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## Diffusional dynamics of hydrogen-bonded liquids: methanol

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**Abstract.** Medium-resolution ( $\Delta E \approx 0.1$  meV) quasielastic neutron scattering spectra have been measured for partially ( $\text{CD}_3\text{OH}$ ) and fully deuterated methanol, ( $\text{CD}_3\text{OD}$ ) in the temperature range between 200 and 300 K. The spectra are analysed in terms of a simplified model which takes into account both coherent and incoherent contributions, and includes translational and rotational motions of the molecular frame as well as the rapid reorientation of the  $\text{CD}_3$  group. Such a procedure enabled the separation of the translational and rotational contributions to the measured intensity. The apparent lack of saturation of the translational linewidths versus the momentum transfer is finally discussed in terms of a phenomenological stochastic model.

### 1. Introduction

The study of the microscopic structure and dynamics of hydrogen-bonded liquids has attracted a great deal of attention in recent times [1]. In particular, water and ionic solutions have been the focus of a number of studies [2] in order to get some insight into their local structure, single-particle dynamics and the possible existence of collective excitations [3].

Although substantial progress has been achieved in the elucidation of local, short-range structure by radiation scattering methods and computer simulation techniques, the strong, cooperative effects caused by the existence of the hydrogen bond (HB) network are still poorly understood.

Despite the relative wealth of models proposed to explain the thermodynamic anomalies in terms of either phenomenological constructs [4] or microscopic models (mainly percolative in nature) [5], there is a dearth of theoretical attempts aimed at obtaining some understanding of HB dynamics. Furthermore, from an experimental point of view the situation becomes still more confusing. The first attempts to interpret the measured quasielastic neutron scattering (QENS) spectra in terms of dynamical models (mainly of stochastic jump type) were developed more than two decades ago [6].

However, the poor resolution achievable at that time as well as oversimplifications in analysing the measured spectra forced the subject into a dormant situation until recent instrumental developments became available [7]. There is now a substantial amount of data concerning the dynamics of water in its liquid and supercooled-liquid states. However, there is no general agreement about the precise meaning of the measured quantities or their subsequent interpretation within some theoretical framework. As a matter of fact, most of the models which have appeared in the literature predict the existence of a number of contributions to the QENS spectrum apart from the idealised, purely translational, component. In particular, it seems nowadays clear that a proper account of the inelastic contributions to the measured intensity coming from rotational and librational motions should be carefully taken into account before trying to decompose the measured  $S(Q, \omega)$  structure factor into individual components. On the other hand, decomposition of the measured intensity into more than a few contributions (two or three) represents a still unsolved problem because of the ill-conditioned nature of such an estimation [8] and very few improvements have appeared concerning this particular topic.

The mentioned difficulties above have led to simplifying assumptions when analysing QENS data where the existence of the HB network is included in a rather marginal fashion [7]. In contrast, there exists sound experimental evidence (from dielectric relaxation) to assign the strong non-ideal behaviour of these liquids to the dynamical characteristics of the bonding network [9].

In the search for a system somewhat simpler than water, liquid methanol appears as a particularly favourable case for study. It can be thought of as being a water molecule where one of the protons has been replaced by an inert, bulkier  $\text{CD}_3$  group and the picture of its liquid structure which emerges from, mainly molecular dynamics, simulations portray it as formed by long HB chains connected through roughly linear H bonds. The available NMR relaxation data [10] have produced a picture where 'the molecule' is considered to be formed by the OH group (because of the HB network) which gives a correlation time about ten times larger than the one measured for the  $\text{CD}_3$  group. The characteristic times for molecular motion seem, therefore, to be reasonably well separated from the relaxation times of the bonding network so that, in principle, the effects of molecular rotation could be separated from those arising from the HB dynamics.

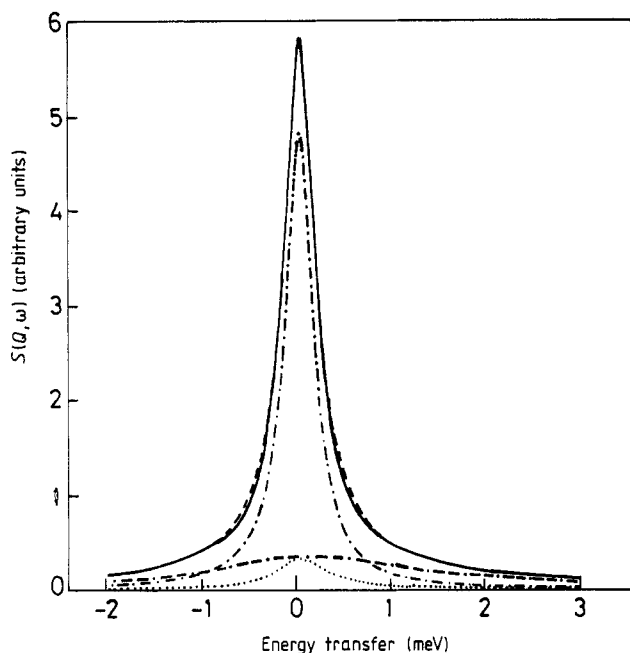
The present work aims to provide some clarification of the existing situation by means of the analysis of QENS spectra of liquid  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  measured at several temperatures within their liquid range.

