Ultrafast optical Kerr dynamics studied with incoherent light

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Femtosecond optical Kerr dynamics in various transparent liquids were measured using incoherent light with a 60 fs autocorrelation width. From the measurement of the optical Kerr effect (OKE) of binary mixtures of CS_2 and various liquids, the contribution of the intermolecular interaction-induced polarizability change to the OKE was found to be affected remarkably by the femtosecond molecular dynamics of CS_2. Especially, data from diluted solutions of CS_2 in nonviscous solvents composed of molecules with a low molecular weight are consistent with the binary collision model in free space. An oscillatory feature, which was attributed to an intermolecular vibrational mode, was found in the OKE dynamics of neat benzene and several benzene derivatives. A theoretical expression for the delay-time dependence of the signal intensity was also derived with no restriction on the statistical properties of the incoherent light. It is expressed in terms of the autocorrelation function of the intensity fluctuation of the incident incoherent light which was utilized as both the pump and the probe.

I. INTRODUCTION

A large amount of information about the molecular dynamics of liquids has been obtained from frequency-domain dynamical light scattering (DLS) spectroscopy. In particular, spectral features in the high-frequency region of Rayleigh scattering spectrum, which have been attributed primarily to an intermolecular interaction-induced (I-I) polarizability change, have provided information about the subpicosecond dynamics of molecules.[1-16] Recently, several time-domain studies have been reported which employ femtosecond optical pulses. In these studies, the femtosecond response of the optical Kerr effect (OKE) of liquids has been measured. The optical Kerr response has been observed to exhibit an initial rise and a fast decay in the femtosecond time domain.[17-26] The short-time behavior observed in the time-domain studies has been tentatively attributed to inhomogeneously frequency-distributed librational motion and/or to the intermolecular oscillations.[17,23] This attribution is in contrast to the theoretical work of Madden *et al.*,[1-3] which showed that the far wing in the DLS spectrum is due mainly to intermolecular translational motion of molecules via I-I effects. Although many theoretical studies and experimental frequency-domain studies have shown that the I-I effects, induced primarily by dipole–induced-dipole (DID) interactions, are responsible for the far wing of DLS spectra of liquids of small molecules, the origin of the subpicosecond response is still poorly understood.

In the present work, a technique using incoherent light instead of ultrashort pulses was applied. The time response of the OKE of carbon disulfide (CS_2) was found to have both fast and slow components, in agreement with the results obtained with femtosecond pulses.[19-21] Signal enhancements and an increase in the relaxation time of the fast component were found upon dilution of CS_2 in hexane and in several other Kerr-inactive liquids. We will show that this can be explained in terms of the motion of CS_2 molecules in the diluted liquids by attributing the fast component mainly to I-I contribution. We also found a slightly oscillatory behavior in the Kerr response of benzene and several benzene derivatives, which may be due to intermolecular vibrational motion.

In a previous paper, theoretical arguments have been presented, which demonstrate that incoherent light (with a correlation time shorter than the OKE relaxation time) can be used to obtain time-resolved measurements of the OKE response as an alternative to the measurement of the OKE response using short pulses with a pulse duration shorter than the OKE relaxation time. In addition, we previously performed the measurement of the OKE response by using incoherent light with a correlation time of about 150 fs.[27-30] In this paper, we report results obtained by the use of incoherent light with a correlation time of 60 fs, offering a time resolution higher than that obtained in previous reports of measurements with short pulses.[17-19]

Theoretical sections precede the description of the experimental results and the discussion. In Sec. II, general features of femtosecond optical Kerr response will be reviewed and theoretical models which are applied to the interpretation of the experimental results will be presented. In Sec. III, a theoretical treatment will show that the delay-time dependence of the signal intensity, from the measurements by degenerate four-wave mixing (DFWM) with incoherent light, can be expressed in terms of the OKE response of the sample and the autocorrelation function of the intensity fluctuation of the incident incoherent light. This result is also applicable to the interpretation of data from measurements of population relaxation dynamics by the use of incoherent light, which was performed by Morita *et al.*[31]

II. FEMTOSECOND OPTICAL KERR RESPONSE

Recent studies have revealed the OKE response of several molecular liquids in the femtosecond time region.[17-26]

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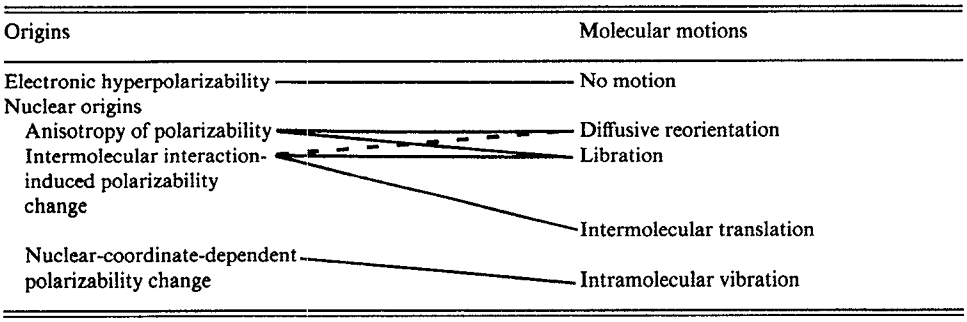
TABLE I. Origins of the optical Kerr effect and associating molecular motions in molecular liquids.



Origins	Molecular motions
Electronic hyperpolarizability	No motion
Nuclear origins	
Anisotropy of polarizability	Diffusive reorientation
Intermolecular interaction-induced polarizability change	Libration
	Intermolecular translation
Nuclear-coordinate-dependent polarizability change	Intramolecular vibration

When the time resolution of the measurement was restricted to the picosecond region or longer, only a couple of exponentially-decaying components were observed in the OKE response of liquids and they have been attributed to diffusive reorientational motions of molecules with anisotropic polarizability.[32,33] In the femtosecond region, however, various types of nonexponential response, such as a rise and oscillations, have been observed, which are due to coherent, or inertial molecular motions.[17–26]

Origins of the optical Kerr effect and associating molecular motions in molecular liquids are summarized in Table I. The electronic response is due to the nonlinear electronic polarizability of the molecules. It is virtually instantaneous and not accompanied by any molecular motions under the nonresonant condition, where the Born–Oppenheimer approximation is valid.[34]

The mechanisms of the nuclear response can be classified as listed in Table I. These mechanisms are coupled with various molecular motions. Those listed in Table I are such molecular motional modes that have a nonnegligible contribution to the OKE response in the picosecond–femtosecond region.

Although the diffusive reorientational motion decays exponentially in the longer delay time region, at short time delays, the reorientational response should inevitably rise continuously from the equilibrium value up to the maximum. The main mechanism of the susceptibility change is the anisotropy of the molecular polarizability. The I-I effect, which is present in the long-time reorientational response, can be neglected since it shows the same time response as the orientational motion in the long time scale. Librational motion is a small-angle oscillation of the orientation of molecules, which can be regarded as a precursor of the diffusive reorientational motion in the OKE response. Librational motion affects the polarizability of the molecular system via the molecular polarizability anisotropy and the I-I effect. Intermolecular translational motion affects the susceptibility only by the I-I effect. The most important term responsible for the OKE response is the two-particle dipole–induced-dipole (DID) polarizability.[1,4,6,35,36] In dense media, intermolecular translational motion can have an oscillatory feature like the librational motion. Raman-active intramolecular vibrational modes are also excited impulsively by short pulses with a duration shorter than the oscillation period of the mode.[37]

A large amount of experimental and theoretical investigation has been done on the molecular dynamics in liquids and gases by studying the dynamical light scattering (DLS) spectra. The OKE response function $G(t)$ is related to the DLS spectrum $I_{\rm DLS}(\omega)$ by the fluctuation–dissipation theorem as

$$I_{\rm DLS}(\omega) \propto [n(\omega)+1]\int_0^\infty dt\, G(t)\sin\omega t. \tag{1}$$

Here, $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the Bose factor and $I_{\rm DLS}(\omega)$ is the light scattering intensity on the Stokes side.[38] In the high temperature limit ($\hbar\omega/kT \ll 1$), we have a simpler relation[38]

$$G(t) \propto -\theta(t)\frac{\partial}{\partial t}\int_{-\infty}^{\infty} d\omega\, I_{\rm DLS}(\omega)\cos\omega t. \tag{2}$$

Here $\theta(t)$ is the normalized step function and the integral in the right-hand side of this equation is proportional to the autocorrelation function of the susceptibility fluctuation of the medium.

