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Third-order nonlinear optical properties of acid green 25 dye by Z‒scan method

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ABSTRACT

Third-order nonlinear optical (NLO) properties of aqueous solutions of an anthraquinone dye (Acid green 25 dye, color index: 61570) have been studied by Z‒scan method with a 5 mW continuous wave (CW) diode laser operating at 635 nm. The nonlinear refractive index (n_2) and the absorption coefficient (β) have been evaluated respectively from the closed and open aperture Z‒scan data and the values of these parameters are found to increase with increase in concentration of the dye solution. The negative sign of the observed nonlinear refractive index (n_2) indicates that the aqueous solution of acid green 25 dye exhibits self-defocusing type optical nonlinearity. The mechanism of the observed nonlinear absorption (NLA) and nonlinear refraction (NLR) is attributed respectively to reverse saturable absorption (RSA) and thermal nonlinear effects. The magnitudes of n_2 and β are found to be of the order of 10^{-7} cm^2/W and 10^{-3} cm/W respectively. With these experimental results, the authors suggest that acid green 25 dye may have potential applications in nonlinear optics.

1. Introduction

The need for nonlinear optical (NLO) materials with large optical nonlinearities and fast response time are essential for applications in optical signal processing, optical data storage, optical phase conjugation, optical limiting and optical switches [1–7]. The large third-order nonlinear optical susceptibilities resulting from the nonlinear response of organic molecules has attracted much attention. Third-order nonlinear optical properties of variety of materials such as, organic dyes [8–12], metal complexes of thiourea [13], gold nanoparticles [14], single crystals of organic molecules [15,16], dibenzylideneacetone [17], TiO_2 nanocomposites [18], liquid crystals [19], alkynyl-ruthenium complexes [20], electroactive ligand and its metal complexes [21], branched oligothienylenevinylenes [22], and azobenzene polymers [23], etc., have been reported in the recent past. The NLO phenomena can be either due to electronic or non-electronic process. The former refers to those radiative interactions between active electrons and optical electric fields. Non-electronic processes are non-radiative interactions such as, temperature, density, phase transition and cis-trans isomerism, etc. [24]. Several experimental techniques currently available, to measure the third-order NLO parameters, are nonlinear interferometry, degenerate four-wave mixing, nearly degenerate three-wave mixing, ellipse rotation and beam-distortion measurements and Z‒scan method. The first three methods, interferometry and wave mixing, are potentially sensitive techniques, but require complex experimental arrangements. Beam-distortion measurements, on the other hand, require precise beam scans followed by detailed wave-propagation analysis [25,26].

The single beam Z‒scan technique, developed by Mansoor Sheik-Bahae et al. is a simple and effective tool for determining the NLO properties of materials [27,28]. This technique employs based on the principle of spatial distortion of the Gaussian laser beam, arising from an optically induced nonlinear self-phase modulation (SPM), when the laser beam propagates inside the sample. SPM changes the phase of an optical pulse resulting from the nonlinearity of the refractive index of material medium [29]. The single beam Z‒scan technique, measures both nonlinear refraction (NLR) and nonlinear absorption (NLA) of samples, which uses the transmittance change of materials. An extremely useful feature of the Z‒scan method that the sign of the nonlinear index of refraction is immediately obvious from the data and the magnitude can also be easily estimated using a simple analysis for a thin medium [27].

In this paper, we report the experimental measurements of nonlinear refractive index (n_2), absorption coefficient (β) and nonlinear susceptibility $\chi^{(3)}$ of aqueous solutions of acid green 25 dye by Z‒scan technique with a 5 mW diode laser operating at 635 nm.

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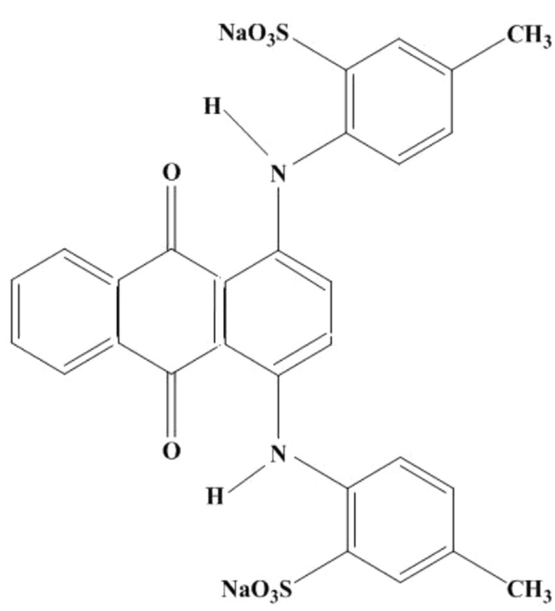
2. Materials

