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Depolarized quasi-elastic light scattering and H-bond cooperative effects in liquid alcohols

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Abstract. Depolarized low-frequency data on the two isomeric pentanols normal-pentanol (n-PeOH) and 2-methyl-2-butanol (2M-2BuOH) are presented. The measurements, performed over a wide temperature range of the liquid phase, allow us to identify two processes that characterize the dynamical response of both the alcohols: the first one, present also in an IQENS experiment performed on the same sample, is connected with the fast rotational jumping of the CH_3 groups and results are independent of the nature of the alcohol; the second one, collective in character, allows—by a comparison with the neutron response—the evaluation of the second-rank static Kirkwood correlation factor g_2 for both of the alcohols. In addition, a large magnitude of the orientational pair correlation function is detected for the more associative n-PeOH, as compared with that of the more molecular 2M-2BuOH. The reorientational dynamics of the two alcohols is also discussed within the framework of the current theories for Rayleigh wing scattering from associated liquids composed of small molecules.

1. Introduction

The physical origin of low-frequency depolarized light scattering in liquid systems, where moderately strong intermolecular interactions such as H-bonds are present, is still an unresolved complex problem (for a comprehensive review on this subject, the reader is referred to [1] and references therein, [2]). Generally speaking in the case of molecular liquids, composed of small weakly interactive molecules, Rayleigh wing studies provide relevant information about the fast relaxation time of reorientational molecular motion [1]. In the case of H-bonded liquids, such as alcohols, the presence of non-negligible orientational pair correlation (OPC) [3, 4] effects makes it difficult to resolve quantitatively the spectral features [5]. This is particularly so in the case of liquid alcohols, where the Rayleigh wing spectrum is determined not only by the molecular rotation of the molecule, as an overall rotation around its symmetry axis, but also by the 'internal' reorientational motion (e.g. the fast jump motion of the CH_3 groups), by the segmental motions induced by some intrinsic flexibility and finally by OPC terms induced by the strong directional $O\cdots H$ potential. This latter effect is mainly connected with the relaxation time of the H-bond-imposed 'local order', i.e. with the time decay of the local order fluctuations [6]. Another important effect observed in alcohols, that adds some difficulty to the explanation of the anisotropic induced spectral features, is the occurrence of isomeric effects that induce different associative properties (and hence different dynamical responses), when the position of the O–H group within the alkyl chain changes. Finally, the possible existence of cross-correlation effects between permanent and induced anisotropic components in the molecular polarizabilities, as well as OPC contributions, do not permit a quantitative data analysis. In the literature a lot of examples are reported for which the possibility of separating the single-particle rotational correlation function contribution with respect to the OPC one [2,7,8] is indicated and performed. It is well known [2] in fact that NMR, Raman and fluorescence decay spectroscopies give information on the self-rotational relaxation time τ_s, whereas dielectric relaxation, Rayleigh wing and Kerr effect spectroscopies probe more directly the collective rotational relaxation time τ_c. A comparison between two experiments performed with two classes of spectroscopy could provide relevant information about the existence of cooperative effects in the liquid under examination.

There exists another possibility for the detection of OPC contributions in liquids, which consists, as indicated by Egelstaff some year ago [9], of comparing the incoherent quasi-elastic neutron scattering (IQENS) rotational contributions with the Rayleigh wing ones. This method appears to be fruitful when hydrogenous molecules (like alcohols) are examined, because of the incoherent nature of the proton cross sections and because the neutron scattering technique probes the single-molecule diffusional motion more directly.

This paper studies the temperature dependence of the Rayleigh wing in the two isomeric alcohols normal-pentanol (n-PeOH) and 2-methyl-2-butanol (2M-2BuOH), which have the same chemical formula $C_5H_{11}OH$ but differ in the position of the OH hydroxyl group within the alkyl chain (n-PeOH) is a primary alcohol whereas 2M-BuOH is a tertiary one).

The aims of the present study are twofold: (i) to verify, if it exists, some difference in the Rayleigh wing spectra of the two isomers as *a priori* supported by the occurrence that they have different physical behaviours in many structural and dynamical properties that could reflect themselves in the reorientational diffusion; and (ii) by comparison with recently available IQENS data [10, 11] if the OPC term enters in the rotational dynamics of the two alcohols, its extent being directly tested by a comparison of the neutron τ^N and the Rayleigh τ^{Ray} reorientational relaxation times.

The present work can be considered as part of an extensive analysis that we have carried out on liquid alcohols by several spectroscopic methods [10, 12, 13]. In particular, the previously obtained results confirmed the existence of linear associative species (n-mers, n = 1,2,3,4) with a zig-zag structure for n-PeOH and a more close packed structure, composed of monomers and linear and cyclic dimers, for the more sterically hindered 2M-2BuOH. Since these associative states are triggered by the existence of the H-bond potential, where the mean lifetime lies in the picosecond region, they are not considered [13] stable entities, but 'transient' species in dynamical equilibrium. The differences between the two conformers, which emerges from the entire body of the experimental results, can be summarized in the following points.

(a) In the case of n-PeOH, we are in the presence of a strongly associated liquid because τ_u (the ultrasonic relaxation time) is lower than τ_D (the dielectric relaxation time) [14]; the ratio η_v/η_s (bulk-to-shear viscosity) is nearly unity; τ_D, τ_u, η_s and D_T (the translational self-diffusion coefficient) show a simple Arrhenius-like T-dependence [10, 14]; and τ_s (the shear relaxation time) and G_∞ (the shear modulus) have a T-dependence that is typical of associated liquids [13].

(b) In the case of 2M-2BuOH, however, a more molecular behaviour has been observed because: $\tau_D \sim \tau_u$; η_v/η_s is greater than 1 over a wide temperature range; and η_s and D_T obey the Vogel–Fulcher–Tamman law as far as their T-dependence is concerned.

These differences are induced, as already mentioned, only by the differences in the 'active' sites of the intermolecular bond, and therefore, following Angell's classification scheme [15], a 'fragile' character can be attributed to the tertiary isomer and a 'strong' one to the primary alcohol.

As will be shown in the next section we confirm that the OPC contribution enters into the rotational relaxations of both the isomers in a wide temperature range, with only a minor effect in the case of 2M-2BuOH.

In addition, the Lorentzian character of the spectral features will allow us to apply the CMMC (correspondence microscopic–macroscopic correlation) theorem [7, 16, 17], which ensures that if the self-rotational correlation function relaxes exponentially in time (and hence Lorentzian-like in the frequency domain) with a decay time τ_s, then the OPC function is also exponential, with a decay time τ_c proportional to τ_s. A comparison of Rayleigh wing and IQENS data will allow us to evaluate the proportionality factor, defined as the ratio between the static and the dynamic OPC.

