

# Two-photon spectra of organic salt trans-4-[p-(N-hydroxyethyl-N-methylamino)styryl]-N-methylpyridinium iodide in two solvents

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Two-photon absorption (TPA) cross sections of an organic dye, trans-4-[p-(N-hydroxyethyl-N-methylamino)styryl]-N-methylpyridinium iodide (abbreviated as ASPI), from 810 to 1100 nm have been measured in two solvents (benzyl alcohol, dimethyl formamide (DMF)) with different polarities. The peak values and positions of ASPI TPA spectra were found to be strongly influenced by the solvents. The maximum molecular TPA cross sections are  $26.42 \times 10^{-48} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$  at 930 nm (in DMF solution) and  $46.81 \times 10^{-48} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$  at 960 nm (in benzyl alcohol solution).

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The two-photon absorption (TPA) process has been the subject of fast-growing interest in fields such as chemistry, photonics, and biological imaging because of a variety of applications of TPA dyes to upconverted lasing<sup>[1,2]</sup>, optical power limiting<sup>[3,4]</sup>, two-photon induced fluorescence microscopy<sup>[5,6]</sup>, and 3D microfabrication<sup>[7,8]</sup>. The development of two-photon technology depends much on the success of synthesizing new molecules with large TPA cross sections at desirable wavelengths<sup>[9,10]</sup>. It is found that the molecular structure has a significant influence on the TPA cross section of molecules. There exist various design strategies employed to enhance the magnitude of the TPA cross section of dyes, for example the charge transfer occurring in the donor-conjugated bridge-accepter systems can lead to a significant enhancement of the third-order response, which is related to the TPA cross section. On the other hand, different environments may also influence the TPA cross section<sup>[11,12]</sup>. In this paper, we report the TPA of spectrum an organic dye trans-4-[p-(N-hydroxyethyl-N-methylamino)styryl]-N-methylpyridinium iodide (abbreviated as ASPI) in different solvents, and find that the peak positions and values of the spectra are greatly influenced by the solvents used.

TPA is a third-order nonlinear optical process. The change in intensity  $I$  of a beam as it propagates through a medium with linear and TPA, is given by<sup>[13]</sup>

$$\frac{dI}{dz} + \alpha I + \beta I^2 = 0, \quad (1)$$

where  $\alpha$  is the linear absorption coefficient (in units of  $\text{cm}^{-1}$ ),  $\beta$  is the TPA coefficient (in units of  $\text{cm}/\text{GW}$ ), related to the imaginary part of the third-order susceptibility  $\chi^{(3)}$ . Under the conditions that the linear absorption is small, and the pump beam has a near Gaussian transverse intensity distribution, the nonlinear transmittance related to the TPA process can be calculated by

$$T(I_0) = \frac{\ln(1 + I_0 L \beta)}{I_0 L \beta}, \quad (2)$$

where  $I_0$  is the incident intensity,  $L$  is the thickness of the solutions. The transmitted intensity  $I(I_0)$  can be shown as

$$I(I_0) = \frac{\ln(1 + I_0 L \beta)}{L \beta}. \quad (3)$$

The value of  $\beta$  can be estimated from Eq. (3) by measuring the transmitted intensity versus incident intensity for a given sample. The molecular TPA cross section  $\sigma_2$  (in units of  $\text{cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$ ) is related to  $\beta$  by

$$h\nu\beta = \sigma_2 N_0 = \sigma_2 N_A d_0 \times 10^{-3}, \quad (4)$$

where  $h\nu$  is the incident photon energy,  $N_0$  is the molecular density ( $\text{cm}^{-3}$ ),  $N_A$  is the Avogadro number, and  $d_0$  is the concentration (mol/L).

The absorption spectra of ASPI were obtained by using a scanning spectrophotometer (Shimadzu UV-2102) with a resolution of 0.5 nm.

