Molecular dynamics of methanol

Far infra-red laser spectroscopy, interferometry and computer simulation

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The far infra-red power absorption coefficients of methanol in the pure and dilute solution states have been measured at 293 K in the wavenumber range 20–230 cm^{-1} with interferometry and laser spectroscopy. The liquid state spectrum shows a peak at 120 cm^{-1} which shifts to below about 80 cm^{-1} upon extreme dilution in cyclohexane. In such solutions a second major peak is observed at 210 cm^{-1}, which probably corresponds to the COH torsion of single molecules as observed at 200 cm^{-1} by Lake and Thompson for methanol vapour. The results are interpreted in a semi-quantitative manner using molecular dynamics simulation. The methanol pair-potential is modelled roughly with a 3×3 site–site representation, made up to Lennard-Jones cores and fixed point charges. While this gives a fairly acceptable result at short-times or far infrared frequencies, it does not continue to do so at longer times. This has been attributed to an insufficient consideration for the long-range hydrogen-bonding in the model.

1. INTRODUCTION

The far infra-red power absorption of the aliphatic alcohols [1–8] is a measure of the extent to which the librational (or torsional oscillatory) motion of the molecular framework is affected by the network of hydrogen bonding. The interpretation of the spectrum therefore requires an adequate consideration of co-operativity among the molecules on the molecular scale. An examination of the spectral data may reveal these details in several different ways.

The intensity of the spectrum may be used to calculate the absorption cross-section per molecule, a factor which may be compared [9] with a gas phase sum rule such as that given by Gordon [10] for simple and rigid molecules. The extent to which the experimentally measured cross-section departs from the sum-rule prediction measures the effect of inter-molecular interactions in the liquid phase both through the induced dipolar absorption and the effective moment of inertia [11] (H-bonding).

The position of the far infra-red absorption peak may be correlated empirically for methanol using the Reid–Evans torque coefficient [12, 13] Tq. The dependence of this factor on a calculable volume of rotation is known to differ appreciably in associated and non-associated molecular liquids [12, 13].

The shape of the infra-red absorption band provides us with the details of the molecular dynamics on a picosecond time scale. The molecular motions evolve in time and result in a dielectric loss at lower frequencies, typically in the MHz and GHz regions. By making dilute solution studies and also studies using supercooled solvents [14] the effects of hydrogen-bonding may be removed. The spectra of the methanol free of hydrogen-bonds may then be interpreted.

The detailed interpretation of molecular motion and interaction in aliphatic alcohols is a formidable task. It is, however, essential to obtain high quality spectra over the MHz to far infra-red range before attempting an empirical or a semi-quantitative interpretation. We have optimized the quality of the far infra-red spectral data produced for this paper by using a combination of two instruments. The magnitude of the absorption coefficient is fixed by a series of spot-frequency measurements using a tunable sub-millimetre laser. By collimating the output beam of the interferometer the spectrum range has been extended to 320 cm^{-1}. This is necessary in order to characterize the main infra-red peak which, in the associated systems peaks at higher frequencies than is usual in non-associated molecular liquids.

The computer simulation [15] on methanol represents an attempt to reproduce the observed far infra-red spectrum with a model of an intermolecular potential. This is based on a three-by-three atom–atom Lennard-Jones core with partial charges on each atomic site. The Lennard-Jones parameters and partial charges are taken from the literature [16–18] and have not been adjusted in any way. This implies, of course, that the pair potential is relatively a crude one. The disadvantage, however, is offset considerably by the fact that the parameters of the potential are easily transferable between molecules. The computer simulation method provides us, in addition, with the ability to produce a variety of dynamic data in a self-consistent way, including the low frequency (GHz) adjunct of the far infra-red spectrum.

