

Optical-heterodyne-detected induced phase modulation for the study of femtosecond molecular dynamics

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A new experimental technique for the study of ultrafast optical response of nonlinear materials, which detects nonrelaxational response in the media with high sensitivity, is introduced. Polarization-selective optical-heterodyne-detection scheme is applied to the measurement of the spectral shift of a probe pulse which is caused by induced phase modulation (IPM) brought about by a pump pulse. This technique, being sensitive to the high-frequency component of the nonlinear response, is especially applicable to the study of intermolecular dynamics in disordered media. The temporal responses of the optical Kerr effect in liquid carbon tetrachloride, benzene, and carbon disulfide are studied using this technique with femtosecond optical pulses. In the response of benzene, damped oscillations are clearly observed which are due to intermolecular vibrational motions of the molecules. The data obtained from benzene and carbon disulfide are analyzed using a Fourier-transform method. The response functions for the IPM measurements are reconstructed, and the Fourier spectra are also obtained. They are discussed in terms of inertial molecular motions and the local structures in these liquids.

I. INTRODUCTION

Inertial nature of orientational and translational molecular motions in liquid phase has been revealed by time-domain measurements with femtosecond time resolution in recent years. The noninstantaneous response of the optical Kerr effect (OKE) of molecular materials, which is due to susceptibility change induced by molecular motions, can be nonrelaxational in the subpicosecond time region, in which inertial effects on the molecular motions become important. Growths and following oscillations in the OKE response have been observed in several transparent organic molecular liquids.¹⁻¹¹

Chesnoy and Mokhtari have investigated oscillatory features in femtosecond nonlinear optical responses of dye solutions which are *resonant* with the excitation light by means of detecting a pump-pulse-induced spectral shift of a probe light pulse.^{12,13} This spectral shift is caused by the induced phase modulation (IPM) of the probe pulse, and is expressed as the time derivative of the real part of the OKE response function in the time scale longer than the duration of the excitation light pulses. IPM technique therefore is suited for the study of the inertial molecular motions, being sensitive only to nonrelaxational responses. In the present paper we apply optical-heterodyne-detection (OHD) technique to the IPM measurements, which results in great enhancement in the sensitivity of the measurements and makes it very feasible to apply the IPM technique to the study of the nonrelaxational response of *nonresonant* molecular liquids.

Extensive investigations have been performed on the molecular dynamics in the liquid phase by studying the dynamical light scattering (DLS) spectrum, which is proportional to the Fourier transform of the susceptibility fluctuation correlation function (SCF) of the medium. The SCF is equated to the orientational correlation function (OCF) of the molecules if intermolecular interaction-induced effects are neglected.¹⁴⁻²⁰ Recently, however, several techniques employing nonlinear optical processes have been applied to the study of the molecular dynamics. These techniques include the time-domain measurements of the OKE response employing ultrashort optical pulses,^{3-8,11,21-25} and frequency-domain ones such as stimulated Raman gain²⁶ and tunable-laser-induced grating measurements.^{27,28} The OKE response function is proportional to the time derivative of the SCF in the high-temperature limit.²⁴ What is directly obtained from the frequency-domain measurements is the Fourier transform of the OKE response function. These time-domain and frequency-domain nonlinear techniques therefore have high sensitivity in the high-frequency region of SCF in proportion to the frequency, and can show oscillatory molecular motions more clearly than linear DLS measurements.²⁴ By employing the IPM technique we can further enhance the sensitivity in the high-frequency region of the response. Furthermore, the IPM response function, given by the time derivative of the nuclear contribution to the OKE response function, directly reflects the angular velocity correlation function (AVCF) of the molecules, which reveals the inertial effects on the molecular motions more clearly than the OCF.

Detailed analyses of the temporal response of the OKE

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in molecular liquids have shown that the molecular motions responsible for the high-frequency portion of the OKE response are of highly intermolecular character, and the frequency of them is inhomogeneously broadened.^{7,8} The analysis of the frequency distribution of the intermolecular modes therefore provides important information about the local structure of molecular liquids as disordered media. McMorro and Lotshaw have reported a Fourier-transform method for the analysis of their results from OKE measurements.^{9,10} We, in the present paper, modify their method for the analysis of the results of IPM measurements.

The OKE responses of benzene and CS₂ are studied by the OHD-IPM technique. Since these liquids exhibit no appreciable monomolecular Raman bands below 400 cm⁻¹, the molecular motions responsible for the IPM signal with 50 fs pulses are purely intermolecular. This makes these liquids ideal for the study of the intermolecular motions in the liquid phase. By using the Fourier-transform analysis the IPM response functions are reconstructed and the Fourier-transform spectra of them are also presented. They provide important information on the ultrafast molecular dynamics and the local structure in the liquid phase.

