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Circular Dichroism of Charge Transfer and Magnetic Dipole Forbidden d–d Transitions. Application to Chiral Chelate Complexes

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Abstract: The circular dichroism (CD) of the charge-transfer transitions of chiral metal complexes is discussed. In tris(bidentate) complexes, it is postulated to arise from direct dipole coupling between the charge-transfer and chelate transition moments, leading to a particularly simple expression for the CD which is readily parametrized from normal absorption data. It is shown to be independent of any coupling between the chelates themselves, but depends directly on their stereochemistry. The model is also applied to the CD of magnetic dipole forbidden d–d transitions, which are postulated to gain their CD through their vibronically or spin-orbit induced electric moments coupling with those of the chelates. The implications of the results for the determination of absolute configurations and conversely for the assignment of the transitions are discussed.

Introduction

The circular dichroism (CD) of chiral metal complexes has received much attention in the literature, both as a test of CD models and as a stereochemical probe. Most attention has focused on the d–d transitions (see, e.g., reviews[1,2] and ref 3) and, in the case of chiral chelate complexes, the coupled chelate bands (e.g., the work of Mason,[4] Bosnich,[5] and references collated in Hawkins' book[1]). Little direct work on the charge-transfer CD has appeared, and it has usually attracted only passing interest in discussions of the other types of transitions.[4] This is especially surprising when it is considered that the charge-transfer (CT) transitions are usually electric dipole allowed, and that the CD mechanisms for electric dipole transitions are generally simpler than those of magnetic dipole allowed ones as encountered, for example, in d–d spectra.

The most probable reason for this is that the separable chromophore (independent systems) approach, which is the basis for most general CD models, assumes that the CD arises from the perturbation of an achiral chromophore (A) by another chromophore (B), there being negligible electron exchange (overlap) between the two. CT transitions are delocalized over both the metal ion and part of the ligand system, the latter also being the source of the chiral perturbation. Thus it is not immediately obvious whether a simple CT chromophore can be defined or not. However, as the CT occurs predominantly from the metal ion to the directly ligating atoms (or vice versa), the bulk of the oscillator strength in the normal absorption spectrum must arise from a fairly localized chromophore (metal ion + ligating atoms). With the CT chromophore chosen in such a way, two contributions to the CT CD may be isolated. The first is due to any intrinsic chirality of the chromophore, and the second, which is present whether the CT chromophore is chiral or achiral, is due to the perturbation by the chiral chelate system of the CT transition moments. These contributions are additive. Only the latter will be discussed in detail in this paper, as it leads to a strong CT CD (especially in tris(chelate) systems) which may be expected to dominate the CD in most complexes.

The other transitions which shall be considered briefly in this paper are the magnetic dipole forbidden d–d transitions, which generally exhibit a far weaker CD than the magnetic dipole allowed ones. The CD of the latter has received copious attention in the literature,[2,3] but, because of the intrinsic dependence on the magnetic dipole transition moment, is difficult to estimate or empiricize from normal absorption data. The CD of the magnetic dipole forbidden transitions, though weaker, has the distinct advantage that it is readily interpreted in terms of the model presented herein, as well as being readily parametrized from normal absorption data.

Circular Dichroism of Electric Dipole Transitions

There are two predominant mechanisms by which an electric dipole allowed transition of an achiral chromophore A (with transition moment $\boldsymbol{\mu}_\mathrm{A}$ centered at the origin of A, and corresponding transition energy ϵ_A) can become CD active through perturbation by another chromophore B (characterized by a single transition r, energy ϵ_r, and an electric transition moment $\boldsymbol{\mu}_\mathrm{B}{}^\mathrm{r}$ if B is intrinsically achiral, or transition moments $\boldsymbol{\mu}_\mathrm{B}{}^\mathrm{r}$, $\mathbf{m}_\mathrm{B}{}^\mathrm{r}$ if B is intrinsically chiral, with $\mathbf{m}_\mathrm{B}{}^\mathrm{r}$ the magnetic dipole transition moment). These arise from first-order perturbation theory (see, e.g., general expansions in ref 6), so that the CD induced at energy ϵ_A in the electric dipole allowed transition

