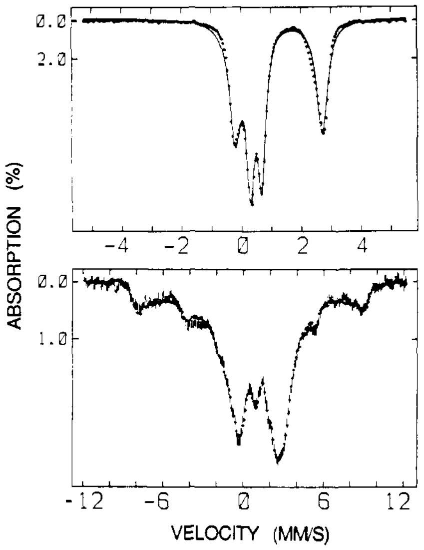

Figure 2. Mössbauer spectra of ^{57}Fe-enriched $[Fe_2(HXTA)(OAc)_2]^{2-}$ in methanol with 0.050 M HOAc/NaOAc at 55 K in zero applied field (top) and at 4.2 K in parallel (crosses) and transverse (hatchmarks) applied fields of 50 mT (bottom).

line width relative to that found in **1** is consistent with the presence of a fast-relaxing high-spin Fe(II) center in the mixed-valence complex.[13,14] The sharpness of the spectra allows us to observe all the protons in **2** and **3**, and we have assigned them by atom substitution experiments.[15,16] The HXTA ligand retains its twofold symmetry, indicating that electron transfer between the metal centers in the complex is fast on the NMR time scale. The bound acetate protons, found at 56 ppm, are in slow exchange with the free acetate in solution, and substitution of acetate with propionate results in CH_2 signals which are diastereotopic.[17] Both observations suggest that the carboxylates bridge the two iron centers; hence the triply bridged diiron structure found in **1** is retained in the mixed-valence form.

The Mössbauer spectrum of **2** at 55 K (Figure 2, top) consists of two quadrupole doublets of equal intensity with isomer shifts of 1.23 and 0.50 mm/s and quadrupole splittings of 2.87 and 0.37 mm/s, respectively, consistent with a high-spin Fe(II)-Fe(III) formulation.[18] The observation of discrete quadrupole doublets for this complex indicates that intervalence electron transfer is slow on the Mössbauer time scale at 55 K. Studies at 110 K show some line broadening, suggesting the onset of intermediate electron exchange. At 4.2 K the Mössbauer spectra (Figure 2, bottom) exhibit magnetic hyperfine interactions, even in zero applied magnetic field, implying a system with half-integer spin.[19] The spectra recorded in parallel (crosses) and transverse (hatchmarks) fields are essentially the same. This suggests a Kramers doublet with uniaxial magnetic properties; such systems produce, at best, only weak EPR signals. Indeed, except for a minor signal at $g = 4.3$ (<0.05 spin/Fe) which can be attributed to iron(III) from the decomposition of the complex in solution, **2** does not exhibit an EPR signal, even at 2 K. A preliminary analysis of the Mössbauer data suggests a coupled Fe(III)-Fe(II) system where the Fe(II) zerofield splitting and the antiferromagnetic coupling between the metal centers are of similar magnitudes. Zerofield splittings for high-spin ferrous centers in non-heme environments are in the range of 10 cm^{-1},[20] while the J value for the complex is estimated to be ca. -5 ± 2 cm^{-1}[21] from the temperature dependence of the NMR isotropic shifts.[22] Further magnetic susceptibility studies on **2** are in progress.[23]

The Mössbauer and EPR properties of **2** recall those of the reduced uteroferrin-phosphate complex, which is also EPR silent despite Mössbauer data indicating a half-integer spin state;[24] **2** thus serves as a potential model for the magnetic properties of this complex. We are currently investigating the properties of Fe(II)-Fe(III) complexes of other binucleating ligands in an effort to understand how ligand environments influence the spectroscopic properties of mixed-valence iron complexes.

Acknowledgment. This work was supported by National Institutes of Health Grants GM-33162 (L.Q.), GM-38767 (L.Q.), and GM-22701 (E.M.). We thank Professor P. G. Debrunner for providing the EPR spectra at 2 K.

Note Added in Proof: We have recently become aware of a paper[25] reporting the electrochemical reduction of $[(Me_3TACN)_2Fe_2O(OAc)_2]^{2+}$, where Me_3TACN is 1,4,7-trimethyl-1,4,7-triazacyclononane. The one-electron reduction of this complex in solution yields a mixed-valence species with EPR features at $g < 2.0$, which are similar to those found in mixed-valence forms of iron-oxo proteins.

