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Reorientational relaxation in a simple polar liquid: CD₃CN. A comparison with light acetonitrile*

Paola Sassi†, Assuntina Morresi, Giulio Paliani and Rosario Sergio Cataliotti‡
Dipartimento di Chimica, Laboratorio di Chimica Fisica, Università di Perugia, via Elce di Sotto
8, 06123 Perugia, Italy
E-mail: spett@unipg.it

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Abstract. FTIR and Rayleigh depolarized scattering experiments have been performed on the isotopomeric couple CH₃CN/CD₃CN in the 5–60 °C temperature range. By using these two techniques, it has been ascertained that the substitution of hydrogen with deuterium weakens the intermolecular interactions so that the local structures of aligned antiparallel dipoles are destroyed at a temperature which is far below the boiling point. The behaviour of the transport quantities versus temperature in liquid CD₃CN thus gives evidence of structural-like relaxations at a temperature falling in the range 35–40 °C. The comparison of thermal and orientational relaxation data obtained for the two isotopomers is the key for a correct interpretation of the dynamics in the two liquids.

1. Introduction

In the study of the molecular dynamics of simple liquids, a molecule like acetonitrile, with its high dipole moment equal to 3.9 D [1], represents an interesting model system because its short-range order in the liquid state is the result of strong dipole–dipole interactions [2–6].

The investigation of the transport properties, i.e. dissipative events associated with the molecular diffusion, viscous flux and thermal conduction, and the interpretation of these properties within the framework of the hydrodynamic theory, can give useful information on the presence of local aggregates in a liquid. It is well known that Rayleigh–Brillouin scattering spectra (RBS) give information on the transport properties of a molecular liquid in the hydrodynamic regime. In fact, from the spectral density analysis of the so-called ‘hydrodynamic triplet’ produced by the longitudinal hyperacoustic waves, thermodynamic and transport properties associated with the density fluctuations in the scattering volume can be derived.

Whereas studies of this type have been extensively carried out on many hydrogenated molecules in the liquid state [7], investigations performed on deuterated analogues are to our knowledge scarce. On the other hand it is assumed that the transport properties of couples of isotopomers should follow the so called ‘dynamic isotope effect’, with a ratio between the transport coefficients proportional to the square root of the ratio between the isotopomer masses.

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† Corresponding author.

‡ Present address: Laboratorio di Superfici e Interfasi (SUPERLAB), Dipartimento di Scienze Chimiche, Università di Catania, Italy.

With the aim of comparing the collective mode dynamics of liquid CH₃CN and CD₃CN in the GHz frequency range, RBS measurements were performed in the 5–60 °C temperature range. We obtained the sound absorption and sound velocity values for the two isotopomers as a function of temperature and wavevectors [8, 9]. Remarkable differences occurring in the physical and dynamical properties of the two liquids have been largely discussed in these previous articles from this laboratory. We found that the weakening of intermolecular interactions due to the isotopic substitution causes partial breakdown of short-range order in the deuterated species. A critical temperature value (~40 °C), above which the head–tail dipolar organization seems to be relaxed, giving a noticeable increase of compressibility factor with respect to the protonated analogue, has been observed in CD₃CN [8, 9].

In this article, we extend the study of dynamics to the reorientational relaxation, by comparing the previous results of the Rayleigh–Brillouin spectra with those obtained from FTIR and depolarized Rayleigh (DR) measurements for CD₃CN in the liquid state, within the frame of a study on the effects of isotopic substitution on intermolecular forces.

2. Experiment

Acetonitrile-d₃ was a spectroscopic grade product from Cambridge Isotope Laboratories Inc, having an isotopic purity of 99.8%. The sample was filtered through a 0.22 μm Millipore filter, directly into the measuring cuvette inside a dry box, thus preventing scattering from suspended atmospheric dust. Temperature control was always maintained by thermostating the sample with a precision of ±0.1 °C, with a Haake thermostat model F6.

FTIR spectra were measured with a Bruker IFS113v instrument, in the 200–6000 cm⁻¹ range, using a cell with CsI windows. Each spectrum was recorded in vacuum and was the average of 200 scans; a four point apodization function was used in the whole region; the spectral resolution was 1 cm⁻¹. For the DR measurements, the sample was irradiated with an argon ion laser line at 514.5 nm with ~200 mW power. The instrumental function was determined using a nanoparticle suspension of latex. Spectral resolution of 0.4 cm⁻¹ was obtained with the apparatus described elsewhere [10].

