

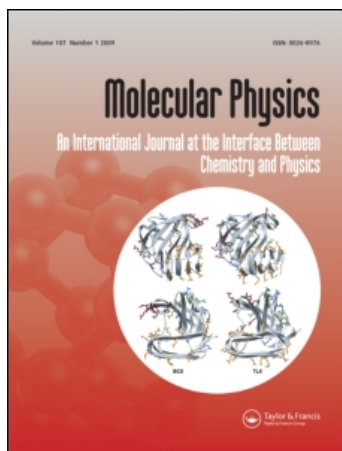
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Concentration effects on collision-induced depolarized Rayleigh lineshapes in CS₂/CCl₄ mixtures

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We report measurements of depolarized Rayleigh spectra of liquid CS₂/CCl₄ mixtures following the procedure proposed by Cox and Madden and recently used by Hegeman and Jonas. We fit a linear function on two distinct regions of the logarithmic spectra. The slopes Δ depend nonlinearly on the mixture composition. A comparison of our results with those of Hegeman and Jones where we follow the number-density dependence seems to be straightforward for further exploration of our experimental data. Our results indicate that, while in the high-frequency range (region III) of the spectrum changes of pressure and number density have very similar effects, these two parameters affect the lower-frequency range (region II) in a quite different way.

1. Introduction

In recent years a larger number of papers have been published reporting attempts to clarify the mechanism of collision-induced spectroscopic effects in liquids [1-8]. For this purpose experimentalists have varied the parameters that are expected to influence the spectra. Thus, by varying the temperature, the collision energy has been controlled [17], while by varying the pressure, the particle density and hence the intermolecular distance have been changed at constant temperature [18]. Despite these efforts, however, we still lack a clear understanding of the complex events at the molecular level underlying collision-induced effects. The reason for this can be seen in the fact that collision-induced effects are extremely sensitive to the very local structure of the liquid and to the complete dynamics of nearby molecules. For both aspects of the liquid state, the static and the dynamic, we still have to turn to rather simple models that are obviously in need of improvement. This situation motivated us to examine the influence of the local environment on collision-induced spectra by studying binary mixtures. Our accompanying molecular dynamics simulations have served to clarify as far as possible the situation for a simple model system [19, 20].

2. Results and discussion

In this short paper we report on preliminary depolarized light scattering results in the system CS₂/CCl₄ at 11°C. The spectra were taken in the neat liquids and at five intermediate mole fractions of $x_{\text{CS}_2} = 0.7, 0.5, 0.3, 0.2$ and 0.1 . CS₂ was chosen because of its axial symmetry, its high optical anisotropy and the quadrupolar character of the leading electric multipole. CCl₄ was chosen as a solvent because of

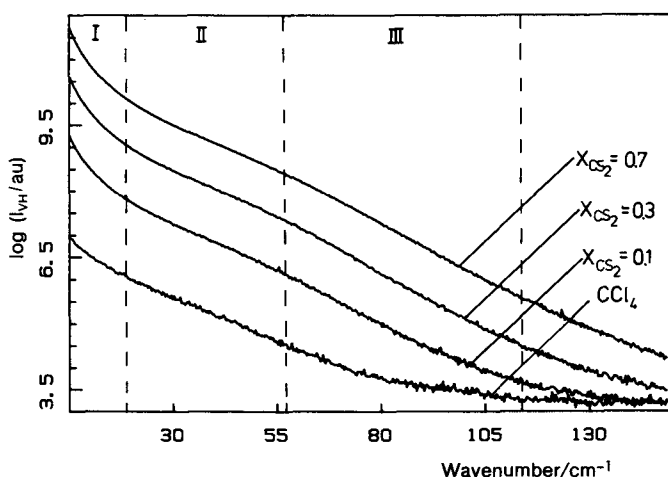


Figure 1. Depolarized Stokes part of the Rayleigh line of several CS_2/CCl_4 mixtures.

its low depolarized scattering intensity, its high symmetry, the octupolar character of the leading electric multipole and, finally, for its good solvent properties. The isotropic polarizabilities of the two molecules are very similar. Both liquids have been comprehensively characterized and extensively studied with several techniques using the available theoretical models [14–25]. The DLS spectra of the mixture CS_2/CCl_4 have already been studied in a narrow low-frequency spectral range reflecting the slow collective reorientational dynamics of the systems [26–28].

Madden and Cox [17] first analysed the depolarized Rayleigh wings of neat liquid CS_2 and distinguished three spectral regions. In analogy to the shape of the collision-induced bands of atomic liquids, they describe the high-frequency wings using an exponential band shape

$$I_{\text{VH}}(\omega) = A \cdot \exp\left(-\frac{\omega}{\Delta}\right), \quad (1)$$

and proposed a dipole-induced dipole (DID) mechanism to explain the regions II and III (see figure 1).

The density and temperature dependence of the depolarized band over a wide spectral range was studied by Hegemann and Honas [18] by applying high pressure. They also analysed the bandshape in terms of (1), and were thus able to separate the free volume effect from the changes in the kinetic energy of the molecules. Geiger and Ladanyi [16, 29] found excellent agreement between their MD simulation results, assuming the DID induction mechanism, and the experimental data from [18].

