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Use of Dispersion-Induced Circular Dichroism (DICD) in Spectroscopic Assignment: Applications to Copper(II) Complexes

Pieter E. Schipper

Contribution from the Department of Theoretical Chemistry, University of Sydney, N.S.W. 2006, Australia.

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Abstract: A new spectroscopic method (DICD) is discussed which permits the direct observation of electronic transitions which are either magnetic or electric dipole allowed. The method is furthermore capable of discriminating between these two types of excitations. The importance of this in the assignment of magnetic dipole transitions is discussed, especially with regard to the d–d excitations of transition metal complexes. The method involves the measurement of the CD spectrum of the (achiral) complex in solution with some nonassociating chiral solute or in a chiral solvent. Application of the method to the assignment of the d–d transitions of Cu(II) complexes is discussed.

1. Introduction

Intensities of absorption lines in conventional absorption spectroscopy are determined almost exclusively by the electric dipole transition moments of the observed transitions and are therefore direct functions of the electric dipole selection rules. Intensity measurements are thus useful for making spectral assignments. Even transitions which are to first-order electric dipole forbidden usually appear in absorption through some mechanism such as vibronic coupling, whereby a small effective electric dipole transition moment is induced through mixing with other electronic states. Intensity contributions from magnetic dipole transition moments are generally swamped even by the contributions of relatively small vibronically-induced electric moments. It is for this reason that magnetic dipole selection rules are of little use in assigning direct absorption bands.

There are numerous systems where a mechanism for measuring the magnetic transition moments would yield valuable information for spectral assignments. Consider, for example, the d–d transitions of metal complexes. These are invariably electric dipole forbidden to first order, but many of them are magnetic dipole allowed. It therefore seems somewhat incongruous to use absorption intensity measurements based on electric dipole transition moments for their assignment.

Is there then some mechanism available for estimating magnetic transition moments? The answer lies in CD techniques. CD measurements depend directly on magnetic transition moments, but are unfortunately restricted to chiral species. MCD has extended CD techniques to the study of achiral molecules, especially in the solid state. This has proved a useful tool in studying degeneracies, but again terms depending on magnetic transition moments are usually swamped by electric dipole terms. Recent theoretical studies[2,3] have, however, led to the development of a new technique which, like MCD, extends CD techniques to the study of achiral complexes, but depends directly on the magnetic transition moment. Referred to as DICD (dispersion-induced circular dichroism), the resultant CD spectrum has measurable peaks only if the transition is *either* electric *or* magnetic dipole allowed. Unlike the direct absorption spectrum, d–d transitions which are magnetic dipole allowed appear through the magnetic dipole contribution, any electric dipole contributions from the small vibronically-induced electric moments being negligible. Electric contributions to DICD arise only when the transition is electric dipole allowed in first order.

DICD is the circular dichroism induced at transition frequencies of achiral species due to the long-range dispersive interactions with other chiral species (all species being orientationally uncorrelated). The effect was first noted in a number of experimental papers,[4,5] and has since been put on a sound theoretical basis.[2,3] It is probably fair to say that the DICD of inorganic complexes is at present further advanced theoretically than it is experimentally. It is the purpose of this paper to encourage narrowing the gap by illustrating the utility of the DICD effect in potentially assigning magnetic dipole transitions. Note that in DICD, the chiral species effectively acts as a source of a chiral electric field which acts on the achiral species. This may be compared with MCD, where a chiral magnetic field is used.

The DICD of the Cu(II) ion is looked at in detail for a number of reasons. The assignment of the d–d transitions for a number of Cu(II) complexes is still uncertain, so that this system poses a challenge to the new technique; Cu(II) complexes have a range of stereochemistries,[7] so that the DICD symmetry rules may be put to the test for a range of molecular symmetries; the d^9 configuration (for which electron repulsion/correlation effects are minimal) leads to a relatively simple energy level scheme (although the general DICD results are as easily applied to more complex electronic systems); and finally, it is one of the few ions whose induced CD has been studied for a few complexes over a wide range of energies in chiral solvents.[8]

Before discussing the theory and applications in some detail, it is important to define the main limitation of the theory and put it into perspective. The DICD theory developed in previous papers assumes that the achiral (A) and chiral (C) species have no orientational correlation; this allows the expressions for induced CD to be averaged (integrated) over all orientations, each orientation assumed equally probable. The reason for this is twofold. It leads to a general result for any A,C pair, independent of their spatial structures, and it yields mathematical expressions for DICD that are both simple to apply in practice and equally simple to comprehend. The range of validity of this assumption may be extended somewhat in the following way. As the DICD is the result of an idealized point chromophore on A interacting with a point chromophore on C, it may still be possible for the chromophores to have sufficient relative orientational freedom to allow the averaged expression to be used even when A and C are associated, provided the sites of association in A and C are sufficiently removed from the chromophores and are not rigidly connected to them. Other possibilities for which the averaged expression is applicable occur when A is surrounded by a large number of C of different orientations or when there are a number of differently oriented A/C pairs in solution. Averaging over molecules or orientations then leads to essentially the same result. A good example of this is the achiral solute/chiral solvent system. Thermodynamic studies of such systems have shown that the DICD has a radial dependence agreeing with that predicted by the completely averaged expression[9] (i.e., as $1/r^6$, where r is the separation of A and C chromophores). There can be little doubt here that the solute and solvent are in relatively intimate contact.