II. DESCRIPTION OF THE METHOD

Light passing through a medium with a refractive index changing with time undergoes phase modulation in proportion to the changing rate of the refractive index. This process, induced phase modulation (IPM), causes spectral shift of the probing light proportional to the time derivative of the refractive index. By causing the index change of the medium with an ultrashort light pulse and probing it with another pulse, the time derivative of the OKE response in the medium can be measured. This has already been demonstrated with transparent molecular liquids^{25,29} and dye solutions.¹³ This method, being a derivative measurement, is more sensitive to the high-frequency component of the OKE response of the medium than ordinary OKE measurements, and effective especially for the investigation of oscillatory features in the dynamics in electronically excited states¹³ and ground states of molecules.^{25,29}

In this paper, we apply the polarization-selective OHD scheme³⁰ to this method, yielding great enhancement in the sensitivity of the measurement. Since the IPM caused by the OKE is a third-order nonlinear optical process, the spectral shift by the IPM process is induced by third-order nonlinear polarization. In our new technique, optical-heterodyne-detected induced phase modulation (OHD-IPM), the nonlinear polarization is heterodyne detected by a weak local oscillator.³¹ The experimental schematic is shown in Fig. 1. The pump pulse is linearly polarized at angle α , usually 45°, from the linear polarization of the probe pulse. A polarization analyzer placed after the sample passes a fraction of the probe light which is polarized at angle β , which is nearly 90°, from the original polarization of the probe light. Thus the component of the nonlinear polarization orthogonal to the incident probe light is heterodyne detected with the fraction of the probe light, which serves as the local oscillator. A grating disperses the light onto a bicell detector. Spectral shift of the light is detected by taking the difference of the

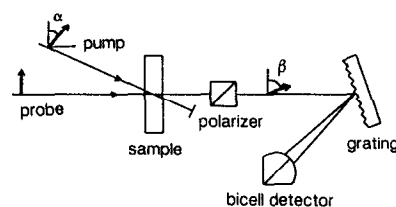


FIG. 1. The schematic of the experiment for the measurement of optical-heterodyne-detected induced phase modulation.

two outputs of the bicell detector. The spectral shift against the delay time of the probe pulse with regard to the pump pulses gives the signal trace of the OHD-IPM measurements.

A simple analysis on the IPM measurements has been presented by Chesnoy and Mokhtari,¹³ who showed that the signal trace is expressed as a convolution of the time derivative of the OKE response function of the medium and the intensity autocorrelation of the excitation light pulses. The contribution of coherent coupling between the pump and the probe pulses, however, greatly modifies the signal trace around the time origin, and it cannot be included in a simple analysis which separates the pumping and the probing processes. In the following, a full description of the IPM signal trace employing the third-order polarization is presented, which includes the coherent-coupling contribution as well.

The nonlinear polarization produced by the third-order process serves as the source term in the nonlinear Maxwell equation and generates electric field with a phase 90° behind the source term. This nonlinear electric field is heterodyne detected by a local oscillator, which is in phase with the probe light. Since the source nonlinear polarization is in phase with the probe light field when the medium is nonresonant with the excitation light, the generated electric field, which is 90° out of phase with the local oscillator, causes spectral shift to the local oscillator. The electric field of the probe light which has undergone the OKE and passed through the analyzer is expressed as

$$E(t)e^{-i\omega_0 t} = [E_{LO}(t) + i\Delta E(t)]e^{-i\omega_0 t}, \quad (1)$$

where $E_{LO}(t)$ is the envelope of the local oscillator, ω_0 is the center angular frequency of the probe light, and $\Delta E(t)$ is proportional to the envelope of the third-order polarization

$$\Delta E(t) \propto P^{(3)}(t). \quad (2)$$

In nonresonant media $P^{(3)}(t)$ is expressed by a linear combination of the contributions of the incoherent process and the coherent coupling as

$$P^{(3)}(t) = \int_{-\infty}^{\infty} dt' R(t-t') [E_0(t)E_0^*(t'+\tau) \times E_0(t'+\tau) + gE_0(t+\tau)E_0^*(t'+\tau)E_0(t')], \quad (3)$$

where $R(t)$ is the temporal response function of the OKE, and $E_0(t)$ is the envelope of the probe light, which is proportional to $E_{LO}(t)$. The probe pulse originates from the same source as that of the pump pulse and is delayed by τ . The factor g is the ratio of the coherent coupling term to the incoherent term and depends on the origin of the nonlinear-

ity and the polarization directions of the pump, the probe, and the detected beams.^{21,32}

The spectral shift of the probe light $\langle \Delta\omega \rangle$ is given by

$$\langle \Delta\omega \rangle = \int_{-\infty}^{\infty} d\Delta \omega \cdot \Delta\omega / (2\pi) \int_{-\infty}^{\infty} dt e^{i\Delta\omega t} G^{(1)}(t), \quad (4)$$

with

$$G^{(1)}(t) \equiv \frac{\int_{-\infty}^{\infty} dt' E^*(t')E(t'+t)}{\int_{-\infty}^{\infty} dt' E^*(t')E(t')}. \quad (5)$$

Here $G^{(1)}(t)$ is the normalized field autocorrelation function of the probe light, and the Fourier transform of it, as appears in Eq. (4), gives the power spectrum of the light. The signal detected by a bicell detector is proportional to $\langle \Delta\omega \rangle$ when higher-order effects can be neglected. By substituting Eq. (1) into Eq. (4) and taking the lowest-order terms with regard to $\Delta E(t)$, we obtain

$$\langle \Delta\omega \rangle = \frac{\int_{-\infty}^{\infty} dt [\Delta E^*(t)\dot{E}_{LO}(t) - E_{LO}^*(t)\Delta\dot{E}(t)]}{\int_{-\infty}^{\infty} dt E_{LO}^*(t)E_{LO}(t)}. \quad (6)$$

Here dots are for the time derivative of the quantity.