A. Reorientational response

DLS spectra of many organic solvents have been investigated for the study of the molecular dynamics in the liquid phase. They are very often composed of a sharp central peak with a Lorentzian line shape and a broad background scattering with an exponentially decaying far wing.[7–9]

Mori's transport theory for correlation functions has developed a method to obtain the equation of motion of the "primary" variable from a generalized Langevin equation.[39] Keyes and Kivelson have applied the Mori theory to the analysis of DLS spectra of liquids.[40] They have shown that the sharp central line is attributed to the reorientational motions, whereas the broad background should be explained in terms of an independent origin other than the molecular orientation.

Ho and Alfano have studied the reorientational relaxation in binary mixtures of organic solvents.[32,33] They explained the relaxation time of the reorientational decay of a series of mixtures with various mixed contents and viscosities by applying Hill's theory of an effective viscosity.[32] They analyzed their later experimental results with an improved signal-to-noise ratio[33] by using a more refined theory of Kivelson and Tsay,[41] where the reorientational relaxation of the system of solute and solvent molecules exhibits two-component exponential decay. We adopted, however, the simpler theory with a single decay component for the analysis of our experimental results since the weaker component of the two can be neglected in the analysis in the present paper, where the dynamic range of the experimental data was not better than 10 for the reorientational OKE response because of a large background signal inherent in the measurement using incoherent light.

The susceptibility fluctuation due to the reorientational motions of molecules in liquids has an exponentially decaying correlation function at sufficiently long delay times, as described by the rotational diffusion equation. This results in a sharp central Lorentzian peak in the DLS spectra or an exponential decay of the OKE response in the long time scale. The deviation from a simple exponential response, however, should be taken into consideration in the femtosecond region, where the molecular moment of inertia cannot be neglected. This effect can be included in the response function by assuming an exponential rise as

$$G_{OR}(t) \propto \theta(t)\exp(-t/\tau_{\mathrm{col}})[1-\exp(-t/\tau_v)]. \quad (3)$$

Here $\theta(t)$ is the normalized step function and τ_{col} is the collective orientational relaxation time, which describes the decay of OKE. The relation of τ_{col} to the single-particle orientational relaxation time was derived by Keyes and Kivelson[40] as

$$\tau_{\mathrm{col}} = (g_2/j_2)\tau_r. \quad (4)$$

where g_2 and j_2 are the static and the dynamic orientational correlation coefficients of the liquid, respectively.

The initial rising behavior, as described in Eq. (3), is a consequence of a finite decay rate of the molecular angular momentum and the rise time τ_v is the relaxation time of the angular momentum. The response function of the angular momentum does not necessarily decay monotonously, but can have oscillatory structure due to the librational effect. In the analysis of the experimental results in the present paper, however, an exponential response is assumed since the time resolution of the measurement was not good enough to observe a short-time oscillatory structure in the response, and any oscillations with a period longer than or comparable to the rise time of the reorientational response can be treated separately as done in the literature.[17,23]

The angular momentum decay time τ_v and the orientational decay time τ_r are correlated to each other by

$$\tau_r\tau_v = J/6kT. \quad (5)$$

This equation is known as the Hubbard relation, which is derived from the Langevin equation describing the orientational motion of the molecule.[39,42,43] In the equation, J, k, and T are the molecular inertial moment, Boltzmann factor, and the temperature, respectively. The exponential rise as in Eq. (3) corresponds to a delta-function autocorrelation of the random torque in the Langevin equation.

If τ_{col} is determined from the long-time OKE relaxation, τ_r can be derived using Eq. (4) and the value of g_2/j_2. In the analysis of the OKE signal from neat carbon disulfide and binary mixtures of carbon disulfide and other liquids, however, we could not determine precisely the relaxation time of the long-time OKE response owing to a large background signal, which is inherent in the method using incoherent light. To circumvent this difficulty, we determined the relaxation time of the orientational component by measuring the viscosity of the mixture. The single-particle orientational relaxation time has been shown to follow the relation[44]

$$\tau_r \propto \eta_{\mathrm{eff}}/kT. \quad (6)$$

Here η_{eff} is the effective viscosity for the relevant molecule, which is expressed approximately as

$$\eta_{\mathrm{eff}} = f_A\eta_{AB} + f_B\eta_B. \quad (7)$$

In this equation, f_A and f_B are the molar fractions of molecule A and B, respectively, and η_{eff} is the effective viscosity relevant to the orientational motions of molecule B. The viscosities of molecules A and B, η_A and η_B, and the mutual viscosity η_{AB} were obtained by fitting the viscosity of the mixture η_m to the Hill's equation[32,45]

$$\eta_m = f_A^2\eta_A a_A/a_m + 2f_Af_B\eta_{AB}a_{AB}/a_m + f_B^2\eta_B a_B/a_m. \quad (8)$$

Here, a_A, a_B, a_{AB}, and a_m are defined by

$$a_A = (M_A/\rho_A N_0)^{1/3}, \quad (9a)$$

$$a_B = (M_B/\rho_B N_0)^{1/3}, \quad (9b)$$

$$a_{AB} = (a_A + a_B)/2, \quad (9c)$$

$$a_m = (M_m/\rho_m N_0)^{1/3}. \quad (9d)$$

In these equations, M_A and M_B are the molecular weights of A and B and M_m is the average molecular weight of the mixture. The densities of these liquids are designated by ρ_A, ρ_B, and ρ_m. N_0 is the Avogadro number.

The decay time of the orientational contribution to the OKE τ_{col} was derived from τ_r by

$$\tau_{\mathrm{col}} = \tau_r[1 + f_B(g_2/j_2 - 1)]. \quad (10)$$

Here, g_2/j_2 is the value for the neat liquid of molecule B and the correction by the orientational correlation of molecule B is assumed to be linear in the molar fraction of B. This model of an effective viscosity, as described above, follows the treatment of Ho *et al.*[32] in their analysis of the reorientational Kerr relaxation in binary mixture liquids.

We use the literature values for the neat CS_2 $\tau_r = 1.45$ ps and $\tau_{\mathrm{col}} = 1.70$ ps, which lead to $g_2/j_2 = 1.17$.[46] The distance between the nitrogen and the carbon atoms in the CS_2 molecule 1.57 Å[47] and the temperature $T = 294$ K yield $\tau_r\tau_v = 1.07\times10^{-25}$ s^2. In neat CS_2, τ_v is obtained to be 74 fs. This is consistent with the values 100 and 75 fs, which were tentatively adopted in the literature.[19,24]

B. Interaction-induced response

The broad background in the DLS spectra of liquids and dense gases has been attributed mainly to the I-I susceptibility change.[1-3,7,11,13] The origin, however, of the fast component in the OKE response, which should correspond to the broad background in the DLS spectra, has not been unambiguously understood in time-resolved studies. Ruhman *et al.* attributed the fast component primarily to librational motions of molecules, which affect the susceptibility of the medium via I-I mechanism.[23] However, McMorrow *et al.*

have tentatively separated the fast part into two components; i.e., an ultrafast component and an intermediate one.[17] They attributed the ultrafast component to librational motions, which affect the susceptibility mainly through the molecular polarizability anisotropy and the intermediate one to an I-I contribution coupled to intermolecular translational motions.

We attributed the fast component observed in the experimentally obtained OKE response of neat CS_2 and binary mixtures to the I-I contribution induced mainly by intermolecular translational motions and fitted it to one function, instead of two as in the analysis by Kalpouzos *et al.*[24] The present results are well reproduced by one function, as shown below. Especially in mixtures of a small content of CS_2 and a liquid with a low polarizability, the fitting was excellent and it is also justified theoretically since librational motions are expected to be suppressed and the I-I effect between two CS_2 molecules should be the main origin of the fast component in these mixtures.

The fast component has been attributed only to I-I contribution in many theoretical and experimental studies on frequency-domain DLS of CS_2. This has also been supported by recent molecular simulations.[36] Theoretical studies have also predicted that the I-I polarizability change is caused mainly by translational motions of the molecules and that the DLS spectrum is not sensitive to the anisotropy of the CS_2 molecule.[1,2,7,48]

Bucaro and Litovitz have derived an expression for the DLS intensity as a function of the angular frequency of the shift ω as

$$I_{\mathrm{DLS}}(\omega) \propto \omega^{q} \exp(-\omega/\omega_0) \tag{11}$$

to describe the I-I DLS spectrum of spherical molecules induced by binary collisions.[49] This equation has very often been used to interpret DLS spectra from nonspherical molecular systems as well.[8,49–52] In the derivation of this equation, an effective polarizability change $\Delta\alpha$ is assumed to be proportional to a power of the distance between the interacting molecules r as

$$\Delta\alpha \propto r^{-m}. \tag{12}$$

The relation between exponent q in Eq. (11) and m in Eq. (12)

$$q = 2(m-7)/7 \tag{13}$$

has been derived[49] and the frequency parameter ω_0 corresponds to the time duration in which the interaction occurs. Although in dense media the assumption of the binary collision does not hold, and the cancellation does occur, this relation has often been used for the analysis of I-I DLS spectra of liquids.[8,49–52] In dense media, ω_0 has been suggested to be correlated to the decay time of the translational motion autocorrelation[9] and q can be regarded as the exponent in an effective function for the intermolecular I-I polarization change.

