Induced transparence on DR19-Cl (Disperse Red – 19 Cloro) solution using picosecond pulses

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Abstract

The Z-scan technique has been used to study the fast nonlinear saturable absorption on DR19-Cl solution. We observed that the effect of transparence is due to the S1 band conformation since this band presents a negligible cross-section. This transparence is proportional to the accumulative population in S1 band, and is a function of the laser pulse intensity and the lifetime. A three-energy-level model was applied to describe this effect and the S0 (cis) cross-section was obtained. This sample present no nonlinear refraction, this results can be associated with the relatively equal conformational cis and trans nonlinear susceptibilities.

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 DR19-Cl/DMSO solutions using the Z-scan technique [11-12] with picosecond laser pulses at 532nm. A three-energy-level model [13], was used to describe the dynamics of the *trans-cis-trans* photoisomezation, allowing the determination of excited state parameters.

Experimental Setup

Our Z-scan experiment have used single pulse extracted from the pulse train of a frequency-doubled Q-switched and mode-locked Nd:YAG laser, operating at 532nm with a 10Hz repetition rate. The FWHM pulse duration was 100ps, and the spatial profile of the laser beam was approximately Gaussian. The laser beam was focused by a f=12cm focal length and the waist size was w_0 = 25μm. The 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.

To measure the lifetime of the nonlinear absorption process we have used the degenerate pump-probe absorption technique. The light source was a tunable OPA pumped by a 150fs with 775nm at 1KHz repetition rate delivered by a Ti:sapphire amplified laser system. The OPA generates a 120fs pulse at 532nm. The beam from OPA was splitted in the strong pump and weak probe beam by a thin beam splitter. The strong pump pulse and weak probe pulse were focused in the nonlinear sample, at same point, by a f=12cm lens. A delay stage was used two scan the time between the two pulses. A big area silicon detector (PIN) and a locking amplifier was used to detect the weak beam and detect the transient absorption caused by the pump beam.

Results and Discussions

The DR19-Cl was dissolved in DMSO at 0.15mg/ml. The linear absorption spectrum of solution was obtained with Cary 17 spectrometer. At room temperature most of molecules are in the *trans* conformation. This solution presents a band associated with n-π^* transition centered at 530 nm.

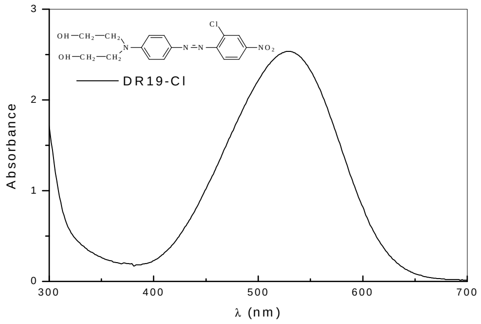

Figure 1: Linear absorbance spectrum and molecular structure of DR19-Cl in DMSO solution.

The results obtained with the Z-scan technique with open aperture (presented in Fig. 3(a)) can be described by the three-energy-level, shown in Fig 2. 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 (τ_t and τ_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, this process is less efficient because the smaller *cis* cross-section. After several photoisomerization cycles, a population of molecules in the S_0 (*cis*) ground state band is created, which generates a different nonlinear absorption.

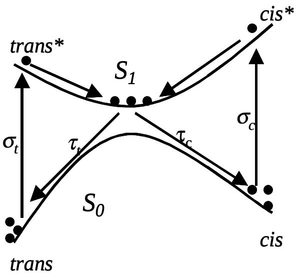

Figure 2: Three-energy-level diagram model used to explain the transparence of DR19-Cl solution.

In Fig. 3(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 $\sigma_c = (9 \pm 0.2)\text{x}10^{-17}\text{cm}^2$. In this fitting, we used the *trans* ground state cross-section $\sigma_t = (11 \pm 0.1)\text{x}10^{-17}\text{cm}^2$, obtained by UV-Vis absorption in a solution with (2.5 ± 0.1) $\text{x}10^{17}$ molecules/cm^3, and the lifetime relaxation (τ_t, τ_c). These times was determined by femtosecond pump-probe experiments, showed in Fig. 3(b), are (2.5 ± 0.4) ps, for both relaxation. These lifetimes are similar to those described by L ednev *et al* [14-15] to azobenzene molecule.

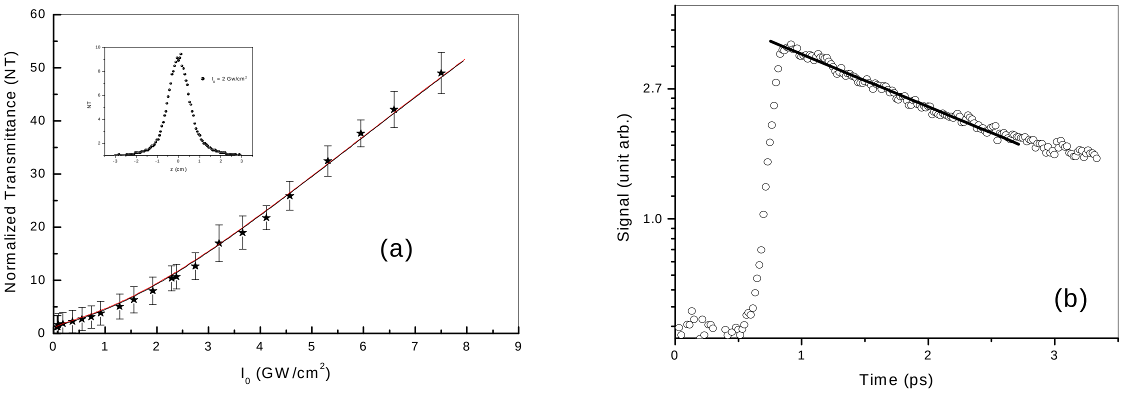

Figure 3: (a) The normalized transmittance (NT) at function of laser irradiance, the star is the experimental data and the solid line is the simulation using a three-energy level model. (b) Transient absorption obtained by femtosecond pump-probe, the open circle is the experimental result and the solid line represent the exponential decay with characteristic time of τ=2.5ps.

Although there is an accumulation of the population in the S_0 (*cis*) state, that presents lower cross-section than the S_0 (*trans*) state, the responsible for the fast and strong transparency is due to the cumulative population in the excited S_1 band. The difference in the cross-section of both fundamental states (*cis* and *trans*) is just about 11:9 ratio, not enough to explain the experimental results. On the other side, the S_1 band presents a negligible absorption cross-section, i.e. a infinity ratio between fundamental and excited state cross-section.

We also have tried to obtain the nonlinear refractive of the DR19-Cl solution with small aperture Z-scan technique, but this solution presents no refractive Z-scan signature at the energy level used. The absence of Z-scan signature indicates that the refractive index of this solution is very small. We can explain this results if the sample has similar susceptibilities of the fundamental and excited states for both conformational configuration.

Conclusion

We investigated the fast transparence effects in a DR19-Cl/DMSO solution.. Open aperture Z-scan measurements have been accomplished with single 100 ps pulses and the nonlinear absorption could be obtained and explained with three-energy-level model. The theoretical model allowed the determine the *cis* conformation absorption cross-section. The fast and strong saturation of absorption could be explained due to an increase in the S_1 molecules population. Using a pump and probe technique we are able to infer the response time of saturation process as about 2.5ps. Finally, the nonlinear refraction was not observed in this compound, this indicates a similar susceptibilities of the fundamental and excited states for both conformational configuration.

Acknowledgements

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