



Evidence of concentration dependence of the two-photon absorption cross section: Determining the “true” cross section value



Aliasghar Ajami^{a,b,*}, Peter Gruber^d, Maximilian Tromayer^c, Wolfgang Husinsky^a, Jürgen Stampfl^d, Robert Liska^c, Aleksandr Ovsianikov^d

^a Institute of Applied Physics, Vienna University of Technology, Wiedner Hauptstrasse. 8-10, 1040 Vienna, Austria

^b Faculty of Physics, Semnan University, Semnan, Iran

^c Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163/MC, 1060 Vienna, Austria

^d Institute of Material Science and Technology, Vienna University of Technology, Favoritenstrasse. 9-11, 1040 Vienna, Austria

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ABSTRACT

The two-photon absorption (2PA) phenomenon is the basis of many unique applications involving suitable chromophores as photoinitiators. Ideally the 2PA cross section should, therefore, be a unique parameter, allowing quantification and comparing 2PA capabilities of different substances. In this report, the most straightforward and widespread method, the Z-scan technique, was used for determining the 2PA cross-section values of three different synthesized photoinitiators and one laser dye as a standard. It is demonstrated that the experimentally obtained values strongly depend on the molar concentration of a measured solution. A tenfold decrease in substance concentration can lead to the doubling of the 2PA cross-section. A similar concentration dependence was confirmed for all three investigated substances. Among the crucial implications of this observed behavior is the questionable possibility to compare the 2PA characteristics of different compounds based on the values reported in the literature. An example of another important consequence of this effect extends i.e. to the calculation of the dose necessary for killing the tumor cells in 2PA-based photodynamic therapy applications. The possible factors responsible for this contra-intuitive behavior are discussed and investigated. Finally, a reliable measurement protocol for comprehensive characterization of 2PA capability of different substances is proposed. Herewith an attempt to establish a standard method, which takes into account the concentration dependence, is made. This method provides means for faultless comparison of different compounds.

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1. Introduction

Two-photon absorption (2PA) cross section is defined as the probability for simultaneous absorption of two photons by an atom or a molecule to be excited from the ground state to an upper energy state [1]. It should therefore represent a unique characteristic allowing quantification and comparing 2PA capability of different substances.

The 2PA phenomenon is the base of many unique applications. The determination of 2PA cross-section is very important for applications such as micro-structuring via two-photon polymerization (2PP) [2,3], 3D optical data stage [4] and even much more crucial for areas such as two-photon photodynamic therapy (2P-PDT) [5] and two-photon induced fluorescence imaging (2PIF) [6]. In

2P-PDT and 2PIF the inaccuracy in the determination of 2PA cross-section due to concentration dependence can cause problematic consequences since the treatments and examinations are often performed on the living cells and tissues. Since different concentration of two-photon absorbers cannot be avoided in various applications, a detailed knowledge of the concentration dependence of the 2PA cross section is needed. Several reports have already indicated that such a dependence exists [7,8]. However, the values reported are exorbitantly high and not very systematic. In this report, the detailed investigations for different photoinitiators and a standard dye at various concentrations ranging from 0.4 milli-molars (mM) to 40 mM is presented.

In order to determine the 2PA cross section of the examined compounds at various concentrations the open aperture Z-scan technique was employed. In the Z-scan method the sample is translated along the propagation direction of a focused laser beam through the focal point. The normalized transmittance as a function of the sample position is given by

* Corresponding author at: Institute of Applied Physics, Vienna University of Technology, Wiedner Hauptstrasse. 8-10, 1040 Vienna, Austria.

E-mail address: ajami@iap.tuwien.ac.at (A. Ajami).

$$T(z) = \sum_{n=0}^{\infty} \frac{(-q_0)^n}{(n+1)^{3/2} (1 + (z/z_0)^2)^n} \quad (1)$$

where z is the sample position measured with respect to the focal point, $q_0 = (N_A \rho \times 10^{-3} / h\omega) L I_0 \sigma_{2PA}$, N_A the Avogadro number, ρ the concentration of solution in mole per liter, L the thickness of the sample, I_0 the peak on-axis intensity at the focus defined as $I_0 = 4 \sqrt{\ln 2 / \pi} E / (M^2 \lambda z_0 \tau)$ (M^2 is the beam quality factor, λ is the wavelength, τ is the pulse duration, E is the pulse energy and z_0 the Rayleigh range) and σ_{2PA} the pure 2PA cross section. It should be pointed out that Eq. (1) has been derived assuming a pure cubic nonlinearity for a thin sample ($z_0 < L$) under approximation of $q_0 < 1$ ($T(0) > 0.76$) [9] hence, the pure 2PA cross section of the examined sample can be extracted by fitting Eq. (1) to the Z-scan experimental data if the contribution of other nonlinear absorption processes is negligible.

