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The Inertial Contribution to Vibrational Optical Activity in Methyl Torsion Modes

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Abstract: Simple expressions are obtained for the Raman and infrared optical activity generated by the oscillations in space of a chiral molecular frame that accompany a methyl torsion vibration in the molecule. Substitution of methyl groups at different points permits the structure of chiral molecules to be probed about different torsion axes. The theory is most straightforward when the torsion axis is a principal axis of inertia of the molecule, and is applied to oscillations of a bridged biphenyl about its twofold proper rotation axis.

Vibrational optical activity spectra can now be obtained using two complementary techniques: infrared circular dichroism (CD), a measure of the small difference in the absorption of left and right circularly polarized infrared radiation;[2,3] and the Raman circular intensity difference (CID), which results from a small difference in the intensity of vibrational Raman scattering in right and left circularly polarized incident visible light.[4-13] Vibrational optical activity is expected to be a useful new means of determining stereochemistry (conformation and absolute configuration) in chiral molecules since, unlike electronic optical rotation and circular dichroism, which only provide stereochemical information about chromophoric groups and their immediate intramolecular environments, every part of a molecule can contribute to a vibrational optical activity spectrum. On account of technical difficulties, related to the fact that the dynamical nature of optical activity reduces its magnitude at low frequencies, the spectral region below about 1600 cm^{-1} is inaccessible to infrared CD at present; most studies have involved carbon-hydrogen stretching modes. On the other hand, the complete vibrational spectrum is accessible to the Raman CID technique, with the region from about 80 to 2000 cm^{-1} (containing, in particular, deformations and torsions) usually showing the largest effects.

It is important to understand how vibrational optical activity is generated in typical structural units in chiral molecules, and to develop simple procedures for extracting stereochemical information from the signs and magnitudes. The methyl group could be valuable in this respect since chiral molecules often contain methyl groups showing distinctive Raman CIDs in some of their characteristic modes of vibration.[5,7,10] The torsion is perhaps the simplest of the characteristic vibrational modes of the methyl group; it provides a novel way of probing the stereochemistry of the rest of the molecule.[7] There seems to be little possibility of observing in the near future vibrational optical activity in methyl torsion modes using infrared CD because the corresponding frequencies occur in the far infrared (from about 100 to 300 cm^{-1}).

The origin of infrared and Raman intensity and optical activity in a methyl torsion vibration can be understood by considering the simplest situation in which the threefold proper rotation axis of the methyl group is also a principal inertial axis of the molecule. Since first- and second-rank tensorial properties of an object with a threefold or higher proper rotation axis are unaffected by rotations about that axis, the electric dipole moment, polarizability, and optical activity of the methyl group, referred to the principal internal axis system, do not change in the course of the torsion vibration. The origin of any infrared or Raman intensity or optical activity must therefore be sought in the rest of the molecule. Two mecha-

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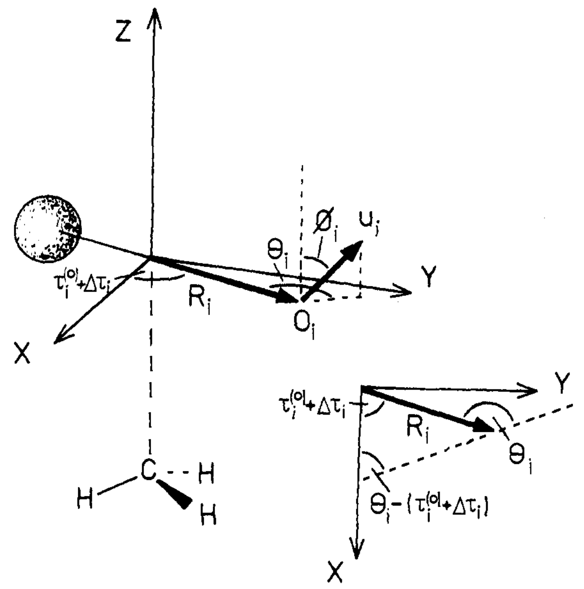

Figure 1. The geometry of the methyl torsion model based on a hindered single-bladed propellor. X, Y, Z are the principal internal axes and $\mathbf{u}_i$ is the axis of the polarizability of the group i located at $\mathbf{R}_i$ in the XY plane. The angles θ_i and ϕ_i are such that $u_{iX} = -\sin\phi_i \cos(\theta_i - \tau_i)$, $u_{iY} = \sin\phi_i \sin(\theta_i - \tau_i)$, and $u_{iZ} = \cos\phi_i$. On reversing $\mathbf{u}_i$, $\phi_i \rightarrow \pi - \phi_i$ and $\theta_i \rightarrow \theta_i + \pi$; on inverting the molecule, $\phi_i \rightarrow \phi_i$ and $\theta_i \rightarrow 2\pi - \theta_i$.

nisms can be distinguished: a coupling of the local methyl torsion mode with other low-frequency modes of the rest of the molecule so that the true normal coordinate embraces a structural unit of appropriate symmetry containing part of the frame together with the methyl group; and an inertial mechanism in which the interaction of the radiation field with the rest of the molecule, via the electric dipole moment vector, polarizability tensor, or optical activity tensor intrinsic to the rest of the molecule, changes as the frame twists in space to compensate the twist of the methyl group, so that the torsion vibration generates zero overall angular momentum. This compensating motion of the rest of the molecule may be unfamiliar to those working with large organic molecules because the methyl group is usually envisaged as twisting against a massive stationary frame. It is, however, familiar in treatments of the microwave and far-infrared spectroscopy of small molecules. For example, the following statement appears in a recent article on torsional frequencies:[14] "Thus, for CH_3CCl_3, it is clear that torsion about the C-C bond leaves the dipole moment unchanged, so that the motion is infrared inactive, whereas torsion of the methyl group in ethyl chloride causes a corresponding oscillation in space of the dipole moment which is fixed in the CH_2Cl group, such that the overall angular momentum is zero, so that the motion is infrared active."

In this article we develop in detail the theory of the inertial contribution to Raman and infrared optical activity for the special case in which methyl torsion vibrations induce oscillations in space of a chiral molecular frame about a principal axis of inertia. The generalization to completely asymmetric molecules is outlined at the end. The treatment falls within the "group dipole" and "group polarizability" theories of infrared and Raman intensities in which the variations of the electric dipole moment and polarizability of the molecule with a normal vibrational coordinate, evaluated at the equilibrium nuclear configuration, are calculated via the variations of intrinsic bond dipoles and polarizabilities with internal vibrational coordinates.[15] Since the normal coordinate for a "pure" methyl torsion involves just one internal coordinate, the development is particularly clear and leads to simple expressions for the infrared and Raman intensity and optical activity in terms of the molecular geometry. Despite the small amplitude of the oscillation in space of the relatively massive frame, very large effects can be generated.

A Single-Bladed Hindered Propellor

Figure 1 shows a model in which an anisotropic, intrinsically achiral, group i with a principal axis of polarizability along the unit vector $\mathbf{u}_i$ is oriented relative to the threefold axis of the methyl group such that the anisotropic group and the threefold axis constitute a chiral structure. Group i is balanced dynamically by a spherical group so that, assuming the existence of a hindering potential, torsional oscillations are executed about the threefold axis of the methyl group. If group i were a benzene ring with $\mathbf{u}_i$ along the sixfold proper rotation axis (neglecting any ring substituents), the structure would have the appearance of a single-bladed propellor.

We first separate the kinetic energy originating in rotation of the whole molecule about the torsion axis from that originating in the internal torsion mode of vibration. If χ_i and χ_{Me} are angles specifying the instantaneous orientations of the two parts of the molecule relative to some nonrotating axis perpendicular to the torsion axis, the total kinetic energy due to rotation about the torsion axis is

$$T = {}^1\!/_2 I_i \dot{\chi}_i{}^2 + {}^1\!/_2 I_{Me} \dot{\chi}_{Me}{}^2 \tag{1}$$

where I_i and I_{Me} are the moments of inertia of the two groups about the torsion axis (I_i refers to group i together with its balancing sphere). If new variables

$$\chi = (I_i \chi_i + I_{Me} \chi_{Me})/I \tag{2a}$$

and

$$\tau = \chi_i - \chi_{Me} \tag{2b}$$

are defined, where $I = I_i + I_{Me}$, the kinetic energy (1) becomes[16]

$$T = {}^1\!/_2 I \dot{\chi}^2 + {}^1\!/_2 \frac{I_i I_{Me}}{I} \dot{\tau}^2 \tag{3}$$

The first term gives the kinetic energy originating in rotation of the complete molecule with the internal rotation frozen, and the second term gives that from the torsion vibration. Since $I\dot{\chi} = I_i \dot{\chi}_i + I_{Me} \dot{\chi}_{Me}$, all of the angular momentum about the torsion axis is associated with changes in the external coordinate χ; none is associated with changes in the internal torsion angle τ defining the relative orientation of the two groups. The Hamiltonian for rotation about the torsion axis is obtained by adding to (3) a potential energy corresponding to the barrier hindering free rotation. For the single-bladed propellor, this would be a symmetric function dominated by the term

$$V = {}^1\!/_2 V_3 (1 - \cos 3\tau) \tag{4}$$

describing three potential minima with intervening barriers of height V_3.

