

Raman Optical Activity of Camphor and Related Molecules

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Raman circular intensity differential spectra between 80 and 2 000 cm^{-1} of (+)-camphor, (+)-3-bromocamphor, (-)-3-bromocamphor-9-sulphonic acid, (+)-3-chlorocamphor, (-)-bornan-2-*endo*-ol, (-)-bornan-2-*exo*-ol, and (+)-3-methylcyclohexanone are presented. Several correlations are pointed out, including large conservative couplets at *ca.* 500 cm^{-1} that might originate in in-plane and out-of-plane carbonyl deformations. It is demonstrated that the conservative couplets which often dominate Raman optical activity spectra originate in coupling of two vibrational modes of appropriate symmetry through a chiral distortion of the molecular framework.

It is now possible to obtain vibrational optical activity spectra by means of two complementary techniques: infrared circular dichroism (c.d.), which measures a small difference in the absorption of right and left circularly polarized infrared radiation;¹⁻³ and Raman circular intensity differential (c.i.d.), which measures a small difference in the intensity of vibrational Raman scattering in right and left circularly polarized incident light.⁴⁻⁶ Vibrational optical activity is expected to be a powerful new means of determining stereochemistry (conformation and absolute configuration) in chiral molecules since, unlike electronic optical rotatory dispersion and circular dichroism, which only provide stereochemical information about chromophoric groups and their immediate intramolecular environment, every part of a molecule can contribute to a vibrational optical activity spectrum. On account of technical difficulties, the spectral region at wavenumbers below *ca.* 2 000 cm^{-1} is inaccessible to i.r. c.d. at present and most studies have involved carbon-hydrogen stretching modes.³ On the other hand, although the complete vibrational spectrum is accessible to the Raman c.i.d. technique, only the region from *ca.* 80 to 2 000 cm^{-1} is studied routinely at present because the modes that occur there (deformations in particular) can show Raman c.i.d. effects much larger than are found for the exclusively stretching modes that occur above *ca.* 2 000 cm^{-1} . Furthermore, unlike the situation in conventional vibrational spectroscopy, vibrational optical activity in deformation modes appears to

be easier to interpret than in stretching modes since lower-order mechanisms are involved.

At this early stage in the development of the subject it is of interest to compare the Raman c.i.d. spectra of series of molecules with similar structural features to see what common effects emerge. In this article the Raman c.i.d. spectra of camphor and related molecules are compared, and several strong correlations are pointed out, although the speculations as to the origin of some may prove incorrect as more data become available.

EXPERIMENTAL

A Raman c.i.d. instrument similar to that described previously⁶ was used, except that a more powerful laser (Spectra-Physics 171-03) was employed. An appropriate experimental quantity is the dimensionless $\Delta = (I_{\alpha}^R - I_{\alpha}^L) / (I_{\alpha}^R + I_{\alpha}^L)$, where I_{α}^R and I_{α}^L are the scattered intensities with α -polarization in right and left circularly polarized incident light. However, it is best to present $I_{\alpha}^R - I_{\alpha}^L$ and $I_{\alpha}^R + I_{\alpha}^L$ separately because the background must be subtracted from $I_{\alpha}^R + I_{\alpha}^L$ before calculation of Δ . Another reason, as shown below, is that equal and opposite $I_{\alpha}^R - I_{\alpha}^L$ values in adjacent bands indicate that the corresponding modes are coupled through a vibrational perturbation originating in skeletal distortions; this diagnostic feature is lost if the Δ values are presented directly, because the Δ values in two such bands are usually very different on account of different $I_{\alpha}^R + I_{\alpha}^L$ values. For reasons discussed previously,^{4,6} only the depolarized components ($\alpha = z$) were sampled.

⁴ L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *J. Amer. Chem. Soc.*, 1973, **95**, 603.

⁵ W. Hug, S. Kint, G. F. Bailey, and J. R. Scherer, *J. Amer. Chem. Soc.*, 1975, **97**, 5589.

⁶ L. D. Barron and A. D. Buckingham, *Ann. Rev. Phys. Chem.*, 1975, **26**, 381.

¹ E. C. Hsu and G. Holzwarth, *J. Chem. Phys.*, 1973, **59**, 4678.

² G. Holzwarth, E. C. Hsu, H. S. Mosher, T. R. Faulkner, and A. Moscovitz, *J. Amer. Chem. Soc.*, 1974, **96**, 251.

³ L. A. Nafie, T. A. Kiederling, and P. J. Stephens, *J. Amer. Chem. Soc.*, 1976, **98**, 2715.

