Measurement of the thermo-optic coefficient and Ring surface profile of sulfadiazine azo dye by using milli watts cw laser beams

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Abstract

We report on the observation of thermal lens as well as multiple diffraction ring patterns due to the irradiation of the azo dye “1.8-Dihydroxy-naphthalin-3, 6 disulfonic acid [2-(4-Azo)]-N-(5-methyl-3-isoxazolyl)-benzene sulfonamide” at same time by three continuous wave, green (λ=532 nm), red (λ=635 nm) and blue (λ=473 nm), laser beams. This effect we observed at power input less than 10 mW for the pump 532 nm green laser and as low as 50 μW of beams from other two wavelengths. The number of rings for all three beams is totally controlled by the level of pump input power. The optical limiting of the azo dye solution using the 532 nm green laser beam is also demonstrated. The change in the material refractive index, Δn, the nonlinear refractive index, n2, and the thermo-optical coefficient dn/dT are calculated based on thermal lens and diffraction ring techniques. The three quantities are found to be in the range of 10−4, 10−7 cm2/W and 10−5 K−1 respectively by both techniques.

Keywords: Thermal effects, diffraction rings, nonlinear refractive index, diffraction ring.

1. Introduction

The various important phenomena (such as the self-focusing and defocusing, self-phase modulation, figuration of spatial rings, and breaking up of beams) are happening and accompanying the laser beam propagated in media with non-linear property and intensity which are dependent on the refractive index and absorption coefficient. [1]. The laser matter-interaction modifies the spatial profile as a result of using Gaussian laser beams. The formation of spatial rings are understood to be induced by the modulation of spatial self-phases which are get up by the laser-induced refractive index [2-4]. Generally, the number of rings are depend on the axis non-linear phase shift experienced during the passage through the medium. Phase shift is depending on optical intensity,
the magnitude and the saturation value of the nonlinear refractive index and the sample thickness. Such effect has attracted enormous work during the last 10 years owing to the potential applications such as data storage, holography, limiting and all optical applications and devices [5-8]. Almost in all related literature, the diffraction ring patterns have been demonstrated experimentally in solids, liquid crystals, thin films and liquids using single laser beam approach [9-11].

In this research paper, we are reported the observation of multiple diffraction rings patterns to azo dye “1.8-Dihydroxy-naphthalin-3,6 disulfonic acid-[2-(4-Azo)]-N-(5-methyl-3-isoxazolyl) – benzene sulfonamide” dissolved in dimethyl sulfoxide solvent at low input power due to irradiation with three different cw laser beams in the visible region at the same time and thermal lens effect at 532 nm. We also demonstrate its z-scan action at 532 nm.

1. Experiment

1.2. The preparation of sulfadiazine azo dye

The sulfadiazine azo dye has been synthesis by same procedure was followed by Fox [12]. The sulfanilamide (C6H8N2O2S) (6 Mm, 1.50170 g) has been dissolved in hydrochloric acid (HCl) (2 ml), and distilled water (10 ml) was added. The Sodium nitrite (NaNO2) (0.4560 g) was dissolved in distilled water (5 ml); thereby, the mixture was saved in an ice medium. The diazonium salt has been synthesis by adding solution of the sodium nitrite (NaNO2) drop wise to the cold amine solution as drop wise with the temperature less than 5 °C under stirring. The diazonium salt was added to the mixture of dissolved chromotropic acid disodium salt dihydrate in distilled water with concentration of 6 mM and sodium hydroxide solution (8 gm) dissolved in distilled water (100 ml) under continuous stirring for five minutes inside an ice bath. The prepared dye should kept in a refrigerator for 24 hrs. The conversion of dye from the sodium salt nature to the hydrogenic was done during the neutralized process by adding the dilute hydrochloric acid (HCl). The final product of azo dye was converted to blood-red under recrystallization process of 93% and the melting point of less than 300 °C. The Infra-red (IR) and Ultra Violet spectrophotometers (UV) were used to investigate the prepared azo dye. Fig. 1. below is showing the chemical structure of prepared azo dye.

