Time Reversal and Molecular Properties

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ABSTRACT

Chemists regularly exploit point group symmetry in their analyses of molecular structure and properties but they rarely utilize time reversal symmetry. The time reversal operator T reverses the momenta and spins of all particles in a system and distinguishes properties which are even under T, such as the electric dipole moment, from those that are odd, such as the magnetic dipole moment. We review the role of T in quantum mechanics and discuss its application to the properties of molecules in electric and magnetic fields. Among the properties considered are natural and magnetic optical activity, magneto-chiral effects, antisymmetric Raman scattering, optical NMR and ESR, chirality, and absolute enantioselection.

Introduction

Symmetry arguments are highly favored by chemists, not only as an aid to understanding molecular structure and reactivity, but also because of their aesthetic appeal.[1] Most chemists are familiar with the spatial symmetry analysis of molecules and the application of point group symmetry arguments to deduce qualitative information. However, spatial symmetry alone may lead to wrong conclusions about the many properties of molecules that depend on motion. One such property is molecular magnetism, which depends on the orbital and spin motions of the constituent electrons and nuclei and on how these are influenced by an external magnetic field, which itself may be generated by the motion of electrons through a coil. To deal with motion-dependent properties, spatial symmetry arguments must be augmented with arguments based on time reversal,[2] which are less familiar to chemists even though they have been used in physics for many years, usually in connection with degenerate quantum states.

Symmetry arguments rest ultimately on the symmetries inherent in the laws of physics, and these depend in turn on certain uniformities that we perceive in the world around us.[3] In quantum mechanics, the invariance of physical laws under an associated transformation often generates a conservation law or selection rule that follows from the invariance of the Hamiltonian H under the transformation. Although the focus of this Account is time reversal, we discuss it along with two other fundamental symmetry operations, namely parity and charge conjugation, to obtain a more complete understanding of molecular behavior.

Parity, represented by the operator P, inverts the coordinates of all the particles in a system through the coordinate origin. If replacing the space coordinates (x,y,z) by $(-x,-y,-z)$ everywhere in equations describing physical laws (e.g., Newton's equations for mechanics or Maxwell's equations for electromagnetism) leaves the equations unchanged, all processes determined by such laws are said to conserve parity. Conservation of parity implies that P commutes with H, so that, if ψ_k is an eigenfunction of H, $P\psi_k$ is also an eigenfunction with the same energy. The associated conserved quantity is the parity eigenvalue ± 1.

Time reversal, represented by the operator T, reverses the motions of all the particles in a system. If replacing the time coordinate t by $-t$ everywhere leaves equations describing physical laws unchanged, all processes determined by such laws are said to conserve time reversal invariance, or to have reversality. A process will have reversality as long as the process with all the motions reversed is in principle a possible process, however improbable it may be. Time reversal is therefore best thought of as motion reversal.[4,5] It does not mean going backward in time! Conservation of time reversal implies that T and H commute, so that, if H is time-independent, the stationary state ψ_k and its time-reversed state $T\psi_k$ have the same energy. T is unusual in that it does not have eigenvalues, so there is no conserved quantity analogous to parity.

Charge conjugation, represented by the operator C, interconverts particles and antiparticles. This operation from relativistic quantum field theory is useful for checking the consistency of equations and has conceptual value in studies of molecular chirality. It appears in the CPT theorem which states that, even if one or more of C, P, or T is violated, invariance under the combined operation CPT will always hold.[6]

By reviewing a number of topics on which we have worked separately and together over many years, we show how time reversal arguments enhance the understanding of molecular behavior. Even at a simple pictorial level, symmetry arguments based on the transformations of an experiment under P, T, and C can be valuable in that they predict the existence or otherwise of new phenomena.[7,8] The main focus here, however, is on time reversal in quantum mechanics.

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Time Reversal in Quantum Mechanics

In classical mechanics, it is usually obvious whether an observable is invariant or changes sign when the motions of all the particles in a physical system are reversed. Examples of time-even observables are energy W, position vector $\mathbf{r}$, electric field $\mathbf{E}$, and electric dipole $\boldsymbol{\mu}$. Time-odd observables include linear momentum vector $\mathbf{p}$, magnetic field $\mathbf{B}$, and magnetic dipole $\mathbf{m}$.

Time reversal in quantum mechanics goes deeper. Taking the complex conjugate of the Schrödinger equation $H\psi(\mathbf{r},t) = i\hbar\partial\psi(\mathbf{r},t)/dt$ and replacing t by $-t$ shows that, for real H, $\psi^*(\mathbf{r},-t)$ rather than $\psi(\mathbf{r},-t)$ is the time-reversed solution of the Schrödinger equation. This means that the interpretation of T as simply reversing the sign of t does not produce a satisfactory quantum-mechanical operator. Instead, the operator

$$T = UK \tag{1}$$

is invoked, where U is a unitary operator and K the operator of complex conjugation.[4,5] Being the product of an antilinear and a unitary operator, T is called an antiunitary operator having the property

$$\langle T\psi|T\varphi\rangle = \langle U\psi^*|U\varphi^*\rangle = \langle\psi^*|U^{\dagger}U|\varphi^*\rangle = \langle\psi|\varphi\rangle^* = \langle\varphi|\psi\rangle \tag{2}$$

(A linear unitary operator A satisfies $\langle A\psi|A\varphi\rangle = \langle\psi|\varphi\rangle$.) For a spinless particle U is the unit operator and for a particle with spin $T = i\sigma_y K$ in the Pauli matrix representation.

