Ultrafast third-order optical nonlinearities in DMSO

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The third-order optical nonlinearities of dimethyl sulfoxide (DMSO) are investigated using the optical Kerr effect (OKE) and Z-scan techniques with femtosecond pulses. We are able to fit the OKE signal theoretically by convolving the autocorrelation of the incident pulse intensity profile with the impulse responses of the samples, illustrating the instantaneous nonlinear response of DMSO. We verify that the purely electronic cloud distortion causes the observed signal for DMSO. The Z-scan technique is used to estimate the third-order susceptibility of DMSO, which is about a quarter of that for CS_2 and mainly comes from the nonlinear refraction with an intensity of less than 140 GW/cm^2.

OCIS codes: 160.4670, 190.3270.
doi: 10.3788/COL201210.111601.

Dimethyl sulfoxide (DMSO) has been widely used as an ideal solvent for many materials due to its high stability and strong solubility. In addition, DMSO has less nonlinearity under nanosecond and picosecond pulses, and thus, its influence on investigated samples can be neglected in some nonlinear measurement experiments. However, in cases of femtosecond pulses, the influence of DMSO should be considered because of the narrow femtosecond pulse width and relatively high intensity. In this letter, we investigate the third-order nonlinearities of DMSO by using the optical Kerr effect (OKE) and Z-scan techniques with 130-fs pulses and 1-kHz repetition rate.

The OKE technique has been widely used for measuring the frequency-domain third-order nonlinear optical susceptibility $|\chi_{\mathrm{s}}^{(3)}(\omega)|$ of various materials, such as clusters, glasses, films, liquids, polymers, and nanoparticles, among others[1−6]. In these works, $|\chi_{\mathrm{s}}^{(3)}(\omega)|$ was estimated using carbon bisulfate (CS_2) as a reference sample[7]. The third-order nonlinear optical susceptibility of CS_2 at 10^{-13} esu is typically used[8].

The third-order nonlinear optical response of a material typically includes three parts, the contributions of the instantaneous electronic motion and the accumulated inter- and intra-molecular motions in response to the incident electric field of a laser pulse. When the width of an incident laser pulse is considerably longer than the slowest response, the overall response can be regarded as instantaneous and the associated function can be taken as a delta function. Therefore, the resultant OKE signal, which is a convolution of the probe pulse intensity and the impulse response function, resembles the intensity distribution at different delay times of the pump beam relative to the probe beam.

Given that inter-and intra-molecular responses are non-instantaneous, the time evolution of the OKE signal no longer resembles the probe intensity when a femtosecond (fs) laser pulse is used to investigate the OKE signal of a sample. Under such circumstance, the time evolution of the OKE signal has to be dealt with in addition to simply determining the magnitude of $|\chi_{\mathrm{s}}^{(3)}(\omega)|$.

Using the OKE technique, we found the response of DMSO to be instantaneous under an fs pulse and ascribed to the contribution of pure electronic cloud distortion. The Z-scan technique was used to obtain the third-order susceptibility of DMSO, which was approximately a quarter of that of CS_2. Third-order susceptibility is mainly generated from the nonlinear refraction within a large intensity range. A brief explanation is given to elucidate the observation.

The laser used in this letter is a mode-locked Ti:sapphire laser (Mira 900, Coherent, USA) combined with a re-generative amplifier (Legend- F, Coherent, USA). This combined system delivers linearly polarized, 800-nm, and 130-fs (full-width at half-maximum, FWHM) pulses at a repetition rate of 1 kHz and an average power of 900 mW. The pulse energy is adjusted using neutral attenuators. We split the beam into two using a thin-film polarizer with an intensity ratio of 10:1. Intense and weak beams were used as pump and probe beams, respectively. A Glan-Taylor polarizer was inserted in the light path of the probe beam to rotate the light polarization by 45° to the linear polarized pump beam. The pump beam passes through an optical delay line driven by a step motor that introduces the delay time of the pump beam to the probe beam. Two lenses with focal lengths of 40 and 20 cm were used to focus the pump and the probe beam at the sample position. The beam waist radii of the pump and probe were approximately 32 and about 16 μm, respectively. The focus was enclosed within a 2-mm-thick sample cell during the measurement. After transmitting through the sample cell, the pump beam was blocked, while the probe beam passed through another Glan-Taylor polarizer. The transmission axis of the pump beam was strictly perpendicular to that of the probe beam. The OKE signal was recorded as a function of pump-probe delay time by using an amplified photodiode and a digital lock-in amplifier. Both the optical delay line and lock-in amplifier were controlled by a personal computer. The Z-scan technique is described in Ref. [9]. The DMSO was a spectrum pure reagent obtained from a chemical reagent company. The
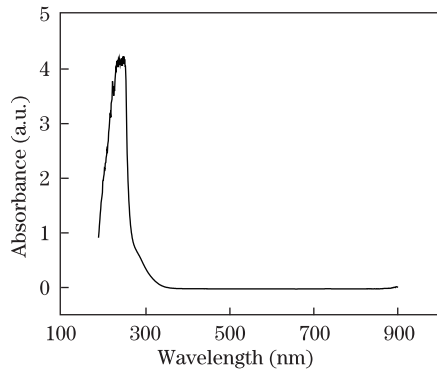
Fig. 1. Linear absorption spectrum of DMSO.