The $I_z^R + I_z^L$ spectra are presented on a linear scale, whereas the $I_z^R - I_z^L$ spectra are presented on a scale that is linear within each decade range, but logarithmic between decade ranges. This enables the exponent in the $I_z^R - I_z^L$ photon count to be recorded, although the spectrum takes on a 'stretched out' appearance in which the statistical noise level appears to be much greater than it really is since, on all but the weakest bands, only values within the

of 10 cm^{-1} at a scan speed of $1 \text{ cm}^{-1} \text{ min}^{-1}$ by using a 3.5 W argon-ion laser beam of $\lambda 488 \text{ nm}$ focused into samples that were either near-saturated solutions or neat liquids.

DISCUSSION

Figures 1—6 show the depolarized Raman circular intensity sum and difference spectra of, respectively,

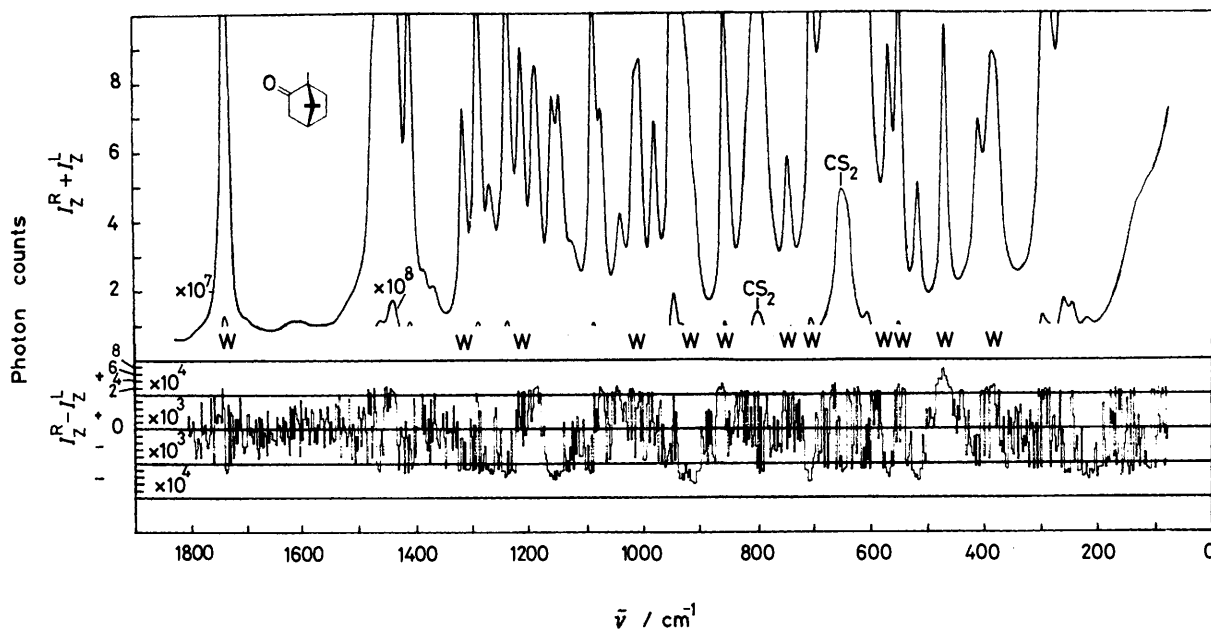


FIGURE 1 Depolarized Raman circular intensity sum ($I_z^R + I_z^L$) and difference ($I_z^R - I_z^L$) spectra of (+)-camphor in carbon disulphide

