

Two-Photon Absorption Dependence on the Temperature for Azoaromatic Compounds: Effect of Molecular Conformation

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This work reports on the effect of temperature on the two-photon absorption cross section of azoaromatic chromophores. A linear decrease in the two-photon absorption cross section with the temperature was observed for several azochromophores. This process was characterized by introducing a two-photon absorption thermal coefficient ($d\delta/dT$), whose typical values are $\sim 2GM/^\circ C$ for all the azochromophores studied here. Such an effect was attributed to thermal induced molecular conformation changes, described by the sum-over-states model and semiempirical calculations, which affect the molecular dipole moments. The characterization of the phenomenon reported here for other nonlinear materials can help in the design of specific applications using two-photon absorption.

Two-photon absorption involves the excitation of a molecular species by the simultaneous absorption of two photons. The quadratic dependence of its rate on the laser intensity allows spatial confinement of the excitation, a property exploited in several applications.^{1–9} Since the first experimental observation of two-photon absorption,^{10,11} several important works have established the foundations of this nonlinear effect. In recent years, the control of nonlinear optical properties has driven the study and design of new nonlinear materials. To date, most of these studies rely on the dependence of the two-photon absorption on the molecular structure, such as conjugation length, molecular symmetry and donor–acceptor lateral groups.^{12–19} In contrast to the extensive study on the structure–property relationship, the effect of molecular conformation on nonlinear processes is still unexplored. As the conformation of the molecule can be altered by external means, for instance by changing the sample temperature, a dynamic control of the two-photon absorption can be achieved.

In this paper, we report the effect of the temperature in the two-photon absorption cross section of azoaromatic chromophores. We observed a decrease in the two-photon absorption cross section with the temperature, which was characterized by introducing a two-photon absorption thermal coefficient. This process was attributed to changes in the molecular conformation with the temperature, which alter the molecule dipole moments as revealed by the sum-over-states model and semiempirical calculations. Thermal induced changes on the two-photon absorption, here described by the two-photon absorption thermal coefficient, may have important implications in the selection of proper conditions or the material to be used for a given application, for example.

For linear and nonlinear optical measurements, we prepared a solution of Disperse Red 19 (DR19) in dimethyl sulfoxide (DMSO) with concentrations of 0.9×10^{17} molecules/cm³ and 4.9×10^{17} molecules/cm³, respectively. The molecular structure of DR19 is shown in the inset of Figure 1. Other azochromophores were also studied; however, we focus only on the results for DR19 in this work, which are illustrative of those

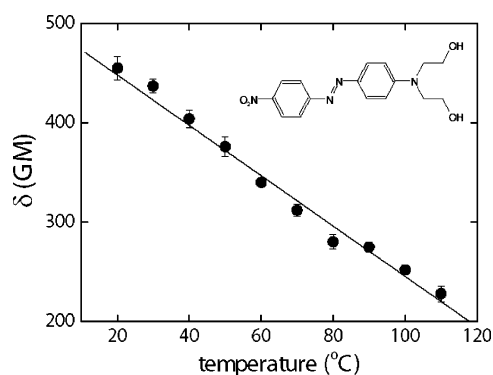


Figure 1. Two-photon absorption cross section as a function of temperature. The solid line represents the fitting obtained with the sum-over-states model described by eq 1. The molecular structure of DR19 is shown in the inset.

obtained for molecules of this class. The sample was placed in 2 mm thick quartz cuvettes for spectroscopic measurements. The linear absorption spectrum was recorded using a Cary 17 spectrophotometer.