2. Experimental procedure and data handling

Depolarized Rayleigh-wing measurements were taken in the −30–131 °C temperature range for n-PeOH and in the −10–96 °C temperature range for 2M-2BuOH. High-purity samples (certified grade quality products) were further purified as previously described [14] and subsequently degassed and filtered inside a dry box, in order to remove dust particles and inhomogeneities. The n-PeOH and 2M-2BuOH samples were successively sealed in optical rectangular silica cells of dimensions 10×10×80 mm and then mounted in an optical thermostat, especially built [12] to avoid any unwanted stray-light contributions. The temperature stability was better than 0.05 °C throughout the investigated temperature range. The high sample purity as well as the optical purity of the sample holder, ensured data collection with a good signal-to-noise ratio and high reproducibility. We used a high-resolution fully computerized Spex–Ramalog triple monochromator in a 90° scattering geometry. As an excitation source we used the 4880 Å vertically (with respect to the scattering plane) polarized line of a unimode Ar^+ laser Spectra Physics mod 165, working at a mean power of 700 mW. We estimated the effective power in the scattering cell to be reduced by ~40%. which in our alcohols does not induce any unwanted thermal effect. The detection apparatus consisted of a photon counting system whose outputs were processed on line by a computer. The scattered photons in horizontal polarization were automatically normalized for the incoming beam intensity and for the CH band intensity, in order to ensure good data reproducibility. Following a well established procedure, previously described [5], a spectral resolution of 0.10 ± 0.05 cm^{-1} (HWHM) in the −3–3 cm^{-1} region, of 0.25 cm^{-1} in the −8 cm^{-1}–8 cm^{-1} region, and of 1.5 cm^{-1} in the −50–50 cm^{-1} was used. The spectra at different resolutions were subsequently numerically matched and corrected for the density ρ, for the refractive index n and for local field effects [18–20]. These corrections correspond to a normalization of the intensity by the factor $n\rho^{-1}(n^2+2)^{-4}$, with $n(T)$ and $\rho(T)$ taken from the literature [14, 21]. Finally the Stokes and anti-Stokes sites of the spectra are properly normalized by means of the 'detailed balance' law. In figure 1 we show, as an example, typical Rayleigh wing spectra for n-PeOH at four temperatures (−30 °C, 10 °C, 60 °C and 131 °C) covering a wide liquid region, in a log–log plot. Figure 2 shows Rayleigh wing spectra, also in a log–log plot, for 2M-2BuOH at four temperatures (−10 °C, 10 °C, 60 °C and 96 °C).

3. Experimental results

It is well known that the Rayleigh wing spectrum in a liquid system is based on by the time correlation $C_\beta^{\mathrm{Anis}}(\boldsymbol{k}, t)$ of the traceless part of the polarizability tensor fluctuations $\delta\beta_{ij}(\boldsymbol{k}, t)$

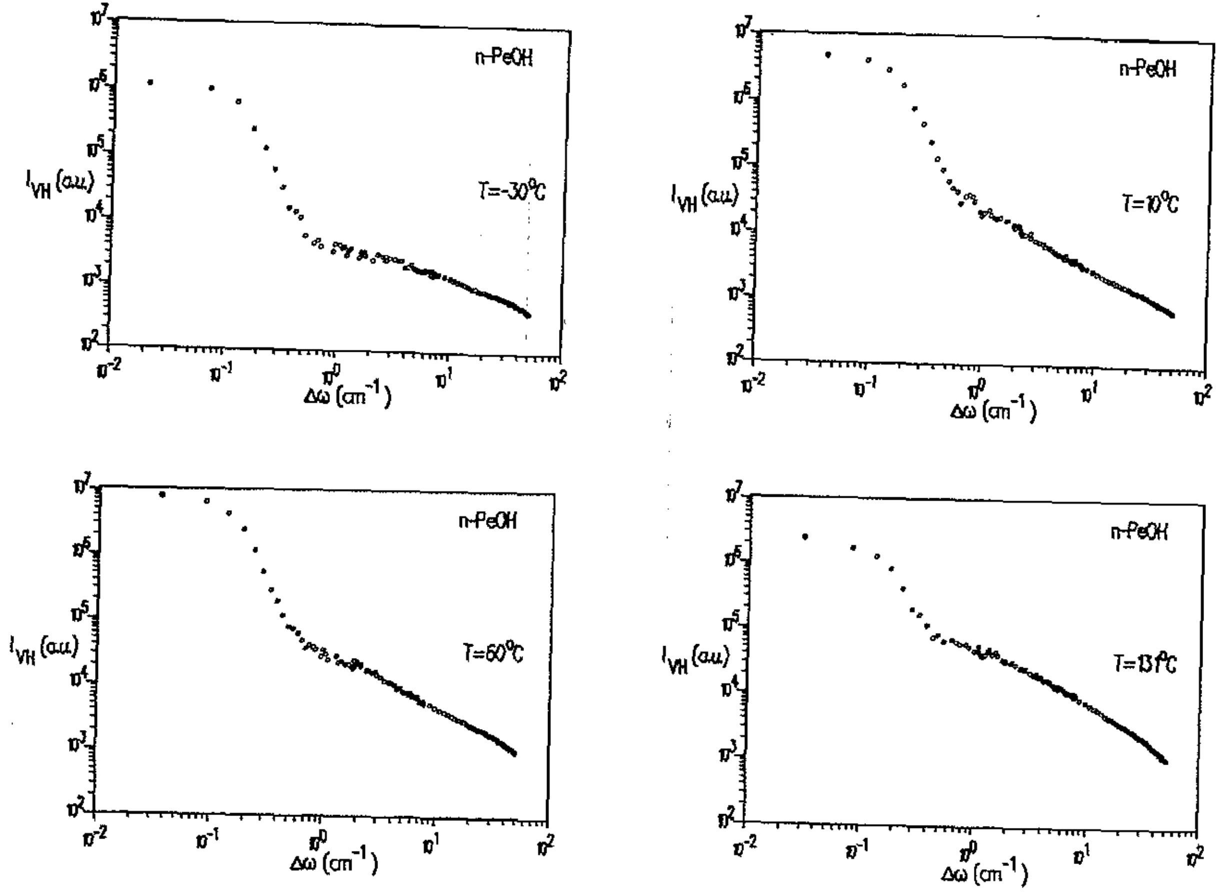

Figure 1. The temperature evolution of depolarized Rayleigh wing spectra in normal-pentanol (n-PeOH). The points are the experimental data represented in a log–log plot.