The paper is divided into two main parts. The first summarizes the theoretical basis of DICD and discusses the symmetry rules and the principle of noninteracting configurations that are so important in applying the theory. The second part looks at the spectroscopy of Cu(II) complexes in a general way and predicts in detail the DICD bands expected for complexes of various stereochemistries. These predictions are compared with recent experimental results and the DICD spectrum tentatively assigned.

2. DICD Theory

The theory of DICD for the purely electronic case has been fully developed elsewhere[2,3] and only the pertinent results will be summarized here. The extensions to the vibronic case,[10] although of primary importance for systems with intense vibronic bands, are not important for d–d transitions and will not be considered in detail here.

The free molecule states of A may be written as $|A^i\rangle$ (i = 0, 1, . . .), with corresponding energies ϵ_i relative to the ground state (i = 0), and the states of C as $|C^j\rangle$ with energies ϵ_j'. The averaged rotatory strength (equal to the area under the DICD curve) for the transition $|A^0\rangle \rightarrow |A^s\rangle$ of A (henceforth referred to as the s transition) may then be shown to be

$$R_A(\mathrm{s}) = R_m(\mathrm{s}) + R_e(\mathrm{s})$$

where

$$R_m(\mathrm{s}) = \Omega_m(\mathrm{s,t})\Lambda_m(\mathrm{u,v})\lambda_m(\epsilon_s,\epsilon_t)$$

$$R_e(\mathrm{s}) = \Omega_e(\mathrm{s})\Lambda_e(\mathrm{u})\gamma_e(\epsilon_s)$$

The quantities

$$\Omega_m(\mathrm{s,t}) = \mathrm{Im}(\boldsymbol{\mu}_A{}^{0t} \times \boldsymbol{\mu}_A{}^{ts} \cdot \mathbf{m}_A{}^{s0})$$

$$\Omega_e(\mathrm{s}) = (\boldsymbol{\mu}_A{}^{0s} \cdot \boldsymbol{\mu}_A{}^{s0})$$

are the *magnetic* and *electric inducibilities* of A, respectively, for the s transition, and

$$\Lambda_m(\mathrm{u,v}) = (\boldsymbol{\mu}_C{}^{0u} \times \boldsymbol{\mu}_C{}^{uv} \cdot \boldsymbol{\mu}_C{}^{v0})$$

$$\Lambda_e(\mathrm{u}) = \mathrm{Im}(\boldsymbol{\mu}_C{}^{0u} \cdot \boldsymbol{\mu}_C{}^{u0}\, \boldsymbol{\mu}_C{}^{0u} \cdot \mathbf{m}_C{}^{u0})$$

are the *magnetic* and *electric inducing powers* of C. The transition moments are defined in terms of point electric ($\boldsymbol{\mu}$) and magnetic (**m**) dipole operators centered on the chromophores of A and C, such that $\boldsymbol{\mu}_A{}^{st} = \langle A^s|\boldsymbol{\mu}_A|A^t\rangle$. The energy factors are defined as

$$\lambda_m(\epsilon_s,\epsilon_t) = -1/18r_{AC}{}^6\Delta\epsilon(\epsilon_t + \epsilon_v' - \epsilon_s)$$

$$\gamma_e(\epsilon_s) = 2/9r_{AC}{}^6\Delta\epsilon^2$$

where it has been assumed for convenience that $\Delta\epsilon = (\epsilon_u' - \epsilon_s) \ll \epsilon_s$ and that $\epsilon_v > \epsilon_u'$. The exact expressions are given elsewhere.[2,10] The quantity r_{AC} is the effective separation of the chromophores on A and C.

The expression is simple both mathematically and physically. The dispersion-induced rotatory strength factors conveniently, so that the inducibilities are simply intrinsic properties of A and the inducing powers are intrinsic properties of C. The contributions R_m(s) and R_e(s) also correspond to different induction mechanisms. These will be discussed in turn. It should be noted in passing that our main interest is in the properties of A, and hence in the inducibility. The factors governing the inducing powers will be returned to later.

Magnetic Inducibility. The magnetic contribution R_m(s) is the induced activity of A if the transition is *magnetic dipole allowed.* From the expression for the magnetic inducibility Ω_m(s,t), this contribution depends on the presence of a state $|A^t\rangle$ (called the intermediate state) such that the transitions $|A^0\rangle \rightarrow |A^t\rangle$ and $|A^s\rangle \rightarrow |A^t\rangle$ are both electric dipole allowed. It vanishes if any two of the transition moments between $|A^0\rangle$, $|A^s\rangle$, and $|A^t\rangle$ in the expression for Ω_m(s,t) are collinear. Some features of this mechanism that will prove important in applications are: (i) the sign of R_m(s) bears no relation to that of the natural CD of the chiral species and may be positive or negative; (ii) it requires the existence of a strongly electric dipole allowed intermediate state; (iii) it is proportional to $1/\Delta\epsilon$; (iv) it is proportional to the magnetic inducing power of the chiral species.

