

## ROTATIONAL RELAXATION STUDIES FROM RAYLEIGH SCATTERING III HALOGENATED METHANES AND ETHYLENE AND CARBON DISULPHIDE

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The Rayleigh scattering profiles of liquid chloroform, bromoform, chloroform-d, dichloromethane, tetrachloroethylene, trichloroethylene and carbon disulphide were recorded using a Ramanor HG2S instrument and He-Ne laser excitation. By splitting the profiles into a low frequency (10 to 25cm<sup>-1</sup>) and a high frequency (25 to 50cm<sup>-1</sup>) region, an average rotational relaxation time was determined in each case and compared with the results obtained for benzene and cyclohexane derivatives.

**Key Words :** Rotational Relaxation; Rayleigh Scattering; Halogenated Methane; Ethylene; Carbon Disulphide; Ramanor HG2S; He-Ne Laser Excitation

### INTRODUCTION

IN previous papers<sup>1,2</sup> (hereafter referred to as I and II), the authors have presented measurements of reorientational relaxation times by depolarized Rayleigh scattering for mono-substituted benzene and cyclohexane derivatives. In this paper, a study of depolarized spectra for some halogenated methanes, ethylene and carbon disulphide which are smaller molecules is presented. However, for all molecules studied in I, II and III, the authors have been able to measure only one relaxation time from the depolarized Rayleigh spectrum which in general corresponds to some overall rotational motion of the molecule. It was found that an important difference between the benzene and cyclohexane derivatives and the halogenated methane and ethylene, and carbon disulphide is that the graphs (see below) are straight lines in both the low and high frequency regions for the halogenated methanes, ethylene, and carbon disulphide, except CHBr<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub>. The straight lines also have different slopes. The second straight line in the high frequency region with different slopes can occur only if the viscosity coefficient  $\eta$  and the elastic constant  $\mu$  (see I) are frequency independent for those molecules.

As it has been shown in their first paper,<sup>1</sup> the intensity of the scattered light  $I(\omega)$  as a function of frequency  $\omega$  for the low frequency region is given by :

$$I(\omega) \propto \tau_r \left\{ \left[ 1 - \left( \frac{I}{4k\Gamma} \right) \omega^2 \right]^2 + \omega^2 \tau_2^r \right\}^{-1}$$

The scattered intensity in the high frequency region is given by :

$$I(\omega) \propto \omega^{12/7} \exp \left( - \frac{\omega}{\omega_0} \right)$$

The rotational relaxation times of the halogenated methane and ethylene, and carbon disulphide have been calculated from the plots of  $I(\omega_0) - I(\omega) / I(\omega)$  vs.  $\omega^2$  using the equation,

$$[I(\omega_0) - I(\omega)] / I(\omega) = \tau_r^2 \omega^2$$

which gives a straight line of slope  $\tau_r^2$ .

#### EXPERIMENTAL

The experimental apparatus was described in their first paper.<sup>1</sup> The Rayleigh wings were recorded from  $10\text{cm}^{-1}$  to  $50\text{cm}^{-1}$ .