T does not have eigenvalues, so it is not possible to classify a quantum state as being even or odd under time reversal. An illustration is the effect of T on the atomic state $|J,M\rangle$, where the total angular momentum is specified by the usual quantum numbers J and M and can have both orbital and spin contributions. Using a particular phase convention, it is found that[8]

$$T|J,M\rangle = (-1)^{J-M+q}|J,-M\rangle \tag{3}$$

where q is the sum of the orbital quantum numbers of all the electrons in the atom. For the special case of the spin states $\alpha = |(1/2),(1/2)\rangle$ and $\beta = |(1/2),-(1/2)\rangle$ for a single electron, (3) gives

$$T\alpha = \beta, \quad T\beta = -\alpha \tag{4}$$

Hence, T interconverts the two spin states (within an essential phase factor ± 1).

Unlike states, quantum-mechanical operators *can* be classified as even or odd under time reversal. Time-even (+) and time-odd (−) operators are defined by[5,8]

$$TA(+)T^{-1} = A(+)^{\dagger}, \quad TA(-)T^{-1} = -A(-)^{\dagger} \tag{5}$$

Operators usually have the same behavior under time reversal as the associated observables. From (2), the

expectation values of a time-even operator have the same magnitude and sign in ψ and $T\psi$, whereas those of a time-odd operator have the same magnitude but opposite sign. Hence, the expectation value of a time-odd operator is zero in a nondegenerate state since ψ and $T\psi$ must be the same state in this case.

Although T does not have eigenvalues, the operator T^2 has the eigenvalue $\epsilon = +1$ for a system with an even number of electrons and -1 for an odd number. This leads to Kramers theorem:[4,5] in the presence of any static electric potential but in the absence of an external magnetic field, the energy levels of a system with an odd number of electrons (or half odd-integral angular momentum) must have an evenfold degeneracy. Pairs of such degenerate states are interconverted by T, with $T\psi$ called the Kramer's conjugate of ψ. Equation 3 provides an example because time reversal converts $|J,M\rangle$ into the new state $|J,-M\rangle$, orthogonal to and degenerate with the original, corresponding to a reversal of the angular momentum.

In contrast, parity does not convert $|J,M\rangle$ into a new atomic state. This is because P, unlike T, *does* have eigenvalues, and states such as $|J,M\rangle$ are eigenstates of parity with eigenvalues $+1$ or -1:[8]

$$P|J,M\rangle = (-1)^q|J,M\rangle \tag{6}$$

This follows from the behavior under space inversion of the spherical harmonics. If two states of opposite parity, such as ψ_{2s} and ψ_{2p_0} in atomic hydrogen, are degenerate, or nearly so, the system can exist in a state of mixed parity and as such can support odd-parity observables such as the electric dipole moment.[8] The fact that pairs of mixed parity states such as $\psi_{\pm} = 2^{-1/2}(\psi_{2s} \pm \psi_{2p_0})$ are interconverted by P suggests a loose analogy in which we can think of states such as $|J,M\rangle$ and $|J,-M\rangle$ as having "mixed time parity" since they are interconverted by time reversal, even though associated states of definite time parity do not exist. "Mixed time parity" is an essential requirement for a state to support time-odd observables.[8]

This distinct behavior of general angular momentum states under P and T lies at the heart of the different behavior of atoms and molecules in electric and magnetic fields, exemplified by the Stark and Zeeman effects. First-order effects require, in the Stark case, a permanent electric dipole moment which has odd parity but is time-even, and in the Zeeman case a permanent magnetic dipole moment which has even parity but is time-odd.

Time Reversal and Group Theory

Spatial symmetry operations must be augmented with time reversal to encompass some of the more subtle aspects of molecular behavior. Permanent electric and magnetic dipole moments provide an example. As far as spatial symmetry is concerned, the difference between

electric and magnetic dipole moments is that μ is a polar vector and so transforms like a translation, whereas $\mathbf{m}$ is an axial (pseudo) vector and so transforms like a rotation. In the elementary theory, if the integrand in $\langle\psi_n|\mu_\alpha|\psi_n\rangle$ contains the totally symmetric irreducible representation, the molecule in the quantum state ψ_n is able to support the α-component of an electric dipole moment. Because the operator μ is time-even, this gives the correct answer, but because $\mathbf{m}$ is time-odd, the same argument applied to $\langle\psi_n|m_\alpha|\psi_n\rangle$ can give the wrong answer because it only has nonzero expectation values in degenerate states.

The usual selection rules for transition matrix elements between states of *different* levels are unchanged whatever the behavior under time reversal of the operators and wave functions, but for matrix elements between component states of the *same* degenerate level, the group-theoretical background to the selection rules must be modified. From the methods of the previous section,[2,5,8]

$$\langle T\psi_j|V|\psi_k\rangle = \epsilon\lambda\langle T\psi_k|V|\psi_j\rangle \qquad (7)$$

where ϵ, the eigenvalue of T^2, equals $+1$ or -1, depending on whether there are an even or odd number of electrons, and λ equals $+1$ or -1, depending on whether the operator V is time-even or time-odd. Hence, depending on whether $\epsilon\lambda$ is positive or negative, $\langle T\psi_j|V|\psi_k\rangle$, and therefore also $\langle\psi_j|V|\psi_k\rangle$,[5] belong to the representation $[\Gamma^2]\times\Gamma_V$ or $\{\Gamma^2\}\times\Gamma_V$, the square and curly brackets denoting the symmetrized and antisymmetrized parts of the direct product, respectively. In the odd-electron case, the representation refers to the appropriate double group.