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of A has two possible contributions:

$$R_1 = \frac{\epsilon_A \epsilon_r}{\hbar(\epsilon_r^2 - \epsilon_A^2)} V(\boldsymbol{\mu}_A, \boldsymbol{\mu}_B^r) \boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B^r \times \mathbf{r}_{BA} \qquad (1)$$

$$R_2 = \frac{-2\epsilon_A}{(\epsilon_r^2 - \epsilon_A^2)} V(\boldsymbol{\mu}_A, \boldsymbol{\mu}_B^r) \operatorname{Im}(\boldsymbol{\mu}_A \cdot \mathbf{m}_B^r) \qquad (2)$$

where

$$V(\boldsymbol{\mu}_A, \boldsymbol{\mu}_B^r) = \boldsymbol{\mu}_A \cdot (\boldsymbol{\mu}_B^r - 3[\boldsymbol{\mu}_B^r \cdot \hat{\mathbf{r}}_{BA}]\hat{\mathbf{r}}_{BA})/r_{BA}^3 = \boldsymbol{\mu}_A \cdot \overline{\boldsymbol{\mu}}_B \qquad (3)$$

$\mathbf{r}_{BA}$ is the vector from the origin of A to that of B, with the cap denoting unit vector. R_1 is the CD due to the coupling of the electric moments on A and B, and is the well-known Kuhn–Kirkwood coupled oscillator contribution.[7,8] R_2 is essentially a CD stealing term in which the transition on A steals its CD directly from that of the chromophore B (which must be intrinsically chiral for this term to be finite). It is interesting to consider the ratio of these terms to gauge their relative importance. If energies are in cm^{-1}, electric moments in eÅ, distance in Å, and magnetic moments in μ_B, the ratio becomes

$$R_1/R_2 = -1.62 \times 10^{-5}\epsilon_r \left[\frac{\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B^r \times \mathbf{r}_{BA}}{\operatorname{Im}(\boldsymbol{\mu}_A \cdot \mathbf{m}_B^r)}\right] \qquad (4)$$

The coupled oscillator contribution R_1 will dominate if the perturber has a strongly allowed electric moment skewed with respect to the moment on A. The R_2 (stealing) mechanism will only be important if the perturber has a strong magnetic transition moment (symmetry allowed) parallel to the moment on A.

Charge Transfer Circular Dichroism of Tris(bidentates)

The discussion here will be restricted to tris(bidentates) of D_3 symmetry, with the metal-ligating atom system having octahedral geometry; generalization to lower symmetries is relatively trivial. The complex is modeled as two separate chromophoric systems.

The Charge-Transfer Chromophore (A). This encompasses the metal and the directly ligating atoms. Under D_3, any electric dipole allowed transitions are either z polarized or (degenerate) x,y polarized in character. As the intrinsic chirality of the CT chromophore is neglected (and hence the magnetic transition moments of the electric dipole allowed transitions assumed to vanish), it is represented solely by the electric moments $\boldsymbol{\mu}^{CT}$ with corresponding transition energies ϵ_{CT}. The symmetry of the CT chromophore may therefore be taken to be that of the moment representation (achiral), conveniently taken to be D_{3d}. Any CT transition will thus be of A_{2u} or E_u symmetry, with the moment defined at the metal (symmetry) origin.

Perturbing Chelate Chromophore System (B). This is represented by the three independent chelate chromophores I (I = 1, 2, 3). Each chelate I is considered to have a single electronic transition moment $\boldsymbol{\mu}_I^r$ centered at some origin in the chelate (e.g., the center of mass), with transition energy ϵ_r. It is necessary to consider only one such state, the final CD results always being summed over all states. The chelate origin is connected to the metal origin by the vector $\mathbf{r}_{IM}$ (directed to the chelate).

It should be noted here that the chromophore definitions ensure that the CT chromophore includes the bulk of the metal-ligand bonding (including, for example, π bonding). Thus energies and absorption intensities will not be significantly affected by the B (chelate) system. This has the distinct advantage in that both moments and energies may be estimated empirically from the absorption spectrum.

