Short Communication

Studies of instantaneous thermal refraction and nonlinear scattering effect in C_{60}/toluene solution

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Nonlinear refraction and scattering effect properties of C_{60}/toluene solution were studied by using the Z-scan technique and 532 nm laser delivering 4 nanosecond (ns) pulses. With single ns pulse, reverse saturable absorption (RSA) and negative nonlinear refraction were observed, and the nonlinear scattering effect in the solution could not be ignored when the pulse energy was large enough. The refraction cross-section of the singlet and triplet excited-state were calculated as $\eta_{S_1} = 8.02 \times 10^{-28} m^2, \eta_{T_1} = 8.52 \times 10^{-28} m^2$, respectively. The nonlinear scattering coefficient was also obtained. PACS: 42.65.Dr; 42.65.Jx; 42.65.Hw

Key words: C_{60}; nonlinear; refraction; scattering

INTRODUCTION

Recently, the fullerene molecules have attracted much attention because, as three-dimensional π-electron conjugated systems they appear promising as new limiting materials Ebbesen et al. (1991). Sahraoui et al. (1999) have found that the asymmetry of intramolecular electronic charge-density essentially influences the optical properties of the C_{60} derivative and caused a charge-density redistribution both on the intramolecular as well as on the intermolecular level (Sahraoui et al., 1999). Wei et al., (2000) have reported the experimental and theoretical study of C_{60}/toluene solution by single picosecond (ps) pulse and trains of ps pulses separated by 7 ns, they used a five-state model to explain the observed RSA in the picosecond regime as well as to distinguish the mechanisms that contribute to ps and nanosecond nonlinear refraction, which show opposite signs when the coexistent nonlinear absorption is eliminated (Wei et al., 2000). Mishra et al. (1996) have observed the nonlinear scattering effect in C_{60}/toluene with long pulse excitation and they explain the reason for the phenomena. In our letter, we investigate instantaneous thermal nonlinear refraction and excited state refraction experimentally and numerically in C_{60}/toluene solution with nanosecond pulse excita-tion, and nonlinear scattering is also

investigated in our letter.

EXPERIMENT RESULT AND DISCUSSION

In this study, we use Nd: YAG laser (Continuum) for ns investigation, which produces 4ns and 10ns laser pluses at 532 nm with a repetition rate of 1 HZ. The spatial distribution of the pulse is nearly a Gaussian profile. The sample solution is placed in quartz cell of 2 mm thickness with the molecular density of $4.0 \times 10^{23} m^{-3}$. The quartz cell was placed on a translation stage controlled by a computer that moved 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 was about $25 \mu m$. The transmittance of the samples is measured with and without an aperture in the far-field. The linear transmittance of the aperture is 0.09. The laser pulses adjusted by an attenuator are separated into two beams by using a splitter. The two beams were simultaneously measured by using two energy detectors (Rjp-735 energy probe) linked to energy meter (Rj-7620 ENERGY RATIOMETER, Laser-probe Corp.). A personal computer is used to collect and process data coming from energy meter through IEEE-488 interface.

Using 4 and 10 ns pulse excitation, we perform the Z-scan measurements on a C_{60}/toluene solution as shown in Figure 1, the solution shows strong nonlinear absorption and nonlinear refraction. The nonlinear optical absorption shows reverse saturable absorption as shown in Figure 1(a). The curve of nonlinear refraction exhibits a peak on the -z side and a valley on the +z side, indicating a negative lensing effect.

