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Abstract. High-resolution ($\Delta E = 15\ \mu eV$) quasielastic neutron spectra have been measured for liquid methanol (CD_3OH) and methane-thiol (CD_3SH) at two temperatures within their liquid ranges. The spectra have been analysed in terms of a previously developed dynamical model which allows for the separation of the translational incoherent parts from the total dynamic structure factors.

The strong differences in linewidths of the incoherent functions between the two compounds are then analysed in terms of a phenomenological model which takes into account the existence of several association states in the alcohol. The sulphur compound is then used as a reference fluid in order to carry out a comparative study of the microscopic dynamics of the two materials.

1. Introduction

Important achievements have been made recently as regards the short-range structure of hydrogen-bonded liquids by radiation scattering methods and computer simulation techniques. However, there have been few attempts, theoretical or experimental, aimed at obtaining a quantitative picture of the effects of the strong molecular association on the microscopic dynamics of these liquids [1]. The work presented herein reports measurements of the quasielastic neutron scattering spectra (QENS) of liquid methanol (CD_3OH) and methane-thiol (CD_3SH) at two temperatures within their liquid ranges. The two molecules are structurally similar and were chosen because of their very different hydrogen-bonding properties. The former is known to form large molecular aggregates whereas, despite the results of a computer simulation study [2], very little association is believed to take place in the thiol compound. Although the same considerations could, in principle, apply for liquid water and H_2S, the larger differences between the ratios of molecular masses and moments of inertia of the two pairs of molecules, as well as their non-overlapping liquid temperature ranges, made the alcohol thiol samples more suitable for the comparison.

The aim of the present report then is to demonstrate the usefulness of QENS spectroscopy for obtaining a quantitative assessment of the effect of the hydrogen-bond network on the centre-of-mass and rotational motions of these molecules within the liquid phase. Medium-resolution time-of-flight ($\Delta E = 50\ \mu$eV) quasielastic [3] and triple-axis inelastic ($\Delta E = 2.5$ meV) [4] experiments are reported elsewhere for the alcohol, whereas only low-resolution QENS data have appeared for the completely hydrogenated thiol compound [5] as well as some relatively old proton NMR measurements [6, 7].

2. Experimental details

The experiment was carried out on the IRIS spectrometer at the ISIS pulsed neutron source at the RAL. IRIS is a back-scattering crystal analyser spectrometer where the wavelength range within the incident neutron pulse provides the energy transfer range. The analyser crystals are pyrolitic graphite and either the 002 or 004 reflections can be used. The former provides an energy resolution of 15 μeV over a Q-range from 0.25 to 1.85 Å^{-1}, whereas the latter has an energy resolution of 50 μeV over a Q-range of 0.5 to 3.7 Å^{-1}. The detector bank spans an angular range of 15° to 165° divided into 51 elements. Only data measured with the 002 configuration are reported in this work. The samples were contained in flat aluminium cells of wall thickness 0.5 mm and sample thickness of 1 mm. The cells were mounted in a variable-temperature liquid helium cryostat at 45° to the incident neutron beam.

The spectral data were converted into $S(Q, \omega)$ results by means of standard RAL software, and a slab correction was applied in order to correct the absorption effects.

The high resolution in energy transfer achievable by the spectrometer has allowed an analysis and separation of the different spectral components to be achieved that is free from some uncertainties present in a previous study performed with a lower-resolution instrument [3].

The spectral analysis was carried out using a dynamical model developed by us along the lines of the Sears approximation, and takes explicit account of both the coherent and incoherent contributions and includes translational and rotational motions of the molecular frame as well as the rapid reorientation of the CD_3 groups [3]. The model scattering law is then written as

$$S(Q, \omega) = \sum_{i=0}^{3} S_i(Q, \omega) \tag{1}$$

where the zeroth contribution contains the dynamical information concerning centre-of-mass motions;

$$S_0(Q, \omega) = \exp(-Q^2 W)(f_{\text{inc}}^2(Q)L(\omega, \Gamma) + f_{\text{coh}}^2(Q)L(\omega, \Gamma^*)S_{\text{CM}}(Q))$$

where $L(\omega, \Gamma)$ is a normalised Lorentzian function with a half-width at half-maximum Γ.

