J. Am. Chem. Soc. **1981**, *103*, 1660–1664

A Two-Group Model for Raman Optical Activity. Application to Methylene Vibrations

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Received March 18, 1980

Abstract: Closed-form expressions are presented which relate the Raman circular intensity differentials associated with the two normal modes resulting from the coupling of two chirally disposed but intrinsically achiral groups to parameters specifying their relative orientations, spatial separation, and components of their derived, electrical polarizability tensors. When the two groups are identical and are of local C_{2v} symmetry, one can show that the ratio obtained when the difference between the Raman intensities produced by alternatively illuminating the "two-group-molecule" with right and left circularly polarized light is divided by their sum depends only on a single parameter other than those specifying the geometry; the former may be determined from the depolarized Raman spectrum. The equations valid in this latter case are applied to the CH_2-scissoring vibrations of four terpenes each containing only two methylene groups. The calculated results are in good agreement with the reported Raman optical activity in that region of their spectra.

Vibrational optical activity has been the subject of several recent publications both of experimental and theoretical nature. Several groups have succeeded in measuring infrared circular dichroism due to vibrations of chiral molecules,[1] and analogous Raman measurements whereby small differences in the Raman scattering cross sections of chiral molecules according to the sense of circular polarization of the incident laser radiation have appeared.[2]

Buckingham and Barron[3] first published the phenomenological equations relating the circular Raman differences to components of products of the molecular polarizability with higher order polarizability tensors. These were reviewed by Barron in ref 4. Since the pertinent polarizability components are in general unknown, one cannot relate immediately the observed circular Raman differentials to the stereochemistry of a molecule, even when vibrational assignments may be made with confidence.

Several attempts to obviate this difficulty have been made. Barron and Buckingham[5] have considered the Rayleigh aand Raman optical activity of two chirally disposed achiral groups each possessing at least a C_3 axis. Stone[6] extended the analysis to groups with C_{2v} symmetry, while Prasad and Burow[7] used the atomic polarizability approach of Applequist[8] to calculate the expected ROA spectrum of fluorochlorobromomethane. More recently the expected ROA of the torsional vibration of a methyl group has appeared.[9]

In this paper we consider the Raman optical activity due to two chirally disposed groups which are intrinsically achiral but otherwise of general symmetry. The results are applied to the coupled vibrations of methylene groups in a series of terpenes.

Two-Group Model

The nomenclature of Buckingham and Barron will be used throughout as it appears in ref 4. Those authors give the expressions

$$S_z{}^{\mathrm{R}} - S_z{}^{\mathrm{L}} = 2C(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - {}^1\!/_3\omega\alpha_{\alpha\beta}A_{\alpha\beta})$$

$$S_z{}^{\mathrm{R}} - S_x{}^{\mathrm{L}} = C(7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}\mathrm{G}'_{\beta\beta} + {}^1\!/_3\omega\alpha_{\alpha\beta}A_{\alpha\beta})$$

$$S_0{}^{\mathrm{R}} - S_0{}^{\mathrm{L}} = 2C(\alpha_{\alpha\beta}G'_{\alpha\beta} + 3\alpha_{\alpha\alpha}G'_{\beta\beta} - {}^1\!/_3\omega\alpha_{\alpha\beta}A_{\alpha\beta})$$

$$S_\pi{}^{\mathrm{R}} - S_\pi{}^{\mathrm{L}} = 4C(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} + {}^1\!/_3\omega\alpha_{\alpha\beta}A_{\alpha\beta})$$

$$S_z{}^{\mathrm{R}} + S_z{}^{\mathrm{L}} = Cc(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}) = 2Cc\gamma^2$$

$$S_x{}^{\mathrm{R}} + S_x{}^{\mathrm{L}} = \frac{C}{2}c(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}) =$$

$$S_0{}^{\mathrm{R}} + S_0{}^{\mathrm{L}} = S_\pi{}^{\mathrm{R}} + S_\pi{}^{\mathrm{L}} = {}^1\!/_3Cc(7\gamma^2 + 45\bar{\alpha}^2) \tag{1}$$

where $C = \omega^4\mu_0E_0{}^2/[480\pi^2c^2r^2\omega_i(1 - \exp -\hbar\omega_i/kT)]$. (The tensor addition convention is used on repeated subscripts in eq 1.) 0, π, x, and z as subscripts refer to forward scattering, backscattering, and 90° scattering polarized normal to and parallel to the scattering plane, respectively. All other quantities are defined in ref 4. Since we are concerned with only Raman scattering, all polarizability components are understood to be derived with respect to the normal coordinate of vibration under consideration. ω_i is its frequency.

Consider two groups, 1 and 2, capable of performing nondegenerate vibrations along coordinate q_1 and q_2 each in the absence of the other. The groups need not be identical. Suppose that they are allowed to interact vibrationally with one another but not with any other group in the molecule. The two normal coordinates of the coupled vibration may be written as

$$Q_\pm = c_1{}^\pm q_1 + c_2{}^\pm q_2$$

The plus signs taken together form one normal coordinate and the minuses form the other. They have been chosen so that in the limit of perfectly coupled identical groups, i.e., in the limit $(c_1{}^\pm, c_2{}^\pm) = (1/2^{1/2}, \pm 1/2^{1/2})$, the Q_+ is the symmetric vibration.

