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FT-Raman spectra of *n*-propanol and selected partially ^{2}H-labelled analogues

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Abstract

Fourier-transform Raman spectra of $CH_3CH_2CH_2OH$ and some of its selectively deuteriated analogues have been obtained. Comparisons of the Raman spectra of the protiated and partially deuteriated species, in conjunction with polarization data, has enabled improved vibrational assignments to be made for the C–H modes. As a result, confirmation of some literature assignments of stretching and bending modes and revision of other tentative assignments for large biopolymer molecules have been proposed.

Keywords: Raman spectra; *n*-Propanol; Deuteriated analogues; Assignments

1. Introduction

In the assignment of the vibrational spectra of large complex molecules of biological interest including wool and cotton [1,2] and biopolymers, such as the human keratotic species skin, hair and nail [3,4], the unequivocal identification of important modes is often difficult because of overlapping spectroscopic features which arise from ν(CH), ν(CO) and ν(CN) bands which occur in similar wavenumber ranges. It is increasingly important for biomedical diagnostic applications of vibrational spectroscopy to be able to assign properly the vibrational bands in materials which have been modified by biological processes. Thus, recent Raman spectroscopic studies of diseased and healthy human tissues [4] revealed that some critical spectroscopic differences have been noted in the ν(CH) and $\delta(CH_2)$ regions. In some cases, it has been possible to relate the observed vibrational band changes to real biological effects such as the de-lipidization of human stratum corneum in the epidermis of diseased tissue samples. Likewise, the molecular basis for the observed role of chemical enhancing agents such as dimethyl sulphoxide on the mechanism of transdermal drug delivery is little understood [5,6] but is believed to involve a lipid transmission mechanism in which the role of water is crucial; this interpretation has yet to be related to the spectroscopic changes in the ν(CH) region of the Raman spectrum.

Further problems can arise in the vibrational assignment of large biological molecules when small molecular species are used as model compounds; in some cases, the rigidity imposed by tertiary skeletal structures can substantially alter the appearance of the spectra. This effect has been noted in previous work from our laboratories on cellulose [3] and bacterial cell walls [7], in which the importance of the β-glycosidic bonds on the biopolymeric structures have a controlling influence on the vibrational skeletal modes and their observed spectra.

We have initiated a programme designed particularly to provide initial identification of ν(CH) and δ(CH) modes of simple organic molecules, in order to assist in the assignment of vibrational bands in more complex biological materials. Improved assignments for the ν(CH) and $\delta(CH_2)$ regions will assist the identification of these features in biopolymers, lipids and proteins, thus improving the understanding of the vibrational modes of which the skeletal structures are composed. In this paper we have applied selective deuterium labelling in specially synthesised

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compounds to address the problems of assigning the ν(CH) and δ(CH_2) vibrational bands in a compound (*n*-propanol) containing the $CH_3CH_2CH_2$-moiety, in order to derive improved molecular vibrational assignments that can be assimilated into more complex species.

2. Experimental

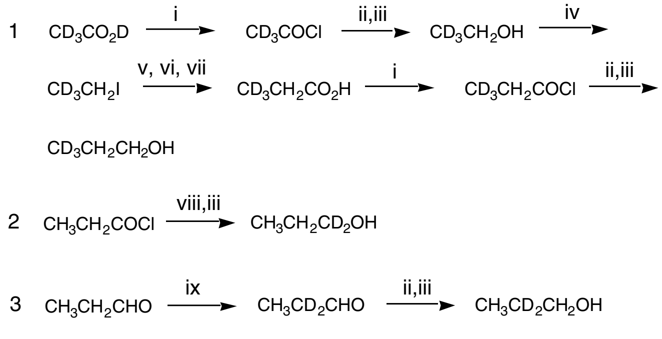
2.1. Origin of specimens

The compounds investigated in this study comprised unlabelled *n*-propanol, $CH_3CH_2CH_2OH$, together with three specifically deuteriated analogues, $CH_3CH_2CD_2OH$, $CH_3CD_2CH_2OH$ and $CD_3CH_2CH_2OH$.

All the unlabelled materials (including *n*-propanol) required for this work were high purity samples obtained from Aldrich or BDH. Isotopically labelled starting materials [D_2O, $LiAlD_4$ and CD_3CO_2D] were obtained from Aldrich and were used without further purification. The labelled alcohols were synthesised by the routes summarised in Scheme 1; details of the procedure for the synthesis of $CH_3CH_2CD_2OH$ and $CH_3CD_2CH_2OH$ are given below; the preparation of $CD_3CH_2CH_2OH$ has been described previously [8]. The isotopic purity of the partially labelled propanols was estimated from their mass spectra to be 96–99%.