By substituting the expression of the third-order polarization, Eqs. (2) and (3), into $\Delta E(t)$ in this equation, the contribution of the incoherent process $S_i(\tau)$ and that of the coherent coupling $S_c(\tau)$ to the spectral shift are obtained as follows:

$$S_i(\tau) \propto - \int_{-\infty}^{\infty} dt \dot{R}(t)G^{(2)}(\tau-t), \quad (7a)$$

$$S_c(\tau) \propto g \int_{-\infty}^{\infty} dt E_{\delta}^*(t+\tau)\dot{E}_0(t) \\ \times \int_{-\infty}^{\infty} dt' R(t-t')E_0(t'+\tau)E_{\delta}^*(t') + \text{c.c.}, \quad (7b)$$

where c.c. stands for the complex conjugate of the preceding term, $G^{(2)}(t)$ is the intensity autocorrelation function of the light, and the OKE response function $R(t)$ was assumed to be real. Thus it is shown that the incoherent contribution to the signal trace, i.e., Eq. (7a), represents the time derivative of the OKE response function convoluted with the intensity autocorrelation function.¹³ Equation (7a) is also proportional to the time derivative of the incoherent contribution to the signal trace of the conventional optical-heterodyne-detected OKE (OHD-OKE) measurement, which is expressed as convolution of the OKE response function and the intensity autocorrelation function.⁴ The above coherent coupling part, in contrast to the incoherent part, is not the time derivative of the coherent coupling contribution to the conventional OHD-OKE signal. When a Fourier-transform limited Gaussian pulse shape is assumed, however, it can be shown that the coherent coupling part is expressed as a linear combination of the intensity autocorrelation function and the time derivative of it for any response function. We use this relation in the analysis of experimental data although the actual pulse shape was not exactly Gaussian.

The OKE response function $R(t)$ is assumed to be real in the present paper. When $R(t)$ is complex, the imaginary part can be measured by inserting a quarter-wave plate in the

probe beam to investigate the excited-state dynamics of resonant media.¹³

III. FOURIER-TRANSFORM ANALYSIS

The transient response in nonlinear optical process can be interpreted from a spectroscopic point of view. Although analysis by fitting the data to some functions has been applied to extract spectroscopic information from time-domain measurements,^{4,23} full information in the frequency domain can be directly obtained by a Fourier-transform analysis. This method has considerable potential especially for the study of the nonlinear response of nonresonant media, where strict correspondence exists between the frequency-domain linear response and the time-domain nonlinear response. Thus accumulated wealth of data by light scattering and infrared studies can be used for the frequency-domain analysis of the OKE response measurements. Separation of the instantaneous electronic and the noninstantaneous nuclear contributions to the experimental data as well as deconvolution of the signal trace to generate the response function to a delta-function excitation is also possible by Fourier transformation.

Fluctuation-dissipation theorem leads to the relation between the OKE response function and the dynamical light scattering (DLS) spectrum as²⁴

$$I_{DLS}(\omega) \propto [n(\omega) + 1] \int_{-\infty}^{\infty} dt r(t) \sin \omega t. \quad (8)$$

Here $I_{DLS}(\omega)$, the Stokes component of the light scattering spectrum, is proportional to the Fourier transform of the correlation function of the susceptibility fluctuation, $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the Bose factor, and $r(t)$ is the nuclear contribution to the OKE response function $R(t)$. In nonresonant media the contributions of the electronic hyperpolarizability and nuclear motions to the OKE response are separable, and the electronic response is instantaneous on the time scale of the applied laser pulse

$$R(t) = b\delta(t) + r(t). \quad (9)$$

Since factor $[n(\omega) + 1]$ is inversely proportional to the frequency in the limit of a high temperature or a low frequency, OKE measurements are more suited than DLS measurements for the study of oscillatory features in the molecular dynamics, which can be obscured by the central peak in the DLS spectrum.²⁴

The Fourier transform of the time derivative of the OKE response function obtained from the IPM measurement is related to the DLS spectrum using Eq. (8) as

$$\int_{-\infty}^{\infty} dt \dot{r}(t) \cos \omega t \propto I_{DLS}(\omega) \omega / [n(\omega) + 1]. \quad (10)$$

As is clear from this relation, the IPM measurement is more sensitive to the higher-frequency component of the OKE response and more useful for the study of vibrational characters of the optical response of materials than conventional OKE measurements.

Shuker and Gammon have shown that the light scattering spectrum in disordered media such as amorphous solids

and liquids is given by

$$I_{\text{DLS}}(\omega) \propto \omega^{-1} C(\omega) g(\omega) [n(\omega) + 1]. \quad (11)$$

Here $g(\omega)$ is the density of vibrational states in the media, $C(\omega)$ is the coupling coefficient between light and the vibrations.^{33,34} Although $C(\omega)$ and $g(\omega)$ cannot be decoupled in Raman-type measurements, which includes OKE and IPM measurements, the reduced Raman spectrum

$$R_2(\bar{\omega}) \equiv I_{\text{DLS}}(\omega) \omega / [n(\omega) + 1] \propto C(\omega) g(\omega) \quad (12)$$

is expected to exhibit features of the density of states of the vibrational modes in the disordered media fairly well, where structures in the coupling coefficient due to spatial symmetry are broad in contrast to those in ordered materials. Fractal characters of several amorphous materials have been clarified by power-law dependence of $R_2(\omega)$ on the frequency.³⁵ From Eqs. (10) and (12) $\dot{r}(t)$, which we designate as the IPM response function, is equated to the Fourier transform of $R_2(\omega)$ as

$$\dot{r}(t) \propto \int_0^\infty d\omega R_2(\omega) \cos \omega t. \quad (13)$$

