

## The Magnetic Circular Dichroism Spectrum of the Tetraiodocobaltate(II) Ion

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**Summary** The magnetic circular dichroism (m.c.d.) spectrum is used to test an assignment of the ligand-field transitions of  $\text{CoI}_4^{2-}$  based on a molecular orbital analysis of electron repulsion and spin-orbit coupling.

MAGNETIC CIRCULAR DICHOISM has proved a powerful technique for the assignment of many classes of optical transition.<sup>1</sup> In order to test a molecular orbital scheme capable of a unified description of ligand-field and charge-transfer states in transition-metal complexes,<sup>2</sup> we have sought systems with a large number of optical transitions of both types. Combining the highest possible point-group symmetry with the need to avoid the vibronic mechanism as a source of the intensity, we have chosen the tetrahedral tetrahalogeno-species of the first transition series. Among these, the cobalt(II) ions combine a large number of ligand-field transitions with a series of readily accessible charge-transfer transitions. We demonstrate here the use of m.c.d. data as applied to the ligand-field transitions of the  $\text{CoI}_4^{2-}$  ion.

Crystals of  $(\text{NEt}_4)_2\text{ZnI}_4$  doped with  $\text{CoI}_4^{2-}$  were grown from nitromethane solution. The habit of these tetragonal crystals is identical with that of  $(\text{NEt}_4)_2\text{NiCl}_4$ , whose structure was determined by Stucky,<sup>3</sup> and to which the analogous  $\text{CoCl}_4^{2-}$  and  $\text{CoBr}_4^{2-}$  salts are isomorphous.<sup>3</sup> The  $\text{CoI}_4^{2-}$  ions lie at sites of  $D_{2d}$  symmetry with their  $S_4$  axes coincident with the optic axis, which in turn is perpendicular to the well developed square crystal face on which it was mounted. M.c.d. spectra were measured at 4.2K,

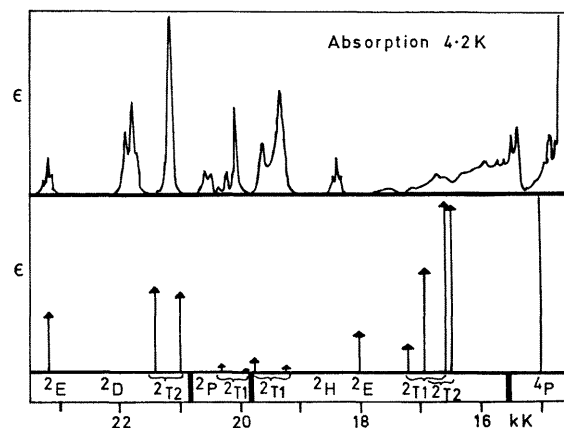


FIGURE 1. Experimental and calculated absorption spectrum of  $\text{CoI}_4^{2-}$  in the doublet ligand-field region. The heights of the vertical lines represent calculated dipole strengths.

using apparatus constructed in this laboratory, in a magnetic field of 25 kg. Absorption spectra at 4.2K were obtained with a Cary 14 spectrophotometer.

The absorption and m.c.d. spectra of the ligand-field doublets are shown in Figures 1 and 2. In contrast to the tetrachloro- and tetrabromo-complexes,<sup>4</sup> little vibrational fine structure is observed in the spectrum of  $\text{CoI}_4^{2-}$  and the

main features arise from separated spin-orbit components of terms arising from the tetrahedral field. For example, the  ${}^2D$  free-ion term gives rise to the  ${}^2E$  and  ${}^2T_2$  terms near 22 kK, the latter being further split into the  $E''$  and  $U'$  spin-orbit components at 21.2 and 21.8 kK, respectively. Temperature variations demonstrate that the dominant contribution to the m.c.d. comes from  $C$  terms<sup>5</sup> whose origin lies in the Zeeman splitting of the  ${}^4A_2$  ground state. Saturation effects have also been observed at high fields and low temperatures.

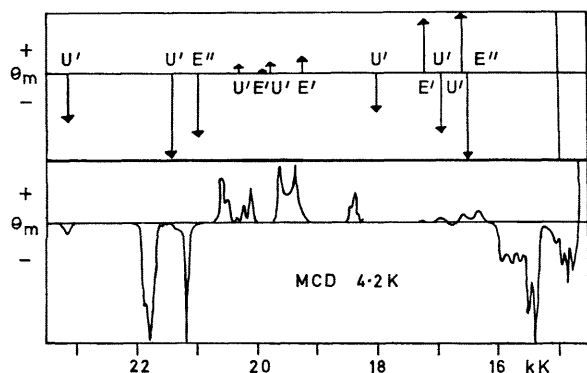


FIGURE 2. Experimental and calculated m.c.d. spectrum of  $\text{CoI}_4^{2-}$  in the doublet ligand-field region.