The subscripts 'coh' and 'inc' correspond to the coherent and incoherent contributions to the molecular form factors $f(Q)$, Γ and Γ^* are the widths associated with the incoherent and coherent spectral components, and $S_{\text{CM}}(Q)$ is the structure factor for the molecular centres. All the geometrical quantities have been derived from previous measurements by neutron diffraction and a detailed account will be given elsewhere [3].
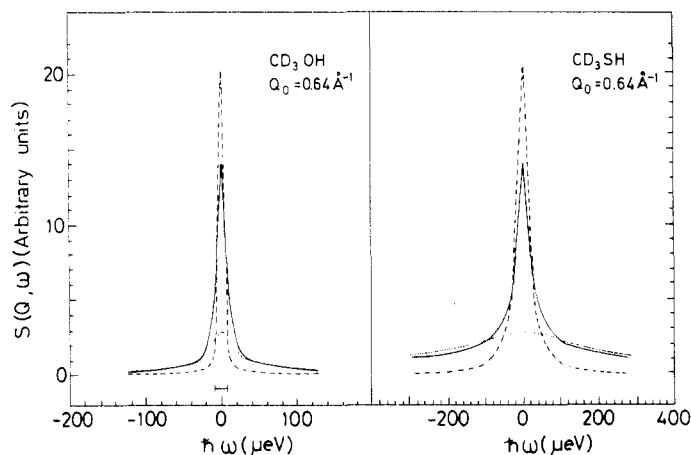
Figure 1. Quasielastic spectra for CD_3OH and CD_3SH at $T = 200$ K and for an average momentum transfer of 0.64 Å^{-1}. The curves underneath the experimental and fitted points (full curves; at this scale the residuals are within these lines) represent the sums of translational (broken curve) and rotational (dotted curve) contributions before convolution with the resolution function. The bar represents the width of the experimental resolution.

The rotational contributions are represented by three sets of Lorentzian functions which are

$$S_i(Q, \omega) = \exp(-Q^2 W) \sum_{l=1}^{\infty} (2l + 1)A_l(Q)^2 L(\omega, D_i(Q)) \tag{2}$$

where the $A(Q)$ are form factors for which explicit expressions are given in [3], and the widths of the rotational Lorentzians are given in terms of the rotational diffusion constant plus the incoherent translational width, the methyl groups jump frequencies plus the incoherent translational width, or a combination of these two. The exponential term is a Debye–Waller factor with amplitude W which, as a simplifying assumption, was set to the same value for the rotational and translational motions. Such an approximation is justified if one takes into consideration the need for reducing the number of free parameters, and amounts to a small adjustment in the relative amplitudes of translational and rotational movements.

3. Results and discussion

Two representative spectra corresponding to the alcohol and thiol compounds at $T = 200$ K are shown in figure 1, together with their decomposition into translational and rotational functions.

The quasielastic linewidths associated with both the incoherent and coherent translational parts of $S(Q, \omega)$ for both compounds at temperatures of $T = 200$ K and $T = 230$ K are shown in figure 2 for a momentum-transfer range up to $Q = 1.24$ Å^{-1}.
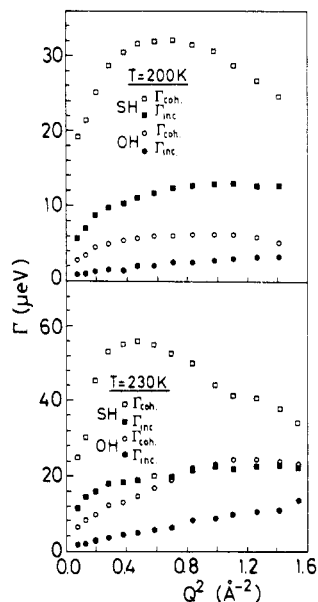
Figure 2. Quasielastic widths for the thiol and alcohol at both temperatures. The symbols Γ denote the incoherent and coherent parts computed by means of (1).
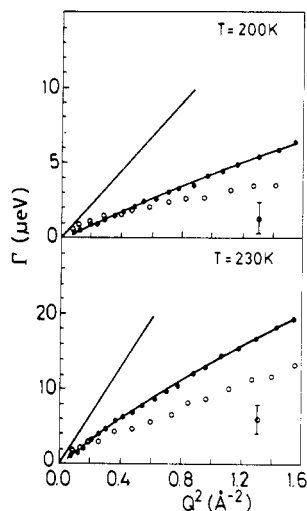
Figure 3. Incoherent quasielastic widths for both temperatures for methyl alcohol (open circles). The straight line represents the Fickian regime with diffusion coefficients computed from [7]. Full circles represent the model calculations performed with the following set of parameters: $T = 200$ K, $t_{HB} = 5$ ps, $T = 230$ K, $t_{HB} = 4$ ps. The temperature dependences of the diffusion coefficients are: $D(n_0) = 182.2\exp(-1059/T) \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$; $D(n_1) = 1164\ \exp(-1445/T) \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$; $\Sigma_{i=0}^{3} f_i D(n_i) = 560\exp(-1615/T) \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$; $f_{i,T=200K} = 0.000, 0.066, 0.875, 0.059$; $f_{i,T=230K} = 0.003, 0.109, 0.824, 0.064$.

