intensity mechanism. The direct sensitivity of VCD to the absolute stereochemistry of the acac rings around the cobalt center is demonstrated. The NH stretching vibrations of the alaninato ligand in differing intramolecular hydrogen bonding environments with respect to an adjacent acac ligand yield a set of VCD spectra that dramatically portray the presence of a vibrationally generated ring current in the Δ- but not the Λ-complex. Sensitivity of VCD to the formation of intramolecular hydrogen bonded rings in molecules is demonstrated. Calculated ring current parameters allow comparison of the strength of this effect in different normal modes in differing environments. These data will provide a basis for theoretical calculations of vibrational ring currents in molecules.

Enhanced Vibrational Circular Dichroism via Vibrationally Generated Electronic Ring Currents

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Abstract: The enhanced vibrational circular dichroism (VCD) observed for some CH and OH stretching vibrations is interpreted in terms of a vibrationally generated electronic ring current mechanism. The molecules investigated include phenylethane derivatives, α-hydroxy acids and esters, and amino acids. The large methine CH stretching VCD in molecules containing an adjacent ring closed by hydrogen bonding or $\pi-\pi$ interaction is not observed in molecules where these rings do not form. For the closed ring, an oscillating magnetic moment can arise from oscillating electronic ring current produced by the methine vibration and is responsible for the large VCD. Enhancement of methyl stretching VCD when through-space interaction between the methyl group and π orbitals is present and enhancement of OH stretching VCD for a hydroxyl group involved in an intramolecular ring provide further examples of vibrationally generated ring currents in VCD. General rules governing the sense of electronic current flow for a given phase of the nuclear motion are proposed which are consistent with all the spectra thus far obtained.

Vibrational circular dichroism[1] (VCD) results from two types of charge displacement occurring simultaneously during infrared excitation of a vibrational mode: linear oscillation of charge producing a nonzero electric dipole transition moment, and angular or circular oscillation of charge producing a nonzero magnetic dipole transition moment. For vibrational modes which involve the strongly coupled motion of chirally disposed oscillators, the magnetic contributions are adequately described by considering only nuclear motion with perfectly following electron density. For example, in the carbon–hydrogen stretching region, the VCD for chiral hydrocarbons arises primarily from this coupled oscillator mechanism and gives rise to conservative VCD spectra, which have no net VCD intensity over the spectral region.[2] In contrast, molecules with regions of delocalizable electron density (π bonds and lone pairs) near the oscillating nuclei often exhibit biased VCD spectra, which have a net positive or negative integrated intensity over the spectral region. In particular, we have observed that the methine C_αH stretching mode in L-amino acids introduces a strong positive bias in the VCD spectra in the CH stretching region for aqueous solutions at neutral pH.[3,4]

Biased VCD intensity in the hydrogen stretching regions requires angular oscillation of electronic charge density which does not perfectly follow the nuclear motion.[5] As an explanation for the strong VCD bias in the CH stretching region in amino acids, amino acid transition metal complexes, and lactic acid, we proposed the following mechanism:[3,4] the C_αH stretch generates an oscillating electronic current in a molecular ring, adjacent to the methine bond, which is closed by hydrogen bonding or transition metal coordination; this oscillating ring current gives rise to a large magnetic dipole transition moment. As depicted in **1** for the C_αH

1
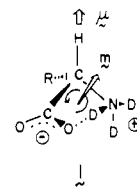
contraction in an L-amino acid, positive current, flowing in the direction N → C_α when electrons are injected into the ring by the C_αH contraction, produces a magnetic dipole transition moment, **m**, with a component in the direction of the electric dipole transition moment, μ. The VCD intensity, represented by the rotational strength $R = \text{Im}(\mu\cdot\mathbf{m})$, is positive, as observed experimentally.

In an effort to determine whether such a mechanism can be applied more generally, we have investigated a number of molecules with a single methine C_αH bond and a variety of other substituents. The CH and OH stretching VCD spectra of several molecules in this class have been surveyed previously in the literature,[6-13] without complete interpretation. For this study, we

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(3) Nafie, L. A.; Oboodi, M. R.; Freedman, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 7449.

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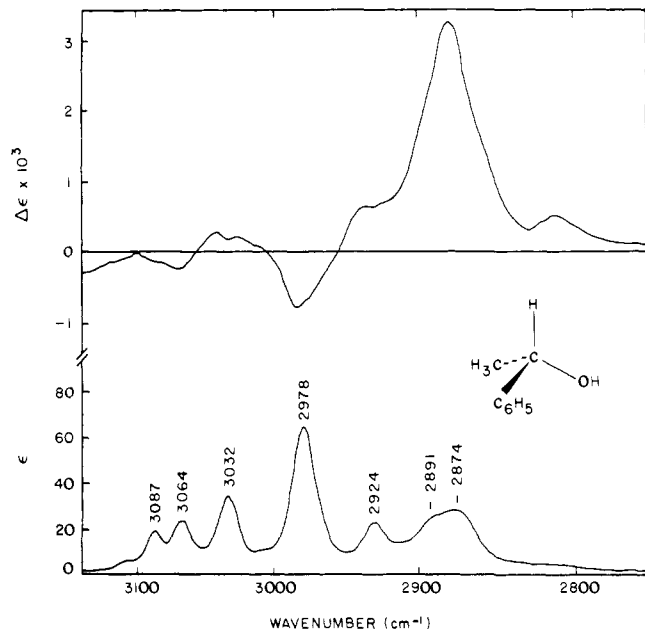
Figure 1. VCD and absorption spectra in the CH stretching region of (S)-(−)-1-phenylethanol, 0.148 M in CCl₄; sample path length 0.1 cm.

Figure 2. VCD and absorption spectra in the CH stretching region of (S)-(−)-1-phenylethanethiol, 0.131 M in CCl₄; sample path length 0.1 cm.

have also recorded the CH stretching VCD in a number of additional molecules.

Although the ring current model was originally introduced in the form of a chirality rule for a specific group of similar molecules, the L-amino acids, the results of the present study provide evidence that vibrationally generated ring currents play a major role as a source of VCD intensity. We have found that methine, methyl, and hydroxyl stretching VCD is enhanced in a wide variety of molecules when the oscillator is in or adjacent to an intramolecular ring. Based on correlations between the sign of the VCD and the structures of the rings, we have derived rules governing the sense of vibrationally generated ring current, which depend only on chemical parameters of the ring. These rules greatly extend the applicability of VCD as a probe of solution stereochemistry.

Experimental Section

Both the *R* and *S* enantiomers of 1-phenylethanol, methyl mandelate, α-phenylglycine, O-acetylmandelic acid, and α-methoxyphenylacetic acid were obtained from commercial sources (Aldrich or Alfa Products, 98–99%) and were used without further purification. (R)- and (S)-1-phenylethanethiol were prepared by the procedure developed by Vollante[14] for (S)-2-octanethiol, using a modified Mitsunobo reaction.[15] (R)- and (S)-1-chloro-1-phenylethane were synthesized using the method of Hoffman and Hughes.[16] All samples were studied as solutions in CCl₄, with the exception of α-phenylglycine which was dissolved in D₂O containing 2 N D₂SO₄ or DCl.

