Optical nonlinearity measurement of 4-(N-methyl, N-hydroxyethl)amino, 4'-nitroazobenzene using a transmittance technique with a phase object (T-PO) with top-hat beams at 600-nm wavelength

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(Received 20 February 2012; revised manuscript received 17 March 2012)

The transmittance technique with a phase object (T-PO), for measuring optical nonlinear coefficients is proposed with a top-hat beam. The sensitivity of the T-PO with a top-hat beam is a factor of 4 greater than that with a Gaussian beam. The validity of this method is verified by measuring the nonlinearity of a well-characterized liquid, CS_2 at 532-nm wavelength. The ease of use of this method has been proved by measuring a new compound 4-(N-methyl, N-hydroxyethyl)amino, 4'-nitroazobenzene(ANAB) at 600-nm wavelength, indicating that this method can be extended to the measurement of optical nonlinearities in a wide-band spectrum.

Keywords: transmittance technique with a phase object (T-PO), phase object, optical nonlinearities

PACS: 42.25.Bs, 42.65.–k **DOI:** 10.1088/1674-1056/21/10/104201

1. Introduction

Development of high power laser sources has inspired extensive research of the optical nonlinearities and optical limiting behaviours of materials. A variety of experimental methods have been used for measuring the third-order nonlinear susceptibility, such as four-wave mixing,[1,2] nonlinear image techniques,[3] and Z-scan.[4,5] Recently, Yang and Song[6] have proposed a Z-scan method with a phase object using a Gaussian beam.[6] Both the magnitude and the sign of the nonlinear coefficients can be obtained from the 'peak' or 'valley' of the curve. Based on the Z-scan technique with a phase object, a transmittance measurement technique with a phase object (T-PO) has been developed to measure the third-order nonlinearities.[7,8] With this simple method, the nonlinear optical coefficients of materials can be easily deduced from the normalized transmittance. In the present paper, the T-PO method with a top-hat beam is studied. The sensitivity of T-PO method with a top-hat beam is greater than that with a Gaussian beam. Meanwhile we compare the results determined from this technique with the results obtained from Z-scan using a top-hat beam. The proposed T-PO method with a top-hat beam is advantageous in high sensitivity and lower stress in fragile materials, since a single pulse is enough to measure the nonlinear coefficients. The reliability is verified by measuring a known liquid CS_2 sample.

In recent years, third-order nonlinear optical materials have been expected to play an essential role in many important photoelectronics and photonics technologies.[9,10] Nowadays, azobenzene functionalized materials have aroused much interest for their potential applications in photonics, optoelectronics, and optical signal processing systems.[11−17] These applications are based on the reversible photochemical isomerization of the azobenzene group upon resonant irradiation with polarized light, which leads to noticeable changes in the physical and optical properties of the material.[18] Polymer containing azobenzene derivatives have good photothermal stability, dissolvability, and easy preparation virtues,[19,20] and have been a well-known nolinear optically active chro-

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mophore due to theirunique optical properties,[21,22] such as photoisomerization and birefringence. However, the maximum of the linear absorption varies with the substituted component of the azobenzene functionalized material. To investigate the optical nonlinearities of the azobenzene derivatives, we should change the wavelength of the laser to avoid the strong single-photo absorption. Unfortunately, the laser beams emitted from an optical parameter generation or oscillation system are not always stable for the well-known Z-scan measurement. On the other hand, a beam with a top-hat profile can be easily obtained by expanding a small part of the beam. Thus, the T-Po method with a top-hat beam has the advantage in measuring the optical nonlinear coefficients at a wide-band spectrum. The optical nonlinear coefficients of a new compound 4-(N-methyl, N-hydroxyethyl)amino, 4'-nitroazobenzene is measured by this method at 600-nm wavelength.

