Raman Optical Activity due to Isotopic Substitution: [α-^{2}H]Benzyl Alcohol

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Summary Observations of Raman optical activity in the carbon–deuterium deformation modes of [α-^{2}H]benzyl alcohol indicate that a new method is available for correlating the absolute configurations of molecules that owe their chirality to isotopic substitution.

Molecules that owe their chirality to isotopic substitution are important in stereochemical studies.[1] However, the determination of their absolute configurations can be difficult on account of very small optical rotations and Cotton effects (if any) because the electronic chirality is very small. On the other hand, in the case of deuterium sub-

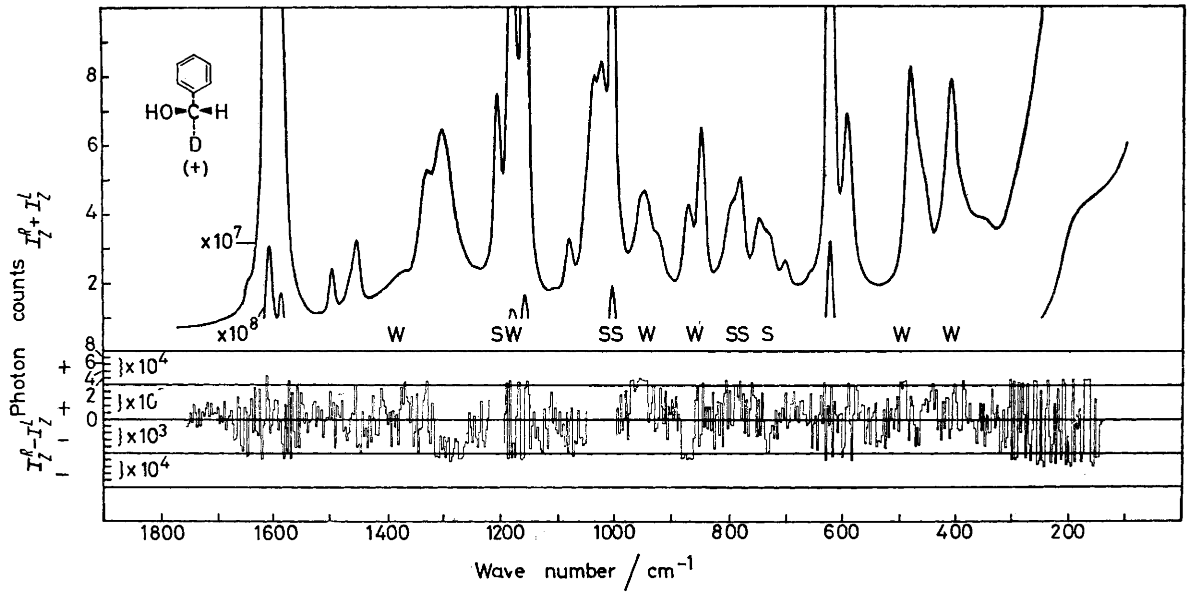

Figure 1. The depolarized Raman circular intensity sum ($I_z^R + I_z^L$) and difference ($I_z^R - I_z^L$) spectra of neat (S)-(+)-[α-^{2}H]benzyl alcohol. s and w denote strongly and weakly polarized Raman bands; all other bands are effectively unpolarized. Instrumental conditions: laser power 5 W, laser wavelength 488·0 nm, slit width 10 cm^{-1}, scan speed 1 cm^{-1} min^{-1}.

stitution, the vibrational chirality of the skeleton in the region of the deuterium atom is expected to be large so vibrational optical activity measurements could provide reliable correlations of absolute configurations (in fact the optical rotation of such molecules is attributed to chiral vibrational perturbations of the electronic states[2]).

Vibrational optical activity can now be measured in two distinct ways: i.r. circular dichroism,[3] which is restricted to the middle i.r. region above *ca.* 2000 cm^{-1} at present, and Raman circular intensity differential,[4,5] which covers the entire vibrational spectrum but is usually restricted to the region from *ca.* 100 to 2000 cm^{-1} since the deformation modes that occur there can show much larger vibrational optical activity than the exclusively stretching modes above *ca.* 2000 cm^{-1}. Small i.r. circular dichroism has been observed in the C–D stretching mode of (−)-[α-^{2}H]neopentyl chloride.[6] We report here a correspondingly much larger Raman circular intensity differential couplet in two C–D deformation modes in (+)-[α-^{2}H]benzyl alcohol (PhCHDOH).