The VCD spectra (∼14 cm⁻¹ resolution) were recorded with a 10-s time constant on the dispersive grating instrument described previously.[17-19] VCD base lines were obtained by comparing the VCD spectra
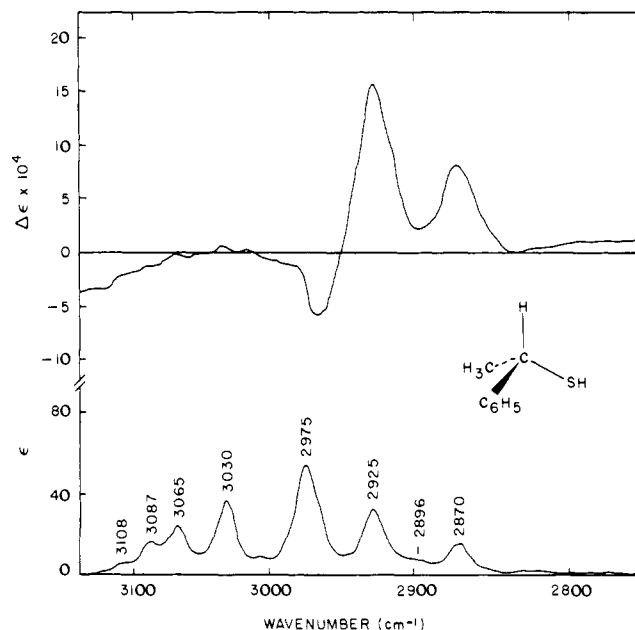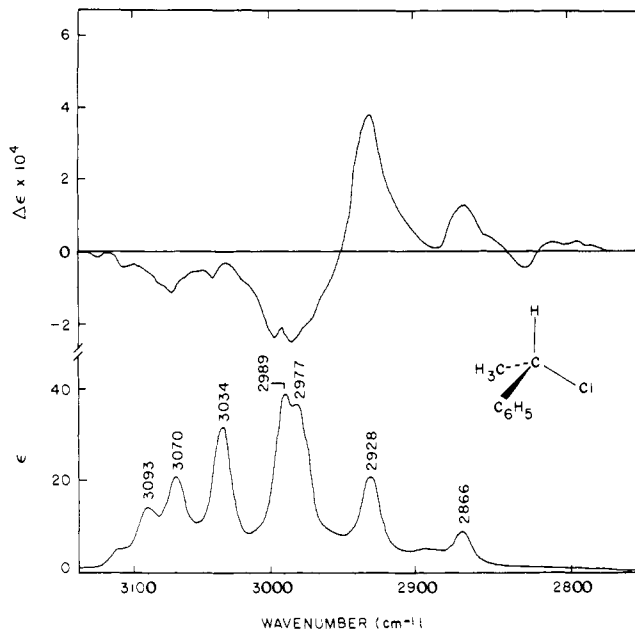

Figure 3. VCD and absorption spectra in the CH stretching region of (S)-(−)-1-chloro-1-phenylethane, 0.299 M in CCl₄; sample path length 0.1 cm.

of the *R* and *S* enantiomers. The absorption spectra (4 cm⁻¹ resolution) were obtained using a Nicolet 7199 FT-IR spectrometer.

Results

The series of $C_\alpha HR_1R_2R_3$ molecules compared here include substituted phenylethanes, α-hydroxy acids and esters, and amino acids and amino acid transition metal complexes. All contain either a phenyl or carboxylate group, or both. The experimental values of the frequency, rotational strength, and anisotropy ratio, $g = \Delta\epsilon/\epsilon$, for the methine and methyl (if present) vibrations for all the molecules studied are compiled in Table I, with the exception of the majority of the amino acids which have been tabulated elsewhere.[4]

The CH stretching VCD spectra of several of the molecules included in this study have been published previously from various laboratories.[6-13] For the purposes of this investigation we have, in addition, recorded the CH stretching VCD spectra of 1-

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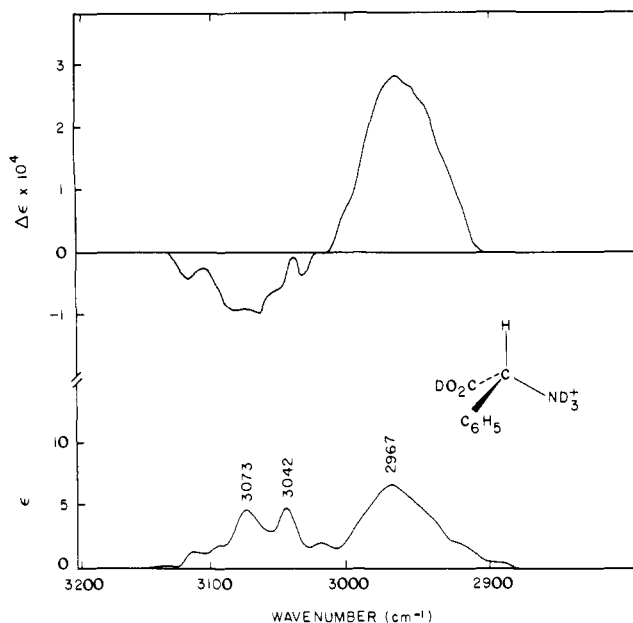(19) Oboodi, M. R. Ph.D. Thesis, Syracuse University, 1982.

Figure 4. VCD and absorption spectra in the CH stretching region of D-α-phenylglycine-*N*-*d*₃, 0.4 M in 2 N DCl in D₂O; sample path length 0.02 cm.
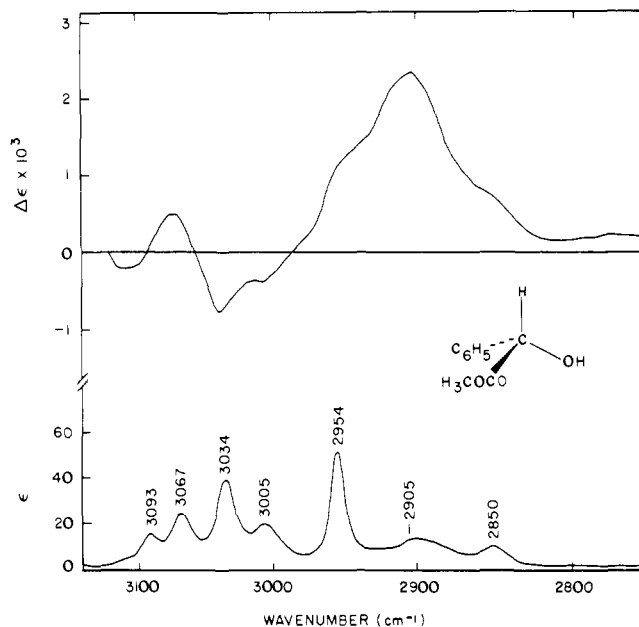

Figure 5. VCD and absorption spectra in the CH stretching region of (*S*)-methyl mandelate, 0.148 M in CCl₄; path length 0.1 cm.

phenylethanol, 1-chloro-1-phenylethane, 1-phenylethanethiol, α-phenylglycine, methyl mandelate, α-methoxyphenylacetic acid, and *O*-acetylmandelic acid. The spectra of these species, with the exception of the last two, are presented in Figures 1–6.

The vibrational assignments in Table I are made based on characteristic absorption patterns observed for the phenyl and methyl groups. In the substituted phenylethanes, the phenyl CH stretching modes remain fairly constant in frequency and are observed at ∼3090, ∼3070, and 3035 cm⁻¹. An additional phenyl mode at ∼3000 cm⁻¹ appears as a shoulder in most of the compounds but gains intensity in some of the mandelic acid derivatives.

A pattern of three bands, ∼2975, 2925, and 2870 cm⁻¹, is observed for a methyl group substituent at the α carbon in the phenylethane derivatives. The highest frequency absorption band arises from the two nearly degenerate antisymmetric methyl stretching modes. Although not resolved, a weaker shoulder to high frequency is detected for 1-phenylethylamine. The remaining two methyl bands arise from the strong Fermi resonance between
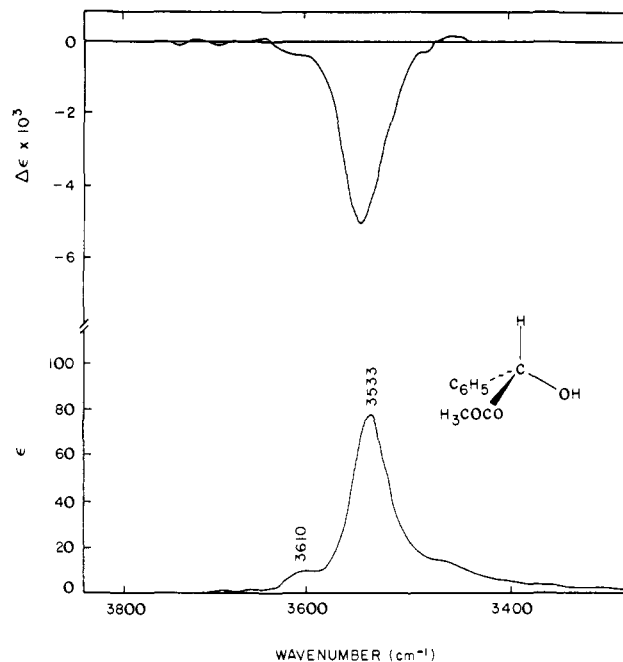