The OKE response function can be derived from the DLS spectrum using the fluctuation–dissipation theorem as follows[37]:

$$G_{\mathrm{II}}(t) \propto \theta(t) \operatorname{Im}[(1 - i\omega_0 t)^{-q-2}], \tag{14}$$

where $\theta(t)$ is the normalized step function. We used this function for the analysis of the experimental data and obtained a good fit for the fast component of experimental OKE response.

III. THEORY OF MEASUREMENT

The time response of OKE in CS_2 and other molecular liquids has been measured by both the transient grating (TG)[53] and Kerr-shutter technique by many researchers.[54] The experimental configuration of both schemes is depicted in Fig. 1. In a TG experiment, two pump beams (using either short pulses or incoherent light) are incident on the sample to prepare a grating via the OKE. The amplitude of the grating with respect to time varies according to the Kerr response within the sample. The intensity of the diffracted portion of the probe beam, which is delayed with respect to the pump beams, yields the time response of the OKE as a function of the delay time. In a Kerr-shutter experiment, the optical anisotropy is detected by the polarization change of the probe. These two methods are special types of DFWM which have both been described in terms of impulsive stimulated scattering.[37,38] In the TG configuration, the combination of the polarization directions of the incident beams and that of the light to be detected can be fixed independently. This makes it possible to discriminate between several contributions which comprise the OKE by detecting their polarization dependence.[19,22] In contrast, in the Kerr-shutter configuration, no grating is produced. The Kerr-shutter technique can be regarded as a special case of the TG configuration, in which the two pump beams are combined and the spatial period of the grating produced by the two pumps goes to infinity. This two-beam configuration makes the experiment easier than the three-beam TG measurement. In this paper, however, theory is presented only for the interpretation of signals measured with the TG configuration, since this configuration is theoretically more general.

In a previous paper, we have reported a time-resolved OKE measurement with incoherent light in phase-conjuga-

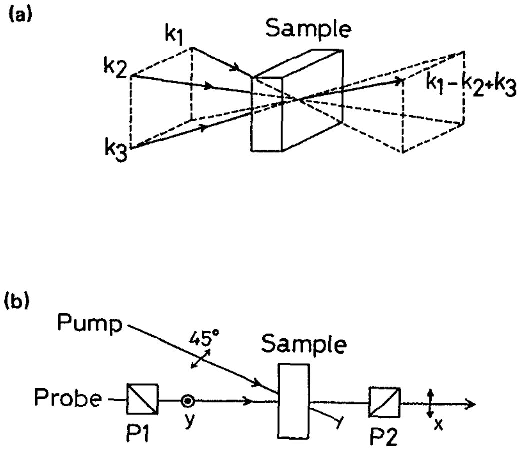


FIG. 1. Schematics for the measurement of dynamics of the optical Kerr effect. (a) Degenerate four-wave mixing (DFWM) in the transient grating configuration. (b) DFWM in the Kerr-shutter configuration.

tion type DFWM.[55] In phase-conjugation configuration, although the optical alignment is easier than in the TG configuration, the part of the signal which exhibits the time response of OKE is much smaller, as shown later in this paper.

The third-order polarization $P^{(3)}(t)$, which is responsible for the signal light in the TG measurements with a transparent medium, can be expressed in terms of the pump light field envelope $E(t)$ and the response function of the OKE $G(t)$ as [28]

$$P^{(3)}(t,\tau) = \int_{-\infty}^{\infty} ds\, G(t-s)[E(t-\tau)E^*(s)E(s) + gE(t)E^*(s)E(s-\tau)], \qquad (15)$$

where $E^*(t)$ is the complex conjugate of $E(t)$, the integral variable s is the time at which the grating is produced, and g is a factor which depends on the combination of the polarization directions of the incident beams and that of the light to be detected and depends also on the relative values of the contributing tensor elements of the third-order susceptibility.[28] In Eq. (15), the instantaneous electronic response is omitted and the probe light is a time-delayed replica of the pump light and the delay time is represented by τ. The second term in the bracket in the right-hand side of Eq. (15) corresponds to the contribution of the coherent coupling of the pump and the probe beams. The intensity of the signal light is proportional to the squared magnitude of the polarization

$$\begin{aligned} I_S(\tau) &\propto |P^{(3)}(t,\tau)|^2 \\ &= \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds'\, G(t-s)G(t-s')[E(t-\tau)E^*(s)E(s) + gE(t)E^*(s)E(s-\tau)] \\ &\quad \times [E^*(t-\tau)E(s')E^*(s') + gE^*(t)E(s')E^*(s'-\tau)]. \end{aligned} \qquad (16)$$

A. In the case of Gaussian light

When the incident light is incoherent, in order to obtain the signal intensity, it is necessary to perform a statistical average of Eq. (16) by assuming the envelope function of the electric field of the incoherent light $E(t)$ to be a random process. Equation (16), which consists of sixth-order moments of the field $E(t)$ can be factorized into products of second-order moments by assuming that $E(t)$ is a complex Gaussian random process, which was sometimes performed for the evaluation of the signal intensity.[56] This factorization procedure for the interpretation of the optical Kerr dynamic measurement has already been described in the previous paper[28] for the limiting case where the response function of the OKE is a single exponential. For a general case of the response function, the factorization procedure is quite analogous to the previous one. This leads to the following expression, which is applicable when the correlation time of the incoherent light t_c (t_c will be used in this paper as a nonspecific time parameter on the order of the width of the field amplitude or the intensity autocorrelation function of the incident light) is much shorter than the decay time of the OKE:

$$\begin{aligned} I_S(\tau) &\propto 1 + g(g+2)|f(\tau)|^2 \\ &\quad + (2/T^{\mathrm{Kerr}}) \int_{-\infty}^{\infty} dt\, |f(t)|^2 G(\tau - t)/G_{\max} \\ &\cong 1 + g(g+2)|f(\tau)|^2 + (2\tau_c'/T^{\mathrm{Kerr}})G(\tau)/G_{\max}, \end{aligned} \qquad (17)$$

where $f(\tau)$ is the normalized autocorrelation function of the envelope of the optical field

$$f(\tau) = \langle E^*(t)E(t+\tau)\rangle / \langle E^*(t)E(t)\rangle, \qquad (18)$$

$G_{\max}$ is the maximum value of $G(t)$, τ_c' is a time parameter for the width of the autocorrelation function as

$$\tau_c' = \int_{-\infty}^{\infty} dt\, |f(t)|^2, \qquad (19)$$

and T^{Kerr} is the characteristic time for the Kerr relaxation defined by

$$T^{\mathrm{Kerr}} = \int_{-\infty}^{\infty} dt\, G(t)/G_{\max}. \qquad (20)$$

The signal intensity profile represented by Eq. (17) consists of the first constant background term, the coherent spike term, and the last signal term, which represents the Kerr response. The ratio of the peak intensity of the signal term to the constant background is on the order of $\tau_c'/T^{\mathrm{Kerr}}$, although the correlation time must be short enough to temporally resolve the Kerr dynamics. When the phase-conjugation configuration is employed for the OKE measurement, the magnitude of the signal term is on the order of $(t_c/T^{\mathrm{Kerr}})^2$ with respect to the coherent spike, as shown previously.[28,55] Therefore, the OKE measurement in the TG or the Kerr-shutter configuration, as presented in this paper, is more advantageous regarding the signal amplitude.

Here it should be noted that the signal term does not represent the squared magnitude of the response function as in the measurements with short pulses,[37] but the response function itself. When short pulses are used, the diffracted signal intensity is proportional to the square amplitude of the grating generated by the pump pulses and relaxes after the excitation according to the Kerr response function. However, with incoherent light, the signal term is proportional to the response function because the diffracted light field is heterodyne detected with the large background signal. Heterodyne detection technique has been employed in the measurement with short pulses, in which there is no inherent background signal, by using a fraction of the probe light as a local oscillator.[17] This heterodyne technique which uses a part of the probe instead of the background signal can also be employed even with incoherent light. Pump–probe measurements performed by Tomita *et al.*[57] correspond to this case in which the imaginary part of the nonlinear susceptibility was detected.

