Observation of broadened and oscillatory optically induced Kerr kinetics in neat liquids

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Broadened and oscillatory Kerr profiles in time were observed in neat liquids by means of intense picosecond optical excitation. This new observation can be used to measure the *molecular* relaxation time and a nonlinear index of refraction.

Ultrafast laser spectroscopy has been extensively applied to study very rapid events that occur in nature.[1] A variety of novel techniques have been used to measure phenomena on a sub-nanosecond time scale, such as the optical Kerr gate,[2] streak camera,[3] excite and probe technique,[4] two-photon absorption induced fluorescence,[5] second harmonic generation,[6] and picosecond continuum.[7] In this paper, we report the first observation of a broadened and oscillatory optical Kerr effect induced by an intense picosecond laser pulse in liquids. The optical Kerr effect was measured at various intensity levels of the orienting laser pulse and compared with theoretically calculated curves. A new technique is derived for measuring the relaxation time and the nonlinear index of refraction in condensed matter.

In the optical Kerr effect (OKE), a linearly polarized laser pulse generates a nonlinear polarization in the medium which induces a transitory optical birefringence. The difference between the induced indices of refraction parallel and perpendicular to the polarization direction of the orienting laser field E_{w2} is given by[8]

$$\delta n(t) = n_2^e \langle E_{w2}^2(t) \rangle$$
$$+ \frac{n_2^0}{\tau_0} \int_{-\infty}^{t} \langle E_{w2}^2(t') \rangle \exp[-(t-t')/\tau_0] dt', \qquad (1)$$

where n_2^e is the nonlinear index of refraction arising from fast relaxation mechanisms[8] (relaxation times are fast compared to the laser pulse width); n_2^0 is the nonlinear index of refraction arising from a molecular relaxation process with a relaxation time τ_0 (slow compared to the pulse width)[8-12]; E_{w2}^2 is the orienting laser field of frequency $w2$; and $\langle E_{w2}^2(t) \rangle$ is the time average of the optical field which is assumed to be

$$\langle E_{w2}^2(t) \rangle = \tfrac{1}{2} E_{20}^2 \exp(-t^2/\tau_l^2), \qquad (2)$$

where τ_l is defined as $1/e^2$ decay time of the

pulse envelope. A probe pulse E_{w1} at a frequency $w1$ (wavelength λ_1), initially polarized at an angle of $45°$ with respect to the polarization direction of the orienting pulse E_{w2}, experience a phase retardation

$$\delta\phi(t) = (2\pi L/\lambda_1)\delta n(t) \qquad (3)$$

between its parallel and perpendicular polarization components upon traveling through an activated Kerr cell of length L. This causes the polarization state of the probe pulse to be altered. The probe signal transmitted through a Kerr gate as a function of delay time τ_D between the probe and the orienting pulse is detected by a slow photodetection system.[2,8,10,13] The normalized signal at τ_D is

$$S_t(\tau_D) = \frac{1}{S_1} \int_{-\infty}^{\infty} \langle E_{w1}^2(t - \tau_D) \rangle \sin^2 \tfrac{1}{2}\delta\phi(t) \, dt, \qquad (4)$$

where S_1 is the signal of the probe light which passes through the Kerr gate when the axes of the analyzer is oriented parallel to the polarization axis of the polarizer, and $\langle E_{w1}^2(t) \rangle$ is assumed to have the same τ_l as $\langle E_{w2}^2(t) \rangle$. The pulse durations measured by TPF for the 1.06- and 0.53-μm pulses are approximately the same [≈ 6 ps within our experimental accuracy ($\pm 15\%$)].

When the intensity of the orienting pulse in the OKE is such that $\delta\phi < 1$, two approximation equations can be derived for $S_t(\tau_D)$ depending on the relative values of τ_0 and τ_l:

(i) When $\tau_0 \ll \tau_l$, Eq. (4) can be approximated by

$$S_t(\tau_D) \approx \frac{1}{S_1} \int_{-\infty}^{\infty} \langle E_{w1}^2(t - \tau_D) \rangle \left(\frac{\delta\phi(t)}{2} \right)^2 dt$$

$$\propto (n_2^e + n_2^0)(E_{20}^2)^2 \exp(-2\tau_D^2/3\tau_l^2) . \qquad (5)$$

In this case, the peak amplitude of the transmitted signal $S_t(\tau_D)$ is a function of $(E_{20}^2)^2$; and the full width at half-maximum (FWHM) of $S_t(\tau_D)$ in time is about $2(\tfrac{3}{2}\ln 2)^{1/2} \tau_l \approx 2\tau_l$.

