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Two-photon absorption spectrum in diazoaromatic compounds

L. De Boni^a, A.A. Andrade^a, S.B. Yamaki^b, L. Misoguti^a, S.C. Zilio^a, Teresa D.Z. Atvars^b, C.R. Mendonca^{a,*}

^aDepartamento de Física e Ciência dos Materiais, Instituto de Física de São Carlos, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil

^bInstituto de Química, Universidade Estadual de Campinas, Unicamp, Caixa Postal 6154, 13084-971, Campinas, SP, Brazil

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ABSTRACT

This Letter studies the degenerate two-photon absorption (2PA) spectra of three diazoaromatic compounds using Z-scan with fs-pulses. The 2PA spectra exhibit resonant enhancement of the nonlinearity as the excitation approaches the linear absorption. The absence of 2PA to the $\pi\pi^*$ band is related to the weaker donor/acceptor groups, and lower symmetry of diazoaromatic compounds, in agreement with our semi-empirical calculations. The higher magnitude of the 2PA cross-section, in comparison with single azoaromatics, demonstrates the positive effect of increasing conjugation. The decrease of 2PA cross-section with temperature is attributed to thermally induced torsions, which decreases the effective conjugation of diazoaromatic molecules.

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1. Introduction

The study of two-photon absorption (2PA) in organic materials has received considerable attention in the last few years, since it can be exploited in an ever-growing number of technological applications [1]. The spatial confinement of excitation and the ability to excite molecules with half of the energy required for linear absorption can be employed in three-dimensional microfabrication [2,3], three-dimensional optical storage [4,5], two-photon fluorescence imaging [6–8], two-photon photodynamic cancer therapy [9,10] and optical power limiting [11,12]. Motivated by these applications, efforts to understand the relationship between molecular structure and 2PA, aiming to design compounds with larger 2PA cross-section, have been carried out, leading to design strategies for novel organic materials [13–17].

Azoaromatic compounds have been extensively investigated due to their potential use in optical devices employing optically induced birefringence [18], surface relief gratings [19] and second harmonic generation [20]. However, the interest in their third-order nonlinear optical properties and its applications is a more recent subject [21–23]. Recently, we studied the correlation between the 2PA and structural molecular features in a series of azoaromatic compounds [24,25], as well as the effect of temperature on their 2PA cross-section, which was related to thermally induced changes in the molecular conformation [26].

In this work, we report a study on the two-photon absorption spectrum of three azoaromatic compounds possessing two azo bonds between three benzene rings, so called diazoaromatics. The nonlinear properties are carried out with a tunable femtosec-

ond optical parametric amplifier operating at nonresonant conditions. The 2PA cross-sections measured in the enhancement region are three times higher than the ones observed for single azoaromatic compounds because of the higher conjugation length. Due to the smaller permanent dipole moments and molecular symmetry, these compounds do not present 2PA around 1000 nm, related to $\pi\pi^*$ transition. We also demonstrated that the decrease of the 2PA cross-section for three Sudans diazoaromatic molecules with the increase of the sample temperature is related to thermally induced torsional motion that diminish the molecular effective conjugation length.

2. Experimental

2PA cross-section was determined in three different diazoaromatic compounds: Sudan III (S3), Sudan IV (S4) and Sudan Red (SR), purchased from Sigma–Aldrich. The molecular structures are shown in Fig. 1. All samples were dissolved in dimethyl sulfoxide (DMSO) and placed in a 2 mm-thick quartz cuvette to perform the linear and nonlinear optical measurements. The linear absorption spectra, in the UV–vis–IR region, were obtained with a Cary 17 spectrophotometer, with samples concentrations of 8×10^{-5} mol/L. Nonlinear measurements were performed with 1.2×10^{-3} mol/L.

Two-photon absorption measurements were carried out with the open aperture Z-scan technique [27], which is a simple and sensitive method to investigate nonlinear optical processes. This technique has been shown to be an excellent option to study nonlinear optical properties of nonfluorescent molecules, as the case of the diazoaromatic compounds studied here. In the Z-scan technique, by monitoring the transmittance change as the sample is scanned through the laser focal plane, an absorptive Z-scan signature is generated. By fitting the experimental curve (normalized transmittance data) [27], we are able to determine the 2PA cross-section,

* Corresponding author. Fax: +55 16 3373 80 85.

E-mail addresses: crmendon@ifsc.usp.br (C.R. Mendonca), crmendon@fas.harvard.edu (C.R. Mendonca).

