

ment, and other parameters on the competition in future investigations.

Prospects

It seems clear that the near future will see many new applications of light-induced electron-transfer processes, along some of the lines indicated in the present Account as well as in new areas. The interfacing of what are basically single electron-transfer processes to achieve multielectron conversions will doubtless be the focus of many studies. Obvious possibilities for accomplishing this include the construction of specialized complexes containing more than one reactive center and the combination of reagents in molecular assemblies perhaps analogous to the chloroplast or similar functional biological systems. While much attention is currently directed toward possible energy applications of light-induced electron-transfer reactions, other applications

including synthesis should not be neglected. Certainly in common with other photochemical reactions, reactor design for efficient use of light and for moderate- to large-scale conversion of reagents remains a major problem and challenge.

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Raman Optical Activity: A New Probe of Stereochemistry and Magnetic Structure

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The introduction of visible lasers in the early 1960s engendered a flourishing renaissance in Raman spectroscopy.¹ The great virtue of Raman spectroscopy is that it uses a visible light source and analyzes visible scattered light: the inelastically scattered visible photon carries information in the form of a loss or gain of a quantum of energy corresponding to a molecular transition which may be translational, rotational, vibrational, or electronic. Visible radiation can be manipulated and detected with ease, and recent advances in optical and electronic technology have made possible many new and exotic Raman experiments. A case in point is the study of vibrational optical activity by measuring a small difference in the intensity of Raman-scattered light from chiral molecules and molecules in magnetic fields, using right and left circularly polarized incident light.

It has been appreciated for some time that the measurement of natural optical activity associated with molecular vibrations could provide a wealth of new stereochemical information. But only in the last few years have vibrational optical activity spectra been obtained by using both infrared and Raman techniques. The significance of vibrational optical activity becomes apparent when it is compared with conventional elec-

tronic optical activity in the form of optical rotatory dispersion (ORD) and circular dichroism (CD) of visible and near-ultraviolet radiation.² These conventional techniques have proved most valuable in stereochemistry, but since the electronic transition frequencies of most structural units in a molecule occur in inaccessible regions of the far ultraviolet, they are restricted to probing chromophores and their immediate intramolecular environments. On the other hand, a vibrational spectrum contains bands from most parts of a molecule, so the measurement of some form of vibrational optical activity should provide much more information.

The obvious method of measuring vibrational optical activity is by extending ORD and CD into the infrared. But there is a fundamental physical difficulty inherent in this approach: optical activity observables are proportional to the frequency of the *exciting* radiation, and infrared frequencies are orders of magnitude smaller than visible frequencies. This snag is side-stepped using Raman optical activity because the Raman effect provides complete vibrational spectra using *visible* exciting light. At the moment there is a striking complementarity between the infrared and Raman approaches to natural vibrational optical activity.³ Infrared CD cannot penetrate much below about 2000 cm⁻¹, and although Raman optical activity covers the complete vibrational spectrum, it is best below about 2000 cm⁻¹. Thus infrared CD is best for studying fundamental

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stretching modes involving hydrogen and deuterium, as well as certain overtone and combination bands, whereas Raman optical activity is best for studying low-frequency skeletal deformation and torsion modes, which in fact carry stereochemical information most directly.

Magnetic field induced Raman optical activity can provide vibrational band assignments, and for molecules in degenerate states it acts as "Raman EPR" since it can measure g values directly. No infrared analogue has been observed to date.

Reviews of Raman optical activity giving more detail than here have been published previously.⁴⁻⁶

Optical Activity in Light Scattering

Polarization studies have always been an important feature in molecular light scattering. In the late 19th century, Lord Rayleigh showed that the light scattered at right angles from spherical molecules should be completely linearly polarized perpendicular to the scattering plane. The observed imperfection in this linear polarization in light scattered from gases was ascribed to a lack of spherical symmetry in the optical properties of the molecules. In 1923, Gans⁷ discussed the possibility of additional polarization phenomena in light scattering from optically active molecules; in particular, he investigated the contribution to Rayleigh scattering from the optical activity tensor alone and claimed to have observed its effect on the depolarization ratio; but de Malleman⁸ pointed out that the anomalies originated in optical rotation of the incident and scattered beams. Also, Gans omitted terms describing interference between the polarizability and optical activity which are central to the discussion of Rayleigh and Raman optical activity. Shortly after the discovery of the Raman effect, Bhagavantam and Venkateswaran⁹ found differences in the relative intensities of some of the vibrational Raman lines of two enantiomers, but these were attributed subsequently to impurities. Although he had no theory, Kastler¹⁰ thought that a difference might exist between the Raman spectra of optically active molecules in right and left circularly polarized incident light, and attempted unsuccessfully to observe it. Perrin¹¹ alluded to the existence of additional polarization effects in light scattered from optically active molecules, but it was Atkins and Barron¹² who showed explicitly that interference between the molecular polarizability and optical activity leads to a dependence of the scattered intensity on the degree of circular polarization of the incident light and to a circularly polarized component in the scattered light. Subsequently, Barron and Buckingham¹³ developed the theory of the Rayleigh and Raman circular intensity difference (CID), defined by eq 1, where I^R and I^L are