Figure 6. VCD and absorption spectra in the OH stretching region of (*S*)-methyl mandelate, 0.148 M in CCl₄; path length 0.1 cm.

the symmetric CH stretching fundamental (unperturbed $\nu \sim$ 2900–2908 cm⁻¹) and the overtone of the antisymmetric methyl deformation at ∼1450–1455 cm⁻¹. The latter is overlapped by a more intense phenyl absorption at 1450 cm⁻¹.[8] For a methyl group substituted at an oxygen, the same absorption pattern is observed, shifted to lower frequency. In the methyl esters, the methyl group transitions occur at 2954, 2905, and 2850 cm⁻¹. In the methoxy-substituted acid, the antisymmetric methyl modes split into bands at 2947 and 2931 cm⁻¹ (average 2938 cm⁻¹) and the Fermi dyad occurs at 2885 and 2828 cm⁻¹. In both lactic acid[4] and alanine,[18–20] the methyl group bands lie at higher frequency, with the average frequency of the antisymmetric modes at ∼3000 cm⁻¹, and the Fermi dyad at 2949 and 2892 cm⁻¹. In general, the methyl group vibrations are identified by an intense antisymmetric stretching band (which may be split), and two weaker bands ∼50 and ∼105 cm⁻¹ to lower frequency, which arise from the symmetric methyl stretching vibration.

The frequency of the methine stretch is much more variable and is influenced by the other α-carbon substituents. In 1-phenylethane-*1,2,2,2*-*d*₄, the lone C_α vibration gives rise to a band at 2910 cm⁻¹.[21] As exemplified by the spectra of α-phenylglycine (Figure 4) and 2,2,2 trifluoro-1-phenylethanol,[7] the methine absorption is normally broad, and it is usually overlapped by methyl vibrations if that group is also present in the molecule. The width of the methine vibration is due to the variation of the $C_\alpha H$ force constant with the conformation of the phenyl or carboxylate groups, as demonstrated by temperature studies of C₆H₅CHD₂.[22] In the amino acids,[4] the methine stretch occurs near 2970 cm⁻¹, and in the α-hydroxy acids and derivatives,[4,10,13] the methine stretching frequency varies between 2900 and 2960 cm⁻¹. In the substituted phenylethanes,[8] the methine stretch occurs as a shoulder to the lowest frequency methyl stretching component in the –OH-, –NH₂-, and –NCO-substituted species. In 1-chloro-1-phenylethane we assign the methine stretch to the feature at 2989 cm⁻¹ (Figure 3). It is unlikely that the 2989-cm⁻¹ band is due to splitting of the antisymmetric methyl modes by the Cl, since NCO and OH do not cause splitting in that mode. Furthermore, the methine stretching frequency in C₆H₅CHCl₂ was assigned at 2992 cm⁻¹ for the conformer with the phenyl group eclipsed to the –CH.[23] The source of the narrower methine bandwidth in

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Table I. Frequencies, Intensities, and Assignments of CH Stretching Modes

molecule (concn/solvent)	frequency, cm^{-1}	assignment[a]	rotational strength $\times 10^{44}$ esu^2 cm^2	anisotropy ratio $\Delta\epsilon/\epsilon$	ref[b]
(S)-(−)-1-phenylethanol	2978	CH$_3{}^{asym}$	−1	−1 × 10^{-5}	this work, 7–9
(0.148 M/CCl$_4$)	2924	CH$_3{}^{sym}$ F.R.	+1	+3.5 × 10^{-5}	
	2890	C*H	+8	+1.5 × 10^{-4}	
	2874	CH$_3{}^{sym}$ F.R.	+sh[c]	positive	
(S)-(−)-1-phenylethylamine	2965	CH$_3{}^{asym}$	−3	−2.5 × 10^{-5}	8, 7
(0.079 M/CCl$_4$)	2925	CH$_3{}^{sym}$ F.R.	+0.7	+1 × 10^{-5}	
	2870	CH$_3{}^{sym}$ F.R.	+sh	positive	
	2850	C*H	+3.7	+7 × 10^{-5}	
(S)-(−)-1-phenylethyl isocyanate	2970	CH$_3{}^{asym}$	−2.7	−2.5 × 10^{-5}	8
(0.087 M/CCl$_4$)	2924	CH$_3{}^{sym}$ F.R.	+(0.7)sh	+1 × 10^{-5}	
	2900	C*H	+4.2	+7.5 × 10^{-5}	
	2875	CH$_3{}^{sym}$ F.R.	+sh	positive	
(S)-(−)-1-phenylethanethiol	2975	CH$_3{}^{asym}$	−0.8	−1 × 10^{-5}	this work
(0.131 M/CCl$_4$)	2925	CH$_3{}^{sym}$ F.R.	+2	+5 × 10^{-5}	
	2896	C*H	<0.5	<2 × 10^{-5}	
	2870	CH$_3{}^{sym}$	+1	+5 × 10^{-5}	
(S)-(−)-1-chloro-1-phenylethane	2989	C*H			this work
(0.299 M/CCl$_4$)	2977	CH$_3{}^{asym}$	−0.6	−6 × 10^{-6}	
	2928	CH$_3{}^{sym}$ F.R.	+0.5	+2 × 10^{-5}	
	2866	CH$_3{}^{sym}$ F.R.	+0.2	+2 × 10^{-5}	
(R)-(−)-2,2,2-trifluoro-1-phenylethanol					
(0.07 M/CCl$_4$)	2910	C*H	+2	+5 × 10^{-5}	27
(0.14 M/CCl$_4$)	2908	C*H	−0.3 (2940 cm^{-1})		7
			+0.7 (2890 cm^{-1})		
neat	2916	C*H	−1.2 (2940 cm^{-1})		8
D-α-phenylglycine	2967	C*H	+0.8	+4 × 10^{-5}	this work
(0.4 M/2 N DCl in D$_2$O)					
L-alanine-N-d_3	3009	CH$_3{}^{asym}$	+0.54	+3.8 × 10^{-5}	18
(1.7 M/D$_2$O)	2989	CH$_3{}^{asym}$	−2.4	−1.7 × 10^{-4}	
	2970	C*H	+5.6	+5 × 10^{-4}	
	2949	CH$_3{}^{sym}$ F.R.	−0.7	−9 × 10^{-5}	
	2892	CH$_3{}^{sym}$ F.R.	−0.4	−8 × 10^{-5}	
L-alanine-N-d_3-C-d_3	2968	C*H	+2.1	+2 × 10^{-4}	18
(1.7 M/D$_2$O)					
L-lactic acid	3010	CH$_3{}^{asym}$	+0.2	+5 × 10^{-6}	4
(5.5 M/D$_2$O)	2992	CH$_3{}^{asym}$	−0.2	−1 × 10^{-5}	
	2948	CH$_3{}^{sym}$ F.R.	sh		
	2920	C*H	+1.5	+1.7 × 10^{-4}	
	2890	CH$_3{}^{sym}$ F.R.			
(S)-methyl mandelate	2954	CH$_3{}^{asym}$	sh		this work
(0.148 M/CCl$_4$)	2910	C*H	+6	+2 × 10^{-4}	
	2905	CH$_3{}^{asym}$ F.R.			
	2850	CH$_3{}^{sym}$ F.R.	sh		
sodium S-(+) mandelate	2900	C*H	+4		10
(4.0 M/D$_2$O)					
(−)-(2S,3S)-tartaric acid-d_4	2900	C*H	+8	+1.6 × 10^{-4}	11
(2.0 M/D$_2$O)					
(−)-2S,3S-dimethyl tartrate	2920	C*H	+17	+3 × 10^{-4}	1a
(0.017 M/CCl$_4$)					
O-acetylmandelic acid	2960	C*H	+5		this work
α-methoxyphenylacetic acid	2960	C*H?	positive		this work

[a] Antisymmetric methyl stretch (CH$_3{}^{asym}$); methine stretch (C*H); Fermi resonance diad involving symmetric methyl stretch (CH$_3{}^{sym}$ F.R.). [b] Numerical data are from first reference listed for each compound. [c] sh = shoulder.

1-chloro-1-phenylethane will be addressed below.

