

Depolarized Rayleigh Light Scattering and Reorientation of Molecular Liquids under High Pressure

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Abstract

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Measurements of rotational relaxation times of pure benzene, toluene, chloroform and methyl iodide have been made by depolarized Rayleigh light scattering at pressures up to 205 MPa using interferometry. A plot of rotational relaxation times for each liquid versus viscosity at constant temperature was found to fit a straight line with non-zero intercept. The results are compared to depolarized Rayleigh data for solutions, high pressure NMR and Raman data, and high pressure depolarized "Rayleigh wing" measurements. The effect of pressure on pair correlations is discussed.

Introduction

Several experimental techniques are currently used to study rotational motion in liquids composed of small molecules. Nuclear magnetic resonance spin-lattice relaxation measurements yield single particle rotational relaxation times [1]. Single particle relaxation times can also be obtained from Raman scattering experiments under conditions where vibrational and rotational motions decouple [2, 3]. Depolarized Rayleigh scattering spectra, however, yield information concerning both single particle rotations and pair correlation effects [4, 5].

Recent depolarized Rayleigh scattering experiments have shown that for some molecules (e.g. benzene and toluene) the pair correlation effects are small [6], while for other molecules (e.g. chloroform and nitrobenzene) the rotational relaxation time varies with solute concentration, suggesting that pair correlations are significant [7]. For molecules showing small or negligible pair correlations, the depolarized Rayleigh rotational relaxation time varies linearly with viscosity at constant temperature, and is independent of solute concentration. When pair correlations do affect the depolarized Rayleigh results, the relaxation times still vary linearly with viscosity at constant concentration and temperature. One of the aims of this study is to determine whether the linear relationship between relaxation times and viscosity still persists at high pressures. By studying pure liquids at different pressures, the viscosity can be varied over a wide range while keeping the chemical composition of the sample constant.

In this paper we present results of depolarized Rayleigh light scattering experiments at high pressures on four molecular liquids: benzene, toluene, chloroform, and methyl iodide. To our knowledge this is the first high pressure study of depolarized Rayleigh light scattering for a series of liquids performed using interferometry. The experiments were run at pressures from 0.1 to 205

MPa. The light scattering rotational relaxation times for benzene and toluene obtained at high pressures are compared to experiments performed at atmospheric pressure [6, 7]. High pressure Raman and/or NMR data are available for chloroform [8] and methyl iodide [9]. By comparing the light scattering results to these data, the effect of pair correlations at high pressure can be studied. Alternatively, the approximations used to obtain the Raman and NMR relaxation times from the experimental results can be examined. High pressure depolarized Rayleigh relaxation times measured using a grating spectrometer have recently been reported [10]. A comparison of these results to those obtained by interferometry and to Raman scattering affords a test of the method used to obtain light scattering rotational relaxation times from the rather complex "Rayleigh wing" spectra.

Theory

Here we will present only those aspects of light scattering theory which are pertinent to our experiments. The subject has been treated by many authors and we follow the formalism and nomenclature of Pecora [4].

Light scattering in any fluid system results from the emission of radiation by an oscillating electric dipole, μ , which is induced by an incident light wave with displacement vector E_0 at the position of the scatterer according to

$$\mu = \alpha \cdot E_0$$

where α is the polarizability tensor. Any dynamic property of the scatterer which affects the polarizability can be studied, in principle, by light scattering techniques. In particular, it has been shown that depolarized light scattering from anisotropic molecules result, in part, from changes in the polarizability due to molecular rotations. For dilute solutions composed of optically anisotropic solute molecules dissolved in an optically isotropic solvent, the intensity of the depolarized scattered light (incident light vertically polarized, scattered light horizontally polarized) at angular frequency ω is given by

$$I_{VH}(K, \omega) = \left(\frac{A}{2\pi} \right) \left[\frac{1}{3}(n^2 + 2) \right]^2 \int_{-\infty}^{\infty} e^{-i\omega t} S(K, t) dt \quad (1)$$

where A is independent of fluctuations in the medium and n is the solution refractive index. K is the scattering vector, defined as $K = k_i - k_s$ where k_i and k_s are the propagation vectors for the incident and scattered beams, respectively.

$S(K, t)$ can be written in terms of an ensemble average over all N scatterers in the scattering volume as

$$S(K, t) = \left\langle \sum_{i,j=1}^N \alpha_{yz}(\Omega_i(t)) \alpha_{yz}(\Omega_j(0)) \times \exp \left\{ iK \cdot [r_i(t) - r_j(0)] \right\} \right\rangle \quad (2)$$

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$\alpha_{yz}(\Omega_i(t))$ is the yz component of the polarizability of molecule i at time t in the laboratory fixed coordinate system, as defined in ref. [6], and is a function of $\Omega_i(t)$, the orientation angle of molecule i at time t . It is this dependence of polarizability on orientation angle which allows us to study rotational motion using light scattering. The K dependence is coupled to the position of the center of mass of the particle at time $t(r_i(t))$ and at time zero ($r_i(0)$), and thus reflects the translational motion of the molecule. It has been shown that for small molecules, one is essentially working in the $K \rightarrow 0$ limit [6]. We therefore omit the K argument in our discussion.