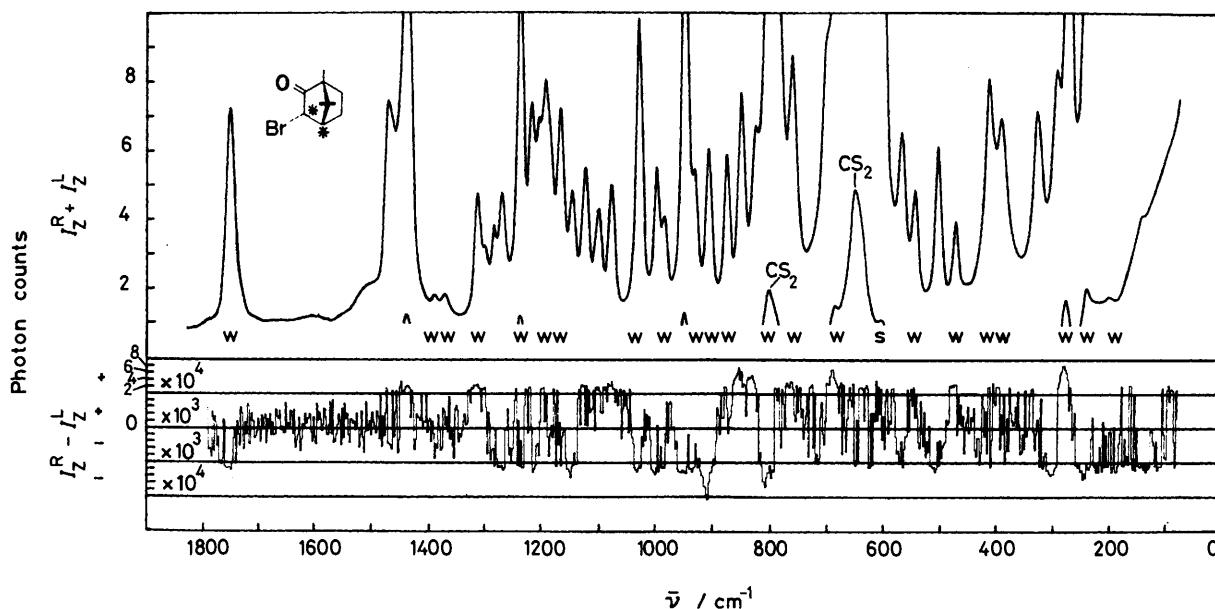


FIGURE 2 Depolarized Raman circular intensity sum and difference spectra of (+)-3-bromocamphor in carbon disulphide

$\pm 10^4$ range are significant. S and W indicate strongly and weakly polarized bands; all other bands are effectively depolarized. All the spectra were recorded with a resolution

(+)-camphor in carbon disulphide, (+)-3-bromocamphor in carbon disulphide, (-)-3-bromocamphor-9-sulphonic acid in water, (+)-3-chlorocamphor in carbon disulphide,

(-)-bornan-2-*endo*-ol in methanol, and (-)-bornan-2-*exo*-ol in methanol. Figure 7 shows the corresponding spectra of neat (+)-3-methylcyclohexanone (for reference).

c.i.d. effects (a normal co-ordinate analysis of camphor⁷ indicates that carbonyl deformations contribute mainly to modes at higher frequency). The corresponding

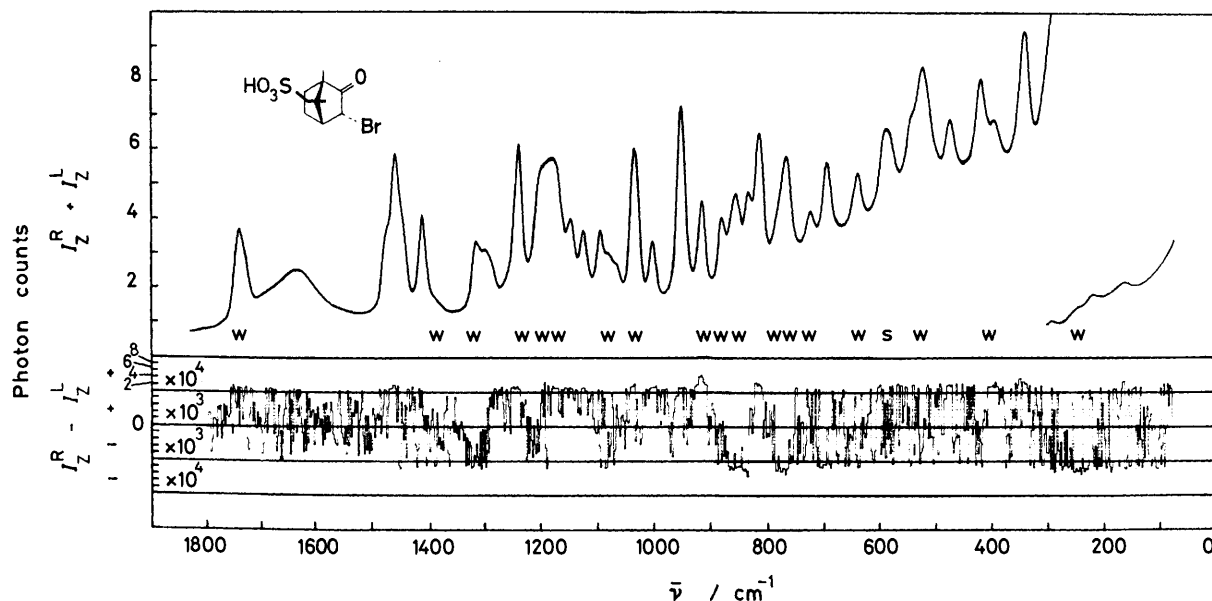


FIGURE 3 Depolarized Raman circular intensity sum and difference spectra of (-)-3-bromocamphor-9-sulphonic acid in water

The most striking feature in the camphor spectrum is the large conservative c.i.d. couplet centred at *ca.* 500 cm^{-1} , associated with two Raman bands of very different intensity. A similar feature occurs in the same region

feature in the spectrum of bromocamphor is much weaker, and in that of chlorocamphor it is barely discernible: possibly the halogen bonded to the carbon adjacent to the carbonyl tends to 'damp' the carbonyl deformations.

