vinyl structure, lying only 0.15 kcal apart, with the cis being the lower lying, bound by $\sim$8 kcal relative to separated $Al + C_2H_2$. However the vinylidene structure lies 12 kcal lower and is the absolute minimum on the AlC_2H_2 potential-energy surface.

Since the vinylidene structure is inconsistent with Kasai, McLeod, and Watanabe's ESR spectrum, there may appear to be a conflict between theory and experiment. However, the barrier height between vinylidene and acetylene is 5–8 kcal and might not be greatly altered by the presence of the Al atom. If this is the case, then the 1,2 hydrogen shift (eq 22) might not occur at all at the liquid helium temperatures of Kasai and McLeod.[92]

$$ \text{(22)} $$
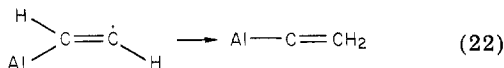
The most challenging feature of Trenary's study[94] is that while the isolated acetylene–vinylidene reaction is *endothermic* by 40 kcal, the same process becomes *exothermic* in the presence of an Al atom. We suspect that other endothermic reactions such as the methylcarbene–ethylene and methylnitrene–methylenimine rearrangements will also become favorable when complexation to a metal atom, metal cluster, or metal surface is achieved. This general mechanism for using metal systems to transform endothermic reactions into nearly degenerate rearrangements may play a key role in catalysis and surface chemistry.

Concluding Remarks

It should be clear that the 1,2 hydrogen shift is a remarkably ubiquitous and important chemical reaction. This simple rearrangement plays a key role in physical organic chemistry, in the chemistry of interstellar space, and in the rapidly developing organometallic-surface-catalysis branch of chemistry. Further studies, both experimental and theoretical, can be expected to yield many new insights during the 1980's.

Optical Activity in Vibrational Transitions: Vibrational Circular Dichroism and Raman Optical Activity

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Natural optical activity in vibrational transitions is emerging as a new branch of molecular spectroscopy. Two distinct yet complementary physical phenomena are the focus of this new field, known as vibrational optical activity (VOA). The first of these is the difference in absorbance of left vs. right circularly polarized infrared radiation, referred to as vibrational circular dichroism (VCD), and the second is the difference in scattered intensity of left vs. right circularly polarized incident laser radiation, which is termed Raman optical activity (ROA). Both theoretically and experimentally, VOA is at an early stage of development. Work is currently in progress to increase the range and efficiency of measurement techniques, to uncover empirical and simple theoretical trends in experimental data, to develop theoretically sound models for calculation, and to compare theoretical and experimental results.

Vibrational optical activity is the convergence of the two established fields of electronic optical activity (EOA) and vibrational spectroscopy. Considered separately, these two fields already provide powerful techniques for obtaining structural information from molecules. The combination of these two fields is expected to generate a number of significant advantages. From the viewpoint of vibrational spectroscopy, VOA should provide configurational and enhanced conformational sensitivity to methods that are already highly structure sensitive. From the viewpoint of optical activity, one can regard the vibrational region as consisting of an abundance of chromophores representing virtually all portions of the molecule. Thus, VOA should provide new chromophores and new sets of criteria for the determination of absolute configuration in molecules. In addition, VOA should also be very sensitive to the conformation of molecules in solution. In fact, the combination of complete VCD and ROA spectra may contain enough stereochemical information to completely determine the conformation of the molecule under study.

The primary difficulty in the measurement of VOA is that signals are four to five orders of magnitude smaller than the parent effects, infrared absorption and Raman scattering. As a result, both VCD[1,2] and ROA[3,4]

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were experimentally discovered and verified only 5 years ago. In order to measure these small signals the sensitive methods of modulation spectroscopy are employed. In ROA, the incident laser radiation is square-wave modulated between left and right circular polarization states, and the resulting scattered intensities, I_L and I_R, in the form of photon counts, are stored and accumulated in separate channels. In VCD the polarization of the incident infrared beam is sinusoidally modulated, leading to an intensity modulation at the detector for circular dichroic samples. The VCD is then obtained by electronic amplification and phase-sensitive detection of the modulation signal.

As VCD and ROA have developed, they have become complementary in a number of ways. The most striking is that VCD is currently limited to vibrational transitions which occur above 2000 cm⁻¹, while ROA has only produced signals below 2000 cm⁻¹. This limits VCD to the fundamental stretching motions of hydrogen and deuterium, as well as certain overtone and combination bands. For ROA, no such vibrational frequency limitations exists; however, the largest effects commonly occur at frequencies below 1000 cm⁻¹. In spite of this mutually exclusive trend, the eventual overlap of VCD and ROA is eagerly awaited in order to look for spectral correlations from the same vibrational transitions.

