

be sensitive to the asymmetry of the surrounding counterion force fields.

### Conclusions

Mixed-cation  $\text{GeO}_2$ -rich glasses that contain equimolar amounts of copper(I) and a second cation exhibit physical property changes that reflect a unique structural situation. These  $\text{GeO}_2$ -rich ternary glasses appear to retain some of the features of both the copper(I) germanate glasses and the alkali or silver germanate glasses. Thus, they may contain (1) some of the linear O—Cu—O arrangements that characterize  $\text{GeO}_2$ -rich copper(I) glasses and (2) some of the  $\text{GeO}_6$  octahedra that are found in the  $\text{GeO}_2$ -rich alkali and silver glasses. The rather voluminous nature of these ternary glasses suggests that they may contain a relatively open arrangement of germanate polyhedra.

Although the mixed-cation copper(I) germanate glasses are more voluminous than their copper(I)-free analogs, the volume—composition relationships of the copper(I) ternary glasses depend upon cation size in a manner similar to that of their copper-free ternary and binary analogs. It is thereby possible to gain an idea of the approximate size of the cation cavity in the mixed-cation copper(I) germanate glasses. Such information could be of possible practical value in a number of ion-exchange processes that involve amorphous oxide materials.

Additional confirmatory evidence for the possible linear O—Cu—O arrangement of copper(I) in binary  $\text{GeO}_2$ -rich glasses was uncovered by this study. It is evident that copper(I) does not experience the structural role encountered by other univalent cations in network-former-rich oxide glasses. The  $3d^{10}$  electronic nature of copper(I) creates a bonding situation that can be quite different from that of  $4d^{10}$   $\text{Ag}^+$ . Caution should be exercised in attempts to substitute or exchange  $\text{Cu}^+$  for  $\text{Ag}^+$  and *vice versa* in oxide environments. Caution will also have to be exercised in attempts to substitute or exchange  $\text{Cu}^+$  for the alkali cations and *vice versa*. This study suggests a new route to possibly unusual amorphous materials *via* the exchange (below the  $T_g$  of the glass) of an alkali ion for a  $\text{Cu}^+$

in surface layers. The alkali ions would find themselves in unusual coordination sites. This could significantly alter selected physical properties of the resultant material.

The enhanced shift to lower frequencies of the main infrared Ge—O vibration that accompanies a change of composition (such as per cent  $\text{GeO}_2$ ) for mixed-cation copper(I) germanate glasses is quite similar to that previously reported for other mixed-cation germanate glasses. While the reasons for the frequency shift observed for the former ternary glasses are more complex, they are readily interpretable in terms of the depolymerization sequences of the corresponding binary glasses. The copper(I) ternary glasses thus offer another example of the usefulness of infrared isofrequency contours as a unique structural probe.

Registry No.  $\text{GeO}_2$ , 1310-53-8;  $\text{Cu}_2\text{O}$ , 1317-39-1;  $\text{Ag}_2\text{O}$ , 20667-12-3.

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## Interpretation of Electronic and Magnetic Circular Dichroism Spectra Using Complete Operator Matrices ( $eZ$ , $L_z$ , $\nabla_x$ ) and Their Application to Evaluate Semiempirical LCAO—MO State Functions of Large Transition Metal Complexes

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Magnetic circular dichroism and electronic absorption parameters of charge-transfer excitations,  ${}^2T_{2g} \rightarrow {}^2T_{1u}{}^{a,b}$  and  ${}^2T_{2u}$ , were computed for the prototype "covalent" transition metal complex  $[\text{Fe}(\text{CN})_6]^{3-}$ . All valence electrons (65) and valence orbitals (57) were included, and a semiempirical LCAO—MO model in common use for such large molecules was employed. The construction and use of the complete multicenter orbital angular momentum ( $L$ ), electric dipole ( $eR$ ), and velocity dipole ( $\nabla$ ) matrices and their artificially incomplete counterparts lead to the conclusions that (i) the MCD Faraday ratios,  $C/D$ , can be computed reliably with unmodified or overlap-optimized iron functions, (ii) these  $C/D$  ratios can be computed reliably with the incomplete, block-diagonal matrix,  $L^{(b)}$ , composed of only the one-center and two-center integrals, (iii) complete electric dipole transition moment matrices should be employed, (iv) the dipole strength of  ${}^2T_{2g} \rightarrow {}^2T_{2u}$  is predicted to be the most intense of the three transitions, as found experimentally, by using either optimized or unmodified iron functions, and (v) the use of optimized iron functions has the advantage of not making  $t_{2g}(\pi)$  and  $t_{1u}(\sim\sigma)$  accidentally degenerate.

### Introduction

It was the premise of this study that the practice of using molecular orbitals of semiempirical LCAO—MO procedures for assigning electronic excitation bands of transition metal complexes by means of magnetic circular dichroism (MCD)<sup>2</sup> is best tested by evaluating all one-, two-, and three-center AO

integrals of appropriate operator matrices. By this means any discrepancy between computed and experimental Faraday parameters can be directly attributed to the molecular orbitals, so that the quality of the latter can become known with certainty. In other words, it was felt necessary to employ this procedure, because using semiempirically derived molecular

Table I. Dipole Strengths,  $D(a \rightarrow j)$ , and Faraday Ratios,  $C(a \rightarrow j)/D(a \rightarrow j)$ , of Charge-Transfer Transitions for  $[\text{Fe}(\text{CN})_6]^{3-}$ 

Ref or Method	${}^2T_{2g} \rightarrow$			Operator matrix
	${}^2T_{1u}^a$	${}^2T_{2u}^a$	${}^2T_{1u}^b$	
	$\Delta E, \text{kK}$			
<i>a</i>	24.04	33.17	38.45	
<i>b</i>	23.897	33.423	38.112	
<i>c</i>	24.5	32.7		
	$D(\text{exptl}), D^2$			
<i>a</i>	1.02	2.1	1.54	
<i>b</i>	1.485	2.691	1.20	
<i>c</i> (290°)	1.54	2.87		
<i>c</i> (12°)	1.61	3.00		
	$D(\text{computed}), D^2$			
I	2.92	7.57	6.40	$eZ$ (complete matrix)
II	5.50	4.76	3.04	$\nabla_x$ (complete matrix)
III	1.76	1.58	1.15	$\nabla_x$ (three-center integrals annihilated)
IV	0.41	0	0.08	$\nabla_x$ (block diagonal)
	$C/D(\text{exptl}), \text{BM}$			
<i>b</i>	-0.605	0.340	-0.283	
<i>c</i> (290°)	-0.43	0.27		
<i>c</i> (12°)	-0.332	0.131		
	$C/D(\text{computed}), \text{BM}$			
II	-0.439	0.439	-0.439	$L_z$ (complete matrix)
III	-0.444	0.444	-0.444	$L_z$ (three-center integrals annihilated)
IV	-0.436	0.436	-0.436	$L_z$ (block-diagonal) ( $=L_z^{(0)}$ )
X	-0.37	0.37	-0.37	$L_z$ (only one-center integrals retained)

<sup>a</sup> Experimental values from ref 28. <sup>b</sup> Experimental values from ref 6. <sup>c</sup> Experimental values from ref 8.

orbitals along with incomplete operator matrices could produce misleadingly good computational results simply because the approximations within each part can mutually cancel.