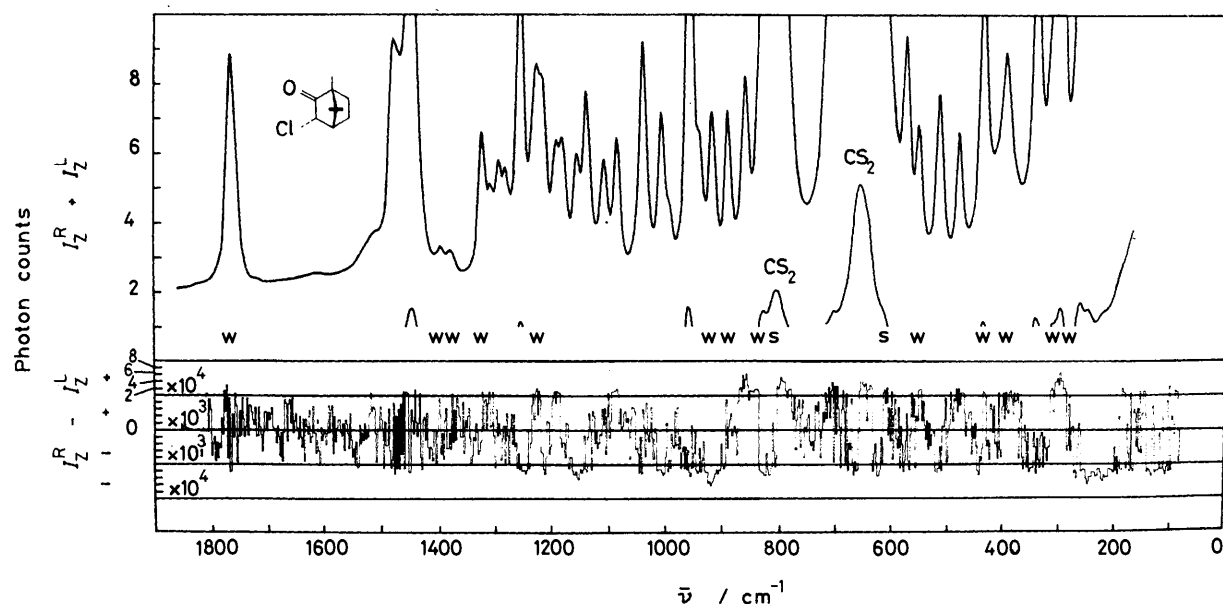


FIGURE 4 Depolarized Raman circular intensity sum and difference spectra of (+)-3-chlorocamphor in carbon disulphide

in the spectrum of 3-methylcyclohexanone. It is possible that these couplets originate in the in-plane and out-of-plane deformations of the carbonyl group since, as shown below, the coupling of these modes through a chiral distortion of the skeleton would produce equal and opposite

Large c.i.d. features centred at *ca.* 280 and 820 cm^{-1} appear in the spectra of bromocamphor and chlorocamphor that are not present in that of camphor itself.

⁷ R. T. Klingbiel and H. Eyring, *J. Phys. Chem.*, 1970, **74**, 4543.

