

## Symmetry Rules for Dispersion-induced Circular Dichroism (DICD) in Achiral Complexes

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*A theory for the circular dichroism bands induced at  $d-d$  transition frequencies of symmetric (achiral) complexes due to long-range dispersive coupling with other chiral species (all species being dissociated in an achiral solvent) is discussed. The conditions for a finite effect are interpreted as symmetry rules restricting the symmetries of the states of the achiral complex that may exhibit the effect. Some suggestions are made as to what type of systems should be studied experimentally.*

### Introduction

The chirality of any dissymmetric species is physically manifest in the appearance of circular dichroism (CD) bands at electronic transition frequencies of the species. Achiral species show no such bands. It has been found experimentally, however, that CD bands located at transition frequencies of achiral species (A) may appear when other chiral species (C) are present in the solution, the solvent being achiral.<sup>1–5</sup> Such bands are best observed when the transition of A lies at lower energies than the transition of C, where the effect is not swamped by the optical activity of the chiral species. The work of Hayward and Totty<sup>2</sup> on organic systems suggests strongly that the effect persists even when there is no association of the chiral and achiral species in solution. The effect was also noted by Bosnich<sup>6</sup>, who reported the CD of the  $\text{PtCl}_4^{2-}$  ion; in this case however a chiral solvent was used as the inducing species. Other workers<sup>5</sup> have since reported the effect for inorganic species in achiral solvents, the achiral species again being square planar metal halides, with organic acid anions used as the inducing agents C. In all these cases, the induced circular dichroism was observed for magnetic-dipole allowed transitions of the achiral species.

A theoretical approach<sup>7,8</sup> to this problem has been presented for the case where the species A and C are assumed to be completely dissociated in an achiral solvent, but coupled to each other by long-range van der Waals or dispersion forces. We shall refer to the

circular dichroism arising from such a mechanism as *dispersion-induced circular dichroism* (DICD). It should be noted that this model can only apply for systems in which the relative orientations of A and C are randomised either in time or over all possible AC pairs in solution. In the absence of association between A and C, it would appear that such an assumption is reasonably valid.

In this paper, the theory of the DICD of  $d-d$  transitions of inorganic complexes is discussed. It will be seen that the expression for the DICD is zero unless a number of symmetry conditions are satisfied for the electronic states involved in the induction process. These conditions are examined in detail, and the symmetry rules applied to complexes of various symmetries.

### Theory I. Method

Consider a given pair of achiral and chiral species A and C in solution with an achiral solvent. We wish to find the CD induced in A by the chiral species C as a function of their separation ( $r_{AC}$ ), and of the intrinsic molecular properties (transition moments) of A and C. This may be done by determining firstly the activity of the AC-system, and then expanding this in terms of the free-molecule (or free-ion) states of A and C in the following way.

The optical activity of the AC-system is described by the optical-rotatory pseudo-tensor,  $\hat{R}_s$ , for each of its transitions, where

$$\hat{R}_s = \text{Im} \langle 0 | \vec{\mu} | S \rangle \langle S | \vec{m} | 0 \rangle \quad [1]$$

$|0\rangle$  is the ground state,  $|S\rangle$  an excited state of the coupled AC-system, with  $\vec{\mu}$  and  $\vec{m}$  being respectively the electric and magnetic dipole operators. It is assumed that the radiation field vectors  $\mathbf{E}$ ,  $\mathbf{B}$  and their first time derivatives ( $\dot{\mathbf{E}}$ ,  $\dot{\mathbf{B}}$ ) may be taken as constant over the system. The rotatory strength (a pseudo-scalar) may then be defined from the above as

$$R_s = \mathbf{b}^\dagger \hat{R}_s \mathbf{b}$$

where  $\mathbf{b}$  is the unit vector along  $\dot{\mathbf{B}}$ . Putting  $\vec{\mu} \cdot \mathbf{b} = \mu^b$ ,  $\vec{m} \cdot \mathbf{b} = m^b$  leads to

$$R_s = \text{Im} \langle 0 | \mu^b | S \rangle \langle S | m^b | 0 \rangle \quad [2]$$

This expression holds for given relative orientations of the radiation field, species A, and species C.