2. Preparation of ANAB

4-Nitrobenzenamine (5.52 g, 0.04 mol) was dissolved in 16-mL concn. hydrochloric acid. After cooling to 0 °C, an ice–water solution of sodium nitrite (3.04 g, 0.044 mol) was added dropwise and stirred for 30 min. 7.88 g (0.084 mol) was dissolved in 60-mL aqueous NaOH (3.36 g, 0.084 mol) solution. The mixture was then added dropwise to a buffered aqueous solution (acetic acid/sodium acetate, pH ≈ 6) containing 2-(methyl (phenyl) amino) ethanol (6.34 g, 0.042 mol) and stirred for 2 h at 0 °C–5 °C. The resulting precipitate was filtered and rinsed twice with water. The crude product was recrystallized twice from ethanol to provide dark green crystal piece crystals in 92% yield. Figure 1 shows the molecular structure of the new compound ANAB. Figure 2 shows the UV-vis spectrum of the compound in THF. It is characterized by two bands at 284 nm and 481 nm, which are assigned to π–π^* electronic transitions of the phenyl and azobenzene chromophore, respectively. Small linear absorption is observed at 600 nm in compound ANAB solution. Therefore, we investigate the optical nonlinearities of this compound at 600-nm wavelength.

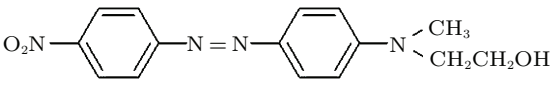


Fig. 1. Molecular structure of the new compound ANAB.

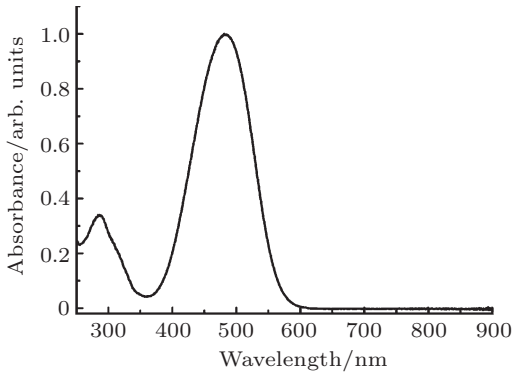


Fig. 2. Normalized absorption spectrum of 4-(N-methyl, N-hydroxyethyl)amino, 4'-nitroazobenzene in THF at a concentration of 1×10^{-5} M.

3. Experiments

The experimental setup for the T-PO with a top-hat beam is shown in Fig. 3. The extracted 21-ps (FWHM) double-frequency pulse (λ = 532 nm) is generated by a Q-switched and mode locked Nd:YAG laser. The beam is first expanded from 8 nm to 64 mm in diameter by convex lenses L_1 and L_2 with focal lengths f_1 = 5 cm and f_2 = 40 cm, respectively. Since the radius of the aperture R_a = 5.6 mm is much smaller than the expanded beam, we consider the part of the beam illuminated in the aperture as a top-hat beam. Then the beam passes through aperture A_1 and the phase object, and is split into two parts: one part of the beam is directed to detector D_1, which monitors the fluctuations of the incident pulse energy; the other part of the beam is tightly focused by convex lenses L_3 and transmits through the sample, then passes through aperture A_2 and detected by D_2. The radius of the phase object is L_p = 0.5 mm, and phase retardation is $\phi_L = 0.5\pi$. The sample is located in a 2-mm width cell. In our experiment, we first place the sample at the focal point, record the ratio between energies detected, respectively, by D_2 and D_1. Then we place the sample away from the focal point, record the ratio between energies, respectively, detected by D_2 and D_1.

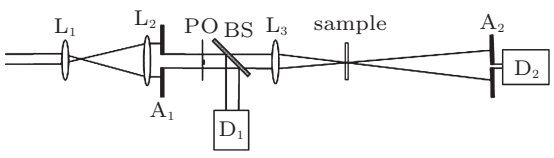


Fig. 3. Experimental apparatus for the T-PO with a top-hat beam technique. L_1, L_2, and L_3 are lenses; D_1 and D_2, detectors; A_1 and A_2, apertures; BS, beam splitter; PO, phase object.

