

# Nonlinear characterization and optical switching in bromophenol blue solutions

Fryad Henari

Department of Basic Medical Sciences, Royal College of Surgeons in Ireland, Medical University of Bahrain, Bahrain;  
[fzhenari@rcsi-mub.com](mailto:fzhenari@rcsi-mub.com)

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## ABSTRACT

In this paper the results from investigations of the nonlinear refractive index and nonlinear absorption coefficient of Bromophenol Blue using the Z-scan technique with a continuous wave laser beam at wavelengths 488 nm and 514 nm are presented. It was observed that the material exhibited reverse saturation absorption and self defocusing behavior. It was found that the increase in solution concentration resulted in linear increase of the nonlinear refractive index. A pump and probe technique was used to obtain the absorption spectrum of triplet state. Furthermore the nonlinear absorption effect was used to demonstrate all optical switching.

**Keywords:** Nonlinear Refractive Index; Nonlinear Absorption; Bromophenol Blue; Cross Phase Modulation; Optical Switching

## 1. INTRODUCTION

In recent decades, there has been considerable interest in searching for materials exhibiting nonlinear optical effects. The application of these effects to photonic devices and optical limiting is of great importance for future technologies. These effects are important for use in applications such as photonic devices and optical limiting [1-5]. The basic properties that are required for nonlinear properties include large nonlinearity and fast response time [6]. A large number of materials have been investigated for example liquid crystals, fullerenes, nanoparticles, organic materials and natural substances such as Chinese tea, Chinese herbal medicine, and solutions of chlorophyll. These materials have been used for application such as optical limiting, optical switching, self actions such as phase modulation, cross phase modulation and self trapping [7,8].

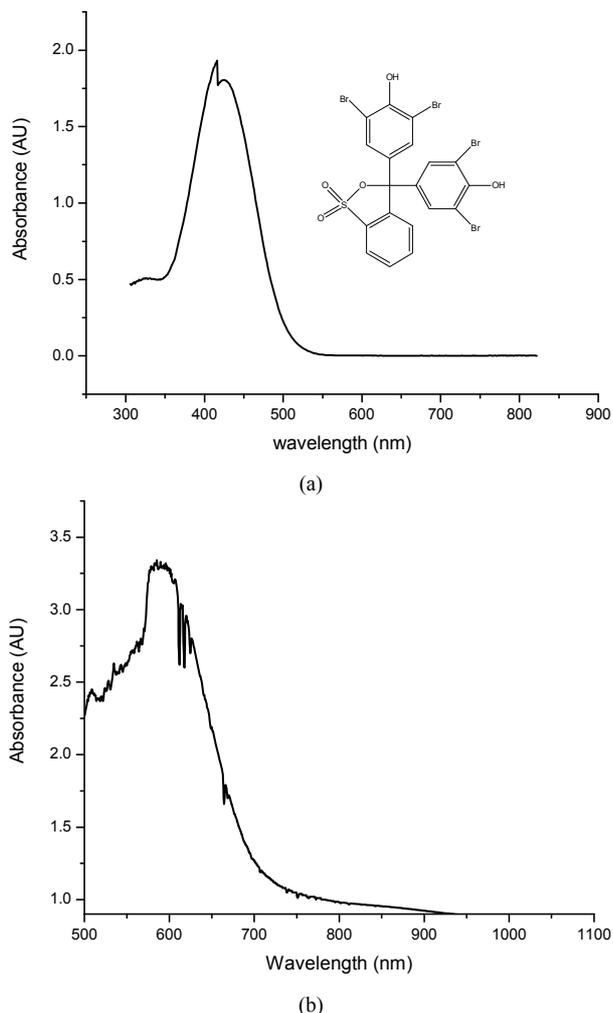
In this paper, the experimental measurements of the nonlinear refractive index  $n_2$  and nonlinear absorption

coefficient  $\beta$  of Bromophenol blue solutions using Z-scan technique are reported [9]. The measurements were performed with the continuous wave (cw) argon ion laser at two different wavelengths 488 nm and 514 nm. We also report observation of phase modulation, cross phase modulation and optical switching. The origin of the observed nonlinearities of the BPB is also discussed.