The CD of the CT transitions in such a model can only arise through coupling between the CT transition moment and that of each of the chelates (I). Each chelate I acts independently (as any interactions between the chelates are ignored) in giving a coupled oscillator term of the form of eq 1, but, as each chelate is separately achiral, all contributions of the form of eq 2 will vanish. Thus the CD strength of a particular CT transition due to a particular chelate I has the form

$$R_I^{CT} = C_\epsilon^{CT} V(\boldsymbol{\mu}^{CT}, \boldsymbol{\mu}_I^r) \boldsymbol{\mu}^{CT} \cdot \boldsymbol{\mu}_I^r \times \mathbf{r}_{MI} \qquad (5)$$

where

$$C_\epsilon^{CT} = \frac{\epsilon_{CT}\epsilon_r}{\hbar(\epsilon_r^2 - \epsilon_{CT}^2)} \qquad (6)$$

with other quantities defined as for eq 1.

Simplification of this expression proceeds through exploiting the generalized selection rules developed elsewhere by this author.[9] This formulation of selection rules reduces any perturbation term to the simplest possible analytic expression under the particular symmetry of the chromophores involved. Under D_{3d}, the CT chromophore moment products $\mu^{CT}(\alpha)\mu^{CT}(\beta)$ (where the argument α denotes the αth Cartesian component of that particular moment) appearing in the expanded form of eq 5 may be replaced by $P^0[\mu^{CT}(\alpha)\mu^{CT}(\beta)]$ where P^0 is the totally symmetric projection operator defined as

$$P^0 = \frac{1}{h}\sum_{\xi=1}^{h} R_\xi$$

The R_ξ ($\xi = 1, \ldots, h$) are the symmetry operations of the group D_{3d} in this case. Noting that

$$P^0[\mu^{CT}(\alpha)\mu^{CT}(\beta)] = 0 \quad \alpha \neq \beta$$

and

$$P^0[\mu^{CT}(z)]^2 = [\mu^{CT}(z)]^2 = |\boldsymbol{\mu}^A|^2$$

$$P^0[\mu^{CT}(x)]^2 = P^0[\mu^{CT}(y)]^2 = \frac{1}{2}\{[\mu^{CT}(x)]^2 + [\mu^{CT}(y)]^2\} = |\boldsymbol{\mu}^E|^2 \qquad (7)$$

it follows that the CD strength separates conveniently into two contributions, one (R_I^A) for z-polarized CT transitions (symmetry A_{2u}, $\boldsymbol{\mu}^{CT} \equiv \boldsymbol{\mu}^A$) and one ($R_I^E$) for x,y-polarized CT transitions (symmetry E_u, $\boldsymbol{\mu}^{CT} \equiv \boldsymbol{\mu}^E$), of the form

$$R_I^A = C_\epsilon^A |\boldsymbol{\mu}^A|^2 [\bar{\mu}_I^r(z)\mu_I^r(x) r_{MI}(y) - \bar{\mu}_I^r(z)\mu_I^r(y) r_{MI}(x)] \qquad (8)$$

$$R_I^E = \frac{1}{2} C_\epsilon^E |\boldsymbol{\mu}^E|^2 [\bar{\mu}_I^r(y)\mu_I^r(z) r_{MI}(x) - \bar{\mu}_I^r(x)\mu_I^r(z) r_{MI}(y)] \qquad (9)$$

If the chelate moment is short axis polarized, it will be perpendicular to $\boldsymbol{\mu}^A$ and coplanar with $\boldsymbol{\mu}^E$; these are precisely the conditions for which coupled-oscillator terms vanish. This is consistent with the previous equation, as then $\bar{\mu}_I(z) = \mu_I(z) = 0$. Long and perpendicular axis polarized transitions of the chelate, however, each yield a nonvanishing contribution to the CT CD strength. Summation over the I and substitution for the geometrical factors for the D configuration (assuming that the metal-ligating atom geometry is octahedral) leads to the overall CD strengths

