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Experimental and theoretical simulation studies on picosecond closed-aperture Z-scan profiles of N,N′−Bis(2,5,-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (DBPI)

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ABSTRACT

The optical nonlinear refractive and absorptive parameters of the dye N,N′−Bis(2,5,-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (DBPI) in 96% sulphuric acid have been obtained by a single closed-aperture (CA) Z-scan technique with picosecond pulses at the wavelength of 532 nm. Here a theoretical model was used to deduce both the refractive and absorptive optical nonlinearity present simultaneously in the CA Z-scan profile. Under the range of concentrations and energies studied here, we found that the effect of saturable absorption (SA) is dominating at higher concentrations (*i.e.* 1.0×10^{-3} M), whereas the reverse saturable absorption (RSA) effect was taken over at dilute concentrations (*i.e.* 1.0×10^{-4} M and 1.0×10^{-5} M). The dominance of absorptive nonlinearity over the refractive nonlinearity results in a low value of the refractive cross-section (σ_r). A relative increase in the value of σ_r is observed with decrease in the dye concentration. Mathematical modeling of CA Z-scan profiles of DBPI shows the existence of peak-valley or valley-peak structure depending upon the contribution of nonlinear absorption. The optical nonlinear parameters have also been estimated by theoretical simulation studies as a function of wavelength and compared with the experimental results. The dye DBPI has been found to be suitable as an important highly photostable molecule for photonic devices in the visible region (400–630 nm).

1. Introduction

Organic dyes having higher order optical nonlinearities are extremely valuable in many applications like optical switching, 3D data storage, optical communications, optical limiting, and saturable absorbers. Saturable absorbers are useful in ultrafast pulse generation as well as bi-stable photonic devices. The refractive and absorptive nonlinear parameters are needed to assess a material for its sensitivity for the ultrafast pulse of high peak energy. By using a single beam Z-scan technique [1,2], these parameters could be easily obtained. Z-scan technique has the advantage by having simple experimental arrangements with high sensitivity [2]. Till date, this technique has been widely used for the measurement of optical nonlinear properties of organic dyes, various materials and proteins in millisecond to femtosecond time scale [3–28]. In a closed-aperture (CA) Z-scan, a finite aperture is kept before the detector, whereas in an open-aperture (OA) Z-scan, the aperture is replaced by a double convex lens to focus all the transmitted light into the detector. CA profiles contain the information of both the refractive and absorptive nonlinearity [2,7], can be used to deduce both types of nonlinearities without performing an OA Z-scan [8]. Previously, this idea has already been tested by a simulation study by Liu et al. [9] and experimentally by Ganeev et al. [10].

In the present study, we have used a single CA Z-scan to estimate both the refractive and absorptive optical nonlinear parameters of the dye N,N′−Bis(2,5,-di-*tert*-butylphenyl)-3,4,9,10-perylenedi carboximide (DBPI) in 96% sulphuric acid. The effects of concentration and energy on the estimated refractive and absorptive optical nonlinear parameters are shown. The optical nonlinear parameters have also been deduced by theoretical simulations as a function of wavelength and compared with those obtained experimentally. Mathematical modeling of CA Z-scan profiles has been

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carried out to show the features of the CA profiles in case of DBPI. The existence of valley-peak or peak-valley structure in a typical CA Z-scan profile is found out depending upon the value of ξ, which is a ratio between the on-axis phase shift due to nonlinear absorption ($\Delta\Psi_0$) to nonlinear refraction ($\Delta\Phi_0$). In addition, we have also studied the ξ dependence of some other profile parameters. Nevertheless, the wavelength dependent profiles were also studied in case of DBPI. DBPI is potentially useful as a laser dye and also in electron and energy transfer studies, site-selection spectroscopy experiments with biological systems and in p-n hetero-junction solar cells [29,30]. Certain photophysical characteristics of DBPI such as fluorescence quenching, high photostability and effect of medium polarity exist in the literature [30–32]. Third order nonlinear susceptibility ($\chi^{(3)}$) values of DBPI have also been reported by using the laser-induced transient grating (LITG) technique [33].

2. Theory

The total refractive index (n (I)) and the total absorption coefficient (α (I)) of a Kerr like sample, in the presence of high irradiance (I), not only depend on linear indices (n_0 and α_0, respectively) but also become functions of nonlinear indices (η_2 (m^2/W) and β (m/W), respectively) as given below

$$n(I) = n_0 + \eta_2 I \quad (1)$$

$$\text{and } \alpha(I) = \alpha_0 + \beta I \quad (2)$$

When a TEM_{00} Gaussian laser beam traveling in the +z direction is focused with a convex lens, the electric field $\vec{E}(z,r,t)$ near the focal plane can be evaluated under the Fresnel's condition as [34].

$$\vec{E}(z,r,t) = \vec{E}_0(t)g(z,r) \quad (3)$$

where $\vec{E}_0(t)$ is the on-axis electric field at the focus and $g(z,r)$ is the normalized spatial profile.

