Saturation effects in nonlinear absorption and refraction of DO3 (Disperse Orange – 3) solution


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Abstract

The Z-scan technique has been used to study the saturation of both absorption and nonlinear refraction ($n_2$) in a DO3 solution. We observed that the saturation of absorption is due to the photoinduced cis conformation. A three-energy-level model was applied to describe this effect and the absorption cross-section was obtained. Besides, a saturation of $n_2$ was observed. Further investigations must be done to determine the origin of this process.

Introduction

Azobenzene undergoes cis-trans photochemical isomerization after excitation to the $S_1(n\pi^*)$ state band, providing the basis for various applications, such as light triggered switches and image storage devices [1-3]. These processes have been extensively investigated by various experimental methods, such as UV-visible absorption [4-7], Raman spectroscopy [8-9] and NMR [10]. Although the optical properties in azobenzene compounds have been widely studied in last few years, there are still some controversies in their excited state structure. In this work, we report the study of resonant optical nonlinearities in DO3/DMSO solutions using the Z-scan technique [11-12] with picosecond laser pulses at 532 nm. A three-energy-level model [13], was used to describe the dynamics of the trans-cis-trans photoisomerization, allowing the determination of excited state parameters.

Experimental Setup

Our Z-scan experiment used single pulses extracted from the pulse train of a frequency-doubled Q-switched and mode-locked Nd:YAG laser, operating at 532 nm with a 10 Hz repetition rate. The FWHM pulse duration was 100 ps, and the spatial profile of the laser beam was approximately Gaussian. The beam waist size ($w_0 = 25 \mu m$) and pulse irradiance were determined by performing Z-scan measurements in a carbon disulfide sample (2-mm cuvette), frequently used as a calibration material. The intensity of laser was varied using a calcite polarizer.

Results and Discussions

The results obtained with the Z-scan technique with open and closed aperture (presented in Fig. 2 (a) and (b)) can be described by the three-energy-level, shown in Fig 1. Azobenzene molecules, initially in the $S_0$ (trans) band, are excited to the $S_1$ (trans*) band, relaxing nonradiatively to the bottom of this band. At this point, there are two possible relaxation pathways: one to $S_0$ (trans) and other to $S_0$ (cis) state, both with similar relaxation life times ($\tau_t$ and $\tau_c$). This process transfers part of the population from $S_0$ (trans) to $S_0$ (cis). An analogous mechanism happens with molecules in $S_0$ (cis). However, in this case the process is less efficient because the cis cross-section is smaller than that of the trans absorption. After several photoisomerization cycles, a population of molecules in the $S_0$ (cis) ground state band is created, which generates the saturable nonlinear absorption and refraction.

Figure 1: Three-energy-level diagram model used to explain the saturation of absorption of DO3 solution.
In Fig. 2 (a), we observe an increase in the normalized transmittance as function of the pulse laser irradiance. This behavior can be explained with the three-energy-level diagram previously described. The solid line in this figure represents the theoretical fitting obtained with a cis absorption cross-section $\sigma_c = (4.2 \pm 0.2) \times 10^{-17}$ cm$^2$. In this fitting, we used the trans ground state cross-section $\sigma_t = (5.2 \pm 0.1) \times 10^{-17}$ cm$^2$, obtained by UV-Vis absorption in a solution with $(5 \pm 0.1) \times 10^{17}$ molecules/cm$^3$. The lifetime ($\tau_c, \tau_t$) determined through the theoretical fitting were $(2.3 \pm 0.4)$ ps, for both relaxation. These lifetimes are similar to those described by Lednev et al [14-15].

Figure 2 (b) shows the nonlinear refraction signal as a function of the pulse irradiance. In this case, it was observed a saturation of the $\Delta T_{pv}$ value for intensities higher than $I = 2 \text{ GW/cm}^2$. To describe this behavior, we used a typical saturation expression where the induced refractive index change $\Delta n$ can be written as function of intensity $I$ according to [16]:

$$\Delta n = n_{2\text{eff}} I / (1 + I / I_s)$$  \hspace{1cm} (1)

where $n_{2\text{eff}}$ is effective refractive index, $I_s$ is the saturation intensity and $I$ is the intensity of Gaussian beam. The dashed line in Fig. 2 (b) represents the fitting obtained for the low intensity regime, where the saturation effect can be neglected. In this case, the refractive nonlinear index found was $n_2 = -1.1 \times 10^{-15}$ cm/W. However, if the saturation effect is considered the effective refractive nonlinear index, solid line in Fig. 2 (b), obtained through the fitting with eq. (1) was $n_{2\text{eff}} = -0.5 \times 10^{-15}$ cm/W. Although a good agreement between the theory and experiment was observed, eq. (1) describes this process just phenomenologically, and further investigations must be done to determine the real origin of the observed effect.

Conclusion

We investigated the nonlinear absorption and refraction effects in a DO3/DMSO solution. The saturation of absorption is due to an increase in the cis molecules population. Open aperture Z-scan measurements accomplished with single 100 ps pulses and the three-energy-level model allowed the cis conformation absorption cross-section determination. The nonlinear refraction was described through a typical phenomenological saturation equation, and the effective $n_2$ value was determined.

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References