Molecules in Electric and Magnetic Fields

Electric and magnetic properties of molecules are characterized by tensors which relate applied fields to the multipole moments they induce. For the time-dependent electric and magnetic components of a radiation field with angular frequency ω, the linearly induced time-dependent electric and magnetic dipole moment vectors and traceless electric quadrupole moment tensor Θ may be written, in Cartesian tensor notation,[8,9]

$$\mu_\alpha = \alpha_{\alpha\beta}E_\beta + \frac{1}{\omega}\alpha'_{\alpha\beta}\dot{E}_\beta + G_{\alpha\beta}B_\beta + \frac{1}{\omega}G'_{\alpha\beta}\dot{B}_\beta + \frac{1}{3}A_{\alpha\beta\gamma}\nabla_\beta E_\gamma +$$
$$\frac{1}{3\omega}A'_{\alpha\beta\gamma}\nabla_\beta\dot{E}_\gamma + \dots \quad (8a)$$

$$m_\alpha = G_{\beta\alpha}E_\beta - \frac{1}{\omega}G'_{\beta\alpha}\dot{E}_\beta + \dots \qquad (8b)$$

$$\Theta_{\alpha\beta} = A_{\gamma\alpha\beta}E_\gamma - \frac{1}{\omega}A'_{\gamma\alpha\beta}\dot{E}_\gamma + \dots \qquad (8c)$$

where $\dot{E}_\alpha = \partial E_\alpha/\partial t$, etc. Perturbation theory gives the following quantum-mechanical expressions for the dynamic molecular property tensors for a molecule in the

nth quantum state at transparent wavelengths:

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}Re(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) = \alpha_{\beta\alpha} \quad (9a)$$

$$\alpha'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}Im(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) = -\alpha'_{\beta\alpha} \quad (9b)$$

$$G_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}Re(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle) \quad (9c)$$

$$G'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}Im(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle) \quad (9d)$$

$$A_{\alpha\beta\gamma} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}Re(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle) \quad (9e)$$

$$A'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}Im(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle) \quad (9f)$$

where $\omega_{jn} = \omega_j - \omega_n$.

Since both sides of (8a)−(8c) must behave the same under time reversal, it follows that $\alpha_{\alpha\beta}$, $G'_{\alpha\beta}$, and $A_{\alpha\beta\gamma}$ are time-even and $\alpha'_{\alpha\beta}$, $G_{\alpha\beta}$, and $A'_{\alpha\beta\gamma}$ are time-odd.[8,10] The symmetric polarizability $\alpha_{\alpha\beta}$ makes the major contribution to phenomena such as light scattering, refraction, and intermolecular dispersion forces; the antisymmetric polarizability $\alpha'_{\alpha\beta}$ generates antisymmetric light scattering, spin-dependent dispersion forces, and, when activated by a magnetic field, magneto-optical phenomena such as the Faraday effect; $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ generate natural optical rotation in chiral samples (the latter only in oriented media) together with other chiroptical phenomena; and $G_{\alpha\beta}$ and $A'_{\alpha\beta\gamma}$ give rise to magneto-chiral phenomena.[11,12]

To accommodate Raman processes, as well as the properties of molecules in degenerate states, these property tensors must be generalized to corresponding *transition* tensors involving different initial and final molecular states $|n\rangle$ and $|m\rangle$. These are best written in complex form. For scattering at transparent wavelengths, the complex transition polarizability is[8,13]

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle}{\omega_{jn} - \omega} + \frac{\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm} + \omega}\right]$$
$$(10)$$

where a tilde denotes a complex quantity. The complex "diagonal" transition polarizability between the same initial and final states, giving the dipole $\tilde{\mu}_\alpha$ induced by the field $\tilde{E}_\beta = E_\beta^{(0)}\exp(-i\omega t)$, is then related to the real and imaginary polarizabilities (9a) and (9b) through

$$(\tilde{\alpha}_{\alpha\beta})_{nn} \equiv \tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} - i\alpha'_{\alpha\beta} \qquad (11)$$

Analogous expressions can be written for the transition optical activity tensors $(\tilde{G}_{\alpha\beta})_{mn}$ and $(\tilde{A}_{\alpha\beta\gamma})_{mn}$.

To apply time reversal arguments to transition tensors, it is necessary to introduce complex polarizability and optical activity operators with well-defined behavior under time reversal. We use the effective polarizability operator[8,14]

$$\hat{\alpha}_{\alpha\beta} = \hat{\alpha}^+_{\alpha\beta} + \hat{\alpha}^-_{\alpha\beta} \tag{12a}$$

$$\hat{\alpha}^+_{\alpha\beta} = \frac{1}{2}(\mu_\alpha O^+ \mu_\beta + \mu_\beta O^+ \mu_\alpha) = \hat{\alpha}^+_{\beta\alpha} \tag{12b}$$

$$\hat{\alpha}^-_{\alpha\beta} = -\frac{1}{2}(\mu_\alpha O^- \mu_\beta - \mu_\beta O^- \mu_\alpha) = -\hat{\alpha}^-_{\beta\alpha} \tag{12c}$$

where

$$O^\pm = \left(\frac{1}{H - \bar{W} + \hbar\omega} \pm \frac{1}{H - \bar{W} - \hbar\omega}\right) \tag{12d}$$