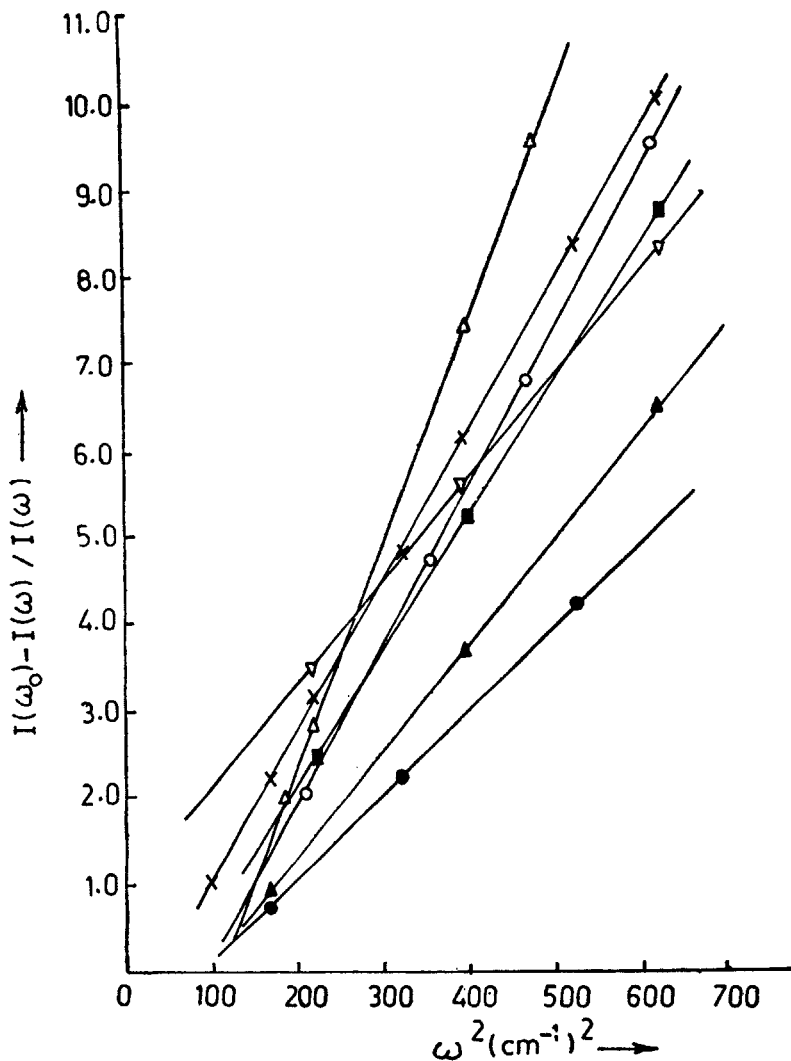


FIG 1 A plot of  $[I(\omega_0) - I(\omega)] / I(\omega)$  vs  $\omega^2$  for  $\text{C}_2\text{HCl}_3$   $\Delta$ ,  $\text{CH}_2\text{Cl}_2$   $\times$ ,  $\text{CS}_2$   $\circ$ ,  $\text{CHCl}_3$   $\blacksquare$ ,  $\text{CCl}_4$   $\nabla$ ,  $\text{CHBr}_3$   $\blacktriangle$ , and  $\text{C}_2\text{Cl}_4$   $\bullet$  (10 to  $25\text{cm}^{-1}$ )

The liquids used for study after distillation were—chloroform, bromoform, chloroform-d, dichloromethane, tetrachloroethylene, trichloroethylene and carbon disulphide. All recordings were made at 22 °C.

## RESULTS AND DISCUSSION

- (i) The plots of  $I(\omega_0) - I(\omega)/I(\omega)$  vs.  $\omega^2$  are given for these liquids in Fig. 1 for the low frequency region and in Fig. 2 for the high frequency region.
- (ii) The plots of  $\log [I(\omega).\omega^{-12.7}]$  vs.  $\omega$  are given for the high frequency region for the liquids in Fig. 3. These are straight lines as per eq. 2 in Ahmed and Thyagarajan.<sup>1</sup>