In the Z-scan technique it is not possible to isolate the pure 2PA from other nonlinear absorption contributions such as higher order nonlinear absorption (e.g. three-photon absorption (3PA) as a fifth order nonlinear absorption), 2PA induced excited state absorption (ESA) (a cascaded χ^3 : χ^1 process defined as a fifth order nonlinear absorption) or one-photon-induced ESA (a cascaded χ^1 : χ^1 process defined as a third order nonlinear absorption). Therefore, to extract the pure 2PA cross section from the Z-scan signal the range of irradiation intensity must be chosen carefully to avoid contribution of other nonlinear processes. Since the measured 2PA cross section depends on many parameters such as the irradiation wavelength, the pulse duration [11,12], the irradiating intensity [13], the specific solvent [14,15] as well as the concentration it is understandable why different authors reported different values for the same compound. To avoid this problem the establishment of a protocol for measuring the 2PA cross sections is of crucial importance [16]. In such a protocol the conditions to be used for the excitation of the molecular system and the standard procedures for the analysis of the data should be carefully selected. In this report, we will propose a measurement protocol accounting for the influence of concentration and light intensity on the measured 2PA cross section. By this way it was possible to extract a value for the 2PA cross section from the Z-scan signal which can be considered as characteristic for the investigated compound.

2. Measurements

Three different two-photon initiators (2PIs), 2,7-bis((4-(dibutylamino)phenyl)ethynyl)-9H-fluoren-9-one (B3FL), (2E,6E)-2,6-bis(4-(dimethylamino)benzylidene)-4-methylcyclohexanone (M2CMK) and (2E,5E)-2,5-bis(4-(dibutylamino)benzylidene)cyclopentanone (B2CPK) [17,18] were used for this study. Fig. 1 shows the molecular structures of the studied compounds.

Fig. 2 shows the linear absorption of the studied compounds with peak absorption at 400 nm for B3FL, 435 nm for M2CMK and 480 nm for B2CPK. Therefore, two photons at 800 nm have sufficient energy to excite these molecules and thus, these compounds can exhibit 2PA.

For all three compounds solutions in Tetrahydrofuran (THF) solvent with different concentration ranging from 0.4 mM to 40 mM were prepared for this investigation. For the highest concentration (40 mM) pulse energy of about 5 nJ was sufficient to obtain a Z-scan signal showing an absorbance of 10% at the focus whereas, for low concentration of 0.4 mM the pulse energy had to be increased up to 100 nJ (intensity of 4.4×10^{11} W/cm²), a threshold above which the THF solvent started nonlinear absorption.

A Ti:sapphire amplifier generating 30 femtosecond pulses at 800 nm with repetition rate of 1 kHz was used as the pulse source in the Z-scan setup. The 10 mm diameter laser beam was focused

