

Investigation of non-linear optical properties in 1,2-Diamino-9,10-Anthraquinone (1, 2-DAAQ) by employing Z-scan technique for two concentrations at low input power laser.

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ABSTRACT;

The amino derivative of anthraquinone dye molecule is studied. Among all the available techniques to measure optical nonlinearity, Z-scan technique is most widely used. Z-scan measurements has been performed for 1,2-DAAQ in methanol at two different concentrations for 1 mM and for 2 mM for the incident peak intensities $I_0 = 10.69 \times 10^2 \text{ W/cm}^2$. The nonlinear absorption coefficient β was evaluated from OA-Z-scan curve. For 1,2-DAAQ induced thermal self-diffraction patterns were observed. The values of β for 1 mM and 2 mM were found to be 0.06293 cm/W and 0.07472 cm/W respectively. The induced self-diffraction patterns were observed for both concentrations and the number of rings increases with the increase in concentration. Studies revealed that the dye 1,2-DAAQ in methanol will be a significant candidate for the future applications in photonic devices.

Keywords; Anthraquinone, Diamino, laser, Non-Linear optics.

1. Introduction

Throughout the long history of optics, it was thought that all optical media were linear. The assumption of linearity of the optical medium has far-reaching consequences:

- Refractive index and the absorption coefficient, are independent of light intensity.
- The principle of superposition holds.
- The frequency of light cannot be altered by passing through the medium.
- Light does not interact with light; two beams of light in the same region of a linear optical medium can have no effect on each other. Thus, light cannot control light.

The invention of the laser in 1960 enabled us to examine the behavior of light in optical materials at higher intensities than previously possible. Many of the experiments carried out made it clear that optical media do exhibit nonlinear behavior, as exemplified by the following observations:

- The refractive index does change with the light intensity.
- The principle of superposition is violated.
- Light can alter its frequency by passing through a nonlinear optical material.
- Light can control light; photons do interact.

The field of nonlinear optics comprises many interesting phenomena. Linearity or nonlinearity is only a property of the medium through which light travels. Nonlinear behavior is not exhibited when light travels in free space. Light interacts with light via the medium. The presence of an optical field modifies the properties of the medium which modify another optical field or even the original field [1].

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, a laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken *et al.* 1961, a short time after the demonstration of the first working laser by Maiman in 1960.

Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field. In order to describe more precisely an optical nonlinearity, let us consider how the dipole moment per unit volume, or polarization $P(t)$, of a material system depends on the strength $E(t)$ of an applied optical field. In the case of conventional (i.e., linear) optics, the induced polarization depends linearly on the electric field strength in a manner that can often be described by the relationship

$$P(t) = \epsilon_0 \chi^{(1)} E(t), \quad (1)$$

Where the constant of proportionality $\chi^{(1)}$ is known as the linear susceptibility and ϵ_0 is the permittivity of free space. In nonlinear optics, the optical response can often be described by generalizing Eq. (1) by expressing the polarization $P(t)$ as a power series in the field strength $E(t)$ as

$$P(t) = \epsilon_0 [\chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \dots] \\ \equiv P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \dots \quad (2)$$

The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear optical susceptibilities, respectively. For simplicity, the fields $P(t)$ and $E(t)$ have been taken as scalar quantities in writing equations (1) and (2). It has been assumed that the polarization at time t depends only on the instantaneous value of the electric field strength [2].

1.2 Non-Linear Optical Phenomena

1.2.1 Non-Linear Absorption

Nonlinear absorption means a nonlinear change in absorption with increasing intensity. It is of two types viz; saturable absorption (SA) or reverse saturable absorption (RSA). Reverse Saturable is observed when excited state absorption (ESA) is greater than ground state absorption. This leads to decrease in transmittance with increase of input intensity. The most important application of RSA is in designing optical limiting devices.

1.2.2 Optical Limiting Effect

Another area of research is optical power limiting. Optical limiting is a nonlinear optical phenomenon in which the transmittance of light decreases with the increasing input intensity such that beyond a certain input intensity the output intensity approaches a constant value. The nonlinear absorption mechanism in organic compounds is due to reverse saturable absorption (RSA), mainly explains the cause of optical limiting effect though there are several mechanisms have been proposed for the explanation of the optical limiting behavior including nonlinear scattering and multiphoton absorption. But the RSA mechanism, by a five-level energy diagram, shown in Figure 1, gives a reasonable explanation for optical limiting in the conjugated organic systems [3]. Such a material can be used to limit the amount of optical power entering a system. This can be used to protect expensive or sensitive equipment such as sensors, can be used in protective goggles, or can be used to control noise in laser beams.

