transition metal complexes have been studied extensively and present particularly difficult problems in establishing generally applicable theories of metal complex optical activity.[75] Solvent perturbations arising from *specific* complex:solvent adduct formation with solvent molecule binding within the first coordination sphere may be easily accommodated in most of the extant theoretical models. In this case, the bound solvent molecules are simply treated as additional perturber groups in the ligand environment and are sensed directly by the metal ion chromophore. However, the influence of solvent molecules bound only in the second, or more distant, coordination sphere, or not specifically bound at all, presents a much more difficult and subtle problem to quantitative (or even qualitative) theoretical analysis. In these cases, the solvent may serve to alter chelate ring conformations, distort the geometrical (structural) parameters of the metal–donor atom cluster, or exert subtle perturbations on the ligand charge distributions. Although a variety of empirical and semiempirical methods and rules have been devised to handle this problem for specific cases, a generally applicable and reliable theory of solvent-dependent d–d optical activity has not yet been formulated.

This review is intended to deal with transition metal complexes which are inherently chiral within their first coordination sphere (defined to include all ligands with donor groups coordinated directly to the metal ion). For this reason we shall not comment extensively on the optical activity *induced* in achiral metal complexes dissolved in chiral solvents or embedded in chiral matrices or crystals. A great deal of progress has been made recently in the development of theories related to the induction of optical activity in achiral systems by chiral media. This work has been done primarily by Schipper,[76–81] Mason,[82] and Craig and co-workers.[83–85]

Special effects associated with the d–d optical activity of transition metal ions (or complexes) situated in enantiomorphic single-crystal systems have been dealt with (theoretically) by a number of workers.[28,30,36,86] The special effects referred to in these cases concern contributions from localized excitations vs. delocalized excitations (exciton motion), dominance of site symmetry vs. unit cell symmetry, and the relative importance of electric quadrupole–electric dipole vs. magnetic dipole–electric dipole molecule–radiation interactions.

III. General Independent Systems/Perturbation Model

A. General Aspects

As was mentioned in the previous section (II), the general independent systems/perturbation (ISP) model of d–d optical activity in chiral transition metal complexes subsumes both the one-electron crystal-field (or static-coupling) model and the dynamic-coupling ligand-polarization model. Its attractiveness derives in large part from the relative simplicity of its underlying physical representation, the simplicity of its associated (perturbation) formalism, and its flexibility in applications to real systems. Its limitations derive primarily from its incomplete and highly approximate representation of metal–ligand interactions (especially of the covalent bonding type). Despite its inherent limitations, the ISP model provides the most promising approach for developing reliable and useful spectra–structure relationships applicable to metal complex d–d optical activity. For this reason, we shall outline the major features of the general ISP model in this section. Various aspects of this model (as applied to metal complex optical activity) have been presented previously (ref 25, 29, 35, 51–54, 57), and each of these will be included in the present general treatment.

B. Description of Model

The basic assumption of the independent systems/perturbation model is that the metal complex may be partitioned into a chromophoric subsystem (the metal ion or the metal–donor atom cluster) and a set of extrachromophoric subsystems. To zeroth order the spectroscopic properties of the chromophoric unit are assumed to be independent of the remainder of the complex. Interactions between the chromophoric and extrachromophoric subsystems are then treated by perturbation techniques and the spectroscopic properties of the perturbed chromophore are calculated from the resultant (perturbed) wave functions of the chromophoric subsystem. Pairwise interactions between the chromophoric and extrachromophoric (perturber) subsystems are generally expressed in terms of bicentric multipolar expansions representing the electrostatic interactions between charge distributions localized on the respective (interacting) subsystems. Exchange interactions (due to overlap) are neglected. Terms in the interaction potential which influence the energies of the d–d spectroscopic states but which do not contribute to d–d rotatory strengths are generally neglected or are absorbed into the zeroth-order representation of the system.

In our present treatment of the general ISP model, we shall find it convenient to express the total *electronic* Hamiltonian of the metal complex as

$$\mathcal{H} = H_A + H_B + V_A + V_{AB} \tag{2}$$

where H_A denotes the electronic Hamiltonian of the achiral chromophoric subsystem (A), H_B denotes the total electronic Hamiltonian of the collection of extrachromophoric subsystems (B) in the ligand environment, V_A allows for a local (chiral) distortion within the chromophoric subsystem (A), and V_{AB} represents all pairwise A–B interactions within the overall complex. In general, the chromophoric subsystem (A) will be taken as a metal–donor atom cluster of an idealized geometry (with, for example, O_h, D_{4h}, or T_d symmetry). Deviations from this idealized (zeroth-order) geometry of A are taken into account by the interaction term, V_A, in eq 2. The B subsystems will be taken as atoms, groups of atoms, or chemical bonds in the ligand environment. The Hamiltonian H_B may be further partitioned as

$$H_B = \sum_r h_r \tag{3}$$

where r labels individual perturber subsystems.

Defining $H^0 = H_A + H_B$ as the zeroth-order Hamiltonian operator in our general ISP model, the zeroth-order basis states of the model may be expressed as product functions of the type:

Ground State

$$|A_0B_0\rangle = |A_0\prod_r b_{r0}\rangle \tag{4}$$

Excited States (singly excited)

$$|A_mB_0\rangle = |A_m\prod_r b_{r0}\rangle \tag{5a}$$

$$|A_0B_{ri}\rangle = |A_0b_{ri}\prod_{s\neq r} b_{s0}\rangle \tag{5b}$$

Excited States (doubly excited)

$$|\mathrm{A}_m\mathrm{B}_{ri}) = |\mathrm{A}_m\mathrm{b}_{ri}\prod_{s\neq r}\mathrm{b}_{s0}) \qquad (6a)$$

$$|\mathrm{A}_0\mathrm{B}_{ri,sj}) = |\mathrm{A}_0\mathrm{b}_{ri}\mathrm{b}_{sj}\prod_{t\neq r,s}\mathrm{b}_{t0}) \qquad (6b)$$

where (r,s,t) label individual B subsystems, (i,j) label excited states localized on the B subsystems, m denotes an excited state of the chromophore (A), and 0 denotes ground state. We note that,

$$H_\mathrm{A}|\mathrm{A}_\alpha) = E_\alpha|\mathrm{A}_\alpha) \qquad (7a)$$

and

$$h_r|\mathrm{b}_{rj}) = E_{rj}|\mathrm{b}_{rj}) \qquad (7b)$$

The inclusion of doubly excited states in the zeroth-order basis set is necessary only if the perturbation expansion of the wave functions is carried to second order.

Applying nondegenerate perturbation theory to second order in $H' = V_\mathrm{A} + V_\mathrm{AB}$, we obtain for the $|\mathrm{A}_m\mathrm{B}_0\rangle$ state:

$$|\mathrm{A}_mB_0\rangle = |A_m\mathrm{B}_0) + \sum_{\alpha\neq m}\sum_{\beta}\frac{(\mathrm{A}_\alpha\mathrm{B}_\beta|H'|\mathrm{A}_m\mathrm{B}_0)}{E_m-(E_\alpha+E_\beta)}|\mathrm{A}_\alpha\mathrm{B}_\beta) + \sum_{\alpha'\neq m}\sum_{\beta'}\left[\sum_{\alpha\neq m}\sum_{\beta}\frac{(\mathrm{A}_{\alpha'}\mathrm{B}_{\beta'}|H'|\mathrm{A}_\alpha\mathrm{B}_\beta)(\mathrm{A}_\alpha\mathrm{B}_\beta|H'|\mathrm{A}_m\mathrm{B}_0)}{(E_m-E_{\alpha'}-E_{\beta'})(E_m-E_\alpha-E_\beta)} - \frac{(A_m\mathrm{B}_0|H'|\mathrm{A}_m\mathrm{B}_0)(\mathrm{A}_{\alpha'}\mathrm{B}_{\beta'}|H'|\mathrm{A}_m\mathrm{B}_0)}{(E_m-E_{\alpha'}-E_{\beta'})^2}\right]|A_{\alpha'}B_{\beta'}) \qquad (8)$$

where $\alpha(\alpha')$ and $\beta(\beta')$ are used as generic indexes for zeroth-order states on the A and B subsystems, respectively. Rounded kets denote zeroth-order state functions and pointed kets denote perturbed wave functions. An expression similar to (8) may be written for the perturbed ground state, $|\mathrm{A}_0\mathrm{B}_0\rangle$, of the metal complex. Equation 8 is appropriate only for nondegenerate systems. However, if we redefine our state indexes (such as m, n, i, j, α, β, etc.) to reflect *components* of degenerate states and further choose zeroth-order degenerate states with components diagonal in H', then we may use eq 8 with the understanding that the summations are taken over states *and* (degenerate) state components.

C. Electronic Rotatory Strengths (General Expressions)

The quantity of primary interest is the electronic rotatory strength. For the 0 → m transition localized on the chromophore (A):

$$R_{0m} = \mathrm{Im}\langle\mathrm{A}_0\mathrm{B}_0|\hat{\mu}|\mathrm{A}_m\mathrm{B}_0\rangle\cdot\langle\mathrm{A}_m\mathrm{B}_0|\hat{\mathrm{m}}|\mathrm{A}_0\mathrm{B}_0\rangle \qquad (9a)$$

$$= \mathrm{Im}(\mathbf{P}_{0m}\cdot\mathbf{M}_{m0}) \qquad (9b)$$

where $\mathbf{P}_{0m}$ and $\mathbf{M}_{m0}$ denote the electric and magnetic dipole transition vectors, respectively. To second order in perturbation theory, the rotatory strength may be reexpressed as:

$$R_{0m} = R_{0m}^{(0)} + R_{0m}^{(1)} + R_{0m}^{(2)} \qquad (10)$$

where

$$R_{0m}^{(0)} = \mathrm{Im}(\mathbf{P}_{0m}^{(0)}\cdot\mathbf{M}_{m0}^{(0)}) \qquad (11a)$$

$$R_{0m}^{(1)} = \mathrm{Im}\,(\mathbf{P}_{0m}^{(0)}\cdot\mathbf{M}_{m0}^{(1)} + \mathbf{P}_{0m}^{(1)}\cdot\mathbf{M}_{m0}^{(0)}) \qquad (11b)$$

and

$$R_{0m}^{(2)} = \mathrm{Im}(\mathbf{P}_{0m}^{(0)}\cdot\mathbf{M}_{m0}^{(2)} + \mathbf{P}_{0m}^{(1)}\cdot\mathbf{M}_{m0}^{(1)} + \mathbf{P}_{0m}^{(2)}\cdot\mathrm{M}_{m0}^{(0)}) \qquad (11c)$$

In eq 10, 11a, 11b, and 11c, the superscripts refer to zeroth (0), first (1), and second (2) order contributions to the rotatory strengths and/or transition moments.

Restricting our treatment to systems with centrosymmetric chromophoric units (A), both $\mathbf{P}_{0m}^{(0)}$ and $R_{0m}^{(0)}$ will vanish for all d–d transitions. The appropriate rotatory strength expression is, therefore, given (to second order) by:

$$R_{0m} = R_{0m}^{(1)} + R_{0m}^{(2)} \qquad (12a)$$

$$= \mathrm{Im}(\mathbf{P}_{0m}^{(1)}\cdot\mathbf{M}_{m0}^{(0)}) + \mathrm{Im}(\mathbf{P}_{0m}^{(1)}\cdot\mathbf{M}_{m0}^{(1)} + \mathbf{P}_{0m}^{(2)}\cdot\mathbf{M}_{m0}^{(0)}) \qquad (12b)$$

To calculate the rotatory strength, eq 12, it is first necessary to evaluate $\mathbf{P}_{0m}^{(1)}$, $\mathbf{P}_{0m}^{(2)}$, $\mathbf{M}_{m0}^{(0)}$, and $\mathbf{M}_{m0}^{(1)}$ using the perturbation model outlined in section III.B. This requires explicit consideration of the perturbation Hamiltonian, $H' = V_\mathrm{A} + V_\mathrm{AB}$, as well as specification of the zeroth-order basis states to be included in the perturbation expansion.

D. Interaction Hamiltonian

We have defined the interaction (perturbation) Hamiltonian, H', as comprised of two parts: V_A and V_AB. The operator V_AB represents electrostatic interactions between charge distributions localized in the extra-chromophoric ligand environment (B) and transition densities associated with (virtual) electronic excitations localized on the chromophore (A). The operator V_A represents all *chiral* components of the metal–ligand interactions *within* the metal–donor atom chromophoric cluster (A). Assuming nonoverlap between the A and B charge distributions and representing V_AB in terms of a sum of bicentric multipolar expansions, the V_AB interaction potential may be expressed as:

$$V_\mathrm{AB} = \sum_r\sum_{\ell_\mathrm{A}=0}^{\infty}\sum_{\ell_r=0}^{\infty}V_{\mathrm{A}r}(\ell_\mathrm{A},\ell_r) \qquad (13)$$

where

$$V_{\mathrm{A}r}(\ell_\mathrm{A},\ell_r) = \sum_{m_\mathrm{A}}\sum_{m_r}T_{m_\mathrm{A},m_r}^{(\ell_\mathrm{A},\ell_r)}(r)D_{m_\mathrm{A}}^{(\ell_\mathrm{A})}(\mathrm{A})D_{m_r}^{(\ell_r)}(r) \qquad (14)$$

In eq 13 and 14, the summation Σ_r is taken over all ligand perturber sites, m_A runs from $-\ell_\mathrm{A}$ to $+\ell_\mathrm{A}$, and m_r runs from $-\ell_r$ to $+\ell_r$. The quantity $T_{m_\mathrm{A},m_r}^{(\ell_\mathrm{A},\ell_r)}$ is the (m_A,m_r) component of a $(\ell_\mathrm{A}+\ell_r)$th rank tensor which describes the orientational dependence of the interaction between a 2^{ℓ_A} multipole on A and a 2^{ℓ_r} multipole on perturber r. The multipole components of the charge distributions on A and r are denoted, respectively, by $D_{m_\mathrm{A}}^{(\ell_\mathrm{A})}(\mathrm{A})$ and $D_{m_r}^{(\ell_r)}(r)$. The general form of the tensor operator, $T_{m_\mathrm{A},m_r}^{(\ell_\mathrm{A},\ell_r)}$, is given by:

$$T_{m_\mathrm{A},m_r}^{(\ell_\mathrm{A},\ell_r)} = \frac{(-1)^{\ell_r+m_r+m_\mathrm{A}}}{R_r^{\ell_\mathrm{A}+\ell_r+1}} \times\left[\frac{(\ell_\mathrm{A}+\ell_r+m_\mathrm{A}+m_r)!(\ell_\mathrm{A}+\ell_r-m_\mathrm{A}-m_r)!}{(\ell_\mathrm{A}+m_\mathrm{A})!(\ell_\mathrm{A}-m_\mathrm{A})!(\ell_r+m_r)!(\ell_r-m_r)!}\right]^{1/2} \times C_{-m_\mathrm{A}-m_r}^{(\ell_\mathrm{A}+\ell_r)}(\Theta_r,\Phi_r) \qquad (15)$$

The multipole moment operators, $D_{m_\mathrm{A}}^{(\ell_\mathrm{A})}(\mathrm{A})$ and $D_{m_r}^{(\ell_r)}(r)$, may be expressed as:

$$D_{m_\mathrm{A}}^{(\ell_\mathrm{A})}(\mathrm{A}) = \sum_\epsilon -er_\epsilon^{\ell_\mathrm{A}}C_{m_\mathrm{A}}^{(\ell_\mathrm{A})}(\theta_\epsilon,\phi_\epsilon) \qquad (16)$$

and

$$D_{m_r}^{(\ell_r)}(r) = \sum_\delta eZ_\delta r_\delta^{\ell_r}C_{m_r}^{(\ell_r)}(\theta_\delta,\phi_\delta) \qquad (17)$$

The electrons on A are labeled by ϵ with coordinates $(r_\epsilon, \theta_\epsilon, \phi_\epsilon)$. The charged particles on perturber r are labeled by δ with coordinates $(r_\delta, \theta_\delta, \phi_\delta)$ and charge $Z_\delta e$ (where e is the magnitude of the electron charge). The position of ligand perturber group r with respect to the chromophoric center (A) is defined by the set of coordinates (R_r, Θ_r, Φ_r). The general form of the $C_m^{(\ell)}(\theta,\phi)$ operator is:

$$C_m^{(\ell)}(\theta,\phi) = [4\pi/(2\ell+1)]^{1/2}Y_{\ell,m}(\theta,\phi) \qquad (18)$$

where $Y_{\ell,m}(\theta,\phi)$ is a spherical harmonic function of rank ℓ. In eq 14, $D_{m_A}^{(\ell_A)}(A)$ and $D_{m_r}^{(\ell_r)}(r)$ are pure electronic operators while $T_{m_A,m_r}^{(\ell_A,\ell_r)}(r)$ is a factor determined entirely by the position of perturber r relative to the chromophoric group A.

