Microscopic Origin of the Optical Kerr Effect Response of CS_2−Pentane Binary Mixtures

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The femtosecond optically heterodyned detected optical Kerr effect (OHD-OKE) response of carbon disulfide/pentane binary mixtures is reported for various concentrations. As pentane is added, three trends are observed: the instantaneous electronic contribution gets more pronounced, the picosecond diffusive reorientation becomes faster, and the subpicosecond inertia-limited response slows down. The corresponding frequency domain representation of the latter component narrows and shifts toward lower frequencies. These spectral changes occur exclusively when the CS_2 concentration is lowered from 100 to 20 vol %; at still lower concentrations no further changes are observed. When the nondiffusive part of the optical response is assigned exclusively to coherent intermolecular vibrations, the spectral changes can be attributed to a reduced inhomogeneous broadening, reflecting a narrowing of the distribution of oscillator frequencies. However, we argue here that because of the observed concentration dependence the validity of this model is questionable. Long-range interaction-induced effects and short-range collision-induced processes are additional scattering mechanisms that may contribute substantially to the observed spectra.

I. Introduction

Light scattering is a very suitable tool for studying intermolecular dynamics in liquids, as was pointed out already in the early days of spectroscopy by Raman.[1] The broadening of the depolarized Rayleigh line was associated with the anisotropy of the molecular polarizability and attributed to several mechanisms such as collision-broadened rotational lines and local density fluctuations.[2] Following many experiments, a large variety of models was proposed for explaining the shape of this line, located close to the zero-frequency shift. However, up to now a full perception of the underlying processes and, hence, of the intermolecular structure and dynamics in liquids is still lacking.

A first quantitative theory of Rayleigh scattering in liquids was formulated in 1941 by Leontovich, who showed that a diffusion-controlled decay of the polarizability anisotropy will lead to a Lorentzian line shape.[3] It was found experimentally by Starunov[4] and by Shapiro and Broida[5] that the depolarized Rayleigh line of simple organic fluids like benzene and carbon disulfide (CS_2) deviates from the predicted Lorentzian shape at frequencies above a few wavenumbers. According to Starunov this might be due to inertial corrections in the diffusion process at early times[6] or due to coherent oscillations of the molecule as a whole in the potential defined by its neighbors.[7,8] Litovitz and co-workers[9,10] reported exponential line shapes at high frequencies (from several tens up to more than hundred wavenumbers) for a number of atomic and molecular liquids. These features, which are not fully described by Starunov's theory, were attributed to short-range electronic overlap effects and molecular frame distortions.[11] A number of other authors evoked long-range dipole−induced dipole (DID) interactions for the explanation of the depolarized Rayleigh wing.[12−22] Also, the possible influence of cooperative effects due to microscopic ordering in the liquid was considered.[13−15,23−25]

When laser pulses with durations of the order of 100 fs became available,[26] a variety of time-resolved spectroscopic techniques was developed to probe the dynamics in the Rayleigh wing.[27−31] Among these methods, which provide information equivalent to the traditionally used spontaneous scattering,[32−34] the optical Kerr effect (OKE)[35−42] is very powerful, since it allows for the implementation of optical heterodyne detection and model-independent deconvolution in frequency space.[42]

While the early light-scattering studies investigated mainly the interplay of the different *scattering mechanisms* responsible for the depolarized Rayleigh wing, the recent time-resolved studies focused more on the *time scale(s) of the fluctuations* that cause the line width.[43−45] The unambiguous separation of the dynamic and static contributions to the line width, often modeled as homogeneous and inhomogeneous dephasing, is crucial for a detailed picture of liquid-state phenomena. The line width of the intermolecular vibrations reflects the distribution and evolution of local potentials but also the possibly frequency[4] or quantum number[46,47] dependent friction due to interactions with the neighboring molecules.

As was shown by Mukamel and co-workers,[48,49] all spontaneous and stimulated nonresonant third-order vibrational spectroscopies measure, in principle, the total spectral density. Because these techniques all depend on the one-time (two-point) correlation function of the polarizability, they are not sensitive to the specific line-broadening mechanism. To characterize the time scale(s) of the underlying dynamics it was proposed to probe higher-order correlation functions by multiple pulse experiments.[48,49] Examples for this approach are the Raman echo[50−52] and temporally two-dimensional fifth-order Raman scattering.[53−60]

Information on the relative importance of the different scattering mechanisms can be obtained from experiments on binary mixtures.[5,16,22,23,61−64] Based on trends in their results, Chang and Castner[62] could assign features in the Rayleigh wing spectrum of formamide in a number of polar solvents to hydrogen networks. McMorrow and coworkers[61,63] reported the optical Kerr effect response of CS_2 in a number of alkanes. The

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observed spectral changes upon dilution were attributed to decreasing intermolecular force constants and a reduced inhomogeneous width.

In this paper we present the optically heterodyned detected optical Kerr effect (OHD-OKE) response of CS_2/pentane binary mixtures for various concentrations, ranging from 100 down to 3 vol % CS_2.[65] As was already observed by McMorrow et al.[61,63] the spectrum shifts toward lower frequencies and becomes narrower upon dilution. These changes occur exclusively at concentrations higher than 20 vol %, indicating that CS_2 is completely "dissolved" when it is on average surrounded by only two pentane molecules. This unexpected feature has not been reported before. The data can be explained quantitatively by a partly inhomogeneously broadened Brownian oscillator model[49] that allows for a continuous change from underdamped to overdamped motion within an inhomogeneous distribution of frequencies. The results of our numerical analysis agree qualitatively with those of ref 61, where the oscillator was described classically: upon dilution the inhomogeneous width decreases, while the homogeneous decay rate does not change significantly. This *decrease* of the inhomogeneous broadening in the CS_2/pentane binary mixture occurs primarily while the distribution of local structures *increases*. It is therefore argued that this interpretation does not provide a complete explanation for the observed concentration dependence. We attribute a large part of the observed spectral changes to the concentration dependence of other mechanisms such as short-range collision-induced effects due to electronic overlap and/or molecular frame distortion and interaction-induced effects.

This paper is organized as follows: In section II, experimental details are given. The results of OHD-OKE experiments on CS_2/pentane binary mixtures are presented in section III. Subsequently, in sections IV and V these results are analyzed. The single-molecule orientational contribution to the OKE response is modeled by a set of Brownian oscillators in section IV. Additional scattering mechanisms are discussed in section V. The paper ends with some concluding remarks.

II. Experimental Section

The third-order nonlinear optical experiments reported in this paper were performed using a home-built CPM laser[26] with a subsequent six-pass bow-tie amplifier[66] that is pumped by a copper vapor laser. Except for some minor modifications the laser system is identical to that used by Nibbering et al.[67] It produces 45 fs laser pulses at 620 nm with a repetition rate of 8.8 kHz and a pulse energy of 1.5 μJ. A set of two prisms in nearly retro reflecting geometry is used to compensate for the group velocity dispersion of the amplifier and the delay setup.

The OHD-OKE experiments were performed in a pump-probe configuration similar to that reported by McMorrow and Lotshaw:[40,42] The probe pulse is split off by an optically flat glass with a reflectivity of 10%, variably delayed by a computer-controlled delay stage, passed through a vertically orientated Glan−Taylor polarizer and a broad-band λ/4 plate, and focused into a 1 mm path length fused silica cell by an uncoated 100 mm focal length achromatic doublet. After the sample the probe beam is recollimated and analyzed by a second, horizontally orientated Glan-Taylor polarizer. The transmitted probe light is detected with a photodiode whose signal is processed by a lock-in amplifier. The pump beam is modulated at 1.2 kHz, polarized by a third Glan-Taylor polarizer that is orientated under 45°, focused with the same doublet lens and blocked after the sample. The pump modulation frequency serves as reference signal for the lock-in amplifier.

