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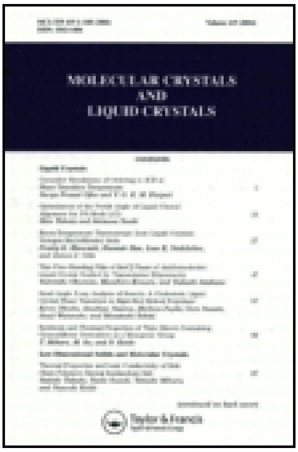

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Structure and Intermolecular Dynamics of Carbon Disulfide/Alcohols Binary Solution

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Published online: 11 Sep 2013.

To cite this article: Takayuki Kiba, Takashi Hirota, Akihiro Murayama & Shin-Ichiro Sato (2013) Structure and Intermolecular Dynamics of Carbon Disulfide/Alcohols Binary Solution, Molecular Crystals and Liquid Crystals, 579:1, 103-109, DOI: 10.1080/15421406.2013.802966

To link to this article: http://dx.doi.org/10.1080/15421406.2013.802966

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Mol. Cryst. Liq. Cryst., Vol. 579: pp. 103–109, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.802966

Structure and Intermolecular Dynamics of Carbon Disulfide/Alcohols Binary Solution

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We investigated the intermolecular vibrational motions of several carbon disulfide/alcohols binary solutions by using Raman-induced Kerr-effect spectroscopy (RIKES). The intermediate decay components that is assigned to the CS_2 polarizability fluctuations induced by the intermolecular collision, showed dependence on the volume concentrations of alcohols. This behavior is very different from CS_2/hexane binary solutions. The reduced spectral densities for fast intermolecular motion were obtained from the time-domain signal. The trend of spectral changes upon dilution were similar to that for CS_2/alkane binary systems,. These results suggest that CS_2 molecules would be mainly localized in the non-polar domains formed by alcohol clusters.

Keywords Intermolecular vibration; nonlinear optical properties; ultrafast spectroscopy

1. Introduction

Intermolecular dynamics such as collective motions of hydrogen-bonding modes play important roles in various chemical and biological processes. Femtosecond Raman-induced Kerr effect spectroscopy (RIKES) is a third-order nonlinear spectroscopy that permits observation of such intermolecular dynamics. In RIKES the Raman-active inter- and intramolecular modes of liquid are impulsively excited by a femtosecond pump pulse, and polarization changes of probe pulse induced by depolarized Raman modes are detected as RIKES signal. This method has been used not only for simple molecular liquids [1–8], but also for complex condensed system such as polymer solutions [9–11],peptide, and protein solutions [12, 13]. There have been several reports of RIKES study on the intermolecular dynamics for mixtures of carbon disulfide (CS_2) with other molecules, such as alkanes [3, 4], polymers [11] and ionic liquids [14]. Since CS_2 has a large polarizability anisotropy which offers a strong RIKES signal, CS_2 has been widely used as a probe molecule to investigate the intermolecular potential of the local environment of solutions. In those studies of CS_2/alkane mixtures, the spectral narrowing and peak-shift toward lower frequencies upon dilution were observed in the low-frequency Raman spectrum obtained from the Fourier-transform (FT) analysis of the time-domain RIKES data [3, 4]. Scodinu *et al.* found that

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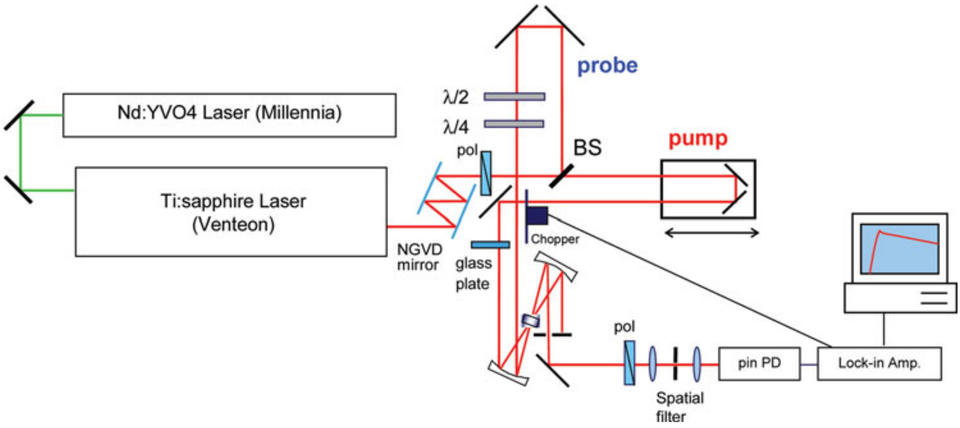

Figure 1. Schematic diagram of the experimental apparatus; pol: polarizer, λ/2: half wave plate, BS: beam splitter.

the microscopic viscosity experienced by CS_2 molecules in the CS_2/alkane binary mixtures differs from the bulk viscosity, and suggested that the microscopic structures of the alkane liquids influence the intermolecular dynamics of CS_2 [3].