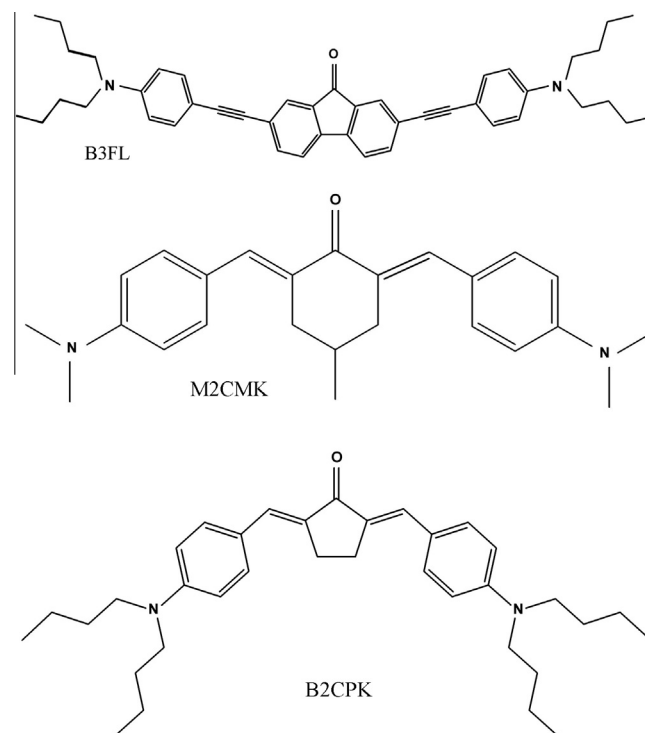


Fig. 1. Molecular structures of the studied compounds.

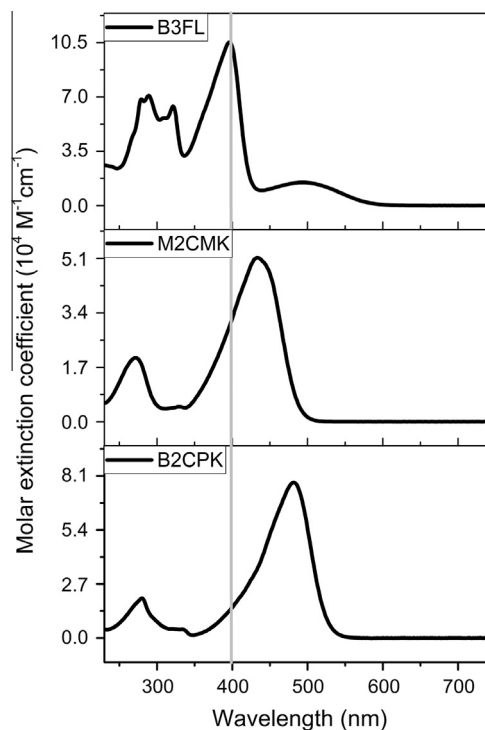


Fig. 2. Linear absorption of the studied compounds.

using a 300 mm focal length lens leading to a beam waist radius of 21.3 μm considering a beam quality factor of 1.4. The Rayleigh range of the focused beam was measured 1.28 mm which is larger than the thickness of the cuvette (1 mm) used as the solution container. The detailed setup and laser pulse and beam characterization can be found somewhere else [10].

It is worth mentioning that the maximum pulse energy which can be used in the Z-scan method is constrained by five factors (a) the threshold pulse energy over which the solvent shows nonlinear absorption, (b) the threshold pulse energy over which the normalized Z-scan transmittance at the focus decreases to lower than 0.76 (corresponding to $q_0 > 1$), (c) the threshold pulse energy over which the spectrum of the transmitted pulse through the sample shows wavelength broadening; This should be avoided due to two reasons: (1) appearance of wavelength broadening indicates that the intensity is high sufficient for the other nonlinear absorptions to take place which actually should be avoided and (2) creating new wavelength in the pulse spectrum might leads to non-degenerate 2PA within the sample which also should be avoided, (d) the threshold pulse energy over which degradation occurs for the compound and (e) the threshold pulse energy over which the contribution of the ESA becomes greater than that of the 2PA. The first three thresholds are easy to determine but determining the fourth one is not straightforward. However, although Eq. (1) has been derived for pure 2PA process it can be used for fitting to the Z-scan data to extract the values for q_0 as long as the contribution of the ESA to the whole nonlinear absorption is less than that of the 2PA. As an essential indication for the pure 2PA it should be noticed that, in the presence of ESA the obtained q_0 show a quadratic dependence on the pulse energy whereas for the pure 2PA it shows a linear dependence.

In order to perform a reliable measurement for each solution all limiting factors on the applied intensity mentioned above were checked as follows. The Z-scan of the pure THF solvent showed a deviation from straight line at 120 nJ pulse energy; an indication of nonlinear absorption in the solvent. Therefore, the Z-scans of the solution were carried out for pulse energies below 100 nJ. The normalized transmittance is easily observed after each scan (Fig. 5) thus, the pulse energy can be controlled to avoid obtaining normalized transmittance below 0.76 (corresponding to $q_0 > 1$). Spectral broadening was also checked for the pure solvent and all solution. As an example, in Fig. 3 the laser spectrum before and after the M2CMK solution with concentration of 10 mM has been compared at two different pulse energies of 130 nJ and 200 nJ. As seen in Fig. 3b, new peaks around 760 nm, 775 nm and 810 nm have been created during irradiating M2CMK solution with pulse energy of 200 nJ however, no spectral broadening was observed for pulse energies up to 120 nJ.