In dealing with chiral distortions within the metal–donor atom cluster, we shall assume it possible to express V_A in precisely the same form as V_{AB}. In this case, however, the extrachromophoric perturber sites r are replaced by ligand donor atoms (denoted by L) displaced with respect to the centrosymmetric reference geometry assumed in our zeroth-order representation of the metal complex. This construct makes less clear the detailed nature of the zeroth-order basis states of the chromophoric subsystem (A), but it should preserve the essential symmetry-determined aspects of the general ISP model.

It is convenient now to partition the interaction potential V_{AB} into its so-called static-coupling (SC) and dynamic-coupling (DC) components. We define the static-coupling component of V_{AB} to be:

$$\mathcal{V}_{AB} = \sum_r \sum_{\ell_A} V_{Ar}(\ell_A,0) \tag{19}$$

or

$$\mathcal{V}_{AB} = \sum_r \sum_{\ell_A} \sum_{m_A} T_{m_A,0}^{(\ell_A,0)}(r) D_{m_A}^{(\ell_A)}(A) D_0^{(0)}(r) \tag{20}$$

The operator $\mathcal{V}_{AB}$ represents the electrostatic interactions between the chromophore (A) multipoles, $D_{m_A}^{(\ell_A)}(A)$, and the net charges (monopoles), $D_0^{(0)}(r)$, of the perturber groups. $\mathcal{V}_{AB}$ thus contains the familiar "crystal-field" potential and is the operator employed in the original one-electron crystal-field models of d–d optical activity.[13,20,21,24,31] The dynamic-coupling component of V_{AB} is defined by:

$$\mathcal{U}_{AB} = \sum_r \sum_{\ell_A} \sum_{\ell_r \geq 1} V_{Ar}(\ell_A,\ell_r) \tag{21}$$

In our subsequent treatment, we shall restrict ℓ_r to $\ell_r = 1$ (dipole components) so that:

$$\mathcal{U}_{AB} = \sum_r \sum_{\ell_A} \sum_{m_A} \sum_{m_r} T_{m_A,m_r}^{(\ell_A,1)}(r) D_{m_A}^{(\ell_A)}(A) D_{m_r}^{(1)}(r) \tag{22}$$

The total interaction potential, V_{AB}, is given by:

$$V_{AB} = \mathcal{V}_{AB} + \mathcal{U}_{AB} \tag{23}$$

The interaction operator $\mathcal{U}_{AB}$ describes the (coulombically) correlated motions of electrons in the A and B subsystems, thus the designation "dynamic-coupling".

Expressions similar to (19)–(23) may be written down for the distortion operator V_A, replacing Σ_r with Σ_L where L denotes displaced donor atoms of the ligands.

The interaction operator V_{AB} (as well as $\mathcal{V}_{AB}$ and $\mathcal{U}_{AB}$) must transform as the totally symmetric irreducible representation of the point group describing the full metal complex. Thus the functions

$$F = \sum_{\ell_A} \sum_{m_A} F(\ell_A,m_A) = \sum_r \sum_{\ell_A} \sum_{m_A} T_{m_A,0}^{(\ell_A,0)}(r) \tag{24}$$

and

$$\bar{F} = \sum_{\ell_A} \sum_{m_A} \sum_{m_r} \bar{F}(\ell_A,m_A,m_r) = \sum_r \sum_{\ell_A} \sum_{m_A} \sum_{m_r} T_{m_A,m_r}^{(\ell_A,1)}(r) \tag{25}$$

must also transform as the totally symmetric irreducible representation of this point group. Referring back to the Schellman's general symmetry analysis of the one-electron theory of optical activity (carried to first-order in perturbation theory),[34] optical activity can be induced in the electronic transitions of the symmetric (achiral) chromophore (A) only if the perturbation potential contains at least one component which transforms as the pseudoscalar irreducible representation in the point group of A. In the present context, this implies that the function F must contain at least one pseudoscalar term (with respect to the symmetry operations contained in the point group of A) in order for the electronic transitions of A to exhibit optical activity to first order. Precisely the same requirement obtains for $\bar{F}$ if the dynamic-coupling model is carried to just first order.[25,35] More succinctly, the *net* first-order rotatory strength associated with any electronic transition of the achiral chromophore (A) will vanish unless either F or $\bar{F}$ contains at least one term which transforms as a pseudoscalar under the symmetry operations of the A point group (which we shall denote by G_A).

Extension of the ISP model to second order (in the wave functions and rotatory strengths) leads to interaction terms whose symmetry transformation properties may be evaluated from product functions of the type:

$$F \times F' = \left[\sum_{\ell_A} \sum_{m_A} F(\ell_A,m_A)\right]\left[\sum_{\ell_A'} \sum_{m_A'} F'(\ell_A',m_A')\right] \tag{26a}$$

$$F \times \bar{F} = \left[\sum_{\ell_A} \sum_{m_A} F(\ell_A,m_A)\right]\left[\sum_{\ell_A} \sum_{m_A} \sum_{mr} \bar{F}(\ell_A,m_A,m_r)\right] \tag{26b}$$

$$\bar{F} \times \bar{F}' = \left[\sum_{\ell_A} \sum_{m_A} \sum_{m_r} \bar{F}(\ell_A,m_A,m_r)\right] \times \left[\sum_{\ell_A'} \sum_{m_A'} \sum_{m_r'} \bar{F}'(\ell_a',m_A',m_r')\right] \tag{26c}$$

Second-order rotatory strength contributions will result only if the direct product representations generated by $F \times F'$, $F \times \bar{F}$, or $\bar{F} \times \bar{F}'$ include a pseudoscalar representation (defined within the G_A point group).[24,25,35,57] To second order, then, neither F nor $\bar{F}$ need transform as a pseudoscalar within the point group of the achiral chromophore. Note that eq 26a pertains to the static-coupling mechanism carried to second order, eq 26c pertains to the dynamic-coupling mechanism carried to second order, and eq 26b pertains to a (simultaneous) static-coupling/dynamic-coupling combination mechanism.

Just as the functions F and $\bar{F}$ reflect the symmetry properties of $\mathcal{V}_{AB}$ and $\mathcal{U}_{AB}$, respectively, so do the functions,

$$f = \sum_{\ell_A} \sum_{m_A} f(\ell_A,m_A) = \sum_r \sum_{\ell_A} \sum_{m_A} D_{m_A}^{(\ell_A)}(A) D_0^{(0)}(r) \tag{27}$$

$$\bar{f} = \sum_{\ell_A} \sum_{m_A} \sum_{m_r} \bar{f}(\ell_A,m_A,m_r) = \sum_r \sum_{\ell_A} \sum_{m_r} D_{m_A}^{(\ell_A)}(A) D_{m_r}^{(1)}(r) \tag{28}$$

The symmetry restrictions of f and $\bar{f}$ (and on products of these functions) in the generation of optical activity in the electronic transitions of A are precisely the same as those discussed above for F and $\bar{F}$. Whereas F and $\bar{F}$ are defined in terms of nuclear positional coordinates, f and $\bar{f}$ are defined in terms of functions of electronic coordinates. For our "fixed-nuclei" model, the electronic symmetry of the complex must at all times be identical with the symmetry of the nuclear framework.

Sector (or "regional") rules for metal complexes may be derived directly from the F and $\bar{F}$ functions upon application of the appropriate symmetry restrictions, whereas the details of the chiral metal–ligand electronic interactions responsible for observed optical activity are best analyzed using the f and $\bar{f}$ functions (and the appropriate symmetry restrictions).

E. First-Order Rotatory Strengths

To first order on our ISP model, the rotatory strength of the $0 \rightarrow m$ electronic transition is given by:

$$R_{0m}^{(1)} = \mathrm{Im}(\mathbf{P}_{0m}^{(1)} \cdot \mathbf{M}_{m0}^{(0)}) \tag{29}$$

where

$$\mathbf{M}_{m0}^{(0)} = (A_m|\hat{\mathbf{m}}|A_0) \tag{30}$$

The electric-dipole transition moment, $\mathbf{P}_{0m}^{(1)}$, may be expressed in terms of a static-coupling (SC) part and a dynamic-coupling (DC) part as follows:

$$\mathbf{P}_{0m}{}^{(1)} = \mathbf{P}_{0m}{}^{(1)}(\mathrm{SC}) + \mathbf{P}_{0m}{}^{(1)}(\mathrm{DC}) \qquad (31)$$

where

$$\mathbf{P}_{0m}{}^{(1)}(\mathrm{SC}) = -\sum_{\alpha\neq 0} (\mathrm{A}_\alpha|\hat{\boldsymbol{\mu}}|\mathrm{A}_m)(\mathrm{A}_\alpha\mathrm{B}_0|\mathcal{V}_{\mathrm{AB}} + \mathcal{V}_{\mathrm{A}}|\mathrm{A}_0\mathrm{B}_0)E_\alpha{}^{-1}$$
$$- \sum_{\alpha\neq m} (\mathrm{A}_0|\hat{\boldsymbol{\mu}}|\mathrm{A}_\alpha)(\mathrm{A}_\alpha\mathrm{B}_0|\mathcal{V}_{\mathrm{AB}} + \mathcal{V}_{\mathrm{A}}|\mathrm{A}_m\mathrm{B}_0)(E_\alpha - E_m)^{-1} \qquad (32)$$

and

$$\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC}) = \sum_{\beta\neq 0} (\mathrm{B}_0|\hat{\boldsymbol{\mu}}|\mathrm{B}_\beta)(\mathrm{A}_0\mathrm{B}_\beta|\mathcal{U}_{\mathrm{AB}} + \mathcal{U}_{\mathrm{A}}|\mathrm{A}_m\mathrm{B}_0)[2E_\beta/(E_m{}^2 - E_\beta{}^2)] \qquad (33)$$

The $\mathcal{V}_{\mathrm{A}}$ and $\mathcal{U}_{\mathrm{A}}$ operators are, respectively, the static-coupling and dynamic-coupling components of the distortion potential V_{A}. The set of states (A_α) are taken from the set of ungerade states localized on the achiral (centrosymmetric) chromophore. These may be described in terms of metal ion excitations (such as, for example, d-p and d-f transitions), ligand-metal charge-transfer states within the metal-donor atom chromophoric cluster, or (composite) ligand-ligand excitations localized on the donor atoms of the chromophoric cluster. The sets of states (B_β) represent excited states localized in the perturbing (extrachromophoric) ligand environment. The first-order rotatory strength may now be expressed as:

$$R_{0m}{}^{(1)} = R_{0m}{}^{(1)}(\mathrm{SC}) + R_{0m}{}^{(1)}(\mathrm{DC}) \qquad (34)$$

where

$$R_{0m}{}^{(1)}(\mathrm{SC}) = \mathrm{Im}[\mathbf{P}_{0m}{}^{(1)}(\mathrm{SC}) \cdot \mathbf{M}_{m0}{}^{(0)}] \qquad (35a)$$

and

$$R_{0m}{}^{(1)}(\mathrm{DC}) = \mathrm{Im}[\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC}) \cdot \mathbf{M}_{m0}{}^{(0)}] \qquad (35b)$$

To first-order, the SC and DC contributions to the rotatory strength are additive and may be treated separately.

As noted previously, in writing $0 \rightarrow m$ we take the ground state (0) to be nondegenerate, and we define m to include all components of any excited state which may be degenerate in the symmetry group G_{A} of the unperturbed achiral chromophore A. For example, if we specify $0 \rightarrow m$ to be the ${}^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{T}_{1g}$ transition of an octahedral (O_h) Co^{3+} chromophoric unit, then R_{0m} corresponds to the total (*net*) rotatory strength associated with this transition.

In order for $R_{0m}{}^{(1)}(\mathrm{SC})$ to be nonvanishing, the static-coupling operator $\mathcal{V} = \mathcal{V}_{\mathrm{A}} + \mathcal{V}_{\mathrm{AB}}$ must contain at least one component which transforms as a pseudoscalar function under the symmetry operations of the G_{A} point group. In order for $R_{0m}{}^{(1)}(\mathrm{DC})$ to be nonvanishing, the dynamic-coupling operator $\mathcal{U} = \mathcal{U}_{\mathrm{A}} + \mathcal{U}_{\mathrm{AB}}$ must contain at least one component which transforms as a pseudoscalar function (in G_{A}).

The static-coupling contribution, $R_{0m}{}^{(1)}(\mathrm{SC})$, arises from the dissymmetric components of the "Stark field" created at the metal ion by the ligand environment (represented as a distribution of point charges). Symmetry considerations dictate that only those components which transform as a pseudoscalar function under the symmetry operations of the G_{A} point group will make nonvanishing contributions to $R_{0m}{}^{(1)}(\mathrm{SC})$. Referring back to eq 24, the lowest order $F(\ell_{\mathrm{A}},m_{\mathrm{A}})$ functions contributing to $R_{0m}{}^{(1)}(\mathrm{SC})$ are listed below for several centrosymmetric G_{A} groups.

G_{A}	$F(\ell_{\mathrm{A}},m_{\mathrm{A}})$	ℓ_α
O_h	$\mathrm{F}(9,m_{\mathrm{A}})$	7, 9, 11
D_{6h}	$\mathrm{F}(7,m_{\mathrm{A}})$	5, 7, 9
D_{4h}	$\mathrm{F}(5,m_{\mathrm{A}})$	3, 5, 7
D_{2h}	$\mathrm{F}(3,m_{\mathrm{A}})$	1, 3, 5
C_{2h}	$\mathrm{F}(1,m_{\mathrm{A}})$	1, 3

ℓ_α denotes the angular momentum quantum numbers allowed among the ungerade A_α states to be mixed into the d-d spectroscopic states. The large values of ℓ_α for $G_{\mathrm{A}} \equiv O_h$ suggest why the first-order SC mechanism is quite often referred to as "unphysical" in its applications to complexes of *erstwhile* O_h symmetry. Sector rules pertaining to $R_{0m}{}^{(1)}$ (SC), expressed in terms of the Cartesian coordinates of the perturber groups, have been listed by Schellman[34] for a wide variety of achiral chromophoric point groups (G_{A}).

