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Investigating some linear and nonlinear optical properties of the azo dye (1-amino-2-hydroxy naphthalin sulfonic acid-[3-(4-azo)]-4-amino diphenyl sulfone)

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ABSTRACT

The optical constants of an azo dye (1-amino-2-hydroxy naphthalin sulfonic acid-[3-(4-azo)]-4-amino diphenyl sulfone) films have been investigated. The transmittance and absorbance spectra were measured in the wavelength range of (300–900) nm. The oscillator energy (E_o), dispersion energy (E_d) and the static refractive index (n_0) have been determined by the Wemple–DiDomenico method. The nonlinear refractive index and the nonlinear absorption coefficient of the azo dye in the ethanol solution were measured by the Z-scan technique using diode laser at 657.2 nm wavelength. The low power optical limiting properties based on the nonlinear refraction of this material have also been studied.

1. Introduction

Recently, the azo dye has become an attractive material due to its optical properties. It has been applied in diverse applications such as the polarized photoinduced anisotropy, nonlinear optics effect and all-photoswitching [1–11]. The azo dye has good photo-thermal stability, dissolvability and easy preparation virtues, so that it can be used as a novel storage medium [12–15]. Most importantly, its structure can be modified to change the absorption property to act as a novel optical limiter for its nonlinear optics effect.

The study of optical absorption transition of azo dye, particularly, the absorption edge has proved to be very useful for the elucidation of the electronic structure of these materials. It is possible to determine the indirect and direct transition occurring in the band gap of the materials by the optical absorption spectra. The transmittance data can be analyzed to determine the optical constants such as refractive index, absorption index and the dielectric constant.

This paper reports the linear optical constants of the azo dye (1-amino-2-hydroxy naphthalin sulfonic acid-[3-(4-azo)]-4-amino diphenyl sulfone) film through an optical spectral analysis, also, the nonlinear optical properties for the azo dye in the ethanol solution were investigated by the use of the Z-scan technique.

2. Experimental

2.1. Sample preparation

An azo dye was prepared by a method similar to that described by Fox [16]. In the present method the dye was prepared as follows:

1. (0.006 mol, 1.4898 g) of the amine was dissolved in 2 ml of conc. HCl and then 10 ml of distilled water was added, then the mixture was stirred and kept in an ice bath.
2. 0.456 g of $NaNO_2$ was dissolved in about 5 ml of distilled water and kept in an ice bath.
3. Diazonium salt was prepared by adding sodium nitrite solution in step (2) dropwise to the cold solution of amine in the step (1) with stirring and keeping the temperature below 5 °C.
4. A coupler was prepared by dissolving (0.006 mol, 2.4017 g) of chromotropic acid disodium salt dehydrate in 25% sodium hydroxide solution and keeping it in ice bath.
5. The diazonium salt was added dropwise to the couplers with a constant stirring, keeping the temperature below 5 °C, the dyes were neutralized with dilute hydrochloric acid solution.
6. The resulting crudes were recrystallized from the methanol; the purity of the resulting azo dye was 94% yield of orange color, the m.p. was >300 °C.

The azo dye has been characterized by the elemental analysis and the IR, and UV spectra. The chemical structure and molecular formula of the chosen azo dye is shown in Fig. 1.

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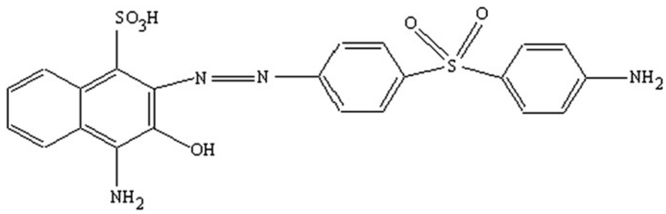

Fig. 1. Chemical structure of the azo dye.

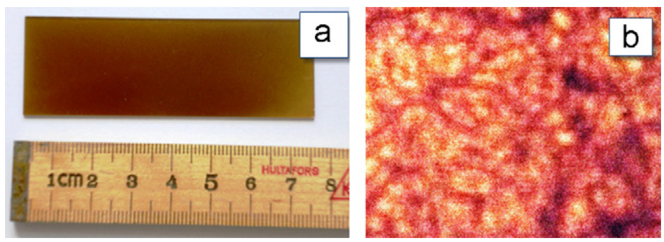

Fig. 2. Images of the azo dye film: (a) photographic image and (b) microscopic image.

