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Analysis of Kerr and thermal nonlinearities in unsatuared polymers with a nanosecond laser

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Nonlinear optical properties of an unsaturated polymer (poly trifluroethyl dipropargyl malonate) are investigated by using a passive Q-switched Nd:YAG laser. Double-peaked structure of phase conjugate signals due to the two-photon-absorption induced thermal effect is clearly observed and a simple method to remove the thermal effect from the overall phase-conjugate signals is demonstrated.

I. INTRODUCTION

Recent progress in the field of high-speed optoelectronics and information processing has encouraged the search for new materials with large nonresonant third-order nonlinear-optical susceptibilities. Among several materials, conjugate polymers seem to be promising candidates for future practical applications in nonlinear optical devices. [1–3] A picosecond pulse has been adapted for investigating electronic third-order nonlinearities of π-conjugate polymers since their nonresonant optical nonlinearities are not generally large.

The contribution of thermal effects being induced in degenerate four wave mixing(DFWM) signals by absorbing photon energies has been studied for DFWM experiments, in which several nanosecond pulses were employed as a light source. [1] Those DFWM signals exhibited two peaks in temporal profiles and often showed higher order dependence. [1] The double-peak feature of DFWM signal was generally attributed to the retardation of the formation of thermal gratings which was added to electronic Kerr gratings. [1,5,6] Therefore, the nonlinearities due to the thermal effect should be removed from the measured signal when long laser pulses were employed. [2]

In this paper, a simple technique to eliminate the contribution of the thermal effect to phase conjugate signals was demonstrated, and $\chi^{(3)}$ of an unsaturated polymer (poly trifluoethyl dipropargyl malonate) measured by using this technique was reported.

II. EXPERIMENT

The "backward" DFWM geometry was utilized in our experiment. A schematic of the experimental geometry using 12 ns(FWHM) 1.064 μm pulses at 10Hz is shown in Fig.1 . A single laser pulse was divided into three pulses by B.S.1. and B.S.2. Two strong beams, forward (E_f) and backward (E_b) pumps, of approximately equal irradiance were incident on the polymer solution in counter-propagating directions. A weaker beam, the probe (E_p), was incident on the sample at an angle, of less than 5 degree with respect to E_f. The intensity ratio of probe beam to pump beam was adjusted to be around 1/10. The intensities of conjugate (E_c) and probe pulses were measured by two pairs of fast photodiodes and pyroelectric energy meters. The pump intensity was varied by neutral density filters to obtain the reflectance of the phase-conjugate signal as a function of the pump intensity.

The waveforms of phase-conjugate signals were captured with the fast photodiodes connected to a digitizing oscilloscope. The captured waveforms of the phase-conjugate pulses were deconvoluted into two peaks to remove the signal due to the thermal grating. The form of the peaks used in the deconvolution was a modified Gaussian function which represented approx-

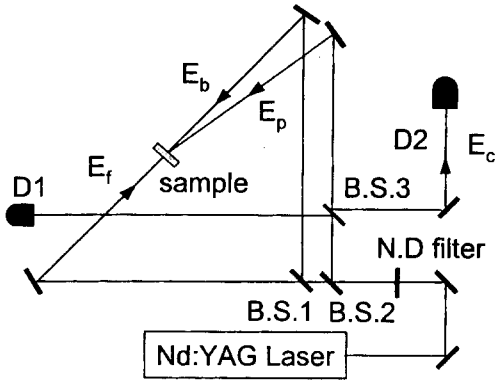

FIG. 1. Schemetic of experimental DFWM apparatus. $D_1(D_2)$ represents pyroelectric energy meter for the probe pulse(the conjugate pulse) energy monitoring or photodiode for temporal profiling.

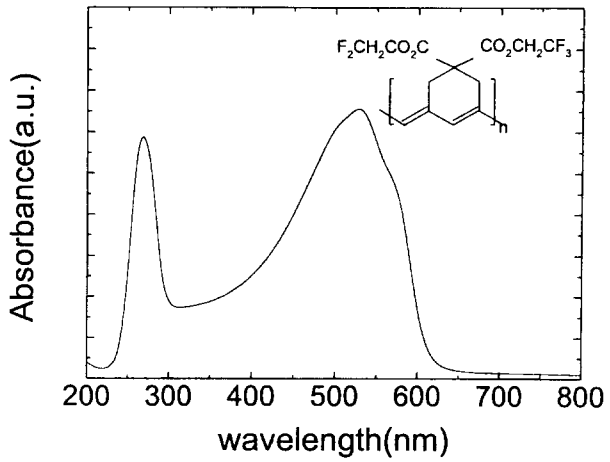

FIG. 2. The structure and absorption spectrum of poly trifluroethyl dipropargyl malonate in tetrahydrofuran. The broad peaks in 400 - 600 nm display the $\pi - \pi^*$ transition of the conjugated polymer.

imately the typical temporal profile of the outputs of the fast photodiode.

The poly trifluroethyl dipropargyl malonate (TFEDPM) used in this experiment has a π conjugation bonding in the chain and contains fluorine in the side chain. The structure and UV-visible spectra of TFEDPM are shown in Fig. 2. [3] Note that the linear absorption at 1.064μm was almost negligible.