$$\Delta = (I^R - I^L)/(I^R + I^L) \quad (1)$$

the scattered intensities in right and left circularly polarized incident light. The first reported Raman CID spectra by Bosnich et al.¹⁴ and Diem et al.¹⁵ originated in experimental artefacts, but the spectra reported shortly afterwards by Barron et al.¹⁶⁻¹⁸ in simple chiral molecules such as α -phenylethylamine and α -pinene have now been confirmed as the first genuine observations.¹⁹⁻²¹

Since all molecules can show ORD and CD in a magnetic field (the Faraday effect), it is not surprising that all molecules should show magnetic Rayleigh and Raman CID. The theory of this effect was worked out by Barron and Buckingham,²² who showed that the magnetic field must be parallel to the incident light beam. Magnetic CIDs were first observed by Barron²³ in the resonance Raman spectrum of ferrocyclochrome *c*. More surprisingly, although there is no simple electrical analogue of the Faraday effect (it would violate parity²⁴), Buckingham and Raab²⁵ pointed out that Rayleigh and Raman optical activity should be shown by any fluid in a static electric field perpendicular to both the incident and scattered directions, and the Rayleigh version has been observed recently by Buckingham and Shatwell.²⁶

Theory

Within a semiclassical model of the interaction of light with matter, the origin of scattered light is considered to be the radiation of electromagnetic waves by the oscillating electric and magnetic multipole moments induced in the molecule by the incident light wave. This approach leads to expressions for observables in terms of molecular property tensors which can be given a quantum-mechanical form.²⁷ The most important experimental situation is an isotropic collection of chiral molecules, in the absence of external magnetic fields, that is transparent to the incident light beam. For light scattered at 90° from an incident beam traveling along the z direction, the following expressions for the CIDs observed through analyzers perpendicular (Δ_x) and parallel (Δ_z) to the scattering plane yz obtain:¹³

$$\Delta_x = \frac{2(7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\lambda\mu}\alpha_{\lambda\mu} + \alpha_{\lambda\lambda}\alpha_{\mu\mu})} \quad (2)$$

$$\Delta_z = \frac{4(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{2c(3\alpha_{\lambda\mu}\alpha_{\lambda\mu} - \alpha_{\lambda\lambda}\alpha_{\mu\mu})} \quad (3)$$

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where²⁷

$$\alpha_{\alpha\beta} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle) = \alpha_{\beta\alpha} \quad (4)$$

$$G'_{\alpha\beta} = -\frac{2}{\hbar} \sum_{j \neq n} \frac{\omega}{\omega_{jn}^2 - \omega^2} \text{Im}(\langle n | \mu_\alpha | j \rangle \langle j | m_\beta | n \rangle) \quad (5)$$

$$A_{\alpha\beta\gamma} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | \theta_{\beta\gamma} | n \rangle) \quad (6)$$

$|n\rangle$ and $|j\rangle$ are the initial and intermediate molecular states, ω is the angular frequency of the incident light, $\omega_{jn} = \omega_j - \omega_n$, and

$$\mu_\alpha = \sum_i e_i r_{i\alpha} \quad (7)$$

$$m_\alpha = \sum_i (e_i / 2m_i) \epsilon_{\alpha\beta\gamma} r_{i\beta} p_{i\gamma} \quad (8)$$

$$\theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i (3r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}) \quad (9)$$

are the electric dipole, magnetic dipole, and electric quadrupole moment operators, particle i at \mathbf{r}_i having charge e_i , mass m_i , and momentum \mathbf{p}_i . The unit alternating tensor $\epsilon_{\alpha\beta\gamma}$ is defined such that $\epsilon_{\alpha\beta\gamma} r_{i\beta} p_{i\gamma}$ is the α component of the vector product $\mathbf{r} \times \mathbf{p}$. The symmetric polarizability $\alpha_{\alpha\beta}$ is supported by all molecules and provides the major contribution to light scattering and refraction. The scalar part of $G'_{\alpha\beta}$, that is, $G'_{\alpha\alpha} = G'_{xx} + G'_{yy} + G'_{zz}$, is supported only by chiral molecules and is familiar from the Rosenfeld equation²⁸ for optical rotation in an isotropic sample. Although $A_{\alpha\beta\gamma}$ does not contribute to optical rotation in isotropic samples, it provides a contribution of the same order as $G'_{\alpha\beta}$ in oriented samples.²⁹ But notice that $A_{\alpha\beta\gamma}$ still contributes to Δ in isotropic samples. Δ_x and Δ_z are called the polarized and depolarized CIDs. Typically, $\Delta \sim 10^{-3}$. The same CID expressions apply to Raman scattering if the polarizability and optical activity tensors are replaced by corresponding transition tensors such as $(\alpha_{\alpha\beta})_{j\nu n\nu} = \langle j_\nu | \alpha_{\alpha\beta} | n_\nu \rangle$, where $|n_\nu\rangle$ and $|j_\nu\rangle$ are the initial and final vibrational states.

