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Concentration dependent nonlinear refraction in chloroaluminum phthalocyanine/ethanol solution*

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Nonlinear refractive properties of chloroaluminum phthalocyanine (CAP) in ethanol solution are studied using the Z-scan technique with picosecond (ps) and nanosecond (ns) laser pulses at a wavelength of 532 nm. A transition from self-focusing to self-defocusing in CAP solution excited by 10 ns pulses is observed during the decrease of its concentration. This transition is due to co-existing excited-state refraction and transient thermal lensing effects. The experimental results are described very well using the rate-equation model and the theory of transient thermal refraction in liquids. The refractive cross sections of the excited-state are also obtained.

Keywords: transient thermal lensing effect, Z-scan, excited-state refraction
PACC: 4265, 4270

1. Introduction

Materials that possess nonlinear optical (NLO) properties have been investigated extensively due to their potential applications in photonic technology.[1−6] Metallophthalocyanines (MPc) are found to exhibit reverse saturable absorption (RSA),[7] which can effectively restrict the output energy of incident light and thus will be used as optical limiters. The excellent properties of MPc as candidates for NLO applications originate not only from their extensive π-electron delocalization and their thermal and chemical stabilities, but also from their ability to be processed by either substituting the peripheral or axial side groups or changing the central metal ion.[8] Chloroaluminum phthalocyanine (CAP) is well known as a saturable absorber at 694 nm, and it was used as an early passive Q-switch for ruby lasers.[9−11] It also exhibits strong RSA and nonlinear refraction at 532 nm.[12] Wei *et al* have used ps pulse and ns pulse trains to study the nonlinear refractive properties of CAP, and they observed opposite signs of nonlinear refraction in CAP dissolved in methanol with these two modes of pulse laser in their work.[13,14] They explained the results of the ns pulse train experiment using the energy-level model and the theory of the steady-state thermal lensing effect in liquids. However, it may not be appropriate to use the steady-state theory to deal with the thermal refraction problem in their experimental circumstances because the interval of the pulse trains is only 7 ns, which is much smaller than the acoustic transit time of 20 ns. It may be necessary to use the theory of the transient thermal lensing effect to explain and fit to the experimental results.

In the present paper, the change in sign of the nonlinear refraction with the decrease in concentration under 10 ns pulse excitation is observed, and its origin is discussed in detail. The nonlinear refraction of the CAP/ethanol solution is investigated using the Z-scan technique[15] with 4 ns, 10 ns and 21 ps pulses separately. By comparing the results of these three cases with those obtained from the rate-equation model and the theory of the transient thermal lensing effect in liquids,[16] the refractive cross sections of the excited state are obtained.

2. Experiment

The NLO properties of CAP/ethanol solution are measured by the Z-scan method with an Nd:YAG laser (continuum), which produces 4 ns FWHM (full

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width at half maximum) and 10 ns FWHM laser pulses (the 10 ns pulses are obtained by adjusting the Q-delay time of the laser) at 532 nm, and a Q-switched and mode-locked Nd:YAG 532 nm laser (EKSPLA, PL2143B) with a 21 ps FWHM, repetition rate of 1 Hz, respectively. The spatiotemporal distributions of these three pulses each exhibit a nearly Gaussian profile. The sample solution is placed in quartz cells of 2 mm thickness. The quartz cells with the sample are placed on a computer-controlled translation stage that can move the sample along the z-axis with respect to the focal point of a 400 mm focal lens. The beam waist radius in the focal plane is about 24.5 μm for these three pulses. The transmittances of the samples are measured separately with and without using an aperture in the far-field. The linear transmittances of the aperture are 0.08, 0.07 and 0.11 for 4 ns, 10 ns, and 21 ps pulses respectively. The laser pulses adjusted by an attenuator are separated into two beams by using a splitter. The two beams are simultaneously measured using two energy detectors (Rjp-765 energy probe) linked to an energy meter (Rj-7620 ENERGY RATIOMETER, Laserprobe). A personal computer is used to collect data coming from the energy meter through the GPIB interface.