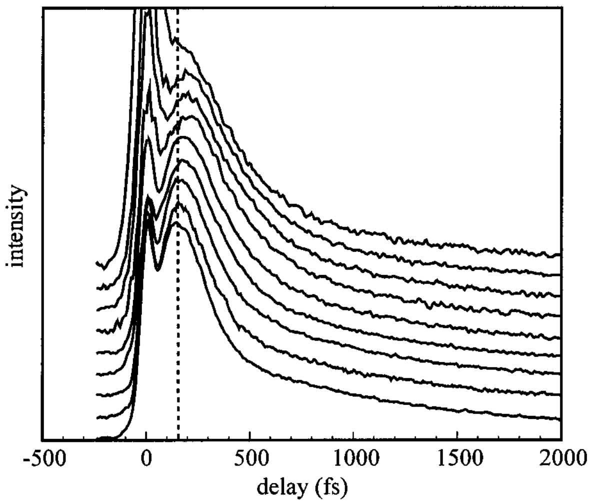

Figure 1. Short-time part of the OHD-OKE response of CS_2/pentane binary mixtures. The volume fractions of CS_2 are (from bottom to top) 100%, 80%, 67%, 50%, 33%, 20%, 11%, 6%, and 3%. Three different contributions can be recognized: (i) at zero delay instantaneous response due to electronic hyperpolarizability; (ii) at long delay (<1 ps) exponential decay due to diffusive reorientation; (iii) In the subpicosecond range inertia-limited response with a finite rise time and a nonexponential decay. The traces are normalized on the maximum of the nuclear response.

Optical heterodyning of the OKE signal is achieved by opening the input polarizer of the probe by 1−2° which introduces a 90° out-of-phase local oscillator.[40,42] The OHD-OKE experiments have been performed using attenuated amplified pulses with pulse energies of less than 20 nJ. The sign of the local oscillator was reversed by rotation of the input polarizer after each third scan which allows for the elimination of the homodyne part of the signal.[68,69]

Fresh samples of CS_2 and pentane (both Merck, spectroscopic grade) were prepared for each experiment. To remove dust particles, the samples were passed through a filter of 0.1 μm pore size when injecting into the cuvet.

III. Results

In Figures 1 and 2 the short- and long-time parts of the OHD-OKE response are presented, respectively. The general features of the Kerr response and their changes upon dilution agree basically with the observations of McMorrow and co-workers.[40,61,63] The sharp peak at zero delay, which follows the second-order intensity autocorrelation of the pump and probe pulses, is due to the instantaneous electronic hyperpolarizability, while the delayed signal arises exclusively from nuclear motions.[32,40] This latter contribution decreases relative to the electronic part as pentane is added, since for neat pentane the ratio of the electronic hyperpolarizability to the nuclear response is much larger than for CS_2 as is evident in Figure 3. Pentane is chosen as cosolvent because it is chemically inert and has, even at the highest concentration, no significant nuclear response compared to that of CS_2.

For delays longer than 2 ps the signal decays single-exponentially with time constants ranging from 1.70 ps for pure CS_2 down to 1.25 ps for a 3 vol % solution of CS_2 in pentane as is shown in Figure 2. In the frequency domain this exponential decay corresponds to the Lorentzian line close to zero frequency that was first discussed by Leontovich.[3] It is attributed to rotational diffusion of the anisotropically polarizable CS_2 molecules. As was found already by Kalpouzos et al. the

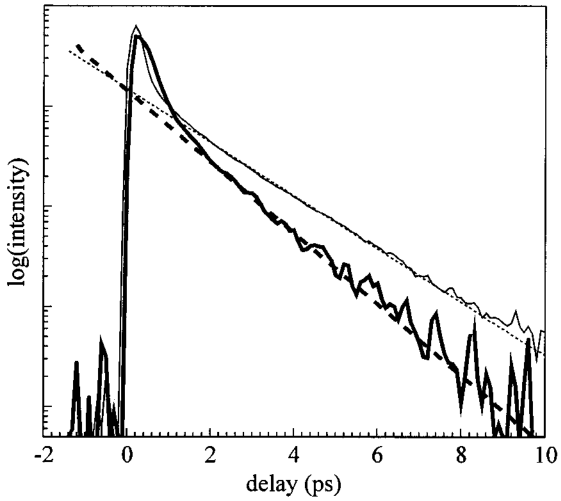

Figure 2. Long-time part of the OHD-OKE response of neat CS_2 (thin solid line) and of 3 vol % CS_2 in pentane (thick solid line). At delays longer than 2 ps the signal intensities fall off exponentially with decay constants of 1.70 ps for the neat liquid (thin dashed) and 1.25 ps for the mixture (thick dashed). For small delays the signals show a distinct nonexponential behaviour. Consult the text for details.

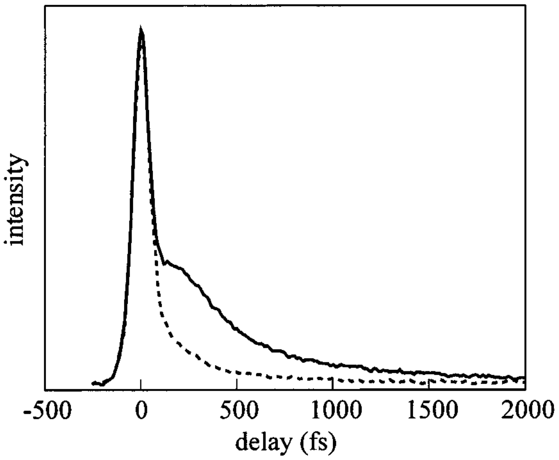

Figure 3. Short-time part of the OHD-OKE response of neat pentane (dashed) and 3 vol % CS_2 in pentane (solid). Even at this low concentration the nuclear signal is mainly due to CS_2. These curves were normalized on the electronic hyperpolarizability.

decay becomes faster with increasing pentane concentration, which can be correlated directly with the bulk viscosity of the mixtures.[61]

At early delay times the signals of Figure 2 deviate from the exponential decays, which corresponds to the non-Lorentzian line shapes at high frequencies first reported by Starunov[4] and by Shapiro and Broida.[5] The microscopic mechanisms responsible for this excess spectral density will be examined thoroughly in the next sections. Here, we first discuss some features that are independent of the specific scattering mechanisms. As shown in Figure 1, the nuclear part of the signal reaches its maximum at finite pump-probe delays of the order of 200 fs, which is followed by a nonexponential decay. With increasing pentane concentration the rise and the subsequent decay both slow down.

The delayed buildup of the response is due to the inertial character of the induced motions:[28,40] During the ultrashort pump pulse the molecules hardly change their position because of their finite moment of inertia. Only after a certain delay time the acquired momentum leads to an appreciable deviation from the initial positions, resulting in a delayed Kerr effect signal. In an OHD-OKE experiment these inertia-limited dynamics are probed by impulsive stimulated Raman scattering:[70−73] All depolarized Raman-active modes of the liquid having a period T longer than the pulse duration τ_p are excited coherently. The 45 fs pulses used here provide access to the spectral density between 0 and 300 cm^{-1}. This region comprises the entire range of the (thermally activated) intermolecular motions.

