Linear and Nonlinear optical properties of Rhodamine 6G

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Abstract

In this study, the linear and nonlinear optical properties of laser dye R6G in methanol solvent were investigated with various concentrations (1x10⁻⁴, 5x10⁻⁴, 1x10⁻⁵, 1x10⁻⁶ and 5x10⁻⁶ mole/liter) at thickness (1mm). To study the non-linear optical properties like refractive index and absorption coefficient (β) Z-Scan technique was used in two modes, the first is the close aperture which can be done by putting the aperture in front of the detector to find the non-linear refractive index. While the second mode is the open aperture which can be obtained by removing the aperture to find non-linear absorption coefficient, using two-wavelength 532 and 1064 nm. The results show that all R6G dye concentrations exhibited self–focusing in closed aperture Z-scan in 532 nm except the (1x10⁻⁴ mol/liter) in 1064 nm which shown a self-defocusing and the change of the effect of saturation absorption in an open aperture in both wavelength.

Key word: Rhodamine; nonlinear; Z-Scan;

Introduction

Recently, organic solid-state lasers (OSSLs) have conducted wide range investigations. Organic dye materials are usually utilized to produce these types of lasers. The bonus of using organic dyes is the simplicity of laser waveguide construction via several coating methods such as dr. blade, drop casting, dip coating and spin coating [1-3]. Rhodamine 6G (R6G) dye is classified as one of the Xanthene organic dyes, that in the visible wavelength range of 500 to 700 nm. It has been extensively used as an active laser media with high efficiency [4].
The interaction of light with materials results in linear and nonlinear optics. Investigations in the linear properties give several indications to improve the understanding of these materials (dyes) behavior. The nonlinear properties of the materials immerged with the discovery of lasers with high intensity. When laser fall on the transparent medium, there is a change in the optical properties such as refractive index, absorption and polarization [5]. To study the non-linear optical properties, the Z-Scan technique is used, which was developed by Sheik-Bahae et.al.in 1989 [6]. It is considered as a simple and sensitive method for measuring the sign and magnitude of the non-linear absorption and refraction for solids and liquids.

In this study the effect of varying the concentrations $1 \times 10^{-4}$, $5 \times 10^{-4}$, $1 \times 10^{-5}$, $1 \times 10^{-6}$ and $5 \times 10^{-6}$ on the linear and nonlinear optical properties of R6G dye has been investigated.

**Experimental**

**Z-scan Set up**

The data of experimental were recorded gradually by moving the sample along the (z) axis and measuring the transmission of the samples in each position (z) [7] ,as shown in figure (1) [8].

![Figure 1: Z-Scan set up](image)

There are two types of Z-Scan technique close aperture to calculate the non-linear refractive index as shown in figure (2), and open aperture to determine the absorption coefficient as in figure (3).

![Figure 2: Z-Scan technique close aperture](image)
Sample preparation

The rhodamines are based structurally on xanthenes [10] and the wavelength region (500-700 nm) and are generally efficient [11], R6G chloride have a high efficiency when used as an effective media in dye lasers. R6G chloride is a red powder that has a chemical formula C<sub>27</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>3</sub> highly soluble with molar mass (479.02 g/mole), the structure of R6G in figure (4).

The powder of R6G dye is accurately weighting by using analytical balances. Solutions of concentrations (1x10<sup>-4</sup>, 5x10<sup>-4</sup>, 1x10<sup>-5</sup>, 1x10<sup>-6</sup> and 5x10<sup>-6</sup> mole/liter) in methanol solvent were prepared using the following equation [13]:

\[ w = \frac{M_w \cdot V \cdot C}{1000} \]  

where \( W \) is the weight of the dissolved dye (gm), \( M_w \) is the molecular weight of the dye which is equal to (479.02gm/mol) for R6G dye, \( V \) is the volume of the solvent (ml) and \( C \) is the dye concentration (mol/l). The prepared solutions were diluted according to the following equation:-

\[ C_1 V_1 = C_2 V_2 \]  

where \( C_1 \) is the primary concentration, \( C_2 \) is the new concentration, \( V_1 \) is the volume before dilution and \( V_2 \) is the volume after dilution.
Linear Optical properties

The linear absorption coefficient \( (\alpha_0) \) of R6G was determined for both wave lengths using the following formula [14]:

\[
\alpha_0 = \frac{1}{t} \ln \frac{1}{T} \tag{3}
\]

where \( t=10\text{mm} \) is the thickness of sample and \( T \) is the transmittance. Furthermore, the extinction coefficient \( (K) \) is calculated using the absorption coefficient \( \alpha_0 \) value by applying the following equation [15] :

\[
K = \frac{\lambda \alpha_0}{4\pi} \tag{4}
\]

