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Electronic and Magnetic Circular Dichroism Spectra of the Triiodide Ion

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Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for the I_3^- ion in CH_3CN and in aqueous iodide (0.050 M I^-, 0.010 M H^+) solution. In addition to the two intense UV bands at 2.8 and 3.4 μm^{-1} a weak shoulder is observed near 1.9 μm^{-1}. The MCD consists of a negative minimum at 1.8 μm^{-1} associated with the weak shoulder in the absorption, a negative *B* term at 2.4 μm^{-1}, a positive *B* term near the maximum of the 2.8-μm^{-1} band, and a positive *A* term (or *pseudo-A* term) in the vicinity of the 3.4-μm^{-1} band. The weak shoulder at 1.9 μm^{-1} is assigned to the parity-forbidden transition to the $\Pi_g(^1\Pi_g)$ state of the $(2\pi_u)^3(2\sigma_u^+)$ excited configuration, while the absorption intensity for the UV bands is attributed to transitions to Σ_u^+ spin–orbit states of the $(\pi_g)^3(2\sigma_u^+)$ and $(\sigma_g^+)(2\sigma_u^+)$ excited configurations. The MCD is interpreted in terms of *B* terms resulting from the magnetic mixing of Π_u spin–orbit states of these same excited configurations with the Σ_u^+ states. The MO model used as a basis for interpretation is constructed from 5p I orbitals and assumes I_3^- remains linear in the excited states responsible for the spectra.

Introduction

The triiodide ion has a characteristic electronic spectrum that is well-known[2-5] and consists of two intense bands in the UV near 353 and 287 nm for aqueous solutions containing I_3^-(aq) and excess I^-. Strong bands at similar wavelengths are observed for KI crystals that contain I_3^- produced additively or electrolytically.[6] The familiar red color of the I_3^- ion, which is presumed to be linear and symmetrical ($D_{\infty h}$) in solution, is caused by the long-wavelength tail of the UV absorption in the visible region. However, the detailed assignment of the I_3^- spectrum has not been established. In fact, disagreement exists as to the interpretation of the specific transitions responsible for the observed bands, and the nature of the lowest energy excited states of this simple triatomic ion is not yet clear. It was early noted[7] that the energy difference between the two intense UV bands (0.63 μm^{-1} for I_3^-(aq)) is similar to the $^2P_{3/2}$–$^2P_{1/2}$ spin–orbit splitting for the I atom (0.79 μm^{-1}).[8] A simple MO description[9,10] of I_3^- associates the lowest energy $\sigma_g \rightarrow \sigma_u$ transition with excited states that correlate with $I_2^-(^2\Sigma_u^+) + I(^2P)$, and therefore the two bands were ascribed to spin–orbit splitting. This interpretation was discredited[4] however when a comparison with a spectrum of Br_3^- showed a larger separation between two strong bands believed to be analogous to those of I_3^-. Since spin–orbit coupling for Br is less than for I ($\zeta_{4p} = 0.2457$ μm^{-1} compared to $\zeta_{5p} = 0.5069$ μm^{-1}),[11] the splitting is expected to be smaller for Br_3^-. An alternative interpretation involving a bent configuration in the lowest excited states was proposed.[4] However, as a result of a more recent examination of the Br_3^- results, the Br_3^- spectrum has now been called into question, and one of the strong bands is believed to be due to molecular Br_2.[6] Thus, the splitting in Br_3^- is likely substantially smaller than originally thought. The assignment of the I_3^- spectrum has also been approached from some valence-bond pseudopotential calculations.[10] These calculations, together with calculations on I_2^- and I_3^{2-}, suggest that the 353- and 287-nm bands result from transitions from the totally symmetric ground state $^1\Sigma_g^+$, which correlates with $I_2(^1\Sigma_g^+) + I^-(^1S)$ to $^1\Sigma_u^+$ correlating with $I_2^-(^2\Sigma_u^+) + I(^2P_{1/2})$ and $^1\Pi_u$ correlating with $I_2^-(^2\Pi_g) + I(^2P_{3/2})$, respectively. More recently, a different assignment of the two intense bands was proposed.[6] The transitions were assigned to *z*-polarized (*z* axis taken parallel to the molecular axis) transitions to Σ_u^+ states alone because *xy*-polarized transitions to Π_u excited states were considered to be too weak to be observed. This conclusion was based on the low absorption cross sections for X_2^- centers in crystals. The 353- and 287-nm bands therefore were assigned to transitions to the spin–orbit states $\Sigma_u^+(^3\Pi_u)$ and $\Sigma_u^+(^1\Sigma_u^+)$, respectively, both of which are strongly intermixed by spin–orbit coupling.