The new spectroscopic information contained in VOA is represented by an intensity as well as a sign for each vibrational transition measured. These intensities and signs in turn contain information regarding the structure, configuration, conformation, and environment of the subject molecule. Initial experimental results of VOA indicate a very high sensitivity to molecular conformation and environment. While this is encouraging from an experimental point of view, it has placed a large burden on the calculation of VOA where suitable theoretical models are still being tested and developed. A central question to be addressed and resolved for VCD calculations is the importance of the electronic contributions to the observed intensity. Regardless of the answer, it is clear that accurate calculations which correctly mimic the sensitivity of VOA to molecular shape and environment will require equally sensitive theoretical procedures. Hopefully such procedures will lie within the range of available calculational methods so that full advantage may be taken of the experimental data.

The strength of a VCD transition can be written in terms of both experimental and theoretical quantities by means of the dissymmetry factor, g, as[5,6] eq 1, where

$$g = \frac{\Delta\epsilon}{\epsilon} = \frac{\epsilon^L - \epsilon^R}{\frac{1}{2}(\epsilon^L + \epsilon^R)} = \frac{4R}{D} \tag{1}$$

ϵ is the average integrated absorption coefficient for left and right circularly polarized light, $\Delta\epsilon$ is the difference $\epsilon^L - \epsilon^R$, and R and D represent the rotational strength and dipole strength of the transition, respectively. For a vibrational transition from gi to gf in the ground electronic state manifold we get eq 2, where μ_α and m_α represent the αth Cartesian component of the electric

$$(g)_{gf,gi} = \frac{4(R)_{gf,gi}}{(D)_{gf,gi}} = \frac{4Im[(\mu_\alpha)_{gf,gi}(m_\alpha)_{gf,gi}]}{Re[(\mu_\alpha)_{gf,gi}(\mu_\alpha)_{gf,gi}]} \tag{2}$$

and magnetic dipole moment operators, the repeated index α indicates summation over x, y, and z, and Im and Re denote imaginary and real parts, respectively. The subscripts of gf, gi for μ_α and m_α indicate a matrix element between the states gi and gf.

For ROA, one measures the circular intensity differential (CID) defined as[7]

$$\Delta = \frac{I^R - I^L}{I^R + I^L} \tag{3}$$

For incident light propagating in the z direction and scattered light in the y direction, the in-plane polarized CID, Δ_z, is more free of artifacts[8] arising from imperfections in the optical path of the experiment than the out-of-plane polarized component, Δ_x; hence we focus on the former. For the transition gi to gf we get[8] eq 4,

$$(\Delta_z)_{gf,gi} = \left[\frac{4(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{2c(3\alpha_{\lambda\mu}\alpha_{\lambda\mu} - \alpha_{\lambda\lambda}\alpha_{\mu\mu})} \right]_{gf,gi} \tag{4}$$

where the subscript gf, gi is carried into all the ROA tensors, giving $(\alpha_{\alpha\beta})_{gf,gi}$, $(G'_{\alpha\beta})_{gf,gi}$, and $(A_{\alpha\beta\gamma})_{gf,gi}$. The Greek subscripts refer to Cartesian components, and again repeated subscripts indicate summation over x, y, and z, while $\epsilon_{\alpha\beta\gamma}$ is the alternating tensor. The tensor symbols α, G', and A refer to the ordinary electric dipole–electric dipole polarizability, the electric dipole–magnetic dipole polarizability, and the electric dipole–electric quadrupole polarizability, respectively.[8]

The principal theoretical differences between VCD and ROA are the simpler way in which the electric and magnetic dipole operators enter the formalism for VCD as well as the presence of the electric quadrupole operator for ROA. Consequently, ROA is much more complex theoretically and somewhat less accessible for model calculations than its complement, VCD.

The Emergence of VOA

Optical activity in the infrared spectral region has been an area of experimental and theoretical interest for nearly five decades. All early VOA experiments were attempted[9] using rotatory dispersion, since the modulation and detection techniques necessary to observe very small circular dichroism signals had not yet been developed. Prior to the experimental discovery of VCD, theoretical studies were pursued investigating the origin and magnitudes of vibrational effects in EOA. This early work was undertaken to explain EOA observed in molecules which were chiral by virtue of isotopic substitution.[10,11] The first calculations carried out to establish the magnitude of the optical activity in vibrational transitions were published by Deutsche and Moscowitz[12] using what has come to be known as the fixed partial charge (FPC) model. In particular,