The states  $|0\rangle$  and  $|S\rangle$  of the AC-system may be determined by perturbation theory. Let the free-molecule states of A be written as  $|A^i\rangle$  ( $i = 0, 1, \dots$ ) with corresponding energies  $\varepsilon_i^A$  relative to the ground state ( $i = 0$ ). The states of C may be similarly written as  $|C^j\rangle$  with energies  $\varepsilon_j^C$ . In the absence of any interaction between A and C, the wave functions of the AC-system have the simple form

$$|ij\rangle = |A^i\rangle |C^j\rangle,$$

exchange effects being neglected. In the presence of the interaction, the species are coupled by the dipole-dipole interaction operator

$$V_{AC} = -\frac{\vec{\mu}_A \cdot \vec{\mu}_C - 3\vec{\mu}_A \cdot \hat{r}_{AC} \vec{\mu}_C \cdot \hat{r}_{AC}}{r_{AC}^3}$$

where  $\hat{r}_{AC}$  is the vector joining A and C, and the  $\sim$  denotes a unit vector.  $\vec{\mu}_A$  is the electric dipole operator for molecule A, and so on. The states of the coupled system may then be found by perturbation theory in terms of the functions  $|ij\rangle$  to include interaction terms up to  $r_{AC}^{-6}$ . In particular, we are interested in the stated  $|0\rangle$  (the perturbed ground state) and  $|S\rangle$  (the perturbed state derived from  $|so\rangle$ ). In the absence of degeneracies, we have

$$\begin{aligned} |0\rangle &= |oo\rangle + P(o0,ij) |ij\rangle + P^2(o0,ij) |ij\rangle \\ |S\rangle &= |so\rangle + P(so,ij) |ij\rangle + P^2(so,ij) |ij\rangle \end{aligned} \quad [3]$$

where

$$\begin{aligned} P(so,ij) &= -\sum_{ij} \frac{\langle ij | V | so \rangle}{\varepsilon_{ij} - \varepsilon_s} \\ P^2(so,ij) &= \sum_{ij} \left( \sum_{i'j'} \left[ \frac{\langle ij | V | i'j' \rangle \langle i'j' | V | so \rangle}{(\varepsilon_{ij} - \varepsilon_s)(\varepsilon_{i'j'} - \varepsilon_s)} \right. \right. \\ &\quad \left. \left. - \frac{\langle so | V | so \rangle \langle ij | V | so \rangle}{(\varepsilon_{ij} - \varepsilon_s)^2} \right] \right). \end{aligned}$$

Note that  $\varepsilon_{ij} = \varepsilon_i + \varepsilon_j$ , where the A and C subscripts have been omitted for convenience. The summations omit any states giving zero denominators.

If any of the states  $|A^i\rangle$  are degenerate, a slightly different procedure is necessary. Consider the state  $|A^s\rangle$  to be  $n$ -fold degenerate, the levels being described by the orthonormal set of functions  $|A_\alpha^s\rangle$ ,  $\alpha = 1, \dots, n$ . The perturbed states of the AC-system are then developed in two steps. Firstly, a state  $|S_\alpha\rangle$  is defined for each  $\alpha$  according to equation [3], except that only states not degenerate with  $|A_\alpha^s\rangle$  are included in the perturbations sums. Secondly, the set  $|S_\alpha\rangle$  is used as a basis for a variation treatment to find the  $n$  new states  $|S_\mu\rangle$  which are diagonal in  $V_{AC}$ . These may be written in the form

$$|S_\mu\rangle = \sum_{\alpha} C_{\mu\alpha} |S_\alpha\rangle. \quad [4]$$

It should be noted that the coefficients  $C_{\mu\alpha}$  are functions of  $V_{AC}$ , and thus of the relative orientations of A and C. Degeneracies in any of the other states may be similarly treated.