The lack of a firm interpretation of the UV spectrum and a coherent description of the important low-lying excited states is disappointing because NQR[12] and Mössbauer[13] studies suggest that the bonding in I_3^- can be considered to a good approximation as resulting from a simple three-centered MO system composed of 5p I orbitals with negligible involvement of 6s or 5d orbitals.[9,14] This description leads to a bond order of 0.5 and provides a prototype for three-centered p-orbital systems believed to be important in compounds of other *n*p block elements. Therefore, prompted in part by our interest in electronic structures of linear two-coordinate complexes and in part by a desire to better understand the nature of the low-lying excited states of I_3^-, we have measured and report here the magnetic circular dichroism (MCD)[15] spectrum for I_3^- in CH_3CN and in aqueous I^- solutions. Our results provide some new insight into the problem of interpreting the I_3^- UV spectrum.

Experimental Section

Solutions of I_3^- in CH_3CN were prepared by combining stoichiometric amounts of I_2 and $(n\text{-}C_4H_9)_4NI$. In all but the most dilute solutions (ca. 10^{-5} M), Beer's law was observed to hold for the I_3^- bands to within ±10%. As solutions were diluted, some weak absorption and characteristic MCD for I^- in CH_3CN[16] were noted at 246 nm (4.07 μm^{-1}) and 206 nm (4.85 μm^{-1}); the relatively small amount of I^- results from the dissociation in eq 1. Both I^- and I_2 are weakly absorbing in the region

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (1)$$

of the I_3^- absorptions. Aqueous solutions were prepared by dissolving I_2 in excess I^- solution because of the low stability of I_3^-(aq) in water (*K* for eq 1 at 25 °C is 1.4×10^{-3} M)[2]. The medium used for spectral measurements was 0.050 M I^- (KI) and and 0.010 M H^+ ($HClO_4$), and Beer's law was obeyed over the concentration range 4.6×10^{-3}–2.8×10^{-5} M. Aqueous solutions prepared with only stoichiometric amounts of I_2 and I^- showed considerable departure from Beer's law due to eq 1.

Absorption spectra were measured by means of a Cary 1501; both 0.100- and 1.00-cm path length cells were used. MCD measurements

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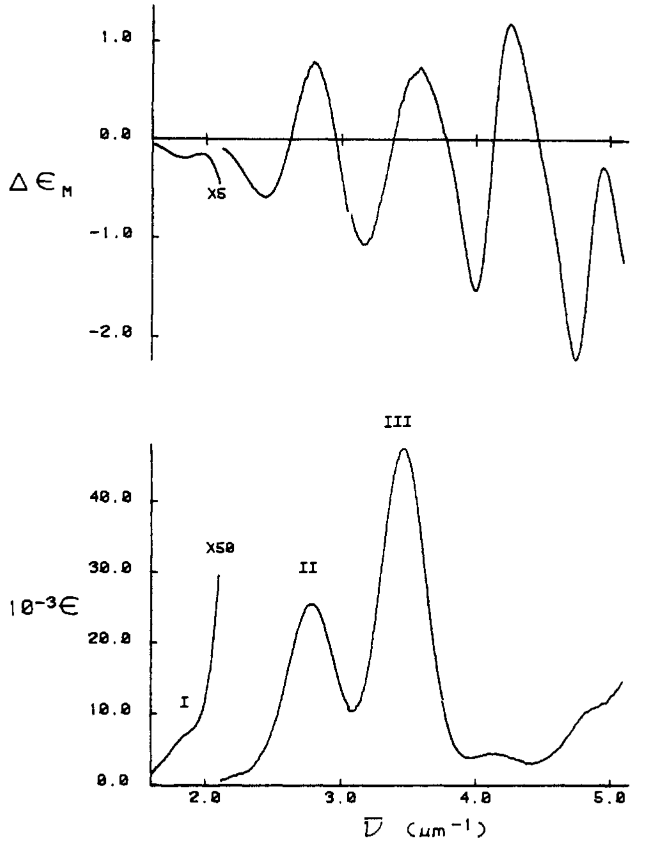