$$R^A = \frac{2\epsilon_A}{(\epsilon_r^2 - \epsilon_A^2)} \frac{|\boldsymbol{\mu}^A|^2}{r_{ML}^3} R_B^A(r) \qquad (10)$$

$$R^E = \frac{\epsilon_E}{(\epsilon_r^2 - \epsilon_E^2)} \frac{|\boldsymbol{\mu}^E|^2}{r_{ML}^3} R_B^E(r) \qquad (11)$$

where

$$-R_B^A(r) = R_B^E(r) = \pm\frac{\epsilon_r}{\sqrt{2}\hbar} r_{ML} |\boldsymbol{\mu}_L^r|^2 \qquad (12)$$

with the upper (+) sign for long axis and the lower (−) for

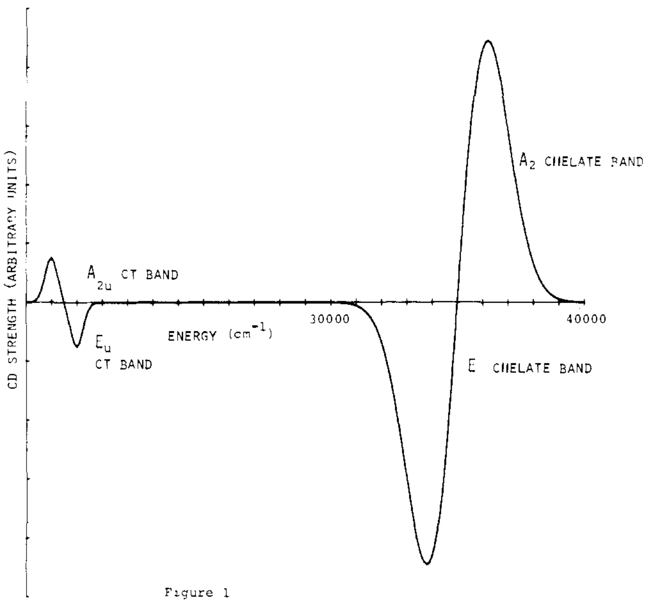

Figure 1. Diagrammatic form of the calculated CD strengths for the values discussed in the text. Note the apparent exciton shape of the CT bands. The signs are for a complex with long axis polarized chelate bands and with Λ configuration.

perpendicular axis polarized chelate transitions. The subscript L refers to any particular chelate I, and has been used simply to stress that the result has been summed over the entire chelate system. The expressions have been written in the form of eq 10 and 11 because the quantities defined in eq 12 are, in fact, the CD strengths of the chelate system itself, as derived from the exciton modification of the Kirkwood-Kuhn mechanism for degenerate transitions by Moffitt[10] and applied to tris chelates by Mason.[4] It is interesting to note that the coupled-oscillator terms *collectively* act much like the CD stealing mechanism of eq 2, and the CT transition of a given polarization simply steals its CD from the chelate band of the same symmetry. The results are totally independent of the so-called exciton splitting of the chelate bands.

A feeling for the magnitude of the CT CD may be obtained from considering the ratio of the CT CD to that of the chelate band of the same symmetry. With the units as defined for eq 4, these ratios become

$$\Delta^{A} = R^{A}/R_{B}^{A}(r) = 2K\frac{\epsilon_{A}}{(\epsilon_{r}^{2} - \epsilon_{A}^{2})}\frac{|\mu^{A}|^{2}}{r_{ML}^{3}} \quad (13)$$

$$\Delta^{E} = R^{E}/R_{B}^{E}(r) = K\frac{\epsilon_{E}}{(\epsilon_{r}^{2} - \epsilon_{E}^{2})}\frac{|\mu^{E}|^{2}}{r_{ML}^{3}} \quad (14)$$

with $K = 1.16 \times 10^5$. For realistic values of $r_{ML} = 3$ Å, $\epsilon_r = 35\,000$ cm^{-1}, $\epsilon_A \simeq \epsilon_E = 20\,000$ cm^{-1}, the ratios are

$$\Delta^{A} \simeq 0.6|\mu^{A}|^2 \qquad \Delta^{E} \simeq 0.3|\mu^{E}|^2$$

These values are typical of, say, Fe(bpy)$_3{}^{2+}$. For CT moments of the order of about 0.5 eÅ, the CT CD is about 15% of that of the chelate bands. This is in good agreement with the observed bands, whose polarizations have been determined by linear dichroism techniques.[11] The agreement in both sign and magnitude is not restricted to this isolated example (see, e.g., spectra in ref 4).

