al Physics 70 (1982) 77–81
-Holland Publishing Company

EXPERIMENTAL ANGULAR VELOCITY CORRELATION FUNCTIONS FOR $CHCl_3$

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Received 7 December 1981; in final form 13 April 1982

The angular velocity correlation function (AVCF) for liquid $CHCl_3$ has been obtained experimentally from the far-infrared absorption and the Raman band shape. The experimental AVCFs are compared with computer simulation results using a 5 X 5 Lennard-Jones atom–atom potential with partial charges situated at the atomic sites.

1. Introduction

Angular velocity fluctuations play a very important role in molecular reorientation processes in dense media. Quite a number of authors have treated theoretically the problem of the relationship between the angular velocity correlation function (AVCF) and intermolecular torque [1–4]. Several authors have shown that the AVCF can, under some conditions, be regarded as the memory function of the angular position correlation function (APCF) [5,6]. A knowledge of the AVCF is therefore essential for a thorough understanding of the microdynamics of liquids.

Most of the investigators interested in the problem accept the fact that the character of the AVCF is non-exponential, often having negative overshoots which arise from a reversal of momentum caused by strong molecular interaction. But up to now both the theoretical and the experimental determination of the exact shape of the AVCF has not been satisfactory.

Experimental studies of the AVCF are rather rare [7–14]. The problem is that many experiments are sensitive to orientational correlation, but only few may reflect the angular velocity correlations because the time scale associated with the latter is shorter. Experiments that may be used for determining the AVCF include infrared absorption spectroscopy, depolarised vibrational Raman scattering, pure rotational Raman scattering and thermal neutron scattering.

The experimental method which gives information about short-time orientational fluctuation of the molecules is far-infrared absorption (Poley absorption). The profile of this absorption reflects not only the orientational motion of a single molecule but also the intermolecular correlation of reorientations. Unfortunately it is very difficult to separate those two pieces of information. There is also the problem of the collision-induced absorption which cannot be determined with acceptable approximation. So in the absence of a molecular dynamics simulation the results one obtains from the shape of the Poley absorption must be analysed with caution.

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The same is true about the AVCF obtained from Raman band shapes. In this case the intermolecular correlations play a negligible role in the band shape but there is a problem with the separation of rotational relaxation from vibrational relaxation. Another difficulty is connected with the fact that the information about the short-time behaviour of reorienting molecule is hidden in the far wings of the vibrational band. One has to be able to detect these wings with ultra-high precision.

In this paper we report some attempts at determining the AVCF from far-infrared absorption and Raman band shape measurements on $CHCl_3$. The experimental results are compared with the computer simulation data recently obtained for $CHCl_3$.

2. Theoretical background

In this section we recall briefly the method of obtaining the AVCF from the experimental data. In a series of papers Kluk et al. [12–14] showed in detail how to extract the AVCF from the APCF using a generalisation of cumulant expansions.

All their results can be summarised in the formulae:

$$G_{\omega_\perp}(t) = \frac{\langle \omega_\perp(t)\,\omega_\perp(0)\rangle}{\langle \omega_\perp(0)\,\omega_\perp(0)\rangle} = -\frac{2}{\langle \omega_\perp^2\rangle\, l(l+1)} \times \left[\frac{1}{G_{\rm rot}}\frac{\mathrm{d}^2 G_{\rm rot}}{\mathrm{d}t^2} - \frac{1}{(G_{\rm rot})^2}\left(\frac{\mathrm{d}G_{\rm rot}}{\mathrm{d}t}\right)^2\right] . \qquad (1)$$

$\omega_\perp$ is the component of the angular velocity perpendicular to the dipole moment (fig. 2), $G_{\rm rot}$ is the rotational function, $l = 1$ for far-infrared, $l = 2$ for Raman scattering.

For far-infrared absorption [15]:

$$G_{\rm rot}(t) = \frac{1}{\pi a}\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t}\,\frac{\alpha(\omega)}{\omega^2}\,\mathrm{d}\omega , \qquad (2)$$

$\alpha(\omega)$ is the absorption spectrum, $\alpha = 4\pi\mu^2/3ckT$, μ is the dipole moment, c the speed of light, k the Boltzmann constant.

