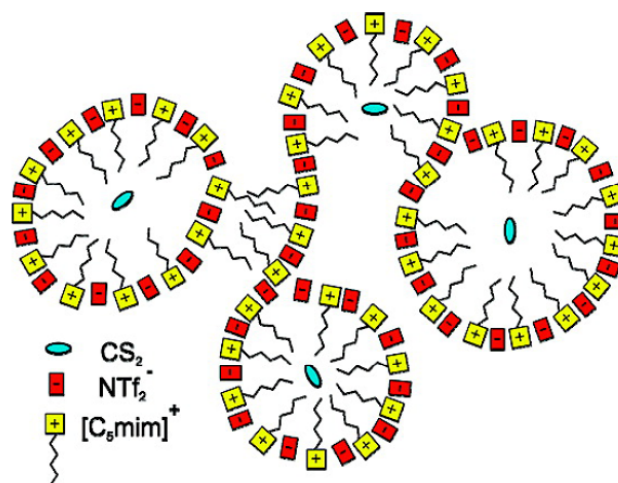


Intermolecular Vibrational Motion of Solute Molecules Confined in Nonpolar Domains of Ionic Liquids

Dong Xiao, Larry G. Hines Jr., Richard A. Bartsch, and Edward L. Quitevis

Abstract



In this study, we address the following question about the dynamics of solute molecules in ionic liquids (ILs). Are the intermolecular vibrational motions of nonpolar molecules confined in the nonpolar domains formed by tail aggregation in ILs the same as those in an alkane solvent? To address this question, the optical Kerr effect (OKE) spectrum of CS_2 in the IL 1-pentyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ($[C_5mim][NTf_2]$) was studied as a function of concentration at 295 K by the use of optical heterodyne-detected Raman-induced Kerr effect spectroscopy. The OKE spectrum broadens and shifts to higher frequency as the CS_2 concentration is decreased from 20 to 10 mol %; at lower concentrations, no further change in the width of the OKE spectrum is observed. Multicomponent line shape analysis of the OKE spectrum of 5 mol % CS_2 in $[C_5mim][NTf_2]$ reveals that the CS_2 and $[C_5mim][NTf_2]$ contributions to the spectrum are separable and that the CS_2 contribution is similar to the OKE spectrum of 5 mol % CS_2 in *n*-pentane with the spectrum being lower in frequency and narrower than that of neat CS_2 . These results suggest that, at this concentration, CS_2 molecules are isolated from each other and mainly localized in the nonpolar domains of the IL.

Results and Discussion

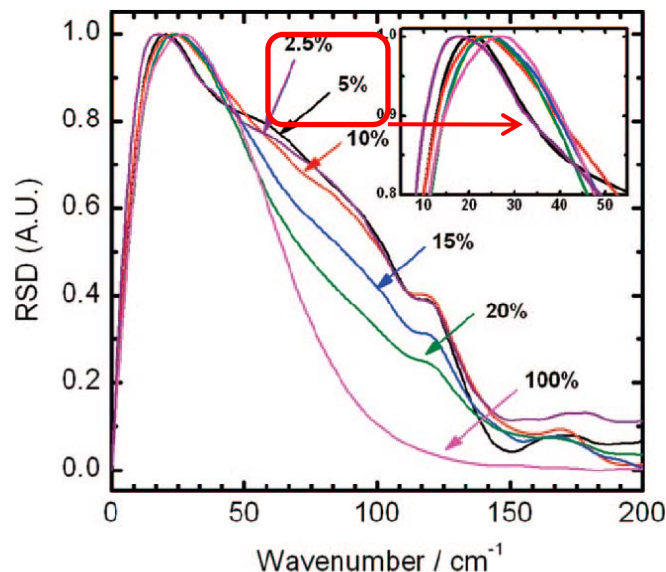


Figure 1. Reduced spectral densities of neat CS_2 and $\text{CS}_2/[\text{C}_5\text{mim}][\text{NTf}_2]$ mixtures at various CS_2 mole fractions at 295 K. The inset is an enlarged view of the region of the peak in the reduced spectral densities.