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they considered a helical molecule of infinite length having fixed, vibrating charges on the atoms. In analogy to the coupled oscillator model in EAO, a similar model for VOA was developed by Holzwarth and Chabay.[13] Schellman subsequently published a harmonic FPC model of VCD and predicted results for methyl-substituted pyrrolidones.[6] Using an exciton coupling model Schellman also calculated VCD for certain polypeptide vibrational modes.[14]

Following the discovery of VCD, a number of theoretical developments appeared. The coupled oscillator model was generalized to include near-degenerate and nondegenerate coupled oscillators.[15] A localized molecular orbital (LMO) model was proposed by Nafie and Walnut in order to account for the dynamic contribution of the electrons to the VCD intensity,[16,17] and the calculation of VCD from overtone and combination bands was made possible by the development of an anharmonic FPC model by Moscowitz, Overend, et al.[18,19] Finally, Craig and Thirunamachandran have provided a vibronic formalism framework for the description of VCD intensities.[20]

The first observation of VCD was achieved in the vibrational combination bands of water in single crystals of $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6D_2O$, and $ZnSeO_4 \cdot 6H_2O$ by Hsu and Holzwarth.[21] The first VCD from a liquid phase sample was reported in the following year for the molecules 2,2,2-trifluoro-1-phenylethanol and neopentyl-1-*d* chloride by Holzwarth et al.[1] and the data were theoretically supported by FPC calculations.[22] The first VCD spectrum was confirmed by Stephens and co-workers,[2] and subsequently Nafie, Keiderling, and Stephens reported VCD spectra of a number of commercially available, organic molecules either as neat liquids or as solutions in CCl_4.[23] This study represented a breakthrough in VCD measurement by providing high-quality spectra for over a dozen molecules where previously VCD of only one molecule had been published. This paper also outlined the general scheme for the design and calibration of VCD spectrometers. Later, reports from the same laboratory demonstrated the presence of VCD of similar magnitude in a number of overtones and combination bands.[24] The papers discussed so far were aimed at demonstrating the feasibility of the measurement of VCD in liquid samples; a detailed interpretation of the observed spectra was not intended and not possible in most cases owing to the complexity of the molecules studied.

The next publications dealing with VCD were aimed at obtaining more interpretable results by examining

smaller molecules of theoretical interest. Moscowitz and co-workers[25] reported VCD in the CH stretching modes of tartaric-d_2 acid-d_2 ($DO_2CCH(OD)CH(OD)$-CO_2D) and were unable to observe spectral features which could be interpreted as resulting from coupling of the two CH stretching motions. Large VCD signals were observed[26,27] in the CH stretching modes of the smallest molecule examined so far, alanine, and interpreted[26] in terms of a perturbed degenerate mode model (vide infra). These observations for the first time dealt with the situation of unfavorably high solvent (D_2O) absorptions in the spectral region of interest. Keiderling and Stephens[28] reported a VCD signal for the OH stretches of dimethyl tartrate in CCl_4 which seems to be the first report of a coupled oscillator, although an alternate interpretation has been offered by Moscowitz et al.[29] VCD of a number of amino acids and peptides were recently reported by the authors of this review[30,31] in both solution and solid phase (mull). These results will be discussed in more detail in the next section.

Raman optical activity has also been an area of research for a number of years.[32] The quantum mechanical basis of the effect was developed by Atkins and Barron,[33] and the detailed formalism was worked out by Barron and Buckingham.[7] Several reviews of ROA have appeared,[8,34,35] so that only a brief outline of the major developments will be given here. ROA was experimentally verified by Barron et al. in 2-substituted phenylethanes[3,36] and in a number of terpenes.[37] In 1975, Hug, Scherer, and co-workers[4] confirmed Barron's work and reported nearly simultaneously with Barron[38] the first circular intensity differentials (CID's) in near-degenerate methyl vibrations. The theory of perturbed, degenerate methyl vibrations has been subsequently developed by Barron[8,39] for ROA and by Nafie[40] for VCD. Raman CID's recently have been obtained for solutions in water, carbon disulfide, methanol, and methyl chloride.[41-43] Some of the recent results seem to suggest a unique sensitivity of ROA to

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molecular conformation[43,44] and configuration.[41,43] Magnetic resonance ROA was observed by Barron[45] in the resonance Raman spectrum of 10^{-4} M ferrocytochrome c solution in water. Theoretical developments of significance include the two-group model[46] which allows ROA to appear in the absence of dynamic coupling between the groups. This zeroth order coupling effect is not possible for VCD, which requires at least first-order coupling. More recently Prasad and Burow have developed an atom dipole approach to ROA[47] which provides a direct method for the calculation of ROA.[48]