---

[13] Swift, T. J. In *NMR of Paramagnetic Molecules: Principles and Applications*; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic: New York, 1973; Chapter 2.

[14] Bertini, I.; Lanini, G.; Luchinat, C.; Messori, L.; Monnanni, R.; Scozzafava, A. *J. Am. Chem. Soc.* **1985**, *107*, 4391-4396.

[15] The acetate, carboxymethyl, and meta protons were selectively deuteriated,[16] while the para methyl group was substituted with chlorine.

[16] Murch, B. P.; Bradley, F. C.; Boyle, P. D.; Papaefthymiou, V.; Que, L., Jr. *J. Am. Chem. Soc.*, in press.

[17] The propionate CH_2 protons would be diastereotopic if **3** adopted a structure similar to that of **1**, which has a twofold rotation axis as its sole symmetry element.

[18] Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971; pp 113-168.

[19] Münck, E. *Methods Enzymol.* **1978**, *54*, 346-379.

[20] Whittaker, J. W.; Solomon, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 835-836. Hodges, K. O.; Wollman, R. G.; Barefield, E. K.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 2746-2751.

[21] This value is in agreement with that obtained from solid susceptibility measurements (80-300 K) on a related complex reported by Suzuki et al.[6]

[22] Maroney, M. J.; Kurtz, D. M., Jr.; Nocek, J. M.; Pearce, L. L.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 6871-6879.

[23] Day, E. P.; Bonvoisin, J. J.; Peterson, J., work in progress.

[24] Pyrz, J. W.; Sage, J. T.; Debrunner, P. G.; Que, L., Jr. *J. Biol. Chem.* **1986**, *216*, 11015-11020.

[25] Hartmann, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.*, in press.

Synthesis and Reactions of Anionic Metallocarboxylates of Iron

Dorothy H. Gibson* and Tek-Sing Ong

Department of Chemistry, University of Louisville
Louisville, Kentucky 40292

Received June 8, 1987

Interest in both metallocarboxylic acids and their conjugate bases derives from their proposed intermediacy in metal carbonyl catalyzed water gas shift (WGS) reactions.[1] However, few of the acids[2] and fewer of the anionic metallocarboxylate complexes[3] have been characterized. Syntheses of the anionic complexes have resulted from either direct carbonation of a metal anion or deprotonation of a metallocarboxylic acid; in only a few cases has isolation been possible. We report here the isolation and characterization of $M[FeCp(CO)(PPh_3)(CO_2)]$ ($M = Li$ and K; $Cp = \eta\text{-}C_5H_5$), their behavior toward electrophiles, and their thermolysis reactions.

---

[1] Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

[2] Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem* **1983**, *22*, 129.

[3] (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082. (c) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604. (d) Forschner, T.; Menard, K.; Cutler, A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 121. (e) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794. (f) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478. (g) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. (h) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

Table I. Carbonyl Chemical Shifts for **2a** and **2b**

compd	solvent	crown[a]	δ_{CO} (mult, J_{PC} (Hz))
2a	acetone-d_6/D_2O[b]		221.67 (d, 34.8) 220.34 (d, 27.1)
2a	acetone-d_6/D_2O[b]	18-crown-6	221.42 (d, 34.3) 218.43 (d, 27.0)
2b	acetone-d_6/D_2O[b]		221.56 (d, 34.5) 219.87 (d, 26.5)
2b	acetone-d_6/D_2O[b]	12-crown-4	221.62 (d, 35.8) 218.71 (d, 27.6)
2b	THF-d_8[c]		221.98 (d, 34.2) 217.93 (d, 26.9)
2b	THF-d_8[c]	12-crown-4	221.61 (d, 36.05) 216.49 (m)

[a] Two equivalents of the crown ether was present. [b] Spectrum was recorded at 20 °C. [c] Spectrum was recorded at -35 °C.