Figure 1. Absorption (lower curves) and MCD (upper curves) spectra of I_3^- in CH_3CN solution. The spectra above 3.9 μm^{-1} do not obey Beer's law; the absorptivities were determined for 6.5 × 10^{-5} M and are apparent values for this concentration. This portion of the spectra is ascribed to I^- (see text).

were made at 7.0 T by means of a computer-controlled spectrometer built at Northern Illinois University[17] equipped with a superconducting magnet (Oxford Instruments SM2-7 fitted with a room-temperature bore). The 7.0-T MCD measurements were accompanied simultaneously and synchronously by absorption measurement along the same light path.

Results and Discussion

Absorption and MCD Spectra. Figure 1 presents absorption and MCD spectra for I_3^- in CH_3CN. The portion of the spectra in Figure 1 above 3.9 μm^{-1} was obtained from a dilute solution (6.5 × 10^{-5} M). The absorption features at 4.07 and 4.85 μm^{-1} and their relatively strong corresponding MCD are due to I^- and compare favorably with absorption and MCD spectra published for I^- in CH_3CN.[16] The apparent absorptivities (Beer's law does not hold above 3.9 μm^{-1}) here for these I^- bands compared to those for I^- alone indicate that at 6.5 × 10^{-5} M the dissociation due to eq 1 is approximately 15–20%. However, with the possible exception of the region near the positive MCD maximum at 3.56 μm^{-1}, there is virtually no overlap between the I_3^- bands at lower energy with those due to I^-. Spectra for I_3^-(aq) in 0.050 M I^- and 0.010 M H^+ were quite similar to Figure 1 below 3.9 μm^{-1}. Above this energy measurements were not possible because of the strong I^-(aq) absorption. Quantitative spectral data for both CH_3CN and aqueous I^- solutions are collected in Table I. In both solutions a weak spectral feature was observed near 1.88 μm^{-1} (ϵ 140–150). This shoulder absorption is near a maximum observed for I_2 in cyclohexane solution (1.9 μm^{-1}, ϵ 940),[18] but the corresponding MCD is significantly different. A clear strong negative *A* term is observed[18] for I_2 extending from 1.7 to 2.3 μm^{-1} whereas only a weak negative minimum is observed here at 1.83 μm^{-1} in CH_3CN or 1.84 μm^{-1} in aqueous I^- solution. This difference, together with the fact that the weak shoulder can be observed clearly only at relatively high I_3^- concentrations where the dissociation to give I_2 (eq 1) would be small, lend support to the interpretation of the weak band as due to an electronic transition of I_3^- rather than I_2.

Table I. Spectral Data

	abs			MCD	
band	λ, nm	$\bar{\nu}$, μm^{-1}	ϵ, M^{-1} cm^{-1}	$\bar{\nu}$, μm^{-1}	$\Delta\epsilon_M$, M^{-1} cm^{-1} T^{-1}
		I_2 + [*n*-Bu_4N]I in CH_3CN			
I	531	1.88	155[a]	1.83	−0.039
				2.42	−0.61
II	363	2.76	25 400	2.77	+0.81
III	292	3.43	45 900	[b] 3.14	−1.07
				3.36	0
				3.56	+0.72
		I_2 + KI in 0.050 M KI-0.010 M $HClO_4$			
I	535	1.87	144[a]	1.84	−0.036
				2.51	−0.48
II	353	2.85	25 300	2.85	+0.55
III	287	3.48	41 400	[b] 3.23	−0.92
				3.47	0
				3.60	+0.59

[a] Shoulder. [b] *A* term or *pseudo-A* term.