These expressions for  $|0\rangle$  and  $|S\rangle$  may now be substituted directly into  $R_s$ . The operators  $\vec{\mu}$  and  $\mathbf{m}$  are expanded as<sup>9</sup>

$$\vec{\mu} = \vec{\mu}_A + \vec{\mu}_C, \quad \mathbf{m} = \mathbf{m}_A + \mathbf{m}_C + \mathbf{M}$$

where  $\vec{\mu}_A$ ,  $\mathbf{m}_A$  are the intrinsic electric and magnetic dipole operators of A, and so on.  $\mathbf{M}$  is that part of the magnetic moment operator which gives rise to magnetic terms due to coupled electric dipoles on different molecules. It may be neglected when dealing with magnetic-dipole allowed transitions.  $R_s$  will then be given as a power series in  $r_{AC}^{-3}$ , which may be truncated at  $r_{AC}^{-6}$  terms. The non-degenerate case is straightforward,  $R_s$  then referring to a single transition. For a degenerate level  $|A^s\rangle$ , we consider the  $n$ -fold degeneracy discussed above. It will be assumed that  $V_{AC}$  does not separate the states  $|S_\mu\rangle$  appreciably energetically, so that  $R_s$  is calculated for all  $|S_\mu\rangle$  assumed to have the unperturbed energy  $\varepsilon_s$ . In this approximation, it follows that

$$R_s = \text{tr} \hat{R} = \text{tr} [\hat{C} \hat{R}^0 \hat{C}^\dagger] = \text{tr} \hat{R}^0$$

where the matrix elements are defined as

$$\begin{aligned} R_{\mu\nu} &= \text{Im} \langle 0 | \mu^b | S_\mu \rangle \langle S_\nu | m^b | 0 \rangle \delta_{\mu\nu} \\ R_{\alpha\beta}^0 &= \text{Im} \langle 0 | \mu^b | S_\alpha \rangle \langle S_\beta | m^b | 0 \rangle \end{aligned}$$

with  $C_{\mu\alpha}$  defined according to equation [4]. Without the assumption that the CD bands for the  $n$  sub-levels are centred at the same energy  $\varepsilon_s$ , it would be necessary to solve explicitly for the coefficients  $C_{\mu\alpha}$  as a function of the relative orientation of A and C (an unenviable task). It then follows that the only effect of degeneracies in this model is to introduce a sum over the degenerate states  $|A_\alpha^s\rangle$  into the expression for  $R_s$ . Other degeneracies are similarly treated.

As the above results hold for A and C in a fixed relative orientation, and the AC-system in a fixed orientation relative to the radiation field, the scalar  $R_s$  must now be averaged over all such orientations. In both averages, all orientations are assumed equally probable. The procedure is fully discussed elsewhere<sup>7</sup>. All terms in  $r_{AC}^{-3}$  vanish, so that the leading terms have an  $r_{AC}^{-6}$ -dependence. For convenience, these results are given in the following section.

## Theory II. Results

As will be discussed further in a later section, the  $d-d$  transitions of metal complexes may be magnetic-

dipole allowed, but are invariably electric-dipole forbidden. We therefore consider the transition  $|A^0\rangle \rightarrow |A^s\rangle$  to be magnetic-dipole allowed, and the averaged induced rotatory strength appearing at energy  $\epsilon_s$  reduces to<sup>7,10</sup>

$$\bar{R}_s = -\frac{1}{18} r_{AC}^{-6} \Omega_A^{os}(t) \mathcal{L}_C^{ou}(v) \lambda_t^{uv}$$

where

$$\Omega_A^{os}(t) = \text{Im} \vec{\mu}_A^{ot} \times \vec{\mu}_A^{ts} \cdot \mathbf{m}_A^{so}$$

$$\mathcal{L}_C^{ou}(v) = \vec{\mu}_C^{ov} \times \vec{\mu}_C^{vu} \cdot \vec{\mu}_C^{uo}$$

and

$$\lambda_t^{uv} = [(\epsilon_u - \epsilon_s)(\epsilon_t + \epsilon_v - \epsilon_s)]^{-1} \text{ for } (\epsilon_u - \epsilon_s) \ll \epsilon_s, \epsilon_u < \epsilon_v$$

