Z-Scan measurements of two-photon absorption for ultrashort laser radiation

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ABSTRACT

We have developed a low cost apparatus for open- and closed-aperture Z-scan measurements of multi-photon absorption (MPA) cross-sections of solid and liquid samples. The experimental setup uses simple diodes for light detection. The signals are recorded with a low-cost two-channel PC-scope. We have developed a LabView based software, which analyzes single laser pulses and allows averaging over several shots. First measurements on a CR-39 polymer demonstrated the functioning of the method. Furthermore, we have shown that for 25fsec ultra short pulses three-photon absorption (ThPa) must be considered in addition to two-photon absorption (TPA). The appropriate nonlinear absorption (TPA-, ThPA-) coefficients and the nonlinear refractive index can be obtained via a best fit of the data to theoretical curves, which have been derived and adapted for ThPA from formulas for TPA accessible in the literature.

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Keywords: Ultra-short lasers, nonlinear optics, multi-photon absorption, photo-polymerization

1. INTRODUCTION

1.1 Physical background

Two-photon absorption is a third-order nonlinear process where two photons are absorbed simultaneously. Since it represents a third-order process, TPA is described by the imaginary part of the third-order susceptibility χ_3 [1,2]. Three-photon absorption is described by the imaginary part of the fifth-order susceptibility χ_5 [2].

There are several different experimental techniques that can be employed to measure TPA cross-section such as nonlinear transmission, up-converted fluorescence emission, transient absorption, four-wave mixing and the Z-scan technique.

By employing the so-called open aperture Z-scan technique[3] one can determine the two-photon and three-photon absorptions coefficients β and α_3. The experimentally obtained (z-) position dependent intensity variation is compared to theoretical curves to extract the desired parameters. Not only the two-photon and three-photon absorptions coefficient, but also the Rayleigh length is determined by fitting the experimental data with the appropriate equations (3) and (4). Furthermore, the nonlinear refractive index γ and n_4 can be determined via the so-called closed aperture z-scan method.

1.2 Motivation

With the development of NIR ultra-short pulsed laser systems in the past few years, Two-Photon Absorption (TPA) in molecular systems has attracted much attention of researchers due to its potential applicability in the field of future photonics such as 3D optical data storage, photonic crystals, photodynamic therapy, two-photon induced photo-

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polymerization (TPIP) and many more. Among many other applications, the development of new organic materials for TPA is a promising area of research.

By means of TPIP, it is possible to produce complex “real” 3D structures with a theoretical spatial fabrication resolution below the diffraction limit of the used wavelength (down to 120 nm). These parts can be used e.g. in polymer-based photonic and micro-electromechanical devices (MEMS), which are beyond the capabilities of other (linear) structuring methods. Optimized photo-initiators (PIs) are essential for nicely shaped structures fabricated by means of TPA based methods.

Representative examples realized in the *Institute of Applied Synthetic Chemistry* at the *Vienna University of Technolgy* are polymer based optical waveguides by a local change of the refractive index by means of TPIP and synthesized PIs based on a triple bond containing cross-conjugated D-π-A-π-D lead structure with an absorption maximum at around 400 nm.

2. EXPERIMENTAL

2.1 Open and closed aperture Z-scan

It was our intention, to realize the Z-scan method at minimal costs and using our ultra-short laser system (FEMTOPOWER PRO). This system delivers ultra short laser pulses with a maximum average power of approximately 500 mW at a repetition rate of 1000 Hz. The pulse duration, estimated as the FWHM of a Gaussian temporal profile, is typically 25 fs and the spectrum is centered at 800 nm.