Figure 1 shows our DLS spectra of neat CCl_4 and three mixtures on a logarithmic scale. We can distinguish three distinct regions, separated by the dashed vertical lines and designated I, II and III. The spectra were taken between 5 and 150 wavenumbers, the data below 5 wavenumbers having been rejected because of spurious effects in this region. Region I was assigned in the literature to collective reorientational motions of the CS_2 molecules [28]. As far as region II is concerned, the break between the two sets of data is quite conspicuous. We believe that the description of this region with a linear fit and its characterization by a slope parameter is artificial and does not reflect the physics of the process. In fact, the change in the spectrum between regions II and

Experimental values for the Δ parameters at different mole fractions CS₂ of the logarithmic DRS spectra in regions II and III at 284 K, the liquid density ρ and the corresponding number density ρ_n of the mixtures.

x_{CS_2}	$\Delta_{\text{II}}/\text{cm}^{-1}$	$\Delta_{\text{III}}/\text{cm}^{-1}$	$\rho/\text{g cm}^{-3}$	$\rho_n/10^{-3} \text{ mol cm}^{-3}$
1.0	25.1	20.9	1.28	16.81
0.7	24.4	19.9	1.41	14.18
0.5	24.1	19.4	1.48	12.87
0.3	23.9	18.9	1.53	11.72
0.2	23.9	19.0	1.56	11.28
0.1	24.2	20.2	1.59	10.89

The error is less than 1.0%.

III in figure 1 is rather reminiscent of a shifted broad spectral band underlying the exponential decay of $I_{\text{VH}}(\omega)$. A tentative simulation of the spectrum has shown that the overall bandshape can be described adequately as the sum of three contributions: a narrow central Lorentzian, an unshifted exponential decay, and a broad shifted band located at 50 cm^{-1} . A similar band has often been invoked on theoretical [30] as well as experimental grounds [31–34]. In fact, an intermolecular highly damped librational mode has been discussed in many instances as a plausible assignment of observed bandshapes [30–36]. Such highly damped librations can be taken to stem from local structures that are stable enough to survive a few oscillation periods. The origin of these structures might be assigned to the survival of a particular solid state local configuration.

In order to analyse the data regions II and III, we fitted separately to (1), following the procedure adopted by Hegemann and Jonas. As the limits of the two ranges are not well defined, we varied the fit ranges until the best correlation between the function and the data was obtained. The table gives the resulting values for Δ_{II} and δ_{III} of the mixtures studied. These data are also illustrated in figure 2, showing the dependence of Δ_{II} and Δ_{III} on the particle density. This figure includes our values and

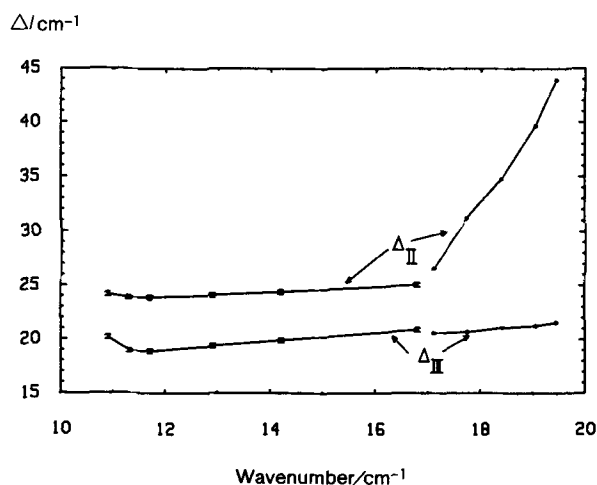


Figure 2. Parameters Δ from the corrected logarithmic DRS spectra of liquid CS₂/CCl₄ mixtures at different mole fractions (■) and from pure CS₂ varying the density (●) by using high pressure [18] versus liquid number density.

those of Hegemann and Jonas. The use of the density as a parameter to analyse the data was suggested by the high-pressure results. In fact, changing both variables, pressure and concentration, amounts to changing, among other things, the liquid number density. However, since the local structure plays a decisive role in collision-induced spectra, it is interesting to check whether the two sets of data—ours and those of Hegemann and Jonas—can be correlated at all. It does indeed appear that, while Δ_{II} behaves quite differently in the two experiments, Δ_{III} seems to follow the same trend for both sets. This means that Δ_{III} decreases slightly when, coming from high pressure, we expand to lower pressures, thus decreasing the number density, and that this trend continues when we further decrease the number density by mixing CS_2 with CCl_4 . It is evident that the two situations—expansion and mixing with another species—are hardly comparable.

If we assume the induction mechanism to be of the DID type, the spectra will in principle contain contributions from $\text{CS}_2 \rightarrow \text{CS}_2$, $\text{CCl}_4 \rightarrow \text{CS}_2$, $\text{CS}_2 \rightarrow \text{CCl}_4$ and $\text{CCl}_4 \rightarrow \text{CCl}_4$ inductions. The contribution of the latter can probably be neglected. We know that the scattered intensity depends not only on the electronic properties of the participating molecules but also on the degree of cancellation between the induction effects in the immediate surrounding of the molecules. On introducing a second component into the mixture, we obtain a new scattering species—a new inducing species—but also we disturb the local structure, which might profoundly affect the cancellation. Whatever effect we consider most important, we expect that the intensity of the DID effect is a sensitive function of the local composition of the mixture. As a consequence, the shape of the total scattering profile will change with the local composition of the two species. At this point it is difficult to predict in more detail the contribution of each of the mentioned effects. When we change the composition of the liquid by mixing CCl_4 and CS_2 , the slopes of the spectral bands in the two ranges as illustrated by the parameters Δ_{II} and Δ_{III} in figure 2 display significantly different behaviour. Also, the dependence of Δ_{II} on the number density is quite different depending on whether the pressure or the concentration is changed. These findings indicate that the mechanisms by which the spectra in range II and III are shaped are different, although little can be said at this stage about the nature of the underlying processes.

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