(ii) When $\tau_0 \gg \tau_i$, Eq. (4) can be approximated by

$$S_t(\tau_D) \approx \frac{1}{S_1} \int_{-\infty}^{\infty} \langle E_{w1}^2(t - \tau_D) \rangle \left(\frac{\pi L}{\lambda_1}\right)^2$$

$$\times \left(n_2^e \langle E_{w2}^2(t) \rangle + \frac{n_2^0}{\tau_0}\right.$$

$$\times \left.\int_{-\infty}^{t} \langle E_{w2}^2(t') \rangle \exp[-(t-t')/\tau_0] dt'\right)^2 dt$$

$$\propto (n_2^0 E_{20}^0)^2 \exp(-2\tau_D/\tau_0) \quad \text{for } \tau_D > 5\tau_i. \quad (6)$$

In this case, the peak amplitude of $S_t(\tau_D)$ is proportional to $(n_2^0 E_{20}^2)^2$; and the decay time of $S_t(\tau_D)$ is equal to $\frac{1}{2}\tau_0$ for $\tau_D > 5\tau_i$.

When the intensity of the orienting pulse is such that $\delta\phi > 1$, the above approximations are no longer valid. Using a focused picosecond laser pulse, $\delta\phi \gg 1$ can easily be achieved. For a peak field of 10^4 stavolt/cm (power density $\approx 12 GW/cm^2$), the phase retardation in a 1-cm-long carbon disulfide (CS$_2$) cell is about 30π and in a 1-cm long nitro-benzene(NB) cell is about 12π. Under these conditions, we have observed a broadened OKE profile in time for the CS$_2$ liquid ($\tau_0 < \tau_i$), and a broadened oscillating OKE profile in time for the NB liquid ($\tau_0 > \tau_i$). These complicated OKE time profiles arise from the birefringence in the wings of the induced phase retardation $\delta\phi(t)$.

A schematic diagram of the experimental apparatus used to measure the intensity dependence of the OKE kinetics is shown in Fig. 1. The single shot picosecond laser technique offers a convenient method for measuring the OKE[14-17] kinetics. A single 1.054-μm (1.05) pulse with ≈ 6 ps duration

generated from an amplified mode-locked Nd: phosphate glass laser system[18] was used to induce the Kerr birefringence in a 1-cm-long sample. A second harmonic 0.527-μm(0.53) pulse was used to interrogate the sample. Its beam diameter was expanded and passed through an echelon. In this manner, the adjacent segments of the interrogating beam (30 pulses) were delayed with a step progression of ≈ 2.5 ps per step. The oblique wave front probed the transitory birefringence induced in the sample. The 0.53-μm step signals transmitted through the Kerr gate were imaged by a camera lens onto the target face of a Hamamatsu GBC SIT videocamera. The video signal was processed by a Hamamatsu Temporal Analyzer. The time axis of the oblique front was calibrated by moving a delay prism in the 0.53-μm laser beam path. The 1.05-μm pulse was incident on the sample at an angle of approximately 3° to the propagation direction of the 0.53-μm beam. The 1.05-μm beam was focused to a diameter of about 3 mm at the sample cell. The area of the segmented 0.53-μm beam profile was focused to a size of 1 mm by 1 mm at the sample site to ensure complete overlap with the 1.05-μm beam profile inside the sample. The energy of the 0.53- and the 1.05-μm pulses were measured by a fast photodiode and oscilloscope on each laser shot. The energy was calibrated using a Hadron thermopile. The peak power density of the pulse $I_{20}[= E_{20}^2(C/8\pi)]$ was calculated from $(W/A\tau_i \sqrt{\pi})$, where W is the measured energy of a single pulse, A is the effective laser beam area, and τ_i is defined by Eq. (2) assuming a Gaussian pulse envelope.[19,20] The chemicals used in this experiment were the highest purity available from
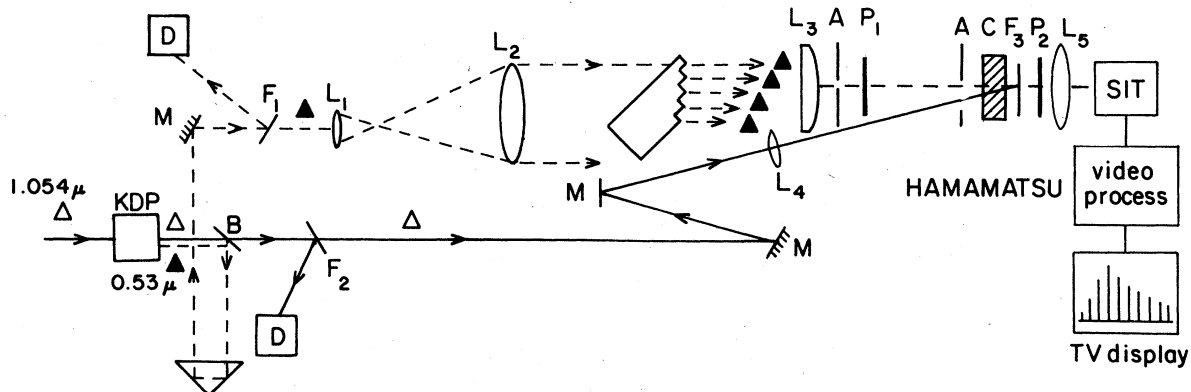

