Raman Optical Activity of Simple Chiral Molecules; Methyl and Trifluoromethyl Asymmetric Deformations

By **Laurence D. Barron**, Chemistry Department, The University, Glasgow G12 8QQ

Raman circular intensity differential spectra between 80 and 2 000 cm^{-1} of (−)-1-phenylethylamine, (+)-1-phenylethanol, (+)-2,2,2-trifluoro-1-phenylethanol, (+)-1-*p*-bromophenylethylamine, and (−)-*N*-benzyl-1-phenylethylamine are presented, and several stereochemical correlations are pointed out. The spectrum of the *p*-bromo-species indicates that the previously reported identification of a couplet with the methyl asymmetric deformations should be used with caution. A couplet at about 520 cm^{-1} in the spectrum of the trifluoromethyl species may originate from the analogous trifluoromethyl asymmetric deformations.

VIBRATIONAL optical activity spectra can now be obtained by 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 visible light.[4-7] Vibrational optical activity is a powerful new probe of stereochemistry since every part of a chiral molecule can contribute to a vibrational optical activity spectrum. The spectral region below about 2 000 cm^{-1} is inaccessible to i.r. c.d. at present, and most observations have involved carbon–hydrogen stretching modes. On the other hand, although the complete vibrational spectrum is accessible to Raman c.i.d., 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 several orders of magnitude larger than found in the exclusively stretching modes that occur above *ca.* 2 000 cm^{-1}. In this article the Raman c.i.d. spectra of 1-phenylethylamine and related compounds are compared, and several stereochemical correlations are pointed out.

EXPERIMENTAL

The Raman c.i.d. instrument was similar to that described previously,[6] except that a more powerful laser (Spectra-Physics 171–03) was used. 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, $I_\alpha^R - I_\alpha^L$ and $I_\alpha^R + I_\alpha^L$ are presented separately because the background must be subtracted from $I_\alpha^R + I_\alpha^L$ before calculating Δ. For reasons discussed previously,[4,6] only the depolarized components ($\alpha = z$) were sampled.

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. S and W indicate strongly and weakly polarized bands; all other bands are effectively depolarized. All the spectra were recorded with a resolution of 10 cm^{-1} at a scan speed of 1 cm^{-1} min^{-1} by using a 4W argon-ion laser beam of λ 488 nm focused into neat liquid samples.

(−)-1-Phenylethylamine (Aldrich), (+)-1-phenylethanol (ICN-K & K) (+)-2,2,2-trifluoro-1-phenylethanol (Burdick and Jackson), and (+)-1-*p*-bromophenylethylamine and (−)-*N*-benzyl-1-phenylethylamine (Norse) were commercial samples.

DISCUSSION

The Origin of Raman C.i.d. Couplets.—The Raman c.i.d. spectra presented here are dominated by couplets that are often conservative (that is, they show equal and opposite optical activities). Without attempting the calculation of magnitudes and signs of Raman c.i.d. effects generated by a particular structural unit in a given absolute configuration, a formidable task, it is still easy to understand the origin of such features in general terms. We consider the simplest case where the Raman optical activity originates in the lifting of vibrational degeneracy by a chiral perturbation since this applies to the methyl and trifluoromethyl asymmetric deformations discussed below.

Consider two vibrational states $|a_v\rangle$ and $|b_v\rangle$ associated with degenerate normal modes Q_a and Q_b localized on an achiral group that is subjected to a small chiral perturbation (v is the number of vibrational quanta present in a particular mode; Q_a and Q_b can also be equivalent modes localized on different achiral groups). We write the ground vibrational state of the two-mode system as the direct product of the ground vibrational states of the individual modes: $|0\rangle = |a_0b_0\rangle$. 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 state is written as in equation (1). Raman optical activity is

$$|1_\pm\rangle = (|a_1b_0\rangle \pm |a_0b_1\rangle)/\sqrt{2} \qquad (1)$$

determined by products such as $\langle v^i|\alpha_{\alpha\beta}|v^f\rangle\langle v^f|G'_{\alpha\beta}|v^i\rangle$, 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 Raman optical

---

[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. Moscowitz, *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.

[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.