3. Results and discussion

Figure 1 gives the nonlinear refraction trace of the CAP solution at four different concentrations under the irradiation of the 10 ns pulse at the same intensity of 0.23 GW/cm^2. The concentrations of the prepared CAP/ethanol solution are 7.62×10^{-4} mol/L, 5.63×10^{-4} mol/L, 3.39×10^{-4} mol/L, and 1.24×10^{-4} mol/L, respectively. At the concentration of 7.62×10^{-4} mol/L, the Z-scan trace exhibits that the valley–peak structure, which shows the nonlinear refraction property of this sample, is self-focusing. However, the peak is suppressed and the valley is enhanced, and there exists a shoulder in the central region of the valley. When the concentration is decreased to 5.63×10^{-4} mol/L and 3.39×10^{-4} mol/L, the peak is reduced further and the shoulder is further increased. Finally, the profile of the Z-scan trace is completely inverted from the valley-to-peak configuration into the peak-to-valley structure at the concentration of 1.24×10^{-4} mol/L.

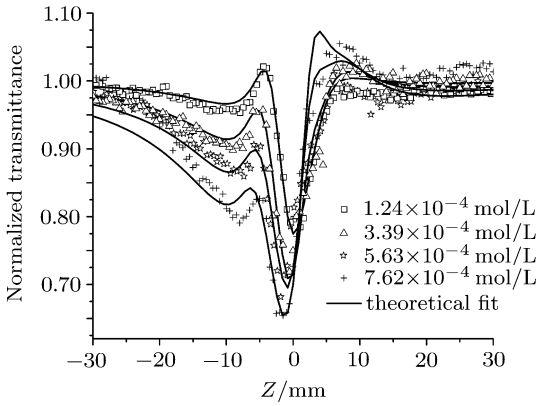


Fig.1. Divided Gaussian Z-scan curves of CAP/ethanol under the irradiation of 10 ns pulses at different concentrations, where the solid lines represent the theoretical fitting to experimental results.

In order to investigate the NLO properties of the CPA solution thoroughly, three different widths of 21 ps, 4 ns, and 10 ns pulses under the Z-scan configuration at 532 nm are used. Figure 2 gives the NLO properties of the CAP solution using 21 ps pulses with pulse energies of 1.18 μJ and 2.08 μJ respectively. The concentration of the solution was prepared to be 1.04×10^{-3} mol/L under these experimental conditions. The experimental results show that CPA/ethanol solution has a strong nonlinear absorption and a positive nonlinear refraction under the 21 ps pulse excitation. The curves in Fig.2(a) are for the open aperture Z-scan results with different input energies, and Fig.2(b) shows the closed aperture Z-scan results divided by the open-aperture scan results of Fig.2(a).

Figure 3 shows the results of the Z-scan under the 4 ns pulse excitation with two different energies: 4.5 μJ (crosses) and 18 μJ (dots). Obviously, the experimental results show that CPA/ethanol solution also has a strong absorption and a positive nonlinear refraction under the 4 ns pulse excitation. We perform the Z-scan measurements on the prepared CPA/ethanol solution with a concentration of 8.03×10^{-4} mol/L. The definitions of Figs.3(a) and 3(b) are the same as those in Fig.2.

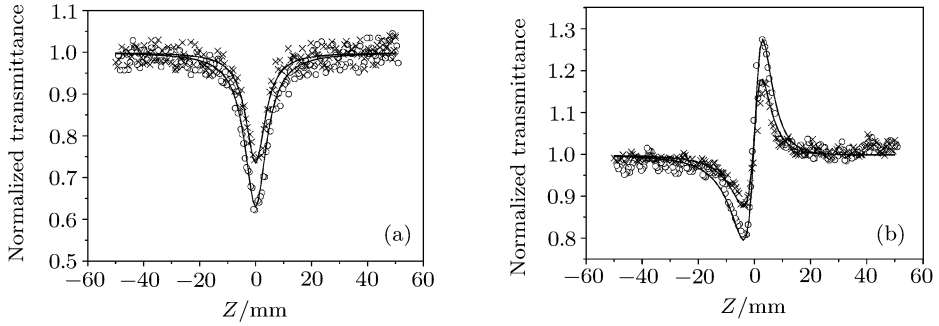


Fig.2. (a) Open aperture Z-scan results of CAP/ethanol for 21 ps with energies of 1.18 μJ (crosses) and 2.08 μJ (dots) separately and (b) divided Z-scan curves of CAP/ethanol for 21 ps with energies of 1.18 μJ (crosses) and 2.08 μJ (dots), where the solid lines are theoretical fits to the experimental results.

