Optics Communications 283 (2010) 1110–1113

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

# The nonlinear optical response of a fluorine-containing azoic dye

Tingjian Jia [a,*], Zhiguo Shang [b], Yongguang Cheng [c]

[a] Department of Physics and Information Engineering, Shangqiu Normal University, Shangqiu 47600, China
[b] The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan
[c] Department of Mathematical and Physical Science, Henan Institute of Engineering, Zhengzhou 450007, China

ARTICLE INFO

*Article history:*
Received 2 October 2009
Received in revised form 28 October 2009
Accepted 28 October 2009

*Keywords:*
Fluorine-containing azoic dye
Electronic effect
Thermal effect
Intersystem crossing

ABSTRACT

The nonlinear optical nonlinearities of a fluorine-containing azoic dye in tetrahydrofuran have been investigated by using *Z*-scan technique with picosecond and nanosecond lasers. The experimental results reveal that the azoic dye has large optical nonlinearity under the excitations of picosecond and nanosecond 532 nm. At the picosecond 532 nm the solution presents negative nonlinear refraction due to the electronic effect, while the larger nonlinear refraction under nanosecond laser excitation is induced by thermal effect. Moreover, the different nonlinear absorption behavior under picosecond and nanosecond excitations is analyzed.



## 1. Introduction

The search for nonlinear optical (NO) materials with large optical nonlinearities and fast response is essential for potential application in optical signal processing, optical limiting (OL) [1,2] and optical storage [3,4]. Though many kinds of nonlinear optical materials have been extensively studied, searching for large nonlinear optical response polymers is still in progress. Azoic dyes have many advantages over other NO materials. Photoisomerization of azoic molecules enables it easy to modify their linear and nonlinear polarizability of them as well as optical nonlinear refraction. Since the optical properties of azoic molecules can be controlled optically, it has intrigued the considerable interest of people [5,6].

The nonlinear optical phenomena of azoic dyes can result from electronic response and/or nonelectronic response. The electronic nonlinearity is induced by either population redistribution or distortion of electronic clouds. A molecule undergoes a transition from its ground state to its excitation state after absorbing a photon. The dipole moment of the molecule changes during such a transition. The change in the dipole moment will give birth to electronic nonlinearity. A nonelectronic response is a non-radiative interaction such as *cis–trans* isomerism, the changes in density and temperature [7–9]. It has been well known that the nonlinear optical behavior of materials can vary greatly by changing different laser duration or different laser wavelengths. Thus, studies about the mechanism of their *t* nonlinear optical response with different laser duration or different laser wavelengths are expected to be more interesting and important. If the nonlinear mechanism is understood for certain laser pulses, the NLO properties optimization can be well accomplished.

*Z*-scan technique is a simple and effective tool to determine the nonlinear properties [10]. It has been widely used in material characterization because it provides not only the magnitudes of the real part and imaginary part of the nonlinear susceptibility, but also the sign of the real part. Both nonlinear refraction and nonlinear absorption in solid and liquid samples can be measured easily by *Z*-scan technique, which use the change of transmittance of nonlinear materials [9]. In this work, we demonstrate the optical nonlinearities of a fluorine-containing azoic dye in tetrahydrofuran (THF) through *Z*-scan technique under picosecond and nanosecond lasers excitation at 532 nm in order to investigate the influence of pulse width on the nonlinear optical response of the fluorine-containing azoic dye.

## 2. Experimental

The molecular structure of the fluorine-containing azoic dye is shown in Fig. 1. The linear absorption spectrum of the dye solution with the concentration of $4.4 \times 10^{-5}$ M in THF is shown in Fig. 2, which was acquired using a UV–VISNIR spectrophotometer (Type: Cary 5000) manufactured by America Varian Company. The absorption spectrum is centered at 370 nm, corresponding to the $S_0 \rightarrow S_1$ transition of the azoic dye molecule. The absorption of the glass substrate was eliminated from the absorption spectrum.