The displacement of the internal torsion angle away from its equilibrium value $\tau^{(0)}$ during the course of the torsion vibration is denoted by the internal coordinate $\Delta\tau$ so that $\tau = \tau^{(0)} + \Delta\tau$. Assuming that no other internal coordinates mix with $\Delta\tau$, the normal coordinate Q_t for the torsion vibration is simply $\Delta\tau$ times a constant. It is possible to write $\Delta\tau$ as the sum of displacements "intrinsic" to each of the two groups

$$\Delta\tau = \Delta\tau_i - \Delta\tau_{Me} \tag{5}$$

provided that the two displacements satisfy

$$I_i \Delta\tau_i = -I_{Me} \Delta\tau_{Me} \tag{6}$$

This last condition follows from the requirement that the contribution to the angular momentum of the molecule about the torsion axis from the torsion vibration be zero; that is

$$I_i\dot{\tau}_i = -I_{\mathrm{Me}}\dot{\tau}_{\mathrm{Me}} \tag{7}$$

where $\tau_i = \tau_i^{(0)} + \Delta\tau_i$ and $\tau_{\mathrm{Me}} = \tau_{\mathrm{Me}}^{(0)} + \Delta\tau_{\mathrm{Me}}$ specify the instantaneous orientations of the two groups relative to a "principal" internal axis, perpendicular to the torsion axis, that remains stationary during the torsion vibration. $\tau_i^{(0)}$ and $\tau_{\mathrm{Me}}^{(0)}$ are the corresponding equilibrium orientations. In Figure 1, this principal internal axis is the X axis.

Referring to Figure 1, the unit vector $\mathbf{u}_i$ along the axis of group i at some instant during the torsion vibration can be written in terms of the unit vectors $\boldsymbol{I}, \boldsymbol{J}, \boldsymbol{K}$ along the principal internal axes X, Y, Z:

$$\begin{aligned} u_{i\alpha} = {} & -I_\alpha \sin\phi_i \cos[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)] \\ & + J_\alpha \sin\phi_i \sin[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)] + K_\alpha \cos\phi_i \end{aligned} \tag{8}$$

Raman Optical Activity

An appropriate experimental quantity in Rayleigh and Raman optical activity is the dimensionless CID

$$\Delta = \frac{I_\alpha^{\mathrm{R}} - I_\alpha^{\mathrm{L}}}{I_\alpha^{\mathrm{R}} + I_\alpha^{\mathrm{L}}} \tag{9}$$

where I_α^{R} and I_α^{L} are the scattered intensities with α polarization in right and left circularly polarized incident light. The components of Δ for Rayleigh light scattered into the y direction from an incident beam in the z direction, polarized parallel (Δ_z) and perpendicular (Δ_x) to the scattering plane yz, are[17]

$$\Delta_z = \frac{4(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{2c(3\alpha_{\gamma\delta}\alpha_{\gamma\delta} - \alpha_{\gamma\gamma}\alpha_{\delta\delta})} \tag{10a}$$

$$\Delta_x = \frac{2(7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\gamma\delta}\alpha_{\gamma\delta} + \alpha_{\gamma\gamma}\alpha_{\delta\delta})} \tag{10b}$$

where ω is the angular frequency of the incident light, $\alpha_{\alpha\beta}$ is the polarizability tensor, and $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ are the electric dipole–magnetic dipole and electric dipole–electric quadrupole optical activity tensors. A repeated Greek suffix denotes a summation over the Cartesian components and $\epsilon_{\alpha\beta\gamma}$ is the third-rank unit antisymmetric tensor.

The same CID expressions apply to vibrational Raman scattering if the polarizability and optical activity tensors are replaced by transition tensors such as $\langle m_{\mathrm{v}}|\alpha_{\alpha\beta}|n_{\mathrm{v}}\rangle$ between initial and final vibrational states n_{v} and m_{v}. The polarizability and optical activity tensor "operators" are expanded as Taylor series in the normal vibrational coordinates Q_p about the equilibrium nuclear configuration, in accordance with Placzek's polarizability theory.[18] The transition polarizability, for example, becomes

$$\langle m_{\mathrm{v}}|\alpha_{\alpha\beta}|n_{\mathrm{v}}\rangle = (\alpha_{\alpha\beta})_{\mathrm{e}}\delta_{m_{\mathrm{v}}n_{\mathrm{v}}} + \sum_p \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_p}\right)_{\mathrm{e}} \langle m_{\mathrm{v}}|Q_p|n_{\mathrm{v}}\rangle + \ldots \tag{11}$$

where a subscript e indicates that the function inside the brackets is to be evaluated at the equilibrium nuclear configuration. The first term on the right of (11) describes Rayleigh scattering, and the second term describes Raman scattering associated with fundamental vibrational transitions ($m_{\mathrm{v}} = n_{\mathrm{v}} \pm 1$). The Raman intensity and optical activity in the fundamental transition associated with the normal vibrational coordinate Q_p are therefore determined by products such as

$$\langle p_0|\alpha_{\alpha\beta}|p_1\rangle\langle p_1|\alpha_{\alpha\beta}|p_0\rangle = \frac{\hbar}{2\omega_p}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_p}\right)_{\mathrm{e}}^{*}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_p}\right)_{\mathrm{e}} \tag{12a}$$

$$\langle p_0|\alpha_{\alpha\beta}|p_1\rangle\langle p_1|G'_{\alpha\beta}|p_0\rangle = \frac{\hbar}{2\omega_p}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_p}\right)_{\mathrm{e}}^{*}\left(\frac{\partial G'_{\alpha\beta}}{\partial Q_p}\right)_{\mathrm{e}} \tag{12b}$$

$$\langle p_0|\alpha_{\alpha\beta}|p_1\rangle\langle p_1|\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}|p_0\rangle = \frac{\hbar}{2\omega_p}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_p}\right)_{\mathrm{e}}^{*}\epsilon_{\alpha\gamma\delta}\left(\frac{\partial A_{\gamma\delta\beta}}{\partial Q_p}\right)_{\mathrm{e}} \tag{12c}$$

the factor $\hbar/2\omega_p$ being the value of $|\langle p_1|Q_p|p_0\rangle|^2$.

Consider first the Raman intensity. The polarizability tensor of the molecule is written as the sum of tensors intrinsic to the two groups,

$$\alpha_{\alpha\beta} = \alpha_{i\alpha\beta} + \alpha_{\mathrm{Me}\alpha\beta} \tag{13}$$

Since the normal coordinate for the torsion contains just $\Delta\tau$, we need only evaluate

$$\begin{aligned} \left(\frac{\partial\alpha_{\alpha\beta}}{\partial\Delta\tau}\right)_0 &= \left(\frac{\partial\alpha_{i\alpha\beta}}{\partial\Delta\tau_i}\frac{\partial\Delta\tau_i}{\partial\Delta\tau}\right)_0 + \left(\frac{\partial\alpha_{\mathrm{Me}\alpha\beta}}{\partial\Delta\tau_{\mathrm{Me}}}\frac{\partial\Delta\tau_{\mathrm{Me}}}{\partial\Delta\tau}\right)_0 \\ &= \frac{I_{\mathrm{Me}}}{I}\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial\Delta\tau_i}\right)_0 - \frac{I_i}{I}\left(\frac{\partial\alpha_{\mathrm{Me}\alpha\beta}}{\partial\Delta\tau_{\mathrm{Me}}}\right)_0 \end{aligned} \tag{14}$$

where we have used (5) and (6). The second term of (14) is zero because $(\partial\alpha_{\mathrm{Me}\alpha\beta}/\partial\Delta\tau_{\mathrm{Me}})_0 = 0$ on account of the threefold axis of the methyl group and the assumption that the torsion axis is a principal inertial axis.