Reaction of [CpFe(CO)$_2$(PPh$_3$)]I, (**1I**), with 2 equiv of KOH in aqueous acetone results, after chilling, in precipitation of dark orange plates of K[FeCp(CO)(PPh$_3$)(CO$_2$)], (**2a**). Similar reaction of **1I** with lithium hydroxide in aqueous acetone affords the lithium salt, **2b**, as a yellow-orange solid:[4]

$$\underset{\textbf{1I}}{[\mathrm{CpFe(CO)_2(PPh_3)}]\mathrm{I}} \xrightarrow[\text{acetone/H}_2\text{O}]{\text{MOH}} \underset{\substack{\textbf{2a},\ \mathrm{M} = \mathrm{K} \\ \textbf{2b},\ \mathrm{M} = \mathrm{Li}}}{\mathrm{M[FeCp(CO)(PPh_3)(CO_2)]}}$$

Hydrolysis of either salt with 1 equiv of HCl in aqueous acetone results in formation of the metallocarboxylic acid, CpFe(CO)(PPh$_3$)COOH (**3**).[5] Treatment of either **2a** or **2b** with excess HBF$_4$·etherate results in re-formation of the cation, **1**BF$_4$.

Solid-state (DRIFTS) IR spectral data of **2a** and **2b**[6] show a broad, weak band in the OH stretching region, which is assigned to coordinated water (the OH region in the spectra of these compounds is similar to that of NaOAc·3H$_2$O). As expected for a metallocarboxylate anion,[3b] the compounds show only weak absorption in the 1600-cm^{-1} region, but show significant bands below 1500 cm^{-1}. The ^{1}H NMR spectrum of the lithium complex, **2b**, in THF-d_8 shows a peak at δ 4.24, which is assigned to coordinated water. Compound **2a** is not sufficiently stable in this solvent, even at low temperature, to allow its spectra to be obtained; however, proton and carbon spectra of the two compounds can be compared in acetone-d_6/D$_2$O and are quite similar.[7] The carbon spectra[8] of both compounds show the terminal and carboxyl carbons as low-field doublets. In an effort to assign these resonances, we have also obtained the carbon spectra of the complexes in the presence of the appropriate crown ethers; the carbonyl chemical shifts, with and without the crowns, are recorded in Table I. With both complexes, the higher field carbonyl resonance shifts upfield when the crown ether is present; the effect is slightly greater for the potassium compound. The magnitude of the effect is much smaller, but is in the same direction as the effect of HMPA on the acyl carbon resonance in the spectra of alkali metal salts of formyl- and acyliron anions;[9] therefore we tentatively assign the upfield carbonyl resonance to the carboxyl carbon in each case.[10]

The behavior of **2a** and **2b** toward various electrophiles has been examined. In contrast to other potassium metallocarboxylates,[3b,g] **2a** provides the corresponding ester, CpFe(CO)(PPh$_3$)COOCH$_3$[5a] (**4**), as a major product from reactions with methylating agents. One equivalent each of methyl iodide, methyl trifluoromethanesulfonate (methyl triflate), and trimethyloxonium tetrafluoroborate afforded isolated yields of 85%, 70%, and 70%, respectively, of **4** and varying amounts of cation **1** (trace, 17%, and 14%, respectively), resulting from oxide transfer to the alkylating agent.[11] Reactions of both **2a** and **2b** with 2 equiv of trityl cation, (Ph$_3$C)BF$_4$, yield trityl ether and **1**BF$_4$; both products are isolated in better than 85% yield from both starting materials. With **2b**, reaction with methyl iodide yields only a trace of the ester, but a 77% yield of cation **1**. Reactions of **2b** with the other alkylating agents yield cation **1** as the only metal carbonyl product. Reaction of 1 equiv of lithium iodide with ester **4** results in ester cleavage; a 91% yield of cation **1I** and only a trace of the ester are recovered from the mixture. Addition of 12-crown-4 to the reaction mixture does not change the results. However, reaction of **4** with KI shows only a slight amount of ester cleavage.

We were also interested in possible oxide transfer behavior of **2a** and **2b** toward a metal carbonyl cation. Reaction of **2a** with [Mn(CO)$_5$(PPh$_3$)]BF$_4$, followed by addition of CH$_3$I, affords **1**BF$_4$ and Mn(CO)$_4$(PPh$_3$)CH$_3$;[13] the latter compound is believed to result from alkylation of the anion formed after CO$_2$ loss from Mn(CO)$_4$(PPh$_3$)(CO$_2$)$^-$ (formed as the oxide transfer product). The same compounds result from **2b**; in both cases the organometallic products are isolated in better than 85% yield. In no case was dissociative loss of CO$_2$ a competing reaction of **2a** or **2b** with any of the electrophiles.

