Environment-Induced Effects on The Nonlinear Refractive Index of Methyl Orange at Different Spectral Regions

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Abstract. The current study investigates the effects of solvent on the linear absorption and nonlinear refraction $n_2$ of Methyl orange dye at different spectral regions. The study shows that the effects of the solvent depend on the excitation wavelength. The peak value of the dye absorbance is similar in water and ethanol. However, the properties of water lead to shift the absorption curve to the short wavelengths side. At wavelengths located outside the resonance band, the dye dissolved in ethanol shows almost identical nonlinear response. This response is lower than that at wavelength within the resonance band. The behaviour of the dye is different in water where $n_2$ is maximum at short wavelength (405 nm) and decreases at longer wavelengths (473 and 532 nm). Water induces dissimilar effects at different wavelengths. Increasing the polarity of water by adding large amounts of NaCl does not clearly affect the absorbance or the nonlinear refraction of the dye.

1. Introduction

The need for faster and smaller optoelectronic devices has stimulated the search for new material that can be employed in this field. Nonlinear materials have been widely used in the field of optoelectronics and other applications due to their favourable characteristics [1,2]. Organic materials, especially organic dyes, have an important role in the field of optoelectronic and other applications of nonlinear materials due to their unique properties [3,4]. The photo-thermal-stability, the rapid nonlinear response, the large nonlinearity, the ability of being included in solutions and solid matrices, the low price, and other properties of organic dyes have made them important materials in the field of nonlinear optics (NLO).

For the optimum used of the nonlinear material, their nonlinearity needs to be precisely characterized. There are several techniques for examining the nonlinearity of materials [5-9]. However, a simple and precise method suggested by S. B. Mansoor et al in 1989 is the $z$-scan method [10,11]. For measuring the nonlinear index of refraction $n_2$, the $z$-scan method depends on detecting the spatial deformation of a single beam inside the nonlinear medium. In addition, the nonlinear absorption coefficient of the medium $\beta$ can be concluded by recording the transmittance of a single light beam passing through the nonlinear medium as a function of the beam intensity. The beam intensity variation in this technique is obtained by scanning the nonlinear sample across the focal plane of the laser beam [10,11].

One of the effects of the real part of the third order susceptibility of material is the nonlinear refraction. This phenomenon causes focusing or defocusing of the laser beam depending on the sign of the refractive index $n_2$. This nonlinear property can be caused by different physical mechanisms depending on the characteristics of the nonlinear medium [12,13]. The significance of the nonlinear refraction and the originating mechanisms depend on the nature of the medium. In addition, the environment that surrounding the nonlinear medium has a significant role on the nonlinear refraction.
[14,15]. This effect has been extensively studied for different materials [13-17]. For instance, the solvent-solute interactions and the general physical properties of the solvent influence the type and the magnitude of the solute nonlinearity. For example, the solvent polarity, its ability of donating or accepting a hydrogen bond, and its thermal parameters can modify the nonlinearity of the solute [13-17].

In this study we investigate the influence of environmental parameters on the nonlinear refraction of Methyl orange (MO) in water and ethanol at three wavelengths 405, 473 and 532 nm. In addition, the effect of salting on \( n_2 \) coefficient of MO has been studied by adding different amounts of NaCl. The nonlinearity has been studied by using the conventional z-scan method with CW light sources.

2. Experimental setup

2.1. Z-scan method

Z-scan technique [10,11] is a simple and sensitive method for characterizing the nonlinearity of low scattering materials. The technique is based on detecting the spatial changes that happen to a single focused laser beam passing through the nonlinear sample as the sample is moving across the focus of the beam. Figure (1) shows the setup of the close aperture z-scan method.