If the axis of group i is a threefold or higher proper rotation axis, (14) can be given a tractable form because the polarizability tensor of group i can be written

$$\alpha_{i\alpha\beta} = \alpha_i(1 - \kappa_i)\delta_{\alpha\beta} + 3\alpha_i\kappa_i u_{i\alpha}u_{i\beta} \tag{15}$$

where

$$\alpha = \tfrac{1}{3}(\alpha_\parallel + 2\alpha_\perp) \tag{16}$$

is the mean polarizability and

$$\kappa = (\alpha_\parallel - \alpha_\perp)/3\alpha \tag{17}$$

is the dimensionless polarizability anisotropy, $\alpha_\parallel$ and $\alpha_\perp$ denoting the polarizability components parallel and perpendicular to the group's principal axis $\mathbf{u}$. Using (8), the polarizability tensor of group i at some instant during the torsion vibration can now be expressed in terms of the unit vectors along the principal internal axes X, Y, Z:

$$\begin{aligned} \alpha_{i\alpha\beta} = {} & \alpha_i(1 - \kappa_i)\delta_{\alpha\beta} \\ & + 3\alpha_i\kappa_i\{I_\alpha I_\beta \sin^2\phi_i \cos^2[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)] \\ & + J_\alpha J_\beta \sin^2\phi_i \sin^2[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)] \\ & + K_\alpha K_\beta \cos^2\phi_i - \tfrac{1}{2}(I_\alpha J_\beta + J_\alpha I_\beta)\sin^2\phi_i \\ & \times \sin 2[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)] - \tfrac{1}{2}(I_\alpha K_\beta + K_\alpha I_\beta)\sin 2\phi_i \\ & \times \cos[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)] + \tfrac{1}{2}(J_\alpha K_\beta \\ & + K_\alpha J_\beta)\sin 2\phi_i \sin[\theta_i - (\tau_i^{(0)} + \Delta\tau_i)]\} \end{aligned} \tag{18}$$

Although the polarizability tensor of group i referred to axes fixed within group i does not change during the torsion vibration, expression (18) for the polarizability tensor referred to the molecule-fixed axes does change, and this is the origin of the effects under discussion. The partial derivative of (18) with respect to the internal coordinate of torsion is

$$\begin{aligned} \left(\frac{\partial\alpha_{i\alpha\beta}}{\partial\Delta\tau_i}\right)_0 = {} & 3\alpha_i\kappa_i[(I_\alpha I_\beta - J_\alpha J_\beta) \\ & \times \sin^2\phi_i \sin 2(\theta_i - \tau_i^{(0)}) \\ & + (I_\alpha J_\beta + J_\alpha I_\beta)\sin^2\phi_i \cos 2(\theta_i - \tau_i^{(0)}) \\ & - \tfrac{1}{2}(I_\alpha K_\beta + K_\alpha I_\beta)\sin 2\phi_i \sin(\theta_i - \tau_i^{(0)}) \\ & - \tfrac{1}{2}(J_\alpha K_\beta + K_\alpha J_\beta)\sin 2\phi_i \cos(\theta_i - \tau_i^{(0)})] \end{aligned} \tag{19}$$

Using (19) in (14), we obtain the following products:

$$\left(\frac{\partial\alpha_{\alpha\beta}}{\partial\Delta\tau}\right)_0\left(\frac{\partial\alpha_{\alpha\beta}}{\partial\Delta\tau}\right)_0 = 9\alpha_i^2\kappa_i^2\left(\frac{I_{\mathrm{Me}}}{I}\right)^2(1 - \cos 2\phi_i) \tag{20a}$$

$$\left(\frac{\partial\alpha_{\alpha\alpha}}{\partial\Delta\tau}\right)_0\left(\frac{\partial\alpha_{\beta\beta}}{\partial\Delta\tau}\right)_0 = 0 \tag{20b}$$

Thus the methyl torsion Raman intensity is a function of the polarizability anisotropy of group i weighted by the square of the ratio of the moment of inertia of the methyl group to that of the complete molecule. No methyl torsion Raman intensity is generated if the principal axis of group i is parallel to the torsion axis (as it would be in CH_3CF_3, for example).

The depolarization ratio of the methyl torsion Raman band, in circularly polarized (and unpolarized) incident light, is found from (20) to be

$$\rho = I_z/I_x$$

$$= \frac{2\left[3\left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)_0 \left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)_0 - \left(\frac{\partial \alpha_{\alpha\alpha}}{\partial \Delta\tau}\right)_0 \left(\frac{\partial \alpha_{\beta\beta}}{\partial \Delta\tau}\right)_0\right]}{7\left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)_0 \left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)_0 + \left(\frac{\partial \alpha_{\alpha\alpha}}{\partial \Delta\tau}\right)_0 \left(\frac{\partial \alpha_{\beta\beta}}{\partial \Delta\tau}\right)_0} = \frac{6}{7} \quad (21)$$

Consider now the Raman optical activity. The optical activity tensors of the molecule are written as sums of tensors intrinsic to the two groups. But unlike the polarizability, these are origin dependent: on moving the origin from **O** to a point **O** + **a**, where **a** is some constant vector, it is found that[19]

$$G'_{\alpha\beta} \rightarrow G'_{\alpha\beta} + \tfrac{1}{2}\omega\epsilon_{\beta\gamma\delta}a_\gamma\alpha_{\alpha\delta} \quad (22a)$$

$$A_{\alpha\beta\gamma} \rightarrow A_{\alpha\beta\gamma} - \tfrac{3}{2}a_\beta\alpha_{\alpha\gamma} - \tfrac{3}{2}a_\gamma\alpha_{\alpha\beta} + a_\delta\alpha_{\alpha\delta}\delta_{\beta\gamma} \quad (22b)$$

This origin dependence was used in a previous article to exploit a simple two-group model of Rayleigh and Raman optical activity;[20] here it is the source of methyl torsion Raman optical activity. It is natural to refer the optical activity tensors of group i to the origin 0 of the principal internal axis system X, Y, Z, in which case

$$G'_{i\alpha\beta}(0) = G'_{i\alpha\beta} - \tfrac{1}{2}\omega\epsilon_{\beta\gamma\delta}R_{i\gamma}\alpha_{i\alpha\delta} \quad (23a)$$

$$A_{i\alpha\beta\gamma}(0) = A_{i\alpha\beta\gamma} + \tfrac{3}{2}R_{i\beta}\alpha_{i\alpha\gamma} + \tfrac{3}{2}R_{i\gamma}\alpha_{i\alpha\beta} - R_{i\delta}\alpha_{i\alpha\delta}\delta_{\beta\gamma} \quad (23b)$$

where $G'_{i\alpha\beta}$ and $A_{i\alpha\beta\gamma}$ are tensors referred to the local origin in group i. Although group i may be intrinsically achiral in the usual sense (it may have improper rotation axes), there are nonetheless certain achiral symmetries, such as C_{2v}, for which nonzero components of $G'_{i\alpha\beta}$ and $A_{i\alpha\beta\gamma}$ exist that can contribute to the methyl torsion Raman optical activity. But we shall henceforth drop these intrinsic group optical activity tensors because they make no contribution when group i has a threefold or higher proper rotation axis, as has been assumed.