The measured OHD-OKE signal is not identical to the true material response because the modes with higher frequencies are excited less efficiently due to the finite duration/bandwidth of the employed laser pulses. The incorporation of optically heterodyning allows us to remove these spectral filter effects by a deconvolution procedure in frequency space: Dividing the Fourier transform of the OHD-OKE signal by the Fourier transform of the intensity autocorrelation gives a frequency representation of the true material response $R^{(3)}(\omega)$ that is free of spectral filter effects.[41,42] All information about the nuclear response is contained in the imaginary part of this complex ratio while the instantaneous electronic response shows up only in the real part. Transformation back to time domain gives the nuclear part of the third-order time domain response function, $R^{(3)}(t)$.

To evaluate the subpicosecond nondiffusive component more carefully, McMorrow and Lotshaw[42] proposed to remove the diffusive component prior to the Fourier deconvolution procedure. Here, we model the exponentially decaying part of the signal by an effective overdamped harmonic mode, which can be characterized either by a damping rate Γ and an effective frequency $\Omega_{eff} = (\Gamma^2/4 - \Omega^2)^{1/2}$ or by exponential rise and decay times τ_R and τ_D:[46,49,58]

$$R^{(3)}_{diff}(t) = e^{-\Gamma t/2}\frac{1}{\Omega_{eff}}\sinh(\Omega_{eff}t) = \frac{1}{2\Omega_{eff}}(1 - e^{-t/\tau_R})e^{-t/\tau_D} \qquad (1)$$

As evident from Figure 2, the decay time τ_D can be determined with high accuracy. The value for rise time τ_R, which is introduced phenomenologically to account for a delayed onset of the diffusion, is not so easily established. As was demonstrated by McMorrow and Lotshaw,[74] the particular choice of τ_R has only a minor influence on the shape of the remaining signal.

We removed the diffusive component before the Fourier transformation, assuming a rise time $\tau_R = 130$ fs for all mixtures. The deconvoluted spectra, shown in Figure 4 for the various solutions, directly display the deviations from the Lorentzian line shape, free of the electronic response and unaffected by any spectral filter effects. Upon dilution, the width of the spectral response decreases and the maximum shifts toward lower frequencies. This could, in principle, be inferred directly from the time domain data of Figure 1, but there these modifications are partly masked by the electronic and diffusive contributions. The main changes in the spectra occur when the volume fraction of CS_2 is decreased from 100% to 33% while no significant changes occur below 20%. This suggests that CS_2 is completely “dissolved” when there are about 2 pentane molecules/CS_2 molecule.[65] This unexpected, rather counterintuitive finding will play a crucial role in the microscopic interpretation of the data, which will be treated in the next two sections.

IV. Single-Molecule Orientational Motion

For the discussion of the microscopic scattering mechanisms responsible for the non-Lorentzian line shape in the Rayleigh wing, we want to refer to concepts originally introduced in depolarized light scattering (DLS). The DLS spectrum $I(\omega)$, which has essentially the same information content as the time-

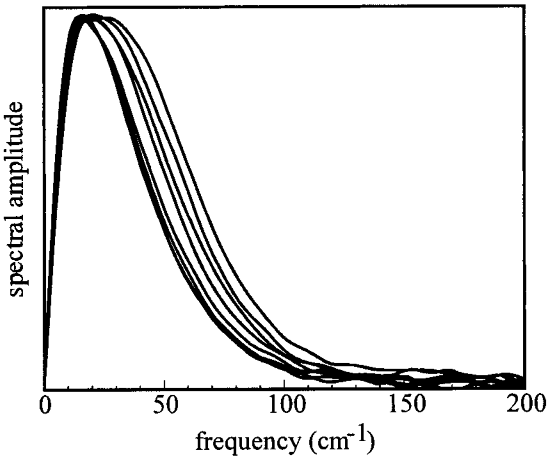

Figure 4. Normalized frequency domain representations of the non-Lorenztian (subpicosecond) part of the deconvoluted OHD-OKE response of all mixtures shown in Figure 1. The spectrum becomes narrower and shifts toward lower frequencies when the concentration of CS_2 decreases. From the right to the left, the curves correspond to CS_2 volume fractions of 100%, 80%, 67%, 50%, and 33%. The curves for 20% and lower concentrations are almost identical.

resolved OHD-OKE experiment,[32−34] is related to the classical correlation function $C(t)$ of the anisotropic part Π_2 of the macroscopic polarizability via the fluctuation-dissipation theorem.[75] $C(t)$ is given by[15,75]

$$C(t) = V^{-1} \langle \mathrm{Tr}\{\mathbf{\Pi}_2(0):\mathbf{\Pi}_2(t)\}\rangle \tag{2}$$

where $\mathbf{\Pi}_2$, an irreducible tensor of rank two, is defined by

$$\mathbf{\Pi} = \Pi_0 \mathbf{1} + \mathbf{\Pi}_2 \tag{3}$$

Here, $\mathbf{1}$ and $\mathbf{\Pi}$ denote the unity tensor and the total macroscopic polarizability tensor, respectively, and Π_0 is defined by $\Pi_0 \equiv {}^1/_3\mathrm{Tr}\mathbf{\Pi}$.

When we neglect local field and collisional effects for the moment (they will be discussed below), the macroscopic polarizability $\mathbf{\Pi}$ is simply the sum of the polarizabilities of all N molecules in the volume V that contribute to the signal:

$$\mathbf{\Pi} = \sum_{i=1}^{N} \boldsymbol{\alpha}_i \tag{4}$$

For molecules with axial symmetry, such as CS_2, the single molecule polarizability $\boldsymbol{\alpha}_i$ of molecule i can be decomposed into an isotropic and an anisotropic part:[19]

$$\boldsymbol{\alpha}_i = \alpha \mathbf{1} + {}^2/_3 \gamma \mathbf{Q}_i \tag{5}$$

where the tensor $\mathbf{Q}_i$ can be expressed in terms of the unit vector $\hat{\mathbf{u}}_i$ along the symmetry axis:

$$\mathbf{Q}_i = {}^3/_2 \hat{\mathbf{u}}_i \hat{\mathbf{u}}_i - {}^1/_2 \mathbf{1} \tag{6}$$

Here, $\hat{\mathbf{u}}_i\hat{\mathbf{u}}_i$ denotes the dyadic product of the vector $\hat{\mathbf{u}}_i$ with itself.

When the correlation function $C(t)$ is expressed in terms of the single molecule orientational coordinates via the unit vectors $\hat{\mathbf{u}}_i$, one obtains

$$C(t) = \frac{\gamma^2}{V} \sum_{i,j=1}^{N} \langle \hat{\mathbf{u}}_i(0)\hat{\mathbf{u}}_i(0):\hat{\mathbf{u}}_j(t)\hat{\mathbf{u}}_j(t)\rangle \tag{7}$$

It is convenient to split the correlation function $C(t)$ into two terms that describe single-molecule orientational motion and dynamic orientational order effects of pairs of molecules, respectively:

$$C(t) = C_S(t) + C_P(t) \tag{8}$$

where the corresponding correlation functions $C_S(t)$ and $C_P(t)$ are given by

$$C_S(t) = N^2 \frac{\gamma^2}{V} \langle \hat{\mathbf{u}}_i(0)\hat{\mathbf{u}}_i(0):\hat{\mathbf{u}}_i(t)\hat{\mathbf{u}}_i(t)\rangle \tag{9}$$

$$C_P(t) = \frac{\gamma^2}{V} \sum_{i \neq j} \langle \hat{\mathbf{u}}_i(0)\hat{\mathbf{u}}_i(0):\hat{\mathbf{u}}_j(t)\hat{\mathbf{u}}_j(t)\rangle \tag{10}$$

For the interpretation of light scattering data, one often assumes a certain functional form for these two functions to fit the spectra. However, the analysis in terms of spectral moments is also a powerful and popular concept.[16,22,23,75]

