Influence of the cumulative effect on the excited state absorption spectra obtained with white-light continuum Z-scan

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Abstract

This work reports on the observation of excited state absorption (ESA) cumulative effect of a resonant nonlinear absorber when ESA spectra are obtained through the white-light continuum Z-scan technique. Besides, from the nonlinear transmittance achieved and simulation procedure, assuming a singlet three level system, the ESA cross-section spectrum can obtain if chirp rate and ground state absorption cross-sections are known.

Introduction

Recently, a new extension of the Z-scan technique known as white light continuum (WLC) Z-scan was proposed [1,2]. It is a simple, fast and efficient tool to obtain a broadband characterization of optical nonlinearities, such as two-photon absorption [1,2] excited state absorption [1] and nonlinear refraction [3] in different materials. From the application’s point of view, the knowledge nonlinearity spectrum is helpful in selecting the best operation wavelength for a specific device. In this work, we discuss the influence of the cumulative effect on the excited state absorption spectra achieved by means of the WLC Z-scan technique. The investigation was developed using an aqueous solution of meso-tetra(sulfonatophenyl) porphyrin molecules (TPPS₄) in its deprotonated and bi-protonated states because the ground and excited state properties are extremely influenced by the protonation state of the porphyrin ring [4]. The different states of protonation can be obtained by changing the pH of the solution. It is also worth point out that these molecules have potential application in cancer photodynamic therapy [4] so that the knowledge of their excited state properties in both states of protonation is imperative.

Experimental Setup

The experimental setup of WLC Z-scan is detailed in Ref. [1]. The WLC generation is achieved from 150 fs laser pulses at 775 nm delivered by a commercial Ti:sapphire chirped pulse amplified system CPA-2001 from Clark-MXR Inc., operating at 1 kHz repetition rate. Figure 1 shows the WLC spectrum and linear absorption spectra for deprotonated and bi-protonated TPPS₄ molecules.

Figure 1: Linear absorption spectra for deprotonated (doted blue line) and bi-protonated (dashed red line) TPPS₄ molecules and WLC spectrum (solid black line).
Results and Discussions

The nonlinear transmittance spectra for TPPS$_4$ obtained with the WLC Z-scan configuration are shown in figures 2(a) and 2(b) for deprotonated and bi-protonated states, respectively. The figure also exhibits the nonlinear spectra obtained through the single wavelength (SW) Z-scan technique using the optical parametric amplifier (OPA) as pump source.

![Figure 2](image_url)

**Figure 2:** Normalized transmittance versus wavelength obtained with WLC (red lines) and single wavelength Z-scan (open circles) for TPPS$_4$ in deprotonated (a) and bi-protonated (b) states. The blue solid line in 2(b) corresponds to the theoretical fitting taking into account the cumulative effect absorption spectra for deprotonated (dotted blue line) and bi-protonated (dashed red line) TPPS$_4$ molecules and WLC spectrum (solid black line).

The nonlinear spectra obtained with both techniques were normalized taking into account the non-absorbing spectral region once the intensities used in the two Z-scan configurations were different. Figure 2(a) indicates a good agreement between WLC and SW configuration for deprotonated sample. On the other hand, an obvious difference can be observed in the excited state spectra for the bi-protonated sample. The disagreement could be attributed to the cumulative effect probed by the blue-green spectral region of the WLC pulse once due to the positive group velocity the red components of the WLC propagates faster than the blue one. As a consequence, the red intrapulses components act first onto the sample promoting the molecules to the first excited state whose fluorescence decay time for TPPS$_4$ in both protonation states is around some nanosecond. In this way, the ground state population is transferred for the first singlet excited state causing the cumulative nonlinear effect probed by blue-green components of WLC pulse. In our experiment, blue-green intrapulse components are delayed in relation to red components by around 4 ps. The WLC chirp rate (18 fs/nm) was determined from optical Kerr effect measurements in hexane, using a strong pump pulse at 775 nm from the CPA laser and a weak WLC beam as a probe. The absence of cumulative effect on the nonprotonated sample is consequence of its very low absorption in the red region, which coincides with the most intense spectral region of the WLC spectrum (figure 1). This avoids an efficient transference of population in an initial moment and consequently the cumulative effect becomes negligible. To confirm the cumulative effect hypothesis, we considered a singlet three level system interacting with the WLC spectral intensity distribution employed in the experiment to calculate the population dynamics during the interaction of the pulse with the solution. Numerical simulation was carried out using the chirp rate value, ground and excited state absorption cross-sections obtained from linear absorbance and SW Z-Scan experiment, respectively. Besides, the respective concentrations were used together with the fluorescence decay time obtained from literature. With this procedure we were able to reproduce the excited state spectrum obtained with WLC Z-Scan (blue line in figure 2b).

Conclusions

In summary, the results indicate that cumulative effect should be taken into consideration when excited state absorption spectra are achieved by means of the WLC Z-scan technique. Besides, the data achieved from the simulation assuming a singlet three level system reveal that excited state absorption cross-section spectrum can be obtained from fitting of the nonlinear transmittance spectrum if known chirp rate and ground state absorption cross-sections.

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References


