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Time-resolved optical Kerr-effect investigation on CS$_2$/polystyrene mixtures

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The relaxation dynamics of carbon disulfide are investigated in mixtures with polystyrene (PS) using the time-resolved optical heterodyne-detected optical Kerr effect (OHD-OKE). The data are analyzed using both the model-dependent approach, which assumes four distinct temporal responses, and the model-independent Fourier transform approach, which generates a spectral response that can be compared with results obtained by depolarized Rayleigh scattering. A slow dynamics is observed for the OHD-OKE transient decaying exponentially with a time constant that varies from 1.68 ps for neat CS$_2$ to 3.76 ps for the most concentrated CS$_2$/PS mixture. The increase of this time constant accompanies an increase in the viscosity of the mixture, so we can associate this component with the diffusive reorientation process of the induced polarizability anisotropy of the carbon disulfide in the mixture. The short-time nuclear response is characterized in the frequency domain by a broad band that peaks around 30 cm$^{-1}$ for neat carbon disulfide, and is associated with a complex relaxation pattern. The vibrational distribution shifts to higher frequencies when the PS concentration is increased in the mixture. This result is discussed in terms of an increase in the interaction strength between the PS phenyl rings and the carbon disulfide molecules. © 2005 American Institute of Physics. [DOI: 10.1063/1.1994850]

I. INTRODUCTION

The dynamics of molecular motion in liquids attracts a lot of attention. Compared to the solid and gas states, liquids are rather poorly understood on a molecular footing. Most organic and inorganic reactions occur in the liquid state. The role of the solvent in promoting a chemical reaction is to alter the energies of the reactant and product states in order to increase the probability of jumping from one electronic state to another. Improving our understanding of the mechanisms of energy dissipation and transfer between solute and solvent opens the possibility to better predict and enhance the reactions of interest. Experimental investigations have utilized numerous techniques including depolarized Rayleigh scattering, far-infrared absorption, and the time-resolved optical Kerr effect. Each of these techniques has strengths and weaknesses, so there is a great interest in correlating their results, allowing the possibility that they can be used in a complementary manner. Time-resolved techniques have the advantage of accessing, in the same experiment, a wide time range, providing a simultaneous picture of the dynamics taking place on different time scales. The time-resolved optical Kerr-effect (OKE) experiment measures the time evolution of the optically induced third-order polarization anisotropy and, to a certain extent, has the capability of separating the different physical processes that lead the system to relax on different time scales. At long times (typically a few picoseconds in liquids) the motion is generally described by orientational diffusion. For simple molecules such as carbon disulfide, the experimental results can be interpreted on the basis of the Debye-Stokes-Einstein hydrodynamic theory. At shorter times (typically 100–1000 fs) the dynamics consist of complex, nondiffusive intermolecular motions (degrees of freedom) associated with the potential formed by nearby molecules through intermolecular forces. There are various contributions to the nondiffusive response (albeit not yet all known and well separated): interaction-induced (II) anisotropy (including binary collisions) that arises from distortions of the molecular polarizabilities induced by the intermolecular interactions; intermolecular vibration, which include orientational (librational) and translational degrees of freedom; molecular frame distortions associated with molecular collisions; and others. Because the librational motion is believed by some to be the most significant contribution to the subpicosecond dynamics, we will refer to the nondiffusive contribution to the data collectively as the “librational response” for the remainder of the paper.

In this paper we present the experimental results obtained with the heterodyne-detected time-resolved optical Kerr-effect technique performed on a series of mixtures of PS in CS$_2$. The dynamical behavior of neat CS$_2$ is described in the literature. Work has been performed on the dynamical behavior of polymers in solution, but more specifically, the polystyrene (PS) molecule was studied with the depolarized Rayleigh technique and also dispersed as the oil phase in an oil-in-water microemulsion experiment. In recent years, the optical heterodyne-detected optical Kerr-effect (OHD-OKE) dynamics of CS$_2$ dissolved in a series of alkane
II. EXPERIMENT

