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SUBMILLIMETRE LASER AND INTERFEROMETRIC SPECTROSCOPY OF THE ALKYL ALCOHOLS

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The far-infrared power absorption of a series of alkyl alcohols has been measured with interferometry and laser spectroscopy. The two techniques are complementary and in good agreement. The vibrational COH torsion and O - - - H stretch have been analysed, particularly for methanol in dilute solutions.

1. Introduction

The brownian motion of alkyl alcohol molecules in the liquid state is restricted by a network of hydrogen bonding [1–4]. In the lower homologues such as methonal and ethanol, the hydrogen bonding is extensive and persists [3] in dilute solution [5,6]. The higher homologues and their isomers tend to form different types of networks depending on the position of the –OH group in the chain and whether the chain is straight or branched [1,7]. In this letter we report briefly on a series of measurements with a view to correlating the behaviour of these alcohols in the radio, microwave and far-infrared [4,8,9] frequency regions. Spectral data prior to this work have been interpreted without involving the complete range of frequency over which the molecular rotational motion manifests itself. The validity of the conclusions reached so far is therefore restricted. Here we present good-quality far-infrared data for methanol and some of the higher *n*-alkyl alcohols. The data are interpreted with reference to the low-frequency dielectric loss peak. The latter is a part of the overall rotational spectrum taken from zero to mid-infrared frequencies. Our study on methanol is combined with the works of Passchier et al. [5,6], and Falk and Whalley [10]. The analysis of the results for pure methanol includes the spectral features up to ≈675 cm^{-1}, where the COH torsional mode appears [10].

2. Experimental

In order to provide for an independent cross-check on the accuracy of the power absorption coefficient $\alpha(\bar{\nu})$, especially for the highly absorbing liquids such as alcohols, we have used two complementary instruments. A Grubb–Parsons/NPL Michelson interferometer has been used to produce broad-band spectra from 20 to 320 cm^{-1}. A tunable submillimetre laser at spot frequencies of 62, 84, 104, 140, 213 and 232 cm^{-1} also provides $\alpha(\bar{\nu})$ values and checks on any tendency for the interferometer to produce distorted bandshapes from beam convergence effects. The submillimetre laser radiation was modulated at 12 Hz. The power is measured as a function of the thickness of the liquid (d) using the Golay detector. The output of the detector is fed to a locking amplifier with a reference signal from the modulator of the laser system. $\alpha(\bar{\nu})$ is calculated using the Beer–Lambert law

$$I = I_0 \exp(-\alpha d),$$

where I is the intensity of the signal for a sample thickness d. A straight line is observed between $\log_e I$ and d. α turns out to have a standard error of estimate less than 2%. The linearity of $\log_e I$ versus d shows that the errors due to reflection of the beam by the windows of the cell are minimal. The method greatly reduces the uncertainty in $\alpha(\bar{\nu})$ due to the sample thickness as (a) d is averaged out, and (b) d for the laser experiment is

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much greater than for the corresponding interferometric experiment because of the higher intensity of the laser beam.

The submillimetre laser radiation is stabilised with a feedback loop from a reference pyroelectric detector interfaced with electronic cavity-stabiliser systems. One of the cavities is locked to the main CO_2 laser system, whereas the other locks onto the methanol line. The time constant of the loop as quoted by the manufacturers is 1 s.

Frequencies of the laser beam were checked to be monochromatic and were measured using the Michelson interferometer to within ± 2 cm^{-1} [11].

3. Results

Results are illustrated in figs. 1, 2 and 3. The previously characterised σ hydrogen-bond stretching frequencies are marked on these figures. In most cases these are corroborated by our results. This mode of absorption is gradually reduced (fig. 2) by dilution, since it involves the relative roto-translation of two or more alcohol molecules linked by the linear H bond. The laser points in fig. 1 and 3 in most cases agree satisfactorily (to within ±5%) with the interferometric results. We remark that the earlier results of Chamberlain et al [4] seem to be in error, in particular on the high-frequency side and also in absolute value in certain cases. In this work, we have defined far-infrared peaks in alkyl alcohols in the region 60–280 cm^{-1}. These are assigned in table 1 and supplemented with literature assignments where relevant.

