10-1-1978

Light scattering studies of orientational fluctuations of CS2

Scott Whittenburg
University of New Orleans, swhitten@uno.edu

Follow this and additional works at: http://scholarworks.uno.edu/chem_facpubs

Part of the Chemistry Commons

Recommended Citation

This Article is brought to you for free and open access by the Department of Chemistry at ScholarWorks@UNO. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of ScholarWorks@UNO. For more information, please contact scholarworks@uno.edu.
Light scattering studies of orientational fluctuations of CS₂

Y. Higashigaki, S. L. Whittenburg, and C. H. Wang

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112
(Received 24 January 1978)

We have measured the depolarized Rayleigh relaxation time of CS₂ as a function of temperature and concentration in an optically isotropic solvent CCl₄. The concentration dependence of the relaxation times indicates the importance of orientational pair correlation in CS₂. The orientational pair correlation factor is found to depend on concentration at high CS₂ concentration, as well as viscosity and temperature, in contrast to what is observed in other small molecules. The single particle reorientation times were obtained by extrapolating from the depolarized Rayleigh relaxation times to infinite dilution. These were compared with the predictions of the hydrodynamic slip and stick models for rotational diffusion. As is usual for small molecules, the slip boundary condition better approximates the experimental results. The single particle reorientation times were also compared with the correlation times obtained by ¹³C NMR and ³²S NQR measurements. They were found to be in good agreement.

I. INTRODUCTION

Depolarized Rayleigh light scattering is a valuable technique for studying molecular reorientation in the liquid state. This is due to the fact that optically anisotropic molecules scatter light with a change in frequency when they reorient. The frequency distribution of the scattered light reflects the molecular reorientation rate.

The characteristic feature of the depolarized spectrum of a single optically anisotropic molecular liquid is a sharp central component having a spectral half-width at half-maximum intensity of the order of 1-5 cm⁻¹ superimposed upon a broad background which extends in many cases to several hundred wavenumbers. While the physical nature of the broad spectral background for a molecular liquid is rather complex, it is now well understood that the mechanism associated with the sharp central component is due to molecular reorientation. If the overdamped shear mode couples to the reorientational motion, a dip at zero frequency may result.¹ The shear mode dip has, however, a negligible effect on the reorientation rate.

Although there are several techniques available for the study of molecular reorientation, depolarized Rayleigh scattering is unusual because it yields information about the cooperative molecular reorientation; the other techniques such as Raman and NMR, when applicable, yield the uncorrelated single particle reorientation time. The depolarized Rayleigh scattering experiment carried out with variation of temperature and dilution of the optically anisotropic molecules in an optically isotropic solvent can provide a method for the study of orientational pair correlation. In this paper we report the results of a detailed study of the temperature and concentration dependence of the depolarized Rayleigh spectra of neat carbon disulfide and solutions of CS₂ in carbon tetrachloride. We have found that the depolarized Rayleigh spectrum of CS₂ is strongly affected by the static orientational pair correlation.

II. EXPERIMENTAL

Since the width of the sharp central component in the depolarized Rayleigh scattering spectrum associated with molecular reorientation is the order of 1 cm⁻¹, in order to obtain an unambiguous experimental result it is necessary to use a Fabry-Perot interferometer to resolve the sharp central component. The depolarized Rayleigh scattering spectra of neat CS₂ and CS₂ in CCl₄ were obtained using the interferometry apparatus described previously.² The light source was an intracavity etalon selected single frequency argon ion laser operating at about 0.6 W at a frequency of 4860 Å. The depolarized component at 90° ± 0.1° from the incident exciting radiation was frequency analyzed with a piezoelectrically scanned Tropel model 360 Fabry-Perot interferometer. The signal from a thermoelectrically cooled photomultiplier was processed by an SSR photon counting system. The amplified signal was displayed on an X-Y recorder and digitized. The digitized spectra were fit to overlapping Lorentzian functions plus a constant background using a nonlinear least square computer program. The spectra were corrected for an instrumental function corresponding to a typical finesse of 50. The depolarized Rayleigh spectrum at 20°C together with the Lorentzian fit is shown in Fig. 1. The free spectral range calibrated with the spacing between the sodium D lines was 855.9 GHz, corresponding to a plate separation of 0.175 mm.

The samples were prepared from spectroquality grade liquids which were repeatedly filtered through 0.22 μm Millipore filters to remove dust. The viscosity of all samples at various temperatures was measured using a Cannon-Ubbelhode viscometer thermostated in an ethylene glycol-water constant temperature bath. The viscosity data are given in Table 1. The indices of refraction of all samples were also measured before and after the light scattering experiment as a check for the accuracy of sample concentration.

