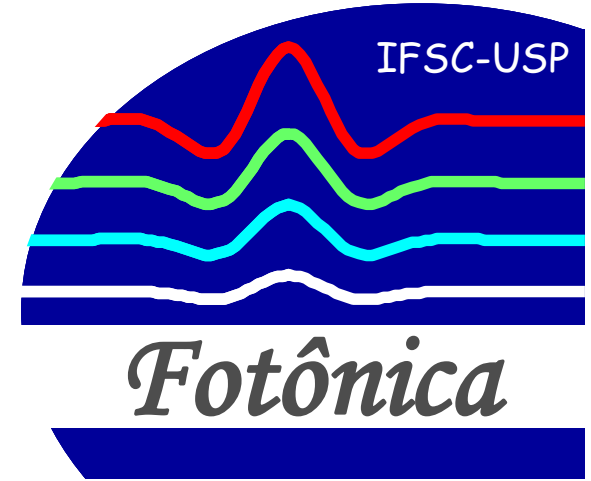# Degenerated two-photon absorption spectra in Azocompounds

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Abstract

This work reports a study of degenerated two-photon absorption (2PA) spectra on several azocompounds dissolved in DMSO. The 2PA spectra was measured with the open aperture Z-scan technique, The results obtained demonstrate that 2PA cross-section depends on the conjugation length and the charge of acceptors and donors groups. In the 2PA spectrum, it was observed two distinct behaviors: the appearing of a peak around 1000 nm and an increase of the 2PA intensity for wavelengths below 750 nm. The 2PA peak occurs at almost twice the position of the lowest energy peak of the corresponding linear absorption, once for asymmetric molecules the selection rules for one and two photon absorption are broken. Thus, the final state by the transition at the 2PA peak must be the same as that by the transition at the one-photon absorption. The enhancement of the 2PA cross-section when the wavelength of excitation approaches the resonance, as expected by the some-over state model.
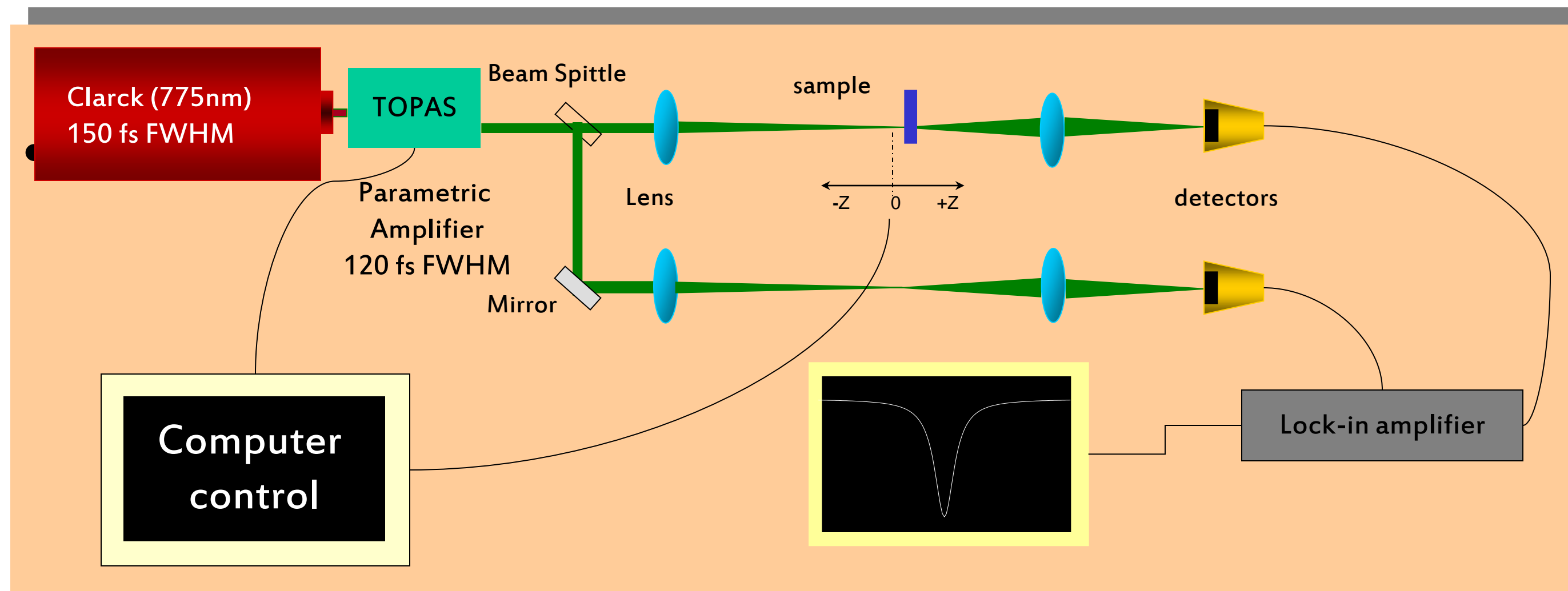
The azobenzene-compounds