From (23) and (14) we obtain the following products:

$$\begin{aligned}\left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)\left(\frac{\partial G'_{\alpha\beta}}{\partial \Delta\tau}\right) &= \frac{1}{3}\omega\left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)\epsilon_{\alpha\gamma\delta}\left(\frac{\partial A_{\gamma\delta\beta}}{\partial \Delta\tau}\right)\\ &= -\frac{1}{2}\omega\left(\frac{I_{\mathrm{Me}}}{I}\right)^2\left(\frac{\partial \alpha_{i\alpha\beta}}{\partial \Delta\tau_i}\right)\epsilon_{\beta\gamma\delta}\left[\frac{\partial(R_{i\gamma}\alpha_{i\delta\alpha})}{\partial \Delta\tau_i}\right]\\ &= -\frac{1}{2}\omega\left(\frac{I_{\mathrm{Me}}}{I}\right)^2\left(\frac{\partial \alpha_{i\alpha\beta}}{\partial \Delta\tau_i}\right)\epsilon_{\beta\gamma\delta}\left[\left(\frac{\partial R_{i\gamma}}{\partial \Delta\tau_i}\right)(\alpha_{i\delta\alpha})\right.\\ &\qquad \left. + (R_{i\gamma})\left(\frac{\partial \alpha_{i\delta\alpha}}{\partial \Delta\tau_i}\right)\right] \quad (24)\end{aligned}$$

Because $\epsilon_{\beta\gamma\delta}$ is antisymmetric in $\beta\delta$ while $\alpha_{\alpha\beta}$ is symmetric in $\alpha\beta$,

$$\left(\frac{\partial \alpha_{i\alpha\beta}}{\partial \Delta\tau_i}\right)_0 \epsilon_{\beta\gamma\delta}(R_{i\gamma})_0\left(\frac{\partial \alpha_{i\delta\alpha}}{\partial \Delta\tau_i}\right)_0 = 0 \quad (25)$$

Since $R_{i\gamma} = R_i[I_\gamma \cos(\tau_i^{(0)} + \Delta\tau_i) + J_\gamma \sin(\tau_i^{(0)} + \Delta\tau_i)]$

$$\left(\frac{\partial R_{i\gamma}}{\partial \Delta\tau_i}\right)_0 = R_i(-I_\gamma \sin\tau_i^{(0)} + J_\gamma \cos\tau_i^{(0)}) \quad (26)$$

Using (26), (25), (19), and (18) in (24) we finally obtain, after some algebra, the following products:

$$\begin{aligned}\left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)_0\left(\frac{\partial G'_{\alpha\beta}}{\partial \Delta\tau}\right)_0 &= \frac{1}{3}\omega\left(\frac{\partial \alpha_{\alpha\beta}}{\partial \Delta\tau}\right)_0\epsilon_{\alpha\gamma\delta}\left(\frac{\partial A_{\gamma\delta\beta}}{\partial \Delta\tau}\right)_0\\ &= \frac{9}{4}\omega R_i\alpha_i{}^2\kappa_i{}^2\left(\frac{I_{\mathrm{Me}}}{I}\right)^2 \sin 2\phi_i \sin\theta_i \quad (27a)\end{aligned}$$

$$\left(\frac{\partial \alpha_{\alpha\alpha}}{\partial \Delta\tau}\right)_0\left(\frac{\partial G'_{\beta\beta}}{\partial \Delta\tau}\right)_0 = 0 \quad (27b)$$

Thus, like the methyl torsion Raman intensity, the optical activity is a function of the polarizability anisotropy of group i weighted by the square of the ratio of the moment of inertia of the methyl group to that of the complete molecule. Equation 27a is reduced to zero if $\theta_i = 0$ or 180° or if $\phi_i = 0$ or 90°.

Using (27) and (20) in (10), we obtain the following expressions for the methyl torsion Raman CID components:

$$\Delta_z = \frac{2\pi R_i \sin 2\phi_i \sin\theta_i}{3\lambda(1 - \cos 2\phi_i)} \quad (28a)$$

$$\Delta_x = \frac{8\pi R_i \sin 2\phi_i \sin\theta_i}{7\lambda(1 - \cos 2\phi_i)} \quad (28b)$$

where $\lambda = 2\pi c/\omega$ is the wavelength of the incident radiation.

Notice that these CIDs are not exclusive to the methyl group; the same results would be obtained for the oscillation of a single-bladed propellor about any well-defined torsion axis. But in practice such effects are only likely to be observed with methyl torsions because the corresponding frequencies occur in an accessible region of the vibrational spectrum. Torsions of other groups with threefold symmetry, such as $-CF_3$, usually occur below about 100 cm^{-1} on account of the much greater mass. Groups such as -OH and $-NH_2$ have torsion vibrations at accessible frequencies, but they are usually more diffuse and harder to identify than methyl torsions; also the above treatment would need to be extended in order to accommodate them because they have lower symmetry than the methyl group and their polarizabilities are changed on rotation about the torsion axis.

These results were developed specifically for a chiral molecule containing a single methyl group with its threefold axis lying on a principal inertial axis; unfortunately such molecules are rare, and a lack of appropriate experimental data has, to date, prevented a detailed application. Nonetheless, this simple theory involving oscillations in space of the molecular frame about a single principal internal axis does lead to a qualitative understanding of the large methyl torsion Raman optical activity that is commonly observed in completely asymmetric molecules. As indicated later, the general theory contains contributions from oscillations in space of the molecular frame about all three principal internal axes.

There is, however, a more common situation to which the model calculations are applicable directly. A molecule containing *two* adjacent methyl groups has vibrational modes corresponding to in-phase and out of phase combinations of the two methyl torsions. These combinations can generate torsion vibrations of the rest of the molecule about well-defined symmetry axes; in *o*-xylene, for example, the in-phase combination generates a torsion about the twofold proper rotation axis. Interesting chiral examples include bridged biphenyls such as (*R*)-(+)-dimethyldibenz-1,3-cycloheptadien-6-one shown in Figure 2. Here, the in-phase combination of the two methyl torsions generates a torsion of the rest of the molecule about its C_2 axis (the Z axis in Figure 2). If the aromatic rings are largely responsible, the inertial contribution to the in-phase methyl torsion Raman optical activity may be calculated easily.

But first we note that, when two or more groups contribute, as in the above biphenyl, a complication arises in that interference between waves scattered from each pair of groups

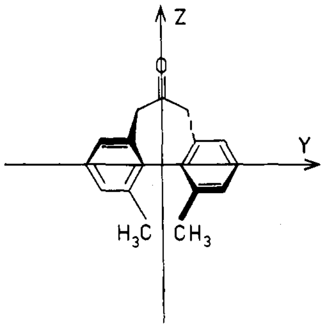

Figure 2. (R)-(+)-dimethyldibenz-1,3-cycloheptadien-6-one. The X axis is perpendicular to the plane of the page. The molecular C_2 axis coincides with the Z axis.

makes a distinct contribution to the Raman intensity and optical activity additional to that arising from interference between two waves scattered from a single group (the latter being the situation in the single-bladed propellor model). This would be an extension of the two-group model published previously.[20] The numerators and denominators of the dimensionless CID components are now sums of contributions from each group, together with cross terms describing interference.

The additional interference terms that contribute in a double-bladed propellor such as the biphenyl provide the same multiplicative factor of $(1 - \cos 2\phi_i)$ in both the numerator and denominator of Δ_z and Δ_x, so after cancellation the CID components (28) that were derived for a single-bladed propellor still apply. Bearing in mind the definitions in the caption to Figure 1, ϕ_i for the absolute configuration shown in Figure 2 is estimated (from a Dreiding model) to be 112.5°, and taking $\theta_i = 90°$, $R_i = 2.5$ Å, and $\lambda = 5000$ Å, we obtain $\Delta_z^{(Z)} = -0.43 \times 10^{-3}$ and $\Delta_x^{(Z)} = -0.74 \times 10^{-3}$. The out of phase combination of the two methyl torsions generates torsions of the rest of the molecule about the X and Y axes in Figure 2. Since $\phi_i = 22.5°$ for torsion about the X axis, the corresponding CID components are $\Delta_z^{(X)} = 2.5 \times 10^{-3}$ and $\Delta_x^{(X)} = 4.3 \times 10^{-3}$. These are much larger than the CIDs for torsion about the Z axis because the denominator, corresponding to the Raman intensity, falls off much faster with decreasing ϕ_i than does the numerator, corresponding to the Raman optical activity. In fact the numerators of $\Delta_z^{(Z)}$ and $\Delta_z^{(X)}$, and of $\Delta_z^{(Z)}$ and $\Delta_x^{(X)}$, are simply equal and opposite. The Raman optical activity for the twisting in space of the biphenyl about the Y axis is simply equal and opposite to that for the "internal" torsion of one aromatic ring with respect to the other; the theory of the Raman optical activity generated by this type of internal twisting mode has been presented elsewhere.[12]

Part of the low-frequency Raman optical activity spectrum of (R)-(+)-dimethyldibenz-1,3-cycloheptadien-6-one has been measured previously[7] (these measurements have not been repeated on our latest instrument because the sample was lost). However, it has not proved possible to obtain a definitive interpretation of any feature in terms of this theory because there appears to be considerable mixing of the methyl torsions with other low-frequency modes. Mixing with C–Me bending modes is anticipated from the fact that the corresponding in-plane and out of plane bending vibrations in toluene have been assigned to bands at about 346 and 217 cm^{-1}.[21] The spectrum contains two broad, barely resolved bands centered at about 234 cm^{-1}; an enormous CID ($\Delta_z \approx -7 \times 10^{-3}$) is found in the lower frequency component, but none in the higher. It was suggested that the two bands originate in the in-phase and out of phase combinations of the two methyl torsions;[7] another possibility is that both are associated with the in-phase combination coupled with C–Me bending modes. A strong band at about 110 cm^{-1} with a large, structured, positive Raman optical activity may involve the out of phase combinations of the two methyl torsions coupled with low-frequency skeletal modes. The large negative CID would then be consistent with the calculations above; the fact that the calculated magnitude is an order of magnitude too small may not be significant because of the sensitivity of the denominator, $I_z^R + I_z^L$, to small changes in ϕ_i, and also because $I_z^R + I_z^L$ might have been underestimated from the observed spectrum because the methyl torsion bands have very broad wings and the background is very high.