The samples, contained in rectangular glass cells, were temperature controlled in an aluminum block with the circulating ethylene glycol-water mixture. The temperature, monitored by a thermocouple, was accurate to within ±1 K.

III. RESULTS AND DISCUSSION

A. Molecular reorientation

We have measured the depolarized Rayleigh scattering spectra of neat CS₂ and solutions of CS₂ in CCl₄.
TABLE I. Depolarized Rayleigh relaxation times.

<table>
<thead>
<tr>
<th>Concentration (volume %)</th>
<th>100</th>
<th>80</th>
<th>60</th>
<th>40</th>
<th>20</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(K)</td>
<td>τ(ps)</td>
<td>n/T</td>
<td>τ(ps)</td>
<td>n/T</td>
<td>τ(ps)</td>
<td>n/T</td>
</tr>
<tr>
<td>273</td>
<td>3.27</td>
<td>1.53</td>
<td>2.92</td>
<td>1.79</td>
<td>2.64</td>
<td>1.82</td>
</tr>
<tr>
<td>278</td>
<td>2.68</td>
<td>1.46</td>
<td>2.55</td>
<td>1.69</td>
<td>2.47</td>
<td>1.80</td>
</tr>
<tr>
<td>283</td>
<td>2.56</td>
<td>1.37</td>
<td>2.38</td>
<td>1.58</td>
<td>2.34</td>
<td>1.82</td>
</tr>
<tr>
<td>288</td>
<td>2.07</td>
<td>1.30</td>
<td>2.24</td>
<td>1.52</td>
<td>2.24</td>
<td>1.69</td>
</tr>
<tr>
<td>293</td>
<td>1.92, 1.54</td>
<td>1.24</td>
<td>2.15, 1.95</td>
<td>1.42</td>
<td>2.14, 2.15</td>
<td>1.58</td>
</tr>
<tr>
<td>298</td>
<td>1.80</td>
<td>1.19</td>
<td>2.06</td>
<td>1.34</td>
<td>2.03</td>
<td>1.48</td>
</tr>
<tr>
<td>303</td>
<td>1.70</td>
<td>1.11</td>
<td>1.95</td>
<td>1.27</td>
<td>1.94</td>
<td>1.41</td>
</tr>
<tr>
<td>308</td>
<td>1.60</td>
<td>1.06</td>
<td>1.89</td>
<td>1.19</td>
<td>1.84</td>
<td>1.32</td>
</tr>
<tr>
<td>313</td>
<td>1.52</td>
<td>1.00</td>
<td>1.84</td>
<td>1.12</td>
<td>1.75</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Note: Units of 10⁻⁸ eP/K.

Rayleigh relaxation times $\tau_{\text{Ray}}$, were obtained from the half-width at half-height (HWHH in Hz) of the Lorentzian spectra according to

$$\tau_{\text{Ray}} = \frac{2\pi \times \text{HWHH}}{1}.$$

The relaxation times were reproducible to better than 10%. The results at various temperatures for several CS₂ concentrations are given in Table I, together with the values obtained previously by Shapiro and Broida. The values of the CS₂ molecular reorientation times of Shapiro and Broida were obtained using a grating monochromator. The $\tau_{\text{Ray}}$, results at various concentrations are plotted as a function of $n/T$ in Fig. 2.

One notes in Table I that the $\tau_{\text{Ray}}$, data reported in Ref. 3 agree within 5% with the present result for concentration above 60%. There is, however, a disagreement below this concentration. At 10% concentration the $\tau_{\text{Ray}}$, value reported in Ref. 3 is 66% longer than the present result. The disagreement is believed to be due to the fact that the depolarized Rayleigh spectrum of CS₂ in CCl₄ narrows with decreasing CS₂ concentration, and at low concentration it cannot be measured accurately using a conventional double-grating monochromator because of its limited resolving power. In fact, the Rayleigh relaxation times of a host of molecules obtained using a grating monochromator have been found to disagree with the Fabry-Perot interferometric results for the same molecules under the same physical conditions. We have discussed the causes for this discrepancy using the two techniques in several of our previous publications.