B. In the case of incoherent light with more general characteristics

In the preceding section, the incident incoherent light is assumed to have Gaussian properties. This makes it possible to obtain the analytical expression of the signal intensity in terms of the second-order autocorrelation of the light field. A more general expression can be obtained by considering higher-order correlations of the incoherent light field. It has been shown by Asaka *et al.* that the signal intensity of accumulated photon echoes can be expressed in terms of the second-order autocorrelation function of the field amplitude of the incoherent light, even when the light is not Gaussian.[58] It has been suggested by Tomita and Matsuoka that the time resolution of the measurement of absorption recovery by the pump–probe technique with incoherent light is determined by the intensity correlation of the incident incoherent light.[57] The lowest-order, i.e., second-order, intensity autocorrelation is a fourth-order correlation of the field amplitude and the sixth-order amplitude correlations in Eq. (16) contain fourth powers of the field amplitude.

In the following section, we will show the following: (1) that the intensity correlation of the incident light determines the time resolution of the OKE measurement and (2) that the signal intensity can be expressed in terms of the second-order intensity autocorrelation function of the incident incoherent light, when the following conditions are satisfied: (i) the statistical properties of the incoherent light are stationary: (ii) $t_c \ll T^{\mathrm{Kerr}}$; and (iii) the intensity and the field amplitude autocorrelation functions are negligible at $|\tau| \gg t_c$.

When the condition

$$|dG(t)/dt|\cdot t_c \ll |G(t)| \tag{21}$$

is satisfied, which corresponds to the condition that $t_c \ll T^{\mathrm{Kerr}}$, each pair of field envelopes in the integrand in Eq. (16) which contains s or s' [i.e., $E^*(s)$, $E(s)$ and $E^*(s')$, $E(s')$] can be replaced by the statistical average of the product of the pair [i.e., $\langle E^*(s)E(s)\rangle$ and $\langle E^*(s')E(s')\rangle$]. This yields

$$\begin{aligned}I(\tau) \propto \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds'\, G(t-s)G(t-s')\,[\,&\langle E^*(t-\tau)E(t-\tau)\rangle\langle E^*(s)E(s)\rangle\langle E^*(s')E(s')\rangle\\
&+ g\langle E^*(t-\tau)E(t)\rangle\langle E^*(s)E(s-\tau)\rangle\langle E^*(s')E(s')\rangle + g\langle E^*(t)E(t-\tau)\rangle\langle E^*(s)E(s)\rangle\\
&\times E^*(s')E(s'-\tau)\rangle + g^2\langle E^*(t)E(t)\rangle\langle E^*(s)E(s-\tau)\rangle\langle E^*(s')E(s'-\tau)\rangle]\\
\propto \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds'\, G(t-s)G(t-s')\,[\,&\langle I\rangle^3 + 2g\langle I\rangle^3|f(\tau)|^2 + g^2\langle I\rangle^3|f(\tau)|^2]\\
= (T^{\mathrm{Kerr}})^2 G_{\max}\langle I\rangle^3[1+g(g+2)|f(\tau)|^2]&.\end{aligned} \tag{22}$$

Here $\langle I\rangle$ is the mean value of the intensity of the incident light. This expression yields the constant background term of 1 and the coherent spike $g(g+2)|f(\tau)|^2$, which both appeared in Eq. (17). The signal term, which represents the OKE response in the general case, as is the last term in Eq. (17), does not appear in this expression since correlations between the second-order autocorrelation functions in Eq. (22) are responsible for the signal term and these correlations are neglected in the averaging procedure, as described above. The first term which results from the expansion of Eq. (16) can be written in terms of the intensity of the incident incoherent light $I(t)$ as

$$I_1(\tau) = \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds' G(t-s)G(t-s') \times \langle I(t-\tau)I(s)I(s')\rangle. \tag{23}$$

Other terms in Eq. (16), which vanish when $|\tau| \gg t_c$, yield only the coherent spike. Equation (23), which is expressed in terms of a third-order correlation function of the light intensity, confirms the important role of the intensity correlation for this type of measurement with incoherent light.[57] When t_c is much shorter than T^{Kerr}, we can obtain an expression of the signal intensity in terms of the second-order intensity autocorrelation function, which can be experimentally measured, as shown in the following:

If the intensity of the incident light is divided into the mean value and the intensity fluctuation as

$$I(t) = \langle I\rangle + \Delta I(t), \tag{24}$$

Eq. (23) can be expressed as

$$I_1(\tau) = \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds'\, G(t-s)G(t-s')\langle [\langle I\rangle + \Delta I(t-\tau)][\langle I\rangle + \Delta I(s)][\langle I\rangle + \Delta I(s')]\rangle. \tag{25}$$

The term in Eq. (25) which contains $\langle I\rangle^3$ is the constant background term of Eq. (22). Besides the background term, only the following terms contribute to the signal intensity:

$$\begin{aligned} I_1'(\tau) = \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds'\, G(t-s)G(t-s')[&\langle I\rangle\langle\Delta I(t-\tau)\Delta I(s)\rangle + \langle I\rangle\langle \Delta I(t-\tau)\Delta I(s')\rangle \\ &+ \langle I\rangle\langle\Delta I(s)\Delta I(s')\rangle + \langle \Delta I(t-\tau)\Delta I(s)\Delta I(s')\rangle], \end{aligned} \tag{26}$$

since the other terms, which are proportional to ΔI, vanish by the statistical average. In Eq. (26), the third term contributes to the constant background signal and can be neglected since it is smaller by a factor of $t_c/T^{\rm Kerr}$ than the background term in Eq. (22). The last term in Eq. (26) can also be neglected since it is on the order of $(t_c/T^{\rm Kerr})^2$ with respect to the background term and on the order of $t_c/T^{\rm Kerr}$ with respect to the other terms. This order evaluation procedure, as described above, is similar to those performed by Asaka *et al.* in the derivation of the expression for the signal intensity of accumulated photon echoes using incoherent light.[58] The other terms, the first and the second terms in Eq. (26), can be approximated as

$$I_1'(\tau) \cong 2\langle I\rangle^3 T^{\rm Kerr} G_{\rm max}\tau_c^I G(\tau), \tag{27}$$

where τ_c^I is defined by

$$\tau_c^I = \int_{-\infty}^{\infty} dt\, \langle \Delta I(0)\Delta I(t)\rangle/\langle I\rangle^2. \tag{28}$$

The summation of expressions in Eqs. (22) and (27) gives the expression for the signal intensity

$$\begin{aligned} I(\tau) &\propto 1 + g(g+2)|f(\tau)|^2 + (2/T^{\rm Kerr})\int_{-\infty}^{\infty} dt\, [G(\tau-t)/G_{\rm max}]\langle\Delta I(0)\Delta I(t)\rangle/\langle I\rangle^2 \\ &\cong 1 + g(g+2)|f(\tau)|^2 + 2(\tau_c^I/T^{\rm Kerr})G(\tau)/G_{\rm max}. \end{aligned} \tag{29}$$

This expression shows that the coherent spike is proportional to the square of the field amplitude autocorrelation function and that the signal term is a convolution of the Kerr response function and the autocorrelation function of the intensity fluctuation of the incident light. This result is employed in the analysis of the experimental results of the present study.

This expression can be also used for the interpretation of the signal intensity obtained by DFWM for the measurement of other processes which are dependent on the light intensity, such as population dynamics.[31] For population dynamics studies by DFWM using incoherent light, only a simple analysis has been reported previously, in which the incoherent light was assumed to be Gaussian and the response function was taken to be an exponential decay.[31] However, an analysis utilizing more general response functions [in Eq. (29)] is required for the OKE, since the response function of the nuclear contribution to the OKE cannot be described by an exponential function in the femtosecond regime. In the femtosecond regime, it is necessary that the response function is zero at $t = 0$.[59]

IV. EXPERIMENT

Measurements of OKE dynamics were performed with the Kerr-shutter configuration. The experimental setup is shown in Fig. 2. Incoherent light was generated by a nanosecond dye laser (Molectron DL-14). Both the oscillator and the amplifier of the dye laser, which were pumped by an excimer laser (Hamamatsu, C2540) contained coumarin 102 (Exciton). No frequency tuning element was employed in the dye laser. The output incoherent light had a peak at 476 nm. The power spectrum was close to a Gaussian shape with a full width at half-maximum (FWHM) of 8 nm. The width and the energy of the output pulse were 5 ns and about 300 μJ, respectively. In the measurement of the OKE, the output light was attenuated by 10% to 20%.

