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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

$\mu = \mathbf{\alpha} \cdot E_{\mathbf{0}}$

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

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

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

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 $\alpha_{ys}(\Omega_i(t))$ 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

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

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

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

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

with α_{\parallel} and α_{\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

$$\langle \alpha_{yz}(\Omega_{i}(t)) \alpha_{yz}(\Omega_{j}(0)) \rangle = \beta^{2} \left\{ \left[\left(\frac{1}{N}\right) + f \right] \times \exp\left[-\frac{t}{\tau_{1}} (1 + gn) (1 + fN)^{-1} \right] - \left(\frac{1}{N}\right) \exp\left(-\frac{t}{\tau_{1}} \right) \right\}$$
(5)

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)

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

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

$$HWHH_{\rm LS} = \frac{1}{2\pi} \left(\frac{1+gN}{1+fN} \right) \left(\frac{1}{\tau_1} \right) \tag{7}$$

We can define a $\tau_{\rm LS}$ by

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

For dilute solutions or cases where pair correlations are small (i.e. $gN \le 1$ and $fN \le 1$), 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

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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

$$r_1 = \frac{1}{6\theta} \tag{9}$$

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

$$\theta = k T / (8\pi \eta a^3) \tag{10}$$

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 CCl₄. When the incident light polarization is horizontal, the intensity of light scattered from CCl₄ 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.



Fig. 1. Light scattering apparatus: (1) argon ion laser; (2) lens A; (3) $\lambda/2$ plate; (4) Glan–Thompson prism; (5) high pressure optical cell; (6) light trap; (7) polarizer with $\lambda/4$ plate; (8) lens B; (9) Fabry-Perot interferometer; (10) lens C; (11) pinhole; (12) photomultiplier tube; (13) pulse amplifier and electronic counter; (14) digital recorder.

The light intensity was measured with an RCA photomultiplier tube whose signal was amplified by a pulse amplifier built in this laboratory. The resulting signal was put into a digital counter and digital recorder. The scan time and digital counter were adjusted such that the intensity of the scattered light was measured at ~ 1 GHz intervals.

The high pressure optical cell has been described in detail elsewhere [17]. For these measurements, fused quartz cell windows, 10 mm in length, were used for the incident and scattered beams. A standard sapphire window was used for the transmitted beam. Quartz is not birefringent and thus the polarization of the incident and scattered beams was not affected by the windows. The cell containing the liquid sample is shown in Fig. 2. It is constructed of quartz and is fitted with flat entrance, exit, and scattering windows. A special plug for the cell was fabricated of black teflon. This plug had a conical inner bore to reduce the backscattered light and was fitted with Viton o-rings. The entire cell, except for the windows, was painted black.

Great care was taken to insure that the samples were as dust free as possible. Spectroquality or reagent grade liquids were filtered through 0.22 μ m Millipore filters. The cell was rinsed with ~50 volumes of the dust free liquid. The toluene and benzene spectra showed no evidence of spurious scattering. For chloroform and methyl iodide, an extremely sharp peak due to scattering from dust was superimposed on the broad depolarized Rayleigh spectrum for about one third of the spectra obtained with a given cell filling. These spectra were easily corrected using a fitting technique (see Results section). For toluene, benzene and methyl iodide, spectra were taken at 298 ±1 K and for chloroform at 299 ±1 K. Viscosities for methyl iodide were extrapolated from data measured by Campbell et al. [8]. Viscosities for the other liquids were obtained from Bridgman's data [18].



Table I. Rotational relaxation times and viscosities

	Pressure/ MPa	HWHH _{LS} / GHz	$ au_{ m LS}/ m ps$	η/mPa s
Benzene	0.1	56	2.85	0.60
	26	46	3.45	0.74
	51	42	3.8	0.91
Toluene	0.1	27	5.6	0.55
	51	22.5	6.8	0.78
	103	20	8.0	1.05
	154	15.5	10.3	1.36
	205	12.7	12.5	1.77
Chloroform	0.1	49	3.2	0.53
	51	41	3.9	0.69
	103	37	4.3	0.88
	154	33	4.85	1.07
	205	29	5.55	1.31
Methyl iodide	0.1	60	2.7	0.47
	51	53.5	3.0	0.57
	103	47.5	3.35	0.69
	150	43	3.7	0.84
	205	37	4.3	0.98