III. RESULT AND DISCUSSION

Phase-conjugate temporal signals as a function of pump beam intensity for a 0.04-M solution of TFEDPM in tetrahydrofuran(THF) are shown in Fig. 3. A double-peaked structure was clearly observed. The ratio of the two peaks varied with the pump energy. Similar double-peaked phase-conjugate pulses

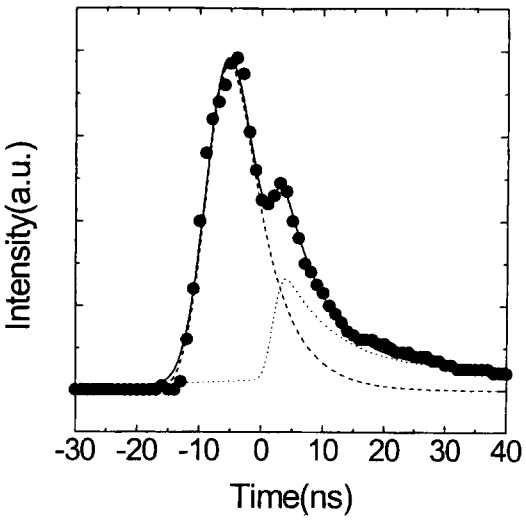

FIG. 3. Experimentally obtained phase-conjugate pulses of DFWM in a 0.04M solution of poly trifluroethyl dipropargyl malonate at pump intensities $32MW/cm^2$. The solid lines are the result of deconvolution of phase-conjugate pulse with two modified Gaussian functions.

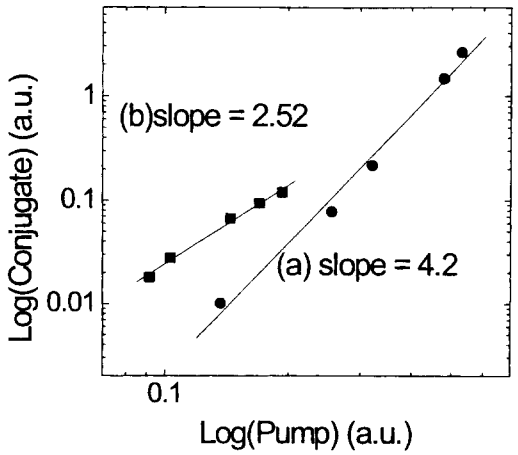

FIG. 4. Log-log plot of DFWM signal detected by (a) energy meter and (b) fast photodiode.

have been investigated by other groups. [1,5,6] This phenomena was attributed to the slow development of a thermal grating which was induced by absorbing photon energies through single or two photon absorption processes and temporally superimposed onto the fast electronic grating. [1,5,6]

Fig. 4(a) exhibits the dependence of the intensity of the double peaked phase conjugate pulses. Since the total energy of two superposed phase conjugate pulses were measured with pyroelectric energy meters, the role of the second peak could be estimated through the analysis of the dependence of the total energy of the phase-conjugate pulses. The best fit gives a power dependence of $I^{4.2}$ instead of the expected $I^{3.0}$ depen-

dence.

Assuming that two photon absorption(TPA) induces thermal gratings, the DFWM signal due to the fast Kerr grating can be written as [9]

$$E_{fast} = i\gamma L E_f(t) E_b(t) E_p^*(t) \tag{1}$$

where $\gamma = 4\pi\omega\chi^{(3)}/c\sqrt{\epsilon}$. According to this equation, the phase-conjugate signal is generated instantaneously with third-order power dependence. The TPA induced thermal grating is described by $\Delta n(x,t) = (dn/dT)\Delta T(x,t)$, where (dn/dT) is the thermo-optic coefficient and $\Delta T(x,t)$ is the absorption-induced temperature distribution. It satisfies the heat diffusion equation,

$$\rho C_p \frac{\partial(\Delta T)}{\partial t} - k_\tau \nabla^2(\Delta T) = \beta I^2(x,t) \tag{2}$$

where ρ, C_p, k_T are the mass density, the specific heat at constant pressure and the thermal conductivity respectively. Note that $I^2 = |E_f + E_b + E_p|^4$ for the DFWM geometry.

The terms which contain $E_f E_p^*$ (for the large period grating) are included and the terms of $|E_p|^2 E_p^*$ are neglected since $|E_p| << |E_f|, |E_b|$. Then the component of I^2 effective in producing a grating leading to the DFWM signal can be written by

$$I_{eff}{}^2(x,t) = (n_o c\epsilon_o/2)^2(|E_f|^2 + 2|E_b|^2)\left[2E_f E_p^* + c.c.\right] \tag{3}$$