The results of time-resolved OHD-OKE experiments, on the other hand, are usually described by time dependent quantum mechanical perturbation theory. The optical Kerr signal is governed by the relevant tensor element of the third-order nonlinear optical response function:[32,46,49]

$$R^{(3)}_{xyxy}(t) = -(\mathrm{i}/\hbar)\mathrm{Tr}\{[\mathbf{P}_2(t),\mathbf{P}_2(0)]\rho(-\infty)\} \tag{11}$$

Here $\mathbf{P}_2(t)$ is the interaction picture representation of the quantum mechanical operator $\mathbf{P}_2$, associated with the classical observable $\mathbf{\Pi}_2$, while $\rho(-\infty)$ denotes the density matrix in thermal equilibrium. The trace is to be taken over the matrix representation of the operator. In the classical limit the quantum mechanical response function is related to the classical correlation function, independent of the specific form of the Hamiltonian H_0, the polarizability operator $\mathbf{P}_2$, and the correlation function $C(t)$, via[76]

$$R^{(3)}_{xyxy}(t) = -\frac{1}{k_B T}\frac{\mathrm{d}}{\mathrm{d}t} C(t) \tag{12}$$

Usually, a certain functional form is assumed for the Hamiltonian H_0 of the system and for the operator $\mathbf{P}_2$ that allows for a closed form calculation of the response function. The most common assumption is that the optical response is dominated by a discrete number or a continuous distribution of harmonic modes $\mathbf{q}$ that change the polarizability with a linear coordinate dependence, according to $\mathbf{P}_2 = \mathbf{P}_2^{(1)}\mathbf{q}$. However, anharmonic potentials and nonlinear coordinate dependence of the polarizability have been treated as well.[49,77] The most straightforward way to relate this approach to the DLS theory is to identify the coordinate $\mathbf{q}$ with the single-molecule orientational variable. The physical process described by this model is then completely analogous to rotational Raman scattering in gases, except for the fact that the rotations in liquids are strongly hindered.[4,7,8]

When it is assumed that the molecule is harmonically bound to an equilibrium position, this yields a spectrum distinctly different from the rotational Raman spectrum: The series of separate lines corresponding to different values of the rotational quantum number J merge to a single line for a harmonic librator. The position of this line depends on the force constant and the reduced moment of inertia of the molecule under consideration.[63] The shape of the line reflects all relevant line-broadening processes due to, e.g., an inhomogeneous distribution of force constants, homogeneous dissipation of energy, or phase relax-

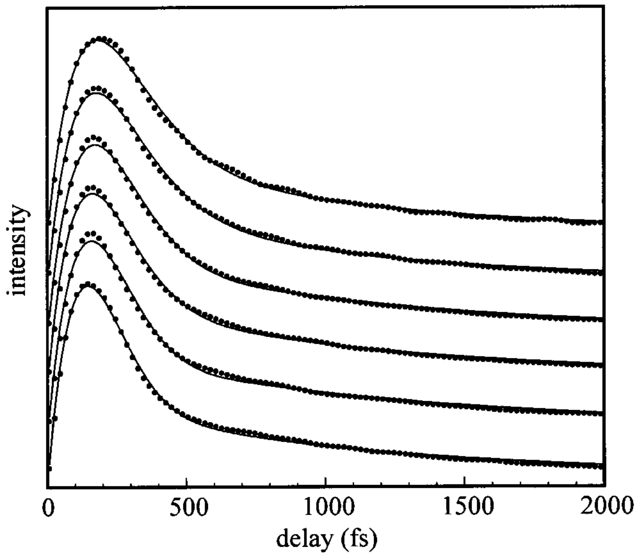

Figure 5. Fits (solid lines) of the deconvoluted optical Kerr response (dots) to a two mode Brownian oscillator model. The CS$_2$ concentrations were 100, 80, 67, 50, 33, and 20 vol % (bottom to top). The parameters of the fits are shown in Table 1.

ation. The observation of oscillatory behavior at low temperatures, which is attributed to librational motion in rigid cages,[44,45,47] supports this assignment. Due to the excitations of the librations the cage configurations and, hence, the equilibrium positions of the molecules change, leading to a net anisotropy of the molecular orientation, which finally decays by rotational diffusion. In the itinerant oscillator model[78] the cage degrees of freedom are projected onto a second effective harmonic coordinate which for strong damping results in a signal according to eq 1. This procedure relies on a time-scale separation between the two involved modes: The collective reorientation has to be much slower than the coherent inertia-limited response.

The coherent librational motion of harmonically bound molecules can be easily described by quantum mechanical perturbation theory.[46,69] Damping can be introduced in this formalism at different levels of sophistication.[46] Coupling with Brownian oscillators is among the most important of these approaches, since it accounts for both the frequency shift of a damped oscillator and for the continuous change from underdamped to overdamped motion.[49,79] For an underdamped libration with frequency ω and homogeneous damping γ the third-order response function reads[46,49,58]

$$R^{(3)}_{libr}(t,\omega) = \mathrm{e}^{-\gamma t/2}\frac{1}{\omega_{\mathrm{eff}}}\sin(\omega_{\mathrm{eff}}t) \qquad (13)$$

where the effective librational frequency is $\omega_{\mathrm{eff}} = (\omega^2 - \gamma^2/4)^{1/2}$. Additional loss of phase coherence can be caused by the fact that there is a distribution of different cage configurations. When the cages change very rapidly this leads to an exponential phase relaxation rate that adds to the homogeneous decay rate γ. In the other limiting case, where the cage configuration changes very slowly on the time scale of the librations, the resulting inhomogeneous broadening due to the static (slowly fluctuating) distribution of librational frequncies $g(\omega)$ can be taken into account by integrating the response function over these frequencies:

$$R^{(3)}_{\mathrm{libr}}(t) = \int_0^\infty \mathrm{d}\omega\, g(\omega)\, R^{(3)}_{\mathrm{libr}}(t,\omega) \qquad (14)$$

TABLE 1: Parameters of the Fits Shown in Figure 5[a]

CS$_2$ (vol %)	ω_0 (rad ps^{-1})	γ (ps^{-1})	σ (rad ps^{-1})	c (rad^2 ps^{-2})	Ω (rad ps^{-1})	Γ (ps^{-1})	τ_R (ps)	τ_D (ps)
100	7.08	10.45	2.77	1.80	2.21	8.87	0.13	1.70
80	6.90	9.55	2.41	1.87	2.24	8.90	0.13	1.65
66	6.65	10.46	2.07	1.72	2.23	8.89	0.13	1.67
50	6.31	9.88	1.84	1.49	2.38	9.04	0.13	1.48
33	5.96	10.32	1.62	1.11	2.49	9.17	0.13	1.35
20	5.87	10.22	1.32	1.02	2.55	9.23	0.13	1.30

[a] The simulated traces were calculated using eqs 1 and 13−16. The parameters for CS$_2$ concentrations below 20% are almost identical (see Figures 1 and 4) and not displayed here.

This equation allows for a continuous change from underdamped ($\omega > \gamma/2$) to overdamped ($\gamma/2 > \omega$) motion over the inhomogeneous distribution. Equation 13 then changes without discontinuity into the form of eq 1. When the cage fluctuations occur on similar time scales as the librational damping itself, the homogeneous and inhomogeneous limits do not apply. It is then more appropriate to apply stochastic approaches to the dynamics. Here, we will discuss the response in terms of (in)-homogeneous dynamics, as described by eqs 13 and 14.