Measurement and Results

The observation of optical activity in molecular vibrational transitions presents considerable experimental difficulties, since the effects are much smaller than those for electronic optical activity. In the case of VCD, the differential absorption between left and right circularly polarized infrared radiation is very small, but the absorption coefficients of infrared bands are generally comparable to those of electronic bands. Typical $\Delta A/A$ (or $\Delta\epsilon/\epsilon$)[49] values for vibrational transitions are in the range of 10^{-5} to 10^{-4}, where A refers to the measured absorbance, although somewhat larger values were recently reported.[30,31] In Raman optical activity, the normalized differential intensity, Δ_z, is generally larger (values between 5×10^{-4} and 5×10^{-3} are typical);[3,34] however, Raman scattered intensities are much harder to observe, particularly for polarization parallel to the scattering plane. Consequently the discovery of both VCD and ROA proved to be difficult, depending critically on technological advances in detectors, electronics, electrooptics, and lasers.

A VCD instrument basically consists of a single-beam infrared spectrometer to which a polarization modulation and a phase-sensitive detection system are added. The IR beam emerging from the monochromator is linearly polarized via a wire grid or prism polarizer. The radiation then passes through a photoelastic modulator (PEM) which will produce alternatively left and right circularly polarized light at a frequency typically in the 50-kHz range. The IR beam then passes through the sample and strikes a high sensitivity InSb ($D^* \sim 10^{11}$ cm Hz$^{1/2}$/W) detector. The ac signal observed at the modulator frequency carries the information about the differential absorption of the sample. The electronic system necessary to obtain ΔA has been discussed elsewhere.[23] The main difficulties encountered are the low efficiency of IR sources and polarization optics and the extremely small magnitude of the ac signal, which necessitates sophisticated techniques for amplification in the presence of detector noise and stray signals. The availability of large area InSb detectors has somewhat reduced the problems of large artifact signals induced by image reducing optics.[23] We were able to obtain straight VCD base lines over a fairly wide frequency range without the use of a polarization scrambler;[23,50]
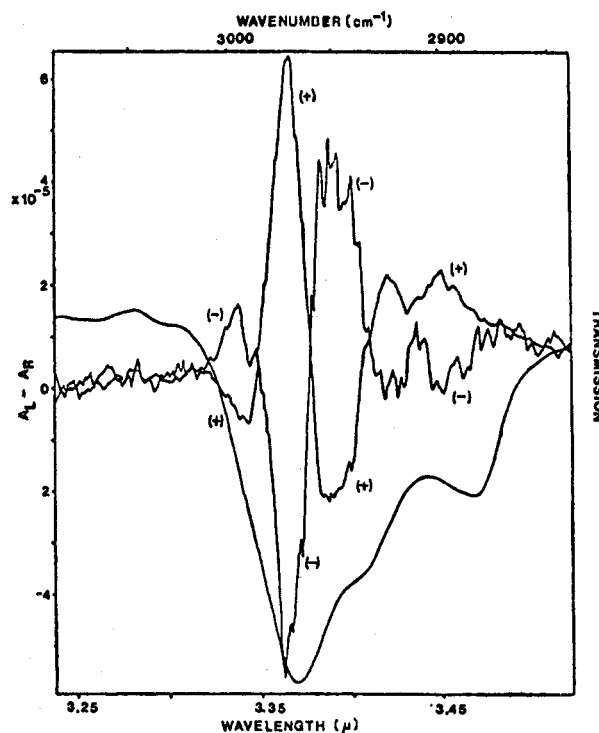
Figure 1. VCD spectrum of (+)- and (−)-camphor in CCl_4 solution (0.5 M) in the C–H stretching region, recorded using a 10-s 18 db roll-off time constant over a 66-min period for each enantiomer. The smooth curve represents the single-beam transmission of the instrument plus sample.

however, different detectors may produce different base lines. In Figure 1 we show the VCD spectrum of (+)- and (−)-camphor in CCl_4, which has been used as a performance standard for VCD spectrometers since these spectra can be obtained relatively easily and are representative in magnitude for VCD observed in C–H stretching modes.

Instrumental improvements will probably include the use of infrared laser sources as well as an extension of the measurement into the mid-infrared region using PbSbTe or HgCdTe detectors.[51] Recently, Nafie and co-workers completed a theoretical description[52] followed by experimental results[53] of VCD obtained via high-frequency modulation Fourier transform spectroscopy. It appears that this technique should present a valuable alternative for the measurement of VCD, particularly in the mid-infrared spectral region, where instrumental throughput becomes more important.