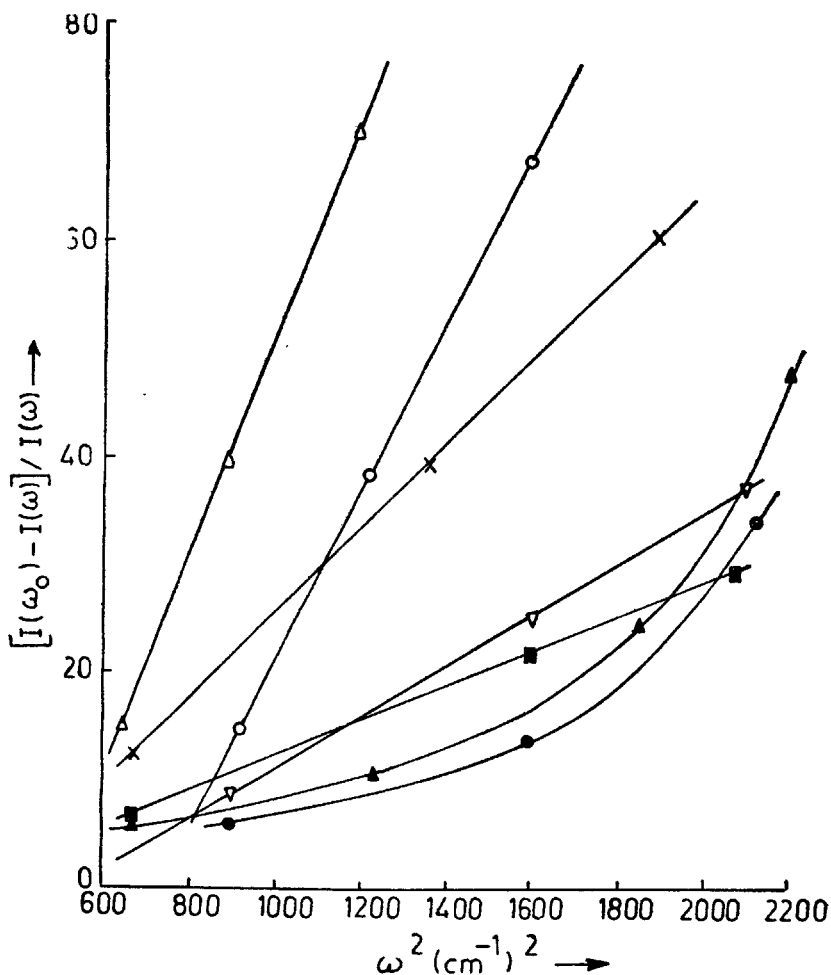


FIG 2 A plot of  $[I(\omega_0) - I(\omega)]/I(\omega)$  vs  $\omega^2$  for  $C_2HCl_3$   $\Delta$ ,  $CS_2$   $\circ$ ,  $CH_2Cl_2$   $\times$ ,  $CDCl_3$   $\nabla$ ,  $CHCl_3$   $\blacksquare$ ,  $CHBr_3$   $\blacktriangle$ , and  $C_2Cl_4$   $\bullet$  (26 to 48  $cm^{-1}$ )

- (iii) The rotational relaxation times obtained from the slopes of the graphs for the low and high frequency regions using eq. 6 (Ref. 1) are given in Table I. The Table also contains data on the moments of inertia, viscosity of the liquids and the value  $\tau_{fr}$ , the free rotator value of the relaxation time. The values of the average rotational diffusion constant ( $D$ ) are also listed in the Table. The results available in the literature using the Fabry-Perot technique for a very low frequency region are given in Table II. The values of  $\tau_r$  for  $CS_2$  are lower compared to that for other liquids, indicating a faster rotation of this molecule. The discrepancy in the case of bromoform compared to the results of the Fabry-Perot method is not clear.

TABLE I  
Correlation times in units of  $10^{-12} S$  at 22 °C for small molecules

Liquid	Viscosity (cp)	Moment of Inertia $\times 10^{-38} gm-cm^2$	$\tau_{fr}$	$\tau_1$	$\tau_2$	Diffusion constant $D = \frac{1}{6\tau_1} \times 10^{12} S^{-1}$
bromoform	1.741	6.720 13.194	0.892 1.249	3.28		0.0508
chloroform	0.514	2.540 4.908	0.548 0.762	3.60	4.71	0.0463
chloroform-d		2.58 4.908	0.553 0.762	3.28	5.52	0.0508
dichloromethane	0.393	0.262 2.529 2.740	0.176 0.547 0.569	4.35	6.60	0.0383
Tetrachloroethylene	0.932			3.26		0.0511
Trichloroethylene	0.566			5.26	9.71	0.0317
Carbon disulphide	0.365			2.65	9.37	0.0628

\* $\tau_1$  calculated from the low frequency region.