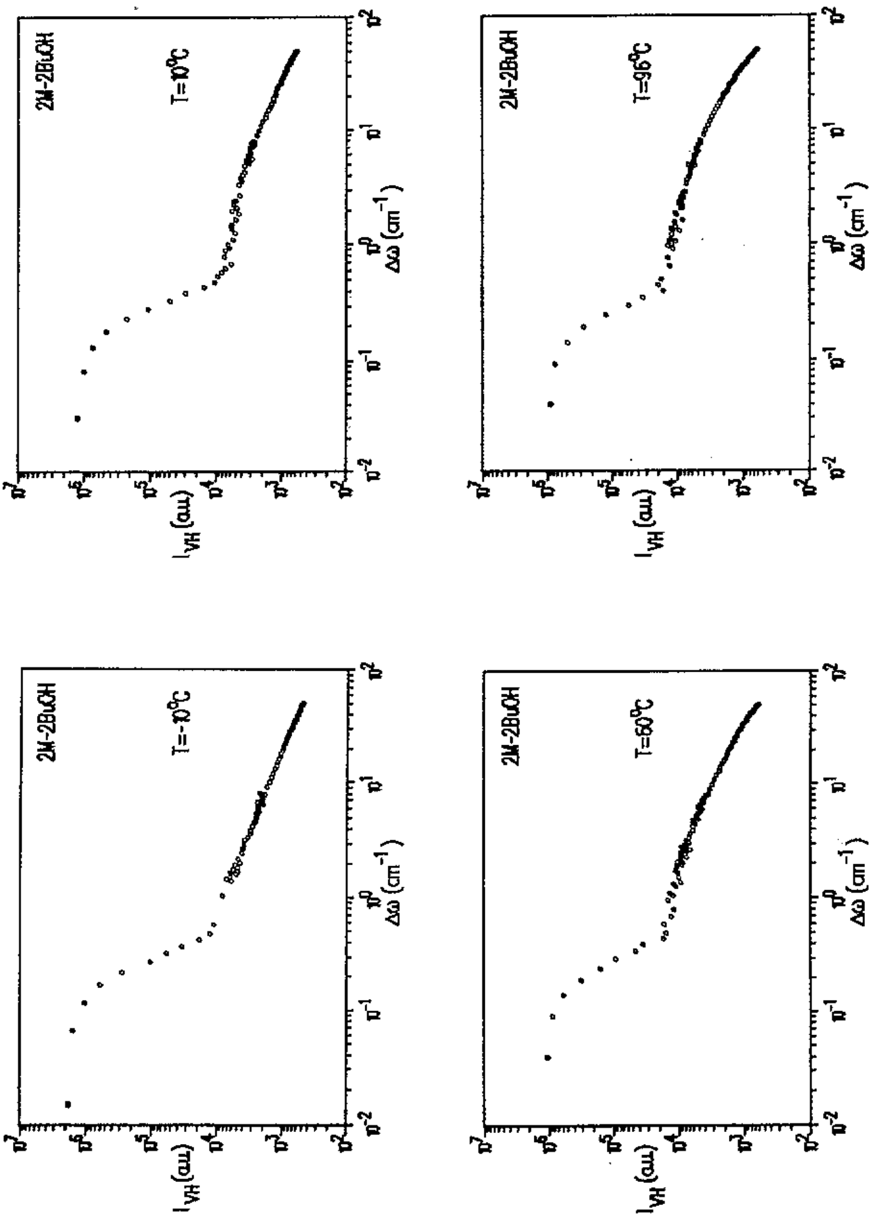

Figure 2. A log–log plot of depolarized Rayleigh experimental spectra in 2-methyl-2-butanol (2M-2BuOH) at four temperatures.

[22]. Usually both the permanent and the induced contributions of this latter effect enter into $C_\beta^{\mathrm{Anis}}(\boldsymbol{k}, t)$. The Rayleigh wing intensity, $I_{\mathrm{VH}}(\boldsymbol{k}, \omega)$, defined as the frequency Fourier transform of $C_\beta^{\mathrm{Anis}}(\boldsymbol{k}, t)$ can be written in the form

$$I_{\mathrm{VH}}(\boldsymbol{k}, \omega) = \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-\mathrm{i}\omega t} \left\{ \langle \delta\beta_{xy}^*(\boldsymbol{k}, 0)\delta\beta_{xy}(\boldsymbol{k}, t)\rangle \sin^2\theta/2 + \langle \delta\beta_{yz}^*(\boldsymbol{k}, 0)\delta\beta_{yz}(\boldsymbol{k}, t)\rangle \cos^2\theta/2 \right\} \tag{1}$$

In equation (1), $\langle \ldots \rangle$ denotes the thermodynamics averaging, θ is the scattering angle and for the scattering geometry we refer to [22] and references therein. $\delta\beta_{ij}$ also takes into account the translational term

$$\delta\beta_{ij}(t) = \frac{1}{V} \sum_a \delta\beta_{ij}^{(a)}(t) \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_a(t)}.$$

In addition the $I_{\mathrm{VH}}(\boldsymbol{k}, \omega)$ contains, as noted in section 1, both the self- and the distinct contributions of the correlation function $C_\beta^{\mathrm{Anis}}(\boldsymbol{k}, t)$.

For relatively low viscous liquids with intermolecular interactions, such as H-bond interactions, under the assumption that no coupling occurs between rotational motion and collective hydrodynamic transport modes [6, 22], in the case of *purely Lorentzian components* in $I_{\mathrm{VH}}(\boldsymbol{k}, \omega)$, the CMMC theorem [7, 16] holds and we can write the following:

(a) For the OPC time

$$\tau_{\mathrm{c}} = \tau_{\mathrm{s}}(1 + N g_2)/(1 + N J_2) \tag{2}$$

where τ_{c} and τ_{s} are the collective and the self-reorientational correlation times, N is the scattering number in the scattering volume, g_l ($l = 2$) is the second-rank static orientational Kirkwood parameter in light scattering experiments:

$$g_l = \sum_j \langle Y_{lm}(1, 0) Y_{lm}(j, 0) \exp\{\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}^1(0) - \boldsymbol{r}^j(0)]\}\rangle_{l=2} \tag{3}$$

Y_{lm} being the normalized spherical harmonic (here we use the same notation as in [2]) and J_2 is the second-rank dynamic orientational Kirkwood parameter that, as tested for many liquids, turns out to be close to zero. By a good approximation, equation (2) can be rewritten as:

$$\tau_{\mathrm{c}} \simeq \tau_{\mathrm{s}}(1 + N g_2). \tag{2$'$}$$

We point out here that when $g_2 = 1$ (the absence of pair correlation) the OPC time τ_{c} becomes equal to τ_{s} [3].