The transition moments are defined as  $\vec{\mu}_A^{ot} = \langle A^0 | \vec{\mu} | A^t \rangle$  and so on. Note that  $u$  and  $v$  refer to the states  $|C^u\rangle, |C^v\rangle$  of the chiral species.  $\mathcal{L}_C^{ou}(v)$  is the *inducing power* of the chiral species, and it should be noted that it is independent of the intrinsic rotatory strength of  $C$ .  $\Omega_A^{os}(t)$  may be called the *inducibility* of  $A$ , and is a measure of the ability of state  $|A^s\rangle$  to exhibit DICD through the intermediate state  $|A^t\rangle$ . The complete result should, of course, be summed over all  $t, u$  and  $v$ , and also over any degeneracies of the states involved. In some cases, however, there may be a certain transition that is much stronger in intensity than any other, so that a single intermediate state  $|A^t\rangle$  need only be considered in that case.

A clearer understanding of this result may be obtained by a simple physical interpretation of the induction process. Although the DICD is independent of the rotatory strength of the chiral species, let us first see how CD arises for the species  $C$ .

The chiral species may be said to be optically-active because it has a state (or states), say  $|C^u\rangle$ , which is accessible from the ground state  $|C^0\rangle$  either by electric or magnetic dipole transitions. In responding to the radiation field, the following virtual process thus leads to the CD band:

$$|C^0\rangle \xrightarrow{\dots \mathbf{m} \dots} |C^u\rangle \quad (\text{Excitation via magnetic dipole})$$

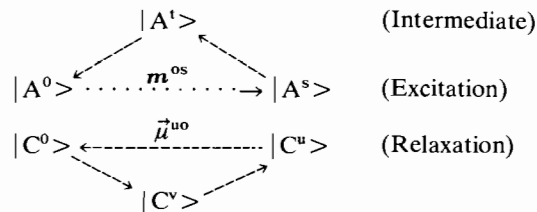
$$|C^0\rangle \xleftarrow{\dots \vec{\mu} \dots} |C^u\rangle \quad (\text{Relaxation via electric dipole})$$

For the achiral species  $A$ , transitions to states  $|A^t\rangle$  may be *either* electric-dipole allowed *or* magnetic-dipole allowed, but not both. It follows that virtual processes analogous to the above are thus impossible. In particular, the process

$$|A^0\rangle \xrightarrow{\dots \mathbf{m} \dots} |A^s\rangle \quad (\text{Excitation via magnetic dipole})$$

can occur, but as it cannot relax through the electric dipole, no CD-band can appear.

Virtual processes leading to CD-bands can occur, however, for the coupled AC-system. In particular, the  $|0\rangle$  to  $|S\rangle$  transition may now become both electrically and magnetically allowed, leading to the DICD of  $A$ . The virtual process may be broken down into its separate  $A$  and  $C$  components in the following way:



Note that the transitions  $|A^s\rangle, |C^u\rangle$  cannot constitute the virtual process alone, as each species must separately return to the ground state. Thus the electric-dipole accessible states  $|A^t\rangle, |C^v\rangle$  are necessary to complete the process, the moments involving  $t$  and  $v$  being coupled through the van der Waals interaction. We shall refer to  $|A^t\rangle$  as the *intermediate* state in the induction of CD in  $|A^s\rangle$ .

### General Symmetry Rules

Both the inducibility of  $A$  and the inducing power of  $C$  involve products of the form  $\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}$ . This product vanishes if any two of the vectors are collinear. This has important consequences in restricting the states of an achiral species participating in the induction process to those of certain symmetries. In this section, the symmetry rules for which the inducibility of  $A$ ,

$$\Omega_A^{os}(t) = \text{Im}(\vec{\mu}_A^{ot} \times \vec{\mu}_A^{ts} \cdot \mathbf{m}_A^{so})$$

is non-zero are discussed (the chiral species will be considered separately in a later section).