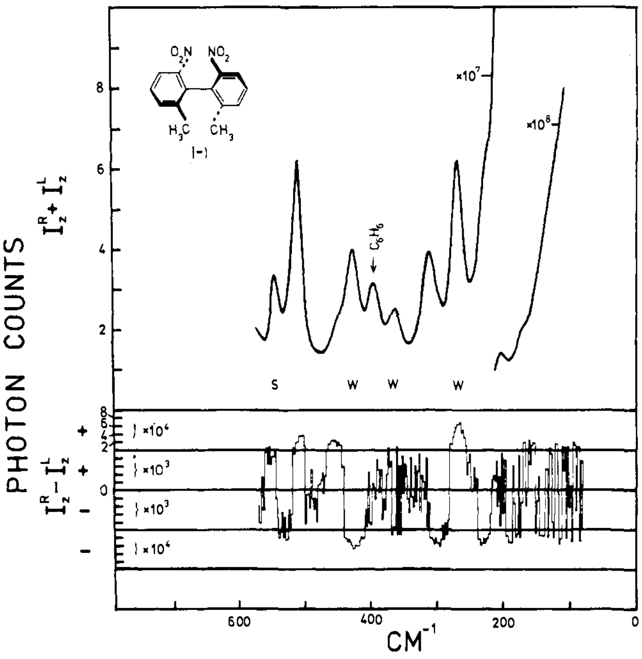

Figure 3. The low-frequency depolarized Raman circular intensity sum and difference spectra of (S)-(−)-6,6′-dinitro-2,2′-dimethylbiphenyl in benzene.

The low-frequency Raman optical activity spectrum of another example, (S)-(−) 6,6′-dinitro-2,2′-dimethylbiphenyl, is shown in Figure 3 (for details of the experimental technique, see ref 6 or 9). If the absolute configuration is as shown, ϕ_i is positive, and taking it to be +45°, together with $R_i = 2.5$ Å and $\lambda = 5000$ Å, we obtain $\Delta_z^{(Z)} = 1.05 \times 10^{-3}$ for the twisting about the C_2 axis associated with the in-phase combination of the methyl torsions. This can be compared with an observed value for Δ_z of about 1.7×10^{-3} for the band at about 270 cm^{-1}. But it would be bold to say that this band does indeed originate in the in-phase combination of the two methyl torsions: the negative–positive–negative pattern of Raman optical activity bands between about 200 and 320 cm^{-1} most likely originates in complicated normal coordinates containing contributions from methyl torsions together with C–Me and C–NO_2 deformations.

Notice that in hindered biphenyls the sign of the Raman optical activity originating in oscillations of the two-bladed propellor about the C_2 axis is the same for all degrees of nonplanarity of the two aromatic rings corresponding to a particular enantiomer (that is, torsion angles between 0 and 180° for one enantiomer, and between 180 and 360° for the other). This can be contrasted with the corresponding optical rotation and circular dichroism, which changes sign on going from torsion angles between 0 and 90° to angles between 90 and 180°.[22,23] This is because the Raman optical activity depends on $\sin 2\phi_i$, where $2\phi_i$ is in this case the angle between effective sixfold axes of the aromatic rings, whereas the optical rotation and circular dichroism depend on $\sin 4\phi_i$.

Clearly there is need for further experimental and theoretical work on series of model compounds before definitive interpretations can be made of observed Raman CIDs in biphenyls.

Infrared Optical Activity

An appropriate experimental quantity in circular dichroism is the dimensionless dissymmetry factor[24]

$$g = \frac{\epsilon^{\mathrm{L}} - \epsilon^{\mathrm{R}}}{1/2(\epsilon^{\mathrm{L}} + \epsilon^{\mathrm{R}})} \tag{29}$$

where ϵ^{L} and ϵ^{R} are the absorption coefficients in left and right circularly polarized incident light. This can be written[25]

$$g = 4R/cD \tag{30}$$

where D and R are the dipole strength and rotational strength of the corresponding electronic or vibrational transition (the factor c in the denominator does not appear when Gaussian units are used). For the transition between initial and final vibrational states n_{v} and m_{v}, assuming an isotropic sample,

$$D = \mathrm{Re}(\langle n_{\mathrm{v}}|\mu_\alpha|m_{\mathrm{v}}\rangle\langle m_{\mathrm{v}}|\mu_\alpha|n_{\mathrm{v}}\rangle \tag{31a}$$

$$R = \mathrm{Im}(\langle n_{\mathrm{v}}|\mu_\alpha|m_{\mathrm{v}}\rangle\langle m_{\mathrm{v}}|m_\alpha|n_{\mathrm{v}}\rangle) \tag{31b}$$

where μ_α and m_α are the electric and magnetic dipole moment vector operators for the molecule.

The single-bladed propellor model is now used, and the electric and magnetic moments of the molecule are written as sums of moments intrinsic to the methyl group and to group i. In writing the intrinsic group magnetic moments, it must be remembered that the magnetic dipole moment is origin dependent in the presence of a time-dependent electric dipole moment, so that for group i

$$m_{i\alpha}(\mathbf{R}_i) = m_{i\alpha} + 1/2\epsilon_{\alpha\beta\gamma}R_{i\beta}\dot{\mu}_{i\gamma} \tag{32}$$

where $m_{i\alpha}$ is the magnetic dipole moment referred to the local origin in group i. When vibrational matrix elements of the origin-dependent part are taken, we invoke the velocity-dipole transformation

$$\langle m_{\mathrm{v}}|\dot{\mu}_{i\alpha}|n_{\mathrm{v}}\rangle = \mathrm{i}\omega_{m_{\mathrm{v}}n_{\mathrm{v}}}\langle m_{\mathrm{v}}|\mu_{i\alpha}|n_{\mathrm{v}}\rangle \tag{33}$$

where $\omega_{m_{\mathrm{v}}n_{\mathrm{v}}} = \omega_{\mathrm{t}}$ is the corresponding vibrational transition frequency. After the effective electric and magnetic dipole moments are expanded in Q_{t}, the dipole strength and rotational strength for the fundamental transition associated with the methyl torsion vibration are determined by the products

$$\left(\frac{\partial\mu_\alpha}{\partial\Delta\tau}\right)_0\left(\frac{\partial\mu_\alpha}{\partial\Delta\tau}\right)_0 = \left(\frac{I_{\mathrm{Me}}}{I}\right)^2\left(\frac{\partial\mu_{i\alpha}}{\partial\Delta\tau_i}\right)_0\left(\frac{\partial\mu_{i\alpha}}{\partial\Delta\tau_i}\right)_0 \tag{34a}$$

$$\left(\frac{\partial\mu_\alpha}{\partial\Delta\tau}\right)_0\left(\frac{\partial m_\alpha}{\partial\Delta\tau}\right)_0 = \frac{1}{2}i\omega_{\mathrm{t}}\left(\frac{I_{\mathrm{Me}}}{I}\right)^2\left(\frac{\partial\mu_{i\alpha}}{\partial\Delta\tau_i}\right)_0\epsilon_{\alpha\beta\gamma}\left[\frac{\partial(R_{i\beta}\mu_{i\gamma})}{\partial\Delta\tau_i}\right]_0 \tag{34b}$$

where $m_{i\alpha}$ is assumed to be zero.