In order to check sample degradation, the solutions were exposed at the focus with pulse energy of 100 nJ for half an hour and then the linear absorption of exposed solution was compared to that of the unexposed solution. Fig. 4 shows the linear absorption of M2CMK solution before and after the exposure. M2CMK solution with concentration of 10 mM was exposed at the focus with pulse energy of 100 nJ. Then, in order to measure the linear absorption using a 200 μm cuvette (the thinnest cuvette we had) the exposed solution was diluted to 1.25 mM. As seen in Fig. 4, the shape and peak position of the exposed solution is the same as the unexposed solution; an indication of identical molecular structure for both exposed and unexposed solutions. The value of absorption coefficient of the exposed solution is a little higher which can be explained as follows. During the exposure (half an hour) the solvent evaporates leading to higher concentration whereas, the same concentration as unexposed solution was assumed in order to obtain the absorption coefficient of the exposed solution. This results in overestimating the absorption coefficient of the exposed solution.

The presence of ESA was verified by investigating the behavior of 2PA cross section versus pulse energy. As long as the extracted 2PA cross section from Z-scan signal stays constant with increasing the pulse energy no ESA has obviously occurred. In the case when the extracted 2PA cross section increases with pulse energy it is

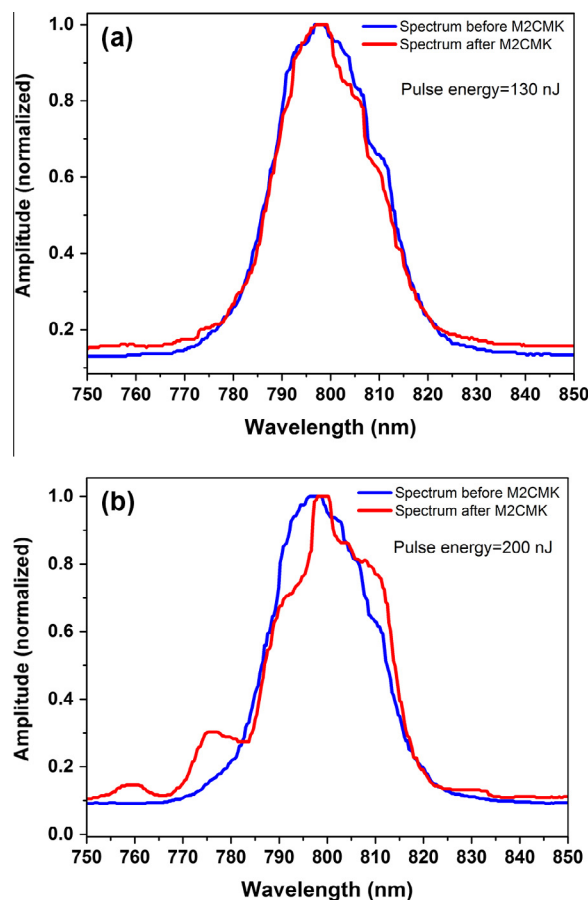


Fig. 3. Spectrum of the laser source used for the Z-scan measurements before the sample (blue curve) and after the M2CMK solution with 10 mM concentration (red curve) exposed with pulse energy of (a) 130 nJ and (b) 200 nJ. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

