Nonlinear Optical Properties of Aurintricarboxylic Acid Compound (B) Using Z-Scan Technique

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Abstract. In the present work, the spectral properties (absorption and fluorescence) for liquid Aurintricarboxylic Acid compound (B) dissolve in dimethy sulfoxide (DMSO) were studied at different concentrations (1×10⁻⁴ and 1×10⁻⁵) M, nonlinear optical parameters was study by use technique of z-scan represented by the nonlinear refractive index and nonlinear absorption coefficients, several testing were done including, Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), results showed the effect of self-focusing in the material at higher intensities, which evaluated n², the effect of two-photon absorption was studied which evaluated β. In addition, the optical limiting behavior has been studied, the results confirmed the capability of the sample to be used as optical limiter device.

1. Introduction

Organic dyes have various applications in many scientific research due to their high fluorescence quantum yield and broad gain bandwidth [1]. The wide bandwidth makes them suitable for tunable ultrafast pulse generation [2]. Organic dyes are fluorescent molecules with large molecular weights, characterized by having conjugated double bonds. In a dye laser, these molecules are dissolved in an organic solvent they usually contain strong absorption spectral somewhere from the ultraviolet to the near infrared [3].

Nonlinear optics is the interaction of light with materials, in the discovery of lasers with high intensity when they fall on the middle transparent there is a change in the optical properties such as refractive index, absorption, polarization, and this is called nonlinear properties.

To study the non-linear optical properties using the simplest method is called Z-Scan technique a simple experiment and a sensitive method for measuring the sign and magnitude of the nonlinear refraction and non-linear absorption for solids and liquids, Z-Scan technique developed by Sheik-Bahae et. al. in 1989, the data of experimental were recorded gradually through moving simple alone axis (z) and measuring the transmission of the samples in(z) position [6]. The main optical properties involved in the light-matter interaction are absorption, which is defined by the nonlinear absorption coefficient, and nonlinear refractive index n² [4, 5], these two parameters are depending on the electric field intensity of laser light, the absorption of the material at high intensity is given by [6]:

\[ \alpha = \alpha_0 + \beta I \]  

(1)
Where

$\alpha_0$: is the linear absorption coefficient and

$\beta$: is the nonlinear absorption coefficient related to the intensity.

At high intensity, the refractive index is given by[7]:

$$n = n_0 + n_2I \quad (2)$$

Where

$n_0$: is the linear refractive index and $n_2$: is the nonlinear refractive index.

Nonlinear optical properties can be investigated by Z-scan technique at which it can be used to determine the nonlinear refractive index when closed-aperture geometry is used and nonlinear absorption coefficient with open aperture.

The nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula[6,8].

$$n_2 = \Delta \Phi_0/ I_0 L_{eff} k \quad (3)$$

Where

$\Delta \Phi_0$: is the nonlinear phase shift,

$$k = 2\pi/\lambda.$$

$\lambda$: is the beam wavelength, $I_0$: is the intensity at the focal spot,

$L_{eff}$: is the effective length of the sample.

$$L_{eff} = (1-e^{-\alpha_0 L})/\alpha_0 \quad (4)$$

Where

$L$: is the sample length and $\alpha_0$: is linear absorption coefficient[9,10].

2. Typical Experimental Procedure for the Preparation

2.1 Aurintricarboxylic Acid

17 milliliters (ML) of concentrated sulphuric acid were mixed with (10 g., 0.014 mol) of solid potassium nitrate. When solution is complete, add 20 g. (0.014 mol) of salicylic acid with stirring. The mixture should then be light red to brown in colour. It is surrounded by an ice-salt bath. Add (1.95 g, 0.065 mol) of formaldehyde is slowly with extremely vigorous stirring. About 100 g of crushed ice is then added, the stirring should be vigorous during the addition. The contents of the flask are stirred until the aurintricarboxylic acid has disintegrated into small pieces, as show in figure(1).

2.2 Aurintricarboxylic Acid Compound (B)

Aurintricarboxylic dyes (0.422 g, 0.001 mol) have been mixed with semecarbazide (0.453 g, 0.003 mol) and POCl₃. The mixture has been refluxed for 36 hours. The mixture poured into crushed ice with continuous stirring. The mixture have been neutralized with potassium bicarbonate, and left for 24 hours to settle down. The precipitate has been filtered and washed wit 100 ML water, as show in figure(1).
3. Solvent

Dimethyl sulfoxide (DMSO) is an organosulfur material with the formula (CH₃)₂SO. DMSO is a dipolar aprotic solvent, solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. It has a relatively high melting point[11]. In state of chemical structure, it has a trigonal pyramidal molecular geometry. Dimethyl Sulfoxide (DMSO) has a low level of toxicity[12].