Molecule structures and absorbance spectra
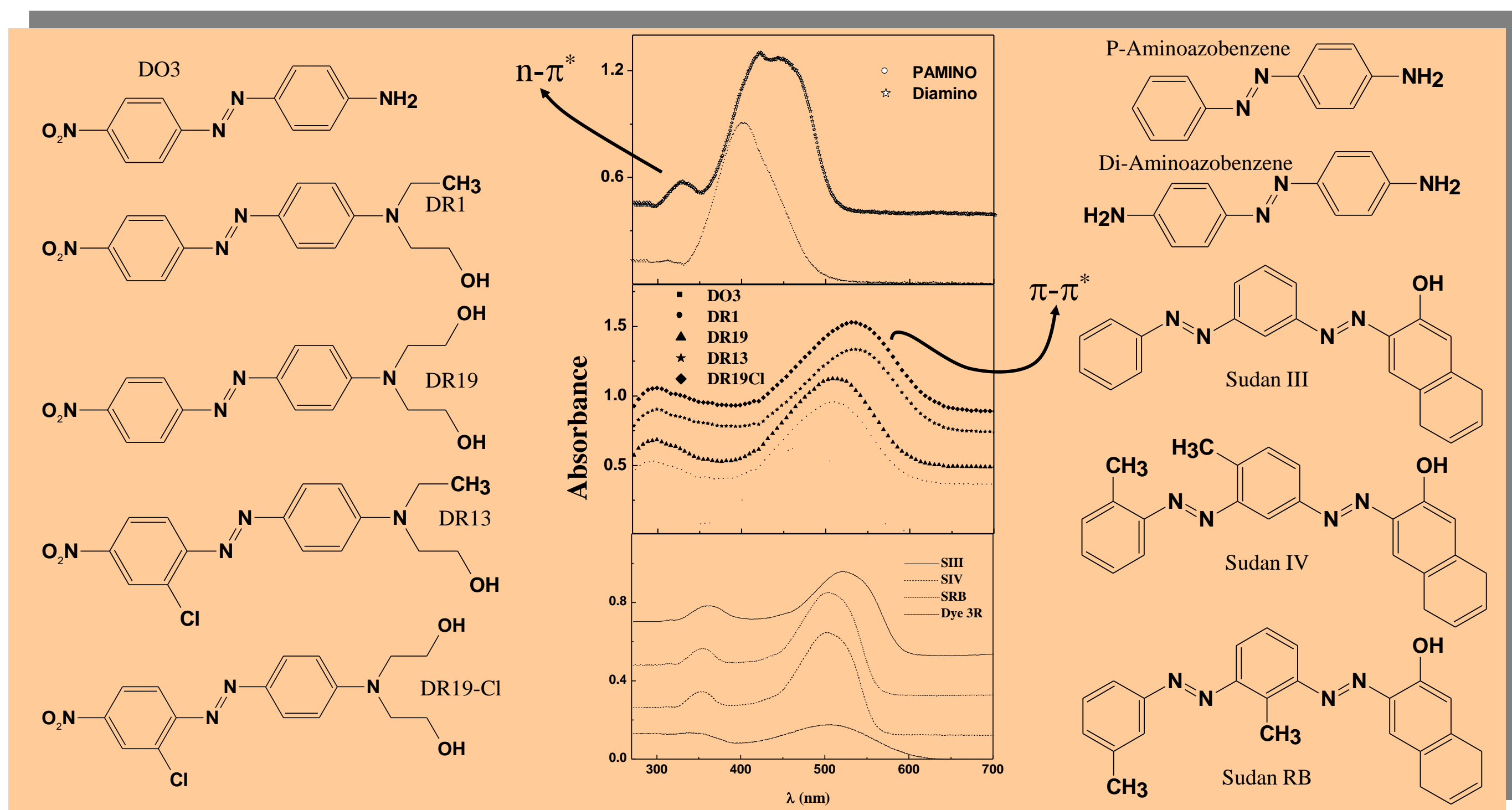
Two real state associated with the azo group and (π that can influence the two-photon transitions.