From Eqs. (2) and (3), the thermal refractive index change due to TPA can be described by

$$\Delta n \approx \frac{1}{2}\int_{-\infty}^{t} I_{eff}^2 dt' \tag{4}$$

where the thermal constant is assumed to be infinite. Since $E_{slow} \propto E_b \Delta n$ due to the thernal nonlinearity, the total intensity dependence of the DFWM signal due to the TPA induced thermal effect can be written in the form of

$$I_{slow} \propto I_b I_p I_f^3 \propto I^5 \tag{5}$$

Assuming the same phase and periodicity of the thermal and Kerr gratings, the phase conjugate signals can be approximated to be [9]

$$I_c(t) \propto |\Delta n(t)|^2 I_p = (|\Delta n_{kerr}(t)|^2 + |\Delta n_{thermal}(t)|^2 + 2|\Delta n_{kerr}(t)\Delta n_{thermal}(t)|)I_p(t) \tag{6}$$

If the delay of formations of the thermal grating longer than the laser pulse width, the third term of the Eq. (6) can be ignored and the phase conjugation signal can be analyzed by two pulse profiles. The first and second terms are originated from the ultrafast Kerr grating and the slowly constructed two-photon-induced thermal grating, respectively. Consequently, the intensity (I_c) of the double-peaked phase-conjugate pulses obtained by using the pyroelectric energy meters can be written as

$$I_c \propto \int_{-\infty}^{+\infty} (I_{fast} + I_{slow})dt \tag{7}$$

where I_{fast} and I_{slow} are the intensities of the first and the second peak, respectively. From Eq. (7), one can see that intensity of the phase-conjugate signal measured by pyroelectric energy meters can display the power dependence $I_p{}^k$,where $3 < k < 5$, if the two terms are comparable to each other.

Since the thermal effect is slower than electronic Kerr effect, the separation of two process can be observed when the fast photodiode with fast response time was employed. In that case, it is inferred strongly that the nonlinearities due to Kerr effect be able to be measured.

Assuming that the output current is proportional to the concentrations of photogenerated free carriers, the temporal output function of a fast photodiode could be calculated by using the following rate-equation.

$$\frac{dn}{dt} = n_o G(t) - \frac{n}{\tau} \tag{8}$$

where n is the time dependent concentration of free carriers, n_o is the total density of photogenerated free-carriers at $t = 0$ and $G(t)$ represents the Gaussian profile of the laser pulse. Photogenerated free-carriers decayed with a time constant τ. A modified Gaussian could be obtained from this equation. Using the obtained results, double-peak phase-conjugate pulses were fitted and broken down into two pulses as shown in Fig. 3. The leading pulse represents the phase-conjugation signal due to the electronic nonlinearities. The following pulse signifies the phase-conjugate signal due to the thermal effect.

For minimizing the interaction between the Kerr and the thermal gratings, the intensity of the pump beam was controlled to be weak enough to keep the ratio of the first peak to the second peak of the phase conjugate signal less than 1/2. Fig. 4(b) shows a log-log plot of the peak-value of the leading pulse versus the input irradiance. The least-squares fit produces a power dependence of $I^{2.5}$, indicating a third order nonlinearity. Therefore, $\chi^{(3)}$ of poly TFEDPM could be determined based on the analysis of the first pulse after removing the second pulse.

DFWM experiments on CS_2 were also performed for determining the value of $\chi^{(3)}$ of poly TFEDPM solution. Only a single peak was observed for CS_2. Differences in refractive index, surface reflectance and lengths of the two samples were accounted and a comparative measurement was performed by using the following relationship. [8]

$$\frac{\left|\chi^{(3)}_{\text{eff}}(\text{sample})\right|^2}{\left|\chi^{(3)}_{\text{eff}}(\text{CS}_2)\right|^2} = \left[\frac{n_{\text{sample}}}{n_{\text{CS}_2}}\right]^4 \times \frac{I_{sample}}{I_{CS_2}} \times \frac{L^2_{\text{CS}_2}}{L^2_{\text{sample}}} \times \frac{(1-R)^4_{\text{CS}_2}}{(1-R)^4_{\text{sample}}} \quad (9)$$

where R is the surface reflectance, I_{CS_2} and I_{sample} represent the peak intensities of the conjugate signals of CS_2 and poly-TFEDPM respectively. Using the value of $\left|\chi^{(3)}_{\text{eff}}(\text{CS}_2)\right|$ in reference [7], $|\chi^{(3)}|$ at 1.064μm was determined to be 4.1×10^{-11} esu from the comparison of the signals from the two materials under identical experimental conditions. This result agrees well agreed with the reported value of 1.1×10^{-11} esu for Poly-4-BCMU which has the same π-conjugate linear chain structure. [2]

IV. CONCLUSION

In order to understand the electronic nonlinearities in the several-nano second regime, the thermal effect on the nonlinearities should be carefully examined since the phase-conjugate signals could show complex thermal effects such as higher-order pump power dependence and double-peaked time profile.

In this paper, we demonstrated a simple technique to remove the thermal components from the phase-conjugate signals so that the electronic and thermal effects could be separated. With this technique, we could measure the value of electronic origin $\chi^{(3)}$ of poly-TFEDPM successfully with nano-second laser pulses. We believe that this simple technique can be utilized to investigate the optical and thermal nonlinear properties of materials in the nano-second regime.

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