The relative amplitudes for the abovementioned contributions, the numerical values obtained for the rotational diffusion constant, and the methyl jump frequencies, as well as some relevant geometrical parameters, are given in table 1.

The first noticeable difference between the widths of the two materials concerns the substantially larger values for the thiol, which are about four times those for the alcohol at $Q^2 = 1.56\,\text{Å}^{-2}$ for $T = 200$ K and double those at the same momentum-transfer value for $T = 230$ K. Such differences, apart from being indicative of the larger motional freedom of the sulphur compound, indicate the clear effect of molecular association. From consideration of the molecular masses of the alcohol ($m_1 = 35$ amu) and thiol ($m_2 = 51$ amu), one would expect that, if the intermolecular forces were comparable, the macroscopic diffusion coefficients should scale as $(m_1/m_2)^{1/2}$ [8], and therefore the diffusion coefficient for the thiol should be about 0.83 times that for methanol. A similar scaling law can be written in terms of the reduced moments of inertia; this is considered to be more appropriate for molecular liquids [9] since it takes explicitly into account the effects of molecular shape. In this latter case the coefficient for the thiol is predicted to be about 0.6 times that from methanol. From consideration of the low-Q values of both

Table 1. Structural parameters and rotational diffusion constants.

Sample	$T(K)$	$D_r{}^a$	$W_m{}^b$	$\langle\mu^2\rangle^c$	$f^2_{inc}(Q=0)^d/f^2_{coh}(Q=0)$
CD_3OH	200	0.055	2.2	0.13	6.848/8.277
		(0.01)		(0.05)	
	230	0.083	2.6	0.18	
		(0.03)		(0.03)	
CD_3SH	200	0.095	2.2	0.22	6.848/6.645
		(0.02)		(0.04)	
	230	0.147	2.6	0.31	
		(0.04)		(0.02)	
CD_3OH	$d_i(r)^e = 0.675, 0.763, 1.367, 1.498, 1.445, 1.445$				
	$i = C, O, H, D_{M1}, D_{M2}, D_{M3}$				
	$I^f = (28.17, 26.80, 7.32)$				
CD_3SH	$d_i(r)^e = 1.138, 0.684, 1.572, 1.844, 1.834, 1.834$				
	$i = C, S, H, D_{M1}, D_{M2}, D_{M3}$				
	$I^f = (50.5, 48.4, 8.28)$				

[a] Units: 10^{12} s^{-1}.
[b] Jump rates for 120° rotational jumps. Set to values found in a previous study on methanol with a larger energy window [3].
[c] Mean square amplitudes. Obtained from fits of the residual elastic intensity versus Q. Units: Å.
[d] Ratios between the incoherent and coherent form factors given in equation (1).
[e] Distances to the centre-of-mass obtained from diffraction experiments. Values are in Å. The subscripts M1, 2, 3 represent the three deuterons of the methyl group.
[f] Principal moments of inertia. Units: amu Å^2.

materials it becomes clear that the apparent diffusion coefficient of the thiol should be of the order of five times larger than that of the alcohol, thus indicating the strong effects of the intermolecular potential on the dynamics of the methanol molecules.

As can be seen upon inspection of figure 2, the Q-dependence of the incoherent translational widths follows substantially different trends in the alcohol and thiol cases. A quasilinear relationship is followed by the OH compound whereas the curves related to the SH compound show a pronounced bending with noticeable saturation at large momentum transfers. From what is already known for most liquids, the trend followed by the sulphur compound conforms to what could be expected for a fluid without strong intermolecular interactions and can be explained in terms of simple jump-diffusion models [10]. The quasilinear behaviour of the alcohol linewidths can be interpreted under the assumption of the existence of more than one diffusive mode which arise from different states of molecular association.