For the measurement of Raman optical activity, an electrooptic modulator (EOM), to produce circularly polarized light, is added to a conventional Raman spectrometer equipped for photon counting. Using synchronous techniques the difference of scattered intensities of the sample between left and right circularly polarized light is obtained directly. There are, however, some severe difficulties in this experiment. Unlike VCD, where over or under modulation (i.e., phase retardations different from $\pm\lambda/4$) are of no major

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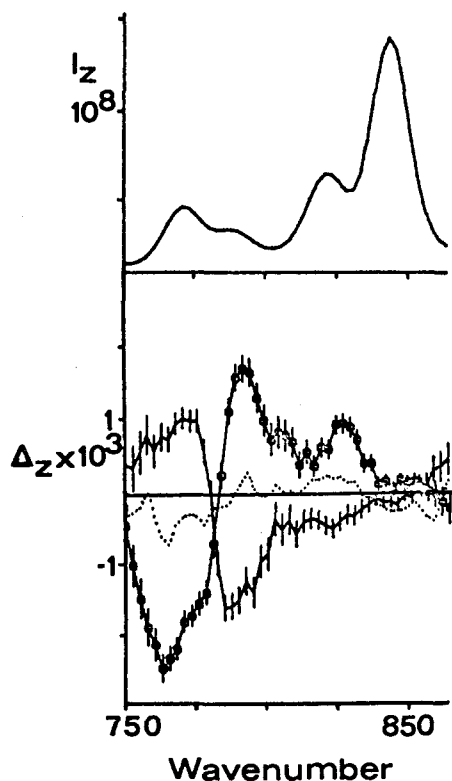
Figure 2. (Top) In-plane polarized Raman spectrum of (±)-α-pinene. (Bottom) ROA spectra of (−)-α-pinene, $[\alpha]^{25}$D 41.9° (plain curve), and (+)-α-pinene, $[\alpha]^{23}$D 46.6° (with circles). Statistical uncertainties are given by vertical bars. The ROA of the racemic modification is represented by a dotted line. Instrumental conditions: laser power, 500 mW at 488 nm; spectral resolution, 10 cm^{-1}; counting time per data point, 300 s; step size, 2.5 cm^{-1}.

consequence, ellipticity will introduce serious artifacts in ROA. Thus, square wave modulation of the EOM and very accurate alignment of the modulation optics are essential. Furthermore, mechanical instability of the optical system and birefringence of the sample cell may produce large, spurious signals. To overcome the inherently weak Raman intensities, high power lasers and large aperture optics are necessary. Despite these difficulties ROA has been observed in a large number of molecules. In Figure 2, we show the normalized couplet CID obtained for (+)- and (−)-α-pinene.[54] This molecule is the ROA calibration analogue of camphor since the pinene couplet, first reported by Barron,[37] can be observed fairly easily owing to its large magnitude and due to the commercial availability of the optically pure pinene enantiomers.

A significantly improved ROA unit was recently reported by Boucher et al.[42] using a spectrograph Raman system and simultaneous detection of scattered frequencies via a multichannel detection system. A similar system having even wider spectral range, lower data acquisition time, and compatibility with pulsed laser sources[55] has been constructed by Hug. Multiplexing instruments of this kind, comparable to the FT–VCD experiment mentioned above, will significantly reduce data acquisition times and increase the sensitivity of the measurement. Thus, it is expected that within the next years superior, high-speed VOA instrumentation will be available which will establish

VOA as a research area of significant value to the scientific community, a value equal to, if not surpassing, that of electronic optical activity at the present time.

