Raman Optical Activity of Bromocamphor Solutions

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Summary Solutions of (+)-3-bromocamphor in CH_2Cl_2 and (−)-3-bromocamphor-π-sulphonic acid in H_2O show similar Raman circular intensity differential bands between 800 and 930 cm^{-1}, but with opposite signs, that probably originate in vibrations of the skeleton in the vicinity of the bromine atom; this indicates that Raman optical activity can correlate absolute configurations by directly probing the appropriate parts of the molecular framework.

We have previously reported theoretical[1–3] and experimental[4–6] studies of vibrational optical activity using a difference in the intensity of Raman scattering in right and left circularly polarized incident light. The relevant experimental quantity is a normalized circular intensity

$$\Delta_\alpha = (I^{R}_{\alpha} - I^{L}_{\alpha})/(I^{R}_{\alpha} + I^{L}_{\alpha}) \qquad (1)$$

differential (C.I.D.) defined by equation (1) where I^{R}_{α} and I^{L}_{α} are the scattered intensities with α-polarization in right and left circularly polarized incident light (I_z and I_x are linearly polarized parallel and perpendicular to the scattering plane).

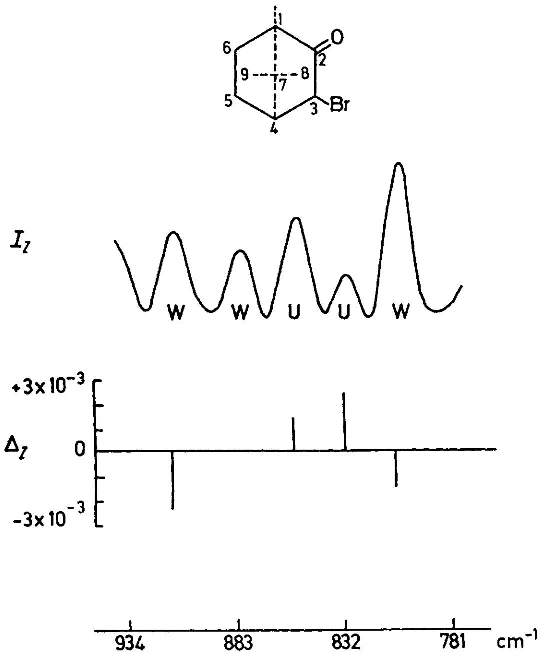

Figure 1. The Raman and Raman C.I.D. spectra of (+)-3-bromocamphor in CH_2Cl_2 for scattered light linearly polarized parallel to the scattering plane. U and W indicate unpolarized and weakly polarized bands. The background was subtracted from the Raman intensities in estimating Δ_z. The Δ_z values are accurate to *ca.* $\pm 2 \times 10^{-4}$. Instrumental conditions: laser frequency 4880 Å; laser power 1 W; slit width 1500 μm.

We have now constructed a new Raman C.I.D. spectrometer, based on a Coderg T800 triple monochromator, with improved sensitivity and stability. As in our previous instrument, the polarization of the laser beam is modulated between right and left circular with a KDP crystal driven with an appropriate square-wave voltage: two matched photon counters (A) and (B) are synchronized with the modulation such that (A) accepts Raman counts when the incident light is right circularly polarized and (B) accepts Raman counts when the incident light is left circularly polarized; the Raman C.I.D. is then Δ = (A − B)/(A + B). The essential features of our earlier results on pure liquids are reproduced easily.

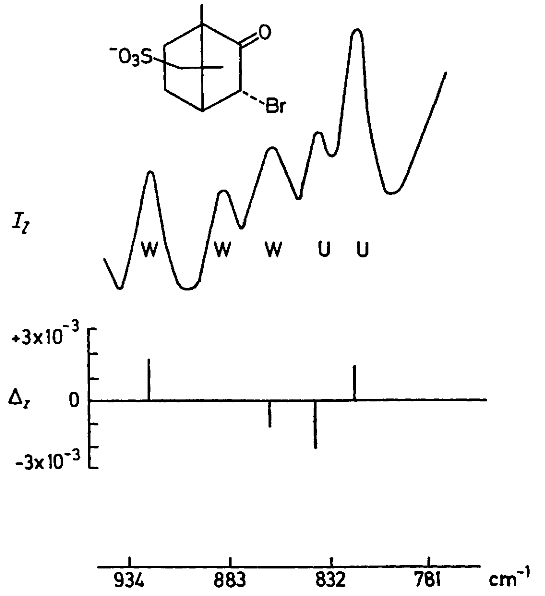

Figure 2. The Raman and Raman C.I.D. spectra of the ammonium salt of (−)-3-bromocamphor-π-sulphonic acid in H_2O. The Δ_z values are accurate to *ca.* $\pm 5 \times 10^{-4}$.

The new instrument has sufficiently improved sensitivity to handle moderately strong solutions, and observations are now reported of large Raman C.I.D.s in saturated solutions of (+)-3-bromocamphor in CH_2Cl_2 (Figure 1) and the ammonium salt of (−)-3-bromocamphor-π-sulphonic acid in H_2O (Figure 2). The component I_z of the light scattered at 90° was sampled since, for reasons discussed previously,[4] only this component is free of artefacts on our instrument. In any event Δ_z is expected to be larger than Δ_x and to provide the best information.[3] There was sufficient Raman intensity from the bromocamphor solution automatically to scan the C.I.D.; the Raman intensity from the bromocamphor-π-sulphonic acid solution was much weaker and the C.I.D. was measured at fixed points. The C.I.D.s are reported as 'stick spectra' giving the maximum C.I.D. in a particular band.

The two solutions show similar Raman C.I.D. spectra between 800 and 930 cm^{-1} (two large C.I.D. couplets), but with opposite signs. The Raman spectrum of camphor is generally similar except in this region, where only two bands are seen and shows no significant C.I.D.s. The observed C.I.D.s are therefore probably associated with skeletal vibrations involving the highly chiral carbon atom **3**, and the two hydrogens at 3 and 4 which together constitute a highly chiral 'dimer' that is not present in camphor; carbonyl bending vibrations may also be involved.

The absolute configurations of *endo*-(+)-3-bromocamphor and *endo*-(−)-3-bromocamphor-π-sulphonic acid, known from *X*-ray studies,[7] are shown in Figures 1 and 2. Our solution of (+)-3-bromocamphor in CH_2Cl_2 is known to contain mainly the *endo* isomer from comparison of the c.d. with reference values [$\Delta\epsilon$ + 2·01(312 nm) in CH_2Cl_2 compared with $\Delta\epsilon$ +1·93 (315 nm) in EtOH[8]]. Assuming that our solution of (−)-3-bromocamphor-π-sulphonic acid in H_2O is also mainly *endo*, the absolute configurations of the parts of the skeletons containing atoms **3** and **4** are opposite in the two molecules. This is consistent with the observed Raman C.I.D. spectra and indicates that Raman C.I.D. can correlate absolute configurations by directly probing the appropriate parts of the molecular framework. It would be of the greatest interest to study these molecules in the less-stable *exo* configuration, and also some deuteriated analogues.

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