The reduced Raman spectrum has also been utilized for the study of the vibrational features in molecular liquids.^{18–20,36} An approximate relation in the low-frequency region,

$$R_2(\omega) \propto I_{\text{DLS}}(\omega) \omega^2, \quad (14)$$

has sometimes been employed instead of Eq. (12) for the calculation of the reduced Raman spectrum.^{20,36}

Spectrum of light scattering of molecular liquids generally exhibits far wings besides the central Lorentzian peak. They are attributed mainly to the interaction-induced (I-I) susceptibility change.^{37–39} The molecular motions inducing the far wings are essentially of intermolecular character, and the density of states of them reflects the local structure of the liquids very sensitively. Librations are a special type of intermolecular vibrations where the motions are mainly oscillations in the molecular orientation. Since the Fourier transform of $\dot{r}(t)$ is directly proportional to $R_2(\omega)$, the IPM measurement is essentially suited for the study of vibrational characters of molecular motions in liquids and other disordered systems.

Here we mention the relation between the angular velocity correlation function (AVCF) of anisotropic molecules and the IPM response. Generally, two types of degrees of freedom in the intermolecular vibrational motions are conceivable separately, namely librational (orientational) and translational motions of molecules. Correspondingly, there are two possible mechanism for the modulation of the optical susceptibility. One is the monomolecular polarizability anisotropy, and the other is the intermolecular I-I susceptibility change. Intermolecular translation vibrations contribute to the OKE response only via the I-I mechanism. On the other hand, librational motions of anisotropic molecules, such as benzene and CS_2 , can affect the bulk susceptibility via both the monomolecular and the I-I mechanisms. Although there have been discussions on the nature of the molecular motions responsible for the ultrafast OKE response of molecular liquids, it is not well understood yet.^{7,8,39} The

monomolecular contribution to the DLS spectrum has, however, sometimes been separated by assuming some conditions on the I-I contribution.^{15–17} The monomolecular orientational contribution to the DLS spectrum $I_{\text{OR}}(\omega)$ is the Fourier transform of the OCF.¹⁴ The AVCF, however, exhibits more clearly the ultrafast librational dynamics of molecules.^{15–17,40,41} It has been shown that in the time region shorter than the reorientational relaxation time the AVCF is given by

$$\langle \omega(0) \omega(t) \rangle = \int_0^\infty d\omega \cos(\omega t) \omega^2 I_{\text{OR}}(\omega), \quad (15)$$

where $\omega(t)$ is the component of the angular velocity perpendicular to the orientation of the molecular axis.^{15,40,42} From Eqs. (13), (14), and (15) it is seen that the orientational contribution to the IPM response $\dot{r}_{\text{OR}}(t)$ is approximately proportional to the AVCF in the low frequency region

$$\dot{r}_{\text{OR}}(t) \propto \langle \omega(0) \omega(t) \rangle. \quad (16)$$

The IPM response function, therefore, directly gives the AVCF of the molecular system at temperatures higher than the corresponding frequency when the I-I contribution to the OKE response can be neglected.

The Fourier-transform analysis of data obtained by conventional OHD-OKE measurements has been described by McMorrow and Lotshaw.^{9,10} The analysis of the IPM data can be performed in a similar way. First, the contribution of the coherent coupling was subtracted from the experimental signal trace as follows. The coherent coupling contribution can be expressed approximately as a linear combination of the intensity autocorrelation and its time derivative, as stated in the preceding chapter. The portion proportional to the intensity autocorrelation was subtracted from the signal trace using the autocorrelation obtained from a second-harmonic-generation measurement so that the time integral of the residual part vanishes. The residual part $S_r(\tau)$ is expressed as a convolution of a modified IPM response and the intensity autocorrelation of the excitation pulse,

$$S_r(\tau) = - \int_{-\infty}^{\infty} dt' [b' \dot{\delta}(t') + \dot{r}(t')] G^{(2)}(\tau - t'), \quad (17)$$

with b' modified from b by the residual coherent coupling contribution. The Fourier transform of the modified IPM response $D(\omega)$ is given as

$$D(\omega) \equiv - \mathcal{F}\{b' \dot{\delta}(\tau) + \dot{r}(\tau)\} = \mathcal{F}\{S_r(\tau)\} / \mathcal{F}\{G^{(2)}(\tau)\}. \quad (18)$$

Here

$$\mathcal{F}\{f(\tau)\} \equiv \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} f(\tau) \quad (19)$$

is the complex Fourier transform of $f(\tau)$. Since the Fourier transform of the derivative of the delta function is given by

$$\mathcal{F}\{\dot{\delta}(\tau)\} = -i\omega, \quad (20)$$

the real part of $D(\omega)$ contains contribution only by the nuclear response

$$\begin{aligned} \text{Re } D(\omega) &= - \text{Re } \mathcal{F}\{\dot{r}(\tau)\} \\ &= - \int_{-\infty}^{\infty} d\tau \dot{r}(\tau) \cos \omega\tau. \end{aligned} \quad (21)$$

It is seen from the comparison of this equation with Eq. (13) that $-\text{Re } D(\omega)$ is proportional to $R_2(\omega)$. Because of causality $\dot{\rho}(t)$ can be reconstructed by inverse Fourier transformation of the real part as

$$\dot{\rho}(t) = \begin{cases} 0 & \text{for } t < 0 \\ -2\mathcal{F}^{-1}\{\text{Re } D(\omega)\} & \text{for } t \geq 0 \end{cases} \quad (22)$$

Thus the nuclear contribution to the IPM response is separated from the electronic response, and $R_2(\omega)$ is obtained directly from the IPM measurement. Experimentally, a high-frequency portion of $D(\omega)$ is cutoff before the inverse Fourier transformation because of the limited bandwidth of the measurement. This corresponds to temporal smoothing of the reconstructed $\dot{\rho}(t)$ trace. Furthermore the AVCF can also be directly obtained provided that the I-I contribution can be neglected. This makes the IPM measurement quite powerful for the study of ultrafast coherent molecular motions.