In this study, we investigated the intermolecular dynamics of CS_2 /alcohols binary mixtures by RIKES measurements. Since alcohol molecule has a hydroxyl group, it has a large polarity and the hydrogen bonding network among them is expected to be formed. These properties of alcohol are very different from non polar alkanes, and will play a different role to affect the intermolecular potentials of CS_2. The purpose of this study is to gain the insight into the microscopic intermolecular structure of alcohols.

2. Experimental Section

The experimental setup of RIKES measurements is shown in Fig. 1. The light source is a 8 fs Ti:sapphire laser (Nanolayers, VENTEON – Pulse:One) pumped by a Nd:YVO4 laser (Spectra Physics, Millenia). The center wavelength of the Ti:sapphire laser was about 750 nm (it spans from 650 to 850 nm) and the repetition frequency was 150 MHz. The output power of the laser was about 450 mW. The extra-cavity positive dispersion compensation is achieved by a pair of negative-group-velocity dispersion mirrors. The cross-correlation measured at the sample position was about 20 fs full width at half maximum (FWHM), assuming a sech^2 pulse shape. The laser output was split into pump and probe beams with an intensity ratio of 95:5, and the probe beam was optically delayed by a mechanically driven optical stage. The pump beam passed through a half-wave plate to set the polarization at 45 degrees from the probe beam. The two beams were focused on the sample with a small intersecting angle. The polarization change of the probe beam after transmitting through the sample was analyzed by a polarizer, and detected by a pin-photodiode and a lock-in amplifier. RIKES measurements were performed on neat CS_2, and binary solutions of ethanol, 1-butanol and 1-hexanol with different volume fractions of 10, 25 and 50%. All chemicals were purchased from Kanto Kagaku. All the measurements were carried out at 295 K.

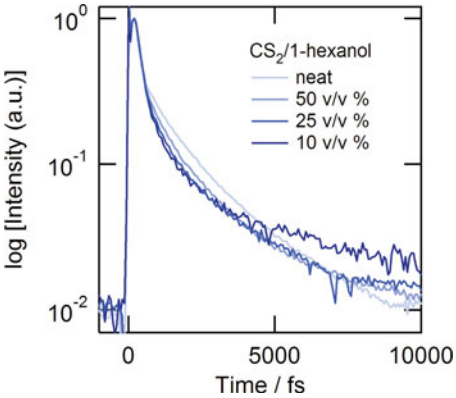

Figure 2. RIKES time-profiles measured for neat CS_2 and the binary mixture of CS_2 and 1-hexanol with different volume fractions.

3. Results and Discussion

Figure 2 compares the RIKES time-profiles of neat CS_2 and the binary mixture of CS_2 with 1-hexanol for different volume fractions. RIKES time-profile contains an instantaneous electronic response at $t = 0$ and a sum of nuclear contributions [3, 4]. The electronic response originates appears at the overlapping region of pump and probe pulses, and does not contain any information for the nuclear dynamics of solutions. The intermolecular nuclear dynamics can be divided into three components as follows; (1) a librational motion of a CS_2 pair (Gaussian-like rise and decay, ca. 150 fs), (2) intermediate collisional motions among CS_2 and between CS_2 and alcohols (sub-picosecond exponential decay with the time constant, τ_{int}) and (3) diffusive reorientational motion of CS_2 molecules (the slowest exponential decay with a few picosecond-scale time constant, τ_{diff}). We analyzed the RIKES time-profiles of binary solutions of ethanol, 1-butanol and 1-hexanol in the time-range after 400 fs, using the following equation,

$$f(t) = A_1 \exp\left(-\frac{t}{\tau_{fast}}\right) + A_2 \exp\left(-\frac{t}{\tau_{int}}\right) + A_3 \exp\left(-\frac{t}{\tau_{diff}}\right). \tag{1}$$

The Gaussian decay tail due to the librational motions of CS_2 was approximated as an exponential decay, τ_{fast}. We will discuss this component later, based on the frequency-domain spectrum separated from the other components by the FT deconvolution analysis. The time constants of intermediate components (τ_{int}) and diffusional components (τ_{diff}) for binary solutions of ethanol, 1-butanol and 1-hexanol with different volume fractions were summarized in Table 1.