Since natural Rayleigh optical activity originates in interference between the scattered waves generated through the same components of the polarizability and optical activity tensors, the symmetry requirement is that the same components of $\alpha_{\alpha\beta}$ and $G'_{\alpha\beta}$ span the totally symmetric irreducible representation of the molecule's point group (although $A_{\alpha\beta\gamma}$ does not transform like $G'_{\alpha\beta}$, the second-rank axial tensor $\epsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta}$ that combines with $\alpha_{\alpha\beta}$ in the expressions for Δ has transformation properties identical with $G'_{\alpha\beta}$). Since it originates in the corresponding transition tensors, the symmetry requirement for natural vibrational Raman optical activity in fundamentals is that the same components of $\alpha_{\alpha\beta}$ and $G'_{\alpha\beta}$ span the irreducible representation of the particular normal vibrational coordinate. This only arises in the chiral point groups C_n , D_n , O , T , and I , which lack improper rotations so that $\alpha_{\alpha\beta}$, which transforms like a second-rank polar tensor, and $G'_{\alpha\beta}$, which transforms like a second-rank axial tensor, have identical transformation properties. Thus all the

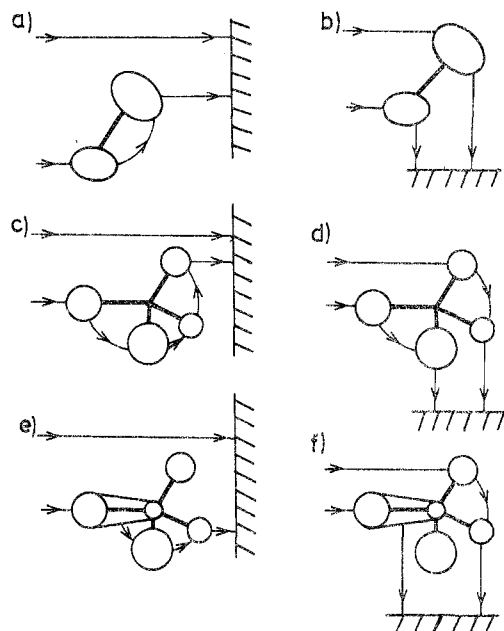


Figure 1. The generation of optical rotation (first column) and Rayleigh and Raman optical activity (second column) in simple model structures.

Raman-active fundamentals in a chiral molecule can show optical activity.

A complete theory of the generation of Raman optical activity within chiral molecules is difficult and will take some time to evolve. Basically, the electronic optical activity tensors $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ (and also $\alpha_{\alpha\beta}$) must be calculated as functions of the normal coordinates of vibration. Considerable physical insight into conventional electronic optical activity has been obtained from "coupling" models which apply when all groups within a molecule are inherently achiral and no electron exchange exists between them.^{30,31} These models are usually applied to isotropic collections of molecules for which only the mean optical activity $G'_{\alpha\alpha}$ is required. To deal with Raman optical activity, they must be extended to generate general components of $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$, taking care to include the origin-dependent parts. As we pointed out some time ago,³² these origin-dependent parts give rise to a mechanism for Rayleigh and Raman optical activity that has no counterpart in optical rotation and circular dichroism. The latter are birefringence phenomena, and therefore originate in interference between transmitted and forward-scattered waves. Thus in the Kirkwood model, the optical rotation generated by a chiral structure comprising two achiral groups involves dynamic coupling: only forward-scattered waves that have been deflected from one group to the other have sampled the chirality and can generate optical rotation on combining with the transmitted wave (Figure 1a). But the transmitted wave is not important in Rayleigh scattering, so interference between two waves scattered independently from the two groups provides chiral information (Figure 1b). This picture can be extended to a chiral tetrahedral structure such as CHFCIBr. Since a pair of dynamically coupled atoms constitutes an anisotropically polarizable group,

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the Born-Boys model of optical rotation, which considers just the four ligand atoms, requires dynamic coupling extending over all four atoms (Figure 1c),³¹ whereas Rayleigh optical activity requires interference between two waves scattered independently from two pairs of dynamically coupled atoms (Figure 1d) or from one atom and three other dynamically coupled atoms. If the central carbon atom is also included, the carbon-ligand bonds constitute anisotropic groups, so less dynamic coupling is required (Figure 1e,f).