Using (8), the electric dipole moment vector $\mu_{i\alpha} = \mu_i u_{i\alpha}$ of group i can be written in terms of the unit vectors along the principal internal axes X, Y, Z. The dipole strength is

$$\left(\frac{\partial\mu_\alpha}{\partial\Delta\tau}\right)_0\left(\frac{\partial\mu_\alpha}{\partial\Delta\tau}\right)_0 = \frac{1}{2}\mu_i^2\left(\frac{I_{\mathrm{Mc}}}{I}\right)^2(1 - \cos 2\phi_i) \tag{35}$$

Thus methyl torsion infrared intensity is only generated if group i has a permanent electric dipole moment that is not oriented parallel to the torsion axis.

The rotational strength is determined by the product

$$\left(\frac{\partial\mu_\alpha}{\partial\Delta\tau}\right)_0\left(\frac{\partial m_\alpha}{\partial\Delta\tau}\right)_0 = -\frac{1}{4}i\omega_{\mathrm{t}}R_i\mu_i^2\left(\frac{I_{\mathrm{Me}}}{I}\right)^2\sin 2\phi_i \sin\theta_i \tag{36}$$

Thus, like the methyl torsion infrared intensity, the optical activity requires group i to have a permanent electric dipole moment. The angular dependence is the same as that of the corresponding Raman optical activity (27a).

Using (35) and (36), we finally obtain the following expression for the methyl torsion infrared dissymmetry factor:

$$g = -\frac{4\pi R_i \sin 2\phi_i \sin\theta_i}{\lambda_{\mathrm{t}}(1 - \cos 2\phi_i)} \tag{37}$$

Apart from the opposite sign (which arises from opposite signs in the definitions of Δ and g), the infrared dissymmetry factor (37) has the same dependence on molecular geometry as the Raman CID components (28). There are, however, important differences between the two methods of measuring methyl torsion vibrational optical activity (apart from instrumental factors). First, group i must have a permanent electric dipole moment for the methyl torsion to be infrared optically active; this is more restrictive than the requirement for Raman optical activity since all nonspherical groups have a polarizability anisotropy. Thus any infrared CD generated by methyl torsion vibrations in a bridged biphenyl such as dimethyldibenz-1,3-cycloheptadien-6-one (Figure 2) would have to originate in the aromatic ring substituents, benzene itself having no dipole moment. Second, the Raman Δ values are larger than the infrared g values by $\lambda_{\mathrm{t}}/\lambda$, where λ_{t} is the fundamental methyl torsion wavelength and λ is the exciting Raman wavelength. Taking λ_{t} = 500 000 Å (corresponding to $\omega_{\mathrm{t}} = 200\ \mathrm{cm}^{-1}$) and λ = 5000 Å, the Raman experiment is 10^2 more favorable. This illustrates explicitly a statement to the effect that the Raman approach to vibrational optical activity, because it uses visible exciting light, has a natural advantage over the infrared approach.[6]

Completely Asymmetric Molecules

In a completely asymmetric molecule, the threefold axis of the methyl group is not a principal inertial axis. For this situation, the rotational kinetic energy is[14,16]

$$T = \frac{1}{2}\sum_{q=1}^{3} I_q\dot{\chi}_q^2 + \frac{1}{2}I_{\mathrm{Mc}}\left(1 - \sum_{q=1}^{3}\frac{I_{\mathrm{Me}}\lambda_q^2}{I_q}\right)\dot{\tau}^2 \tag{38}$$

where I_q and $\dot{\chi}_q$ are the moment of inertia and angular velocity about the qth principal inertial axis of the complete molecule with the internal rotation frozen, and λ_q is the cosine of the angle between the threefold axis of the methyl group and the qth principal axis; as before, I_{Me} is the moment of inertia of the methyl group about its threefold axis, and $\dot{\tau}$ is the internal angular velocity of the methyl group relative to the rest of the molecule. Notice that, when the methyl torsion axis is also a principal inertial axis, (38) reduces to (3) for the kinetic energy about the torsion axis, plus the kinetic energy about the other two principal inertial axes.

Since the angular momentum about each principal axis q must be zero at any instant during the torsion vibration,

$$I_{iq}\Delta\tau_{iq} = -I_{\mathrm{Me}}\Delta\tau_{\mathrm{Me}}\lambda_q \tag{39}$$

where I_{iq} is the moment of inertia of the rest of the molecule about the qth principal axis (so that $I_q = I_{iq} + 1/2 I_{\mathrm{Me}}(1 + \lambda_q^2)$) and $\Delta\tau_{iq}$ is the "intrinsic" displacement of the rest of the molecule about the qth axis. Again, $\Delta\tau_{\mathrm{Me}}$ is the "intrinsic" displacement of the methyl group about its threefold axis. The internal coordinate for the methyl torsion can be written

$$\begin{aligned}\Delta\tau &= \sum_{q=1}^{3}\Delta\tau_{iq}\lambda_q - \Delta\tau_{\mathrm{Me}} \\ &= \left(\sum_{q=1}^{3}\Delta\tau_{iq}\lambda_q\right) + \frac{I_{iq}}{I_{\mathrm{Me}}\lambda_q}\Delta\tau_{iq}\end{aligned} \tag{40}$$

so that

$$\left(\frac{\partial\Delta\tau}{\partial\Delta\tau_{iq}}\right)_\lambda = \frac{I_{iq} + I_{\mathrm{Me}}\lambda_q^2}{I_{\mathrm{Me}}\lambda_q} \tag{41a}$$

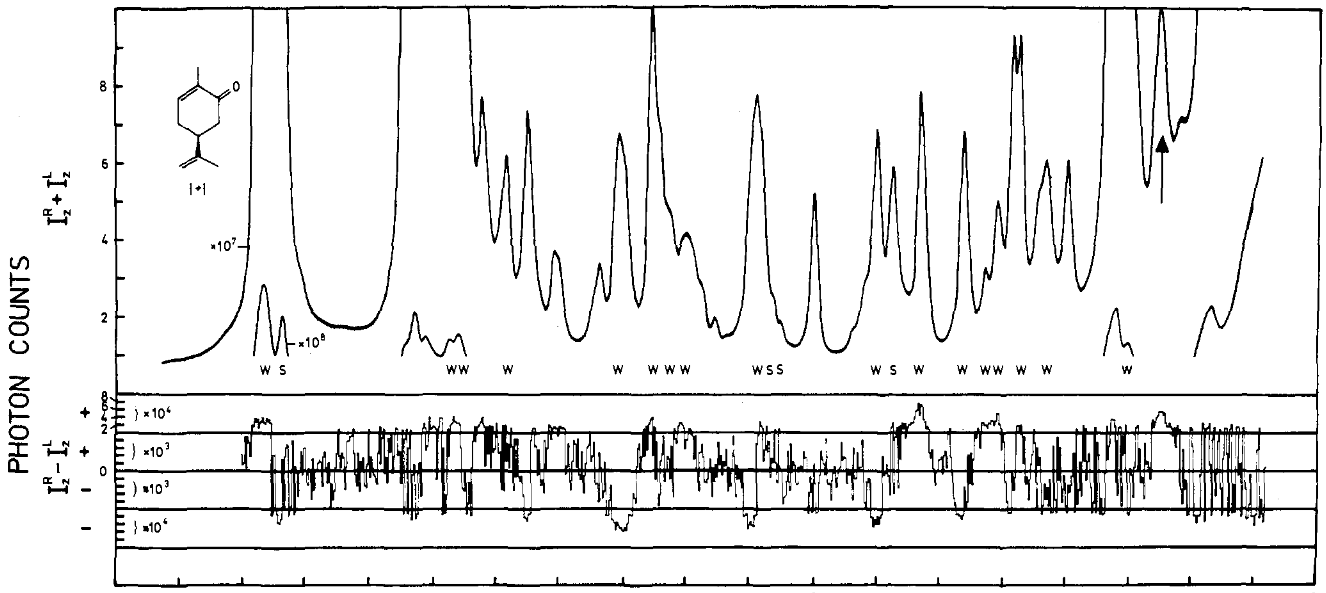

Figure 4. The depolarized Raman circular intensity sum and difference spectra of neat (+)-carvone.