IV. EXPERIMENTAL

Detailed description of the femtosecond light source will be given in a separate paper.⁴³ Briefly, a standard combination of a colliding-pulse mode-locked (CPM) ring dye laser and a multiple-pass amplifier pumped by a copper vapor laser was employed.⁴⁴ A 3 mm flow cell was used for the amplification, and the output of the CPM laser was amplified six times.⁴⁵ The amplifying medium as a 3×10^{-4} mol/l solution of rhodamine 640 in a 1:3 volume ratio mixture of methanol and water with 4% Ammonyx LO. The output was passed through a sequence of four prisms to minimize the pulse width at the sample by compensating for the group-velocity dispersion of optical components. The repetition rate, the energy, and the wavelength of the amplified pulses were 10 kHz, 2 μ J, and 620 nm, respectively. The output pulses were attenuated for the measurement down to a 100 nJ level to avoid any higher-order effects. The pulse width was 55 fs, which was calculated from the second-harmonic autocorrelation measurement, assuming a hyperbolic-secant squared pulse shape.

The amplified light was divided by a beam splitter into the pump and the probe beams. Both beams were passed through delay lines, one of which could be varied by a stepping-motor-driven translation stage. The polarization direction of the pump light was rotated to 45° from that of the probe light by a quartz halfwave plate. A Glan-Thompson (GT) polarizer was inserted in front of a focusing lens in the probe beam line. Another GT polarizer was inserted also in the pump beam line to compensate for the group-velocity dispersion.

For OHD-IPM measurements, a third GT polarizer was employed as an analyzer to transmit a small fraction of the probe after passing through the sample cell. This fraction served as the local oscillator of the OHD measurement. The intensity of the local oscillator was adjusted so that it was greater than about 20 times of that of the nonlinear signal field in order to ensure linear detection of the OKE response. The polarization angle of the analyzer was typically 1° to 2° from orthogonal to the input polarization direction. The output of the analyzer was collimated by a lens and dispersed

by a grating onto a bicell photodiode (BiPD). The pump beam was chopped at 2.3 kHz, and the difference of the two outputs of the BiPD was fed to a lock-in amplifier. The BiPD was positioned so that the two outputs balanced when the pump beam was intercepted.

Conventional OHD-OKE measurements⁴ were also performed for the comparison with the OHD-IPM measurements. For the OHD-OKE measurements, a quartz quarter-wave plate was inserted in the probe beam after the sample cell. One of the axes of the quarter-wave plate was fixed to be parallel to the polarization direction of the probe light. The analyzer was oriented by a small angle from an orthogonal direction to the input probe light polarization. The intensity of the output of the analyzer was detected by a photodiode.

All the measurements were performed at 22 ± 1 °C. The sample liquids of CCl_4 , benzene, and CS_2 were in a 1 mm glass cell.

V. RESULTS AND DISCUSSION

Figure 2 shows results of a conventional OHD-OKE measurement and an OHD-IPM measurement from liquid CCl_4 . The sign of the latter, which is arbitrary depending on the sign of the local oscillator field, is fixed so that the IPM data correspond to the time derivative of the ordinary OKE data. The oscillations in the data are due to intramolecular vibrational modes of 218 and 314 cm^{-1} . The OKE data are consistent with those reported by McMorro *et al.*⁴ In the figure also the time integral of the OHD-IPM data is shown in order to confirm the validity of the time-derivative technique by OHD-IPM measurements. The integral is expanded and vertically shifted to match the OHD-OKE data. The agreement between the OHD-OKE and the time integral of the OHD-IPM signal is remarkably good except the misfit around time zero and the baseline shift at negative delay

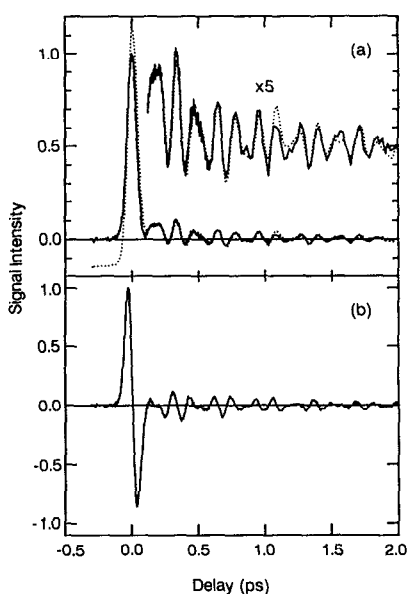


FIG. 2. Signal traces obtained from CCl_4 . (a) The OHD-OKE data (solid line) are plotted with the time integral of the OHD-IPM signal trace (dotted line). Also displayed are the oscillating parts of them, which are expanded fivefold after shifted vertically. (b) Original signal trace of OHD-IPM measurements.