(b) For the integrated intensity of the Rayleigh wing

$$I_{\mathrm{VH}} \equiv \int_{-\infty}^{\infty} \mathrm{d}\omega I_{\mathrm{VH}}(\omega) = A\langle\beta\rangle^2 N(1 + N g_2) \tag{4}$$

A being a form factor that marks the shape of the molecule in the liquid of mean anisotropy $\langle\beta\rangle$.

As already noted, these equations can correctly describe the spectral features of the Rayleigh wing under the assumption of Lorentzian character of the observed lineshapes. We have observed, as can be seen in figures 3 and 4, that two Lorentzian lines provide good fits for our Rayleigh wings in both the n-PeOH and 2M-2BuOH systems. Thus, as a consequence, we can apply the CMMC theorem. By returning now to figures 3 and 4, the

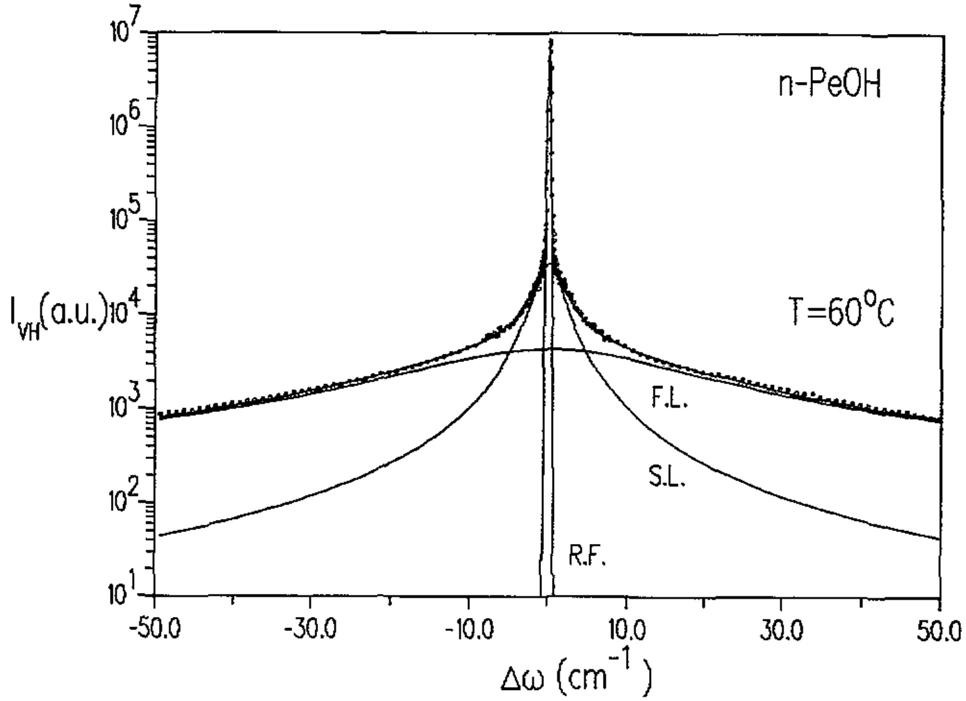

Figure 3. A semilog plot of the experimental Rayleigh wing spectrum (points) of n-PeOH at $T = 60$ °C, fitted with two Lorentzian components, a resolution-enlarged Gaussian component, plus a baseline. The fitted results are shown as full curves (see text for details).

two Lorentzian lines, composed of a 'fast' (FL) and a 'slow' (SL) component, are the fitted results of our Rayleigh wing spectra at $T = 60$ °C with the scattering law

$$I_{\mathrm{VH}}(\omega) = R(\omega) + L^{\mathrm{Slow}} + L^{\mathrm{Fast}} + B \tag{5}$$

where $R(\omega)$ represents the 'ultranarrow' resolution-enlarged Gaussian component that could be induced by unwanted parasitic light coming from the polarized component not completely rejected by the polarizer film, which in any case does not induce any variation in the $L^{\mathrm{Slow}}(\omega)$ parameters, as estimated by a convolution of the Lorentzian $L^{\mathrm{Slow}}(\omega)$ with the Gaussian $R(\omega)$. $L^{\mathrm{Slow}}(\omega)$ and $L^{\mathrm{Fast}}(\omega)$ are Lorentzian lines related to the exponential time decays of two different rotational relaxation processes and B is a small flat background contribution. B turns out to range from 20 counts s^{-1} to 40 counts s^{-1}, which results from the small contribution of dark counts plus a very small fluorescence signal.

Each Lorentzian line provides two relevant parameters; the relaxation time $\tau = (2\pi c\Gamma)^{-1}$ (Γ being the HWHM linewidth) and the integrated area I_{VH}, which correspond to equations (2′) and (4), respectively. The Rayleigh wing spectra, shown for n-PeOH and 2M-2BuOH at $T = 60$ °C in figures 3 and 4, are well fitted to equation (5) throughout the investigated temperature range. Figures 5 and 6 show, for comparison, the Rayleigh wing experimental spectra (points) together with the best fits to equation (5) (full curves) taken at the extreme temperatures investigated, for n-PeOH and 2M-2BuOH, respectively. As can be seen, good fits for the anisotropic low-frequency contribution in both the isomeric alcohols, without invoking a sum of exponentials in the ω-domain, as reported in [23] (whose physical meaning cannot be clearly recovered) are obtained for the two investigated isomers. In the next section we will try to give a possible explanation for the obtained parameters, with the help of IQENS results on the same system.