[7] M. Diem, M. J. Diem, B. A. Hudgens, J. L. Fry, and D. F. Burow, *J.C.S. Chem. Comm.*, 1976, 1028.

activity associated with transitions to the two degenerate excited states (1) is therefore determined by expressions of the form (2).

$$\langle 0|\alpha_{\alpha\beta}|1_{\pm}\rangle\langle 1_{\pm}|G'_{\alpha\beta}|0\rangle = \tfrac{1}{2}\{(\langle a_0|\alpha_{\alpha\beta}|a_1\rangle\langle a_1|G'_{\alpha\beta}|a_0\rangle + \langle b_0|\alpha_{\alpha\beta}|b_1\rangle\langle b_1|G'_{\alpha\beta}|b_0\rangle) \pm (\langle a_0|\alpha_{\alpha\beta}|a_1\rangle\langle b_1|G'_{\alpha\beta}|b_0\rangle + \langle b_0|\alpha_{\alpha\beta}|b_1\rangle\langle a_1|G'_{\alpha\beta}|a_0\rangle)\} \quad (2)$$

The first term of (2) is zero because $|a_1\rangle$ and $|b_1\rangle$ are orthogonal modes of the achiral group and so are not spanned by the same components of $\alpha_{\alpha\beta}$ and $G'_{\alpha\beta}$.[8] The second term contributes if the degeneracy of the $|1_+\rangle$ and $|1_-\rangle$ states is lifted by means of a chiral interaction between $|a_1\rangle$ and $|b_1\rangle$.[8] This contribution is of equal magnitude and opposite sign in the $|1_+\rangle$ and $|1_-\rangle$ states and so is probably responsible for conservative couplets associated with two close (or unresolved) Raman bands. Significant asymmetry in a couplet indicates that other mechanisms contribute, in particular that the vibrational perturbation couples more than two modes.

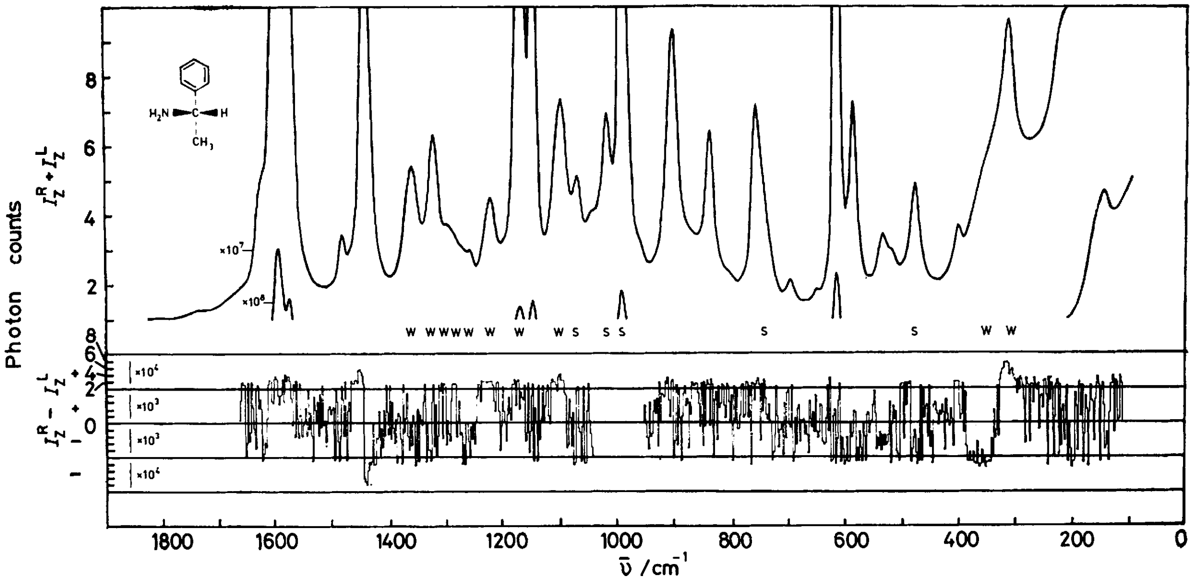

FIGURE 1 Depolarized Raman circular intensity sum ($I_z^R + I_z^L$) and difference ($I_z^R - I_z^L$) spectra of neat (−)-1-phenylethylamine

The theory can be generalized to the coupling, by a chiral vibrational perturbation, of modes of appropriate symmetry that are not degenerate, in which case the magnitude of the c.i.d. couplet is inversely proportional to the energy separation of the two modes.[8,9]

Present Results.—Figures 1—5 show the depolarized Raman circular intensity sum and difference spectra obtained. The complete Raman c.i.d. spectrum of (+)-1-phenylethylamine has been published previously;[5] apart from the use of a linear scale and computer smoothing, it is very similar to Figure 1 but with reversed signs.