2.1.1. $CH_3CH_2CD_2$ OH

A suspension of lithium aluminium deuteriide (5.0 g, 0.119 mol) in triglyme [triethylene glycol, dimethyl ether, $CH_3O(CH_2CH_2O)_3OCH_3$, (150 cm^3)] was stirred magnetically under a nitrogen atmosphere. The temperature was maintained between 30 and 50 °C by means of external cooling (ice/salt bath) during the dropwise addition over a period of 2 h of a solution of propionyl chloride (19 g, 0.205 mol) in triglyme (50 cm^3). Stirring was continued overnight, after which tetragol [tetraethylene glycol, $HO(CH_2CH_2O)_3OH$, (80 cm^3)] was added dropwise over 1 h. Careful distillation gave a colourless liquid product (12.1 g, 95%) having b.p. 96–99 °C; redistillation through a 5 cm helically packed column gave *n*-propanol-1,1-d_2 (10.4 g, 84%) having b.p. 98–99 °C.



Scheme 1. Reagents and conditions: (i) excess PhCOCl, distil., (ii) excess $LiAlH_4$, triglyme, stir 24 h, (iii) excess tetragol, (iv) I_2, red P, (v) Mg, $(C_2H_5)_2O$, (vi) excess CO_2, −78 °C, (vii) HCl/H_2O, (viii) excess $LiAlD_4$, triglyme, stir 24 h, (ix) excess D_2O, pyridine, reflux 72–96 h; repeat twice.

2.1.2. $CH_3CD_2CH_2$ OH

$CH_3CD_2CH{=}O$. A mixture of redistilled *n*-propionaldehyde (32 g, 0.55 mol), deuterium oxide (48 g, 2.4 mol) and pyridine (4 g, 0.05 mol) was refluxed in a nitrogen atmosphere for 72–96 h. The isotopically enriched aldehyde was removed by distillation through a 10 cm helix-packed column (b.p. 47–48 °C) and subjected to two further exchanges with fresh portions of deuterium oxide (35 g, 1.75 mol) and pyridine (4 g, 0.05 mol). The final yield of *n*-propionaldehyde-2,2-d_2 having b.p. 47–48 °C was 13.5 g (41%), but additional batches of aldehyde could be exchanged in somewhat higher yields using the deuterium oxide employed for the first batch of aldehyde.

2.1.3. $CH_3CD_2CH_2OH$

A solution of *n*-propionaldehyde-2,2-d_2 (18 g, 0.30 mol) in triglyme (50 cm^3) was added dropwise during a period of 1.3 h to a magnetically stirred suspension of lithium aluminium hydride (8.7 g, 0.23 mol) in triglyme (300 cm^3) under a nitrogen atmosphere. The temperature was kept below 40 °C by means of external cooling (cold water bath) during the early stages of the addition when the reaction was moderately vigorous. Stirring was continued overnight, after which tetragol (50 cm^3) was added dropwise over 1 h. Careful distillation gave an almost colourless liquid (16.6 g, 89%) having b.p. 95–101 °C (bulk 98–99 °C); redistillation through a 5 cm helix packed column gave *n*-propanol-2,2-d_2 (16.8 g, 89%) having b.p. 98–99 °C.

2.2. Raman spectroscopic instrumentation

Fourier-transform Raman spectra were recorded using a Bruker FRA106 Raman module attachment on an IFS66 infrared optics system. A Nd^{3+}/YAG laser operating at 1064 nm was used as an excitation source and the laser beam focussed to a 100 μm diameter spot at the sample. Samples of the propanols were contained in sealed capillary tubes mounted in a specially constructed holder. Laser powers of up to 500 mW were used with typically 2000 scans at 4 cm^{-1} spectral resolution being collected; the average spectral accumulation time was estimated as 60 min per specimen under these conditions. A liquid-nitrogen cooled germanium detector with extended spectral bandwidth was used over the normal scan range of 50–3500 cm^{-1}; spectra were corrected for the instrument response and the observed band wavenumbers, calibrated against the internal laser frequency, are correct to better than 1 cm^{-1}. The depolarization ratio measurements were made with an optical vector rotator (90°) in the incident laser beam.

3. Vibrational theory

For C_S molecular symmetry as indicated diagrammatically in Fig. 1, the vibrational modes may be classified as follows:

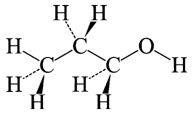


Fig. 1. Molecular structure of propanol, $CH_3CH_2CH_2OH$, on the basis of C_S molecular symmetry; molecular plane of symmetry in plane of paper.

$$\Gamma_{vib} = 18A' + 12A''$$

all of which are Raman-active and 18 bands are expected to be polarized in the Raman spectrum.