A general "bond-polarizability" theory of Raman optical activity has been developed⁶ in which the variation of the molecular polarizability and optical activity tensors with a normal coordinate of vibration is calculated by way of the variation of the tensors with local internal coordinates such as bond stretches and angle bends. By writing the molecular tensors as sums of local bond or group tensors and taking account of the origin dependence of $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$, one can relate the products that determine the Raman intensity and optical activity to the details of the molecular structure. For example,

$$\begin{aligned} \langle p_0 | \alpha_{\alpha\beta} | p_1 \rangle \langle p_1 | G'_{\alpha\beta} | p_0 \rangle = & \\ - \frac{\hbar\omega}{4\omega_p} \epsilon_{\beta\gamma\delta} \left\{ \sum_{i < j} (R_{ji\gamma})_0 \left[\sum_q \left(\frac{\partial \alpha_{i\alpha\beta}}{\partial s_q} \right)_0 L_{qp} \right] \times \right. & \\ \left[\sum_r \left(\frac{\partial \alpha_{j\delta\alpha}}{\partial s_r} \right)_0 L_{rp} \right] + & \\ \left[\sum_i \sum_q \left(\frac{\partial \alpha_{i\alpha\beta}}{\partial s_q} \right)_0 L_{qp} \right] \times & \\ \left. \left[\sum_j (\alpha_{j\delta\alpha})_0 \sum_r \left(\frac{\partial R_{j\gamma}}{\partial s_r} \right)_0 L_{rp} \right] \right\} + & \\ \frac{\hbar}{2\omega_p} \left[\sum_i \sum_q \left(\frac{\partial \alpha_{i\alpha\beta}}{\partial s_q} \right)_0 L_{qp} \right] \left[\sum_j \sum_r \left(\frac{\partial G'_{j\alpha\beta}}{\partial s_r} \right)_0 L_{rp} \right] & \end{aligned} \quad (10)$$

where $\alpha_{i\alpha\beta}$ etc. are tensors intrinsic to the i th group. s_q is the q th internal coordinate, and L_{qp} is the \mathbf{L} matrix element, determined from a normal coordinate analysis, that gives the relative contribution of the p th normal mode to the q th internal coordinate. The first term is a sum over all pairs of groups that constitute chiral structures, in accordance with the mechanism illustrated in Figure 1b, \mathbf{R}_{ji} being the vector from the local origin in group i to that in j . The second term involves changes in the position vector \mathbf{R}_j of a group relative to the molecule-fixed origin: normal coordinates containing contributions from changes in either the length of \mathbf{R}_j , or its orientation, or both, will activate this term. Changes in the orientation of \mathbf{R}_j can generate a significant "inertial" contribution in deformation and torsion modes. The last term involves the product of intrinsic group polarizability and optical activity tensors. The complete expression is invariant to both the choice of molecular origin and the local group origins.

If a normal coordinate analysis is available, the bond-polarizability expressions enable the sign and magnitude of the Raman CIDs to be calculated for every normal mode, and such calculations are now in hand in Glasgow. But since the theory is based on bond

properties, together with the position and orientation of the bonds within the molecule, it is possible to extract from it simple geometrical expressions that apply to local archetypal chiral units, such as two-group structures, in larger molecules.⁶

In another approach to the calculation of Raman CIDs, the "atom-dipole interaction" theory,^{3,33,34} the molecule is broken down into its constituent atoms, rather than bonds, so dynamic coupling needs to be invoked at the outset since mechanisms such as that in Figure 1d are involved. It might be thought that even the bond-polarizability theory needs to invoke dynamic coupling in order to cope with molecules such as CHFClBr, but in fact the inertial term in (10) makes the dominant contribution in deformations.³⁵

Experiment

In principle, the Raman CID experiment is simplicity itself. But from the heated controversy that surrounded the original observations, it will be gathered that there are snags! In the first generation of instruments, an electrooptic modulator, for switching the polarization of the incident laser beam between right and left circular, was added to a conventional Raman spectrometer arranged to detect scattering at 90° and equipped for photon counting. Using synchronous detection techniques, the difference in the Raman-scattered intensity in right and left circularly polarized incident light is obtained directly. The difficulties arise from the fact that imperfections in the modulation system and the optical train can generate large artefacts in the $I^R - I^L$ spectrum. As discussed in detail elsewhere,^{4,16} the artefacts originate in the modulation of linear polarization components in the incident light beam: the secret of success in the original Cambridge experiments¹⁶ was the use of square-wave modulation to switch the polarization of the laser beam between pure right and pure left circular with careful gating of the photon counters to avoid collecting counts at the crossover points. The first generation Raman CID instrument that has been working in Glasgow for the last few years uses up to 4 W of argon ion laser power to produce well-defined $I^R - I^L$ spectra at a resolution of 10 cm⁻¹ and a scan speed of 1 cm⁻¹ min⁻¹.