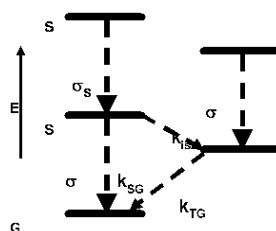


Figure 1 Five level energy diagram

1.2.3 Thermal Self Diffraction

When the Gaussian beam illuminates the dye in the liquid/solid media, the medium absorbs the light and its temperature rises. The raise in temperature results in change of refractive index and induces Self-diffraction [4]

1.3 Aim of the present work

With the extensive use of high-power laser in many different fields, interest has been directed towards the search for new nonlinear optical materials. Organic compounds with delocalized π -electrons showing large values of nonlinear optical parameters are gaining interest among researcher because of their potential applications in field of optoelectronics such as optical communication, optical computing, optical switching and image processing [5,6]. Organic molecules are good candidates for nonlinear devices as they are chemically flexible, and they show large and fast nonlinear optical response, as a result of which, their optical and electronic properties can be tuned. Several groups have investigated organic dye molecules for Reverse Saturable Absorption (RSA), optical limiting effect and thermal self-diffraction. Concentration plays an important role on nonlinear optical behavior of organic dye molecules [7].

The amino derivative of anthraquinone dye molecule is chosen for the present study. Amino derivatives have the potential applications in the area of pharmaceutical industry, industrial synthetic dyes and pigments [8-10]. Anthraquinones are the class of organic compounds derived from aromatic compounds exchanging an even number of groups with necessary arrangement of double bonds leading to conjugation with the aromatic struc-

ture. Organic compounds with electron donating group on one side of the molecule and electron accepting group on other side have been studied by experimental and theoretical scientists for NLO properties [12]. The amino substituted quinonoid structure, contain amino group being an electron donors and carbonyl groups as an acceptor. In the past years few anthraquinones have attracted for exhibiting the third order non-linear optical behavior [12].

The present work aimed to investigate non-linear optical properties in 1,2-Diamino-9,10-Anthraquinone (1, 2-DAAQ) by employing Z-scan technique for two concentrations at low input power laser.

2. EXPERIMENTAL DETAILS

Material and Experimental Details

The dye 1,2-DAAQ was purchased from sigma Aldrich and used without further purification. Figure 2 shows the molecular structure of 1,2-DAAQ.

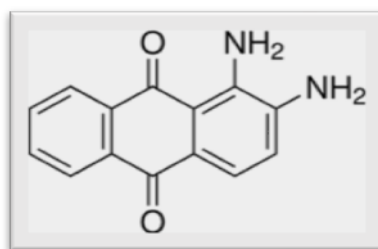


Figure 2 Molecular structure of 1,2-DAAQ

Experimental Technique: Z-scan method

Among all the available techniques to measure optical nonlinearity, Z-scan technique is most widely used. The technique was developed by Sheik- Bahae et.al [13], based on the principle of spatial distortion of laser beam arising from an optically induced nonlinear self-phase modulation while the laser beam propagates inside the sample. It is well known that nonlinear absorption can be determined by open aperture (OA) technique. The basic idea of experiment is self-focusing or self-defocusing of a Gaussian beam, focused by a convex lens onto a thin sample, sample is moved in the focal plane of the lens and at different position with respect to the focus ($z=0$) and the corresponding transmittance is measured. The sample exhibits variation in intensity at different position and thus intensity dependent change in transmittance can be calculated. At focus, the beam has maximum intensity and decreases symmetrically on the either side of focus. So, with this transmission information nonlinear absorption coefficient can be calculated.