Dividing the obtained two energy ratios, we derive the normalized transmittance. The distance between the sample and the aperture A_2 is $d = 0.8$ m. In our arrangement, the edge of the aperture A_2 is adjusted to coincidence with the edge of diffraction image of the PO to acquire high accuracy. The corresponding optimal radius of aperture A_2 is $r_a = 1.0$ mm.

4. Theoretical calculations and discussion

The electric field $E(r,t)$ of the top-hat beam incident on the front surface of the PO can be generally expressed as

$$E(r,t) = E_0 \exp\left(-\frac{t^2}{2\tau^2}\right) \mathrm{circ}\left(\frac{r}{R_a}\right), \tag{1}$$

where E_0 is the amplitude of the electric field, and $\mathrm{circ}(r/R_a)$ represents a circular function and $\mathrm{circ}(r/R_a) = 1$ when $r \le R_a$; $\mathrm{circ}(r/R_a) = 0$ when $r > R_a$. The value of E_0 is given by $E_0 = \sqrt{\varepsilon/(\pi^{3/2}R_a^2\tau)}$, where ε is the pulse energy. The output electric field of the PO can be expressed as

$$E_1(r,t) = E(r,t)\exp(\mathrm{i}\phi_L \mathrm{circ}(r/L_p)). \tag{2}$$

With the help of Fresnel diffraction formula, the electric field in the front surface of L_3 can be obtained as

$$E_2(r_1,t) = \frac{\mathrm{e}^{\mathrm{i}kf_3}\,\mathrm{e}^{\mathrm{i}kr_1^2/2f_3}}{\mathrm{i}\lambda f_3}\int_0^\infty 2\pi r E_{01}(r,t) \times \mathrm{e}^{\mathrm{i}kr^2/2f_3}\mathrm{J}_0(rr_1)\,\mathrm{d}r, \tag{3}$$

where f_3 is the focal length of L_3, and J_0 is the Bessel function of zero order. The output electric field in the back surface of L_3 is

$$E_2(r_1,t) = E_2(r_1,t)\exp\left(-\frac{\mathrm{i}kr_1^2}{2f_3}\right). \tag{4}$$

Using the Fresnel diffraction formula, the incidence beam on the sample can be expressed as

$$E_3(r_2,t) = \frac{\mathrm{e}^{\mathrm{i}kf_3}\,\mathrm{e}^{\mathrm{i}kr_2^2/2f_3}}{\mathrm{i}\lambda f_3}\int_0^\infty 2\pi r_1 E_2(r_1,t) \times \mathrm{e}^{\mathrm{i}kr_1^2/2f_3}\mathrm{J}_0(r_1r_2)\mathrm{d}r_1. \tag{5}$$

The equations governing the irradiance and phase changes are

$$\frac{\mathrm{d}I}{\mathrm{d}z'} = -\alpha_0 I - \beta I^2, \tag{6}$$

$$\frac{\mathrm{d}\Delta\phi}{\mathrm{d}z'} = k\Delta n. \tag{7}$$

Here, I and ϕ represent the irradiance and phase change respectively; z' is the penetration depth; α_0, β, and Δn denote the linear absorption coefficient, two photon absorption coefficient, and change of refractive index, respectively. The irradiance is expressed as $I = |E_3(r_2,t)|^2$, and the laser induced refractive index change is $\Delta n = n_2 I$, where n_2 represents the Kerr nonlinear refraction coefficient. The output electric field in the back surface of the sample is $E_4(r_2,t) = E_3(r_2,t)\exp(\mathrm{i}\Delta\phi)$. The electric field in the aperture plane is

$$E_5(r_3,t) = \frac{\mathrm{e}^{\mathrm{i}kd}\,\mathrm{e}^{\mathrm{i}kr_3^2/2d}}{\mathrm{i}\lambda d}\int_0^\infty 2\pi r_2 E_4(r_2,t) \times \mathrm{e}^{\mathrm{i}kr_2^2/2d}\mathrm{J}_0(r_2r_3)\,\mathrm{d}r_2. \tag{8}$$