If bringing together the two groups perturbs the derived polarizability components only slightly, then in eq 1 we may write

$$\alpha_{\alpha\beta}{}^\pm = c_1{}^\pm\alpha_{\alpha\beta}{}^{(1)} + c_2{}^\pm\alpha_{\alpha\beta}{}^{(2)} \tag{2a}$$

$$\alpha_{\alpha\beta}{}^\pm\mathbf{G}'_{\alpha\beta}{}^\pm = c_1{}^\pm c_2{}^\pm(\omega\epsilon_{\alpha\delta\gamma}\alpha_{\alpha\beta}{}^{(1)}\alpha_{\beta\gamma}{}^{(2)}r_\delta{}^{(1)} + \alpha_{\alpha\beta}{}^{(1)}G'_{\alpha\beta}{}^{(2)} + \alpha_{\alpha\beta}{}^{(2)}G'_{\alpha\beta}{}^{(1)})$$

$$\frac{\omega}{3}\alpha_{\alpha\beta}{}^\pm\mathbf{A}_{\alpha\beta}{}^\pm = c_1{}^\pm c_2{}^\pm\left(\omega\epsilon_{\alpha\delta\gamma}\alpha_{\alpha\beta}{}^{(1)}\alpha_{\beta\gamma}{}^{(2)}r_\delta{}^{(1)} + \frac{\omega}{3}\alpha_{\alpha\beta}{}^{(1)}A_{\alpha\beta}{}^{(2)} + \frac{\omega}{3}\alpha_{\alpha\beta}{}^{(2)}A_{\alpha\beta}{}^{(1)}\right)$$

$$\mathbf{G}'_{\alpha\alpha}{}^\pm = 0 \tag{2b}$$

where the superscripts ±, (1), and (2) on α, G', and A are un-

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(1) G. Holzwarth, E. C. Hus, H. S. Mosher, T. R. Faulkner, and A. Moskowitz, *J. Am. Chem. Soc.*, **96**, 251 (1974); L. A. Nafie, J. C. Cheng, and P. J. Stephens, *ibid.*, **97**, 3842 (1975); L. A. Nafie, T. A. Keinderling, and P. J. Stephens, *ibid.*, **98**, 2715 (1976); C. Marcott, H. A. Habel, J. Overend, and A. Moskowitz, *ibid.*, **100**, 7088 (1978).

(2) For a review see L. D. Barron in "Optical Activity and Chiral Discrimination", S. F. Mason, Ed., D. Reidel Publishing Co., Boston, Mass., pp 219–262, 1979, and reference 4.

(3) L. D. Barron and A. D. Buckingham, *Mol. Phys.*, **20**, 1111 (1971).

(4) L. D. Barron, "Advances in Infrared and Raman Spectroscopy", R. J. H. Clark and R. E. Hester, Eds., Heyden, London, 1978, Chapter 6.

(5) L. D. Barron and A. D. Buckingham, *J. Am. Chem. Soc.*, **96**, 4769 (1974).

(6) A. J. Stone, *Mol. Phys.*, **33**, 293 (1977).

(7) P. L. Prasad and D. F. Burow, *J. Am. Chem. Soc.*, **101**, 800, 806 (1979); P. L. Prasad and L. A. Nafie, *J. Chem. Phys.*, **70**, 5582 (1979).

(8) J. Applequist, *Acc. Chem. Res.*, **10**, 79 (1979).

(9) L. D. Barron and A. D. Buckingham, *J. Am. Chem. Soc.*, **101**, 1979 (1979).

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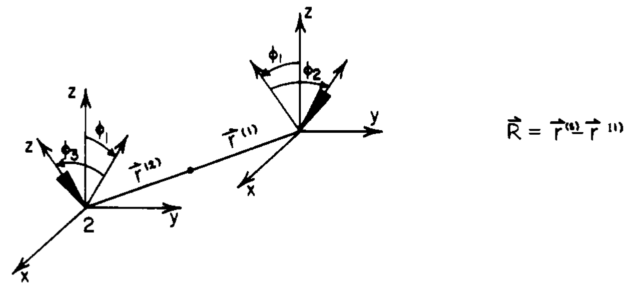

Figure 1. Angles and lengths specifying the relative orientation and separation of the two groups.

derstood to mean in the context of Raman scattering $\partial/\partial Q_\pm$, $\partial/\partial q_1$, and $\partial/\partial q_2$, respectively, and must be chosen appropriately for the two normal modes.

Equations 2a and 2b are similar to those given by Barron and Buckingham[5] in the limit in which $(c_1^\pm, c_2^\pm) = (1/2^{1/2}, \pm 1/2^{1/2})$. In eq 2a,b the components of $\mathbf{G}'$ and $\mathbf{A}$ superscripted with 1 and 2 are defined with respect to origins local to each group. Each of the two local origins is a distance $|r^{(1)}|$ from a common origin, and $\mathbf{r}^{(1)}$ is defined in Figure 1.