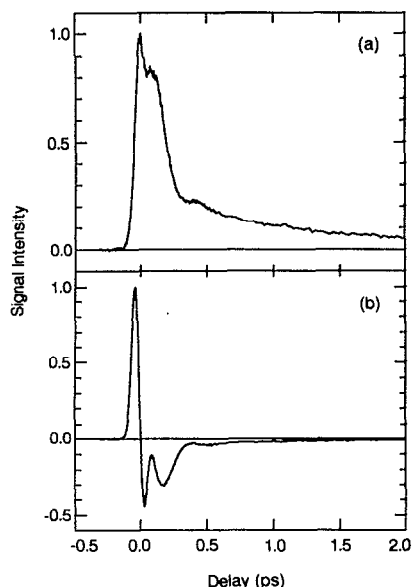


FIG. 3. Signal trace of benzene obtained by (a) OHD-OKE and (b) OHD-IPM measurements.

times. These disagreements are due to the contribution of the coherent coupling, since that to the OHD-IPM signal trace is not the time derivative of that to the OHD-OKE signal trace, as shown in Sec. II.

Figure 3 shows the OHD-OKE and OHD-IPM data obtained from liquid benzene. Damped oscillations are apparent in the OHD-IPM data. The dynamics of the OKE response of benzene has been studied by a conventional transient-grating measurement with femtosecond pulses⁶ and by a Kerr-shutter experiment with temporally incoherent light.^{11,23} Although the oscillations are discernible in the previously reported data^{6,11,23} and also in the present OHD-OKE data, the advantage of the time-derivative technique by OHD-IPM measurements for the study of vibrational dynamics of molecular systems is clear. The OHD-IPM signal trace can be decomposed into three following contributions: (1) the nearly antisymmetric signal with a large amplitude around time zero due to the electronic and the coherent coupling contributions; (2) damped cosine oscillations with a period of about 400 fs; and (3) slowly decaying negative signal. The oscillations in the OKE and the IPM data are attributed to an *intermolecular* vibrational mode since benzene has no low-frequency *intramolecular* modes in the wave number region below 400 cm^{-1} .⁴⁶ The character of the intermolecular mode, however, is not clear.

Molecular dynamics in liquid benzene has also been studied by means of the measurement of the DLS spectrum. The AVCF of benzene molecules in liquid has been calculated from the DLS spectrum by several groups.^{15–17} They separated the DLS spectrum into the I-I contribution $I_{\text{int}}(\omega)$ and the orientational contribution $I_{\text{OR}}(\omega)$ by assuming the functional form of the I-I contribution, and calculated the AVCF using Eq. (15). We reconstructed the time derivative of the nuclear contribution to the OKE response function $\dot{r}(t)$ following the procedure described in Sec. III for the comparison with those results since it should be nearly equal

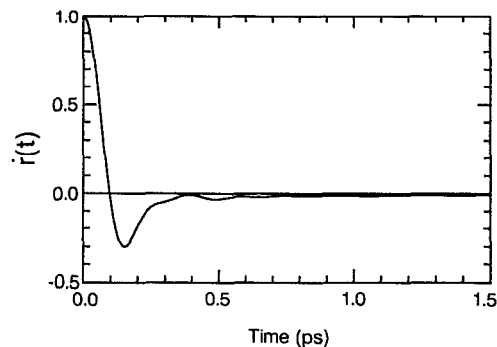


FIG. 4. Reconstructed IPM response function $\dot{r}(t)$ of benzene, which is due to the nuclear response.

to the AVCF if the I-I contribution can be neglected. Figure 4 shows the reconstructed IPM response function $\dot{r}(t)$ for benzene. The $R_2(\omega)$ spectrum up to 200 cm^{-1} was used for the Fourier inverse transformation. It clearly shows damped oscillations with a period of about 400 fs. The humps around 250 and 550 fs, which are not seen in the original experimental data, are probably artifacts due to the truncation of the Fourier spectrum at 200 cm^{-1} or due to imperfect separation of coherent-coupling and electronic contributions. The reconstructed IPM response agrees well with the AVCFs obtained from the DLS spectrum^{15–17} except for these humps and a slowly decaying negative feature in the present data. It should correspond to the I-I contribution which has been subtracted from the DLS spectrum before the calculation of the AVCFs. In this paper, however, we do not attempt to separate the I-I and the orientational contributions to $\dot{r}(t)$ in order to obtain the AVCF since the assumption of a specific functional form of the I-I contribution does not have sufficient theoretical ground, and it is not clear whether the main origin of the oscillatory feature is the librational or the translational motions of molecules. The agreement between the present $\dot{r}(t)$ and the AVCF calculated from the DLS spectrum, however, shows the exact correspondence between the nonlinear response and the fluctuation in the linear susceptibility of nonresonant media, which is a consequence of the fluctuation–dissipation theorem.

The conventional OHD-OKE data and the OHD-IPM data obtained from CS_2 are shown in Fig. 5. In the IPM signal trace of CS_2 the oscillatory character is not so apparent as in that of benzene. The IPM response function of CS_2 reconstructed from the IPM signal trace is shown in Fig. 6. The Fourier transform up to 100 cm^{-1} was used. The oscillation almost damps in a single period, which is about 600 fs. Although the femtosecond OKE response of CS_2 has already been reported by several groups,^{3,4,7,8,11} the present IPM data, being closely related to the AVCF, exhibit more directly the features of the coherent molecular motions in CS_2 liquid.