The transmitted energy though aperture A_2 is obtained by spatially integrating $E_5(r_3,t)$ up to aperture radius $r_a = 1$ mm, as

$$P_c = \int_{-\infty}^{+\infty}\int_0^{r_a} 2\pi r_3 |E_5(r_3,t)|^2\,\mathrm{d}r_3\,\mathrm{d}t. \tag{9}$$

Also, we can remove aperture A_2 and the transmitted energy can be easily obtained by spatially integrating $E_5(r_3,t)$ up to $r_a = +\infty$. In this open aperture case, Eq. (13) can be written as

$$P_{op} = \int_{-\infty}^{+\infty}\int_0^{+\infty} 2\pi r_3 |E_5(r_3,t)|^2\,\mathrm{d}r_3\,\mathrm{d}t. \tag{10}$$

Assuming β to equal zero, the open aperture transmitted energy P_{op0} in linear situation is derived using Eq. (10). The open aperture normalized transmittance is given by $T_{op} = P_{op}/P_{op0}$. Similarly, assuming β and n_2 to equal zero, using Eq. (9) the close aperture transmitted energy P_{c0} is derived. The close aperture normalized transmittance is given by $T_c = P_c/P_{c0}$. We find that nonlinear absorption has little influence on T_c, and we can easily determine the sign of the nonlinear refraction from the normalized transmittance: $T > 1$ indicating the positive nonlinear refraction; indicating the negative nonlinear refraction. Since the nonlinear refraction gives no influence on open aperture normalized transmittance, the

nonlinear absorption coefficient (β) of nonlinear material can be deduced from the open aperture experiment with help of equations mentioned above. The obtained nonlinear absorption coefficient can be used to fit the closed aperture experiment data. Table 1 shows the experimental results of CS_2 using T-PO with a top-hat beam and the theoretical fits. Using, $n_2 = 3.3 \times 10^{-18}$ m^2/W, the best fit is obtained. The parameter is in quite good agreement with the reported value $n_2 = 3.2 \times 10^{-18}$ m^2/W.[23]

Table 1. Nonlinear parameters of CS_2, measured by the T-PO with a top-hat beam.

ε/μJ	T_c	T_{op}	ΔT_c	ΔT_{op}	$n_2/(10^{-18}$ m^2/W)	$\beta/(10^{-11}$ m/W)
0.22	2.80	1.00	1.80	0	3.3	0

The sensitivity of T-PO method with a top-hat beam changes with the radius of aperture A_2 and the distance between the sample and A_2. Fixing distance $d = 0.8$ m, we calculate the closed-aperture normalized transmittance changes with r_a in CS_2 sample with an input pulse energy of 0.22 μJ. The normalized transmittance with respect to L_p is shown in Fig. 4. As can be recognized from this figure, $r_a = 1$ mm is optimal for the best sensitivity. The adding of a PO in this arrangement strongly changes the interference of the beam in the far field at the PO diffraction zone. It is just like the principle of phase contrast. The phase change of the laser beam is converted into the amplitude change by the introduction of PO. The positive or negative refraction will be reflected from the amplitude change: $T_c > 1$ or $T_c < 1$.

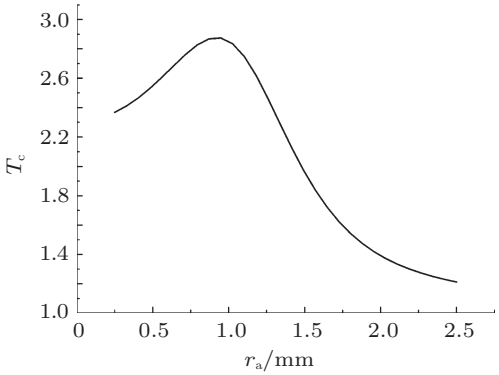


Fig. 4. Closed-aperture normalized transmittance T_c varying with r_a.