experiment was conducted at room temperature, and the DMSO was in liquid state. Figure 1 shows the linear absorption spectrum of the DMSO, where the DMSO exhibited very little linear absorption at the 800-nm wavelength.

The OKE signal detected in the OKE experiment arose from the third-order effect, i.e., the laser intensity dependent birefringence and coherent-coupling effect[10]. The laser beam induced instantaneous electronic motion and non-instantaneous nuclear motion when it irradiated the liquid media. The instantaneous electronic motion response can be described using a delta function $\delta(t)$. The nuclear motion can be separated into two categories, namely, intra- and inter-molecular motions. In the intramolecular motion, the nuclear resonance involves a normal vibration that gives rise to quantum interference (QI)[11,12]. The response function $\phi_{\mathrm{intra}}(t)$ can be expressed as[12]

$$\phi_{\mathrm{intra}}(t) = A_\Omega \mathrm{e}^{-\Gamma_\Omega t} \sin \Omega t, \tag{1}$$

where A_Ω is a constant and Ω is the angular frequency of the molecular normal vibration difference between the ground and the first excited state of the vibration. In the inter-molecular motion, three dynamic processes have different response times. The diffusive reorientation that originated from the molecular reorientation following the diffusion equation is the slowest dynamic process. The molecular polarizability distortion induced by inter-molecular collisions (translational and rotational) is the faster dynamic process[13]. The molecular libration, which occurs as a molecule that is momentarily torqued and released by the incident radiation field, is the fastest dynamic process.

According to the inertial Debye dephasing-inhomogeneous oscillator model[14], the response function of the inter-molecular motion can be represented as[15]

$$\phi_{\mathrm{inter}}(t) = A_\mathrm{D}\mathrm{e}^{-\Gamma_\mathrm{D}t}\sinh(\omega_0 t) \\ + A_\mathrm{T}\mathrm{e}^{-\Gamma_\mathrm{T}t}\sinh(\omega_0 t) + A_\mathrm{L}\mathrm{e}^{-\alpha^2 t^2/2}\sin(\omega_0 t), \tag{2}$$

where Γ is the Debye relaxation rate, $1/\tau_\mathrm{i}$ is the intermediate dephasing rate, ω_0 is the oscillator frequency, and α the inhomogeneous broadening rate; $\Gamma_\mathrm{D} \equiv \Gamma + \omega_0$ and $\Gamma_\mathrm{T} \equiv 1/\tau_\mathrm{i} + \omega_0$. The ω_0 factor determines the initial rise of the respective responses. A_D, A_T, and A_L are constants determined by fitting with the experimental

data. The three terms in the right hand side of denote the diffusive reorientation, molecular polarizability distortion, and molecular libration, respectively. Therefore, the overall response function may be taken as a linear superposition of electronic and molecular contributions as[16]

$$\phi^{(3)}(t) = \delta(t) + \phi_{\mathrm{inter}}(t) + \phi_{\mathrm{intra}}(t). \tag{3}$$

The observed OKE signal may be taken as a convolution of the background-free laser pulse autocorrelation function $G^{(2)}(t)$[17] by using the real third-order response function $\phi^{(3)}(t)$ as[16]

$$S(\tau) = \int_{-\infty}^{\infty} G^{(2)}(t-\tau)\phi^{(3)}(t)\mathrm{d}t, \tag{4}$$

where τ is the delay time of the pump beam to the probe beam. The induced anisotropy of the molecular skeletons in liquid cannot occur instantaneously when the incident laser pulse is sufficiently short[18]. The magnitude of the inertial effect is assumed to be similar for all non-instantaneous nuclear responses. Thus, the quantity $\beta \equiv \omega_0^{-1}$ was set to be identical for all three inter-molecular dynamics[19].

