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RAMAN OPTICAL ACTIVITY OF TARTARIC ACID AND RELATED MOLECULES

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Abstract—The Raman optical activity spectra of (2*R*, 3*R*) (+)- and (2*S*, 3*S*) (−)-tartaric acid, (2*R*, 3*R*) (+)-dimethyl tartrate, (2*R*, 3*R*) (−)-2,3-butanediol and (2*S*, 3*S*) (+)-dibenzoyl tartaric adid are presented. A large couplet at about 500 cm^{-1} in the first three molecules, which probably originates in deformations of a chiral structural unit, might serve as an indicator of conformation and absolute configuration.

A small difference in the intensity of Raman scattering from chiral molecules in right and left circularly polarized incident light provides a measure of vibrational optical activity.[1-8] At this early stage in the development of the subject it is of interest to compare the Raman optical activity spectra of series of related compounds to see what common features emerge: here the spectra of tartaric acid and a few related molecules are presented. It is gratifying that the molecule instrumental in establishing the concept of molecular chirality shows a striking Raman optical activity spectrum reflecting both its conformation and absolute configuration.

EXPERIMENTAL

The instrument used has been described previously.[2,7] The samples were run as near saturated solutions or neat liquids. The instrumental conditions were as follows: laser wavelength 488.8 nm, laser power 4 W, slit width 10 cm^{-1}, scan speed 1 cm^{-1}min^{-1}. As before,[2,7] only the depolarized Raman circular intensity sum $(I_z^R + I_z^L)$ and difference $(I_z^R - I_z^L)$ spectra between 100 and 2000 cm^{-1} were recorded, the difference spectra being presented on a scale that is linear within each decade range but logarithmic between decade ranges since 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. The NMR spectra were run on either a Perkin-Elmer R32 or a Varian-XL-100 spectrometer.

Discussion of the spectra

In all of the molecules studied, intramolecular H-bonding is expected to be an important factor in determining which of the three rotational conformers that can exist for each molecule is preferred.[9] However, intramolecular hydrogen bonding will not necessarily be the dominant factor because, at the very high sample concentrations used in these measurements, intermolecular associations might be overwhelming. Unfortunately, Raman optical activity instruments are not yet sufficiently sensitive for measurements to be made at high dilution (unless the resonance Raman phenomenon is involved).

Figure 1 shows the Raman optical activity spectra of (2*R*, 3*R*) (+)- and (2*S*, 3*S*) (−)-tartaric acid in water. There is good reflection symmetry between the spectra

