

## Study of resonant nonlinearities with time-resolved fluorescence using picosecond train of pulses

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### Abstract

*The Z-scan technique has been used to study the nonlinearities of a variety of photosensitive materials. In resonant condition, the excited states determine the nonlinear properties. Using a Q-switched and modelocked Nd:YAG laser, that delivery trains with about 20 strong modelocked pulses with 70ps duration spaced by 13ns at 532 nm, we are able to resolve the dynamic of several nonlinear effects such as saturable and reverse saturable absorption. Here, looking at the fluorescence, we have mapped the first singlet excited state dynamic. A five or three-energy-level model were applied to describe the dynamic of these effects. The absorption cross-section, lifetimes of excited states and intersystem crossing rate could be obtained.*

### Introduction

The Z-scan technique has been used to study the nonlinear properties in a variety of photosensitive materials. Traditionally, this technique is used extensively to study refractive and absorptive nonlinearities. In resonant condition, the excited states determine the nonlinear properties. Recently, we have introduced a simple experimental technique to study the refractive and the absorptive nonlinear dynamics with pulse train [1, 2]. By this technique, we are able to determine several important parameters from the nonlinear sample such as cross-sections and lifetime dynamics of the excited states. Since several interesting nonlinear materials presents fluorescence, here we also extended our pulse train method to map the excited state dynamics looking at the fluorescence behavior.

### Materials and Methods

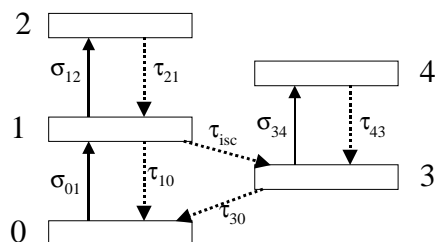
There are several materials with interesting nonlinear effects that can be used in devices. The performance of these devices relies on the type and the magnitude of these nonlinearities. For example, there are materials where the nonlinear effects suffer saturation. In this case, there is two type of opposite behavior: one presents a saturation of the absorption (SA) and other a reverse saturation of the absorption (RSA). These nonlinear effects play important role in several devices such as in optical limiters, switches and memory, for example.

Using a Q-switched and modelocked Nd:YAG laser, that delivery trains with about 20 strong pulses with 70ps duration spaced by 13ns at 532nm, we can resolve the dynamics of resonant nonlinear effects in the picosecond and nanosecond time scale. Several resonant nonlinear material exhibits long excited states lifetime. Indeed, a cumulative nonlinearity can take place in a sample if the lifetime of one excited state, responsible for one nonlinear process, is longer than the separation of the excitation pulses. Looking at the fluorescence we also can observe a cumulative effect if any slow or dark (non-fluorescent) state take place in the transition process during the pulse train interaction. We have observed that pulse train fluorescence (PTF) can be used as complementary measurements with absorptive and refractive ones to obtain the dynamic of nonlinear effects due to their high sensitivity and low noise.

To demonstrate this new method, experiments have been carried out on a fluorescent porphyrin (PPhs) solution. This molecule presents excited singlet and triplet states. Porphyrins are macro-cyclic aromatic molecules having four pyrrole rings occupying position at four corners of square and connected by a unsaturated bridge. To assure structure stability, the PPh ring presents a central part constituted by either two protons or a metal ion, M<sup>2+</sup>. The porphyrins belong to a class of important material for their potential

application in photo-dynamic therapy (PDT), for example. Considerable effort has been directed towards creating new efficient porphyrins for PDT application. These molecule presents excited singlet and triplet states. The triplet state play the most important role to the mechanism of action of drugs base on porphyrins molecules.

A five-energy-level model were applied to describe the dynamic of the effects.



**Figure 1:** Five-level diagram: fundamental level (0), singlet excited states (1) and (2), and triplet excited states (3) and (4). The cross-sections and lifetimes for each transition are  $\sigma$  and  $\tau$ , respectively.

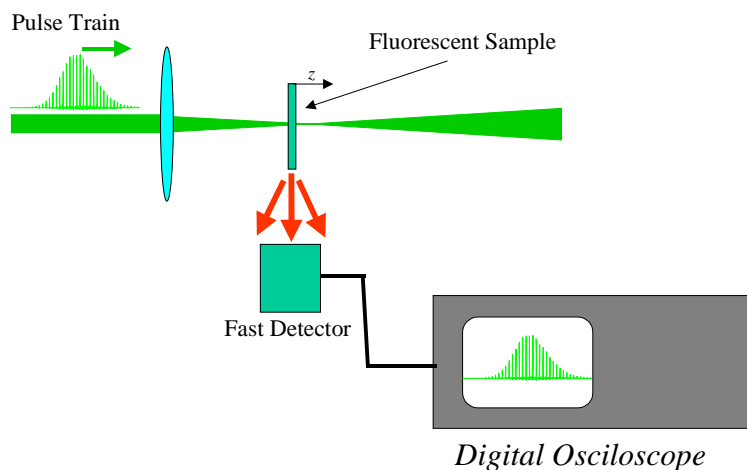
The rate equation for all five-energy-level can be described by:

$$\begin{aligned}\frac{dN_0}{dt} &= \frac{-\sigma_{01}I(t)}{\hbar\omega} N_0 + \frac{N_1}{\tau_{10}} + \frac{N_3}{\tau_{30}} \\ \frac{dN_1}{dt} &= \frac{-\sigma_{12}I(t)}{\hbar\omega} N_1 + \frac{\sigma_{01}I(t)}{\hbar\omega} N_0 + \frac{N_2}{\tau_{21}} - \frac{N_1}{\tau_{10}} - \frac{N_1}{\tau_{isc}} \\ \frac{dN_2}{dt} &= \frac{\sigma_{12}I(t)}{\hbar\omega} N_1 - \frac{N_2}{\tau_{21}} \\ \frac{dN_3}{dt} &= \frac{-\sigma_{34}I(t)}{\hbar\omega} N_3 + \frac{N_1}{\tau_{isc}} - \frac{N_3}{\tau_{30}} + \frac{N_4}{\tau_{43}} \\ \frac{dN_4}{dt} &= \frac{\sigma_{34}I(t)}{\hbar\omega} N_3 - \frac{N_4}{\tau_{43}}.\end{aligned}$$

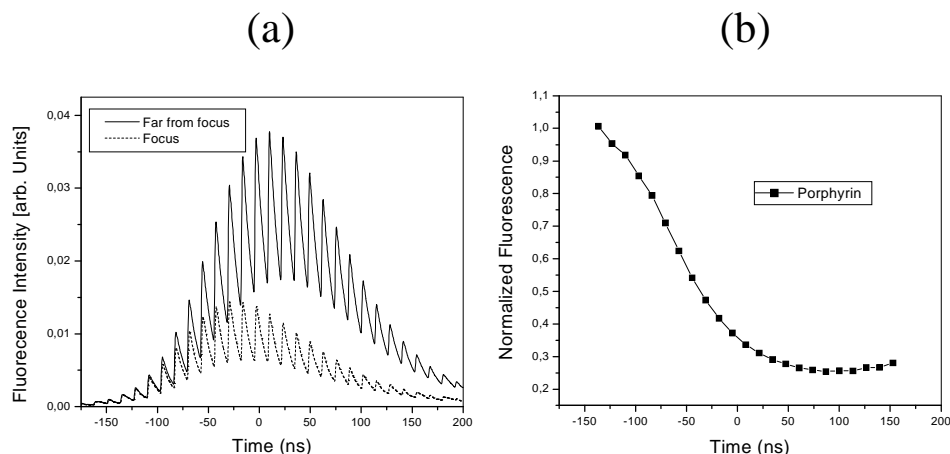
Porphyrin molecules, initially in the fundamental state  $S_0$  (0), are excited to the  $S_1$  state (1). At this point, there are two possible relaxation pathways: one back to  $S_0$  and other to  $T_1$  (3) states, both with relaxation lifetimes  $\tau_{10}$  and  $\tau_{isc}$ , respectively. This process transfers part of the population from singlet to triplet state. At same time, part of population of  $S_1$  state can be transferred to  $S_2$  (2) state and from  $T_1$  (3) to  $T_2$  (4) state. The effective absorption is determined by the density of the population at each state and by their cross-sections. The population and the cross-section of the singlet state can be probed with single fast picosecond pulse. Considering that the intersystem crossing time is about some nanoseconds, the pulse trains can be used to probe the population density, the lifetime of excited states, the cross-section and the intersystem crossing rate by measuring the nonlinear absorption dynamic. We also are able to map the excited state dynamic looking at the fluorescence signal. The fluorescence signal is proportional to the population density of the first singlet excited state  $S_1$ . So, it carry information of singlet excited state density, lifetime and intersystem crossing rate.

## Results and Discussions

Our Z-scan experiment used a single pulse or a pulse trains from a frequency-doubled Q-switched and mode-locked Nd:YAG laser, operating at 532 nm with 10 Hz of repetition rate to avoid thermal effects. The FWHM of the pulse is 70 ps, with a gaussian spatial profile. First, we have measured the nonlinear absorption properties looking at the absorption behavior [1, 2]. Second, using the PTF technique, we were able to better determine the intersystem crossing dynamic.



**Figure 2:** Experimental setup of fluorescence measurements with pulse train.



**Figure 3:** Fluorescence signal of a porphyrin in DMSO solution obtained by a fast photodetector (a). The normalized fluorescence (NF) corresponds to the ratio between the peak of fluorescence signal at focal point (high intensity) with signal far from focal point (low intensity).

The decrease of the NF signals at functions of pulse sequence reveal the contribution of triplet state since it is a non-fluorescent state. The lifetimes of first excited states and intersystem crossing rate can be obtained by fitting the normalized fluorescence signal at function of pulse train sequence. These results can be compared with the data obtained with the absorption method. So far, good agreements between these pulse trains techniques have been obtained. For this particular porphyrin, we have obtained  $\tau_{10} \approx \tau_{isc} = 14 \pm 2$  ns,  $\sigma_{12} = 4 \times 10^{-17}$  cm<sup>2</sup> and  $\sigma_{34} = 2.1 \times 10^{-17}$  cm<sup>2</sup>. Also, this technique can be used, at least, to determine the singlet lifetime and intersystem crossing rate in sample that possess same cross-sections of fundamental and the excited states where the absorption methods can not be used.

## Conclusions

In this work we have developed a new technique to study the dynamic of excited states population using train of picosecond pulses. The train of pulses induces a type of fluorescent signal that carry information about the dynamic of excited states. The lifetimes of excited states and intersystem crossing rate can be obtained. Due to its simplicity, this technique can be very useful to researcher who wants to study the intersystem crossing rate of any type of fluorescent sample.

## Acknowledgements

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## References

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