The ultrafast OHD-OKE measurements were carried out using linearly polarized laser pulses with duration of approximately 100 fs and with a center wavelength of 780 nm (the pulse is characterized by the modified Grenouille method\(^{14}\) and the temporal envelope is well described by a square-root hyperbolic secant). The pulses were generated in a commercial Kerr-lens mode-locked Ti:Sapphire laser (Mira 900 Coherent) pumped by a 5-W (CW) intracavity-doubled diode-pumped Nb:YVO\(_4\) laser (Coherent Verdi). The 250-mW femtosecond laser beam was split into pump (95%) and probe (5%) beams, and the pump beam was optically delayed using a stepper motor resulting in a 16.7-fs/step delay resolution (Fig. 1). Once the polarization of pump beam is determined, a polarizer is placed in the probe beam to achieve a 45° angle relative to the pump. A 20-cm focal-length lens was used to focus the two beams into the sample. To enhance the sensitivity of the signal detection, we used a phase-sensitive lock-in amplifier with a chopper that modulates the pump beam at 1.38 kHz and the probe beam at 1.02 kHz. The signal was detected at the beat frequency of 2.4 Hz. At the sample position, the pulse temporal width was measured with a two-photon absorption photodiode. The ultrafast birefringence signal was obtained with a shot-noise-limited, balanced-detection scheme, as described elsewhere.\(^{15}\) In this setup, the probe beam is circularly polarized with a quarter-wave retardation plate after the sample. Parallel and perpendicular components are separated with a Glan-Thompson polarizer and sent to a pair of photodiodes that are connected to the input channels of the lock-in amplifier. Because the signal is obtained by electronically subtracting the horizontal from the vertical component, both homodyne and background components are canceled out. In turn, the pure heterodyne signal is recorded in a single shot. In addition, balanced detection reduces the effects of random fluctuations of the laser power, and achieves a significant improvement in the signal-to-noise ratio.

Carbon disulfide of spectroscopic grade was obtained from Merck and used without further purification. Styrene from Merck, free from stabilizer, was freshly distilled. The samples were prepared in sealed quadratic glass cuvettes, following a filtration of the liquid mixtures through a 22-μm Millipore filter and several freeze-pump-thaw cycles. The polymerization of the styrene-containing samples was performed in the cuvettes at 333 K as described elsewhere.\(^{16}\) The molecular weight (\(M_n\)) of the polystyrene in the mixtures was determined by GPC\(^{17}\) to be between 1.4×10\(^6\) and 1.5×10\(^5\) g/mol for the different samples, having a broad molecular distribution. All measurements were carried out at a temperature of 293 K.

For determining the femtosecond nondiffusive dynamics, short scans over 2.5 ps were measured with steps of 16.7 fs/point, while to ascertain the diffusive dynamics longer scans over 10 ps were taken with steps of 83.5 fs/point. Each point was averaged over 20 samples and each data set was an average of ten scans. The baseline established before zero time delay was averaged and subtracted from the data, and then normalized prior to fitting. Because the autocorrelation and OHD-OKE signal are measured independently, zero time delay has some uncertainty associated with it. In our experiments this value is around 16.5 fs and is handled in the data analysis as described below.

III. RESULTS AND DISCUSSION

An extensive quantity of time-resolved OKE measurements has been performed on dilutions of CS\(_2\) in a series of alkane solvents, including \(n\)-pentane, isopentane (2-methylbutane), isoheptane (2-methylhexane), \(n\)-tetradecane, and \(n\)-hexadecane.\(^{8,12,13,18}\) In those cases, CS\(_2\) was considered the solute, and the data were interpreted in terms of changes in the intermolecular dynamics when dissolved in the alkane solvents, resulting in spectral changes that were attributed to decreasing intermolecular force constants and a reduced inhomogeneous width. An interesting question that the presents work tries to elucidate is what are the changes in the dynamical properties of CS\(_2\) when considered as a solvent for a complex solute like PS? First, we analyze the molecular dynamical behavior of neat CS\(_2\) (this result can be compared with known literature\(^{7,8,19}\)). Figure 2(a) illustrates a typical short-scan OHD-OKE response for neat CS\(_2\) at 293 K together with the fitted complete nonlinear-response function and the constituent functions that compose it (next we discuss the model functions we used). To examine how the signal relaxes for longer times, Fig. 2(b) shows a semilog plot of a long scan, together with a response generated to reproduce the measured 1.68-ps decay time of the diffusive reorientation process. In order to better reveal the ultrafast dynamics, Fig. 2(c) presents the data with this orientational response subtracted off. The residual curve has a shoulder at zero delay that relaxes rapidly (≈100 fs), and an exponential decay exhibiting a time constant of ≈400 fs. Including the instantaneous electronic component, the signal must be de-
scribed by four dynamically distinguishable contributions. Similar results have been obtained for the OHD-OKE for various anisotropic molecular liquids investigated to date, including acetonitrile, benzene, chloroform, and methyl iodide.