Using eq 2 in eq 1 one obtains

$$S_z^{\mathrm{R}} - S_z^{\mathrm{L}} = K + 6L - 2M$$

$$S_z^{\mathrm{R}} - S_x^{\mathrm{L}} = 2K + 7L + M$$

$$S_0^{\mathrm{R}} - S_0^{\mathrm{L}} = 2L - 2M$$

$$S_\pi^{\mathrm{R}} - S_\pi^{\mathrm{L}} = 4K + 12L + 4M$$

$$K^\pm = 4C\omega\epsilon_{\alpha\delta\gamma}\alpha_{\alpha\beta}{}^{(1)}\alpha_{\beta\gamma}{}^{(2)}r_\delta{}^{(1)}c_1{}^\pm c_2{}^\pm$$

$$L^\pm = C(\alpha_{\alpha\beta}{}^{(1)}G'_{\alpha\beta}{}^{(2)} + \alpha_{\alpha\beta}{}^{(2)}G'_{\alpha\beta}{}^{(1)})c_1{}^\pm c_2{}^\pm$$

$$M^\pm = \frac{C\omega}{3}(\alpha_{\alpha\beta}{}^{(1)}A_{\alpha\beta}{}^{(2)} + \alpha_{\alpha\beta}{}^{(2)}A_{\alpha\beta}{}^{(1)})c_1{}^\pm c_2{}^\pm \qquad (3)$$

One should recall that quantities superscripted with (1) or (2) refer to quantities derived with respect to q_1 or q_2, respectively, having made the assumption that $\alpha_{\alpha\beta}{}^{(1)}$ is not a function of q_2 and vice versa. When only two groups couple $c_1{}^+c_2{}^+ + c_1{}^-c_2{}^- = 0$ and therefore $(S^{\mathrm{R}} - S^{\mathrm{L}})^+ = -(S^{\mathrm{R}} - S^{\mathrm{L}})^-$ for all of the cases considered above; i.e., the circular intensity differential spectrum will consist of a couplet whose components are of opposite sign but of equal magnitude. Since, however, the Raman intensity of the two components, i.e., $(S^{\mathrm{R}} + S^{\mathrm{L}})$, will not be equal, the quantity $\Delta = (S^{\mathrm{R}} - S^{\mathrm{L}})/(S^{\mathrm{R}} + S^{\mathrm{L}})$ will, in general, not be of equal magnitude for the two normal vibrations.

When each of the two groups has C_{3v} symmetry or higher, L and M vanish, and if those groups are identical and perfectly coupled, one is left with the result of Buckingham and Barron[5]

$$K^+ = C\omega r_y{}^1\gamma^2 \sin 2\theta = -K^-$$

$$\gamma^{2+} = \gamma^2(5 + 3\cos^2 2\theta)/4$$

$$\gamma^{2-} = 3\gamma^2 \sin^2 \theta/2$$

$$\bar{\alpha}^+ = \sqrt{2}\,\bar{\alpha}$$

$$\bar{\alpha}^- = 0$$

where γ^2 and $\bar{\alpha}$ are the anistropy and trace of $\alpha^{(1)} = \alpha^{(2)}$ and θ is the angle between the C_3 symmetry axes of the two groups defined as positive when the triple vector product, $\mathbf{u}_1 \times \mathbf{u}_2 \cdot \mathbf{R}$, is positive, $\mathbf{u}_{1,2}$ being line segments directed along the C_3 axes of the two groups and $\vec{\mathbf{R}}$ being a vector joining their local origins taken in the sense $\mathbf{R} = \mathbf{r}^{(2)} - \mathbf{r}^{(1)}$. In that limit, $\Delta_z{}^+$, $\Delta_z{}^-$, $\Delta_x{}^-$, and $\Delta_\pi{}^-$ depend only on θ and $r_y{}^1$ while $\Delta_x{}^+$, $\Delta_\pi{}^+$, and $\Delta_0{}^+$ are functions of $\gamma^2/\bar{\alpha}^2$ as well. In that particular limiting case $\mathbf{G}^{(1)}$, $\mathbf{G}^{(2)}$, $\mathbf{A}^{(1)}$, and $\mathbf{A}^{(2)}$ are purely antisymmetric if the origins of the groups are respectively taken to be anywhere on their symmetry axes.

Barron has extended the above model by including a tilt in the orientation of the symmetry axes of the two groups out of the xz plane.[4] This, however, does not generalize the model since one can always find a line joining two lines which is perpendicular to both. Consequently one is able to define a single distance and a single angle in terms of which the CID's may be written (see Appendix).

In the general case of two arbitrary achiral groups, the K contributions in eq 3 arise from the origin-dependent parts of the tensors $\mathbf{G}'$ and $\mathbf{A}$.[10] It contains only components of the derived polarizability which may, in many cases, be deduced from the ordinary Raman spectrum of the molecule and geometric parameters (r_δ). The terms L and M, on the other hand, contain contributions from the tensors $\mathbf{G}'$ and $\mathbf{A}$ belonging to each of the two groups. These are generally not available. However, the comparison of a theoretically derived value of K with an experimentally derived one is possible since K can be found from the measurement of three of the ΔS's given by eq 3. Unfortunately it is only the ΔS_z spectrum which is normally measured. When K is the dominant contribution to the ROA, it should be possible to compute the correct sign and order of magnitude of the CID intensities and hence determine the absolute configuration of a molecule from a ΔS_z spectrum alone.

We will now show that the K contribution will indeed be the largest one in many practical circumstances.