3. Results

FTIR and DR spectra at room temperature are shown in figure 1. The ν₁ bandwidths from FTIR spectra of CH₃CN and CD₃CN have been evaluated with a fitting procedure after deconvolution of instrumental linewidth. Reorientational relaxation times, both from IR and DR bandwidths, have been evaluated by using the following equation:

$$\tau_{or} = 1/(2\pi c \text{ HWHH}) \quad (1)$$

where HWHH is the half width at half height of ν₁ or the Rayleigh peak, in wavenumber units.

In figure 2, the reorientational relaxation times (τ_{or}^{IR}) obtained from FTIR spectra for the ν₁ mode (C–H, C–D stretching vibration) of the two isotopomers are reported as a function of the viscosity/temperature ratio. We clearly observe a linear plot in the case of CH₃CN; for CD₃CN the linearity is achieved only above 1.1 × 10⁻³ cP K⁻¹ of the ratio η/T. In evaluating τ_{or}^{IR} we have assumed that the total width of the band is the sum of vibrational and rotational contributions, and that the vibrational contribution to the ν₁ band width is the same as that estimated from the Raman isotropic profile: (Δν₁)_{vib} = 3.9 cm⁻¹, in the whole range of explored temperature [10, 11].

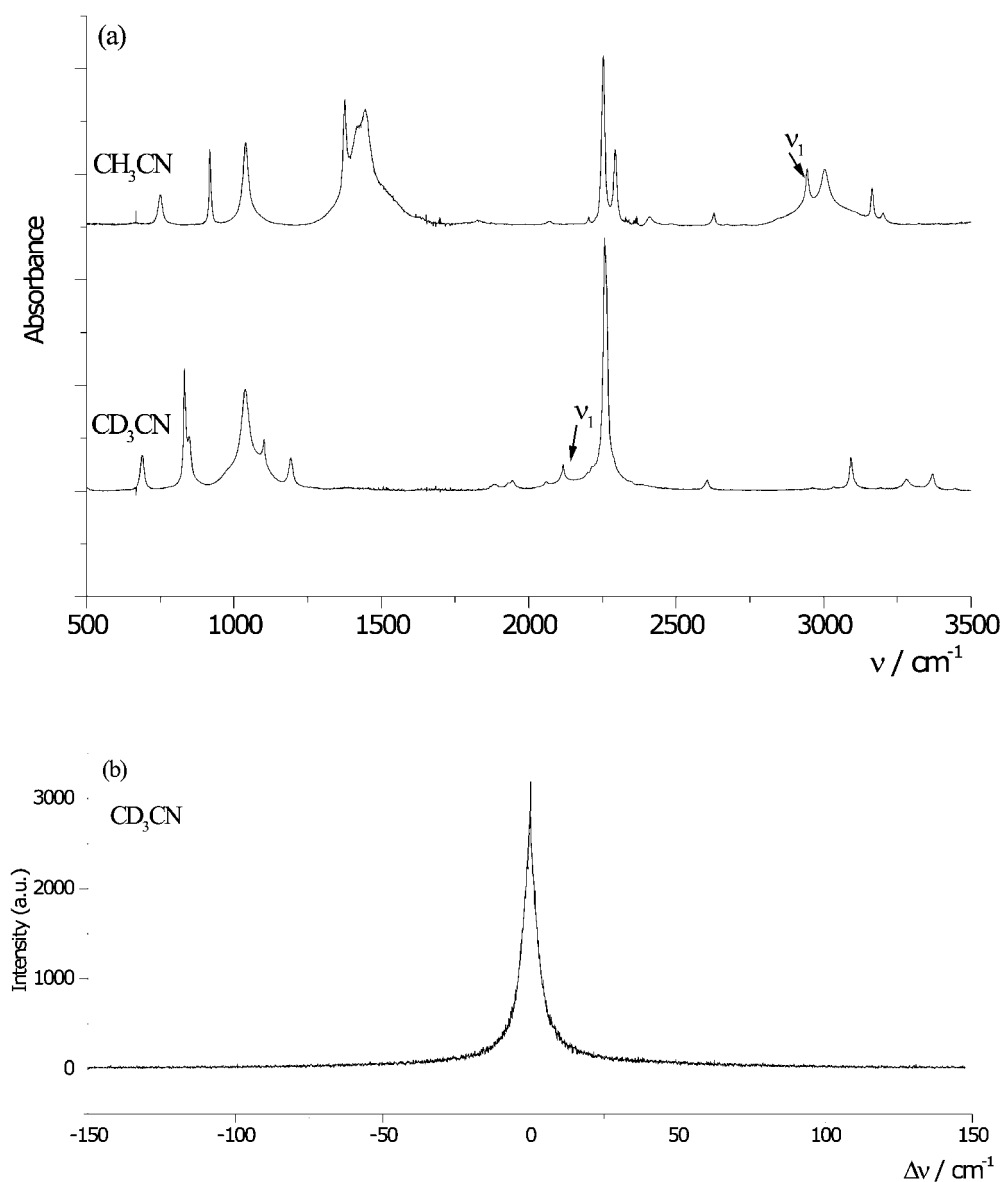


Figure 1. FTIR (a) and DR (b) spectra of acetonitrile at room temperature.

The connection between reorientational relaxation time and viscosity is usually expressed by the Stokes–Einstein–Debye equation (SED):

$$\tau_{or} = C\eta/T + \tau_0 \quad (2)$$

where η is the viscosity, T the absolute temperature and C a coefficient equal to the hydrodynamic volume V_h divided by the Planck constant. τ_0 is the value of τ_{or} extrapolated to zero viscosity.

Looking at our data, one can observe that there is a linear dependence of τ_{or}^{IR} for both liquids when T goes from 5 to 35 °C, with the hydrodynamic volume being about