The MCD and electronic spectra of  $[\text{Fe}(\text{CN})_6]^{3-}$  are good test cases because (i) the Faraday  $C$  terms were recently measured, (ii) the three charge-transfer bands in question are nicely separated, (iii) the molecule is not too large for obtaining its molecular orbitals by currently used semiempirical LCAO-MO procedures, and (iv)  $[\text{Fe}(\text{CN})_6]^{3-}$  is representative of a large number of transition metal complexes having significant metal-ligand covalency and  $\pi$  bonding, e.g.,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Ru}(\text{N}\equiv\text{N})(\text{NH}_3)_5]^{2+}$ , and  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{V}$ ).

The previous sources of information about the Faraday effect of  $[\text{Fe}(\text{CN})_6]^{3-}$  in the 20–45-kK region of its three  $\text{CN}^- \rightarrow \text{Fe}^{3+}$  charge-transfer bands (Figure 1) are as follows. Two reports of the magneto-optical rotatory dispersion were given in 1964 by Shashoua and Briat,<sup>3</sup> and in 1965 Stephens<sup>4</sup> assigned the symmetry of the two low-energy bands ( $\sim 25$  and  $\sim 33$  kK) to  ${}^2T_{2g}(t_{2g}^5) \rightarrow {}^2T_{1u}(t_{1u}\sigma^5 t_{2g}^6)$  or  $t_{1u}\pi^5 t_{2g}^6$  and  ${}^2T_{2g}(t_{2g}^5) \rightarrow {}^2T_{2u}(t_{2u}\sigma^5 t_{2g}^6)$  by estimating their Faraday ratios,  $C/D$ , where in general  $C(a \rightarrow j) = (1/2da) \sum_{a,j,m,\mu} \langle a|\mu|a \rangle \cdot \text{Im}[\langle a|m|j \rangle \times \langle j|m|a \rangle]$  and  $D(a \rightarrow j)$  is the electric dipole strength,  $(1/da) \sum_{a,j,m} |\langle a|m|j \rangle|^2$ . Among the later developments are the MCD measurements of all three charge-transfer bands<sup>5–7</sup> and the association<sup>6</sup> of these bands with the charge-transfer excited states,  $T_{1u}^a[t_{1u}^5(\sim\sigma)t_{2g}^6] < {}^2T_{2u}(t_{2u}^5(\pi)t_{2g}^6) < {}^2T_{1u}^b[t_{1u}^5(\sim\pi)t_{2g}^6]$ . Finally, the dependence of these MCD bands on temperature was measured by Gale and McCaffery<sup>8</sup> in order to separate the Faraday  $B(a \rightarrow j)$  and  $C(a \rightarrow j)$  parameters, i.e.,  $\theta(a \rightarrow j) = -(24NH/\hbar c) \cdot (f(\nu))[B(a \rightarrow j) + C(a \rightarrow j)/kT]$ , where  $\theta$  is the intensity and  $f(\nu)$  is the shape function of the band. The authors concluded that the Faraday  $C$  parameters for  ${}^2T_{1u}^a$ ,  ${}^2T_{2u}$ , and  ${}^2T_{1u}^b$  were as shown in Table I (values denoted by footnote *c* in the table).

It was the object of the present study to compute these  $C(a \rightarrow j)/D(a \rightarrow j)$  ratios by using operator matrices containing all their one-, two-, and three-center integrals and then to transform these into molecular orbital space by the use of

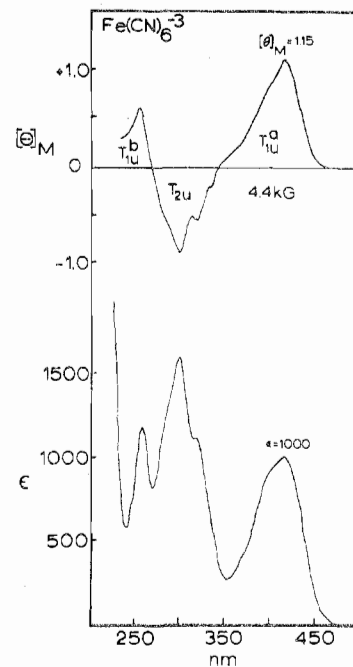


Figure 1. MCD (4.4-kG magnetic field) and electronic absorption spectra of an aqueous solution of  $[\text{Fe}(\text{CN})_6]^{3-}$  at room temperature.  $[\theta]_M$  is the molar ellipticity per Gauss. Spectra recorded in this laboratory.

semiempirically derived molecular orbitals. Ground-state functions are tested by this step. We also evaluated the electric dipole strengths of these three transitions,  ${}^2T_{2g} \rightarrow {}^2T_{2u}$ ,  ${}^2T_{1u}^a, {}^b$ , so as to ascertain the usefulness of such semiempirical molecular orbitals for constructing excited-state functions. In order to accomplish this testing, the task was undertaken (i) to generate such molecular orbitals and (ii) to compute complete operator matrices of the required multicenter integrals in double precision on an IBM 360/170 for the operators  $z$ ,  $\nabla_x$ , and  $L_x$ .  $z$  is the coordinate of an electron,  $\nabla_x \equiv \partial/\partial x$ ,

and  $L_z \equiv (\hbar/2\pi i)[x(\partial/\partial y) - y(\partial/\partial x)]$ . The effects of optimizing metal orbitals were also studied. Finally, the conclusions reached for this molecule ion would be indicative of what to expect for several other computations; *i.e.*, the operators used here also occur in several other places, *e.g.*, in Faraday  $A$ ,  $B$ , and  $C$  terms and in electric dipole strengths,  $D(a \rightarrow j)$ , magnetic dipole strengths, permanent electric dipole moments, and optical rotatory strengths.

### Computations

The nonoptimized basis consisted of all valence orbitals of iron (3d, 4s, 4p), carbon (2s, 2p), and nitrogen (2s, 2p). Slater orbitals<sup>9</sup> were used for the last two atoms, and multi- $\zeta$  functions,<sup>10,11</sup> for iron orbitals ( $\text{Fe}^+$ ); *i.e.*

$$\psi(3d) = 0.5060(\zeta_{3d} = 4.05) + 0.6750(\zeta_{3d} = 1.80)$$

$$\psi(4s) = -0.02078(\zeta_{1s} = 25.38) + 0.07052(\zeta_{2s} = 9.75) - 0.1744(\zeta_{3s} = 4.48) + 1.0124(\zeta_{4s} = 1.40)$$

$$\psi(4p) = 0.04091(\zeta_{2p} = 10.60) - 0.14364(\zeta_{3p} = 4.17) + 1.00932(\zeta_{4p} = 1.25)$$