The first-order electric dipole transition moment $\mathbf{P}_{0m}{}^{(1)}$ (SC), defined in eq 32, may be written more explicitly as eq 36,

$$\mathbf{P}_{0m}{}^{(1)}(\mathrm{SC}) = -\sum_{\alpha\neq 0}\sum_q\sum_{\ell_{\mathrm{A}}}\sum_{m_{\mathrm{A}}} (A_\alpha|D_q{}^{(1)}(\mathrm{A})|\mathrm{A}_m)(\mathrm{A}_\alpha|D_{m_{\mathrm{A}}}{}^{(\ell_{\mathrm{A}})}(\mathrm{A})|\mathrm{A}_0)E_\alpha{}^{-1}$$
$$\times \left[\sum_r Q_r T_{m_{\mathrm{A}},0}{}^{(\ell_{\mathrm{A}},0)}(r) + \sum_L Q_L T_{m_{\mathrm{A}},0}{}^{(\ell_{\mathrm{A}},0)}(L)\right]$$
$$- \sum_{\alpha\neq m}\sum_q\sum_{\ell_{\mathrm{A}}}\sum_{m_{\mathrm{A}}} (\mathrm{A}_0|D_q{}^{(1)}(\mathrm{A})|\mathrm{A}_\alpha)\,(\mathrm{A}_\alpha|D_{m_{\mathrm{A}}}{}^{(\ell_{\mathrm{A}})}(\mathrm{A})|\mathrm{A}_m)$$
$$\times (E_\alpha - E_m)^{-1}\left[\sum_r Q_r T_{m_{\mathrm{A}},0}{}^{(\ell_{\mathrm{A}},0)}(r) + \sum_L \mathrm{Q}_L T_{m_{\mathrm{A}},0}{}^{(\ell_{\mathrm{A}},0)}(L)\right] \qquad (36)$$

where q denotes the (spherical) components of the electric dipole operator ($\hat{\mu}_q \equiv D_q{}^{(1)}$), Σ_r runs over all perturber sites in the extrachromophoric ligand environment, Σ_{L} runs over the donor atoms (distorted from the chromophore reference geometry), and Q_r and Q_L denote, respectively, charge parameters for the rth and Lth perturbers.

The dynamic coupling contribution to the first-order rotatory strength, $R_{0m}{}^{(1)}(\mathrm{DC})$, arises from a dissymmetric coupling between electric dipole transition vectors located in the ligand environment with multipolar transition moments associated with the chromophoric d-d transitions. The physical basis of this mechanism can be viewed in terms of an *induction* of (virtual) electric dipole transitions in the ligand environment by (radiation) field-induced excitation localized in the chromophoric group (A). The entire first-order electric dipole transition moment, $\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC})$, appearing in eq 35 is located in the ligand environment. Equation 33 for $\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC})$ may be written more explicitly as,

$$\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC}) = \sum_r\sum_{i\neq 0}\sum_{\ell_{\mathrm{A}}}\sum_{m_{\mathrm{A}}}\sum_{m_r}\sum_q T_{m_{\mathrm{A}},m_r}{}^{(\ell_{\mathrm{A}},1)}(r)$$
$$\times (\mathrm{B}_0|D_q{}^{(1)}(r)|B_{ri})(\mathrm{A}_0|D_{m_{\mathrm{A}}}{}^{(\ell_{\mathrm{A}})}(\mathrm{A})|\mathrm{A}_m)(\mathrm{B}_{ri}|D_{m_r}{}^{(1)}(r)|\mathrm{B}_0)$$
$$\times [2E_{ri}/(E_m{}^2 - E_{ri}{}^2)] + \sum_L\sum_{j\neq 0}\sum_{\ell_A}\sum_{m_A}\sum_{m_L}\sum_q T_{m_{\mathrm{A}},m_L}{}^{(\ell_{\mathrm{A}},1)}$$
$$\times (L)(\mathrm{B}_0|D_q{}^{(1)}(L)|\mathrm{B}_{Lj})(\mathrm{A}_0|D_{m_{\mathrm{A}}}{}^{(\ell_{\mathrm{A}})}(\mathrm{A})|\mathrm{A}_m)$$
$$\times (B_{Lj}|D_{m_L}{}^{(1)}(L)|\mathrm{B}_0)[2E_{Lj}/(E_m{}^2 - E_{Lj}{}^2)] \qquad (37)$$

where q denotes the (spherical) components of the electric dipole operator ($\hat{\mu}_q = D_q{}^{(1)}$), Σ_r runs over all perturber sites in the extrachromophoric ligand environment, Σ_i runs over all excited states localized on the perturbers $\{r\}$, Σ_L runs over the donor atoms (distorted from the chromophore reference geometry), and Σ_j runs over all excited states of the donor atoms L. $\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC})$ represents a vector sum of electric dipole transition moments arrayed in the ligand environment of the metal complex.

For spherically symmetric perturber groups, only the $m_r = q$ and $m_L = q$ terms in eq 37 survive. We define

$$\alpha_r(q,q) = -\sum_{i\neq 0} (\mathrm{B}_0|D_q{}^{(1)}(r)|\mathrm{B}_{ri}) \times (\mathrm{B}_{ri}|D_q{}^{(1)}(r)|\mathrm{B}_0)[2E_{ri}/(E_m{}^2 - E_{ri}{}^2)] \qquad (38)$$

as the qth diagonal component of the polarizability tensor for the *r*th perturber group at the frequency $\nu_m = E_m/h$. We define a similar set of quantities, $\alpha_L(q,q)$, for the *L* donor atoms. Restricting our attention to spherically symmetric perturber groups (*r* and *L*), we replace $\alpha_r(q,q)$ and $\alpha_L(q,q)$ by "average" polarizabilities, $\overline{\alpha}_r(\nu_m)$ and $\overline{\alpha}_L(\nu_m)$, and rewrite eq 37 as,

$$\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC}) = \sum_q P_{0m;q}{}^{(1)}(\mathrm{DC}) \tag{39}$$

where

$$P_{0m;q}{}^{(1)}(\mathrm{DC}) = -\sum_r \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} T_{m_\mathrm{A},q}{}^{(\ell_\mathrm{A},1)}(r)\overline{\alpha}_r(\mathrm{A}_0|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_m) - \sum_L \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} T_{m_\mathrm{A},q}{}^{(\ell_\mathrm{A},1)}(L)\overline{\alpha}_L(\mathrm{A}_0|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_m) \tag{40}$$

$P_{0m;q}{}^{(1)}(\mathrm{DC})$ is the *q*th (spherical) component of the first-order DC electric dipole transition moment of the 0 → *m* transition. In this approximation, the first-order dynamic-coupling rotatory strength is given by

$$R_{0m}{}^{(1)}(\mathrm{DC}) = -\mathrm{Im}\left\{\sum_q \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} (\mathrm{A}_0|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_m) \times (\mathrm{A}_m|\hat{m}_q|\mathrm{A}_0)\left[\sum_r \overline{\alpha}_r T_{m_\mathrm{A},q}{}^{(\ell_\mathrm{A},1)}(r) + \sum_L \overline{\alpha}_L T_{m_L,q}{}^{(\ell_\mathrm{A},1)}(L)\right]\right\} \tag{41}$$

where $\hat{m}_q$ represents the *q*th component of the magnetic dipole moment operator (with an origin within the A chromophoric group).

In the general case (where the perturber groups are *not* necessarily spherically symmetric), we have:

$$\mathbf{P}_{0m}{}^{(1)}(\mathrm{DC}) = \sum_q P_{0m;q}{}^{(1)}(\mathrm{DC}) \tag{42}$$

where

$$P_{0m;q}{}^{(1)}(\mathrm{DC}) = -\sum_r \sum_{\ell_\mathrm{A}}\sum_{m_\mathrm{A}}\sum_{q'} T_{m_\mathrm{A},q'}{}^{(\ell_\mathrm{A},1)}(r)\alpha_r(q,q') \times (\mathrm{A}_0|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_m) - \sum_L \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} \sum_{q'} T_{m_\mathrm{A},q'}{}^{(\ell_\mathrm{A},1)} \times (L)\alpha_L(q,q')(\mathrm{A}_0|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|A_m) \tag{43}$$

and

$$\alpha_r(q,q') = -\sum_{i\mp 0} (\mathrm{B}_0|D_q{}^{(1)}(r)|\mathrm{B}_{ri}) \times (\mathrm{B}_{ri}|D_{q'}{}^{(1)}(r)|\mathrm{B}_0)[2E_{ri}/(E_m{}^2 - E_{ri}{}^2)] \tag{44}$$

It is clear from eq 29 that only the *magnetic dipole allowed* d–d transitions gain *net* rotatory strength to first order on the ISP model presented here. Furthermore, eq 34 expresses the fact that to first order the static-coupling and dynamic-coupling mechanisms are complementary with respect to their contributions to the *net* rotatory strength. For a side-by-side comparison of the SC vs. DC mechanisms as applied to a series of chiral Co(III) diamine complexes, the reader is referred to an excellent paper recently published by Mason and Seal.[53]

F. Second-Order Rotatory Strengths

1. Magnetic Dipole Forbidden Transitions

The second-order contribution to the rotatory strength of a magnetic dipole-forbidden d–d transition is given by

$$R_{0n}{}^{(2)} = \mathrm{Im}(\mathbf{P}_{0n}{}^{(1)} \cdot \mathbf{M}_{n0}{}^{(1)}) \tag{45}$$

Proceeding as before, we may partition both $\mathbf{P}_{0n}{}^{(1)}$ and $\mathbf{M}_{n0}{}^{(1)}$ into their respective SC and DC components so that:

$$\mathbf{P}_{0n}{}^{(1)} = \mathbf{P}_{0n}{}^{(1)}(\mathrm{SC}) + \mathbf{P}_{0n}{}^{(1)}(\mathrm{DC}) \tag{46}$$

$$\mathbf{M}_{n0}{}^{(1)} = \mathbf{M}_{n0}{}^{(1)}(\mathrm{SC}) + \mathbf{M}_{n0}{}^{(1)}(\mathrm{DC}) \tag{47}$$

and, finally

$$R_{0n}{}^{(2)} = \mathrm{Im}[\mathbf{P}_{0n}{}^{(1)}(\mathrm{SC}) \cdot \mathbf{M}_{n0}{}^{(1)}(\mathrm{SC})] + \mathrm{Im}[\mathbf{P}_{0n}{}^{(1)}(\mathrm{DC}) \cdot \mathbf{M}_{n0}{}^{(1)}(\mathrm{DC})] + \mathrm{Im}[\mathbf{P}_{0n}{}^{(1)}(\mathrm{SC}) \cdot \mathbf{M}_{n0}{}^{(1)}(\mathrm{DC}) + \mathbf{P}_{0n}{}^{(1)}(\mathrm{DC}) \cdot \mathbf{M}_{n0}{}^{(1)}(\mathrm{SC})] \tag{48}$$

or

$$R_{0n}{}^{(2)} = R_{0n}{}^{(2)}(\mathrm{SC}) + \mathrm{R}_{0n}{}^{(2)}(\mathrm{DC}) + R_{0n}{}^{(2)}(\mathrm{SC,DC}) \tag{49}$$

Unlike the first-order case where the SC and DC contributions are strictly additive, the second-order rotatory strength $R_{0n}{}^{(2)}$ includes contributions from mechanisms involving combinations of (simultaneous) static-coupling and dynamic-coupling between the metal ion chromophore and the ligand environment.

The first-order electric dipole transition moments, $\mathbf{P}_{0n}{}^{(1)}(\mathrm{SC})$ and $\mathbf{P}_{0n}{}^{(1)}(\mathrm{DC})$, appearing in eq 48 have been written down previously in eq 36 and 37, respectively. Collecting all perturber groups (*r* and *L*) into a single set labeled by *r*, the first-order magnetic dipole transition moment, $\mathbf{M}_{n0}{}^{(1)}(\mathrm{SC})$, may be expressed as

$$\mathbf{M}_{n0}{}^{(1)}(\mathrm{SC}) = -\sum_r \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} Q_r T_{m_\mathrm{A},0}{}^{(\ell_\mathrm{A},0)}(r) \times \left[\sum_{\gamma\mp 0} (\mathrm{A}_n|\hat{\mathbf{m}}(\mathrm{A})|\mathrm{A}_\gamma)(\mathrm{A}_0|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_\gamma)E_\gamma{}^{-1} + \sum_{\gamma\mp n} (\mathrm{A}_\gamma|\hat{\mathbf{m}}(\mathrm{A})|\mathrm{A}_0)(\mathrm{A}_n|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_\gamma)(E_\gamma - E_n)^{-1}\right] \tag{50}$$

where $\hat{\mathbf{m}}(\mathrm{A})$ denotes a magnetic dipole operator centered on the A chromophore and Σ_γ runs over a set of *gerade* states localized on A. The dynamic-coupling contribution to the first-order magnetic dipole transition moment may be expressed as

$$\mathbf{M}_{n0}{}^{(1)}(\mathrm{DC}) = \sum_r \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} \sum_{m_r} \sum_{i\mp 0} T_{m_\mathrm{A},m_r}{}^{(\ell_\mathrm{A},1)}(r) \times (\mathrm{B}_{ri}|\hat{\mathbf{m}}'(r)|\mathrm{B}_0)(\mathrm{A}_n|D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A})|\mathrm{A}_0) \times (\mathrm{B}_0|D_{m_r}{}^{(1)}(r)|\mathrm{B}_{ri})[2E_n/(E_n{}^2 - E_{ri}{}^2)] \tag{51}$$

where

$$\hat{\mathbf{m}}'(r) = \hat{\mathbf{m}}(r) + (e/2m_\mathrm{e}c)\mathbf{R}_r\mathbf{X}\hat{\mathbf{p}}(r) \tag{52}$$

Here, m_e denotes electron mass and we have used *r* to label all perturber sites. The magnetic dipole operator, $\hat{\mathbf{m}}(r)$, *and the linear momentum operator*, $\hat{\mathbf{p}}(r)$, are centered on the respective perturber groups. The vector $\mathbf{R}_r$ defines the position of perturber site *r* with respect to an origin located within the A chromophore.

The magnetic dipole matrix elements in eq 51 may be rewritten as follows:

$$(\mathrm{B}_{ri}|\hat{\mathbf{m}}'(r)|\mathrm{B}_0) = (\mathrm{B}_{ri}|\hat{\mathbf{m}}(r)|\mathrm{B}_0) + (e/2m_\mathrm{e}c)\mathbf{R}_r\mathbf{X}(\mathrm{B}_{ri}|\hat{\mathbf{p}}(r)|\mathrm{B}_0) = \mathbf{m}_{i0}(r) + (i\pi E_{ri}/hc)\mathbf{R}_r\mathbf{X}\boldsymbol{\mu}_{i0}(r) \tag{53}$$

where $\boldsymbol{\mu}_{i0}(r) = (\mathrm{B}_{ri}|\hat{\boldsymbol{\mu}}(r)|\mathrm{B}_0)$ and $\mathbf{m}_{i0}(r) = (\mathrm{B}_{ri}|\hat{\mathbf{m}}(r)|\mathrm{B}_0)$. In writing eq 53 we have made use of the relation

$$(\psi_i|\hat{\mathbf{p}}|\psi_j) = -\psi_j|\hat{\mathbf{p}}|\psi_i) = (2\pi i m_\mathrm{e}/e)(E_i - E_j)(\psi_i|\hat{\boldsymbol{\mu}}|\psi_j) \tag{54}$$

Since we are restricting the dynamic-coupling chromophore (A)–perturber (B) interaction potential to A (multipole) B (dipole) terms, the only ligand (perturber) transitions contributing to eq 51 are those which possess nonvanishing electric dipole character.