Nonlinear optical properties

To determine the \( T_p \) and \( T_v \), Z-Scan technique with close aperture mode should be used. The non-linear refractive index was measured by the formulas [14], [16] and [17]:

\[
n_2 = \frac{\Delta \phi_0}{I_0 L_{\text{eff}} k} \tag{5}
\]

where \( \Delta T_{p-v} = 0.406 \Delta \phi_0 \) .......

\[
\Delta T_{p-v} = T_p - T_v \tag{7}
\]

\[
k = \frac{2\pi}{\lambda} \tag{8}
\]

\[
I_0 = \frac{2p}{\pi W_0^2} \tag{9}
\]

\[
L_{\text{eff}} = \frac{(1 - \exp^{-\alpha_0 t})}{\alpha_0} \tag{10}
\]

where \( I_0 \) is intensity of th laser beam at the focus \( (Z = 0) \), \( P \) is the power of laser beam, \( W_0 \) is the beam radius at the focal point. As well as, \( L_{\text{eff}} \) is the effective length of the sample, \( t \): is the sample thickness , \( \alpha_0 \) : linear absorption coefficient.

From the open aperture Z-scan data, the nonlinear absorption coefficient is estimated [13] as the following equation:

\[
\beta = \frac{2\sqrt{2}}{L_{\text{eff}}} \Delta T \tag{11}
\]

where \( \Delta T \) is the one peak value at the open aperture Z-scan curve.

Results and discussions
Spectral properties of the liquid dye solution (R6G)

1. Spectra of absorption and fluorescence

The Spectra of absorption and fluorescence for solution dye R6G in methanol for different concentration are shown in figures 5 and 6 respectively. The absorption spectra in figure 5 show red shifting and correspondingly the intensity reduced by reducing the concentration. Furthermore, a shoulder between 475 nm to 500 nm was noted. Generally, there is a reduction in the width of absorption peaks by reducing the concentration except for concentration 1x10^-4 M. This decrement ascribed to the amount of molecules of R6G which considered as absorbance sites and then effected the total absorbance spectra. As example, the R6G molecules in concentration of 5 x 10^-4 M is 100 times more than the molecules with concentration of 5 x10^-6 M, therefore the absorbance of R6G is reduced by reducing the concentration (increasing dilution) of the dye. Electronic excitations are escorted by vibrational transitions. These transitions happened from the ground state to many higher levels of excited electronic states. Therefore at UV portion of spectra photons with high energy excite many molecules and hence increase the vibrations of these molecules. Consequently, the spectra exhibited many peaks that cannot be resolved by the spectrophotometer, those appeared as broad spectra. Meanwhile at lowest energy level photons with higher wavelength excited less molecules which narrowed the spectra.

Meanwhile, the fluorescence spectra in figure 6 show peaks in the range from 530 nm to 650 nm which is the typical fluorescence of R6G dye in water. As well as, an enhancement in the intensity of the fluorescence spectra by reducing the concentration was also observed, as example the 5x10^-4 M which is the highest concentration exhibited the lowest fluorescence peak. The enhancement in the fluorescence displays a non-monotonic performance with concentration of R6G dye. As well, the fluorescence spectra are drastically blue shifted due to the aggregates with reducing the dye concentration. The shifting could be attributed to the reduction in surface polarity due to the interaction between nearest molecules.

The absorbance spectra is a characteristic property that indicate the categories of dimers formation. Particularly the construction of H-dimers or J-dimers can be distinguished. The blue shift peak could be assigned to the H-dimers formation meanwhile the red shift represents the J-dimer. Thus, the R6G aqueous solutions show aggregation that were ascribed to the creation of non-fluorescent H-dimers [18]. It could be noticed that, revising the fluorescence spectra offer informative details. Principally, by studying the shift difference value of the fluorescence emission spectral many parameters could be determined, such as the pH of the environment and the concentration of dye. Therefore, by studying the fluorescence shifting of the dyes could be used in a very wide range of application.

The absorbance of R6G with various concentrations at wavelength range from 450 nm to 550 nm are listed in Table 1. It show that by reducing the R6G concentration, the absorption goes towards longer wavelengths red shift, meanwhile the fluorescence pushed towards smaller wavelengths blue shift.
Figure (5) spectra of Absorption for different concentration

Figure (6) spectra of Fluorescence for different concentration
Table 1. Absorption pushed wavelengths and the top fluorescence pushed

| C mole/liter | λ_{abs.} (nm) | λ_{fluo.} (nm) |
|--------------|---------------|----------------|
| 5×10^{-4}   | 492           | 566            |
| 1×10^{-4}   | 523           | 558            |
| 1×10^{-5}   | 532           | 562            |
| 5×10^{-6}   | 523           | 557            |
| 1×10^{-6}   | 526           | 555            |

Linear Optical properties

The linear absorption coefficient of R6G was determined for both wavelengths using the following formula (3) and (4) [14].