For any spectrum an inhomogeneous distribution $g(\omega)$ can be constructed that perfectly fits the data.[48] To facilitate the numerical simulations, we assume here the presence of a modified Gaussian distribution that ensures zero spectral amplitude as the frequency approaches zero:[73]

$$g(\omega) = \omega \exp\left\{-\frac{(\omega - \omega_0)^2}{2\sigma^2}\right\} \qquad (15)$$

In this expression, the central frequency and the width of the distribution are denoted as ω_0 and σ, respectively.

In Figure 5 the best fits to the deconvoluted nuclear response functions are shown for mixtures of 100% down to 20 vol % CS$_2$. Both the single molecule librations and the diffusive nuclear response are taken into account here, according to the formula

$$R^{(3)}(t) = R^{(3)}_{\mathrm{libr}}(t) + cR^{(3)}_{\mathrm{diff}}(t) \qquad (16)$$

where c denotes the relative amplitude of the diffusive response, and $R^{(3)}_{\mathrm{diff}}$ and $R^{(3)}_{\mathrm{libr}}$ are given by eqs 1 and 14, respectively. As mentioned already in connection with the itinerant oscillator model, this description of the collective and the librational motions by two independent modes relies on the time scale separation between these two types of motions, which for neat CS$_2$ is fairly valid.[82]

The corresponding parameters for the various mixtures are given in Table 1. Some care should be taken here, since a smaller (larger) inhomogeneous width can to some extent be compensated for by a larger (smaller) homogeneous width. The quality of the fits then is only slightly affected, as was demonstrated for neat CS$_2$ in our previous work.[58] Also, modifications of the functional form of $g(\omega)$ may yield equally good fits, with different parameters. However, despite these uncertainties we may summarize the following overall trends: Upon dilution of CS$_2$ from 100 to 20 vol %, the centre frequency ω_0 becomes smaller and the inhomogeneous width σ decreases, while the homogeneous damping rate γ is not much affected. The collective decay time τ_D decreases as well. Similar features were found by McMorrow and co-workers.[61,63] However, it is not straightforward to compare our numerical results, since their parameters were reported for a classical model with three independent modes and a somewhat different frequency distribution.

At a first glance, it seems that the changes of the spectrum can be easily explained by the lower interaction energy between CS_2 and pentane, compared to that of two CS_2 molecules. The reduced interaction energy accounts for (i) a lower viscosity, hence a shorter collective decay time τ_D; (ii) a decrease of the libration frequency ω_0 of the CS_2 molecules; (iii) a narrower distribution $g(\omega)$ of these libration frequencies.

Although these conclusions seem logical, there are some surprising aspects that need further explanation and these, in fact, induced us to look for alternative explanations for the microscopic origin of the optical response. In general, the mixing of two species is governed by both entropy and the interaction energies between the two species. For rather weakly interacting molecules such as CS_2 and pentane, none of which has a permanent dipole, one might expect that the mixing will be largely determined by entropy. In the ideal case of identical interaction, the distribution of local configurations for the CS_2 molecules becomes broader upon dilution, until a ratio of 1:1 is reached. Then, a reduction of the number of available configurations sets in. Finding a *decrease* of the inhomogeneous width of librational frequencies while at the same time expecting an *increase* of possible local configurations is not necessarily impossible in view of the reduced intermolecular interaction between CS_2 and pentane molecules. However, in that case one would expect a further reduction of the inhomogeneous width for concentrations below 20 vol %, since CS_2 is not fully surrounded by pentane molecules, yet, and the distribution of local environments changes substantially upon further dilution.

The rather narrow range of concentrations over which the spectral changes of the inertial response occur casts serious doubt on the validity of the approach taken so far. From a physical point of view, this is not at all surprising, considering the crudity of treating the optical response only at the single-molecule level. In the analysis outlined above, dynamic pair correlations, local field corrections and the influence of collisions were ignored. In reality, these effects probably determine to a large extent the optical response. In the next section we will discuss to which extent these processes can provide alternative explanations for the observed spectral changes upon dilution.

V. Alternative Scattering Mechanisms

Dynamic correlations between molecules can lead to changes in the polarizability that are not accounted for in the single-molecule model described in the previous section. Such correlations are directly related to the molecular shapes and the strength of the interaction energies. They can be particularly important for strongly interacting molecules, e.g., in the presence of hydrogen bridges, but may show up in CS_2/pentane mixtures as well. The quadrupole moment[83,84] of CS_2 may give rise to aggregate-like structures in the liquid, resembling small clusters.[74] Like in gas-phase clusters, collective low-frequency vibrations are then expected to contribute significantly to the observed Rayleigh-wing spectra.[74,85]

In the DLS theory, the collective local modes are described by the dynamic pair correlation function $C_p(t)$, defined in eq 10. At $t = 0$ this quantity is closely related to the static orientational correlation parameter g_2 which is a measure for the average local ordering in the liquid.[13-15,23-25] For finite times, $C_P(t)$ describes the decay of the two-particle correlation in the liquid. The experimental determination of g_2 is far from simple, because its extraction from experimental data relies on several assumptions about the specific form of the single-molecule orientational motion and the contributions due to interaction- and collision-induced effects (see below). For pure CS_2 values of g_2 between 1.2 and 2.1 have been reported.[24,25] While for CS_2 and pentane there are, to our knowledge, no data available about the dependence of g_2 on the composition of the mixture, MD simulations for binary mixtures of CS_2 and CCl_4 revealed a maximum of the static orientational order parameter at a CS_2 mole fraction of 0.75.[86,87,88] Although it is not straightforward to extrapolate this result to a CS_2/pentane mixture, it indicates that the local structure may depend significantly on the composition of the mixture.

In recent literature, the collective local motions in liquids have also been analyzed in terms of instantaneous normal modes (INM).[89,90] Compared to the pair correlation function $C_p(t)$ discussed above, this alternative concept provides a rather natural formulation of the many-body dynamics since it avoids the description in terms of pairs of molecules. Moreover, there is a direct way to incorporate the results of an INM analysis into the theoretical description of the OKE response of section IV, since the instantaneous normal modes are modeled by harmonic oscillators. It should be noted, however, that within the INM picture the modes are undamped, which corresponds to pure inhomogeneous broadening. This description holds for very short times but is expected to break down at longer times. Therefore, additional homogeneous damping has to be introduced (eqs 13 and 14), while the slow reorientational diffusion was modeled by an overdamped mode, according to eq 1.

Due to our limited knowledge of the intermolecular potentials in a mixture of CS_2 and pentane, it is difficult to estimate how the collective local modes are changed upon dilution. When pentane is added the average interaction between molecules decreases because pentane, in contrast to CS_2, is less polarizable and does not have any prominent multipole. Therefore, one might anticipate a decrease of the collective vibrational motions, corresponding to a decrease of $C_p(t)$. This change would lead to a narrowing and a net shift to lower frequencies, thus providing a qualitative explanation for the observed modifications of the spectrum. It is, however, not directly evident that the collective modes would change exclusively at concentrations above 20 vol % of CS_2. This may indicate the formation of CS_2 dimers or higher aggregates which do not change their size as more pentane is added. Whether this is indeed true can be answered only by quantum chemical calculations. In view of the rather weak interactions in the CS_2/pentane mixtures, we do not think that this explanation is very plausible, though.