Considering only contributions from the *r* perturber groups in the ligand environment, the $R_{0n}{}^{(2)}(\mathrm{SC})$ term of eq 49 may be expressed as eq 55,

$$\begin{aligned}
R_{0n}{}^{(2)}(\mathrm{SC}) &= \mathrm{Im}[\mathbf{P}_{0n}{}^{(1)}(\mathrm{SC}) \cdot \mathbf{M}_{n0}{}^{(1)}(\mathrm{SC})] \\
&= (-i) \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} \sum_{\ell_\mathrm{A}'} \sum_{m_\mathrm{A}'} \left[\sum_{r} \sum_{r'} Q_r Q_{r'} T_{m_\mathrm{A},0}{}^{(\ell_\mathrm{a},0)}(r) T_{m_\mathrm{A}',0}{}^{(\ell_\mathrm{A}',0)}(r') \right] \\
&\quad \times \sum_q \Bigg[\sum_{\alpha \neq 0} \sum_{\gamma \neq 0} (\mathrm{A}_\alpha | D_q{}^{(1)}(\mathrm{A}) | \mathrm{A}_n) \\
&\quad \times (\mathrm{A}_n | \hat{m}_q(\mathrm{A}) | \mathrm{A}_\gamma)(\mathrm{A}_\alpha | D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A}) | \mathrm{A}_0) \\
&\quad \times (\mathrm{A}_0 | D_{m_{\mathrm{A}'}}{}^{(\ell_{\mathrm{A}'})}(\mathrm{A}) | \mathrm{A}_\gamma) E_\alpha{}^{-1} E_\gamma{}^{-1} \\
&\quad + \sum_{\alpha \neq n} \sum_{\gamma \neq n} (\mathrm{A}_0 | D_q{}^{(1)}(\mathrm{A}) | \mathrm{A}_\alpha) \\
&\quad \times (\mathrm{A}_\gamma | \hat{m}_q(\mathrm{A}) | \mathrm{A}_0)(\mathrm{A}_\alpha | D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A}) | \mathrm{A}_n) \\
&\quad \times (\mathrm{A}_n | D_{m_{\mathrm{A}'}}{}^{(\ell_{\mathrm{A}'})}(\mathrm{A}) | \mathrm{A}_\gamma)(E_\alpha - E_n)^{-1}(E_\gamma - E_n)^{-1} \\
&\quad + \sum_{\alpha \neq 0} \sum_{\gamma \neq n} \mathrm{A}_\alpha | D_q{}^{(1)}(\mathrm{A}) | \mathrm{A}_n) \\
&\quad \times (\mathrm{A}_\gamma | \hat{m}_q(\mathrm{A}) | \mathrm{A}_0)(\mathrm{A}_\alpha | D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A}) | \mathrm{A}_0) \\
&\quad \times (\mathrm{A}_n | D_{m_{\mathrm{A}'}}{}^{(\ell_{\mathrm{A}'})}(\mathrm{A}) | \mathrm{A}_\gamma) E_\alpha{}^{-1}(E_\gamma - E_n)^{-1} \\
&\quad + \sum_{\alpha \neq n} \sum_{\gamma \neq 0} (\mathrm{A}_0 | D_q{}^{(1)}(\mathrm{A}) | \mathrm{A}_\alpha) \\
&\quad \times (\mathrm{A}_n | \hat{m}_q(\mathrm{A}) | \mathrm{A}_\gamma)(\mathrm{A}_\alpha | D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A}) | \mathrm{A}_n) \\
&\quad \times (\mathrm{A}_0 | D_{m_{\mathrm{A}'}}{}^{(\ell_{\mathrm{A}'})}(\mathrm{A}) | \mathrm{A}_\gamma) E_\gamma{}^{-1}(E_\alpha - E_n)^{-1} \Bigg] \qquad (55)
\end{aligned}$$

where Σ_q goes over the (spherical) components of the electric and magnetic dipole operators. Recall that for $R_{0n}{}^{(2)}(\mathrm{SC})$ to be nonvanishing, the quantity

$$\begin{aligned}
F \times F' = &\left[\sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} \sum_{r} T_{m_\mathrm{A},0}{}^{(\ell_\mathrm{A},0)}(r) \right] \\
&\times \left[\sum_{\ell_{\mathrm{A}'}} \sum_{m_{\mathrm{A}'}} \sum_{r'} T_{m_\mathrm{A}',0}{}^{(\ell_\mathrm{A}',0)}(r') \right] \qquad (56)
\end{aligned}$$

must contain components which transform as the pseudoscalar representation under the symmetry operations of the G_A point group.

Again considering only contributions from the r perturber groups in the ligand environment, the $R_{0n}{}^{(2)}(\mathrm{DC})$ term of eq 49 may be expressed as (57).

$$\begin{aligned}
R_{0n}{}^{(2)}(\mathrm{DC}) &= \mathrm{Im}[\mathbf{P}_{0n}{}^{(1)}(\mathrm{DC}) \cdot \mathbf{M}_{n0}{}^{(1)}(\mathrm{DC})] \\
&= (-i) \sum_r \sum_{r'} \sum_{\ell_\mathrm{A}} \sum_{m_\mathrm{A}} \sum_{\ell_\mathrm{A}'} \sum_{m_\mathrm{A}'} \sum_{m_r} \sum_{m_r} [T_{m_\mathrm{A},m_r}{}^{(\ell_\mathrm{A},1)}(r) T_{m_\mathrm{A}',m_r}{}^{(\ell_\mathrm{A}',1)}(r')] \\
&\quad \times \sum_{i \neq 0} \sum_{j \neq 0} [(\mathrm{B}_0 | \hat{\boldsymbol{\mu}}(r) | \mathrm{B}_{ri}) \cdot (\mathrm{B}_{r'j} | \hat{\mathbf{m}}'(r') | \mathrm{B}_0)] \\
&\quad \times [(\mathrm{A}_0 | D_{m_\mathrm{A}}{}^{(\ell_\mathrm{A})}(\mathrm{A}) | \mathrm{A}_n)(\mathrm{B}_{ri} | D_{m_r}{}^{(1)}(r) | \mathrm{B}_0) \\
&\quad \times (\mathrm{A}_n | D_{m_{\mathrm{A}'}}{}^{(\ell_{\mathrm{A}'})}(A) | \mathrm{A}_0)(\mathrm{B}_0 | D_{m_{r'}}{}^{(1)}(r') | \mathrm{B}_{r'j})] \\
&\quad \times \left[\frac{4 E_{ri} E_n}{(E_n{}^2 - E_{ri}{}^2)(E_n{}^2 - E_{r'j}{}^2)} \right] \qquad (57)
\end{aligned}$$

The mixed static-coupling/dynamic-coupling term in eq 49 may be formed from eq 36, 37, 50, and 51 for the respective first-order electric and magnetic dipole transition moments.

2. *Magnetic Dipole Allowed Transitions*

The second-order contribution to the rotatory strength of a magnetic dipole allowed d–d transition is given by

$$R_{0m}{}^{(2)} = \mathrm{Im}(\mathbf{P}_{0m}{}^{(1)} \cdot \mathbf{M}_{m0}{}^{(1)} + \mathbf{P}_{0m}{}^{(2)} \cdot \mathbf{M}_{m0}{}^{(0)}) \qquad (58)$$

Detailed expressions for the first term in eq 58 may be developed in precisely the same manner as was done for eq 45 in the previous section (III.F.1). The second term in eq 58 may be expanded to the following form:

$$\begin{aligned}
R_{0m}{}^{(2)} = \mathrm{Im}[&\mathbf{P}_{0m}{}^{(2)}(\mathrm{SC}) + \mathbf{P}_{0m}{}^{(2)}(\mathrm{DC}) \\
&+ \mathbf{P}_{0m}{}^{(2)}(\mathrm{SC,DC})] \cdot \mathbf{M}_{m0}{}^{(0)} \qquad (59)
\end{aligned}$$

The next step is to obtain general expressions for the second-order electric dipole transition moments, $\mathbf{P}^{(2)}$. In doing this we shall use the "contracted" notation listed in Table I.

The static-coupling contribution to $\mathbf{P}_{0m}{}^{(2)}$ is given by eq 60.

$$\begin{aligned}
\mathbf{P}_{0m}{}^{(2)}(\mathrm{SC}) = &\sum_{\alpha \neq 0} \mathbf{P}_{\alpha m}{}^{(0)} \Bigg[\sum_{\alpha' \neq 0} V(\alpha 0, \alpha' 0) \\
&\times V(\alpha' 0, 00) E_\alpha{}^{-1} E_{\alpha'}{}^{-1} - V(\alpha 0, 00) V(00, 00) E_\alpha{}^{-2} \Bigg] \\
&+ \sum_{\alpha \neq m} \mathbf{P}_{0\alpha}{}^{(0)} \Bigg[\sum_{\alpha' \neq m} V(\alpha 0, \alpha' 0) V(\alpha' 0, m0) \\
&\times \Delta E_{m\alpha}{}^{-1} \Delta E_{m\alpha'}{}^{-1} - V(\alpha 0, m0) V(m0, m0) \Delta E_{m\alpha}{}^{-2} \Bigg] \\
&- \sum_{\alpha \neq 0} \sum_{\alpha' \neq m} \mathbf{P}_{\alpha\alpha'}{}^{(0)} V(\alpha 0, 00) V(00, \alpha' 0) E_\alpha{}^{-1} \Delta E_{m\alpha'}{}^{-1} \\
&- \sum_{\alpha \neq ,0m} \mu_{00} V(00, \alpha 0) V(\alpha 0, m0) E_\alpha{}^{-1} \Delta E_{m\alpha}{}^{-1} \qquad (60)
\end{aligned}$$

The dynamic-coupling contribution to $\mathbf{P}_{0m}{}^{(2)}$ is given by eq 61.

$$\begin{aligned}
\mathbf{P}_{0m}{}^{(2)}(\mathrm{DC}) = &\sum_{\alpha \neq 0} \mathbf{P}_{\alpha m}{}^{(0)} \\
&\times \sum_{\beta \neq 0} \sum_{\alpha' \neq 0,\alpha} V(\alpha 0, \alpha' \beta) V(\alpha' \beta, 00) E_{\alpha' \beta}{}^{-1} E_\alpha{}^{-1} \\
&+ \sum_{\alpha \neq m} \mathbf{P}_{0\alpha}{}^{(0)} \sum_{\beta \neq 0} \sum_{\alpha' \neq m,\alpha} V(\alpha 0, \alpha' \beta) \\
&\times V(\alpha\beta, m0) \Delta E_{m\alpha}{}^{-1} (E_m - E_{\alpha' \beta})^{-1} \\
&+ \sum_{\beta \neq 0} \mu_{0\beta} \sum_{\beta' \neq 0,\beta} \sum_{\alpha \neq 0,m} [V(0\beta, \alpha\beta') \\
&\times V(\alpha' \beta', m0) \Delta E_{m\beta}{}^{-1} (E_m - E_{\alpha\beta'})^{-1} \\
&+ V(m\beta, \alpha\beta') V(\alpha\beta', 00) E_{m\beta}{}^{-1} E_{\alpha\beta'}{}^{-1}] \\
&- \sum_{\alpha \neq 0} \sum_{\alpha' \neq m,0} \mathbf{P}_{\alpha\alpha'}{}^{(0)} \sum_{\beta \neq 0} V(\alpha\beta, 00) \\
&\times V(\alpha', \beta, m0) E_{\alpha\beta}{}^{-1} (E_m - E_{\alpha'\beta})^{-1} \\
&- \sum_{\beta \neq 0} \sum_{\beta' \neq 0} \mu_{\beta\beta'} \sum_{\alpha \neq 0,m} V(\alpha\beta, 00) \\
&\times V(\alpha\beta', m0) E_{\alpha\beta}{}^{-1} (E_m - E_{\alpha\beta'})^{-1} \qquad (61)
\end{aligned}$$

The "mixed" static-coupling/dynamic-coupling contributions to $\mathbf{P}_{0m}{}^{(2)}$ are given by eq 62.

Expressions 60, 61, and 62 can be reduced to simpler form only upon consideration of specific systems with prescribed symmetry properties. We note that $\mathbf{P}_{0m}{}^{(2)}(\mathrm{DC})$ includes terms with metal-localized electric dipole transition moments as well as terms with ligand-localized electric dipole transition moments.

3. *Comments on Second-Order Rotatory Strengths*

The details of the physical mechanisms subsumed in the second-order contributions to the d–d rotatory strengths are indeed quite complex. Some discussion of these physical mechanisms and their implications with regard to structure elucidation have appeared in the literature (ref 22, 24–27, 29, 35, 52–54, 57). Richardson and co-workers[24–27] have dealt primarily (but not entirely) with the $R^{(2)}(\mathrm{SC})$ terms, whereas Mason and co-workers[53] have dealt primarily with the dynamic-coupling contributions. Carrying the dynamic-coupling

TABLE I. Contracted Notation

A. Interaction Matrix Elements

1. General

$$V(\alpha\beta,\alpha'\beta') \equiv (\mathrm{A}_\alpha\mathrm{B}_\beta|\mathcal{V}_\mathrm{A} + \mathcal{V}_\mathrm{AB} + \mathcal{U}_\mathrm{A} + \mathcal{U}_\mathrm{AB}|\mathrm{A}_{\alpha'}\mathrm{B}_{\beta'})$$

2. Static Coupling

$$\mathcal{V}(\alpha,\alpha') \equiv (\mathrm{A}_\alpha|\mathcal{V}_\mathrm{A} + \mathcal{V}_\mathrm{AB}|\mathrm{A}_{\alpha'}) \equiv (\mathrm{A}_\alpha\mathrm{B}_0|\mathcal{V}_\mathrm{A} + \mathcal{V}_\mathrm{AB}|\mathrm{A}_{\alpha'}\mathrm{B}_0)$$

3. Dynamic Coupling

$$\mathcal{U}(\alpha\beta,\alpha'\beta') \boxminus (\mathrm{A}_\alpha\mathrm{B}_\beta|\mathcal{U}_\mathrm{A} + \mathcal{U}_\mathrm{AB}\mathcal{V}\mathrm{A}_{\alpha'}\mathrm{B}_{\beta'})$$

B. Transition Energy Sums and Differences

$$E_{\alpha\beta\gamma} = E_\alpha + E_\beta + E_\gamma$$

$$\Delta E_{\alpha\beta} = E_\alpha - E_\beta$$

C. Transition Dipole Matrix Elements

1. Metal Ion Chromophore

$$\mathbf{P}_{\alpha\gamma}{}^{(0)} \equiv (\mathrm{A}_\alpha|\hat{\boldsymbol{\mu}}(\mathrm{A})|\mathrm{A}_\gamma); \qquad \mathbf{M}_{\alpha\gamma}{}^{(0)} \equiv (\mathrm{A}_\alpha|\hat{\mathbf{m}}(\mathrm{A})|\mathrm{A}_\gamma)$$

