Inorganica Chimica Acta, *122* (1986) 25–30

d–d Transitions of Co(III) Complexes Studied by Associated Induced Circular Dichroism

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(Received May 26, 1986)

Abstract

The circular dichroism (CD) induced, by tartatic acid, into magnetic dipole allowed d–d transitions of a range of Co(III) complexes, is studied experimentally and theoretically. With the aid of the results from a symmetry analysis of the independent systems/perturbation approach to CD, it is possible to interpret the experimentally determined spectra. The relative band signs and band magnitudes are found to be consistent only with a second order, geometry dependent mechanism. The results can be extended to other systems where the preferred chiral inducer/achiral chromophore adduct geometry is defined by the symmetry of the achiral chromophore.

I. Introduction

Circular dichroism (CD) of magnetic dipole allowed d–d transitions has proved to be a useful tool in the study of metal complexes [1–3]**. Generally the complexes studied have been intrinsically chiral complexes, where the aim has been to determine the absolute configuration of the complex, or the conformation of its ligands. More recently, the use of CD has been extended, both theoretically [4, 5] and experimentally [5] to achiral metal complexes by considering solutions containing chiral species which do not preferentially orient themselves with respect to the metal complex of interest (dispersion induced CD, DICD). In between the extremes of natural CD and DICD is the situation where a chiral molecule associates in the second coordination sphere of an achiral metal complex with a preferential orientation thus inducing CD (associated induced CD, AICD) into the transitions of the complex. Most CD studies in this physical limit have focused on electric dipole allowed (eda) transitions of organic systems in which the CD is induced by the coupled oscillator mechanism [8, 9]**. Nordén [10] suggested AICD as a means of studying the geometry of an achiral metal complex/chiral molecule adduct (though his analysis in terms of an octahedral pseudoscalar regional rule is inconsistent with the results of this work). As yet little is known about the AICD of magnetic dipole allowed (mda) transitions. There is no reason to expect its behaviour to resemble that of either natural CD or DICD of related systems. The purpose of this work is to investigate the phenomenon of AICD, both theoretically and experimentally, aiming to understand the observed CD and its relationship (if any) to natural CD and DICD.

A CD spectrum is most useful when it can be interpreted in terms of an applicable well-defined theoretical model which links the observed spectrum to the electronic structure of the species being investigated. Whether a given theoretical model is applicable to a given situation is not always readily apparent. A means of resolving this dilemna has been provided, at least in part, by ref. 11 in which the independent systems/perturbation (ISP) approach is used to generate distinct models whose behaviour as a function of system symmetry are quite different. Thus by performing a systematic study of a series of systems in which symmetry is the main variable, it should be possible to elucidate the dominant CD mechanism (or mechanisms) and hence to interpret the spectra. As a general rule, it appears that where simple empirical rules have been successfully applied, system symmetry and the ISP approach can be used to give a theoretical justification for that success.

In this work we have chosen to study the CD induced by L-(+)-tartaric acid into the lowest energy d–d transition of a series of Co(III) complexes of varying symmetry. Such systems are appropriate for a systematic AICD study as is discussed below; in addition data from the previous DICD study of Co(III) complexes [6] will prove useful in the analysis of the spectra. In order to provide background with which to understand the experimental data given in section III, section II contains a qualitative discussion of the ISP approach. Discussion of the relevant equations is postponed until section IV where they are used to understand the observed AICD spectra.

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**And refs. therein.

0020-1693/86/$3.50

II. The ISP Approach

In the ISP approach to CD the chiral system being studied is *sub*-divided into separate non-exchanging chromophoric units such that the CD-active transition is essentially localized in an achiral chromophore (**A**) which is chirally perturbed through its interaction with the remainder of the system (**C**). Systems for which such a division is not possible do not concern us here since they are unique and cannot be seen as part of a series.