The experimental and data treatment aspects will be presented in § 2. The dynamical model is summarised in § 3, and the results obtained are finally discussed in § 4.

## 2. Experimental aspects

The relevant molecular parameters have been obtained from diffraction measurements [11], and the high-quality data necessary for the measurements of static structure factors at low temperatures have recently been obtained using the Liquids and Amorphous Diffractometer (LAD) of the ISIS pulsed source. A detailed account of the structural characteristics of the liquids will be given elsewhere [12].

The QENS experiments were carried out using the focusing time-of-flight spectrometer IN6 [13], situated on one of the cold neutron guides of the High-Flux Reactor of



**Figure 1.** Representative spectrum for  $\text{CD}_3\text{OH}$  at 300 K,  $2\theta = 44.7^\circ$ . Full curve, experimental intensity; broken curve, fitted model scattering law,  $S_{\text{model}}(Q, \omega)$ , (equation (15)); chain curve, translational ( $S^0(Q, \omega)$ ) component; dotted curve,  $S^1(Q, \omega)$  (equation (13)) showing the function resulting from the sum of the first four harmonics; dash-dash-dot curve;  $S^2(Q, \omega)$  (equation (13)), same number of contributions.

the Institut Laue–Langevin, Grenoble, France. The instrument operates in the direct geometry and the fixed incident wavelength was set to  $5.12 \text{ \AA}$  ( $3.121 \text{ meV}$ ).

A high statistical accuracy was achieved ( $\approx 0.1\%$  at peak maxima) by counting over relatively large periods.

The 337 detectors which span an angular range from  $10$  to  $115^\circ$  were grouped into nine bins with elastic momentum transfer between  $0.33$  and  $1.96 \text{ \AA}^{-1}$ , with an energy resolution better than  $\Delta E \approx \mu\text{eV}$  FWHM (full width at half maximum).

The sample was contained between two concentric aluminium cylinders of  $30 \text{ mm}$  outer diameter and  $29 \text{ mm}$  inner diameter and a height of  $50 \text{ mm}$ .

The temperature regulation was achieved using a standard 'orange' cryostat with a stability better than  $0.5 \text{ K}$ .

Two different samples were studied,  $\text{CD}_3\text{OH}$  at temperatures  $200$ ,  $230$  and  $300 \text{ K}$ , and  $\text{CD}_3\text{OD}$  at  $200$  and  $250 \text{ K}$ . Typical spectra are shown in figure 1, where it can be seen that, apart from substantial broadening, no noticeable inelastic structure is apparent.

The sample transmission was about  $96\%$  so that multiple-scattering effects are estimated to be smaller than  $5\%$  of the total scattered intensity.

The conversion from time-of-flight spectra into  $S(Q, \omega)$  dynamical structure factors was achieved by means of standard ILL software using vanadium foil rolled into the sample container for normalisation and resolution.

Although the incoherent cross section dominates, in the case of  $\text{CD}_3\text{OH}$ , the coherent contribution cannot be ignored since it contributes about 30% of the scattering power, and the converse is also true for  $\text{CD}_3\text{OD}$ .

The two isotopic compositions were used in order to check the physical relevance of the dynamical parameters obtained, since the same motional constants should be able to explain the measured spectra in both cases.

The first problem that appears in the analysis of QENS spectra concerns the number of components contributing to the observed intensity. Up to now, there is no generally accepted agreement about the correct approach to this question.

Under such circumstances, one has to appeal to some physically sound model or to estimate the minimum number of components by means of the analysis of misfit statistics.

In this work we have started the analysis by estimating the minimum number of lorentzians required to reproduce the spectrum. In a further step we have adopted a simplified model in order to assign a physical origin to the parameters entering the lorentzians.

In order to guarantee some sort of globality for the parameters estimated, we have adopted the following strategy. (a) Initial estimates were obtained from the analysis of the quasielastic region of the spectra ( $-2 \text{ meV} \leq \hbar\omega \leq 2 \text{ meV}$ ). (b) A subsequent search covering the energy window of interest ( $-2 \text{ meV} \leq \hbar\omega \leq 8 \text{ meV}$ ) was carried out by means of a direct search algorithm of a modified Simplex type with the parameters subjected to simple bounds. Although this kind of algorithm is quite inefficient in comparison with traditional gradient methods it allows the alleviation of problems caused by multiple local minima. (c) The estimates obtained were allowed to be refined by means of a conjugate gradient method. (d) In some cases it was useful to examine sets of linear combinations of parameters leading to extreme errors, following standard statistical techniques.

Since the original spectra were taken at constant angle, the  $Q$ -values were calculated for all the energy transfers in every spectrum at the first iteration step.

The model  $S(Q, \omega)$  was finally folded with the resolution function measured with the vanadium standard to give the intensity function to be compared with the experimental one.

### 3. The model

On empirical grounds, all the spectra (for the two samples and all temperatures) can be decomposed into a sum of three lorentzian functions without considering any background. Such an approximation gives excellent fits for a wide energy transfer range ( $-2$  to  $8 \text{ meV}$ ).