We conducted the OKE experiments of DMSO and reference sample CS_2 under the pump beam intensity of 60 GW/cm^2. The transient OKE signal of the liquid DMSO obtained in the experiment was plotted against the delay time in Fig. 2. Figure 3 shows the experimental results of CS_2, where the OKE signal of DMSO contained two parts, namely, a pulse limited rise and a fast decay, which is delta-like impulse response function. The temporal profile of the OKE signal was Gaussian symmetrical. Based on Fig. 2, we conclude that both the intra-molecular motion and diffusive reorientation have no contribution to the DMSO response. The first conclusion was drawn based on the fact that no vibration QI beats were observed in the DMSO OKE signal, which was induced by intra-molecular motion, such as the vibration of $C_2H_4Br_2$[14]. Thus, the contribution to the OKE signal from intra-molecular motion can be neglected. The second conclusion was drawn based on the fact that the diffusive reorientation was a slow process that lasted for a few ps, such as that in CS_2[20]. Figure 3 shows the slow decay component of CS_2 observed in the experiment. No slowly decaying component was observed in the OKE signal of DMSO. Therefore, the OKE
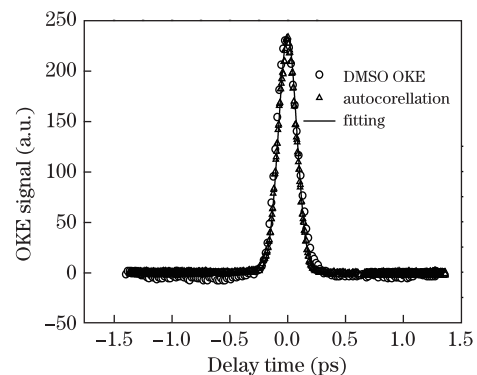

Fig. 2. (Color online) OKE signal of DMSO under the pump beam intensity of 60 GW/cm^2 and the autocorrelation signal of the pulse intensity.
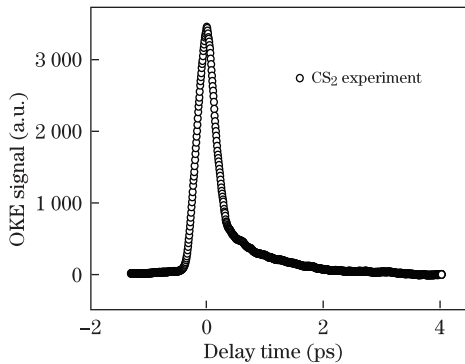
Fig. 3. OKE signal of CS$_2$ obtained under the pump beam intensity of 60 GW/cm^2.

signal did not include the contribution of the diffusive reorientation involved in the inter-molecular motion. We measured the pulse width by using a single-shot autocorrelator (SSA) to explore the origin of the OKE signal for DMSO. Figure 2 shows the plot of the autocorrelation signal measured using SSA (triangles). For comparison, the autocorrelation signal was adjusted to the same amplitude as that of the OKE signal of DMSO. We found the width of the OKE signal of DMSO to resemble that of the autocorrelation signal of the laser pulse. Therefore, the response of liquid DMSO can be regarded as instantaneous in response to the incident electric field of a fs-laser pulse. Moreover, the two fast responses of inter-molecular motion are not involved in the OKE signal of DMSO. Based on the analyses above, the responses of DMSO, with the exception of the intra-molecular and inter-molecular motions, were found to mainly come from the contribution of the electronic motion. The peak value of the OKE signal for CS$_2$ was approximately 3 500, as shown in Fig. 3, and that of DMSO was approximately 240, as shown in Fig. 2. The third-order nonlinear susceptibility of DMSO can be estimated using CS$_2$ as a reference sample[7]. The third-order nonlinear susceptibility of DMSO was approximately a quarter of that of CS$_2$.

As can be seen in Fig. 2, the measured autocorrelation signal was a standard Gaussian distribution. The laser autocorrelation function can be represented in the following form by fitting the autocorrelation signal:

$$G^{(2)}(t) = A \exp\left(-\frac{2t^2}{T^2}\right), \tag{5}$$

where A is the magnitude, $T = W_1/\sqrt{\ln 4}$, t is the time, and W_1 is the width (FWHM) of the measured autocorrelation signal. The W_1 value of 185.32 fs was obtained by fitting the experimental data (uncertainty was approximately 5%). The laser pulse width (FWHM) can be obtained by dividing the width (FWHM) of the autocorrelation signal by $\sqrt{2}$. The obtained laser pulse width value was approximately 131 fs[21], which was nearly equal to the pulse width used in the experiment. This result further confirms the good accuracy of the experiment.

The OKE signal of DMSO was fitted using Eq. (4) and the autocorrelation function obtained with the delta function $\delta(t)$. The fitting result is indicated by the solid line in Fig. 2, which is in agreement with the experimen-

tal data. The results confirm the view that the response of DMSO to the incident electric field of an fs pulse is instantaneous and mainly comes from electronic instantaneous motion. The instantaneous response may be attributed to the relatively large molecule and symmetrical structure of DMSO, making it difficult to move during the fs pulse duration. In contrast, a rod-like molecule, such as the CS$_2$, can move easily.