Electric Inducibility. If the s transition is *electric dipole allowed,* only an electric inducibility contribution R_e(s) will appear. From the expression for R_e(s), this mechanism: (i) leads to DICD bands of the same sign as that of the natural CD associated with the inducing transition of the chiral species; (ii) is proportional to the intensity of the s transition in the normal absorption spectrum; (iii) is proportional to $1/\Delta\epsilon^2$; (iv) is proportional to the electric inducing power of the chiral species.

These differences between the two mechanisms are vitally important in determining the nature of a particular DICD band.

The expressions given earlier in this section are strictly for transitions that are either electric or magnetic dipole allowed. As is well known, however, mechanisms such as vibronic and spin–orbit coupling may give finite transition moments to otherwise forbidden transitions. The theory of the DICD of vibronic states[10] suggests that the DICD of such states may be evaluated using the purely electronic expressions, but substituting the vibronic (or spin–orbit) induced moments for $\boldsymbol{\mu}_A{}^{s0}$ or $\mathbf{m}_A{}^{s0}$. It has been suggested[10] on the basis of experimental evidence[11] that such vibronic contributions are only significant if the corresponding band in absorption has intensities comparable to those of electric dipole allowed transitions. For transition metal complexes, the vibronically-induced DICD terms for d–d transitions should be neglibible in most cases.

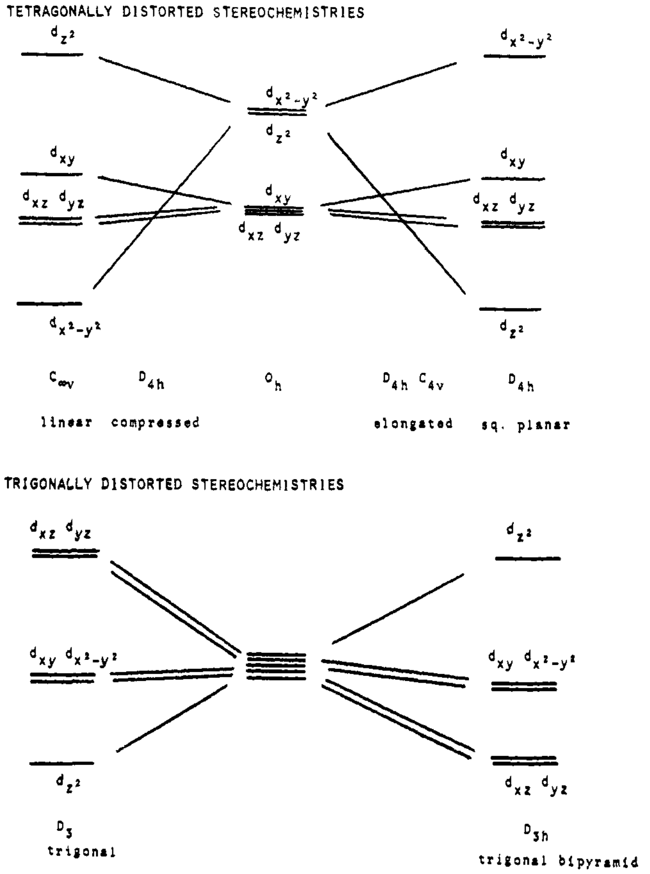

Figure 1. Energy level diagrams for various stereochemistries.

3. Symmetry Rules and Noninteracting Configurations

The expressions for the inducibilities of A contain matrix elements of the dipole operators μ and $\mathbf{m}$, which can only connect states of certain symmetry. In addition, the expression for the magnetic inducibility has the vector product form $\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}$, which vanishes if any two of the vectors are collinear, further restricting the symmetries of the states that can give finite magnetic inducibilities. These conditions may be collected to give symmetry rules, which determine the possible combinations of $|A^0\rangle$, $|A^s\rangle$, and $|A^t\rangle$ that can give finite DICD in the s transition. The symmetry rules for the electric inducibility are simply that the s transition be electric dipole allowed, and thus are equivalent to the selection rules of absorption spectroscopy. Those for the magnetic inducibility are more complex and have been discussed in detail elsewhere.[3] The results may be summarized by listing all DICD-active combinations for each achiral point group. The tables for selected point groups to be used later appear in the Appendix.

Certain intermediate states $|A^t\rangle$ allowed by symmetry as intermediates for DICD of a particular s transition may still yield vanishing matrix elements, and hence a vanishing magnetic inducibility. These may be referred to as noninteracting configurations. Consider the ground state $|A^0\rangle$ written as a single determinant in the usual way:[12]

$$|A^0\rangle = \frac{1}{\sqrt{N!}} \sum_{\nu=1}^{N} (-1)^\nu P_\nu \{\phi(a_1|1)\phi(a_2|2)\ldots\}$$

where $\phi(a_k|k)$ is a spin orbital indexed by a_k and occupied by an electron labeled by k. N is the total number of electrons and P_ν permutes the electron labels among themselves, ν being the ordinal number of the permutation. An excited state of the system in this case can be approximated by the single determinant

$$|A^r\rangle = \frac{1}{\sqrt{N!}} \sum_{\mu=1}^{N} (-1)^\mu P_\mu \{\phi(a_1'|1)\ldots\}$$