The K contribution arises from the origin-dependent parts (odp) of the tensors $\mathbf{G}$ and $\mathbf{A}$, which themselves arise from the odp of the multipoles $m_\alpha{}^{(1)}$, $\theta_{\alpha\beta}{}^{(1)}$, $m_\alpha{}^{(2)}$, and $\theta_{\alpha\beta}{}^{(2)}$. These are given in ref 4. For $m_\alpha{}^{(1)}$ this odp is

$$(m_\alpha{}^{(1)})_{\mathrm{odp}} = \epsilon_{\alpha\beta\gamma}\sum_k \frac{e_k}{2m_k} r_\beta{}^{(1)} p_{k\gamma}$$

and for $\theta_{\alpha\beta}{}^{(1)}$

$$(\theta_{\alpha\beta}{}^{(1)})_{\mathrm{odp}} = \frac{3}{2}\sum_k e_k(r_{k\alpha}{}^{(0)} r_\beta{}^{(1)} + r_{k\beta}{}^{(0)} r_\alpha{}^{(1)} - {}^1\!/_3 \mathbf{r}_k{}^{(0)} \cdot \mathbf{r}^{(1)} \delta_{\alpha\beta})$$

where $\mathbf{r}_k{}^{(0)}$ is the displacement from the particle i to the origin of group 1; $r^{(1)}$ is defined in Figure 1. The contributions L and M arise from an expression similar to those above but using the origin of the group itself. For $m_\alpha{}^{(1)}$, it is

$$(m_\alpha{}^{(1)})_0 = \sum_k \frac{e_k}{2m_k}(\epsilon_{\alpha\beta\gamma} r_{k\beta}{}^{(0)} p_{k\gamma} + g_k s_{k\alpha})$$

and for $\theta_{\alpha\beta}{}^{(1)}$

$$(\theta_{\alpha\beta}{}^{(1)})_0 = \frac{1}{2}\sum_k e_k(3r_{k\alpha}{}^{(0)} r_{k\beta}{}^{(0)} - (r_k{}^{(0)})^2 \delta_{\alpha\beta})$$

g is the gyromagnetic ratio and $s_{k\alpha}$ is the spin operator on particle k.

Note, again, that these equations are similar to the preceding ones, except that $r_k{}^{(0)}$ replaces $r^{(1)}$. Therefore one may ignore the L and M contributions when the dimensions of the individual groups are small with respect to the distance between them. When such is the case, all three CID components, $S_z{}^{\mathrm{R}} - S_z{}^{\mathrm{L}}$, $S_x{}^{\mathrm{R}} - S_x{}^{\mathrm{L}}$, and $S_\pi{}^{\mathrm{R}} - S_\pi{}^{\mathrm{L}}$, are expected to yield the same information, although with different absolute magnitudes, while $S_0{}^{\mathrm{R}} - S_0{}^{\mathrm{L}}$ will be effectively zero. Except for certain accidental relative orientations of the two groups in which the origin-dependent contribution to K becomes small, the above argument applies directly only to *Rayleigh* scattering and it is not immediately obvious that it should also hold for Raman scattering where $G'_{\alpha\beta}$ stands for terms such as $(\partial G'_{\alpha\beta}/\partial \mathrm{q})$. With the assumption however, that $G'_{\alpha\beta}$ is not a slowly varying function of q, then the maximum value reached by $(G'_{\alpha\beta})_{\mathrm{odp}}$ will, according to the previous argument, handily exceed the maxima reached by $(G'_{\alpha\beta})_{\mathrm{intrinsic}}$. Hence $(\mathrm{G}'_{\alpha\beta}/\partial\mathrm{q})_{\mathrm{odp}}$ will, in general, be larger than the intrinsic contributions except near maxima and minima of $(G'_{\alpha\beta})_{\mathrm{odp}}$.

We will henceforth restrict ourselves to the case where the odp contributions dominate and derive an expression for the quantity

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(10) A. D. Buckingham and H. C. Longuet-Higgins, *Mol. Phys.*, **14**, 63 (1968).

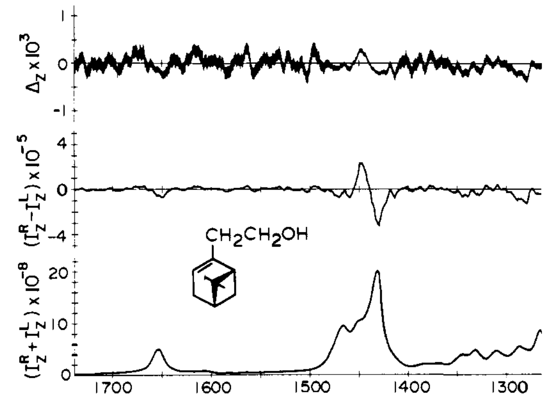

Figure 2. ROA spectrum of (−)-nopol.

K in terms of the three angles specifying the relative orientations of the two groups, the distance between them, and components of the tensor $\alpha^{(1)}$ in the molecule-fixed frame of the group in which it is diagonal. Making reference to Figure 1, one defines the three angles ϕ_1, ϕ_2, and ϕ_3 as follows.

One begins with two identical, space-fixed, coordinate systems fixed on each of the two groups. These are called xyz. Suppose the two molecule-fixed coordinate axes in which the two groups individually yield diagonal-derived polarizability tensors are labeled $x_1y_1z_1$ and $x_2y_2z_2$; then rotation of group 1 about its local y axis through ϕ_1 transforms the local x axis into x_1. A second rotation about the x_1 axis through an angle ϕ_2 brings group 1 into its final position. The same procedure is followed with group 2 but using ϕ_1 and ϕ_3 (in place of ϕ_2). The sign convention used to define a positive sense of rotation and the positive direction of directed line segments may be deduced from Figure 1.