2. Ligand (Perturber) Group

$$\boldsymbol{\mu}_{0\beta} \boxminus (\mathrm{B}_0|\hat{\boldsymbol{\mu}}(\mathrm{B})|\mathrm{B}_\beta); \qquad \hat{\mathbf{m}}_{0\beta}{}' \equiv (\mathrm{B}_0|\hat{\mathbf{m}}'(\mathrm{B})|\mathrm{B}_\beta)$$

Summations over all perturber sites r are implicit in the operators $\hat{\boldsymbol{\mu}}(\mathrm{B})$ and $\hat{\mathbf{m}}'(\mathrm{B})$.

$$\begin{aligned}
\mathbf{P}_{0\mathrm{m}}{}^{(2)}(\mathrm{SC,DC}) = \sum_{\beta\mp 0}\Bigg[&\sum_{\alpha\mp 0}\mathbf{P}_{\alpha m}{}^{(0)}V(\alpha 0,\alpha\beta) \\
&\times V(\alpha\beta,00)E_\alpha{}^{-1}E_{\alpha\beta}{}^{-1} \\
&+ \sum_{\alpha\mp m}\mathbf{P}_{0\alpha}{}^{(0)}V(\alpha 0,\alpha\beta)V(\alpha\beta,m0)\Delta E_{m\alpha}{}^{-1}(E_m - E_{\alpha\beta})^{-1}\Bigg] \\
&- \sum_{\beta\mp 0}\boldsymbol{\mu}_{0\beta}[\mathrm{V}(m0,m0)V(m0,0\beta)\Delta E_{m\beta}{}^{-2} \\
&+ V(00,00)V(00,m\beta)E_{m\beta}{}^{-2} \\
&- V(0\beta,00)V(00,m0)E_m{}^{-1}\Delta E_{m\beta}{}^{-1} \\
&- V(m\beta,m0)V(m0,00)E_{m\beta}{}^{-1}E_m{}^{-1}] \\
&+ \sum_{\beta\mp 0}\sum_{\beta'\mp 0}\boldsymbol{\mu}_{0\beta}[V(0\beta,0\beta') \\
&\times V(0\beta',m0)\Delta E_{m\beta}{}^{-1}E_{m\beta'}{}^{-1} \\
&+ V(m\beta,m\beta')V(m\beta',00)E_{m\beta}{}^{-1}E_{m\beta'}{}^{-1}] \\
&+ \sum_{\beta\mp 0}\sum_{\alpha\mp 0,m}\boldsymbol{\mu}_{0\beta}[V(0\beta,\alpha 0)V(\alpha 0,m0)\Delta E_{m\beta}{}^{-1}\Delta E_{m\alpha}{}^{-1} \\
&+ V(m\beta,\alpha 0)V(\alpha 0,00)E_{m\beta}{}^{-1}E_\alpha{}^{-1} \\
&- V(\alpha\beta,00)V(\alpha 0,m0)E_{\alpha\beta}{}^{-1}\Delta E_{m\alpha}{}^{-1} \\
&- V(\alpha 0,00)V(\alpha\beta,m0)E_\alpha{}^{-1}(E_m - E_{\alpha\beta})^{-1}] \\
&+ \sum_{\beta\mp 0}\boldsymbol{\mu}_{0\beta}\Bigg[\sum_{\alpha\mp 0}V(m\beta,\alpha\beta)V(\alpha\beta,00)E_{m\beta}{}^{-1}E_{\alpha\beta}{}^{-1} \\
&+ \sum_{\alpha\mp m}V(0\beta,\alpha\beta)V(\alpha\beta,m0)\Delta E_{m\beta}{}^{-1}(E_m - E_{\alpha\beta})^{-1}\Bigg] \qquad (62)
\end{aligned}$$

model to second order, Strickland and Richardson[54] calculated the d–d optical activity for a series of Cu(II) complexes of amino acids, dipeptides, and tripeptides. More recently, Schipper[57] has presented a theoretical treatment of d–d optical activity based on the independent systems/perturbation model and focused his attention primarily on what we have denoted as $R^{(2)}$(DC) and $R^{(2)}$(SC,DC), that is, the second-order dynamic-coupling and "mixed" static-coupling/dynamic-coupling contributions. Of special interest in the Schipper study is the assertion that the rotatory strengths of magnetic dipole allowed d–d transitions arise *predominantly* from $R^{(2)}$(DC) contributions involving dipole (metal ion chromophore)–dipole (ligand) interactions.

Schipper[57] discounts the "pure" static-coupling and "mixed" static-coupling/dynamic-coupling mechanisms as dominant contributors to the d–d rotatory strengths in most metal complexes since the chiral components of the static part of the ligand field potential are generally expected to be weak. Exceptions to this would occur in those cases where *charged* ligand groups are dissymmetrically disposed about the metal ion chromophoric unit. Schipper also discounts the $R^{(1)}$(DC) contributions as being dominant due to the necessity in this case of including multipolar ($\ell_\mathrm{A} > 1$)-dipole terms in the metal ion–ligand interaction potential. The dominance of $R^{(2)}$(DC) over $R^{(1)}$(DC), according to Schipper, may be attributed to the dominance of dipole–dipole over multipole ($\ell_\mathrm{A} > 1$)-dipole interaction terms in the metal ion chromophore-ligand dynamic-coupling mechanism.

Although Schipper's arguments for the dominance of $R^{(2)}$(DC) via dipole–dipole coupling would appear to be plausible from *qualitative* physical considerations, no numerical or quantitative calculations have yet been reported to support these arguments. To date, all calculations of d–d rotatory strengths based on the dynamic-coupling model have relied on chiral multipole ($\ell_\mathrm{A} >$ 1)-dipole metal–ligand interactions to induce optical activity. Furthermore, all of the sector rules proposed for d–d CD spectra have been based on the expressions for $R^{(1)}$(SC), $R^{(2)}$(SC), $R^{(1)}$(DC), and the multipole ($\ell_\mathrm{A} > 1$)-dipole parts of $R^{(2)}$(DC). These theoretical analyses (in which the dipole–dipole coupling terms in $R^{(2)}$(DC) have been ignored) have enjoyed some moderate success in accounting for the empirically observed CD data, both qualitatively and semiquantitatively. However, given the extensive parameterization of the assumed models, this success cannot be taken as conclusive evidence for the correctness of the models. *Quantitative* analyses based on the dipole–dipole coupling terms in $R^{(2)}$(DC) are required before further conclusions can be reached regarding the dominant mechanism in d–d optical activity.

An example of a dipole–dipole coupling term in $R^{(2)}$(DC) is given by (for a magnetic dipole *allowed* transition 0 → m),

$$\begin{aligned}
-iV_\mathrm{dd}(0\beta,\alpha\beta')V_\mathrm{dd}(\alpha\beta',m0)\Delta E_{m\beta}{}^{-1}& \\
\times (E_m - E_{\alpha\beta'})^{-1}[\boldsymbol{\mu}_{0\beta}\cdot\mathbf{M}_{m0}{}^{(0)}]&
\end{aligned}$$

where $\beta \neq 0$, $\beta' \neq 0,\beta$, and α is coupled to both the ground state (0) and the excited state (m) via an electric dipole operator $\hat{\boldsymbol{\mu}}(\mathrm{A})$ located on the chromophore A. Here, V_dd denotes the dipole–dipole coupling term in the interaction potential. In this case, the matrix element product on B (the ligand environment) has the form

$$\mu_{0\beta}\mu_{\beta\beta'}\mu_{\beta'0}$$

and the matrix element product on A has the form

$$P_{0\alpha}{}^{(0)}P_{\alpha m}{}^{(0)}M_{m0}{}^{(0)}$$

This contribution to the rotatory strength of the 0 → m transition will be maximized when

$$\boldsymbol{\mu}_{0\beta} \times \boldsymbol{\mu}_{\beta\beta'}\cdot\boldsymbol{\mu}_{\beta'0}$$

is maximized; i.e., the electric dipole transition moments on B are all strongly allowed *and* mutually orthogonal. A detailed account of the electronic selection rules and stereochemical sector rules inherent to the dipole–dipole coupling terms of $R^{(2)}$(DC) may be found in Schipper's article.[57]

Another example of a dipole–dipole coupling term in $R^{(2)}$(DC) is given by

$$\begin{aligned}
-iV_\mathrm{dd}(\alpha 0,\alpha'\beta)V_\mathrm{dd}(\alpha'\beta,m0)\Delta E_{m\alpha}{}^{-1}& \\
\times (E_m - E_{\alpha'\beta})^{-1}[\mathbf{P}_{0\alpha}{}^{(0)}\cdot\mathbf{M}_{m0}{}^{(0)}]&
\end{aligned}$$

where $\beta \mp 0$, $\alpha' \mp \alpha$, and α' is connected to both α and m via an electric dipole operator. In this case, an electric dipole transition moment ($\mathbf{P}_{0\alpha}{}^{(0)}$) is induced on the chromophore A via the mediation of the ligand environment.

G. Assessment of Model

The independent systems/perturbation model has been valuable in the development of d–d optical activity as a structure probe of metal complexes. In the majority of its applications it has provided useful *qualitative* guidelines and working hypotheses with regard to correlating CD spectral observables with stereochemical and electronic structural details. In some cases, calculations based on this model have been of semiquantiative and quantitative value in understanding or rationalizing d–d CD spectra. The model is extraordinarily simple in its physical assumptions and details, and the formalism associated with it is straightforward. However, it provides only a *limited* physical representation of transition metal complexes and, when carried to second-order, calculations based on it can become extremely cumbersome. It has not yet been clearly established that such calculations may be simplified by assuming dominance of just one or two mechanisms operative within the general model. Furthermore, sector rules based on this model are unambiguous and straightforward to apply only when dominant mechanisms can be identified for specific classes of metal complex systems.

Improvements and refinements in the application of the independent systems/perturbation model to interpreting the d–d optical activity of transition metal complexes depend upon further detailed characterization of d–d, charge-transfer, and ligand-localized spectroscopic transitions in these systems. Additional theoretical calculations *and* empirically based spectra–structure correlation studies are also required to identify the dominant metal–ligand coupling mechanisms for specific classes of metal complexes.

IV. Vibronic Interactions

In developing the theory presented in section III we dealt exclusively with *pure* electronic transitions. The states connected by these transitions were taken as eigenstates of an electronic Hamiltonian operator defined with the nuclei "fixed" in their equilibrium configuration. In considering the *detailed* structure of CD spectra one must examine the rotatory strengths associated with individual vibrational-electronic (vibronic) transitions. Furthermore, the possible consequences of vibronic coupling interactions must be considered.

Vibronic interactions play an *essential* role in determining most of the spectroscopic properties of the d–d transitions in metal complexes which are centrosymmetric. All of the electric dipole intensity observed in the d–d absorption (and emission) bands of such systems arise from vibronically induced mixings between ungerade excited states of the metal complex and the gerade d–d states. In this case, the gerade and ungerade states mix under the perturbative influence of the ungerade vibrational modes of the system. Vibronic interactions retain an important (although, in general, a nonessential) role in determining the d–d absorption intensities in metal complexes which are noncentrosymmetric. If the deviation from centric symmetry is only slight, then the noncentrosymmetric components of the ligand field are generally small and are relatively ineffective in mixing the d–d gerade states with ungerade states which will lead to observable electric dipole absorption intensity. In most cases, the principal mechanism by which the ligand-field transitions acquire intensity is through vibronically induced mixings with electric dipole allowed transitions.

Generally the gerade ligand-field states and the ungerade states with which they can mix via a vibronic coupling mechanism are sufficiently separated in energy that the vibronic coupling energy can be assumed small compared to the energy separation. Under these conditions the so-called Herzberg–Teller (HT) 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 HT 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 HT theory is not applicable. Under these conditions, the nuclear motions are modified by the electronic motions leading to a deformation of the potential energy surface associated with the coupling mode(s). In this case, a nonadiabatic 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.[88] PJT or JT interactions *within* the manifold of d–d states of a metal complex cannot produce or enhance d–d absorption (or emission) intensities. However, such interactions can have a significant influence on how the *total* intensity is distributed among the vibronic components of the transitions.

Richardson and co-workers have investigated (theoretically) the influence of PJT and JT vibronic interactions upon the d–d chiroptical spectra of dissymmetric trigonal complexes[61] and dissymmetric pseudo-tetragonal complexes.[60,62,63] Additionally, Richardson and Hilmes[30] incorporated vibronic interactions of the PJT type into their treatment of the optical activity of crystalline Cu^{2+}:$ZnSeO_4 \cdot 6H_2O$. In these studies, the active vibrational modes (i.e., those involved in vibronic coupling) were assumed to be localized within the metal ion–donor atom cluster (the so-called "skeletal" modes of the systems), and only the d-electron states of the metal ion chromophore were allowed to couple via vibronic interactions. The d-electron basis states were taken as eigenfunctions of an electronic Hamiltonian defined for the (dissymmetric) equilibrium geometry of the metal complex under consideration. The chirality of the metal complex was fully reflected, therefore, in the nonvibronic representation of the system. The vibronic interactions operating within the manifold of d-electron states did not introduce any additional chirality into the system; their main effect was to redistribute rotatory strength (or CD intensity) among the perturbed vibronic components of d-electron state parentage. The *net* (or total) d–d rotatory strength was determined entirely by the stationary dissymmetric potential created by the ligand field, but how this *net* rotatory strength was distributed across the d–d CD spectrum was found to be extraordinarily sensitive to the nature and strength of the vibronic interactions. In cases where several d-electron states are nearly degenerate or where the vibronic interaction energies may be assumed large (relative to the energy spacings between electronic energy levels), it was shown that assignments of specific features in the CD spectra to specific electronic transitions may not be valid. Under these conditions the states involved in the spectroscopic transitions cannot be characterized or described in terms of well-defined electronic quantum numbers. The only meaningful designations of these states are the set of vibronic quantum numbers, reflecting the strong vibrational-electronic coupling. This has important implications regarding the validity of procedures in which spectra–structure correlations are based on the use of just one (or several) CD band(s) as diagnostic indicators of ligand stereochemistry. In these procedures it is usually assumed that each CD band can be assigned a specific electronic identity. The sensitivity of d–d CD intensity distributions to PJT vibronic interactions is demonstrated in the numerous simulated CD spectra calculated by Richardson and co-workers.[60–63]

The influence of vibronic coupling between the d-electron states and states outside the d-electron state manifold upon d–d chiroptical spectra has not yet been dealt with quantitatively. In this case, the adiabatic approximation is most likely valid and the HT theory of vibronic coupling may be applied. Harding[64] has considered this case in a qualitative way for d–d optical activity using the vibronic coupling formalism of Weigang and co-workers.[65-68] The Weigang model employs the adiabatic approximation.