## 2. ABSORPTION SPECTRUM

Bromophenol Blue (BPB) (Tetrabromophenolsulfonphthalein) is a halochromic chemical that indicates, the degree of acidity or basicity of a solution through characteristic colour changes [10]. A general structure and formula of the BPB are shown in **Figure 1**. The BPB samples at four concentrations of 0.1, 0.15, 0.2 and 0.4 g/L were prepared in ethanol to give a solution with a yellowish colour. The samples were placed in a 1 mm thick quartz cuvette. The ground state  $S_0 - S_1$  absorption spectra of BPB solution at concentration of 0.2 g/L were recorded and the absorption peak is found to occur at  $\lambda = 420$  nm as shown in **Figure 1(a)**. The absorption spectrum of  $T_1$  excited state was obtained through the following procedure: An argon ion cw laser beam of wavelength 488 nm (close to resonance) was used as a pump (excitation source) and was focused by a lens of 5 cm focal length to the beam waist of 30  $\mu\text{m}$ . A Halogen lamp was used as probe beam and focused on the sample by the same lens.

The sample is moved to a postfocusing position (minimum transmission in Z scan experiment (see below)). The intensity change of the probe beam was detected by CCD spectrometer (Model BRC112E-USB-Vis NIR) and transferred to a computer. The population of triplet excitations achieved by population of  $S_1$  state through excitation of the  $S_0 - S_1$  transition by cw excitation beam, where the  $S_1$  states undergo intersystem crossing, producing population in  $T_1$  states. Because of the long lifetime of  $T_1$  state, its population dominates that of other excited states. **Figure 1(b)** shows the  $T_1$  absorption spectrum of BPB in ethanol. A absorption



**Figure 1.** (a) Ground state absorption spectrum, (b) Triplet state absorption spectrum (AU) of bromophenol blue.

peak occurs at 590 nm.

### 3. EXPERIMENTS

The nonlinear coefficients of the BPB samples were measured by the Z-scan technique. Z-scan is a well-known technique that allows the simultaneous measurement of both nonlinear absorption coefficient ( $\beta$ ) and the nonlinear refractive coefficient ( $n_2$ ). The Z-scan technique relies on the fact that the intensity varies along the axis of the convex lens and is maximum at the focus. Hence, by shifting the sample through the focus, the nonlinear absorption and the nonlinear refraction can be measured by observing the spot size variation at the plane of finite aperture/detector combination.

The experiment was performed with an air-cooled Ar ion laser beam operating at 488 nm and 514 nm with an average power of 5 - 40 mW. The beam was focused to a beam waist of 30  $\mu\text{m}$  with a lens of 5 cm focal length,

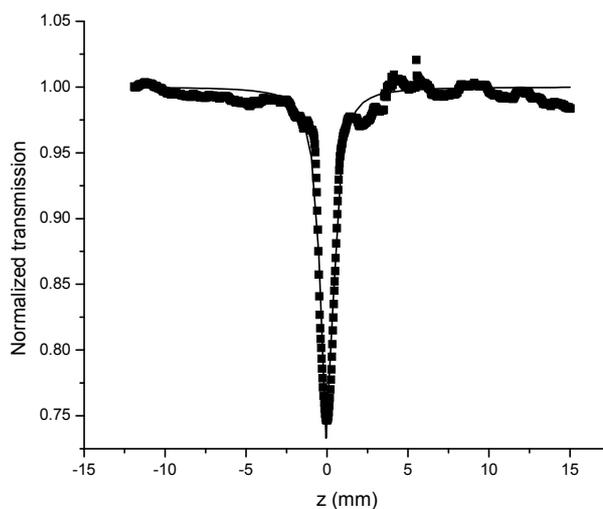
giving a typical power density of  $1.42 \times 10^7 - 1.00 \times 10^8 \text{ W/m}^2$ . The sample was placed in 1 mm thick quartz cuvette and positioned on the translation stage. The transmission for the sample was measured with and without an aperture in the far-field of the lens, as the sample moved through the focal point. This enables the nonlinear refractive index (closed aperture) to be separated from that of the nonlinear absorption (open aperture).

### 4. RESULTS AND DISCUSSION

**Figure 2** shows the normalizing transmission for open aperture case. The transmission is symmetric with respect to the focus ( $z = 0$ ), where it has minimum transmission. This is an indicative that the sample exhibits reverse saturation absorption, (RSA) (optical limiting). The conditions required for RSA are as follows: 1) Incident photons with the same wavelength can be absorbed by molecules in the ground state and also by excited states. 2) The absorption of the excited states must be larger than that of the ground state. For most organic molecules excited by a laser wavelength of weak ground state absorption, these conditions usually can be met. Open aperture Z-scan was performed also with a pure solvent. In this case, no nonlinear absorption was observed within the limit of the intensity used in the experiment. We conclude that the effect seen is due to BPB