Table II. Excited Configurations and States

confign[a]	zero-order states	spin-orbit states[b]
$(2\pi_u)^3(2\sigma_u^+)$	$^1\Pi_g$	(Π_g)
	$^3\Pi_g$	$(\Pi_g, \Sigma_g^+, \Sigma_g^-, \Delta_g)$
$(\pi_g)^3(2\sigma_u^+)$	$^1\Pi_u$	Π_u
	$^3\Pi_u$	$\Pi_u, \Sigma_u^+, (\Sigma_u^-, \Delta_u)$
$(\sigma_g^+)(2\sigma_u^+)$	$^1\Sigma_u^+$	Σ_u^+
	$^3\Sigma_u^+$	$\Pi_u, (\Sigma_u^-)$

[a] Filled orbitals omitted. [b] Forbidden states in parentheses.

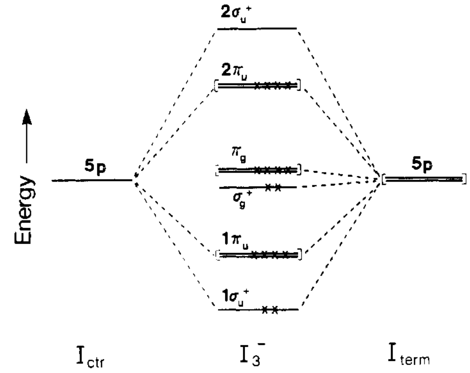

Figure 2. Molecular orbital energy levels for I_3^- constructed from 5p atomic orbitals. I_{ctr} is the central I atom; I_{term} are the terminal I atoms.

Energy Levels and Excited States. In order to provide a basis for interpreting the absorption and MCD spectra, Figure 2 presents a MO energy level scheme for the $D_{\infty h}$ I_3^- ion. This scheme is constructed with the approximation that the atomic orbitals of the I atoms important for bonding are primarily 5p. As noted earlier this approximation is consistent with the results of NQR and Mössbauer studies of salts of I_3^-.[12,13] The *z* axis is taken to be the molecular axis, and the highest filled orbital is $2\pi_u$. The ground state is thus totally symmetric, is diamagnetic, and is designated $^1\Sigma_g^+$. The lowest energy excited configurations together with their associated electronic states in $D_{\infty h}$ symmetry are listed in Table II. In $D_{\infty h}$ symmetry only transitions to Σ_u^+ (*z* polarized) and Π_u (*xy* polarized) states are allowed by electric dipole selection rules. However, because of the strong I 5p spin–orbit coupling, singlet and triplet states of Σ_u^+ or Π_u symmetry will be intermixed and transitions to states of formally triplet parentage can have significant intensity. The spin–orbit states expected for the lowest energy excited configurations are also included in Table II; they

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are characterized by a lack of spin multiplicity superscripts. The Σ_u^+ and Π_u spin–orbit states can be determined in terms of the zero-order singlet and triplet states in the absence of spin–orbit coupling. These states are given by eq 2 and 3, where a_j–e_j are

$$|\Pi_u(j)\rangle = a_j|^1\Pi_u\rangle + b_j|^3\Pi_u\rangle + c_j|^3\Sigma_u^+\rangle \qquad (2)$$

$$|\Sigma_u^+(j)\rangle = d_j|^3\Pi_u\rangle + e_j|^1\Sigma_u^+\rangle \qquad (3)$$

mixing coefficients that are determined by diagonalizing the secular determinants in eq 4 and 5. In eq 4 and 5, the energies

$$\begin{vmatrix} ^1\Pi_u - E & i\zeta/2 & -{}^1/_2\zeta \\ -i\zeta/2 & ^3\Pi_u - E & -i\zeta/2 \\ -{}^1/_2\zeta & i\zeta/2 & ^3\Sigma_u^+ - E \end{vmatrix} = 0 \qquad (4)$$

