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Two-photon solvatochromism III: Experimental study of the solvent effects on two-photon absorption spectrum of *p*-nitroaniline

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ABSTRACT

We report on the solvent influence on the two-photon absorption spectra of *p*-nitroaniline. Measurements of the two-photon absorption cross section values were performed in three solvents (1,4-dioxane, propylene carbonate, dimethyl sulfoxide) using the Z-scan technique. The most important finding in this report is the observation that two-photon absorption cross section value, corresponding to the intramolecular charge-transfer state, is significantly intensified with the solvent polarity increase. In the case of a strongly positive solvatochromic molecule, the two-level model correctly predicts the observed two-photon absorption cross section value increase caused by the solvent polarity change.

1. Introduction

In this work we continue our systematic studies regarding the solvent effects on the two-photon absorption (2PA) of organic chromophores demonstrating strong negative or positive solvatochromic shift of the electronic UV–Vis absorption peaks. In our previous experimental reports (part I and II) in different contexts we have considered the solvent effect on the 2PA spectra of the prototypical solvatochromic chromophores *i.e.*, 4-dimethylamino-4'-nitrostilbene (DANS) and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, commonly referred to as Reichardt's dye (RD) or B30 [1,2]. In the case of the strongly negatively solvatochromic Reichardt's dye we have observed an inverse dependence of 2PA cross section (σ^{2PA}) maximum values on solvent polarity increase. The obtained results were consistent with the theoretical predictions [2]. A more complicated case of the moderately solvatochromic DANS occurred to be not fully conclusive. The changes of the σ^{2PA} maximum values versus solvent polarity increase turned out to be non-monotonic [1]. This conclusion was fully confirmed by a theoretical calculation performed by Murugan et al. [3].

Observations concerning the solvatochromic behavior of molecules were originally conducted in the field of the linear spectroscopy and have a long history [4–17]. Quantitative analysis of the solvent effect conducted in one-photon regime allows for the discussion of conformational changes of molecules placed in different environments, evaluation of the origins of intermolecular interactions, determination of the dipole moments and polarizabilities and many other molecular properties. With no doubt, solvatochromism of a chemical species provides a lot of valuable data about its properties. The largest shifts of the absorption band maximum as a function of the solvent polarity are usually observed for an important class of organic molecules, the donor-acceptor π-conjugated compounds (D-π-A). It is well established that such compounds exhibit an intense low-lying ($\pi \rightarrow \pi^*$) transition in the UV–Vis spectral region which is assigned to the intramolecular charge-transfer (CT) occurring along the molecular axis. The value and direction of the UV–Vis electronic absorption band shift as a function of the solvent polarity can be explained on the basis of the theory of intermolecular solute-solvent interactions in the ground and Franck-Condon excited states [4,5,9–15,17,18]. In contrast to this picture, origins of the absorption band intensity and shape modifications are still not precisely determined theoretically nor fully understood.

Lately, the scientists attention has been attracted by the solvent effects on the two-photon absorption (2PA) defined as a simultaneous absorption of two photons by a single molecule. Presently available experimental works have shown that the environment

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(solvent) plays a remarkable role in the consideration of the 2PA cross sections (σ^{2PA}) of different molecular systems including the D-π-A type chromophores [1,2,19–38]. In the context of interactions with the environment some unconventional molecular systems have also been investigated. For example, Vivas et al. published the research concerning the influence of solvent on the induction of coil to helix conformational change generating the modification of the σ^{2PA} values [30]. Kavitha et al. presented the solvent effect on 2PA of ZnO nanoparticles [39]. Also, environments other than the type of solvent have been examined. Woo et al. [23], and more recently Bairu et al. [35], have demonstrated that the micellar systems, in particular the concentration [23] and different micropolarity of the micelle's Stern layers [35], can have a substantial influence on σ^{2PA}. Another recent idea is the issue of the solvent effect on three-photon absorption (3PA) cross section. Pioneering work, both in the theoretical and experimental area, have been already published [40,41]. As one can see, the research on this novel and fascinating field is still in progress. However, our knowledge about the 2PA solvatochromism is not deep enough and far from universal. Probably the first theoretical and experimental research of the solvent effect on 2PA of molecules was published in 1971 by Aslanidi et al. [19]. Later, in 1988, Mohler and Wirth published the work considering the solvent effect on the excited state symmetry of randomly oriented molecules by 2PA [42]. In this very important report based on theoretical considerations the authors have shown that solvent perturbs the excited state symmetry of the fluorene molecule, which enabled gaining the information about macroscopic properties of the solvent environment. Thorough inspection of the newly published electronic spectra for a variety of molecules (not only D-π-A) in solutions shows that the solvent effect on the 1PA bands intensity is less important than its influence on the 2PA bands. This conclusion can be supported by investigations presented by Drobizhev et al. for the fluorescent proteins [43]. In particular, authors present a significant sensitivity of σ^{2PA} of the polar chromophore to the local electric field generated by different “Fruit” proteins while for the same systems the 1PA extinction coefficient varies only relatively slightly. The examples presented there are very important for considerations introduced in this contribution and clearly show that σ^{2PA} can be manipulated by changing the chemical environment of the investigated molecule.