The components of $\alpha^{(1)}$ in the frame xyz which will be called $\alpha^{(1)\prime}$ are

$$\alpha_{xx}' = \alpha_{xx} + (\alpha_{zz} - \alpha_{xx}) \sin^2 \phi_1 + (\alpha_{yy} - \alpha_{zz}) \sin^2 \phi_1 \sin^2 \phi_2$$

$$\alpha_{yy}' = \alpha_{xx} + (\alpha_{zz} - \alpha_{xx}) + (\alpha_{yy} - \alpha_{zz}) \cos^2 \phi_2$$

$$\alpha_{zz}' = \alpha_{xx} + (\alpha_{zz} - \alpha_{xx}) \cos^2 \phi_1 + (\alpha_{yy} - \alpha_{zz}) \cos^2 \phi_1 \sin^2 \phi_2$$

$$\alpha_{xy}' = -(\alpha_{yy} - \alpha_{zz}) \cos \phi_2 \sin \phi_1 \sin \phi_2$$

$$\alpha_{xz}' = (\alpha_{zz} - \alpha_{xx} + (\alpha_{yy} - \alpha_{zz}) \sin^2 \phi_2) \sin \phi_1 \cos \phi_1$$

$$\alpha_{yz}' = -(\alpha_{yy} - \alpha_{zz}) \sin \phi_2 \cos \phi_2 \cos \phi_1 \tag{4}$$

The components of $\alpha^{(2)\prime}$ are related to those of $\alpha^{(2)}$ by using expressions similar to eq 4 but with $-\phi_1$ and $-\phi_3$ in place of ϕ_1 and ϕ_2. Equation 4 and its analogue for $\alpha^{(2)\prime}$ may then be entered into the expression for K of eq 3 in order to determine the origin-dependent contribution to the CID's $S_z^R - S_z^L$ etc.

Then K^+ and K^- can be obtained in closed form as

$$K^+ = -K^- = 4\pi Cc(\alpha_{yy} - \alpha_{zz})^2[\zeta + \eta + \zeta]C_1^+C_2^+$$

$$\zeta = +\frac{R_x}{\lambda} \cos \phi_1[\tau \sin^2 \phi_1(\sin 2\phi_2 + \sin 2\phi_3) + \sin (\phi_2 + \phi_3)(\cos \phi_2 \cos \phi_3 - \cos 2\phi_1 \sin \phi_2 \sin \phi_3)]$$

$$\eta = \frac{-R_y}{\lambda} \sin 2\phi_1[(\tau + \sin^2 \phi_2) \times (\tau + \sin^2 \phi_3) \cos 2\phi_1 - \tfrac{1}{4}(\sin 2\phi_2 - \sin 2\phi_3)]$$

$$\xi = \frac{-R_z}{\lambda} \sin \phi_1[\tau \cos^2 \phi_1(\sin 2\phi_2 - \sin 2\phi_3) + \tfrac{1}{2} \sin 2(\phi_3 - \phi_2)]$$

$$\tau = (\alpha_{zz} - \alpha_{xx})/(\alpha_{yy} - \alpha_{zz}) \tag{5}$$

In order to determine the CID associated with either Q_+ or Q_-, one need know only the geometrical parameters ϕ_1, ϕ_2, ϕ_3, and $|\vec{R}|$ and the quantities τ and $(\alpha_{yy} - \alpha_{zz})$. We will now show that for Δ_z^-, i.e., the ratio $(S_z^R - S_z^L)/(S_z^R + S_z^L)$ associated with Q_-, the last quantity need not be known, so that there remains only one quantity, τ, derived from the polarizability of the vibrating group, which must be determined.

Using eq 4 in eq 2a, one finds that

$$\alpha_{xx}^- = \frac{1}{\sqrt{2}}(\alpha_{yy} - \alpha_{zz}) \sin^2 \phi_1(\sin^2 \phi_2 - \sin^2 \phi_3)$$

$$\alpha_{yy}^- = \frac{1}{\sqrt{2}}(\alpha_{yy} - \alpha_{zz})(\cos^2 \phi_2 - \cos^2 \phi_3)$$

$$\alpha_{zz}^- = \frac{1}{\sqrt{2}}(\alpha_{yy} - \alpha_{zz}) \cos^2 \phi_1(\sin^2 \phi_2 - \sin^2 \phi_3)$$

$$\alpha_{xy}^- = \frac{-1}{\sqrt{2}}(\alpha_{yy} - \alpha_{zz}) \sin \phi_1(\sin 2\phi_2 - \sin 2\phi_3)$$

$$\alpha_{yz}^- = \frac{-1}{2\sqrt{2}}(\alpha_{yy} - \alpha_{zz}) \cos \phi_1(\sin 2\phi_2 + \sin 2\phi_3)$$

$$\alpha_{zx}^- = \frac{1}{\sqrt{2}}(\alpha_{yy} - \alpha_{zz})[\tau + \tfrac{1}{2}(\sin^2 \phi_2 + \sin^2 \phi_3)] \sin 2\phi_1 \tag{6}$$

where τ is as in eq 5.