Although such a model-free approach can encompass all the observed spectral features, in practice it becomes quite difficult to assign a physical meaning to each spectral component

Alternatively one can consider some simplified model and examine the QENS spectra in terms of a relatively small set of model parameters. The simplest approach relies on the decoupling of the rotational and translational motions as well as on the uncorrelated rotational motions of neighbouring molecules. Although such assumptions are clearly unphysical for the class of fluids we are interested in, we have undertaken such an exercise for the following two reasons: (a) these are the only ones giving an analytically

tractable form and (b) most of the work reported previously (on liquid water) [14] has been carried out along the same lines.

Furthermore, the use of an analytically simple model is required if one aims to separate the different motional processes and, in particular, the translation and rotational motions.

In essence, the approximation referred to above amounts to a consideration of a model similar to the one proposed by Sears [15] for weak rotational hindering.

### 3.1. Basic formulae

The measured double differential cross section, is expressed in terms of an intermediate scattering function  $\sigma(Q, t)$

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{K_f}{K_i} \frac{1}{2\pi} \int e^{-i\omega t} \sigma(Q, t) dt$$

$$\sigma(Q, t) = \sum_{j,j'=1}^N \sum_{v,v'=1}^n [b_{\text{coh}}^{jv} b_{\text{coh}}^{j'v'} + \delta_{jj'} \delta_{vv'} (b_{\text{inc}}^{jv})^2] \langle \exp[-i\mathbf{Q} \cdot \mathbf{R}_{jv}(0)] \exp[-i\mathbf{Q} \cdot \mathbf{R}_{j'v'}(t)] \rangle \quad (1)$$

where the first summation runs over the  $N$  molecules in the sample, each of these composed of  $n$  atoms characterised by the  $b^{jv}$  coherent and incoherent bound scattering lengths, with time-dependent spatial coordinate  $\mathbf{R}(t)$ .

From the relative widths and intensities of the three lorentzians composing the spectra, we are led to consider three different motions: a centre-of-mass motion, spherical rotational tumbling of the molecule as a whole, and a fast rotation of the methyl group relative to the C—O axis. As an additional assumption, we consider the two rotational motions to be independent, so that the intermediate scattering function can be factorised as follows:

$$\begin{aligned} \sigma(Q, t) = & \sum_{j \neq j'=1}^N \sum_{v, v'=1}^n b_{\text{coh}}^{jv} b_{\text{coh}}^{j'v'} \langle \exp[-i\mathbf{Q} \cdot \mathbf{R}_j(0)] \exp[i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)] \rangle \\ & \times \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{jv}(0)] \rangle \langle \exp[i\mathbf{Q} \cdot \mathbf{r}_{j'v'}(t)] \rangle \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}'_{jv}(0)] \rangle \langle \exp[i\mathbf{Q} \cdot \mathbf{r}'_{j'v'}(t)] \rangle \\ & + \sum_{j=1}^N \sum_{v, v'=1}^n (b_{\text{coh}}^{jv} b_{\text{coh}}^{jv'} + \delta_{vv'} (b_{\text{inc}}^{jv})^2) \langle \exp[-i\mathbf{Q} \cdot \mathbf{R}_j(0)] \exp[i\mathbf{Q} \cdot \mathbf{R}_j(t)] \rangle \\ & \times \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{jv}(0)] \exp[i\mathbf{Q} \cdot \mathbf{r}_{jv}(t)] \rangle \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}'_{jv}(0)] \exp[i\mathbf{Q} \cdot \mathbf{r}'_{jv}(t)] \rangle \end{aligned} \quad (2)$$

where the positions of the  $j$ th,  $v$ th nucleus is specified by the coordinate

$$\mathbf{R}_{jv} = \mathbf{R}_j + \mathbf{r}_{jv} + \mathbf{r}'_{jv} \quad (3)$$

$\mathbf{R}_j$  being the coordinate of the centre-of-mass of the  $j$ th molecule,  $\mathbf{r}_{jv}$  the position of the  $v$ th atom relative to the molecular centre of mass and  $\mathbf{r}'_{jv}$  a relative position of the  $v$ th atom with respect to some reference, which is zero except for the three deuterons of the methyl group. It is then clear that  $\sigma(Q, t)$  is split into two contributions comprising intermolecular and intramolecular terms.

The averages  $\langle \exp(i\mathbf{Q} \cdot \mathbf{r}_v) \rangle$ , due to the isotropy of the liquid, give rise to form factors

$$\begin{aligned} f_v(\mathbf{Q}) &= \langle \exp(i\mathbf{Q} \cdot \mathbf{r}_v) \rangle = j_0(Qr_v) \\ g_v(\mathbf{Q}) &= \langle \exp(i\mathbf{Q} \cdot \mathbf{r}'_v) \rangle = j_0(Qr'_v) \end{aligned} \quad (4)$$

whereas those containing two exponentials will give rise to the intermediate scattering functions