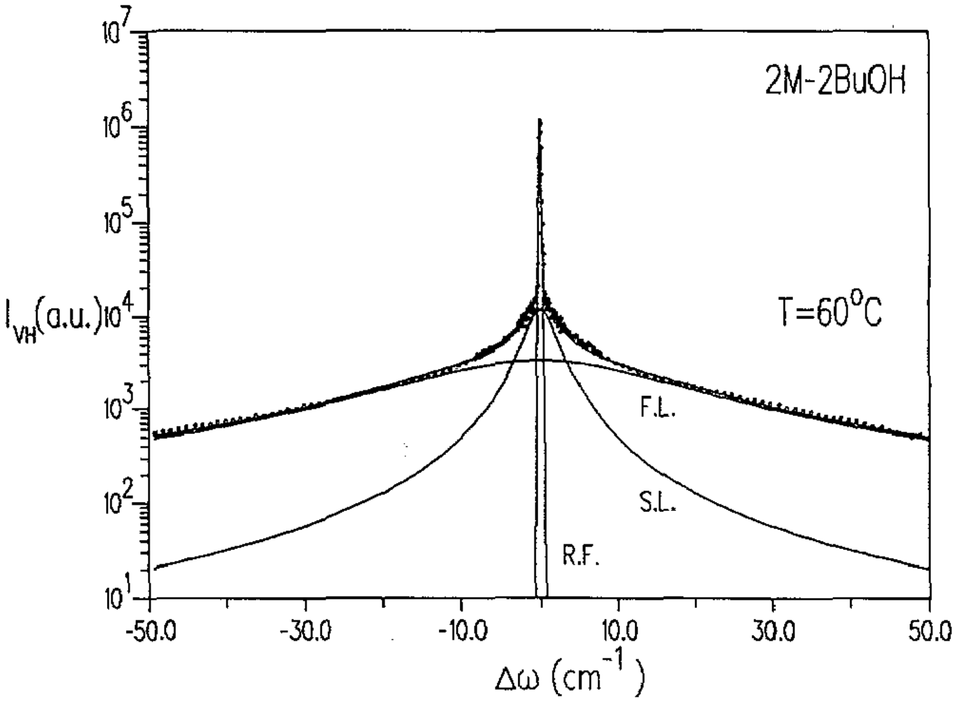

Figure 4. A semilog plot of the experimental Rayleigh wing spectrum (points) of 2M-2BuOH at $T = 60$ °C, fitted with two Lorentzian components, a resolution-enlarged Gaussian component, plus a full curve (see text for details).

4. Discussion of the results

In table 1 the results of the analysis of the Rayleigh wing data for both the alcohols as a function of temperature are reported. It is to be noted that subscript '1' refers to the 'slow' Lorentzian component parameters whereas subscript '2' refers to the 'fast' Lorentzian component parameters. Furthermore, figure 7 shows the behaviour of the Rayleigh wing rotational relaxation times τ^{Ray} as obtained by evaluating at each temperature the fast and the slow Lorentzian linewidths for n-PeOH and 2M-2BuOH. In the same figure are reported, for comparison, the IQENS τ^{N}, measured as a function of temperature in both the alcohols during an IQENS experiment [11] performed with the MIBEMOL TOF spectrometer at the ORPHEE reactor in Saclay, France. The τ^{N} values, as noted above, give direct information about the single-molecule reorientational relaxation time τ_s ($\equiv \tau^{\mathrm{N}}$) = $[l(l+1)D_r]^{-1}$, with $l = 2$ for a direct comparison with the light scattering data. At the same time the τ^{Ray} reorientational relaxation times give direct information on the OPC time τ_c ($\equiv \tau^{\mathrm{Ray}}$). We are, by an inspection of figure 7, in the presence of two distinct behaviours concerning the 'fast' F and the 'slow' S rotational times,

(i) The 'fast' relaxation times $\tau^{\mathrm{Ray}}_{\mathrm{Fast}}$ turn out to be almost independent of the nature of the alcohols, they reveal a weak T-dependence, and they are near-coincident (within experimental uncertainties) with the neutron $\tau^{\mathrm{N}}_{\mathrm{Fast}}$ times. All these purely experimental results point to the fact that we are in the presence of the ultrafast jump of the CH_3 methyl group, because the mean value ($\simeq 0.3$ ps) is equal to other unambiguous determinations of this rotational parameter [24, 25]. This rotational relaxation time, which seems to be present also in the Rayleigh wing spectrum in spite of its scarce anisotropic scattering contribution,

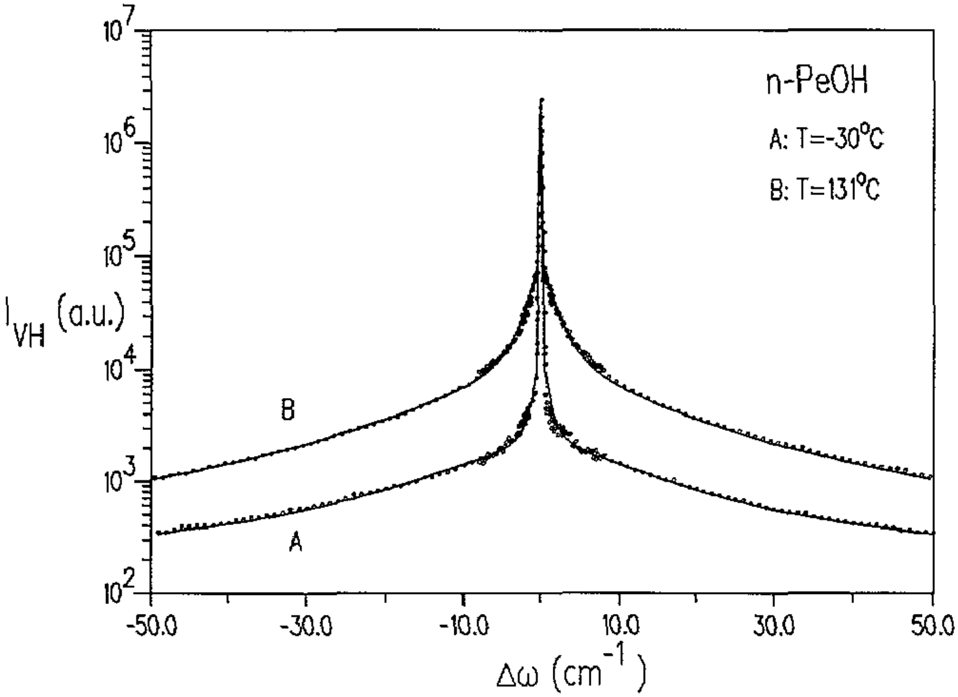

Figure 5. Experimental VH spectra (points) of n-PeOH at $T = -30$ °C (A) and $T = 131$ °C (B) in a semilog plot. The full curves represent the best-fit results to equation (5).

is, as expected, not influenced by cooperative linkage of the non-interactive CH_3 group, so that g_2 is equal to zero and, as verified,

$$\tau_{\mathrm{Fast}}^{\mathrm{Ray}}/\tau_{\mathrm{Fast}}^{\mathrm{N}} \equiv \tau_{\mathrm{c,Fast}}/\tau_{\mathrm{s,Fast}} = 1 .$$

(ii) The 'slow' relaxation times $\tau_{\mathrm{Slow}}^{\mathrm{Ray}}$, which are evaluated by the narrow Lorentzian linewidths, turn out to be dependent on the nature of the alcohol ($\tau_{\mathrm{Slow}}^{\mathrm{Ray}}$ for n-PeOH is bigger than $\tau_{\mathrm{Slow}}^{\mathrm{Ray}}$ for 2M-2BuOH), they suffer the same T-dependence (they both fulfil an Arrhenius-like law, with an activation enthalpy ΔH equal to $\sim$1 kcal mol^{-1}), and both are definitively higher with respect to the $\tau_{\mathrm{Slow}}^{\mathrm{N}}$ ones. The differences between $\tau_{\mathrm{Slow}}^{\mathrm{Ray}}$ and $\tau_{\mathrm{Slow}}^{\mathrm{N}}$ for the two alcohols indicate, as noted above, 'the extent to which rotational diffusion is a cooperative phenomenon', as shown by Egelstaff [9]. In our case we have

$$\frac{\tau_{\mathrm{Slow}}^{\mathrm{Ray}}}{\tau_{,\mathrm{Slow}}^{\mathrm{N}}} \equiv \frac{\tau_{\mathrm{c,Slow}}}{\tau_{\mathrm{s,Slow}}} = 1 + N g_2 \simeq \begin{cases} 3.5 \text{ for n-PeOH} \\ 2.7 \text{ for 2M-2BuOH.} \end{cases}$$