- upon dilution with $[\text{C}_5\text{mim}][\text{NTf}_2]$, the RSD broadens and shifts to higher frequency, which is not expected given that the RSD of $[\text{C}_5\text{mim}][\text{NTf}_2]$ is higher in frequency and broader ($\langle\omega\rangle \sim 75 \text{ /cm}$; $\Delta\omega \sim 120 \text{ /cm}$) than that neat CS_2 .
- Spectral moment $\langle\omega\rangle$ increases smoothly with decreasing concentration in the range 2.5 to 20 mol %
- Peak frequency ω_{pk} decreases with decreasing concentration in the 2.5 to 20 mol %
- 120 and 169 /cm smaller peaks : intramolecular vibrations of the NTf_2 ion

TABLE 1: Spectral Parameters for $\text{CS}_2/[\text{C}_5\text{mim}][\text{NTf}_2]$ Mixtures

mol % CS_2	$\langle\omega\rangle^a$ (cm^{-1})	ω_{pk}^b (cm^{-1})	$\Delta\omega^c$ (cm^{-1})
2.5	66.7	17.8	97.6
5	63.4	20.5	97.9
10	63.3	23.2	96.3
15	60.5	24.4	81.7
20	58.8	24.1	66.4
100	43.0	25.5	58.8

^a First spectral moment: $\langle\omega\rangle \equiv \int \omega I_{\text{RSD}}(\omega) d\omega / \int I_{\text{RSD}}(\omega) d\omega$, where $I_{\text{RSD}}(\omega)$ is the reduced spectral density with integration limits 0–200 cm^{-1} . ^b Peak frequency. ^c Full width at half-maximum.

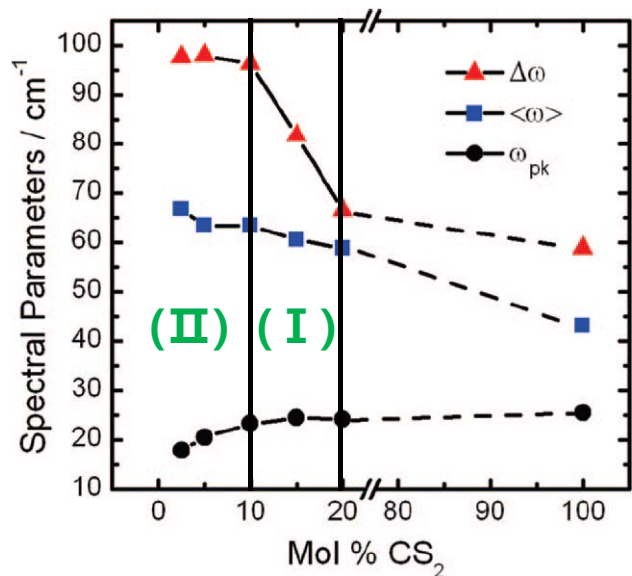
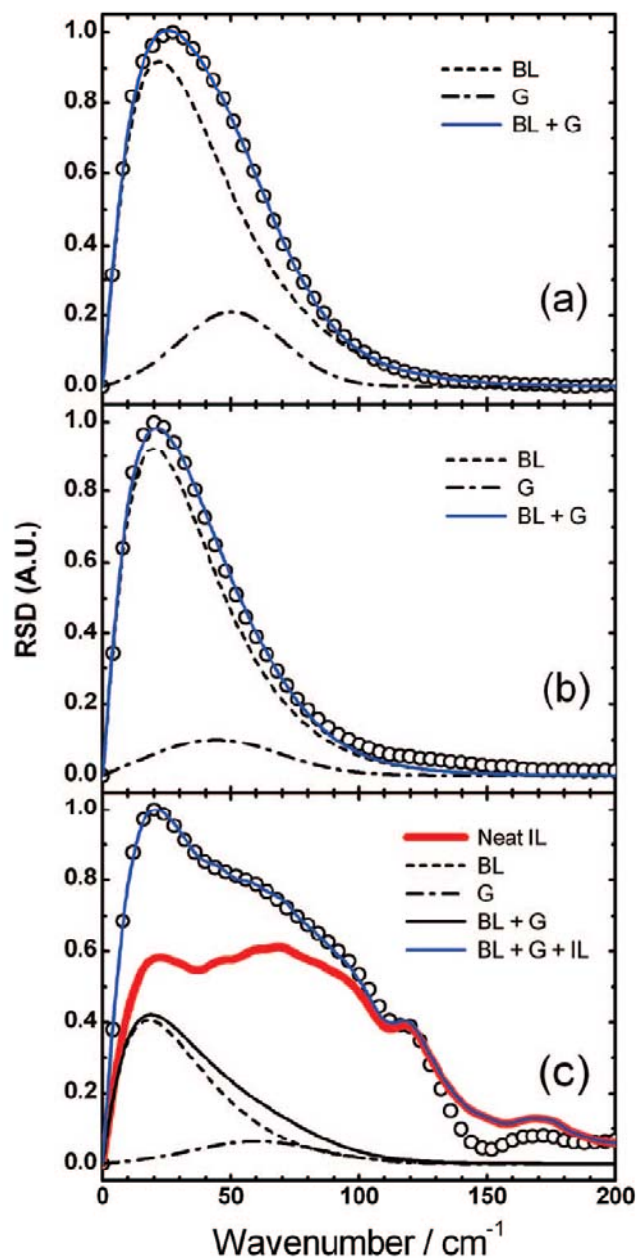


