Study optical properties of R6G dye doped in polymer PVA

K J Tahir1*, H H. Obeed1 and N M Shiltagh1, 2
1Department of physics, college of science, University of Kerbala, Karbala, Iraq
2Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, UK
*Corresponding author: khawla.taher@uokerbala.edu.iq

Abstract. The linear and nonlinear optical properties for laser dye R6G is investigated in solvent methanol at different concentrations (5x10^{-4}, 1x10^{-4}, 1x10^{-5}, 5x10^{-6} and 1x10^{-6} Ml) at thickness (2µm). The nonlinear optical properties as refractive index \( n^2 \) and the nonlinear absorption coefficient \( \beta \) were studied by using Z-Scan technique in two parts; one part by putting aperture in front of the detector (close aperture) to find the nonlinear refractive index, however in second part is by removing the aperture (open aperture) to find nonlinear absorption coefficient, these by using two wavelengths 532, 1064 nm. The results show the effects of self–focusing in 532 nm and other concentrations in 1064 nm and the change of the saturation absorption effect in open aperture in both wavelengths. The higher nonlinear refractive index is found \( (n^2=29.93cm^2/mw) \) in the concentration \( (1*10^{-4} Ml) \), while the higher nonlinear absorption coefficient is \( (\beta=8.88cm/mw) \) in the concentration \( (5*10^{-6} Ml) \) at the wavelength 532 nm.

Key words: R6G, Z-Scan technique, optical properties.

1. Introduction
The most efficient type of laser dyes is the rhodamine 6G (R6G) which has characterized by high efficiency fluorescence band around 560 nm. Therefore, R6G dye is utilized potentially in applications as emitted light diode and the signal amplification in optics [1,2]. Rhodamine days are fluorophores that have a place with the group of xanthenes alongside fluorescein and eosin days. The general structures of xanthenic chromophore and rhodamine days are shown in Fig. 1 The phenomenal photostability properties are other features of R6G, which found to use as laser days [3,4,5].

Figure 1. The structure of R6G [6].
R6G dye has a wide area in applications such as optical switching, solar cell with concentrators, optical communications, optical limiting power, optoelectronics, laser dye, gain medium, as an active medium for dye lasers and photonics devices [7,8].

Z-scan technique was used to study the nonlinear optics properties (NLO)[9,10]. This technique is the simplest method and a sensitive for measuring the sign and magnitude of the non-linear refraction and non-linear absorption for solids and liquids. It was developed by Sheik-Bahae et.al. 1989 [11,12,13].

Recently, a considerable number of studies are devoted to investigate the optical properties of R6G. The most important of these studies is (Deng et.al. 2007 [1] who investigated the fluorescence and nonlinear optical properties of R6G/PMMA films by using z-scan technique. Modification strategies of the R6G applications as fluorescent probes that linked to another (bio) molecule were discussed widely in review by (Mariana et.al. 2009 [6]. In this basic survey the procedures for adjustment of Rhodamine dye and a discussion on the assortment of uses of these new subordinates as fluorescent tests are given.

Hence, in order to obtain a thin film R6G/PVA with good properties, it is necessary to test a variety amount of concentrations of R6G laser dye (500 – 700) nm. Aiming to do that, optical properties (linear and nonlinear) consisting of absorption and fluorescence spectra were investigated. Where, normally the absorption of Rhodamine 6G increases by depending the second harmonic of Nd: YAG laser (532 nm). Thus, in this work the control of concentration of R6G dye is the key factor in the linear and nonlinear optical properties of R6G/PVA, which were measured by z-scan technique laser Nd-YAG.

2. Experimental

2.1 Sample preparation

The powder of R6G dye is accurately weighting by using analytical balances. Solutions of concentrations (1x10^{-4}, 5x10^{-4}, 1x10^{-5}, 1x10^{-6} and 5x10^{-6} mole/liter) in methanol solvent were prepared by eq. (1) [14]:

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

(1)

Where;
W: weight of the dissolved dye (gm).
Mw: molecular weight of the dye (479.02 gm/mol).
V: the volume of the solvent (ml).
C: the dye concentration (mol/l).