$$\begin{aligned} I_d(\mathbf{Q}, t) &= \langle \exp[-i\mathbf{Q} \cdot \mathbf{R}_j(0)] \exp[i\mathbf{Q} \cdot \mathbf{R}_j(t)] \rangle (N-1) \\ I_s(\mathbf{Q}, t) &= \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_j(0)) \exp[i\mathbf{Q} \cdot \mathbf{R}_j(t)] \rangle \\ \chi_{vv'}(\mathbf{Q}, t) &= \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{jv}(0)] \exp[i\mathbf{Q} \cdot \mathbf{r}_{jv'}(t)] \rangle \\ K_v(\mathbf{Q}, t) &= \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}'_{jv}(0)] \exp[i\mathbf{Q} \cdot \mathbf{r}'_{jv}(t)] \rangle \end{aligned} \quad (5)$$

so that

$$\sigma(\mathbf{Q}, t) = [u(\mathbf{Q})I_d(\mathbf{Q}, t) + v(\mathbf{Q})I_s(\mathbf{Q}, t)\chi_{vv'}(\mathbf{Q}, t)K_v(\mathbf{Q}, t)]N$$

where  $u(\mathbf{Q})$ ,  $v(\mathbf{Q})$  are molecular form factors given in terms of  $f_v(\mathbf{Q})$  and  $g_v(\mathbf{Q})$  and scattering lengths.

### 3.2. Rotational tumbling

The third function in (5) represents rotational tumbling, and can be calculated by means of the expansion:

$$\chi_{vv'}(\mathbf{Q}, t) = \sum_{l=0}^{\infty} (2l+1)j_l(Qr_v)j_l(Qr_{v'})P_l(\cos \theta_{vv'})S(t) \quad (6)$$

where the arguments of the spherical Bessel functions contain the modulus of the  $r_v$  position vectors,  $P_l$  is a Legendre polynomial with argument  $\cos \theta_{vv'}$ , where  $\theta$  is the angle between the vectors  $r_v$  and  $r_{v'}$ , and  $S(t)$  is a rotational relaxation function which contains all the details about the molecular reorientation. Although for our samples  $S(t)$  is not known, several simplified approximations are available to model it. Apart from idealised inertial models, only valid for dilute gases,  $S(t)$  can be modelled on the basis of rotational jumps, infinitesimal reorientations (rotational diffusion) or an equal mixture of both of these [15]. For simplicity we have considered the rotational diffusion case where

$$S(t) = \exp[-l(l+1)D_r]t \quad (7)$$

for the isotropic case (spherical rotations) and  $D_r$  is a rotational diffusion constant, or

$$S(t) = \sum_{m=-1}^1 \exp[l(l+1)D_1 + m^2D_2]t$$

with

$$D_1 = \frac{1}{2}(D_{xx} + D_{yy}) \quad D_2 = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) \quad (8)$$

for the axially symmetric motion.

### 3.3. Methyl group reorientation

For the methyl group reorientation we have adopted a three-site jump model [16]

$$K_v(\mathbf{Q}, t) = \left[\frac{1}{3} + \frac{2}{3}A(Q)\right] + \left[\frac{2}{3} - \frac{2}{3}A(Q)\right] \exp\left(-\frac{2}{3}W_M t\right)$$

$$A(Q) = 3j_0(Qr'\sqrt{3}) \quad \frac{1}{\tau_M} = W_M \quad (9)$$

where  $\tau_M$  represents the dwell time on a site and  $r'$  is the radius of rotation whose value was set to 0.77 Å (distance to the axis of rotation).

### 3.4. Spectral components

As a consequence of the adopted approximations, the model predicts, in the frequency domain, the existence of the following components.

**3.4.1. Translational motion.** The quasielastic intensity comprising both coherent and incoherent contributions may be written as

$$S^0(Q, \omega) = \exp\left(-\frac{\langle\mu^2\rangle}{3}Q^2\right) \left( f_{\text{inc}}^2(Q) \frac{\Gamma_Q}{\omega^2 + \Gamma_Q^2} + f_{\text{coh}}^2(Q) \frac{\Gamma_Q^*}{\omega^2 + (\Gamma_Q^*)^2} S_{\text{cm}}(Q) \right) \quad (10)$$

where the  $f^2(Q)$  are structure factors defined as:

$$f_{\text{inc}}^2(Q) = \left( \sum_{v=1}^n (b_{\text{inc}}^v)^2 j_0^2(Qr_v) \right) \left[ \frac{1}{3} + \frac{2}{3}j_0(Qr'\sqrt{3}) \right]$$

$$f_{\text{coh}}^2(Q) = \left( \sum_{v=1}^n b_{\text{coh}}^v j_0(Qr_v) \right)^2. \quad (11)$$

The width  $\Gamma_Q$  associated with the incoherent intermediate scattering function  $I_s(\mathbf{Q}, t)$  (equation (5)) was treated as a free parameter, and that related to the coherent component was computed from  $\Gamma_Q$  and the elastic structure factor of the molecular centres  $S_{\text{cm}}(Q)$  by means of the Sköld approximation [17]:

$$\Gamma_Q^* = \Gamma_Q / S_{\text{cm}}(Q). \quad (12)$$

The Debye–Waller term appearing as a prefactor was also used as a free parameter and the obtained mean-square amplitudes  $\langle\mu^2\rangle$  are given in table 1.