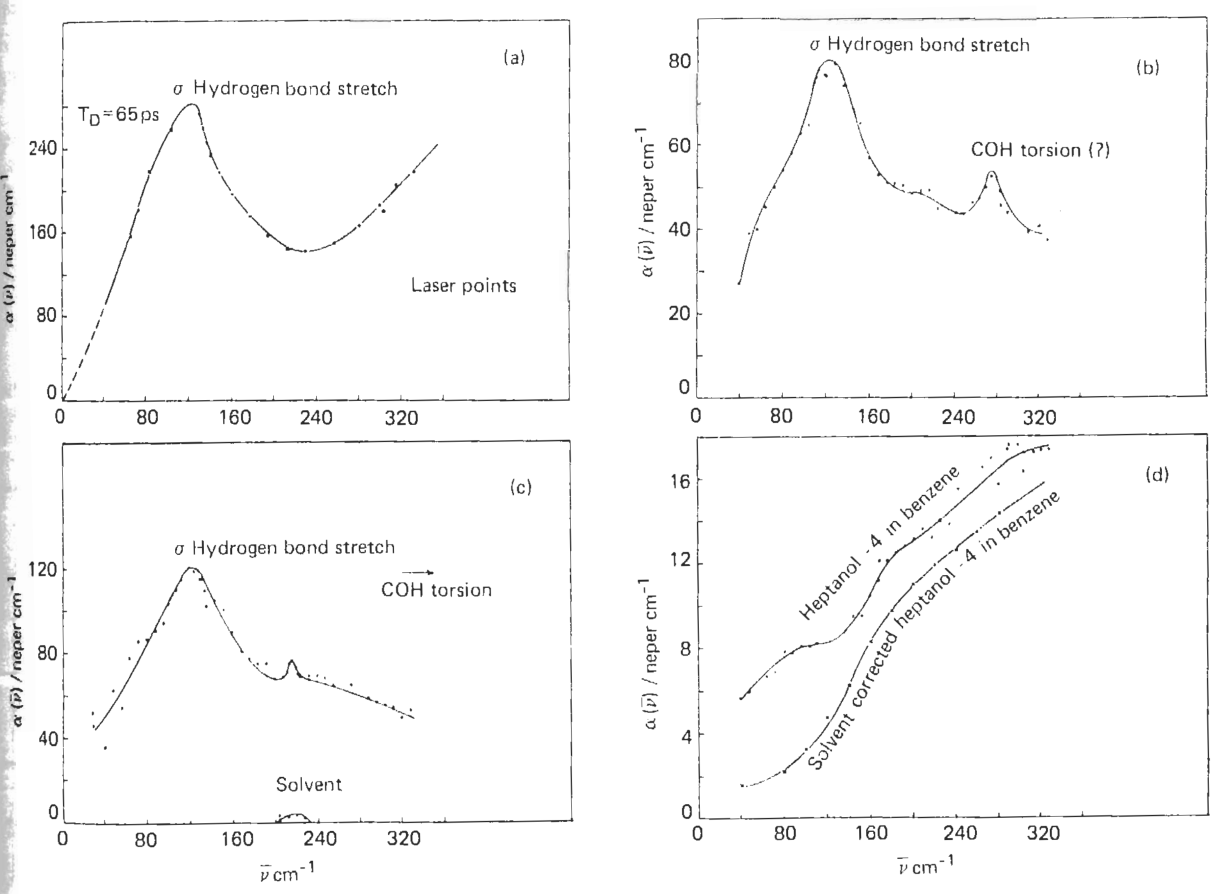

Fig. 1. Far-infrared power absorption of methanol and 4-heptanol solutions. Solvent corrected unless otherwise stated. (∗) laser points, (•) interferometric data. (a) Pure methanol, (b) 50% V/V CH_3OH/CCl_4 (uncorrected), (c) 25% V/V CH_3OH/CCl_4, (d) 5% V/V heptanol-4 in benzene.