For Raman scattering [13]:

$$G_{\rm rot}(t) = \int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t} I_{\rm rot}\,\mathrm{d}\omega \Big/ \int_{-\infty}^{\infty} I_{\rm rot}\,\mathrm{d}\omega , \qquad (3)$$

where $I_{\rm rot}$ is obtained using the Bartoli–Litovitz separation method [16]:

$$I_{\rm vib}(\omega) = I_{\rm VV}(\omega) - \tfrac{4}{3} I_{\rm VH}(\omega) ,$$

$$I_{\rm VH}(\omega) = (I_{\rm rot} * I_{\rm vib})(\omega) .$$

$I_{\rm VV}$ and $I_{\rm VH}$ are the scattered intensities with the polarisation parallel and perpendicular to the incoming beam polarisation respectively.

3. Experimental

The shape of the $CHCl_3$ Poley absorption band was obtained using three kinds of instrumentation:

(1) A fast scanning Fourier-transform spectrometer DIGILAB FTS-14. The region covered was 15–120 cm^{-1}. The liquid was placed between quartz windows prepared in a special way to avoid spurious interference. The TPX and polyethylene windows are not suitable for chloroform as they strongly absorb this substance. The resolution was 2 cm^{-1} and the path length 0.5 mm.

(2) A series of carcinotrons which produce monochromatic waves. The region covered was 2–15 cm^{-1}.

(3) Klystrons which produce frequencies below 1 cm^{-1}.

The Raman spectra were recorded on a Cary-82 spectrometer. An Ar^+ ion laser operating at 514.5 nm and at powers of 100 mW was the excitation source. The slid width was 1 cm^{-1}.

The chloroform used was a Merck product "for spectroscopy". Small amounts of ethyl alcohol (present as a stabiliser) were removed by distillation over molecular sieves.

4. Results

The profiles of the absorption band for three temperatures are shown in fig. 1. The data for room temperature are in good agreement with the profiles of Chantry [17] but they differ from the results of Goulon et al. [18] and Rosenthal et al. [19].

We have checked the microscopic sum role for this band [20]:

$$\int_0^{\infty} \alpha(\bar{\nu})\,\mathrm{d}\bar{\nu} = \frac{\mu^2 (n^2+2)^2 N}{6cl\xi_0 \cdot 9nV} ,$$

$\xi_0 = 8.85 \times 10^{-12}$ F m, n is the refractive index ($n =$

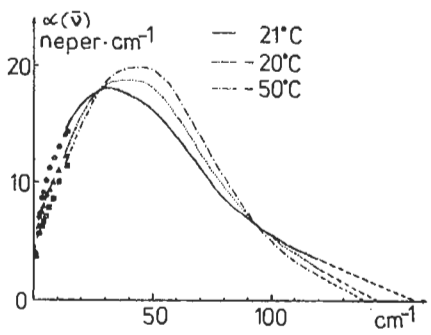

Fig. 1. Far-infrared absorption band of $CHCl_3$ at three temperatures. ○, △ and □ are the carcinotron data at 21, −20 and −50°C, respectively.

1.45), N the number of molecules in the volume V, I the moment of inertia (for $CHCl_3$, $I = 254 \times 10^{-40}$ g cm^2).

At room temperature the integral of the experimental band is 0.142 in SI units. The value of the rhs of eq. (5) is 0.096. So the theoretical value is ≈70% of the experimental one. If the shape of molecule is taken into consideration the coefficient $[(n^2+2)/3]^2$ in (5) should be replaced by $[1 + D(n^2 - 1)]^2$, where D stands for the depolarisation factor which for $CHCl_3$ is equal to 0.46. In such a case the rhs of (5) is 0.121 which is 85% of experimental value. It is also worth mentioning that the integral of the experimental band for pure chloroform agrees very well with that obtained for 10% v/v solution in decalin (0.0147 SI units) [21]. In calculating the AVCF from the absorption profile we have neglected induced absorption.

The Raman C–H stretch band was measured at two polarisations. We checked the value of the rotational second moment

$$M_{\mathrm{rot}}(2) = \int \omega^2 I_{\mathrm{rot}}(\omega)\,\mathrm{d}\omega / \int I_{\mathrm{rot}}(\omega)\,\mathrm{d}\omega \qquad (6)$$

to be 12% higher than the theoretical value ($M_{\mathrm{rot}}^{\mathrm{exp}}(2) = 308$ cm^{-2}, $M_{\mathrm{rot}}^{\mathrm{theor}}(2) = 274$ cm^{-2}) which may result from the scattering by induced collisions, mentioned in earlier work [22].