$\tau_2$  calculated from the high frequency region.

TABLE II  
Correlation times in units of  $10^{-12} S$  at 22 °C for small molecules

Liquid	This work	Literature values			
bromoform	3.28	11.53[3]	11[4]	10.1[5]	—
chloroform	3.6	5.9[4]	2.58[3]	2.95[6]	2.9[6]
chloroform-d	3.28	2.9[5]			
$CS_2$	2.65	1.86[7]	1.96[7]	2.3[3]	1.76[4]

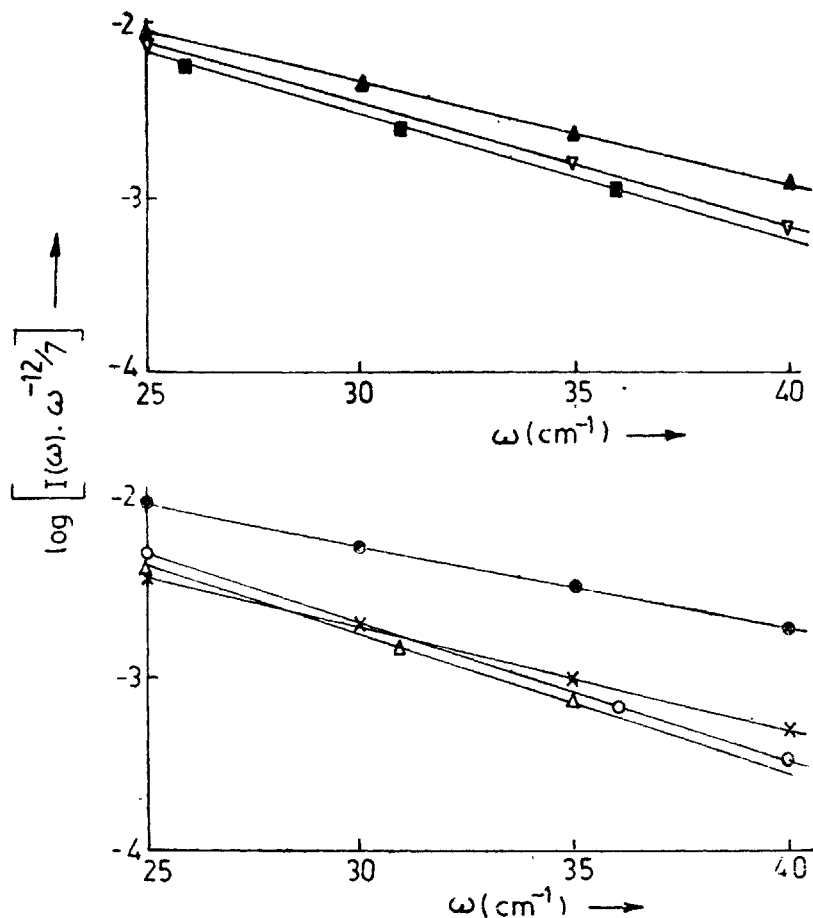


FIG 3 Plots of  $\log [I(\omega) \cdot \omega^{-12/7}]$  vs  $\omega$  for  $\text{CHBr}_3$ ,  $\blacktriangle$ ,  $\text{CDCl}_3$ ,  $\nabla$ ,  $\text{CHCl}_3$ ,  $\blacksquare$ ,  $\text{C}_2\text{Cl}_4$ ,  $\bullet$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\times$ ,  $\text{CS}_2$ ,  $\circ$  and  $\text{C}_2\text{HCl}_4$ ,  $\triangle$

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