![Figure 1. The experimental setup of the close aperture z-scan.](image)

The changes in the spatial phase of the beam due to the nonlinearity of the sample lead to change the beam size at the far field. This leads to change the amount light transmitted through a small aperture located at the far field, as shown in figure (1). The shape of change in the transmittance as a function of the sample position depends on the sign of \( n_2 \) of the sample and, for a fixed aperture size, the amount of the changes depends on the absolute value of \( n_2 \). For a Gaussian-profile beam, the difference between the maximum of the aperture transmittance and its minimum \( \Delta T_{p-v} \) is related to the phase difference \( \Delta \Phi_o \) as [16]

\[
\Delta T_{p-v} \approx 0.406(1 - S)^{0.255} |\Delta \Phi_o| 
\]

with

\[
S = 1 - \exp(-2r_a^2/w_a^2) \\
\Delta \Phi_o = \frac{2\pi}{\lambda} n_2 I_o L_{eff} \\
L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha} 
\]
Equation (1) is valid for small changes, i.e. $|\Delta \Phi_0| < \pi$ [16]. The transmittance curve can be easily obtained by moving the sample across the focal plane of the beam and recording the transmittance of the aperture as a function of the sample position. This leads to define the value of $\Delta T_{p-v}$ which can be used to find the value of $n_2$ by using equations (1) and (3).

2.2. Material and instruments
The Methyl orange dye has been obtained from (BDH) and used without further purification. The samples have been prepared by dissolving the dye into spectroscopic-purity ethanol and water. The light sources used in this work are three CW diode lasers having wavelengths of 405, 473 and 532 nm and Gaussian-profile beams. A 1 mm thick quartz cell has been used to characterize the samples in the z-scan experiment.

3. Results and discussion
Figure (2 a) shows the spectra of the linear absorption of the MO dye dissolved in water and ethanol.

![Figure 2](image)

**Figure 2.** The absorption spectra of (a) pure MO dye dissolved in water and ethanol and (b) MO dye dissolved in water with different amounts of NaCl.

The peak absorbance value of MO seems to be not affected by the solvent. However, using water leads to slightly shift the absorption curve toward the short wavelengths side relative to the absorbance curve of the dye dissolved in ethanol. This shift indicates that the energy value of the ground state level is changed due to the polarity of the solvent [16]. In general, not only the polarity of the solvent that can affect the linear properties of the solute but also the other properties of the solvent such as the ability of the solvent of denoting and accepting a hydrogen bond. These parameters act as a combination to determine the type of the solvent-solute interactions which in turns influence the spectral properties of the solute.

For investigating the effects of increasing the polarity of the solvent we have measured the absorbance of MO dissolved in water with different amounts of NaCl. The results are shown in figure (2 b). NaCl increases the polarity of the aqueous solution [18] and also its viscosity [19]. As can be seen, even with large amount of NaCl, the absorption spectra show negligible changes represented by a very small increase in the peak absorbance with the increase of the added NaCl. This indicates that the polarity of the solvent alone cannot affect the spectral properties of the MO dye. Instead, the combination of the total properties of the solvent can influence the spectral characteristics of the solute with different contribution of each property.

The nonlinear properties of the MO dye have been investigated by the z-scan procedure. Figure (3 a-c) depicts the close aperture curves of MO dissolved in water and ethanol at different excitation wavelengths. The pure effect of $n_2$ is obtained by dividing the close aperture curves by the corresponding open aperture curves. However, the curves of the dye dissolved in ethanol at excitation wavelengths 405 and 473 show the residual effect of the nonlinear absorption on the shape of the close aperture curves.
As can be seen, the dye possesses a negative nonlinear refraction index in the two solvents and at all the used wavelengths. The values of $n_2$ of the dye are listed in table (1).

![Graphs showing close aperture curves of 0.5 mM of MO dissolved in water and ethanol at excitation wavelengths 405, 473, and 532 nm.](image)

**Figure 3.** The close aperture curves of 0.5 mM of MO dissolved in water and ethanol at excitation wavelength (a) 405, (b) 473, and (c) 532 nm.

The $n_2$ values of the dye in ethanol at wavelengths 405 and 532 nm, which are located slightly outside the resonance band of the dye, are almost identical. However, at excitation wavelength within the...
The resonance band of the dye, the nonlinearity slightly increases. At this wavelength, dissolving the dye in water, despite all different properties of water, does not clearly affect the value of $n_2$. However, at the excitation wavelengths 405 and 532 water induces opposite effects.