In order to test the behaviour of the width function against  $Q$ , a set of fits was carried out where its value was computed using a well-known random-jump model

$$\Gamma_Q = \frac{D_T Q^2}{1 + D_T Q^2 \tau_0}$$

where  $D_T$  was set to the value obtained by pulsed-field-gradient NMR and  $\tau_0$  was treated as a free parameter. Such an approach, which leads to a saturation in the linewidth at high  $Q$ -values, was abandoned since it gave unphysical values for  $\tau_0$ , so that an approximate linearity of  $\Gamma_Q$  against  $Q$  was retained.

**3.4.2. Rotational motion.** The rotational inelastic contribution to the scattering law is then composed of three sets of lorentzian functions, which for isotropic reorientation of the molecule as a whole become:



**Table 1.** Dynamical parameters for CD<sub>3</sub>OH and CD<sub>3</sub>OD.

Sample	T (K)	$D_T^a$	$D_T^b$	$D_T^c$	$D_T^d$	$W^e$	$\tau_M^f$	$\langle \mu^2 \rangle^{1/2g}$
CD <sub>3</sub> OH	200	0.168 ± 0.03	0.174	—	0.054 ± 0.12	2.211 ± 0.62	0.45	0.12
	230	0.482 ± 0.05	0.498	—	0.089 ± 0.11	2.6 ± 0.58	0.38	0.19
	300	2.601 ± 0.02	2.567	2.50	0.147 ± 0.06	2.8 ± 0.71	0.36	0.21
CD <sub>3</sub> OD	200	0.183 ± 0.08	0.174	—	0.062 ± 0.09	2.3 ± 0.42	0.43	0.16
	250	0.917 ± 0.06	0.875	—	0.109 ± 0.10	2.7 ± 0.64	0.37	0.23

<sup>a</sup> Obtained from fits of  $Q_O$  against  $Q^2$ .

<sup>b</sup> From [18a].

<sup>c</sup> Taken from [18b]. Data refer to the fully hydrogenated compound. Units for  $D_T$  are  $10^5 \text{ cm}^2 \text{ s}^{-1}$ .

<sup>d</sup> Units are  $10^{12} \text{ s}^{-1}$ .

<sup>e</sup> Jump rates for  $120^\circ$  rotational jumps. Defined in equation (3).

<sup>f</sup>  $\tau_M = W_M^{-1}$ , in  $10^{12} \text{ s}$ .

<sup>g</sup> Mean-square amplitudes. Obtained from fits of the quasielastic intensity against  $Q$ . ( $= \exp(-Q^2 \langle \mu^2 \rangle / 3)$ ). Values given in angstroms.

$$S^i(Q, \omega) = \exp\left(-\frac{\langle \mu^2 \rangle}{3} Q^2\right) \left( \sum_{l=1}^{\infty} (2l+1) A_l^2(Q) \frac{\Gamma_{i,Q}}{\omega^2 + (\Gamma_{i,Q})^2} \right) \quad i = 1, 2 \quad (13)$$

and

$$S^3(Q, \omega) = A_0^2(Q) \frac{\Gamma_{3,Q}}{\omega^2 + (\Gamma_{3,Q})^2}$$

with

$$A_l^2(Q) = \left( \sum_{v,v'=1}^n (b_{\text{coh}}^v b_{\text{coh}}^{v'} + \delta_{vv'} (b_{\text{inc}}^v)^2) j_l(Qr_v) j_l(Qr_{v'}) P_l(\cos \theta_{vv'}) \right) B_M(Q)$$

where

$$B_M(Q) = \begin{cases} \frac{1}{3} + \frac{2}{3} j_0(Qr' \sqrt{3}) & \text{for } i = 1 \\ \frac{2}{3} - \frac{2}{3} j_0(Qr' \sqrt{3}) & \text{for } i = 2, 3 \end{cases}$$

and the resulting width functions are

$$\Gamma_{1,Q} = l(l+1)D_T + \Gamma_Q \quad \Gamma_{3,Q} = \frac{2}{3} W_M + \Gamma_Q \quad \Gamma_{2,Q} = \Gamma_1 + \frac{3}{2} W_M \quad (14)$$

For the case of an axially symmetric reorientation this would become

$$\Gamma_{1,m} = l(l+1)D_1 + m^2 D_2 + \Gamma_Q \quad m = -1, 0, 1$$

which would result in three components for every  $\Gamma_i$ . Similar substitutions would have to be written for  $\Gamma_{2,m}$  and  $\Gamma_{3,m}$ . The total observed intensity is then analysed in terms of the model function

$$S_{\text{model}}(Q, \omega) = S^0(Q, \omega) + \sum_{i=1}^3 S^i(Q, \omega). \quad (15)$$

As a further, simplifying, assumption only one Debye–Waller factor was used which would therefore encompass all the relevant motions.

**Table 2.** Geometrical parameters<sup>a</sup> for CD<sub>3</sub>OH/D<sup>b,c</sup>.

	C	O	H	D <sub>1</sub>	D <sub>2,3</sub>
C	0.67	171.8	145.3	41.8	46.2
O		0.76	42.7	130.0	137.6
H			1.37	172.8	110.9
D <sub>1</sub>				1.49	75.6
D <sub>2,3</sub>					1.44

<sup>a</sup> From [11].