CS₂ is a linear molecule. Reorientation of the molecule about the molecular axis does not modulate the molecular polarizability and hence this motion does not induce depolarized Rayleigh scattering. The reorientation of the molecular axis involves displacements of other molecules and is thus expected to greatly change the molecular polarizability. The CCl₄ solvent has a negligible depolarized Rayleigh scattering intensity. Therefore, we expect that the depolarized Rayleigh spectra of neat CS₂ and CS₂ in CCl₄ solutions are associated with the reorientation of the CS₂ molecular axis, and the half-width at half-height of the Lorentzian spectrum is a measure of the average rate of reorientation of this axis.

However, as pointed out above, owing to the fact that Rayleigh scattering is a coherent process, the depolarized Rayleigh spectrum contains information about correlated molecular reorientation, and the $\tau_{\text{Ray}}$, values obtained for CS₂ at finite concentrations do not represent the uncorrelated single particle molecular reorientation time.

B. The pair reorientational correlation time

The Rayleigh relaxation time is affected by temperature, viscosity, and concentration. As shown by the previous work on small molecules in the absence of strong solvent-solute interactions (such as hydrogen bonding, dimerization, etc.), the pair correlation effect present in the depolarized Rayleigh spectrum can be...
studied by measuring $\tau_{\text{Ray}}$, as a function of concentration, but keeping the solution's viscosity fixed to the value of the neat liquid. This method has been applied to some small molecules in our laboratory and using this technique we have found that pair correlation is significant in part as due to free rotor reorientation. However, for symmetric top molecules, the pair correlation effect on $\tau_{\text{Ray}}$ is only about 20%, whereas the viscosity of CCl$_4$ is about 0.36 cP, whereas the viscosity of CCl$_4$ is about 0.96 cP. In the CS$_2$-CCl$_4$ system the solution viscosity increases as the CS$_2$ concentration is decreased. The linear molecules, it has been shown that $\tau_{\text{Ray}}$ increases as the concentration of molecule $i$ with respect to some external reference coordinate system, $n$ is the number density of CS$_2$ molecules, $P_2(x) = \frac{1}{2}(3x^2 - 1)$, and $f = \langle P_2(\cos \theta_i)P_2(\cos \theta_j) \rangle / \langle P_2(\cos \theta_i) \rangle^2$.

According to Eq. (3), $\tau_s$ can be determined from the concentration dependence of $\tau_{\text{Ray}}$ by extrapolating the $\tau_{\text{Ray}}$, values at fixed $\eta/T$ to zero solute concentration. The results obtained for $\tau_s$ in this manner are shown as a function of $\eta/T$ in Fig. 3. A linear least squares fit of the data to the equation

$$\tau_s = C\eta/T + \tau_0$$

gives $C = 5.6 \times 10^4$ Kps/P and $\tau_0 = 0.87$ ps.

The experimental value of the slope $C$ can be compared with the Stokes-Einstein equation modeling CS$_2$ as an ellipsoid with slip and stick boundary conditions. The results are given in Table II. As is usual for small molecules, the slip boundary condition more closely fits the experimental slope. For CS$_2$ we observe a nonzero intercept, in contradiction with the hydrodynamic model used to derive the Stokes-Einstein relation. The physical significance of $\tau_0$ is unclear at present but has been interpreted in terms of the free rotor reorientation time. Previous depolarized Rayleigh scattering studies have found both vanishing and nonvanishing $\tau_0$ values for some molecules.

Also included in Fig. 3 are the single particle rotational correlation times obtained from the $^{14}$C spin-lattice relaxation times and from $^{32}$S nuclear quadrupole resonance linewidth data. The light scattering data are about 10% lower than the NMR results, but the...
The Stokes–Einstein slope for a sphere with stick boundary conditions is $2.85 \times 10^2 \text{ ps K/P}$. For an ellipsoid with stick boundary conditions, it is $2.95 \times 10^2 \text{ ps K/P}$, and with slip boundary conditions, it is $6.20 \times 10^4 \text{ ps K/P}$. The experimental slope is $5.6 \times 10^6 \text{ ps K/P}$.

The overall agreement between the two results is satisfactory.

The $\tau_{\text{Re}}$ data at all concentrations can also be represented according to an Arrhenius-type of equation given by

$$\tau_{\text{Re}} = \tau_{\text{Re}}^0 \exp(E_a/kT),$$

where $E_a$ is the activation energy. A fit of the $\tau_{\text{Re}}$ to Eq. (4) yields an activation energy $E_a$ which depends on concentration. The concentration dependence of $E_a$ is shown in Fig. 4. At a concentration greater than $80\%$, the activation energy is seen to increase rapidly. This is considered as due to the pair orientational correlation which renders the reorientation of the $\text{CS}_2$ molecular axis difficult. Below $80\%$, the activation energy decreases slightly with decreasing $\text{CS}_2$ concentration.