Z-Scan experimental setup and typical results

Our Z-scan experiment employ laser pulses from a commercial optical parametric amplifier (TOPAS) pumped by a 150 fs pulses at 775 nm delivered by a Ti:sapphire chirped pulse amplified system (CPA-2001, from Clark-MXR Inc.), operating at 1kHz repetition rate. The FWHM pulse duration from TOPAS was about 120 fs, and the spatial profile of the laser beam presented an approximately Gaussian distribution.
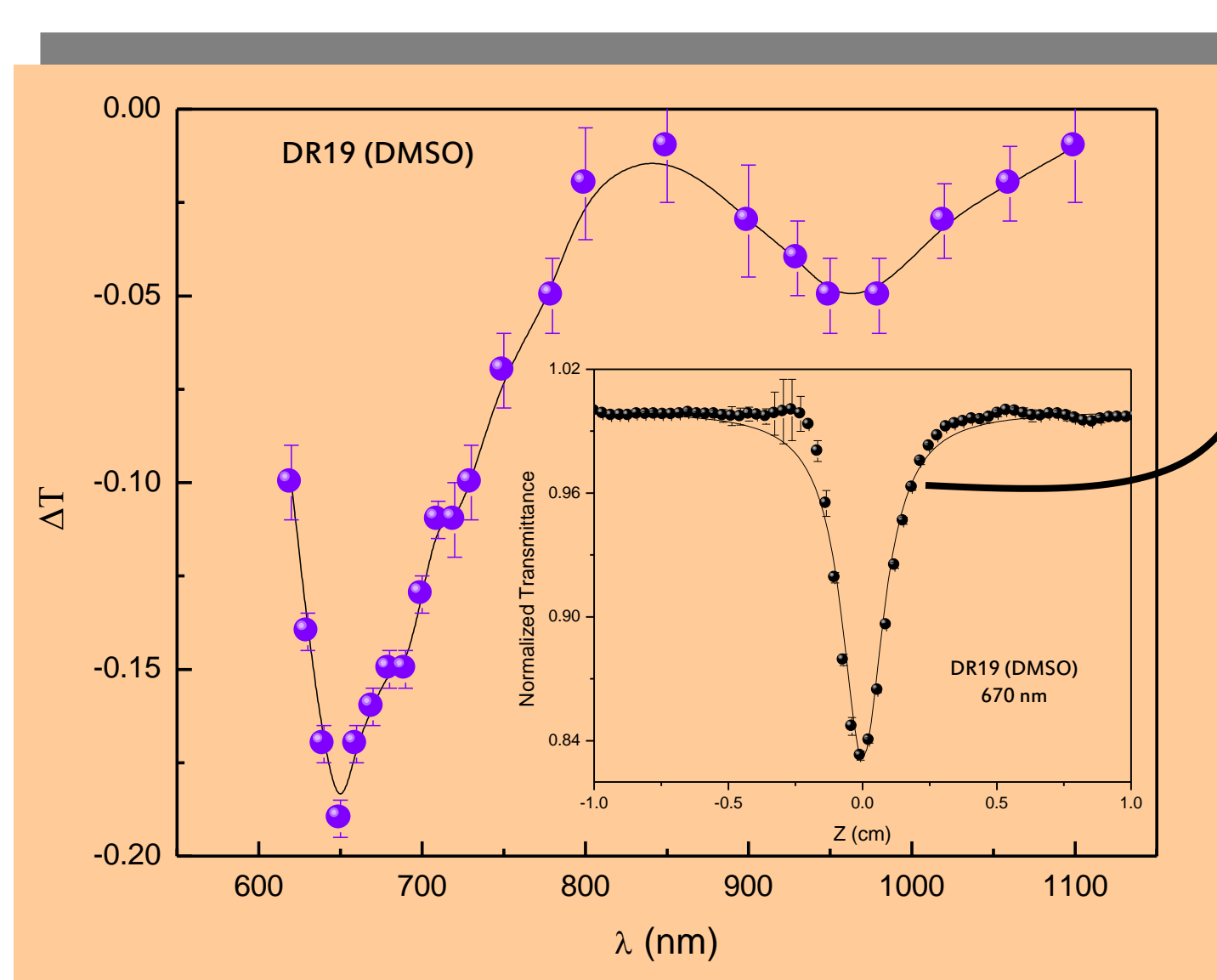
Typical curve of 2PA. The fit are obtained by rate equations that describe two–energy-level diagram.
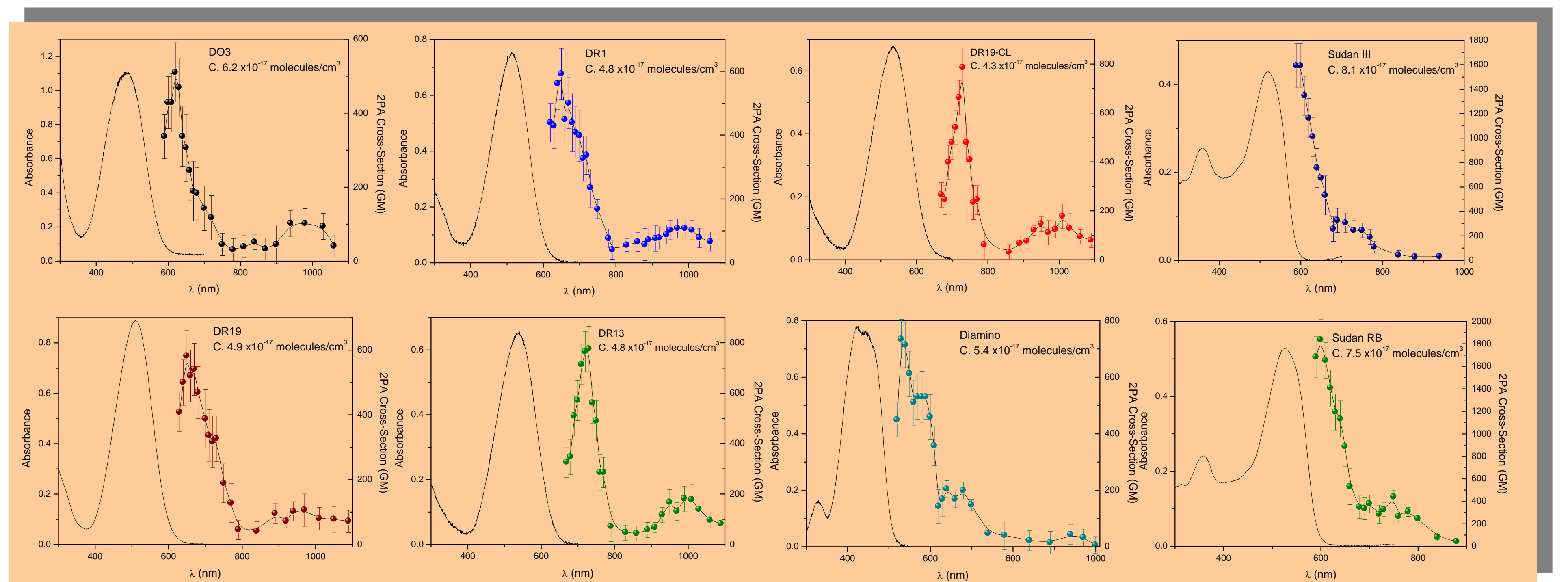
ΔT versus wavelength excitation