Results

Depolarized Rayleigh spectra were obtained for toluene, chloroform and methyl iodide at pressures up to 205 MPa. Spectra for benzene were recorded at pressures up to 51 MPa (benzene freezes at 60 MPa at room temperature). The data are presented in Table I. Linewidths were reproducible to better than $\pm 7\%$. Typical spectra showing the effect of pressure on the linewidth are shown in Fig. 3. Also shown is a Lorentzian fit to the spectra. The experimental spectrum is a convolution of the true depolarized Rayleigh spectrum with an instrumental spectrum. Alms et al. [6], have shown that when the true spectrum is a Lorentzian and the instrumental shape a Voigt function, it is a simple matter to obtain the true widths from the experimental widths using a table of Voigt functions [19]. For toluene this correction was at most 5% of the experimental width and for the other liquids the correction was less than 1%. Experimental spectra were fitted to a single Lorentzian plus baseline using a non-linear leastsquares fitting program which corrected for the overlap of adjacent orders. For those spectra having a sharp spike at zero frequency due to scattering from dust, data points within ~10 GHz of the maximum were omitted when fitting the spectra to a Lorentzian. Alternatively, the spectra were smoothed by hand. Both techniques gave the same result for the HWHH_{LS}.

Depolarized spectra were recorded in all three polarization configurations: VH, HV and HH. Linewidths for all three configurations were the same within experimental error, as were the intensities of the VH and HV spectra. The values in Table I are averages of from three to six spectra. Values of $\tau_{\rm LS}$ were obtained from the HWHH_{LS} according to $\tau_{\rm LS} = (2\pi \rm HWHH_{LS})^{-1}$. The uncertainty in $\tau_{\rm LS}$ values is ± 0.2 ps.

Plots of $\tau_{\rm LS}$ versus pressure for each liquid are given in Figs. 4–7. All four liquids show a significant increase in $\tau_{\rm LS}$ with pressure. In order to compare our results with those of other workers, we have replotted our $\tau_{\rm LS}$ as a function of η/T in Figs. 8–11. In all cases the data fit well to a straight line

$$\tau_{\rm LS} = \frac{A\eta}{T} + \tau_0 \tag{11}$$

where τ_0 is the zero viscosity (or infinite temperature) intercept.

Fig. 2. Liquid sample cell.



Fig. 3. I_{VH} spectra of pure toluene: + + +, experimental points; —, calculated fit to one Lorentzian plus a baseline.

Discussion

A. Benzene and toluene

Using interferometry, Alms et al. [6] have measured $\tau_{\rm LS}$ for benzene and toluene both in the pure liquid and as solutions in isotropic solvents. They found that for these two liquids, the relaxation times varied only with viscosity and not with the molecular nature of the solvent. Their data are included in Figs. 8 and 9. Their relaxation times for benzene were independent of concentration, suggesting that pair correlations in this liquid are small. Our high pressure results substantiate this conclusion. Even at densities approaching the freezing point, the relaxation time measured by depolarized Rayleigh scattering remains the same linear function of viscosity. We therefore conclude that for benzene we are measuring the single particle relaxation time.

Proton spin lattice relaxation times have been measured for benzene at high pressure by Bull and Jonas [20]. The reorientational relaxation time changed from 1.7 ps at 0.1 MPa to 1.8 ps at 50 MPa, thus showing little or no pressure dependence. The proton relaxation time is affected both by rotations parallel and perpendicular to the C_2 symmetry axis, whereas the $\tau_{\rm LS}$ depends only on rotations perpendicular to the axis. Bull and Jonas point out that spinning of benzene about its axis is relatively free and should show little pressure dependence. This explanation of the NMR results is in agreement with our conclusion that in benzene we are measuring the τ_1 single particle relaxation time for rotation perpendicular to the symmetry axis.

Recently Dill et al. [10] have reported values of $\tau_{\rm LS}$ for benzene

at high pressures as measured with a grating spectrometer. Their values are also included in Fig. 8. Except for the highest pressure, their values are in agreement with our values measured using interferometry. We feel, however, there are inherent limitations involved in measuring depolarized Rayleigh rotational relaxation times using a grating spectrometer. This subject will be dealt with in detail when we discuss our results for methyl iodide.