$\bar{W}$ is the mean of the energies W_n and W_m of the initial and final states. By summing over a complete set of states $|j\rangle\langle j|$ inserted after $O^\pm$ and using the approximation $\omega_{jn} \approx \omega_{jm}$, it is easily verified that $\langle m|\hat{\alpha}_{\alpha\beta}|n\rangle$ generates the complex transition polarizability (10). Effective optical activity operators $\hat{G}_{\alpha\beta}$ and $\hat{A}_{\alpha\beta\gamma}$ can also be defined with μ_β in (12) replaced by m_β and $\Theta_{\beta\gamma}$, respectively, but without the symmetric and antisymmetric behavior of $\hat{\alpha}^+_{\alpha\beta}$ and $\hat{\alpha}^-_{\alpha\beta}$ under permutation of the tensor subscripts.[8] These operators have the following characteristics: $\hat{\alpha}^+_{\alpha\beta}$ and $\hat{A}^+_{\alpha\beta\gamma}$ are time-even and Hermitian, $\hat{\alpha}^-_{\alpha\beta}$ and $\hat{A}^-_{\alpha\beta\gamma}$ are time-odd and anti-Hermitian, $\hat{G}^+_{\alpha\beta}$ is time-odd and Hermitian, and $\hat{G}^-_{\alpha\beta}$ is time-even and anti-Hermitian. Using

$$\langle T\psi|A(\pm)|T\varphi\rangle = \pm\langle\varphi|A(\pm)|\psi\rangle \tag{13}$$

which follows from (2) and (5), we obtain the following properties of the associated transition tensors:[8,14]

$$\langle m|\hat{\alpha}_{\alpha\beta}|n\rangle = \langle Tn|\hat{\alpha}_{\beta\alpha}|Tm\rangle = \langle Tm|\hat{\alpha}_{\alpha\beta}|Tn\rangle^* \tag{14a}$$

$$\langle m|\hat{G}_{\alpha\beta}|n\rangle = -\langle Tm|\hat{G}_{\alpha\beta}|Tn\rangle^* \tag{14b}$$

$$\langle m|\hat{A}_{\alpha\beta\gamma}|n\rangle = \langle Tm|\hat{A}_{\alpha\beta\gamma}|Tn\rangle^* \tag{14c}$$

Despite the approximations used here to simplify their derivation, (14a)−(14c) are valid for all Raman processes, transparent and resonant.[15]

As for the permanent magnetic dipole moment, spatial symmetry arguments alone can lead to erroneous conclusions about time-odd property tensors. For example, in a molecule with C_{4h} symmetry, the combination $(xy - yx)$ of translations (and the component R_z of rotations) transforms as the totally symmetric representation A_g, but because $\hat{\alpha}^-_{\alpha\beta}$, the antisymmetric part of the polarizability operator, is time-odd, it would be wrong to conclude that a C_{4h} molecule in its ground state can support the xy component of the antisymmetric polarizability. Further considerations involving the selection rule (7) are required.[8]

Applications to Molecular Properties

Antisymmetric Light Scattering. Antisymmetric tensors in Rayleigh and Raman scattering were first considered by Placzek.[13] The main characteristic is "anomalous polarization", corresponding to a value for the depolarization ratio greater than the maximum possible value of 3/4 for conventional anisotropic (symmetric) scattering in incident light linearly polarized perpendicular to the scattering plane. Pure antisymmetric scattering generates an infinite depolarization ratio.

A two-fold Kramers-degenerate level with component states e and e', such as the electron spin states α and β, provides a source of antisymmetric tensors in atoms and molecules. Using (4) for the effect of the time reversal operator on e and e', the first equality in (14a) reveals that the "spin−flip" transition polarizability $\langle e|\hat{\alpha}_{\alpha\beta}|e'\rangle$ is purely antisymmetric, and the second equality shows that the "diagonal" transition polarizabilities $\langle e|\hat{\alpha}_{\alpha\beta}|e\rangle$ and $\langle e'|\hat{\alpha}_{\alpha\beta}|e'\rangle$ can have real symmetric and imaginary antisymmetric parts. Antisymmetric scattering associated with spin degeneracy has been observed in resonance Raman scattering from dilute solutions of odd-electron transition metal complexes[16] and in resonance Rayleigh scattering from atomic Na vapor.[17]

The symmetry aspects of general vibrational Raman transitions are analyzed using the generalized matrix element selection rule (7) which combines time reversal and spatial symmetry arguments.[8,18] Thus, if Γ_e is the irreducible representation spanned by the degenerate electronic states, Γ_v that spanned by the normal vibrational coordinate, and Γ_a that spanned by an antisymmetric tensor (or axial vector) component, then because $\hat{\alpha}^-_{\alpha\beta}$ is time-odd, for *even*-electron systems antisymmetric scattering in a fundamental vibrational Raman transition is possible if $\{\Gamma_e^2\} \times \Gamma_a$ contains Γ_v, and for *odd*-electron systems if $[\Gamma_e^2] \times \Gamma_a$ contains Γ_v.