The methine stretching mode in 1-phenylethanethiol is apparently quite weak, and it is difficult to locate. No large frequency shift from the methine stretch in the alcohol is expected. For example, in ethanethiol, the average frequency of the methylene CH stretching modes is 2906 cm^{-1} in an argon matrix.[24] We therefore assign the weak shoulder at 2896 cm^{-1} (Figure 2) to the methine stretch in 1-phenylethanethiol.

In the VCD spectra of this group of molecules, features corresponding to most of the absorption bands are observed. The phenyl group gives rise to weak, indistinct VCD features, which yield little structural information at this time. In contrast, the methyl and methine groups at the asymmetric carbon generate characteristic, fairly intense VCD patterns. The antisymmetric methyl stretching modes give rise to a bisignate couplet in alanine

and lactic acid, whereas in the phenylethane derivatives, the absorption band for these modes is not resolved and only a single VCD feature is observed, corresponding to an excess of VCD intensity for one of the two antisymmetric methyl stretches. The two components of the Fermi resonance dyad involving the symmetric methyl stretching mode give rise to VCD of the same sign and with proportionate intensity, as expected.

The VCD bands corresponding to the methine CH stretch are broad, as are the corresponding absorption features. The intensity of the methine CH stretching VCD varies greatly over the series of molecules studied and appears to be quite sensitive to the molecular environment.

VCD spectra have also been recorded in the OH stretching region of α-hydroxy acids and esters.[10,12,13] The large negative VCD for the S enantiomers (Figure 6) corresponds to the maximum of the absorption spectrum (~3530 cm^{-1}) which has been assigned to OH hydrogen bonded to the ester carbonyl oxygen. In (R)-2,2,2-trifluoro-1-phenylethanol, a negative OH stretching VCD band is also observed. The frequencies and intensities for the OH region are compiled in Table II.

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(24) Barnes, A. J.; Hallam, H. E., Howells; J. D. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 737.

Table II. Frequencies and Intensities of OH Stretching Modes

molecule (concn/solvent)	frequency, cm^{-1}	rotational strength $\times 10^{44}$ esu^2 cm^2	anisotropy ratio $\Delta\epsilon/\epsilon$	ref[a]
(S)-(+)-methyl mandelate (0.148 M/CCl_4)	3533	−12	−6 × 10⁻⁵	this work, 10
(S)-methyl lactate (0.006 M/CCl_4)	3555	−11	−4.5 × 10⁻⁵	12
(2S)-dimethyl malate (0.042 M/CCl_4)	3550	−19	−2.5 × 10⁻⁵	13
(S)-methyl 3-hydroxybutyrate (0.008 M/CCl_4)	3585	+2		12
	3545	−2		
(R)-2,2,2-trifluoro-1-phenylethanol				
neat	3400	−40		7
0.35 M/CCl_4	3620	−2	−1 × 10⁻⁵	27, 7
(R)-2,2,2-trifluoro-1-phenylethanol-d_1	2670	negative		27

[a] Numerical data are from first reference listed for each compound.

Discussion

Ring Current Mechanism. Our interpretation of the methine, methyl, and hydroxyl stretching VCD in this group of molecules is derived from the following observations. (1) The intensity of $C_\alpha H$ stretching VCD is large in molecules which can form intramolecular hydrogen-bonded rings adjacent to the methine bond: the weaker the hydrogen bond, the lower the methine intensity. (2) The sign of the $C_\alpha H$ VCD depends on the absolute stereochemical arrangement of the ring relative to the methine bond. (3) The pattern of the VCD due to methyl group stretching vibrations correlates with the orientation of an adjacent carboxyl or phenyl group, but shows no correlation with the frequency of the methine vibration. (4) Hydroxyl stretching VCD is observed in molecules which form strong intramolecular hydrogen bonds and occurs at the frequency assigned to intramolecularly hydrogen-bonded OH stretch. (5) When a closed ring is present, appreciable VCD intensity is observed for $C_\alpha H$, OH, or CH_3 stretching modes even when there is very little contribution to the normal mode from the motion of other nuclei in the molecule.

Specific evidence for these correlations will be provided below in the discussion of individual molecules. These observations demonstrate that the enhanced VCD intensity observed for the modes considered here is primarily due to intrinsic contributions from a single local oscillator, rather than arising from the coupled nuclear motion of two or more chirally oriented oscillators. The correlation of enhanced VCD with the presence of an intramolecular ring associated with the local oscillator and the correlation of the sign of the VCD with a specific relative orientation of the oscillator and ring, in those cases for which other evidence for a preferred structure is available, provide the basis for the ring current mechanism for VCD.

The main premise of the ring current mechanism is that the nuclear motion of a driving oscillator can generate an electronic current around an intramolecular loop, and this current produces a magnetic moment.

The magnetic moment due to constant current in a planar loop is given by

$$\mathbf{m} = (I/c)\mathbf{S} \tag{1}$$

where I is the current flowing around the loop and $\mathbf{S}$ is a vector whose magnitude is the area of the loop, and direction is given by the right-hand rule for positive current flow in the loop. For excitation of normal mode Q_a, the electronic contribution to the magnetic dipole transition moment from ring current is proportional to

$$\left(\frac{\partial \mathbf{m}}{\partial P_a}\right)_0 = \frac{1}{c}\left(\frac{\partial I_{loop}}{\partial P_a}\right)_0 \mathbf{S}$$

where P_a is the momentum conjugate to Q_a and zeros denote equilibrium values. The current derivative $(\partial I_{loop}/\partial P_a)_0$ can be equated to $(\partial \xi_{loop}/\partial Q_a)_0$, the amount of charge, ξ_{loop}, which flows around the loop due to the normal mode Q_a. The contribution to the magnetic dipole transition moment due to vibrationally generated electronic ring current will therefore increase with

increased ring size and with increased current. The latter will be influenced by the strength of the bond closing the ring. For the cases discussed below, charge flow around a closed ring on the order of 10^{-3} electron per vibrational half-cycle is sufficient to generate the observed VCD intensity.

Although angular oscillation of electronic charge through a limited arc, rather than an enclosed loop, also contributes to the magnetic dipole transition moment, such motion causes concentrations of electronic charge and separation of positive and negative charges which is less favorable energetically. An enclosed pathway permits current flow at constant electron density. Vibrationally generated ring current involves correlation of nuclear and electronic momenta, and the theoretical description, which lies beyond the Born–Oppenheimer approximation, will be discussed in more detail separately.[25] Our emphasis here is to present experimental evidence for the vibrationally generated ring current mechanism and to show how the model can be used to obtain information on solution conformation.

Two types of ring current have been identified in our investigations, electronic current generated by an oscillator adjacent to the ring and current generated by an oscillator within the ring.

Enhancement of the methine stretching VCD arises due to nuclear oscillation external to an intramolecular ring. The descriptive model that we apply to the $C_\alpha H$ stretch in individual cases below is shown schematically in **2**, where an intramolecular hy-

2
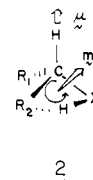
drogen bond is formed between the substituents XH and R_2. Contraction of $C_\alpha H$ corresponds to an electric dipole moment derivative $(\partial\mu/\partial Q)_0$ (where Q is the normal mode) directed toward the α hydrogen. The $C_\alpha H$ contraction causes electron density to be injected into the ring, preferentially toward the heteroatom X. When a closed ring is present, a positive current around the ring can be generated in the direction shown in **2** (H → X → C_α → R_2) which gives rise to the magnetic dipole transition moment **m**. In the opposite phase of vibration, $C_\alpha H$ elongation, both μ and the sense of current (and hence **m**) change sign, since now electrons are *withdrawn* preferentially from the C_α–X bond. This sense of vibrationally generated ring current is due to the fact that, relative to the other bonds to the α-carbon, the electron density in the C_α–X bond is less tightly held, and more able to follow the electron density oscillation in the driving $C_\alpha H$ bond. The C_α–X bond is more reactive, more labile, and usually not as strong. For example the bond strength for $C_6H_5CH_2$–OH (77 kcal mol⁻¹) is lower than that for C_6H_5–CH_3 (102 kcal mol⁻¹), and for a methine contraction in 1-phenylethanol, electron flow would be preferentially to the OH rather than phenyl group. As a second example, from CNDO atomic populations, for L-alanine-N-d_3 (assuming no ring), we calculate electronic charge flow away from C_α due to methine contraction that is 2.5 times larger for the C_α–N bond

compared to the C_α–CO_2^- bond.[25]   Electron flow at constant density generated by the methine contraction around a ring closed by $ND_3^+\cdots CO_2^-$ hydrogen bonding would reasonably follow this same preferred path toward the nitrogen.