Suppose the point group of  $A$  has been determined, and the irreducible representations (IR's) designated as  $\Gamma$ . The axes ( $xyz$ ) are chosen in accord with the usual conventions for that point group.<sup>11</sup> The states  $|A^0\rangle, |A^s\rangle, |A^t\rangle$  may then be taken to be bases for the IR's  $\Gamma_o, \Gamma_s, \Gamma_t$  respectively. Let the IR's generated by  $m_x, m_y, m_z$  (the Cartesian components of  $\mathbf{m}$ ) be denoted by (i)  $\Gamma_{m_x, m_y, m_z}$  if they are the basis for a three-dimensional IR, (ii)  $\Gamma_{m_x, m_y}, \Gamma_{m_z}$  if  $m_x, m_y$  are the basis for a two-dimensional IR, and  $m_z$  is that for a one-dimensional IR, and so on. The IR's generated by the components of  $\vec{\mu}$  are analogously defined.

The symmetry rules for a finite inducibility may then be stated as follows:

#### I. If All IR'S One-dimensional

- (i)  $\Gamma_o \otimes \Gamma_s$  must contain  $\Gamma_{m_i}$  ;
- (ii)  $\Gamma_o \otimes \Gamma_t$  must contain  $\Gamma_{\mu_i}$  ;

- (iii)  $\Gamma_t \otimes \Gamma_s$  must contain  $\Gamma_{\mu_k}$  ;  
 (iv)  $i \neq j \neq k \neq i$  where  $i, j, k$  each run over  
 Cartesians  $x, y, z$ .

The  $\otimes$  denotes direct products. Rules (i) to (iii) arise simply from the conditions for finite matrix elements, whereas (iv) embodies the condition for the vector product to be non-vanishing.

## II. Multidimensional IR'S

For multidimensional IR's, the procedure is only slightly modified. For example, if the pair  $\mu_j, \mu_k$  are the basis of the two-dimensional IR  $\Gamma_{\mu_j \mu_k}$ , it follows that (ii) and (iii) above become

- (ii)  $\Gamma_0 \otimes \Gamma_t$  must contain  $\Gamma_{\mu_j \mu_k}$  ;  
 (iii)  $\Gamma_t \otimes \Gamma_s$  must contain  $\Gamma_{\mu_j \mu_k}$  .

The other conditions remain unchanged.

Although these conditions may seem slightly complex, they are deceptively easy to employ in practice with recourse to a set of character tables.<sup>11</sup> Their utility lies in the immediate prediction of which states  $|A^s\rangle$  are potentially inducible, and which states  $|A^t\rangle$  can act as intermediates in the induction process. For example, if there is only one strong electric-dipole allowed transition  $|A^0\rangle \rightarrow |A^t\rangle$  in the observed spectrum of A (or one which is appreciably more intense than any others), it should be possible to predict which states  $|A_s\rangle$  (if any) may exhibit DICD. Alternatively DICD could be used to assign the symmetry of a transition if it is magnetic-dipole allowed, or possibly locate it when conventional techniques fail. It is worth pointing out here that the dependence of the DICD on both the nature of  $|A^s\rangle$  and  $|A^t\rangle$  could lead to information which could supplement that obtainable from MCD techniques,<sup>12,13</sup> which depend to a first approximation only on the state  $|A^s\rangle$ .

To apply the symmetry rules, it is necessary to know the IR's generated by the cartesian dipole components and the direct product rules for the representations of the achiral point groups. These are generally available in standard texts.<sup>11</sup>

It is instructive to work through a simple case. Consider a species of  $D_{4h}$  symmetry (e.g. Pt  $Cl_4^{2-}$ ) with an  $A_{1g}$  ground state. From character tables,<sup>11</sup> it follows that

$$\Gamma_{m_x m_y} = E_g, \Gamma_{\mu_x \mu_y} = E_u, \Gamma_{m_z} = A_{2g}, \Gamma_{\mu_z} = A_{2u}$$

The magnetic dipole can lie either in the  $z$ -direction or in the  $xy$ -plane. In the first case, DICD-active states must satisfy the following symmetry rules:

- (i)  $A_{1g} \otimes \Gamma_s$  must contain  $A_{2g}$  ;  
 (ii)  $A_{1g} \otimes \Gamma_t$  must contain  $E_u$  ;  
 (iii)  $\Gamma_s \otimes \Gamma_t$  must contain  $E_u$  .

TABLE I. DICD-allowed Symmetries for Octahedral and Square-Planar Complexes.