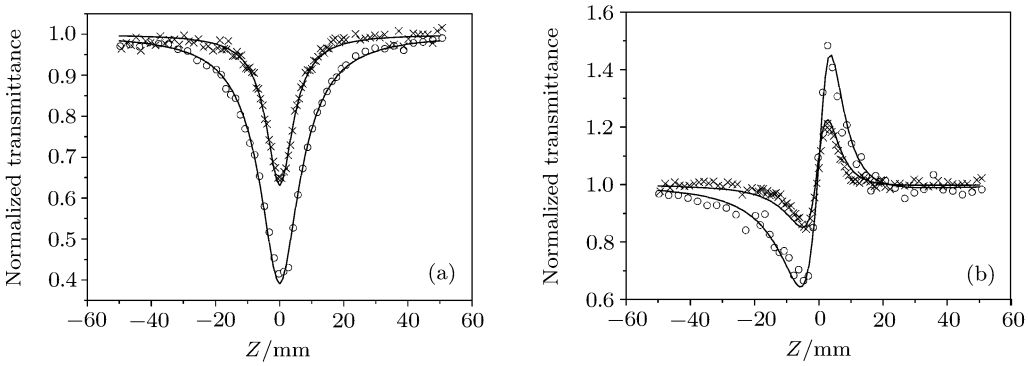


Fig.3. (a) Open aperture Z-scan of CAP/ethanol solution for 4 ns pulses with energies of 4.5 μJ (crosses) and 18 μJ (dots), and (b) divided Z-scan curves of CAP/ethanol solution for 4 ns pulses with energies of 4.5 μJ (crosses) and 18 μJ (dots), where the solid lines are theoretical fits to the experimental results.

For CAP it is most appropriate to use a five-level model shown in Fig.4 to explain the experimental results.[13] The process of absorption in a five-level system is as follows. Pumped by a laser pulse at 532 nm, the molecules are promoted to the first excited singlet state S_1 via a one-photon process, or to a higher excited singlet state S_2 via a two-photon process. From the first excited singlet state S_1, one of three things may happen. The electron can relax to the ground state by a radiative or nonradiative transition (with a constant time of $\tau_{S_1} = 12.1$ ns.[14]). The second possibility is for the electron to undergo a spin-flip transition to the lowest triplet state T_1. This process is called intersystem crossing (with a constant time of $\tau_{\rm ISC} = 17.5$ ns[14]). The third possibility is that the molecule may absorb another photon, which promotes the electron to a higher excited singlet state S_2, from which it then relaxes very rapidly back to the first excited singlet state(with a constant time of $\tau_{S_2} = 900$ fs[17]). For an electron in the lowest triplet state T_1, two possibilities exist. One is that it may relax by phosphorescence to the ground state S_0. The other is that the molecule absorbs another photon, promoting the electron to a higher-lying triplet state T_2. The electron then relaxes very rapidly back to the lowest triplet state T_1 Accompanying each absorption process mentioned above, an instantaneous refraction takes place according to the Kramers–Krönig relation. Following each relaxation, a temperature rise (ΔT) occurs, thus inducing an additional refractive index change $\Delta n_{\rm thermal}$. Since ΔT is larger around the beam axis than off the axis for $\rm TEM_{00}$ mode laser excitation, the resulting nonuniform spatial distribution of $\Delta n_{\rm thermal}$ produces a thermal lensing effect with either a positive or negative sign depending on the sign of $({\rm d}n/{\rm d}T)$.

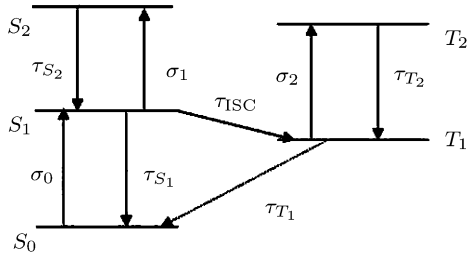


Fig.4. Five-level model showing nonlinear absorption behaviours of the sample in singlet states (S) and triplet states (T).