The asymptotic activation energy at zero concentration is found to be $1.58 \text{ kcal/mole}$. This value agrees well with the values of 1.42 and 1.28 kcal/mole obtained from $^{13}\text{C}$ and $^{32}\text{S}$ magnetic resonance measurements, respectively. The Arrhenius plot of the single particle orientation correlation times extrapolated from the present light scattering experiment is shown in Fig. 5.

Having obtained the single particle times, it is now possible to use Eqs. (2) and (3) to obtain the orientational pair correlation factor $f$ according to

$$f = \frac{\tau_{\text{Re}}}{}.$$

The result for $f$ in $\text{CS}_2$ is found to depend on the concentration of $\text{CS}_2$, in contrast to the $\text{CH}_3\text{I}$ result, in which $f$ is found to be independent of concentration. We plot in Fig. 6 the pair correlation factor $f_n$ as a function of $n$. $f_n$ increases more or less linearly with increasing $n$ below $60\%$ $\text{CS}_2$ concentration. Above such a concentration, $f_n$ increases nonlinearly with increasing $n$. We also studied the viscosity and temperature dependence of $f$ and have found that the condition of high viscosity or low temperature favors the presence of pair orientational correlation. The results of $f_n$ versus $n$ for different $\eta/T$ are also shown in Fig. 6.

The alignment of $\text{CS}_2$ molecules about a central $\text{CS}_2$ molecule depends significantly on the molecular environment, as is indicated by the viscosity dependence. Previous studies on the pair correlation factor have indicated that molecular shape is the determining factor for $f$. The present result for $\text{CS}_2$ indicates that the long-range attractive force may also play an important role in $f$.

$\text{CS}_2$ is a linear molecule and thus has no dipole moment. Previous studies have also indicated that the interaction between molecules through the dipole moment is insignificant as far as the short-range pair orientation correlation is concerned. The $\text{CS}_2$ molecule has a significant electric quadrupole moment, and is also readily polarizable. In addition to the short-range repulsive potential, the interaction through the quadrupole moment may play an important role in determining $f$. However, the certainty of such a speculation must await a future systematic study of the orientational pair correlation of anisotropic molecules in the liquid state.

IV. SUMMARY AND CONCLUSIONS

We have measured the depolarized Rayleigh relaxation time of $\text{CS}_2$ as a function of temperature and concentration in an optically isotropic solvent. $\tau_{\text{Re}}$ was found to depend on the $\text{CS}_2$ concentration and to be a nonlinear function of $\eta/T$, indicating the importance of static orientational pair correlation in $\text{CS}_2$. From the concentration dependence of $\tau_{\text{Re}}$, we have obtained the single particle reorientation time. $\tau_{s}$ was found to agree well with the values obtained by $^{13}\text{C}$ NMR and $^{32}\text{S}$ NQR measurements. Comparison of $\tau_{s}$ to the Stokes–

---

TABLE II. Comparison of the theoretical Stokes–Einstein slope to the experimental slope.

<table>
<thead>
<tr>
<th>Stokes–Einstein slope for a sphere with stick boundary conditions</th>
<th>$2.85 \times 10^2 \text{ ps K/P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stokes–Einstein slope for an ellipsoid with stick boundary conditions</td>
<td>$2.95 \times 10^2 \text{ ps K/P}$</td>
</tr>
<tr>
<td>Stokes–Einstein slope for an ellipsoid with slip boundary conditions</td>
<td>$6.20 \times 10^4 \text{ ps K/P}$</td>
</tr>
<tr>
<td>Experimental slope</td>
<td>$5.6 \times 10^6 \text{ ps K/P}$</td>
</tr>
</tbody>
</table>

FIG. 4. Activation energy for reorientation as a function of concentration.
Einstein hydrodynamic model showed better agreement modeling CS$_2$ as an ellipsoid with slip boundary conditions, as is usual for small molecules. The fit of $\tau_s$ to the Stokes–Einstein relation yielded a nonzero intercept, in contradiction to the hydrodynamic model used to derive the relation. The static orientational pair correlation factor obtained from $\tau_{\text{REW}}$ and $\tau_s$ was found to depend nonlinearly on $\eta/T$ in contrast to dependence seen in other molecules.

ACKNOWLEDGMENT

Acknowledgment is made to the National Science Foundation and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.