The molecular orbitals were obtained by solving the secular equation of an oblique AO basis  $[\mathbf{H} - \mathbf{E}\mathbf{S}]\mathbf{C} = \mathbf{0}$ , where  $\mathbf{S}$  is the completely evaluated overlap matrix,  $\mathbf{C}$  is the matrix of molecular orbitals, and  $\mathbf{H}$  is the semiempirically generated Hamiltonian matrix. The diagonal elements of  $\mathbf{H}$  for transition metal orbitals were taken as

$$H_{ii} = -\sum_k d_k(\text{VOIP})_k$$

according to Basch, Viste, and Gray,<sup>12</sup> where the valence orbital ionization energy (VOIP) for the  $k$ th configuration (*e.g.*,  $3d^6 4s^1$  for  $\text{Fe}^+$ ) is  $(\text{VOIP})_k = A_k Q_m^2 + B_k Q_m + C_k$  ( $Q_m$  is the charge of the metal). Other details of the procedure are fully given elsewhere.<sup>12</sup> Carbon and nitrogen diagonal elements were taken as  $H_{ii}(L) = -CL$  as given by Ballhausen and Gray.<sup>13</sup> All off-diagonal elements were obtained by using the Wolfsberg-Helmholz equation<sup>14</sup> with  $K = 1.9$ . Since an oblique basis was employed, *i.e.*,  $[\mathbf{H} - \mathbf{E}\mathbf{S}]\mathbf{C} = \mathbf{0}$ , with  $\mathbf{S} \neq \mathbf{1}$ , the latter secular equation had to be transformed into standard eigenproblem form as follows. The overlap matrix is the Hermitian, positive definite metric of the oblique atomic basis, so that the original secular equation may be written in eigenproblem form

$$[\mathbf{M} - \mathbf{E}]\mathbf{T} = \mathbf{0}$$

using standard matrix analysis as follows.<sup>15</sup> The molecular orbital coefficient matrix,  $\mathbf{C}$ , of the oblique basis is related to the molecular orbital coefficient matrix,  $\mathbf{T}$ , of an orthonormal basis by

$$\mathbf{C} = \mathbf{P}\mathbf{T}$$

where  $\mathbf{P} = \mathbf{U}\mathbf{S}^{-1/2}$ .  $\mathbf{U}$  is the unitary matrix which will diagonalize  $\mathbf{S}$ ,  $\mathbf{S}^{-1/2}$  derives<sup>15</sup> from the diagonalized form of  $\mathbf{S}$ ,  $\mathbf{M}$  is the conjugate of  $\mathbf{H}$ , or  $\mathbf{M} = \mathbf{P}^{-1}\mathbf{H}\mathbf{P}$ , and  $\mathbf{T}$  is obtainable because it diagonalizes  $\mathbf{M}$ . A Mulliken population analysis<sup>16</sup> was carried out to obtain atom charges,  $q$ , from  $\mathbf{C}$  and  $\mathbf{S}$ . For atom  $A$

$$P_A = \sum_k \sum_i^{\text{MOA}} N_k C_{ik}^2 + \sum_k \sum_{i \neq j}^{\text{MOA}} N_k C_{ik} C_{jk} S_{ij}$$

and  $q_A = z_A - P_A$ , the atom charge, where  $z_A$  is the charge of the atomic core (numerically equal to the number of valence electrons),  $P_A$  is the number of electrons on atom  $A$ , and the other symbols in the present notation can be found elsewhere.<sup>17</sup> Iterations were carried out, as given in ref 17, which varied matrix  $\mathbf{C}$  until it produced self-consistent charges on two successive cycles.

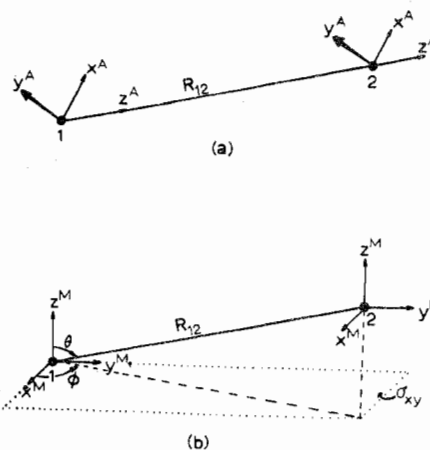


Figure 2. The aligned coordinate system (a) recognized by subroutine INTE and the molecular coordinate system (b) employed in the molecular orbital calculation.

The elements of the overlap matrix,  $\mathbf{S}$ , were obtained by using subroutine INTE (QCPE, Program 82.1). This subroutine as received from QCPE was found to be accurate after extending the number of  $B$  functions,  $B_k(t)$ , to be used for each integral from the fixed number 10 to such a number  $n$  so that another term,  $B_{n+1}(t)$ , would contribute only  $10^{-8}$  or less to the sum of terms preceding it. The routine is the coding of formulas by Kuppermann, Karplus, and Isaacson<sup>18</sup> over single- $\zeta$  STO's. Since this subroutine evaluates the integrals in the aligned coordinate system of Figure 2a it was necessary to express the atomic orbitals of the molecular orbital coordinate system (Figure 2b) as linear combinations of aligned atomic orbitals (Figure 2a), *i.e.*, for the sets of  $p_m$  and  $d_m$  orbitals in the molecular coordinate system  $m$

$$p_m = \mathbf{A}_p p_a$$

$$d_m = \mathbf{B}_p d_a$$

where  $p_a$  and  $d_a$  are orbitals in the aligned coordinate system. The transformation matrices  $\mathbf{A}$  and  $\mathbf{B}$  were derived using the Euler angles and Goldstein matrices<sup>19</sup> in the conventional manner.

The one-center and several types of two-center electric dipole integrals were evaluated with INTE. However, in order to evaluate three-center integrals,  $\langle \chi_i(\text{C}) | e z(\text{A}) | \chi_j(\text{B}) \rangle$ , the operator on center  $A$ , or  $\text{Fe}$  here, had to be transformed onto center  $B$ . This had the effect of changing every three-center moment integral into a linear combination of two-center integrals. This can be carried out for the general case by recognizing that the coordinates of an electron with respect to center  $A$  can also be expressed with respect to those of center  $B$ , and the relationship is shown in Figure 3. These coordinates, in fact, are related geometrically by

$$X_A = X_B + R \sin \theta \cos \phi$$

$$Y_A = Y_B + R \sin \theta \sin \phi$$

$$Z_A = Z_B + R \cos \theta$$

where  $\theta$ ,  $\phi$ , and  $R$  are defined by the geometry of the complex.

The alternative method of computing electric dipole transition moment integrals was also used.<sup>20</sup> This method employs the differential operator  $\nabla q = \partial/\partial q$  ( $q = x, y, \text{ or } z$ ) in place of the components of the distance operator,  $q = x, y, \text{ or } z$ ; *i.e.*, for the transition  $a \rightarrow j$

$$\langle a | q | j \rangle = -\frac{\hbar^2}{m^2 (E_a - E_j)} \langle a | \partial/\partial q | j \rangle$$