The prepared solutions were diluted according to the eq. (2) [14]:

\[ C_1 \times V_1 = C_2 \times V_2 \]  

(2)

Where;
C₁: primary concentration.
C₂: new concentration.
V₁: the volume before dilution.
V₂: the volume after dilution.

2.2 Fabrication of the films (R6G dye doped polymer PVA)
Dye R6G doped PVA polymer films were fabricated by using the casting method. The prepared solution of the polymer was produced by dissolving amount of polymer (0.7 gm from PVA in 10 ml of water solvent) at temperature 35. The mixture of ratio (2/3) of the polymer solution with water is added to (1/3) of the R6G dye in methanol solution. Then, the final mixture of all these material is placing in Baker with a constant stirring of the mixture to obtain a homogeneous mixture. Finally, in order to solidify the mixture, it pours upon a glass slide (2.5x7.5 cm) at room temperature and leave the slide for 24 hours to obtain film under different concentrations at a constant thickness (t=2μm).

3. Results and discussions
The nonlinear optical properties were studied for films R6G & PVA as following:

3.1 Spectral properties of the films R6G & PVA

3.1.1 Spectra of absorption and fluorescence
The Spectra of absorption and fluorescence for films R6G & PVA were investigated in methanol for different concentrations (1x10^{-4}, 5x10^{-4}, 1x10^{-5}, 1x10^{-6} and 5x10^{-6} mole/liter) at thickness (2µm). Figures (2) and (3) show the spectra of absorption and Fluorescence for R6G & PVA in different concentrations.

![Figure 2](image-url)  
**Figure 2.** Spectra of Absorption for different concentration.

From Fig. (2) it can be seen that the absorption increases with increase the concentrations, where the spectra increase slightly at low concentrations. Then it increases significantly at 5x10^{-4} Ml.
In terms of spectra of fluorescence as shown in Fig. (3), they increase and present red shift towards high wavelength by increasing the concentrations.

3.1.1.1 Linear optical properties

The linear absorption coefficient of R6G & PVA was determined for both wavelengths using the formulae (3) [14].

\[
\alpha_0 = \frac{1}{t} \ln \frac{T}{T_0}
\]

where \((t)\) is the thickness of sample and \(T\) is the transmittance. Table (1), gives the values of the linear optical properties \(\alpha_0\), \(T\), \(n\) and \(K\). It has been realized that the coefficient of refractive index \((n)\) and the absorption \((\alpha_0)\) increase with increase the concentration for both wavelengths. So in this case, this work use \((532, 1064)\) nm, while in [4] used 532 nm.

Table 1. Linear optical properties for R6G & PVA in different concentration (1x10^{-4}, 5x10^{-4}, 1x10^{-5}, 1x10^{-6} and 5x10^{-6} mole/liter) at thickness (2µm).

| C(M/L) | T% 532nm | \(\alpha_0/\text{cm}^{-1}\) | \(n\) | T% 1064nm | \(\alpha_0/\text{cm}^{-1}\) | \(n\) | \(K\times10^{-7}\) 532nm | \(K\times10^{-7}\) 1064nm |
|--------|----------|-----------------|--------|----------|-----------------|--------|-----------------|-----------------|
| 5x10^{-4} | 27.7561 | 6408.57 | 7.0641 | 98.527 | 74.2 | 1.1885 | 271445.8 | 6285.7 |
| 1x10^{-4} | 74.0866 | 1499.68 | 2.2563 | 97.878 | 61.02 | 1.1695 | 63521.48 | 5169.2 |
| 1x10^{-5} | 88.9356 | 586.29 | 1.6385 | 99.256 | 37.34 | 1.1302 | 24833.3 | 3163.2 |
| 5x10^{-6} | 88.7574 | 596.32 | 1.6457 | 99.421 | 29.03 | 1.1139 | 25258.14 | 2459.23 |
| 1x10^{-6} | 87.2634 | 681.2 | 1.7056 | 99.689 | 15.57 | 1.0822 | 28853.38 | 1318.99 |