Measurements were made with an instrument described previously;[5,7] as before, the depolarized Raman circular intensity sum ($I_z^R + I_z^L$) and difference ($I_z^R - I_z^L$) spectra are presented separately on a scale that is linear within each decade range but logarithmic between ranges. The sample of (*S*)-(+)-[α-^{2}H]benzyl alcohol {$[\alpha]_D^{24}$ + 1·43 (neat)}, prepared by fermentation,[8] was optically pure but diluted with *ca.* 14% of benzyl alcohol.

Figure 1 shows the Raman optical activity spectrum from 100 to 2000 cm^{-1}. The only significant effects are a couplet associated with two weakly polarized bands at *ca.* 860 and 950 cm^{-1}, and a smaller negative band associated with two unpolarized Raman bands between *ca.* 1250 and 1350 cm^{-1}. These are the very regions where the Raman spectrum differs from that of benzyl alcohol; the higher-frequency region is consistent with C–H and O–H deformations[9] and the lower-frequency region with C–D deformations (the approximate frequency of a C–D bending mode is found by multiplying the frequency of the analogous C–H mode by 0·7[10]). Figure 2 shows the Raman optical activity spectrum between 700 and 1000 cm^{-1} at higher sensitivity; the corresponding Raman spectrum of benzyl alcohol is also displayed to demonstrate that the optical activity couplet is associated mainly with two new bands assigned to C–D deformations. This type of couplet is expected to arise from the coupling of two orthogonal modes by a chiral vibrational perturbation.[7] An analogous couplet in the C–H deformation region is absent probably because strong coupling between C–H and O–H deformations[9] precludes the existence of well defined C–H deformations. No significant effects were found in the C–D stretch at *ca.* 2150 cm^{-1} and in the C–H stretch at *ca.* 2900 cm^{-1}.

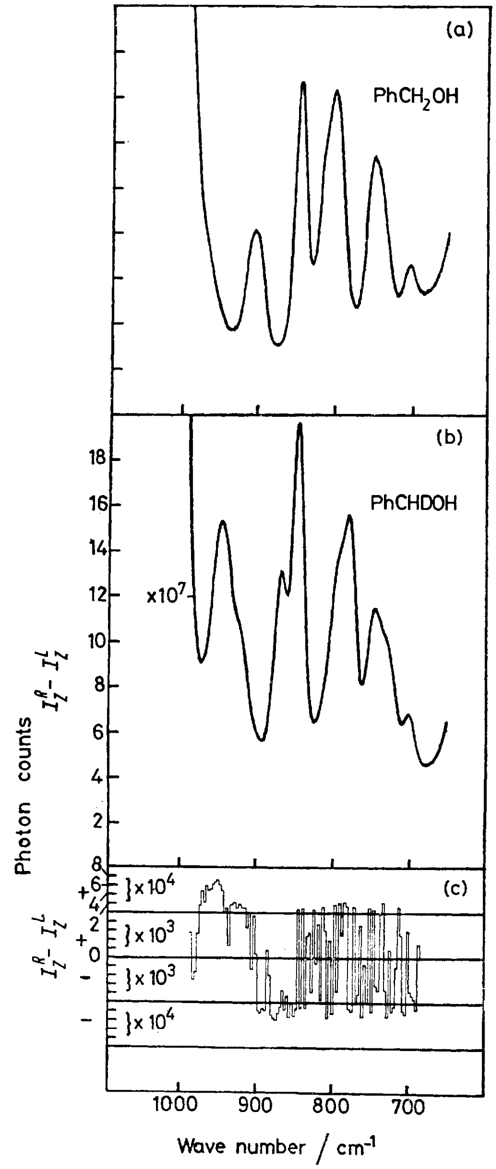

FIGURE 2. (a): depolarized Raman circular intensity sum spectrum (arbitrary intensity units) of benzyl alcohol. (b) and (c): The depolarized Raman circular intensity sum and difference spectra of (S)- (+)-[α-^{2}H]benzyl alcohol with instrumental conditions as for Figure 1, except for a slit width of 15 cm^{-1} and a scan speed of 0·5 cm^{-1} min^{-1}.

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