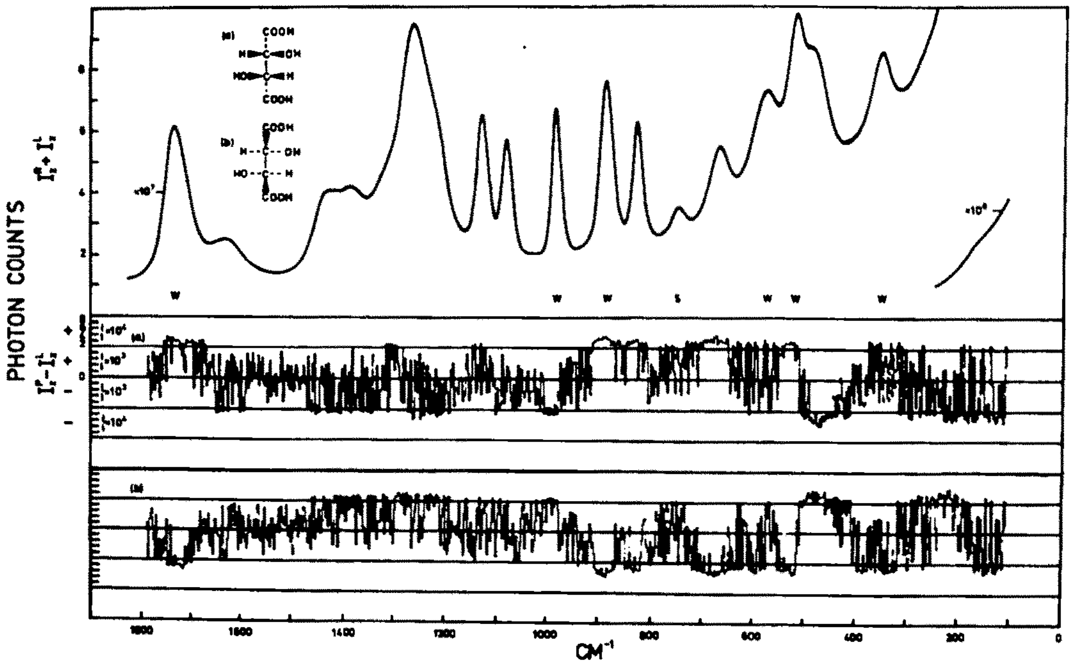


Fig. 1. The depolarized Raman circular intensity sum $(I_z^R + I_z^L)$ and difference $(I_z^R - I_z^L)$ spectra of (2*R*, 3*R*) (+)-tartaric acid (a) and (2*S*, 3*S*) (−)-tartaric acid (b) in water.

of the two optical isomers. The simplicity of the Raman and Raman optical activity spectra indicates that one of the three possible staggered conformations 1, 2 and 3 (which refer to the (2*R*, 3*R*) (+)-isomer) dominates at room temperature. This is consistent with an NMR coupling constant of the two vicinal protons of 3 Hz, indicating that the two protons are gauche as in conformers 1 and 3;[10] however, the NMR results alone cannot distinguish between 1 and 3. Both the Raman and Raman optical activity spectra were essentially unchanged when the tartaric acid was dissolved in methanol and dimethylsulphoxide, indicating that no conformation change was induced.

Figure 2 shows the Raman optical activity spectrum of (2*R*, 3*R*) (+)-dimethyl tartrate diluted with a small amount of water. The relative complexity of the Raman spectrum, together with the rather weak Raman optical activity compared with tartaric acid, indicates that two or more of the conformers 4, 5 and 6 are present in significant proportions. Unfortunately, experimental difficulties prevented measurement of the NMR coupling constant of the two vicinal protons.

Figure 3 shows the Raman optical activity spectrum of neat (2*R*, 3*R*) (−)-2, 3-butanediol. Again the relative complexity of the Raman spectrum and the rather weak optical activity indicates that two or more of the conformers 7, 8 and 9 are present in significant proportions. The NMR coupling constant of the two vicinal protons was found to be about 6.3 Hz, indicating a mixture of all three conformers. Since a coupling constant of about 8.5 Hz is expected for 8,[11] this conformer might be present in the largest proportion.

Figure 4 shows the Raman optical activity spectrum of (2*S*, 3*S*) (+)-dibenzoyl tartaric acid in methanol. Now the relative simplicity of the Raman spectrum (bearing in mind the complexity of the groups present) and the strong Raman optical activity indicates that one of the conformers 10, 11 and 12 dominates. Again the NMR coupling constant of the two vicinal protons could not be measured.

A striking feature in the Raman optical activity spectrum of tartaric acid is a couplet associated with an unpolarized Raman band at about 470 cm^{-1} and a weakly polarized Raman band at about 520 cm^{-1}. Similar couplets appear in this region in dimethyl tartrate and in 2,3-butanediol. Two infrared bands in this region in liquid ethylene glycol have been assigned to in-phase and out-of-phase combinations of the two in-plane C–C–O