The double summation in eq. (2) can be expanded and written in terms of ensemble averages for single particles and for pairs of particles as

$$S(t) = N \langle \alpha_{yz}(\Omega_i(t)) \alpha_{yz}(\Omega_i(0)) \rangle + N(N-1) \langle \alpha_{yz}(\Omega_i(t)) \alpha_{yz}(\Omega_j(0)) \rangle \quad (3)$$

Keyes and Kivelson [5] have derived expressions for both the singlet and pair terms for pure liquids using Mori's [11] statistical mechanical theory of fluctuations. They found that for symmetric top molecules

$$\langle \alpha_{yz}(\Omega_i(t)) \alpha_{yz}(\Omega_i(0)) \rangle = \beta^2 \exp(-t/\tau_1) \quad (4)$$

where β , the optical anisotropy of the scattering molecule, is defined by

$$\beta = \alpha_{\parallel} - \alpha_{\perp}$$

with $\alpha_{\parallel}$ and $\alpha_{\perp}$ the molecule-fixed components of the polarizability parallel and perpendicular to the molecular axis, respectively. The single particle rotational relaxation time is thus given by τ_1 . The pair correlation term becomes

$$\begin{aligned} \langle \alpha_{yz}(\Omega_i(t)) \alpha_{yz}(\Omega_j(0)) \rangle &= \beta^2 \left\{ \left[\left(\frac{1}{N} \right) + f \right] \right. \\ &\times \exp \left[-\frac{t}{\tau_1} (1 + gN) (1 + fN)^{-1} \right] - \left(\frac{1}{N} \right) \exp \left(-\frac{t}{\tau_1} \right) \left. \right\} \quad (5) \end{aligned}$$

where f and g measure the strength of static and dynamic pair correlations. Eqs. (4) and (5) can be combined to yield the total $S(t)$

$$S(t) = \frac{N\beta^2}{15} (1 + fN) \exp \left[-\left(\frac{1 + gN}{1 + fN} \right) \frac{t}{\tau_1} \right] \quad (6)$$

Thus, the observed light scattering spectrum, $I_{\text{vh}}(\omega)$, will be a single Lorentzian [12] with a half width at half height (HWHH_{LS}) in Hz equal to

$$\text{HWHH}_{\text{LS}} = \frac{1}{2\pi} \left(\frac{1 + gN}{1 + fN} \right) \left(\frac{1}{\tau_1} \right) \quad (7)$$

We can define a τ_{LS} by

$$\tau_{\text{LS}} = \left(\frac{1 + fN}{1 + gN} \right) \tau_1 \quad (8)$$

For dilute solutions or cases where pair correlations are small (i.e. $gN \ll 1$ and $fN \ll 1$), the relaxation time measured by light scattering will equal the single particle relaxation time.

Both Raman light scattering and nuclear magnetic resonance techniques measure the single particle relaxation time directly. In obtaining τ_1 from Raman measurements, one must assume

vibration and rotation are decoupled and also that non-orientational relaxation processes affect the isotropic and anisotropic Raman spectra in the same manner [3]. By comparing rotational relaxation times measured for pure liquids using depolarized Rayleigh light scattering with those measured using Raman and NMR, the effects of pair correlations in the liquid can be studied.

In the rotational diffusion approximation, the single particle relaxation time for rotations perpendicular to the molecular symmetry axis, τ_1 , measured in depolarized Rayleigh, Raman or NMR experiments, is related to the rotational diffusion coefficient of the symmetry axis, θ , by

$$\tau_1 = \frac{1}{6\theta} \quad (9)$$

For spherical hydrodynamic particles in the limit of "stick" boundary conditions, the Stokes-Einstein relation [13] predicts that the rotational diffusion coefficient is related to the viscosity of the medium, η , and the temperature, T , by

$$\theta = kT / (8\pi\eta a^3) \quad (10)$$

where a is the particle radius. Perrin [14] has derived expressions for ellipsoidal particles and recently Hu and Zwanzig [15] have extended the theory to "slip" boundary conditions. Although the rotational diffusion model does not seem to apply rigorously to liquids composed of small molecules, the linear dependence of rotational relaxation time on η/T seems quite general [3, 6, 7]. By plotting τ versus η/T we can compare relaxation times for a given molecule measured under different conditions and by different techniques.

Experimental

All depolarized Rayleigh scattering spectra were taken using the apparatus shown in block form in Fig. 1. The apparatus is similar to that used previously in this laboratory [16]. The incident light at 514.5 nm was obtained from a Coherent Radiation Model 5 argon ion laser. The experiments were run using between 100 and 250 mW of power. Lens A focused the laser beam in the center of the high pressure scattering cell. A $\lambda/2$ plate and Glan-Thompson prism were used together to adjust the polarization of the incident beam to be either perpendicular to or in the scattering plane. The light scattered at 90° passed through a polarizer which was coupled to a $\lambda/4$ plate permitting polarization analysis of the scattered light and insuring that the light entering the interferometer and photomultiplier tube was circularly polarized. The polarizers were carefully adjusted by measuring the light scattered from CCl_4 . When the incident light polarization is horizontal, the intensity of light scattered from CCl_4 is a minimum. The $\lambda/2$ plate was adjusted such that this was the case. The polarizers could then be adjusted by insuring that the intensity was a minimum when they were crossed with the $\lambda/2$ plate. The scattered light was collimated by lens B through the Tropel piezoelectrically scanned Fabry-Perot interferometer. The free spectral range (FSR) of the interferometer was determined by measuring the plate separation using a specially constructed gauge. This value was checked by observing the doublet spectrum from a sodium lamp. For all measurements reported here the FSR was 241 ± 1 GHz corresponding to a plate separation of 0.62 mm. The finesse was typically 60 and was frequently checked by measuring the polarized scattering from a Ludox solution. The frequency analyzed light was focused by lens C on a pinhole.