In this work we are interested in the AICD of mda transitions (and in particular that of the T_{1g} d–d transition of Co(III) metal complexes), for which the ISP approach of ref. 11 is appropriate (other approaches were analysed in that work and will not be discussed here). In this approach, the CD induced into a mda transition of an achiral chromophore, **A**, by the chiral perturbation of **C** is expressed, using perturbation theory. If the **A**–**C** interaction is represented by a multipole expansion, then the CD strength can be written as a sum of terms dependent only on (i) **A** and **C** transition multipole moments and transition energies, (ii) the **A**–**C** distance, r_{AC}, and (iii) the position of **C** in the **A** coordinate system, denoted $r_{AC}(X, Y, Z)$. The key feature of the analysis of ref. 11 is that the component terms of the full perturbation expression for the CD strength are grouped according to their operator products and then analysed using the Generalized Selection Rules (GSR) of Schipper [13] in a manner made possible by the point group augmentation procedure of ref. 14. The main factor which determines the relative significance of those terms surviving the GSR procedure proves to be the $r_{AC}{}^{-n}$ component of each term: the larger n, the smaller the term. As n increases both with increasing order of perturbation theory and with increasing order of the multipoles in each term, this results in second order perturbation theory being necessary and sufficient for our purposes, and only two mechanisms, which we shall denote R′ and R″, being significant. R′ results from first order perturbation theory and is essentially the well known 'dynamic coupling' mechanism [15]. R″ results from second order perturbation theory and in the limit of rotational averaging of **A** with respect to **C** gives the DICD mechanism of Schipper [4].

The main difference between R′ and R″ from the point of view of identifying whether or not they contribute significantly to an observed spectrum is that R′ is extremely sensitive to the symmetry of the **A** chromophore, whereas R″ is not. The sensitivity of R′ is apparent in two ways. Firstly the R′ CD contributions for transitions of different polarization (e.g. the A_{2g} and E_g bands of a D_{4h} Co(III) complex) generally depend on different orders of multipole moments, thus have different r_{AC} dependence, and so have completely different magnitudes of CD strengths. Secondly, within a series of compounds, increasing the **A** symmetry increases the order of the multipoles on **A** required by the first non-vanishing term, thus increases the power of its inverse distance dependence, and so reduces the magnitude of the observed CD. The limiting case of this behaviour is for spherically symmetric or rotationally averaged systems where all the first order CD mechanisms vanish.

The T_{1g} d–d bands of d[Co(en)$_3$]$^{3+}$ and l-[Co(mal)$_2$en]$^-$ provide a clear illustration of the symmetry dependence of R′. Purely from geometrical considerations we can deduce that en distorts the Co(N)$_6$ d–d chromophore resulting in a D_{3d} **A** chromophore, and the [Co(mal)$_2$en]$^-$ d–d chromophore C_{2v} symmetry. Now, if R′ is the dominant mechanism one would expect the D_{3d} system to have a larger E band (quadrupole dependent, hence $r_{AC}{}^{-4}$), and a smaller A_2 band (hexadecapole dependent, hence $r_{AC}{}^{-6}$). In addition one would expect the C_{2v} system to have 3 bands, 2 dipole dependent and 1 quadrupole dependent. So, unless cancellation effects obscure this one would expect 2 larger and 1 smaller band. What is observed [1] is in fact completely consistent with these predictions: d-{Co(en)$_3$]$^{3+}$ has two T_{1g} component bands, the E band with $\Delta\epsilon = 1.89$ and the A_2 band with $\Delta\epsilon = -0.17$, and l-[Co(mal)$_2$en]$^-$ has 3 T_{1g} components with $\Delta\epsilon = 2.8, -2.3$ and 1.0.

By way of contrast with R′, the magnitude of the R″ contribution to the observed CD is not a sensitive function of the symmetry of the system. The first non-vanishing R″ CD contribution always depends only on **A** dipole moments, and always has $r_{AC}{}^{-6}$ distance dependence. This fact was illustrated by the DICD spectra of ref. 6 where the only effect of increasing the **A** symmetry was to reduce the number of peaks observable in the spectra.

We shall make use of the symmetry dependence of R′ and symmetry independence of R″ to determine the relative significance of the two mechanisms in the series of AICD experiments which are discussed in the next section. As we shall see, R″ proves to be dominant, so section IV is devoted to a brief discussion of the actual form of the R″ terms followed by the interpretation of the AICD spectra. Some indication of the application to which R′ can be put has been given in this work and reference 11, further discussion of this is postponed until a later publication.