We use a five-energy-band model shown to interpret the experimental results (Wei et al., 2000). Each band is conventionally named as S_m for the singlet manifold or T_m for the triplet manifold, where the subscript m refers to the state formed from certain electr-

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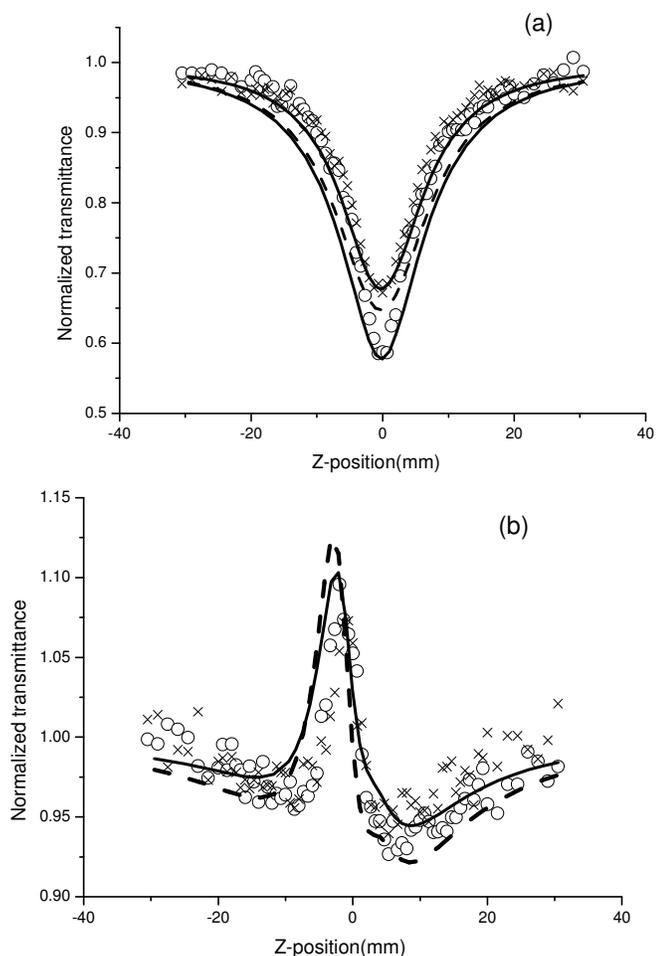
Figure 1. The Z-scan results of C_{60}/toluene solution using 4 ns pulses. (a): nonlinear absorption, cross: experimental results of $0.1GW/m^2$, circle: experimental results of $0.14GW/m^2$, solid line: simulation of the experimental results. (b): cross: experimental results of $0.1GW/m^2$, nonlinear refraction of $0.14GW/m^2$, circle: experimental results of $0.14GW/m^2$, solid line and dash line: simulation of the experimental results.

onic configurations in molecular orbital. Pumped by a laser pulse at 532 nm, the molecules are prompted to the first excited singlet state S_1 via a one-photon process, and then undergo one of the following three processes: (1) internal conversion (with a time constant of $\tau_{IC}=30$ ns) to the bottom of S_0, (2) intersystem crossing (with a time constant of $\tau_{ISC}=1.2$ ns) to T_1 (Li et al., 1994), or (3) one-photon excitation to a vibronic level of S_2. Those excited to the vibronic levels of S_2 nonradiatively decay to a vibronic level of S_1 in sub-picoseconds (Ebbesen et al. 1991). Those relax to T_1 can further be excited to T_2 if the pulse duration is comparable with τ_{ISC} or longer.

As previous estimated, the local thermal equilibrium time is about 299 ps (Wei et al., 2000), in our experiment, we use 4ns laser pulse, both the thermal lensing effect and the triplet transition are relevant based on the thermal equilibrium time and the ns S_1 state lifetime. As a result, nonlinear absorption and refraction arise from transitions among the singlets and triplets, and the irradiance and

phase changes are determined by the equations below (Wei et al., 1998)

$$\frac{dI}{dz'} \equiv -\alpha I = -[\sigma_{S0}N_{S0}+\sigma_{S1}N_{S1}+\sigma_{T1}N_{T1}]I \tag{1}$$

$$\frac{d\phi}{dz'} \equiv k\Delta n = \eta_{S0}N_{S0}+\eta_{S1}N_{S1}+\eta_{T1}N_{T1}+kn_2I+k\Delta n_{thermal} \tag{2}$$