The schematic of the experimental setup is shown in Fig. 1. The beam is split in two orthogonal directions, one being used as intensity reference (detected at the reference diode D_r). The other is directed to a focusing lens (20 cm focal length) and then through the sample. At this stage, the target used was a CR-39 polymer, 1 mm thick and mounted on a translating stage that can be moved across 25 mm through the beam focus. The transmitted intensity is then collected by a lens (10 cm focal length) and directed to the diode D_o (open aperture configuration) or through a small aperture and to the Diode D_c. (closed aperture configuration). According to our intention to keep the costs minimal, we have used diodes as detector. This requires adjusting the absolute intensity at the diodes (Neutral Density Filters NDF) to fall into the dynamic range of the diodes. The signal at the diodes is recorded with a low-cost two-channel PC Oscilloscope (Picoscope). The computer software analyzes the intensity of individual laser pulses (including averaging over several laser shots) and also handles the movement of the translation stage as well as the entire data acquisition process (LabView). The setup in Fig. 1 shows both, the so-called open aperture and closed-aperture Z-scan methods, which yield the TP (and/or three photon-) absorption coefficients and the nonlinear refractive index respectively.

2.2 CR-39 target for calibration

In order to test and calibrate the apparatus and the method, we have performed measurements of the nonlinear absorption for a polymer called CR-39 [4], which is made by polymerization of diethyleneglycol bis allylcarbonate (ADC) in presence of diisopropyl peroxydicarbonate (IPP) catalyst. It is colorless and completely transparent in the visible spectrum and almost completely opaque in the ultraviolet and infrared. Its density is about half of that of glass and its linear refractive index (1.501) is only slightly lower than that of crown glass. For these reasons, it is an advantageous and dominant material for eyeglasses and sunglasses lenses.

CR-39 is used for different applications. These include up-to-date studies in nuclear and fission physics, alpha, neutron and charged particle radiography, cosmic ray studies and astrophysics, porosity and micro-filters, alpha- and neutron-dosimetry, uranium prospection and radon-emanation measurements, radiological protection and monitoring, radiobiology and nuclear medicine measurements made on meteorites, lunar samples, in stratospheric balloons and from space vehicles, as well as the search for super heavy elements [4].

2.3 Two- and three-photon absorption

The Z-scan technique has been first introduced in 1989 by Shaik-Bahae et al [3] and has been developed since then. For the open aperture geometry, in addition to the equation given in [3] for fitting the z-scan intensity curve assuming TPA, we have derived the analog formula under the assumption of three-photon absorption.

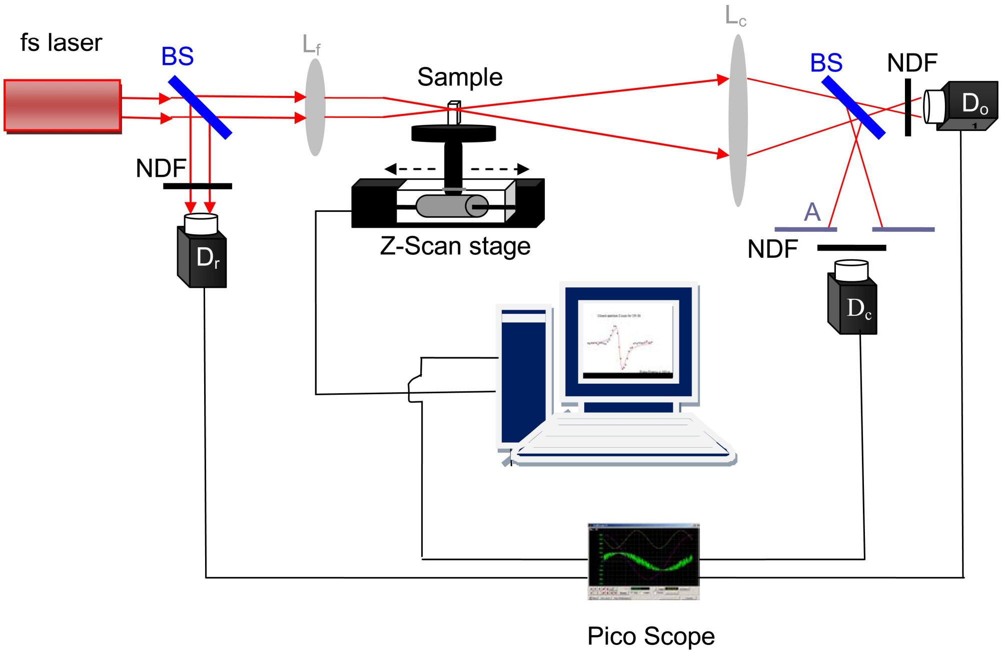

Fig.1: Experimental realization of an open and closed aperture Z-scan experiment.