Using  $\nabla q$  in this manner has been termed the velocity dipole

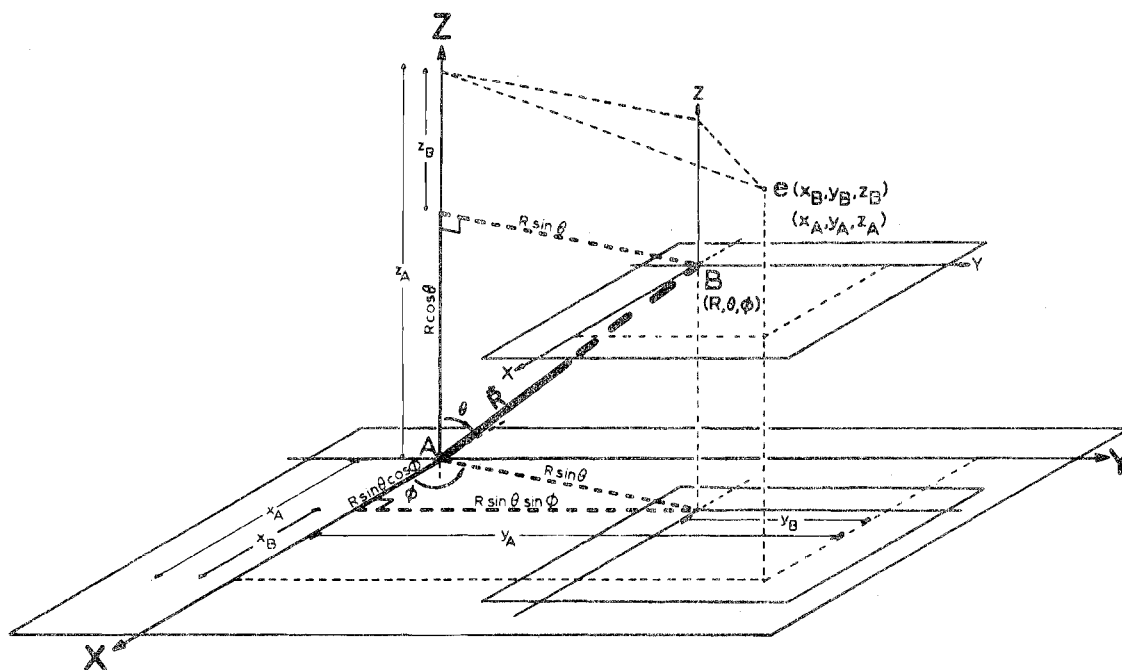


Figure 3. Coordinates of an electron with respect to two atoms, A and B.

procedure (using  $q$  being the electric dipole procedure), and experimental energy differences were employed here to compute the dipole strength,  $D$ . The integrals of the velocity dipole operator,  $\nabla$ , were evaluated by first deriving the analytical functions obtained by operating on the oblique atomic orbital,  $\chi_m$ , in the manner  $\nabla|\chi_m\rangle$ , this action creating a new function. For example

$$\nabla_z(A)|2p_x(B)\rangle = -N_b \zeta_b e^{-\zeta_b r_b} \sqrt{\frac{3}{4\pi}} \frac{X_b Z_b}{r_b}$$

so that

$$\langle \chi_m(C) | \nabla_z(A) | 2p_x(B) \rangle = -\frac{1}{2} \sqrt{\frac{3}{\pi}} N_b \zeta_b \langle \chi_m(C) | \frac{X_b Z_b}{r_b} e^{-\zeta_b r_b} \rangle = \text{constant } x \text{ overlap integral}$$

The reduced matrix element  $\langle {}^2T_{2g} || \mu_L || {}^2T_{2g} \rangle$  of the Faraday ratio<sup>6</sup>  $C/D$  or

$$\frac{C}{D} ({}^2T_{1u}^{a,b}) = -\frac{C}{D} ({}^2T_{2u}) = \frac{\sqrt{2}}{4i} \langle {}^2T_{2g} || \mu_L || {}^2T_{2g} \rangle$$

was evaluated in all the possible combinations of bases allowed by Griffith's table of Clebsch-Gordon coupling coefficients.<sup>21</sup> For example

$$\langle {}^2T_{2g} || \mu_L || {}^2T_{2g} \rangle = \sqrt{2} \langle {}^2T_{2g} \xi | L_z | {}^2T_{2g} \eta \rangle$$

where the integral on the right-hand side was evaluated as usual

$$\langle {}^2T_{2g} \xi | L_z | {}^2T_{2g} \eta \rangle = \psi^T ({}^2T_{2g} \xi) L_z \psi ({}^2T_{2g} \eta)$$

$\psi ({}^2T_{2g} \xi)$  ( $=C({}^2T_{2g} \xi)\chi$ ) is the Slater determinant of molecular orbitals for  ${}^2T_{2g} \xi$ ,  $L_z$  is the  $57 \times 57$  operator matrix of  $L_z$  over the atomic orbitals, and  $\chi$  is the column matrix of these atomic orbitals. Integrals of the many-center angular momentum matrix  $L_z$  were evaluated as described by an example given in the Appendix.

The overlap optimization of metal orbitals was carried out in the following manner. First of all, the 3d orbital of  $Fe^+$  was used as given by Richardson, *et al.*,<sup>10</sup> in view of previous experience by Fenske and Radtke.<sup>22</sup> The other two orbitals,

4s and 4p, were overlap-optimized as follows.<sup>22</sup> The starting orbitals were taken from papers of Richardson, *et al.*,<sup>10,11</sup> *i.e.*,

$$\psi^0(4s) = -0.02078(\zeta_{1s} = 25.38) + 0.07052(\zeta_{2s} = 9.75) - 0.1744(\zeta_{3s} = 4.48) + 1.0124(\zeta_{4s} = 1.40)$$

$$\psi^0(4p) = 0.04091(\zeta_{2p} = 10.60) - 0.14364(\zeta_{3p} = 4.17) + 1.00932(\zeta_{4p} = 1.25)$$

and the core orbitals (1s, 2s, 2p, 3s, 3p) of iron were as previously given.<sup>10</sup> The procedure for optimizing  $\psi^0(4s)$  was to (i) change the above value of  $\zeta_{4s}$ , (ii) reevaluate  $C_4$  (1.0124) by using the requirements that  $\psi(4s)$  be orthonormal to the core, and (iii) compute the overlap integral with the 2p( $\sigma$ ) orbital of the bonded carbon atom. The result is a more contracted orbital

$$\psi(4s) = -0.04968(\zeta_{1s} = 25.38) + 0.16997(\zeta_{2s} = 9.75) - 0.44492(\zeta_{3s} = 4.48) + 1.07902(\zeta_{4s} = 2.06)$$

which gave the largest overlap integral.  $\psi(4p)$  was found similarly by changing  $\zeta_{4p}$ , reevaluating  $C_3$ , but then computing the two overlap integrals  $S_\sigma$  and  $S_\pi$  with the adjacent carbon orbitals 2p( $\sigma$ ) and 2p( $\pi$ ). The optimum value of  $\zeta_{4p}$ , in the sense that  $1/2(S_\sigma + S_\pi)$  was maximized, was taken to define  $\psi(4p)$

$$\psi(4p) = 0.08042(\zeta_{2p} = 10.60) - 0.29063(\zeta_{3p} = 4.17) + 1.03763(\zeta_{4p} = 1.65)$$