For the tetra-atomic skeletal modes only, the following vibrational classification applies:

$$\Gamma_{vib}^{skeletal} = 5A' + 1A''$$

for which five bands will be polarized in the Raman spectrum, comprising ν(CO) and ν(CC) stretching (of which there are two, one involving the terminal carbon atom and the other the carbon atom bound to the OH group), and the δ(CCO) and δ(CCC) in-plane bending vibrations.

All three deuteriated species substituted at the α-, β- and γ-carbon atoms, like the protiated parent molecule, belong to the C_S molecular point group.

4. Results and discussion

The FT-Raman spectrum of protiated $CH_3CH_2CH_2OH$ is shown in Fig. 2; even for such an apparently simple molecule, the complexity of the ν(CH) and $\delta(CH_2)$ wavenumber regions indicates the problems faced in molecular assignments. However, investigation of partially deuteriated propanols in which specific CH_2 or CH_3 groups have been replaced by CD_2 or CD_3 groups should facilitate the identification of the CH modes which arise from these units in the molecule; the assumption is made that there is little or no vibrational coupling between adjacent CH_3 and CH_2 groups in the molecules. Consequently, the isotopically labelled materials chosen for this study were $CH_3CH_2CD_2OH$, CH_3CD_2OH and $CD_3CH_2CH_2OH$. The Raman spectra of the three partially deuteriated analogues of propanol are shown as a stackplot in Fig. 3; comparison of these spectra reveals the influence of deuterium substitution on the α-, β- or γ-carbon atoms in the carbon backbone on the molecular vibrations.

The wavenumbers of the bands in the Raman spectra of the protiated and deuteriated compounds are given in Table 1 with the proposed vibrational assignments. Generally, the latter have been deduced from the literature [9] with specific reference to earlier studies [10] made in our laboratories for 3-methoxy-1-propene (allyl methyl ether), $CH_2{=}CHCH_2OCH_3$, and deuteriated analogues.

Broadly, the molecular vibrational assignments may be classified as modes involving CC, CO, OH stretching and CCC, CCO and COH bending modes (in-plane and out-of-plane); the in-plane modes will be polarized in the Raman spectrum for C_S molecular symmetry whereas the out-of-plane modes will be depolarized. For simplicity, the polarized and depolarized components of the individual spectra are not shown in the stackplots in Fig. 3, but the polarization properties of the modes can be seen in Fig. 4a, b and c for the deuteriated compounds and the details have been summarised in Table 1. It is appropriate to consider each vibrational wavenumber region separately:

4.1. 3400–1900 cm^{-1} region

This is the region where ν(CH), ν(OH) and ν(CD) stretching are expected [9], the strongest ν(CH) bands are found between 2800 and 3000 cm^{-1} for saturated aliphatic molecules, whereas the ν(CD) modes are expected to lie in the region of 2000–2200 cm^{-1}. The ν(OH) stretching vibrations of medium–weak intensity expected around 3238–3250 cm^{-1}, occur in the spectra of all samples since the —OH group is present in each compound. However, deuteriation at the α-, β- and γ-carbon atoms produces a shift of −12, −7 and −5 cm^{-1}, respectively, from the protiated molecular ν(OH) stretching wavenumber at 3250 cm^{-1}. We considered the preparation of a deuteriated analogue of the *n*-propanol substituted on the OH group but this proved rather difficult to purify; since the assignments of the hydroxyl group are not primarily in question here,

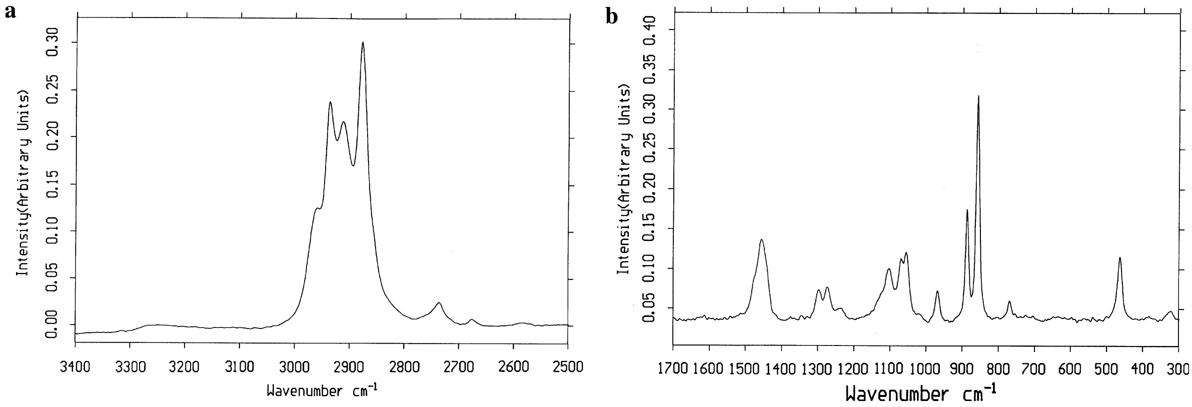


Fig. 2. FT-Raman spectrum of $CH_3CH_2CH_2OH$. (a) 2500–3400 cm^{-1} and (b) 300–1700 cm^{-1}; wavelength of excitation 1064 nm; 2000 accumulated scans at 4 cm^{-1} resolution.