The change of the two-photon absorption cross section, δ , with the sample temperature was measured using the open aperture Z-scan technique,²⁰ which has been successfully applied to measure the two-photon absorption cross section of several compounds, which gives results similar to the ones obtained by two-photon excited fluorescence methods. As the azochromophores studied in this work do not fluoresce, the Z-scan method appears to be an excellent option to measure the two-photon absorption cross section. The Z-scan measurements were carried out using a 150 fs, 775 nm, and 1 kHz Ti:sapphire laser as the pump for an optical parametric amplifier delivering 120 fs pulses. Although the two-photon absorption cross section spectrum of DR19 presents a peak at ~ 1000 nm,¹⁷ its magnitude is smaller than the one obtained in the resonant enhancement region. For this reason, we choose to perform the measurements at 680 nm (region of the resonance enhancement of the nonlinearity¹⁷) in order to improve the signal/noise ratio. The output beam of the optical parametric amplifier was spatially filtered to produce a Gaussian beam profile. The two-photon nonlinear absorption coefficient, β , can be determined by fitting

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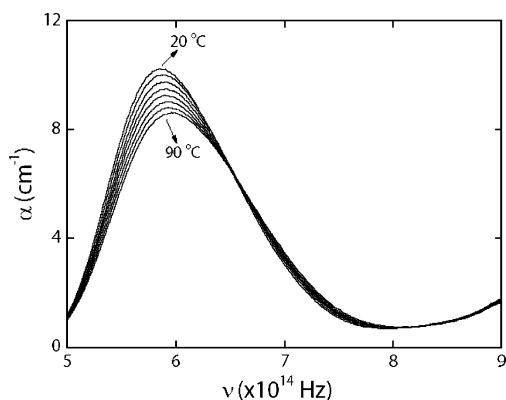


Figure 2. Linear absorption spectrum of DR19 as a function of the temperature. The highest curve was measured at 20 °C, with the subsequent ones obtained in temperature intervals of 10 °C up to 90 °C.

the normalized transmittance data.²⁰ The two-photon absorption cross section is determined through $\delta = \beta h\nu/N_0$, where $h\nu$ is the photon excitation energy and N_0 is the number of molecules/cm³. For linear and nonlinear optical measurements, the sample temperature was controlled through a thermo-electric cooler.

Figure 1 shows that the two-photon absorption cross section at 680 nm decreases linearly with the sample temperature. The slope of this decrease, defined as the two-photon absorption thermal coefficient ($d\delta/dT$), characterizes the change in the two-photon absorption cross section with the temperature. For the DR19 solution, we determined $d\delta/dT = -2.5GM/^\circ\text{C}$. We obtained values in the same order of magnitude for other azoaromatic compounds (Disperse Red 13, Disperse Orange 3, and Disperse Red 19–Cl). It is important to mention that the observed changes in the two-photon cross section with the temperature are completely reversible, demonstrating that no thermal degradation takes place. In Figure 1, the solid line represents the fitting obtained with a sum-over-states model assuming temperature dependencies to the transition dipole moment and $\pi \rightarrow \pi^*$ transition of the azochromophore, which will be described later in this paper.

The solid line in Figure 1 was obtained by fitting the experimental data with a sum-over-states model, described by

$$\delta(T) = \frac{4}{5\pi} \frac{(2\pi)^4}{(hc)^2} \frac{\nu^2}{(\nu_{01}(T) - \nu)^2 + \Gamma_{01}^2} \left[\frac{|\mu_{12}(T)|^2 |\mu_{01}(T)|^2 \Gamma_{02}}{(\nu_{02} - 2\nu)^2 + \Gamma_{02}^2} \right] \quad (1)$$

where h is Planck's constant, c is the speed of light, and ν is the laser frequency. ν_{mn} , Γ_{mn} , and μ_{mn} represent, respectively, the transition energy, damping constant and transition dipole moments of the $m \rightarrow n$ transition.^{21–25} In eq 1, the term inside the brackets corresponds to the line-shape of a two-photon transition to a state $|2\rangle$ in the UV region. For the two-photon absorption tensor term, outside the brackets, we assumed that only one intermediate state contributes to the virtual state in the sum-over-states. The $\pi \rightarrow \pi^*$ transition, which corresponds to the band around 6×10^{14} Hz shown in Figure 2, was assumed to be the one giving the major contribution to the virtual intermediate state represented as $|1\rangle$ in eq 1. The highest curve in Figure 2 was obtained at 20 °C, with all the subsequent ones obtained in temperature intervals of 10 °C up to 90 °C. As can be seen, the $\pi \rightarrow \pi^*$ band shifts to high energies, and its amplitude decreases when the temperature is increased. This process is also completely reversible, showing that no thermal induced degradation occurs as mentioned before. On the basis