Then, for a one-electron operator

$$U = \sum_k U_k$$

where k is summed over the N electrons, the matrix element $\langle A^0|U|A^r\rangle$ vanishes if any two or more of the $\phi(a)$ are different from the $\phi(a')$ [after as much ordering as possible has been carried out]. The generalization of this well-known rule to the matrix elements in the expression for the magnetic inducibility (the condition applies to each matrix element independently) leads to the following restrictions on the possible configurations $|A^t\rangle$. Let the s transition correspond to the one-electron excitation from the orbital indexed by a_i to that indexed by a_j (viz., $a_i \rightarrow a_j$), and $|A^0\rangle \rightarrow |A^t\rangle$ to the transition $a_k \rightarrow a_l$. The only possible interacting configurations $|A^t\rangle$ will be those for which

$$a_k = a_i \text{ or } a_l = a_j$$

The above derivation is for the simple case where the excited configurations may be represented by single determinants. If configuration interaction is important, so that $|A^s\rangle$ and $|A^t\rangle$ are linear combinations of singly excited configurations $|A^x\rangle$ and $|A^y\rangle$, respectively, viz.

$$|A^s\rangle = \sum_x |A^x\rangle, \; |A^t\rangle = \sum_y |A^y\rangle$$

then extension of the above leads simply to the condition that $|A^t\rangle$ is a noninteracting configuration if *all* the configurations $|A^y\rangle$ are noninteracting relative to *each* $|A^x\rangle$. Application of the rules in such cases requires some knowledge of the wave functions and would need to be looked at separately for each case in which the single determinant approximation is inadequate.

These noninteracting configuration rules are thus important in determining the possible intermediate states for the magnetic induction mechanism.

4. Energy Levels of the Cu(II) Ion

d-Electron Spectra. The $3d^9$ outer electron configuration of the Cu(II) ion may be thought of as a positive hole in an otherwise d^{10} configuration. Lack of extensive configuration interaction (electron repulsions being minimal in such an effectively inverted d^1 system) leads to simple crystal-field models being adequate for setting up energy-level diagrams for a range of stereochemistries. The d^9 configuration also lacks cubic symmetry and thus leads to distorted forms of the basic stereochemistries,[7] so that the Cu(II) ion is reluctant to take up a regular octahedral or tetrahedral stereochemistry. For example, under O_h symmetry, the degenerate ground state (with the unpaired electron in either the $d_{x^2-y^2}$ or d_{z^2} orbitals) undergoes a Jahn–Teller distortion via an e_g vibration. This can lead to either an expanded tetragonal octahedral structure (i.e., the z ligands move outwards) if the lone electron is in the $d_{x^2-y^2}$ orbital [of which the four-coordinated square-planar structure is the limit], or a compressed structure (ligands in the xy plane move inwards) if the lone electron is in the d_{z^2} orbital. The elongated structures are generally energetically more favorable. Further distortions of both types may also occur for other reasons (e.g., σ-bond square-planar complexes need the stabilization of "semi-coordinated" z ligands). Steric factors can also play a role in favoring either structure. Chelation in the equatorial plane, however, has little effect.[7] Structural factors may also lead to five-coordinated structures such as trigonal bipyramidal or square-based pyramidal, especially the latter.

The crystal-field energy levels for these various stereochemistries are summarized in Figure 1. Note that although the simple crystal-field picture is generally capable of giving the ground state (i.e., specifying the highest singly occupied orbital), the relative ordering of the other occupied orbitals may vary considerably. The following qualitative diagrams will, however, be sufficient for the purposes of this discussion. One important point[6] that has led to copious confusion in papers on Cu(II) spectra is the different Cartesian notation for D_{4h} and D_{2h} complexes. The axis system used for the d-orbital classification under O_h and D_{4h} symmetry is the same as the Cartesian system used for the point-group character tables. This is not so for D_{2h}, where the point-group axes pass between and not through the ligating atoms (the z axis being the same). In this paper, this confusion will be avoided by using unprimed axes (xyz) to refer to the O_h system (x,y passing through the ligand atoms) and primed coordinates ($x'y'z$) to refer to the D_{2h} character table system (with the x,y axes passing between the ligand atoms). Thus, for example, the $d_{x^2-y^2}$ ground state under D_{4h} becomes $d_{x'y'}$ under D_{2h}.

In each case, electron jumps are possible from any of the lower, doubly occupied levels to the singly occupied topmost (ground-state) level. Such transitions will be written as actual electron jumps: e.g., $d_{z^2} \rightarrow d_{x^2-y^2}$. Note, however, as the hole transition is the reverse of this, and the symmetry of the states essentially follow that of the hole, the transition above becomes $B_{1g} \rightarrow B_{2g}$ in symmetry notation.

Charge-Transfer Spectra. In addition to the d-d spectra, charge-transfer transitions involving the ligand orbitals are a feature of transition metal spectra.[13] In this case, an electron jumps from an essentially metal orbital to one localized largely on the ligand, or vice versa. Ligand to metal charge transfer is most common, yielding very intense electric dipole allowed bands. It may be expected that in the elongated tetragonal octahedral complexes, little contribution to the charge-transfer spectrum would come from axial ligation, though the reverse would apply for the rarer compressed complexes. Metal to ligand charge transfer is favored by unsaturated and aromatic ligands. The nature of these bands depends strongly on the nature of the ligands and thus must be considered separately for each individual case.