The far field pattern of the beam at the detector plane can be obtained through a zeroth-order Hankel transformation of the complex electric field $\vec{E}_e(z,r,t)$ at the exit of the sample of thickness L and linear absorption coefficient α_0. Hence for propagation of a Gaussian beam profile in the low irradiance limit (for smaller changes in phase), the normalized transmittance T up to first order irradiance is given by Refs. [7,8].

$$T(z) = 1 + \frac{4x}{(x^2+9)(x^2+1)}\Delta\Phi_0 - \frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\Psi_0 \quad (4)$$

where $x = z/z_0$, in which z_0 is the Rayleigh range, $\Delta\Phi_0 = k\eta_2 I_0 L_{eff}$ (on-axis phase shift due to nonlinear refraction) and $\Delta\Psi_0 = \beta I_0 L_{eff}/2$ (on-axis phase shift due to nonlinear absorption) in that I_0 is the on-axis beam irradiance at focus, k is the wave number, $L_{eff} = [1\text{-exp}(-\alpha_0 L)]/\alpha_0$ is the effective length of the sample.

By expressing $\Delta\Psi_0$ in terms of $\Delta\Phi_0$ by introducing a coupling factor "ξ" Eq. (4) can be rewritten as [9].

$$T(z) = 1 + \frac{2(-\xi x^2 + 2x - 3\xi)}{(x^2+9)(x^2+1)}\Delta\Phi_0 \quad (5)$$

where ξ is the ratio of $\Delta\Psi_0$ to $\Delta\Phi_0$ and given as $\xi = \beta/2k\eta_2$.

Eq. (5) can be used as a model to analyze the CA profiles for combined effect of refractive and absorptive nonlinearity and it is the basis for the present study.

3. Experimental

From Aldrich chemical co. the dye DBPI was purchased and used as received from the company. Hitachi, UV-3400 spectrophotometer was used to record the absorption spectrum of the dye in a 1 mm thick quartz cell. For the CA Z-scan experiments, we have used the second harmonic of a Nd: YAG laser (Continuum Model YG601, 532 nm, 35 ps, 10 Hz) at different pulse energies as an excitation source. The experimental setup is shown in Fig. 1. At the far field, the transmittance through the sample was measured (D2/D1) as a function of its position by scanning the sample in the focal plane of a double convex lens of focal length 20 cm. Before the detector D2, a circular aperture of 2 mm diameter is used at the far field. To minimize the statistical fluctuations of the laser irradiance that may lead to systematic transmittance trace change, which could mask the effect of nonlinear refraction, a reference detector D1 was used. The beam was nearly Gaussian with TEM_{00} mode and 86% beam criterion was considered [35]. The radius of the beam waist (w_0) was ~18 μm with a corresponding Rayleigh range of ~2 mm. To fulfill the thin sample approximation condition, the sample thickness was less than the Rayleigh range [2]. The detectors used here are photodiodes (Becker and Hickl, PDI-400). The solvent sulphuric acid was of spectrograde quality and was used as received. The experimental setup was standardized with a standard reference nonlinear material (CS_2). Theoretical simulations and the data analysis were carried out by homemade software.

4. Results and discussion

From the absorption spectra of DBPI, the value of absorbance at the working wavelength (532 nm) in 96% sulphuric acid was obtained (Fig. 2). Inset of Fig. 2 shows the molecular structure of the dye DBPI. From Fig. 2 it was found that the peak wavelength of absorption is at 605 nm. At 532 nm the value of absorbance is ~$2.2 \times 10^4\ M^{-1}\ cm^{-1}$, which is lower by ~5.5 times at 605 nm *i.e.* the pump wavelength is away from the peak of the absorption. Therefore, the effect of varying degree of absorption (due to the change of concentration) on the refractive and absorptive parameters of the optical nonlinearity at a particular input pulse energy have been studied along with theoretical simulations. Profiles at other pulse energies were also taken for comparison.

In a CA Z-scan experiment, the translation of the sample in the focal plane leads to an intensity dependent refractive index due to the change in the input irradiance in the focal plane. Therefore, by keeping an aperture at the far field, we can estimate the sign as well as the magnitude of η_2 for the sample by measuring the transmission through the sample. A prefocal transmittance minimum (valley) followed by a postfocal transmittance maximum (peak) is a signature of positive refractive nonlinearity (*i.e.* positive η_2), whereas, a negative nonlinear refraction (*i.e.* negative η_2) gives rise to an opposite peak-valley configuration. In addition, due to high absorbance of the sample, the effect of saturable absorption (SA) might be observed if the working wavelength is near the peak of the absorption. In principle, the SA effect in the sample will suppress the valley along with the relative enhancement of the peak. Similarly, due to low absorbance of the sample, the effect of reverse saturable absorption (RSA) might be observed under working wavelengths far from the peak of the absorption. These effects will enhance the valley and relatively suppress the peak in the measured profile. The effect of RSA could be either due to two-photon absorption or excited state absorption (ESA).

4.1. Experimental CA Z-scan profiles of DBPI

We measured the CA Z-scan profiles of DBPI in 96% sulphuric