Optical Materials 47 (2015) 524–529

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

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

ARTICLE INFO

Article history:
Received 12 February 2015
Received in revised form 5 June 2015
Accepted 16 June 2015
Available online 22 June 2015

Keywords:
Two-photon absorption
Two-photon cross section
Nonlinear optics
Femtosecond pulses
Photoinitiator

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.

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 photoinitiotors 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).

http://dx.doi.org/10.1016/j.optmat.2015.06.033
0925-3467/

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

where z is the sample position measured with respect to the focal point, $q_0 = (N_A\rho \times 10^{-3}/\hbar\omega)LI_0\sigma_{2PA}$, 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/cm^2), 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 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].

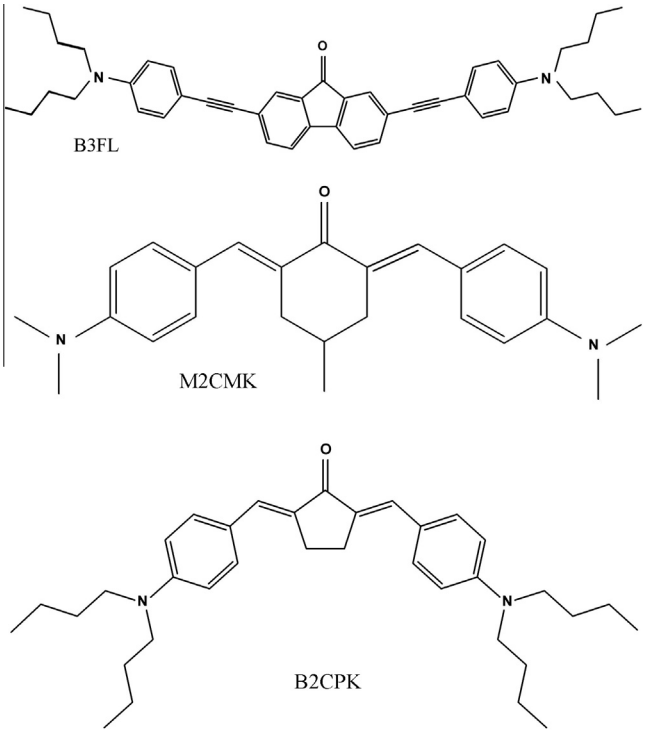

Fig. 1. Molecular structures of the studied compounds.

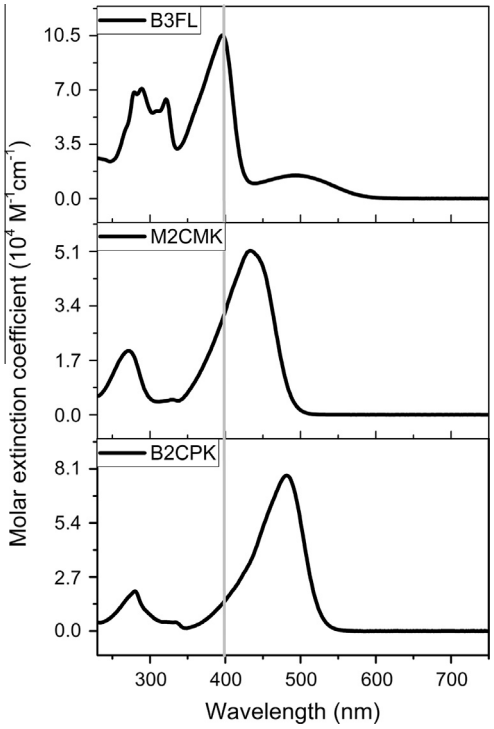

Fig. 2. Linear absorption of the studied compounds.