Considering a thin medium and using the slowly varying envelope approximation, we can separate the beam propagating equation into a couple of equations, one for the phase and the other for the irradiance, given as follows:[15]

$$\frac{\partial I}{\partial z'} = -\alpha I, \tag{1}$$

and

$$\frac{\mathrm{d}\phi}{\mathrm{d}z'} = k\Delta n, \tag{2}$$

where I and ϕ represent the irradiance and the phase respectively, and z' refers to the propagation length in the sample; α and Δn denote the absorptive coefficient and the change of refractive index respectively. The irradiance and the phase of a laser pulse, incident on the sample at z, can be written as

$$I(z,r,t) = \left[\frac{\omega_0^2}{\omega^2(z)}\right] I_0 \exp\left[-\frac{2r^2}{\omega^2(z)}\right] \exp\left[-\left(\frac{t}{\tau}\right)^2\right], \tag{3}$$

and

$$\phi(z,r,t) = \frac{kr^2}{2R(z)}, \tag{4}$$

where $\omega(z) = \omega_0[1 + (z/z_0)^2]^{1/2}$ is the beam radius at z; z is the sample position away from the focus on the axis; $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam; ω_0 is the beam radius at focus; I_0 is the on-axis peak irradiance at focus and can be calculated from $I_0 = 4\sqrt{\ln 2}E/(\pi^{3/2}\omega_0^2\tau)$; E is the pulse energy; τ is the laser pulse width (FWHM).

In our investigation with 21 ps pulses, because the picosecond pulse duration is rather shorter than the temporal duration of the population transfer from the singlet excited state to the triplet state, i.e. $\tau_{\mathrm{ISC}} \gg$ 21 ps, the contribution of the triplet state is very small and can be neglected. Thermally induced optical nonlinearity buildup time is determined by the time required for a sound wave to propagate across the beam size, $\tau_{\mathrm{ac}} = \omega_0/v_{\mathrm{s}}$, where v_{s} is the sound speed in the sample. In our experiment, the laser beam radius at focus w_0 is about 24.5 μm, and the sound speed in ethanol is $v_{\mathrm{s}} = 1200$ m/s; the rise time of the thermal nonlinearity τ_{ac} is obtained to be about 20.4 ns. The pulse width $\tau_{\mathrm{p}} = 21$ ps is much smaller than the buildup time of the thermally induced optical nonlinearities, so the thermally induced optical nonlinearity is very small and can be neglected according to the previous results.[16] The nonlinear absorption and the nonlinear refraction arise from transitions among the singlet states alone. A three-level model, including the ground state S_0 and two singlet excited states S_1 and S_2, is adequate to describe the observed picosecond nonlinear behaviour, and the population-change rates of the states are

$$\begin{aligned}
\frac{\mathrm{d}N_0}{\mathrm{d}t} &= -\frac{\sigma_0 I}{\hbar\omega}N_0 + \frac{N_1}{\tau_{S1}} - \frac{\beta N_{S_0} I^2}{2\hbar\omega},\\
\frac{\mathrm{d}N_1}{\mathrm{d}t} &= \frac{\sigma_0 I}{\hbar\omega}N_0 - \left(\frac{\sigma_1 I}{\hbar\omega} + \frac{1}{\tau_{S_1}}\right)N_1 + \frac{N_2}{\tau_{S_2}},\\
\frac{\mathrm{d}N_2}{\mathrm{d}t} &= \frac{\sigma_1 I}{\hbar\omega}N_1 - \frac{N_2}{\tau_{S_2}} + \frac{\beta N_{S_0} I^2}{2\hbar\omega},
\end{aligned} \tag{5}$$

where the absorptive coefficient α and the change of refractive index Δn in Eqs.(1) and (2) are expressed as

$$\alpha = \sigma_0 N_0 + \sigma_1 N_1 + \beta N_0 I^2, \tag{6}$$

and

$$\Delta n = \Delta\eta_1 N_1 + \gamma I N_0 + n_2 I, \tag{7}$$

where σ_0 is the ground-state absorption cross section; σ_1 is the excited-state absorption cross section from the excited-state S_1; $\Delta\eta_1$ denotes the contrast of the refractive index between the S_1 and S_0; β and γ represent the two-photon absorptive coefficient and Kerr nonlinear refractive coefficient of the S_0 state respectively; N_0 and N_1 represent the number densities of states S_0 and S_1, respectively; n_2 is the Kerr nonlinear refractive coefficient of the solvent, and its value of 1.1×10^{-19} m^2/W is obtained by the 21 ps Z-scan experiment.