In the same solvent, the variation of the excitation wavelength can result in changing the physical process that produces the nonlinear refraction. In addition, if the nonlinear refraction is a result of a combination of multiple mechanisms, the contribution of each mechanism to the total refraction can be different at different wavelength regions. This can lead to change the value of $n_2$ by changing the excitation wavelength.

Table 1. The nonlinear index of refraction of 0.5 mM of MO dissolved in water and ethanol

| Solvent  | $n_2 \times 10^{-12}$ (m$^2$/W) |
|----------|-------------------------------|
|          | at 405 nm | at 473 nm | at 532 nm |
| Ethanol  | - 2.47    | - 3.57    | - 2.39    |
| Water    | - 4.86    | - 3.53    | - 1.65    |

The effect of the solvent is also evident from the results at wavelengths 405 and 532 nm. These changes are not due to the differences in the linear absorption, because the absorbance values of the dye at these wavelengths are almost equal. In addition, the increase in the value of $n_2$ at 405 nm indicates that the nonlinear refraction at this wavelength is not of thermal origin. This is because the thermal conductivity of water and its heat capacity are larger than those of ethanol. This means that if the nonlinear refraction of MO at 405 nm is due to thermal lensing, the value of $n_2$ in water would be smaller than its value in ethanol, which is not the case.

The effects of solvent may be attributed to the polarity and the hydrogen bonding ability of water. The properties of the solvent determine the type and the strength of the solvent-solute interactions. These interactions affect the geometry of the dye molecule which directly leads to modify its nonlinear response [14]. In addition, the results of the current study reveal that the effect of the solvent is not similar at all excitation wavelengths. The influence of the solvent can induce an enhancement in the nonlinearity of the dye at a particular wavelength, while it can weaken the nonlinearity at another spectral region, as can be seen in table (1).

Investigating the effects of solvent polarity on the nonlinear properties of the solute by using a set of solvents with different polarities, in fact, includes the effects of changing the other properties of the solvent. Thus the resulting effects on the solute nonlinearity represent the effects of the combination of all properties of solvent but not only its polarity. In this study we show the effect of increasing the polarity of the same solvent by adding NaCl with different amounts. Figure (4) presents an example of the close aperture curves of the MO dye dissolved in water with different amounts of NaCl at excitation wavelength 405 nm.

![Figure 4. The close aperture curves of MO dissolved in water with different amounts of NaCl at excitation wavelength 405 nm](image-url)
As shown, even with large amounts of NaCl, the increase in water polarity does not clearly influence the value of $n_2$ of the MO dye. The behavior of the dye at wavelengths 473 and 532 is similar to that at 405 nm. This indicates that the change in the nonlinearity of the solute by changing the solvent is not solely due to the change in the polarity of the solvent but due to the combination of all the properties of the solvent.

According to the results of the current study, for applications that require a large $n_2$, employing MO dye at wavelengths 405 and 532 nm has many advantages. Firstly, the dye possesses relatively large $n_2$. Secondly, the linear absorbance of the dye at these wavelengths is negligible which means minimum losses. Thirdly, the nonlinearity of the dye is not affected by the polar impurity of the solvent.

4. Conclusion
The effect of environment properties on the linear absorption and nonlinear refraction of Methyl orange (MO) dye is investigated in water and ethanol. The results show that the value of linear absorbance of the dye is not affected by the change of the solvent. However, the absorption curve is shifted to shorter wavelengths by dissolving the dye in water. The polarity of the solvent alone does not influence the spectral and the nonlinear properties of the MO dye. However, the combination of the solvent properties, such as the polarity and its ability of donating and accepting a hydrogen bond, does influence the optical properties of the dye. The MO dye shows dissimilar nonlinear properties in water and ethanol at different wavelengths. The dye dissolved in ethanol possesses maximum nonlinearity at 473 nm and almost identical nonlinearities at 405 and 532 nm. However, maximum nonlinearity of the dye in water happens at 405 nm and decreases by increasing the excitation wavelength. The influence of the solvent is not likely to be due to the differences in the linear absorption of the dye or the thermal properties of the solvent at wavelengths 405 and 473 nm.

5. References
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