Enhancement of methyl and hydroxyl stretching VCD arises due to nuclear oscillation within a ring, closed by $XH\cdots Y$ interaction for $XH = OH$ or CH and Y = phenyl or carboxylate group. In this case the sense of current can be deduced from the following considerations: elongation of the XH bond decreases the hydrogen bond length and causes increased $H\cdots Y$ orbital overlap, thereby strengthening the bond by means of a flow of electrons from the electron-rich substituent Y into the hydrogen-bonded region. XH contraction weakens the hydrogen bonding interaction and generates the opposite sense of flow.

In the following sections we interpret the hydrogen stretching VCD spectra for specific molecules in terms of these two types of vibrationally generated ring currents.

Methine Stretching VCD.   In interpreting individual VCD spectra, we aim to explain the sign and magnitude of features which cannot be explained by nuclear coupling effects alone. Although the room-temperature infrared absorption spectra may not exhibit much sensitivity to the rotameric distributions present in solution, the VCD depends more strongly on the precise stereochemistry since both sign and magnitude are affected. Rotameric distribution is possible for several substituents in each molecule, and, in analyzing spectra, we must necessarily restrict our consideration to those conformations which are likely to be stable due to steric interactions or intramolecular association, including hydrogen bonding, alkyl/π, and alkyl/lone-pair attraction,[26] or lone pair/π repulsion.[27]

For the substituted phenylethanes, we will consider the conformers with the phenyl group eclipsed or nearly eclipsed to the methine. This conformation, which appears to be the predominant one for α,α-dichlorotoluene[23] and 1-phenyl-1-fluoro-2-chloro-ethane,[28] is reasonable for bulky R_2 and R_3 groups, and allows phenyl π interaction with R_2 or R_3.

The first molecule for which liquid-phase VCD was recorded is 2,2,2-trifluoro-1-phenylethanol (TFPE).[6]   In the neat liquid, the methine vibration in the R enantiomer gives rise to a broad absorption at 2916 cm^{-1} and a large negative VCD peak at 2940 cm^{-1}. As the molecule is diluted in CCl_4, the absorption shifts to 2908 cm^{-1}, the negative VCD at 2940 cm^{-1} decreases, and positive VCD at 2910–2890 cm^{-1} is observed.[7,29]   Upon dilution the broad OH stretching band at 3400 cm^{-1} decreases and a narrower band at 3614 cm^{-1} is observed.[7]   Since the methine stretch is not significantly mixed with other nuclear motion, fixed partial charge calculations, which consider only perfect nuclear following for the electrons, yield rotational strengths which lie an order of magnitude below the observed VCD results.[29]

Two types of hydrogen bonding are possible in TFPE, shown in **3** and **4** as viewed down the $C_\alpha H$ bond with the phenyl group
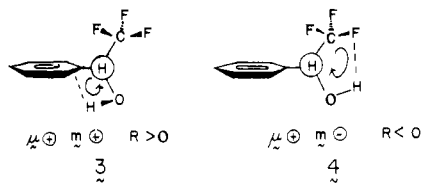
eclipsed to $C_\alpha H$. These diagrams represent an alternate stereoprojection of the schematic model **2**. For a methine contraction, positive μ is directed out the page (+). In **3**, vibrationally generated current around the ring closed by O–H hydrogen bonding

to the π orbitals on the phenyl group will generate a magnetic dipole transition moment **m** with a component directed out of the page, and thus positive VCD from the ring current. Although the stability of this conformation may be influenced by oxygen lone pair/phenyl π repulsion[27] as well as $OH\cdots\pi$ bonding attraction, the current direction can be determined by the $OH\cdots\pi$ pathway.

In the conformer **4**, with an O—H$\cdots$F—C hydrogen bond, vibrationally generated current produces **m** into the page (–) and negative VCD. The concentration of the latter conformer would increase at higher concentrations where the dimer **5** can form and
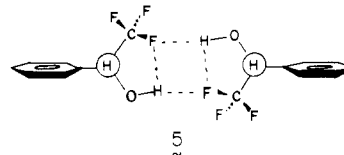

can be associated with the negative VCD band at 2940 cm^{-1} which increases in intensity with increasing concentration. The shift in the methine absorption peak also reflects this change in rotameric population.

The positive VCD feature in (–)TFPE at 2890 cm^{-1} therefore corresponds to the $C_\alpha H$ stretch in conformer **3**. In (S)-(–)-1-phenylethanol, only hydrogen bonding to the phenyl π system is possible, as in **6**.   Although for this molecule VCD features
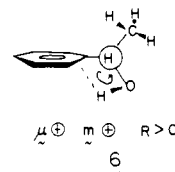

corresponding to methyl vibrations are also observed, the VCD (Figure 1) is clearly positively biased and dominated by the large broad positive methine VCD band at 2890 cm^{-1}, which has the same sign and nearly the same frequency as the methine VCD in the corresponding conformer, in **3**, in R-(–)TFPE.

The phenylethane derivatives for which the fourth substituent is NH_2 or NCO,[8] while not showing distinctly biased VCD in the CH stretching region, also exhibit positive methine VCD for the corresponding S-(–) conformations.   Contribution from ring current is also necessary to explain the methine VCD in these two molecules, since VCD due to nuclear coupling between the methine (ν 2850 or 2900 cm^{-1}) and the symmetric methyl stretch (unperturbed frequency 2905 cm^{-1}) would produce two VCD bands of opposite sign, not both positive as observed. Coupling with the antisymmetric methyl stretches near 2980 cm^{-1} should not be significant. The origin of the large methyl stretching VCD in these molecules is addressed later in this discussion.
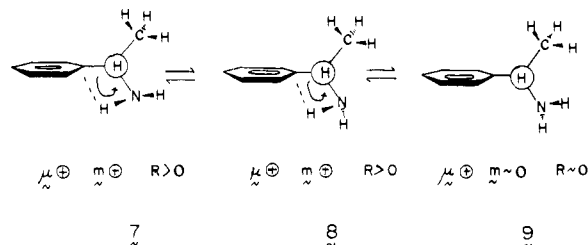
Two of the three staggered NH_2 rotamers **7** to **9** in (S)-(–)-1-phenylethylamine have possible N—H$\cdots\pi$ hydrogen-bonded rings in which vibrationally generated ring current is possible. Conformation **9** is also less favorable due to π-lone-pair repulsion. Conformation **10**, in which π–π overlap between the phenyl and
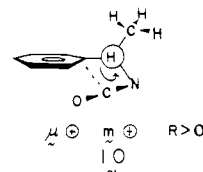
(25) Nafie, L. A.; Freedman, T. B., unpublished results.
(26) Uzawa, J.; Zushi, S.; Kodama, Y.; Fukuda, Y.; Nishihata, K.; Umemura, K.; Nishio, M.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3623.
(27) Abraham, R. J.; Bakke, J. M. *Acta Chem. Scand., Ser. B* **1983**, *37*, 865.
(28) Lere-Porte, J. P.; Bonniol, A.; Petrissans, J.; Charlon, C.; Luu-Duc, G. *J. Mol. Struct.* **1983**, *98*, 77.
(29) Faulkner, T. R.; Marcott, C.; Moskowitz, A.; Overend, J. *J. Am. Chem. Soc.* **1977**, *99*, 8160.

the isocyanate group provides a pathway for ring current, is sterically favorable for (S)-(−)-1-phenylethyl isocyanate and involves favorable CH$_3$···lone-pair interaction. In these two molecules, positive VCD due to ring current is therefore predicted, as observed experimentally. The intramolecular association is weaker than in 1-phenylethanol, and the methine stretching VCD is correspondingly weaker.