Previous experiments with this experimental setup used rhodamine 6G as the laser dye.[27] The output light was found to closely approximate the Gaussian light. This result was obtained from the comparison of the intensity autocorrelation, the field amplitude autocorrelation, and the power spectrum of the output of a strongly saturated and a nonsaturated amplifier.[60] In the present study, in which coumarin 102 was used, the Gaussian statistical properties of the laser light could not be verified, since phase matching cannot be achieved with the SHG crystal KDP at 476 nm. However, significant deviations from Gaussian properties of the light are not expected. Non-Gaussian contribution from saturation of the gain or the absorption, which can suppress the intensity fluctuation of the light, is not expected to occur in the subpicosecond region.[61]

The dye laser output was divided into the pump and the probe beams by a beam splitter, with an intensity ratio of about 70/30. The pump beam, which was linearly polarized

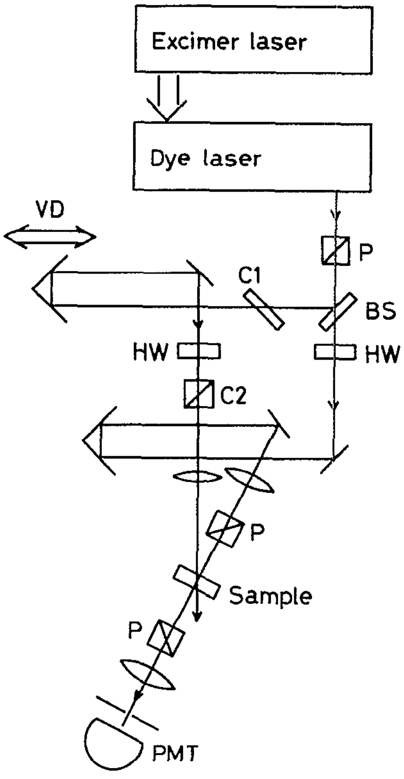


FIG. 2. Experimental setup for the measurement of femtosecond optical Kerr dynamics. BS, beam splitter; C1 and C2, dispersion compensators for the beam splitter and the Glan–Thompson polarizer, respectively; HW, half-wave retarders; P, Glan–Thompson polarizers; PMT, photomultiplier tube; VD, variable delay. Details are described in the text.

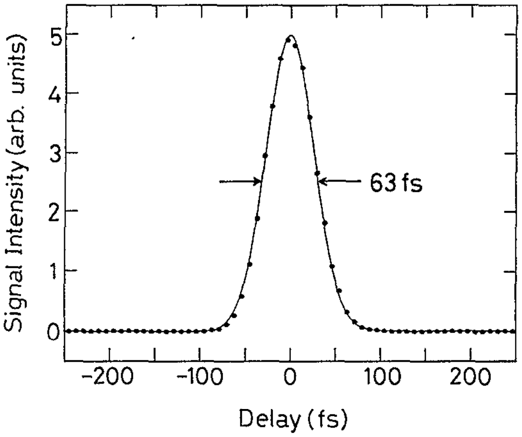


FIG. 3. A typical autocorrelation curve of the incoherent light obtained by the thermal-grating measurement. The line is a Gaussian function with a FWHM of 63 fs.

at 45° with respect to the linear polarization of the probe beam, was focused to a 1 mm glass cell. The probe beam traveled through a variable delay line and a Glan–Thompson polarizer, which was positioned in front of the sample cell to eliminate any polarization change that occurred in the optical elements. After the probe was focused into the sample, the probe was passed through a polarization analyzer and the intensity of the signal light, whose polarization direction was perpendicular to that of the incident probe light, was detected by a photomultiplier tube. The rotation of the polarization of the probe light in the sample of less than 1×10^{-6} could be detected. The signal intensities were averaged typically over 500 laser shots. The laser pulse energy was monitored by a photodiode and any shots with a pulse energy outside $\pm 2\%$ of the average laser pulse energy were excluded. The dispersion of the beam splitter and the polarizer was compensated for by inserting the same optical components in the other arm of the delay line. The pump and the probe beams must undergo the same group-velocity dispersion to achieve the time resolution determined by the Fourier transform of the power spectrum of the incident light.

To obtain the autocorrelation function of the incident incoherent light, the OKE due to a thermal grating or a population grating produced by the interference of the pump and the probe was measured with benzene solution of 4-diethyl-4′-aminonitrostilbene (DEANS). Since DEANS has a broad absorption band at the laser wavelength of 476 nm, the intensity of the signal should be proportional to the squared magnitude of the field amplitude autocorrelation of the incident light.[62] A typical autocorrelation trace is shown in Fig. 3, which can be well fitted to a Gaussian function with a width of 63 fs. In the measurement of the OKE, incoherent light with an autocorrelation width of 57–65 fs was employed. This correlation width corresponds to a coherent pulse width of 40–46 fs, which is below those of femtosecond pulses employed in the Kerr measurements.[17–19] From the fit of the data using a Gaussian function, both tails of the autocorrelation curve were found to decay as $\exp(-\tau^2)$. This result is in contrast to the exponential tails observed with femtosecond pulses, obtained by a colliding-pulse mode-locked ring laser.[63]

Mixtures of CS_2 and various solvents were prepared for the OKE measurement. The viscosities of them were measured with an Ostwald viscosimeter. All the measurements of the OKE and the viscosity were performed at 22 ± 1 °C.

V. RESULTS AND DISCUSSION

A. Carbon disulfide and carbon tetrachloride

The Kerr signal intensity from CS_2 is shown in Fig. 4, as a function of the delay time. The background signal, which was about 50% of the total signal intensity at zero delay, has been subtracted from the data shown here. The large signal at zero delay time agrees with the autocorrelation data shown above. It is attributed to the coherent spike and to a contribution from the instantaneous electronic response. The maximum intensity of the noninstantaneous nuclear Kerr response was ten times smaller than that of the coherent spike. Besides the coherent spike, two other components were observed in the signal. The first component appears at early delay times with a peak at ~140 fs and then decays

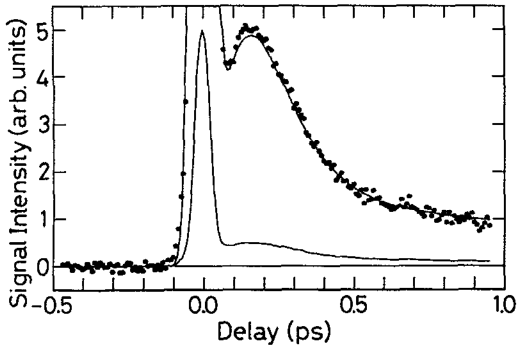


FIG. 4. The delay-time dependence of the OKE signal intensity obtained from carbon disulfide. The lower line is the experimental data. Circles are the data expanded by a factor of 10. The upper line is the fitting curve. The fitting procedure is described in Sec. V B and the fitting parameters are given in Table III.

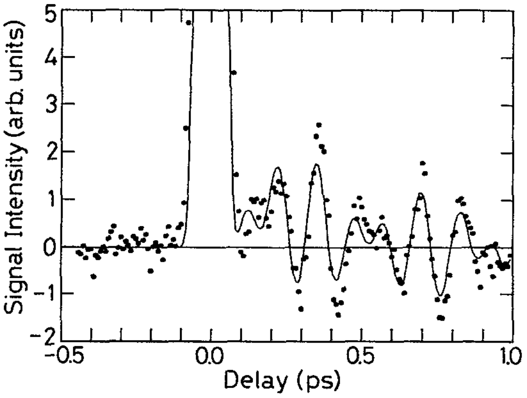


FIG. 5. Signal intensities obtained from carbon tetrachloride. Circles are the experimental data and the line is the fitting curve. The fitting functions and the parameters are described in the text.

until ≈ 500 fs. The other component remains after the disappearance of the fast component and slowly decays from 500 fs until 1 ps, which was the longest delay time used. These two components have also been observed with femtosecond pulses.[17,23,24] The OKE response of CS_2 was first time resolved by Ippen and Shank by using picosecond optical pulses and a 2.1 ps decay time was observed.[54] Measurements with subpicosecond resolution were performed by several groups later and another component with a decay time of 0.20–0.36 ps was reported.[53,64,65] The fast component in the present data decays at 360 fs if an exponential decay is assumed and the decay time of the slow component is 1.7 ps. Recent measurements with sub-100 fs pulses, however, have revealed the inertial feature of the OKE response of CS_2 and inappropriateness of the description of the fast component by a simple exponentially decaying response function.[19-21] The delay in the nuclear response of the optical Kerr effect in the femtosecond region has been widely observed with many molecular liquids and it is now well understood that the existence of the delay is essential because of the inertial character of the nuclear motions.[17,18,22-26,66,67] The procedure of fitting of the obtained data, fully taking account of this inertial character, is described in the next section.