Figure 3 shows the schematic diagram of the experimental set up of z scan technique used for open aperture. The experiment was performed at room temperature by using a single beam CW diode pumped solid state laser of wavelength 532 nm as an excitation source. The laser beam is focused with lens of focal length $f=20$ cm on the liquid sample placed in a 1mm quartz cuvette. The laser beam waist w_0 at the focus was measured to be $77.14\mu\text{m}$ and the Rayleigh length is $z_0 = 35.13$ mm. The beam waist was measured by employing knife edge method. The experiments were performed with peak intensity $I_0 = 10.69 \times 10^2 \text{W/cm}^2$. The sample was moved

along the axial direction i.e. the direction of the propagation of laser beam with the motorized translational stage with step size of 150 microns. For an open aperture the transmission of the beam was then focused with a lens of focal length $f=10$ cm placed in the far field and fed in to the photo detector connected to digital power meter (Melles-Griot-PEM001).

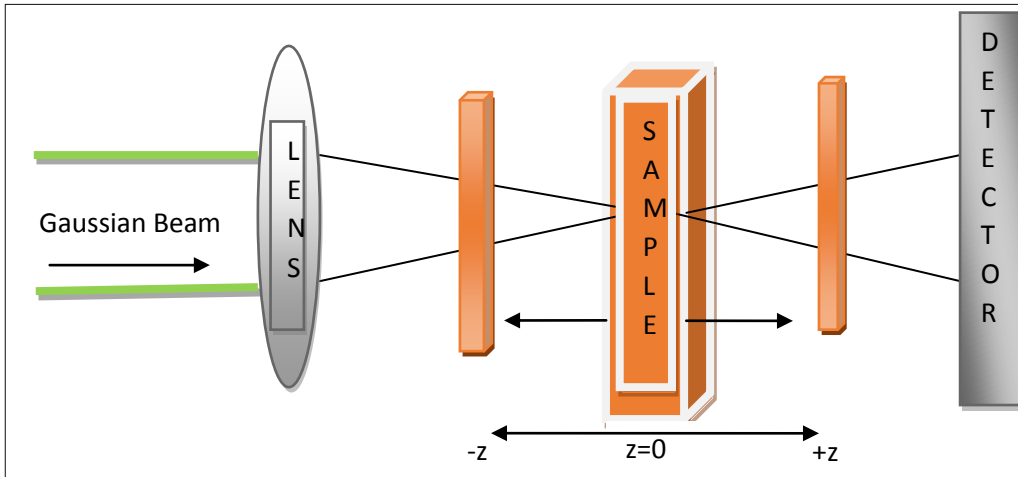
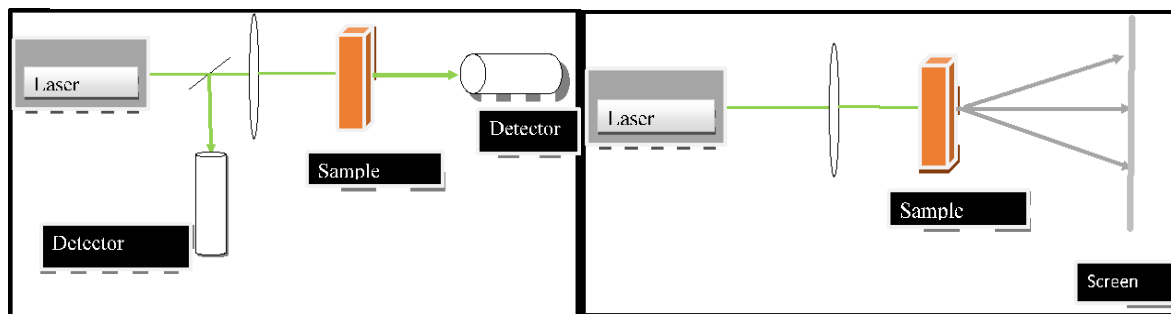


Figure 3 experimental set-ups for Z-scan measurements

Optical limiting measurements were performed with cw-diode-pumped solid-state laser working in the range of 2 mW-50 mW. The experimental set up is shown in Figure 4. The laser beam was guided onto the sample through a lens of focal length 20 cm. The dye solution was placed in 1mm path length quartz cuvette, placed at the focal plane of lens. The incident power of the laser was controlled by varying the intensity of the laser. Output power transmitted through the sample was detected by the Melles-Griot-PEM001 power meter. The experiments were performed at room temperature. Typical Optical limiting behavior was obtained by varying the input power of DPSS laser, ranging from 2 mW-35 mW.