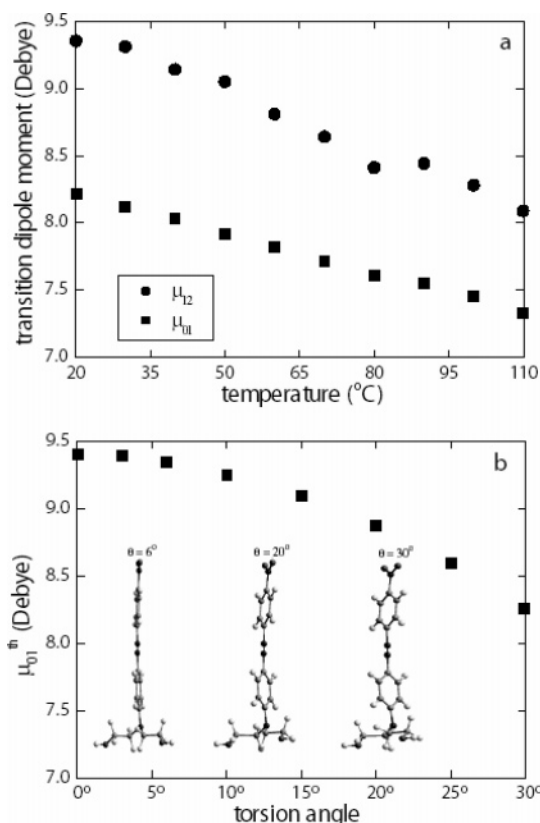


Figure 3. (a) Transition dipole moments μ_{01} and μ_{12} as a function of the temperature. (b) Theoretical values μ_{01}^{th} obtained through PM3 quantum chemical calculations as function of the torsion angle. The inset shows the molecular structure for three distinct torsion angles.

of these observations, we assumed temperature dependencies to the transition dipole moments ($\mu_{01}(T)$ and $\mu_{12}(T)$) and to the $\pi \rightarrow \pi^*$ transition frequency ($\nu_{01}(T)$) in eq 1.

To fit eq 1 to the data in Figure 1, we determined the transition dipole moment as a function of temperature, $\mu_{01}(T)$, through the oscillator strength obtained from the absorption spectra in Figure 2.²⁶ These values are presented in Figure 3a (■). $\nu_{01}(T)$ was extracted from the peak of the absorption spectra shown in Figure 2. The damping constants $\Gamma_{01} = 2000 \text{ cm}^{-1}$ and $\Gamma_{02} = 10\,000 \text{ cm}^{-1}$ were obtained from ref 17. In this way, the excited-state transition dipole moment, $\mu_{12}(T)$, is the only adjustable parameter in the fitting procedure. As seen by the solid line in Figure 1, the sum-over-states model assuming temperature dependencies to the transition dipole moment and $\pi \rightarrow \pi^*$ transition (eq 1) fits very well with the linear decrease experimentally observed.

Figure 3a shows that μ_{12} , determined by the fitting in Figure 1, decreases with the temperature with a slope similar to that observed for μ_{01} , indicating that our results are related to changes in the molecular conformation induced by the temperature. Attempts to model the data in Figure 1 considering only the shifts in the absorption band, which will affect the two-photon absorption cross section line shape (eq 1), were not successful. We observed that this process produces only a slight decrease in the two-photon absorption cross section, indicating that changes in the transition dipole moment due to temperature induced molecular conformation play a major role in the observed effect.