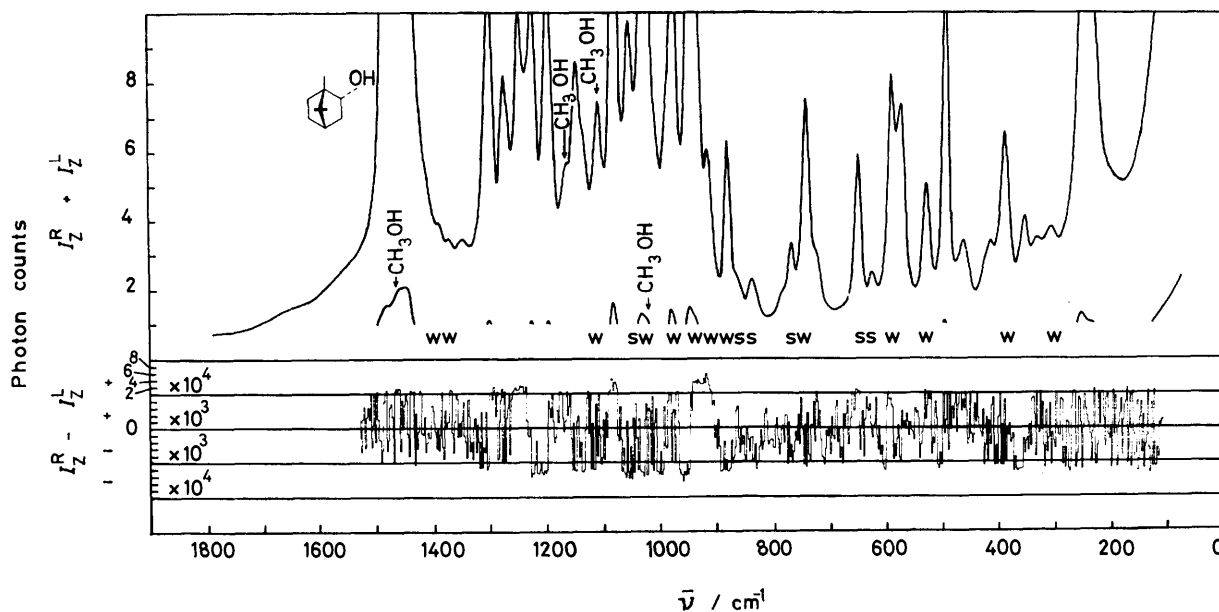


FIGURE 5 Depolarized Raman circular intensity sum and difference spectra of (-)-bornan-2-endo-ol in methanol

The new low-frequency c.i.d. effects almost certainly originate in carbon-bromine deformations, but the origin of the new high-frequency c.i.d. features is not clear.

(-)-3-Bromocamphor-9-sulphonic acid and (+)-3-bromocamphor have very similar c.i.d. spectra between

the appropriate parts of suitable molecules.⁸ Also (+)-3-chlorocamphor shows c.i.d. features in this region almost identical with those in the spectrum of (+)-3-bromocamphor.

No large c.i.d. effects appear in the spectra of the

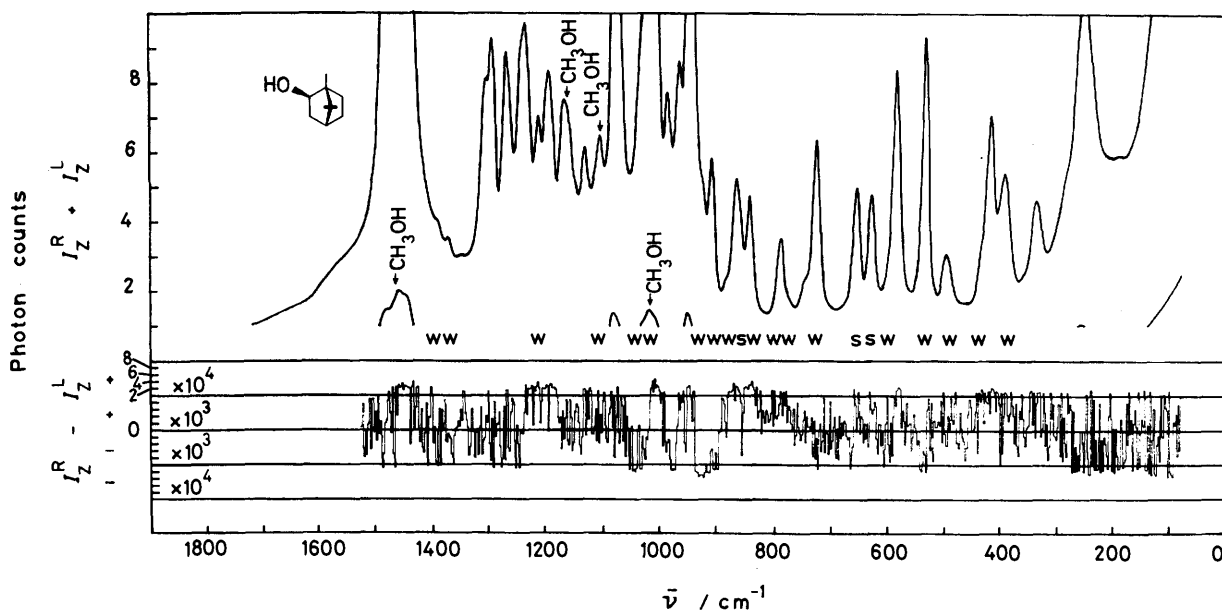


FIGURE 6 Depolarized Raman circular intensity sum and difference spectra of (-)-bornan-2-exo-ol in methanol

ca. 700 and 950 cm^{-1} , except that the signs are reversed, since these particular isomers have opposite absolute configurations in the structural units that are common to both. This particular comparison has been reported previously as an example of how Raman optical activity can correlate absolute configurations by directly probing

(-)-bornan-2-ols below *ca.* 800 cm^{-1} , which is consistent with the absence of a carbonyl group. Both molecules show a couplet centred at *ca.* 900 cm^{-1} (overlapping slightly with a couplet of opposite sign at higher frequency)

⁸ L. D. Barron and A. D. Buckingham, *J.C.S. Chem. Comm.*, 1974, p. 1028.

which invites comparison with couplets at similar frequency in the spectra of camphor, bromocamphor, bromocamphorsulphonic acid, and chlorocamphor. Since methyl rocking and C-C(H₃) stretching frequencies can occur in this region,⁹ one stereochemical feature consistent with the relative signs of these c.i.d. effects is the presence of a substituent on a secondary bridge adjacent to the bridgehead methyl group, which results in the latter being no longer symmetrically disposed relative to the geminal dimethyl group. But another possibility is that these couplets originate in modes of the two methylene groups in the unsubstituted

bon atom attached to OH, together with O-H deformations.