For pump, probe, and local oscillator pulses derived from a single transform-limited optical pulse, the OHD-OKE signal is the convolution of the autocorrelation, $A_\tau(t)$, and the molecular nonlinear-response function, $R(t)$,

$$I(\tau) \propto \int_{-\infty}^{\infty} dt A_\tau(t) R(\tau-t)$$

$$= A_\tau(t) \otimes R(t) = A_\tau(t) \otimes [\sigma(t) + r(t)].$$  

(1)

The analysis of Eq. (1) was developed by McMorrow et al.

For optical pulses far from an electronic resonance, the Born-Oppenheimer approximation holds and the response function $R(t)$ can be written as the sum of electronic, $\sigma(t)$, and nuclear contributions, $r(t)$. When analyzing experimental data, it is interesting to describe the dynamics of the sample under study in terms of a simple model that achieves all the features of the signal and that minimizes the number of free-fitting parameters. The fast electronic contribution can be simply described by a Dirac delta function multiplied by a real constant that depends on the sample under study. The nuclear part of the nonlinear-response function can be treated as a sum of contributions $r(t) = \sum r_j(t)$. In making this sum, it is assumed that the different processes described by each response function are independent and generally relax on different time scales. Now, we have to assume model functional forms for the different response functions, $r_j(t)$, with the various parameters left to be adjusted to obtain the best agreement with the experimental data. For intermolecular dynamics of simple symmetric species (such as CS$_2$ and CH$_3$CN, for example), the experimental OHD-OKE data have revealed the existence of three distinct time scales resulting in a minimum of three terms in the sum when the individual $r_j(t)$ are treated as exponential and damped sinusoidal functions. The assignment of the three contributions to specific nuclear coordinates of well-defined physical processes, however, lacks rigorous physical justification. The three nuclear-response functions are modeled as

$$r_1(t) = a_1 \exp \left( -\frac{t}{\tau_{\text{diff}}} \right) \left[ 1 - \exp \left( -\frac{t}{\tau_{\text{rise1}}} \right) \right],$$

(2)

$$r_2(t) = a_2 \exp \left( -\frac{t}{\tau_{\text{int}}} \right) \left[ 1 - \exp \left( -\frac{t}{\tau_{\text{rise2}}} \right) \right],$$

(3)

$$r_3(t) = a_3 \exp \left( -\frac{\alpha^2 t^2}{2} \right) \sin(\omega_0 t).$$

(4)

Equations (2) and (3) correspond, respectively, to the diffusive ($\tau_{\text{diff}}$) and intermediate ($\tau_{\text{int}}$) relaxation processes observed in the OHD-OKE signal. The intermediate process is intriguing in the sense that this time is too short to be associated with a collective diffusive reorientation process. This response function has been discussed in the OKE literature, and at the moment the most promising interpretation is given by McMorrow and co-workers in terms of an inhomogeneously broadened harmonic-oscillator model of intermolecular nuclear coordinates. In that model, the oscillators are strongly damped, but are always underdamped (they approach the classical critically damped case in the low-frequency limit), giving rise to the constructive and destructive interference resulting in the unique temporal profiles that are characteristic of the femtosecond OKE dynamics of liquids. To account for the inertial response of the nuclear motion, it is necessary to include a rise time. Our model requires two rise times [Eqs. (2) and (3)] which, in fact, cannot be measured independently, and we note that the other fitting parameters are quite independent of these times. Correspondingly, we set the two equal to a value of $\tau_{\text{rise}} = 140$ fs that is consistent with values used in the literature.