The theoretical curves superposed on the data in Fig.1 are obtained by solving Eqs.(1), (2) and (5) and using a single set of parameters, i.e. $\sigma_1 = 23 \times 10^{-22}$ m^2, $\Delta\eta_1 = 2.1 \times 10^{-21}$ m^2, $\beta = 2.5 \times 10^{-36}$ m^4 /W and $\gamma = 0.8 \times 10^{-36}$ m^4/W. Here, $\sigma_0 = 1.5 \times 10^{-22}$ m^2 is provided by the linear absorption measurements. It is confirmed that the theoretical fitting is in very good agreement with the experimental result.

Under 4 ns pulse excitation, the triplet state populations come into play. Although the pulse duration is smaller than the intersystem crossing time τ_{ISC}, there should be a certain population transferring from the singlet states S_1 to the triplet state T_1 and the population of the triplet state will be more and more cumulative because of the long lifetimes of the triplet state T_1 and the first singlet excited-state S_1. Because the lifetimes of energy levels S_2 and T_2 are very short, the populations of these two levels can be neglected in the nanosecond case. The two-photon absorption, the Kerr nonlinear refraction of the solvent and the Kerr

nonlinear refraction of the S_0 state are very small and also can be neglected because of the relatively weak irradiance. Meanwhile, the thermal lensing effect can come into play even though the laser pulse width is smaller than the buildup time of the thermally induced optical nonlinearities $\tau_{\rm ac}$, which belongs to the problem of thermally induced optical nonlinearities in liquids in the transient regime.[16] Thus, the observed nanosecond nonlinear behaviour can be well described by another three-level model, including the ground states S_0 and two excited states S_1 and T_1. Now the rate equations for these three levels, the absorptive coefficient α and change of refractive index Δn in Eqs.(1) and (2) are expressed as

$$\begin{aligned}\frac{{\rm d}N_0}{{\rm d}t} &= -\frac{\sigma_0 I}{\hbar\omega}N_0 + \frac{N_1}{\tau_{S_1}} + \frac{N_3}{\tau_{T_1}},\\ \frac{{\rm d}N_1}{{\rm d}t} &= \frac{\sigma_0 I}{\hbar\omega}N_0 - \frac{N_1}{\tau_{S_1}} - \frac{N_1}{\tau_{\rm ISC}},\\ \frac{{\rm d}N_3}{{\rm d}t} &= \frac{N_1}{\tau_{\rm ISC}} - \frac{N_3}{\tau_{T_1}},\end{aligned} \tag{8}$$

$$\alpha = \sigma_0 N_0 + \sigma_1 N_1 + \sigma_2 N_3, \tag{9}$$

and

$$\Delta n = \Delta\eta_1 N_1 + \Delta\eta_2 N_3 + n_2 I + \Delta n_{\rm thermal}, \tag{10}$$

where σ_2 is the excited-state absorption cross section from the excited-state T_1, $\Delta\eta_2$ is the contrast of the refractive index between T_1 and S_0, and N_3 represents the number density of states T_1.

In most previous studies on thermally induced refractive change in the transient regime, numerical simulations are obtained by solving photo-acoustic and electromagnetic wave equations simultaneously.[16] However, this process demands complicated computation and takes much computing time. In fact, it is not yet possible to compute the pulsed laser beam propagation through nonlinear optical materials when we consider the thermal lensing effect using Eqs.(1) and (2) if the sample thickness is smaller than the value of z_0. We only need to acquire the real-time thermally induced nonlinear refraction change $\Delta n_{\rm thermal}$ in the nanosecond pulse duration by solving the photo-acoustic equation. The energy will be released along with the nonradiative decays from the higher excited-states (S_2, T_2) to the first excited-states (S_1, T_1) and from the excited-state S_1 to the ground state S_0. The energy which is released from the triplet state T_1 to the ground-state S_0 can be neglected because of the long lifetime of the state T_1. On the other hand, because the lifetime of the higher excited-state (S_2, T_2) is much shorter than the duration of the nanosecond pulse, we think that the photon energy, which is absorbed by the solute molecules to promote the electron from the states (S_1, T_1) to the higher excited singlet states (S_2, T_2), is the total energy released within the nanosecond pulse duration. The released energy turns into heat within the molecule at the speed of