Figure 2. Dependence of spectral parameters for CS₂/[C₅mim][NTf₂] mixtures on the concentration of CS₂. $\Delta\omega$, full width at half-maximum; $\langle\omega\rangle$, first spectral moment; ω_{pk} , peak frequency. The dashed lines connecting the points at 20 and 100 mol % are only intended to show the change in the spectral parameters in going from neat CS₂ to CS₂/[C₅mim][NTf₂] mixtures. Note that CS₂ and [C₅mim][NTf₂] are immiscible for 50 mol % CS₂ and higher concentrations. See Table 1 for values of the spectral parameters.

- Regime I
 - : intermediate concentration between 10 and 20 mol %
 - : RSD dominated by CS₂ contribution

- Regime II
 - : width of RSD independent of concentration
 - : RSD in the region of peak of RSD narrower than RSDs at higher concentration
 - : at 5 mol % average distance between CS₂ molecules $\sim 20 \text{ \AA}$, approximately twice the correlation length $D \sim 11.4 \text{ \AA}$, as determined by small- wide- angle X-ray scattering (D corresponds to the average size of the domain, which includes the alkyl tail domain size and thickness of the charged shell)

- At a CS₂ concentration of 5 mol %, the population of CS₂ molecules in the nonpolar domains of the IL is low.



The intermolecular dynamics of the $\text{CS}_2/[\text{C}_5\text{mim}][\text{NTf}_2]$ mixtures in regime II

$$I_{\text{mix}}(\omega) = \alpha I_{\text{CS}_2}^{\text{mix}}(\omega) + \beta I_{\text{IL}}^{\text{mix}}(\omega) \quad (1)$$

The OKE spectra associated with intermolecular vibrational motions of CS_2 were modeled by two-component line shape function

$$I(\omega) = I_{\text{BL}}(\omega) + I_{\text{G}}(\omega) \quad (2)$$

The low-frequency component is the Bucaro-Litovitz line shape function

$$I_{\text{BL}}(\omega) = A_{\text{BL}} \omega^a \exp(-\omega / \omega_{\text{BL}}) \quad (3)$$

The high-frequency component is the antisymmetrized Gaussian line shape function

$$I_{\text{G}}(\omega) = A_{\text{G}} \{ \exp[-(\omega - \omega_{\text{G}})^2 / 2\varepsilon^2] - \exp[-(\omega + \omega_{\text{G}})^2 / 2\varepsilon^2] \} \quad (4)$$

Figure 3. Reduced spectral density of (a) neat CS_2 (points) with fit of the two-component line shape function (eq 2), (b) 5 mol % CS_2/n -pentane mixture (points) with fit of the two-component line shape function (eq 2), and (c) 5 mol % $\text{CS}_2/[\text{C}_5\text{mim}][\text{NTf}_2]$ with fit of the model line shape function (eq 1). The component bands used in the fit of the reduced spectral densities are also shown. BL, Bucaro–Litovitz line shape function; G, antisymmetrized Gaussian line shape function; IL, reduced spectral density of neat $[\text{C}_5\text{mim}][\text{NTf}_2]$.