It should be mentioned that the polarized CID Δ_x is much more susceptible to artefacts than the depolarized CID Δ_z .^{4,16} For this reason only depolarized CIDs have been measured routinely on the first generation instruments. This is not too restrictive, however, since depolarized CIDs are easier to interpret and no stereochemical information is lost; but for more fundamental studies it would be nice to have polarized CIDs as well.

The instrument just described is now obsolete. Moskovits, Bosnich, et al.^{21,36} reported a new Raman CID instrument based on an optical multichannel spectrograph that records large chunks of a spectrum simultaneously, which decreases the data acquisition time dramatically. Subsequently, Hug and Surbeck³⁷ reported an even faster multichannel instrument with sufficient control of artefacts that polarized CIDs could

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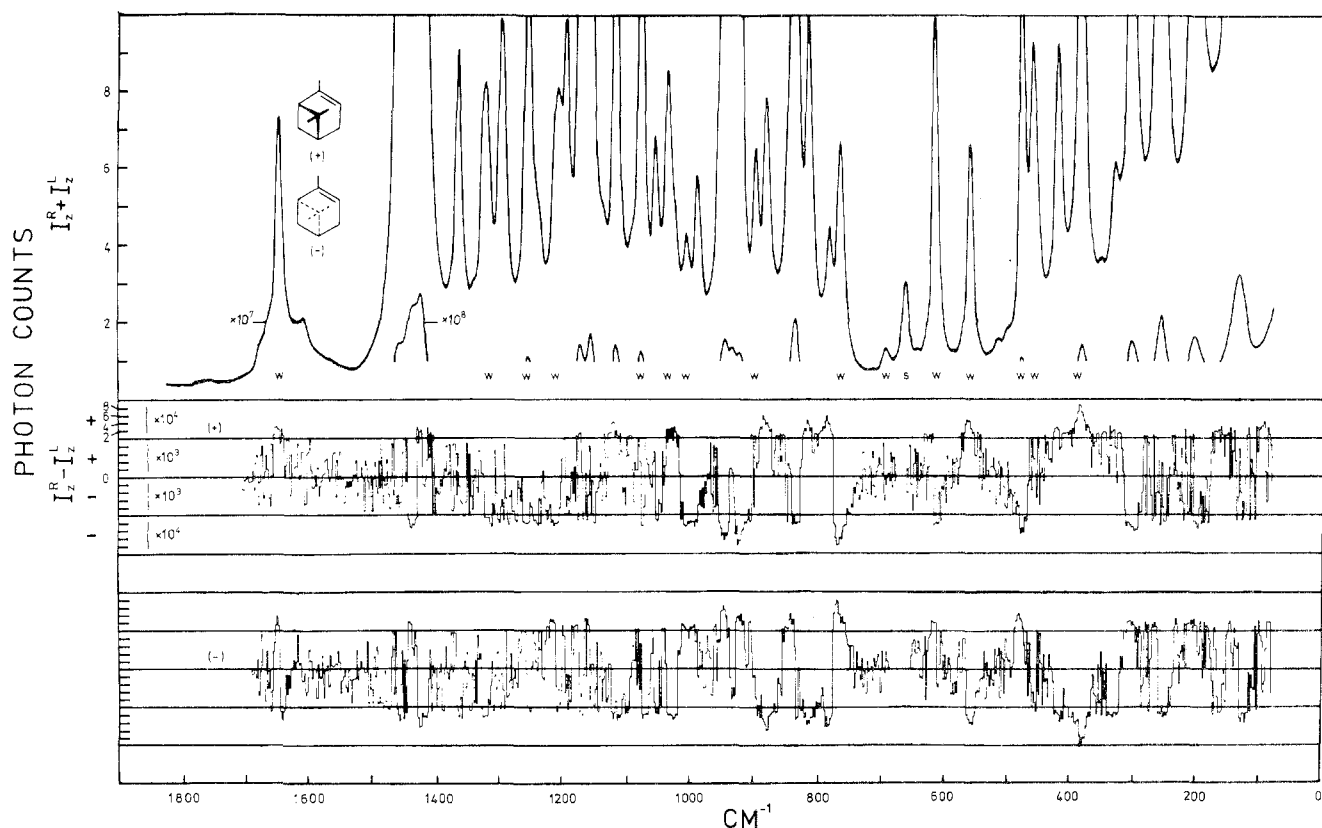