The normalize transmittance for the open aperture is given by [9].

$$\Delta T(z) = 1 - \frac{\Delta\phi}{(1+x^2)} \quad (1)$$



**Figure 2.** Normalized transmittance (open aperture) of Bromophenol blue for 0.2 g/l solution at an incident intensity  $I = 4.27 \times 10^7 \text{ W/m}^2$  at  $\lambda = 488 \text{ nm}$ . The solid line is a fit of the data to **Equation (1)**.

where  $x = z/z_o$  (with  $z_o = \pi w_o^2/\lambda$ ) is the diffraction length of the Gaussian beam,  $w_o$  is the beam waist and  $\Delta\phi$  is the nonlinear phase change. The nonlinear absorption  $\beta$  is then related to  $\Delta\phi$  by [9]

$$\beta = \frac{2\sqrt{2}\Delta\phi\alpha}{I_o(1-e^{-\alpha l})} \quad (2)$$

where  $\alpha$  is the linear absorption coefficient at  $\lambda = 488$  nm ( $\alpha = 0.235/\text{mm}$ ) and  $l$  is the thickness of the sample and  $I_o$  is the peak intensity at the focus. A fit of **Equation (1)** to the experimental data is depicted in the **Figure 2**, and yields the value of nonlinear absorption  $\beta = 4.28 \times 10^{-3}$  cm/W. This value is in the same of the nonlinear absorption measured for zinc porphyrin polymer and triphenylmethane measured with the z-scan method [10,11] and two orders higher than fast green FCF dye observed under cw excitation at 633 nm [12].

**Figure 3** shows the normalizing transmission for a closed aperture case at  $\lambda = 514$  nm for a solution with a concentration of 0.1 g/l solution at an incident intensity  $I = 1.4 \times 10^7$  W/m<sup>2</sup>. The peak valley configuration indicates that the sign of the nonlinear refractive index  $n_2$  is negative (self-defocusing occurs).

The difference between normalized peak-valley transmittance  $\Delta T_{p-v}$  is given by

$$\Delta T_{p-v} = 0.406(1-s)^{0.25} |\Delta\phi| \quad (3)$$

where  $|\Delta\phi|$  is the on axis nonlinear phase shift at focus,  $s$  is the nonlinear transmittance of the aperture and is given by  $s = 1 - \exp(-2r^2/w^2)$  here  $r$  is the radius of the aperture and  $w$  is the radius of the beam at the entrance of the aperture.

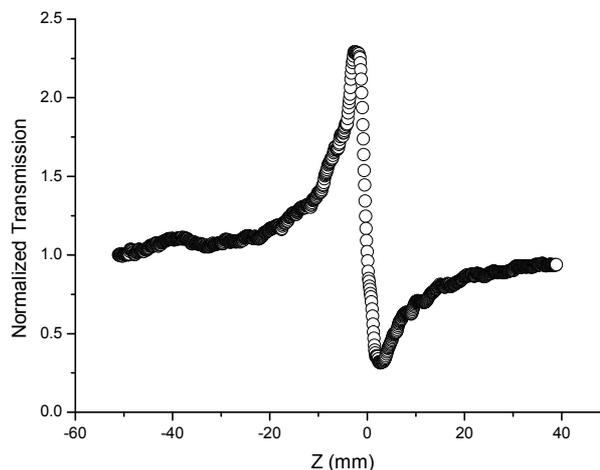
The nonlinear refractive index  $n_2$  is related to  $\Delta\phi$  by

$$n_2 = \frac{\Delta\phi\alpha\lambda}{2\pi I_o(1-e^{-\alpha l})} \quad (4)$$

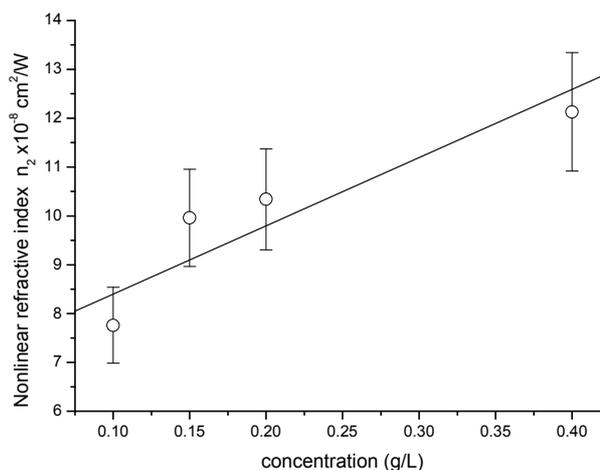
where  $\alpha$  is the linear absorption coefficient,  $l$  is the thickness of the sample,  $I_o$  is the peak intensity at the focus, and  $\lambda$  is the wavelength of the laser beam.