(a) (b)

Figure 4.(a)Experimental set-up for measuring optical limiting effect in 1,2-DAAQ, (b) experimental set-ups for Self-diffraction



The experimental setup for induced self-diffraction is shown in Figure 4(b). A diode pumped solid state cw-laser of $\lambda = 532$ nm is used as the excitation source. The laser beam is focused by a convex lens of focal length $f = 20$ cm. The sample in liquid form is placed at the focus of lens and the diffracted patterns were observed at the screen placed 30 cm away from the focal point. The induced patterns were recorded by taking digital photographs. Multiple concentric rings were obtained with the intensity of laser beam equal to 18.72×10^2 W/cm².

3. RESULTS AND DISCUSSION

3.1 Nonlinear absorption in 1,2-DAAQ

Z-scan measurements has been performed for 1,2-DAAQ in methanol at two different concentrations (a) 1 mM (b) 2 mM for the incident peak intensities $I_0 = 10.69 \times 10^2$ W/cm². The nonlinear absorption coefficient β was evaluated from OA-Z-scan curve. Figure (6a) and (5b) show the nonlinear optical response of 1,2-DAAQ for concentrations 2mM and 1mM respectively, for incident peak intensity at focus $I_0 = 10.69 \times 10^2$ W/cm².

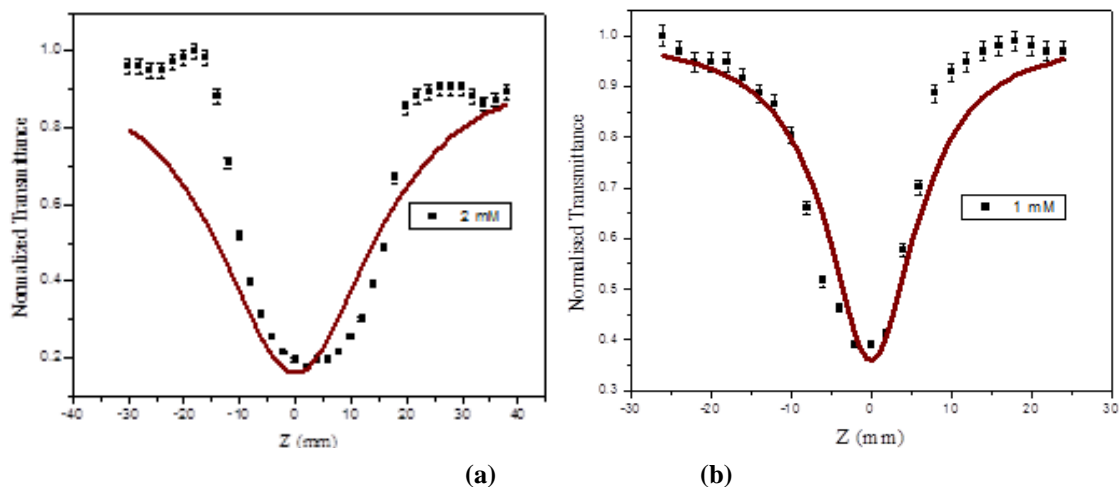


Figure 5, (a) Open-aperture Z-scan curve for 1,2-diamino-9,10-anthraquinone

The obtained Z-scan curves are symmetric with respect to the focus of the lens ($z=0$), showing the normalized transmittance valley. The decrease in normalized transmittance is the feature of RSA and corresponds to positive nonlinear absorption characteristic. Materials exhibiting RSA possess a higher excited state absorption cross-section σ_{ex} compared to that of ground state σ_g . RSA behavior is induced either by excited state absorption (ESA) or two photon absorption (TPA) process that requires the intensity of the order of $\approx 10^8$ W/cm² or above [14]. The nonlinear absorption observed at this low intensity of the order $\approx 10^2$ W/cm² is significant.

The normalized transmittance obtained from OA Z-scan is expressed by the summation form [14]:

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad (3)$$

Solving the summation and for $\alpha \ll 1$;

$$T(z) = 1 - \frac{\beta L I_0}{2^{3/2} \left(1 + \left(\frac{z^2}{z_0^2} \right) \right)} \quad (4)$$

Where $q_0(z) = (\beta I_0 L_{eff}) / ((1 + (z^2 / (z_0^2)))$; $L_{eff} = (1 - e^{-\alpha L}) / \alpha$ = effective length; I_0 = intensity at the focus, β = nonlinear absorption coefficient; α = linear absorption coefficient; z_0 = diffraction length = $\pi w_0^2 / \lambda$; w_0 = minimum beam radius at the focus; λ = excitation wavelength.