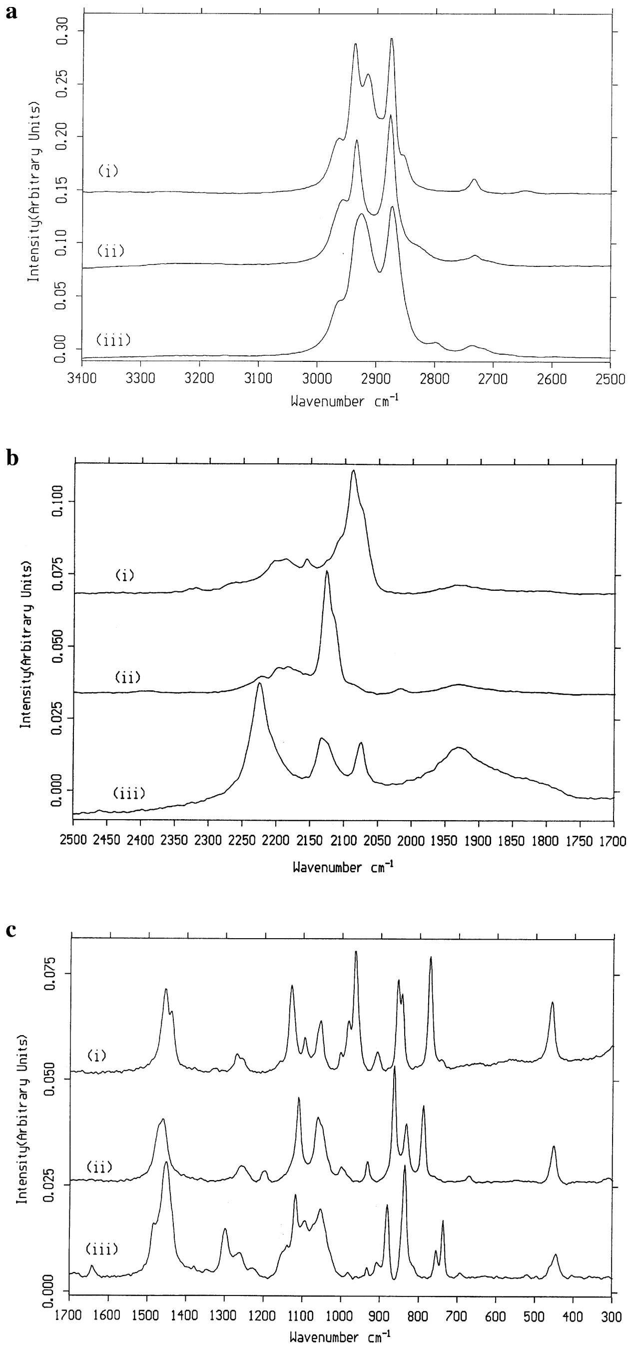


Fig. 3. FT-Raman spectra of partially deuteriated analogues of propanol. (a) 2500–3400 cm^{-1}, (b) 1700–2500 cm^{-1} and (c) 300–1700 cm^{-1}; conditions as for Fig. 2; samples: (i) $CH_3CH_2CD_2OH$, (ii) $CH_3CD_2CH_2OH$ and (iii) $CD_3CH_2CH_2OH$.

the only advantage in the current work in having such a deuterium substituted compound would be in an assignment verification of the skeletal C—C—OH bending mode which is expected near 1000 cm^{-1}. The $\nu(CH_3)$ and $\nu(CH_2)$ assignments follow generally from the deuteriation pattern and theses are tabulated in Table 1.

It should be noted, however, that for C_S molecular symmetry one CH_3 symmetric and one CH_3 asymmetric stretching mode are both of A′ symmetry species and should hence appear polarized in the Raman spectrum. One CH_3 asymmetric stretching band will be depolarized and each CH_2 group will contribute one polarized and one depolarized stretching band in this wavenumber region. Hence, for this molecular symmetry, there should be a total of 4A′ and 3A″ CH stretching modes observable in the Raman spectrum.