Figure 2. The depolarized Raman CID spectra of the two enantiomers of α -pinene.

be recorded for the first time: their preliminary report indicates that valuable information can be gained on the relative importance of the individual tensor invariants that can contribute to Raman CID. Hug and Surbeck also introduced a "chirality number", q , defined in terms of differential scattering cross sections, rather than raw intensities, which has the advantage of being representative of an enantiomerically pure sample. For such a sample, their chirality number is related to the dimensionless CID by $q = -2\Delta$.

The depolarized Raman CID spectra of about 100 chiral molecules have been obtained on the first generation Glasgow instrument. The $I^R - I^L$ and $I^R + I^L$ spectra are presented separately because the background must be subtracted from $I^R + I^L$ before calculating Δ . The $I^R + I^L$ spectra are presented on a linear scale, whereas the $I^R - I^L$ spectra are presented on a scale that is linear within each decade range but logarithmic between decade ranges. This enables the exponent in the $I^R - I^L$ photon count to be recorded, although the spectrum takes on a stretched out appearance in which the statistical noise level looks much greater than it really is since, on all but the weakest bands, only values within the $\pm 10^4$ range are significant.

Figure 2 shows the depolarized Raman circular intensity sum and difference spectra of the two neat enantiomers of α -pinene. The features between about 380 and 900 cm^{-1} are assigned to skeletal vibrations of pinane-type molecules and to out-of-plane olefinic hydrogen deformations.³⁸ Allowing for different methods of presentation, the CID spectra of α -pinene published by Hug et al.¹⁹ and Moskovits, Bosnich, et al.^{21,36} are virtually identical.

(38) L. D. Barron and B. P. Clark, *J. Chem. Soc., Perkin Trans. 2*, 1171 (1979).

Raman CID spectra can be used at different levels of analysis. At the lowest level, one can simply compare spectra of series of related compounds without enquiring into the origins of the effects. The richness of the spectra, with many features correlating in sign and magnitude, often enables absolute configurations to be assigned with confidence. A good example is provided by substituted menthols: a complicated CID structure between about 1100 and 1400 cm^{-1} in (-)-menthol is repeated almost exactly in (-)-menthylamine and (-)-menthyl chloride.³⁹ Camphors also provide some good correlations.⁴⁰

The next level of analysis is the comparison of CID features in Raman bands in related molecules that originate in well-defined modes of vibration. The methyl group could be particularly useful in this respect since several of its characteristic modes often show significant CIDs. For example, when the methyl group is attached to the same chiral carbon atom as an unsubstituted phenyl group, the band at about 1450 cm^{-1} originating in the degenerate methyl asymmetric deformations often shows a sharp CID couplet, the sign of which provides consistent correlations of absolute configuration.^{19,41-43} The methyl torsion should also be useful: this sets up oscillations in space of the rest of the molecular frame from which the absolute configuration and geometry of the frame relative to the torsion axis can be probed through the associated Raman CID.⁴⁴

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(43) L. D. Barron and B. P. Clark, *J. Chem. Res. (S)*, 36 (1979).

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It is gratifying that the molecule instrumental in establishing the concept of molecular chirality, tartaric acid, shows a splendid Raman CID spectrum.⁴⁵ One significant feature is a large couplet centered at about 500 cm^{-1} which also appears in this region in dimethyl tartrate and 2,3-butanediol. If these couplets originate in deformations of the twisted O-C-C-O or C-C-C-C units, then knowing the absolute configuration, it would be possible to distinguish between the three staggered conformers (and vice versa).

Significant effects have also been observed in molecules that are chiral on account of deuterium substitution.^{46,47} For example, (+)- α -D-benzyl alcohol shows a CID couplet associated with two Raman bands at about 860 and 950 cm^{-1} .⁴⁶ These bands are not present in benzyl alcohol itself, and are assigned to C-D deformations.