$$\frac{dn_g(t)}{dt} = -n_g(t)W_{g1} + \frac{n_1(t)}{\tau_{1g}}$$

$$\frac{dn_1(t)}{dt} = +n_0(t)W_{g1} - \frac{n_1(t)}{\tau_{1g}}$$

$$W_{g1} = \frac{\delta_{g1}I^2}{2h\nu}$$

$$\beta(t) = \frac{N}{h\nu}(\delta)$$

Degenerated 2PA cross-section (δ)

The results obtained demonstrate that 2PA cross-section depends on the conjugation length and the charge of acceptors and donors groups. In the 2PA spectrum, it was observed two distinct behaviors: the appearing of a peak around 1000 nm and an increase of the 2PA intensity for wavelengths below 750 nm.

Sum-over states (S.O.S) analyses

$$\delta(\nu) \propto \frac{\nu_p^2}{(\nu_{j0} - \nu_p)^2 + \Gamma_{j0}^2} \times \left[\frac{A_1}{(\nu_{f_10} - 2\nu_p)^2 + \Gamma_{f_10}^2} + \frac{A_2}{(\nu_{f_20} - 2\nu_p)^2 + \Gamma_{f_20}^2} \right]$$

Γ_{j0} is the Linewidth of the first state

$\Gamma_{f_10}, \Gamma_{f_20}$ are Linewidths of the 2PA transitions

ν_{j0} is the one-photon transition frequency

ν_{f_10}, ν_{f_20} are 2PA transitions frequencies
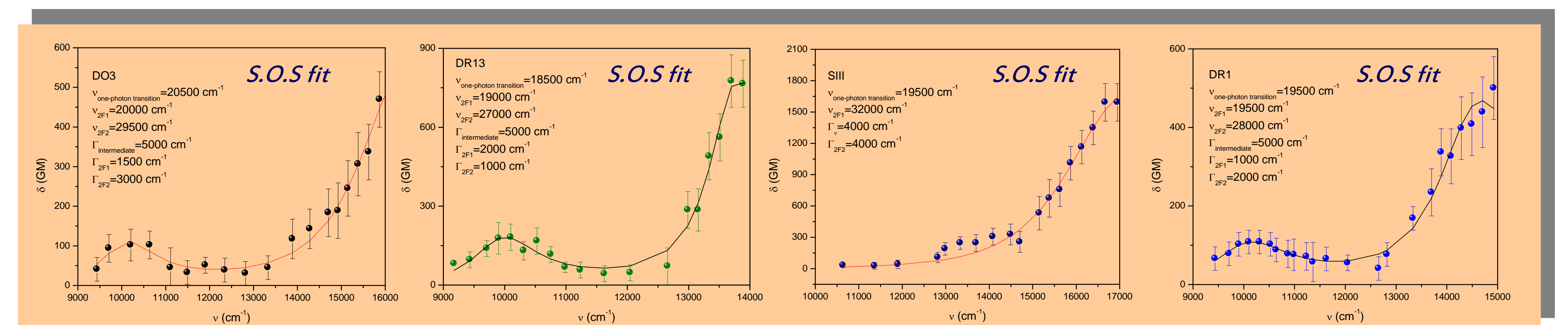
Conclusions

The 2PA peak occurs at almost twice the position of the lowest energy peak of the corresponding linear absorption, once for asymmetric molecules the selection rules for one and two photon absorption are broken. Thus, the final state by the transition at the 2PA peak must be the same as that by the transition at the one-photon absorption. The enhancement of the 2PA cross-section when the wavelength of excitation approaches the resonance, as expected by the some-over state model. Thanks to Prof. Dr. O.N. Oliveira Jr., Prof Dra. T.Z. Atvars, S.B. Yamaki and D.S. dos Santos for helpful discussions