In addition, because the percentage of the monomers in both the liquids is less than 5% in the temperature range studied [12] and $N \simeq 1$, we estimate the value of g_2 to be $\simeq$2.5 for n-PeOH and, as expected, a lower value ($\simeq$1.7) in the case of 2M-2BuOH. We specify that such values are considered as mean ones within the investigated temperature range.

As far as the integrated intensities are concerned, figures 8 and 9 represent the temperature dependences of the intensities in the cases of n-PeOH and 2M-2BuOH, respectively, obtained from the fitting of the experimental lineshapes to equation (5). As can be noticed, we observe that: (i) the I_{VH} values are, as expected, almost the same for the

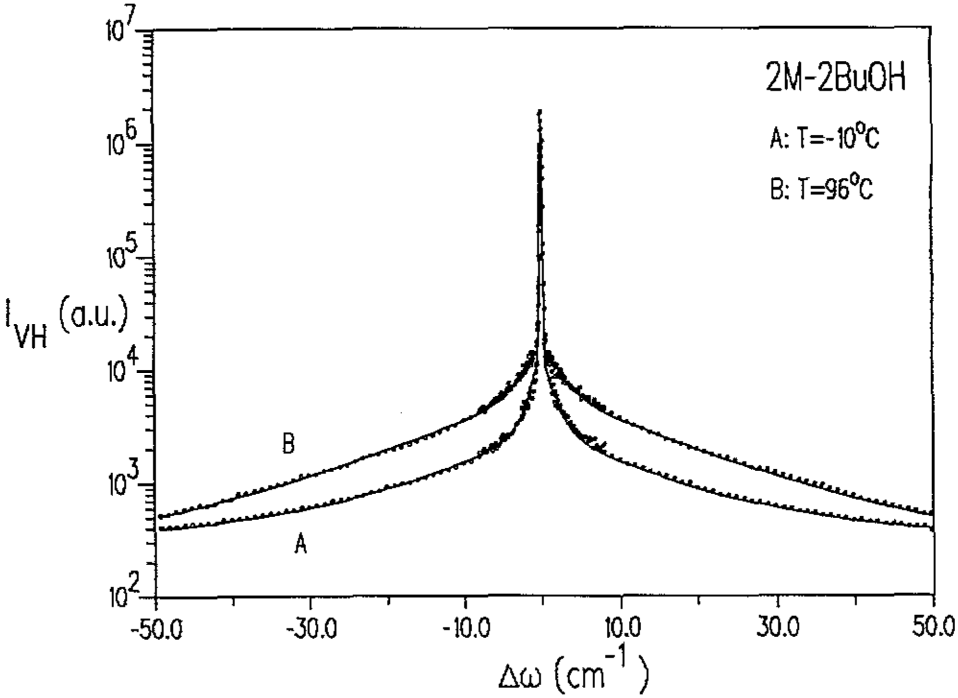

Figure 6. Experimental VH spectra (points) of 2M-2BuOH at $T = -10$ °C (A) and $T = 96$ °C (B) in a semilog plot. The full curves represent the best-fit results to equation (5).

Table 1. The temperature dependence of the slow (1) and fast (2) Lorentzian fitting parameters in 2M-2BuOH and in n-PeOH isomers: A, intensity;, Γ, HWHM; τ, relaxation time.

2-Methyl-2-Butanol

T (°C)	A_1	Γ_1(cm^{-1})	τ_1(psec.)	A_2	Γ_2(cm^{-1})	τ_2(psec.)
−10	13623	1.37	3.87	24833	16.21	0.327
+10	14481	1.75	3.04	38146	17.2	0.309
+60	24354	2.1	2.53	59877	18.6	0.285
+96	26400	2.45	2.16	71824	19.04	0.279

n-Pentanol

T(°C)	A_1	Γ_1(cm^{-1})	τ_1(psec.)	A_2	Γ_2(cm^{-1})	τ_2(psec.)
−30	21998	0.8	6.64	25674	15.8	0.336
−10	29767	1.2	4.42	37878	16.3	0.326
+10	45992	1.3	4.08	44328	17.9	0.296
+60	61096	1.75	3.03	79476	19.5	0.272
+110	93780	1.82	2.91	105982	20.25	0.262
+131	102840	1.98	2.68	109778	20.6	0.258

two alcohols in the case of the 'fast' component connected with the CH_3 internal rotational motion (see the values A_2 in table 1). The small observed differences between n-PeOH and 2M-2BuOH can be connected, by following equation (4), which in such a case becomes