The slowest time-constants (τ_{diff}) due to the diffusive reorientation became slower as the alkyl chain length was increased. In general, the diffusive reorientation time is known to be proportional to the bulk viscosity of the solution, in accordance with the qualitative expectations of the Debye-Stokes-Einstein theory [4]. In Fig. 3, the slowest time-constants (τ_{diff}) were plotted as a function of solution's macroscopic viscosities, which were measured by using an Ubbelohde viscometer. The time-constants (τ_{diff}) increased exponentially with the solution viscosities, not linearly. The discrepancy with the Debye-Stokes-Einstein theory can be explained by the existence of a microscopic viscosity that differs from the bulk viscosity [3]. This result suggests that the reorientational motion of CS_2 can be affected by

Table 1. Time-constants for binary mixture of CS_2 and ethanol, 1-butanol and 1-hexanol with different volume fractions

Solvents	ethanol		1-butanol		1-hexanol	
CS_2 (vol%)	τ_{int} (fs)	τ_{diff} (fs)	τ_{int} (fs)	τ_{diff} (fs)	τ_{int} (fs)	τ_{diff} (fs)
100	470	1700	470	1700	470	1700
50	—	—	600	1900	670	2200
25	570	1900	750	3000	930	3500
10	580	2900	860	6200	1000	8100

the local structure of alcohols, which will be discussed later based on the frequency-domain analysis.

On the other hand, the intermediate decay components (τ_{int}), which was previously ascribed to the CS_2 polarizability fluctuations induced by the intermolecular collisions [6, 7], showed a dependence on the mole fraction of alcohols, as shown in Fig. 4. This behavior of the intermediate components is very different from CS_2/hexane binary solutions. In CS_2/hexane binary solutions the intermediate components was $\tau_{int} \approx 470$ fs, showed no dependence on the volume concentrations of hexane (shown together in Fig. 4). τ_{int} became longer as the increasing volume fraction of alcohols, and the lengthening of alkyl chain of alcohols intensified the change in τ_{int} lengthening; τ_{int} at the 10% (v/v) CS_2 concentration was 580 fs (ethanol), 860 fs (1-butanol), and 1000 fs (1-hexanol). The τ_{int} dependence of CS_2/alcohols mixtures seems to be originated from the networking or clustering property of alcohols through hydrogen bonding. That is, the microscopic structure of alcohols varies with its concentration because of the clustering, although the microscopic structure of alkanes does not change and are uniform with its concentrations. Because τ_{int} was fastest for neat CS_2 and became slower with the increasing alcohol concentrations, the fluctuation of CS_2 polarizability that contributes to τ_{int} should be larger for the interactions for a CS_2-CS_2 pair than for CS_2-alcohols and CS_2-alkanes pairs. This result can be rationalized by the

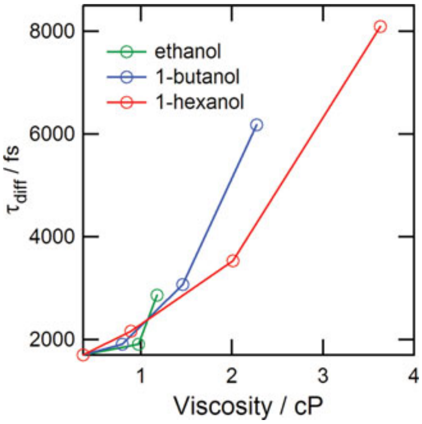

Figure 3. The slowest time-constants (τ_{diff}) for binary mixture of CS_2 and ethanol, 1-butanol and 1-hexanol as a function of viscosity.