For example, the orthonormalizations to obtain  $\psi(4s)$  were carried out using the following expressions.<sup>23</sup> For the coefficient of  $\phi_{4s}$  in  $\psi(4s)$

$$C_{4s,4} = [1 - \sum_{k=1}^3 \langle \phi_{4s} | T_{ks} \rangle^2]^{-1/2}$$

and for the other three coefficients,  $i = 1, 2, \text{ or } 3$ , in  $\psi(4s)$

$$C_{4s,i} = \sum_{k=1}^3 C'_{4s,k} \alpha_{ks,i}$$

where

$$C'_{4s,k} = -\langle \phi_{4s} | T_{ks} \rangle / C_{4s,4}$$

The  $T_{ks}$  are the orthonormal 1s, 2s, and 3s core functions,<sup>10</sup> or  $T_{ks} = \sum \lambda \alpha_{ks, \lambda} \phi_\lambda$  and  $\phi$  is a single- $\zeta$  STO. The internuclear

distances of  $[\text{Fe}(\text{CN})_6]^{3-}$  were used as previously given.<sup>6,24</sup> Finally, from previous experience<sup>25</sup> in this laboratory it was found that the single- $\zeta$  Clementi-Raimondi orbital exponents<sup>26</sup> for lighter atoms (*e.g.*, C and N) are very nearly as good as the multi- $\zeta$  ("double- $\zeta$ ") orbitals of Clementi.<sup>27</sup> This conclusion derives from comparing two-center and three-center electric dipole moment integrals and overlap integrals.<sup>25</sup> With this in mind the present calculations were carried out using the single- $\zeta$  exponents of Clementi and Raimondi.<sup>26</sup> The molecular Hamiltonian matrix elements,  $H$ , for these optimized-orbital calculations were evaluated as described above, except that the diagonal ligand elements are evaluated by means of the equation

$$H_{ii}(\text{L}) = -[A_L Q_L^2 + B_L Q_L + C_L]$$

where the coefficients  $A$ ,  $B$ , and  $C$  are given by Basch, Viste, and Gray,<sup>12</sup> and  $Q_L$  is the charge of ligand atom L (C or N).

### Results and Discussion

Regarding the use of nonoptimized Fe functions, Table I is the collection of experimental data and computational results for dipole strengths,  $D(a \rightarrow j)$ , and Faraday ratios,  $C(a \rightarrow j)/D(a \rightarrow j)$ , for the three  $\text{CN}^- \rightarrow \text{Fe}^{3+}$  charge-transfer transitions  ${}^2T_{2g} \rightarrow {}^2T_{1u^a}[t_{1u^5}(\sim\sigma)]$ ,  ${}^2T_{2u}$ , and  ${}^2T_{1u^b}[t_{1u^5}(\sim\pi)]$ . These transitions are at  $\sim 24,000$ ,  $\sim 33,000$ , and  $\sim 38,000$   $\text{cm}^{-1}$  in the same order, and the bands are shown in Figure 1. There is a bit of variation of the magnitudes of the experimental dipole strengths,<sup>6,8,28</sup> and the ranges are 1.02–1.64, 2.1–3.0, and 1.20–1.54  $\text{D}^2$  for  ${}^2T_{1u^a}$ ,  ${}^2T_{2u}$ ,  ${}^2T_{1u^b}$ , respectively. However, it is unambiguous that the middle band,  ${}^2T_{2u}$ , has the largest dipole strength (Table I). There is a similar uncertainty about the Faraday ratio,  $C/D$ , of each of  ${}^2T_{1u^a}$  and  ${}^2T_{2u}$ ; *i.e.*, for the first of these the measured ratios fall between  $-0.332$  and  $-0.605$  BM, and for the second one the reported values are 0.13, 0.27, and 0.340 BM (Table I). For  ${}^2T_{1u^b}$  only one value,  $-0.283$  BM, has been reported.<sup>6</sup> The room-temperature MCD spectrum obtained here is given in Figure 3 for easy reference, and this figure also shows how the electronic spectrum compares with the MCD spectrum. It is somewhat surprising that the absolute values of these extracted  $C/D$  ratios are not more similar, since it can easily be shown, and has been,<sup>6</sup> that theory predicts them to be equal, *i.e.*

$$\frac{C}{}{D}({}^2T_{1u^a,b}) = -\frac{C}{}{D}({}^2T_{2u}) = \frac{\sqrt{2}}{4i} \langle {}^2T_{2g} || \mu_L || {}^2T_{2g} \rangle$$

where  $\mu_L \equiv L \sum_i i^{\pm 1} L(i)$ . However, the difference of absolute magnitudes of these experimentally extracted  $C/D$  ratios probably arises in large part from the uncertainties inherent in curve fitting electronic and MCD spectra and due to the presence of d-d character in some of these charge-transfer band envelopes.

The computational results are as follows. On using the complete orbital angular momentum operator matrix,  $L_z$ , the computed Faraday ratios ( $|C/D| = 0.439$  BM) were found to be in quite good agreement (calculation II, Table I) with the experimental values (Table I) and had the correct signs. It is also quite interesting that the ratio  $|C/D| = 0.5$ , computed by Schatz, *et al.*, is quite close to our value, in spite of the few momentum integrals of  $L_z$  those authors evaluated.<sup>6</sup> This led us to annihilate arbitrarily certain types of blocks in our complete matrix,  $L_z$ , so as artificially to produce defective matrices to be used with the same state function as with the complete  $L_z$ . For example, it was found that on annihilating all three-center integrals,  $\langle \chi_A | L_z(\text{Fe}) | \chi_B \rangle$  ( $A \neq B \neq \text{Fe}$ ), the Faraday ratio changed by only  $\sim 1\%$  (calculation III, Table I). Furthermore, by calculation IV (Table I), with  $\langle \chi_A | L_z(\text{Fe}) | \chi_B \rangle = 0$  for all  $A \neq B$ , it was evident that on further simplifying  $L_z$  to block-diagonal form the  $|C/D|$  ratio again

differed very little from that of calculation II which used the complete momentum matrix. This block form of  $L_z$  for calculation IV has the same form as would an overlap matrix in which the overlap between each pair of neighboring orbitals vanishes. In fact, on making the most severe approximation of retaining only  $\langle L_z \rangle$  values of the iron orbitals (calculation X), it was found that the reduced matrix element still gave the correct sign and approximately the right magnitude, *e.g.*,

$$\frac{C}{}{D}({}^2T_{1u^a,b}) = -0.37 \text{ BM}$$

However, it must be admitted that this ratio is a more sizable change ( $\sim 15\%$ ) of magnitude from the value obtained on using the complete operator matrix (calculation II). Also, this deviation is held to  $\sim 15\%$  because the  $t_{2g}$  orbitals in  $[\text{Fe}(\text{CN})_6]^{3-}$  are so high in iron content, *i.e.*, 74% Fe, that two-center and three-center integrals do not play a very important role. The more fundamental reason for this result is that the reduced matrix element of states simplifies to the expectation value over  $t_{2g}$  molecular orbitals, *e.g.*

$$\begin{aligned} \frac{C}{}{D}({}^2T_{1u^a,b}) &= \frac{\sqrt{2}}{4i} \langle {}^2T_{2g} || \mu_L || {}^2T_{2g} \rangle \\ &= \frac{1}{2i} \langle {}^2T_{2g} \xi | L_z | {}^2T_{2g} \eta \rangle \\ &= \frac{1}{2i} \langle t_{2g} \xi | L_z | t_{2g} \eta \rangle \end{aligned}$$

The multicenter integrals of  $L_z$  are expected to contribute to an even smaller extent to the  $C/D$  values of more ionic complex species, *e.g.*,  $[\text{FeCl}_4]^-$ , so that it can be expected that the inclusion of only one-center angular momentum integrals will lead to the correct sign and approximately correct magnitude of such excitations.