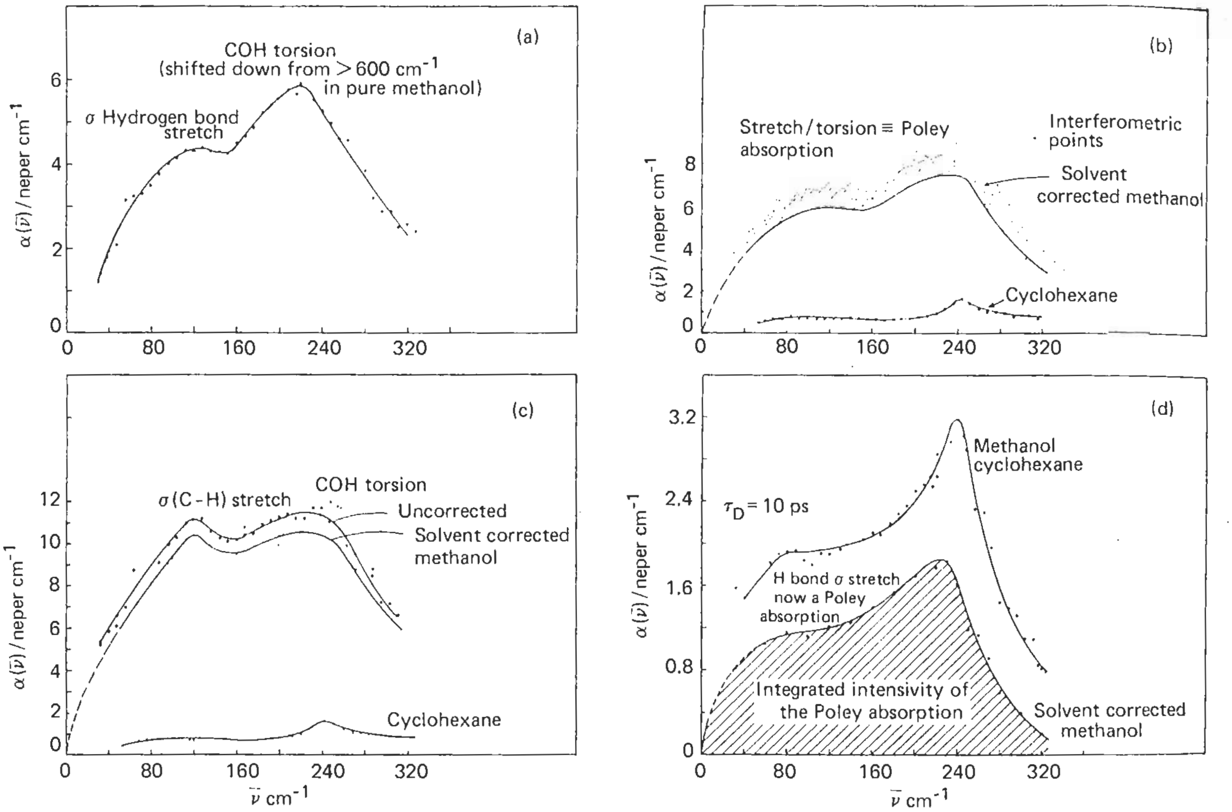

Fig. 2. Far-infrared power absorption of CH_3OH/cyclohexane solutions. (a) 10% V/V, (b) 5% V/V, (c) 2.5% V/V, (d) 1.25% V/V.