Organic dyes are the most attractive optical materials exhibiting large third-order nonlinear optical properties. NLO properties of organic dye molecules have been the subject of numerous investigations [30]. The dye chosen for the present study belongs to the family of anthraquinone. Anthraquinone is an important class of synthetic dyes, the resonance structure from the aromatic rings and the carbonyl groups provide the chromophores for these dyes. They possess a highly delocalized π-conjugated electron system not only in its nucleus, but also in the substituent's [31]. Anthraquinone dyes have gained considerable attention in nonlinear optics due to their excellent optical qualities and high thermal stabilities [31,32]. These dyes have vast applications in optical switches, light emitting diodes, photovoltaic devices, organic semiconductors, reprographics, thermal printing, biology, pharmaceutical industries, medical purposes like wound healing and photodynamic therapy, etc. [33]. In the present investigations, an anthraquinone dye (Acid green 25; color index: 61570) was chosen as the material for the study. Acid green 25 dye is of interest because it possess π-conjugated planar structural system with electron donating and accepting groups and hence suitable for the study of NLO properties. The structural flexibility supports for increasing the optical nonlinearity of the dyes. With this view, an attempt has been made to investigate the third-order NLO properties of acid green 25 dye. This dye was purchased from Merck India and has been used for the study without any further purification. Acid green 25 dye is in the form of dark green powder and highly soluble in water. The chemical structure and molecular formula of acid green 25 are shown in Fig. 1. The UV–vis absorption spectra of aqueous solution of acid green 25 dye with 0.01 mM concentration was recorded using UV–vis spectrophotometer (UV-1601 PC Shimadzu) which exhibits a absorption peak (λ_{max}) at 638 nm as shown in Fig. 2.

3. Experimental

The well known Z–scan method consists in translating a nonlinear sample through the focal plane of a tightly focused Gaussian laser beam and monitoring the transmittance changes in the far field position. For a purely refractive nonlinearity, the light field induces an intensity



Molecular Formula: $C_{28}H_{20}N_2Na_2O_8S_2$

Fig. 1. The chemical structure and molecular formula of acid green 25 dye.

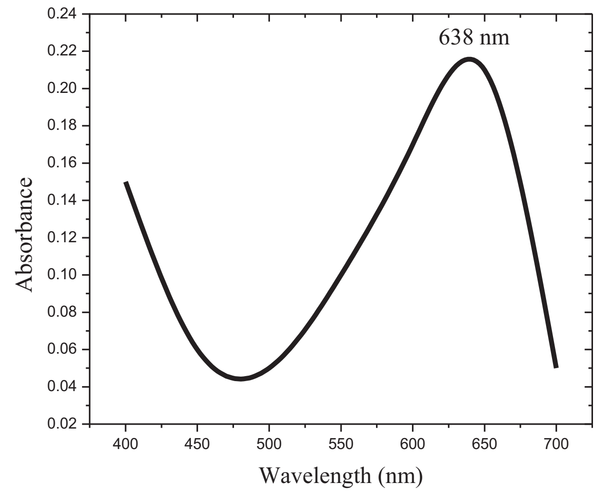


Fig. 2. UV–vis absorption spectra of aqueous solution of acid green 25 dye.

dependent nonlinear phase and, as consequence of the transverse Gaussian intensity profile, the sample presents a lens like behavior. The induced SPM has the tendency of defocusing or re-collimating the incident beam, depending on the Z–position with respect to the focal plane. By monitoring the transmittance changes through a finite circular aperture placed in the far field position (Closed aperture Z–scan), it is possible to measure the nonlinear refractive index (n_2). The nonlinear absorption coefficient (β) can be measured where the aperture is removed (Open aperture Z–scan) and hence the entire transmittance of the beam is collected through a suitable lens.

To work out how the Z–scan transmittance as a function of sample position (z) is related to the nonlinear refraction of the sample, it is assumed that the medium with negative nonlinear refractive index and thickness smaller than the diffraction length of the focused beam. This can be considered as a thin lens of variable focal length. Beginning far from the focus ($z < 0$), the beam irradiance is low and nonlinear refraction is negligible. In this condition, the measured transmittance remains constant (i.e., z–independent). As the sample approaches the beam focus, irradiance increases, which leads to self-lensing in the sample. A negative self-lens before the focal plane tends to collimate the beam on the aperture in the far field, increasing the transmittance measured at the iris position. After the focal plane, the same self-defocusing increases the beam divergence, which leads to widening of the beam at the iris and thus reducing the measured transmittance. Far from the focus ($z > 0$), again the nonlinear refraction is low resulting in a transmittance z-independent. A pre-focal transmittance maximum (peak), followed by a post-focal transmittance minimum (valley) is a Z–scan signature of a negative nonlinearity. An inverse Z–scan curve (i.e., A valley followed by a peak) characterizes a positive nonlinearity.

The schematic of the experimental set up used is shown in Fig. 3. The Z–scan experiments were performed with a 635 nm continuous wave diode laser with 5 mW of total power. The laser beam was focused by a positive lens, with 5 cm of focal length, which produces a beam waist ω_0 of 16.84 μm and the Rayleigh length, Z_R of 1.4 mm in the sample. A cuvette of 1 mm thickness containing the aqueous solution of acid green 25 dye is translated across the focal region along the axial direction i.e., is the direction of propagation of the laser beam. The transmittance of the beam through an aperture placed in the far field was measured using an optical power meter (Field Master™ GS, Coherent). The condition for the Rayleigh length $Z_R > L$, is satisfied in our case and therefore the thin sample approximation is reasonably valid.

4. Results and discussion

Third-order nonlinear refraction index (n_2) and the nonlinear