In-Ligand Transitions. Transitions occurring within the ligands themselves may appear in the spectrum if such bands are of sufficiently low energy. For example, $\pi \rightarrow \pi^*$ transitions of unsaturated ligands may appear as very intense high-energy bands in some complexes.[14]

5. DICD of Cu(II) Complexes

The three different types of transitions in metal complexes discussed in the previous section differ both in intensity and energy in the absorption spectrum, allowing some unraveling of the experimental spectrum. As will be shown in this section, the DICD of these three types of transitions is also quite different. We treat each of these in turn.

DICD of the d-d System. As discussed previously, d-d transitions can only appear in absorption through such mechanisms as vibronic coupling. MCD bands appear through an analogous mechanism. This induced electric moment is sufficiently small, however, to lead to a negligible electric inducibility. It follows that DICD for these transitions appear through the magnetic induction mechanism, depending directly on the magnetic transition moment.

For a given d-d transition $|A^0\rangle \rightarrow |A^s\rangle$, the symmetry rules and conditions for noninteracting configurations lead to three general conditions for the s transition to be DICD active through the magnetic mechanism. (i) The s transition must be magnetic dipole allowed. (ii) The symmetry of the intermediate state $|A^t\rangle$ must be such that the symmetry rules are satisfied. This includes the condition that the transitions $|A^0\rangle \rightarrow |A^t\rangle$ and $|A^s\rangle \rightarrow |A^t\rangle$ both be electric dipole allowed. It follows that $|A^t\rangle$ must be ungerade and either (a) a charge transfer state or (b) an electric dipole allowed in-ligand state. Any vibronically-induced d-d electric moments will be far too weak to act as intermediates. (iii) The configuration $|A^t\rangle$ must be an interacting configuration with respect to $|A^0\rangle$ and $|A^s\rangle$. In terms of the notation used previously, a_i and a_j must index pure d states; it follows that the transition $|A^0\rangle \rightarrow |A^t\rangle$ (or $a_k \rightarrow a_l$) must satisfy

$$\textit{either } a_k = a_i \textit{ or } a_l = a_j$$

i.e., either a_k or a_l must also correspond to a pure d state. This corresponds to two different physical situations: (a) $a_k = a_i$: this describes a d electron in the metal being excited to a ligand state and hence a metal → ligand charge transfer; (b) $a_l = a_j$: in this case, the ligand state is occupied in the ground state, leading to ligand → metal charge transfer. This severely restricts the possible intermediate states, eliminating completely any in-ligand transitions even if they are allowed by the symmetry rules (see iib). This, however, is as useful as it is restrictive, for DICD can thus be used as a probe for both d-d and charge-transfer states without the complications of the sometimes broad and intense in-ligand transitions.

The symmetry rules may be applied directly to the d-d transitions of Cu(II) complexes of various stereochemistries by means of the DICD tables for the corresponding point groups (see Appendix). With the d-orbital notation expressed in terms of the O_h (xyz) system, the one-electron transitions and the possible intermediate states for DICD activity are presented in Tables I and II. Transitions for which no intermediate charge-transfer states are given are DICD inactive.

The DICD activity can be seen to be a function of stereochemistry. For the elongated tetragonal octahedra (square planar in the limit), the number of DICD bands allowed by symmetry increases with decreasing symmetry. For O_h, only one band is expected (through T_{1u} or T_{2u}). Under D_{4h}, this band splits into two, one appearing through an E_u intermediate, and another through a B_{2u} charge-transfer state. If one of these charge-transfer states is especially intense or nearby energetically, then the corresponding d-d band may be considerably stronger in the DICD spectrum (or even be the only one to appear). The number of symmetry-allowed DICD active transitions is not affected by reduction to C_{4v}. Further reductions to D_{2h} or C_{2v}, however, lead to a maximum of four bands. For D_{2h}, three are allowed through B_{2u}, three through B_{3u}. Under C_{2v}, three are allowed through B_1, three through B_2, and two through A_2.

For compressed stereochemistries, only one DICD band appears for O_h, D_{4h}, and C_{4v}, and a maximum of three for D_{2h} and C_{2v}, the number depending on the possible intermediate charge-transfer states of the complex. Finally, under D_{3h}, only one possible band is allowed.

Thus the higher the symmetry, the more selective is the DICD technique. (Compare this with natural CD.) Even for lower symmetries such as D_{2h}, one might expect the D_{4h} symmetry rules to apply if, for example, the complex involves two bidentate ligands, whose stereochemistry with respect to the chelating *atoms* remains approximately D_{4h}. As square-planar copper complexes are especially resilient to chelate effects, we might therefore expect only *two* DICD bands even for D_{2h} under these circumstances.

One feature of the magnetic induction mechanism is that the sign of each DICD band may be positive or negative and the transition moments must be calculated explicitly before the sign can be estimated theoretically. The inducibility is, however, constant for given states $|A^s\rangle$ and $|A^t\rangle$ and this fact may be exploited to investigate the signs of the relative inducing powers of a range of chiral inducing species.