Magnetic Raman Optical Activity

Magnetic Rayleigh and Raman optical activity originate in interference between waves scattered through the symmetric polarizability $\alpha_{\alpha\beta}$, given by (4), and the antisymmetric polarizability $\alpha'_{\alpha\beta}$, given by eq 11.

$$\alpha'_{\alpha\beta} = -\frac{2}{\hbar} \sum_{j \neq n} \frac{\omega}{\omega_{jn}^2 - \omega^2} \text{Im}(\langle n | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | n \rangle) = -\alpha'_{\beta\alpha} \quad (11)$$

Complete expressions for the magnetic CID components, which are linear in the applied magnetic field, can be found elsewhere.^{5,22,48} $\alpha'_{\alpha\beta}$ is supported only by molecules in degenerate states and is responsible for antisymmetric light scattering.⁴⁹ But $\alpha'_{\alpha\beta}$ is supported by all molecules in a static magnetic field, when it generates the Faraday effect.⁵⁰

The magnetic Raman CID experiments in Glasgow use the same basic instrument as for natural Raman CID, with the addition of a permanent magnet with holes bored through the pole pieces to pass the laser beam. This arrangement provides a magnetic field of about 0.7 T parallel to the laser beam.

The first observations were in a number of the resonance Raman bands originating in porphyrin ring modes of ferrocytochrome c.^{23,51} These effects originate in the Zeeman splitting of the orbitally degenerate excited electronic resonant states, although the detailed mechanism is still not clear. Recently, large effects have been observed in smaller systems such as the low-spin d^5 complex IrCl_6^{2-} , the high-spin d^5 complex FeBr_4^- and the d^9 complex CuBr_4^{2-} ,⁵² which have a simpler explanation in terms of transitions between the Zeeman levels of the Kramers-degenerate ground states. This is illustrated in Figure 3 for the simplest case of a twofold degeneracy. The magnetic field lifts the degeneracy, and the two "off-diagonal" Raman transitions lead to frequency shifts, equal to the Zeeman splitting,

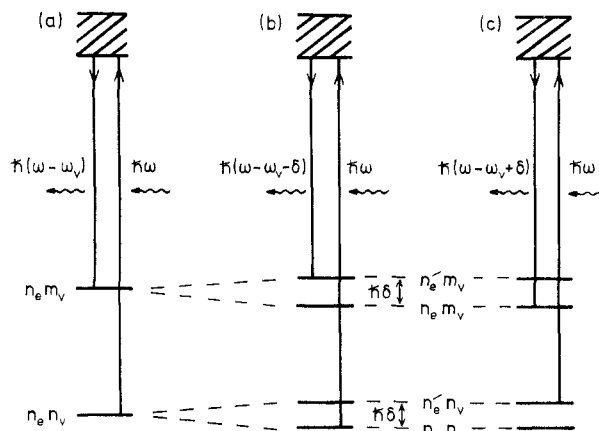


Figure 3. (a) A conventional Stokes Raman vibrational transition process from the ground vibrational state within the ground electronic level, $n_e n_v$, to an excited vibrational state within the ground electronic level, $n_e m_v$. (b) and (c) show the two distinct "off-diagonal" Raman processes that are generated if a twofold degeneracy in the ground electronic level is lifted by a magnetic field.

on either side of the vibrational Raman frequency. Magnetic optical activity of equal magnitude, but opposite sign, is associated with the two "off-diagonal" transitions, so a CID couplet is observed.

Time-reversal arguments lead to the following fundamental property of the complex transition polarizability $\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} - i\alpha'_{\alpha\beta}$.⁴⁹

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = (\tilde{\alpha}_{\beta\alpha})_{n^T m^T} = (\tilde{\alpha}_{\alpha\beta})_{m^T n^T}^* \quad (12)$$

where $|n^T\rangle$ and $|m^T\rangle$ are the time-reversed versions of the initial and final molecular states. This result enables definitive statements to be made about the permutation symmetry of the transition polarizability. Of relevance here is that the complex transition polarizability generated by an "off-diagonal" Rayleigh scattering process is pure antisymmetric.⁴⁹ The same conclusions apply to resonance Raman scattering in totally symmetric modes of vibration. Thus the appearance of a magnetic CID couplet in a totally symmetric resonance Raman band is a sensitive new test for antisymmetric scattering which, following observations by Koningstein and Mortensen in metal ions,⁵³ Spiro and Strekas in heme proteins,⁵⁴ and Hamaguchi et al. in metal halides,⁵⁵ has assumed great importance in resonance Raman spectroscopy.