Although toluene is an asymmetric top molecule, our spectra could be described very well by a single Lorentzian, making attempts to fit the spectra to more than one Lorentzian unjustified. The $\tau_{\rm LS}$ for toluene is a linear function of the viscosity. Alms et al. have discussed the possible significance of the fact that this asymmetric top molecule has a single relaxation time [6]. Our values of $\tau_{\rm LS}$ for toluene lie only slightly above those measured by Alms et al. They found the values for pure toluene and 75% solution (by volume) of toluene in isopentane to be ~10% greater than the rest of their data when plotted versus solution viscosity (their data included values for concentrated toluene solutions in other solvents). This could imply the existence of relatively small pair correlation effects in toluene. Our results show that pair correlations, if they are present, do not seem to influence the viscosity dependence of the singlet relaxation time.

Bucaro et al. [21] have also studied depolarized Rayleigh scattering of toluene at high pressures. They detected the *K*dependent doublet feature, as predicted by Stegeman and Stoicheff [22], at a pressure of 400 MPa. We found no evidence of this doublet in our spectra at 205 MPa.



Fig. 4. Light scattering rotational relaxation time for benzene versus pressure.



Fig. 5. Light scattering rotational relaxation time for toluene versus pressure.



Fig. 6. Light scattering rotational relaxation time for chloroform versus pressure.

Parkhurst et al. [23] have determined the effect of pressure on the proton spin lattice relaxation time of toluene $-d_3$. They found a significant increase in the rotational relaxation time with pressure. The rotational relaxation time for toluene, as measured using NMR, reflects both spinning and tumbling of the molecular axis, and we feel detailed comparisons of the NMR data to our depolarized Rayleigh data are not justified.

B. Chloroform

Our high pressure light scattering results for pure chloroform in Fig. 10 show $\tau_{\rm LS}$ to be a linear function of viscosity at constant temperature. Also shown in Fig. 10 are data of Campbell and Jonas [8] for rotational relaxation times at high pressures measured using both Raman scattering and NMR.

The light scattering rotational relaxation time for chloroform has been shown by Alms et al. [7] to be strongly concentration dependent, suggesting pair correlations are affecting the light scattering data at high concentrations. They report values for fN and gN of 1.0 ± 0.1 and 0.0 ± 0.1 , respectively, for the pure liquid.

Both Raman and NMR measure rotations perpendicular to the symmetry axis and in the absence of complicating effects, should yield the same value of τ_1 under the same conditions. It is readily seen from Fig. 10 that this is not the case, except at atmospheric pressure. Campbell and Jonas suggested the differ-



Fig. 7. Light scattering rotational relaxation time for methyl iodide versus pressure.



Fig. 8. Rotational relaxation times for benzene versus viscosity $\times T^{-1}$: •••, pure liquid, high pressure Rayleigh, 298 K, this work; $\Box \Box \Box$, solution, Rayleigh, 297 K, ref. [6]; $\triangle \triangle \triangle$, pure liquid, high pressure Rayleigh, 296 K, ref. [10]. The line is a least squares fit of the • high pressure data.

ence might be due to a change in the proton quadrupolar coupling constant with pressure. If we compare our $\tau_{\rm LS}$ results to the τ_1 Raman results, it appears that pair correlations are decreasing as pressure is increasing.

Using eq. (8) and the reported values of fN and gN, we find that τ_{LS} should increase faster than τ_1 with increasing pressure simply due to the increase in N, the number of scatterers in the scattering volume. This does not appear to be the case from Fig. 10. It is possible that either f or g, or both, are changing with pressure, and this change could explain the observed results. There is also the possibility that some assumptions used in obtaining τ_1 from the Raman data are not applicable at high pressure. Specifically, there may be significant vibration-rotation interaction at high pressures and/ or the non-orientational relaxation processes may not affect the isotropic and anisotropic Raman spectra in the same way [24]. This could also help explain the large discrepancy between the Raman and NMR data.