Degeneracy in the initial, final, or intermediate states is not required for antisymmetric Raman scattering in a fundamental mode of vibration that transforms according to an antisymmetric irreducible representation.[8] This is encountered in antisymmetric resonance Raman scattering in B_{1g} modes of annulenes of D_{2h} symmetry,[19] for which no degeneracies exist, and in A_{2g} modes of porphyrins of D_{4h} symmetry,[20] where the degeneracy present in the intermediate states is not essential.[8] For Raman scattering at transparent wavelengths, the Placzek approximation[8,13] may be invoked in which the antisymmetric polarizability $\alpha'_{\alpha\beta}$ in the ground electronic state now acts as an effective operator bringing about vibrational transitions. However, being a time-odd property, $\alpha'_{\alpha\beta}$ must be expanded in the conjugate momentum of the normal vibrational coordinate,[14,21] rather than the coordinate itself, similar to the development of the magnetic dipole operator in VCD theory (vide infra). Such antisymmetric scattering is expected to be very weak. An analogous mechanism may generate the antisymmetric third-rank hyperpolarizability tensor responsible for resonant sum-frequency vibrational optical activity in chiral liquids.[22]

Raman EPR. Antisymmetric resonance Raman scattering associated with spin−flip transitions generated by tensors such as $\langle e|\hat{\alpha}_{\alpha\beta}|e'\rangle$ is exploited in a novel technique
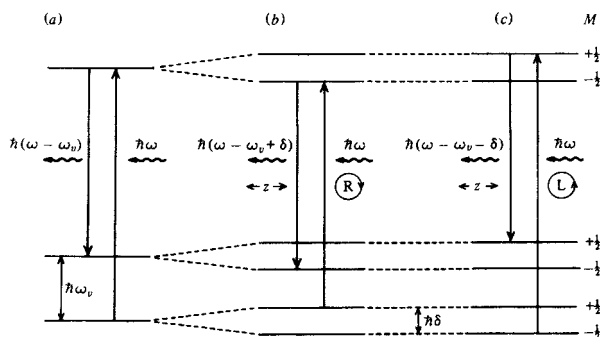
FIGURE 1. Spin—flip Raman scattering pathways involving a vibrational transition associated with a two-fold spin degeneracy in the electronic level. Each scattering pathway can be envisaged as the longitudinal and transverse Zeeman effects back-to-back: the incident circularly polarized photon generates a $\Delta M = \pm 1$ change in the molecule, and the 90°-scattered z-polarized photon a $\Delta M = 0$ change. Two depolarized Raman lines shifted in frequency by the Zeeman splitting δ on either side of the Stokes vibrational Raman line at $(\omega - \omega_v)$ are thereby generated: right circularly polarized light generates the line shifted to frequency $(\omega - \omega_v + \delta)$, and left circularly polarized light generates that shifted to frequency $(\omega - \omega_v - \delta)$.

called Raman EPR (electron paramagnetic resonance), which is a manifestation of magnetic Raman optical activity (ROA).[8,23] Figure 1a shows a conventional vibrational Stokes resonance Raman process, while parts b and c show the polarization characteristics of the two distinct spin—flip Raman processes for scattering at 90° if a two-fold spin degeneracy in the initial and final levels is lifted by a magnetic field parallel to a circularly polarized light beam incident along z.

Even if the resolution is insufficient to detect these magnetic-field-induced Raman shifts directly, they can be detected by measuring a Raman difference spectrum in right and left circularly polarized incident light. A residual positive—negative magnetic ROA couplet is generated from incomplete cancellation of the two partially overlapping bands. Raman EPR was first observed in resonance Raman scattering from dilute solutions of odd-electron transition metal complexes such as $IrCl_6^{2-}$.[24] Figure 2 shows the Raman EPR spectrum of this species remeasured with more modern equipment. Raman EPR was subsequently observed in dilute magnetic semiconductors in which the Zeeman splitting can be sufficiently large that the two spin—flip transitions are observed directly at low temperature.[25] Spin—flip transitions are not a prerequisite for Raman EPR: for example, $\Delta M = \pm 1$ transitions between Zeeman-shifted levels in even-electron systems such as uranocene show the effect.[23]

Raman EPR provides information about the magnetic structure of ground and low-lying excited states, including the sign of the g-factor, and how the magnetic structure changes when the molecule is in an excited non-totally symmetric vibrational state. Interestingly, the absolute sign of the Raman EPR couplet associated with the A_{1g} vibrational Raman band in Figure 2 reveals that the ground-state g-factor of $IrCl_6^{2-}$ is *negative*, as predicted.[5] The opposite signs for the Raman EPR couplets associated
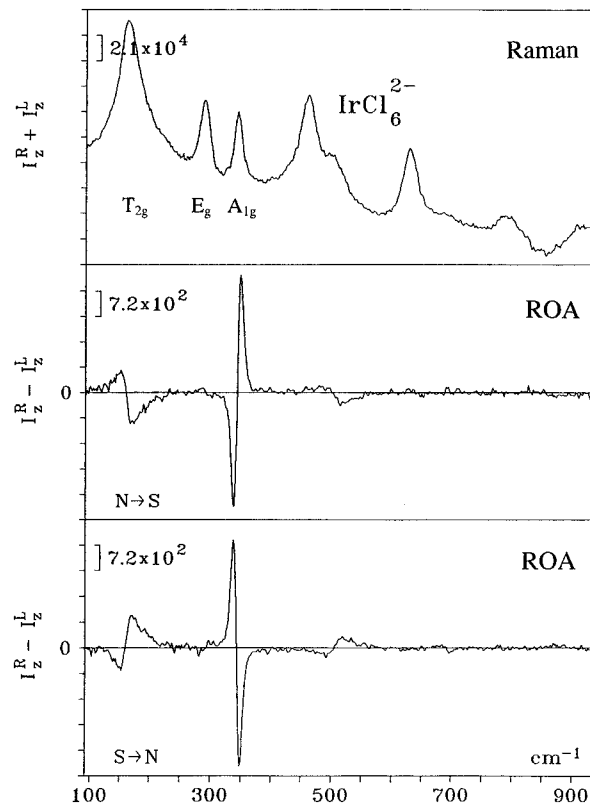

FIGURE 2. Depolarized resonance Raman and associated Raman EPR (magnetic ROA) spectra of $IrCl_6^{2-}$ in dilute aqueous solution for positive (N $\rightarrow$ S) and negative (S $\rightarrow$ N) magnetic fields using 488 nm excitation.

with the T_{2g} and A_{1g} bands in Figure 2 indicate that changes in magnetic structure can be dramatic for degenerate vibrations.