Symmetry of Ground State $ A^0\rangle$	Symmetry of $ A^s\rangle$	Symmetry of $ A^t\rangle$
<i>Octahedral (<math>O_h</math>)</i>		
$A_{1g}$	$T_{1g}$	$T_{1u}$
$A_{2g}$	$T_{2g}$	$T_{2u}$
$E_g$	$T_{1g}$	$T_{1u}, T_{2u}$
	$T_{2g}$	$T_{1u}, T_{2u}$
$T_{1g}$	$A_{1g}$	$T_{1u}$
	$E_g$	$T_{1u}, T_{2u}$
	$T_{1g}$	$A_{1u}, E_u, T_{1u}, T_{2u}$
	$T_{2g}$	$E_u, T_{1u}, T_{2u}$
$T_{2g}$	$A_{2g}$	$T_{2u}$
	$E_g$	$T_{1u}, T_{2u}$
	$T_{1g}$	$E_u, T_{1u}, T_{2u}$
	$T_{2g}$	$A_{2u}, E_u, T_{1u}, T_{2u}$
<i>Square-Planar (<math>D_{4h}</math>)</i>		
$A_{1g}$	$A_{2g}$	$E_u$
	$E_g$	$A_{2u}$
$A_{2g}$	$A_{1g}$	$E_u$
	$E_g$	$A_{1u}$
$B_{1g}$	$B_{2g}$	$E_u$
	$E_g$	$B_{2u}$
$B_{2g}$	$B_{1g}$	$E_u$
	$E_g$	$B_{1u}$
$E_g$	$E_g$	$A_{2u}$
	$A_{2g}$	$E_u$

Note that rule (iv) has already been satisfied by choosing the combination  $[m_z, \mu_x, \mu_y]$ . It follows directly from the product rules that  $\Gamma_s = A_{2g}, \Gamma_t = E_u$ . For the magnetic dipole in the  $xy$ -plane, the analogous treatment leads to  $\Gamma_s = E_g, \Gamma_t = A_{2u}$ . These are the only two possibilities for the  $A_{1g}$  ground state: DICD can appear at an  $A_{2g}$  state (through the intermediate  $E_u$ ) or at an  $E_g$  state (through an intermediate  $A_{2u}$ ).

In Table I, the symmetry rules have been used to determine the possible symmetries of the states  $|A^s\rangle, |A^t\rangle$  for various ground state symmetries for octahedral ( $O_h$ ) and square planar ( $D_{4h}$ ) complexes. Similar tables are readily compiled for any other point group using the symmetry rules.

Finally, it should be noted that the states  $|A^0\rangle, |A^s\rangle, |A^t\rangle$  should all have the same multiplicity so that all transitions between them will be spin-allowed.

## Applications

The lowest energy transitions of metal complexes are usually the  $d-d$  transitions of the metal ion, the  $d$ -orbitals being strongly perturbed by the ligands.<sup>14,15</sup> If the ligand field has inversion symmetry about the metal ion (e.g.  $O_h$  and  $D_{4h}$  complexes), such transi-

tions may be magnetic-dipole allowed but are electric-dipole forbidden. It follows that such transitions may exhibit DICD (provided they are magnetic-dipole allowed) but cannot act as intermediates in the induction process. Although the  $d-d$  transitions may become weakly electric-dipole allowed through such mechanisms as vibronic coupling, it is highly unlikely that they could contribute to the induction process by acting as intermediates as DICD is already a small effect and thus will be seen only for large inducibilities. It may be expected therefore that the intermediate states in the induction process are the charge transfer states that are common in coordination compounds, as these are generally strongly electric-dipole allowed. If the ligand field does not have inversion symmetry, some of the  $d-d$  transitions may become electric-dipole allowed by symmetry. In general, however, the  $d-d$  transitions are still relatively weak, so that charge transfer states would seem to be the intermediates in such systems as well.