The quantity $(S_z^R + S_z^L)^-$ may be formed by using the quantities defined in eq 6 and the appropriate member of eq 1. In the special case in which $\phi_2 = \phi_3$, $(\gamma^2)^-$ takes on the simple form

$$(\gamma^2)^- = 6(\alpha_{yy} - \alpha_{zz})^2 \cos^2 \phi_1[(\tau + \sin^2 \phi_2)^2 \sin^2 \phi_1 - \tfrac{1}{4} \sin^2 2\phi_2] \tag{7}$$

The components of α^+ analogous to those of α^- given in (6) are rather more complicated. They are not needed, however, since

$$\text{trace}(\alpha^+) = \sqrt{2}\,\text{trace}(\alpha)$$

$$(\gamma^2)^+ = 2\gamma^2 - (\gamma^2)^- \tag{8}$$

where γ^{2+}, γ^{2-}, and γ^2 are the anisotropics of the tensors α^+, α^-, and α.

It is clear, therefore, that the quantity $(\alpha_{yy} - \alpha_{zz})^2$ cancels out in forming Δ_z^-. The quantity τ, moreover, may be determined from the ratio $(\gamma^2)^+/(\gamma^2)^-$ which, in turn, may be obtained from the depolarized spectrum of the molecule. Determining the angles ϕ_1, ϕ_2, and ϕ_3 requires knowledge of the molecular geometry and in addition the orientation of the frame in which α is diagonal. The latter may be a problem in the case of groups with local C_s symmetry. Most substituents, however, contain sufficient symmetry to allow this special frame to be determined by inspection or, for nontotally symmetric vibrations (locally), by performing a simple similarity transformation.

The above equations will now be applied to the scissoring vibrations of two coupled methylene groups. Brocki et al.[11] have recently shown that a negative–positive couplet was a persistent feature in the methylene deformation region of the ROA spectrum of a series of chiral terpenes. An example is shown in Figure 2. Four of the terpenes considered by those authors contained only two methylene groups. We will assume, as have Brocki et al.,[11] that the couplet originates primarily from the coupling of the two methylenes. This assumption is not entirely without question since the molecules contain several methyl groups in addition to the two methylenes. We will suppose, however, that the coupling with the methyl groups is considerably weaker since the two methylenes form part of a rigid ring while the methyl groups are situated on substituents and are more distant.

The structures of the four terpenes considered, (+)-α-pinene, (−)-myrtenol, (−)-nopol, and (−)-myrtenal, are given in Table I. Using a commercial molecular model with C—C and C═C bond lengths of 1.54 and 1.34 Å, respectively, and assuming the four

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[11] T. Brocki, M. Moskovits, and B. Bosnich, *J. Am. Chem. Soc.*, in press.

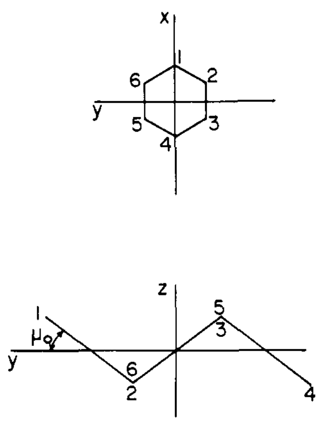
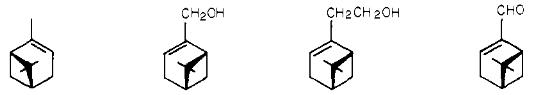


Figure 3. Axis convention and atomic numbering for cyclohexane.

Table I. Summary of Observed and Calculated ROA Results

(+)-α-pinene (−)-myrtenol (−)-nopol (−)-myrtenal



A B C D

	A	B	C	D
ν^-, cm^{-1}	1434	1434	1434	1419
ν^+, cm^{-1}	1446	1455	1450	1449
I^+/I^-(exptl)	0.76	0.76	0.47	0.42
I^+/I^-(calcd)[a]	0.61	0.61	0.61	0.61
$10^4\Delta_z^-$(exptl)[b]	+1.1	−1.25	−1.25	−1.5
$10^4\Delta_z^-$(theor)[c]	+1.15	−1.15	−1.15	−1.15
$10^4\Delta_z^-$(theor)[d]	+1.40	−1.40	−1.40	−1.40
$10^4\Delta_z^-$(theor)[e]	+0.90	−0.90	−0.90	−0.90

[a] Using eq 6 and 1 and $\tau = 1.90$. [b] In order to minimize the effect of experimental error, we calculated this quantity from the average of $(S_z^R - S_z^L)^+$ and $(S_z^R - S_z^L)^-$, keeping, of course, the appropriate sign. Data are from ref 11. [c] Calculated with eq 5 using $\tau = 1.90$. [d] With $\tau = 1.40$. [e] With $\tau = 2.69$.

Table II. Summary of Assignments for the Methylene Scissoring Modes in Cyclohexane

	δ(CH_2)				
A_{1g}[a](R)	1443	1465	1451	1465	1465
E_u			1457		
E_g(R)	1443	1443	1443	1444	1443
A_{2u}			1451		1449
ref	12	13	14	15	16

[a] Frequencies are in cm^{-1}; (R) indicates Raman active.

carbons on the cyclohexene ring which are not part of the double bond to lie in a plane, one finds that for those four compounds $\phi_1 = -59°$, $\phi_2 = -16°$, and $\phi_3 = +85°$ while $R_x = -2.495$ Å, $R_y = +0.95$ Å, and $R_z = -0.29$ Å. If one chooses axis as defined in Figure 4, these quantities can now be used in eq 5 and 1 to obtain Δ_z^- if τ were known. Because of overlap with other bands in this region, a precise value of τ is difficult to obtain from the depolarized Raman spectrum of the four terpenes reported by Brocki et al.[11] To decide which of the above four values most reasonably represents the case where only methylenes couple, we calculated a value of τ from the spectrum of cyclohexane liquid.