Figure 1 shows the experimental setup for the measurement of the TPA spectra. The pump laser beam comes from an optical parametric oscillator (OPO, Continuum Panther plus) pumped by a Nd:YAG laser (Continuum PR11 8010). The tunable wavelength range, pulse duration and repetition are 410–2186 nm, 6 ns and 10 Hz, respectively. After passing a diaphragm and a variable attenuator, and collimated by lenses  $L_1$  and  $L_2$ , the laser beam was focused by a 15-cm focal length lens at the center of the 1-cm-path quartz cuvette containing ASPI sample solution. The radius at the focal was  $79 \mu\text{m}$  approximately. The transmitted laser beam via a high-pass filter was detected by an optical energy meter (Laser Probe, Rm-3900) with a large detection area of  $1 \text{ cm}^2$ . The variable attenuator made by two crossed Glan polarizers was used to adjust the energy of the laser beam. During the experiment, we have measured the nonlinear optical properties of ASPI in the wavelength ranges of 810–1100 nm. The pumping energy and the transmitted energy are recorded every 10 nm and each of them was an average of 300 laser pulses. The precision of our apparatus is about  $\pm 15\%$ .

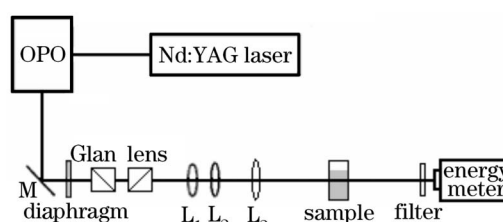


Fig. 1. Experimental setup for TPA spectra measurements.

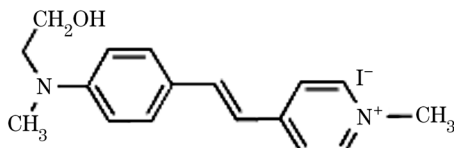


Fig. 2. Molecular structure of organic salt ASPI.

Figure 2 presents the molecular chemical structure of ASPI. It is a D- $\pi$ -A conjugated system with an electron-donating amino group (one end) and an electron-accepting pyridinium group (the other end). Figure 3 shows the linear absorption spectra of ASPI solution samples in two different solvents of benzyl alcohol and dimethyl formamide (DMF). Their molecular permanent electronic dipole moment ( $\mu_0$ ) values (measured in gas phase) are 1.71D (benzyl alcohol) and 3.82D (DMF)<sup>[14]</sup>. The two solutions are all with the same concentration of  $d_0 = 1 \times 10^{-5}$  mol/L. The absorption peaks are located at 497 (benzyl alcohol) and 479 nm (DMF) respectively. An obviously blue shift can be seen with increasing the polarity of the solvent. This is a negative solvatochromism.

During the measurement of TPA spectra, for each wavelength, we have measured the transmitted intensity versus incident intensity and Eq. (2) has been used to get the best-fitting parameter of  $\beta$ . We found the  $\beta$  is independent of the input intensity within experimental uncertainty. Therefore, under our experimental conditions, the measured values of ASPI solution are reliable. Figure 4 shows the transmissivity of ASPI in benzyl alcohol with the concentration of 0.01 mol/L versus the incident intensity at 960 nm. One can see the experimental data fit well with the theoretical curve.

The dotted line is given by Eq. (2) with a fitting parameter of  $\beta=1.36$  cm/GW.

Figure 5 gives the  $\sigma_2$  of ASPI in DMF and benzyl alcohol respectively. The concentration of these two solutions is 0.01 mol/L. The largest molecular TPA cross sections are  $26.42 \times 10^{-48}$  cm<sup>4</sup> · s · photon<sup>-1</sup> at 930 nm (in DMF solution) and  $46.81 \times 10^{-48}$  cm<sup>4</sup> · s · photon<sup>-1</sup> at 960 nm (in benzyl alcohol solution). At 1064 nm, the TPA cross sections are  $3.43 \times 10^{-48}$  cm<sup>4</sup> · s · photon<sup>-1</sup> (in DMF solution) and  $6.64 \times 10^{-48}$  cm<sup>4</sup> · s · photon<sup>-1</sup> (in benzyl alcohol solution), which are much smaller than their maximum TPA cross sections. According to the report by He *et al.*<sup>[2]</sup>, the TPA cross-section value of ASPI measured in benzyl alcohol solution at 1064 nm by using a 10-ns laser pulse is almost the same as the value measured in our experiment. This can also prove that the TPA cross sections of ASPI solutions measured by us are accurate.