![Chemical structure of the prepared azo dye.](image)
2.2. IR spectrum of sulfadiazine azo dye

The infrared spectroscopy characterization of prepared azo dye illustrated in Fig. 2. It’s clear, at (3448.490) cm\(^{-1}\) the spectrum has a broad and strong band which refers to the hydrogen bond hydroxyl group. The strong bands hide the weak bands relatively which were expected to the NH bands (which usually appear in the same area). The stretching vibration of the O-H groups appeared at the region (3448.490) cm\(^{-1}\) whereas the one pertinence to the N-H group assumed to interfered with H-O bond at (3448.490) cm\(^{-1}\). Moreover, the band at (1502.440) cm\(^{-1}\) attributed to the C=C bond (the stretching vibration band of aromatic structure). The band at (1436.870) cm\(^{-1}\) assigned for azo group band (N=N). Finally, the vibration of O=H bonding was noticed at (835.120) cm\(^{-1}\). The elemental analysis of C\(_{20}\)H\(_{15}\)N\(_{5}\)O\(_{10}\)S\(_{3}\) calculated. C 38.17, H 2.60, N 8.35; found: C 38.69, H 2.20, N 8.81.

![Fig. 2. IR-spectrum of the prepared azo dye.](image)

2.3 UV–visible characterization of sulfadiazine azo dye

The absorbance (A) of the specimen measurement was carried out using U-1500-HITACH “double beam UV–visible Spectrophotometer” under room temperature. The absorbance spectral distribution of the specimen in the range of (350–650nm) and the absorption peak was noted at 510 nm as illustrated in Fig. 3.
3. The setup of experimental

The experimental arrangement, comprised an azo dye sample in a quartz cell 1mm thick. Three conventional solid state lasers operating on the lowest order transverse mode give Gaussian spatial distributions with wavelength 532 nm (green), 635 nm (red) and 473 nm (blue) respectively. A glass lens of 20 cm focal length, three screens and a digital camera “DSC-WX1/B-10MP-Sony”. The green beam passes perpendicularly through the lens only while the three beams intersect at the same position just inside the cell containing the sample. The angle between the green-blue and green-red beams was 30°. The diffraction ring patterns induced by each beam showed instantaneously post irradiation on each screen. The experimental set up is shown in Fig.4.

We used the solid state laser operating at 532 nm for the Z-scan experiments. The experiment work is including the optical transmittance as a function to the sample position at far field by using the double convex lens with focal length 5 cm. A circular aperture is used before the detector at far field for closed aperture Z-scan techniques. Whereas, a large diameter double convex lens is used in situation of the circular aperture for open aperture Z-scan techniques. The beam was nearly Gaussian. A 1 mm wide optical cell containing the sample was moved step by step along the propagation direction of the Gaussian beam.
4. Nonlinear refractive index of sulfadiazine azo dye

Suppose the optical transmission of radiation through an absorbing medium was done with a confirmed intensity. According to technique of the thermal lens (TL) [13], thermal gradient established after absorption and thermal relaxation of sample results in a change in intensity at the beam center owing to the incident beam divergence. The signal of thermal lens is referred as the relative change in power [14]

\[ \theta = \frac{I_{\text{in}} - I_{\text{out}}}{I_{\text{out}}} \]  

(1)

\[ \theta = \frac{\Delta I}{I_{\text{out}}} = \frac{\alpha L_{\text{eff}} P}{2K} \left( -\frac{dn}{dT} \right) \]  

(2)

where \( I_{\text{in}} \) and \( I_{\text{out}} \) are the transmitted optical power before and after the construction the thermal lens respectively, \( \alpha \) and \( L_{\text{eff}} \) refer to the linear absorption coefficient and effective thickness of the sample which is given by the equation \( L_{\text{eff}} = \frac{1}{\alpha} \left( 1 - e^{-\alpha L} \right) \) [15], \( L \) is the sample thickness, \( P \) is the laser input optical power, \( \lambda \) is the pump laser wavelength, \( K \) is the thermal conductivity and \( dn/dT \) is the thermo-optics coefficient.

For the thermal nonlinearity and steady state case, the on axis change in refractive index, \( \Delta n \), can be expressed as [16]:

\[ \Delta n = \frac{dn}{dT} \cdot \frac{1}{4} \frac{\alpha L_{\text{eff}}}{K} \]  

(3)

I is the intensity of light \( ( = 2P / \pi \omega^2 ) \) [17] and \( \omega \) defined as beam radius at the sample\( ( = 21.63 \text{ } \mu \text{m}) \).