The conclusions are significant for instructing the application of DMSO. For example, the DMSO can be substituted for CaF$_2$ and LiF plates to measure the fs pulse width by using the OKE technique because of the instantaneous response of DMSO to the incident fs pulse. The DMSO with instantaneous response can also be used as a sample in the OKE technique to determine the zero time delay between the pump beam and the probe beam in the pump-probe experiment.

We conducted a Z-scan experiment for DMSO and reference sample CS$_2$ under the same conditions to explore the origin of the third-order susceptibility of DMSO. Figure 4 shows the divided Z-scan experimental results under the incident intensity of 41 GW/cm^2. The divided Z-scan experimental data were fitted using standard Z-scan equations and Huygens-Fresnel propagation integral[22,23]. We obtained the third-order nonlinear refractive index γ of DMSO and CS$_2$, which were approximately 0.60×10^{-19} and 2.3×10^{-19} m^2/W, respectively. Moreover, the same results can be obtained using the fs-pulsed Z-scan analytical method[24]. The CS$_2$ had a nonlinear refraction index of approximately 2.4×10^{-19} m^2/W[25]. No nonlinear absorptions of DMSO and CS$_2$ were observed under such conditions. Therefore, the third-order nonlinear susceptibility of the two liquids mainly comes from nonlinear refraction, as shown in

$$\gamma = \chi^{(3)}/c\varepsilon_0 n_0^2 (\text{m}^2/\text{W}), \tag{6}$$

$$\chi^{(3)}(\text{SI}) = \frac{4\pi}{(10^{-4}c)^2}\chi^{(3)}(\text{esu}), \tag{7}$$

where c is 3.0×10^{-8} m/s of light velocity, n_0 is the linear refractive index of DMSO, and ε_0 is dielectric constant in vacuum. Using the expressions above, the third-order nonlinear susceptibility of CS$_2$ of approximately 1.15×10^{-13} esu was obtained, and this value agrees with the 10^{-13} esu reported in Ref. [8]. The calculated third-order nonlinear susceptibility of DMSO was approximately 3.0×10^{-14} esu, which was approximately a quarter of that of CS$_2$.
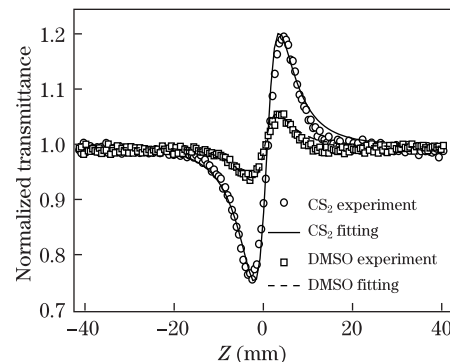

Fig. 4. Divided Z-scan experimental data of DMSO and CS$_2$ and the fitted results under the intensity of 40 GW/cm^2.
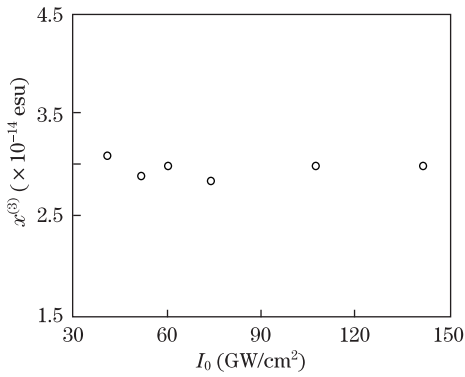
Fig. 5.   The third-order susceptibility of DMSO under different intensities.

The value obtained using the Z-scan experiment is in accordance with the value obtained using the OKE experiment.   Therefore, the influence of solvent DMSO should also be considered in the measurement of nonlinear materials.

The Z-scan measurement of DMSO was conducted under different intensities.   The divided Z-scan results were found to be fitted well using the third-order theory when the incident intensity was less than 140 GW/cm^2. The calculated third-order susceptibility was almost constant, as shown in Fig. 5.   No nonlinear absorption was observed within this intensity range.   However, when the intensity was larger than 140 GW/cm^2, the experimental results were not fitted well using the third-order theory only, indicating that a higher-order nonlinear effect or other effects may appear.   The intensity needed for the emergence of higher order nonlinearity in DMSO was twice of that for $CS_2^{[9]}$.   Therefore, in the fs domain, using DMSO as standard sample is more appropriate than CS_2 when the incident intensity is relatively large.

In conclusion the third-order nonlinearities of liquid DMSO under the excitation of fs laser pulses are investigated using time-resolved OKE technique.   The results show that the nonlinear optical response of DMSO is instantaneous and originates from the pure electronic cloud distortion.   Intra-molecular and inter-molecular motions are found to have no contributions to the OKE signal. Using Z-scan technique, we obtain the third-order susceptibility of approximately 3.0×10^{-14} esu, which was approximately a quarter of that of CS_2.

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