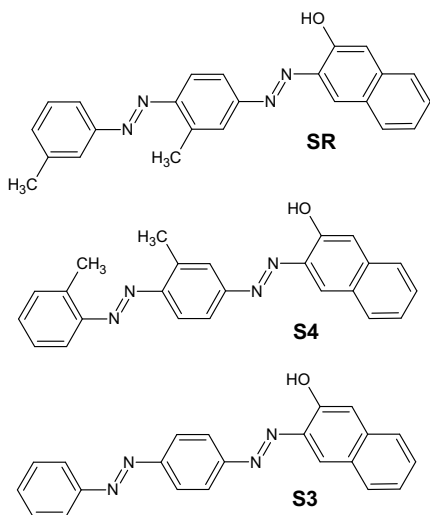


Fig. 1. Molecular structures of Sudan R (SR), Sudan 4 (S4) and Sudan 3 (S3).

δ , which is usually expressed in Göppert–Mayer units (GM), with $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s molecules}^{-1} \text{ photon}^{-1}$. The Z-scan measurements were performed using 120 fs laser pulses from an optical parametric amplifier, pumped by a Ti:sapphire laser system (150 fs, 775 nm and 1 kHz). A Gaussian distribution of the beam profile was achieved by spatial filtering.

Two-photon absorption measurements as function of temperature were carried out using the same laser system. In this experiment, the sample temperature was controlled using a Peltier element. Temperature range was from 18 to 110 °C. Samples were thermally equilibrated for five minutes before the Z-scan measurements at every temperature.

3. Results and discussion

The molecules used in the present study are a homologue series of Sudan dyes, whose chemical structure are showed in Ref. [24] (Fig 1). The main difference lies in the presence of two azoaromatic groups in the conjugated bridge, and a naphthyl moiety added to one of the azo groups. Thus, the diazoaromatic compounds studied here have almost three times longer conjugation length than single-azoaromatic molecules.

The linear (dashed line) and two-photon (circle) absorption spectra of three samples are presented in Fig. 2. The linear absorption spectra for the diazoaromatic compounds (dashed line in Fig. 2) present a peak at approximately 500 nm, which corresponds to the lower energy $\pi \rightarrow \pi^*$ electronic transition, being completely transparent in the near infrared region. Therefore, the two-photon absorption measurements were carried out only in the linear absorption transparent region. In Fig. 2, each circle represents the 2PA cross-section for a specific excitation wavelength, obtained by fitting the Z-scan curve at that wavelength with the expression given in Ref. [28].

As seen in Fig. 2 (circles), a monotonic increase of the 2PA cross-section was observed in the spectral region close to the onset of the linear absorption. This behavior is attributed to the resonant enhancement of the nonlinearity, as predicted by the increase of the denominator in the sum-over-states model first term in Eq. (1), when the excitation wavelength approaches the linear absorption band [29–31]. The 2PA cross-sections, observed in Fig. 2, are about three times higher than those reported for single azoaromatic compounds [24], for the enhancement region. The molecules used in the present study have a similar structure, in general, to

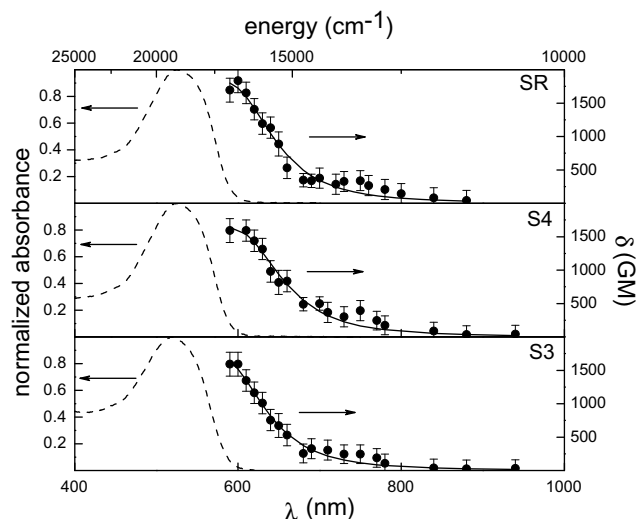


Fig. 2. Linear (left axes) and degenerate two-photon absorption (right axes) spectra for the diazoaromatic compounds. The solid line represents the theoretical fitting obtained with the sum-over-states model.

those of Ref. [24]. The main difference lies in the presence of two azoaromatic groups in the conjugated bridge, and a naphthyl moiety added to one of the azo groups. In this way, the diazoaromatic compounds studied present almost three times the conjugation length of single-azoaromatic molecules. The 2PA cross-section for S3, S4 and SR, at the enhancement region ($\delta \sim 1600 \text{ GM}$), is much higher than that observed for azobenzene type compounds ($\delta \sim 500 \text{ GM}$) [24,25]. Such values are directly related with the conjugation length of these molecules.