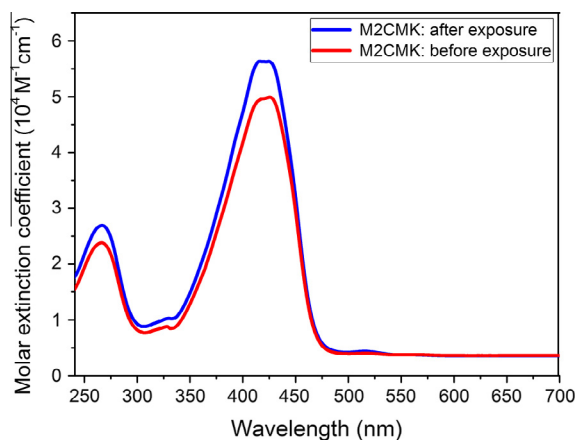


Fig. 4. Linear absorption of M2CMK. Red curve shows the spectrum for the fresh solution and blue curve shows the spectrum for the exposed solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

proposed to used pulse energies for which the measured 2PA cross section grows two times larger than its pure value. As can be seen from Fig. 7 the measured 2PA cross section of B3FL and B2CPK solution with concentration of 1 mM at 100 nJ pulse energy is less than double of their pure value (extrapolated to zero pulse energy).

For each compound at each concentration the experiment was repeated over a range of pulse energies limited to a pulse energy that results in a Z-scan curve giving $q_0 = 1$.

Fig. 5 presents Z-scans of B2CPK solution with concentration of 20 mM for different energy ranging from 6 nJ up to 22 nJ. The points show the measured data and the solid curves depict the best fits to the measured data using Eq. (1) from which the value of q_0 can be extracted for different scans corresponding to different pulse energy. The 2PA cross section can be obtained from the slope of the plot of q_0 versus pulse energy (E).

3. Results and discussions

Fig. 6a shows the plots of q_0 versus pulse energy for compound B2CPK in THF solution with a range of concentration from 40 mM to 0.4 mM. The data points are the extracted values from fit to Z-scans using Eq. (1). In this figure the zero intercept of those curves labeled with 10, 20 and 40 presents a definite indication of the pure 2PA in the solutions with concentrations of 10 mM, 20 mM and 40 mM (no contribution of ESA). However, at concentrations lower than 10 mM the negative intercept of the plots indicates the presence of ESA. This happens as a consequence of irradiating the solutions with higher intensity laser pulses required to obtain a detectable change in the Z-scan transmittance (i.e. since $q_0 = (N_A \rho \times 10^{-3} / h\omega) L I_0 \sigma_{2PA}$ lower value of concentration ρ should be compensated with higher value of intensity I_0). Although in the presence of ESA the q_0 must show a quadratic dependence on the pulse energy it is hard to distinguish the upward curvature in the plots of q_0 versus pulse energy due to the limited range of q_0 values ($q_0 < 1$). Therefore, the solid lines in Fig. 6a, obtained by fitting the linear relation $q_0 = (N_A \rho \times 10^{-3} / h\omega) L I_0 \sigma_{2PA} + b$ to the data, represent sufficiently good fit curves.

By ignoring the negative intercept, the measured 2PA cross section extracted from the slope of the plots of q_0 versus pulse energy showed a decrease of 7-fold as the concentration was increased from 0.4 mM to 40 mM (Fig. 6b). A decrease by 35-fold in 2PA cross section has been reported by Gu et al. [7] when the concentration increased from 0.2 mM to 20 mM, a 10 folds decrease in 2PA cross section has been reported by Elim et al. [8] when the concentration increased from 0.1 mM to 10 mM (in both reports the highest concentration examined was 100 times higher than the lowest concentration, i.e. the same ratio as in our experiment) and also a 4-fold reduction in 2PA cross section has been reported by Wang et al. [19] even at very low concentrations ranging from 0.001 mM to 0.01 mM. Although the procedure for the data

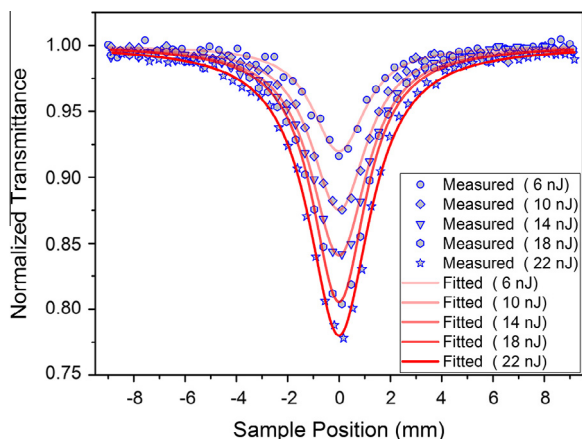


Fig. 5. Z-scans of B2CPK with concentration of 20 mM for different pulse energies.