Clearly, examination of the Raman spectra and tabulated data shown in Table 1 reveals that the medium intensity, depolarized band at 2970 cm^{-1} in $CH_3CH_2CH_2OH$ which is present at 2965 and 2958 cm^{-1}, respectively, for the $CH_3CH_2CD_2OH$ and $CH_3CD_2CH_2OH$ species and is absent from the spectrum of the $CD_3CH_2CH_2OH$ species must therefore be a CH_3 mode and should be assigned to the CH_3 asymmetric stretching mode on the basis of the polarization data. The progressive change in the observed wavenumber of this CH_3 band with CD substitution at the CH_2 group in the alkyl chain is strongly suggestive of the presence of some degree of vibrational coupling through the CCC skeleton. Likewise, the medium strong intensity polarized band in the range 2937–2926 cm^{-1} can be assigned to the CH_2 symmetric stretching mode as it is present in all four species studied here. In contrast, the medium strong intensity depolarized band occurring in the range 2912–2917 cm^{-1} is seen to be absent from the spectrum of the $CH_3CH_2CD_2OH$ molecule and this can be therefore confidently assigned to the A″ symmetry class CH_2 stretching mode at the α-carbon atom. The CH stretching band in the range 2878–2874 cm^{-1} appears as a polarized band in all four molecules and this therefore places it firmly as an A′ class CH_2 symmetric stretching mode, located at either the β- or γ-carbon atoms. The band in the range 2860–2830 cm^{-1} is again seen to be present for the CH_3 molecules but absent from the CD_3 substituted species, so identifying it as another CH_3 stretching mode belonging to the A′ symmetry class. Hence we have identified two of the three expected CH_3 modes and three of the expected four CH_2 modes predicted on the basis of the C_S molecular symmetry. We can only conclude that the missing CH_3 A″ symmetry class mode and the CH_2 A″ symmetry class mode are accidentally degenerate with other observed bands in the Raman spectrum of the suite of molecules studied.

The four identified polarized ν(CH) modes in the region of 3000–2800 cm^{-1} move to the 2200–2000 cm^{-1} region on deuteriation, where three polarized bands may be identified; these correspond to the $\nu(CD_2)$ or $\nu(CD_3)$ modes of the α-, β- and γ-carbon atom substituents.

Generally, the assignment of the bands in this region concurs with the literature [9] for alkane, haloalkane and alcohol molecules. On substitution of D for H in $CH_3CH_2CH_2OH$ the $\nu(CH_3)$ asymmetric and symmetric stretching bands move from 2970, 2878 and 2860 cm^{-1} to 2227, 2127 and 2076 cm^{-1}, respectively, for $CD_3CH_2CH_2OH$; the isotopic ratios of ν^H to ν^D for the $\nu(CH_3)$ and $\nu(CH_2)$ bands observed here range from 1.35 to 1.38. The CH_3 asymmetric stretching band of A′ symmetry class, identified as the 2860 cm^{-1} band, and similarly the CH_2

Table 1
Wavenumbers and vibrational assignments for $CH_3CH_2CH_2OH$ and deuteriated analogues