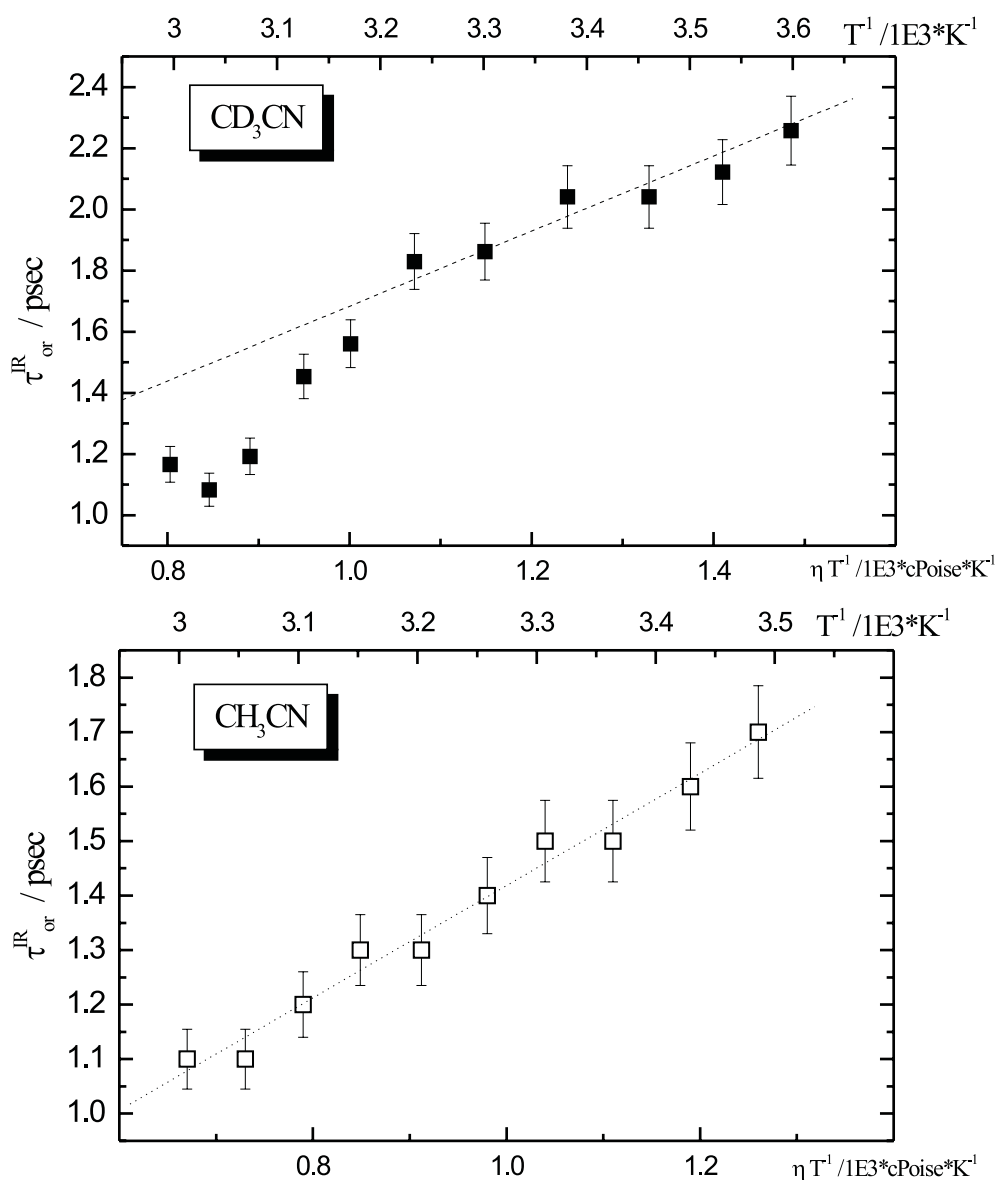


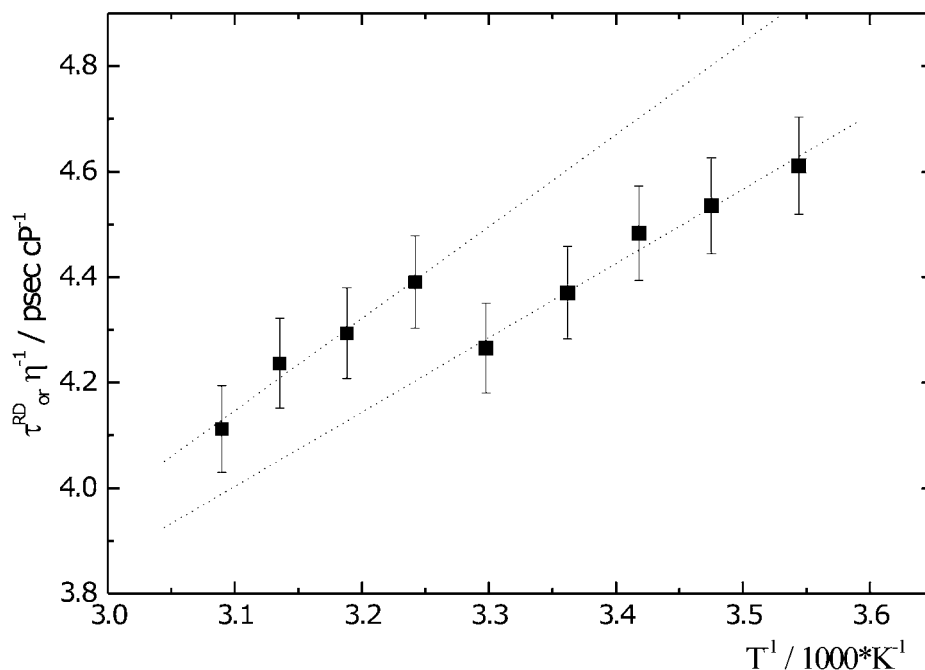
Figure 2. Reorientational relaxation times of CH₃CN and CD₃CN from ν_1 bandwidth of IR spectra. The lines are the linear regressions of SED plots for CD₃CN and CH₃CN data in the ranges of temperature reported in table 1.

20% higher in the heavy species (see table 1). Even though the physical meaning of 'hydrodynamic volume' is yet not well defined, the connection between this parameter and the strength of intermolecular forces is certain [12]. For this reason, the results of the SED equation are in perfect agreement with the sound velocity behaviour. In figure 6 of [7], the sound velocity values of the two isotopomers are reported as a function of temperature. This figure clearly shows that the decrease of sound velocity due to the substitution of hydrogen with deuterium is far greater than the difference in the mass density (5–7%)

Table 1. Parameters of SED equation for ν_1 band of CH₃CN and CD₃CN^a.

	τ_0^{IR} (ps)	C (ps K cP ⁻¹)	Temperature range (°C)
CH ₃ CN	0.388	1030	5–60
CD ₃ CN	0.436	1227	5–35

^a For the deuterated molecule the SED plot cannot be performed in the whole range of temperature (see figure 2), thus the parameters are obtained for η/T values between 1.1×10^{-3} and 1.5×10^{-3} cP K⁻¹.

**Figure 3.** SED plot of reorientational relaxation times obtained from DR spectra of CD₃CN.

[8]; therefore it is reasonable to assume that the isotopic substitution appreciably affects the intermolecular interactions. The same assumption can be derived from the increase of hydrodynamic volume in heavy species. Weaker van der Waals forces and/or dipole interactions can cause a higher free volume for each particle inside the liquid, as well as a higher compressibility factor (lower sound velocity) of the liquid itself in comparison with the CH₃CN isotopomer.