<sup>b</sup> The figures on the diagonal correspond to distances from the referred nuclear position to the molecular centre of mass ( $r_i$ ) (in Å).

<sup>c</sup> The off-diagonal figures are the angular values between the vectors  $r_i, r_j$  taken with respect to the molecular centre of mass.  $D_{1,2,3}$  represent the deuterons of the methyl group. Computed moment of inertia = {28.17, 26.80, 7.32} amu Å<sup>2</sup>.

Once the random-jump approximation has been discarded, the model is completely defined by a set of three parameters  $\Gamma_Q$ ,  $D_r$  and  $W_M$  where the first is allowed to vary in  $Q$ -space whereas both  $D_r$  and  $W_M$  are optimised to single values at each temperature in order to represent the  $Q$ - and  $\omega$ -dependences of the rotational contribution.

The required geometrical parameters as well as the  $S_{\text{cm}}(Q)$  structure factor are, in principle, obtainable from diffraction measurements [11], and some relevant parameters are given in table 2.

#### 4. Results and discussion

The quasielastic scattering spectra of liquid methanol shows rather different features than those reported for liquid water up to the present moment [14, 19]. The main features differentiating this liquid are discussed below.

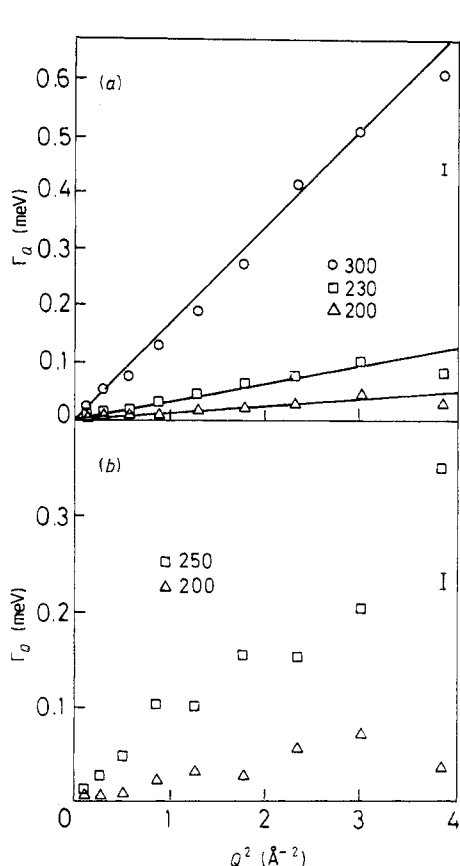
##### 4.1. Quasielastic widths

The dependence of the quasielastic widths  $\Gamma_Q$  as a function of  $Q^2$  for both partially and fully deuterated samples is shown in figure 2. As can be seen from the figure, except for the points corresponding to the largest momentum transfer ( $1.96 \text{ \AA}^{-1}$ ) the experimental data follow a quasilinear behaviour, closely resembling the linear  $D_T Q^2$  trend predicted by the hydrodynamic theory, with a translational diffusion coefficient measured from pulsed, field-gradient NMR.

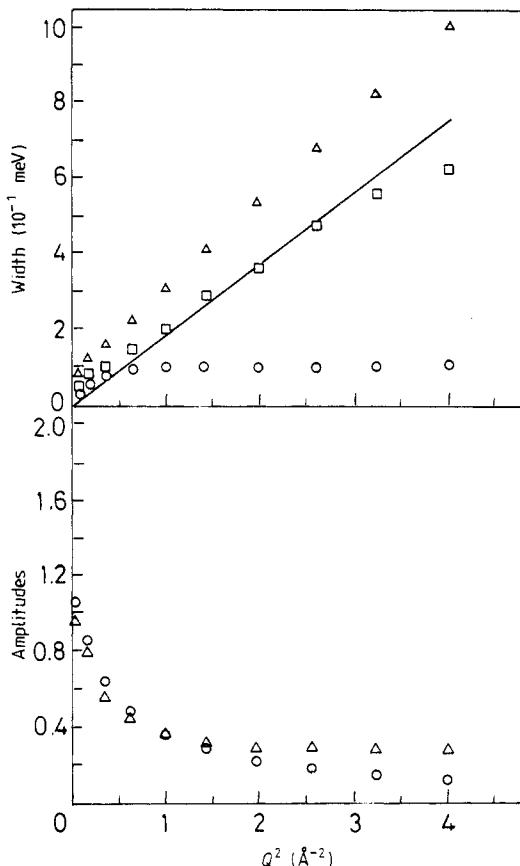
Such behaviour is in agreement with estimates of the total width for CH<sub>3</sub>OH made two decades ago [20].

In order to confirm this fact we tried to fit a jump diffusion model by following the procedure adopted for the analysis of QENS spectra of water. The fits produced using such a model were of a rather poor quality ( $\approx 10$  times worse than with a lorentzian) and tended to force the optimised values of the parameter representing the residence time towards unphysical regions.