V. Spin-Orbit Interactions

Only one study has been reported concerning the influence of spin-orbit interactions upon the chiroptical spectra of spin-allowed d-d transitions. Hilmes, Caliga, and Richardson[63] investigated the influence of (simultaneous) spin-orbit and vibronic interactions upon the rotatory strengths of nearly degenerate d-d transitions in metal complexes of pseudo-tetragonal symmetry. A model system was considered in which three nearly degenerate d-d excited states are coupled via both spin-orbit and vibronic interactions. Vibronic interactions among the three nearly degenerate d-d electronic states were assumed to arise from a PJT (pseudo-Jahn-Teller) mechanism involving three different vibrational modes of the undistorted metal complex system. The model was *conservative* with respect to the total (or *net*) rotatory strength associated with transitions to the vibronic sublevels of the three perturbed d-d excited states. The rotatory strength distribution among these transitions was found to be sensitive to both the vibronic and spin-orbit coupling parameters. Furthermore, it was found that the vibronic and spin-orbit effects could be additive, subtractive, or mutually interactive, depending upon the transitions considered and the coupling parameters used. It was further concluded that spin-orbit coupling effects upon the spin-allowed d-d transitions of first row metal ions would be sufficiently small to preclude their significantly perturbing the observed chiroptical spectral properties.

The essential role of spin-orbit coupling in generating optical activity in the spin-forbidden d-d transitions of chiral transition metal complexes has been studied by a number of workers.[69-74] These studies have employed straightforward perturbation techniques in which the spin-orbit interaction operator was assumed to mix d-electron states of different spin multiplicities. The spin-forbidden d-d transitions were assumed to acquire their optical activity by "stealing" rotatory strength from the optically active spin-allowed d-d transitions. Only single-center (metal ion) spin-spin interactions were considered.

VI. Spectra-Structure Relationships

A. Stereochemistry

The sources of dissymmetry in an optically active metal complex may generally be classified as follows: (1) *inherent dissymmetry* within the metal ion-donor atom coordination cluster, (2) *configurational dissymmetry* due to a chiral arrangement of chelate systems about the metal ion, (3) *conformational dissymmetry* due to chiral conformations within individual chelate rings, and (4) *vicinal dissymmetry* due to asymmetric sites located within the coordinated ligands. Identification and separation of the contributions made by these types of dissymmetry to the observed d-d chiroptical spectra can provide at least "rough-grained" stereochemical information about a metal complex.

One class of metal complexes which are *inherently dissymmetric* due to the distribution of achiral monodentate ligands about the metal ion is represented by *all-cis*-$[M(A)_2(B)_2(C)_2]$, where M denotes the metal ion and A, B, and C denote chemically dissimilar monodentate ligands (see Figure 1). Two examples of metal complexes of this type are: (*R*)-(+)-*all-cis*-$[Co(NH_3)_2(H_2O)_2(CN)_2]^+$ and (*S*)-(+)-*all-cis*-$[Co(NH_3)_2(H_2O)_2(NO_2)_2]^+$. These two complexes have recently been synthesized and resolved,[89] and their electronic absorption and circular dichroism spectra have been reported.[89] Mason[90] has calculated the optical activity of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ Co(III) d-electron transition for these systems using the independent systems/perturbation model carried to third- and fourth-order in the dynamic-coupling terms. (Mason refers to the dynamical coupling aspects of the independent systems/perturbation model as the *ligand-polarization model*.) Mason found that the third-order rotatory strengths vanish if the coordination octahedron of the complex is geometrically regular, but not those of the fourth-order model, which is based upon the pairwise mixing of the three components of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ d-d transition, mediated by the Coulombic potential between the individually correlated induced dipoles in different ligands. The sum of the third- and fourth-order contributions were found to reproduce the signs and a significant fraction of the magnitude of the observed rotatory strengths exhibited by the two complexes for which data are available. In performing these calculations, Mason neglected all static-coupling and "mixed" static-coupling/dynamic-coupling contributions. He further neglected all mixing between the $^1T_{1g}$ and $^1T_{2g}$ octahedral d-electron states of Co(III).

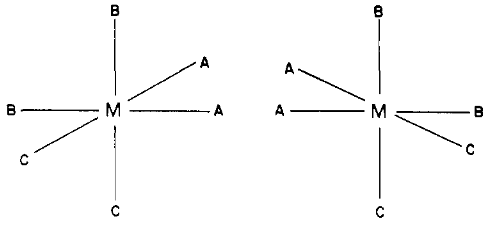
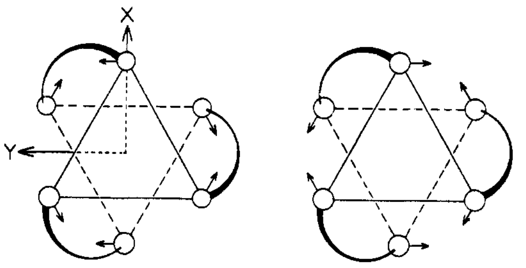


Figure 1. Enantiomeric forms of an *all-cis*-$[M(A)_2(B)_2(C)_2]$ complex in which A, B, and C denote chemically dissimilar, achiral, and monodentate ligands.

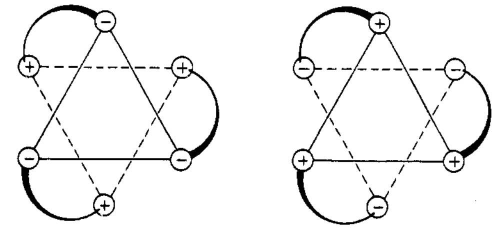
Examples of complexes which possess inherent dissymmetry within the metal ion-donor atom cluster as well as configurational dissymmetry due to chiral distributions of chelate rings are $Co(ox)_3^{3-}$ and $Cr(ox)_3^{3-}$, where ox denotes an oxalato dianion. The MO_6 clusters in these complexes are trigonally distorted octahedra possessing exact trigonal dihedral (D_3) symmetry, and the planar ox ligands are arrayed about the metal ion with exact D_3 symmetry. The relative contributions of the donor atoms vs. the chelate bridging atoms (or groups) to the optical activity of these systems have never been sorted out or determined conclusively. Trigonal distortion operations on the ML_6 cluster of a tris(bidentate ligand) metal complex with D(Λ) absolute configuration are depicted in Figure 2. These distortion operations are classified as azimuthal twists about the C_3 axis of the system or as polar elongations (or compressions) along the C_3 axis.[91] As depicted in Figure 2, the azimuthal twists exert an ungerade perturbation upon the (erstwhile) octahedral system, whereas the polar distortions exert a gerade perturbation. An azimuthal twist within the ML_6 cluster is *essential* to producing optical activity within the d-d transitions of such complexes so long as all the donor atoms are identical and the chelate bridging atoms (or groups) are ignored. The polar distortions cannot produce d-d optical activity in the absence of an azimuthal twist.[24,31] The tris(oxalato) and tris(ethylenediamine) complexes of Co(III) are examples of systems in which the ML_6 cluster suffers polar compression/azimuthal contraction (at least in crystalline media).[16] The tris(malonato) complex of Cr(III) in crystalline form reveals a polar elongation/azimuthal expansion of the CrO_6 cluster.[16] The tris(trimethylenediamine) complex of Co(III) also exhibits polar elongation/azimuthal expansion in its crystalline form.[16]

All of the structures shown in Figure 2 have a D(Λ) absolute configuration defined with respect to the distribution of chelate rings about the metal ion. If the chelate bridging atoms determine (or make the dominant contributions to) the d-d rotatory strengths, then one may readily correlate the d-d optical activity observables to the absolute configuration of tris(symmetric bidentate ligand) complexes. On the other hand, if the signs and



a. Azimuthal Contraction

b. Azimuthal Expansion



c. Polar Compression

d. Polar Elongation

Figure 2. Trigonal distortion operations on the ML_6 cluster of a tris(bidentate ligand) metal complex with D(Λ) absolute configuration.

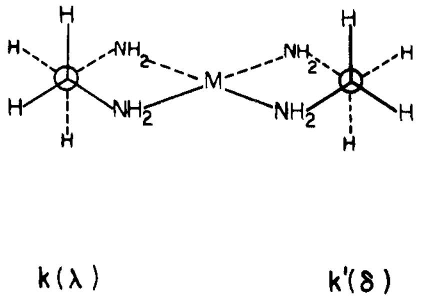


Figure 3. Conformational isomers of coordinated ethylenediamine. The view is along a direction parallel to the C–C bonds in the en ligands.

magnitudes of the d–d rotatory strengths are primarily determined by distortions within the ML_6 cluster, then great care must be exercised in deducing absolute configurations from the optical activity observables. Uncertainties regarding the relative importance of inherent dissymmetry (within the ML_6 cluster) vs. configurational dissymmetry (due to the distribution of chelate rings) to producing optical activity in the d–d transitions of tris(bidentate ligand) complexes have retarded progress in developing reliable and generally applicable spectra–structure relationships for such systems.

The independent systems/perturbation model outlined in section III neglects metal ion–donor atom bonding interactions and ignores the detailed orbital nature of the ligand electronic distributions. For these reasons this model is not very suitable for treating effects due to distortions within the ML_6 cluster.

An example of a complex in which there are three sources of dissymmetry (inherent, configurational, and conformational) is $Co(en)_3^{3+}$, where en ≡ ethylenediamine ligand. In this complex the CoN_6 cluster is trigonally distorted with a polar compression/azimuthal contraction distortion (see Figure 2), the distribution of chelate rings reflects one of two enantiomeric configurations (Λ or Δ), and each five-membered chelate ring may exist in one of two enantiomeric conformational types, k(λ) or k′(δ). The possible configurational–conformational isomers for $Co(en)_3^{3+}$ are: Λ(δδδ), Λ(δδλ), Λ(δλλ), Λ(λλλ), Δ(δδδ), Δ(δδλ), Δ(δλλ), and Δ(λλλ). The conformational isomers of coordinated ethylenediamine are depicted in Figure 3. In crystalline media, $Co(en)_3^{3+}$ has been found to exist in the Λ(δδδ) or Δ(λλλ) enantiomeric forms. Conformational analysis calculations indicate that these should be the most stable isomers of free $Co(en)_3^{3+}$.[92] In the Λ(δδδ) isomer, the axes of the C–C bonds of the en ligands are parallel (*lel*) to the C_3 axis of the complex. Likewise, in the Δ(λλλ) isomer the C–C bonds of the en ligands are parallel to the C_3 symmetry axis. In the Λ(λλλ) and Δ(δδδ) isomers, the C–C bonds of the en ligands are oblique (*ob*) to the C_3 symmetry axis (see Figure 4). Conformational analysis indicates that for free $Co(en)_3^{3+}$ the order of stability for the various isomers is Λ(δδδ) = Δ(λλλ) > Λ(δδλ) = Δ(λλδ) > Λ(δλλ) = Δ(λδδ) > Λ(λλλ) = Δ(δδδ), with Λ(δδδ) being about 1.8 kcal/mol more stable than Λ(λλλ). There remains considerable uncertainty regarding the relative stabilities of these isomers in solution media.

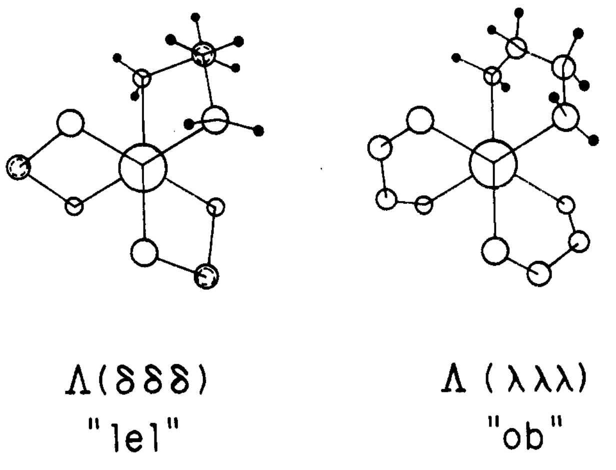


Figure 4. The "lel" and "ob" forms of a Λ-$[M(en)_3]$ complex.

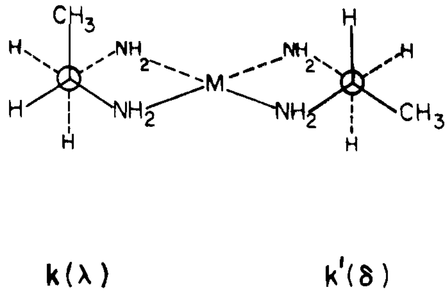


Figure 5. Conformational isomers of coordinated (*S*)-propylenediamine. The view is along a direction parallel to the C–C bonds in the *S*-pn ligands.

Examples of metal complexes in which there are four sources of dissymmetry (inherent, configurational, conformational, and asymmetric centers within the ligands) are $Co(S\text{-}pn)_3^{3+}$ and $Co(R\text{-}pn)_3^{3+}$, where pn ≡ propylenediamine ligand. These systems can assume any of the eight configurational-conformational isomeric forms discussed above for $Co(en)_3^{3+}$ and each ligand in these complexes has one asymmetric carbon atom (which is a bridging atom in the five-membered chelate rings). The methyl substituent in *R*-pn is equatorial to the chelate ring in the λ conformation and is axial to the chelate ring in the δ conformation. The methyl substituent in *S*-pn is equatorial to the chelate ring in the δ conformation and is axial to the chelate ring in the λ conformation. The most stable isomer of $Co(R\text{-}pn)_3^{3+}$ is Δ(λλλ), whereas the most stable isomer of $Co(S\text{-}pn)_3^{3+}$ is Λ(δδδ).[92] The conformational isomers of coordinated *S*-pn are depicted in Figure 5.

Examples of complexes possessing dissymmetry only from chiral chelate ring conformations and asymmetric centers within the ligands are *trans*-$[Co(S\text{-}pn)_2(NH_3)_2]^{3+}$ and *trans*-$[Co(S\text{-}ala)_2(H_2O)_2]^+$, where ala ≡ alaninato ligand. An example of a metal complex which has only one source of dissymmetry, an asymmetric carbon atom in one of its ligands, is $[Co(NH_3)_5($*S*-

amH)]$^{2+}$, where *S*-amH is an amino acid ligand coordinated only through its carboxylate group (i.e., it is bound unidentate).

One of the principal objectives of theoretical research dealing with the d–d optical activity of chiral transition metal complexes is to show how each of the sources of dissymmetry discussed above is manifested in the observed CD spectra of these systems. More specifically, one would like to relate the band splittings, sign patterns, relative band intensities, and total (*net*) CD intensity to the structural characteristics of the metal complex. These structural characteristics include distortions within the metal ion–donor atom cluster, the distribution of donor atoms about the metal ion, absolute configuration, conformational features of chelate rings, and the spatial disposition of ligand substituent groups. Developing such spectra–structure relationships is an ambitious task and the current theories of d–d optical activity are not yet entirely adequate for this purpose. The theories have been reasonably successful in providing *a posteriori* interpretations and rationalizations of the experimental data, but their predictive value has been somewhat more limited. However, there now exist a number of reasonably reliable spectra–structure relationships for several structural classes of chiral metal complexes. Most of the relationships may be considered semiempirical in the sense that they were derived from systematic correlations of empirical data and were made to conform to (or be consistent with) general theoretical principles.

The most comprehensive investigations of spectra–structure relationships within the context of the independent systems/perturbation model with static-coupling (ISP–SC) were carried out by Richardson.[24–27,31] These studies included consideration of all sources of dissymmetry in four-coordinate and six-coordinate complexes belonging to a variety of structural and symmetry classes. Given the simplicity of the model employed (ISP–SC), these studies led to rather remarkable qualitative correlations between the CD observables and various structural features of metal complexes. Applications of the sector rules derived for six-coordinate dissymmetric complexes were given special attention in ref 27, and applications of the sector rules derived for four-coordinate dissymmetric complexes were considered in ref 26. Complexes of trigonal dihedral (D_3) symmetry were treated in ref 24, and complexes of pseudo-tetragonal symmetry were the subject of ref 25. Mason[29,35] has also examined the sector rules and other spectra–structure relationships inherent in the static-coupling parts of the general independent systems/perturbation model of d–d optical activity.