A phenomenological model has been proposed [11] that takes into account this fact and is capable of explaining the different Q-dependencies of the two species. Such an approach leads to the computation of the single-particle structure factor as a sum of four different Lorentzians representative of the states where the molecules are linked through 0, 1, 2 or 3 bonds:

$$S_s(Q, \omega) = \sum_{i=0}^{3} B_i(Q)L(\omega, D_i(Q)) \tag{3}$$

where the amplitudes B_i and widths D_i are computed from the solution of the differential system for the intermediate scattering function:

$$\dot{F}_{si}(Q, t) = - D(n_i)Q^2 F_{si}(Q, t) + \sum_{j=0}^{3} (K_n)_{ij} F_{sj}(Q, t) \qquad i = 0, 1, 2, 3 \tag{4}$$

where the dot stands for the time derivative, the $D(n_i)$ are diffusion coefficients for each ith state, and **K** is a kinetic matrix with elements (rate constants for formation or breaking of hydrogen bonds) given in terms of hydrogen bond lifetimes. The total intermediate function is then computed as

$$F_s(Q, t) = \sum_{i=0}^{3} f_i F_{si}(Q, t) \tag{5}$$

where the f_i are population factors for the four bonding states.

In order to compute the spectral widths the present data have been used to parametrise such a model, which requires some knowledge of the diffusion constants for each of the association states, as well as the f_i-factors, and an estimate of t_{HB}, the hydrogen bomb lifetime.

In the present work, the f_i-factors have been computed from molecular dynamics simulations performed at both temperatures [12], and the following *ansatz* was adopted in order to estimate the $D(n_i)$ coefficients.

(i) $D(n_0)$, which gives the coefficient for the unassociated state, was computed from the thiol, low-Q data (fits to a straight line, Fickian regime) and scaled to match the molecular mass of methanol.

(ii) $D(n_3)$, corresponding to molecules with three intact hydrogen bonds, was assumed to be of the same order of magnitude as that for amorphous methanol, i.e. 10^{-7} cm^2 s^{-1} (estimated from the spectra of the amorphous phase obtained by rapidly quenching of the liquid, $T = 140$ K).

(iii) The coefficient $D(n_2)$ corresponding to molecules with two hydrogen bonds was taken to be equal to an estimate corresponding to the diffusion coefficient for the supercooled liquid phase, i.e. 1.1×10^{-6} cm^2 s^{-1}, and was assumed to be independent of temperature. The value given above was set to a value estimated from a recent molecular dynamics simulation [12].

(iv) The coefficient for the state with only one intact hydrogen bond was computed taking into account the above-mentioned assumptions as well as the fact that the sum of the four different coefficients weighted by the f_i-factors must be equal to the value obtained for the long-wavelength regime (Fickian) by means of pulsed-field-gradient NMR [7].

The only free parameter was then t_{HB}, for which there are no reliable data available. It was therefore set to a value that gave the best approximation to the present data. Taking the set of parameters given above, the model predicts the existence of four Lorentzian functions contributing to the observed incoherent structure factor, of which only the more intense one is relevant for the energy window we are working with.

The values obtained for the incoherent widths for both temperatures are shown in figure 3, where the values representing the Fickian regime [7] are given as straight lines. The estimated values for t_{HB} were 5 ps and 4 ps respectively, which are in reasonable agreement with the prediction made for $T = 298$ K: 2 ps [11].

From inspection of figure 3, it can be seen that the model computations closely resemble the measured linewidths up to momentum transfers of 0.6 Å^{-1}. The reasons for the discrepancies at larger Q-values may well be due to the fact that at such length

scales such a model could break down, since that region is located well inside the kinetic regime and a more detailed account of the molecular shapes and forces becomes necessary. In this respect, a recent calculation on supercooled water [11] has shown that the agreement with the measured widths could be improved if allowance were made for different values of the lifetimes t_{HB} for each of the associative states. Although the introduction of additional free parameters would clearly make the computations unmanageable, the use of such an approach could be exploited if such dynamical information could be obtained from other sources (i.e. depolarised Rayleigh scattering or molecular dynamics computations).