From Fig. 5, one can see that the TPA spectra of ASPI in various solvents have similar figure, but their peak values and positions are dramatically different. The difference is related to the polarity of the solvents used. For polar dye, the polar substituent can interact with the dipoles of the solvent to shift the energy levels of the dye. The different dipoles in different solvents will result in the different shifts of the dye's energy levels. This will lead to different two-photon resonance conditions.

Furthermore, for the two solvents, both the maximum of the TPA cross sections are located at shorter wavelength than the twice of their one-photon absorption

peak, the shifts are about 28 nm for DMF and 34 nm for benzyl alcohol. This phenomenon can be explained by the maximum wavelength dependence of the overlap integral of the wave functions in the transition probability. For the molecules that have central symmetry, two photon transitions only happen between initial and final states with the same parity, but for one photon transitions, different parity must be ensured between initial and final states. On the other hand, for the molecules without a center of inversion symmetry, every state is of mixed parities, and so has the possibility of being the TPA final state, but which is the most probability two-photon transition state depending on the characteristics

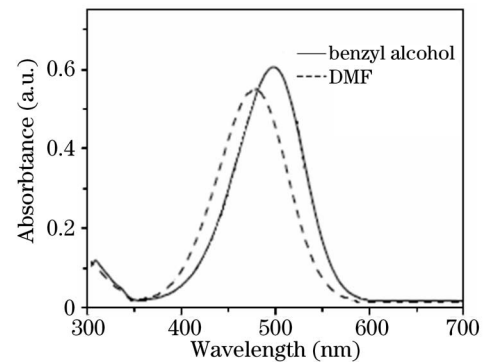


Fig. 3. Linear absorption spectra of ASPI in different solvents with the same concentration  $d_0 = 1 \times 10^{-5}$  mol/L.

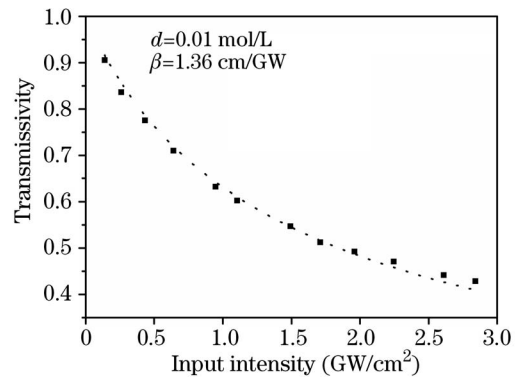


Fig. 4. Measured transmissivity of ASPI in benzyl alcohol with the concentration of 0.01 mol/L versus the incident intensity at 960 nm.

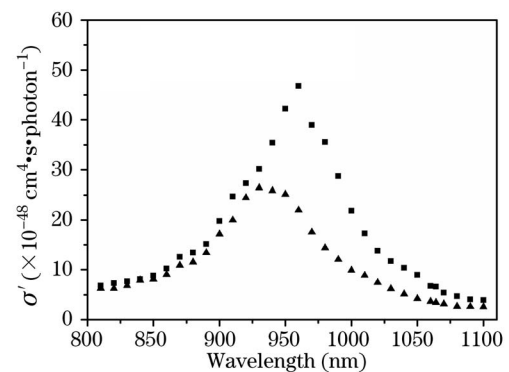


Fig. 5. TPA cross sections  $\sigma_2$  of the 0.01-mol/L ASPI in benzyl alcohol (squares) and DMF (triangles).

of the wave functions. Our experiment results show that the most probability two-photon transition vibrational excited state are energetically above the most probability one-photon transition vibrational excited state in the ASPI dye.

TPA cross section spectra of ASPI in benzyl alcohol and DMF at the wavelength from 810 to 1100 nm have first been obtained by nonlinear transmission method. With the increase of the polarity of the solvents, the peak values of the TPA spectra decrease, meanwhile, there is about 30-nm blue shift of their peak positions. These differences might caused by the interaction between the polar substituent and the dipoles of the solvent, which, consequently, changes the energy levels and the two-photon absorption probability of the dye when in different molecular environment.

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