Nonlinear optical absorption dynamics in free base tetrapyridyl porphiryn (H_2TPyP)

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ABSTRACT

This work report the nonlinear absorption dynamics in free base Tetrapyridyl porphyrin (H_2TPyP) solution, using a frequency doubled Q-switched and mode-locked Nd:YAG laser. A five-energy-level diagram was used to model the time evolution of nonlinear absorption of H_2TPyP, which allows the determination of excited state cross-sections and the intersystem crossing time. Single pulse and pulse trains measured shows a reverse saturable absorption (RSA).

Introduction

During the last years, nonlinear optical properties of porphyrin complex is under intensive investigation [1-2]. The interest in these materials has been stimulated not only by a quest for understanding their optical nonlinearities but also by their potential applications, such as optical limiters [3]. The dominant mechanism responsible for optical limiting in porphyrins is the reverse saturable absorption (RSA) [4], occurring when the excited absorption cross-section exceed that of the ground state, which decreases the transmittance of the material when the excited state is sufficiently populated.

The present work reports on the photo-physical study of Tetrapyridyl porphyrin (H_2TPyP) dissolved in $CH_3OH/CHCl_3$, using several techniques like: linear absorbance, time resolved fluorescence and Z-scan with pulse trains (ZSPT) [5]. In the last, pulse trains are produced by a frequency-doubled Q-switched and mode-locked Nd:YAG laser. A five-energy-level diagram was used to describe the time evolution of nonlinear absorption for H_2TPyP. This procedure enables us to study the nonlinear dynamics and yields excited state spectroscopic parameters.

We found a cumulative RSA process when the dynamics was investigated with Q-switched and mode-locked pulse trains. When 70 ps single pulse were employed, a RSA process was also observed. However, since in this case there is no significant population in the triplet state, because there is no time for the intersystem crossing to occurs, the RSA process is totally due to the excited singlet state.

Results and Discussions

The excited spectroscopic parameters can be determined by fitting the experimental data with the solution of a set of rate equations, associated with the five-energy-level diagram ilustrated in Figure 1. In this diagram, molecules excited to a vibronic state of the level $|1\rangle$ decay non-radiatively to the bottom of this band, with a characteristic time τ_{relax}, due to interaction beteween the molecules and the surroundings, transferring energy to the solvent. At this point, molecules in level $|1\rangle$ can decay radiatively to level $|0\rangle$ or undergo an intersystem crossing to the triplet state $|3\rangle$

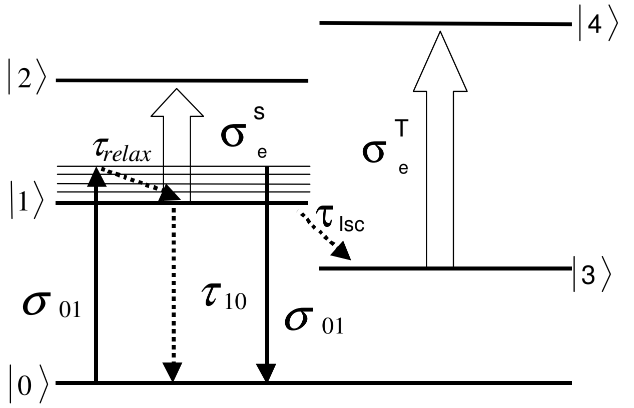
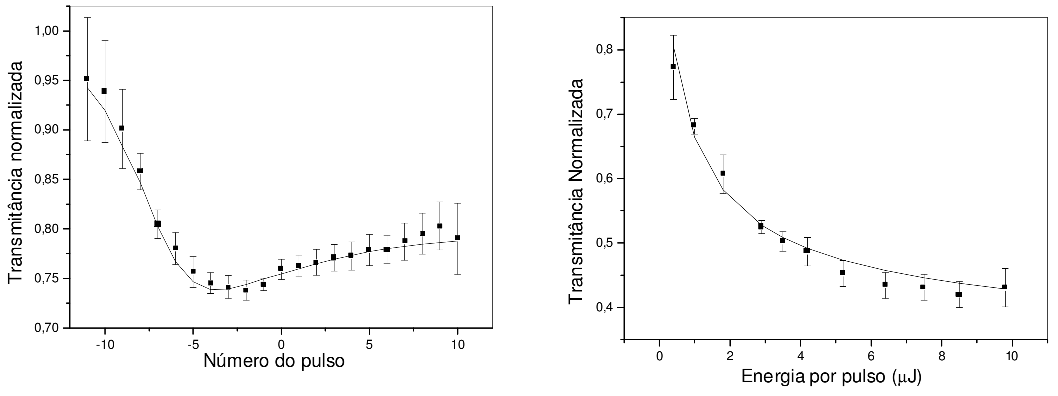


Figure1: Five-level-energy diagram used to explain the results of H_2TPyP

The relaxation time of the singlet excited state was estimated to be 50ps for fitting of both experiments (single pulse and pulse trains Z-scan) and is in agreement with the literature [6]. That of the fitting shows a high T_{isc}, about 32 ns, and a triplet absorption cross-section lower than singlet what explains the decrease of efficiency of RSA process with accumulative effect. The singlet absorption cross-section found is about tree times higher than ground state absorption cross-section, which explains the result of RSA for single pulse measurement. Both the measurements are show in the Figure 2.



(a) (b)

Figure2: (a) pulse trains and (b) single pulse results for TPyP

Conclusions

We investigated the nonlinear absorption dynamics of H_2TPyP and observed a reverse saturable absorption process. The linear absorbance gave a ground absorption cross-section of about $1.6\text{x}10^{17}$ cm^2, and the time resolved fluorescence yielded a singlet life time of about 8ns. Z-scan measurements with single pulse and pulse trains together with the five-energy-level diagram fitting gave us a 50ps relaxation time for the singlet excited state, 35 ns of intersystem crossing time, and $6\text{x}10^{-17}$ cm^2 and $2.1\text{x}10^{-17}$ cm^2 for the singlet and triplet absorption cross-sections, the value of of vibronic singlet relaxation time suggests that it is due to the cooling of molecules by interaction with the surrounding giving extra energy for solvent molecules.

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