A striking feature in each of the first two spectra is a conservative couplet centred at *ca.* 1 450 cm^{-1}. It is gratifying that the two couplets have opposite signs since the two molecules have opposite absolute configurations according to the *R*,*S*-convention. The corresponding Raman bands originate mainly in the two degenerate methyl asymmetric deformations,[10] and it has been suggested that the attachment of the methyl group to the asymmetric carbon atom effectively destroys its threefold symmetry axis, thereby lifting the degeneracy and inducing equal and opposite Raman optical activities in the two split components.[5,11] Although no splitting can be seen in the corresponding Raman bands at the low resolution used here, it was suggested that shoulders observed under high resolution were due to the splitting of the methyl asymmetric deformations.[11] The detailed mechanism was thought to involve the activation of the second term of equation (2) by a chiral distortion of the carbon tetrahedron of the methyl group brought about through interactions with three other groups of different effective volume or polarizability;[8] this was supported by the fact that molecules such as amphetamine, lactic acid, alanine, and 3-methylcyclohexanone do not show distinctive couplets.

However, no corresponding Raman c.i.d. couplet appears in the spectrum of (+)-1-*p*-bromophenylethylamine (Figure 4): instead a new Raman band, associated with a large positive c.i.d. effect, appears at *ca.* 1 410 cm^{-1}, and is almost certainly the lower frequency semicircle stretching mode of the substituted aromatic

---

[8] L. D. Barron, Advances in Infrared and Raman Spectroscopy,' ed. R. J. H. Clark and R. E. Hester, vol. 3, Heyden, London, in the press.

[9] L. D. Barron, *J.C.S. Perkin II*, 1977, 1074.

[10] N. B. Colthup, L. H. Daly, and S. F. Wiberley, ' Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1975.

[11] L. D. Barron, 1975, *Nature*, **255**, 458.

ring, which shifts from between 1 465 and 1 430 cm^{-1} for mono, *ortho*-, and *meta*-substitution to between 1 420 and 1 400 cm^{-1} for *para*.[10,12] (The higher frequency semicircle stretching mode appears between 1 510 and 1 470 cm^{-1} for mono-, *ortho*-, and *meta*-substitution, and between 1 525 and 1 480 cm^{-1} for *para*;[10,12] both semicircle stretching modes are seen clearly in the Raman spectrum of (+)-2,2,2-trifluoro-1-phenylethanol in Figure 3, the lower frequency one having a small positive c.i.d. effect. Furthermore, no shoulder appears in the methyl asymmetric deformation band under high resolution. Consequently, the appealing interpretation that the c.i.d. couplets in 1-phenylethylamine and 1-phenylethanol originate in the two split methyl asymmetric deformations is too simple. It may be that the isolated methyl asymmetric deformations are insufficiently split for a c.i.d. couplet to be observed and require the lower frequency semicircle aromatic stretch to be sufficiently close in frequency to induce more splitting, or the c.i.d. couplet may involve one or both of the methyl asymmetric deformations together with the semicircle