III. Experimental

Systems Studied

The achiral chromophore, **A**, and the chiral inducer, **C**, in an AICD experiment must satisfy the following criteria:

(i) **A** and **C** must be mutually soluble in an achiral solvent;

(ii) **A** and **C** systems must associate in a preferential orientation;

(iii) **A** and **C** must not react during the course of the experiment;

(iv) **C** must be spectroscopically transparent in the region of the **A** transition(s) which are being studied, so that any observed CD is AICD, not natural CD of **C**;

(v) The AICD must be large enough to be detectable.

In addition, for our mechanistic studies, we require that the **A** chosen must have a range of symmetries.

The systems chosen for this work which satisfy all the above criteria are the following series of achiral Co(III) complexes in 1M (+)-L-tartaric acid/H_2O solutions: $[Co(NH_3)_6]Cl_3$, *trans*-$[Co(en)_2Cl_2]Cl$, $[Co(NH_3)_5Br]Br_2$, *cis*-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$, *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$. There are a few points to note about the systems chosen in relationship to the list of requirements given above.

(i) In general, the concentrations of the complex solutions were ~0.03 M, though the relative insolubility of $[Co(NH_3)_5Br]Br_2$ meant concentrations of 0.007 M were used.

(ii) Tartaric acid is known to associate to Co(III) amine complexes in the second coordination sphere [10, 12, 16].

(iii) $[Co(NH_3)_4H_2OCl]^{2+}$ does in fact react with the tartaric acid on the timescale of minutes, so repeat scans (see below) could not be performed on a single sample. (As an aside, it is interesting to note that the AICD provides a very convenient technique for monitoring the substitution reaction since the reactant and product have significantly different T_{1g} d–d transition energies).

(iv) Tartaric acid is known to induce CD into Co(III) complexes in a detectable manner [10, 16] although there has been no systematic experimental and theoretical symmetry study of the kind attempted in this work.

(v) The complexes chosen have the required symmetry range in their d–d chromophores (metal and directly ligating atoms), *viz.* O_h, D_{4h}, C_{4v}, C_{2v}, C_s (order is the same as that of the list of complexes given above).

In addition, there is basic information available about the d–d spectroscopy of Co(III) complexes including the previous DICD study of these complexes provides information that will prove useful later.

Method

The CD spectra were measured on a Jasco-500C spectropolarimeter with the DP-500N data processor attachment. The data processor enabled the baselines to be subtracted directly from the stored spectra and, with the exception of the aquo-chloro complex discussed above, enabled accumulation of repeated scans of the spectra and thus reduction in noise. The error bar in Fig. 1 includes concentration errors and the uncertainty in the magnitude of the CD. The general features of each spectrum as illustrated were reproducible on newly prepared solutions. All complexes were recrystallized prior to use. The (+)-L-tartaric acid was commercially available. Normal absorption spectra were run on each sample directly after the CD spectrum. The presence of the tartaric acid made no detectable difference to the normal absorption (unless a substitution reaction had occurred). The normal absorption spectra are given in Fig. 2 for completeness. Temperature was maintained at 20 ± 2 °C.

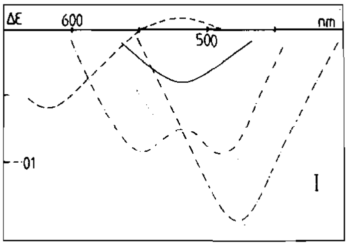

Fig. 1. AICD induced into $[Co(NH_3)_6]^{3+}$ — · —; *trans*-$[Co(en)_2Cl_2]^+$ – – –; $[Co(NH_3)_5Br]^{2+}$ – ·· –; $[Co(NH_3)_4(H_2O)_2]^{3+}$ ……; and $[Co(NH_3)_4H_2OCl]^{2+}$ ——; by 1 M (+)-L-tartaric acid (extinction coefficients given per mol of Co(III)).

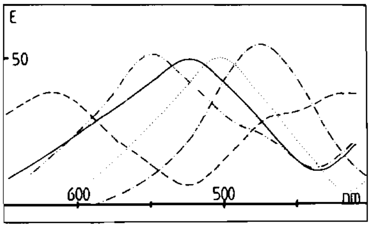

Fig. 2. Normal absorption spectra corresponding to the AICD spectra of Fig. 1.

Inspection of Fig. 1 shows that the behaviour of the CD magnitude as a function of symmetry is inconsistent with the symmetry dependence of the R′ mechanism: the smallest CD signal belongs to the lowest (rather than highest) symmetry d–d chromophore, the largest belongs to the highest symmetry d–d chromophore, and the remaining spectra show no trend of magnitude *versus* symmetry. This suggests that R″ is dominant for these systems.