Where I and ϕ represent the irradiance and phase, and z' is the propagation length in sample. α and Δn denote the absorptive coefficient and change of refractive index. N represents the population density of the state specified by the subscripts. n_2 is the Kerr nonlinear refractive coefficient of the solvent, its value is $5.5\times10^{-19}m^2W^{-1}$ [7]. $\Delta n_{thermal}$ is the thermally induced nonlinear refraction change. For Eqs.(1) and (2), the associated population-change rates of the states involved are:

$$\frac{dN_{S_0}}{dt} = -\frac{\sigma_{S_0}N_{S_0}I}{h\varpi}+\frac{N_{S_1}}{\tau_{S_1}}+\frac{N_{T_1}}{\tau_{T_1}} \tag{3}$$

$$\frac{dN_{S_1}}{dt} = \frac{\sigma_{S_0}N_{S_0}I}{h\varpi}-\frac{N_{S_1}}{\tau_{S_1}}-\frac{N_{S_1}}{\tau_{ISC}}+\frac{N_{T_1}}{\tau_{T_1}} \tag{4}$$

$$\frac{dN_{T1}}{dt} = \frac{N_{S_1}}{\tau_{ISC}}-\frac{N_{T_1}}{\tau_{T1}} \tag{5}$$

The irradiance and phase of a switched-out single pulse, incident on the sample at z, can be written as [8]

$$I = I(z,r,t) = [\frac{\varpi_0^2}{\varpi^2(z)}]I_0\exp[-\frac{2r^2}{\varpi^2(z)}]\exp[-(\frac{t}{\tau})^2] \tag{6}$$

and

$$\phi_0 = \phi(z,r) = \frac{kr^2}{2R(z)} \tag{7}$$

In Eq. (6), the origin of time is set as the pulse maximum; the argument r refers to the lateral distribution of the laser beam. $\varpi(z)=\varpi_0[1+(z/z_0)^2]^{1/2}$ is the beam radius at z, $R(z)=z[1+(z_0/z)^2]$ is the curvature radius of the wave front at z, $z_0=k\varpi_0^2/2$ is the diffraction length of the beam, τ is the pulse duration, and $k=2\pi/\lambda$ is the wave vector, all in free space. I_0 is the on-axis peak irradiance at the focus, and can be calculated from $I_0=4\sqrt{\ln 2}E/(\pi^{3/2}\varpi_0^2\tau)$. E is the pulse energy, and τ is the laser pulse width.

Consider the thermal lensing effect by using the Eqs.(6)-(7) if the sample thickness is smaller than z_0, we need to acquire the real-time thermally induced nonlinear refraction change $\Delta n_{thermal}$ 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-state (S_2, T_2) to the first excited-state (S_1, T_1) and from the excited-state S_1 to the ground state S_0. The released energy turns into heat and the temperature change ΔT in the sample occurs after the intermolecular heat dissipates throughout the surrounding solvent molecules. We can neglect the

diffusion term in the diffusion equation of conduction of heat, because it does not occur on the nanosecond time scale, and ΔT at time t can be obtained as (Jiao et al., 2007).

$$\Delta T(r,z,t) = \frac{1}{\rho_0 C_p} \int_{-\infty}^{t} \alpha(r,z,t)I(r,z,t)dt \qquad (8)$$