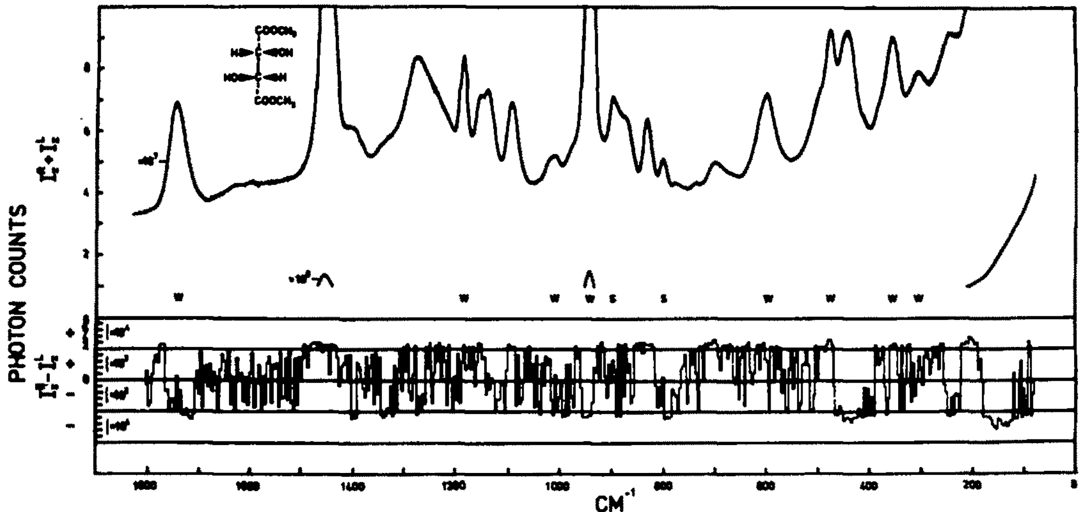


Fig. 2. The depolarized Raman circular intensity sum and difference spectra of (2*R*, 3*R*) (+)-dimethyl tartrate.

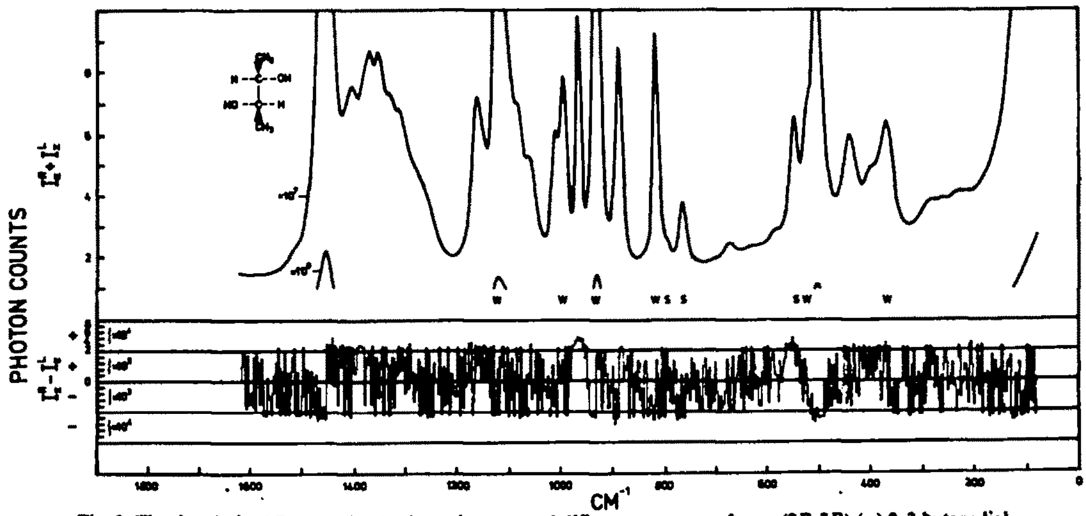


Fig. 3. The depolarized Raman circular intensity sum and difference spectra of neat (2*R*, 3*R*) (−)-2, 3-butanediol.