The AVCFs obtained from FIR spectra are shown in fig. 2. The AVCF from the Raman band is shown in fig. 3. The Raman AVCF oscillates more than that from the FIR but the time at which the AVCF starts to be negative is the same for both, i.e. 0.23 ps. In the case of the FIR there is clearly no temperature dependence of that time (fig. 2). This behaviour is the same as that

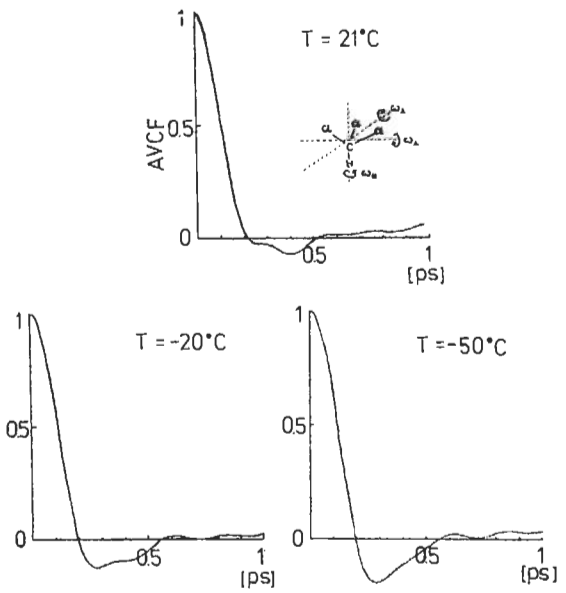

Fig. 2. Angular velocity correlation functions of $CHCl_3$ obtained from FIR absorption spectra.

found for C_6H_6 in experimental work [9] and for HCl in computer simulations [23]. This zero-crossing time is a measure of the "time between collisions" τ_{BC}. Its value is higher than that obtained by Moradi-Araghi and Schwartz [24]. They obtained a value of 0.13 ps for τ_{BC}, which in their paper is a parameter affecting the efficiency of relaxation by vibrational dephasing. They used Rotschild's [25] general expression for the isotropic correlation function with τ_{BC} as a parameter.

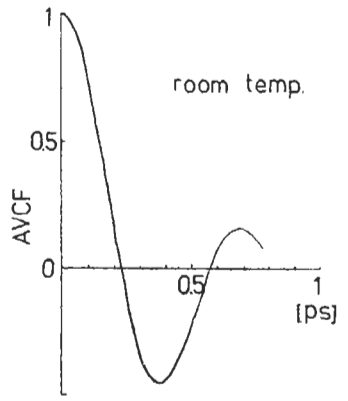

Fig. 3. Angular velocity correlation function of $CHCl_3$ obtained from Raman band shape.

5. Computer simulation of the molecular dynamics in $CHCl_3$

The details of this extensive computer simulation (at 293 K, 1 bar) will be published elsewhere [26]. In this paper we will briefly describe the algorithm and computational procedures and illustrate the angular velocity autocorrelation function produced by the simulation.

The algorithm was developed from one written by Singer et al. and made available to us by SERC CCP5. The original was modified by Ferrario and Evans [26] to include charge–charge interaction and a force cut-off criterion based on the intermolecular centre-of-mass distance. The translational equations of motion are now solved with a third-order predictor algorithm and the rotational ones using as coordinates the angular momentum and the three unit vectors of the principal moment of inertia frame.

In the absence of reliable experimental (e.g. dielectric virial) information on the pair potential of $CHCl_3$ we built up a model potential energy of 5 × 5 atom–atom Lennard-Jones type with partial charges at the atomic sites:

for H–H $\sigma = 2.75$ Å, $\epsilon/k = 13.4$ K;
For Cl–Cl $\sigma = 3.50$ Å, $\epsilon/k = 175.0$ K;
for C–C $\sigma = 3.20$ Å, $\epsilon/k = 51.0$ K,

with cross terms evaluated with the usual empirical formulae

$$(\epsilon/k)_{AB} = [(\epsilon/k)_A(\epsilon/k)_B]^{1/2} ,$$

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_A + \sigma_B) .$$

The σ parameter for Cl–Cl interactions was optimised to 3.50 Å. This is different from the equivalent parameter in a parallel CH_2Cl_2 simulation [26], 3.35 Å. Otherwise the same set of Lennard-Jones parameters was used in both simulations. The value of σ influences the intersection point of the AVCF with the time axis. For $\sigma = 3.15$ Å the AVCF starts to be negative at 0.27 ps.