As can be seen in figure 2, for the heavy species the situation changes above 35–40 °C ($\eta/T = 1.1 \times 10^{-3}$ cP K⁻¹). In fact, the relaxation process described with the Brillouin experiment [8, 9] is also evident by the S-shaped curve of acetonitrile-d₃ τ_{or}^{IR} data.

The τ_{or} values evaluated from DR spectra of the deuterated species (τ_{or}^{DR}) are reported in figure 3 as τ_{or}^{DR}/η against $1/T$. This plot is different from that of figure 2 only because this representation gives a more immediate description for the behaviour of the relevant parameters of heavy acetonitrile as a function of temperature.

Applying the equation of the SED theory to this parameter, we have found that for CD₃CN there are two distinct hydrodynamic regimes, one below 35 °C, giving a value of 15.27 \AA^3 , and

one above 35 °C giving a value of 15.85 Å³ for the hydrodynamic volume (see data in table 2 showing a 4% increase).

The increase of the slope at higher temperatures, shown in figures 2 and 3, being connected to the V_h values, can be related to the increase of compressibility, due to a less rigid packing of CD₃CN molecules, because of the vanishing of dipole–dipole oriented interaction.

4. Discussion

Dynamic isotope effects have been reported for several isotopomer couples in molecular liquids [13–18]. Substantially the isotopic effect consists in the effect produced on the transport properties of a fluid by the change of the molecular mass and is quantitatively expressed by the so called ‘square-root mass law’ [15], as follows:

$$D_1/D_2 = \eta_2/\eta_1 = (m_2/m_1)^{1/2}. \quad (3)$$

Here indices 1 and 2 refer to the components of the isotopomer couple.

To date, the experiments on this effect have been directed to measurements of self-diffusion coefficient (D), shear viscosity coefficient (η) and rotational correlation times derived by NMR experiments [15–17].

Failures in the application of equation (3) have been attributed to slightly different relaxation dynamics occurring in the two isotopomers considered, i.e. to a different magnitude of the energy coupling between translational and rotational molecular motions [17]. In such cases, in order to accord the experimental results with the empirical mass law, it has been proposed to use the ratio of momenta of inertia in place of the mass ratio in equation (3) [16].

Previous RBS studies from this laboratory [8,9] have shown that in the range of temperature between 5 and 60 °C the viscosity ratio for the CH₃CN/CD₃CN couple is different from the $(m_2/m_1)^{1/2}$ value. Furthermore, this ratio is not constant with the temperature variation, so that it is reasonable to assume that some differences in the energy coupling between translational and rotational degrees of freedom are operative in this isotopomer couple.

The present FTIR and DR experiments, together with the previous RBS data [8,9], put therefore in evidence the same experimental picture. Even though the short-range order relaxation concerns only the dipole–dipole interactions, the disruption of local structures enhances the compressibility of the fluid and reduces the local viscosity so much as to speed up the reorientational dynamics. The effect is produced not only on the relaxation time of a single molecule (FTIR data), but also on pair and collective dynamics, probed by DR and RBS experiments.

As in translational diffusion experiments, the interpretation of the reorientational relaxation by the SED equation suggests that the hydrodynamic limit is applicable, but with the occurrence of two distinct hydrodynamic regimes within the 5–60 °C temperature range. Unfortunately, the limitations of the hydrodynamic theory become evident when we try to compare the hydrodynamic volume values, obtained from the C slope, with molecular volumes, regardless of the method used to estimate their values [19].

We think that a further development for interpreting the behaviour of the rotational relaxation time in CD₃CN can be found in the free-volume theory [20], even if this involves one of the few attempts to correlate τ_{or} to free-volume data [21]. Free-volume theory is usually referred to supercooled liquids; nevertheless, our attempt of interpreting also in this temperature range the behaviour of reorientational relaxation times with this model only has the purpose of focusing our attention on the dependence of dynamical properties of the liquid

Table 2. Comparison between experimental and theoretical values of molecular volume in CD₃CN. V^{tumb} and V^{spin} refer to the theoretical values for the tumbling and spinning rotation respectively of the molecular ellipsoid, and are independent of temperature.

T (K)	V^a (Å ³)	V_f^b (Å ³)	V_0^b (Å ³)	V_0^{SED} (Å ³)	V^{spin} (Å ³)	V^{tumb} (Å ³)
283.65	85.91	22.36	63.54	15.27		
287.64	86.62	22.87	63.74	15.27		
291.64	87.26	23.39	63.86	15.27		
297.75	87.95	24.06	63.88	15.27		
302.74	88.69	24.83	63.86	15.27	40.80	71.00
307.64	89.36	25.19	64.16	15.85		
314.15	90.04	25.89	64.14	15.85		
317.34	90.77	26.52	64.24	15.85		
325.35	91.42	27.27	64.15	15.85		

^a From density measurements.