FIG. 1. Schematic diagram of the experimental setup. A, 1-mm slot; B, beam splitter; C, 1-cm-long optical cell; D, Hamamatsu photodiodes; F1; Corning 4-96 filter; F2; Corning 7-99 filter; F3, Corning 4-96 filter; L1, $f=$ 4-cm lens; L2, $f=$ 40-cm lens; L3, $f=$ 30-cm cylindrical lens; L4, $f=$ 30 cm lens; L5, 50 mm/f1.8 camera lens; and M, dielectric coated mirrors. P1 and P2, polaroid HN22 polarizers; polarized along the directions 45° and $-45°$, respectively. TV, Hamamatsu Temporal Analyzer video system. Echelon: 30 pieces of 1-mm thickness glass oriented at Brewster's angle with respect to the polarization direction of E_{w1}.

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The measured transmitted signals from a CS_2 and a NB gate at various orienting intensity levels are plotted in Figs. 2(a) and 3(a), respectively. The corresponding calculated curves are plotted in Figs. 2(b) and 3(b) by assuming values of the parameters I_{20}, τ_l, τ_0, n_2^e, and n_2^0 for Eq. (4). Since the power density and pulse durations of the laser pulse fluctuate within $\pm 20\%$, these parameters were accurate within that variation. The nor-
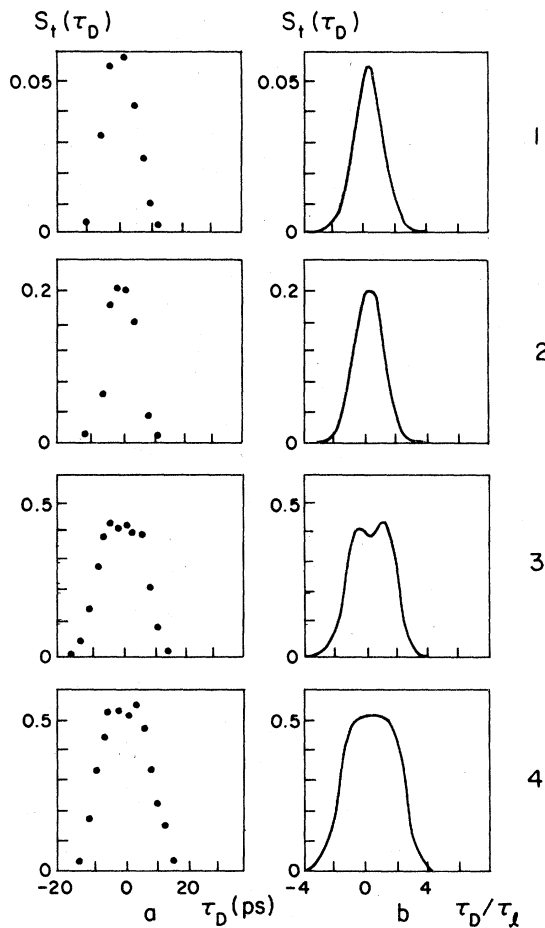