Considering the experimental error of our measurements, no 2PA peak was observed at twice the wavelength of the $\pi\pi^*$ absorption band for the samples studied here. Such result indicates the absence of the dipolar contribution on the two-photon absorption process for the diazoaromatic compounds, probably because of its small permanent dipole moment. In order to check for that, we used AM1 and PM3 semi-empirical calculations. With these methods, we were able to calculate μ_{11} and μ_{00} , from which we obtained $\Delta\mu_{01} = \mu_{11} - \mu_{00}$ of approximately 0.3 D. This value is much smaller than the ones observed for others azoaromatic compounds ($\sim 10 \text{ D}$) [25] and stilbene type molecules ($\sim 7 \text{ D}$) [39], which explains the absence of the 2PA band in infrared region.

In order to be able to relate the nonlinear optical response only to a few transition energies in the sum-over-states treatment [32], we used a simplified three-energy model [33–37]. In such approximation, the sum-over-states formula is truncated by assuming that there is a single excited state, $|1\rangle$, that is strongly one-photon allowed, and that there is only one upper-lying two-photon allowed excited state, $|2\rangle$, that is strongly coupled to $|1\rangle$. In this case, the expression for the 2PA cross-section δ is given by:

$$\delta(\nu) = \frac{4}{5\pi} \frac{(2\pi)^4}{(ch)^2} \frac{\nu^2}{(\nu_{01} - \nu)^2 + \Gamma_{01}^2} \cdot \frac{|\mu_{12}|^2 \cdot |\mu_{01}|^2 \cdot \Gamma_{02}}{(\nu_{02} - 2\nu)^2 + \Gamma_{02}^2} \quad (1)$$

where, h is the Planck constant, c is the speed of light and ν is the optical frequency. ν_{nm} , Γ_{nm} and μ_{nm} represent the transition energy, damping constant and transition dipole moments, respectively, of the $n \rightarrow m$ transition. This expression contains a two-photon term, which is related to the excited state, $|2\rangle$. The term outside the brackets describes the enhancement of the nonlinearity when the one photon transition is approached.

The solid line in Fig. 2 represents the fit of Eq. (1) to the experimental 2PA cross-section, with $\Gamma_{02} = 5000 \text{ cm}^{-1}$ taken from Ref.

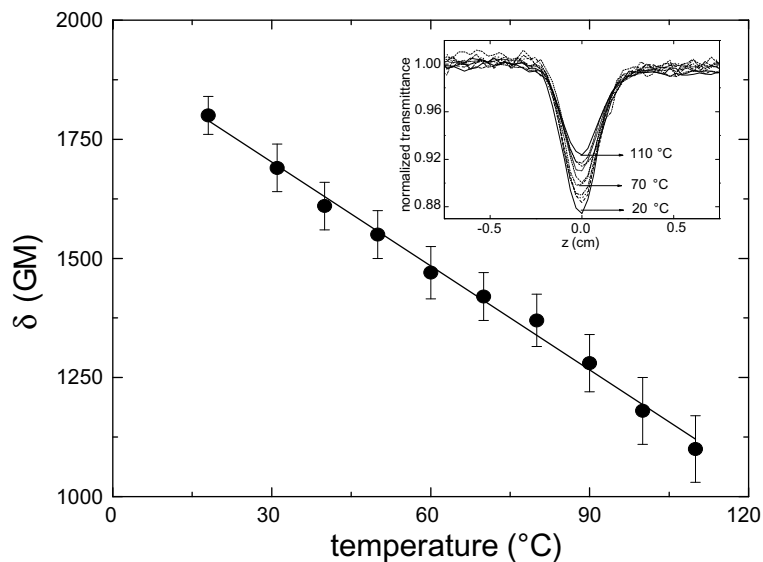


Fig. 3. Two-photon absorption cross-section as a function of temperature for SR at 650 nm. The solid line represents the fitting obtained with the sum-over-states model. The slope of this curve, $-7 \text{ GM}/^\circ\text{C}$, gives the thermal two-photon absorption coefficient, $d\delta/dT$. The inset shows the Z-scan measurements for different temperatures.