To interpret the spectra in detail, we assume that the intensity of the doublets is derived from an admixture of quartet wavefunctions *via* second-order spin-orbit coupling. Contributions are to be expected not only from  ${}^4T_1$  ligand-field transitions but also from the nearby charge-transfer transition of the same symmetry.<sup>6</sup> First-order spin-orbit coupling splits  ${}^4T_1(P)$  into  $E'$ ,  $E''$ ,  $3/2 U'$  and  $5/2 U'$  components for which  $C/D$  is predicted to be  $-5/2$ ,  $3/2$ ,  $-1$ ,  $3/2$  Bohr magnetons.<sup>7</sup> Figure 3 shows the absorption and m.c.d. spectra of  ${}^4T_1(P)$ . We assign the transitions at 14.45, 13.75, 13.22, and 12.78 kK to the  $E'$ ,  $3/2 U'$ ,  $E''$ , and  $5/2 U'$  components, respectively, in agreement with previous experiments on  $\text{CoCl}_4^{2-}$ .<sup>7</sup> Whereas the signs and magnitudes of  $C/D$  for the  $E'$  and  $E''$  doublet components are determined by those of the corresponding quartets, the  $U'$  doublet states reflect the relative contributions of the  $3/2 U'$  and  $5/2 U'$  quartet components, and thus constitute a test of the doublet wavefunctions, which we have attempted to calculate.

Empirical molecular-orbital eigenvectors were derived by least-squares fitting term energies, calculated from a molecular-orbital treatment of electron-electron repulsion parameters,<sup>3</sup> to the experimental baricentres. These eigenvectors were in turn employed in a diagonalisation of

the complete molecular spin-orbit interaction using a molecular orbital basis set. The basis includes charge-transfer as well as ligand-field configurations. The relative absorption intensities and  $C$  terms were computed from the resulting eigenfunctions and are shown diagrammatically in the Figures. Many detailed features of both absorption and m.c.d. spectra are satisfactorily reproduced. For example the components of  ${}^2D$ , near 22 kK, referred to previously are correctly predicted in energy, relative intensity, and magnitude of the  $C$  terms.

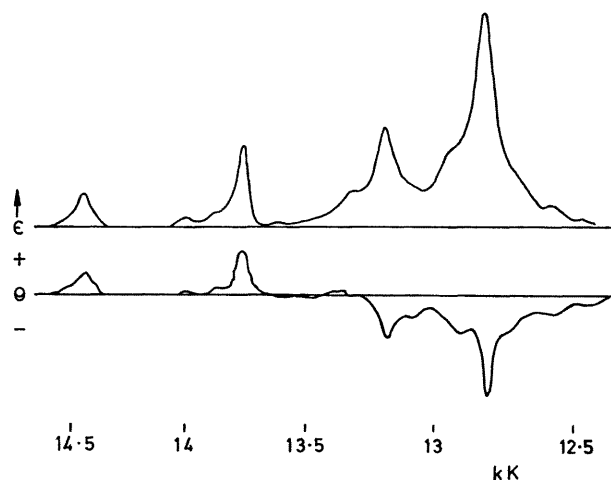


FIGURE 3. Absorption and m.c.d. spectra of  $\text{CoI}_4^{2-}$  in the  ${}^4T_1(P)$  region.

The negative m.c.d. of  $U'({}^2T_2, D)$  is particularly informative in that the sign of this component is only predicted negative if the contributions of charge-transfer states dominate the intensity mechanism.

The relative intensities and m.c.d. parameters of the lower-energy doublets are also satisfactorily accounted for, though the energies of these bands, which were not included in the original least-squares fitting procedure, appear uniformly shifted from those observed. Only one band, which we have assigned to  $U'({}^2E, H)$  at 18.4 kK, has an experimental  $C$ -term sign disagreeing with our prediction.

Corresponding data on the doublet states of  $\text{CoCl}_4^{2-}$  and  $\text{CoBr}_4^{2-}$  have also been obtained under conditions of higher resolution,<sup>4</sup> and will be reported later.

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<sup>1</sup> See, e.g., *Symposia Faraday Soc.*, 1969, 3.

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