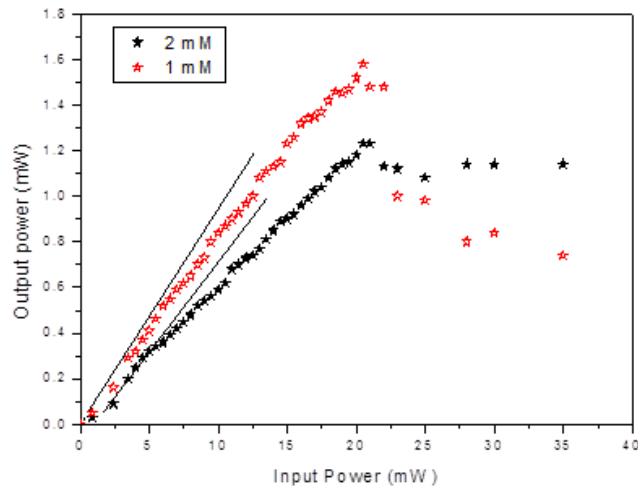
Experimental data points obtained by z-scan measurements were theoretically fitted with equation (3) and the nonlinear absorption coefficients β , for two concentrations were obtained from the best fit calculations. In Figure 5, scattered points are experimental data and solid line is theoretical best fit curve. The obtained values of β are shown in Table I. The value of nonlinear absorption coefficient is concentration dependent for 1,2-DAAQ, showing its nonlinear optical behavior with the change in input intensity. From curves 5(a) and 5(b) it can be seen clearly the drop down in normalized transmittance as the concentration increases. Transmittance reduces from 0.4 to 0.2 as the concentration increases from 1 mM to 2 mM. The increase in contribution is attributed to the increase in number of dye molecules as the concentration increases, more particles get thermally agitated resulting in enhanced effect. The results obtained were similar to reports in the literature published [14].

Table I. Measured value of nonlinear absorption coefficient, β (cm/W) and linear absorption coefficient, α (mm)⁻¹ for concentrations 1mM and 2 mM

Sample Concentration	β (cm/W)	α (mm) ⁻¹
1 mM	0.06293	0.33
2 mM	0.07472	0.35

3.2 Optical Limiting Effect in 1,2-DAAQ

The optical limiting measurements were performed for two concentrations of 1, 2-DAAQ in methanol. For investigating optical limiting behavior in 1,2-DAAQ, sample in 1mm path length cuvette is placed at the focus of 20 cm convex lens and the transmitted power is obtained at different input power by varying the input current of laser. As, it can be seen from Figure 6, output power, varied linearly and the transmittance obeyed Beer's law i.e. $I = I_0 \exp(-\alpha L)$, at low input power, where I , I_0 , α , L are the output intensity, incident intensity, the absorption coefficient and the sample length, respectively. For the explanation of optical limiting behavior several mechanisms have been proposed including RSA, nonlinear scattering and multiphoton absorption. But RSA mechanism is considered to be more explained. From the same Figure it can be seen as there is a drop down in output power as the concentration increases. It is well known concentration plays an important role in the optical limiting action. The optical limiting effect is enhanced and the transmittance is decreased with the increase in concentration. This is because a sample with increase in concentration has more molecules per unit volume participating in the interaction during nonlinear absorption. However, the concentration of the sample should be chosen carefully. When the concentration of the sample is too high, the result is very poor transmission while at low concentration the optical limiting effect is weak. We got poor transmission at concentration above 2 mM solutions of 1,2-DAAQ. From the data obtained we can deduce that optical threshold is inversely proportional to concentration as well as clamping level is observed. The observed results are confirmed from the previous findings that the concentration plays an important role in optical limiting effect [7].

Figure 6 Optical limiting effect in 1, 2-DAAQ in methanol with concentrations 1 mM, 2mM

3.3 Thermal self-diffraction in 1,2-DAAQ

For 1,2-DAAQ induced thermal self-diffraction patterns were observed. Absorbing nonlinear dye molecules, illuminated by Gaussian beam show diffracted ring patterns observed for some meter distance at the exit of the nonlinear media, these ring patterns are circular in shape. As the laser radiation was passed through the sample, the molecules absorb some of the incident energy and get excited to higher energy state. The subsequent deexcitation process can occur radiatively or nonradiatively. The thermal lensing in the sample is due to nonradiative process. The increase in temperature generates a volume expansion in the sample and a density change which results in change in refractive index and induces self-diffraction ring formation [15].