Methanol has previously been studied by Mandel *et al.* [5, 6] in the range 100 to 500 cm^{-1} and by Davies [11] up to 200 cm^{-1}. The 120 cm^{-1} band of methanol has been attributed by these authors to the stretching of the hydrogen bond between the oxygen atom of one molecule and the hydrogen atom of another. It is claimed that below a concentration of 0·12 mol. l^{-1} on dilution the 120 cm^{-1} band ' disappears '. This appears to be inconsistent with the expectation of a Poley absorption in dilute solutions. We intend to supplement and explain the behaviour of the methanol molecules by making use of the more accurate data and developments in the computer simulation of molecular dynamics.

2. Experimental

Broad-band spectra were taken with a Grubb-Parsons/NPL interferometer in phase modulation, with a beam diameter restricted to about 2·8 cm. This improved the collimation and increased the range of the instrument to about 320 cm^{-1} on the high frequency side. The cells used were standard VC-01 or VT-01 variable path length in design with TPX windows (poly-4-methyl-pent-1-ene).

The system for scanning the far infra-red spectrum has been improved by interfacing the interferometer to a 380Z microcomputer system which, in turn,

is linked to a Honeywell 6080 mainframe computer. This system ensures a rapid analysis of the interferometric data by fast Fourier transformation. The accuracy in the power absorption coefficient is maximized by repeated averaging of the interferogram ratios. This was double-checked using a sub-millimeter laser as described below.

An Apollo Instruments CO_2 laser was used to pump several of the lines of methanol contained in a resonant cavity. The emitted radiation was checked for monochromicity using the Grubb–Parsons interferometer and its wave-number was measured [19] to within $\pm 2 \mathrm{~cm}^{-1}$. The power absorption co-efficient was determined using the Beer Lambert law

$$I = I_0 \exp\left(-\alpha d\right), \tag{1}$$

where I is the intensity of the laser beam after traversing the sample thickness d in cm. The logarithm of the intensity is plotted against the sample thickness d. The linearity of the plot (figure 1) shows the stability of the laser system both in amplitude and frequency. Using this method, some systematic un-certainties inherent in the broad-band interferometric method may be removed. Among these are convergent beam effects which may sometimes distort the base line of the Fourier transform and errors due to the reflection losses. The major advantage of the laser system however is that the extra power may be used to penetrate an accurately measurable thickness of these intensely absorbing liquids. In fact, the difference in the sample thickness, for the beam intensities of I and I_0, is used in equation (1) rather than the actual thickness of the sample. An accuracy of ± 5 per cent in $\alpha(\bar{\nu})$ for intensely absorbing liquids, such as methanol, is estimated.
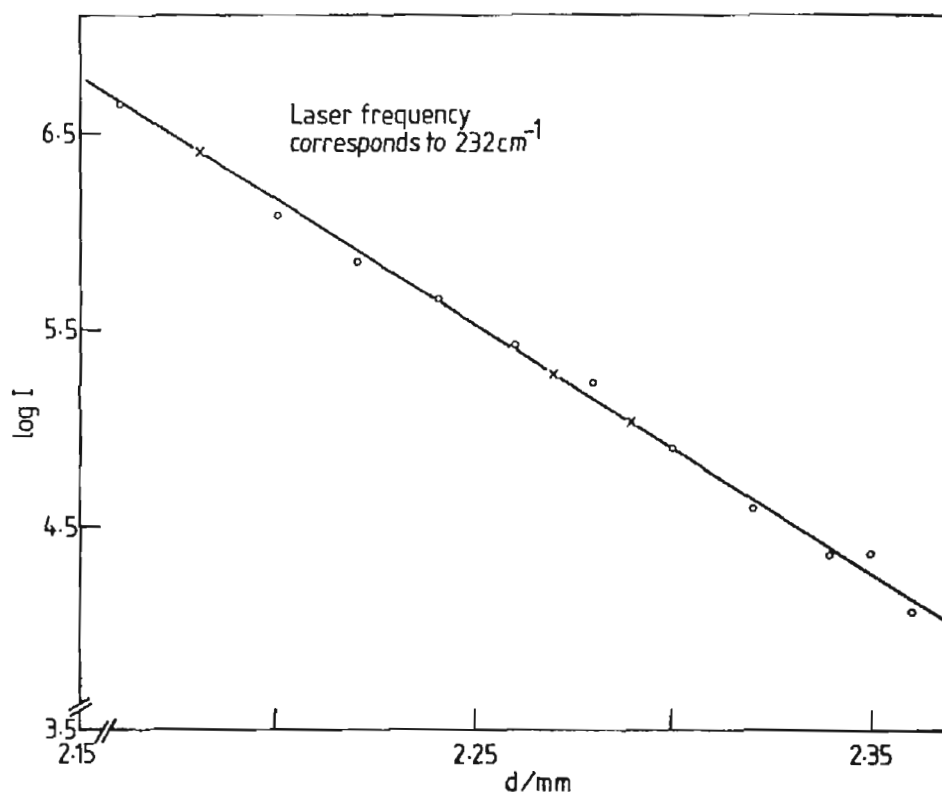