Collision-induced (CI) changes of the molecular polarizability arise through the fact that neighboring molecules in liquids temporally approach each other so closely that the electron clouds and/or molecular frames are seriously distorted.[9-11] The CI mechanism was first proposed to explain certain features in the Raman and infrared spectrum of carbon tetrachloride.[11] It is not an easy task to derive an expression for the polarizability change as a function of the mutual distances and orientations of the involved molecules and then average over all the rapidly changing configurations that are possible. To quantify this effect for molecular systems, Bucaro and Litovitz[9] showed that in a Lennard-Jones liquid the polarizability depends on the 13th power of the inverse distance provided that all collisions have a zero impact parameter. Based on these assumptions, they derived an exponentially decaying line shape that indeed was observed in the Rayleigh wing of atomic and some molecular liquids. However, they stressed that their approach is rather suspicious for highly anisotropic molecules such as CS_2.[9] Within the quantum-mechanical perturbation picture, often used for OKE experiments, the CI effects at the repulsive part of the potential may be accounted for by incorporating a strong dependence of the polarizability on the internuclear separation.

From this elementary description of the CI effects, it is clear that we may expect this contribution to the optical response to decrease when CS_2 molecules, with their extended electron clouds on the sulfur atoms, are replaced by pentane where the electrons are more confined to the backbone. Since the CI effects are believed to govern the high-frequency part of the spectrum,[9] we can anticipate the narrowing of the spectrum as apparent in Figure 4. It is, however, quite surprising that these changes occur exclusively at relatively high concentrations of CS_2. Intuitively, one would expect a further narrowing of the spectrum until each CS_2 molecule is surrounded by pentane molecules only.

Changes of the molecular polarizability can also be accomplished by dipole−induced dipole (DID) interactions, that occur on a much longer range.[12−22] It should be noticed that the Lorentz−Lorenz theory,[91] which accounts for the change of the local field due to a dielectric continuum around the molecule under consideration, is not capable of dealing with a surrounding composed of discrete polarizable matter that is free to move. The relation between the optical response and the probed microscopic dynamics is, in fact, very complicated.[92,93]

In general, the electric field $\mathbf{E}_i$ at molecule i is the superposition of an externally applied field $\mathbf{E}_{\mathrm{Ex}}$ and the local field corrections $\mathbf{E}_i^{\mathrm{Lo}}$ at this molecule, resulting from the (induced) dipoles $\boldsymbol{\mu}_j$ and higher multipoles of all other molecules: $\mathbf{E}_i = \mathbf{E}_{\mathrm{Ex}} + \mathbf{E}_i^{\mathrm{Lo}}$. When the contribution of the induced dipoles is dominant, one finds

$$\mathbf{E}_i^{\mathrm{Lo}} = \sum_{j\neq i} \mathbf{T}(\mathbf{r}_{ij})\cdot\boldsymbol{\mu}_j = \sum_{j\neq i} \mathbf{T}(\mathbf{r}_{ij}):\boldsymbol{\alpha}_j\cdot\mathbf{E}_j \tag{17}$$

Here $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the distance between the centers of mass of molecules i and j, and $\mathbf{T}(\mathbf{r}) = (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{1})/r^3$ is the dipole tensor expressed in terms of the unit vector $\hat{\mathbf{r}} = \mathbf{r}/r$.

Note that the local field correction at molecule i depends on the total field $\mathbf{E}_j$ at molecule j and, hence, on the local field corrections $\mathbf{E}_j^{\mathrm{Lo}}$ of all other molecules. This implies that, in general, the problem has to be solved self-consistently for all molecules. Often, these local field effects are treated by a perturbative approach, where one first approximates $\mathbf{E}_j \approx \mathbf{E}_{\mathrm{Ex}}$ on the right-hand side of eq 17. The resulting $\mathbf{E}_i$ is then used to define an effective polarizability $\boldsymbol{\alpha}_i^{\mathrm{Eff}}$ via: $\boldsymbol{\alpha}_i^{\mathrm{Eff}}\cdot\mathbf{E}^{\mathrm{Ex}} \equiv \boldsymbol{\alpha}_i\cdot\mathbf{E}_i$ that can be used as a new starting point for the calculation of the local field correction. It has been demonstrated by Ladanyi[17] that this iterative procedure works well for molecules with small polarizabilities. For highly polarizable molecules such as CS_2 the difference between the applied and the local field are substantial and the iterative method is not appropriate.[19] Dorfmüller and co-workers showed that for CS_2/CCl_4 mixtures the difference between the first- and the all-order method becomes smaller with decreasing CS_2 concentration.[87]

The fluctuations of the surrounding molecules give rise to changes in the induced dipole moment and polarizability and hence to absorption or scattering of light. The DID mechanism explains the observation of symmetry-forbidden lines, e.g., the FIR absorption of nonpolar molecules and the depolarized Rayleigh scattering of atomic systems,[16] but it might also contribute considerably to symmetry-allowed transitions. However, it is not an easy task to experimentally separate the DID contributions from the other mechanisms discussed in the previous sections.[15,18,19]

The DID scattering is particularly sensitive to local density fluctuations. To illustrate this, we note that the induced dipoles of isotropically polarizable molecules in a highly symmetric microscopic structure cancel.[21] Only when the symmetry is partly broken, there is a residual correction to the local field. For anisotropically polarizable molecules the situation is even more complicated because then both the mutual distances and orientations are important.[15]

Due to these complexities it is virtually impossible to derive closed form expressions for the line shapes resulting from DID interactions in condensed matter systems. The only way to quantitatively investigate the effect is offered by MD simulations.[15,17−19] Because the fields induced by the different molecules nearly compensate for each other, this method is very sensitive to the accuracy of the intermolecular potentials and molecular polarizabilities. In most simulations one typically assumes an effective, gas-phase-like molecular polarizability that is independent of the surrounding molecules. Therefore, this approach does not include any CI-effects.

In their MD study of the depolarized Rayleigh spectrum of CS_2/CCl_4 binary mixtures, Dorfmüller and co-workers[87] found that the CS_2 molecules were responsible for the main part of the DID signal. In the case of CS_2/pentane we foresee a similar but even more pronounced role of the carbon disulfide molecules in the DID contribution. As a first approximation one can expect that the DID effects scale with the average polarizability, normalized by the average density of the mixture.[15] Both CS_2 and pentane have nearly equal average molecular polarizabilities (8.8 and 10 Å^3, respectively)[94] but the density of CS_2 is 2 times higher than that of pentane. Therefore, a decrease of the DID contribution to the spectral density is expected when CS_2 is diluted in pentane.

It should be noted, however, that the DID contribution does not necessarily scale linearly with the index of refraction of the mixture. As discussed above, at high concentrations of CS_2 small corrections occur because the local fields originating from different molecules partly compensate for each other. This cancellation effect, which in the light-scattering literature is often discussed in terms of the so called three-body term, depends in general on the local symmetry. It has been proposed to quantify these effects by investigating the integrated scattering intensity as a function of the composition of the mixture.[95] This method has been applied successfully to the analysis of symmetry-forbidden *intra*molecular modes of CS_2 in several cosolvents.[95] However, in the low-frequency spectrum investigated here, the character of the intermolecular vibrations may change considerably upon dilution (see the discussion on clustering at the beginning of section V) which also leads to a modification of the integrated intensity. The same holds for the coherent orientational motion discussed in section IV: As pentane is added, it may be expected that the amplitude of the librations becomes larger because the potential is presumably less steep, which also results in a concentration dependence of the integrated intensity. Therefore, the intensity dependence of the signals does not provide a direct measure of the DID contribution to the signal. Despite these difficulties in quantifying the exact size and form of the DID effect, we conclude that this mechanism provides an alternative explanation for the narrowing and the red-shift of the spectrum. This conclusion is supported qualitiatively by the MD results on neat CS_2[19,20] and on CS_2/CCl_4 mixtures,[87] which showed that the DID effects are prominent at the high-frequency part of the spectrum.