Molecular motions in liquid CS_2 have been studied by Tildesley and Madden using computational simulation.⁴¹ They calculated the AVCF of CS_2 at 294 K, which is very similar to the $\dot{r}(t)$ shown in Fig. 6 except for the following points: (1) The negative peak value of the AVCF around 300 fs is 10% of the initial positive value, in contrast to the

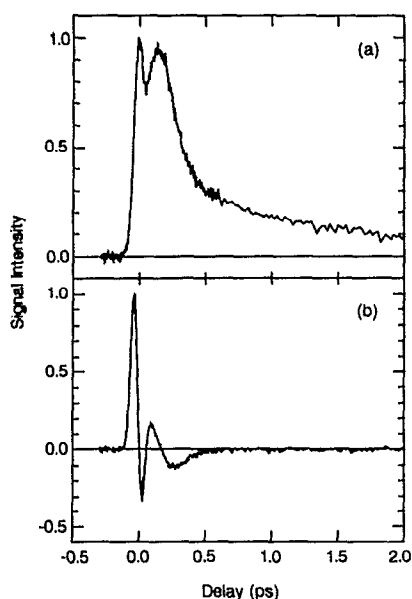


FIG. 5. Signal trace of CS₂ obtained by (a) OHD-OKE and (b) OHD-IPM measurements.

ratio of 45% for $\dot{r}(t)$ presented here; (2) The zero-crossing time is about 215 fs, whereas that is 180 fs for $\dot{r}(t)$. These differences should be due to the I-I contribution to the OKE response, which does not contribute to the AVCF. Molecular dynamics simulations on the subpicosecond OKE response of CS₂ have been presented by Madden³⁷ and by Geiger and Ladanyi,⁴⁷ They used similar models, and there is no pronounced difference in the results. It was found from their simulation that the I-I contribution dominates the OKE response for $t < 200$ fs, and the peak of I-I contribution occurs earlier than the orientational peak. This is consistent with the present result since the I-I contribution to $\dot{r}(t)$ should have a large positive value earlier than about 200 fs and a large negative value between 200 and 500 fs due to the fast rise and decay of the response. This explains the larger negative value and the smaller zero-crossing time than those of the AVCF obtained from the simulation studies.

Thus the present experimental results are consistent with those of the simulation studies. Although the dipole-induced-dipole (DID) effect on the susceptibility is found to be the main origin of the I-I contribution by theoretical and

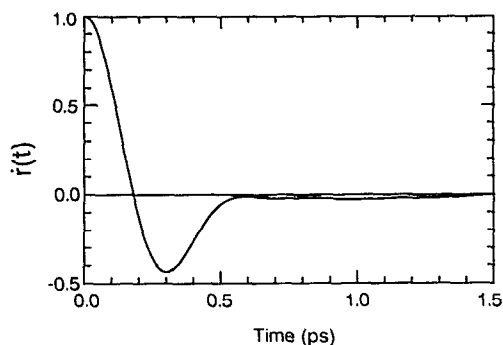


FIG. 6. Reconstructed IPM response function $\dot{r}(t)$ of CS₂, which is due to the nuclear response.

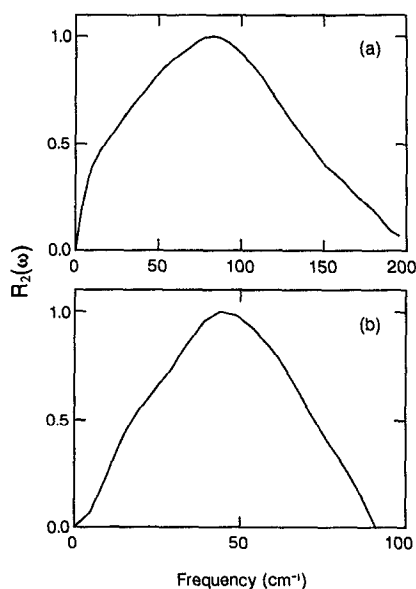


FIG. 7. The reduced Raman spectra $R_2(\omega)$ of (a) benzene and (b) CS₂.

simulation studies,^{38,47} the molecular motions which induce the susceptibility change are not well characterized yet. Calculations by Madden and Cox predict that the I-I effect due to translational intermolecular motion dominates the high-frequency region of the DLS spectrum of CS₂.⁴⁸ However, since the time scales of the I-I and the orientational contributions are comparable, these two contributions can interfere with each other in subpicosecond time region.³⁷ Librational motions of molecules, therefore, may affect the I-I response of CS₂ in this time region as suggested by Ruhman *et al.*⁷ Detailed simulation studies will be required to clarify the character of the molecular motions which induce the I-I response.

In Fig. 7 are shown the reduced Raman spectra $R_2(\omega)$ of benzene and CS₂ calculated from the IPM signal trace by the Fourier-transform procedure described in Sec. III. Their peak frequencies are 80 and 45 cm⁻¹ for benzene and CS₂, respectively. The $R_2(\omega)$ spectrum of benzene has been calculated from the DLS spectrum using the exact relation, Eq. (12),¹⁸ or the approximate form as in Eq. (14).²⁰ The peak frequency of the reported spectra at 75 or 78 cm⁻¹ and the spectral shape agree well with the present spectrum obtained by the OHD-IPM technique. The present peak frequency for CS₂ data also agrees with the reported value of 46.4 cm⁻¹ at 333 K obtained from the DLS spectrum.⁴⁹

It has been shown that the damping of the oscillatory OKE response of molecular liquids is primarily due to the inhomogeneous distribution of the frequency of intermolecular vibrational modes.^{7,8} Since the frequency of the intermolecular vibrations depends highly on the local structure of the liquid, the study of the oscillatory OKE response should provide substantial information about the local order of liquids, of which little is known yet. For the discussion of the distribution of vibrational modes in disordered media, the Fourier-transform analysis is straightforward and powerful since $R_2(\omega)$, which is the Fourier transform of the IPM response function, directly corresponds to the density of states of vibrational modes, as shown in Sec. II.