* Corresponding author.
*E-mail address:* tingjianjia@yahoo.cn (T. Jia).

0030-4018/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.optcom.2009.10.110

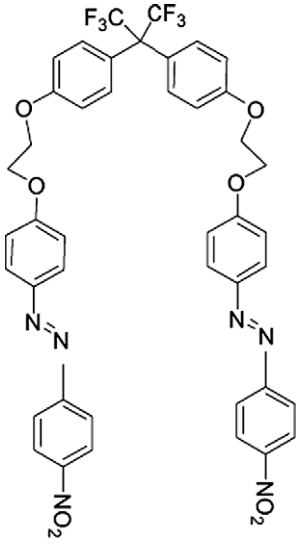


**Fig. 1.** The molecular structure of the fluorine-containing azoic dye.

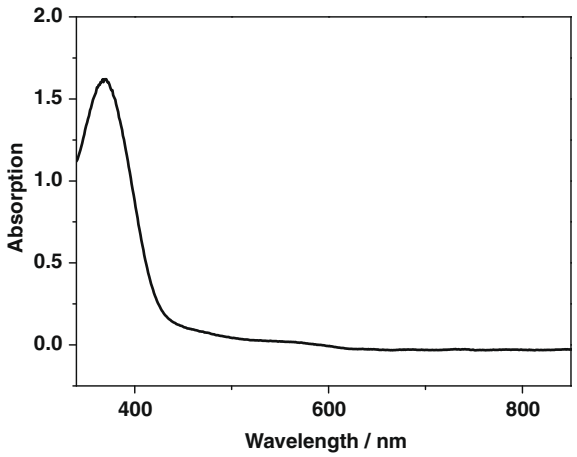


**Fig. 2.** The absorption of azoic dye in THF with the concentration of $4.4 \times 10^{-5}$ M.

In this work, picosecond and nanosecond lasers were adopted as excitation source in the *Z*-scan measurements [10]. For the picosecond *Z*-scan measurement, the radius of the beam waist ($w_0$) are 26.03 μm, and the corresponding Rayleigh length $z_0$ can be calculated to be 4 mm, much longer than the thickness of the quartz cell. This experiment was carried out using a mode-locked Nd:YAG laser (PY61C-10, Continuum) as the light source with a repetition rate of 10 Hz, pulse width of 38 ps and wavelength of 532 nm. The pulse *Z*-scan experimental system was calibrated by measuring the nonlinear refractive index of conventional $CS_2$ solution. The mean error of the experimental data, mostly arising from the fluctuation of the laser power, is below 10%. In the nanosecond *Z*-scan measurement, the excitation source is a Q-switched Nd:YLF laser (LABest Sunlight-200), with 6 ns pulse duration, 10 Hz a repetition rate and wavelength of 532 nm. The radius of the beam waist and the corresponding Rayleigh length are 29.10 μm and 5 mm, respectively. The dye solution with the concentration of $1.5 \times 10^{-3}$ M was placed in a quartz cell with 1 cm path length to perform *Z*-scan measurements.

## 3. Results and discussion

The nonlinear refractive index $n_2$ ($cm^2/W$) and nonlinear absorption $\beta$ (cm/W) are evaluated by carrying out the measurements of *Z*-scan. The difference between normalized peak and valley transmittance $\Delta T_{p-v}$ (denoting $T_P - T_V$) can be directly measured by *Z*-scan technique. The variation of this quantity as a function of $|\Delta\Phi_0|$ is given by

$$\Delta T_{p-v} 0.406(1-s)^{0.25}|\Delta\Phi_0|, \tag{1}$$

where $s = 1 - \exp(-2r_0^2/\omega_0^2)$ is the aperture linear transmittance with $r_0$ denoting the aperture radius and $\omega_0$ denoting beam radius at the aperture in the linear region. $\Delta\Phi_0$ can be obtained from Eq. (2):