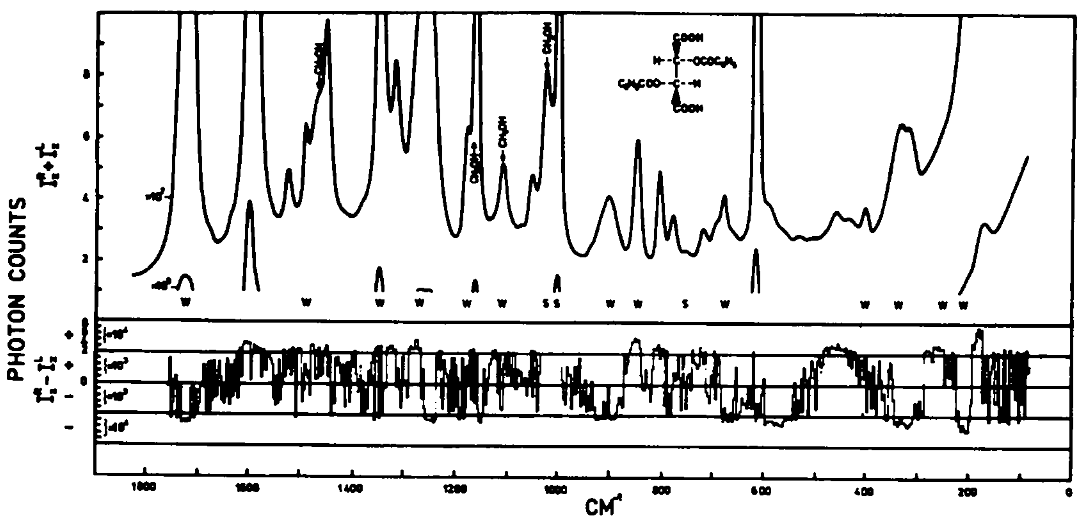
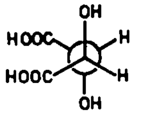


Fig. 4. The depolarized Raman circular intensity sum and difference spectra of (2S,3S) (+)-dibenzoyl tartaric acid in methanol.



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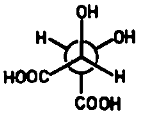

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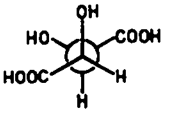

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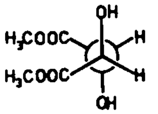

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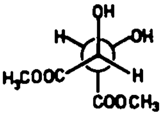

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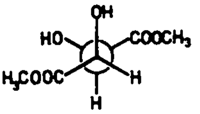

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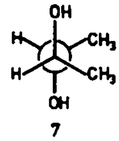

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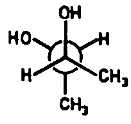

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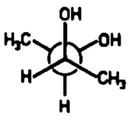

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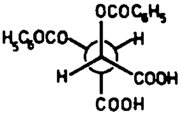

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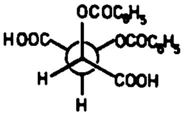

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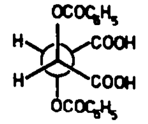

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deformations.[12] In 2, 3, 5, 6, 8 and 9 the O–C–C–O unit constitutes a twisted, highly chiral structure, and coupling between the in-phase and out-of-phase combinations of the two deformations is expected to generate a Raman optical activity couplet from which the absolute configuration can be deduced if the in-phase and out-of-phase bands can be identified.[2,3,13] Since this couplet has the same relative signs in (2R,3R) (+)-tartaric acid, (2R,3R) (+)-dimethyl tartrate and (2R,3R) (−)-2,3-butanediol we could speculate that conformers 3, 6 and 8 are responsible because, if we assume that the lower-frequency component arises from the in-phase combination, the associated negative Raman optical activity indicates a left-handed twist in the O–C–C–O structure.[2,3,13] One difficulty with this argument is that the Raman band arising from the in-phase combination should be polarized, yet the lower-frequency component is unpolarized. Also several other modes of vibration could be involved in these Raman optical activity features. For example, C–C–C–C deformations occur in this region;[14] also contributions from the out-of-plane hydrogen bonded O–H deformation, which becomes a torsion in the absence of H-bonding,[15] have been ascribed to infrared bands at 650 and 330 cm⁻¹ in liquid ethylene glycol.[12] So it must be stressed that much more data is required on model structures before such arguments can be applied with confidence.

Discussion of the remaining Raman optical activity features, particularly the large conservative couplets that extend throughout the spectrum of dibenzoyl tartaric acid, will be postponed until further data are available for comparison. But it should be apparent that Raman optical activity is a powerful new method for studying the stereochemistry of chiral molecules that can exist in several conformers on account of internal rotation: for example, once the Raman bands in a molecule such as tartaric acid have been properly assigned, knowing the absolute configuration it should be possible to distinguish between conformers such as 1, 2 and 3. In another related example of Raman optical activity in conformational studies, couplets in bands originating in carbon-halogen stretching modes in 1-halo-2-methylbutanes were ascribed to rotational conformers with opposite chiralities.[5]

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