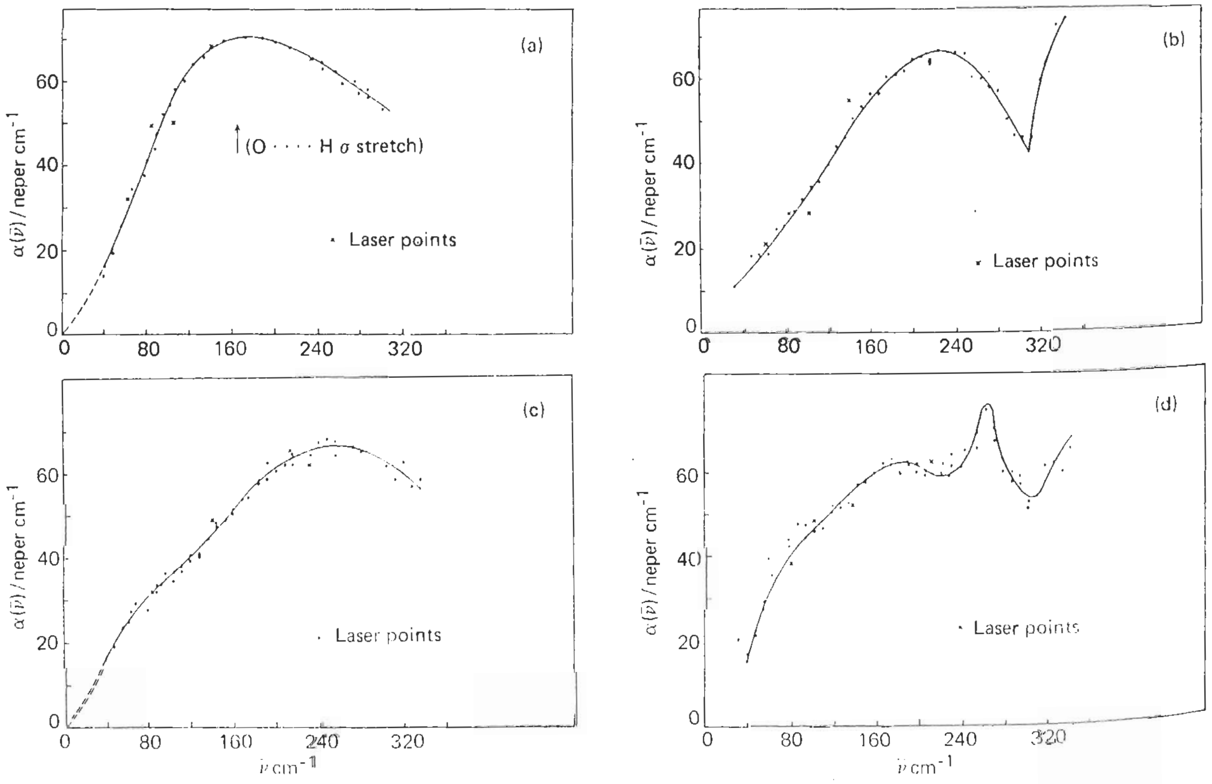

Fig. 3. The heptanols (pure liquids) (a) heptanol-1, (b) heptanol-3, (c) heptanol-4, (d) 5-methyl-2-hexanol.

Table 1
Far-infrared absorptions of the alkyl alcohols

Alcohol	Far-infrared peak (cm^{-1}) and assignment	Dielectric relaxation time (ps)
methanol (pure)	675: COH torsion 130: σ O - - - H stretch	65
ethanol (pure)	110: σ O - - - H stretch 250: $-CH_3$ torsion	154
propanol-1 (pure)	145: σ O - - - H stretch 225: $-CH_3$ torsion	430
pentanol-1 (pure)	150: σ O - - - H stretch 255 shoulder: $-CH_3$ torsion	920
hexanol-1 (pure)	160: σ O - - - H stretch Higher frequency shoulder, CH_3 torsion	1210
heptanol-1 (pure)	190: σ O - - - H stretch compounded with some CH_3 torsion	1380
heptanol-3 (pure)	245: σ O - - - H stretch compounded with CH_3 torsion	1180
heptanol-4 (293 K)	225: σ O - - - H stretch compounded with some CH_3 torsion 360: closed *n*-mer lattice modes	1180
heptanol-4 (343 K)	230: O - - - H stretch compounded with some CH_3 torsions 360: closed *n*-mer liquid lattice mode	–
heptanol-4 (5% *V*/*V* in benzene)	Shoulder at ≈ 200: remains of the σ O - - - H stretch. A rising continuum absorption due to CH_3 torsion	–
t-butyl alcohol (pure)	75: Poley absorption of the dimer 150: σ O - - - H stretch >320 cm^{-1}: COH torsion	–
t-butyl alcohol (10% *V*/*V* in cyclohexane)	60: Poley absorption of a mixture of monomers and dimers 150: weak mode due to σ O - - - H stretch in the dimer 230: COH torsion, shifted down from high frequencies by dilution	–
methanol solutions: 50% *V*/*V* in CCl_4	120: σ O - - - H stretch of the dimer 280: a possible COH torsion	–
25% *V*/*V* in CCl_4	120: σ O - - - H stretch of the dimer 230: a possible COH torsion	–
10% *V*/*V* in cyclohexane	120: weak mode due to σ O - - - H stretch of the dimer 230: COH torsion shifted down from 675 cm^{-1} by releasing the H-bonding	–
2.5% *V*/*V* in cyclohexane	120: shoulder due to removal of the σ O - - - H stretch 230: COH torsion	–
1.25% *V*/*V* in cyclohexane	80: shoulder due to torsional oscillation of the monomers – the Poley absorption 220: COH torsion superimposed on the Poley absorption of the monomer	–