Figure 1. $\log_{10} I$ versus d (sample thickness), $\circ$, d increasing ; $\times$, d decreasing.

3. Results

Figure 2 shows $\alpha(\bar{\nu})$ as a function of $\bar{\nu}$ for methanol. The laser points at spot frequencies of 62, 84, 104, 140, 213 and 232 cm^{-1} fix the absolute values of the ordinate scale within ± 5 per cent. Figure 3 shows the absorption spectrum of pure methanol up to 980 cm^{-1}. The spectral features from 320 cm^{-1} upwards are taken from the works of Mandel and his co-workers [5, 6] and the Aldrich infra-red catalogue [20]. Figure 4 shows $\log \epsilon''$ for methanol as a function of $\log f$. The microwave dielectric data is taken from the literature [21]. The far infra-red power absorption shows up as a broad shoulder on the low frequency ϵ''. A twin peak spectrum in the 20–320 cm^{-1} range is observed for a 50 per cent v/v methanol–acetone. Figures 5 and 6 show a similar dependence of $\alpha(\bar{\nu})$ on $\bar{\nu}$ for dilute solutions of methanol (1·25 per cent v/v in cyclohexane and decalin saturated with methanol).
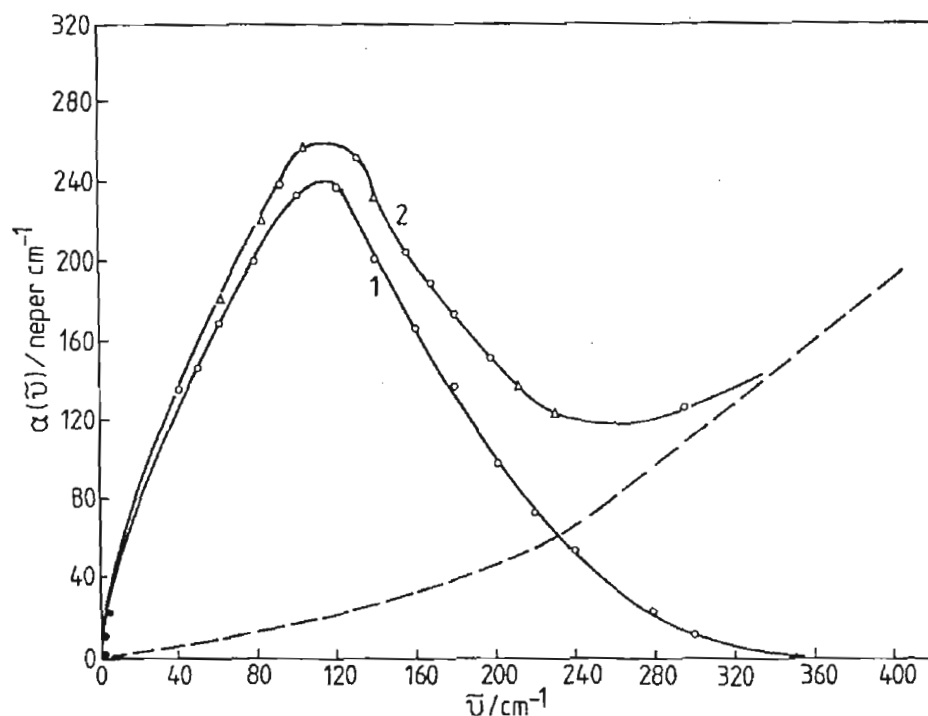

Figure 2. Far infra-red power absorption of pure methanol: interferometric. ●, microwave ϵ'' measurements (data from [21]); ▷, laser points. Curve 1, corrected from higher frequency dispersion (shown by dotted lines); Curve 2, experimental.