DICD of the Charge-Transfer Transitions. The main feature of charge-transfer bands in absorption spectra is their relatively high intensity compared with that of the d-d transitions, a

Table I. DICD for Tetragonal Stereochemistries

	O_h	T_t	D_{4h}	T_t	C_{4v}	T_t	D_{2h}	T_t	C_{2v}	T_t
Elongated										
$d_{z^2} \rightarrow d_{x^2-y^2}$			$B_{1g} \rightarrow A_{1g}$		$B_1 \rightarrow A_1$		$B_{1g} \rightarrow A_g$	B_{2u} B_{3u}	$A_2 \rightarrow A_1$	B_1 B_2
$d_{xy} \rightarrow d_{x^2-y^2}$	$E_g \rightarrow T_{2g}$	T_{1u} T_{2u}	$B_{1g} \rightarrow B_{2g}$	E_u	$B_1 \rightarrow B_2$	E	$B_{1g} \rightarrow A_g$	B_{2u} B_{3u}	$A_2 \rightarrow A_1$	B_1 B_2
$d_{xz} \rightarrow d_{x^2-y^2}$			$B_{1g} \rightarrow E_g$	B_{2u}	$B_1 \rightarrow E$	B_1 E	$B_{1g} \rightarrow B_{2g}$	B_{3u}	$A_2 \rightarrow B_1$	A_2 B_1
$d_{yz} \rightarrow d_{x^2-y^2}$							$B_{1g} \rightarrow B_{3g}$	B_{2u}	$A_2 \rightarrow B_2$	A_2 B_2
Compressed										
$d_{x^2-y^2} \rightarrow d_{z^2}$			$A_{1g} \rightarrow B_{1g}$		$A_1 \rightarrow B_1$		$A_g \rightarrow B_{1g}$	B_{2u} B_{3u}	$A_1 \rightarrow A_2$	B_1 B_2
$d_{xy} \rightarrow d_{z^2}$	$E_g \rightarrow T_{2g}$	T_{1u} T_{2u}	$A_{1g} \rightarrow B_{2g}$		$A_1 \rightarrow B_2$		$A_g \rightarrow A_g$		$A_1 \rightarrow A_1$	
$d_{xz} \rightarrow d_{z^2}$			$A_{1g} \rightarrow E_g$	A_{2u}	$A_1 \rightarrow E$	A_1 E	$A_g \rightarrow B_{2g}$	B_{1u} B_{3u}	$A_1 \rightarrow B_1$	A_1 B_1
$d_{yz} \rightarrow d_{z^2}$							$A_g \rightarrow B_{3g}$	B_{1u} B_{2u}	$A_1 \rightarrow B_2$	A_1 B_2

Table II. DICD for Trigonal Stereochemistry

	D_{3h}	
	$\Gamma_0 \rightarrow \Gamma_s$	Γ_t
$d_{x^2-y^2} \rightarrow d_{z^2}$ $d_{xy} \rightarrow d_{z^2}$	$A_1' \rightarrow E'$	
$d_{xz} \rightarrow d_{z^2}$ $d_{yz} \rightarrow d_{z^2}$	$A_1' \rightarrow E''$	E' A_2''

result of their electric dipole character. The DICD of such bands may therefore be expected to occur through the electric induction mechanism and thus have the same sign as the CD of the inducing transition in the chiral species. Furthermore, the DICD intensity will have an inverse square dependence of the energy difference of the charge-transfer state and the inducing transition of the chiral species.

The proportionality of electrically-induced DICD to the CD of the chiral species may be utilized to measure the relative rotatory strengths of the inducing transitions for any number of inducing chiral species, provided the transition energies are roughly known and the same achiral species is used. This could be useful in studying transitions of the chiral species, which are beyond the limits of present CD instrumentation.

It is possible for magnetically allowed charge-transfer transitions, which would be swamped in direct absorption, to appear in the DICD spectrum. Whether they will be suitably resolved remains an open question.

DICD of In-Ligand Transitions. Although the in-ligand transitions cannot interact with any d-d configurations and thus are ineffective as intermediates in the DICD of the d-d transitions, they may exhibit DICD in their own right by either mechanism. If these transitions are intense in absorption, one may expect correspondingly intense electrically-induced DICD bands. Again, other bands could potentially appear in the DICD due to magnetic dipole allowed in-ligand transitions, and could thus show up with signs different from (or the same as) that of the chiral species.

Separation of the Two Mechanisms. A given chiral species may be specified completely (within this model) by (a) its electric and magnetic inducing powers and (b) the energies of the transitions involved. The fact that the magnetic and electric inducing powers of a given chiral species are *independent* (they have only the factor μ_C^{0u} in common) can be exploited in discriminating between the electric and magnetic induction mechanisms. By studying *experimentally* a large number of chiral inducing species, it should be possible to find, for example, a chiral species C_m with a large magnetic inducing power, small electric inducing power, and another chiral species C_e with a small magnetic and large electric inducing power. Then by measuring the DICD of a species A with C_m and then with C_e, it should theoretically be possible to effect a separation of the magnetically induced spectrum from that appearing through the electric mechanism; this follows directly by noting that the magnetically-induced transitions lose intensity in going from C_m to C_e, whereas the electrically-induced bands will have the higher intensity in C_e.

Another flexible parameter in the choice of chiral species is its lowest transition energy. In the previous discussion, it has been assumed to lie above all the transitions of interest in the achiral molecule. This is simply to avoid confusion of the CD band systems of the achiral and chiral species. In cases where only the d-d spectra were of interest, it would be advantageous to use a chiral species with its lowest transition considerably closer to (but still higher than) the d-d bands themselves. This could give greater resolution and intensity of the d-d DICD bands.