Equation (4) represents the dephasing of a Gaussian distribution of low-frequency oscillators around the principal fre-
The LV algorithm did not show consistency in the model fitting results, mainly because of the great number of free parameters. Its convergence is highly dependent on the initial parameters, i.e., if the time-constant decays are previously known, it will fit properly. However, for the data of this paper that is not the case. The use of the EvoAlg is much more flexible in this prerequisite. The EvoAlg approach has been used in several applications. One of the authors has used it in the data analysis of pump and probe experiments to fit complex relaxation phenomena in biomolecules such as β-carotene. In this work, the EvoAlg is adapted to fit OHD-OKE data. It uses several vectors, called “individuals,” which compose a generation. Each vector is formed by parameters related to the time-constant decays (diffusive and intermediate), amplitudes, and parameters of the model already discussed above. The first generation is created randomly within a certain range at the first interaction. For example, for neat CS₂, the diffusive term was typically allowed to vary between 1.3 and 2.0 ps. For the mixtures the range was kept about the same, but was translated to slower decays, as suggested in the literature. For other parameters, since they were unknown prior to this work, the range was fixed to the limits plus 50% of similar systems. The randomly generated first population maps all the space formed by all variables with its 196 different individuals. The best individuals, i.e., those with the smallest difference (actually $\chi^2$) between the experimental transients and the associated fitting are mutated and recombined to form a new generation. This process is repeated again with the new best individuals. This search converges when a variation of the $\chi^2$ smaller than $10^{-5}$ between successive generations is reached. It is important to note that the EvoAlg does not give error bars for the best individual. The error is calculated after several “runs” of the algorithm. The best individuals of each run are averaged and the error of each parameter is calculated. The lack of convergence of a run or a large error bar may indicate that the fitting model is not adequate or the data quality is not good. In this work, in all fitting analysis the algorithm converged consistently.

In Fig. 3 we show the measured signal for neat CS₂ and for the three different mixture concentrations with PS together with the traces obtained adjusting the model (dashed lines). From top to bottom: Neat CS₂, 20% by wt PS, 40% by wt PS, 60% by wt PS. The curves are offset vertically for clarity.

![Figure 3](image-url)
To eliminate the hypotheses that there is some contribution to the diffusive relaxation coming from the PS molecules in the mixtures, we show Fig. 4, which is the OHD-OKE signal of a mixture of 80% by wt PS in CCl4 solvent. This solvent possesses an isotropic polarizability; that is, all relaxations associated with orientational motion are absent, except for a small amplitude contribution due to interaction-induced anisotropy, as also extracted from OKE measurements. The polymer is composed of styrene monomer units that have a considerable polarizability anisotropy (5.4 Å³), suggesting that the major contribution to the signal comes from it. As can be seen, the signal relaxes on a time scale of 700 fs. This result has been reported previously and can be associated to the librational dynamics of the phenyl rings that are attached to the carbon-chain backbone. To account for this relaxation contribution it is necessary to introduce another exponential term like Eq. (3). This contribution is listed in Table I as $\tau_{pol}$, and the amplitude $a_4$ is only 6% of the total signal amplitude. It is interesting to note that the intermediate time constant does not change when more PS is added to the mixture, suggesting that the physical mechanism that leads to this relaxation is not altered as the polymer concentration is varied, lending no new insight into the origin of this decay that has been challenging several groups. Concerning the librational motion of CS$_2$, the parameter associated with the half-width Gaussian distribution of librational frequencies, $\alpha$, also does not change with variations of polymer concentration in the mixture, suggesting that the intermolecular inhomogeneity is not altered by the PS introduction. Nevertheless, an interesting result is the increase in the characteristic frequency of the librational distribution, $\omega_0$, reflecting a strengthening of the intermolecular potential in which the CS$_2$ molecules librate, so we take a closer look at these spectral features.

To describe the nondiffusive part of the nuclear response, we follow the Fourier transform deconvolution procedure developed by McMorrow and Lotshaw. Briefly, taking the Fourier transform of the OHD-OKE signal we have

$$\mathcal{F}\{I(t)\} = \mathcal{F}\{A_c(t)\} \mathcal{F}\{R(t)\},$$

(5)

where we used the property of the Fourier transform for the convolution. The deconvolution is accomplished by computing the complex quotient

$$\frac{\mathcal{F}\{I(t)\}}{\mathcal{F}\{A_c(t)\}} = \mathcal{F}\{R(t)\} = D(\omega).$$

(6)

Since the instantaneous electronic contribution is simply described by a real constant that multiplies a Dirac delta function, this will not contribute to the imaginary part of the spectral distribution. So, as modeled, the information about all possible nuclear motions is contained in the imaginary part of the spectral distribution, Im[$D(\omega)$].