Although the spectrum only up to 200 cm^{-1} is shown here, this time-domain technique has a potential bandwidth up to 400 cm^{-1} , where the magnitude of the Fourier-transform spectrum of the intensity autocorrelation of the excitation pulses is still about 5% of the peak value. It is difficult, in contrast, to obtain an $R_2(\omega)$ spectrum up to 300 cm^{-1} from the DLS spectrum since the intensity of the DLS spectrum drops rapidly at the wings because of the factor of $\omega/[n(\omega) + 1]$, as shown in Eq. (12).

The structures of disordered media have been investigated by studying the density of states of localized vibrational modes. $R_2(\omega)$ spectra calculated from the light scattering spectra have been utilized for the study of polymers and other amorphous media, and a power-law dependence of the spectra in a certain frequency region has suggested a fractal structure of the media.^{35,50,51} Recently, possibility of fractal ordering of the structure of liquids has been suggested.⁵² $R_2(\omega)$ spectra of many molecular liquids show the power-law dependence in a frequency region around 10 cm^{-1} , and the intermolecular vibrational modes in this region might be understood as fractons, which are the vibrational modes localized in fractal structures.^{53,54} In the fracton picture the peak frequency of the $R_2(\omega)$ spectrum corresponds to the high-frequency edge of the fracton region, which can be equated to the sound velocity in the medium divided by the size of the unit of the fractal structure. By using the sound velocity of 1295 m/s for benzene and 1149 m/s for CS_2 , the unit sizes are calculated reasonably to be 5.4 and 8.5 \AA , respectively, being a few times the size of each molecule.

Analyses of x-ray and neutron scattering data and simulation studies,⁵⁵⁻⁵⁹ however, have shown that the orientation of benzene molecules in liquid state tends to be perpendicular to nearest neighbors, which is similar to the local structure in the crystalline phase.⁶⁰ On the other hand, it has been reported that although CS_2 molecules tend to be aligned parallel to one another, the orientational correlation in the liquid phase is small.^{56,61} A larger unit size therefore of the fractal structure of benzene than that of CS_2 should be expected, contrary to the values calculated above. A more realistic model is required for the interpretation of the $R_2(\omega)$ spectra of molecular liquids.

Librational molecular motions may have significant effects on the density of states of localized vibrational modes in these liquids since the intermolecular modes in liquids of anisotropic molecules inevitably have a librational, i.e., orientational, character to some extent. In the Raman spectrum of the crystalline CS_2 low frequency peaks due to libron modes have been observed at 73 and 83 cm^{-1} at 77 K .^{62,63} Crystalline benzene has two libron modes with appreciable Raman intensities at 53 and 73 cm^{-1} at 195 K .⁶⁴ These frequencies do not correspond to the peak frequencies of $R_2(\omega)$ spectra. However, since the frequencies of librational modes in crystalline benzene are slightly below the peak of the $R_2(\omega)$ spectrum, the librational modes in benzene should affect the nature of intermolecular vibrational motions significantly also in the liquid phase.

More comprehensive study on the OKE response of molecular liquids is required to reveal the nature of the intermolecular motions including their frequency distribution in

molecular liquids. The study of femtosecond OKE response, however, is potentially very powerful for the study of the dynamics and the structure of molecular liquids since it is sure that the local structure greatly affects the dynamics or the frequency distribution of intermolecular motions of the molecules, which usually damp in the subpicosecond time region.

VI. CONCLUSIONS

The optical-heterodyne technique for the sensitive detection of the spectral shift due to induced phase modulation (OHD-IPM) was developed, and its application to the study of the molecular dynamics in several liquids were described. We derived the expression for the signal trace of OHD-IPM measurements using third-order nonlinear polarization. The signal trace was found to consist of the incoherent and the coherent-coupling contributions. The incoherent part is expressed as a convolution of the IPM response function, which is the time derivative of the response function of the optical Kerr effect (OKE), and the intensity autocorrelation of the excitation pulses. The coherent-coupling part has a more complicated form, which should also be accounted for in the analysis of the experimental results. The IPM response function was shown to approximate the angular velocity correlation function (AVCF) of anisotropic molecules if the interaction-induced effect on the susceptibility is neglected. The Fourier transform of the IPM response function was shown to be equal to the reduced Raman spectrum $R_2(\omega)$ shown by Eq. (12).

Experiments on the OKE response of benzene and CS_2 clearly showed the oscillatory character of the intermolecular motions in these liquids. The reconstructed IPM response functions and the reduced Raman spectra for these liquids were obtained using a Fourier-transform technique. The obtained IPM response of benzene was found to be consistent with the AVCF calculated from the light scattering spectrum. The results on CS_2 confirmed a significant contribution of the interaction-induced effect to the femtosecond OKE response, which is in agreement with simulation studies.

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