[38]. Based on the $\pi\pi^*$ bandwidth of the diazoaromatic compounds, we obtained $\Gamma_{01} = 2000 \text{ cm}^{-1}$, which was used as a fixed parameter in the fitting procedure. ν_{01} was determined from the maximum of the $\pi\pi^*$ band. μ_{01} was calculated through the oscillator strength for the transition $|0\rangle \rightarrow |1\rangle$ ($\pi\pi^*$ band), according to Ref. [39]. μ_{12} and ν_{12} were treated as adjustable parameters. The 2PA spectrum is a combination between the one-photon enhancement effect and the two-photon excitation to state $|2\rangle$ in the UV region. If this state is not taken into account, only the one-photon enhancement term is not enough to depict the nonlinear effect observed. The fit of the experimental data gives $\nu_{12} = 30000 \text{ cm}^{-1}$ ($\sim 330 \text{ nm}$) for the second state.

Fig. 3 shows the 2PA as function of the temperature (circles) for SR. The Z-scan measurements as a function of the temperature (inset of Fig. 3) were carried out at 650 nm, close to the maximum value of the 2PA. In Fig. 3, the solid line represents the fit obtained with sum-over-states model, considering temperature dependence for the transition frequency, ν_{01} , in the resonance enhancement term (outside the brackets) [26]. For this fitting, the dipolar contribution to the 2PA was ruled out, as before. We used the same values for Γ_{01} and Γ_{02} , obtained in 2PA fitting (Fig. 2). For each temperature, ν_{01} was obtained from the maximum of the linear absorption, that shows a blue shift of $\pi\pi^*$ band with the temperature (data not shown here). This blue shift of the $\pi\pi^*$ band is completely reversible, indicating that there is no sample degradation. In the range of temperatures investigated, the blue shift is of only a few nanometers, and there is no change of the bandwidth. In the fitting procedure, the product $|\mu_{12}|^2 \cdot |\mu_{01}|^2$ was treated as adjustable parameters.

The dependence of the 2PA with the temperature can be explained by changes in the conjugation length due to thermally induced torsions in the N–C and N=N bonds. Such decrease in the effective conjugation length leads to a decrease in the transition dipole moments, which are consequently indirectly dependent of the temperature. It is important to mention that the density of DMSO (boiling point at 189°C) decreases only approximately 3% when the temperature changes from 20 to 60°C [40]. Such change in density with temperature is much smaller than the one observed for the 2PA cross-section, reason why this effect was neglected here.

From the slope of the curve in Fig. 3, we obtained the thermal two-photon absorption coefficient ($d\delta/dT$). For the three com-

pounds studied, this value is about $-7 \text{ GM}/^\circ\text{C}$, which is approximately three times greater than the values obtained for single-azoaromatic molecules, around $-2.5 \text{ GM}/^\circ\text{C}$ [26]. This is approximately equivalent to the ratio between the conjugation lengths of di- and single-azoaromatic molecules. In addition, the contribution of the naphthyl groups to the thermal induced torsion is smaller than their contribution to the conjugation length, due to their rigidity. As shown in Ref. [26], rigid molecules do not present measurable variation of the 2PA cross-section with temperature. Accordingly, the segments of the diazoaromatic molecules, which are sensitive to changes in temperature and consequently undergo torsion, are the N–C and N=N bonds. As diazoaromatic molecules present twice as much of such segments than single azoaromatic compounds, it is expected they will exhibit a higher thermal two-photon absorption coefficient, as observed in this work.

4. Conclusion

We carried out an investigation on the 2PA spectrum of diazoaromatic compounds (S3, S4 and SR) using the Z-scan technique with fs-pulses. The results obtained shown that the 2PA cross-sections, in the enhancement region, are three times higher than those of single-aromatic compounds. This behavior was explained by the longer conjugation length in diazoaromatics. On the other hand, 2PA transition for first excited state ($\pi\pi^*$ band) is improbably due to the absence of strong donor/acceptor charge groups. This result indicates that the presence of donor/acceptor groups is the main factor to obtain high 2PA cross sections in azoaromatic compounds, as the conjugation via azo groups ($-\text{N}=\text{N}-$) is weak.

2PA effect as a function of temperature gave a thermal two-photon absorption coefficient three times higher than the ones for single-azoaromatics compounds. It seems to be related with the number of bonds that can easily rotate in the conjugated system.

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