Thus, three distinct types of reactions can be observed for metallocarboxylate anions in the presence of alkylating agents: (a) dissociative loss of CO$_2$ followed by alkylation of the metal anion,[3b,d] (b) alkylation of a carboxylate oxygen,[3d,g] and (c) oxide transfer to the alkylating agent.[14] Reactions of type a can be suppressed by sequestering the CO$_2$ ligand with a strongly bound metal cation (e.g., Mg^{2+})[3d], by making the transition-metal center highly electron rich,[3h] or by using a highly oxophilic alkylating agent.[3g] However, even these techniques will not ensure that reaction with an alkylating agent will result in formation of a stable ester; the oxophilicity of the metal counterion can also play a significant role in partitioning the reaction between alkylation and oxide transfer.

In the first report of **2a**,[5a] it was indicated that the compound was a yellow microcrystalline precipitate, stable at 100 °C in dry DMF. In our hands, compounds **2a** and **2b** are rapidly decomposed to Cp$_2$Fe$_2$(CO)$_3$(PPh$_3$)[15] in dry organic solvents at room

---

(4) More detailed procedures for the preparation of **2a** and **2b** will be published elsewhere: Gibson, D. H.; Ong, T.-S. *Organometallic Syntheses*, Vol. 4, in press.

(5) (a) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. (b) Gibson, D. H.; Ong, T.-S. *Organometallics* **1984**, *3*, 1911. (c) Gibson, D. H.; Ong, T.-S. *Organometallic Syntheses*, Vol. 4, in press.

(6) The IR (DRIFTS) spectrum of **2a** (mp 57–60 °C) shows the following bands: 3700–2700 (w, centered at 3370), 1885 (s), 1877 (sh, s), 1588 (w, br), 1479 (s, br) cm^{-1}. Compound **2b** (mp 65–68 °C) shows IR (DRIFTS) bands at 3638 (w), 3291 (vw, br), 1912 (s), 1899 (sh, s), 1615 (w), 1479 (m), and 1436 (s) cm^{-1}.

(7) ^{1}H NMR (1:1 acetone-d_6/D$_2$O, 20 °C) for **2a**: δ 7.39 (m), 7.24 (m), 4.33 (s). ^{1}H NMR for **2b** (2:1 acetone-d_6/D$_2$O, 20 °C): δ 7.43 (m), 7.27 (m), 4.35 (s); (THF-d_8, −35 °C): δ 7.65 (m), 7.31 (m), 4.48 (s), 4.24 (s, br).

(8) ^{13}C NMR for **2a** (1:1 acetone-d_6/D$_2$O, 20 °C): δ 221.67 (d, J_{PC} = 34.8 Hz), 220.34 (d, J_{PC} = 27.1 Hz), 138.08 (d, J_{PC} = 41.5 Hz), 133.48 (d, J_{PC} = 9.8 Hz), 129.81 (s), 128.15 (d, J_{PC} = 8.8 Hz), 84.86 (s). ^{13}C NMR for **2b** (2:1 acetone-d_6/D$_2$O, 20 °C): δ 221.56 (d, J_{PC} = 34.5 Hz), 219.87 (d, J_{PC} = 26.5 Hz), 138.23 (d, J_{PC} = 41.3 Hz), 133.52 (d, J_{PC} = 9.4 Hz), 129.74 (s), 128.12 (d, J_{PC} = 9.2 Hz), 84.85 (s); (THF-d_8, −35 °C): δ 221.98 (d, J_{PC} = 34.2 Hz), 217.93 (d, J_{PC} = 26.9 Hz), 139.67 (d, J_{PC} = 36.9 Hz), 134.53 (s, br), 129.76 (s), 128.45 (d, J_{PC} = 7.6 Hz), 85.58 (s).

(9) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.

(10) The carbonyl chemical shifts are similar to those reported for other metallocarboxylate anions.[3g,h] Assignments of the carboxyl and carbonyl resonances reported by Cutler[3g] for CpFe(CO)$_2$CO$_2^-$Li$^+$ are unequivocal; in THF-d_8 the carboxyl carbon is at 217.0 ppm and the carbonyl carbons are at 200.7 ppm. The corresponding methyl ester shows upfield shifts of both resonances (213.3 and 200.8 ppm), with the carboxyl carbon shifted by the greater amount. Comparisons of the resonances of **2b** (Table I: 221.98 and 217.93 ppm) with those of the corresponding acid[5c] (220.90 and 214.10 ppm) and methyl ester (220.81 and 212.18 ppm), all in THF-d_8, show the same trends. These comparisons provide further support for the assignments of the carbon resonances for **2a** and **2b** given in the text.