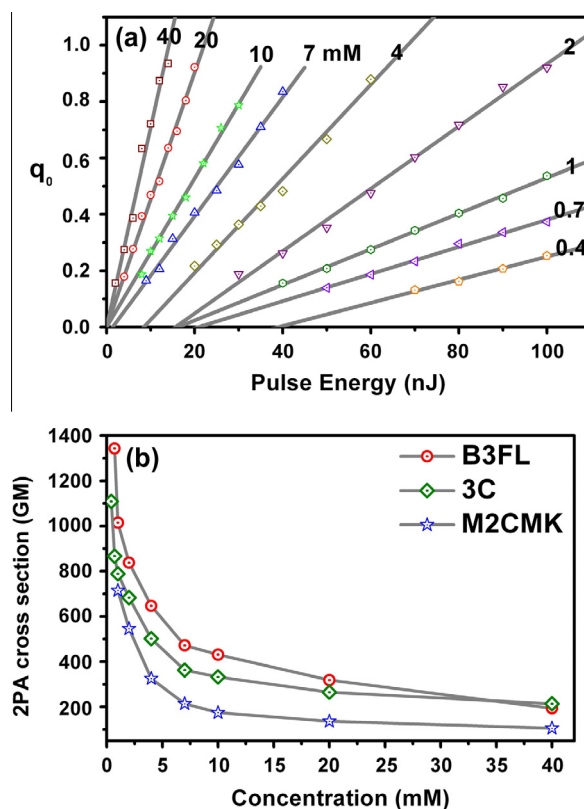


Fig. 6. q_0 (defined in Eq. (1)) versus pulse energy (E) at different concentrations of B2CPK in THF (a) and 2PA cross section versus concentration for different compounds (b). (These data extracted from the slope of q_0 versus E at different concentrations for all compounds).

analysis was not explicitly described in Ref. [7,8], it is most likely that the 2PA cross section values were calculated from the slope of the linear fit to the plot of q_0 versus pulse energy without accounting for the presence of ESA. Thus, the sharp increase in the measured 2PA cross section with decreasing the concentration arises from the substantial contribution of ESA as a consequence of applying higher pulse energies which are required to detect non-linear absorption in the lower concentration solutions. As will be shown in this report, the pure 2PA cross section is although concentration dependent, the change in the concentration cannot lead to such a huge change in the value of the pure 2PA cross section.

In order to determine the pure 2PA cross section and also verify the contribution of the ESA, the Z-scan experiment must be repeated over a range of several pulse energies. At each pulse energy the 2PA cross section of the compound can be directly extracted by fitting Eq. (1) to the Z-scan data. If the measured 2PA cross section remains constant over the range of applied pulse energies it is concluded that the ESA is negligible and thus the measured 2PA cross section can be considered as the pure 2PA cross section. In the presence of ESA the measured 2PA cross section (σ_{meas}) shows a linear increase with pulse energy governed by equation $\sigma_{\text{meas}} = \sigma_0 + k\sigma_{\text{ESA}}E$ where σ_0 is the 2PA cross section at zero pulse energy which can be defined as the pure 2PA cross section, σ_{ESA} is the ESA cross section, E is the pulse energy and k is a constant. Fig. 7a–c shows the measured 2PA cross section as a function of pulse energy for three various 2Pis at different concentrations. For high concentration solutions, where low pulse energies are sufficient to detect the nonlinear absorption from Z-scan experiment, the measured 2PA cross section at each concentration remained constant over the range of energies used in the experiment. In order to examine the lower concentration