$$\begin{vmatrix} ^3\Pi_u + {}^1/_2\zeta - E & -({}^1/_2)^{1/2}\zeta \\ -({}^1/_2)^{1/2}\zeta & ^1\Sigma_u^+ - E \end{vmatrix} = 0 \qquad (5)$$

of the singlet and triplet zero-order states appear along the diagonal and $\zeta = \zeta_{5p}$ for I. The elements of these determinants are determined by approximating the MO's as combinations of pure 5p atomic orbitals.

MCD Terms.[15] Since the ground state of I_3^- is nondegenerate, only *A* and *B* terms are expected in the MCD (*C* terms will be absent). *A* terms originate from Zeeman splitting of degenerate states by the magnetic field and therefore may be observed only for the excited Π_u states of I_3^-. However, both the Π_u and Σ_u^+ states may exhibit *B* terms, which result from mixing of states by the field. For the space-averaged case appropriate for I_3^- in solution, the magnitudes of these terms are determined by the $\bar{A}_1$ and $\bar{B}_0$ parameters given by eq 6–8.[15] In eq 6–8 μ_B is the Bohr

$$\bar{A}_1(\Pi_u(j)) = (-1/2^{1/2}\mu_B)\langle\Pi_u(j)||\mu^{\Sigma_g^-}||\Pi_u(j)\rangle\ \bar{D}_0(\Pi_u(j)) \qquad (6)$$

$$\bar{B}_0(\Pi_u(j),\Pi_u(k)) = \mathrm{Re}\left(\frac{-2}{3(2^{1/2})\mu_B}\sum_{k\neq j}\frac{\langle\Pi_u(j)||\mu^{\Sigma_g^-}||\Pi_u(k)\rangle}{\Delta W_{kj}} \times \langle\Sigma_g^+||m^{\Pi_u}||\Pi_u(j)\rangle\langle\Pi_u(k)||m^{\Pi_u}||\Sigma_g^+\rangle\right) \qquad (7)$$

$$\bar{B}_0(\Sigma_u^+(j),\Pi_u(k)) = \mathrm{Re}\left(\frac{-2}{3\mu_B}\sum\frac{\langle\Sigma_u^+(j)||\mu^{\Pi_u}||\Pi_u(k)\rangle}{\Delta W_{kj}} \times \langle\Sigma_g^+||m^{\Sigma_u^+}||\Sigma_u^+(j)\rangle\langle\Pi_u(k)||m^{\Pi_u}||\Sigma_g^+\rangle\right) \qquad (8)$$

magneton, μ and m are the magnetic and electric moment operators, respectively, $\bar{D}_0(\Pi_u(j)) = -{}^1/_3\langle\Sigma_g^+||m^{\Pi_u}||\Pi_u(j)\rangle\langle\Pi_u(j)||m^{\Pi_u}||\Sigma_g^+\rangle$, the electric dipole strength of the $\Sigma_g^+ \rightarrow \Pi_u(j)$ transition, and $\Delta W_{kj} = W_k - W_j$, the energy difference between the states k and j. When the spin–orbit $|\Pi_u(j)\rangle$ and $|\Sigma_u^+(j)\rangle$ states of eq 2 and 3 are substituted into eq 6–8, the resulting equations may be simplified to eq 9–11, where $m_\gamma = \langle\sigma_g^+|m_\gamma|2\sigma_u^+\rangle$ and γ

$$\bar{A}_1(\Pi_u(j)) = (|a_j|^2 + |b_j|^2 + 2|c_j|^2)|a_j|^2\bar{D}_0(^1\Pi_u) \qquad (9)$$

$$\bar{B}_0(\Pi_u(j),\Pi_u(k)) = -(2/\Delta W_{kj})(a_j^*a_k + b_j^*b_k + 2c_j^*c_k)a_ja_k^*\bar{D}_0(^1\Pi_u) \qquad (10)$$

$$\bar{B}_0(\Sigma_u^+(j),\Pi_u(k)) = (1/\Delta W_{kj})[4id_j^*b_k - 2(2^{1/2}) \times (d_j^*c_k + e_j^*a_k)]e_ja_k^*m_z(m_x^* - m_y^*) \qquad (11)$$