In Fig. 5, the OKE signal from neat carbon tetrachloride is shown. The signal intensity was fitted with two vibrational components and an I-I contribution. The former are damped sine functions with a 2 ps exponential decay and the periods are obtained, by the fitting, to be 164 and 116 fs. For the I-I component, the function shown in Eq. (14) was used. These three functions were convoluted with the autocorrelation data and the coherent spike and a constant background were used besides them for the fitting. The I-I component was necessary to fit the appreciable shift of the center of the oscillation above the background value at delay times shorter than 400 fs. These three features have also been observed with the use of femtosecond pulses by McMorrow *et al.*[17] The oscillations of the signal intensity with the delay time have been attributed to the scissoring and the deformation modes with wave numbers of 218 and 314 cm^{-1}, respectively.

The results shown above are consistent with the previous results of McMorrow *et al.*,[17] except that the intensity ratio of the vibrational components to the I-I component was enhanced by five to ten times in the present experiment. This discrepancy can be explained by the difference in the spectral width of the excitation light. In experiments employing the impulsive stimulated scattering, vibrational modes are excited by combinations of two frequencies, within the excitation light spectrum, with a difference frequency in resonance with the relevant mode. In the experiment of McMorrow *et al.*, light of 180 cm^{-1} FWHM was employed. The 8 nm width of the incoherent excitation light at 476 nm corresponds to a FWHM of 350 cm^{-1}, which is larger than the frequencies of the two vibrational modes.

Thus, the measurement of CS_2 and CCl_4 demonstrated that the incoherent light technique, which has been applied in time-resolved measurements of various processes, such as electronic dephasing,[30,68] vibrational dephasing,[69] population relaxation,[57] and fluorescence decay,[70] can also be applied to obtain the OKE response with a femtosecond time resolution.

B. Binary mixtures of CS_2 and other solvents

Kalpouzos *et al.* measured the Kerr dynamics of CS_2 in binary mixtures with alkane solvents.[24] They observed an increase in the amplitude of the intermediate component by a factor of 2 upon dilution of CS_2 in each solvent. This enhancement was explained by cancellation between the two-, three-, and four-body interaction terms in the effective molecular polarizability, which has been observed also in the density dependence of the DLS of compressed rare gases.[4-6] However, an increase by a factor of 2 is too small compared to the theoretical estimate of the reduction of the amplitude of the I-I contribution by the cancellation mechanism to be two orders of magnitude.[1]

Therefore, we measured the Kerr response of binary mixtures of CS_2 with liquids less viscous than those used in the measurement by Kalpouzos *et al.*[24] to clarify the origin of the fast component in the OKE response, since I-I contri-

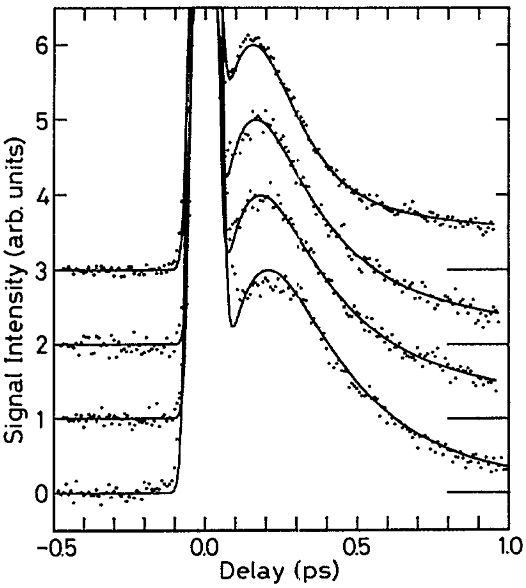


FIG. 6. The delay-time dependence of the signal intensity obtained from binary mixtures of CS_2 and hexane. The signal intensity, after the background intensity was subtracted from it, was multiplied by a factor of 6–12 in order to normalize the intensity of the shoulder part of the signal. The volume fractions of CS_2 are 100%, 50%, 25%, and 10% from the top to the bottom. Dots are the experimental data points and the lines are the fitting curves. The fitting functions are described in the text and the obtained fitting parameters are presented in Table III.

bution should be reduced in viscous solvents by the hindrance of the translational motions of CS_2 molecules by surrounding solvent molecules, resulting in the amplitude enhancement smaller than expected from the decrease of the cancellation effect. Mixtures with five liquids were measured. Four liquids—hexane, methanol, ethanol, and butanol—exhibit only an instantaneous electronic Kerr response. Chloroform, in contrast, has a small nuclear contribution to the OKE.[25]

The signal intensity obtained from mixtures with hexane are shown in Fig. 6. Upon dilution, both the rise and the decay times of the fast component become longer and the amplitude increases with respect to the reorientational contribution. The enhancement of the amplitude ratio of the fast component to the reorientational contribution is attributed mainly to enhancement of the amplitude of the fast component, as shown later.

Analysis of these results, including those obtained from other mixtures, is performed by fitting them using two functions, i.e., the reorientational response and the I-I response as expressed in Eqs. (3) and (14) for the nuclear response.

Using the relations shown in Sec. II and the literature value of τ_r of neat CS_2,[46] we can obtain τ_r of the mixture by measuring the viscosity of the binary mixture as a function of the mixing ratio. The obtained values of viscosities η_B, η_{AB}, and η_A are summarized in Table II, with the molecular weight and the density of each molecule. Since the effective viscosity, which affects the reorientational motion of CS_2 molecules as a frictional force, changes by 40% at most; as seen in Table II, the peak value of the reorientational contribution per molecular density should vary by no more than 40%. Therefore, the change in the amplitude ratio of the fast component to the reorientational contribution, which was observed in the mixing ratio dependence of the OKE response, is attributed mainly to a change in the amplitude of the fast component.

TABLE II. Viscosities and mutual viscosities of CS_2 and various solvents obtained from the measurement of viscosities of the binary mixtures. In this table, B designates CS_2. The molecular weight and the density of each solvent are also summarized. The molecular weight and the density of CS_2 are 76.14 cP and 1.258 g/cm^3, respectively.

	η_B (cP)	η_{AB} (cP)	η_A (cP)	Molecular weight	density (g/cm^3)
Hexane	0.36	0.31	0.29	86.18	0.657
Methanol	0.33	0.53	0.56	32.04	0.789
Ethanol	0.35	0.50	1.15	46.07	0.787
Butanol	0.36	0.43	2.79	74.12	0.808
Chloroform	0.35	0.41	0.54	119.38	1.484

The cross correlation between the I-I contribution and the orientational one was neglected, which is justified since the time scales of these two contributions are different from each other by one order of magnitude.[35] The experimentally obtained data were fitted with these two components convoluted with the coherent spike, besides the constant background and the coherent spike, following Eq. (29).

Figure 7 shows the experimental data for the CS_2/methanol binary mixture series, together with the best fits and curves for the two components—I-I, and orientational ones. The results of the data analysis for the different mixtures are presented in Table III. In this table, $M(2)$ is the second-order moment of the I-I contribution to the DLS spectrum, which is defined by

$$M(2) = \int_0^\infty d\omega\, \omega^2 I_{\rm DLS}(\omega) \Big/ \int_0^\infty d\omega\, I_{\rm DLS}(\omega). \tag{30}$$

By using Eq. (11), $M(2)$ can be expressed as

$$M(2) = (q+2)(q+1)\omega_0^2. \tag{31}$$

This second-order moment has been used in the literature[4,6,7] as a measure of the broadening of the DLS spectrum, or the relaxation rate of the Kerr response. For the data from mixtures with chloroform, the intramolecular vibrational mode of 262 cm^{-1} was included in the data analysis besides the I-I and the orientational components.

From the data shown in Fig. 7 and Table III, several trends are found for mixtures with three solvents, i.e., hexane, methanol, and ethanol: (1) q decreases upon dilution down to -0.6 to -0.8; (2) ω_0 does not vary essentially; (3) $M(2)$ decreases upon dilution: (4) the peak ratio of the I-I component to the orientational one increases upon dilution and the amplitude of the orientational component becomes negligible at the CS_2 volume fraction of 10%. An error in the amplitude of the orientational component is less than 10% of that of the I-I component.