The dominance of a second order mechanism over a first order one may at first sight be somewhat surprising. However, the reason for this is not difficult to find. The geometries postulated for the **A**–**C** adducts (see below) all have either $X = 0$ or $Y = 0$, and the C_{2v} complex has both $X = 0$ and $Y = 0$. Inspection of the R′ ICD expressions of ref. 11 shows that these geometries cause the isotropic (and hence larger) polarizability contributions to R′ to vanish, resulting in R″ being dominant. Thus, the results of this work can be applied to all systems where similar **A**–**C** adduct geometries are relevant. Effectively this reduces to those cases where the adduct geometry is defined by **A** symmetry.

IV. R″ and the AICD Spectra

The R″ CD mechanism results from the second order independent systems approach. Its significance was first realized by Schipper [17] when he considered rotationally averaged systems (the DICD limit) for which all first order mechanisms vanish. The fact that even in the rotationally averaged limit R″ requires only dipole–dipole coupling and hence r_{AC}^{-6} distance dependence [4] suggests that R″ (in its unaveraged form) may also be significant in non-DICD situations. In fact we have just seen this to be the case (though R″ is not as widely applicable as initially envisaged by Schipper [18]). The relevant R″ theoretical expressions are given below and discussed in relationship to the spectra of Fig. 1. The full derivation of the expressions is given elsewhere [11] so not included here.

R″ CD Expressions (Transition Polarizations are those of the Magnetic Dipole Moment)

C_{2v}, D_{2h} and z-polarized transitions of C_s, C_{2h}:

x-polarized:

$$R'' = r_{\mathrm{AC}}^{-6}\beta_{\mathrm{C}}(\mu_z m_x \mu_y - \mu_y m_x \mu_z)(2 - 3X^2) \qquad (1)$$

y-polarized:

$$R'' = r_{\mathrm{AC}}^{-6}\beta_{\mathrm{C}}(\mu_x m_y \mu_z - \mu_z m_y \mu_x)(2 - 3Y^2) \qquad (2)$$

z-polarized:

$$R'' = r_{\mathrm{AC}}^{-6}\beta_{\mathrm{C}}(\mu_y m_z \mu_x - \mu_x m_z \mu_y)(2 - 3Z^2) \qquad (3)$$

Point groups with x and y degenerate:

x/y-polarized:

$$R'' = (1/2) r_{\mathrm{AC}}^{-6}\beta_{\mathrm{C}}(\mu_x m_y \mu_z - \mu_y m_x \mu_z + \mu_z m_x \mu_y - \mu_z m_y \mu_x)(1 + 3Z^2) \qquad (4)$$

z-polarized:

$$R'' = r_{\mathrm{AC}}^{-6}\beta_{\mathrm{C}}(\mu_y m_z \mu_x - \mu_x m_z \mu_y)(2 - 3Z^2) \qquad (5)$$

Point groups with x, y and z degenerate:

$x/y/z$-polarized: $R'' = r_{\mathrm{AC}}^{-6}\beta_{\mathrm{C}}(\boldsymbol{\mu} \times \boldsymbol{m}\cdot\boldsymbol{\mu}) \qquad (6)$

The notation used in eqns. (1)–(6) is as follows.

(1) The expressions are given only for transitions whose polarization is defined by symmetry.

(2) Explicit mention of states, transition energies and 'Im' (the imaginary part of) have been removed for clarity. The full expression can readily be recovered using ref. 11 since the ordering of the operators has been strictly retained. So little data is available about both the charge transfer transitions of the complexes being studied and the UV and higher transitions of tartaric acid that explicit inclusion of states and transition energies is irrelevant for our purposes. It is sufficient for us to note that states of all symmetries are available so that state selection rules [13] do not offer any further simplification of the CD expressions.

(3) $\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)$ and $\boldsymbol{m} = (m_x, m_y, m_z)$ are, respectively, the electric and magnetic dipole transition moment operators of the achiral d–d chromophore **A**. $\beta_{\mathrm{C}} = (1/6)(\boldsymbol{\mu}_{\mathrm{C}} \times \boldsymbol{\mu}_{\mathrm{C}}\cdot\boldsymbol{\mu}_{\mathrm{C}})$ is the operator isotropic hyperpolarizability of **C** (tartaric acid in our case), where $\boldsymbol{\mu}_{\mathrm{C}}$ is an electric dipole transition moment of **C**·(X, Y, Z) is the position of the **C** origin in the symmetry determined coordinate system of **A** (the origin of tartaric acid is in the centre of the centre C–C bond).