In 1-phenylethanethiol, intramolecular hydrogen bonding is expected to be considerably less important since a four-membered ring containing SH would be required. A broad distribution of −C−S−H rotamers would therefore have similar energies, and the lack of a distinct methine absorption feature may thus be due to a very large bandwidth resulting from the presence of a wide range of conformers. The three VCD features (Figure 2) clearly correspond to the methyl vibrations. With little intramolecular association present, the methine VCD is too weak to be observed. Similarly, when the NH···π hydrogen bonding in (S)-(−)-1-phenylethylamine is eliminated by methyl substitution to form (S)-(−)-N,N-dimethyl(1-phenylethyl)amine, no positive methine VCD is observed near 2850 cm^{-1}.[7]

The final compound in this group, (S)-1-chloro-1-phenylethane (Figure 3), exhibits a distinct, fairly sharp methine absorption at 2989 cm^{-1}, which probably reflects a large population of a single conformation, due to the large chloro substituent that restricts the phenyl rotation and is itself monatomic. The VCD features correspond primarily to the methyl stretching modes. The methine vibration does not generate significant positive VCD, consistent with the lack of a good pathway for vibrationally generated ring current through the phenyl group. The methine appears, in fact, to contribute weak negative, rather than positive VCD in the *S* enantiomer, which may result from an attractive interaction between the methyl hydrogens and the chlorine lone pairs creating a current path.

In the α-hydroxy acids and derivatives, strong intramolecular hydrogen bonding is possible. The infrared absorption spectra in the OH stretching region for dilute solutions are consistent with a predominant conformation containing an intramolecular hydrogen bond between the hydroxyl and carbonyl groups.[30] The large positive VCD bias in the CH stretching region in lactic acid has been previously attributed to vibrationally generated current in the C—OH···O=C ring.[3,4] (S)-Methyl mandelate (Figure 5) and sodium (S)-(+)-mandelate-d$_1$[10] have similar, positive C$_\alpha$H VCD, indicative of an excess of structure **11**, rather than **12**, and

11   12
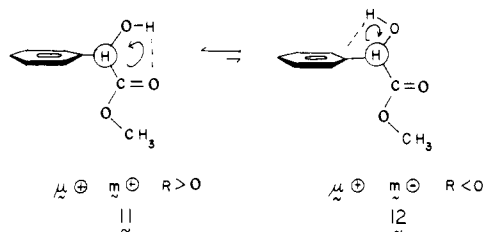
suggesting that the hydroxyl hydrogen rather than the acid hydrogen (if present) is involved in the hydrogen bonding in this series. The methine stretching VCD in (2S,3S)-tartaric acid-d$_4$[11] and (2S,3S)-(−)-dimethyltartrate[1a] (**13**) are also large and positive.


13
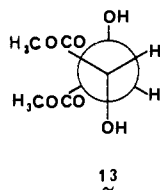
In these two molecules both five- and six-membered hydrogen bonded rings can form, either individually or simultaneously, as shown in **14** for a conformation consistent both with NMR evi-

14
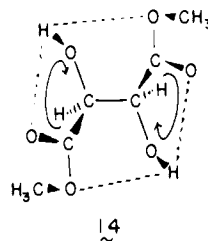
dence requiring vicinal CH groups, and with the OH- and CO-stretching VCD couplets arising due to the coupled oscillator mechanism.[31,32] The monosignate CH stretching VCD in these two molecules is clearly not due to coupled methine CH motions. However, the vibration of each individual methine can generate ring current around the adjacent five-membered ring, which would result in a positive contribution to the rotational strength. Any ring current generated in the adjacent six-membered ring would produce a magnetic moment nearly orthogonal to the electric dipole transition moment for that methine, and therefore no intrinsic rotational strength contribution. Our interpretation of the VCD spectra therefore requires that five-membered rings be formed in solutions of tartaric acid and dimethyl tartrate.

In the final two α-hydroxy acid derivatives, substitution at the hydroxyl hydrogen forces any intramolecular hydrogen bonding to occur through the acid hydrogen. In O-acetylmandelic acid, either a five-membered ring, **15**, or seven-membered ring, **16**, is

15   16
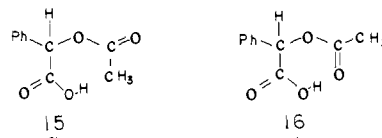
possible. Either structure can give rise to a positive VCD based on the ring current mechanism, and, in fact, the VCD of this compound consists of a weak positive VCD signal at 2960 cm^{-1} riding on an extremely broad negative background. Although the absorption spectrum similarly rides on an intense broad background due to OH stretching in the acid dimer, a weak OH absorption at ∼3505 cm^{-1} is observed which may be attributed to intramolecular hydrogen bonding. In α-methoxyphenylacetic acid, only a five-membered ring is possible. The VCD for this compound is difficult to assign due to features which apparently arise from the methoxy group. A positive VCD feature does occur at 2960 cm^{-1}, the same frequency as in the acetyl-substituted acid.

In both the amino acids (**17**) and α-hydroxy acids (e.g., **11**) enhancement of methine VCD due to ring current is optimized by a carboxylate group approximately orthogonal to the methine CH bond. This orientation is rigidly maintained in the L-amino acid transition metal complexes which exhibit a two- to fourfold increase in positive VCD bias in the CH stretching region relative to the zwitterion alone. Crystal structure determinations for some of the α-hydroxy acid derivatives[33] indicate approximately coplanar acid and hydroxyl oxygens, which also result in orthogonal methine and acid groups.

The large positive bias in the CH stretching VCD in the L-amino acids in neutral solution is greatly reduced at low pH.[4,34] Detailed analysis of this pH dependence will be presented separately.[34] It

17   18
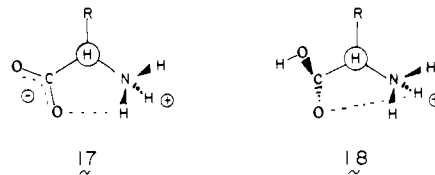
is probable that the N—H···O interaction is weaker when the

(30) Mori, N.; Omura, S.; Kobayashi, N.; Tsuzuki, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2149.

(31) Su, C. N.; Keiderling, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 511.
(32) Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 8061.
(33) (a) Okaya, Y.; Stemple, N. R.; Kay, M. I. *Acta Crystallogr.* **1966**, *21*, 237. (b) Kroon, J.; Kanters, J. A. *Acta Crystallogr., Sect. B* **1973**, *29*, 1278; **1972**, *28*, 714.
(34) Zuk, W. M.; Freedman, T. B.; Nafie, L. A., unpublished results.

carboxylate is protonated and therefore not charged. Any alkyl/carboxylate interaction is also decreased. At low pH, steric repulsion may then become relatively more important and serve to depopulate orientations such as **17** and favor orientations such as **18** in which the magnetic dipole transition moment due to ring current is more nearly orthogonal to μ for the methine stretch, also resulting in decreased VCD.

The methine stretching VCD in α-phenylglycine in acid solution (Figure 4) is positive for the D enantiomer, in contrast to the other amino acids in neutral solution, which exhibit positive VCD for the L enantiomer. Phenylglycine is not soluble at neutral pH. The VCD bias for phenylglycine is readily explained using the ring current model. Although interaction between the acid and amino groups apparently does not produce enhanced methine VCD at low pH in other amino acids, in α-phenylglycine (**19**) a second


$\mu\oplus$ $m\oplus$ $R>0$

19
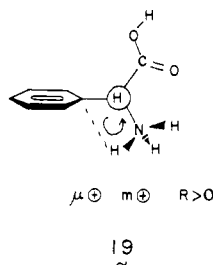
type of ring can be formed simultaneously, closed by N—H$\cdots\pi$ interaction with the phenyl group, identical with that proposed for (S)-1-phenylethylamine. Current generated in this ring results in positive methine stretching VCD for the D enantiomer, as observed. The $C_\alpha H$ stretching anisotropy ratio for α-phenylglycine is comparable to that in (S)-1-phenylethylamine, but is considerably smaller than that observed for molecules with rings involving a carboxylate group.