The nonlinear refractive index, \( n_2 \), given by [18]:

\[ n_2 = \frac{\Delta n}{I} \]  

(4)
The total refractive, \( n \) and the background refractive index, \( n_b \) can be related through the following expression [19]:

\[
n = n_b + \Delta n
\]  

(5)

Based on the absorption coefficients and thermo-optical coefficient measured in experiment, the theoretical values of \( n_2 \) in Eq. (4) are calculated and they are shown in Fig.5.

![Fig.5. Variations of nonlinear refractive index and thermo-optic coefficient of azo dye at \( \lambda = 532nm \)](image)

The nonlinear refractive index of the azo dye solution under cw laser illumination is also calculated by the well-known closed Z-scan set up formulated by “Sheik-Bahae et al.” [20].

The difference between the normalized peak and valley optical transmission (\( \Delta T_{p,v} \)) is given by the on axis phase shift terms \( \Delta \phi_o \) at the focus [21].

\[
\Delta T_{p,v} = 0.406(1-S)^{0.25}|\Delta \phi_o|
\]  

(6)

Here \( S \) refers to the linear transmittance of the aperture-defined as \( S = 1 - \exp(-2r_a^2/\omega_a^2) \) [22] where \( r_a \) defined as the aperture radius and \( \omega_a \) refers to the beam spot radius on the aperture. The nonlinear refractive index is expressed by following [23].

\[
n_2 = \frac{\lambda \Delta T_{p,v}}{0.812\pi(1-S)^{0.25}L_{eff}I_o}
\]  

(7)

where \( I_o \) is the optical intensity of the laser beam at focus \( z = 0 \).

From the open aperture z-scan data, the nonlinear absorption coefficient \( \beta \) is estimated using [24]:

\[
\beta = \frac{2\sqrt{2} \Delta T}{L_o L_{eff}}
\]  

(8)
where $\Delta T$ is the one valley value at the open aperture $z$-scan curve.

Fig. 6 (a) shows the experimental closed aperture Z-scan data for azo dye with incident intensity 2.449 KW/cm$^2$ and 532 nm wavelength. Also, its showing that the normalized optical transmittance is plotted as a function of sample position, $z$. Analysis of nonlinearity in the azo dye was showed that the dye has the negative (self-defocusing) nonlinearity. Self-defocusing effect was due to local variation of refractive index with temperature. A pre-focal optical transmittance maximum (peak) and followed by a post-focal transmittance minimum (valley) in the Z-scan experiment is a signature of the negative nonlinearity. The optical nonlinearity in this dye may be due to laser heating induced nonlinear effect. An optical laser beam, whereas passing through an absorbed media, induces temperature degree and density gradients that are changing the refractive index profile. This intensity-induced localized change in the refractive index ($n$) results in lensing effect on the optical beam. The measured data in situation of the open aperture Z-scan was illustrated in Fig.6 (b). The large dip has been noted around the focal position due to the non-linear absorption. In measurement of the Z-scan technique, the intensity “which dependent on optical transmission of the measured sample without an aperture (open aperture scan)” gives information on purely absorptive nonlinearity while the apertured scan (closed aperture) is including the information about the nonlinear optical absorption and nonlinear refractive index ($n_2$). The ratio of the normalized closed aperture and open aperture scans generates a Z-scan due to the purely nonlinear refractive index, and results are shown in Fig.6 (c). The nonlinear optical absorption coefficient $\beta$ (cm/W) and nonlinear refractive index $n_2$ (cm$^2$/W) are calculated from the open and closed aperture optical normalized transmittance in Figs. 6 (b) and 6 (c) respectively. The obtained $\beta$ and $n_2$ for azo were $1.740 \times 10^{-4}$ cm/W and $0.4010 \times 10^{-7}$ cm$^2$/W.
5. The technique of diffraction ring patterns

The ring patterns for 635, 473 and 532 nm wavelengths are shown in Fig. 7. The ring structure exhibit asymmetry in the vertical direction because of distortion “as a result of thermal convection”. The number of rings for the three beams increases with increasing input optical power of green wavelength 532 nm light only, nonlinearly, as shown in Fig. 7.

![Diffraction ring patterns](image)

Fig. 7. Diffraction ring patterns spontaneously induced via irradiation with the three colored beams at the same time 635nm, 473nm and 532nm.

![Diffraction ring patterns](image)

Fig. 8. Diffraction ring patterns using green light (532nm) with input power (a) 25mW (b) 45 mW.