The rotational velocity autocorrelation function $(C_{\dot{\mu}(t)})$ has been obtained by taking the Fourier transforms of the absorption spectrum of a very dilute solution of methanol in cyclohexane (1·25 per cent v/v) and is shown in figure 7. This a.c.f. is approximately rotational as it contains a small component arising from the torsional motion of dipoles and a small component from the rotational–translational (r.t.) coupling in addition to the purely rotational motion of molecules. This experimental a.c.f. is compared with that obtained from computer simulation on methanol molecules in the absence of hydrogen bonding.
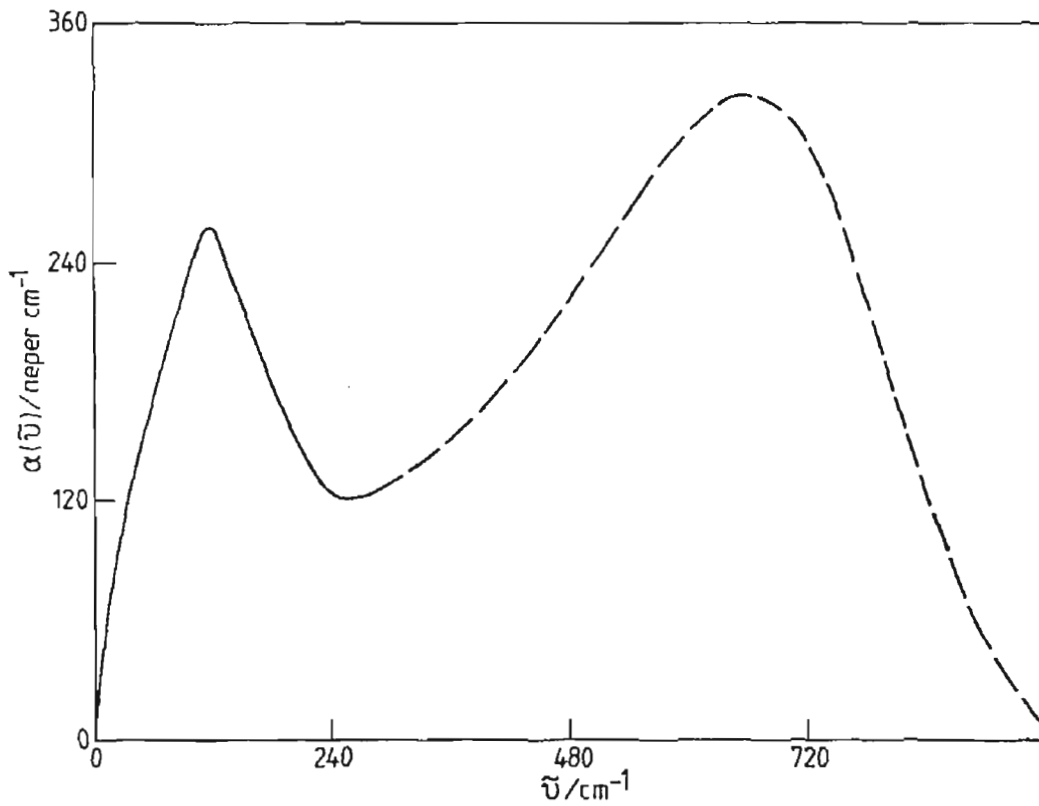
Figure 3.   Power absorption of pure methanol in far infra-red and mid infra-red wave regions with the latter taken from [20].
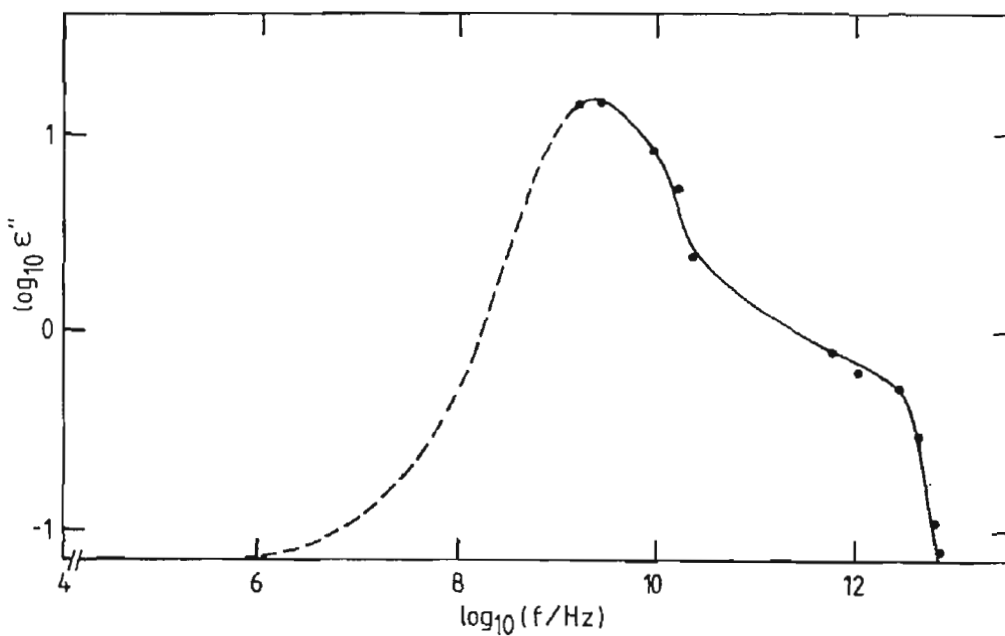