It is also informative to look at the quality of the computed electric dipole strengths of these three parity allowed bands. While it is generally conceded that this is a difficult quantity to calculate correctly, it was of interest to ascertain whether the semiempirical molecular orbitals would predict that  ${}^2T_{2g} \rightarrow {}^2T_{2u}$  is the most intense excitation of the three (Table I). Indeed the method was found capable of making this prediction when we used the complete matrix of the distance operator,  $eZ$ ; *viz.*, the predicted magnitudes (calculation I) were 2.92, 7.57, and 6.40  $\text{D}^2$  for  ${}^2T_{1u^a}$ ,  ${}^2T_{2u}$ , and  ${}^2T_{1u^b}$ , while the experimental values are 1.02–1.61, 2.1–3.0, and 1.2–1.54  $\text{D}^2$  in the same order.

On using these same state functions for evaluating the electric dipole strengths by means of the complete matrix of the velocity dipole operator,  $\nabla$ , the three predicted values were of comparable magnitude again (5.50, 4.76, and 3.04  $\text{D}^2$ ) as found experimentally, although the middle band,  ${}^2T_{2u}$ , was not computationally the most intense one. We proceeded artificially to simplify the operator matrix  $\nabla$  so as to investigate whether three-center and two-center integrals are as dispensable as they were found to be for evaluating the ground-state orbital magnetic moment of the ratio  $C/D$ . It was discovered that the dipole strengths were significantly sensitive to the presence of the three-center integrals, since deletion of the latter (calculation III) from  $\nabla$  led to greatly reduced dipole strengths compared to using the proper complete operator matrix  $\nabla$  (compare calculations II and III, Table I). In fact, if one had carried out these dipole strength calculations by deleting these more difficult to evaluate three-center integrals for the sake of convenience, one would have been led to the erroneous conclusion that the state functions are excellent. The computational result on simplifying the operator matrix were worst when the three-center integrals plus those two-center integrals which involve orbitals on different centers (see result of calculation IV, Table I) were artificially an-

Table II. Computed<sup>a,b</sup> Dipole Strengths<sup>c</sup> and Faraday Parameter Ratios,  $C(a \rightarrow j)/D(a \rightarrow j)$ , for Charge-Transfer Bands of  $[\text{Fe}(\text{CN})_6]^{3-}$ 

Method	${}^2T_{2g} \rightarrow$			Operator matrix
	${}^2T_{1u}^a$	${}^2T_{2u}$	${}^2T_{1u}^b$	
	$\Delta E, \text{kK}$			
	~24	~33	~38	
	Computed Dipole Strength, $D_c, D^2$			
A	1.8	5.3	3.3	Complete matrix; no optimization
B	0.62	6.0	3.7	Complex matrix; optimization
C	0.31	2.68	1.83	Three-center integrals annihilated
D	3.72	0	0.15	Block-diagonal operator matrix
	Computed Faraday Ratio, $C/D, \text{BM}$			
A	-0.40	0.40	-0.40	
B	-0.418	0.418	-0.418	
C	-0.411	0.411	-0.411	
D	-0.428	0.428	-0.428	

<sup>a</sup> See Table I for experimental values. <sup>b</sup> Optimized orbitals. <sup>c</sup> Velocity dipole operator,  $\nabla$ .

annihilated; *i.e.*, the computed dipole strengths are 0.41, ~0, and 0.08  $D^2$  for  ${}^2T_{1u}^a$ ,  ${}^2T_{2u}$ , and  ${}^2T_{1u}^b$ , respectively.

We conclude that the use of dipole strength calculations as a criterion of testing semiempirical wave functions of charge-transfer states requires one to use the complete operator matrix. On the other hand, the multicenter integrals of the orbital angular momentum operator,  $L_q$ , are much less important relative to the one-center integrals, when used to evaluate the angular momentum of the ground state. It also seems reasonable to suggest from this experience that Faraday  $B$  terms will be computationally accessible, if very few states get magnetically mixed into the excitation  $a \rightarrow j$ . The effects of optimizing the metal 4s and 4p orbitals are given in the remainder of the paper.

The suggestion has been made in a recent paper that overlap-optimized atomic orbitals for metal-ligand pairs of atoms in transition metal complexes ought to be used for LCAO-MO calculations of such large, many-electron systems.<sup>22</sup> It is our premise that this intuitively reasonable practice is best tested by computing molecular orbital coefficients with ( $C^0$ ) and without ( $C$ ) this optimization, and then to compute expectation values corresponding to experimental observables by employing completely generated AO operator matrices,  $M^0$  and  $M$ , along with  $C^0$  and  $C$ , respectively. This approach offers advantage over the one of assessing the relative merits of such coefficients by inspecting bond orders and atomic charges, generated on subjecting  $C^0$  and  $C$  to a population analysis, since these parameters are not related to observables in the concise manner of operators. For this reason the Faraday ratios,  $C(a \rightarrow j)/D(a \rightarrow j)$ , of MCD electronic excitations, and electric dipole strengths,  $D(a \rightarrow j)$ , of electronic absorption bands are explored, and the remainder of this paper concerns itself with determining what the improvements are, if any, on employing optimized metal basis orbitals (see Computations).

The dipole strength matrix computed by method B is the most complete of the three using optimized iron functions (see Table II), since the complete velocity dipole matrix,  $\nabla_x$ , was employed to derive the dipole strengths,  $D$ , of 0.62, 6.0, and 3.7  $D^2$ . This computation (Table II) clearly predicts  ${}^2T_{2u}$  to be the most intense band, as found experimentally. When all the three-center integrals of the operator matrix are artificially annihilated (calculation C), as one might be tempted to do in order to be able to save computer cost, it was discovered that each of the three dipole strengths decreased by *ca.* 50% from their respective values of calculation B, in which the full matrix,  $\nabla_x$ , was employed (Table II). The second feature of interest about the practice of using the incomplete operator matrix,  $\nabla_x^{(i)}$ , which is improperly devoid of its three-center integrals, is that the computed dipole strengths for  ${}^2T_{2u}$  (2.68  $D^2$ ) and  ${}^2T_{1u}^b$  (1.83  $D^2$ ) (but not  ${}^2T_{1u}^a$ ) are in better agreement

with the experimental values, 2.1–3.0  $D^2$  ( ${}^2T_{2u}$ ), and 1.2 and 1.58  $D^2$  ( ${}^2T_{1u}^b$ ), than were the ones obtained with the properly complete matrix,  $\nabla_x$ . The point here is that, if one had used the incomplete  $\nabla_x^{(i)}$ , one would have been led to the erroneous conclusion that the molecular orbital coefficients are excellent. (It was also possible to reach this conclusion by using the simpler, nonoptimized basis, along with the distance operator in place of the velocity dipole analog (*vide supra*). There is another, and more grave, discrepancy between the results as obtained using the complete operator matrix,  $\nabla_x$ , and the one artificially devoid of three-center integrals,  $\nabla_x^{(i)}$ . The sign of the unsquared electric dipole moment integral  $\langle a | m | j \rangle$  of  ${}^2T_{2g} \rightarrow {}^2T_{1u}^a$  changed when the incomplete matrix,  $\nabla_x^{(i)}$ , was employed to evaluate it! This behavior would have dire consequences in computing rotational strengths,  $R$ , of natural optical activity in similar transition metal complexes, since this unsquared moment appears here

$$R(a \rightarrow j) = \text{Im} \langle a | m | j \rangle \langle j | \mu | a \rangle$$