$= x, y$, or z. In development of eq 9–11 the one-electron MO's were approximated by pure 5p atomic orbitals, and the summations in eq 7 and 8 were truncated to include only the states within the $(\pi_g)^3(2\sigma_u^+)$ and $(\sigma_g^+)(2\sigma_u^+)$ configurations because contributions from all others will be much smaller due to larger ΔW_{kj}. Equations 9–11 are sufficient to predict the sign of the MCD parameters, but in view of the approximations involved they are probably not adequate to give quantitative values. For example, $\bar{D}_0(^1\Pi_u)$ and the m_γ integrals are two-centered, involving the $5p_z$ orbital of the central I atom and 5p orbitals on the terminal I atoms, and are thus difficult to calculate exactly. Overlap considerations indicate that $\bar{D}_0(^1\Pi_u)$ is positive but may be quite small (see later), m_z and m_x^* are positive, and m_y^* is negative with our choice of coordinate system and conventions.

Spectral Assignment and MCD Interpretation. The weak shoulder observed near 1.9 μm^{-1} in the absorption spectrum (Figure 1, band I), together with the somewhat better resolved MCD feature associated with this band, is assigned on the basis of energy and intensity to the transition to the $\Pi_g(^1\Pi_g)$ state of the $(2\pi_u)^3(2\sigma_u^+)$ excited configuration. Transitions to all of the states of this configuration (Table II) are parity forbidden and are expected to be weak. However, the $\Pi_g(^1\Pi_g)$ state would have the largest singlet character and therefore would exhibit the most intense band. Unfortunately, the MCD in the region of band I is not very informative. A broad negative minimum is observed, but a definite term assignment is not possible because of overlap with the stronger negative MCD to higher energy.

The two intense bands at 2.8 μm^{-1} (band II) and 3.4 μm^{-1} (band III) are undoubtedly due to allowed transitions to states of the $(\pi_g)^3(2\sigma_u^+)$ and $(\sigma_g^+)(2\sigma_u^+)$ excited configurations. The MCD in the region of these bands however is comparatively weak. For band II, $(\Delta\epsilon_M)/\epsilon$ is 3×10^{-5} for CH_3CN solution, whereas for example $(\Delta\epsilon_M)/\epsilon$ for the I^- band at 4.08 μm^{-1} in CH_3CN is approximately 4×10^{-3}.[16] The MCD consists of a negative *B* term at 2.4 μm^{-1}, which has no corresponding absorption feature, a positive *B* term associated with the maximum of band II, and what appears to be a positive *A* term in the region of band II with $\Delta\epsilon_M = 0$ very near the band maximum. The MCD in the region of band III could also be due to two *B* terms of opposite sign forming a *pseudo-A* term.[15]

The earlier assignment of bands II and III to transitions to spin–orbit Σ_u^+ states (eq 3) was based upon a cogent argument that the *z*-polarized $\sigma_g^+ \rightarrow 2\sigma_u^+$ transition in I_3^- is expected to be considerably more intense than the *xy*-polarized $\pi_g \rightarrow 2\sigma_u^+$ transition.[6] Higher intensities for $\sigma \rightarrow \sigma^*$ transitions compared to $\pi \rightarrow \sigma^*$ transitions are also predicted from ground- and excited-state orbital overlap arguments and have been used by us[19] and by others[11,20] to interpret relative intensities of ligand-to-metal charge-transfer (LMCT) transitions in a number of metal–halo complexes. As a result of this intensity argument, transitions to the Π_u states of I_3^- (eq 2) were previously neglected altogether.[6]