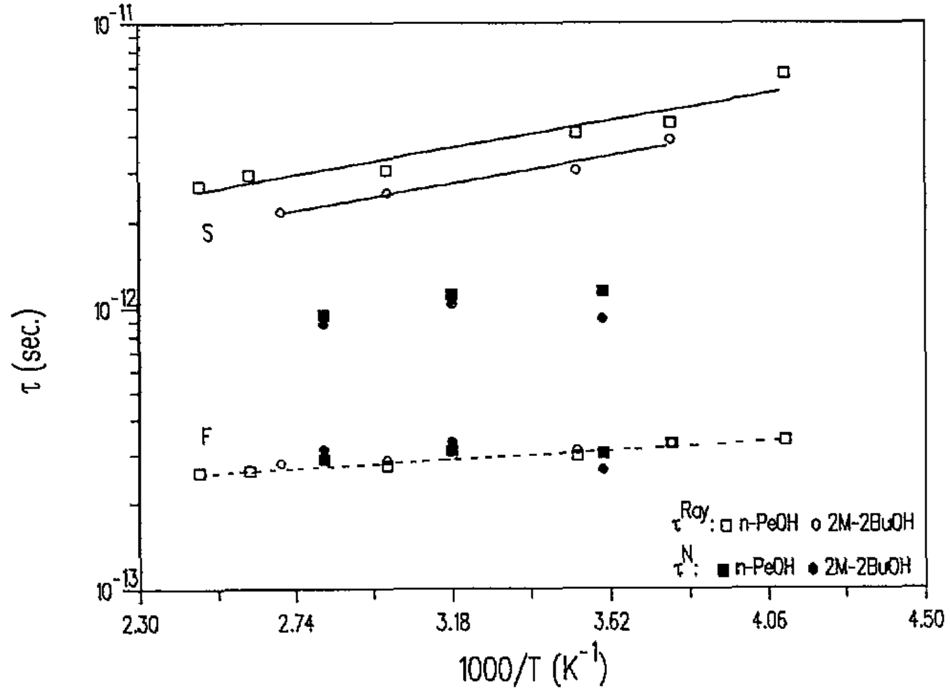

Figure 7. A semilog plot of the light scattering orientational time τ^{Ray} versus T^{-1} for n-PeOH (□) and 2M-2BuOH (○). The IQENS orientational times τ^{N} for n-PeOH (□) and 2M-2BuOH (○) are also shown. The symbols S and F refer to 'slow' and 'fast' spectral Lorentzian lineshapes. In the same figure the full lines represent the Arrhenius-like best fit.

$I_{\mathrm{VH,Fast}} = A\langle\beta^2\rangle N$ (due to the ~ 0 value of the g_2 parameter), to the small different values of the shape A and of the $\langle\beta^2\rangle$ parameters because of a more compact structure of the tertiary alcohol aggregation state which, in turn, could locally influence the rotating CH_3 entities: (ii) in the case of the 'slow' components, the integrated intensities $I_{\mathrm{VH,Slow}}$, on the basis of equation (4), give rise to higher intensities in the case of n-PeOH with respect to its isomers. This occurrence is, as expected, correctly understood because g_2 (n-PeOH) is higher than g_2 (2M-2BuOH).

As far as the temperature evolution of $I_{\mathrm{VH,Slow}}$ in both the alcohols is concerned, we can apply the model previously adopted in the case of the Rayleigh wing analysis of other associated liquids, such as molten $SbCl_3$ [26] and supercooled water [5]. The model is formally analogous to the Angell's 'bond-lattice' model, which hypothesizes that an associated liquid can be viewed by an ensemble of 'intact' and 'broken' bonds (states 'on' and 'off'). The transition from one state to the other is considered to be a thermally activated process and the anisotropic component of the polarizability tensor is modified according to the level of occupancy of the two states. In such a case the integrated intensity of the Lorentzian lines (in the case of time exponential rotational density) is proportional to the binding energy ΔG, which represents the difference between the energies of the 'on' and of the 'off' states. It has been demonstrated [26], in addition, that this integrated intensity is proportional to the conditioned probability $p_{\mathrm{B}}(1-p_{\mathrm{B}})$ of finding a bond in the 'on' state, namely:

$$I_{\mathrm{VH,Slow}} \propto p_{\mathrm{B}}\left(1-p_{\mathrm{B}}\right) \tag{6}$$

$$p_{\mathrm{B}} = \left[1+\exp(-\Delta G/RT)\right]^{-1}. \tag{7}$$

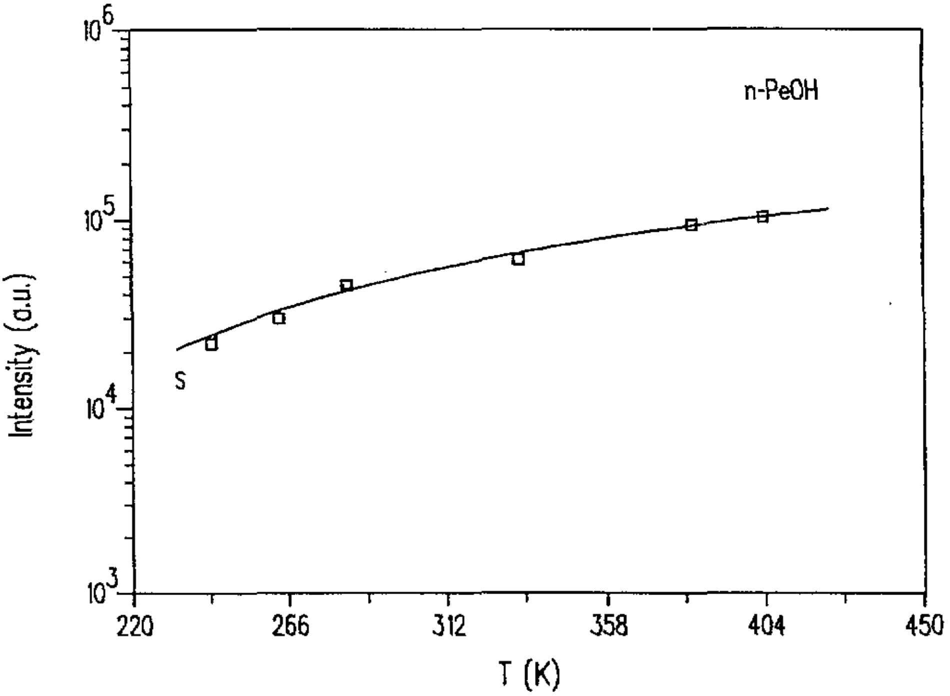

Figure 8. The temperature dependence of the integrated intensity I_{VH} of the 'slow' Lorentzian (S) for n-PeOH. The squares are the experimental data and the full curve is the best-fit result to equation (6).

The fitting of our integrated intensities to equation (6), shown as full curves in figures 8 and 9, gives a binding energy $\Delta G \simeq 1.93$ kcal mol^{-1} (for the 'Slow' rotational process) in the case of n-PeOH, whereas it gives $\Delta G \simeq 1.53$ kcal mol^{-1} for the same process in the case of 2M-2BuOH.

5. Concluding remarks

In summary, we have studied the nature of the quasi-elastic anisotropically induced (Rayleigh wing) spectral lineshape in two isomeric alcohols in the liquid phase as a function of temperature. The spectroscopic data allow us to obtain some information on the orientational pair correlation (OPC) time τ_c by comparing the light scattering response with the IQENS one. In such a way we have been able to extract some information about the value of the second-rank Kirkwood correlation factor g_2 independently, from the theoretical models used for describing the molecular reorientation under the assumption of validity of the CMMC theorem. The value of g_2 for n-PeOH is higher with respect to that evaluated for the other isomeric alcohol. This occurrence is in agreement with a high extent of the spatial correlations, H-bond-imposed, in the linear more associative n-PeOH, on which n-mers ($n = 1,2,3,4$) are hypothesized to exist, whereas the more compact structures (monomers and dimers) of the tertiary 2M-2BuOH induce a lower value of g_2. This kind of information is useful [2] because the reorientational molecular process can act as a specific probe of the local order around a given molecule as well as give relevant information regarding the dynamical problem itself, when the rotational correlation function is written as a function of the set of 'slow' hydrodynamic variables [2] that are necessary to describe all the relevant