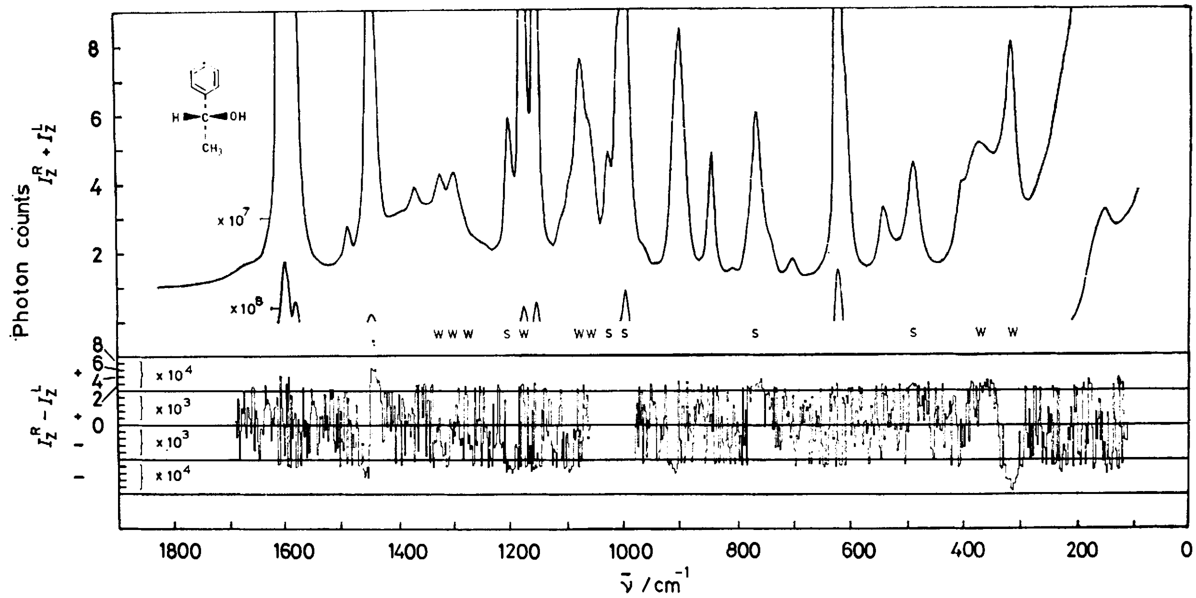

FIGURE 2 Depolarized Raman circular intensity sum and difference spectra of neat (+)-1-phenylethanol

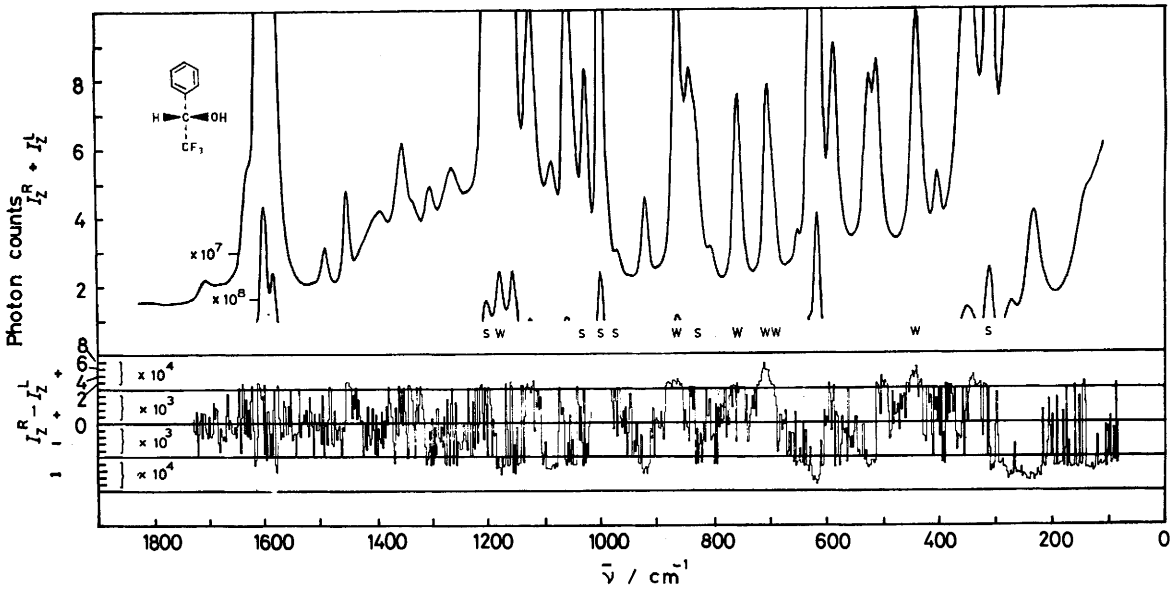

FIGURE 3 Depolarized Raman circular intensity sum and difference spectra of neat (+)-2,2,2-trifluoro-1-phenylethanol

---

[12] F. R. Dollish, W. G. Fateley, and F. F. Bentley, ' Characteristic Raman Frequencies of Organic Compounds,' Wiley, New York, 1974.

aromatic stretch. Methyl asymmetric deformation c.i.d. couplets should therefore be used with caution in assigning absolute configurations.