^b By fitting of equation (4).

on the short-range local structure. In this respect, the description of this simple polar liquid is completely new and gives a new insight on the dynamics of the liquid acetonitrile, both in its protonated [22] and deuterated form. In particular it is possible to observe that even strong dipole–dipole interaction can diminish the simple, molecular behaviour in favour of an associative, fragile character of the liquid.

In the framework of Flory's theory [23], we may consider that the free-volume redistribution associated with the relaxation of the local structure has an activation energy which is of the same order of magnitude of the rotational diffusion in the hydrodynamic regime. This fact is due to the strong connection existing between the translational and reorientational relaxation processes on one hand and the shear viscosity on the other.

Assuming a single relaxation process, the Arrhenius-like behaviour of τ_{or}^{RD} can be expressed by the Doolittle equation [20]:

$$\tau_{or}^{RD} = \tau'_{or} \exp(E_a/kT) = \tau'_{or} \exp(V/V_f) \quad (4)$$

where V_f is the free volume equal to $V - V_0$, V the average volume per molecule and V_0 the molecular volume for close-packed rigid spheroids, i.e. the van der Waals volume. The values of V used are those derived from the number density measurements [8].

In the case of CD₃CN, the V_f and V_0 values obtained by fitting τ_{or}^{RD} experimental data within equation (4) are listed in table 2. A comparison can be made between the V_h values obtained by applying the SED equation (V_0^{SED}), and those calculated for a prolate spheroid with the shorter a (1.775 Å) and the longer b (3.090 Å) semi-axes.

It can be seen that the numerical evaluation of molecular volume is much better for applying free-volume theory (equation (4)) than SED theory (equation (2)). V_h values are useful in the description of the different dynamical properties of heavy and light species, and of the different behaviour of CD₃CN below and above the critical temperature value. Unfortunately, the agreement between this parameter and any value of geometrical molecular volume (V^{spin} or V^{tumb} in table 2) is very poor. Furthermore, the V_h value is more comparable with that of V_f , but we believe that this is only accidental, and has no physical meaning.

It is possible to recognize that the main effect for a structural-like rearrangement that tends toward a higher compressibility is on the free volume. The increase of this parameter is about 20% ranging from 5 to 60 °C; in contrast, the molecular volume V_0 changes within the experimental error. This confirms the assumption that there is a change in the local structure

of the liquid CD₃CN that does not produce a dramatic change in the physical properties of the single molecule (i.e. V_0), but, in contrast, greatly affects the dynamics of the liquid.

5. Conclusions

Deuterated acetonitrile offers an interesting example of the dynamic isotope effect. For many years, phenomenological theories, especially on viscosity and volume, have been developed to interpret the temperature dependence of transport properties in dense liquids. The Stokes–Einstein–Debye equation is usually successful in describing the properties of liquids in conditions of low viscosity ($\eta \approx 10^{-2}$ P). However, it has severe limits because the hydrodynamic volume values are strongly dependent on the technique used to derive reorientational relaxation times. Moreover, it correlates a macroscopic quantity, such as the viscosity, with a microscopic molecular property as τ_{or} .

When fluidity decreases and viscosity increases to the limiting value of the glass state ($\eta \approx 10^4$ – 10^{15} P), the free-volume model is better used to calculate all the thermodynamic quantities of interest. In the liquid–glass transition, one can assume that the same microscopic process underlies rotational diffusion, viscosity and structural relaxation; this means that volume and viscosity relaxations have the same activation energy. Present data on CD₃CN largely confirm that the translational motions are strongly coupled to both vibrational and rotational degrees of freedom. For this reason, we believe that the free-volume theory is particularly suitable for interpreting the dynamics of this short-range ordered molecular liquid.

The basic idea of this theory does not give a detailed description of the motion of each particle, but rather it emphasizes the importance of entropy and its redistribution from glasslike to liquid-like domain. The free-volume model is commonly applied in the computation of translational diffusion coefficient near the liquid–glass transition. Nevertheless, we think that in the case of heavy acetonitrile the free-volume theory is more appropriate than the SED one for modelling the reorientational dynamics. This occurs because of the existence of a local-structure relaxation process at a temperature that is in the range explored in our experiment.

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