$CH_3CH_2CH_2OH$	$CH_3CH_2CD_2OH$	$CH_3CD_2CH_2OH$	$CD_3CH_2CH_2OH$	Approximate assignment of vibrational mode
3250 mw, br, pol	3238 mw, br, pol	3243 mw, br, pol	3245 mw, br, pol	$\nu(\mathrm{OH})$ stretching; free and hydrogen-bonded
2970 m, sh, depol	2965 m, depol	2958 m, depol		$\nu(\mathrm{CH_3})$ asymmetric A''
2937 ms, pol	2938 s, pol	2935 s, pol	2926 s, br, pol	$\nu(\mathrm{CH_2})$ symmetric A'
2912 ms, depol	2917 ms, depol		2915 br, sh	$\nu(\mathrm{CH_2})$ asymmetric A''
2878 s, pol	2877 s, pol	2878 s, pol	2874 s, pol	$\nu(\mathrm{CH_2})$ symmetric A'
2860 m, sh, pol	2860 m, sh, pol	2830 m, sh, pol		$\nu(\mathrm{CH_3})$ symmetric A'
			2799 mw, pol	$\nu(\mathrm{CD_3\text{-}CH_2})$ stretching
2737 mw, pol	2735 mw, pol	2733 mw, pol	2738 mw, pol	$\nu(\mathrm{CH_2\text{-}CH})$ stretching combination
			2720 mw, pol	$\nu(\mathrm{CH_2\text{-}CD_3})$ stretching combination
2676 w, pol	2648 w, pol			$\nu(\mathrm{CH_3\text{-}CH_2})$ stretching combination
	2210 mw,pol	2222 mw, pol	2227 mw, pol	$\nu(\mathrm{CD_3})$ asymmetric; $\nu(\mathrm{CD_2})$ symmetric
		2197 mw, depol		$\nu(\mathrm{CD_2})$ asymmetric
	2187 mw, pol	2184 mw, pol		$\nu(\mathrm{CD_2})$ symmetric
	2157 mw	2157 w		$\nu(\mathrm{CD_2})$ asymmetric
		2127 s, pol	2127 s, pol	$\nu(\mathrm{CD_3})$; $\nu(\mathrm{CD_2})$ symmetric
	2110 w sh	2110 w, sh		
	2089 s, pol	2090 mw, pol	2076 s, pol	$\nu(\mathrm{CD_2})$ symmetric
	2070 mw, depol	2078 w		$\nu(\mathrm{CD_3})$; $\nu(\mathrm{CD_2})$ asymmetric
	1936 mw, br, depol	1932 mw, br, depol	1931 mw, br, depol	
			1485 mw, depol	$\delta(\mathrm{CH_2})$
1470 m, sh, pol				$\delta(\mathrm{CH_2})$ scissors
1456 ms, depol	1456 ms,depol	1460 ms, br, depol	1452 ms, br, depol	$\delta(\mathrm{CH_2})$ scissors
	1440 m, depol			$\delta(\mathrm{CH_2})$ scissors
1350 w, depol	1350 w, depol		1350 w, depol	$\delta(\mathrm{CH_2})$ wagging
1298 m, depol			1298 mw, depol	$\delta(\mathrm{CH_2})$ wagging
1274 m, depol	1272 mw, depol			$\delta(\mathrm{CHO})$
	1260 w	1258 m, br, depol	1260 mw, depol	$\delta(\mathrm{CHO})$
1230 w, depol			1230 w, depol	
		1197 mw, depol		
	1132 mw, pol		1140 w, sh	$\nu(\mathrm{CC})$
1120 w, pol		1111 s, pol	1118 ms, pol	$\nu(\mathrm{CO})$
	1097 mw, depol		1097 mw, pol	$\nu(\mathrm{CC})$
1075 m, pol	1070 mw, sh			$\nu(\mathrm{CCO})$ o-o-p
		1061 ms, pol		$\delta(\mathrm{CD_2})$ scissors
1056 ms, pol	1056 br, pol	1050 sh, pol	1054 ms, br, pol	$\nu(\mathrm{CO})$
1015 vw	1005 w, depol	1000 mw, depol	1000 w	$\delta(\mathrm{COH})$
	980 m, pol			$\delta(\mathrm{CD_2})$
969 m, depol	968 s, pol			$\rho(\mathrm{CH_3})$
		933 m, pol		$\delta(\mathrm{CD_2})$ wagging
	910 mw, depol		905 w	
888 ms, pol			882 ms, pol	$\nu(\mathrm{CCC})$
859 s, pol	857 s, pol	865 s, pol		$\nu(\mathrm{CCC})$; $\nu(\mathrm{CCO})$ ip
	847 ms, pol			$\nu(\mathrm{CCC})$ ip
		834 ms, pol	837 ms, pol	$\nu(\mathrm{CCC})$ symmetric
800 vw				
		789 s, pol		
780 m, pol	774 s, pol			$\delta(\mathrm{CCC})$
	750 w, depol		755 m, pol	$\delta(\mathrm{CCC})$
			737 m, pol	$\delta(\mathrm{CCC})$,$\rho(\mathrm{CD_3})$
		680 mw, pol		$\rho(\mathrm{CD_2})$
464 ms, pol	459 ms, pol	452 ms, pol	445 m, pol	$\delta(\mathrm{CCO})$
322 mw, br, depol				$\delta(\mathrm{CCC})$
	320 mw, br, depol	308 mw, br, depol	297 mw, br, depol	$\delta(\mathrm{CCC})$

stretching band of A' symmetry class at 2937 cm^{-1} could each now comprise a CH_2 stretching mode, one of which is part of the terminal carbon group and the other attached to the OH group, which were not positively identified in the analysis earlier. Selective deuteriation of the CH_2 attached to the terminal carbon group shows that this band is responsible for the observed feature at 2938 cm^{-1}, whereas the other CH_2 group gives rise to the band at 2935 cm^{-1}; these move to 2187 and 2184 cm^{-1}, respectively, upon deuteriation, with an isotopic ratio of 1.35. The deuteriation pattern seems to confirm the degeneracy of the CH_2 mode pattern alluded to here.