$$\Delta\Phi_0 = kL_{eff}n_2I_0 = (2\pi/\lambda)L_{eff}n_2I_0, \tag{2}$$

where $I_0$ is the intensity of the laser beam at focus $z = 0$, $L_{eff} = ([1-\exp(-aL)]/a)$ is the effective thickness of the sample, $a$ is the linear absorption coefficient and $L$ is the thickness of the sample. The nonlinear refractive index $n_2$ ($cm^2/W$) can be obtained from Eqs. (1) and (2). $\Delta n_0 = n_2 I_0$ with $I_0$ being the on-axis irradiance at the focus represents the change in $n_2$ at the focus.

Fig. 3a shows the closed aperture (CA) *Z*-scan curve of the azoic dye solution. From the unsymmetric curve, there is obvious nonlinear absorption existing in the solution, and the closed transmittance is affected by the nonlinear refraction and absorption. As a result, the determination of $n_2$ is less straight-forward from the closed aperture *Z*-scan measurement. It is necessary to separate the effect of nonlinear absorption by performing the open aperture experiment. Fig. 3b shows the open aperture (OA) *Z*-scan curve of the solution while the closed aperture curve divided by open aperture (CA/OA) curve of the solution is shown in Fig. 3c. The theoretical expression of the CA/OA curve can be written as:

$$T(z,\Delta\Phi_0) = 1 - 4\Delta\Phi_0\chi/(\chi^2+9)(\chi^2+1), \tag{3}$$

where $\chi = z/z_0$, $z_0 = k\omega_0^2$ is the diffraction length of the beam, $k = 2\pi/\lambda$ is the vector and $\lambda$ is the laser wavelength, all in free space.

In the picosecond *Z*-scan measurement, the effective thickness of the sample was $L_{eff} = 0.85$ mm. The linear transmittance of the aperture was $s = 0.5$. The optical intensity at the focus point is $1.49 \times 10^9$ W/$cm^2$. From the theoretical fit result, the nonlinear absorption coefficient was obtained to be 5.58 cm/GW. The value of $\Delta T_{p-v}$ can be obtained to be 0.39 and the third-order nonlinear index is calculated to be $-7.64 \times 10^{-14}$ $cm^2$/W ($-2.64 \times 10^{-11}$ esu). The nonlinear refractive index of THF was reported in order of $10^{-13}$ esu [11], which was much smaller than that of azoic dye solution, so the contribution of solvent was negligible. $\Delta n_0$ of solution under picosecond 532 nm excitation was calculated as $1.14 \times 10^{-4}$.

The value of the nonlinear optical susceptibility $\chi^{(3)}$ (esu) could be evaluated from the nonlinear refractive index $n_2$. The relation is defined as follows [12]:

$$\chi^{(3)}\,(\text{esu}) = \frac{n_0^2 c}{12\pi^2}10^{-7}n_2\left(\frac{\text{cm}^2}{W}\right) = 25.313 n_0^2 n_2\left(\frac{\text{cm}^2}{W}\right) \tag{4}$$

where $n_0$ is the linear refractive index. For the solution sample, we use the refractive index value of the pure solvent. The values of $\chi^{(3)}$ (esu) for the solution is calculated to be $-4.06 \times 10^{-12}$ esu. The second hyperpolarizability of molecule in an isotropic media is related to the nonlinear optical susceptibility by the following [13]:

$$<\gamma> = \chi^{(3)}/(L^4N), \tag{5}$$

where $N$ is the number density of the molecules in $cm^{-3}$ and $L$ is the local field correction factor given by $[(n^2+2)/3]$. Under 532 nm excitation, the number density of the molecules in the solution in $cm^{-3}$ was $N = 9.03 \times 10^{17}$ $cm^{-3}$, so the corresponding second hyperpolarizability was $<\gamma> = 1.28 \times 10^{-30}$ esu at picosecond 532 excitation.