$$\frac{{\rm d}Q}{{\rm d}t} = \frac{\hbar\omega N_1}{\tau_{S_1}} + \sigma_1 N_1 I + \sigma_2 N_3 I, \tag{11}$$

where Q denotes the thermal energy accumulated within the solute molecules per unit volume. The temperature change ΔT in the sample occurs after the intermolecular heat (Q) has dissipated through the surrounding solvent molecules. The diffusion equation of conduction of heat is[16]

$$\rho_0 C_{\rm p}\frac{\partial\Delta T(r,z,t)}{\partial t} - \kappa\nabla\Delta T(r,z,t) = \frac{{\rm d}Q}{{\rm d}t}, \tag{12}$$

where κ is the thermal conductivity of the sample. Here, we can neglect the diffusion term, which does not occur on the nanosecond time scale. As a result, ΔT at time t can be obtained as

$$\Delta T(r,z,t) = \frac{1}{\rho_0 C_{\rm p}}\int_{-\infty}^{t'}\frac{{\rm d}Q}{{\rm d}t}{\rm d}t', \tag{13}$$

where $C_{\rm p}$ denotes the isobaric specific heat and equals 1.9×10^3 J/(kg·°C) for ethanol,[18] and ρ_0 is the density of ethanol. When the leading edge of a nanosecond pulse ($t=-\infty$) encounters the sample, $\Delta T(r,z,-\infty)=0$. The thermal index change induced by the propagation of a nanosecond laser pulse through the sample can be described by the following photo-acoustic wave equation:[16]

$$\begin{aligned}&\frac{\partial^2\Delta n(r,z,t)}{\partial t^2} - v_{\rm s}^2\nabla^2\left(\Delta n(r,z,t)\right)\\ =&\frac{\gamma_{\rm e}\beta v_{\rm s}^2}{2n_0}\nabla^2(\Delta T(r,z,t)),\end{aligned} \tag{14}$$

where $\beta=-(1/V)(\partial V/\partial T)_{\rm p}$ is the thermal expansion coefficient; $\gamma_{\rm e}=\rho_0[\partial(n^2)/\partial\rho]_T=(n_0^2-1)(n_0^2+2)/3$ is the electrostrictive constant and can be obtained from the Lorentz–Lorenz law;[16] n denotes the linear refractive index of the solvent. ${\rm d}n/{\rm d}T=\gamma_{\rm e}\beta/2n_0$ is the thermo-optic coefficient. For the interaction of a nanosecond pulse with the sample, we substitute ΔT derived from expression (13) into Eq.(14) to obtain Δn with the initial condition, i.e. $\Delta n=0$ and $\dfrac{\partial(\Delta n)}{\partial t}=0$ at $t=-\infty$.

There are two parameters, σ_2 and $\Delta\eta_2$, which are undetermined in the 21 ps pulse Z-scan experiments. Using $\sigma_2 = 1.2 \times 10^{-21}$ m^2 and $\Delta\eta_2 = -2.3 \times 10^{-21}$ m^2, we best fit the results with $\Delta n_{\text{thermal}}$ determined by Eq.(14). Here, $\mathrm{d}n/\mathrm{d}t = 3.9 \times 10^{-4}$ (K^{-1}) is cited from Ref.[18]. We also let $\mathrm{d}n/\mathrm{d}t = 0$ for fitting the experiment results and find that the change of the theoretical fitting line is very small, which indicates that the thermal lensing effect is very small under the 4 ns pulse excitation, which is due to the fact that the pulse duration is only about 0.2 times the thermal forming time and the contribution of the singlet excited-state is too large to cover up the thermal lensing effect.