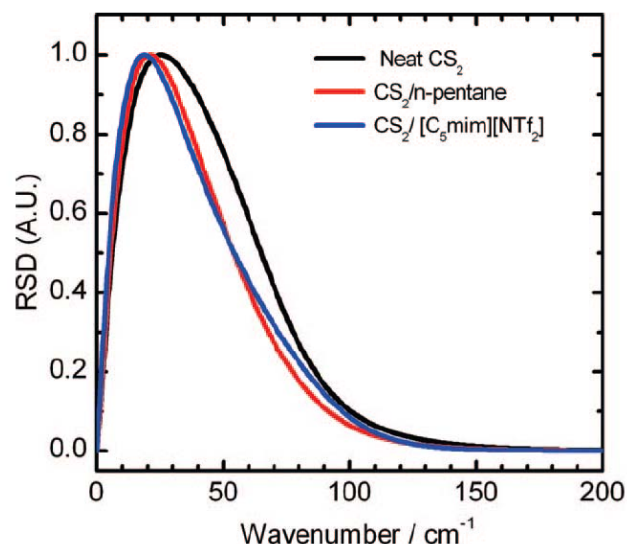


Figure 4. Spectra of the intermolecular vibrations of CS₂ obtained from the sum of the Bucaro–Litovitz and antisymmetrized Gaussian functions (eqs 2–4) corresponding to the reduced spectral densities in Figure 2. See Table 2 for fit parameters.

- The CS₂ contribution to the CS₂/ [C₅mim][NTf₂] mixture is strikingly similar to the CS₂/n-pentane mixture : $\omega_{\text{pk}} \sim 19 \text{ /cm}$, $\Delta\omega \sim 49.7 \text{ /cm}$ for $I_{\text{CS}_2}^{\text{mix}}(\omega)$; and $\omega_{\text{pk}} \sim 21 \text{ /cm}$, $\Delta\omega \sim 48.6 \text{ /cm}$ for the RSD of the CS₂/n-pentane mixture
- Mechanism for shift to lower frequency and narrowing of $I_{\text{CS}_2}^{\text{mix}}(\omega)$ must be similar to that CS₂/n-pentane mixture, which is due to softening of the intermolecular potential by dilution in weakly interacting alkane solvent : because CS₂ – n-pentane interaction are weaker than CS₂–CS₂ interaction, the average intermolecular potential that a CS₂ molecule sees in a dilute n-pentane solution will be weaker than in neat CS₂

TABLE 2: Fit Parameters for Intermolecular Spectra of Neat CS₂, CS₂ in *n*-Pentane, and CS₂ in [C₅mim][NTf₂]

liquid	ω_{pk}^c (cm ⁻¹)	$\Delta\omega^d$ (cm ⁻¹)	Bucaro–Litovitz ^a			antisymmetrized Gaussian ^b		
			A_{BL}	a	ω_{BL} (cm ⁻¹)	A_{G}	ω_{G} (cm ⁻¹)	ϵ (cm ⁻¹)
neat CS ₂	25.5	58.8	0.084	1.14	19.4	0.21	50.2	20.3
CS ₂ /n-pentane ^e	21.0	48.6	0.087	1.18	16.9	0.1	44.0	25.0
CS ₂ /[C ₅ mim][NTf ₂] ^e	19.0	49.7	0.12	1.10	16.4	0.15	60.0	25.0

^a See eq 3 for definition of parameters. ^b See eq 4 for definition of parameters. ^c Peak frequency of the two-component line shape function (eq 2). ^d Full width at half-maximum of the two-component line shape function (eq 2). ^e 5 mol % mixture.

Conclusions

- The OKE spectrum broadens and shifts to higher frequency as the CS₂ concentration is decreased from 20 to 10 mol % ; at lower concentration no further change in the width of the OKE spectrum is observed
- Multicomponent line shape analysis of the OKE spectrum 5 mol % CS₂ in [C₅mim][NTf₂] reveals that the CS₂ and [C₅mim][NTf₂] contributions to the spectrum are separable and that the CS₂ contribution is similar to the OKE spectrum being lower in frequency and narrower than of neat CS₂
- These results suggest that at concentration of 5 mol % or less, CS₂ molecules are isolated from each other and mainly localized in the nonpolar domains of the ionic liquid.