The weaker features in the Raman spectra in the 2600–2750 cm^{-1} region are assignable to combination modes of the fundamentals of the terminal $CH_3{-}CH_2$ moiety [11]; selective deuteriation has permitted their

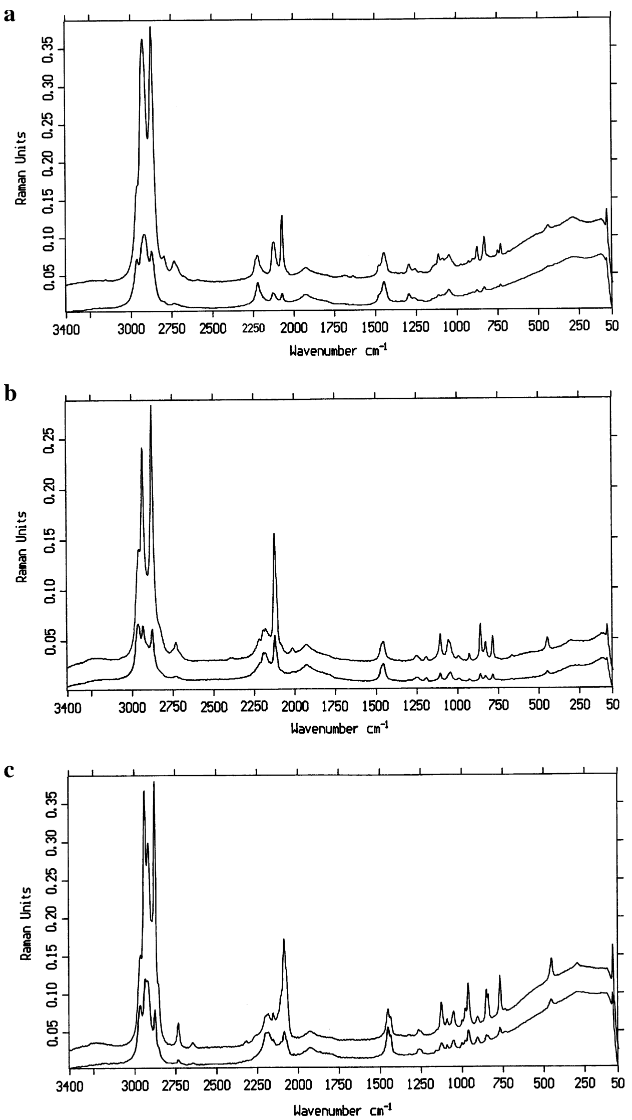


Fig. 4. FT-Raman spectra of partially deuteriated analogues of propanol. (a) CD_3CH_2 CH_2OH, (b) $CH_3CD_2CH_2OH$ and (c) $CH_3CH_2CD_2OH$; 100–3400 cm^{-1} wavenumber range, 2000 scans accumulated at 4 cm^{-1} spectral resolution, 1064 nm excitation; upper spectrum—depolarized, lower spectrum—polarized.

assignment as shown in Table 1. The combination modes at 2680, 2648 cm^{-1}, move to ~1936 cm^{-1} upon deuteriation with an isotopic ratio of 1.38. Other weak features in this region are assignable to combination bands of fundamentals involving CC and CO stretching modes.

4.2. 1800–250 cm^{-1} region

In this wavenumber region we expect to observe the six skeletal modes predicted, including the ν(CC), ν(CO) and δ(CCO), δ(CCC) modes; the five skeletal polarized bands of A′ symmetry can be identified as ν(CO)/ν(CC) at ~1130 cm^{-1}, ν(CO) at 1056 cm^{-1}, ν(CCO) in-plane at ~850 cm^{-1}, δ(CCC) at ~770 cm^{-1} and δ(CCO)/δ(CCC) at ~460 cm^{-1}. Variations in the skeletal stretching wavenumbers from the values observed in $CH_3CH_2CH_2OH$ are ascribed to mass-effects of CD_3 and CD_2 substitution on adjacent carbon atoms of the skeletal mode concerned. Thus, the δ(CCO)/δ(CCC) vibrational mode at 464 cm^{-1} for $CH_3CH_2CH_2OH$ shifts to 445 cm^{-1} for CD_3CH_2 CH_2OH and the ν(CCC)/ν(CCO) band at 859 cm^{-1} moves to 837 cm^{-1} for the same two molecular species. Theoretically, the skeletal modes should be independent of ν(CH) substitution by ν(CD). In practice, however, significant wavenumber shifts may be observed; these are ascribed to the influence of mode mixing, primarily with CH_2 and CH_3 deformation modes in the same symmetry classes. Even the O^{13}-substitution of the oxygen atom, undertaken in a recent investigation of allyl methyl ether in an attempt to derive unambiguous information about the ν(CCO), ν(CCC) and δ(CCO) and δ(CCC) vibrational modes, was determined to be not without interference from mode mixing of this sort [10]. In this region, therefore, for the $CH_3CH_2CH_2OH$ and its deuteriated analogues, in addition to the six modes expected for the CCCO skeleton, we would expect a further 16 modes ($7A' + 9A''$) arising from CH_2 and CH_3 motion. These will consist of deformations of the type δ(CH_2), δ(CCH), δ(CH_3) and rocking or wagging modes of the type ρ(CH_2) and ρ(CH_3).