In the remainder of this section, we review the progress made in the last 2 years in our laboratory. The goal of this work was establishing VCD as a sensitive, new chiroptical probe of molecular stereochemistry. Thus, the molecules examined had to be sufficiently small to allow interpretation of the spectra; it was also desirable that a large number of chemically related molecules would be available to allow correlation of the results. Thus, a detailed study of some amino acids and related peptides was initiated. The major disadvantage of studying these molecules proved to be their insolubility in any common solvent but water, and we were faced with rather large background absorption levels in the spectral region of interest[30] which degraded the signal-to-noise ratio of the spectra. Fortunately the VCD instrument at Syracuse proved to be very stable, so that very long, data-averaged VCD scans did not present significant difficulties.
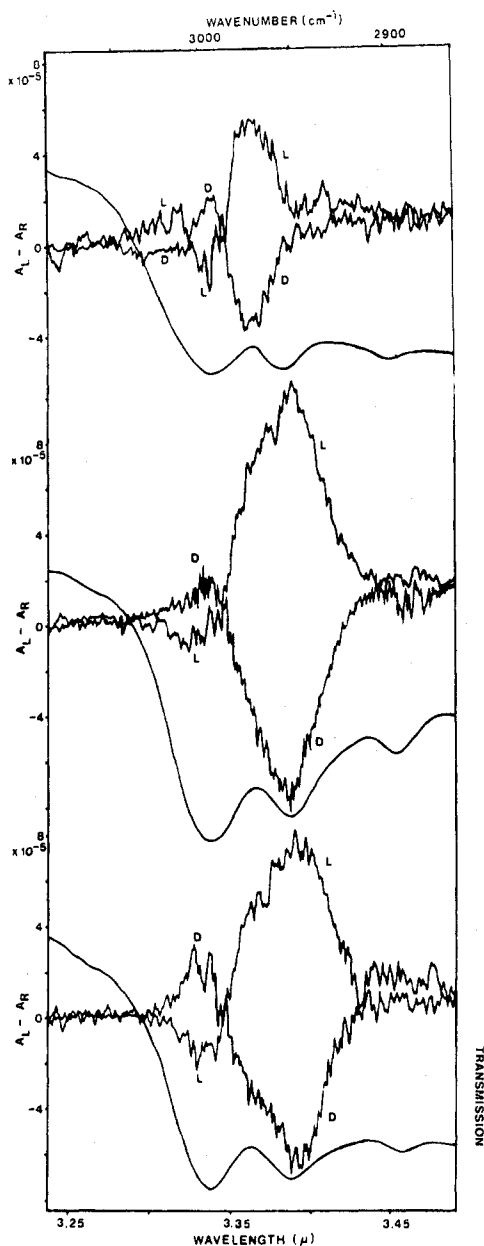
The spectra of alanine (Ala), alanylalanine (Ala-Ala), alanylalanylalanine (Ala-Ala-Ala), alanylglycine (Ala-Gly), and glycylalanine (Gly-Ala) as solutions in D_2O were recently reported,[30] and Figure 3 contains the VCD spectra of alanine and the alanyl homopeptides. The alanine spectrum was interpreted using the perturbed degenerate mode model[40] and an overlap of the resulting VCD couplet with the VCD signals of the remaining CH stretching modes. For the qualitative interpretation of all spectra, including that of alanine itself, an empirical correlation was found which relates the intensity of the VCD signals of the symmetric methyl stretching modes to the chemical environment of the methyl group. In this manner, the analogies of the VCD spectra of Ala-Ala and Gly-Ala and the enormous differences between the spectra of Gly-Ala and Ala-Gly could be explained. Calculations of VCD intensities of alanine are nearly completed and will be published after a careful normal coordinate analysis has been completed.[56]

The $\Delta A/A$ values for serine are about five times smaller than those of alanine, and computer-averaging techniques had to be employed.[31] Although the small optical activity in the C–H stretching vibrations of serine may partially be due to cancellation of VCD intensities of different conformers of the CH_2OH group, it is tempting to argue that the main difference between Ala and Ser is the absence of perturbed degenerate methyl vibrations in serine; it is argued that such modes contribute strongly to the VCD intensity in alanine.

Both Ala and Ser have high solubilities in water, and their VCD spectra in the 2800–3100 cm^{-1} range are not limited in quality by solubility problems. A number of other amino acids could not be dissolved in sufficiently high concentrations to allow observation of VCD spectra. Thus, we have obtained VCD of polycrystalline samples as mulls in halocarbon oil.[31] This method has proved to be a rather simple sampling technique which allows VCD data to be collected between 3600 and 1800 cm^{-1}. Thus, a large number of vibrations, including CH, NH, OH, ND, and OD stretching modes, can be studied. Correlation of liquid (solution) and solid (mull) phase

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WAVENUMBER (cm^{-1})

Figure 3. VCD and transmission in the C–H stretching region of L- and D-alanine-d_3 (top), L,L- and D,D-alanylalanine-d_3 (middle), and L,L,L- and D,D,D-alanylalanylalanine-e_3 (bottom) in D_2O.

singlet ground electronic states. This comes about because this electronic contribution in the Born–Oppenheimer approximation is just the expectation value of the magnetic dipole moment operator for the ground state. Since the ground-state wavefunction is purely real and the operator is purely imaginary, the contribution vanishes. Alternately, there is no magnetic moment associated with a nondegenerate singlet state.