3.2 Nonlinear optical properties

Z-Scan technique has used close aperture to determine the \(T_P\) and \(T_V\). The nonlinear refractive index was measured by the formula (4) [15].

\[
\frac{T}{T_0} = 1 - \frac{4}{n^2} \alpha_0 \frac{L}{t} + \frac{2}{n^4} \alpha_0^2 \frac{L^2}{t^2}
\]
\[ n_2 = \frac{\Delta \phi_0}{I_0 L_{\text{eff}} k} \]  

(4)

\[ I_0 \]: Is the intensity of the laser beam at the focus (Z = 0).

\[ \Delta \phi_0 \]: Non-linear phase shift [15].

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

(5)

\[ L_{\text{eff}} \]: the effective length of the sample, \( t \): is the sample thickness , \( \alpha \): linear absorption coefficient .

From the open aperture Z-scan data, the nonlinear absorption coefficient is estimated [15].

\[ \beta = \frac{2\sqrt{\Delta T}}{l_{\text{eff}}} \]  

(6)

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

After putting the sample (R6G/PVA) at thickness 2µm on the base of z-scan system, the normalized transmission were recorded by using 532 nm of Nd-Yag laser for closed and open aperture. The first group of results with closed aperture is given by Fig. 4 under different concentrations.

Figure 4. Closed aperture Z-Scan for R6G & PVA in wavelength 532 nm in different concentrations with (\( t = 2\mu m \)).
It can be seen from Fig. (4) that the nonlinear refractive index which is represented by valley-peak changes between positive (self-focusing : that mean valley-peak) and negative (self-defocusing: that mean peak-valley).

The second case with open aperture gives the spectra that are shown in Fig. 5.

![Figure 5](image)

**Figure 5.** Open aperture Z-Scan for R6G & PVA in wavelength 532 nm in different concentration with \((t= 2\,\mu m)\).

From Fig. 5, the spectra that were obtained with open aperture present the peaks only with no valley. Upon decreasing the concentrations the spectra of transmission increase and become narrow. The nonlinear absorption coefficient of R6G/PVA that was measured with Z-Scan technique exhibits the behavior of
saturated absorption. The values of \((n_2)\) and \((\beta)\) are listed in table 2. Case 1; at \(\lambda=532\) nm and \(I_0 = 49.147 \times 10^3 mW/cm^2\).

Table 2. The results of the nonlinear optical properties for R6G & PVA by the Z- scan.

| C(Ml)    | \(\Delta T_{P-V}\) | \(\Delta \Phi\) (Rad) | \(n_2\) \(\left(\frac{cm^2}{mw}\right)\times 10^{-7}\) | \(T_{max}\) | \(\beta\) \(\left(\frac{cm}{mw}\right)\) |
|----------|---------------------|------------------------|--------------------------------------------------|-------------|------------------------|
| 5x10^{-4} | 0.5                 | 1.23                   | 18.8                                             | 17.4        | 8.88                   |
| 1x10^{-4} | 1.22                | 3                      | 29.93                                            | 18.83       | 6.27                   |
| 1x10^{-5} | 0.53                | 1.31                   | 12.08                                            | 19.5        | 6                      |
| 5x10^{-6} | 0.55                | 1.35                   | 12.34                                            | 20          | 6.11                   |
| 1x10^{-6} | 1.08                | 2.66                   | 24.52                                            | 20.5        | 6.3                    |

From above table it can be seen that the higher value of nonlinear refractive index \((n_2)\) was obtained when the concentration is \((1*10^{-6}\) Ml\)). Additionally, higher non-linear absorption coefficient \((\beta)\) obtained when the concentration equals to \((5*10^{-4}\) Ml\)) as well.

Furthermore, another laser was used with a different wavelength 1064 nm. For this kind of laser the two cases of closed and open apertures were applied as well. In the closed aperture, the results were presented in Fig. 6.