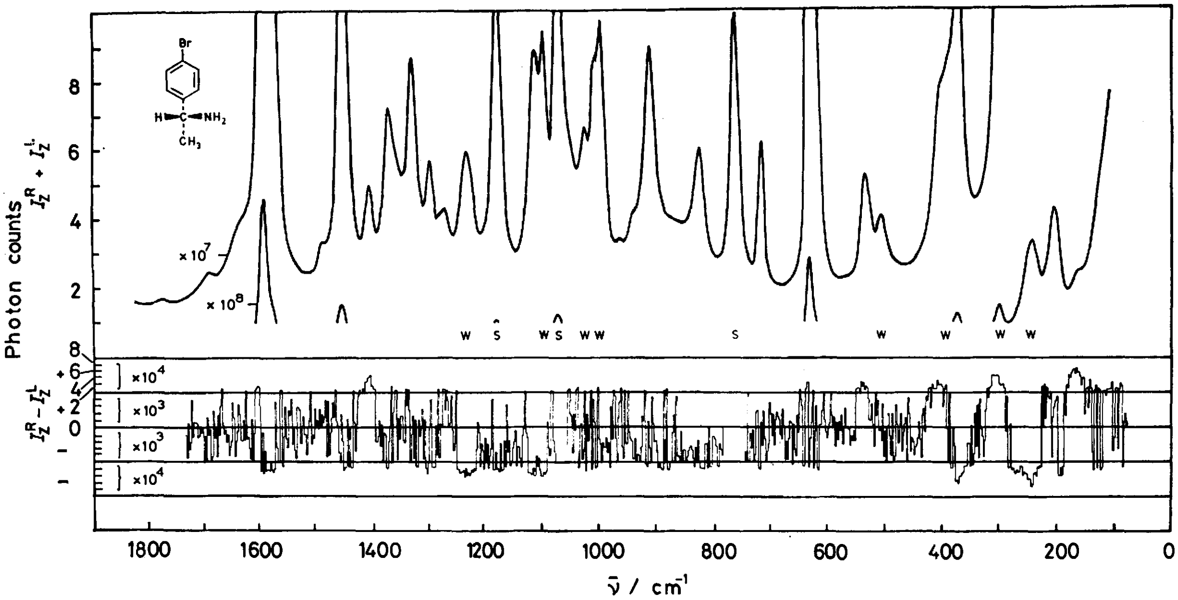

FIGURE 4 Depolarized Raman circular intensity sum and difference spectra of neat (+)-1-*p*-bromophenylethylamine; the absolute configuration was deduced by comparing the spectrum with that of (—)-1-phenylethylamine (Figure 1)

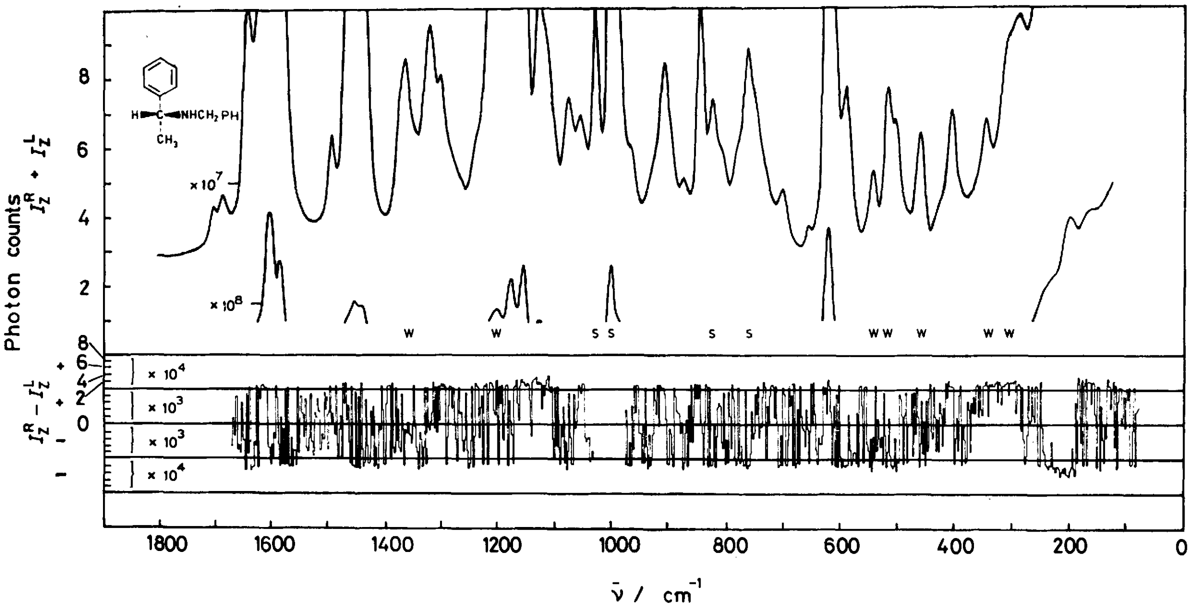

FIGURE 5 Depolarized Raman circular intensity sum and difference spectra of neat (—)-*N*-benzyl-1-phenylethylamine: the absolute configuration is speculative