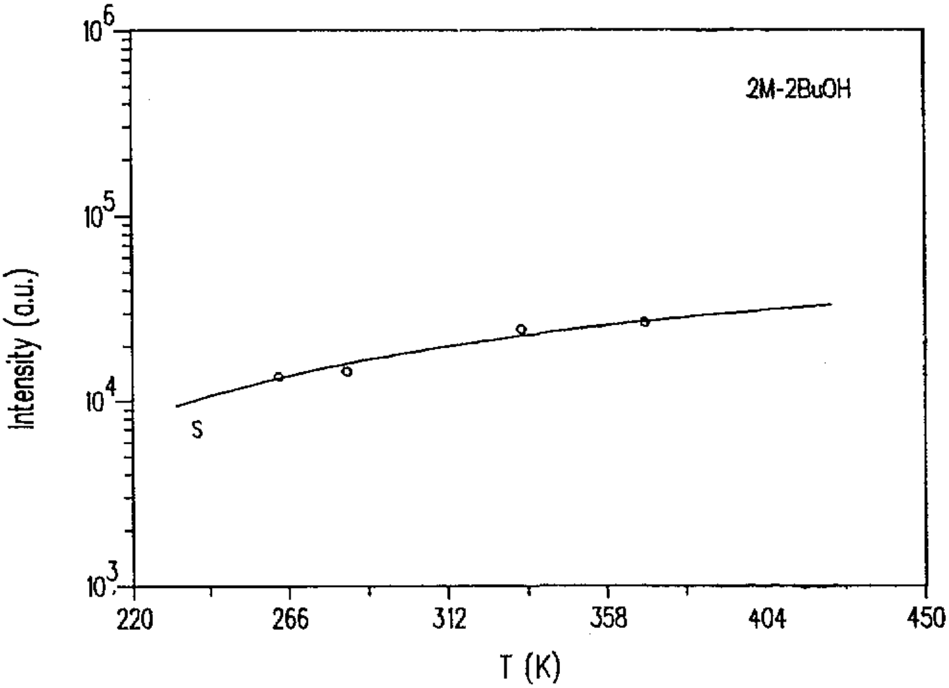

Figure 9. The temperature dependence of the integrated intensity I_{VH} of the 'slow' Lorentzian (S) for 2M-2BuOH. The circles are the experimental data and the full curve is the best-fit result to equation (6).

low-frequency motions. The presence for both the isomers of a 'fast' rotational term in the Rayleigh wing, which is also present in the rotational lineshape of an IQENS experiment, both having the same mean value of ~0.3 ps, has been identified as the fast rotational jump of the CH_3 methyl group. Furthermore, from the temperature evolution of the integrated intensities of the slow Lorentzian line, we can obtain information about the binding energy which confirms the presence of the OPC term in the reorientational dynamics of the two isomers, the H-bond intermolecular interaction being, as expected, the origin of the observed collective rotational processes.

References

[1] Clarke J H R 1978 *Advances in Infrared and Raman Spectroscopy* vol 4, ed R J H Clark and R E Hester (London: Heyden) pp 109–93

[2] Kivelson D 1987 *Rotational Dynamics of Small and Macromolecules, Lecture Notes in Physics* vol 293, ed Th Dorfmüller and R Pecora (Berlin: Springer) pp 1–14

[3] Gierke T D and Flygare W H J 1974 *Chem. Phys.* **61** 2231

[4] Bertucci S J, Burnham A K, Alms G R and Flygare W H 1988 *J. Chem. Phys.* **66** 605

[5] Aliotta F, Vasi C, Maisano G, Majolino D, Mallamace F and Migliardo P 1986 *J. Chem. Phys.* **84** 4731

[6] Quentrec B 1976 *Phys. Rev.* A **15** 1304

[7] Keyes T and Kivelson D 1972 *J. Chem. Phys.* **56** 1057

[8] Dorfmüller Th 1987 *Rotational Dynamics of Small and Macromolecules, Lecture Notes in Physics* vol 293, ed Th Dorfmüller and R Pecora (Berlin: Springer) pp 65–88

[9] Egelstaff P A 1970 *J. Chem. Phys.* **53** 2590

[10] Aliotta F, Bellissent-Funell M C, Donato D I, Migliardo P and Vasi C 1992 *Physica* B **180–1** 861

[11] Migliardo P 1993 *J. Mol. Struct* at press

[12] D'Aprano A, Donato D I, Migliardo P, Aliotta F and Vasi C 1988 *Phys. Chem. Liq.* **17** 279

[13] Magazu S, Majolino D, Mallamace F, Migliardo P, Aliotta F, Vasi C, D'Aprano A and Donato D I 1989 *Mol. Phys.* **66** 819

[14] D'Aprano A, Donato D I, D'Arrigo G, Bertolini D, Cassettari M and Salvetti G 1985 *Mol. Phys.* **55** 475

[15] Angell C A 1984 *Relaxation in Complex Systems* ed K L Ngai and G B Write (National Technical Information Service, US Department of Commerce) pp 3–11

[16] Guillot B and Bratos S 1979 *Mol. Phys.* **37** 991

[17] Kivelson D and Madden P 1975 *Mol. Phys.* **30** 1749

[18] D'Arrigo G, Maisano G, Mallamace F, Migliardo P and Wanderlingh F 1981 *J. Chem. Phys.* **75** 4264

[19] Eckardt G and Wagner W G 1966 *J. Mol. Spectrosc.* **19** 407

[20] Burham A K, Alms G R and Flygare W H 1975 *J. Chem. Phys.* **62** 3289

[21] D'Aprano A, Donato D I and Agrigento V 1981 *J. Solut. Chem.* **10** 673

[22] Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley) pp 310–26
Volino F 1977 *Microscopic Structure and Dynamics of Liquids* ed J Dupuy and A J Dianoux (New York: Plenum) pp 221–300

[23] Benassi P, Mazzacurati V, Nardone M, Ruocco G and Signorelli G 1989 *J. Chem. Phys.* **91** 6752

[24] Bermejo F J, Batallan F, Enciso E, White R, Dianoux A J and Howells W S 1990 *J. Phys.: Condens. Matter* **2** 130

[25] Bee M 1988 *Quasielastic Neutron Scattering* (Bristol: Hilger) pp 183–203

[26] Aliotta F, Maisano G, Micali N, Migliardo P, Vasi C, Wanderlingh F, Triolo R and Smith G P 1982 *J. Chem. Phys.* **76** 3987

[27] Angell C A 1971 *J. Chem. Phys.* **75** 3698