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نشانه هایی از وابستگی سطح مقطع جذب دو فوتونی به چگالی: تعیین مقدار واقعی سطح مقطع

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چکیده - پدیده جذب دوفوتونی پایه کاربرهای زیادی است که از آغازگرهای دوفوتونی بهره می برند. به طور ایده آل سطح مقطع جذب دوفوتونی می بایستی پارامتری مختص هر ماده باشد تا امکان اندازه گیری و قیاس توانایی جذب دوفوتونی مواد مختلف فراهم آید. در این گزارش نشان داده شده است که سطح مقطع جذب دوفوتونی به چگالی ماده حل شده در یک محلول بستگی دارد. از آنجایی که استفاده از چگالیهای متفاوت یک ماده در کاربردهای مختلف اجتناب ناپذیر است پس اطلاعات کامل درباره بستگی سطح مقطع جذب دوفوتونی به چگالی و روش صحیح اندازه گیری آن ارائه شده است.

کلید واژه- آغازگرهای دوفوتونی، اپتیک غیر خطی، پالسهای لیزری فوق کوتاه، جذب دوفوتونی

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

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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. 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. 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.

Keywords: Nonlinear optics, Two-photon absorption, Two-photon initiator, Ultrashort laser pulses

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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], 3D optical data stage [3] and even much more crucial for areas such as two-photon photodynamic therapy (2P-PDT) [4] and two-photon induced fluorescence imaging (2PIF) [5]. 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. In this report, the detailed investigations for different photoinitiotors at various concentrations ranging from 0.4 milli-molars (mM) to 40 mM are presented.
In order to determine the 2PA cross section of the examined compounds at various concentrations the open aperture Z-scan technique [6] was employed.

2 Results and discussion

In our Z-scan setup a Ti:sapphire amplifier generating 25 femtosecond pulses at 800 nm with repetition rate of 1 kHz was employed. The 15 mm diameter laser beam was focused using a 300 mm focal length lens leading to a beam waist radius of 20.3 Micron considering a beam quality factor of 2. The detailed setup and laser pulse and beam characterization can be found somewhere else [7].

In the Z-scan technique it is not possible to isolate the pure 2PA from other nonlinear absorption contributions such 3PA, 2PA induced excited state absorption (ESA) or 1PA induced ESA. Therefore, to extract the pure 2PA cross section from the Z-scan signal the establishment of a protocol [8] for measuring the 2PA cross sections is of crucial importance. For instance, the range of irradiation intensity must be chosen carefully [9] 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.

Three different PIs (B3FL), (M2CMK) and (3C) [10] at concentration ranging from 0.4 mM to 40 mM were investigated. 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 but 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/cm^2), a threshold at which the solvent showed nonlinear absorption. It is worth mentioning that the maximum pulse energy which can be used in the Z-scan method is constrained by two factors a) the threshold pulse energy over which the solvent shows nonlinear absorption and b) the threshold pulse energy over which the normalized Z-scan transmittance at the focus becomes lower than 0.76.
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 from the Z-scan data. If the measured 2PA cross section stays constant over the range of applied pulse energies it is concluded that 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 $\sigma_{meas}=\sigma_0+k\sigma_{ESA}E$ 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. Figures 1(a), 1(b) and 1(c) show 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 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 contribution of ESA to the whole nonlinear absorption was less

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than that of the 2PA (figure 2) and c) the Z-scan normalized transmittance at the focus remained greater than 0.76. However, as a consequence of high irradiation the measured 2PA cross section showed linear dependence on intensity due to the contribution from ESA process. In such a case the intercept of the plot of σ_{meas} versus E represents the pure 2PA cross section. Although the measured 2PA cross section may or not show intensity dependent behavior depending on the range of pulse energies used, the pure 2PA cross section corresponding to the 2PA cross section at zero pulse energy always shows a concentration dependent as shown in figures 1(a), 1(b) and 1(c). The obtained results for all three investigated compounds demonstrate that the pure 2PA cross section of each compound decreases with increasing concentration over the whole range of concentrations examined. 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 [11]. 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. 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 concentrations no longer actually reflects the intrinsic molecular characteristics.