Figure 4 shows the depolarized resonance magnetic Raman circular intensity sum and difference spectra of a dilute solution of IrCl_6^{2-} in aqueous HClO_4 .⁵² The three bands are assigned to the three Raman-active fundamentals of the octahedral MX_6 structure: ν_1 (A_{1g} , 341 cm^{-1}), ν_2 (E_g , 290 cm^{-1}), and ν_5 (T_{2g} , 161 cm^{-1}). Using irreducible tensor methods for the octahedral spinor group,⁵⁶ calculations of the appropriate components of $\alpha_{\alpha\beta}$ and $\alpha'_{\alpha\beta}$ for the particular vibrational-electronic scattering transitions that generate each resonance Raman band give CIDs that agree in sign and relative

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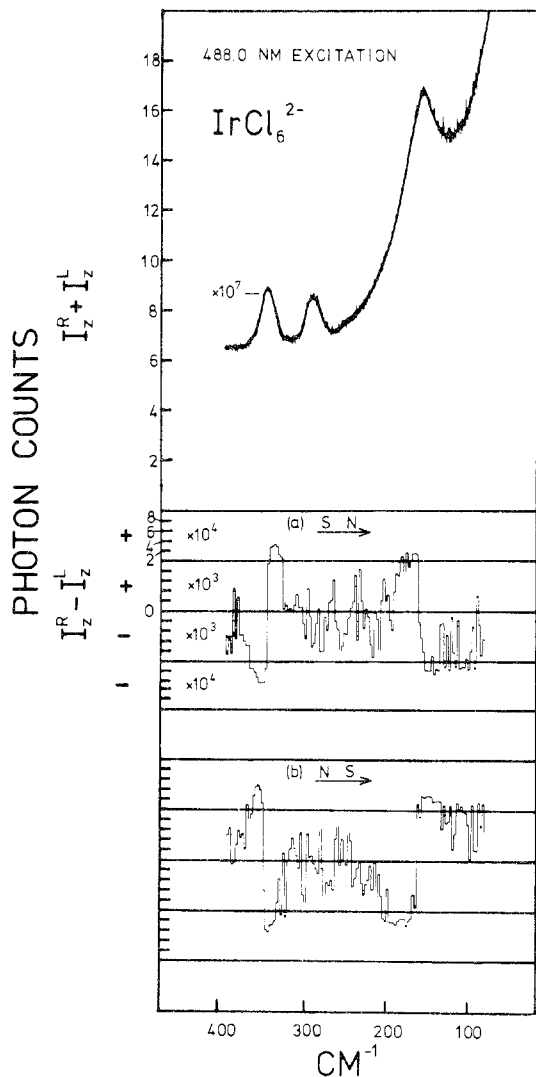


Figure 4. The depolarized resonance magnetic Raman CID spectra of IrCl_6^{2-} for magnetic fields antiparallel (a) and parallel (b) to the incident laser beam.

magnitude with these observations.⁵⁷ This indicates that magnetic Raman CID can give vibrational band assignments.

Concluding Remarks

The work outlined in this Account has demonstrated that Raman optical activity probes molecular stereochemistry and magnetic structure in novel and diverse ways. Now that the measurements have received a tremendous boost from optical multichannel detection methods, the technique should find wide application in chemistry. In conclusion, some possible future developments are surveyed.

With chiral molecules, it is hoped that the ultimate level of analysis will be the extraction of the *total*

stereochemistry (absolute configuration, conformation, and bond angles) from the complete Raman CID spectrum. This should be possible once reliable theories have been developed. One can envisage the use of a computer to synthesize the complete CID spectrum and to vary the stereochemical parameters until the observed spectrum is reproduced exactly.

Raman CID should be particularly useful with molecules that owe their chirality to isotopic substitution. Studies of stereochemical aspects of enzyme reactions often depend on determinations of the absolute configurations of such molecules, yet this can be uncertain on account of very small ORD and CD (if any!) because the electronic chirality is so small. But the large vibrational chirality generates Raman CIDs sufficiently large and specific for reliable correlations of absolute configuration to obtain. One potentially unique application is to the chiral phosphate group $-\text{OP}^{16}\text{O}^{17}\text{O}^{18}$,^{58,59} for which no existing physical method provides a reliable absolute configuration.

Optical activity measurements are important in biochemistry and biophysics since they are sensitive to the delicate stereochemical features that determine biological function. Vibrational optical activity should be particularly useful in this respect, and by combining the resonance Raman⁶⁰ and Raman CID techniques it should be possible to obtain new stereochemical information at sites of biological function in large biological molecules in aqueous media, even on surfaces in particulate samples such as membranes in highly scattering suspensions.

In addition to the study of fundamental resonance Raman processes and vibrational band assignment, magnetic Raman CID could provide *g* values directly (although only the Rayleigh effect gives the true ground-state *g* value). The resolution of the spectra obtained so far is not good enough to extract *g* values from the separation of the peaks in the magnetic CID couplets, but this should be possible by using a multichannel spectrograph and a superconducting magnet. The ability to measure *g* values through resonance Raman scattering, including changes due to the lower effective symmetry of a molecule while executing non-totally symmetric vibrations, has intriguing possibilities in the study of odd-electron inorganic systems and organic free radicals. One can also envisage the use of "resonance Raman spin probes" at appropriate sites in large biological molecules.

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