Optical Activity and Degeneracy. Time reversal arguments can help unravel the distinct optical activity phenomena shown by chiral and achiral molecules in degenerate states. Consider natural optical rotation in an odd-electron chiral molecule. In isotropic systems such as a solution, this is linear in $G'_{\alpha\alpha}$, the trace of the imaginary part of the electric dipole—magnetic dipole tensor.[8,9] For a two-fold Kramers degeneracy, we deduce from (14b) that[8]

$$(G'_{\alpha\alpha})_{ee} = (G'_{\alpha\alpha})_{e'e'} \tag{15a}$$

$$(G'_{\alpha\alpha})_{ee'} = - (G'_{\alpha\alpha})_{e'e} \tag{15b}$$

Equation 15a shows that the natural optical rotations in the two states e and e' are equal in sign and magnitude, so the two contributions reinforce. This contrasts with magnetic optical rotation (the Faraday effect), which depends on components of $\alpha'_{\alpha\beta}$.[8,9,26] From (14a) we deduce that

$$(\alpha'_{\alpha\beta})_{ee} = - (\alpha'_{\alpha\beta})_{e'e'} \tag{15c}$$

$$(\alpha'_{\alpha\beta})_{ee'} = (\alpha'_{\alpha\beta})_{e'e} \tag{15d}$$

Equation 15c shows that, for equal populations of e and e' and light propagating along z, the optical rotation

contributions $(\alpha'_{xy})_{ee}$ and $(\alpha'_{xy})_{e'e'}$ cancel, hence the necessity for a magnetic field along z to lift the degeneracy and so generate a residual effect. On the other hand, (15b) and (15d) show that the associated spin−flip processes tend to cancel in the natural case but reinforce in the magnetic, but these do not contribute to optical rotation. Since an electric field does not lift the degeneracy, there is no simple electric analogue of the Faraday effect (which would violate P and T[7,8]). However, since they break P and T, certain coherent complex superposition states of chiral molecules should support electric field optical activity.[27] Furthermore, an oscillating electric field $\dot{E}_z$, which is odd under T, can induce optical rotation.[28]

Faraday-type rotations can be generated by other time-odd influences, such as rapid rotation of the sample about an axis parallel to the propagation direction of the light beam.[29]

Magneto-Chiral Phenomena. The interplay of chirality and magnetism can give rise to new phenomena, such as magneto-chiral birefringence and dichroism, which are small differences in the refractive indices and absorption coefficients, respectively, of chiral molecules in a static magnetic field parallel and antiparallel to the propagation direction of an *unpolarized* light beam.[11,12] Both have been observed recently.[30,31] They originate in components of $G_{\alpha\beta}$, the real part of the electric dipole−magnetic dipole tensor, and $A'_{\alpha\beta\gamma}$, the imaginary part of the electric dipole−electric quadrupole tensor.[12] For the case of a two-fold Kramer's degeneracy, we deduce from (14b) that

$$(G_{\alpha\beta})_{ee} = - (G_{\alpha\beta})_{e'e'} \tag{15e}$$

$$(G_{\alpha\beta})_{ee'} = (G_{\alpha\beta})_{e'e} \tag{15f}$$

Equation 15e shows why a magnetic field is necessary: the two Kramer's conjugate states generate equal and opposite effects, so their degeneracy must be lifted. This parallel behavior of the tensors $G_{\alpha\beta}$ and $\alpha'_{\alpha\beta}$ follows from the fact that both are generated by time-odd operators ($\hat{G}^+_{\alpha\beta}$ and $\hat{\alpha}^-_{\alpha\beta}$). Similar results obtain for $A'_{\alpha\beta\gamma}$.

Optical NMR and ESR. The antisymmetric polarizability $\alpha'_{\alpha\beta}$ also features in theories of the possible influence of a circularly polarized light beam on magnetic resonance spectra.[32,33] In the NMR case, the circularly polarized light wave induces electronic angular momentum in the atomic electrons which generates a bulk magnetic moment proportional to the intensity, corresponding to the inverse Faraday effect, parallel to the propagation direction, together with a local magnetic field at all nuclei. For a right (+) or left (−) circularly polarized light beam propagating along z, the magnetic field $B_z^{(I)}$ induced at nucleus I in a freely tumbling molecule is[33]

$$B_z^{(I)} = \mp (E^{(0)2}/12)\epsilon_{\alpha\beta\gamma}\alpha'_{\alpha\beta\gamma}(m^I) \tag{16}$$

where $E^{(0)}$ is the amplitude of the electric vector of the light wave and $\alpha'_{\alpha\beta\gamma}(m^{(I)}) = \partial\alpha'_{\alpha\beta}/\partial m_\gamma^{(I)}$, with $m_\gamma^{(I)}$ the magnetic moment of nucleus I. Like the chemical shift, the shifts caused by the circularly polarized light beam are strongly dependent on the local electronic structure.

Unfortunately, they are too small to be of analytical use in chemistry with laser beams of reasonable intensity.[34] Resonant laser frequencies would greatly enhance the effects.