We want to end this discussion with the remark that the projection of CI and DID effects on harmonic oscillators seems to be quite dubious. In addition, interfering cross terms between these interaction-induced effects and orientational motion complicate the description even more. Currently, no comprehensive theory is available that takes all these effects properly into account and allows for signal analysis in terms of closed form expressions.

VI. Conclusions

In this paper the OHD-OKE responses of neat CS_2 and CS_2/pentane binary mixtures were presented as typical examples of the results obtained with nonresonant third-order experiments. The signals are composed of three distinct components: an instantaneous contribution around zero delay due to the electronic hyperpolarizability, a delayed nuclear response with an inertia-limited rise time of the order of 200 fs, and a slow diffusion-controlled decay on a picosecond time scale. Upon dilution in pentane the relaxation rate of the diffusive component increases, which is attributed to a decrease in the bulk viscosity, while the buildup and decay time of the subpicosecond component become slower. The non-Lorentzian part of the spectral density narrows and shifts toward lower frequencies as pentane is added. Concentration-dependent experiments showed that the main spectral changes occur at intermediate concentrations where there is approximately 1 CS_2 molecule/pentane molecule. For mixtures with less than 20 vol % CS_2 no spectral changes are observed.

There are at least four different scattering mechanisms that can in general contribute to the observed nuclear response: (i) single-molecule orientational motions of the anisotropically polarizable molecules, (ii) low-frequency collective vibrations of transient aggregate structures, (iii) short-range collision-induced effects that result from polarizability changes due to molecular frame distortions and/or electronic overlap of adjacent molecules, and (iv) long-range interaction-induced effects that are caused by electrostatic dipole or higher multipole interactions.

From the discussion of these scattering mechanisms it is clear that a reliable description of the observed Rayleigh-wing line shapes is extremely difficult. It is far from trivial to derive well-justified, closed form expressions that accurately describe the collision- and interaction-induced effects. From the trends upon dilution the relative importance of the various mechanisms cannot be determined unambiguously. It was proposed by McMorrow and co-workers[61,63] that the narrowing of the spectra at intermediate concentrations should be due to a decrease of the inhomogeneous width of the coherent intermolecular vibrations. As was discussed in section V, a *broader* distribution of local configurations may indeed lead to a *smaller* distribution of vibrational frequencies in the case of CS_2/pentane binary mixtures.

The spectral changes, however, were found exclusively at CS_2 concentrations above 20 vol %. For weakly interacting molecules such as CS_2 and pentane, the changes in the distribution of local structures and, hence, the spectral changes are expected over a much broader range of concentrations. The narrowing of the spectra at intermediate concentrations is therefore probably for a substantial part determined by collision- and interaction-induced effects, as well. Moreover, the observed line narrowing may be partly due to changes in the homogeneous damping. The homogeneous and inhomogeneous contributions to the overall line shape can be determined unambiguously only by higher order nonlinear optical techniques. In a forthcoming paper we will report experimental results on the fifth-order response of CS_2/pentane mixtures, which should provide additional information on the role of the different scattering mechanisms and on the relevant time scales of the intermolecular dynamics.[96]

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References and Notes

(1) Raman, C. V.; Krishnan, K. S. *Nature* **1928**, *122*, 278; **1928**, *122*, 882.

(2) Weiler, J. *Z. Phys.* **1931**, *68*, 782.

(3) Leontovich, M. A. *J. Phys. USSR* **1941**, *4*, 499.

(4) Starunov, V. S. *Opt. Spectrosc.* **1965**, *18*, 165.

(5) Shapiro, S. L.; Broida, H. P. *Phys. Rev.* **1967**, *154*, 129.

(6) See, e.g.: McConnell, J. *Rotational Brownian motion and dielectric theory*; Academic Press: London, 1980.

(7) Ginzburg, V. L. *Sov. Phys. JETP* **1958**, *7*, 170.

(8) Steele, W. A. *J. Chem. Phys.* **1963** *38*, 2404; **1963**, *38*, 2411.

(9) Bucaro, J. A.; Litovitz, T. A. *J. Chem. Phys.* **1971**, *54*, 3846.

(10) Dardy, H. D.; Volterra, V.; Litovitz, T. A. *J. Chem. Phys.* **1973**, *59*, 4491.

(11) Gabelnick, H. S.; Strauss, H. L. *J. Chem. Phys.* **1968**, *49*, 2334.

(12) Buckingham, A. D.; Stephen, M. J. *Trans. Faraday Soc.* **1957**, *53*, 884.

(13) Cox, T. I.; Madden, P. A. *Chem. Phys. Lett.* **1976**, *41*, 188.

(14) Cox, T. I.; Battaglia, M. R.; Madden, P. A. *Mol. Phys.* **1979**, *38*, 1539.

(15) Frenkel, D.; McTague, J. P. *J. Chem. Phys.* **1980**, *72*, 2801.

(16) Birnbaum, G.; Ed. *Phenomena induced by intermolecular interactions*; Plenum Press: New York, 1985.

(17) Ladanyi, B. M. *Chem. Phys. Lett.* **1985**, *121*, 351.

(18) Madden, P. A.; Tildesley, D. J. *Mol. Phys.* **1985**, *55*, 969.

(19) Geiger L. C.; Ladanyi, B. M. *J. Chem. Phys.* **1987**, *87*, 191.

(20) Geiger L. C.; Ladanyi, B. M. *Chem. Phys. Lett.* **1989**, *159*, 413.

(21) Madden, P. A. In ref 22, p 124ff.

(22) Steele, D., Yarwood, J., Eds. *Spectroscopy and Relaxation of Molecular Liquids*; Elsevier: Amsterdam, 1991.

(23) Besnard, M.; Lascombe, J.; Cavagnat, R. *J. Phys.* **1981**, *42*, 593.

(24) Battaglia, M. R.; Cox, T. I.; Madden, P. A. *Mol. Phys.* **1979**, *37*, 1413.

(25) Madden, P. A.; Battaglia, M. R.; Cox, T. I.; Pierens, R. K.; Champion, J. *Chem. Phys. Lett.* **1980**, *76*, 604.

(26) Fork, R. L.; Greene, B. I.; Shank, C. V. *Appl. Phys. Lett.* **1981**, *38*, 671.

(27) Halbout, J. M.; Tang, C. L. *Appl. Phys. Lett.* **1982**, *40*, 765.

(28) Greene, B. I.; Farrow, R. C. *J. Phys. Chem.* **1982**, *77*, 4779.

(29) Ruhman, S.; Williams, L. R.; Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1987**, *91*, 2237.

(30) Vöhringer, P.; Scherer, N. F. *J. Phys. Chem.* **1995**, *99*, 2684.

(31) Cong, P. J.; Chang, Y. J.; Simon, J. D. *J. Phys. Chem.* **1996**, *100*, 8613.

(32) Hellwarth, R. W. *Prog. Quantum Electron.* **1977**, *5*, 1.

(33) Giorgini, M. G.; Foggi, P.; Cataliotti, R. S.; Distefano, M. R.; Morresi, A.; Mariani, L. *J. Chem. Phys.* **1995**, *102*, 8763.

(34) Kinoshita, S.; Kai, Y., Yamaguchi, M.; Yagi, T. *Phys. Rev. Lett.* **1995**, *75*, 148.

(35) Marker, P. D.; Terhune, R. W.; Savage, C. M. *Phys. Rev. Lett.* **1964**, *12*, 507.

(36) Mayer, G.; Gires, F. *C. R. Acad. Sci. Paris* **1964**, *258*, 2039.