Number of diffraction rings N_{rings} can be used to determine the maximum variation in refractive index Δn_{max} from the following relation [16]:

$$\text{Maximum index change } \Delta n_{\text{max}} = \frac{\lambda_{\text{beam}}}{L_{\text{mat}}} N_{\text{rings}} \quad (5)$$

Where λ_{beam} is the wavelength and L_{mat} is sample thickness. Thus, a linear variation of Δn_{max} with the concentration can be expected.

Figure 7 shows the induced self-diffraction patterns for the concentrations 1 mM and 2mM. As shown in figure, number of rings increases with increasing concentration of the sample. The reason behind this is a sample with the higher concentration has more molecules per unit volume to contribute to the laser heating induced nonlinear effect, causing more interference leading to increased number of rings. From relation (5) maximum change in refractive index for 1mM is 1.596×10^{-3} and for 2 mM is 3.724×10^{-3} . Therefore, change in refractive index is proportional to concentration. The value of refractive index change obtained for 1, 2-DAAQ is comparable to that of other non-linear molecules reported in literature [8].

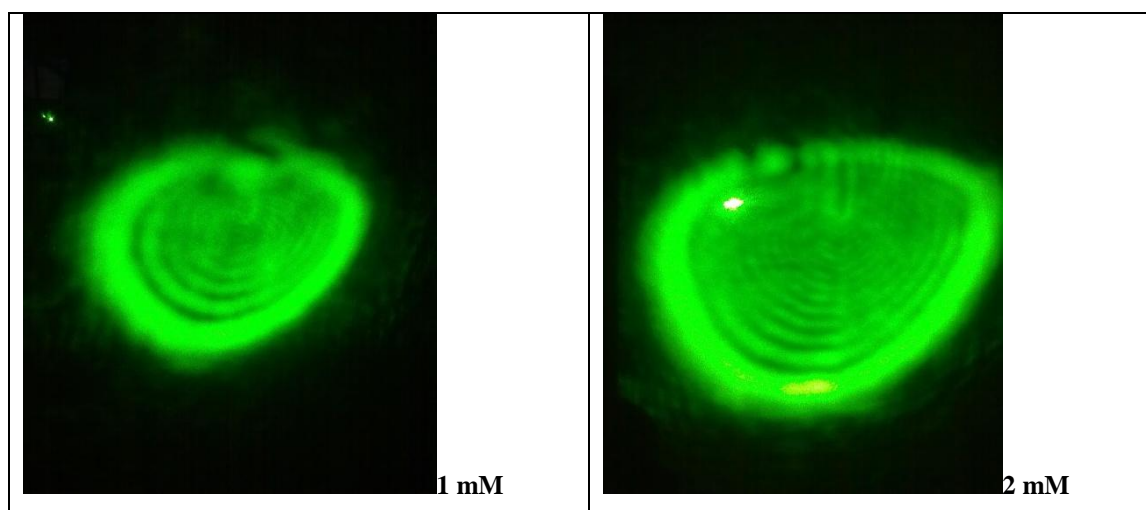


Figure 7 Induced self-diffraction pattern obtained for 1,2-DAAQ at intensity 10.69×10^2 w/cm²

4. CONCLUSIONS

The nonlinear optical properties of 1,2-Diamnino-9,10-Anthraquinone (1,2-DAAQ) have been investigated by employing Z-Scan technique using low power continuous wave diode pumped solid state laser at $\lambda = 532$ nm. The nonlinear absorption coefficient (β) has been calculated for two concentrations 1mM and 2 mM in methanol as a solvent and it was found that with the increase of concentration the value of β increases. The values of β for 1 mM and 2 mM were found to be 0.06293 cm/W and 0.07472 cm/W respectively. Reverse Saturable absorption (RSA) behavior has been observed for 1, 2-DAAQ indicating the application of 1,2-DAAQ as an optical limiter. Optical limiting measurements were also performed for the above concentrations. Moreover, the induced self-diffraction patterns were observed for both concentrations and the number of rings increases with the increase in concentration. Studies revealed that the dye 1,2-DAAQ in methanol will be a significant candidate for the future applications in photonic devices.

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