( $\mu$  being the magnetic dipole operator), *i.e.*, using the incomplete matrix,  $\nabla_x^{(i)}$ , may lead to erroneous sign predictions of the rotational strengths. The very same computational error would appear in assigning excited states on the basis of computing  $B$  parameters, which for the cubic problem would be

$$B(a \rightarrow j) = \text{Im} \left\{ \sum_{k \neq a} \frac{\langle k | \mu_z | a \rangle}{h\nu_{ka}} [M_x^a M_y^b - M_y^a M_x^b] + \sum_{k \neq j} \frac{\langle j | \mu_z | k \rangle}{h\nu_{kj}} [M_x^a M_y^c - M_y^a M_x^c] \right\}$$

where  $M_x^a M_y^b = \langle a | m_x | j \rangle \langle j | m_y | k \rangle$ , etc.<sup>2</sup> In other words, here too one finds unsquared moment integrals, and using incomplete operator matrices,  $\nabla_x^{(i)}$ , may lead to erroneous signs of Faraday  $B$  parameters. Calculation D, the result of which is summarized in Table II, consisted of computing the dipole strengths with the defective block-diagonal operator matrix

$$\nabla_x^{(b)} = \{A_1(\text{Fe})^{(9)} A_2(\text{C}_1)^{(4)} A_3(\text{N}_1)^{(4)} \cdot \cdot A_4(\text{N}_6)^{(4)}\}$$

with the operator centered at Fe, so that  $A_1$  is the one-center matrix of dimensions  $9 \times 9$  (one 4s, three 4p, five 3d orbitals), and the remainder of diagonal blocks are "same-center" two-center integrals at carbon, C<sub>1</sub>, nitrogen, N<sub>1</sub>, etc. The result of using this defective matrix,  $\nabla_x^{(b)}$ , was severe when transformed to compute the electric dipole strengths,  $D$ ; *i.e.*, the latter values were 3.72, 0, and 0.15  $D^2$ . This approximation should, therefore, be avoided at all cost for charge-transfer excitations. Again, the moment integral for the excitation to  ${}^2T_{1u}^a$  had the opposite sign from that obtained on using the proper, complete matrix  $\nabla_x$ . The reasonably successful relative

dipole strength computation of method B (optimized orbitals and complete operator matrix  $\nabla_x$ ) should now be compared with those of method A, in which nonoptimized iron orbitals were used but the operator matrix  $\nabla_x$  was also complete.

The three relative dipole strengths (1.8, 5.3, 3.3 D<sup>2</sup>) for the three excitations to  ${}^2T_{1u}(\sim\sigma)$ ,  ${}^2T_{2u}(\pi)$ , and  ${}^2T_{1u}(\sim\pi)$ , when computed with unmodified iron functions of Richardson, *et al.*,<sup>10,11</sup> are somewhat in better agreement with experiment (Table II) than the ones (0.62, 6.0, 3.7 D<sup>2</sup>) computed using the optimized functions (method B). It is of interest to point out that the  ${}^2T_{2g} \rightarrow {}^2T_{1u}(\sim\sigma)$  excitation is most sensitive computationally to this choice of functions, since the most covalent Fe-CN molecular orbitals are being involved in the intensity calculation. In fact, the sensitivity of this  ${}^2T_{1u}(\sim\sigma)$  intensity can be used to advantage; *viz.*, since the computed dipole strength using optimized iron functions is somewhat too small (0.62 D<sup>2</sup> compared to the low experimental value of 1.02 D<sup>2</sup>), it can be concluded that the molecular orbital procedure employed leads to  $t_{1u}(\sim\sigma)$  molecular orbitals which are a bit too covalent, if one assumes that the AO basis is correct. The only objection we can put forth here with regard to using nonoptimized metal functions along with this semiempirical LCAO-MO procedure is that  $t_{1u}(\sim\sigma)$  and  $t_{2g}$  are found to be very nearly accidentally degenerate. This causes electron population analysis problems. On the other hand, use of the optimized metal functions with this molecular orbital procedure led to the molecular orbital order  $t_{1u}^6(\sim\pi) < t_{2u}^6(\pi) < t_{1u}^6(\sim\sigma) < t_{2g}^5(\pi)$  which is most reasonably consistent with the order of states, or  ${}^2T_{2g} > {}^2T_{1u}^2(\sim\sigma) > {}^2T_{2u}(\pi) > {}^2T_{1u}(\sim\pi)$ .

The computational results of Table II for evaluating  $C/D$  ratios are as follows. First, employing the complete operator matrix,  $L_z$ , gave quite good answers, or  $|C/D| = 0.418$  BM (method B: complete  $L_z$  and optimized Fe orbitals). However, when we artificially deleted all three-center integrals from  $L_z$  (calculation C) or when we went farther by removing, in addition to all three-center integrals, those two-center integrals which had orbitals on different centers (calculation D:  $L_z$  became block-diagonal), it was discovered that neither of these two approximations is severe (Table II). A similar conclusion is reached from the calculation in which nonoptimized AO's of iron were employed (*vide supra* and Table II). This result was somewhat surprising to us, since inorganic chemists view  $[\text{Fe}(\text{CN})_6]^{3-}$  as having quite covalent iron-carbon bonds, which in turn led us to believe that two-center integrals of the type  $\langle \chi_k(\text{Fe}) | L_z(\text{Fe}) | \chi_l(\text{C}) \rangle$  would contribute prominently to the value of  $\langle {}^2T_{2g} | \mu_z | {}^2T_{2g} \rangle$ . The underlying cause for being able to use a defective operator matrix,  $L_z$ , for  $\langle {}^2T_{2g} | \mu_z | {}^2T_{2g} \rangle$  appears to be the large metal character in the open shell,  $t_{2g}^5$ ; *i.e.*, after transforming the molecular orbital coefficients  $C$  of the oblique basis,  $\chi$ , to molecular orbital coefficients,  $T$ , of an orthogonal basis,  $\chi_t$ , *i.e.*

$$T = P^{-1}C$$

(*vide supra*), we find from  $T$  that the 3d(Fe) orbital content of  $t_{2g}$  indeed is 69%.  $C/D$  for nonoptimized Fe functions are good for the same reason.

We conclude from the calculation of these Faraday ratios,  $C/D$ , that (i) a block diagonal operator matrix,  $L^{(b)}$ , of one- and two-center integrals is sufficiently complete to compute these Faraday ratios, (ii)  $L^{(b)}$  may be computed with optimized metal orbitals or with the unmodified ones as given by Richardson, *et al.*,<sup>10,11</sup> and (iii) the  $L^{(b)}$  type matrix may be used for computing Faraday ratios,  $C/D$ , for nearly all other transition metal complexes since they will be even less covalent than  $[\text{Fe}(\text{CN})_6]^{3-}$  (a few molecules such as perhaps  $\text{V}(\text{CO})_6^{2-}$  may turn out to be exceptions). In contrast, electric dipole strengths of charge-transfer transitions such as these ought to be evaluated with complete operator matrices.