Large conservative Raman c.i.d. couplets have been reported in methyl asymmetric deformation modes at *ca.* 1450 cm⁻¹ in molecules such as 1-phenylethylamine.^{5,12} These couplets originate in the lifting of the degeneracy of the methyl asymmetric deformations on attachment of the methyl group to a structure of lower symmetry: the mechanism appears to require a chiral distortion of the carbon tetrahedron of the methyl group brought about through interactions with three other groups of very different effective volume attached to the asymmetric

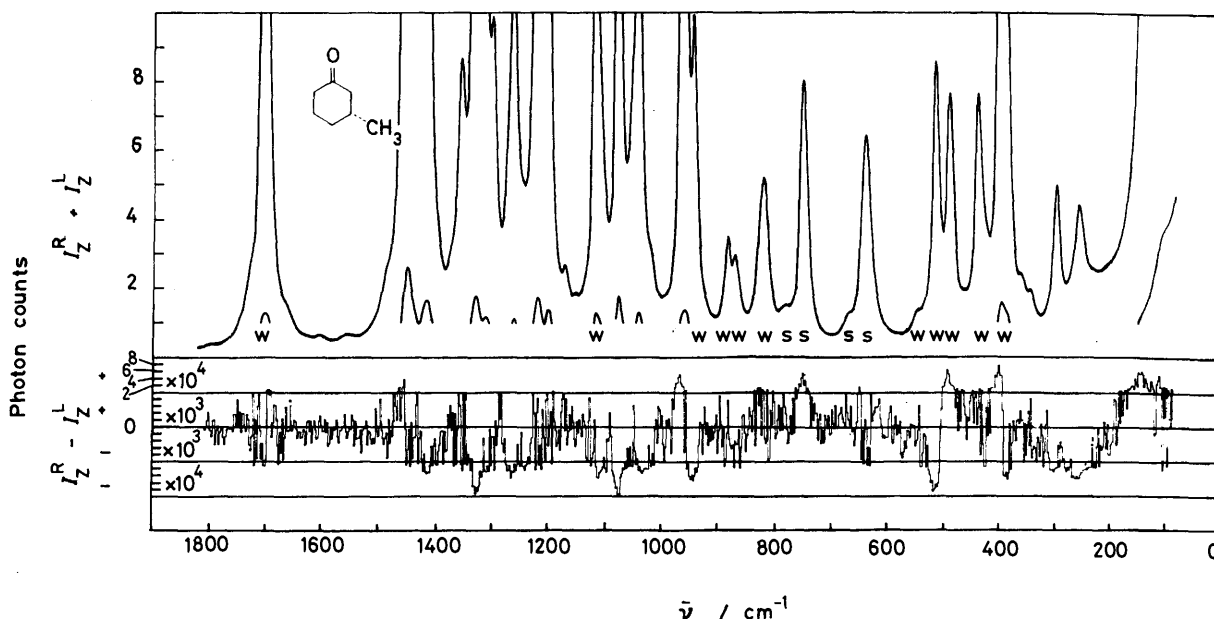


FIGURE 7 Depolarized Raman circular intensity sum and difference spectra of neat (+)-3-methylcyclohexanone

secondary bridge which are twisted relative to each other on account of the twist in the norbornane skeleton.^{10,11}

A small c.i.d. couplet, associated with four Raman bands, appears at *ca.* 1300 cm⁻¹ in the spectrum of bromocamphor but not in that of camphor itself. Since this is the frequency region for C-H deformations,⁹ the structural feature responsible could be the C-H groups at the asterisked positions, which together constitute a rigid twisted unit that is not present in camphor. 3-Bromocamphor-9-sulphonic shows a similar couplet here but with opposite sign (in keeping with the opposite absolute configuration) associated with two broad unresolved Raman bands. It is disappointing that a similar couplet does not occur in the spectrum of chlorocamphor, although additional c.i.d. features appear at slightly lower frequencies that might be related. In the spectrum of bornan-2-*exo*-ol there is a broad positive c.i.d. band at *ca.* 1200 cm⁻¹ and in that of the 2-*endo*-ol a large c.i.d. couplet centred at *ca.* 1250 cm⁻¹: both features might involve deformations of the C-H at the car-

bon atom.¹³ No such c.i.d. couplets appear in the Raman bands originating in the methyl asymmetric deformations in any of the spectra shown here, consistent with the fact that all the methyl groups in these molecules are attached to ring systems, so any 'chiral crowding' of the methyl groups is minimal.