In the spectrum of (+)-2,2,2-trifluoro-1-phenylethanol (Figure 3) a small conservative c.i.d. effect associated with two adjacent depolarized Raman bands appears at about 510 cm^{-1}: this region is appropriate for trifluoromethyl asymmetric deformations,[13,14] although the frequencies are much more variable than the corresponding methyl frequencies. Since the two components are now well resolved, the original description of the origin of the methyl asymmetric deformation c.i.d., which has proved to be over-simplified, may well be valid for the trifluoromethyl asymmetric deformations. Notice that the signs of the high and low frequency components of the c.i.d. couplet are the same as in the methyl analogue that has the equivalent absolute configuration (Figure 2).

The couplets at about 340 cm^{-1} in the spectra of

---

[13] J. R. Nielsen and R. Theimer, *J. Chem. Phys.*, 1957, **27**, 891.

[14] O. Risgin and R. C. Taylor, *Spectrochim. Acta*, 1959, **15**, 1036.

(−)-1-phenylethylamine and (+)-1-phenylethanol (Figures 1 and 2), which were the first genuine Raman c.i.d. effects to be observed,[4] could originate in deformation vibrations of the central carbon tetrahedron that are degenerate in a similar molecule of higher symmetry. Torsion modes of the methyl group could also be involved. A similar c.i.d. couplet, associated with a similar Raman band structure, occurs in the spectrum of (+)-1-*p*-bromophenylethylamine at *ca.* 390 cm^{-1} (Figure 4): this has an opposite sign to that in the case of (−)-1-phenylethylamine, in keeping with an opposite absolute configuration. In the remaining two spectra (Figures 3 and 5) there are much broader c.i.d. couplets at lower frequency that might have similar origins.

A small nonconservative couplet appears at *ca.* 1 250 cm^{-1} in the spectrum of (−)-1-phenylethylamine (Figure 1). The same feature appears in the spectrum of the mirror-image isomer, but with opposite sign,[5] so it is probably genuine. It also appears in the spectrum of (+)-1-*p*-bromophenylethylamine (Figure 4), but with opposite sign, in keeping with an opposite absolute configuration, but does not appear in the remaining three spectra. The effects might involve carbon–hydrogen deformations, and perhaps even the elusive NH_2 twist.[15]

The large Raman c.i.d. couplet at *ca.* 290 cm^{-1} in the spectrum of (+)-1-*p*-bromophenylethylamine (Figure 4) almost certainly involves carbon–bromine deformations since it does not occur in the spectrum of 1-phenylethylamine and is reminiscent of large c.i.d. features in the same region in bromocamphor that were identified with carbon–bromine deformations.[9]

In the spectrum of (+)-2,2,2-trifluoro-1-phenylethanol (Figure 3) a large negative Raman c.i.d. effect associated with a strong depolarized Raman band at *ca.* 620 cm^{-1}, originating from a well characterized deformation of the monosubstituted benzene ring,[10,12] is paired with an equal and opposite c.i.d. effect at *ca.* 710 cm^{-1} associated with a weakly polarized Raman band that might originate from the symmetric deformation of the trifluoromethyl group.[13,14] This could be an example of the generation of Raman c.i.d. through the coupling of modes of appropriate symmetry and similar frequency through a chiral distortion of the skeleton;[8,9] in which case analogous effects are not seen in the other spectra because the methyl symmetric deformation occurs at higher frequency (*ca.* 1 375 cm^{-1}),[10] so any coupling is much smaller. The mode corresponding to the weakly polarized Raman band at *ca.* 440 cm^{-1} is probably the degenerate partner in benzene itself of the mode corresponding to the 620 cm^{-1} band.[10,12] This has a positive c.i.d. effect and so may also be coupled by the chiral perturbation to the 620 cm^{-1} mode. On account of interactions with other modes, the frequencies of the symmetric and antisymmetric trifluoromethyl stretches are very variable and can range between *ca.* 870 and 1 400 cm^{-1},[12] so it is possible that they are involved in the c.i.d. couplet associated with the weakly polarized and depolarized Raman bands at *ca.* 870 and 920 cm^{-1}, or indeed in the couplet at *ca.* 1 100 cm^{-1}.

I thank the S.R.C. for an equipment grant.

[7/279 *Received*, 15*th February*, 1977]

---

[15] J. R. Durig, S. F. Bush, and F. G. Baglin, *J. Chem. Phys.*, 1968, **49**, 2106.