The data for the thiol compound could be analysed along the same lines if one were to assume the existence of association. However, the fact that no data for the diffusion coefficient are available, either from NMR or macroscopic (tracer-diffusion) sources, precluded such an analysis, since it would require the introduction of too many free parameters. Therefore, the widths for the thiol compound can be more conveniently analysed in terms of a simplified jump model of the Singwi–Sjölander [13] type, which is more appropriate for this, predominantly unassociated liquid. In short, such a model assumes that the molecules execute a librational motion for a characteristic time t_0 and then diffuse continuously for a subsequent period t_1. If we assume that, due to the relatively low temperatures studied, we have $t_1 \ll t_0$, then the model scattering law is a Lorentzian with a half-width at half-maximum given by

$$D = (1/t_0)[1 - \exp(-Q^2 W)/(1 + Q^2 D_T t_0)]$$

where D_T is a diffusion coefficient. The results for the residence times t_0 for both temperatures, estimated from the observed incoherent widths, were 49.3 and 26.2 ps for $T = 200$ K and $T = 230$ K respectively; the corresponding self-diffusion coefficient values were 1.45 and 2.74 $\times$ 10^{-5} cm^2 s^{-1}, which can be favourably compared with those measured for H_2S (3.7) and 6.0 $\times$ 10^{-5} cm^2 s^{-1} respectively [14]).

Finally, in order to show the validity of our assumption of considering the thiol liquid as a reference state, we have applied the principle of corresponding states along the same lines as for the water/H_2S comparison [14]. For this purpose we have computed the reduced self-diffusion coefficients given by [14]

$$D_{Rcd}(T^*) = D^*(T^*)/D^*(0.667) = D(T)/D(0.667\,T_c) \tag{6}$$

where T^* stands for the reduced temperature and

$$D^*(T^*) = (1/V_c^{1/3})(m/k_B T_c)^{1/2} D(T)$$

where the subscript c denotes critical volume and temperature, m is the molecular mass, $D(T)$ is the diffusion coefficient, and the scaling to 0.667 T_c was chosen in order to normalise the values to the middle of the liquid range.

The results for the thiol and alcohol liquids are shown in figure 4 as well as some supplementary data taken from [14] and [15].

As can be easily seen from inspection of figure 4, the data corresponding to the unassociated liquids are close to following a universal scaling law, whereas both the curve drawn for methanol and that for water substantially deviate from such behaviour. Such characteristic behaviour shows the extent to which both liquids, H_2S and CD_3SH, could be considered as valid reference fluids (with no hydrogen bonding) for the kind of theoretical approximation followed in this work.
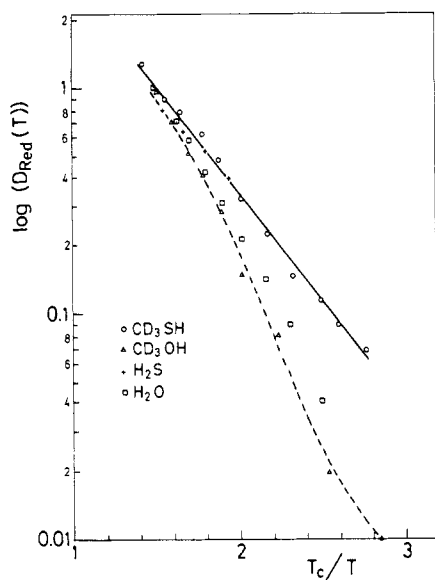
Figure 4. Reduced self-diffusion coefficient (equation (6)) versus reduced temperature. The data for methanol have been computed from an Arrhenius equation given in [7], and those for water from the same procedure with an equation given in [15]. Data for hydrogen disulphide were taken from [14] and the corresponding ones for the thiol are extrapolations using an Arrhenius equation parametrised with the diffusion coefficient values obtained by application of the Singwi–Sjölander model to the observed incoherent linewidths. Both the full and broken curves have been drawn as guides to the eye.

4. Conclusions

The purpose of this work was to examine the effect of strong molecular association upon the microscopic translational dynamics of two structurally related fluids by means of high-resolution QENS spectroscopy. The substantial differences in linewidth found were interpreted on the basis of a model that takes the thiol liquid as a reference state. Further work is needed in two directions: first, an adequate model for decomposing the observed spectra into constituent response functions, going beyond the Sears approximation [10], is still lacking; second, the model used to explain the differences between the linewidths of the two liquids should be extended in order to predict the correct behaviour for unassociated liquids. In the meantime, valuable information can be obtained from the concurrent use of neutron spectroscopy and light scattering data, as well as computer simulation results.

Acknowledgments

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