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### Appendix

The evaluation of the three-center integral,  $J = 1.31891i$  BM =  $\langle 2p_y(N_1) | L_z(\text{Fe}) | 2p_x(C_2) \rangle$ , is exemplary of the computational steps necessary for constructing the orbital angular momentum matrix,  $L_z$ . First, the operator is transformed from Fe to the carbon atom  $C_2$ . This will have the convenient effect of changing  $J$  into a linear combination of two-center integrals. In general, since  $L_z = -i\hbar[x(\partial/\partial y) - y(\partial/\partial x)]$ , it is necessary to know that

$$X_{\text{Fe}} = X_{C_2} + R_{\text{Fe}-C_2} \sin \alpha \cos \beta \quad (1)$$

$$Y_{\text{Fe}} = Y_{C_2} + R_{\text{Fe}-C_2} \sin \alpha \sin \beta \quad (2)$$

This follows directly from Figure 3, and the angles are defined by

$$\alpha = \cos^{-1} \left( \frac{Z_{C_2} - Z_{\text{Fe}}}{R_{\text{Fe}-C_2}} \right) \quad (3)$$

$$\beta = \tan^{-1} \left( \frac{Y_{C_2} - Y_{\text{Fe}}}{X_{C_2} - X_{\text{Fe}}} \right) \quad (4)$$

After substituting eq 3 and 4 into eq 1 and 2 and putting the explicit form of eq 1 and 2 into the expression of  $L_z$ , subsequent manipulations give

$$L_z(\text{Fe}) = L_z(C_2) - i\hbar R_{\text{Fe}-C_2} (\sin \alpha) \left[ (\cos \beta) \frac{\partial}{\partial y(C_2)} - (\sin \beta) \frac{\partial}{\partial x(C_2)} \right] \quad (5)$$

Substitution of (5) into  $J$  then gives

$$\begin{aligned} J = \langle 2p_y(N_1) | L_z(\text{Fe}) | 2p_x(C_2) \rangle = & -i\hbar \langle 2p_y(N_1) | X(C_2) \frac{\partial}{\partial y(C_2)} | 2p_x(C_2) \rangle + \\ & i\hbar \langle 2p_y(N_1) | Y(C_2) \frac{\partial}{\partial x(C_2)} | 2p_x(C_2) \rangle - \\ & i\hbar R_{\text{Fe}-C_2} (\sin \alpha \cos \beta) \langle 2p_y(N_1) | \frac{\partial}{\partial y(C_2)} | 2p_x(C_2) \rangle + \\ & i\hbar R_{\text{Fe}-C_2} (\sin \alpha \sin \beta) \langle 2p_y(N_1) | \frac{\partial}{\partial x(C_2)} | 2p_x(C_2) \rangle \quad (6) \end{aligned}$$

Next, we operated to the right in each of the four terms so as to create new functions from each operation. The final result was that it was possible to evaluate each of these four terms as a linear combination of overlap integrals. For the integral above we obtained 1.31891*i* BM using the following input

	Coordinates, A		
	X	Y	Z
C <sub>2</sub>	1.900	0.0	0.0
N <sub>1</sub>	3.050	0.0	0.0
Fe	0.0	0.0	0.0

The carbon and nitrogen orbitals were<sup>26</sup>

$$R(C_2; p) = N_1 e^{-1.5679r}$$

$$R(N_1; p) = N_2 e^{-1.9170r}$$

and the overlap integrals were evaluated using INTE (*vide supra*). Other integrals of  $L_z$  were evaluated similarly.

Registry No.  $\text{Fe}(\text{CN})_6^{3-}$ , 13408-62-3.

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## Intensity Studies on the Raman-Active Fundamentals of Some Square-Planar ( $\text{MX}_4^{n-}$ ) Ions and of the $\text{ICl}_2^-$ Ion. Calculation of Parallel and Perpendicular Bond Polarizability Derivatives and Bond Anisotropies

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The Raman spectra of solid samples and aqueous acid solutions of the anions  $\text{MX}_4^{n-}$  ( $M = \text{Pt}, \text{Pd}, \text{or Au}; X = \text{Cl or Br}$ ) and of acetonitrile solutions of the  $\text{ICl}_4^-$  and  $\text{ICl}_2^-$  ions have been recorded, and accurate values of the Raman-active fundamentals in each state are reported. The intensities in solution of all the Raman bands of each ion relative to that of the  $935\text{-cm}^{-1}$  band of the perchlorate ion have been measured at four different exciting frequencies. On the basis of these measurements, bond polarizability derivatives,  $\alpha'_{\text{MX}}$ , at zero exciting frequency have been calculated. A procedure for the calculation of both the parallel and the perpendicular components of  $\alpha'_{\text{MX}}$  for square-planar and linear ions is outlined, both for the case in which the MX bond is assumed to have cylindrical symmetry and for that in which it does not, and the magnitudes of these quantities are calculated for the ions in question and discussed. The quantity  $\alpha''_{\text{MX}}$  is a measure of the degree of covalent character of a bond. Values for the bond anisotropy  $\gamma_{\text{MX}}$  have also been deduced for the square-planar ions from the intensity of the Raman-active bending mode of each ion.

### Introduction

Previous studies of the intensities of Raman-active fundamentals of molecules and ions have primarily been concerned with octahedral,<sup>1-4</sup> tetrahedral,<sup>5-8</sup> linear,<sup>9,10</sup> and trigonal-planar<sup>5,11</sup> species. The present study, the first involving square-planar ions, has been carried out in order to establish values for the MX bond polarizability derivatives ( $\alpha'_{\text{MX}}$ ) for this interesting class of ions for comparison with the  $\alpha'_{\text{MX}}$  values of related ions of different stereochemistries. A procedure has been developed for the calculation of parallel and perpendicular bond polarizability derivatives in square-planar and linear ions, and the magnitudes of the quantities so calculated are discussed with reference to the degrees of covalent character of the MX bonds involved in the normal modes of vibration. Bond anisotropy derivatives as well as bond anisotropies have been deduced.

In all cases the intensities of the Raman-active fundamentals were measured relative to the  $935\text{-cm}^{-1}$  band of the perchlorate ion as internal standard. All intensity measurements were carried out by use of the rotating-sample technique at four

different exciting frequencies in order that suitable corrections for the preresonance Raman effect could be made. In the course of the work, accurate values for all the Raman-active fundamentals of each species have been determined.

### Experimental Section

**Samples.** The compounds  $\text{KAuCl}_4$ ,  $\text{KAuBr}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_2\text{PdCl}_4$ ,  $\text{K}_2\text{PdBr}_4$ , and  $(\text{NH}_4)_2\text{PtCl}_4$  were obtained from Johnson Matthey and Co. Ltd.  $\text{K}_2\text{PtBr}_4$  was obtained from K & K Laboratories, Inc.  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{AuCl}_4]$  and  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{AuBr}_4]$  were prepared by standard procedures.<sup>12</sup> The compounds  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ICl}_4]$  and  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ICl}_2]$  were prepared according to the method of Popov and Buckles,<sup>13</sup> and their Raman spectra were recorded in dried acetonitrile, the  $919\text{-cm}^{-1}$  band of the latter being used as internal standard. This band was subsequently calibrated against the  $935\text{-cm}^{-1}$  band of the perchlorate ion. In all other cases the samples were dissolved in aqueous solutions of the appropriate hydrohalic acid to minimize hydrolysis and then sodium or potassium perchlorate was added in known amounts as internal standard.

Each solution was studied at two different relative concentrations of standard to solute. The approximate mole ratios (number of moles of solute/number of moles of perchlorate) used for each anion studied