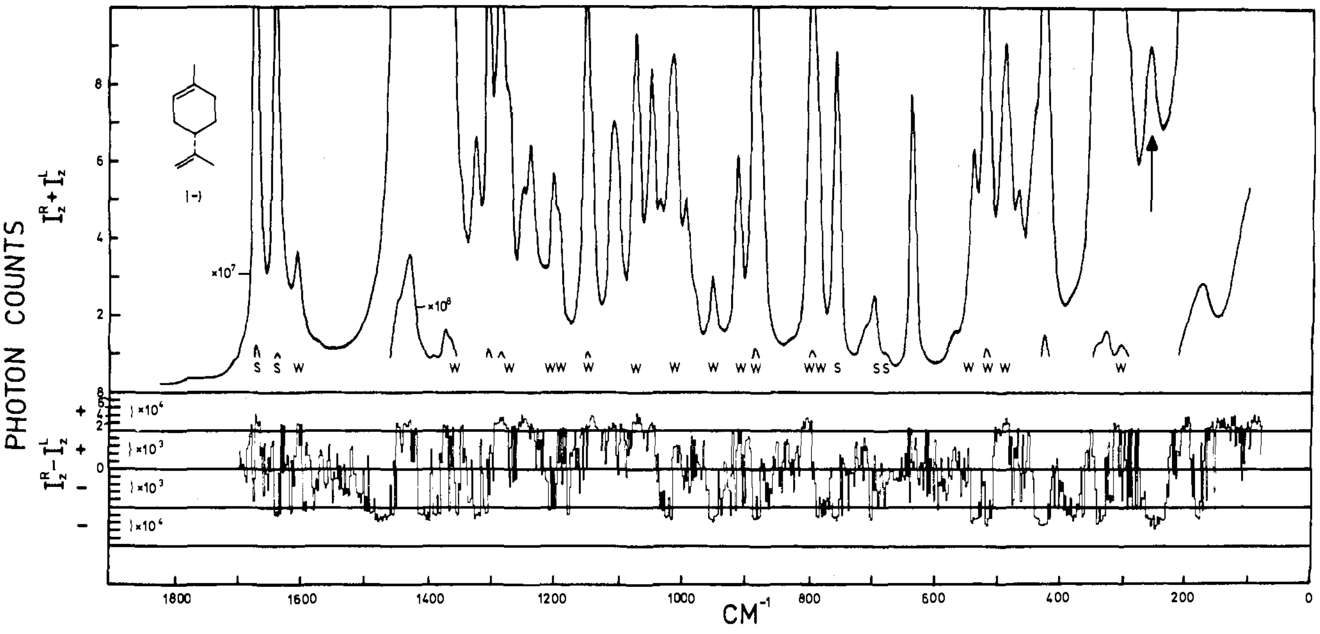

Figure 5. The depolarized Raman circular intensity sum and difference spectra of neat (−)-limonene.

$$\left(\frac{\partial\Delta\tau}{\partial\lambda_q}\right)_{\Delta\tau_i} = -\left(\frac{I_{iq} - I_{\mathrm{Me}}\lambda_q{}^2}{I_{\mathrm{Me}}\lambda_q{}^2}\right)\Delta\tau_{iq}$$

$$= \left(1 - \frac{\dfrac{I_{\mathrm{Me}}\lambda_q{}^2}{I_{iq}}}{\lambda_q}\right)\Delta\tau_{\mathrm{Me}} \quad (41\mathrm{b})$$

Polarizability derivatives such as (14) are now generalized to

$$\left(\frac{\partial\alpha_{\alpha\beta}}{\partial\Delta\tau}\right)_0 = \sum_{q=1}^{3}\left\{\left(\frac{\partial\alpha_{i\alpha\beta}}{\partial\Delta\tau_{iq}}\frac{\partial\Delta\tau_{iq}}{\partial\Delta\tau}\right)_0 + \left(\frac{\partial\alpha_{i\alpha\beta}}{\partial\lambda_q}\frac{\partial\lambda_g}{\partial\Delta\tau}\right)_0 + \left(\frac{\partial\alpha_{\mathrm{Me}\alpha\beta}}{\partial\lambda_q}\frac{\partial\lambda_q}{\partial\Delta\tau}\right)_0\right\} \quad (42)$$

The terms in $\partial\alpha_{i\alpha\beta}/\partial\lambda_q$ and $\partial\alpha_{\mathrm{Me}\alpha\beta}/\partial\lambda_q$ are present because there is in general a reorientation of λ on internal rotation and this changes the anisotropic group polarizabilities. As in (14), $(\partial\alpha_{\mathrm{Me}\alpha\beta}/\partial\Delta\tau_{\mathrm{Me}})_0 = 0$.

In using (42) to generalize results such as (20) and (27) for the Raman intensity and optical activity, a complication arises in that cross terms such as $(\partial\alpha_{i\alpha\beta}/\partial\Delta\tau_{iq})_0\,(\partial\alpha_{i\alpha\beta}/\partial\Delta\tau_{iq'})_0$, describing interference between the changes in the polarizability with respect to two different principal internal axes q and q', are not zero in general. Thus the Raman intensity and optical activity are not simply weighted sums of contributions from torsions about the three separate principal internal axes. In fact this complication arises in the case of the oscillations in space about the X and Y axes of the biphenyl that accompany the out of phase coupled mode of the two methyl torsions (it does not arise for the pure oscillations about the Z axis associated with the in-phase coupled mode). A further complication is that the methyl group itself will make a contribution

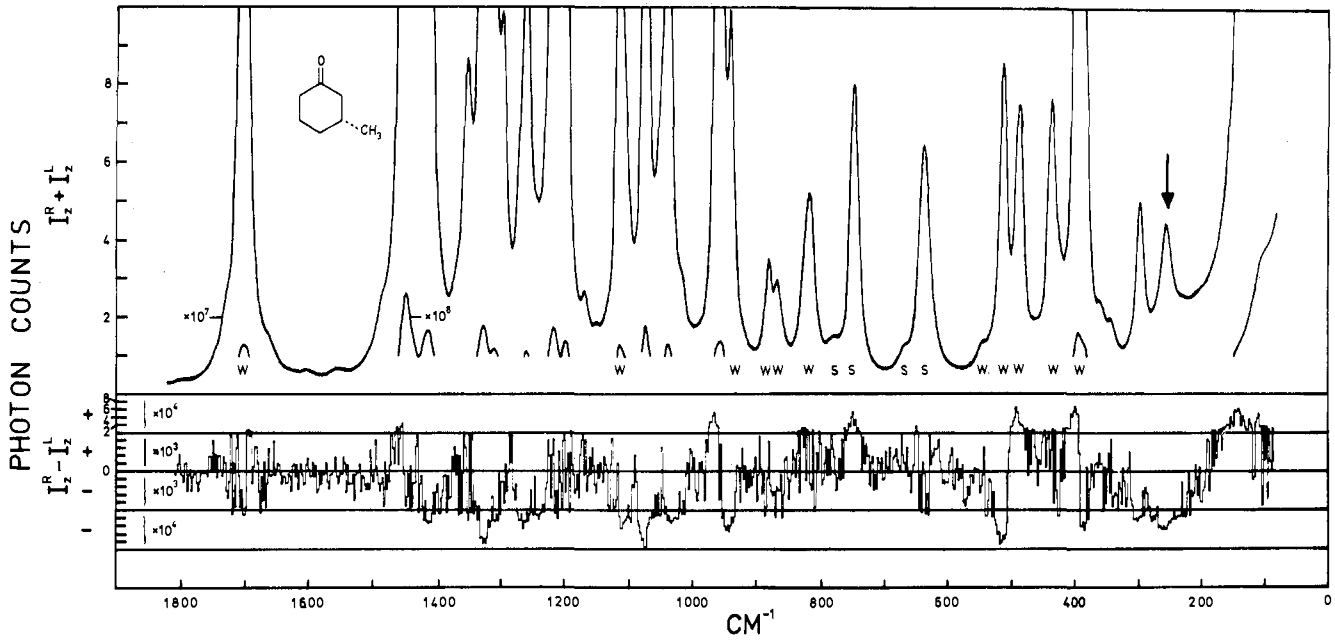

Figure 6. The depolarized Raman circular intensity sum and difference spectra of neat (+)-3-methylcyclohexanone.