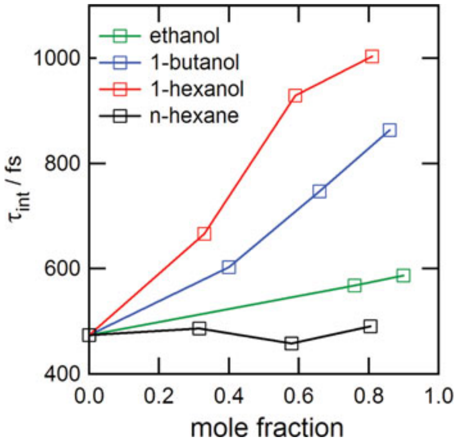

Figure 4. The intermediate time-constants (τ_{int}) for binary mixture of CS_2 and ethanol, 1-butanol and 1-hexanol as a function of mole fraction.

prominent large polarizability of CS_2. Therefore, the reason for the τ_{int} slowing will be due to the isolation of a CS_2 monomer by the incorporation into micelle-like alcohol cluster. This CS_2 isolation model can also explain the result that the larger τ_{int} slowing effect for 1-hexanol than for ethanol; since the longer alkyl chain can give rise to the larger-size micelle clusters, isolation distance among CS_2 monomers should be longer for 1-hexanol than for ethanol.

In order to discuss the fastest intermolecular dynamics due to librational motion for a CS_2 pair, we analyzed the RIKES time-domain signal using Fourier transform deconvolution method [3, 4]. The intermolecular librational response in the time-domain was obtained by subtraction of τ_{int} and τ_{diff} decaying components from a raw RIKES time-profile. Then, a reduced spectral density can be obtained by the Fourier transform of the subtracted time-domain signal, which represent the low-frequency Raman spectra for the librational motion. Figure 5 shows the reduced spectral densities of neat CS_2 and mixture of CS_2 and 1-hexanol

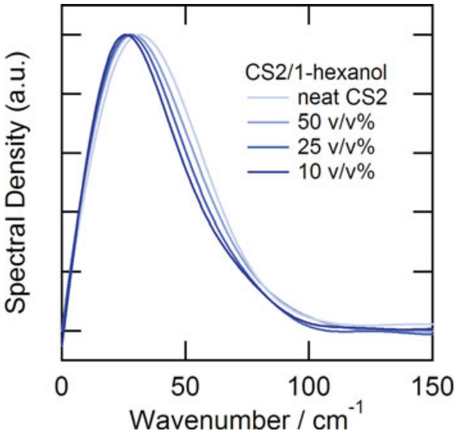

Figure 5. Normalized reduced spectral densities for neat CS_2 and 10, 25 and 50 v/v % of CS_2 in 1-hexanol.

with different volume ratio. As can be seen, the spectra became narrower and red-shifted to the lower frequency region by the dilution with alcohol. Although the trend is similar to that observed for CS_2/alkane binary systems [3, 4], amounts of the low-frequency shift and narrowing are much less than those observed for CS_2/alkane binary systems. The tendency of the low-frequency shift and narrowing of the spectrum suggests that CS_2 molecules are mainly localized in the non-polar domains of alcohol solvent. It is well known that the cluster of alcohol molecules can be formed via hydrogen bonding and the hydrophobic interactions. The similar low-frequency shift and narrowing of the spectrum of CS_2 within the non-polar local domain has also reported in the RIKES study of CS_2 in ionic liquid [14]. Therefore, we conclude that the CS_2 monomer and dimer (or more) are confined in the non-polar domain of the micelle-like alcohol clusters. The low-frequency shift of the librational peak can be explained by the softening of the intermolecular potential between a CS_2 pair by the additional interaction with alcohol molecules upon dilution. The smaller amounts of low-frequency shifts upon dilution would be explained by the increasing amounts of a CS_2 monomer, of which no librational motion is expected.

4. Conclusion

We investigated the intermolecular vibrational motions of several carbon disulfide (CS_2)/alcohols (ethanol, 1-butanol, 1-hexanol) binary solutions by using Raman-induced Kerr-effect spectroscopy (RIKES). The RIKES time-profiles of the binary solutions exhibited three decaying components. The intermediate decay components that is assigned to the CS_2 polarizability fluctuations induced by the intermolecular collision, showed dependence on the volume concentrations of alcohols. This behavior of the intermediate components is very different from CS_2/hexane binary solutions, in which the intermediate components showed no dependence on the volume concentrations of hexane. The reduced spectral densities for fast intermolecular motion were deconvoluted from the time-domain signal by Fourier transform analysis. The trend of spectral changes (lower shift and narrowing) upon dilution was similar to that for CS_2/alkane binary systems, although the amount of the changes was small. These results suggest that the solvent structure of alcohols is inhomogeneous, and CS_2 molecules would be mainly localized in the non-polar domains formed by alcohol clusters.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 24550004) from MEXT Japan, and by Grant-in-Aid for JSPS Fellows (No. 20-2850) from JSPS.

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