4. Experimental Work for Solutions preparation:

Solutions of concentrations (10⁻⁴ and 10⁻⁵) M for organic dyes in (DMSO) solvent were prepared.

The powder was weighted by using an electronic balance type (BL 210 S), Germany, having a sensitivity of four digits. Different concentrations were prepared according to the following equation[13]:

\[ W = \frac{M_W \times V \times C}{1000} \]  

Where, \( W \): Weight of the dissolved in material (g), \( M_w \): Molecular weight of the material (g/mol), \( V \): Volume of the solvent (mL) and \( C \): The concentration (M).

The prepared solutions were diluted according to the following equation[13].

\[ C_1V_1 = C_2V_2 \]  

Where: \( C_1 \): Primary concentration, \( C_2 \): New concentration, \( V_1 \): The volume before dilution and \( V_2 \): The volume after dilution.

5. Results and Discussion
The preparation dye was measured by using FTIR-Affinity-1 SHIMADZU devise around (400-4000) cm\(^{-1}\) using a potassium bromide (KBr) for solid material. Aurintricarboxylic Acid dye was detected by FTIR. The IR spectrum showed a wide absorption band at (3340-2924) cm\(^{-1}\) around the vibrations that include stretching bond (OH), and absorption band around the vibrations the carbonyl acid group at 1676 cm\(^{-1}\) as shown in figure(2).

Figure (2): FTIR Spectrum of Aurintricarboxylic acid.

The H-NMR spectrum of compound Aurintricarboxylic acid has shown the appearance of a singlet peak at 5.35 ppm due to the phenyl hydroxyl group, also the appearance of doublet peak at 6.40 ppm related to the two protons of quinone group. The doublet peak at (7.1-7.5) ppm attributed to the six aromatic protons. Beside, the one proton of quinone group (the ortho to the carboxyl group) that appeared at 8.1 ppm. The carboxylic OH group appeared at 11 ppm figure (3).

Figure (3): H-NMR spectra of Aurintricarboxylic acid.

The infrared spectra of Aurintricarboxylic Acid compounds (B) was measured by using FTIR-Affinity-1 SHIMADZU devise around (400-4000) cm\(^{-1}\) using a KBr for solid material. Aurintricarboxylic compounds (B) was detected by FT-IR. The IR spectrum showed a wide absorption band at (3340-2924) cm\(^{-1}\), around the vibrations that include stretching bond (OH), and absorption band around the vibrations the carbonyl acid group at 1676 cm\(^{-1}\) as shown in figure(4).
The HNMR spectrum of compound B has shown the appearance of a singlet peak at 5.35 ppm due to the phenyl hydroxyl group, also the appearance of doublet peak at 6.40 ppm related to the two protons of quinone group. Also, the appearance of singlet peak at 6.66 ppm attributed to the six protons of the three amines groups. The doublet peak at (7.1-7.5) ppm attributed to the six aromatic protons. Beside, the one proton of quinone group (the ortho to the carboxyl group) that appeared at 8.1 ppm. The disappearance carboxylic OH group at 11 ppm figure (5).

The nonlinear optical properties were study Aurintricarboxylic acid compound (B) for solvent (DMSO) using continuous wave (CW) diode pump solid state blue laser at (457 nm) wavelength and (84 mW) power. There are two parts were used to measure the nonlinear properties of the material by Z-Scan technique. The first part is closed-aperture Z-Scan and the second part is the open-aperture Z-Scan.

The normalized transmittances of Z-Scan investigated as a function of distance as in figure(6), the nonlinear effect region is extended from (-3) mm to (3) mm. The peak followed by a valley transmittance curve obtained from the closed aperture Z-Scan data indicates that the sign of the refraction nonlinearity is positive ($n_2 > 0$), leading to self-focusing lensing in these samples. This behaviour agrees with the study in reference [13].
The nonlinear absorption coefficient of the Aurintricarboxylic compound (B) were measured by open-aperture Z-Scan technique. The performed open aperture Z-Scan exhibits an increasing in the transmission about the focus of the lens, The behaviour of transmittance starts linearly at different distances from the far field of the sample position (-Z), at the near field, the transmittance curve begins to decrease until it reaches the minimum value ($T_{\text{min}}$) at the focal point, where ($Z= 0 \text{ mm}$) as show in figure (7).

The transmittance begins to increase towards the linear behavior at the far field of the sample position (+Z). The change of intensity, in this case, is caused by two photon absorption.
The open-aperture Z-Scan defines variable transmittance values, which was used to determine absorption coefficient\[13\]. The behaviour of Z-Scan curves was in good agreement with the study in reference [14].