An assignment of bands II and III to transitions to Σ_u^+ states alone, while reasonable on intensity grounds, cannot explain the MCD observed for I_3^-. The magnetic field cannot mix different Σ_u^+ states ($\langle\Sigma_u^+(j)||\mu||\Sigma_u^+(k)\rangle$ are zero), and therefore *B* terms for them will be zero (*A* terms of course will be absent because Σ_u^+ states lack degeneracy). The observed MCD thus requires the presence and mixing of Π_u states in the region of bands II and III. It is reasonable therefore to expect that both the Σ_u^+ states proposed earlier[6] and the Π_u states of the same $(\pi_g)^3(2\sigma_u^+)$ and $(\sigma_g^+)(2\sigma_u^+)$ configurations are present and that *B* terms result from the mixing of different Π_u states (eq 10) and from the mixing of Π_u and Σ_u^+ states (eq 11) by the applied field. The Π_u states may also lead to the observation of *A* terms, but if the transitions to Π_u states are weak ($\bar{D}_0(^1\Pi_u)$ of small magnitude in eq 9), then the *A* terms expected will also be weak and could be overshadowed by stronger *B* terms. In order to test these possibilities within the spin–orbit model adopted here for I_3^- and to aid in spectral interpretation, some rough calculations of spin–orbit energies and mixing coefficients were made by eq 4 and 5. Estimated energies of the zero-order singlet and triplet states and ζ_{5p} served as input for these calculations. The results of a typical calculation are collected in Table III, together with the predicted $\bar{B}_0$ parameters determined from eq 10 and 11. The calculations are rather crude

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Table III. Spin-Orbit Energies and Coefficients[a] and MCD $\bar{B}_0$ parameters

state	calcd energy, μm^{-1} $(\bar{B}_0)^b$	obsd MCD B term $(\Delta\epsilon_M)^c$	calcd coeff a $(^1\Pi_u)$	b $(^3\Pi_u)$	c $(^3\Sigma_u^+)$	d $(^3\Pi_u)$	e $(^1\Sigma_u^+)$
$\Sigma_u^+(2)$	3.56 (+17)	3.56 (+0.72)				−0.629	0.777
$\Pi_u(3)$	3.43 (−18)	3.14 (−1.1)	0.915	$-0.284i$	−0.284		
$\Pi_u(2)$	3.12	. . .	0.000	$0.707i$	−0.707		
$\Sigma_u^+(1)$	2.83 (+2.7)	2.79 (+0.81)				0.777	0.629
$\Pi_u(1)$	2.46 (−2.3)	2.43 (−0.61)	0.402	$0.647i$	0.647		

[a] Input parameters (in μm^{-1}): $^1\Sigma_u^+ = {}^1\Pi_u = 3.27$; $^3\Sigma_u^+ = {}^3\Pi_u = 2.87$; $\zeta_{5p} = 0.50$. [b] Contributions from the sum of $\bar{B}_0(\Sigma_u^+(j),\Pi_u(k))$ (eq 11) in units of $m_z(m_x^* - m_y^*)/(\mu m^{-1})$. The contributions from $\bar{B}_0(\Pi_u(j),\Pi_u(k))$ were very small and were taken to be zero. [c] From Table I, CH_3CN solution.