The ESR case is more straightforward. For an alkali metal atom, the change in ESR frequency for the transition $\Delta S_z = 1$ in right (+) or left (−) circularly polarized light is[35]

$$\Delta\nu_\pm = \pm (E^{(0)2}/h)\alpha'_{xy} \tag{17}$$

where α'_{xy} is the antisymmetric polarizability of the α spin state. These shifts should be observable at near-resonant optical frequencies and would provide a direct measure of the antisymmetric polarizability.

Spin-Dependent Intermolecular Forces. The antisymmetric polarizability $\alpha'_{\alpha\beta}$ can make small contributions to intermolecular dispersion forces. The dispersion energy obtained from second-order perturbation theory can be cast in the form[9]

$$W = - \left(\frac{1}{4\pi\epsilon_0}\right)^2\left(\frac{\hbar}{2\pi}\right)T_{\alpha\beta}T_{\gamma\delta}\int_0^\infty [\alpha_{1\alpha\gamma}(iu)\alpha_{2\beta\delta}(iu) + \\ \alpha'_{1\alpha\gamma}(iu)\alpha'_{2\beta\delta}(iu)]\,du \tag{18}$$

where $\alpha_{\alpha\beta}(iu)$ and $\alpha'_{\alpha\beta}(iu)$ are the dynamic polarizabilities (9a) and (9b) at the imaginary frequency iu, and $T_{\alpha\beta} = (3R_\alpha R_\beta - R^2\delta_{\alpha\beta})R^{-5}$, where $\boldsymbol{R} = \boldsymbol{R}_2 - \boldsymbol{R}_1$ is the vector from the origin on molecule 1 to that on 2. The first term of (18) is nonzero for any pair of molecules and generates the London equation. The second term is only nonzero for pairs of molecules in degenerate states and has been applied to atomic Na.[36]

An additional dispersion interaction between pairs of chiral molecules involving the product of the optical activity tensors $G'_{\alpha\beta}$ has opposite signs for pairs with the same absolute configuration and pairs with opposite absolute configurations.[37] There are also spin-dependent contributions between pairs of odd-electron chiral molecules involving the product of the tensors $G_{\alpha\beta}$ which have characteristics similar to those of the interactions involving $\alpha'_{\alpha\beta}$, with additional features due to the fact that, unlike $\alpha'_{\alpha\beta}$ (and also $G'_{\alpha\beta}$), $G_{\alpha\beta}$ has a static limit.[37]

Velocity-Dependent Property Surfaces and Vibrational Circular Dichroism. Vibrational circular dichroism (VCD) is the differential absorption of left and right circularly polarized infrared radiation associated with the vibrational frequencies of a chiral molecule.[38−40] For an isotropic sample, the differential absorption associated with a molecular transition from state n to state j is proportional to the rotational strength

$$R_{jn} = Im(\langle n|\mu_\alpha|j\rangle \langle j|m_\alpha|n\rangle) \tag{19}$$

which contains the scalar product of electric and magnetic dipole transition moments. The magnetic dipole vibrational transition moment vanishes when attempts are made to evaluate it using the same formalism as for electric dipole transition moments within the Born−Oppenheimer approximation. Thus, the electric dipole transition moment between vibrational states ψ_v and $\psi_{v'}$

would be written $\langle v'|\mu_\alpha(Q)|v\rangle$, where $\mu_\alpha(Q)$ is an effective operator associated with the permanent electric dipole moment of the molecule in the ground electronic state, being parametrically dependent on the normal vibrational coordinate Q. Subsequent Taylor expansion of $\mu_\alpha(Q)$ about the equilibrium geometry provides terms such as $(\partial\mu_\alpha/\partial Q)_0 Q$, which can bring about vibrational transitions. However, the corresponding magnetic dipole $m_\alpha(Q)$ vanishes for closed-shell molecules because it is the expectation value of a time-odd operator and so is zero at all fixed nuclear configurations. The problem is resolved by realizing that m_α is a function of the conjugate momentum $\dot{Q}$ as well as of Q itself; so, by developing the parametric dependence on $\dot{Q}$, terms such as $(\partial m_\alpha/\partial \dot{Q})_0 \dot{Q}$ emerge which bring about the vibrational transition.[41,42]

We can understand this within the context of time reversal. Essentially, $(\partial m_\alpha/\partial Q)_0$ and $(\partial m_\alpha/\partial \dot{Q})_0$ are molecular electronic properties, the first being time-odd and the second time-even, so if the molecular electronic state is nondegenerate, it can support only the latter. The time-odd aspect of the original magnetic dipole operator is now embodied in the operator $\dot{Q}$, which can bring about the $\Delta v = \pm 1$ transition between nondegenerate vibrational states, even though $\dot{Q}$ itself does not have expectation values.

By introducing a vibronic perturbation of the electronic part ψ_e of the Born−Oppenheimer wave function, the electronic contribution to the magnetic dipole transition moment may be transformed to[42,43]

$$\langle ev'|m_\alpha|ev\rangle = -2\hbar \sum_p \langle v'|\ \dot{Q}_p|v\rangle Im[\langle (\partial\psi_e/\partial B_\alpha)_0|(\partial\psi_e/\partial Q_p)_0\rangle] \quad (20)$$

The required derivatives may be computed routinely at SCF and higher levels with density functional theory (B_α is a "fake" static magnetic field). Testimony to the power of this formalism is the close agreement between observed and calculated VCD spectra.[40]

True and False Chirality. There is no disagreement when the term "chiral" is applied to a static handed object displaying distinguishable enantiomers under space inversion P (or mirror reflection). But when the term is applied to less tangible enantiomorphous systems in which motion is an essential ingredient, time reversal arguments are required to clarify the concept.