Figure 6. Closed aperture Z-Scan for R6G & PVA at wavelength 1064 nm in different concentrations with \((t=2\mu m)\).
In Fig. 6, the nonlinear refractive index changes between positive (self-focusing: that mean valley-peak) and negative (self-defocusing: that mean peak valley).
In the second case with open aperture and for the same laser, the result was shown in Fig. 7.

![Graph showing nonlinear refractive index changes](image)

**Figure 7.** Open aperture Z-Scan for R6G & PVA in wavelength 1064 nm in different concentrations with (t= 2µm). Case 2: In λ=1064 nm and \( I_0 = 72.737 \times 10^3 mW/cm^2 \)

From Fig. 7, the nonlinear absorption coefficient of R6G/PVA that was measured with Z-Scan technique exhibits the behavior of saturated absorption. The values of \( n_2 \) and \( \beta \) are listed in table 3.
Table 3. The results of nonlinear optical properties for R6G & PVA by the Z- scan.

| C(Ml)  | ΔT_{σ-ν} (Rad) | Δφ (Rad) | n^2 (cm^2/mW) × 10^{-7} | T_{max} | β (cm/mW) |
|--------|----------------|----------|--------------------------|---------|-----------|
| 5×10^{-4} | 0.32           | 0.79     | 9.27                     | 28.69   | 5.62      |
| 1×10^{-4} | 5.5            | 13.55    | 158.78                   | 28.95   | 5.66      |
| 1×10^{-5} | 3.19           | 7.86     | 91.88                    | 27.93   | 5.45      |
| 5×10^{-6} | 0.42           | 1.03     | 12.03                    | 27.77   | 5.41      |
| 1×10^{-6} | 1.3            | 3.2      | 37.3                     | 22.44   | 4.37      |

From this table it can be seen that the higher value of the nonlinear refractive index (n^2) is obtained when the concentration is (1×10^{-4} Ml), and the higher value of the non-linear absorption coefficient (β) obtained when the concentration is (1×10^{-4} Ml).

After that, the effect of the concentration changes on the energy gap (E.g) was studied and the results are shown in the table 4. Fig. 8 shows the relation between the E.g and the concentration as well.

Table 4. The results of E.g at different concentrations.

| C(Ml)  | E.g   |
|--------|-------|
| 5×10^{-4} | 2.23  |
| 1×10^{-4} | 2.22  |
| 1×10^{-5} | 2.2   |
| 5×10^{-6} | 2.15  |
| 1×10^{-6} | 2.1   |

Table (4) shows that the energy gap increases with increasing the concentrations.

Figure 8. Energy gap for different concentrations.
In comparison with other research, it has been realized that there is agreement in some findings. One of these agreements is found with Deng Yan [1], in the behavior of the closed aperture. However, this research did not address the study of the open aperture. In addition, there was a difference in the values of the linear refractive index (0.65 – 28.9) × 10^{-7} cm^2/mW with varying concentration [4]. These differences might attributed to add particles of silver in research [4].

On the other hand, excited and emitted spectra of polymeric (PMMA) films that doped with R6G dye were investigated by Tanyi E [16]. In contrary with several studies, this study suggests that ~495 nm shoulder in the absorption spectrum is chiefly not due to a dimer formation, but is likely owing to vibronic transitions. With an increase of the dye concentration, the area of the Gaussian band representing the shoulder of the absorption spectrum increases linearly.

4. Conclusion

The spectral and optical properties of the models used in the search were investigated by applying theoretical calculations on practical (experimental) results that obtained in this research. It has been realized that absorption and fluorescence spectra of the samples (solid state) for different concentrations drift towards longer wavelengths with increasing concentration of the dye. Additionally, the nonlinear absorption coefficient of the solid state exhibits behaviour of saturated absorption of certain concentrations, which leads to increases the value of the nonlinear absorption coefficient solutions with increase concentrations. However, the nonlinear refractive index (n_2) of solid changes between the positive and negative values and increases with increasing of the concentrations.

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