Figure 4.   A plot of $\log_{10} \epsilon''$ versus $\log_{10} f$ for pure methanol.
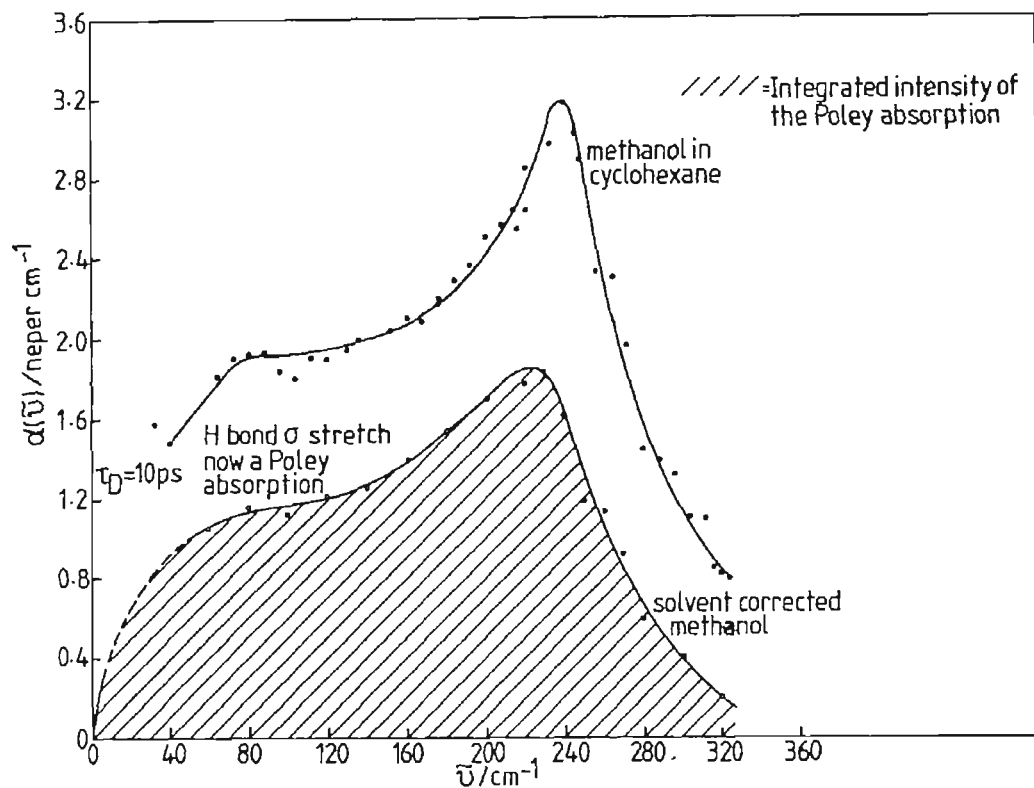
Figure 5.   Far infra-red power absorption of 1·25 per cent v/v methanol–cyclohexane
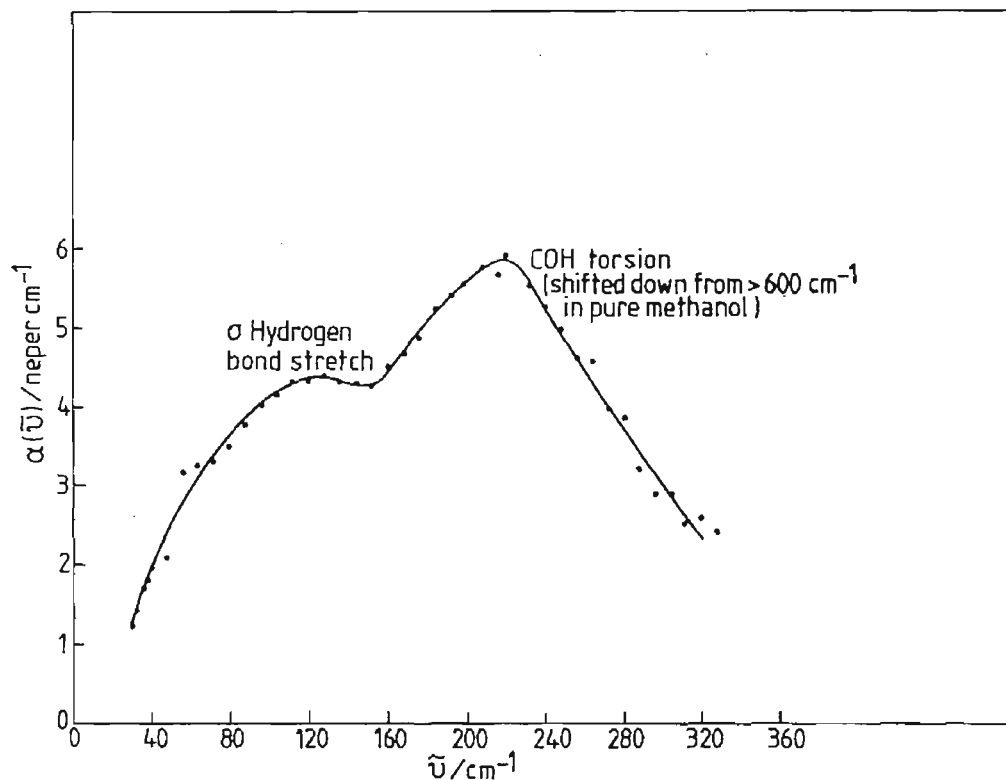solution.