Methyl Stretching VCD. The CH stretching VCD spectra of the substituted (S)-phenylethanes (NH_2, Cl, SH, OH, NCO) exhibit a characteristic VCD pattern (Figures 1–3) due to the vibrations of the methyl group, that is, a negative feature for the antisymmetric stretches and positive features due to the Fermi resonance dyad involving the symmetric methyl stretch. VCD intensity calculations based on nuclear coupling and perfect electronic following have not been able to account for the magnitude of methyl stretching VCD bands.[18,21]

An explanation for enhanced VCD based on induced ring currents can also be formulated for the methyl group vibrations. It is unlikely that the ring responsible for the methine enhancement is also involved in the methyl group VCD intensity since the electric dipole moment for the symmetric stretch is nearly orthogonal to the magnetic moment generated in that ring, and the antisymmetric stretching modes cannot inject electron density into the hydrogen-bonded ring. However, a direct interaction between one of the methyl group CH bonds and the π orbitals of the phenyl group can form an additional closed pathway for current flow. Evidence for an attractive CH$\cdots\pi$ interaction between phenyl and alkyl groups has been obtained from NMR conformational studies.[26]

For the methyl group, one oscillator, a methyl CH bond, is contained in the ring, but the electric dipole transition moments, due to oscillation of all three methyl CH bonds, have a component perpendicular to the ring (when the phenyl group is not orthogonal to the methyl group). In this case the sense of current can be determined by the second rule, for an oscillator contained in a ring: CH elongation causes increased orbital overlap, strengthening the C—H$\cdots\pi$ bond and causing a flow of electrons from the electron-rich π system into the bonded region; CH contraction weakens the interaction resulting in the opposite sense of flow.

The electric and magnetic dipole transition moments for the methyl stretching modes in a phenylethane derivative are depicted in **20** and **21**, viewed down the $C_\alpha H$ bond, with the phenyl group eclipsed to the methine bond. The region of interaction of one methyl CH bond is also shown. The other two methyl CH bonds are not in bonding directions. In **20** and **21a**, the elongation Δr_1

$\nu_{CH_3}{}^{s y m}$ $R>0$ $\nu_{CH_3}{}^{a s y m}$ $R<0$ $\nu_{CH_3}{}^{a s y m}$ $R\sim0$

20   **21a**   **21b**
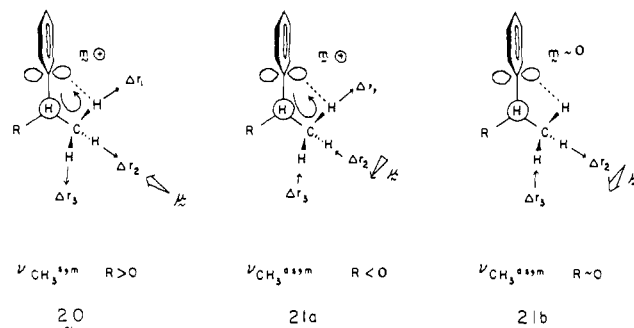
generates a ring current producing a magnetic dipole transition moment **m** out of the page. In the symmetric methyl stretch $3^{-1/2}$ ($\Delta r_1 + \Delta r_2 + \Delta r_3$), **20**, μ has a component out of the page resulting in positive VCD as observed. In **21a**, the antisymmetric stretching mode $6^{-1/2}$ ($2\Delta r_1 - \Delta r_2 - \Delta r_3$) has an electric dipole transition moment μ with a component into the page, producing negative VCD, while in the other antisymmetric stretch **21b**, $2^{-1/2}$ ($\Delta r_2 - \Delta r_3$), no ring current is generated. Other assumed perpendicular orientations for the two antisymmetric stretching modes also predict net negative VCD, as observed.

In L-alanine-C_α-d_1-N-d_3, any nuclear coupling of methyl and methine motions is removed, and the methyl stretching VCD is comparable in intensity to that in the phenylethane derivatives, but exhibits the opposite sign pattern, with the symmetric stretching VCD negative and net positive VCD in the antisymmetric stretching region. In the amino acids, the intramolecular hydrogen bonding favors a carboxylate more nearly eclipsed to the amino group rather than to the methine; that is, the methyl$\cdots\pi$ orientations are approximately mirror images in alanine and the phenylethane derivatives. For alanine-C_α-d_1-N-d_3, the ring current due to interaction between one methyl CH bond and the carboxylate π orbitals therefore results in negative VCD for the symmetric stretch, **22**.


$\nu_{CH_3}{}^{s y m}$ $R<0$

22
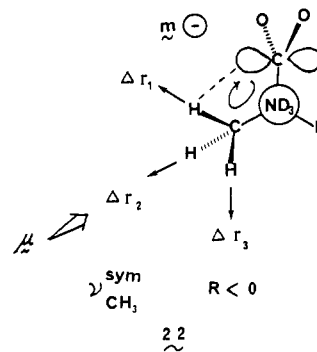
In L-lactic acid, a similar carboxyl group orientation, eclipsed to the $C_\alpha O$ bond, also results in negative ring current enhanced VCD for the symmetric methyl stretch. The nuclear coupling between the methine and methyl stretching motion predicts a positive VCD contribution for the methyl symmetric stretch.[4] However, the observed VCD spectrum for lactic acid is more consistent with negative VCD due to $\nu_{CH_3}{}^{s y m}$ (2948 cm^{-1}) distorting the contour of the large broad positive methine CH stretching VCD (2920 cm^{-1}).[4]

Hydroxyl Stretching VCD. The VCD spectrum of (S)-methyl mandelate in Figure 6 is representative of the negative VCD observed[10,12] for the OH stretching mode in the α-hydroxy esters (S enantiomer). This mode is isolated and involves little nuclear motion beyond the stretch of the OH bond. The strong absorption and negative VCD at 3533 cm^{-1} is assigned to the OH intramolecularly hydrogen bonded to the carbonyl oxygen, while the weak shoulder at 3610 cm^{-1} corresponds to OH bonded to the methoxy oxygen.[30] By a mechanism similar to that proposed for enhancement of the VCD due to methyl motions, the OH stretch can generate an oscillating current in the H—O—C_α—C=O ring. Elongation of the OH bond shortens the hydrogen bond, increasing the strength of the bond and promoting flow of electrons

VCD via Electronic Ring Currents

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from the electron-rich oxygen. The electric dipole transition moment is directed O → H for OH elongation. For the five-membered hydrogen-bonded ring shown in **23** viewed down the


23
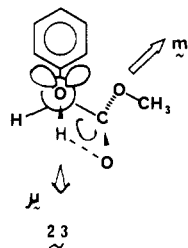
C_α–O bond, where the hydrogen lies above the four other atoms in the ring, the rotational strength due to the vibrationally generated ring current is negative. In this orientation, the OH bond lies trans to the C–CH$_3$ bond of methyl lactate or the C–Ph bond in methyl mandelate which permits a symmetric interaction between the lone pairs on the hydroxyl oxygen and the methyl or phenyl group. This orientation is also consistent with strong positive ring current enhanced methine stretching VCD and negative symmetric methyl stretching VCD (in lactic acid) as discussed above, and directs the methoxy lone pair away from the phenyl π system in methyl mandelate. Rotating the OH bond in **23** to a position cis to the carbonyl bond results in a planar ring for which no enhanced OH stretching VCD can occur. Rotating the OH bond trans to the methine CH results in positive OH stretching VCD. The observed negative hydrogen stretching VCD is therefore most consistent with a large population of the conformation shown in **23**. For a similar trans orientation of the hydroxyl and trifluorophenyl groups in (R)-2,2,2-trifluoro-1-phenylethanol (**24**), negative VCD from vibrational ring current


24
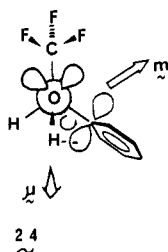
is also predicted for the OH stretch, as observed in dilute solution[7] for the band at 3614 cm^{-1} assigned to the OH⋯π conformation. FPC calculations for this band give rotational strengths two orders of magnitude too low.[29]
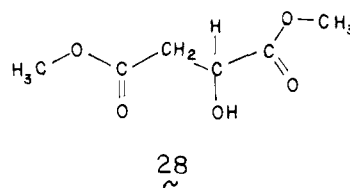
Methyl 3-hydroxybutyrate (**25**) forms a six-membered intra-

25
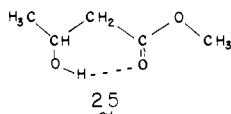
molecularly hydrogen-bonded ring. The OH stretch in the ring gives rise to a broad absorption band at 3555 cm^{-1} and a weak bisignate VCD feature[12] centered at 3565 cm^{-1}. Nakao et al.[12] tentatively assigned the two lobes to two conformations due to rotation about the C–OH bond. An alternative assignment is suggested by the ring current model. Maintaining the OH and C–CH$_3$ bonds trans as in methyl lactate, rotation of the carboxylate group from above to below the C–O–H plane would change the sign of the rotational strength due to vibrationally generated ring current from positive to negative for the *S* enantiomer, **26** and **27**, respectively.