The most comprehensive investigations of spectra–structure relationships within the context of the independent systems/perturbation model with dynamic-coupling (ISP–DC) have been carried out by Mason and co-workers.[29,35,51–53,90,93] Comparisons of the sector rules derived from the DC and SC parts of the general independent systems/perturbation model were given explicit consideration, and a number of quantitative calculations were carried out within the polarizability approximation for representing ligand contributions to the electric dipole transition moments of the perturbed d–d transitions. Richardson[25,54] has also employed the ISP–DC model to examine the spectra–structure relationships appropriate to a series of pseudo-tetragonal complexes. Detailed calculations based on the ISP–DC model carried to second order were reported for the d–d optical activity in Cu(II) complexes of amino acids, dipeptides, and tripeptides.[54]

The most complete set of symmetry rules applicable to the d–d optical activity of chiral transition metal complexes have been set forth in the work of Schipper.[57,94,95] These symmetry (selection) rules apply to the spectroscopic moments appearing in the d–d rotatory strength expressions and may be related in a straightforward way to sector rules pertaining to ligand structural (stereochemical) features. Schipper's work is based on the general independent systems/perturbation model (which he refers to as the "separable chromophore model") and includes consideration of both static-coupling and dynamic-coupling.

The only source of dissymmetry in metal complexes which poses a serious problem for the general ISP model is that of inherent dissymmetry within the metal ion–donor atom cluster. The neglect of covalent bonding interactions between the metal ion and the ligand donor atoms (or groups) may be expected to be a poor approximation when dealing with ML_n dissymmetry (where L denotes donor atoms). However, Mason[90] has achieved some success in treating the d–d optical activity of *all-cis*-[$M(A)_2(B)_2(C)_2$] complexes using the ISP–DC model, and Richardson[24–27] has simply incorporated the ligand donor atoms into the ligand perturber set in his applications of the ISP–SC model. The extent to which the general ISP model can be successfully and usefully applied to sorting out the configurational, ligand conformational, and ligand vicinal contributions to d–d optical activity is determined in large part by how one chooses to partition the ligand environment into perturber fragments. The greater the number of perturber fragments (atoms, groups, *or* bonds) represented in the model, the better the chances are of accurately reflecting all of the stereochemical subtleties of the ligand environment. Of course, the greater the number of ligand perturber fragments included, the greater the scope of the calculations and the greater the demand for spectroscopic information about the ligands (and their component parts).

The molecular orbital and related methods for calculating d–d optical activity (ref 39–41, 43, 44, 46–48) have not proved to be particularly useful in sorting out spectra–structure relationships. The models and calculations dealing only with the metal ion–donor atom cluster (ML_n) have, perhaps, yielded some insights regarding the sensitivity of d–d rotatory strengths to metal–donor atom orbital interactions (especially with regard to orbital overlaps and orbital hybridization—on the metal ion *and* on the ligand donor atoms).[39–41,43,48] These models are possibly the most appropriate for treating inherent dissymmetry within the ML_n cluster. The models and calculations which have included *all atoms* of the complexes[44,46,47] have yielded results which are useful primarily as checks or tests of results obtained empirically or from alternative calculational methods. These calculations have produced few, if any, new spectroscopic or structural insights.

It should be mentioned here that a great deal of experimental work has been done on the problem of sorting out the relative contributions of the various sources of dissymmetry (*inherent, configurational, conformational,* and *vicinal*) to the d–d optical activity of a variety of structural classes of transition metal complexes. The laboratories of Bodie Douglas (University of Pittsburgh), Clifford Hawkins (University of Queensland), Brice Bosnich (University of Toronto), and Stephen Mason (University of London King's College) have been particularly active in this regard. Additionally, a great deal of effort has been devoted to developing empirically based sector rules for d–d optical activity. Among the more active research groups in this area have been those of Hawkins, Bosnich, Mason, and Bruce Martin (Univeristy of Virginia). Discussion and comment on these empirically based studies lie outside the scope of this review article. However, these studies have played an essential role in guiding the development of d–d optical activity theory.

B. Characterization and Assignment of Transitions

The principal utility of CD studies in the characterization and assignment of electronic transitions is differentiation between magnetic-dipole-allowed and magnetic-dipole-forbidden transitions. The CD intensity of a transition, *i* → *j*, is governed by the rotatory strength quantity

$$R_{ij} = -i\langle \psi_i | \hat{\boldsymbol{\mu}} | \psi_j \rangle \cdot \langle \psi_j | \hat{\mathbf{m}} | \psi_i \rangle = -i\boldsymbol{\mu}_{ij} \cdot \mathbf{m}_{ji} = |\boldsymbol{\mu}_{ij}|\,|\mathbf{m}_{ji}| \cos\theta \quad (63)$$

where $|\mu_{ij}|$ and $|\mathbf{m}_{ji}|$ are, respectively, the absolute (real) values of μ_{ij} and $\mathbf{m}_{ji}$, and θ is the angle between the electric and magnetic dipole transition vectors. The absorption intensity of the same transition is governed by the dipole strength quantity,

$$D_{ij} = |\mu_{ij}|^2 + |\mathbf{m}_{ij}|^2 \qquad (64)$$

The rotatory strength, R_{ij}, may be determined from CD data according to

$$R_{ij} = 22.9 \times 10^{-40} \int \Delta\epsilon(\nu)\, d\nu/\nu \text{ esu}^2 \text{ cm}^2 \qquad (65)$$

and the dipole strength, D_{ij}, may be determined from absorption data according to

$$D_{ij} = 91.8 \times 10^{-40} \int \epsilon(\nu)\, d\nu/\nu \text{ esu}^2 \text{ cm}^2 \qquad (66)$$

where the integrations in eq 65 and 66 are taken over the CD and absorption band profiles, respectively. $\Delta\epsilon = (\epsilon_L - \epsilon_R)$ and $\epsilon = (\epsilon_L + \epsilon_R)/2$, where $\epsilon_{L(R)}$ is the molar decadic extinction coefficient for left (right) circularly polarized light. We may further define

$$g_{ij} = [\int \Delta\epsilon(\nu)\, d\nu/\nu]/[\int \epsilon(\nu)\, d\nu/\nu] = 4R_{ij}/D_{ij} \qquad (67)$$

which is referred to as the dissymmetry factor, or anisotropy factor, of the transition. Ignoring the magnetic dipole contributions to the dipole strength of the transition, eq 67 may be reexpressed as follows:

$$g_{ij} = 4(m/\mu) \cos \theta \qquad (68)$$

where $m = |\mathbf{m}_{ji}|$ and $\mu = |\mu_{ij}|$.

In writing eq 68 we have assumed that both μ_{ij} and $\mathbf{m}_{ij}$ have unique and fixed (constant) polarization directions across the CD and absorption band profiles. This may or may not be the case depending upon the extent of vibronically induced mixings within the electronic transition $i \rightarrow j$.[65-68,96]

To exhibit optical activity it is not sufficient that a transition have nonvanishing magnetic dipole character. The transition must also have some electric dipole character, and the electric and magnetic dipole transition vectors must have a nonvanishing projection one upon the other (i.e., $\cos \theta \neq 0$). Generally it is assumed that values of $|g|$ greater than 10^{-2} indicate transitions with strong magnetic dipole character and only weak electric dipole character. This has been widely used as a criterion for establishing the inherent magnetic-dipole-allowedness of electronic transitions in chiral molecular systems and its validity has considerable empirical support. Among chiral transition metal complexes with near centrosymmetric ML_n chromophoric units, it is generally found that $|g| > 10^{-2}$ for d–d transitions which are magnetic-dipole-allowed (according to selection rules based on the symmetry of the ML_n chromophore). Values of $|g| < 10^{-3}$ are generally characteristic of magnetic-dipole-forbidden d–d transitions in these systems. For metal complexes in which the ML_n chromophoric unit deviates significantly from centric symmetry, the d–d transitions may acquire substantial *inherent* electric dipole strength and, consequently, the $|g|$ values may be $<10^{-2}$–10^{-3} even when these transitions are magnetic dipole allowed.

Although values of $|g| > 10^{-2}$ may nearly always be considered diagnostic of magnetic-dipole-allowed d–d transitions in metal complexes (no matter what the metal ion or the symmetry of the ML_n chromophore), values of $|g| < 10^{-2}$ are not necessarily reliable indicators of the magnetic-dipole-forbidden nature of transitions. The $|g|$ value of a transition may be small for reasons other than a small magnitude of the magnetic dipole transition moment (m in eq 68). Small values of $\cos \theta$ and/or large values of μ will also reduce the magnitude of g.

The use of observed g values for differentiation between magnetic-dipole-allowed and magnetic-dipole-forbidden d–d transitions has proved to be of significant value, and it appears to be valid and reliable so long as it it employed with some circumspection. There are, of course, d–d transitions in metal complexes of certain symmetry types which are rigorously forbidden in magnetic dipole radiation. For example, the ${}^1A_1({}^1A_{1g}) \rightarrow {}^1A_1({}^1T_{2g})$ transition in Co(III) complexes of D_3 symmetry is rigorously magnetic dipole forbidden and exhibits no optical activity ($g = 0$). The trigonal partner of this transition, ${}^1A_1({}^1A_{1g}) \rightarrow {}^1E({}^1T_{2g})$, is magnetic dipole allowed by D_3 selection rules, but is magnetic dipole forbidden by O_h selection rules. This latter transition exhibits only weak optical activity ($|g| < 10^{-2}$) in most trigonal dihedral Co(III) complexes, reflecting its strong octahedral parentage. The ${}^1A_1({}^1A_{1g}) \rightarrow {}^1A_2({}^1T_{1g})$ and ${}^1A_1({}^1A_{1g}) \rightarrow {}^1E({}^1T_{1g})$ transitions in D_3 Co(III) complexes are magnetic dipole allowed by both D_3 and O_h selection rules, and they generally exhibit strong optical activity ($|g| > 10^{-2}$).

The sign and splitting patterns observed within the d–d absorption region of a CD spectrum may also be used to identify and assign specific transitions. For example, nearly degenerate transitions split out of a common parent state (degenerate) of a ML_n chromophoric cluster are found quite frequently to exhibit CD bands of opposite signs and very nearly equal magnitudes (couplets). This has been used frequently to identify the components of A $\rightarrow$ E type transitions in chiral complexes of pseudotetragonal symmetry. One must be very careful in making correlations of this kind, however, except when overwhelming empirical evidence is available. The d–d optical activity models and theories can given guidance in this regard, but they are by no means sufficiently refined to yield completely reliable predictions.

VII. Single Crystal Spectra

Let us consider a sample of fixed orientation in space having uniaxial (cylindrical) macroscopic symmetry about an axis γ (also fixed in space). Let us further assume that this (macroscopic) sample is comprised of an assembly of noninteracting chromophoric units each of which is orientationally fixed. If we perform a CD experiment with radiation propagating along the γ axis of the sample, then to lowest order of the expansion of the vector potential of the radiation field the rotatory strength of an electronic transition $i \rightarrow j$ (localized on a chromophoric unit) is given by

$$\begin{aligned} R_{ij} = (3/2)\mathrm{Im}[&\langle \psi_i | \hat{\mu}_\alpha | \psi_j \rangle \langle \psi_j | \hat{m}_\alpha | \psi_i \rangle \\ &+ \langle \psi_i | \hat{\mu}_\beta | \psi_j \rangle \langle \psi_j | \hat{m}_\beta | \psi_i \rangle] \\ &- (3/4)(2\pi\nu_{ji}/c)\mathrm{Re}[\langle \psi_i | \hat{\mu}_\alpha | \psi_j \rangle \\ &\times \langle \psi_j | \hat{q}_{\beta\alpha} | \psi_i \rangle - \langle \psi_i | \hat{\mu}_\beta | \psi_j \rangle \langle \psi_j | \hat{q}_{\gamma\alpha} | \psi_i \rangle] \end{aligned} \qquad (69)$$

where $\nu_{ji} = (E_j - E_i)/h$, the indices (α,β,γ) refer to a space-fixed orthogonal coordinate system, and $\hat{q}_{\beta\gamma}$ and $\hat{q}_{\gamma\alpha}$ are, respectively, the $\beta\gamma$ and $\gamma\alpha$ components of the electric quadrupole tensor operator. If the sample is a crystal of uniaxial macroscopic symmetry, then γ must correspond to the principal (or optic) axis of the crystal. If the sample is a crystal of cubic symmetry, then the choice of γ (with respect to the crystallographic axes) is entirely arbitrary. The components of the electronic operators in eq 69 are referred to the (α,β,γ) coordinate system. Furthermore, the operators may be defined *within* the respective chromophoric units since the chromophoric units have been assumed to be noninteracting. The wave functions, ψ_i and ψ_j, correspond to *localized* chromophoric state functions and reflect the site symmetry (and dissymmetry) of the chromophoric units.

If the chromophoric units of the sample are interacting (coupled), then eq 69 must be modified to reflect excitation delocalization (exciton motion) or electron delocalization among the coupled chromophoric units. In this case the wave functions, ψ_i and ψ_j, reflect crystal (or unit cell) symmetry and correspond to crystal state functions. Furthermore, the operators in eq 69 can no longer be defined simply with respect to origins located within individual chromophoric units. The general problems attendant to treating the optical activity of crystalline samples comprised of interacting or noninteracting chromophoric subsystems have been addressed elsewhere[28,36,87,97] and will not be dealt with further here.

Two principal questions have arisen in the theoretical analyses of d–d optical activity exhibited by crystalline samples of transition metal complexes. One question regards the relative contributions of the electric dipole–magnetic dipole vs. the electric dipole–electric quadrupole terms in eq 69, and the other question regards the relative contributions of site (local) dissymmetry vs. unit cell dissymmetry to the overall, observed d–d optical activity. In their detailed theoretical treatment (formal and computational) of the d–d orbital activity exhibited by crystalline $NiSO_4 \cdot 6H_2O$[28] and crystalline $Cu^{2+}:ZnSeO_4 \cdot 6H_2O$,[30] Richardson and co-workers concluded that the electric dipole–electric quadrupole terms contributed only minimally (less than 5%) to the rotatory strengths, even for transitions which are formally electric quadrupole allowed according to cubic (O_h) selection rules. They further concluded that the d–d states in these systems could be considered localized on the MO_6 clusters and that site dissymmetry is entirely responsible for the observed optical activity. For $NiSO_4 \cdot 6H_2O$, the d–d optical activity was attributed entirely to inherent dissymmetry within the $Ni(H_2O)_6^{2+}$ unit and to the dissymmetric field created at each Ni^{2+} site by the four nearest-neighbor SO_4^{2-} anions. Similarly for $Cu^{2+}:ZnSeO_4 \cdot 6H_2O$, all of the optical activity of the Cu^{2+} d–d transitions was attributed to $Cu(H_2O)_6^{2+}$ dissymmetry (inherent) and to the four nearest-neighbor SeO_4^{2-} anions. The calculations carried out by Richardson and co-workers[28,30] were based on the static-coupling variant of the independent systems/perturbation model carried to second order, and considerable attention was given to the sensitivity of the results to parameter variations within the constraints of this model. The calculated results were in substantial agreement with experimental observation.[98-102]

Kato[36] has carried out a theoretical analysis of the d–d optical activity of a whole series of $M^{2+}:ZnSeO_4 \cdot 6H_2O$ systems (where $M^{2+} = Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}$, and Mn^{2+}). This analysis was also based on the static-coupling terms of the general independent systems/perturbation model carried to second order. Local (site) dissymmetry was found to be the dominant source of optical activity in these systems, and contributions from the electric dipole–electric quadrupole terms of eq 69 were found to be negligible.