because of the various approximations involved, and little attempt was made to optimize the energies. Consequently, the magnitude of the calculated $\bar{B}_0$ parameters given in Table III are only of qualitative significance since they are sensitive to the energies ΔW_{kj} and the coefficients a_j–e_j. Nevertheless, the results of Table III are encouraging in that the energies of the spin–orbit states are consistent with the absorption spectra, and the calculated $\bar{B}_0$ parameters correctly predict the B term signs in the MCD spectra. For example, the $\bar{B}_0$ for the lowest energy state $\Pi_u(1)$ is found to be negative, in agreement with the negative B term at 2.4 μm^{-1}. Since there is no corresponding absorption feature for this state, the dipole strength for the transition must be small. The calculation shows that $\Pi_u(1)$ is only 16% $^1\Pi_u$, and from the intensity arguments earlier $\bar{D}_0(^1\Pi_u)$ is not expected to be large. Similarly, the A term for $\Pi_u(1)$ is expected to be small ($\bar{A}_1$ determined from eq 9 is $+0.20\bar{D}_0(^1\Pi_u)$), and thus it is not surprising that the B term dominates the MCD. The second lowest energy state in contrast is $\Sigma_u^+(1)$ and is calculated to be near the maximum of band II. This state has 40% $^1\Sigma_u^+$ character; therefore, the substantial intensity of band II can be rationalized. The $\bar{B}_0$ for $\Sigma_u^+(1)$ is predicted to be positive, again consistent with experiment. The next higher energy state $\Pi_u(2)$ is calculated to have virtually no singlet character and therefore is not expected to contribute to either the absorption or MCD spectra. The MCD in the vicinity of band III can be ascribed to a positive *pseudo-A* term originating from the negative and positive B terms associated with the $\Pi_u(3)$ state (lower energy) and $\Sigma_u^+(2)$ state (higher energy), respectively. The intensity of band III can be interpreted as due primarily to $\Sigma_u^+(2)$, which has 60% $^1\Sigma_u^+$ character. The signs of the calculated $\bar{B}_0$ parameters for $\Pi_u(3)$ and $\Sigma_u^+(2)$ are consistent with this assignment, but it should be pointed out that the A term for the $\Pi_u(3)$ state, which is calculated to be 84% $^1\Pi_u$, is also predicted to be positive ($\bar{A}_1$ calculated from eq 9 is $+0.90\bar{D}_0(^1\Pi_u)$. The observed MCD may thus be a combination of the positive *pseudo-A* term and the positive A term. The two contributions cannot be easily separated, but the observed position of the positive MCD maximum at higher energy than the absorption maximum of band III, together with the value of $\Delta\epsilon_M = 0$ near the absorption maximum, would argue for a nonnegligible contribution from the A term for $\Pi_u(3)$. Finally, the comparative weakness of the MCD noted earlier can be explained qualitatively by reference to eq 6–8. The magnitudes of $\bar{D}_0(^1\Pi_u)$ and the individual $\pi \rightarrow \sigma^*$ type dipole integrals, $\langle \Sigma_g^+ \| m \| \Pi_u \rangle$, are expected to be smaller than the $\sigma \rightarrow \sigma^*$ type, $\langle \Sigma_g^+ \| m \| \Sigma_u^+ \rangle$. The $\bar{B}_0$ parameters of eq 8 for example contain the small $\langle \Sigma_g^+ \| m \| \Pi_u \rangle$ factor, which in turn will affect their overall magnitude.

In summary, the foregoing discussion shows that the absorption and MCD spectra for the I_3^- ion can be interpreted within the simple MO model provided I spin–orbit coupling is included. The intensity of the two UV absorptions is primarily due to transitions to the Σ_u^+ spin-orbit states of the $(\pi_g)^3(2\sigma_u^+)$ and $(\sigma_g^+)(\sigma_u^+)$ excited configurations, but the MCD requires the presence and magnetic interaction of the Π_u states of these configurations. The simple MO model assumes the I_3^- ion remains linear in the excited states of these configurations and that the π_g and σ_g^+ orbitals are energetically close and nearly nonbonding, since they are orbitals based on the terminal I atoms. Since this description provides a self-consistent interpretation of the solution absorption and MCD spectra, it is unlikely that there are significant contributions from the higher energy 6s and 5d I orbitals, and therefore the π_g, σ_g^+, and $2\sigma_u^+$ orbitals are composed of 5p I orbitals to a good approximation. The observation of band I at low energy attributed to the $(2\pi_u)^3(2\sigma_u^+)$ configuration is interesting and indicates nonzero π interaction of the $5p_x$ and $5p_y$ orbitals in I_3^-. This interaction of course does not lead to bonding because both the bonding $1\pi_u$ and antibonding $2\pi_u$ orbitals are filled in the ground state. The bonding in I_3^- is still best described as a simple three-centered σ system delocalized over all three I atoms.[9,14]

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