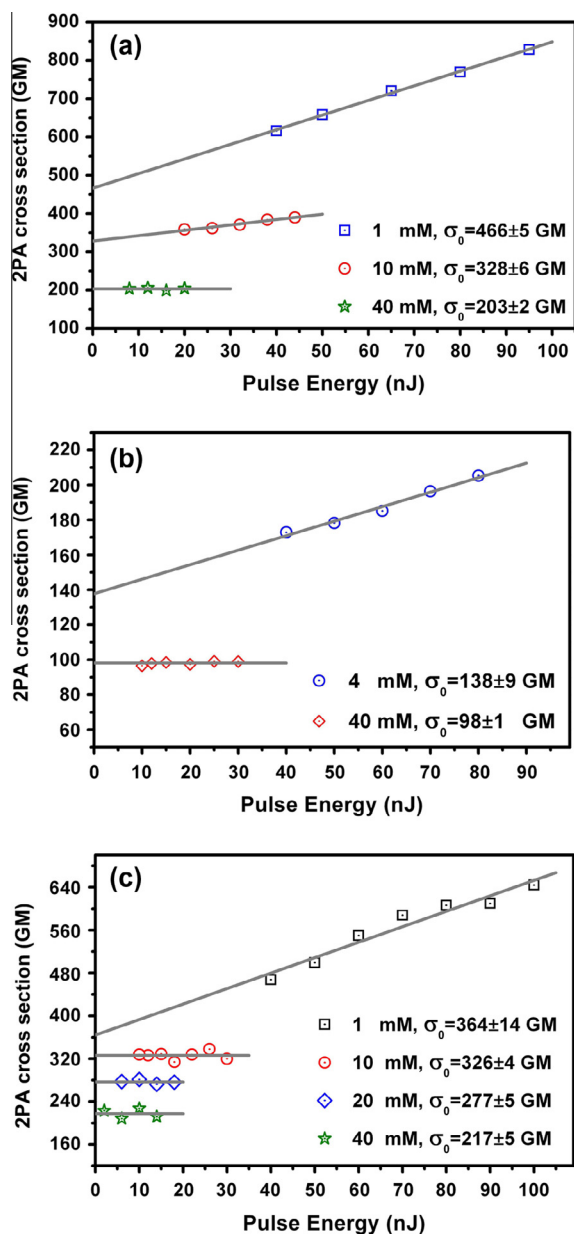


Fig. 7. 2PA cross section versus pulse energy for B3FL (a), M2CMK (b) and B2CPK (c).

solutions the pulse energy has to be increased. The pulse energies up to 100 nJ could be used since below 100 nJ (a) the solvent did not show any nonlinear absorption, (b) the normalized transmittance at the focus was measured larger than 0.76, (c) the contribution of ESA to the whole nonlinear absorption was less than that of the 2PA (Fig. 7) thus Eq. (1) is still valid to be used to fit to the Z-scan transmittance in order to extract the 2PA cross section and (d) no sample degradation or wavelength broadening was observed during the exposure even when the sample traveled through the focus. However, as a consequence of high irradiation the measured 2PA cross section showed linear dependence on pulse energy (corresponding to peak intensity at the focus) due to the contribution of ESA process. In such a case the intercept of the plot of σ_{meas} versus E represents the pure 2PA cross section.

As seen in Fig. 7a–c, the pure 2PA cross section determined as the 2PA cross section at zero pulse energy showed dependence on concentration. In addition, for low concentration solution the

measured 2PA cross section showed intensity dependent behavior since higher pulse energy were used to perform the Z-scan measurements.

The obtained results for all three investigated compounds, summarized in Table 1, demonstrate that the pure 2PA cross section of each compound decreases with increasing concentration over the entire range of concentrations examined. The same behavior was also observed for Rhodamine B (data are not shown here). This behavior can be explained as follows. It has been reported that by increasing the concentration of a solution the number of molecules forming an aggregate – and thus determine the size of the aggregate – increases [20]. As the number of molecules in an aggregate increases the efficiency of the interaction of light per molecule decreases (screening effect) resulting in an overall reduction in 2PA cross section per unit molecule. Thus the tendency of molecules to form larger aggregates at higher concentrations leads to a lower measured 2PA cross section than expected. It is worth mentioning that formation of aggregates at very low concentrations where individual molecules start to aggregate results in an enhancement of the 2PA cross section as reported by Collini et al. [21]. In this case no screening effect is expected, but strong collective effects dominate. However, they also found that as the concentration increased (from 0.25 mM to 1 mM) and thus larger aggregates were formed the 2PA cross section decreased (from 1200 GM to 900 GM). This trend is consistent with our results which were obtained in concentration range from 0.4 mM to 40 mM. Thus the same behavior of decreasing of the 2PA cross section with increasing concentration (except for very low starting concentrations) is a general trend (Refs. [7,8,19,21]). This behavior can be ascribed to the growing the size of aggregates with increasing the concentration. As mentioned above, a screening of individual molecules from the incoming field might be an explanation. Hence, the 2PA cross section measured at high concentration no longer represents the 2PA probability of a single molecule which actually depends on the molecular structure (and also the irradiation wavelength).