The number and shape of rings for the 532nm laser beams and shape are the same and vary by the same manner as the input green beam power varies. All patterns are invariant neither in shape nor in
number with time. We can estimate the induced refractive index change, $\Delta n$, and the effective nonlinear refractive index, $n_2$, as follows. Because the laser beam used in the experiment has a Gaussian distribution, the relative phase shift, $\Delta \Phi$, suffered by the beam while traversing a sample of thickness, $d$, can be written as [25]:

$$ (\Delta \Phi)_\text{max} = \frac{2\pi}{\lambda} \Delta n d \quad (9) $$

The total number of ring can be related to the relative phase shift, $\Delta \Phi$, as follow [26]:

$$ N = \frac{(\Delta \Phi)_\text{max}}{2\pi} \quad (10) $$

where $N$ is the maximum number of observed rings and the results are listed in table 1, which shows the variation of the number of rings with input green light power and nonlinear parameters.

| Power (mW) | Number of rings (N) | $\Delta n \times 10^{-4}$ | $n_2 \times 10^{-7} \text{ cm}^2 / \text{W}$ | $dn / dT \times 10^{-5} \text{ K}^{-1}$ |
|-----------|---------------------|--------------------------|---------------------------------|-----------------------------------|
| 25        | 3                   | 0.827                    | 0.243                           | 0.148                             |
| 45        | 7                   | 0.193                    | 0.315                           | 0.192                             |

According to the obtained results it seems that the concave lens effect initiated by the green pump beam act as the source for the diffraction ring patterns of the red and blue beams too although the input power of red and blue beams was very low in comparison with pump beam. The beam which used in the experiment work has Gaussian intensity distribution and given by [27].

$$ I = I_0 e^{-\frac{2r^2}{\omega^2}} \quad (11) $$

where $\omega$ is the beam radius. A part of the incident radiation absorbed by the sample leading to local heat of the medium. The temperature distribution in the medium was similar of the beam profile of the excitation beam and hence a refractive index ($n$) gradient is created in the medium. Due to this modification in refractive index, the medium act as a lens, it is called thermal lens. Thermal lens generally has a negative focal length since most materials expand upon heating and hence have negative temperature coefficient of refractive index. This negative lens causes beam divergence.
The observed rings patterns could be understood from the self-phase modulation effect [28,29]. A pump beam with a Gaussian intensity profile should induce a bell-shaped transverse profile of the phase shift, $\Delta \Phi$, so that maximum constructive and destructive interferences occurs when $\Delta \Phi_1 - \Delta \Phi_2 = m\pi$ for $m$ being even or odd integers respectively.

6. Ring surface profile

When a Gaussian TEM$_{00}$ laser beam shines the azo dye in the media-liquid media-, the medium was absorbing some part of the incident laser and then its temperature increase. The elevation in temperature induces changes in, $n$ and $dn/dT$, and then the self-diffraction is induced which thereby seems in the pattern shape of diffraction rings [30,31]. From the rings profiles (as shown in Fig. 9), we can understood the thermally induced effects as the ability of the Gaussian excitation beam to induce spatial variation of the $n$, leading to a phase shift that depends on the transverse distance from the beam axis. The transverse phase shift modulation implicated in the emergence of rings in the pattern of transmitted light.

Fig.9. Profile ring surface scan distribution of observed patterns corresponding to the 45mW input power
8. Conclusion

In this communication we observed thermal lens effects as well as multiple diffraction patterns occurring in azo dye “1,8-Dihydroxy-naphthalin-3,6 disulfonic acid-[2-(4-Azo)]-N-(5-methyl-3-isoxazolyl)–benzene sulfonamide” due to multiple irradiation with three different laser beams at the same time. The number of rings for all beams are governed by the power level of pump beam. The semicircular shape of each pattern is attributed to the upward convection of liquid with temperature. This is an indicator of the thermal effect. The change in the refractive index, $\Delta n$, the nonlinear refractive index, $n_2$, and the thermo-optic coefficient $dn/dT$ are calculated based on thermal lens and diffraction ring techniques, and are found to be of the same order for both techniques. We have measured the nonlinear refraction index coefficient $n_2$ and the nonlinear absorption coefficient $\beta$ for azo dye solvent in DMSO using the Z-scan technique. Based on nonlinear refraction the sample behaved as good optical nonlinear parameter indicating this sample find potential applications in optical device and signal processing applications.

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