4. Discussion

4.1. *Methanol*

Falk and Whalley [10] and Passchier et al. [5] have observed the absorption band centred at 675 cm^{-1} in liquid methanol. This has been attributed to the COH torsion mode. In a 50% *V*/*V* solution of methanol in CCl_4, we observe that the band moves down to 280 cm^{-1} (fig. 1b). On further dilution by 100% the band merges into the solvent peak at 230 cm^{-1} (fig. 1c). For methanol in dilute solutions of cyclohexane (figs. 2a–2d) we observe a small gradual shift of the torsion mode from 230 to 210 cm^{-1}. These results supplement the measurements on methanol vapours by Lake and Thompson [12], where a band near 200 cm^{-1} was observed. Dilution tends to isolate the methanol monomers, freeing them from hydrogen bonding. The energy involved in COH torsion is consequently reduced with a decrease in frequency of absorption. The monomer peak at 120 cm^{-1} is similar to that observed for water [13] in extremely dilute solutions. In the pure liquid, however, the Debye time of 64 ps is indicative of a slow and cooperative process involving several hydrogen-bonded molecules. The broadened modes at 130 and 675 cm^{-1} are the faster motions, assigned as above, superimposed on the slow motions. However, in a 1.25% V/V dilute solution of methanol in cyclohexane, we believe that the 120 cm^{-1} σ H-bond stretch evolves into a Poley band with its origin in molecular roto-vibrations. Furthermore, the low-frequency relaxation time shortens to less than 10 ps and, consequently, the dielectric loss peak becomes observable as a low-frequency (<10 cm^{-1}) shoulder in $\alpha(\bar{\nu})$ (fig. 2d).

4.2. Higher alkyl alcohols

Our spectra of higher alcohols differ considerably from those of Chamberlain et al. [4]. These spectra show finer details than given in the literature. These are summarized in table 1 and are shown for heptanols in fig. 3. Based on an analysis of the results on higher alkyl alcohols, Vij et al. [1] remarked that n-alkanols yield a semi-circular Cole–Cole arc. The isomers, and in particular those involving branched chains, show skewed-arc behaviour. This type of difference in behaviour is also reflected in the far infrared. The spectrum of 1-heptanol is a Poley-type absorption but with a less steep rise of α and peaks at 195 cm^{-1}. This consists mainly of σ O - - - H stretch bands. On account of a chain-like regular structure in n-heptanol, CH_3 torsions are comparatively restricted. These torsions therefore contribute less significantly in the experimental range of the spectrum. However, for a branched 3-heptanol, there are two CH_3 groups attached to each end of the molecule. The spectrum is therefore compounded with CH_3 torsions. In contrast, the spectrum of 5-methyl-2-hexanol is twin peaked; the peak at 270 cm^{-1} is rather sharp. Since the dielectric studies provide evidence for a closed multimer structure in the branched alcohol isomers, it is reasonable to conclude that the 270 cm^{-1} peak is due to lattice vibrations [14] of a closed multimer structure. CH_3 torsions in the structure appear to be severely restricted due to steric hindrance. The spectrum of 4-heptanol is intermediate to that of 3-heptanol and 5-methyl-2-hexanol. We remark that an early interpretation of the dielectric loss of alcohols in terms of secondary or tertiary Cole–Cole arcs needs to be re-examined in conjunction with accurate far-infrared data.

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