Table 2. Linear optical properties of R6G dye solution

| C (MI) | T% | α₀ cm⁻¹ | K* 10⁻⁷ | n |
|--------|----|---------|---------|---|
|        | 532nm | 1064nm | 532nm | 1064nm | 532nm | 1064nm |
| 5*10⁻⁴ | 0.148 | 95.964 | 6.516 | 0.041 | 275.99 | 3.473 | 1.3229 |
| 1*10⁻⁴ | 1.655 | 97.777 | 4.1 | 0.022 | 173.66 | 1.864 | 1.3281 |
| 1*10⁻⁵ | 1.564 | 95.941 | 4.158 | 0.041 | 176.12 | 3.473 | 1.3298 |
| 5*10⁻⁶ | 1.532 | 95.172 | 4.179 | 0.049 | 177 | 4.151 | 1.3277 |
| 1*10⁻⁶ | 1.37 | 95.952 | 4.29 | 0.041 | 181.71 | 3.473 | 1.3284 |

Nonlinear optical properties

Z-Scan technique close aperture to determine the \( T_p \) and \( T_v \).

The nonlinear refractive index was measured by the formula.
Figure 7  closed aperture Z-Scan for R6G solution in wavelength 532 nm at different concentration.
Case 1:
In $\lambda=532$ nm and $I_0 = 45.415 \times 10^3$

Table 3. The results of nonlinear optical properties for R6G by the Z-scan

| C (mI) | $\Delta T_{p-v}$ | $\Delta \varphi$ (Rad) | $n_2 \left( \frac{cm^2}{mw} \right) \times 10^{-10}$ | $T_{max}$ | $\beta \left( \frac{cm}{mw} \right) \times 10^{-3}$ |
|--------|-----------------|------------------------|-----------------------------------------------|-----------|-----------------------------------------------|
| $5\times10^{-4}$ | 0.26            | 0.64                   | 7.709                                         | 4.52      | 1.85                                          |
| $1\times10^{-4}$ | 1.17            | 2.882                  | 22.132                                        | 4.7       | 1.22                                          |
| $1\times10^{-5}$ | 0.97            | 2.389                  | 18.578                                        | 4.58      | 1.209                                         |
| $5\times10^{-6}$ | 3.6             | 8.867                  | 69.247                                        | 12.21     | 3.24                                          |
| $1\times10^{-6}$ | 1.82            | 4.483                  | 35.92                                         | 18.77     | 5.1                                           |
From this table it can be shown that higher nonlinear refractive index ($n_2$) has been obtained when the concentration is ($5 \times 10^{-6}$ Ml), we also note that higher nonlinear absorption coefficient ($\beta$) obtained when the concentration is ($1 \times 10^{-6}$ Ml). with decreasing the concentration

Figure 9 closed aperture Z-Scan for R6G solution in wavelength 1064 nm at different concentration.
Figure 10: open aperture Z-Scan for R6G solution in wavelength 1064 nm at different concentration.

Case 2:
In \(\lambda=1064\) nm and \(I_0 = 72.737 \times 10^3\)

**Table 4.** The results of nonlinear optical properties for R6G by the Z-scan
| CMI | \(\Delta T_{P-V}\) | \(\Delta \phi\) (Rad) | \(n_2\left(\text{cm}^2/\text{mw}\right) \times 10^{-10}\) | \(T_{\text{max}}\) | \(\beta\left(\text{cm}/\text{mw}\right) \times 10^{-3}\) |
|-----|-----------------|----------------|-----------------|----------------|----------------|
| \(5 \times 10^{-4}\) | 5.14 | 12.66 | 30.13 | 24.32 | 0.966 |
| \(1 \times 10^{-4}\) | 2.02 | 4.975 | 11.73 | 21.83 | 0.858 |
| \(1 \times 10^{-5}\) | 8.87 | 21.847 | 51.99 | 24.36 | 0.967 |
| \(5 \times 10^{-6}\) | 2.4 | 5.911 | 14.11 | 23.54 | 0.938 |
| \(1 \times 10^{-6}\) | 6.3 | 15.517 | 36.93 | 23.72 | 0.942 |

From this table it can be shown that higher nonlinear refractive index \((n_2)\) has been obtained when the concentration was \((1 \times 10^{-5}\text{Ml})\), we also note that the higher nonlinear absorption coefficient \((\beta)\) obtained when the concentration is \((1 \times 10^{-5}\text{M l})\).

**Conclusion**

The optical properties of the models used in this research were studied by applying theoretical calculations on experimental results (spectra) that obtained in this research. It has been realized that the absorption spectra of the samples (liquid state), are reduced and correspondingly red shifted with some discrepancy between the absorbance spectra of R6G with reducing concentration of the dye. But, the fluorescence emission spectra of R6G dye are blue shifted with the reduction of concentration. Additionally, the nonlinear absorption coefficient of exhibits behavior of saturated absorption of certain concentrations, nonlinear refractive index\((n^2)\) increase with decreasing the concentration. It could also noted that the absorption coefficient of nonlinear\((\beta)\) decrease with decreasing the concentration.

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