(37) Duguay, H. A.; Hansen, J. W. *Appl. Phys. Lett.* **1969**, *15*, 192.

(38) Ippen, E. P.; Shank, C. V. *Appl. Phys. Lett.* **1975**, *26*, 92.

(39) Greene, B. I.; Fleury, P. A.; Carter, H. L.; Farrow, R. C. *Phys. Rev. A* **1983**, *29*, 471.

(40) McMorrow, D.; Lotshaw, W. T.; Kenney-Wallace, G. A. *IEEE J. Quantum Electron.* **1988**, *QE-24*, 443.

(41) McMorrow, D.; Lotshaw, W. T. *Chem. Phys. Lett.* **1990**, *174*, 85.

(42) McMorrow, D.; Lotshaw, W. T. *J. Phys. Chem.* **1991**, *95*, 10395.

(43) McMorrow, D.; Lotshaw, W. T. *Chem. Phys. Lett.* **1991**, *178*, 69.

(44) Ruhman, S.; Nelson, K. A. *J. Chem. Phys.* **1991**, *94*, 859.

(45) Waldman, A.; Banin, U.; Rabani, E.; Ruhman, S. *J. Phys. Chem.* **1992**, *96*, 10842.

(46) Steffen, T.; Fourkas, J. T.; Duppen, K. *J. Chem. Phys.* **1996**, *105*, 7382.

(47) Farrer, R. A.; Loughnane, B. J.; Deschenes, L. A.; Fourkas, J. T. *J. Chem. Phys.* **1997**, *106*, 6901.

(48) Loring, R. F.; Mukamel, S. *J. Chem. Phys.* **1985**, *83*, 2116.

(49) Tanimura, Y.; Mukamel, S. *J. Chem. Phys.* **1993**, *99*, 9496.

(50) Vanden Bout, D.; Muller, L. J.; Berg, M. *Phys. Rev. Lett.* **1991**, *43*, 3700.

(51) Muller, L. J.; Vanden Bout, D.; Berg, M. *J. Chem. Phys.* **1993**, *99*, 810.

(52) Inaba, R.; Tominaga, K.; Tasumi, M.; Nelson, K. A.; Yoshihara, K. *Chem. Phys. Lett.* **1993**, *211*, 183.

(53) Tominaga, K.; Yoshihara, K. *Phys. Rev. Lett.* **1995**, *74*, 3061.

(54) Tominaga, K.; Yoshihara, K. *J. Chem. Phys.* **1996**, *104*, 1159.

(55) Tominaga, K.; Yoshihara, K. *J. Chem. Phys.* **1996**, *104*, 4419.

(56) Steffen, T.; Duppen, K. *Phys. Rev. Lett.* **1996**, *76*, 1224.

(57) Tokmakoff, A.; Fleming, G. R. *J. Chem. Phys.* **1997**, *106*, 2569.

(58) Steffen, T.; Duppen, K. *J. Chem. Phys.* **1997**, *106*, 3854.

(59) Tokmakoff, A.; Lang, M. J.; Larsen, D. S.; Fleming, G. R. *Chem. Phys. Lett.* **1997**, *272*, 48.

(60) Steffen, T.; Duppen, K. *Chem. Phys. Lett.* **1997**, *273*, 47.

(61) Kalpouzos, C.; McMorrow, D.; Lotshaw, W. T.; Kenney-Wallace, G. A. *Chem. Phys. Lett.* **1988**, *150*, 138; **1989**, *155*, 240.

(62) Chang, Y. J.; Castner, Jr., E. W. *J. Chem. Phys.* **1993**, *99*, 113.

(63) McMorrow, D.; Thantu, N.; Melinger, J. S.; Kim, S. K.; Lotshaw, W. T. *J. Phys. Chem.* **1996**, *100*, 10389.

(64) Neelakandan, M.; Pant, D.; Quitevis, E. L. *Chem. Phys. Lett.* **1997**, *265*, 283.

(65) The number densities can be calculated easily from the molecular weights and the densities of CS_2 (76.14 and 1.263 g cm^{-3}) and pentane (72.15 and 0.6262 g cm^{-3}). For instance, in a mixture of 50 vol % there are twice as many CS_2 molecules than pentane molecules.

(66) Knox, W. H.; Downer, M. C.; Fork, R. L.; Shank, C. V. *Opt. Lett.* **1984**, *9*, 552.

(67) Nibbering, E. T. J.; Duppen, K.; Wiersma, D. A. *J. Photochem. Photobiol. A: Chem.* **1997**, *62*, 347.

(68) Alavi, D. S.; Hartman, R. S.; Waldeck, D. H. *J. Chem. Phys.* **1991**, *94*, 4509.

(69) Cho, M.; Du, M.; Scherer, N. F.; Fleming, G. R.; Mukamel, S. *J. Chem. Phys.* **1993**, *99*, 2410.

(70) Yan, Y.-X.; Nelson, K. A. *J. Chem. Phys.* **1987**, *87*, 6240.

(71) Yan, Y.-X.; Nelson, K. A. *J. Chem. Phys.* **1987**, *87*, 6257.

(72) Ruhman, S.; Joly, A. G.; Nelson, K. A. *IEEE J. Quantum Electron.* **1988**, *QE-14*, 460.

(73) Ruhman, S.; Kohler, B.; Joly, A. G.; Nelson, K.A. *IEEE J. Quantum Electron.* **1988**, *QE-14*, 470.

(74) McMorrow, D.; Lotshaw, W. T. *Chem. Phys. Lett.* **1993**, *201*, 369.

(75) Berne, B. J.; Pecora, R. *Dynamic light scattering*, Wiley: New York, 1976.

(76) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.

(77) Okamura, K.; Tanimura, Y. *Chem. Phys. Lett.* **1997**, *278*, 175.

(78) Hill, N. E. *Proc. Phys. Soc. (London)* **1963**, *82*, 723.

(79) Grabert, H.; Schramm, P.; Ingold, G. L. *Phys. Rep.* **1988**, *168*, 115.

(80) Lynden-Bell, R. M.; Steele, W. A. *J. Chem. Phys.* **1984**, *88*, 6514 and references therein.

(81) Steffen, T.; Duppen, K. *Chem. Phys.*, in press.

(82) Madden, P. A. In ref 16, p 643.

(83) Maroulis, G. *Chem. Phys. Lett.* **1992**, *199*, 250.

(84) De Luca, G.; Russo, N.; Sicilia, E.; Toscano, M. *J. Chem. Phys.* **1996**, *105*, 3206.

(85) Schaeffer, M. W.; Maxton, P. M.; Felker, P. M. *Chem. Phys. Lett.* **1994**, *224*, 544.

(86) Mittag, U.; Samios, J.; Dorfmüller, Th. *Mol. Phys.* **1989**, *66*, 51.

(87) Stassen, H.; Dorfmüller, Th. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 995.

(88) Mittag, U.; Samios, J.; Dorfmüller, Th. *Mol. Phys.* **1994**, *81*, 1143.

(89) Stratt, R. M. *Acc. Chem. Res.* **1995**, *28*, 201.

(90) Saito, S.; Ohmine, I *J. Chem. Phys.* **1998**, *108*, 240.

(91) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: New York, 1952.

(92) Mukamel, S. In ref 76, Chapter 16.

(93) Samson, R.; Pasmanter, R. A.; Ben-Reuven, A. *Phys. Rev. A* **1976**, *14*, 1224.

(94) Lide, D. R., Ed. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1994.

(95) Cox, T. I.; Madden, P. A. *Mol. Phys.* **1981**, *43*, 307.

(96) Steffen, T.; Nakashima, S.; Duppen, K., manuscript in preparation.