6. Comparisons with Experiment

Little experimental work has appeared in this area. Solution MCD work by Kato[15] illustrates the complexity of the calculations needed with relatively little reward when MCD methods are applied to nondegenerate d-d transitions. This stems directly from the dependence of the MCD bands on the electric dipole transition moments, and hence on vibronic coupling terms in these electric dipole forbidden transitions.

In a recent paper,[8] Murakami and Hatano have measured the induced CD curves of achiral Cu(II) β-diketonates over a wide wavelength range (visible to ultraviolet) dissolved in optically active bases (D-α-phenylethylamine and nicotine). There is little doubt that the axial positions of the diketonate complexes (square planar) are occupied by the basic nitrogen positions of the respective solvents, but the D_{2h} (or approximately D_{4h} in the oxygens) symmetry is presumably retained about the central ion. Although the nicotine is relatively rigid, the phenyl chromophore in the D-α-phenylethylamine is relatively free orientationally with respect to the central metal atom of the complex, even in the presence of the axial ligation through the nitrogen. Thus one may interpret the induced CD in the latter solvent in terms of the DICD model discussed in this paper. This is supported by the following observations.

d-d Region. One strong DICD band appears at low d-d energies, with a weaker one developing in some of the com-

Table III

	T_0	T_s	T_t
O_h	A_{1g}	T_{1g}	T_{1u}
	A_{2g}	T_{2g}	T_{2u}
	E_g	T_{1g}	T_{1u},T_{2u}
		T_{2g}	T_{1u},T_{2u}
	T_{1g}	A_{1g}	T_{1u}
		E_g	T_{1u},T_{2u}
		T_{1g}	A_{1u},E_u,T_{1u},T_{2u}
		T_{2g}	E_u,T_{1u},T_{2u}
	T_{2g}	A_{2g}	T_{2u}
		E_g	T_{1u},T_{2u}
		T_{1g}	E_u,T_{1u},T_{2u}
		T_{2g}	A_{2u},E_u,T_{1u},T_{2u}
D_{4h}	A_{1g}	A_{2g}	E_u
		E_g	A_{2u}
	A_{2g}	A_{1g}	E_u
		E_g	A_{1u}
	B_{1g}	B_{2g}	E_u
		E_g	B_{2u}
	B_{2g}	B_{1g}	E_u
		E_g	B_{1u}
	E_g	E_g	A_{2u}
		A_{2g}	E_u
C_{4v}	A_1	E	A_1,E
	A_2	A_1	E
		E	A_2,E
	B_1	B_2	E
		E	B_1,E
	B_2	B_1	E
		E	B_2,E
	E	A_1	A_1,E
		A_2	A_2,E
		B_1	B_1,E
		B_2	B_2,E
		E	A_1,A_2,B_1,B_2
D_{2h}	A_g	B_{1g}	B_{2u},B_{3u}
		B_{2g}	B_{1u},B_{3u}
		B_{3g}	B_{1u},B_{2u}
	B_{1g}	A_g	B_{3u},B_{2u}
		B_{2g}	B_{3u}
		B_{3g}	B_{2u}
	B_{2g}	A_g	B_{3u},B_{1u}
		B_{1g}	B_{3u}
		B_{3g}	B_{1u}
	B_{3g}	A_g	B_{2u},B_{1u}
		B_{1g}	B_{2u}
		B_{2g}	B_{1u}
C_{2v}	A_1	A_2	B_1,B_2
		B_1	A_1,B_1
		B_2	A_1,B_2
	A_2	A_1	B_1,B_2
		B_1	A_2,B_1
		B_2	A_2,B_2
	B_1	A_1	A_1,B_1
		A_2	A_2,B_1
		B_2	A_1,A_2
	B_2	A_1	A_1,B_2
		A_2	A_2,B_2
		B_1	A_1,A_2
D_{3h}	A_1'	A_2'	E'
		E''	E',A_2''
	A_2'	A_1'	E'
		E''	E',A_1''
	E'	E'	A_1',A_2',E'
		A_1''	A_2',E''
		A_2''	A_1',E''
		E''	E',E''
	A_1''	A_2''	E''
		E'	A_2',E''
	A_2''	A_1''	E''
		E'	A_1',E''
	E''	E'	E',E''
		A_1'	E',A_2''
		A_2'	E',A_1''
		E''	A_1'',A_2'',E''

plexes at higher energies. Under approximate D_{4h} symmetry, these would correspond to the

$$d_{xy} \rightarrow d_{x^2-y^2} \text{ and } d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$$

transitions, respectively, the former through an E_u charge-transfer state, the latter through a B_{2u}. The charge-transfer states presumably originate from the oxygen to metal charge transfer, though the reverse cannot be ruled out. The variation in the sign of the DICD for these two observed DICD bands confirm their magnetic origin and also suggests that different charge-transfer states may be acting as intermediates in different complexes.

Charge-Transfer Region. At least one charge-transfer band appears at about 25 000 cm^{-1}, with a DICD whose sign is always the same as that of the CD of the chiral species. This supports the electric induction mechanism and agrees with the intensity of the band in direct absorption. In some of the complexes, the band appears only as a shoulder on a considerably stronger DICD band having its origin in the in-ligand transitions.