The azo dye film used in the present study was prepared as follows: 0.5 g of the azo dye powder was dissolved in 10 ml of ethanol, the dye solution was stirred at room temperature for 45 min and then the solution was filtered through a 0.2 μm syringe filter. The film was prepared by the repeat-spray method on a clean glass slide substrate of 25 mm × 25 mm × 1 mm in a size that is heated up to 70 °C. A smooth film without dust and solvent residues were obtained. The thickness of the film was about 30 μm. Electronic microscopy observations showed that the surface of the azo dye film was dense and uniform without cracks or voids (see Fig. 2). Optical quality of this film was checked by passing 5 mW laser beam. No distortions in the output beam confirm the optical quality of the films.

2.2. UV–visible Spectroscopic studies

A UV–visible spectroscopy has been used to characterize the azo dye film in the spectral range (300–900 nm). The transmittance (T) and the absorbance (A) of the sample measurements using double beam UV–visible Spectrophotometer (U-1500-HITACH). These measurements were performed at room temperature. Fig. 3 shows the spectral distribution of absorbance sample in the spectral range (300–900 nm) and the peak of absorption is located at 305 nm.

2.3. Z-scan measurement

The Z-scan is a simple and popular experimental technique to measure the intensity dependent third-order nonlinear susceptibility of the materials. It allows the simultaneous measurement of both the nonlinear refractive index and the nonlinear absorption coefficient. By this method, the sample is translated in the z-direction along the axis of a focused Gaussian and the far field intensity is measured as a function of the sample position. By properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), the intensity can be measured depending on the absorption of the sample. When both of the methods (the open and the closed apertures) are used for the measurements, the ratio of the signals determines the nonlinear refraction of the sample.

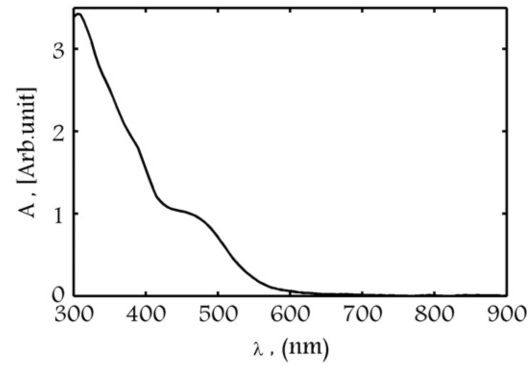

Fig. 3. Spectral absorption of the azo dye film as a function of wavelength.

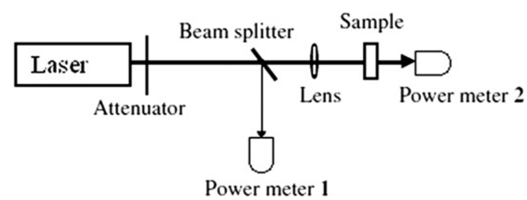

Fig. 4. Experimental setup for optical limiting measurements of azo dye.

A diode laser at 657.2 nm was used as a source of light in the Z-scan experiment. The Z-scan experiment was performed using a Gaussian beam. A lens of a focal length (+50 mm) was used to focus the laser beam onto 1 mm quartz cuvette, which contained the azo dye in the ethanol solution. The resulting beam waist radius at the focused spot was 19.37 μm; this corresponds to the Rayleigh length of 1.79 mm. Thus the sample thickness of 1 mm was less than the Rayleigh length and therefore, it can be treated as a thin medium. The scan was obtained with $S=0.39$, an aperture at an incident intensity $I_o=5.09$ kW/cm^2. The transmission of the beam through the aperture was measured by the use of a photodetector fed to the power meter.

2.4. Optical limiting property

The experimental setup for the demonstration of optical limiting of the laser beam by azo dye
(1-amino-2-hydroxy naphthalin sulfonic acid-[3-(4-azo)]-4-amino diphenyl sulfone) under CW laser illumination is shown in Fig. 4.

This is very similar to the standard Z-scan geometry and the same parameters were used as for the Z-scan experimental setup. Additionally a variable beam splitter (VBS) was used to vary the input power. A 1 mm quartz cuvette containing azo dye in the ethanol solution is kept at the position where the transmitted intensity shows a valley in closed aperture Z-scan curve. An aperture of variable diameter is used to control the cross-section of the beam coming out of the sample cuvette. This beam is then made to fall on the photodetector (PD). The input laser intensity is varied systematically and the corresponding output intensity values are measured by the photodetector.

3. Results and discussion

3.1. Linear optical properties

3.1.1. Refractive index dispersion

The transmission (T) and the absorbance (A) measurements of the azo dye film were used to determine the optical absorption