**Equations 3** and **4** were used to calculate the value of the nonlinear refractive index and it was found to be  $n_2 = 7.76 \times 10^{-8}$  cm<sup>2</sup>·W<sup>-1</sup>. This value is three orders higher than the nonlinear refractive index measured for C60 with z-scan method [13] and in agreement with results measured in ref. [11,12,14].

The nonlinear refractive index dependence on concentration of the BPB solution was investigated. **Figure 4** shows the nonlinear refractive index as a function of concentration at an incident intensity of  $2.83 \times 10^7$  W/m<sup>2</sup>. It has been found that the nonlinear refractive index is linearly dependent on the concentration with the range of the concentrations studied. One can conclude that the



**Figure 3.** Normalized transmittance (closed aperture) of Bromophenol Blue for 0.2 g/l solution at an incident intensity  $I = 4.27 \times 10^7$  W/m<sup>2</sup> at  $\lambda = 514$  nm.



**Figure 4.** Nonlinear refractive index  $n_2$  as a function of concentration for Bromophenol blue solution.

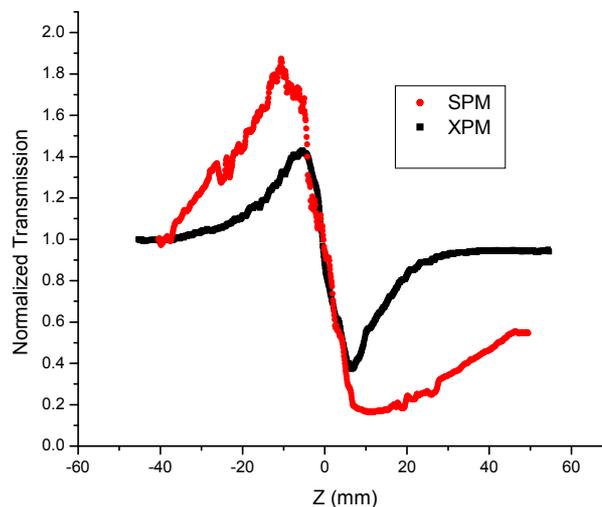
higher concentration of the sample gives higher nonlinearities. Experiments were performed to study the concentration dependence on the nonlinear absorption coefficient and it has been found that the nonlinear absorption coefficient is linearly dependent on the concentration. In fact, the nonlinear absorption coefficient is more easily obtained at higher concentration. The increase of  $n_2$  and  $\beta$  with increase of concentration may arise from the fact that the number of BPB molecules increases as the concentration increases, therefore more molecules are thermally agitated resulting in an increase of nonlinear effects.

Nonlinear optical phenomena can be due to: electronic and non-electronic processes [15]. The former refers to those radiative interactions between the active electron and the optical electric field. Usually, they are very fast, of the order of ps. The latter refers to thermal processes

due effect of heating (due light absorption). Usually they are slow, of the order of ms. The type of the laser used in this experiment to probe the nonlinear effects of the material is a cw laser. Therefore the optical nonlinearities observed in this experiment may be of thermal origin and arising from thermally induced refractive index changes. The nonlinear absorption may arise according to the Kramers-Kroing relation, which states that the change in the refractive index at any frequency is associated with a change of the absorption coefficient. The time resolved Z scan method was also performed at different chopping frequencies all showing the maximum transmittance (peak) followed by minimum transmission (valley). No discrimination on the sequences of peak and valley were observed, usually for electronic nonlinearities (valley first then peak) and thermal nonlinearities (peak followed by valley). This is another indication that the nonlinear optical response is predominately of thermal origin.