The values of the translational diffusion constant  $D_T$  obtained from fits of the experimental points (low- $Q$  data) are given in table 1 and compared with data from other sources. All the remaining dynamical quantities which have been derived from



**Figure 2.** Quasielastic translational widths for the  $\text{CD}_3$  and  $\text{CD}_3\text{OD}$  measurements. (a)  $\text{CD}_3\text{OH}$ , incoherent component. The straight lines represent the  $D_T Q^2$  values with the translational diffusion coefficient calculated from equation (36) of [18a]. (b)  $\text{CD}_3\text{OD}$  coherent component, calculated using equation (10). Representative estimates of the errors are shown as bars on the right-hand side of the figures.



**Figure 3.** Quasielastic widths and the associated amplitudes computed using the model described in [21]. The straight line represents the Fickian regime with diffusion coefficient taken from [18a] for 300 K. Open circles and triangles represent the widths and amplitudes of the first two lorentzians. Squares show the effective width of the curve composed of the sum of the two contributions.

the fits, such as the molecular rotational diffusion constant  $D_r$  and the methyl group jump frequency are also given in table 1.

A way to explore the significantly different behaviour of this liquid when compared with water can be found using some phenomenological approaches which take into account the nature and dynamics of the HB network. In particular, we have taken the prescription due to Bertolini *et al* [21] for the analysis of the translational part of the quasielastic spectra. Such an approach was adopted since although it is purely phenomenological in nature, it allows the computation of dynamical quantities, such as the quasielastic widths, in terms of a simple kinetic model where most of the parameters required are obtainable from macroscopic measurements (diffusion coefficients) or from

computer simulations (fraction of molecules with a given number of intact H bonds, and H bond lifetimes).

In order to specify the model several assumptions need to be introduced. The first one concerns the number of states (number of intact H bonds) available for each molecule. Such questions can be easily answered on the basis of three independent computer simulations performed with different model potentials [22] which lead to the conclusion that four different states, with relative populations which depend upon the potential employed, exist.

The remaining parameters (diffusion coefficients for every one of the four states  $D_T(x_i)$ ) were approximated following a similar scheme to that used for water [21]. The calculation of the dynamical structure factor for self-correlations

$$S_s(Q, \omega) = \sum_{i=0}^3 \frac{A_i(Q)\lambda_i(Q)}{\omega^2 + [\lambda_i(Q)]^2} \quad (16)$$

thus requires the specification of the  $\lambda_i$ ,  $A_i$  widths and amplitudes for the four lorentzian lines. Such quantities are easily obtained from the integration of a first-order linear differential system by specifying the time behaviour of the four self-intermediate scattering functions in terms of the  $D_T(x_i)$  diffusion coefficients and a kinetic matrix (for details see [21]). The dynamical quantities  $A_i$ ,  $\lambda_i$  are easily calculated using standard methods [23] from a spectral analysis of the steady state solution of the linear system referred to. Some representative results of the calculation are given on a graph showing the behaviour of the two narrower (and more intense) lorentzians dotted against  $Q^2$  which is shown in figure 3.

As can be seen from the figure, the narrowest lorentzian saturates to a constant width at relatively low  $Q$ -values ( $Q^2 \approx 0.6$ ) whereas the second translation component approximately follows a trend proportional to  $D_T Q^2$  without showing any bending up to the highest  $Q$ -value considered ( $2 \text{ \AA}^{-1}$ ). It is then clear that the combination of the two lorentzians will result in a quasielastic part of the spectrum which does not show saturation, at least in measurements performed with the resolution achieved in the present work.

#### 4.2. Rotational diffusion constants

The rotational dynamics of liquid methanol has been the subject of extensive NMR investigations (for a review see [10]) since it constitutes one of the simplest molecules suited for the study of intramolecular and intermolecular dynamics at the same time. The picture that emerges from the studies portrays a rather slow rotation of the OD part of the molecule due to its coupling to the dynamics of the HB network, and a second rotational mode arising from the internal reorientation of the methyl group.

In order to test the possibility of discriminating between isotropic and anisotropic rotational diffusion models, several trials were carried out using equation (8), this time introducing two free parameters  $D_1$  and  $D_2$ . No substantial improvement in the quality of the fits was achieved and, on the other hand, one of the parameters tended to go towards unphysical regions. The reason for the insensitivity to the rotational anisotropy may be the low momentum transfer explored in the present experiment.

Although from principal moments of inertia considerations (see table 2) one would expect a marked degree of anisotropy of the molecular reorientation, the available NMR data suggest that it can be adequately understood in terms of a spherical isotropic

**Table 3.** Comparison of rotational motion constants.

T (K)	$\tau_r^{\text{NMR a}}$	$\tau_r^{\text{QENS b}}$	$\tau_{\text{CD}_3}^{\text{NMR c}}$	$\tau_{\text{CD}_3}^{\text{QENS d}}$	$\tau_r^{\text{diel e}}$
200	71.0	27.8	1.94	0.39	—
230	27.0	16.8	1.35	0.32	192
250	17.0	13.8	1.16	0.30	131
300	6.6	10.2	0.74	0.27	34

<sup>a</sup> Units are  $10^{12}$  s, taken from [2].

<sup>b</sup> Units as before, computed using  $\tau_r^{\text{QENS}} = \frac{3}{2}D_r^{\text{QENS}}$ .

<sup>c</sup> Taken from [24].