Figure 6.   Far infra-red power absorption of saturated decalin with methanol (solvent
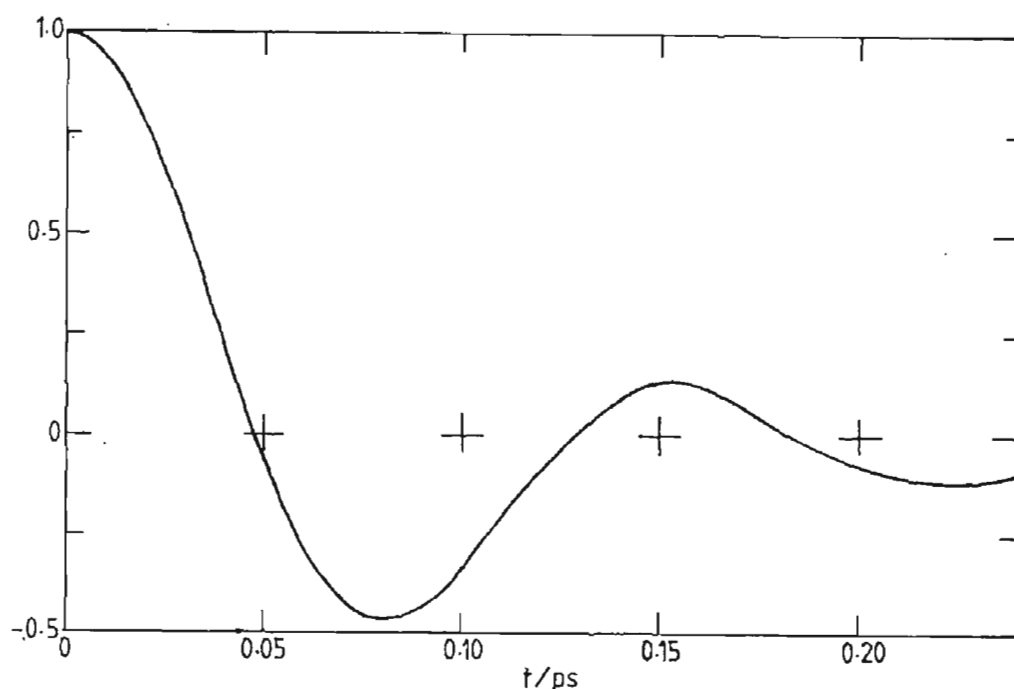corrected).