The Raman spectrum of cyclohexane has been reported by several authors,[12-16] and their assignments in the CH_2 deformation region are summarized in Table II. The symmetry of the molecule is D_{3d} with A_{1g} and E_g Raman active. Their normal modes may be written as follows, assuming the methylenes couple only with one another and not with any other groups within the molecule

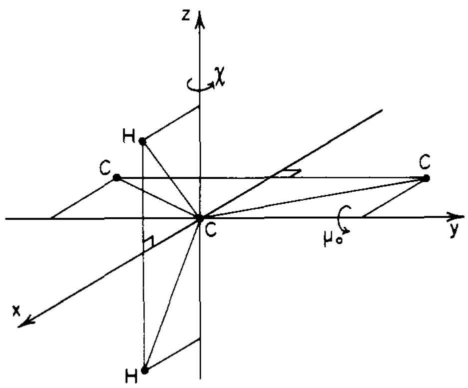


Figure 4. Axis convention for methylene.

$$Q_{A_{1g}} = \frac{1}{\sqrt{6}}(1, 1, 1, 1, 1, 1)$$

$$Q_{E_g^a} = \frac{1}{2\sqrt{3}}(2, -1, -1, 2, -1, -1)$$

$$Q_{E_g^b} = \tfrac{1}{2}(0, 1, -1, 0, 1, -1) \tag{9}$$

in which the vector components refer to the motion of the individual methylene groups. In turn, the components of the derived polarizability tensor of the *n*th methylene group written in a common frame are as

$$\alpha_{xx}^n = \alpha_{yy} + (\alpha_{xx} - \alpha_{zz}) \cos^2\theta \cos^2\mu + (\alpha_{zz} - \alpha_{yy}) \cos^2\theta$$

$$\alpha_{yy}^n = \alpha_{yy} + (\alpha_{xx} - \alpha_{zz}) \sin^2\theta \cos^2\mu + (\alpha_{zz} - \alpha_{yy}) \sin^2\theta$$

$$\alpha_{zz}^n = \alpha_{yy} + (\alpha_{xx} - \alpha_{zz}) \sin^2\mu + (\alpha_{zz} - \alpha_{yy})$$

$$\alpha_{xy}^n = \sin\theta \cos\theta[(\alpha_{xx} - \alpha_{zz}) \cos^2\mu + (\alpha_{zz} - \alpha_{yy})]$$

$$\alpha_{yz}^n = -\sin\theta \sin\mu \cos\mu(\alpha_{xx} - \alpha_{zz})$$

$$\alpha_{zx}^n = -\cos\theta \sin\mu \cos\mu(\alpha_{xx} - \alpha_{zz}) \tag{10}$$

using the numbering and coordinate systems shown in Figures 3 and 4. The values of θ are 0, $\pi/3$, and $-\pi/3$ for methylenes 1, 2, and 6, respectively, while those of μ are μ_0, $-\mu_0$, and $-\mu_0$ in the same order where μ_0, defined in Figure 3, is related to the C–C–C angle, χ, in cyclohexane through the expression

$$\tan^2 2\mu_0 = (1 - \cos^2\chi - \sin^2\chi/2)/\cos^2\chi$$

The value of χ found for alkane[17,18] averages around 112°; hence μ_0 is approximately 24°.

The values of $\alpha_{\alpha\beta}^n$ for carbons 3, 4, and 5 are equal to those of 6, 1, and 2, respectively, for reasons of symmetry, and the polarizability components on the right-hand side of eq 10 refer to the derived polarizability for the scissoring motion of a methylene group defined for the coordinate frame shown in Figure 4 in which the tensor is diagonal.

With eq 9 and 10 and the definition of γ^2 in eq 1, one obtains

$$\gamma_{A_{1g}}^2 = \tfrac{3}{2}(\alpha_{yy} - \alpha_{zz})^2[\tau(3\cos^2\mu_0 - 2) - 1]^2$$

$$\gamma_{E_g}^2 = \tfrac{9}{4}(\alpha_{yy} - \alpha_{zz})^2[(\tau\cos^2\mu_0 + 1)^2 + \tau^2\sin^2 2\mu_0] \tag{11}$$

and $\bar{\alpha}_{A_{1g}} = (1/6^{1/2})\bar{\alpha}$ while $\bar{\alpha}_{E_g} = 0$.

It is evident from Table 2 that while there is no doubt in the assignment of the E_g vibration, different authors assign A_{1g} differently. We choose Miller, Snyder, and Forel's assignment as

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(17) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

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it relies on polarization measurements. Snyder[15] gives quantitative measurements for $\gamma_{A_{1g}}^2$ and $\gamma_{E_g}^2$ which are 0.018 and 2.264 Å^4 amu^{-1}, respectively, from which one calculates (with eq 11) two values of τ: 2.69 and 1.40. These values of τ yield, using eq 6, the ratios 0.64 and 0.57 for I^+/I^-. By comparing these ratios with the experimental ones measured on the four terpenes (cf. Table I), we conclude that the lower frequency corresponds to the asymmetric vibration Q^-. These values of τ also yield values of Δ_z^- for (+)-α-pinene of $+1.40 \times 10^{-4}$ and $+0.90 \times 10^{-4}$, respectively, values that straddle the experimentally determined value of $(+1.1 \times 10^{-4})\gamma^2$ values of highly polarized bands are generally too high, however, as a result of errors introduced by collisional effects and by the finite angle over which the scattered light is gathered. As $\gamma_{A_{1g}}^2$ decreases, the two values of τ which eq 11 produces approach one another until, in the limit of $\gamma_{A_{1g}}^2 = 0$, τ has only a single value of 1.90. With this value one calculates Δ_z^- for (+)α-pinene to be $+1.15 \times 10^{-4}$, close to the experimental value. These data are summarized in Table I.