According to the two-level model, proposed as a simplified formula enabling a relatively good estimation of σ^{2PA} or two-photon transition probability (δ) [18,44–47], in the case of the chromophores exhibiting large negative solvatochromism the presence of a polar environment should lead to the substantial decrease of the 2PA cross section with the solvent polarity increase. Opposite tendencies should be observed for the chromophores exhibiting positive solvatochromism. However, the presented theoretical procedure is restricted to 2PA from the ground to the CT excited state. Moreover, in the early studies, the importance of one of variables, namely the linewidth parameter (Γ) and its influence on the σ^{2PA} in different solvents had been underrated. This, as it lately has been realized, very relevant quantity contains the information about both homogeneous and inhomogeneous broadening of the resonance lines corresponding to the 2PA transition. The latter contribution is present in the condensed phases and is directly related to the intermolecular interaction between the two-photon absorbing chromophore and molecules constituting the environment. It is obvious that Γ has to change from one molecule to another and depends on the solvent as well as the temperature. Important examples are reported in the recent works describing the influence of the solvent on 2PA of the DANS molecule. Without the quantitative analysis including the influence of Γ, it was not possible to fully explain the nonmonotonic behavior of the 2PA cross section of that molecule, considered in the solvents of different polarity [1,3]. Recently, the significance of Γ has been appreciated and a significant progress in this field has been achieved [3,48–50].

In this study we focus on the investigations of the influence of solvent on the 2PA spectra of *p*-nitroaniline (pNA). The 2PA cross sections of pNA in various solvents such as propylene carbonate (PC), 1,4-dioxane and dimethyl sulfoxide (DMSO) were measured with femtosecond (fs) laser pulses using the Z-scan measurement technique [51]. The relation between the solvent effects in the linear (1PA) and nonlinear (2PA) spectroscopy is considered. PNA is a classic model for experimental as well as theoretical investigations of charge-transfer (CT) properties including aspects related with the solvent effect and second-order nonlinear optical properties [52–88]. For this important D-π-A molecule a large change in the dipole moment (9.3 D in 1,4-dioxane) upon electronic transition to the intramolecular CT excited state is observed [56]. It leads to a large sensitivity on the polarity of solvent (~5000 cm^{-1} solvatochromic shift) [52–57,88,89] enabling one to verify the two-level model predictions for the positively solvatochromic system. Until now, only two experimental reports concerning the 2PA cross section have been published for this molecule [90,91]. In both cases the measurements were conducted only in DMSO. Therefore, the motivation for the present study was to extend the current knowledge about the 2PA processes occurring in this important chromophore in condensed phases.

2. Experimental details

The *p*-nitroaniline (purity ≥ 99%, Fig. 1) was purchased from Sigma-Aldrich company and used as received. The linear (1PA) spectra were recorded with 1 nm resolution using a Perkin Elmer Lambda 20 spectrophotometer in a 1 mm quartz cell for three different concentrations (in order to obtain the molar extinction coefficient (ε)). However, in the further measurements of Z-scan relatively large sample concentrations were required. Therefore, in order to check for possibility of autoaggregation of the molecules we have also carried out 1PA measurements of the pNA samples at the concentrations used in the nonlinear measurements. This was performed using ultra thin 10 μm path length quartz cuvettes. No additional absorption bands were observed, however, the existing absorption bands were very slightly wider than in the case of the diluted solutions. Due to a relatively low solubility of pNA in common solvents (like chloroform or dichloromethane), a somewhat non-standard set of solvents was selected, namely 1,4-dioxane, dimethyl sulfoxide (DMSO) and propylene carbonate (PC). All solvents were purchased from Sigma-Aldrich and used without further purification. Parameters of the selected solvents are presented in Table 1.

The 2PA data were recorded using the Z-scan measurement technique [51]. A standard measurement setup and procedures used in our laboratory have been described in detail elsewhere [1,2,92]. However it is important to stress here that in order to avoid any undesirable one-photon sequential (i.e. excited state absorption) or thermal effects [93–96], short, approximately 130 fs, laser

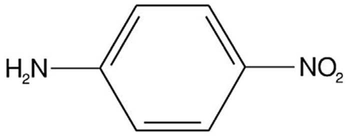

Fig. 1. Structural formula of the pNA molecule.