For azoaromatic compounds, temperature induced conformation changes would most likely appear as a twist of the aromatic rings around the azo group ($-\text{N}=\text{N}-$). As a consequence of this torsion, the effective conjugation length of the azochro-

mophore decreases, leading to a decrease in the optical nonlinearity. In order to test this hypothesis, we performed PM3 CIS/semiempirical (15 eV as the energy criterion) quantum chemical calculations (Hyperchem 7.5) of the transition dipole moment, μ_{01}^{th} , for distinct torsion angles, defined as the angle between the azo group and the aromatic ring. As an illustration, the inset in Figure 3b displays the molecular structure for three different torsion angles. Figure 3b shows that μ_{01}^{th} decreases by 12% as the torsion angle changes from 0° to 30°. This decrease is approximately the same observed for μ_{01} when the temperature varies from 20 °C to 110 °C as observed in Figure 3a (■). These results indicate that, indeed, thermally induced molecular conformation changes are taking place, leading to changes in the two-photon absorption cross section due to the change in the molecular conjugation. It should be pointed out that although the transition dipole moments obtained through the CIS/semiempirical method overestimates the experimental ones, the quantum chemical calculations provide enough information to our temperature induced torsion hypothesis.

In addition to the change in the transition dipole moment, our semiempirical calculation also revealed a shift in the absorption maximum to higher energies as a result of the molecule torsion, with a trend similar to the one observed in Figure 2. That is, for an increase in the torsion angle, the energy of the transition is blue-shifted in agreement with a smaller conjugation-length.

The same general results were observed for other azoaromatic chromophores, namely, Disperse Red 13, Disperse Orange 3, and Disperse Red 19–Cl. The structure of azoaromatic molecules, possessing aromatic rings symmetrically linked to a central azo group, facilitates changes in the molecular conformation induced by heat (temperature). Such changes affect the molecular conjugation length and dipole moments, resulting in modification in the two-photon absorption cross section. As mentioned earlier, all these azochromophores present thermal two-photon absorption coefficient ($d\delta/dT$) in the same order of magnitude of the one presented for DR19, for approximately the same spectral region. The observed effect depends on the microscopic viscosity of the solution, being smaller as the viscosity increases. Furthermore, the use of modified molecules, where the aromatic groups' torsion is hindered, can be employed as a strategy to avoid the temperature effect on the two-photon absorption cross section.

To further verify the molecular conformational origin of the observed process, we studied the influence of temperature on the two-photon absorption process of perylene tetracarboxylic derivatives,^{18,27,28} molecules structurally distinct from the azoaromatic chromophores. Perylene tetracarboxylic derivatives (PTCD) present a central perylene moiety, where the conjugation is localized.^{18,19,27} Attached to this central region are distinct lateral groups, which do not affect the molecular conjugation. For these molecules, no thermal induced change on the two-photon absorption cross section was observed for excitation around 600 nm (resonance enhancement region). Such a result can be explained by the structural rigidity of the central portion of PTCDs,¹⁹ whose conformation is unaffected by the temperature. As the nonlinear optical properties of PTCD are mainly determined by the central region of the chromophore, no changes in the two-photon absorption with temperature are expected. This result indicates that only molecules with significant structural mobility will present a measurable two-photon absorption thermal coefficient.

In summary, we showed that the two-photon absorption cross section of azochromophores decrease with the temperature. This

process was explained by thermal induced conformational changes that affect the transition dipole moments. Our experimental results were described by the sum-over-states model, considering temperature dependences to the transition dipole moments and to the $\pi \rightarrow \pi^*$ frequency. Semiempirical quantum chemical calculations revealed that different torsions of the aromatic rings around the azo group leads to changes in the transition dipole moment. Such changes are compatible to the ones observed through the sum-over-states model, corroborating the molecular conformation hypothesis.

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