When the leading edge of a nanosecond pulse ($t=-\infty$) encounters the sample, $\Delta T(r,z,-\infty)=0$. In Eqs. (8) C_p denotes the isobaric specific heat and equals 1.71 J/g°C for toluene (Jiao et al., (2007). Index change induced by propagation of a nanosecond laser pulse through the sample can be described by the following photo-acoustic wave equation (Kovsh et al., 1999a; Kovsh et al., (1999b)

$$\frac{\partial^2 \Delta n(r,z,t)}{\partial t^2} - v_s^2 \nabla^2 \left(\Delta n(r,z,t) \right) = \frac{\gamma_e \beta v_s^2}{2n_0} \nabla^2 (\Delta T(r,z,t))$$

$$(9)$$

Where, $\beta = -(1/V)(\partial V/\partial T)_p$ is the thermal expansion coefficient, $\gamma_e = \rho_0 [\partial(n^2)/\partial\rho]_T = (n_0^2-1)(n_0^2+2)/3$ is the electrostrictive constant and can be obtained from the Lorentz-Lorenz law (Yariv 1991); n denote the linear refractive index of the solvent. It is used to use $dn/dT = \gamma_e \beta/2n_0$ representing the thermal-optic coefficient. For the interaction of a nanosecond pulse with the sample, we substitute ΔT derived from Eqs.(8) into Eqs.(9) to solve for Δn with the initial condition of $\Delta n=0$ and $\partial(\Delta n)/\partial t=0$ at $t=-\infty$ (Jiao et al., 2007)

When the intensity of $0.1GW/m^2$ is used, the experimental result is shown in Figure 1 for cross, to fit the experimental result, we take, $\sigma_{S_0}=3.1\times10^{-22}m^2, \sigma_{S_1}=1.6\times10^{-21}m^2, \quad \sigma_{T_1}=0.95\times10^{-21}m^2$, and $\eta_{S_0}=8.44\times10^{-28}m^2, \quad \eta_{S_1}=8.02\times10^{-28}m^2, \quad \eta_{T_1}=8.52\times10^{-28}m^2$, the thermal-optic coefficient $dn/dt=5.7\times10^{-4}K^{-1}$, and the simulation fits the experimental result well, as the top line in Fig.1(a) and the solid line in Figure 1(b) shown . We assume the contributions to the nonlinear refraction are excited state refraction induced by excited state absorption and thermal lencing effect.

When we use intensity of $0.14GW/m^2$ for excitation, with the same parameters, we simulate the dash line in Figure 1(a), the bottom of the simulation cannot arrive at the bottom of the experimental result, and we assume there is nonlinear scattering effect in the solution when the pulse energy increases. Here we consider the nonlinear scattering effect in the solution, we define μ as nonlinear scattering coefficient, and we take $\mu=4.5\times10^{-11}m^2W^{-1}$, as the bottom solid line in Figure 1(a) and dash line in Figure 1(b) shown, the theoretical result fits the experimental result well. S. R. Mishra et al. have reported the contribution of nonlinear scattering effect in C_{60}/toluene, they used 30ns, 527 nm laser pulse for excitation, with the input fluence of $1J/cm^2, 1.5J/cm^2, 2J/cm^2$, they observed the nonlinear scattering in the solution and concluded that the origin of scattering in C_{60}/toluene solution appears to be due to formation of absorption induced in homogeneity in the solution (Mishra et al., 1996). Here our input fluence is $0.8J/cm^2$, lower than theirs for the width of our pulse is shorter than theirs. As a result, the contributions to the nonlinear refractive index induced by the nanosecond pulse are the instantaneous thermal effect, excited state refraction, and nonlinear

scattering, the nonlinear refraction for the contributions is associated with a negative sign.

Conclusion

With the pulse of 4ns and the different energy of the laser pulse excitation at the wavelength of 532 nm, we performed Z-scan technique to investigate the nonlinear optical properties of C_{60}/toluene solution. The experimental results indicate that C_{60}/toluene solution has reverse saturable absorption (RSA) and negative nonlinear refraction under our conditions. There are three contributions to nonlinear refraction, that is, instant-neous thermal effect, excited state refraction and nonlinear scattering effect. The theoretical results are accord with the experimental results. When we use the pulse intensity of $0.14GW/m^2$, the nonlinear scattering effect in the solution must be considered, and when the pulse intensity declines to $0.1GW/m^2$, the nonlinear scattering disappears in the solution.

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