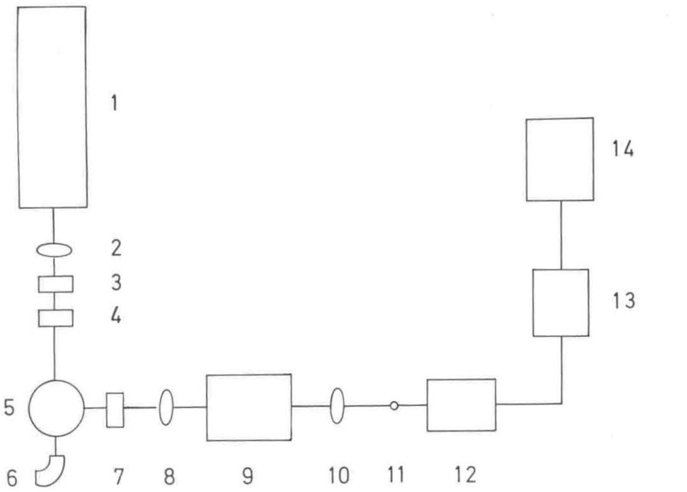

Fig. 1. Light scattering apparatus: (1) argon ion laser; (2) lens A; (3) $\lambda/2$ plate; (4) Glan–Thompson prism; (5) high pressure optical cell; (6) light trap; (7) polarizer with $\lambda/4$ plate; (8) lens B; (9) Fabry-Perot interferometer; (10) lens C; (11) pinhole; (12) photomultiplier tube;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

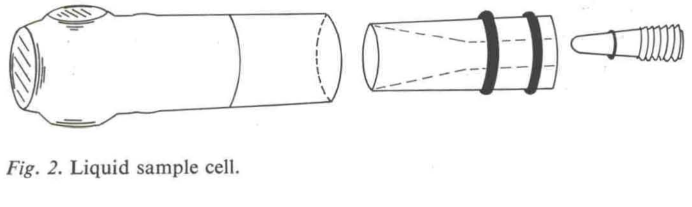

Fig. 2. Liquid sample cell.

Table I. *Rotational relaxation times and viscosities*

	Pressure/ MPa	$\mathrm{HWHH_{LS}}$/ GHz	τ_{LS}/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 ±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 least-squares 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 $\mathrm{HWHH_{LS}}$.

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 τ_{LS} were obtained from the $\mathrm{HWHH_{LS}}$ according to $\tau_{LS} = (2\pi \mathrm{HWHH_{LS}})^{-1}$. The uncertainty in τ_{LS} values is ±0.2 ps.

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

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

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

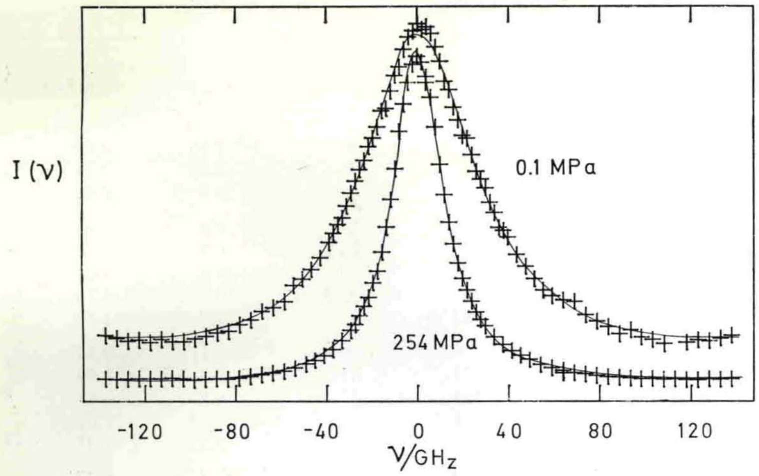

Fig. 3. I_{VH} spectra of pure toluene: + + +, experimental points; ——, calculated fit to one Lorentzian plus a baseline.

Discussion

A. *Benzene and toluene*

Using interferometry, Alms et al. [6] have measured τ_{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 τ_{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 τ_{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 τ_{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 τ_{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.

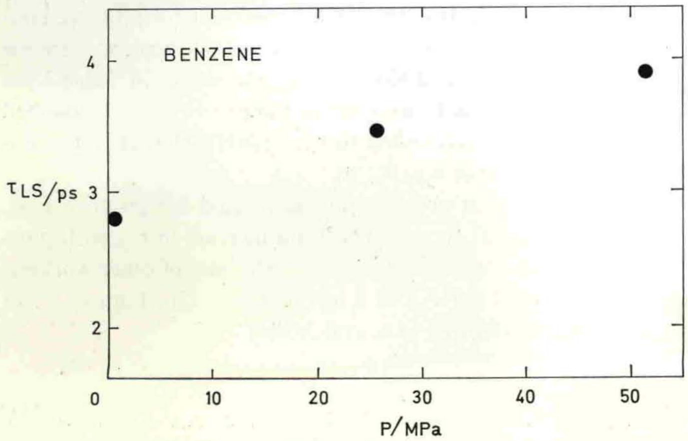

Fig. 4. Light scattering rotational relaxation time for benzene versus pressure.

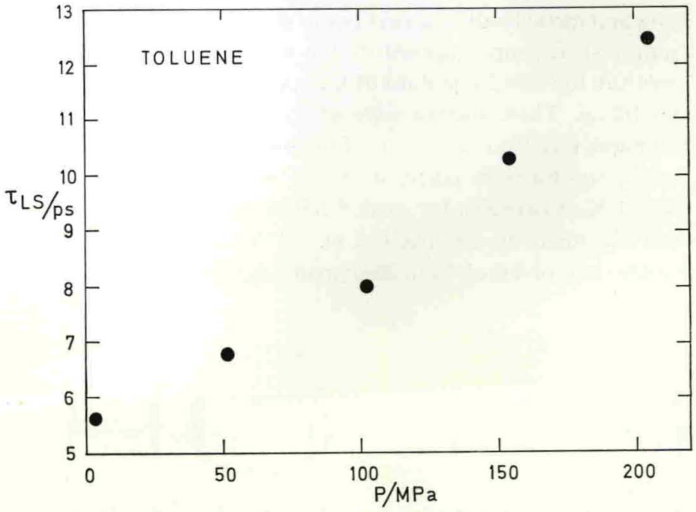

Fig. 5. Light scattering rotational relaxation time for toluene versus pressure.