C. Methyl iodide

Our high pressure depolarized Rayleigh relaxation times for methyl iodide measured using interferometry are given in Fig. 11, along with high pressure Raman results of Campbell et al. [9], and high pressure depolarized Rayleigh results of Dill et al. [10]



Fig. 9. Depolarized Rayleigh rotational relaxation times for toluene versus viscosity $\times T^{-1}$: •••, pure liquid, high pressure, 298 K, this work; $\Box \Box \Box$, solution, 297 K, ref. [6]. The line is a least squares fit of the high pressure data.



Fig. 10. Rotational relaxation times for pure chloroform versus viscosity $\times T^{-1}$: •••, high pressure Rayleigh, 298 K, this work; $\Box \Box \Box$, high pressure Raman, 296 K, ref. [8]; $\triangle \triangle \triangle$, high pressure NMR, 296 K, ref. [8]; • Rayleigh, 295 K, ref. [7]; • NMR, 295 K, ref. [7]. The line is a least squares fit of the high pressure data.

measured using a grating spectrometer. Again, the Raman experiments should yield single particle relaxation times. In comparing our $\tau_{\rm LS}$ results to the τ_1 Raman times we find a situation similar to that for chloroform, that is, pair correlations appear to be significant at atmospheric pressure. However, the $\tau_{\rm LS}$ of Dill et al. do not agree with our $\tau_{\rm LS}$ values and are significantly smaller than the Raman times.

The depolarized Rayleigh spectra obtained using spectrometers consist of two prominent features: an intense narrow peak at the laser frequency, and a broad "Rayleigh wing" which extends, in many cases, for several hundreds of wavenumbers. In an interferometric experiment this "wing" appears as a flat background due to the overlapping of adjacent orders and does not interfere with measurement of the narrow component. In order to obtain the narrow component from the experimental grating spectrometer spectrum the contribution of the "wing" must be "subtracted out" in some manner.

Since the nature of the wing spectrum is not totally understood, Dill et al. separated out the narrow part by assuming the second moment of the narrow band was the classical, single particle value, 6kT/I. The second moment will differ from the classical value in the presence of pair correlations. There is also evidence that the single particle second moment can differ signifi-



Fig. 11. Rotational relaxation times for pure methyl iodide: $\bullet \bullet \bullet$, high pressure Rayleigh, 298 K, this work; $\Box \Box \Box$, high pressure Raman, 303 K, ref. [9]; $\triangle \triangle \triangle$, high pressure Rayleigh, 296 K, ref. [10]. The line is a least squares fit of the \bullet high pressure data.

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cantly from 6kT/I. Campbell et al. [9] have measured the second moment of methyl iodide at pressures up to 200 MPa and at temperatures ranging from 273 K to 363 K. In all cases the second moment was found to be significantly less than 6kT/I. Other investigations have yielded various values for the second moment of methyl iodide.

In the absence of knowledge concerning the magnitude of pair correlations and reliable second moment values we feel there are limitations involved in obtaining τ_{LS} values from depolarized Rayleigh experiments performed using grating spectrometers.

Our τ_{LS} values and the Raman τ_1 values approach each other at high pressures, as was the case for chloroform. This behaviour can be explained as arising either from changes in f and g with pressure, or effects of vibration-rotation interaction and nonorientational processes on the Raman spectra, or both.

Conclusion

We have shown that accurate depolarized Rayleigh light scattering measurements using interferometry can be performed at high pressure. By changing the pressure, the viscosity can be varied over a wide range while keeping chemical composition constant.

The light scattering relaxation times of pure benzene and toluene measured at high pressures are a linear function of viscosity at constant temperature. This viscosity dependence agrees well with previous results obtained over a range of concentrations at atmospheric pressure. The effect of pair correlations on the light scattering relaxation time is small and one is essentially measuring the single particle relaxation time. For chloroform and methyl iodide the light scattering relaxation time is also a linear function of viscosity. Pair correlations seem to be significant in these two liquids. At higher pressures, the light scattering and Raman rotational relaxation times approach each other. This suggests either the magnitude of the static and dynamic contributions to the pair correlations are changing with pressure, or the approximations used to obtain the single particle Raman rotational relaxation times from the polarized and depolarized Raman spectra are not valid at high pressure, or both.

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