It is worth noting that, whenever there are two CT states, one of A_{2u} and one E_u symmetry, close together energetically, the resultant CT CD spectrum will mimic the exciton shape characteristic of the chelate band. Mason has cited the exciton type shape of the CT bands as supporting an intrinsically chiral CT chromophore,[4] but it is obvious from the earlier expressions that this is by no means necessarily the case. The spectrum calculated for the typical values discussed above is illustrated (diagrammatically) in Figure 1 for the particular case for which $|\mu^E|^2/|\mu^A|^2 = 2$. This choice is not fundamental, as it is, in fact, inherent in the definition of the chromophore that these two moments are not symmetry related, and the ratio is determined empirically. Thus there is no symmetry reason for the CT CD to appear as a conservative positive-negative couplet, a feature which occurs only for the particular ratio used above.

The interesting feature of the examples cited above is that the CT CD for such complexes have been ascribed solely to contributions from the intrinsic chirality of the CT chromophore. Mason[4] has attempted to estimate this contribution using the following model. The CT transition is assumed to arise from the coupling of separate contributions from a predominantly metal d state ψ_M to chelate states ψ_I (I = 1, 2, 3). Each such contribution is represented by a moment of the form $\mu_I = \langle\psi_M|\mu|\psi_I\rangle$ with an origin centered somewhere between the metal and the chelate I. The CD is then taken to originate in a degenerate coupling of the μ_I moments in a manner analogous to that used for determining the chelate CD, leading to exciton-type CT bands.

Such an approach is pictorially simple, but difficult to justify quantum mechanically when one considers that the coupled-oscillator approach (for degenerate or nondegenerate moments) explicitly assumes that each moment is on a separate chromophore. Considering that the same metal state (ψ_M) is involved in the definition of all three moments μ_I, the assumption that each moment arises from a different chromophore with negligible mutual electron overlap is unjustified.

The contribution from any intrinsic chirality should be estimated by explicit evaluation of the electric and magnetic transition moments at the metal origin for a suitable choice of wave functions, i.e., between the metal state ψ_M and some suitable linear combination of the ψ_I. Only one origin should be defined for each chromophore. It appears from this work, however, that the coupling of the electric transition moments of the CT chromophore to that of the chelate system is sufficiently strong to dominate the CT CD, and that the contributions from any intrinsic chirality are generally negligible (provided, of course, that the chirality does not arise from the identity of the ligating atoms).

Circular Dichroism of Magnetic Dipole Forbidden d-d Transitions

Magnetic dipole forbidden d-d transitions may also be characterized solely through their weak electric transition moments $\Delta\mu^{dd}$ (defined at the metal origin) arising through such mechanisms as vibronic or spin-orbit coupling. This moment and the corresponding transition energy ϵ_{dd} may be obtained directly from the absorption spectrum, so that the details of the mechanism through which the intensity derives are immaterial. The CD of such a transition will arise in a way analogous to that of the CT transitions. As $\Delta\mu^{dd}$ is either z or x,y polarized, the CD has the same form as eq 10 and 11 where the ϵ_A, ϵ_E, R^A, and R^E now correspond to the transition energies and CD strengths of the d-d transition of the appropriate polarization, and $\mu^A \equiv \Delta\mu^{dd}$ (if z polarized), $\mu^E \equiv \Delta\mu^{dd}$ (if x,y polarized). Again the CD is stolen directly from the chelate CD. Neglecting the energy factors, the approximate ratio of the d-d CD to that of the CT band of the same polarization is equal to

$$|\Delta\mu^{dd}|^2/|\mu^{CT}|^2$$

The magnitude of the effect predicted by the above model is in good agreement with the observed bands, and should provide a simple method for assigning such d-d transitions.