(11) Reactions were conducted at −30 to −40 °C by adding a cold solution of the alkylating agent in CH$_3$CN to the solid metallocarboxylate maintained at the same temperature under N$_2$. The mixtures were stirred at low temperature for a time and then slowly warmed to room temperature. Solvent was removed and the residues were triturated with CH$_2$Cl$_2$/hexane to separate the ester from cation **1**. Ester **4** partially ionizes in polar solvents, but returns to the covalent form upon removal of solvent.

(12) (a) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794. (b) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1467.

(13) The corresponding methyl ester, Mn(CO)$_4$(PPh$_3$)COOCH$_3$, is stable under the reaction conditions.

(14) Cooper[3h] has observed that Li$_2$[W(CO)$_5$(CO$_2$)] yields W(CO)$_6$ as the main organometallic product from reactions with various organic electrophiles; these may represent further examples of oxide transfers to electrophiles promoted by lithium ion.

(15) Compound **3** decomposes to the same product.[5b]

temperature in a nitrogen-filled glovebox. It was not easily apparent how the two sets of results could be so different; however, if **2a** is allowed to stand in water at room temperature, the color of the solid changes from dark orange to yellow and its spectral properties change also. The new compound, **5**, shows carbonyl absorptions at 1940 and 1610 cm^{-1} (Nujol mull), reacts with methyl alcohol to give ester **4**, and reacts with excess acid to give cation **1**. We suggest that **5** may be the anhydride, $[CpFe(CO)(PPh_3)C(O)]_2O$, a member of a currently unknown class of organometallic compounds, and that it was **5** and not **2a** which was studied earlier. Efforts are in progress to characterize compound **5**. The lithium salt, **2b**, is more stable to further reaction with water, but slowly degrades after standing overnight; compound **5** does not appear to be formed from **2b**.

Efforts are in progress to probe further for differences in the chemical behavior of metallocarboxylates **2a** and **2b** and their sodium and calcium analogues.

Acknowledgment. Support of this work by the Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), is gratefully acknowledged.

Theory of Vibrational Circular Dichroism: *trans*-1(*S*),2(*S*)-Dicyanocyclopropane

K. J. Jalkanen and P. J. Stephens*

Department of Chemistry
University of Southern California
Los Angeles, California 90089

R. D. Amos and N. C. Handy

Department of Theoretical Chemistry
Cambridge University, Cambridge, UK

Received April 6, 1987

Vibrational circular dichroism (VCD) reflects the stereochemistry of a chiral molecule and, in principle, provides a tool for its elucidation. More than a decade since the earliest observations[1-3] the measurement of VCD is now nearly routine.[4,5] However, until recently, the absence of a convincing theory of VCD has impeded the analysis and application of VCD spectra.[5]

Recently, an a priori theoretical formalism of vibrational rotational strengths has been derived by Stephens, allowing for the first time direct calculation of VCD spectra from molecular wave functions.[6] Stephens' equation for the rotational strength, R_i, of the fundamental transition in the ith normal mode requires the computation of two molecular tensors: $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ at the molecular equilibrium geometry, $\mathbf{R}_o$. $P^{\lambda}_{\alpha\beta}$ is the familiar atomic polar tensor (APT)[7]

$$P^{\lambda}_{\alpha\beta} = [\partial(\mu^{G}_{\text{el}})_{\beta}/\partial X_{\lambda\alpha}]\mathbf{R}_o \qquad (\alpha, \beta = x, y, z)$$

where μ^{G}_{el} is the adiabatic electric dipole moment of the ground electronic state G and $X_{\lambda\alpha}$ is a Cartesian displacement coordinate from $\mathbf{R}_o$ of nucleus λ. $I^{\lambda}_{\alpha\beta}$ is a new tensor given by

$$I^{\lambda}_{\alpha\beta} = \left\langle \left(\frac{\partial\psi_G(\mathbf{R})}{\partial X_{\lambda\alpha}}\right)_{\mathbf{R}_o} \middle| \left(\frac{\partial\psi_G(\mathbf{R}_o,H_\beta)}{\partial H_\beta}\right)_{H_\beta=0} \right\rangle$$

where $\psi_G(\mathbf{R})$ is the adiabatic electronic wave function of G, and $\psi_G(\mathbf{R}_o,H_\beta)$ is the wave function of G at $\mathbf{R}_o$ in the presence of a magnetic field perturbation. $P^{\lambda}_{\alpha\beta}$ alone determines dipole strengths, D_i, and absorption spectra of vibrational transitions.