To investigate a cross phase modulation (XPM), the Z scan experiment was performed with a pump and probe beams. Cross-phase modulation is the change in the optical phase of a light beam caused by the interaction with another beam in a nonlinear medium. This can be described as a change in the refractive index,  $\Delta n = 2n_2 I_o$ , where  $n_2$  is the nonlinear refractive index of the material and  $I_o$  is the intensity of pump beam which causes a refractive index change for probe beam. In this experiment, the pump beam was Argon Ion ( $\lambda = 488$  nm, power 20 mW) and the probe beam was He-Ne ( $\lambda = 633$  nm, power 0.5 mW). The two beams propagate simultaneously at the same direction in the nonlinear medium. The pump, which produces the effect, was blocked by the filter and monochromator and the intensity of the probe beam was monitored as the sample moved through the plane of the lens. The maximum transmission (peak) followed by the minimum transmission (valley) was observed. The observed behaviour is due to cross-phase modulation from pump beam to probe beam [7,16]. We believe in this case the thermal lens (TL) effect is responsible for above observation; however, further experiments are needed to investigate the mechanism involved in XPM. **Figure 5** shows typical z scan results and used to determine the nonlinear refractive index for SPM (z scan with pump beam only) and XPM (z scan with pump and probe). The nonlinear coefficient can be calculated using Equations (3) and (4), for pump beam  $n_2 = 7.7 \times 10^{-8}$  cm<sup>2</sup>/W and for probe beam (with pump is on)  $n_2 = 3.4 \times 10^{-8}$  cm<sup>2</sup>/W. Please note the value  $n_2$  for XPM is nearly one order lower.

The pump and probe experiment was used to demonstrate inverted optical switching. In the experiment a cw argon ion laser beam of wavelength 488 nm and power



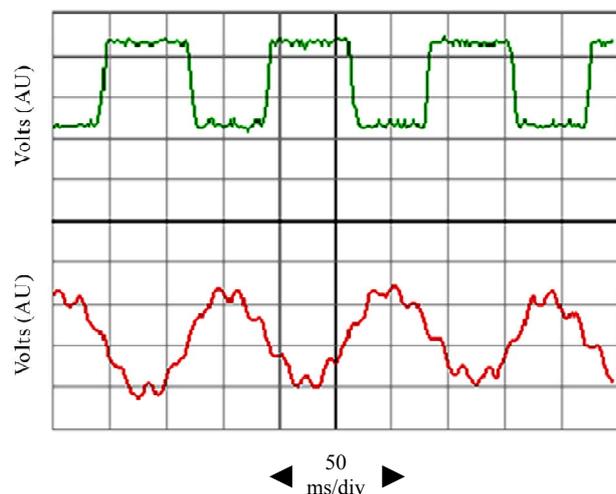
**Figure 5.** Normalized transmission (closed aperture) of bromophenol blue with pump beam only (SPM, diamonds) and with pump and probe beams (XPM, squares).

20 mW was used as a pumping beam and was focused with a lens of 5 cm to a beam waist of 30 mm. A weak laser beam of wavelength 633 nm and power = 0.5 mW from HeNe laser was used as a probe beam and focused on the sample by the same lens. The pump beam was modulated with mechanical chopper beam.

The mechanism of optical switching which is based on nonlinear absorption and maybe explained as follows: The absorption spectra of BPB of the ground state  $S_0$  and triplet state  $T_1$  are different. Absorption of the  $T_1$  state is much higher in the region of 600 nm than that of the ground state  $S_0$ , (see **Figure 1**). The cw probe beam with a wavelength ( $\lambda = 633$  nm) off absorption peak of the ground state but close to the absorption peak of triplet state  $T_1$  passes through the sample; the output intensity is in the switch-on states because of lower linear absorption and higher transmittance of 633 nm. When the sample is pumped by a strong laser beam with wavelength of 488 nm, the population of  $T_1$  is greatly enhanced through intersystem crossing from  $S$  state to triplet  $T$  state. The probe beam is intensively absorbed. The output intensity would be in the switched off state. **Figure 6** shows the oscilloscope trace (below) of transient optical inversion switching.

## 5. CONCLUSIONS

In conclusion, nonlinear absorption coefficient and nonlinear refractive index have been investigated for BPB solution using Z scan experiment at wavelengths 488 nm and 514 nm. The Z-scan measurements indicated that the BPB exhibited large nonlinear optical properties. We have shown that the nonlinear absorption can be attributed to a reverse saturation absorption process (op-



**Figure 6.** Waveform traces for the pump beam (upper trace) and the probe beam (lower trace).

tical limiting). The absorption spectrum of T1 excited state was obtained using cw irradiation at 488 nm as pump beam and halogen lamp as a probe beam. Optical switching based on absorption of the probe beam by the triple stat was demonstrated. Focusing, defocusing and nonlinear absorption in such materials can be applied for designing various photonic devices. Low power pumping is important for device manufacturing with respect to cost and compactness and threshold damage. Another advantage of BPB over other materials is its stability and it is easily synthesized in comparison with C60 and liquid crystals.

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