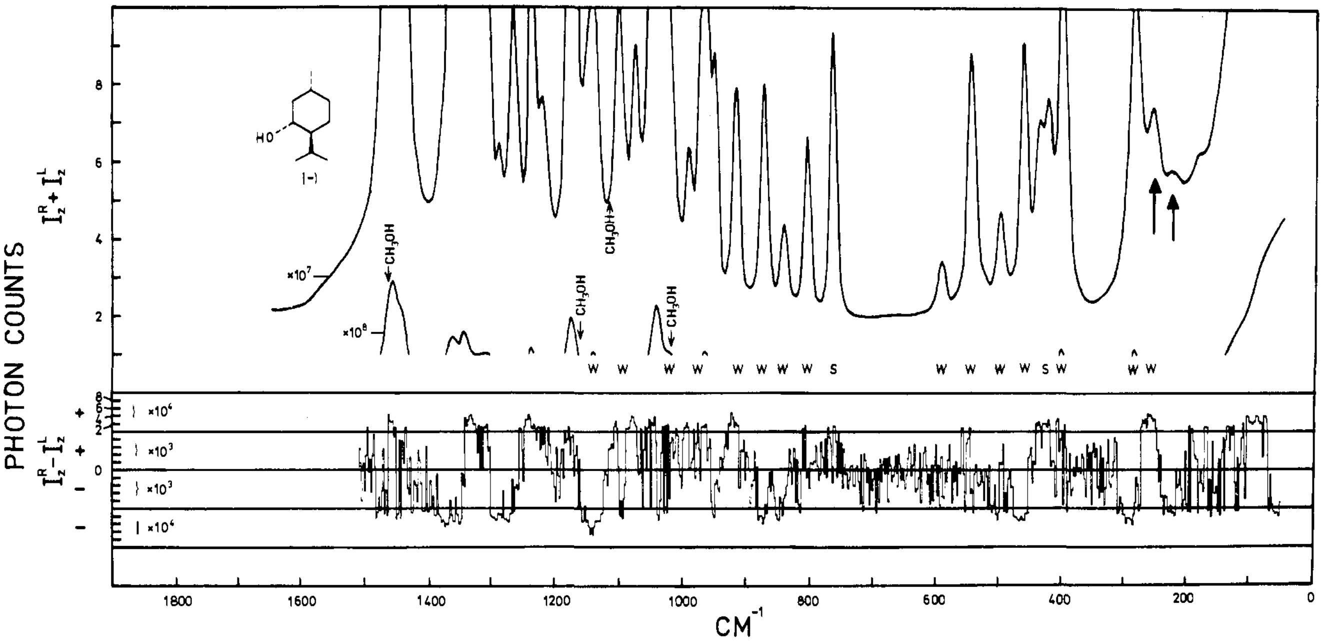

Figure 7. The depolarized Raman circular intensity sum and difference spectra of (−)-menthol in methanol.

depending on the disposition of its principal axis relative to the principal internal axes of the complete molecule; this in turn leads to yet another contribution, mentioned previously, involving interference between waves scattered independently from the methyl group and the rest of the molecule. Again this complication arises in the out of phase mode in the hindered biphenyl, but it is probably a good approximation to ignore such additional contributions from the two methyl groups compared with those from the aromatic rings.

Thus general expressions for methyl torsion Raman (and infrared) optical activity in completely asymmetric molecules are of considerable complexity, and are not presented here. But in some cases a good approximation might be obtained by considering oscillations of the rest of the molecule about a single principal internal axis if the associated contributions to the Raman (or infrared) optical activity are much larger than from oscillation about the other two axes.

To date, it has not been possible to apply this theory explicitly. However, we have obtained many Raman optical activity spectra in which certain large features at low frequency probably contain contributions from the inertial methyl torsion mechanism. The assignment of methyl torsion bands is often uncertain; but the broad characteristic line shape can be helpful, and also, perhaps, the Raman optical activity itself. Figures 4–8 contain possible examples of large Raman optical activity features at low frequency (marked with arrows) in which methyl torsions make significant contributions. In carvone and limonene (Figures 4 and 5) a large inertial contribution is anticipated in torsions of the isopropenyl methyl group and the opposite signs in the bands at about 250 cm^{-1}

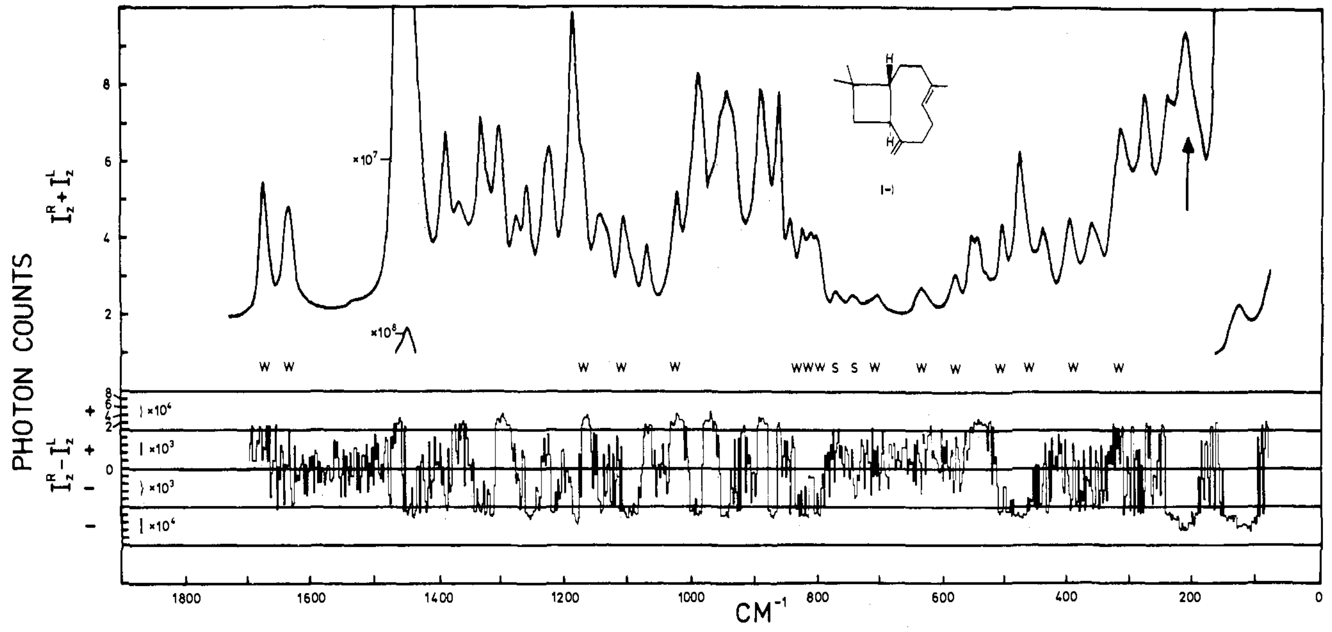

Figure 8. The depolarized Raman circular intensity sum and difference spectra of neat (−)-caryophyllene.

in (+)-carvone and (−)-limonene correlate with the opposite absolute configurations of the structural features common to both molecules.[7] The methyl torsion optical activity in (+)-3-methylcyclohexanone at about 260 cm^{-1} [7] (Figure 6) is probably too large to originate mainly in the inertial mechanism; the fact that it has a partner of equal magnitude and opposite sign at lower frequency indicates that much of the optical activity is generated through coupling of the methyl torsion with a low-frequency skeletal vibration (there are no obvious equal and opposite partners to the optical activity bands assigned to methyl torsions in carvone and limonene). Other possible examples are the bands at about 225 and 250 cm^{-1} in (−)-menthol (Figure 7) and the band at about 215 cm^{-1} in (−)-caryophyllene (Figure 8).

In these large, low-symmetry molecules the methyl torsion is likely to mix considerably with other low-frequency modes, so that it is unreasonable to expect "pure" inertial contributions in methyl torsion modes. Rather, the inertial mechanism should be viewed as part of a more general theory of Raman optical activity which would involve an extension of a generalized two-group theory presented previously (section 4.6 of ref 12). In this theory sums are taken over all pairs of bonds, constituting chiral structures, which are embraced by a true normal coordinate. For simplicity, contributions involving changes in $\mathbf{R}_i$ were neglected;[12] but if these are retained (with $\mathbf{R}_i$ carefully specified as the distance of group i from the origin of the principal internal coordinate system) the inertial mechanism is included automatically.

If methyl torsion Raman optical activity is to be of value in stereochemical studies, it is essential that the methyl torsion bands be assigned unequivocally (the assignments above are tentative suggestions). Deuteration should be particularly useful in this respect since the CD_3 torsion occurs at about 0.7 of the frequency of the CH_3 torsion in the corresponding molecule. Also identification of the $v = 1 \rightarrow v = 2$ methyl torsion overtone could provide additional evidence since this can have a significant intensity and a slightly lower frequency than the fundamental.

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