The hallmark of a chiral system is that it can exhibit time-even pseudoscalar (odd parity) observables, such as natural optical rotation,[8] which are only supported by quantum states with mixed parity but which are invariant under time reversal. This leads to the following definition:[44]

True chirality is exhibited by systems existing in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation.

True chirality can therefore be thought of as a time-invariant enantiomorphism, meaning that time reversal cannot undo the effect of space inversion. A simple example is the magneto-chiral influence comprising a static magnetic field $\boldsymbol{B}$ collinear with the propagation vector $\boldsymbol{k}$ of an unpolarized light beam. Since $\boldsymbol{B}$ is a time-odd axial vector and $\boldsymbol{k}$ is a time-odd polar vector, the distinct enantiomeric parallel and antiparallel arrangements are interconverted by P but not by T.[44,45] An example of a time-*non*-invariant enantiomorphism, and therefore of false chirality, is a collinear arrangement of static uniform electric and magnetic fields: since $\boldsymbol{E}$ is a time-even polar vector and $\boldsymbol{B}$ is a time-odd axial vector, the distinct enantiomeric parallel and antiparallel arrangements are again interconverted by P, but now they are also interconverted by T.[44,45] A similar type of false chirality is shown by a stationary cone spinning about its symmetry axis, but a cone translating along the axis of spin becomes truly chiral. Indeed, the combination of a rotation with a linear motion is a common source of true chirality, as in a circularly polarized photon or a translating spin-polarized electron. A molecular example of false chirality is a complex coherent chiral superposition state,[27] since this breaks P and T simultaneously but is PT-invariant overall.

The distinction between true and false chirality has proved fruitful in several areas, including chiral effects in electron scattering by molecules[46] and the characterization of external fields and forces used in attempts to induce absolute enantioselection.[44,45] For example, since the magneto-chiral influence is truly chiral, it is able, in principle, to induce enantioselection in all circumstances, including a reaction allowed to reach thermodynamic equilibrium. The use of a magneto-chiral influence to induce absolute enantioselection has recently been demonstrated experimentally.[47] Particularly interesting is the idea that a false chiral influence can induce a breakdown in microscopic reversibility in reaction and transport processes involving chiral molecules, with symmetry recovered by means of a new principle of *enantiomeric microscopic reversibility* based on overall PT invariance with P and T individually broken.[45,48] Although not yet observed in molecular processes, a breakdown in microscopic reversibility is observed in elementary particle processes associated with CP violation in decays of the neutral K-meson.[4] As in the particle case, the apparently contradictory kinetic and thermodynamic aspects of a breakdown in microscopic reversibility in certain chiral molecular processes are reconciled by invoking the unitarity of the scattering matrix (which corresponds to the transition probabilities from a given state to all possible final states summing to unity) together with PT invariance.[48] This is consistent with the fact, which deserves to be more widely known in chemistry, that Boltzmann's *H*-theorem and hence the second law of thermodynamics depends on unitarity, not microscopic reversibility as often used in textbook derivations, and so still hold even when microscopic reversibility breaks down.[49]

Due to parity violation in the electroweak force, a tiny energy difference exists between a chiral molecule and its mirror-image enantiomer. Strict degeneracy is recovered on going to the antiworld, for the CP enantiomer of a chiral molecule (i.e., the mirror-image molecule com-

posed of antiparticles) has identical energy to the original.[8,45] It is intriguing that this strict degeneracy survives even if *CP* itself is violated, provided *CPT* invariance is maintained,[50] which suggests that the force responsible for *CP* violation exhibits false chirality with respect to *CP* enantiomorphism. This insight exposes an analogy between *CP* violation, the most enigmatic of all physical phenomena discovered to date, and chemical catalysis since in both cases the kinetics, but not the thermodynamics, are affected.[45,50]

The Photon's Static Magnetic Field. Although time reversal with spatial symmetry arguments gives correct results when applied to atoms and molecules, it can lead to error when applied to elementary particles. An example is the proposal that a circularly polarized light beam or photon in free space carries a static magnetic field parallel or antiparallel to the propagation direction depending on the sense of circular polarization, thereby introducing the concept of a "light magnet" which can generate a new range of magneto-optical phenomena.[51] However, the idea is not supported by experiment.[34] This is not surprising for, although such a magnetic field is allowed by both time reversal and parity,[51] it is forbidden by charge conjugation and therefore does not exist.[52]

The photon is a relativistic object that is simultaneously its own antiparticle,[6] so its attributes must be analyzed using the full trinity of parity, time reversal, and charge conjugation symmetries. A consequence of the *CPT* theorem is that the electromagnetic properties of particles and antiparticles are equal in magnitude but opposite in sign,[6] so the nonexistence of the photon's magnetic field is a consequence of the identity of the photon with its antiparticle. The only reason for seeking it experimentally would be as a test of the limits of *CPT* invariance.

Concluding Remarks

We hope that this Account will encourage a greater awareness of the value in chemistry of time reversal arguments, which are expected to become increasingly important as new aspects of molecular behavior are explored and applied to problems in science and technology. The interplay of chirality and magnetism seems to be a particularly fruitful area for further study, especially since the first three-dimensional chiral molecular magnets have been reported recently.[53] We invite the reader to think of a system that is able to support a time-odd pseudoscalar, which is the symmetry characteristic of the elusive magnetic monopole![4]

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