Figure 7. Normalized rotational velocity a.c.f. ($C_{\dot{u}(t)}$) for 1·25 per cent v/v of methanol in cyclohexane.

4. DISCUSSION

One of the most intriguing problems [22] in dielectrics for over half-a-century has been the fact that a most complicated system like water or alcohols with strong dipole–dipole coupling show a perfect Debye dispersion with a semi-circular Cole–Cole plot. Systems with a weak dipole–dipole coupling are known, however, to have a distribution of Debye times. The development of the millimeter wave dielectric measuring techniques by Smyth and his co-workers [23] made it possible for the discovery of a supplementary 'foot' on the high frequency side of the Cole–Cole plot for the higher series of the aliphatic alcohols [1]. This has been attributed to the 'internal rotation' of the –OH segment with respect to the main molecular framework. However, the microwave dielectric measurements for methanol above a frequency range of 75 GHz do not appear to be reported in the literature. Nevertheless, an observation of such a suplementary foot for methanol is also possible. In pure methanol (figure 8), $\epsilon_\infty = 5·0$, whereas $n_D{}^2$ is 1·77. An extremely large difference of $\epsilon_\infty - n_D{}^2$ is indicative of a strong high frequency power absorption. The millimetre wave dielectric loss ϵ'' appears to be a part of the $\alpha(\bar{\nu})$ spectrum (figure 4). In other words, the high frequency power absorption spectrum of methanol and the low frequency dielectric loss are pictures of the same dynamical process. One feature of the spectrum cannot be interpreted in isolation from the other. This becomes clear upon dilution, when the dielectric relaxation time shifts considerably [27] from 65 ps to below 10 ps and the 120 cm^{-1} peak simultaneously shifts to below 80 cm^{-1} (figure 5). In a 50 per cent v/v methanol–CCl$_4$ methanol–CCl$_4$ system, an absorption peak has been observed [24] to appear at 280 cm^{-1}. This peak is seen to shift to 230 cm^{-1} with a 100 per cent further increase in dilution. The same trend is reflected by the dilute solutions of methanol in cyclohexane and decalin. For 1–2 per cent