Table I. Calculated and Experimental Vibrational Frequencies[a] of TDCCP-d_0

symmetry[b]	expt[c]	unscaled	scaled (one param)	scaled (six params)
B	3119	3419	3081	3112
B	3052	3364	3032	3062
A	3052	3362	3031	3061
A	3035	3322	2994	3024
A	2247	2621	2362	2247
B	2247	2621	2362	2247
A	1443	1636	1475	1460
A	1385	1556	1402	1388
B	1297	1447	1304	1288
A	1190	1312	1183	1176
B	1131	1260	1136	1122
B	1104	1226	1105	1090
A	1075	1223	1103	1089
A	1048	1191	1074	1064
B	992	1091	984	978
B	908	1041	938	915
A	871	995	897	893
A	809	887	799	797
B	778	852	768	763
B	553	613	553	542
B	530	587	529	535
A	518	575	519	513
A	497	546	492	498
B	270	290	262	252
A	237	252	227	232
B	129	169	152	154
A	88	128	115	107
		RMS Deviation from Experiment[a]		
		182	37	13

[a] In cm^{-1}. [b] Calculated. [c] Reference 18.

VCD spectra calculated with Stephens' equations have to date been compared to experiment for two small chiral molecules: propylene oxide and *trans*-1,2-dideuteriocyclobutane.[5,8] SCF wave functions at the 4-31G basis set level[9] were used. The derivatives determining $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ were obtained by finite difference procedures.[10] The results were in encouraging agreement with experiment. However, the use of finite difference procedures for the calculation of $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ is extremely cumbersome and only practical for very small molecules and basis sets. State-of-the-art calculations of $P^{\lambda}_{\alpha\beta}$ now employ vastly more efficient analytical derivative techniques.[11-15] We have therefore developed the methodology for the calculation of $I^{\lambda}_{\alpha\beta}$ as well as $P^{\lambda}_{\alpha\beta}$ using analytical derivative methods and implemented it in the Cambridge Analytical Derivatives Package (CADPAC) program.[16] This now permits the efficient prediction of VCD spectra for much larger molecules and basis sets than heretofore practicable.

We report here the first application of this new calculational technology. The VCD spectra of the d_0 and *trans-1,2-d*$_2$ isotopomers of *trans*-1(*S*),2(*S*)-dicyanocyclopropane (TDCCP) are predicted by using SCF wave functions and the 6-31G** basis set[9] and compared to the experimental spectra of Heintz and Keiderling.[17]

---

(1) Holzwarth, G.; Hsu, E. C.; Mosher, H. S.; Faulkner, T. R.; Moscowitz, A. *J. Am. Chem. Soc.* **1974**, *96*, 251.

(2) Nafie, L. A.; Cheng, J. C.; Stephens, P. J. *J. Am. Chem. Soc.* **1975**, *97*, 3842.

(3) Nafie, L. A.; Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 2715.

(4) Nafie, L. A. *Adv. Infrared Raman Spectrosc.* **1984**, *11*, 49.

(5) Stephens, P. J.; Lowe, M. A. *Ann. Rev. Phys. Chem.* **1985**, *36*, 213.

(6) Stephens, P. J. *J. Phys. Chem.* **1985**, *89*, 748.

(7) Person, W. B.; Newton, J. H. *J. Chem. Phys.* **1974**, *61*, 1040.

(8) Lowe, M. A.; Stephens, P. J.; Segal, G. A. *Chem. Phys. Lett.* **1986**, *123*, 108.

(9) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: 1986.

(10) Lowe, M. A.; Segal, G. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 248.

(11) Amos, R. D.; *Chem. Phys. Lett.* **1984**, *108*, 185.

(12) Amos, R. D. *Chem. Phys. Lett.* **1985**, *114*, 10; **1985**, *122*, 180.

(13) Amos, R. D. *Chem. Phys.* **1986**, *104*, 145.

(14) Yamaguchi, Y.; Frisch, M.; Gaw, J.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262.

(15) Amos, R. D. *Adv. Chem. Phys.* **1987**, *67*, 99.

(16) Amos, R. D.; Handy, N. C.; Jalkanen, K. J.; Stephens, P. J. *Chem. Phys. Lett.* **1987**, *133*, 21.

0002-7863/87/1509-7193$01.50/0