These Lennard-Jones parameters are based *almost exactly* on values available in the literature for other, simpler, liquids such as Cl_2. The fractional charges were taken directly from a simple calculation by del Re [27], aimed at reproducing the experimental dipole moment.

With these parameters, satisfactory thermodynamic characteristics were obtained with 108 molecules after ≈2500 time steps of 0.005 ps each. These initial steps were rejected and the next 5000 or so used to build up a wide variety of dynamical and static (equilibrium) information. Input state point was 293 K, 1 bar. Some of the major conclusions of this simulation are:

(i) the rotational diffusion of $CHCl_3$ (in contrast to CH_2Cl_2 [26]) is very nearly isotropic;

(ii) the Kirkwood factor is nearly unity;

(iii) the liquid is *nevertheless* highly structured (from the atom–atom pair distribution functions);

(iv) using small sub-spheres the autocorrelation functions and cross-correlation functions of orientation and rotational velocity are almost identical;

(v) the transient statistics of linear and angular momentum are non-gaussian;

(vi) there are subtle effects of rotation/translation coupling which defy conventional analytical analysis, and which show up in the mixed autocorrelation functions

$$\langle J^2(0)\, v^2(t)\rangle / \langle J^2(0)\rangle \langle v^2(0)\rangle ,$$

where v is the centre-of-mass linear velocity.

The AVCF obtained from computer simulation is drawn in fig. 4 and it compares well with the experimental AVCFs of the far-infrared analysis, but not so well with the AVCF from the Raman analysis. This confirms the validity of both the FIR [28] and simulation probes of liquid-state molecular dynamics as used in this paper. The situation is clearly poised for an effort at quantifying the pair interaction potential by accurate measurements of B_ϵ, the second dielectric

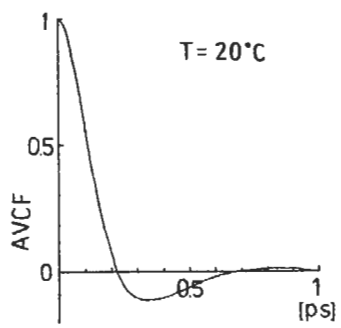

Fig. 4. Angular velocity correlation function of $CHCl_3$ obtained by computer simulation.

virial coefficient [29]. An improvement of our knowledge in this area is fundamental to further progress because algorithms such as TETRA now allow us to go directly from a given intermolecular potential to a wide variety of spectra.

6. Discussion

As can be seen from figs. 2, 3 and 4, the shape of the AVCF in the time region 0–30 ps seems to be well determined. The results of two experiments and an independent computer simulation agree within this time regime. For longer times the agreement starts to get worse.

We have stressed at the beginning of this paper that the far-infrared absorption profile contains "too much" information for it all to be properly assimilated. We have to neglect some processes when explaining the data using correlation function language and this could lead to errors in the shape of the correlation functions we obtain. However, it does seem that we have for the first time the important confirmation that induced absorption in $CHCl_3$ is *not* an important source of uncertainty in the pure liquid at 293 K, 1 bar. This follows from the fact that the computer simulation *does not deal in polarisability*, and cannot describe the process of collision induction. Despite this, the AVCF obtained in two totally independent ways, each with its assumptions, agree in the important respects of axis cut-time, depth of overshoot and long-tail characteristics.

In the Raman technique there is always a doubt whether we can separate vibrational and rotational relaxation, and this doubt persists.

Acknowledgement

The authors would like to thank Dr. K. Pasterny and Dr. T. Żerda for their computer programs to process the FIR and Raman data. We would like to thank Professor W. Kęcki for enabling us to use the Cary 82 Raman spectrometer, Dr. J.M. Janik for stimulating discussions concerning the Raman measurements, and Messrs. Sokołowski and Sarga for the technical help at these measurements. M.W.E. wishes to thank SERC for support and Professor K. Singer and Dr. M. Ferrario for advice and help.

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