R < 0

26

R > 0

27
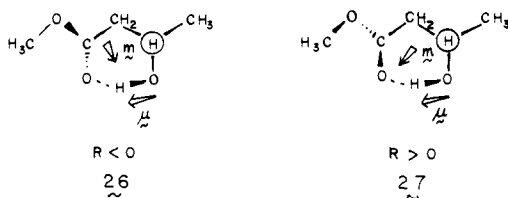
(S)-(–)-dimethyl malate **28** can form a single five- or six-

28

membered ring. The absorption and VCD spectra[31] correspond to those of methyl lactate, rather than to those of methyl 3-hydroxybutyrate, indicative of a preference for the five-membered ring conformation. For this molecule, a distinct negative VCD band is also reported for the weak absorption at 3615 cm^{-1} due to the OH⋯methoxy oxygen ring.

Conclusions

Our analysis has shown that, in addition to VCD arising primarily from coupled nuclear motion extending over a chiral frame, highly localized nuclear motion, such as isolated CH and OH stretching modes, can also generate significant VCD in certain situations. Enhanced VCD in these modes correlates with the presence of an intramolecular ring, having a region of delocalizable electron density, near the localized oscillator. We have proposed a second major general mechanism for VCD (in addition to nuclear coupling) to explain this enhancement, whereby a large magnetic dipole transition moment arises from oscillating electronic current around the ring, generated by the local vibrational transition. Two rules have been devised for determining the sense of current flow in the ring.

Rule 1: When an oscillator attached to a ring contracts, electrons are inserted into the ring such that positive current flows preferentially toward the inducing oscillator along the bonded region having less tightly held electron density. Elongation of the oscillator withdraws electrons from the ring, generating the opposite sense of positive current.

Rule 2: When an oscillator involved in the hydrogen-bonding interaction elongates, the hydrogen bond length decreases, strengthening the bond and generating electron flow from the more electron rich of the hydrogen-bonding atoms into the hydrogen-bonded region. For X—H⋯Y, positive current flows from the hydrogen-bonded region toward Y, the electron-rich substituent, during X–H elongation, and away from Y during X–H contraction.

For oscillators in the ring, a component of the electric dipole transition moment must lie out of the ring for enhanced VCD to be observed. Striking examples of the second rule for NH stretching modes in transition metal complexes are presented elsewhere.[35]

Vibrationally generated electronic ring currents represent a new chemical phenomenon which has not been previously recognized. This study has provided further evidence for the widespread occurrence of vibrational ring currents beyond their initial postulation to explain the amino acid VCD spectra, and this mechanism should be considered whenever biased VCD spectra are encountered.

Since VCD enhancement due to vibrationally generated ring current is possible only for specific rotameric conformations, the observed VCD may arise from only a fraction of the molecules in the sample. Thus, variations in VCD intensity reflect not only variations in hydrogen bond strength, but also other factors which determine the conformational distribution in solution. The VCD spectra can serve as a unique probe of factors which influence this distribution.

Vibrationally generated ring currents provide a source of magnetic dipole character which does not contribute to the electric dipole strength, and cannot be calculated by determining charge redistributions at the extremes of a vibrational cycle. Previous calculations of VCD intensities using molecular orbital models developed in our laboratory[5,36] have predicted biased CH stretching

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(35) Young, D. A.; Lipp, E.; Nafie, L. A. *J. Am. Chem. Soc.*, preceding paper in this issue.

VCD. These earlier models take into account electronic motion distinct from nuclear motion, but ignore ring currents, and for isolated bands the calculated anisotropy ratios $\Delta\epsilon/\epsilon$ lie well below the experimental values. Efforts are currently underway to provide a more quantitative description of the ring current mechanism and to carry out calculations using recently developed vibronic coupling formulations[37,38] which implicitly include ring current effects.

As a basis for the qualitative interpretation of observed VCD spectra, the ring current model provides a new direct way to probe both solution conformation and intramolecular interactions. The conformations which we have postulated based on ring current enhancement of VCD are in agreement with those postulated from other evidence, when available, and have provided a consistent explanation of the OH and CH stretching VCD in a wide range

of molecules. The VCD spectra for bond-stretching motions considered here are easily recorded. Ring current enhancement can often be detected as a biased component superimposed on the VDC arising from coupled nuclear motion, allowing conformational information to be obtained without the precise vibrational analysis needed to interpret the nuclear coupling VCD. The role of ring currents generated by bending vibrations remains to be investigated, but may prove significant in the midinfrared where weak absorptions with large anisotropy ratios, and hence, significant magnetic dipole character, have been recorded.

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Heteronuclear Transition-Metal Cluster Ions in the Gas Phase. Photodissociation and Reactivity of VFe⁺

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Abstract: The transition-metal cluster ion VFe⁺ was synthesized in the gas phase by reaction of V⁺ with Fe(CO)₅, followed by appropriate collisional activation pulses. Photodissociation of VFe⁺ to generate V⁺ exclusively reveals two peaks at 260 ± 10 and 340 ± 10 nm with a threshold dissociation at 380 ± 10 nm. A cross-section $\sigma(340 \text{ nm}) = 6 \pm 3 \times 10^{-18} \text{ cm}^2$ is determined for the photodissociation of VFe⁺. The threshold at 380 ± 10 nm yields $D°(V^+–Fe) = 75 \pm 5$ kcal/mol, which implies $D°(Fe^+–V) = 101 \pm 5$ kcal/mol, $\Delta H_f°(VFe^+) = 302 \pm 5$ kcal/mol, and IP(VFe) = 5.4 eV. No reaction is observed between VFe⁺ and linear or cyclic alkanes. VFe⁺ is also unreactive with all linear alkenes through hexene but reacts with C₆ and C₇ cycloalkenes. The primary reaction between VFe⁺ and cyclohexene (or benzene) produces VFe(C₆H₆)⁺, which upon collisional activation readily eliminates C₆H₆. Collisional activation of VFe(C₆H₆)₂⁺, formed by a secondary reaction with cyclohexene, produces loss of Fe to yield V(C₆H₆)₂⁺. VFe⁺ abstracts a carbene from cycloheptatriene, indicating $D°(VFe^+–CH_2) > 70$ kcal/mol. The oxide chemistry of VFe⁺ is also modified from that of V⁺ or Fe⁺. VFe⁺ reacts very slowly with O₂ to yield VO⁺ and Fe⁺ whereas VFe(CO)ₓ⁺ (*x* = 2–4) reacts quickly with O₂ to produce VFeO₂⁺, which then abstracts an oxygen from O₂ to form VFeO₃⁺. VFe⁺ will react sequentially with ethylene oxide to abstract up to three oxygens, producing VFeO⁺, VFeO₂⁺, and VFeO₃⁺. No reaction is observed between VFe⁺ and N₂O, although both V⁺ and Fe⁺ will abstract an oxygen from N₂O.

The production and examination of small metal clusters have become topics of considerable interest over the past decade.[1] Transition-metal clusters are particularly important in astronomy, homogeneous nucleation,[2] and surface science, specifically heterogeneous catalysis.[3]

Metal clusters are thought to mimic metal surfaces, particularly when the clusters are ligand free.[4] Gas-phase techniques are well suited for studying bare transition-metal cluster ions. Most of the metal cluster ions examined thus far have been generated by electron impact[5] or multiphoton ionization[6] of metal carbonyls.

Smalley and others have recently developed novel beam expansion techniques for generating neutral clusters of various sizes for study in the gas phase.[7]

A convenient method of generating heteronuclear transition-metal cluster ions in the gas phase has allowed the reactivity of CoFe⁺ to be examined in detail.[8] In order to further probe the nature of these cluster ions, the VFe⁺ ion was chosen since it combines both an early and a late transition metal. In this cluster, the electron density should be polarized and the resulting charge localization might greatly influence the reactivity of the cluster.

Photodissociation of VFe⁺ provides an indirect measure of the absorption spectrum of the ion, as well as a thermodynamic threshold which provides bond energy information. In order to observe the photodissociation process, AB⁺ + hν → A⁺ + B, the

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