Another previously reported characteristic Raman c.i.d. feature is a single band associated with a methyl torsion mode in molecules such as 3-methylcyclohexanone, where the electronic potential barrier hindering the rotation of the methyl group has a large chiral part (this is the band at *ca.* 250 cm⁻¹ in Figure 7).¹² There are hints of such methyl torsion c.i.d. features in several of the spectra shown here, but the situation is complicated by the presence of more than one methyl group.

The Origin of Raman C.i.d. Couplets.—Many Raman c.i.d. spectra, in particular the examples shown in this article, are dominated by couplets which are often con-

⁹ N. B. Colthup, L. H. Daly, and W. E. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1975.

¹⁰ C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995.

¹¹ F. H. Allen and D. Rogers, *J. Chem. Soc. (B)*, 1971, p. 632.

¹² L. D. Barron, *Nature*, 1975, **255**, 458.

¹³ L. D. Barron, in preparation.

servative. It is now shown that such features originate in coupling between vibrational modes of appropriate symmetry brought about through a chiral distortion of the molecular framework.

Consider two vibrational states, $|a_v\rangle$ and $|b_v\rangle$, associated with two normal modes Q_a and Q_b localized on achiral groups (Q_a and Q_b can also be different modes of the same group) where the subscript v indicates the number of vibrational quanta present in a particular mode. We can write the ground vibrational state of the two-mode system as the direct product of the ground vibrational states of the two modes [equation (1)].

$$|0\rangle = |a_0 b_0\rangle \quad (1)$$

In the first excited vibrational state Q_a can be excited with Q_b in its ground state, or *vice versa*, so the first excited vibrational states are written as in equations (2) and (3).

$$|1_+\rangle = \cos \theta |a_1 b_0\rangle + \sin \theta |a_0 b_1\rangle \quad (2)$$

$$|1_-\rangle = \sin \theta |a_1 b_0\rangle - \cos \theta |a_0 b_1\rangle \quad (3)$$

The coefficients $\cos \theta$ and $\sin \theta$ depend on the energy separation $W_{a_1} - W_{b_1}$ of the two modes and on the vibrational perturbation V that couples them, and are obtained from equation (4).¹⁴ If the two modes are

$$\tan 2\theta = 2\langle a_1 b_0 | V | a_0 b_1 \rangle / (W_{a_1} - W_{b_1}) \quad (4)$$

degenerate, $\cos \theta = |\sin \theta| = 2^{-1/2}$; if the energy separation is very large, $\sin \theta \rightarrow 0$ and $\cos \theta \rightarrow 1$. The energies of the two states are given by equation (5). Raman

$$W_{\pm} = \frac{1}{2}(W_{a_1} + W_{b_1}) \pm \frac{1}{2}[(W_{a_1}^2 - W_{b_1}^2) + 4|\langle a_1 b_0 | V | a_0 b_1 \rangle|^2]^{\frac{1}{2}} \quad (5)$$

optical activity is determined by products such as $\langle v^i | \alpha_{\alpha\beta} | v^f \rangle \langle v^j | G'_{\alpha\beta} | v^i \rangle$, where $\alpha_{\alpha\beta}$ is the electric dipole-electric dipole polarizability tensor, $G'_{\alpha\beta}$ is the electric dipole-magnetic dipole optical activity tensor and $|v^i\rangle$ and $|v^f\rangle$ are the initial and final vibrational states.⁶ The optical activities of the Raman bands associated with the vibrational states represented by equations (2) and (3) are therefore determined by expressions of the form (6) and (7). The first terms of (6) and (7) generate Raman

$$\begin{aligned} \langle 0 | \alpha_{\alpha\beta} | 1_+ \rangle \langle 1_+ | G'_{\alpha\beta} | 0 \rangle = & (\cos^2 \theta \langle a_0 | \alpha_{\alpha\beta} | a_1 \rangle \langle a_1 | G'_{\alpha\beta} | a_0 \rangle + \\ & \sin^2 \theta \langle b_0 | \alpha_{\alpha\beta} | b_1 \rangle \langle b_1 | G'_{\alpha\beta} | b_0 \rangle) \\ & + \sin \theta \cos \theta (\langle a_0 | \alpha_{\alpha\beta} | a_1 \rangle \langle b_1 | G'_{\alpha\beta} | b_0 \rangle + \\ & \langle b_0 | \alpha_{\alpha\beta} | b_1 \rangle \langle a_1 | G'_{\alpha\beta} | a_0 \rangle) \quad (6) \end{aligned}$$