As is evident from the table, the equations derived above for the two-group model reproduce acceptably the magnitude and signs of the Δ_z's associated with what was assigned as the in-phase and out-of-phase coupled methylene scissoring vibrations in the four terpenes shown in Table I. As such, this constitutes a determination by Raman optical activity of the absolute configuration of those molecules.

Generalizing the model to include more than two groups would enable one to calculate the Raman and Raman CD intensities of any normal vibration of a molecule, and we are currently engaged in its solution. One looks forward to the day when the entire stereochemistry of a molecule with a given configuration may be solved by ROA, provided of course that equal advances are made in the field of vibrational assignments.

Acknowledgment. The authors are indebted to the Natural Sciences and Engineering Council of Canada, the Atkinson Foundation, and the University of Toronto for financial support. We also wish to thank Dr. L. D. Barron for transmitting to us several manuscripts before their publication.

Appendix

We wish to demonstrate that Barron's modified two-group model[4] may be written in terms of a single angle and a single distance and is therefore not physically different from the model proposed by the authors in ref 5.

Define $\mathbf{u}_1$ and $\mathbf{u}_2$ as unit vectors along the main axes of the two groups of ref 5. If $\mathbf{R}_{12}$ is a vector of magnitude R_{12} directed along a line joining the origins of the two groups, one can show that the quantities $\cos\theta$ and $R_{12}\sin\theta$, in terms of which all the pertinent quantities Δ_x^+, Δ_x^-, Δ_z^+, and Δ_z^- of ref 5 are defined, may be written as

$$\cos\theta = \mathbf{u}_1 \cdot \mathbf{u}_2$$

$$R_{12}\sin\theta = \mathbf{u}_1 \times \mathbf{u}_2 \cdot \mathbf{R}_{12}$$

If one now tilts group 1 through δ_1 and group 2 through δ_2 out of the x–z plane, then $\mathbf{u}_1$ and $\mathbf{u}_2$ become

$$\mathbf{u}_1 = (0, \sin\delta_1, \cos\delta_1)$$

$$\mathbf{u}_2 = (-\sin\theta\cos\delta_2, -\sin\delta_2, \cos\theta\cos\delta_2)$$

(assuming $\mathbf{u}_1$ was originally along the x axis). $\mathbf{R}_{12} = (0, -R_{12}, 0)$. The inner and vector-triple products now become

$$\mathbf{u}_1 \cdot \mathbf{u}_2 = \cos\theta\cos\delta_1\cos\delta_2 - \sin\delta_1\sin\delta_2$$

$$(\mathbf{u}_1 \times \mathbf{u}_2 \cdot \mathbf{R}_{12}) = R_{12}\sin\theta\cos\delta_1\cos\delta_2$$

When these quantities are now used in place of $\cos\theta$ and $R_{12}\sin\theta$ in the equations of ref 5, one obtains the new equations of reference 4. In other words, one may define a new angle θ' and a new distance R'_{12} such that

$$\cos\theta\cos\delta_1\cos\delta_2 - \sin\delta_1\sin\delta_2 = \cos\theta'$$

and

$$R_{12}\sin\theta\cos\delta_1\cos\delta_2 = R'_{12}\sin\theta'$$

in terms of which all the ROA of the modified, two-group model of reference 4 may be written.

Tungsten-183 NMR and X-ray Study of a Heteropolyanion $[As_2W_{21}O_{69}(H_2O)]^{6-}$ Exhibiting a Rare Square-Pyramidal Environment for Some Tungsten(VI)

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Received July 31, 1980

Abstract: The compound $H_2Rb_4[As_2W_{21}O_{69}(H_2O)]\cdot 34H_2O$ was synthesized and its crystal structure determined. It crystallizes in the hexagonal space group $P6_3/mmc$; the lattice constants are as follows: $a = b = 16.926$ (7) Å, $c = 18.767$ (8) Å; $Z = 2$. The structure has been refined by full-matrix least squares to a final R factor of 0.059 for 1572 reflections collected at room temperature. As confirmed by the ^{183}W NMR study, the $[As_2W_{21}O_{69}(H_2O)]^{6-}$ heteropolyanion is made of two AsW_9O_{33} units, joined together in an asymmetrical way by three tungsten atoms among which one is octahedrally surrounded and two are in a square-pyramidal environment.

Some structures of heteropolyanions with As(III) as a heteroatom have been recently published: $(NH_4)_7[H_2AsW_{18}O_{60}]\cdot 16H_2O$[1] and $(NH_4)_{23}[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]\cdot nH_2O$.[2]

These two structures contain the AsW_9O_{33} unit derived from the Keggin structure[3] by removing a W_3O_{13} group. The lone pair of arsenic(III) points toward the outside of the shell made by the nine-linked WO_6 octahedra. It prevents this unit from catching a fourth W_3O_{13} group to give a Keggin heteropolyanion or to

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