The validity of the direct substitution for $\Delta\mu^{dd}$ into the first-order perturbation expression for the CD of electric dipole allowed transitions is readily verified using, for example, a simple vibronic coupling model. The procedure is analogous to that discussed elsewhere for vibronic contributions to DICD (dispersion-induced CD).[12] As the induced moment is itself first order in vibronic coupling, the CD strength is effectively third order overall (substitution of the square of the induced moment into a first-order CD term), and will thus be roughly about three orders of magnitude smaller than the chelate CD.

This contribution will also arise for magnetic dipole allowed d-d transitions, but it is then swamped by an effectively second-order term involving the magnetic transition moment.[3]

Applications

It follows from the previous theory that the signs of the CD of the chelate bands, and hence that of the CT bands, are direct indicators of the absolute configuration of the complex, provided that the polarizations of the bands are determined by some independent technique. The lower intensity and energy of the CT transitions make polarization data as determined from oriented crystal spectra more accessible than direct studies of the chelate bands. In addition, with the increasing development of linear dichroism (LD) techniques,[11] CT spectra may be assigned for certain tris bidentates (e.g., using flow orienting techniques for the complex bound to DNA). Such an approach in which all the quantities appearing in the CD expression may be determined by independent techniques should give considerably more reliable stereochemical correlations than alternative approaches involving, for example, energy splitting calculations of chelate bands[4] for systems exhibiting clear CT spectra. Conversely, of course, if the absolute configuration is known, the CT CD may be used to assign the CT transitions.

Similar applications may be envisaged for the CD of the magnetic dipole forbidden transitions, especially considering that polarization data for such transitions from solid-state studies are generally easily accessible. It is somewhat paradoxical that these transitions may ultimately give a more direct approach to assignment of absolute configuration than the intensively studied magnetic dipole allowed transitions. Of broader spectroscopic interest, however, is that the polarization and hence symmetry assignment of magnetic dipole forbidden transitions for complexes in which the absolute configuration is known follow readily from the sign of the CD.

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Vibrational Circular Dichroism in Amino Acids and Peptides.[1] 3. Solution- and Solid-Phase Spectra of Alanine and Serine

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Abstract: Vibrational circular dichroism (VCD) in solution and solid phases is reported for alanine and serine in vibrational modes involving hydrogen and deuterium stretching motions. The quality of the solution-phase VCD spectra was significantly enhanced by on-line computer averaging techniques. Solid-phase spectra were obtained as mulls in halocarbon oil and this method promises to be a useful new sampling technique in VCD spectroscopy. VCD signals in the solid phase are considerably larger than the solution spectra for the same molecules. The increased magnitude is attributed to such effects as conformational uniformity, local ordering, and crystal lattice interactions between molecules. A new vibrational assignment of solution-phase alanine in the carbon-hydrogen stretching region is presented as determined from the solid-phase Raman spectra of alanine-d_0 and alanine-C^*-d_1. The basic features of the observed VCD spectra of alanine and serine are discussed in terms of their constituent normal modes and the chiral perturbation of locally symmetric groups.

I. Introduction

Over the past few years, vibrational circular dichroism (VCD) and Raman optical activity (ROA) have been observed in a variety of optically active compounds,[3] and recent results of these studies suggest a unique sensitivity of these techniques to the elucidation of molecular stereochemistry.[4-6] In order to obtain results which can be interpreted in terms of empirical correlations, and in order to test existing models of the origin of VCD intensities, we have studied the vibrational circular dichroism of a number of amino acids and simple peptides. We have already reported results of our studies on alanine[6a] and some alanylpeptides;[6d] this series of molecules was of particular interest for the following reasons. First, alanine is one of the smallest molecules for which VCD has been observed and the small size allows a reasonably detailed vibrational analysis which in turn facilitates the interpretation of the observed spectral features. Second, this series allows comparison of the spectra of a parent molecule with the spectra of a number of derivatives,[6d] leading to the conclusion that VCD is, indeed, very sensitive to small changes in molecular structure and stereochemistry.

We have since obtained VCD spectra of a number of amino acids, among them valine, proline, arginine, and serine. We

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