Typical of complexes showing strong charge transfer bands are octahedral hexacarbonyls and hexahalides. A few particular examples should suffice to illustrate the features of such systems. The hexacarbonyls Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub> have ground state symmetries <sup>1</sup>A<sub>1g</sub>, so that application of the symmetry rules predicts that states of symmetry <sup>1</sup>T<sub>1g</sub> (which are magnetic-dipole allowed) may be DICD-active through intermediate states of symmetry <sup>1</sup>T<sub>1u</sub>. Spectroscopic studies<sup>16</sup> of these complexes have shown that there is a <sup>1</sup>T<sub>1g</sub> state at about 30,000 cm<sup>-1</sup>, and strong <sup>1</sup>T<sub>1u</sub> charge transfer states at 35,000 and 43,000 cm<sup>-1</sup>. Thus a DICD band should be observable in the region of the <sup>1</sup>T<sub>1g</sub> transition. The hexahalides of the  $d^6$  ions of the Fe, Co, Ni groups also have <sup>1</sup>A<sub>1g</sub> ground states, with strong low-lying <sup>1</sup>T<sub>1u</sub> charge transfer states.<sup>17</sup> In this case then the <sup>1</sup>T<sub>1g</sub> states should also be DICD-active.

Another interesting example is that of the D<sub>4h</sub> halide complexes (square-planar) of the Ni group (Ni, Pd, Pt). The ground state is <sup>1</sup>A<sub>1g</sub>, so that from Table I it follows that the <sup>1</sup>A<sub>2g</sub> may be DICD-active through <sup>1</sup>E<sub>u</sub>, or the <sup>1</sup>E<sub>g</sub> through the <sup>1</sup>A<sub>2u</sub>. It appears that the <sup>1</sup>E<sub>2u</sub> bands are much stronger than the <sup>1</sup>A<sub>2u</sub> bands in these complexes,<sup>17</sup> so that the <sup>1</sup>A<sub>2g</sub> may be expected to have the stronger DICD. This is indeed found to be the case for PtCl<sub>4</sub><sup>2-</sup>, where Bosnich<sup>6</sup> found that CD was induced in the <sup>1</sup>A<sub>2g</sub>, but not the <sup>1</sup>E<sub>g</sub>.

The appearance of strong low-energy charge transfer bands seems quite general for halide complexes, and these would seem to be good systems for future DICD studies, especially if the chiral species is also chosen to be negatively charged to avoid association. The necessity for having relatively low-lying charge transfer states is the appearance of the transition energy  $\epsilon_t$  in the denominator of the induced rotatory strength; however, equally if not more important is the necessity for both  $\vec{\mu}^{st}$ ,  $\vec{\mu}^{to}$  to be large, *i.e.* both transitions

$|A^0\rangle \rightarrow |A^t\rangle$  and  $|A^s\rangle \rightarrow |A^t\rangle$  must be strongly electric-dipole allowed.

### The Inducing Power

Thus far the major concern has been the determination of the conditions for a non-vanishing inducibility of the achiral species A. It remains to discuss the properties of the chiral species C which lead to strong DICD in A.

The first excited state of C,  $|C^u\rangle$ , should lie energetically above the state of the achiral species  $|A^s\rangle$  so as not to mask the DICD of A. At the same time, however, the transition energies  $\epsilon_s$ ,  $\epsilon_u$  should be as close as possible to maximise the effect. This follows from the appearance of the quantity  $(\epsilon_u - \epsilon_s)$  in the denominator of the induced rotatory strength.

A high inducing power requires the existence of two states  $|C^u\rangle$ ,  $|C^v\rangle$  which are both linked to the ground state and to each other by strong electric dipole transition moments, no two of which may be colinear. As a general rule therefore the chiral species should lack as many symmetry elements as possible, and preferably be asymmetric as distinct from merely chiral. Again, it may be noted that  $d-d$  transitions of chiral complexes are still generally weak, so that these will be unsuitable as inducing agents unless several strongly-allowed ligand transitions exist with the required combinations of electric transition moments; asymmetric organic species should, in general, be used.

The chiral species should also be chosen judiciously so that association with the achiral species may be neglected. This may be done by avoiding systems where A and C are of apposite charge and using, if possible, species of similar or zero charge. Once the chiral species is chosen, it may be characterised by its inducing power and its transition energies. These may then be assumed constant and the effect for a range of achiral species measured or predicted.

### References

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