Dynamics nonlinear optical properties in indocyanine green solutions

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Abstract

Dynamic nonlinearities of Indocyanine Green solutions were studied by different Z-scan techniques. The excited singlet and triplet cross-sections of this molecule and the intersystem crossing times were obtained solving numerically rate equations.

Introduction

Indocyanine green (ICG) is an organic dye with application in several distinct areas. In lasers, it is used as the active medium [1] and as a saturable absorber [2]. In medicine, ICG has been mainly used for diagnosis [3] and photo-dynamic therapy (PDT) of cancer [4,5]. Regarding photonics, it can be applied in optical limiting devices [6] due to its efficient reverse saturated absorption (RSA). The results obtained here have shown that the excited singlet and triplet states cross sections of this molecule are extremely high with respect to the ground state one, describing a RSA with a fast intersystem crossing time.

Experimental Setup

In this work we studied the dynamic of the nonlinear absorption of ICG (Fig. 1) diluted in water and dimethyl sulfoxid (DMSO). We used two configuration of the Z-scan technique to obtain the singlet and triplet states dynamics, independently. One configuration is the traditional single pulse Z-scan technique [7] that consists in translating the sample through the focal plane of a Gaussian beam and monitoring the changes in the intensity in the far-field as a function of the sample-focal position. The other configuration is the pulse train (PTZ-scan) Z-scan technique [8], which is able to verify the nonlinear dynamics in the nanosecond time scale.

The experimental apparatus is similar to the traditional Z-scan. In this case, the sample is also moved through the focal plane, and several pulse trains are acquired and the amplitudes of each pulse are normalized to the one obtained when the sample is far from the focus. The excitation of the sample was made at 532 nm, being the second harmonic of a Nd:YAG Q-switched and mode-locked laser (Antares Quantronix). The characteristic laser pulse delivered from Antares contains a pulse train with about 20 pulses, separated by 13 ns and with 100 ps of FWHM. This pulse configuration was used in PTZ-scan. For the single pulse Z-scan technique, the pulse train pass through a Pockels cell placed between two crossed polarizes, which is used to extracted a single pulse envelope.

Figure 1: Indocyanine green structure.
In order to measure the nonlinear properties of ICG, we used a concentration of approximately 1.2x10^{17} molecules/cm^3. The UV-Vis absorption spectrum was obtained with a Cary-17A spectrometer at room temperature, with a concentration six times more diluted than used in the nonlinear measurements.

**Results and Discussions**

Figure 2 shows the UV-Vis absorption spectrum of ICG diluted in water (solid line) and in DMSO (dash line) for a concentration of 2x10^{16} molecules/cm^3. It presents a strong band around 800 nm related to the \( \pi \rightarrow \pi^* \) transition. This band changes its intensity with increasing the temperature, as showed in the inset. For temperatures lower than 60°C, this optical process is reversible. However, for temperatures higher than 60°C it does not recover the initial absorption, which is probably associated with sample degradation. Due to this thermal behavior, we have just carried out the nonlinear measurements at room temperature.

![Figure 2: Absorption spectrum of indocyanine green in water (solid line) and in DMSO (dashed line). The inset shows the absorption changes with the sample heating in water solvent.](image)

Employing the single pulse Z-scan technique we obtained the normalized transmittance (TN) as a function of pulse irradiance for both samples, as shown in Fig. 3. Each point in this figure is the minimum value extracted from a single open-aperture Z-scan measurement (insets in Fig. 3). The solid lines represent the fittings using a three singlet energy level diagram, that provides the absorption cross-sections \( \sigma_{1s}^{\text{water}} = (13 \pm 1) \times 10^{-17} \text{ cm}^2 \) and \( \sigma_{1s}^{\text{DMSO}} = (12 \pm 1) \times 10^{-17} \text{ cm}^2 \). We can also observe a saturation effect of the TN. This behavior is due to the accumulation of molecules in the singlet excited state and to the depleting of the ground state. In the ICG diluted in DMSO, the saturation occurs for low intensities due to its fluorescence time (500 ps) [9], that is 25 times higher than that of the ICG-water (20 ps). In this way, saturation intensity of the first excited state for ICG-DMSO is lower than for ICG-water. This implies that for the same pulse irradiance, more population is accumulated in singlet excited state to ICG-DMSO, which causes a premature saturation of RSA effect. With more molecules excited in the first state, more transitions can occur to second excited state, that present a small absorption cross-section. This process can be visualized in the change of the slope on the fitting in Fig. 3(b), around 3 GW/cm^2, or also in the focal position \( z=0 \) in the inset of the same figure, where the TN present a discontinuously in comparison with the inset of Fig. 3(a).
In the Fig. 4 we show the results obtained using the Z-scan with pulse train (PTZ-scan) [8]. In this technique the long duration of the Q-switch envelope (about 200 ns) and the 13 ns time interval between consecutive pulses is employed to map the evolution of the nonlinearity. These results reveal an accumulative process due to the triplet state population and can be explained considering a five-energy-level diagram. When a pulse of the envelope excites the molecule to the level $S_1$, it can be promoted to a second excited state, return to the ground state or decay to the excited triplet state $T_1$ (intersystem crossing process). With the arrival of the next pulses from the same envelope, additive contributions to the optical nonlinearity can appear due to the population build up in triplet state. The experiment results obtained here demonstrated that both samples exhibit RSA due to the higher absorption cross section relative to the ground state ($\sigma_{\text{water}} = (9 \pm 1) \times 10^{-17} \text{cm}^2$ and $\sigma_{\text{DMSO}} = (7 \pm 1) \times 10^{-17} \text{cm}^2$). The intersystem crossing times determined using PTZ-scan were 1 ns and 9 ns for water and DMSO, respectively, in agreement with the literature [9,10]. The fittings are represented by lines in Fig 4.

Conclusions

In conclusion, the results obtained with both techniques have shown that the excited singlet and triplet cross-sections of ICG in both solvents are extremely high in relation to the ground state. If compared with the ground state, the singlet excited state present a value 50 times larger for water and 75 times larger for DMSO. In triplet state, this difference is lower than the singlet excited state one. In this case, the values are 33 and 45 times larger for water and DMSO, respectively. The high singlet and triplet excited states cross section and a high population in the triplet state makes ICG a good candidate for photodynamic therapy and optical limiting devices.

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References