(4) It has been assumed that the isotropic hyperpolarizability of tartaric acid is significantly larger than the non-isotropic hyperpolarizability.

We are now in a position to analyse eqns. (1)–(6). Each equation has four factors: the **A**–**C** distance dependence, the operator isotropic hyperpolarizability of **C**, an **A** moment product and a factor dependent on (X, Y, Z) which gives the geometry dependence. We shall discuss the significance of each of these components in turn.

r_{AC} is always positive, so does not affect the CD band sign. In addition in eqns. (1)–(6) the r_{AC} dependence is the same, so, for a given **A**–**C** system, the distance dependent factor is the same for all transitions of that system. Thus, for example, any magnitude variation between the A_2 and E of $[\mathrm{Co(NH_3)Br}]^{2+}$ is due to the other three factors. This is in contrast to the R′ mechanism as noted above.

As β_{C} is a constant in all the experiments recorded here it suffices to say that its magnitude is determined by the nature of **C** and its sign determined by the handedness of **C**.

The final factor is in many ways the most interesting in this context as it is the one factor that played no part in the earlier analysis of DICD spectra. It can be determined directly from the geometry of the tartaric acid/metal complex adduct, and it modifies both the sign and the magnitude of the observed CD band. For our purposes electrostatic arguments (tartaric acid/halide repulsions etc.) provide sufficiently accurate adduct geometries. The approximate geometries illustrated in Fig. 3 have (X, Y, Z) values

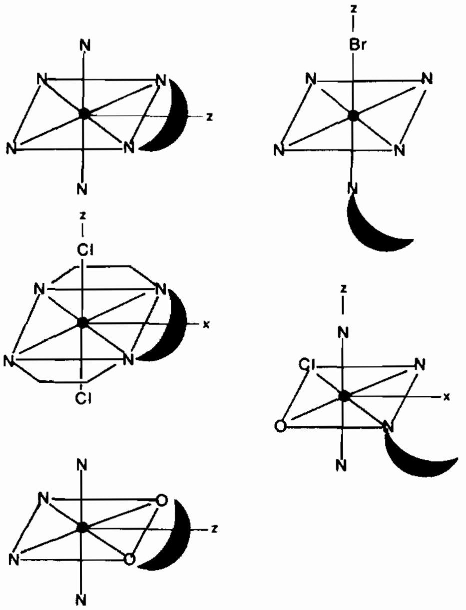

Fig. 3. Schematic illustration of the most probable tartaric acid/metal complex adduct geometries determined using electrostatics.

as follows (order as for the list of complexes above): (0, 0, 1), (0, 1, 0), (0, 0, $>\sqrt{3}/2$), (0, 0, 1) and (0, 0, $<\sqrt{3}/2$). In order to tie the discussion together we must digress to consider DICD expressions. Expressions for dispersion induced CD are derived from eqns. (1)–(6) by integrating out the geometry dependence. In addition we note that (i) in any series of spectra with the same chiral inducer, β_C is a multiplicative constant, and (ii) r_{AC}^{-6} is the same for all transitions of a given complex/inducer adduct. Thus, although information about the states involved in the **A** moment product is not readily available, the problem can be circumvented by making use of the DICD spectra of the same Co(III) complexes, if we also assume that the implicit energy terms do not cause any erratic behaviour in the sign or magnitude of the DICD spectra (hence the choice of fructose).