It is hardly surprising, perhaps, that the δ(COH) mode is not uniquely identifiable from the Raman spectra, since it occurs as a medium–weak feature near the 1000 cm^{-1} region, where the δ(CO, CHO), and δ(CD_3,CD_2) modes also occur. It is possible that the Raman spectrum of oD substituted propanol would assist in the clarification of this assignment, but as mentioned earlier the preparation of a sufficiently pure sample of this material was not possible in this study. The skeletal C—C and C—O stretching modes show little difference from their wavenumbers for the *n*-alkanes; the masses of C and O do not differ greatly and a strong interaction is to be expected here; the infrared spectra exhibit some differences in observed band intensity between alkanes and alcohols in this region because of the C—O band polarity. However, in several cases in Table 1 the deuteriation assists materially in the identification of a specific CH mode (e.g., the 1274 cm^{-1} band assigned to a δ(CHO) mode).

The δ(CH_2) and δ(CH_3) modes expected around 1300–1470 cm^{-1} will occur around 960–1080 cm^{-1} for the analogous CD_2 and CD_3 species. Unfortunately, the deformation modes of the CD_2 and CD_3 moieties occur in a similar wavenumber region as the rocking vibrations for CH_2 and CH_3 groups, whose deuteriated modes are themselves expected around 640–680 cm^{-1} and this complicates the observed spectra in this wavenumber region.

In the low wavenumber region, the modes are best described as mixed modes, particularly of δ(CCO) and δ(CCC) vibrations. Hence, the listing of modes in Table 1 is again subject to mode mixing; nevertheless, several features of interest are apparent. For example, the band at 1298 cm^{-1} in the spectrum of $CH_3CH_2CH_2OH$ also occurs at 1298 cm^{-1} in the spectrum of $CD_3CH_2CH_2OH$ but not in those of $CH_3CD_2CH_2OH$ and $CH_3CH_2CD_2OH$. This band is assigned here to a $\delta(CH_2)$ wagging mode, because it must be ascribed to a $-CH_2CH_2-$ grouping, rather than a $-CD_2CH_2-$ or $-CH_2CD_2-$ moiety.

The conclusions of this study demonstrate the value of isotopic substitution (particularly D for H) especially in the CH_3 and CH_2 stretching, bending and rocking regions of the spectrum. For example, the combined polarization and deuteriation data clearly confirm the assignment of the 2860 cm^{-1} band to a $\nu(CH_3)$ symmetric stretch, which had been tentatively proposed in the literature to hitherto correspond to a $\nu(CH_2)$ mode [1,10]. However, the 2878 cm^{-1} mode is clearly a $\nu(CH_3)$ asymmetric stretch and this has formerly been ascribed only tentatively [1,10] to a $\nu(CH_2)$ symmetric stretching mode. Likewise, the 2730 cm^{-1} band, previously assigned to a $\nu(C{=}CH)$ aliphatic mode [3,9] cannot be of this description as it is present in the protiated and deuteriated saturated alcohols studied here; it is clearly assignable on the basis of the present work to $\nu(CH_2CH_2)$ or $\nu(CH_2CD_2)$ stretching. On the other hand, the earlier tentative assignment on a literature basis [9] of a band at 1450 cm^{-1} in keratotic tissue [1] as a $\delta(CH_2)$ scissors mode is reaffirmed as such by this deuterium-labelling study. Similarly, a band at 1298 cm^{-1} which has also been ascribed in biological tissues to a $\delta(CH_2)$ mode, is also confirmed in assignment on the basis of this work [3].

The band at 968 and 969 cm^{-1} observed here in both the parent protiated and CH_2 deuteriated molecules is assigned to a $\rho(CH_3)$ terminal methyl mode; it is absent from the spectrum of $CD_3CH_2CH_2OH$, and a new band appears at 737 cm^{-1} so this assignment better fits the evidence than does the current literature [9], where it is tentatively ascribed to a $\nu(CC)$ stretching mode. A band at 883 and 891 cm^{-1} observed in biological specimens and ascribed to a $\rho(CH_2)$ rocking mode is shown to be mis-assigned and more accurately described as a $\nu(CCC)/\nu(CCO)$ mode.

We propose to extend this study to other series of specifically labelled analogues of simple organic compounds which serve as models for larger biological molecules, so as to refine the tentative assignment of bands in several regions of interest, thereby enhancing the value of Raman spectroscopy for biological molecular applications.

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