FIG. 2. Kerr transmitted signal of CS_2 liquid at various intensitites of the orienting 1.05-μm pulse. (a) Experimental data; (b) calculated curves from Eq. (4). The parameters chosen are $\lambda_1 = 0.53\mu$m, $L = 1$ cm, n_2^e $= 0.4 \times 10^{-11}$ esu, $n_2^0 = 1.6 \times 10^{-11}$ esu, $\tau_0 = 1.8$ ps, and $\tau_l = 5$ ps. The measured power densities were accurate to within $\pm 20\%$. The location of zero ($\tau_D = 0$) for the experimental data was chosen where S_t (τ_D) reaches its maximum value for the CS_2 gate. (1) $I_{20} = 68(MW/cm^2)$ [$\delta\phi(0) \approx 0.21\pi$], (2) $I_{20} = 135$ MW/cm^2[$\delta\phi(0) \approx 0.42\pi$], (3)$I_{20}$ $= 680$ MW/cm^2[$\delta\phi(0) \approx 2.1\pi$], (4)$I_{20} = 3.4$ GW/cm^2[$\delta\phi(0)$ $\approx 10.6\pi$].

malized Kerr signals for the CS_2 gate are plotted in Fig. 2 for different power density levels of the orienting 1.05-μm pulse of 0.068, 0.135, 0.68, and 3.4 GW/cm^2. The salient feature of the data presented in Fig. 2 is that the Kerr kinetic profile for CS_2 broadens in time as the power density of the orienting pulse is increased. The normalized Kerr signals for the NB gate are plotted in Fig. 3 for different power density levels of the 1.05-μm orienting pulse of 0.135, 0.68, 3.4, and 13.5 GW/ cm^2. The salient features of the data displayed in Fig. 3 are that the Kerr kinetic profiles from NB first broadens [Fig. 3(a)–(2)], and then becomes a complex oscillating pattern [Fig. 3(a)–(3) and (4)] as the power density of the orienting pulse is increased to 13.5 GW/cm^2. Since the echelon in our setup spans about 75 ps on a single laser flash, the experimental curve displayed in Fig. 3(a)–(4) is a combination of three different laser flashes which cover different overlapped time regions. This may account for the slight differences between the measured [Fig. 3(a)–4] and the calculated [Fig. 3(b)–(4)] curves.

In the analysis of the CS_2 gate data, the orientational relaxation time and the total nonlinear index of refraction was chosen to be 1.8 ps (Refs. 21 and 22) and 2×10^{-11}esu ($n_2^0 = 4n_2^e$),[19] respectively. When I_{20} is less than 0.1 GW/cm^2($\delta\phi < 1$), the Kerr transmitted signal can be fitted to the calculated function of $\exp(-2\tau_D^2/3\tau_l^2)$; and the FWHM of $S_t(\tau_D)$ is about $2\tau_l = 10$ ps. When the intensity of the laser beam is increased to 0.13 GW/cm^2 ($\delta\phi > 1$), the FWHM of $S_t(\tau_D)$ is wider than $2\tau_l$, and it monotonically increases with I_{20}. Because $\tau_0 < \tau_l$, the oscillation period of $\sin^2[\frac{1}{2}\delta\phi(t)]$ for the CS_2 gate is much faster than the pulse duration of the probe beam.[13] As expected, we did not observe any appreciable oscillations in the curve of S_t vs τ_D. In the above analysis, we have neglected photoinduced absorptions in CS_2. When I_{20} exceeds 4 GW/cm^2, multiphoton absorption[23,24] about 3500 Å may be observed[25] in a CS_2 liquid.

In our analysis of the NB gate data,[13] the molecular orientational relaxation time was taken to be 35 ps.[10,26,27] When $\delta\phi(t) \gg \pi(I_{20} > 3$ GW/cm^2), the curve of S_t vs τ_D is complex. Since the oscillation period of $\sin^2[\frac{1}{2}\delta\phi(t)]$ in the tail of the $\delta\phi(t)$ curve is slower than the probe pulse duration, the last valley of $S_t(\tau_D)$ is approximately located at a delay time

$$\tau_D[\delta\phi(t) = 2\pi] \approx \tau_0 \ln(n_2^0 E_{20}^2 \sqrt{\pi} \ \tau_l L/2\lambda_1\tau_0) , \qquad (7)$$

for $\tau_D > 5\tau_l$ and $\tau_0 \gg \tau_l$, and the last maximum of $S_t(\tau_D)$ is approximately located at a delay time