The theoretical approaches to VCD which avoid this problem are the coupled oscillator model[13] and the fixed partial nuclear charge (FPC) model.[6] The coupled oscillator model expresses the rotational strengths of two degenerate vibrational transition moments, μ_1 and μ_2, in a geometrical way which requires, in addition, only the vector $\mathbf{R}_{12}$ which connects these two moments. Coupling results in symmetric (+) and antisymmetric (−) vibrations. In the more general case, the magnetic dipole moments $\mathbf{m}_1$ and $\mathbf{m}_2$ must also be included, and the rotation strengths for the (+) and (−) modes are given by eq 5.[25] In the absence of rotational strength

$$R^{\pm} = \tfrac{1}{2}Im(\mu_1 \cdot \mathbf{m}_1 + \mu_2 \cdot \mathbf{m}_2) \pm$$
$$\tfrac{1}{2}[Im(\mu_1 \cdot \mathbf{m}_2 + \mu_2 \cdot \mathbf{m}_1) - (\omega/2c)(\mu_1 \times \mu_2) \cdot \mathbf{R}_{12}] \quad (5)$$

from the individual subunits, the term in square brackets contributes oppositely to the (+) and (−) modes. This results in a VCD couplet as long as the two modes move sufficiently apart in frequency as a result of their interaction. As mentioned earlier, no definitive observation of this mechanism has been established, although its simplicity is appealing.

The harmonic FPC model has a much wider range of application. In this approach one assigns partial charges to the atomic positions which represent the nuclear charge screened by an amount due to the electrons. As the nuclei vibrate, the partial charges generate electric and magnetic dipole moments which result in infrared absorption and VCD. To apply the model to the αth normal mode, the displacement vectors $\mathbf{s}_{n\alpha}$ for the set of nuclei labeled n as well as a set of partial charges, e_n, are required. The expression for the rotational strength for the transition from v to $v + 1$ is given by eq 6,[6] where $\mathbf{R}_{nn',o}$ denotes the sep-

$$R^{\alpha}_{v+1,v} = [e^2 \hbar (v + 1)/4c] \sum_{n>n'} e_n e_{n'} \, \mathbf{R}_{nn',o} \cdot \mathbf{s}_{n\alpha} \times \mathbf{s}_{n'\alpha} \quad (6)$$

spectra is difficult; in view of the sensitivity of VCD to the stereochemistry and molecular environment, it is not surprising that mull and solution spectra are rather different.

Theory and Calculations

The current theoretical descriptions of VCD and ROA have contrasting strengths and weaknesses. The basic expressions for VCD are simple, but formal difficulties prevent a straightforward application of the Born–Oppenheimer approximation,[15,17,18] while for ROA, the basic expressions are more complex, yet no formal difficulties are apparent. As a consequence, VCD calculations have relied upon models which avoid the Born–Oppenheimer approximation, and ROA calculations have only begun to appear.[48]

The theoretical impediment in VCD is the vanishing of the electronic contribution to the magnetic dipole moment operator for molecules with nondegenerate

aration vector between $\mathbf{R}_{n,o}$ and $\mathbf{R}_{n',o}$ at the equilibrium conformational position. The resemblence of this expression to the $\mathbf{R}_{12}$ term of the coupled oscillator model exhibits its basic form as a summation over all pairs of coupled nuclear motions for each normal mode. The model is popular due to its simplicity, but it has not been derived from first principles and it may neglect important contributions from electronic motion at the vibrational frequency which, in general, does not exactly follow the individual nuclei. Indeed, in many instances the FPC model predicts lower VCD intensities than the corresponding observations.[15,22]

In an attempt to account for at least part of this electronic motion, the LMO model restores the full nuclear charge, Z_n, and then describes the motion of the centroids of charge of localized orbitals, labeled k, which have equilibrium positions, $\mathbf{r}_{ko}$, and displacements in the αth normal mode, $\sigma_{k\alpha}$. These orbitals correspond to inner shell atomic orbitals, bonding orbitals, and lone-pair electron orbitals. The expression for the

rotational strength analogous to the FPC expression in eq 6 is

$$R^{\alpha}_{v+1,v} = [e^2\hbar(v + 1)/4c][\sum_{n>n'} Z_n Z_{n'}\mathbf{R}_{nn',o}\cdot\mathbf{s}_{n\alpha} \times \mathbf{s}_{n'\alpha} +$$

$$\sum_{k>k'} \mathbf{r}_{kk',o}\cdot\sigma_{k\alpha} \times \sigma_{k'\alpha} - \sum_{n,k} Z_n(\mathbf{R}_{n,o} - \mathbf{r}_{k,o})\mathbf{s}_{n\alpha} \times \sigma_{k\alpha}] \quad (7)$$

where $\mathbf{r}_{kk',o} = \mathbf{r}_{k,o} - \mathbf{r}_{k',o}$. This equation can be derived from first principles by two independent pathways involving somewhat different sets of assumptions.[16,17] Both, however, involve the formal introduction of corrections to the Born–Oppenheimer approximation to maintain the magnetic dipole electronic contribution. These corrections are necessary due to the absence of *velocity* correlation between the electronic and nuclear motion in the Born–Oppenheimer approximation, and these correlations are necessary to describe the magnetic dipole moment operator involving $\mathbf{r}_i \times \mathbf{p}_i$ for the ith electron. The resulting electronic contribution in eq 7 is in agreement with intuition and involves no obscure effect. The major drawback to the LMO model is the requirement of an LMO calculation, not only at equilibrium but also at displaced positions along normal coordinates, in order that the vector sets $\mathbf{r}_{k,o}$ and $\sigma_{k,\alpha}$ are known. LMO calculations from our laboratory are envisioned once preliminary FPC calculations for certain molecules of interest have been thoroughly worked out.