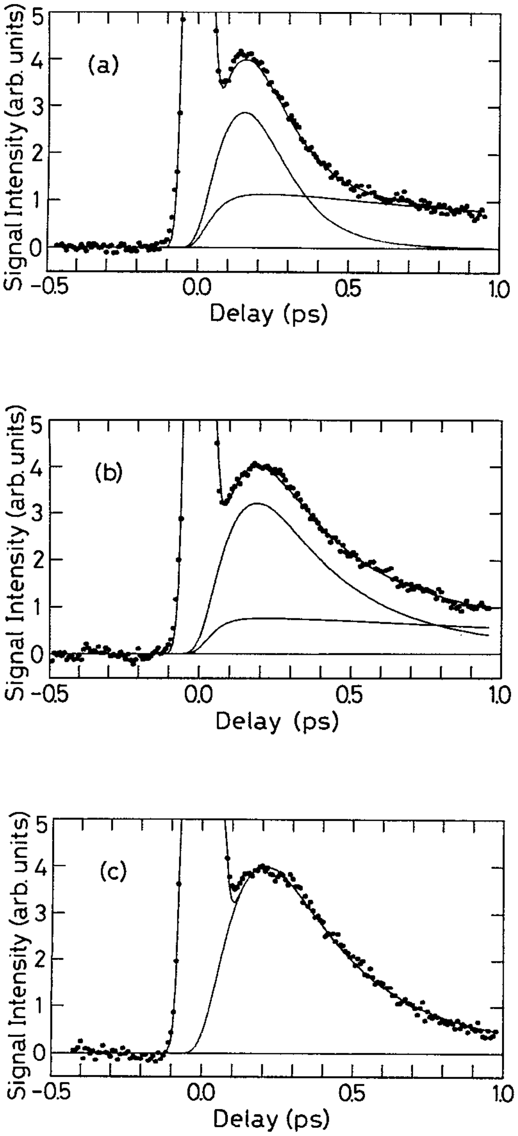


FIG. 7. The delay-time dependence of the signal intensity from binary mixtures of CS_2 and methanol. Closed circles are experimental data. Fitting curves together with two components—I-I and orientational contributions—are displayed. The volume fractions of CS_2 are (a) 100%; (b) 33%; and (c) 10%. The fitting functions are described in the text and the obtained fitting parameters are presented in Table III.

These trends have also been observed in the DLS studies of rare gases. Density dependence of light scattering from argon, krypton, and xenon in a compressed gas phase and liquid phase has been reported.[4–6,10,11] In the I-I DLS of these neat gases, a decrease in amplitude and a broadening of the spectra upon increase in the density have been observed. This dependence on density has also been observed by theoretical and simulation studies[4,6,12–14] and has been attributed to the three- and four-body correlations which cancel the two-body correlation contribution to the I-I polarizability fluctuation. Especially, polarizability fluctuation at low frequency is reduced efficiently, which results in the spectral broadening, or a decrease in decay time, at high densities.

At low densities, on the other hand, the description of the I-I polarization change, or the I-I OKE, by binary interactions is appropriate. The I-I polarization change in CS_2 has been attributed primarily to DID interaction, which is proportional to the cubic inverse of the intermolecular distance.[1] When the binary collision model, in which the molecules are assumed to be in free space, is applied,[49] the exponent q in Eq. (11) is derived to be $-8/7$ at low volume fractions of CS_2, in which the binary collision approximation is good, by using Eqs. (12) and (13). The present obtained values, as shown in Table III, of -0.6 to -0.8 are close to this theoretical value. This shows that molecular motions of CS_2 in dilute solutions in these solvents are fairly free in spite of the presence of the solvent. The good fitting and the consistent change of parameters in a series of binary mixtures with different mixing ratios support the attribution of the fast OKE component mainly to the I-I effect even in neat CS_2.

The trends mentioned above have also been observed by Kalpouzos *et al.*[24] in their study of the OKE response of a series of CS_2/alkane binary solutions. Although comparison cannot be done straightforwardly between our results and theirs because of the different sets of fitting functions, it can be seen that in their data, the change in the ratio of the amplitudes of the fast component to the slow one upon dilution of CS_2 is much smaller than that in ours. This difference should be due to the difference of the solvents. In their study, relatively viscous alkanes were used as the Kerr-inactive solvent, which affect the motion of CS_2 molecules and presumably conceal the cancellation effect of the I-I contribution due to many-body correlation.

In the mixtures with butanol and chloroform, on the other hand, the change in the parameters obtained by the fitting is much smaller than with the other three solvents, as presented in Table III. This result shows that the translational motions of CS_2 molecules, which contribute primarily to the I-I polarizability change, are suppressed by solvent molecules. As shown in Table II, butanol is a viscous solvent, compared with the other four, and the molecular weight of chloroform is much larger than the other. Therefore, the motions of CS_2 molecules in these solvents are expected to be hindered by surrounding solvent molecules. This hindrance should reduce the I-I contribution in the mixtures at low volume fractions of CS_2. Therefore, the present experimental result can be explained in terms of the suppression of translational motions of CS_2 molecules in the femtosecond time regime in these mixtures.

Although we analyzed the data shown above by fitting the fast component to the nonoscillatory response function as given in Eq. (14) in order to focus on the molecular dynamics in dilute CS_2 solutions, where the fitting is excellent, we do not exclude the possible contribution of a damped oscillatory component, as supposed in some reports[21,24] in neat CS_2. Ruhman *et al.* have reported that oscillatory responses are observed in the OKE response of neat CS_2 at low temperatures below 240 K.[23] Even at the room temperature, a possibility of any contribution of intermolecular vibrational motions to the OKE response may not be disregarded,

TABLE III. Parameters obtained from the fitting of OKE signal intensities. τ_{col}'s are calculated values using viscosities. Peak ratios are the ratios of the peak values of the I-I contribution to the orientational contribution before convolution with the coherent spike. $\cdots$ shows that the best fit was obtained without the orientational contribution.

Volume (molar) fraction of CS_2	τ_{col} (ps)	q	ω_0^{-1} (fs)	$\tilde{\nu}_0 = \omega_0/2\pi c$ (cm^{-1})	$M(2)/(2\pi c)^2$ (cm^{-2})	Peak ratio
1.00(1.00)	1.70	0.580	400	13.3	721	2.6
Hexane						
0.50(0.68)	1.56	−0.759	265	20.0	65	11.4
0.25(0.42)	1.44	−0.756	290	18.3	102	8.7
0.10(0.19)	1.35	−0.622	357	14.9	115	$\cdots$
Methanol						
0.33(0.25)	2.17	−0.768	300	17.7	90	4.2
0.10(0.07)	2.25	−0.591	361	14.7	125	$\cdots$
Ethanol						
0.50(0.49)	1.92	0.052	410	13.0	363	3.0
0.10(0.10)	2.06	−0.801	310	17.1	68	$\cdots$
Butanol						
0.10(0.14)	1.72	−0.009	367	14.5	413	2.2
Chloroform						
0.10(0.13)	1.66	−0.054	247	21.4	847	6.3

although we suppose that they are essentially of translational character and affect the susceptibility of the medium mainly through the I-I effect.[1,7,11,13]

However, the mutual viscosities of CS_2 with these two solvents are not appreciably larger than with the other three, as shown in Table III. Since the viscosity of liquids is a measure of the frictional force which is relevant to the macroscopic motions of the liquid, the molecular motions of CS_2 in the macroscopic scale are not suppressed appreciably by the presence of these two solvent molecules. This difference in the molecular motions which depend on the time scale and on the spatial scale requires further studies of the molecular dynamics in liquids.