In-Ligand Transitions. The very intense DICD band at 28 000-32 000 cm^{-1} corresponds to electrically induced DICD of the $\pi \rightarrow \pi^*$ ligand transition. There is a marked increase in the intensity of this band as $\Delta\epsilon$ decreases, which is qualitatively consistent with the $1/\Delta\epsilon^2$ behavior expected from the electric induction mechanism. This electric dipole allowed transition is only one of the possible exciton-type states of the overall ligand system and it is not too difficult to show that a long-axis polarized $\pi \rightarrow \pi^*$ transition of the diketonate ligands can lead to both an electric and magnetic dipole in-ligand transition of the overall complex. The latter could lead to a magnetically induced band, which could have either sign. This could explain the positive peaks in this region for some of the complexes and also suggests a method of observing both components of such exciton states.

It would seem that the agreement between theory and experiment for the above system is certainly more than fortuitous and there is little doubt that a comparison of the DICD spectra in different chiral solvents would effect the separation of the electric and magnetic DICD bands, thus clarifying some of the remaining ambiguities.

In summary, the model proposed here supports the assignment of the lowest DICD band as a z-polarized magnetic dipole allowed transition, as suggested by Murakami and Hatano, but further identifies it as the $d_{xy} \rightarrow d_{x^2-y^2}$ and not the $d_{z^2} \rightarrow d_{x^2-y^2}$, which is DICD-inactive under D_{4h}, and would be expected to be only weak under D_{2h} in this case. A second DICD band is assigned as that involving the d_{xz},d_{yz} state. These results agree with the most recent assignments made on the basis of detailed vibronic analysis of the absorption spectrum.[14] (The primed coordinate system is used in their analysis.) Earlier literature is discussed in reference.[8]

Summary

The DICD technique is seen to yield selection rules that facilitate assignment by simply referring to the DICD spectrum and the relevant table derived from the DICD symmetry rules. The results are qualitative, the calculation of absolute intensities requiring knowledge of all transition moments in the relevant expressions. Usually only a few are known (from oscillator strengths in absorption). When these quantities are determined theoretically, better comparisons with experiment will be possible. As discussed earlier, however, the use of suitable chiral inducing agents should be able to effect a separation of the magnetic and electric dipole allowed transitions and lead to a more definitive assignment of the entire spectrum, even without quantitative estimates of all the transition moments.

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Appendix

DICD-Allowed Symmetries for Various Stereochemistries. In Table III, the possible combinations of $|A^0\rangle$, $|A^s\rangle$, and $|A^t\rangle$ are given for point group symmetries common to Cu(II) complexes. These are the only combinations that lead to DICD activity in the s transition through the magnetic induction mechanism. If more than one symmetry of $|A^t\rangle$ is given for a certain $|A^s\rangle$, then any one of those states is a potential intermediate state for inducing DICD in the s transition. The symmetry of state $|A^r\rangle$ will be denoted Γ_r.

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An Analysis of the Endostatic Transformation of Thermodynamic Functions

Gary L. Bertrand*[1a] and Thomas F. Fagley[1b]

Contribution from the Departments of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401, and Tulane University, New Orleans, Louisiana 70118.

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Abstract: The endostatic transformation of the standard state properties of a solute in a mixed solvent system has been analyzed in terms of the hypothetical experiment on which the transformation is based, the relationships between transformed functions, and the behavior of transformed functions for a simple model system. This analysis reveals serious flaws in the structure of endostatic transformations.

In a recent article, Grunwald and Effio proposed a transformation of the thermochemical properties of a solute in a mixed solvent system from the normal condition of fixed solvent composition to a hypothetical condition of fixed activity ratios.[2] This transformation was based on a hypothetical experiment in which the addition of solute to a solution was accompanied by transfer of solvent components between the solution and reservoirs containing the individual solvents and solute at the same solute mole fraction as the solution so that the total number of moles of solvent and the ratio of solvent activities in the solution were unchanged. This transformation was designed to simplify interpretation of the thermodynamic properties of the solute in a mixed solvent by making these functions analogous to corresponding functions in one-component solvents. The utility of considering processes at constant solvent activity ratios cannot be denied. Some processes actually occur under these conditions, i.e., the osmotic experiments designed by Scatchard[3a] and many other processes in biological systems. Treiner[3b] has observed that mixed solvents obey Raoult's law (as it was originally stated) under these conditions. However, these processes have an important distinction from the endostatic process described by Grunwald and Effio (GE) in that the real processes occur in a system in which the chemical potentials of the solvent components are uniform throughout the system, while the endostatic process occurs in a system containing solvent components in different free energy states. One can conceive a reversible process occurring in an osmotic experiment with two solutes in chemical equilibrium. This process could not occur reversibly under endostatic conditions, except in highly specific cases. Because of this difference between endostatic and osmotic conditions we have analyzed the endostatic experiment described by GE on the basis of the definition of the hypothetical experiment, the relationships between transformed functions, and the behavior of transformed functions for a simple model system. We have found that the fundamental concept is flawed in that: (1) the hypothetical experiment cannot be applied to the addition of a finite quantity of solute, (2) the temperature dependence of transformed standard state properties is much more complex than in the normal case, and (3) interpretation of solvent effects on transformed properties is hampered by complexities even in the case of an ideal binary solvent. These flaws appear to arise from the properties of the hypothetical system on which transformations are based, rather than from the properties of