We can write the tartaric acid AICD for a given complex and transition polarization in terms of the corresponding DICD as

$$
\begin{aligned}
&(j\text{-polarized T AICD})\\
&\quad\approx \{r_{AC}^{-6}A_j\beta_C\}_F \times \{(r_{AC})_T/(r_{AC})_F\}^{-6}\\
&\qquad\times \{(\beta_C)_T/(\beta_C)_F\} \times \{\text{geometry factor}\}\\
&\quad\approx \{j\text{-polarized F DICD}\}\\
&\qquad\times [(r_{AC}^{-6}\beta_C)_T/(r_{AC}^{-6}\beta_C)_F]\\
&\qquad\times \{\text{geometry factor}\} \qquad (7)
\end{aligned}
$$

where T denotes tartaric acid and F denotes fructose. The sign of the term in square brackets is constant for any tartaric acid and fructose series so we can write

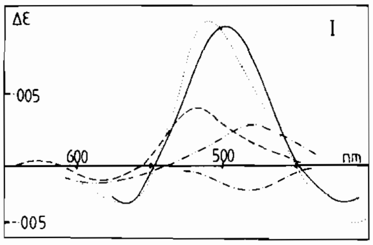

Fig. 4. DICD spectra corresponding to the AICD spectra of Fig. 1.

$$
\begin{aligned}
&(j\text{-polarized T AICD})\\
&\quad\approx \{\pm\} \times \{j\text{-polarized F DICD}\}\\
&\qquad\times \{\text{geometry factor}\} \qquad (8)
\end{aligned}
$$

Equation (8) together with the adduct geometries given above and the fructose DICD given in Fig. 4 enables us to determine the relative band signs predicted by R″ for the tartaric acid AICD. The information required to predict the band signs, the predictions and the observed band signs are given in Table I together with the assignments of the transitions deduced in ref. 6. The assignments are required in order to make the comparison between experiment and theory. Conversely one could use the relative band signs to assign the transitions.

The agreement shown in Table I between the theoretical predictions of the geometry dependent R″ CD mechanism and the observed AICD confirms the dominance of R″ for the tartaric acid/metal complex AICD since R′ cannot explain the observed band sign behaviour. In fact the band sign behaviour of the observed AICD is different from that common to both natural CD and DICD (in general both natural CD and DICD exhibit oscillating band signs under a T_{1g} band). For example, the natural CD [1] and DICD [6] of T_{1g} d–d transitions in complexes with *x*/*y* degenerate d–d chromophores generally exhibit two bands of opposite sign. This is also the case for the D_{4h} AICD of Fig. 1, but not for the C_{4v} AICD. A convincing explanation of this difference is provided by the geometry dependence of R″ as summarized in Table I. A similar example is that of the C_{2v} complex where on the basis of the natural CD and the DICD one might expect to see at least two and generally three transitions under the T_{1g} band. However only one band can be seen in the AICD, since (*cf.* Table I) the sign of the AICD for the three component transitions is the same so the three transitions overlap to give the appearance of a single transition.

No attempt has been made in this work to examine band magnitudes (except to note the effect

TABLE I. Summary of Information Required to Predict the AICD Band Signs Using the Geometry Dependent R″ Mechanism Together with the Observed AICD Band Signs for Various Tartaric Acid/Metal Complexes Adducts

Assignment (order of increasing energy)	$[Co(NH_3)_6]^{3+}$	$[Co(en)_2Cl_2]^+$		$[Co(NH_3)_5Br]^{2+}$		$[Co(NH_3)_4(H_2O)_2]^{3+}$			$[Co(NH_3)_4H_2OCl]^{2+}$		
	T_{1g}	E	A_2	E	A_2	B_1	A_2	B_2	A_2	–	–
Fructose DICD sign	–	–	+	–	+	–	+	–	–	+	–
Geometry factor	+	+	–	+	+	+	–	+	+		
Predicted relative AICD sign	–	–	–	–	+	–	–	–	–		
Observed AICD sign	–	–	–	–	+		–			–	

of the **A**–**C** distance) since such a study does require more detailed information about transition energies and moments than is provided by a parallel DICD study. This information is not available in the literature for the systems being studied and the energies of most relevant transitions are too high to be experimentally accessible.

V. Conclusion

In conclusion then we can say that the geometry dependent R″ mechanism is dominant for the tartaric acid/Co(III) complex AICD and that the theoretical analysis of the mechanism proved to be a means of understanding the observed spectra. It is reasonable to hypothesise that R″ is also dominant for AICD systems where the **A**–**C** linkage is related to the symmetry determined axes of **A**. As was illustrated in section IV, the analysis of spectra where the geometry dependent R″ mechanism is dominant is considerably abetted by the results from a complementary DICD study. In this context, and in the wider context of CD studies in general, the importance of well-defined theoretical models, with simple criteria for discriminating between them, and of a systematic study must not be underestimated.

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