Under the 10 ns pulse excitation more populations will transfer from the singlet state S_1 to the triplet state T_1 and the contribution of the triplet state to the nonlinear refraction will increase. Meanwhile, the thermal lensing effect also increases. As shown in Fig.1, the transition from self-focusing to self-defocusing illustrates that the contribution of thermal lensing effect to the Z-scan curve surpasses the excited-state refraction gradually with the decrease of concentration. In order to further discuss the influence of concentration on nonlinear refraction of CAP solution, we investigate separately the variations of pure excited-state nonlinear refraction and pure transient thermal lensing effect with concentration in theory. We define that the difference between the extrema of the normalized transmittance peak and valley of Z-scan curve, ΔT_{pv} is positive for excited-state refraction, and negative for thermal lensing effect. The curves for the variation of ΔT_{pv} as a function of concentration for pure excited-state refraction and pure transient thermal lensing effect are shown in Fig.5. These curves exhibit that the thermal lensing effect and the excited-state refraction decrease as the concentration of the solution decreases. However, the decrease rate of the thermal lensing effect is smaller than that of the excited-state refraction. As a result, the thermal lensing effect surpasses the excited-state refraction gradually with decreasing concentration. We still use the obtained parameters to simulate the 10 ns Z-scan experimental results. The excellent agreement between the numerical simulations and the data reported here indicates that our theoretical model and these parameters are accurate to describe the photo-physical dynamics of the sample.

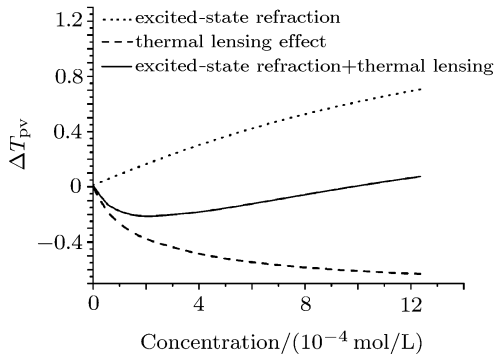


Fig.5. Curves for ΔT_{pv} as a function of concentration.

We also compare our results with those in the work by Wei *et al.*[14] First, we repeat the theoretical fitting given by Wei *et al.* Second, we obtain the theoretical curve using their parameters and the theory of the transient thermal lensing effect. Finally, we obtain the theoretical curve using our parameters and the theory of the transient thermal refraction. We find that the theoretical curve obtained using our obtained parameters and the theory of the transient thermal lensing effect is in good agreement with their experimental results. However, there is an obvious discrepancy between the theoretical curve obtained by using the theory of the transient thermal lensing effect and the theoretical curve obtained using the theory of the steady-state thermal lensing effect, which indicates that it is not appropriate to use the steady-state theory to deal with the transient thermal lensing effect problem under their experimental conditions, as shown in Fig.6.

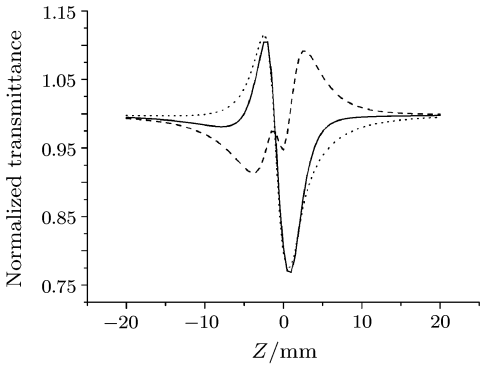


Fig.6. Theoretical curves obtained using the different parameters and the theory model separately, where the solid line is for the theoretical curve obtained using Wei *et al*'s parameters and the theory of the steady-state thermal lensing effect, the dash line is for the theoretical curve obtained using Wei *et al*'s parameters and the theory of the transient thermal lensing effect, and the dot line is for the theoretical curve obtained using our parameters and the theory of the transient thermal lensing effect.

4. Conclusions

We use the Z-scan technique with 4 ns, 10 ns and 21 ps laser pulses to investigate the nonlinear refractive properties of CAP/ethanol solution. The experimental results are described very well using the rate-equation model and the theory of the transient thermal lensing effect in liquids. The refractive cross sections of the excited state are obtained, and the refractive cross section of the triplet excited-state is confirmed to be smaller than that of the ground-state.

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