Moreover, a top-hat Z-scan experiment without the phase object is compared with this method. The top-hat Z-scan experimental condition including the pulse energy and the Airy radius at the focal plane of L_3 are kept the same as those with the top-hat T-PO. The experimental result is shown in Fig. 5 with a dotted line. The difference in the normalized transmittance between peak and valley is $\Delta T_{p-v} = 1.30$. This implies that the top-hat T-PO method has greater sensitivity than the top-hat Z-scan method in measuring the nonlinear refraction coefficient. Additionally, we compare the top-hat T-PO experimental results with those with a Gaussian beam at the same input pulse energy 0.22 μJ. The Airy radius of the focused point of the top-hat beam is given by $\omega_0 = 0.61\lambda f_3/R_a$ (23 μm) which is the same as the waist of the used Gaussian beam in the T-PO experiments.[7] The measured transmittance difference is $\Delta T = 0.45$ for the T-PO with a Gaussian beam. This implies that the sensitivity of top-hat T-PO is a factor of 4 greater than that of T-PO with a Gaussian beam.

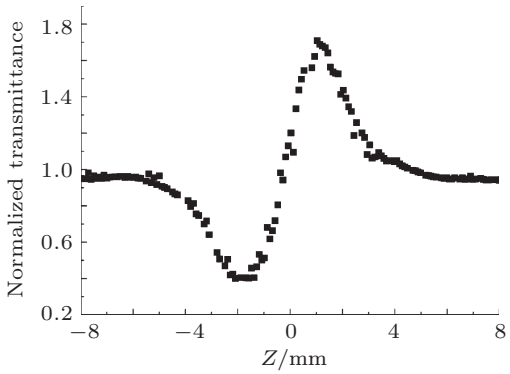


Fig. 5. Z-scan measured nonlinear refraction curve.

Since the feasibility and the high sensitivity of the top-hat T-PO has been proved, we use this method to measure optical nonlinearity of compound ANAB dissolved in DMF with a pulse width of 21 ps at 600 nm. The experimental results and the theoretical fit are shown in Table 2. Excluding the derived nonlinear absorption and the refraction coefficient of the solvent, the pure solute nonlinear absorption coefficient $n_2 = -0.2 \times 10^{-18}$ m^2/W and nonlinear absorption coefficient $\beta = 0.25 \times 10^{-11}$ m/W are obtained by theoretical fitting.

Table 2. Nonlinear parameters of ANAB/DMF at 600-nm wavelength, measured by the T-PO with a top-hat beam.

ε/μJ	T_c	T_{op}	ΔT_c	ΔT_{op}	$n_2/(10^{-18}$ m^2/W)	$\beta/(10^{-11}$m/W)
1.01 (DMF)	1.56	1.00	0.56	0	0.2	0
1.01 (ANAB/DMF)	1.00	0.86	0	–0.14	0	0.25
ANAB					–0.2	0.25

5. Conclusion

In this paper, the T-PO with a top-hat beam is developed to investigate optical nonlinearities. The feasibility of this method is demonstrated by the CS_2 sample. The proposed method is advantageous and imposes a lower stress in the cases of fragile material, since a single shot of laser pulse is enough to determine its nonlinear refractive index as well as nonlinear absorption coefficient. One of the advantages of this scheme is the relative ease of producing the top-hat beam, thus this method can be expanded to a wide-range spectrum. Moreover, experimental results indicate the high-accuracy measurements of nonlinear coefficient using a top-hat beam. With this method, the optical nonlinear coefficients of a new sample ANAB are easily determined at 600 nm.

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