As shown in this report, decreasing the concentration of the solution leads to an increase of the pure 2PA cross section of the compound resulting in an increase of the overall 2PA. On the other hand, by decreasing the concentration the overall 2PA decreases due to decreasing of the number density of the two-photon absorbers. Although the former effect cannot compensate the latter one (i.e. the overall 2PA reduces with decreasing concentration), it is proposed to use the as low concentration as solutions that is capable to give the appropriate results. However, selecting the suitable concentration depends also on the light intensity which is available and safe for a specific purpose.

In conclusion, the following procedure is proposed to determine the 2PA cross section which can more likely be considered as a characteristic for the examined compound. In a first step, the 2PA cross section of the given compound at a certain concentration should be determined over a range of pulse energies (from a low value which is sufficient to induce detectable 2PA to the threshold value at which solvent shows nonlinear absorption, sample degradation occurs, wavelength broadening observed or the normalized transmittance at the focus becomes less than 0.76). If the measured 2PA cross section shows intensity dependent behavior (an indication of ESA) then higher concentration solution must be investigated because the Z-scan experiment can be performed using lower pulse energies. The experiment must be repeated at higher concentrations until the dependence of 2PA cross section on the intensity is eliminated. Ultimately, the lowest concentration at which the 2PA cross section becomes intensity independent can be determined for the examined compound. At such a concentration, on one hand, the ESA will not contribute to nonlinear absorption leading to determine a pure 2PA cross section and, on the

Table 1

Pure 2PA cross section of the investigated 2PIs at different concentrations.

Concentration	40 mM	20 mM	10 mM	7 mM	4 mM	2 mM	1 mM	0.7 mM	0.4 mM
σ_0 of B3FL (GM)	203 ± 2	298 ± 4	328 ± 6	383 ± 5	407 ± 6	437 ± 6	466 ± 5	468 ± 6	473 ± 7
σ_0 of M2CMK (GM)	98 ± 1	122 ± 4	129 ± 7	134 ± 6	138 ± 9	140 ± 8	142 ± 9	... ^a	... ^a
σ_0 of B2CPK (GM)	217 ± 5	277 ± 5	326 ± 4	334 ± 4	347 ± 8	358 ± 7	364 ± 14	367 ± 9	371 ± 11

^a The Z-scan signal was not detectable in the range of pulse energy used.

other hand, the screening effect due to the existence of large aggregates is weaker than in case of higher concentration leading to determine the more realistic pure 2PA cross section. Therefore, the obtained 2PA cross section at concentration determined with the above procedure can be considered as the characteristic for the investigated compounds and provides a sensible measure to compare the two-photon activities of different compounds. As shown in Fig. 7c, 10 mM was found the lowest concentration for the compound B2CPK at which 2PA cross section showed no intensity dependent behavior thus, 326 GM can be reported as the characteristic pure 2PA cross section for this compound. For compounds B3FL and M2CMK the lowest concentration, at which only pure 2PA was observed, was determined 20 mM. At this concentration the 2PA cross section was obtained 298 GM for B3FL and 122 GM for M2CMK.

4. Conclusion

This report presents the results of investigating the effect of concentration of solutions on their 2PA cross section. The aim of this paper is to verify the concentration dependence of the 2PA cross section and establish a procedure to determine the pure 2PA cross section. Three different 2PIs and a standard dye were investigated over a concentration ranging from 0.4 mM to 40 mM and a pulse energy ranging from 2 nJ to 100 nJ. In addition to intensity dependent behavior for 2PA cross section, which has been well understood due to the contribution of the ESA, a concentration dependent behavior was observed for all examined compounds. The results of investigations show that the pure 2PA cross section decreases with increasing the concentration. This could be ascribed to the screening effect due to the formation of large aggregates in high concentration solutions. Thus, in order to measure the more realistic 2PA cross section it is recommended to use lower concentration. The intensity independent 2PA cross section at lowest concentration can be considered as the pure 2PA cross section.

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