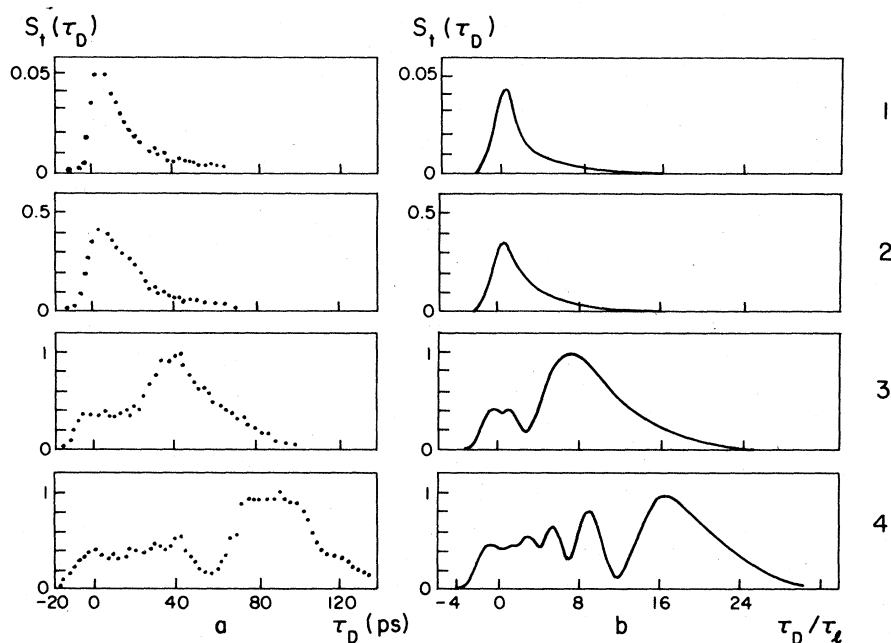$$\tau_D[\delta\phi(t) = \pi] \approx \tau_0 \ln(n_2^0 E_{20}^2 \sqrt{\pi} \ \tau_l L/\lambda_1\tau_0), \qquad (8)$$

FIG. 3. Kerr transmitted signal for NB liquid at various intensities of the orienting 1.05-μm pulse. (a) Experimental data; (b) calculated curves from Eq. (4). The parameters chosen are $\lambda_1 = 0.53$ μm, $L = 1$ cm, n_2^e $= 0.5 \times 10^{-11}$ esu, $n_2^0 = 2 \times 10^{-11}$ esu, $\tau_0 = 35$ ps, and $\tau_l = 5$ ps. (1) $I_{20} = = 35$ MW/cm^2 [$\delta \phi (0)$ $\approx 0.16\pi$], (2) $I_{20} = 680$ MW/ cm^2 [$\delta \phi(0) \approx 0.78\pi$], (3) I_{20} $= 3.4$ GW/cm^2 [$\delta \phi (0) \approx 3.9\pi$], (4) $I_{20} = 13.5$ GW/cm^2 [$\delta \phi (0)$ $= 15.5\pi$].

for $\tau_D > 5\tau_l$ and $\tau_0 \gg \tau_l$. The time separation between the last valley and the last peak of $S_t(\tau_D)$ is calculated from Eqs. (7) and (8) to be $\tau_0 \ln 2$. A value of 25 ps is measured for the time separation from the data in Fig. 3(a)–(4), which yields $\tau_0 = 36$ ps for NB. In addition, the value of $n_2^0 E_{20}^2$ estimated from the values of $\tau_D(2\pi)$ and $\tau_D(\pi)$ excludes any contribution from the fast nonlinear index of refraction. Using the peak power density of 13.5 GW/cm^2, a value of $n_2^0 = 2.1 \times 10^{-11}$ esu is calculated for NB. These values (τ_0 and n_2^0) for NB are in excellent agreement with published values. Similar effects have also been observed in benzene, toluene, m- nitrotoluene liquids.

In conclusion, the optically induced Kerr kinetics in various liquids have been measured with the aid of intense picosecond laser pulses. Complex Kerr decay profile curves were observed at power densities exceeding 1 GW/cm^2. The location of the last peak of the oscillating Kerr kinetic profile is a function of τ_0, n_2^0, and E_{20}^2. The separation time between the last valley and the last maximum in the oscillatory Kerr kinetic profile is equal to $\tau_0 \ln 2$.

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