The perturbed degenerate mode (PDM) model was first discussed by Barron for degenerate methyl deformation modes in ROA.[8] Empirical evidence suggests that this model is also important for the hydrogen stretching in VCD.[26,30] Its principal manifestation is the frequent appearance of a positive–negative couplet at the frequency of the near-degenerate antisymmetric methyl stretching modes. The methyl group can be regarded as a symmetric chromophore having X–Y degeneracy. The general coupled oscillator model described by eq 5 can be applied to a pair of degenerate methyl vibrations. The symmetry of the chromophore eliminates contributions from the first term, while the location of both of the degenerate vibrations on the same chromophore eliminates the third term involving $\mathbf{R}_{12}$. The symmetry selection rules associated with the remaining exchange term follow the same pattern as ROA as demonstrated by Barron,[8] and a large couplet effect should ensue. Frequency splitting of the two vibrational modes is aided by their spatial superposition, and this strong splitting increases the observed magnitude of otherwise canceling VCD intensities. This advantage is not enjoyed by widely separated hydrogen stretching modes which appear to couple only weakly, leading to a paucity of observations of the coupled oscillator model in the high-frequency region.[24,29]

Theoretical work in ROA has been predominantly noncalculational in character. Due to the complexity of the fundamental equations,[8] simplified models have been developed which extract the essence of the ROA phenomena in restricted situations. The most notable of these are the simple two-group model,[8,46] the theory of degenerate methyl deformations and other degenerate modes,[8] the theory of twisting modes,[8] and a general two-group model of ROA.[8] It is interesting to note a close relationship between the last two terms of the coupled oscillator model of VCD and the corresponding terms in the simple two-group model of ROA.

The numerical calculation of ROA has just recently been carried out[47,48] for the first time by combining the atom–dipole interaction (ADI) model of the molecular polarizability with a complete normal coordinate analysis. The molecule studied was bromochlorofluoromethane for which, unfortunately, there is yet no experimental VOA data. The equations of the ADI model can be shown to be the same as those developed by Barron for the general two-group model.[57] In the former model, spherical atomic polarizabilities become individually chiral through dipolar interactions; however, the latter model advocates direct calculations using symmetric bond polarizabilities. Consequently, the ADI model includes the additional effects of optical rotation which arise from the chirality of individual local polarizability units.[57]

Both theoretical and experimental projects in ROA are currently being pursued in our laboratory. Of particular interest are molecules such as chlorofluoroethane and alanine which possess chirally perturbed methyl groups.

As procedures become established for calculating ROA and VCD, simultaneous calculations of both effects should appear, since a major portion of the work required for such calculations is the preliminary equilibrium conformational analysis and the normal-coordinate analysis. Correlations between VCD and ROA using comparably sophisticated models and the same vibrational analysis should yield interesting data regarding the relative sign and magnitudes of calculated signals. Comparison with corresponding experimental data should prove to be even more informative, especially with regard to the utility of the theory of VCD and ROA.

Conclusion

VOA is still in an intense period of development, experimentally, empirically, theoretically, and computationally. To a certain degree, the measurement of VCD and ROA has been established, although many improvements are underway or envisioned. Most of the fundamental aspects of the theory have been worked out, but some subtle points still need to be clarified. Several theoretical models have been proposed, but their utility as interpretative aids has not yet been fully tested or verified. Calculational procedures are still rough, and as a result, a reliable connection between experiment and theory, or spectra and interpretation, is not yet available.

The sensitivity of VOA to configuration and conformation has been demonstrated by a growing body of experimental data. The translation of these data into molecular information appears to be a formidable task. It is clear, though, that the gradual achievement of these goals will reveal a great deal of information regarding the equilibrium conformation of molecules, intra- and possibly intermolecular forces, the displacement vectors of vibrational normal coordinates, and the equilibrium distribution and vibrational rearrangement of electronic charge in molecules. Furthermore, the convergence of VCD and ROA into the same domain of applicability will reinforce and intensify these interpretive efforts.

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