<sup>d</sup> Computed using  $\tau_{\text{CD}_3}^{\text{QENS}} = \frac{1}{2D_r} \frac{1}{3 + W_M/2D_r}$ .

<sup>e</sup> In  $10^{-12}$  s. Taken from [8] and computing  $\tau_r$  with a hydrogen bond lifetime of 2 ps.

rotational diffusion law [24], the reason for this being the three directions in which a hydrogen bond can be formed with the OD fragment.

The characteristic time of this motion is linked to the rotational diffusion constant through  $\tau_c = \frac{1}{6}D_r$ . Some representative values, taken from Versmold [24] are given in table 3.

Some difficulty is encountered when trying to compare rotational correlation times measured from NMR and inelastic neutron scattering, because of the several definitions used in the literature. In the approach followed in this work, that is of Brownian rotational diffusion, a time constant can be defined as

$$1/\tau_l = l(l+1)D_r$$

and, following Powles [25] the characteristic time for the rotational motion should be

$$\tau_R \cong 3\tau_1.$$

A comparison of the values measured using the deuteron relaxation rates in NMR experiments with values reported in this work (table 3) shows systematic differences in both absolute values of  $\tau_r$  and its temperature dependence.

Although the information obtainable from deuteron relaxation studies always has to be extracted assuming the same value for the quadrupole coupling constant, which may be affected by large errors, the extent of the deviations with respect to the QENS data cannot be attributed to such an origin. A plausible explanation for such a discrepancy can be considered to arise from the energy transfer window used in the present experiment. It is then clear that the large values found by NMR at lower temperature would give rise to a spectral component comparable with the instrumental resolution and of the same order of magnitude as the translational component.

On the other hand, following the same lines as those given in the previous section for the translational diffusion, it may be argued that a realistic model to represent the rotational motion should encompass the several different environments encountered by the rotating molecule. In such a case it should be said that, although a similar calculation to that performed for the translational components can be carried out, the main difficulty lies in the evaluation of the four required  $D_r(x_i)$  rotational diffusion coefficients for which we were not able to obtain a set consistent with the available NMR and dielectric relaxation data. However, the fact that according to computer simulation results, only

a very small fraction of molecules ( $\approx 2.0\%$ ) are free to rotate, introduces an additional uncertainty in the analysis of the present data.

On an empirical basis (without appealing to any particular model for the rotation) we found that one of the three lorentzians composing the spectra could be assigned to a rotational mode with a geometry (defined by the residual elastic intensity) consistent with a centre-of-mass outside the molecule. Although such a fact can be interpreted as an indication of intermolecular association, the lack of a model with only a few adjustable parameters prevented us from reaching any definite conclusion.

As expected, the dynamics of the  $\text{CD}_3$  group proved to be considerably faster than that for whole molecule reorientation. It is again difficult to compare the jump frequencies in this work with the rotational correlation times derived from NMR relaxation measurements. The simplest relationship is

$$\tau_{\text{CD}_3}^{\text{NMR}} = \frac{1}{2D_r} \left| \frac{1}{3 + W_M/2D_r} \right|$$

where again only the isotropic diffusion coefficient is considered, due to the lack of sensitivity of the present data to discriminate between isotropic and anisotropic models. Representative results of this comparison are given in table 3.

Finally it is worth comparing some results from dielectric relaxation studies with those given in this work. Although some early work [26] claimed that it was possible to measure three dispersion regions with relaxation times of orders of  $10^{-10}$ ,  $10^{-11}$  and  $10^{-12}$  s, respectively, these results have not been confirmed in more recent investigations [9], where only one relaxation time was apparent over a wide range of temperatures. From the reported data it is possible to derive a microscopic relaxation time  $\tau_r$  in the form

$$\tau_r = \tau^{\text{diel}}(2\varepsilon_0 + \varepsilon_\infty)/3\varepsilon_0$$

where  $\tau^{\text{diel}}$  is the dielectric relaxation time (macroscopic) and  $\varepsilon_0$  and  $\varepsilon_\infty$  are the static dielectric constant and its limiting value respectively. The microscopic  $\tau_r$  relaxation times are also given in table 3. It is then clear that  $\tau_r$  should sample motions quite different from those accessible to QENS or NMR. For the latter two spectroscopic techniques, only motions relative to the mobile fraction (unassociated molecules and dimers) seem to be accessible, whereas most of the dielectric relaxation results seem to be sampling collective processes linked to the dynamic of the HB network.

## 5. Conclusions

The dynamics of liquid methanol, either partially or fully deuterated has been studied by QENS spectroscopy comprising a wide range of energy and momentum transfers.

Although a simplified model which does not take into account the associative nature of this liquid can explain all the observed spectral features of the two samples the dependence with  $Q^2$  of the  $\Gamma_Q$  linewidths show a qualitatively different behaviour from what could be expected for an associated liquid. Such a quasilinear trend may be rationalised as arising from two different diffusion processes linked to two associative states.

The rotational part of the spectra can be explained as being composed of at least two motions arising from molecular tumbling and fast rotation of the  $\text{CD}_3$  group. The

discrepancies observed with respect to NMR relaxation studies could also be explained by means of a similar stochastic model to the one employed for the translational motion.

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