Figure 5(a) shows the low-frequency spectral distribution for neat CS$_2$. A valid spectrum is obtained if the time reference (zero delay between pump and probe) of the auto-correlation and OHD-OKE signals is identical. We used the same criteria from literature that is, we empirically corrected the zero delay of the signal by up to two step values (25 fs) in order to obtain a spectrum that is positive from 0 cm$^{-1}$ to the highest possible frequency, while at the same time minimizing any background. To better access the nondiffusive nuclear part, we subtracted the diffusive component prior to the deconvolution procedure.

Figure 5(b) shows the spectral distribution for neat CS$_2$ and for the three mixtures. The full width at half maximum of the observed frequency distribution remains unaltered, reflecting the analogous behavior observed for the parameter $\alpha$. The most noticeable result is the displacement of the librational distribution to higher frequencies as the concentration of PS is increased. This corroborates the work of da Silveira et al., in which the CS$_2$/PS system was analyzed by means of the depolarized Rayleigh-scattering technique.
Motivated by these results, another work of da Silveira et al.\textsuperscript{11} showed an \textit{ab initio} determination of the C\textsubscript{6}H\textsubscript{6} – CS\textsubscript{2} cluster stabilization energy. The results of that work indicate the existence of weakly bound complexes between benzene and CS\textsubscript{2}. The benzene molecule was chosen in that study as the best analog to the phenyl ring that composes the styrene monomer. In this sense, the shift of the spectral distribution may reflect the expected interaction between the phenyl ring and the CS\textsubscript{2} molecules when the concentration of PS in the mixture increases.\textsuperscript{1} This is most evident in passing from the 40% by wt to the 60% by wt of PS, which shows the greatest spectral shift. Given that the molecular weight of the styrene molecule is 104.15, and that of the carbon disulfide molecule is 76.14, the 60% by wt mixture has a molar fraction of 0.52, corresponding to the situation where the number of molecules of each component of the mixture is approximately the same (that is, the CS\textsubscript{2} molecules and the styrene monomers that compose the polymer), resulting in the best structural conformation in the sample.

IV. CONCLUSIONS

Using the heterodyne-detected time-resolved optical Kerr-effect technique, we investigate the time evolution of the molecular dynamics for a series of mixtures of PS in the CS\textsubscript{2} probe solvent. This technique, combined with the Fourier transform data analysis, is particularly well suited for probing low-frequency intermolecular motions in liquids. The experimental data fitting were performed using the evolutionary-genetic procedure. The first important result of our work is that the decay of the orientational anisotropy of the CS\textsubscript{2} molecules, associated with the diffusive reorientation time, varies with the microviscosity of the polymer solutions; that is, the relaxation time varies from 1.68 ps for neat CS\textsubscript{2} to 3.76 ps for the most concentrated CS\textsubscript{2}/PS mixture. We associate this result with the frictional intermolecular forces experienced by the CS\textsubscript{2} molecules that change when the concentration of the mixture increases. No observable change occurs for the intermediate time decay when PS is added to the mixture, suggesting that its physical mechanism is unaltered in the mixtures in relation to the neat CS\textsubscript{2}. Concerning the nondiffusive subpicosecond motion, which we refer in a simplified form as librational motion, the results are as follows. The parameter associated with the half-width Gaussian distribution of librational frequencies, \( \alpha \), does not change with the increase of polymer concentration in the mixture, indicating that the system inhomogeneity is not altered by the PS introduction. Through variations in the concentration of the mixture, it is possible to vary the effective intermolecular potential in a nearly continuous fashion. Our results show that as the PS concentration is increased the principal librational frequency \( \omega_0 \) shifts to higher frequency, consistent with a strengthening of the intermolecular forces between the phenyl rings of the PS molecules and the CS\textsubscript{2} molecules. This association is corroborated by the fact that as CS\textsubscript{2} molecules are replaced by the more strongly interacting phenyl rings, the net effect is to increase the curvature of the intermolecular potential. This result is consistent with an intermolecular vibrational model, in which the molecules execute a constrained, or hindered, angular motion (or librational motion). As the potential acquires a more positive curvature through intermolecular interactions, the librational motion frequency increases.

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