Table (1) show the properties of Aurintricarboxylic compound (B) the nonlinear refractive indices and absorbance coefficient have a high valve with the order of \((10^{-11}, 10^{-3})\) respectively.

Table 1. The linear and nonlinear optical parameters for Aurintricarboxylic compound (B) at \(\lambda=457\)nm.

| Material | Concentration (M) | Limiting Threshold(mw) | Limiting Amplitude(mw) |
|----------|-------------------|-------------------------|------------------------|
| Compound(B) | \(10^{-4}\) | 112 | 10 |
|           | \(10^{-5}\) | 115 | 14 |

6. Optical Limiting Behavior:

The optical limiting behaviour of Aurintricarboxylic compound (B) were performed by open - aperture Z-Scan with the same laser used in Z-Scan technique. Figures(8) give the optical limiting characteristics at room temperature for samples. The samples show very good optical limiting behaviour arising from nonlinear refraction as show in table (2). The output power rises initially with the increasing in input power, but after a certain threshold value, the sample starts defocusing the beam.

Table 2. The optical limiting response for Aurintricarboxylic compound (B).

| Material | Concentration (M) | Limiting Threshold(mw) | Limiting Amplitude(mw) |
|----------|-------------------|-------------------------|------------------------|
| Compound(B) | \(10^{-4}\) | 112 | 10 |
|           | \(10^{-5}\) | 115 | 14 |
Figure (8): The optical limiting response for Aurintricarboxylic compound (B).

7. Conclusions

The nonlinear refraction as a function of intensity was investigated for Aurintricarboxylic compound (B) solution by z-scan technique by using continues wave (cw) diode laser at 457 nm and incident intensity I0= 111*10^-4 W/cm². The Z-scan indicated that the dye exhibited large nonlinear optical properties for (10^-4 and 10^-5)M concentration of the dye solution, the n_2 and β value were found to be high value, (Higher n_2 and β2) for this dye have better nonlinear optical response and can, be chosen as ideal candidates with high prospects of applications in nonlinear optics the measured absorption curves indicate that the nonlinear absorption is saturation absorption process with self-focusing therefore the dyes solution have been observed as a very interesting as optical limiting material.

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References

[1] Fontalvo M, Garcia A, Valbuena S and Racedo F 2016 Measurement of nonlinear refractive index of organic materials by z-scan J. Phys. Conf. Ser. 687 012100.

[2] Hamdan A 2009 Baghdad J. Opti. & Lase. Techn. 41 415-418.

[3] Schäfer F and Drexhage K 1973 Dye Lasers (New York: Springer).

[4] Carstea E 2012 Fluorescence Spectroscopy As a Potential Tool For situmonitorin of Dissolved Organic Matter in Surface Water (Romania :Intech Open Access Publisher).

[5] Sheik-Bahae M, Said A, Wel T, Hagan J and Van E 1990 Sensitive Measurement of Optical Nonlinearities Using a Single Beam J. Qua. Elec. 26 760-769.

[6] Papadopoulos M, Sadlej A and Leszczynski J 2006 Nonlinear Optical Properties of Matter (Dordrecht: Springer).

[7] Sharifi S, Rakhshanizadeh F, and Peyghami S, 2019 Methods to Study of L-phenylalanine Concentration In Mediums: Nonlinear Optics J. Sen. Lette. 17 144-149.

[8] Naser B 2016 Preparation and Study Non-linear Optical Properties of Nematic Liquid Crystal Materials Doped by Nanoparticles Ph.D.Thesis (University of Babylon).

[9] Al-Ahmad A, Hassan Q, Badran H and Hussain K 2012 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) J. Opti. & Las. Tech. 44 1450-1455.

[10] N.Abdulkadim 2019 Non-Linear Optical Study of Liquid Crystal MS.c Theise, (University of Babylon).

[11] Sperling S and Larsen I 2009 Toxicity of Dimethylsulfoxide (DMSO) to Human Corneal Endothelium J. Act. Ophth. 57 891-898.

[12] Lyubartsev A and Laaksonen A 2001 Molecular Dynamics Simulations of Dimethyl Sulfoxide and Dimethyl Sulfoxide–Water Mixture J. Phy. Che. A. 105 1702-1710.

[13] Q.Hassan, 2007 Third-order nonlinearities and optical limiting properties of rose Bengal at 532 nm wavelength J. Basr. Rease. (Sciences) 33 76-81.

[14] AL-Adel k and Badran H 2012 The Study of the Nonlinear Optical Properties of cw Laser Illumination J. of Basr. Rease. (Sciences) 38 73-78.