The optical activity caused by exciton dispersion in chiral crystals has been treated formally by Kato, Tsujikawa, and Murao,[86] and crystalline $CsCuCl_3$ belonging to the optically active space group $D_6^2(P6_122)$ or $D_6^3(P6_522)$ was considered as a case where such optical activity might be observed. No calculations were reported in this study, however.

Barron[87] has proposed that the electric dipole–electric quadrupole term of eq 69 may contribute significantly to (or dominate) the optical activity of d–d transitions which are magnetic dipole forbidden (or only weakly allowed) but which are electric quadrupole allowed. He suggested that the ${}^1A_1({}^1A_{1g}) \rightarrow {}^1E({}^1T_{2g})$ transition of Co(III) in crystalline $2[(+)\text{-}Co(en)_3Cl_3] \cdot NaCl \cdot 6H_2O$ might be a case where the electric dipole–electric quadrupole contribution would dominate. Order-of-magnitude calculations and a comparison of solution vs. crystal CD intensity in the region of this transition suggest that Barron's proposal is certainly plausible. Barron further suggested that the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions in crystalline $NiSO_4 \cdot 6H_2O$ may acquire most of their optical activity via the electric dipole–electric quadrupole term in eq 69. This latter suggestion is not supported by the calculations performed by Strickland and Richardson.[28] At this point it is safe to say that the relative importance of the electric dipole–magnetic dipole vs. the electric dipole–electric quadrupole terms of eq 69 in determining the optical activity of electric-quadrupole-allowed transitions has not yet been decided for any particular case.

A great deal of experimental work has been carried out on the optical activity of metal complexes in crystalline media. Some of this work has dealt with achiral molecular units, such as $NiSO_4 \cdot 6H_2O$, in chiral crystals, and other work has dealt with chiral molecular units, such as $Co(en)_3^{3+}$ and $Co(ox)_3^{3-}$, in (necessarily) chiral crystals. A review and discussion of this experimental work lies outside the scope of this article. Suffice it to say that these studies on single crystal systems have been of great value to the development of d–d optical activity theory.

VIII. Other Topics

There are several aspects of d–d optical activity theory which will not be dealt with in this review article. These include (a) solvent-induced optical activity (achiral complex in a chiral solvent), (b) the Pfeiffer effect, and (c) optical activity induced in an achiral complex by outer-sphere association of chiral species. Theoretical studies related to these phenomena have been reported by a number of workers[76-85,103-106] over the past five years, and significant progress has been made in understanding the underlying interaction mechanisms and spectroscopic processes. The reader is especially referred to the recent series of papers authored by Schipper.[76-81,104-106] This series of papers encompasses all of the above-mentioned phenomena and represents the most comprehensive and detailed work on the related theory.

As was mentioned in the Introduction, the optical activity associated with metal ↔ ligand charge-transfer transitions and with ligand-localized transitions lies outside the scope of this review article. We have dealt only with the ligand-field (d–d) transitions localized on the metal ion chromophore. However, ligand-localized transitions entered into our independent systems/perturbation (ISP) model by providing electric dipole character to the d–d transitions via the dynamic-coupling interaction mechanism. Similarly, the metal ↔ ligand charge-transfer transitions entered into our ISP model by providing electric dipole character to the d–d transitions via the static-coupling interaction mechanism. By the ISP model, therefore, the spectroscopic properties of the d–d, metal ↔ ligand charge-transfer, and ligand-localized transitions are related (interdependent), and there is some artificiality involved in discussing their chiroptical properties separately. However, the d–d contributions to the CD spectra of metal complexes can generally be separately identified and assigned, and it remains useful to treat these contributions with only indirect reference to other types of transitions which may occur in the complexes.

Acknowledgments. This work was supported by the National Science Foundation and by a Teacher-Scholar Award from the Camille and Henry Dreyfus Foundation.

IX. References

(1) A. Cotton, *C. R. Acad. Sci.*, **120**, 989, 1044 (1895).
(2) Alfred Werner 1866–1919, *Helv. Chim. Acta*, Commemoration Volume, IXth Meeting of the ICCC, Zurich, 1966.
(3) F. M. Jaeger, "Spatial Arrangements of Atomic Systems and Optical Activity", George Fisher Baker Lectures, Vol. 7, Cornell University, McGraw-Hill, New York, 1930.
(4) J. P. Mathieu, "Les Theories Moleculaires du Pouver Rotatoire Naturel", Gauthier-Villars, Paris, 1946.
(5) W. Kuhn and K. Bein, *Z. Phys. Chem., Abt. B*, **24,** 335 (1934).
(6) W. Kuhn and K. Bein, *Z. Anorg. Allg. Chem.*, **216,** 321 (1934).
(7) W. Kuhn, *Naturwissenschaften*, **19,** 289 (1938).
(8) W. Kuhn, *Z. Phys. Chem., Abt. B*, **4,** 14 (1929).
(9) W. Kuhn, *Trans. Faraday Soc.*, **26,** 293 (1930).
(10) W. Kuhn, *Z. Phys. Chem., Abt. B*, **20,** 325 (1933).
(11) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Acta Crystallogr.*, **8,** 729 (1955).
(12) For the accepted nomenclature and notation regarding absolute configuration designations for coordination compounds, see (a) IUPAC Information Bulletin, No. 33, 68 (1968); (b) *Inorg. Chem.*, **9,** 1 (1970).
(13) W. Moffitt, *J. Chem. Phys.*, **25,** 1189 (1956).
(14) E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, **5,** 753 (1937).
(15) S. Sugano, *J. Chem. Phys.*, **33,** 1883 (1960).
(16) See, for example, Y. Saito, *Coord. Chem. Rev.*, **13,** 305 (1974).

(17) L. Rosenfeld, *Z. Phys.*, **52**, 161 (1928).
(18) (a) H. Bethe, *Ann. Phys.*, **5**, 133 (1929); (b) J. H. Van Vleck, *Phys. Rev.*, **41**, 208 (1932); (c) W. G. Penney and R. Schlapp, *ibid.*, **41**, 194 (1932).
(19) N. K. Hamer, *Mol. Phys.*, **5**, 339 (1962).
(20) H. Poulet, *J. Chim. Phys.*, **59**, 584 (1962).
(21) T. S. Piper and A. Karipedes, *Mol. Phys.*, **5**, 475 (1962).
(22) M. Shinada, *J. Phys. Soc. Jpn.*, **19**, 1607 (1964).
(23) D. J. Caldwell, *J. Phys. Chem.*, **71**, 1907 (1967).
(24) F. S. Richardson, *J. Phys. Chem.*, **75**, 692 (1971).
(25) F. S. Richardson, *J. Chem. Phys.*, **54**, 2453 (1971).
(26) F. S. Richardson, *Inorg. Chem.*, **10**, 2121 (1971).
(27) F. S. Richardson, *Inorg. Chem.*, **11**, 2366 (1972).
(28) R. W. Strickland and F. S. Richardson, *J. Chem. Phys.*, **57**, 589 (1972).
(29) S. F. Mason, *J. Chem. Soc. A*, 667 (1971).
(30) F. S. Richardson and G. Hilmes, *Mol. Phys.*, **30**, 237 (1975).
(31) G. Hilmes and F. S. Richardson, *Inorg. Chem.*, **15**, 2582 (1976).
(32) S. Sugano and M. Shinada, Abstracts, International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962.
(33) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).
(34) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).
(35) S. F. Mason in "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism", F. Ciardelli and P. Salvadori, Ed., Heyden and Son Ltd., New York, 1973, Chapter 3.6.
(36) T. Kato, *J. Phys. Soc. Jpn.*, **32**, 192 (1972).
(37) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).
(38) Th. Bürer, *Mol. Phys.*, **6**, 541 (1963).
(39) A. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).
(40) A. Liehr, *J. Phys. Chem.*, **68**, 3629 (1964).
(41) A. Karipedes and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).
(42) T. S. Piper and A. G. Karipedes, *Inorg. Chem.*, **4**, 923 (1965).
(43) R. W. Strickland and F. S. Richardson, *Inorg. Chem.*, **12**, 1025 (1973).
(44) R. S. Evans, A. F. Schreiner, and P. J. Hauser, *Inorg. Chem.*, **13**, 2185 (1974).
(45) K. Nakatsu, *Bull. Chem. Soc. Jpn.*, **35**, 382 (1962).
(46) C. Y. Yeh and F. S. Richardson, *Inorg. Chem.*, **15**, 682 (1976).
(47) G. Hilmes, C. Y. Yeh, and F. S. Richardson, *J. Phys. Chem.*, **80**, 1798 (1976).
(48) C. E. Schäffer, *Proc. R. Soc. London, Ser. A*, **297**, 96 (1968).
(49) C. E. Schäffer, *Struct. Bonding (Berlin)*, **5**, 68 (1968).
(50) C. E. Schaffer and C. K. Jorgensen, *Mol. Phys.*, **9**, 401 (1965).
(51) R. H. Seal, Ph.D. Thesis, London University, 1974.
(52) S. F. Mason and R. H. Seal, *J. Chem. Soc., Chem. Commun.*, 331 (1975).
(53) S. F. Mason and R. H. Seal, *Mol. Phys.*, **31**, 755 (1976).
(54) R. W. Strickland and F. S. Richardson, *J. Phys. Chem.*, **80**, 164 (1976).
(55) I. Tinoco, *Adv. Chem. Phys.*, **4**, 113 (1962).
(56) E. G. Höhn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).
(57) P. E. Schipper, *J. Am. Chem. Soc.*, **100**, 1433 (1978).
(58) R. G. Denning, *Chem. Commun.*, 120 (1967).
(59) F. S. Ham, *Phys. Rev. A*, **138**, 1727 (1965).
(60) D. Caliga and F. S. Richardson, *Mol. Phys.*, **28**, 1145 (1974).
(61) F. S. Richardson, D. Caliga, G. Hilmes, and J. J. Jenkins, *Mol. Phys.*, **30**, 257 (1975).
(62) F. S. Richardson, G. Hilmes, and J. J. Jenkins, *Theor. Chim. Acta*, **39**, 75 (1975).
(63) G. Hilmes, D. Caliga, and F. S. Richardson, *Chem. Phys.*, **13**, 203 (1976).
(64) M. J. Harding, *J. Chem. Soc., Faraday Trans. 2*, **68**, 234 (1972).
(65) O. E. Weigang, *J. Chem. Phys.*, **42**, 2244 (1965).
(66) O. E. Weigang, *J. Chem. Phys.*, **43**, 3609 (1965).
(67) S. E. Harnung, E. C. Ong, and O. E. Weigang, *J. Chem. Phys.*, **55**, 5711 (1971).
(68) O. E. Weigang and E. C. Ong, *Tetrahedron*, **30**, 1783 (1974).
(69) S. Kaizaki, J. Hidaka, and V. Shimura, *Inorg. Chem.*, **12**, 142 (1973).
(70) G. L. Hilmes, H. G. Brittain, and F. S. Richardson, *Inorg. Chem.*, **16**, 528 (1977).
(71) S. Kaizaki and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 3611 (1975).
(72) S. F. Mason and B. J. Peart, *J. Chem. Soc., Dalton Trans.*, 937 (1977).
(73) C. J. Ballhausen, *Mol. Phys.*, **5**, 461 (1963).
(74) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **43**, 1100 (1970).
(75) See, for example: (a) C. J. Hawkins, G. A. Lawrence, and R. M. Peachy, *Aust. J. Chem.*, **30**, 2115 (1977); (b) B. Bosnich and J. M. Harrowfield, *J. Am. Chem. Soc.*, **94**, 989 (1972); (c) B. Bosnich and J. M. Harrowfield, *ibid.*, **94**, 3425 (1972).
(76) P. E. Schipper, *J. Am. Chem. Soc.*, **98**, 7938 (1976).
(77) P. E. Schipper, *Mol. Phys.*, **29**, 1705 (1975).
(78) P. E. Schipper, *Inorg. Chim. Acta*, **14**, 161 (1975).
(79) P. E. Shipper, *Chem. Phys.*, **12**, 15 (1976).
(80) P. E. Schipper, *Chem. Phys. Lett.*, **30**, 323 (1975).
(81) P. E. Schipper, *Inorg. Chim. Acta*, **12**, 199 (1975).
(82) S. F. Mason, *Chem. Phys. Lett.*, **32**, 201 (1975).
(83) D. P. Craig, E. A. Power, and T. Thirunamachandran, *Chem. Phys. Lett.*, **27**, 149 (1974).
(84) D. P. Craig and P. J. Stiles, *Chem. Phys. Lett.*, **41**, 225 (1976).
(85) D. P. Craig, E. A. Power, and T. Thirunamachandran, *Proc. R. Soc. London, Ser. A*, **348**, 19 (1976).
(86) T. Kato, I. Tsujikawa, and T. Murao, *J. Phys. Soc. Jpn.*, **34**, 763 (1973).
(87) L. D. Barron, *Mol. Phys.*, **21**, 241 (1971).
(88) R. Englman, "The Jahn-Teller Effect in Molecules and Crystals", Wiley-Interscience, New York, 1972.
(89) T. Ito and M. Shibato, *Inorg. Chem.*, **16**, 108 (1977).
(90) S. F. Mason, *Mol. Phys.*, in press.
(91) See ref 24 and 43 for more explicit descriptions of these trigonal distortion operations.
(92) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, 1971, Chapter 3.
(93) J. A. Hearson, S. F. Mason, and R. H. Seal, *J. Chem. Soc., Dalton Trans.*, 1026 (1977).
(94) P. E. Schipper, *Chem. Phys.*, **23**, 159 (1977).
(95) P. E. Schipper, *J. Am. Chem. Soc.*, **100**, 3658 (1978).
(96) W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).
(97) See, for example: (a) C. W. Deutsche, *J. Chem. Phys.*, **53**, 1134 (1970); (b) R. Strickland and F. S. Richardson, *ibid.*, **57**, 589 (1972).
(98) P. L. Meridith and R. A. Palmer, *Chem. Commun.*, 1337 (1969).
(99) R. Grinter, M. J. Harding, and S. F. Mason, *J. Chem. Soc. A*, 667 (1970).
(100) E. C. Hsu and G. Holzwarth, *J. Chem. Phys.*, **59**, 4678 (1973).
(101) T. Kato, T. Ban, and I. Tsujikawa, *J. Phys. Soc. Jpn.*, **32**, 152 (1972).
(102) K. D. Gailey and R. A. Palmer, *Chem. Phys. Lett.*, **13**, 176 (1972).
(103) B. Norden, *Chem. Scripta*, **7**, 14 (1975).
(104) P. E. Schipper, *Inorg. Chim. Acta*, **12**, 199 (1975).
(105) P. E. Schipper, *Chem. Phys.*, **23**, 159 (1977).
(106) P. E. Schipper, *J. Am. Chem. Soc.*, **100**, 1079 (1978).