$$\begin{aligned} \langle 0 | \alpha_{\alpha\beta} | 1_- \rangle \langle 1_- | G'_{\alpha\beta} | 0 \rangle = & (\sin^2 \theta \langle a_0 | \alpha_{\alpha\beta} | a_1 \rangle \langle a_1 | G'_{\alpha\beta} | a_0 \rangle + \\ & \cos^2 \theta \langle b_0 | \alpha_{\alpha\beta} | b_1 \rangle \langle b_1 | G'_{\alpha\beta} | b_0 \rangle) \\ & - \sin \theta \cos \theta (\langle a_0 | \alpha_{\alpha\beta} | a_1 \rangle \langle b_1 | G'_{\alpha\beta} | b_0 \rangle + \\ & \langle b_0 | \alpha_{\alpha\beta} | b_1 \rangle \langle a_1 | G'_{\alpha\beta} | a_0 \rangle) \quad (7) \end{aligned}$$

optical activities of the same sign in the two bands and probably originate in electronic chirality; the second terms generate equal and opposite Raman optical acti-

vities in the two bands and, as now shown, originate in vibrational chirality.

We consider explicitly the situation where the energy separation of the two modes is much larger than the vibrational perturbation so that $|\langle a_1 b_0 | V | a_0 b_1 \rangle / (W_{a_1} - W_{b_1})| \ll 1$. Then we obtain equations (8) and (9). Neglecting the first terms in (6) and (7) we see that,

$$\cos \theta = 1 - \frac{1}{2} \frac{|\langle a_1 b_0 | V | a_0 b_1 \rangle|^2}{(W_{a_1} - W_{b_1})^2} + \dots \quad (8)$$

$$\sin \theta = \frac{\langle a_1 b_0 | V | a_0 b_1 \rangle}{W_{a_1} - W_{b_1}} + \dots \quad (9)$$

to a first-order approximation in V , conservative Raman optical activity couplets are determined by equation (10).

$$\begin{aligned} \langle 0 | \alpha_{\alpha\beta} | 1_{\pm} \rangle \langle 1_{\pm} | G'_{\alpha\beta} | 0 \rangle = & \pm \frac{\langle a_1 b_0 | V | a_0 b_1 \rangle}{\hbar \omega_{a_1 b_1}} (\langle a_0 | \alpha_{\alpha\beta} | a_1 \rangle \langle b_1 | G'_{\alpha\beta} | b_0 \rangle + \\ & \langle b_0 | \alpha_{\alpha\beta} | b_1 \rangle \langle a_1 | G'_{\alpha\beta} | a_0 \rangle) \quad (10) \end{aligned}$$

The significance of (10) is best appreciated by considering a specific example. Most appropriate here are the in-plane and out-of-plane deformation modes of the carbonyl group which belong to symmetry species B_1 and B_2 in the local C_{2v} symmetry point group. Since $\alpha_{\alpha\beta}$ is a second-rank polar tensor (which transforms like the product of two co-ordinates) and $G'_{\alpha\beta}$ is a second-rank axial tensor (which transforms the same as $\alpha_{\alpha\beta}$ except for a sign change under improper rotations), B_1 is spanned by α_{xz} and G'_{yz} , and B_2 is spanned by α_{yz} and G'_{xz} . In the expression (10) the vibrational perturbation V must contain a product of the normal co-ordinates of the two modes in order to couple them and it is therefore of symmetry species A_2 : such a perturbation can only arise through a chiral distortion of the skeleton (*i.e.* to C_2 or C_1 symmetry). The absolute signs depend on the sign of $\langle a_1(B_1) b_0 | V | a_0 b_1(B_2) \rangle$, which depends on the absolute configuration, and on the sign of $(\langle a_0 | \alpha_{xz} | a_1(B_1) \rangle \langle b_1(B_2) | G'_{yz} | b_0 \rangle + \langle b_0 | \alpha_{yz} | b_1(B_2) \rangle \langle a_1(B_1) | G'_{xz} | a_0 \rangle)$, which is an intrinsic property of the carbonyl group and should be the same from molecule to molecule. These quantities have not yet been calculated, so it is not possible at present to predict absolute configurations *a priori* by using this model.

The method could be extended to more than two modes, leading to complex Raman optical activity patterns, provided that the corresponding symmetry species are appropriate and the Hamiltonian that determines the vibrational motion contains chiral perturbation terms involving products of all the relevant normal co-ordinates.

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¹⁴ A. S. Davydov, 'Quantum Mechanics,' Pergamon, Oxford, 1965, p. 177.