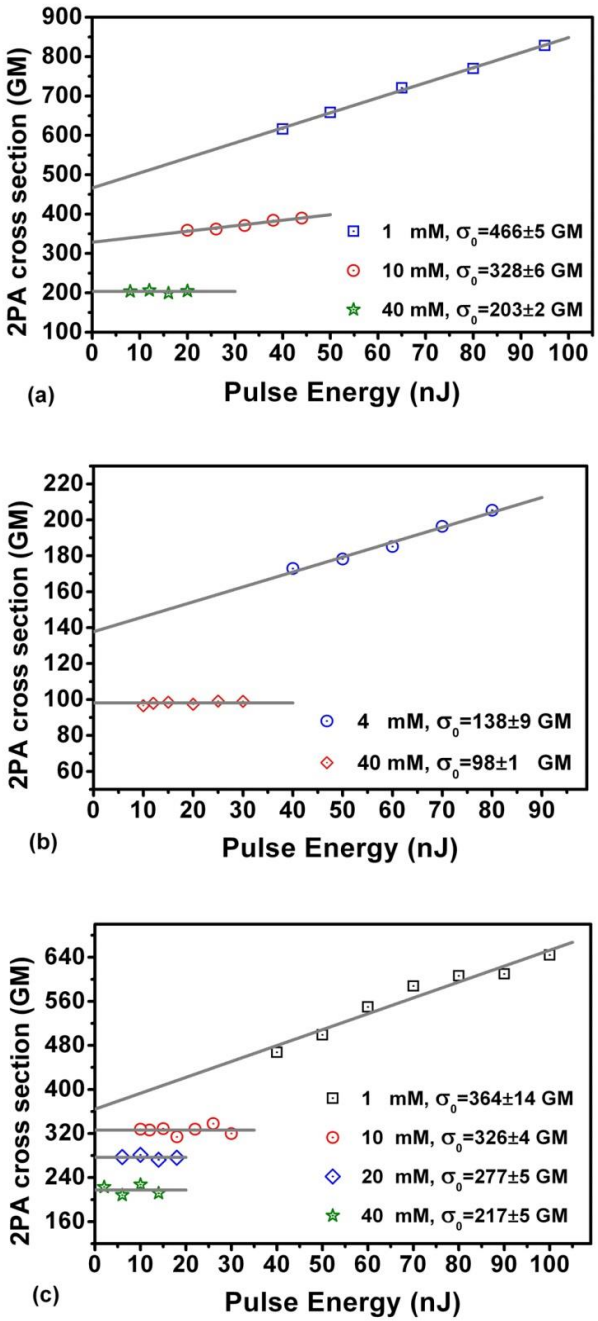


Figure 1. 2PA cross section versus pulse energy for B3FL (a), M2CMK (b) and 3C (c)

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. If the measured 2PA cross section shows intensity dependent behavior (an indication of ESA) then higher concentration solution must be investigated since it can be examined using lower pulse

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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 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. As shown in the figure 1(c), 10 mM was found the lowest concentration for the compound 3C at which 2PA cross section showed no intensity dependent behavior thus, 326 MG can be reported as the characteristic pure 2PA cross section for this compound. For compounds B3FL and M2CMK the lowest concentration, at which only the pure 2PA is observed, was determined 20 mM. At this concentration the 2PA cross section was obtained 298 GM for B3FL and 122 GM for M2CMK.

3 Conclusions

The concentration dependent behavior of 2PA cross section is attributed to the tendency of aggregates to grow their size with increasing the concentration. Finally, a measurement protocol for comprehensive characterization of 2PA capability of different substances is proposed.

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