C. Benzene and benzene derivatives

The signal intensities of the OKE measurement from neat liquids of benzene, toluene, fluorobenzene, chlorobenzene, and *m*-xylene are shown in Fig. 8. These liquids—benzene and mono- or disubstituted benzene derivatives—show very similar OKE response. In the data, besides the coherent spike, there is a feature which rises until 100 fs and decays fast until about 300 fs and there is also a slowly decaying feature. Optical Kerr dynamics of benzene and chlorobenzene have been reported using femtosecond pulses[26,66] and the present data are consistent with them. The fast component in the OKE response of benzene has been attributed primarily to an I-I contribution from the study of the DLS spectrum.[15]

Another feature which is common in the data shown in Fig. 8 is a slightly oscillatory behavior of the slow component. This oscillatory feature is also seen in the data from benzene obtained by Etchepare *et al.* using femtosecond pulses, although it was not mentioned.[26] It was not seen in the data from chlorobenzene reported by Lotshaw *et al.*,[66] which may be due to its worse time resolution. Similar oscillatory response has been observed in the femtosecond optical Kerr dynamics of CS_2 at temperatures lower than 240 K and attributed to a librational motion of CS_2 molecules.[23]

The oscillatory feature observed from benzene and its derivatives should be attributed to an intermolecular vibrational mode. Librational motions of molecules, which are orientational intermolecular vibrations, can affect the optical susceptibility via the molecular polarizability anisotropy or via the intermolecular I-I effective polarizability change. Intermolecular translational vibration can also contribute to the oscillatory behavior of the susceptibility via the I-I mechanism. The oscillatory feature in the OKE response, therefore, can be attributed to either of these two origins.

Dill *et al.* have argued about the librational motions of benzene molecules in the study of the DLS spectrum of neat benzene.[51] They separated the DLS spectrum into I-I and orientational contributions by assuming the spectral shape of the I-I contribution to be $\omega^{12/7}\exp(-\omega/\omega_0)$. From this analysis, they concluded that the orientational motions of benzene are librational in the subpicosecond time domain, which have a period of ≈ 300 fs and decay until ≈ 600 fs. These values are consistent with the oscillatory feature observed in the present data. However, this result is a consequence of the assumption of the spectral shape of the I-I contribution, which yields a nonoscillatory time response. Therefore, the attribution of the oscillatory feature in the Kerr response to the librational motions is not proved by their analysis.

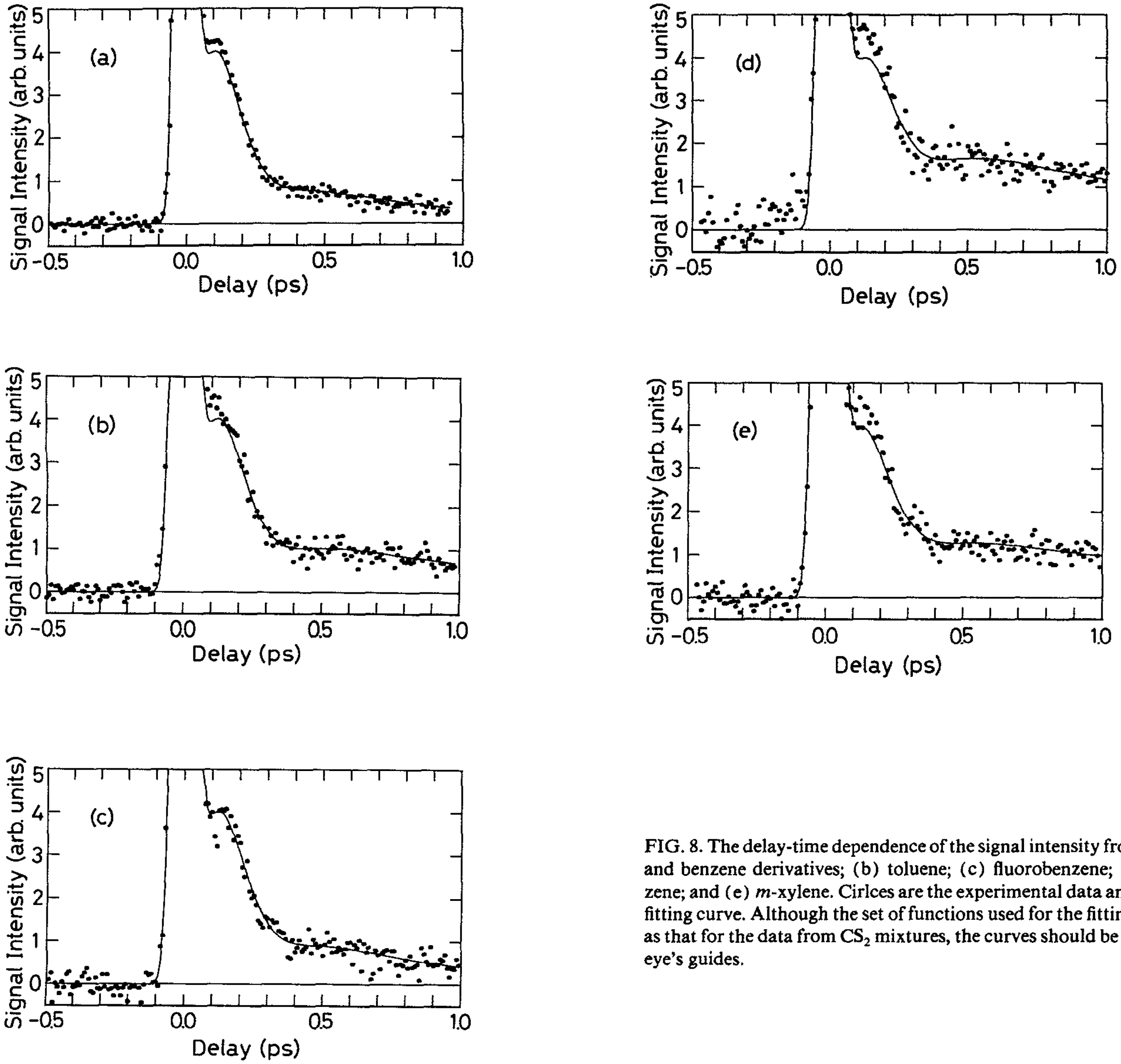


FIG. 8. The delay-time dependence of the signal intensity from (a) benzene and benzene derivatives; (b) toluene; (c) fluorobenzene; (d) chlorobenzene; and (e) *m*-xylene. Cirlces are the experimental data and the line is the fitting curve. Although the set of functions used for the fitting was the same as that for the data from CS_2 mixtures, the curves should be regarded as the eye's guides.

Here, we discuss the possibility of an I-I origin of this oscillatory feature. The orientation of benzene molecules is known to be highly correlated to each other in neat liquid and the bimolecular configuration has been suggested to have a "T"-shaped geometry, in which the molecular planes are perpendicular to each other and the edge of one molecule is close to the center of the other.[16] The existence of benzene dimers in molecular beams has also been reported.[71] Theoretically, the binding energy of the dimer was calculated to be 2 kcal/mol in the T orientation. This strong coupling between molecules is attributed to short-distance interactions, such as permanent-quadrupole–permanent-quadrupole interaction, dispersion force, and electron overlap.[72] Because of this short-distance strong intermolecular coupling, translational and orientational motions of each benzene molecule in liquid phase are expected to be highly correlated with those of the surrounding molecules. Intermolecular vibrational modes are likely distributed in an appreciably narrow spectral region since the strong orientational correlation between molecules does not allow a wide distribution in the local configuration of the liquid. Spectrally narrow distribution is required for the vibration to be observed as oscillations in the OKE response. Intermolecular motions should affect the effective polarizability by the I-I mechanisms, as shown above. Even librational motions, which can affect the susceptibility via the molecular polarizability anisotropy, should have a large I-I contribution in highly polarizable liquids such as benzene. The same discussion can be applied to benzene derivatives, since the small substituents are not expected to prevent contact between benzene rings of these molecules. Therefore, the I-I origin of the oscillatory feature in the optical Kerr response of benzene and benzene derivatives cannot be excluded. Further experimental and theoretical studies are required to clarify the physical origin of this oscillatory behavior.

VI. CONCLUSION

In the theoretical section, we derived an expression for the signal intensity of the OKE measurement using incoherent light. A Gaussian assumption on the statistical properties of the incoherent light was not employed in the derivation. The time resolution for the OKE response is determined by the width of the autocorrelation function of the intensity fluctuation of the incident incoherent light. This expression can also be applied to the analysis of the signal intensity of the measurement of the population dynamics using incoherent light.

Experimentally, femtosecond dynamics of the optical Kerr effect in various neat and mixed liquids were measured by the use of incoherent light with a correlation time of 60 fs. From the measurement of the OKE of binary mixtures of CS_2 and various solvents, the I-I contribution to the OKE was found to be affected remarkably by the femtosecond molecular dynamics of CS_2. Especially, data from diluted solutions of CS_2 in nonviscous solvents composed of molecules with a low molecular weight are consistent with the binary collision model in a free space.

An oscillatory feature was found in the OKE dynamics of neat benzene and several benzene derivatives. This feature was attributed to intermolecular vibrational modes, which change the optical susceptibility of the liquids either via the molecular polarizability anisotropy or via the I-I effective polarizability change.

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