Starting point is the fifth-order nonlinearity where the absorption coefficient α can be expressed in terms of the linear (α_0) and the three-photon absorption coefficient α_3 by

$$\alpha = \alpha_0 + \alpha_3 I^2 \tag{1}$$

The amplitude of the electric field $\sqrt{I}$ and its phase as a function of z' (coordinates inside the sample) are described by a differential equations as follows:

$$\frac{dI}{dz'} = -\left(\alpha_0 + \alpha_3 I^2\right) I \tag{2}$$

After some lengthy calculations the (measured) normalized transmittance $T(z)$ defined as the quotient of transmitted and incident energy is obtained as:

$$T(z) = \sum_{m=0}^{\infty} (-1)^m \frac{P_0(0)^{2m}}{(2m+1)^{3/2} 2m!(1+x^2)^{2m}} \tag{3}$$

In equation (3) $P_0(0) = \sqrt{2\alpha_3 L'_{eff} I_0(0)}$, $I_0(0)$ is the maximum on-axis intensity at the focus, $x = z/z_0$ with z the position of the sample measured with respect to the beam waist, and z_0 is the Rayleigh length. $L'_{eff} = (1-e^{-2\alpha L})/2\alpha$ is called the effective sample length.

The normalized transmittance for purely two-photon absorption derived in [3] is given by

$$T(z)=\sum_{m=0}^{\infty}\frac{\left(-q_0(0)\right)^m}{(m+1)^{3/2}\left(1+x^2\right)^m} \tag{4}$$

Where $q_0(0)=\beta L_{eff} I_0(0)$ with $I_0(0)$ the on-axis intensity in the focus and β the TPA coefficient.

The experimental curves can be fitted with (3) or (4) or the sum of both respectively to obtain α_3 and β.

In a similar way, a formula can be derived for the closed aperture case, in which the nonlinear refractive index is the major parameter to be determined from the experimental data by the best fit.

The analogous normalized transmittances for TPA and ThPA and the closed aperture geometry have been derived and are given in equations (5) and (6)

$$T(z)=1+\frac{4\Delta\Phi_0(t)x-q_0(t)\left(x^2+3\right)}{\left(1+x^2\right)\left(9+x^2\right)} \tag{5}$$

with the phase change due to induced changes of the (nonlinear) refractive index: $\Delta\Phi_0(t)=k\gamma L_{eff} I_0(t)$.

$$T(z)=1+\frac{8\Delta\Phi_0(t)^2x-\frac{1}{2}p_0(t)^2\left(x^2+5\right)}{\left(x^2+25\right)\left(x^2+1\right)} \tag{6}$$

In (6) the phase change becomes $\Delta\Phi_0(t)^2=kn_4L'_{eff}I_0(t)^2$.

n_4 and α_3 are related to the real and imaginary part of the fifth order susceptibility χ_5 respectively. It should be mentioned, that equation (3) is valid in this relative simple form only under the condition that the absorption remains below approx. 10% (or equivalent low laser intensities). For higher intensities simplifications in the derivation of (3) are not accurate anymore.

3. RESULTS AND DISCUSSION

A series of open-aperture experiment for the polymer CR-39 were performed for different laser intensities. The results are shown in Fig. 2 and 3. In Fig. 2 the experimental data for different laser intensities are shown. The multi-photon absorption cross-section increases with increasing laser intensity. The increase of the absorption maxima in Fig. 2 is approximately proportional to I^2.

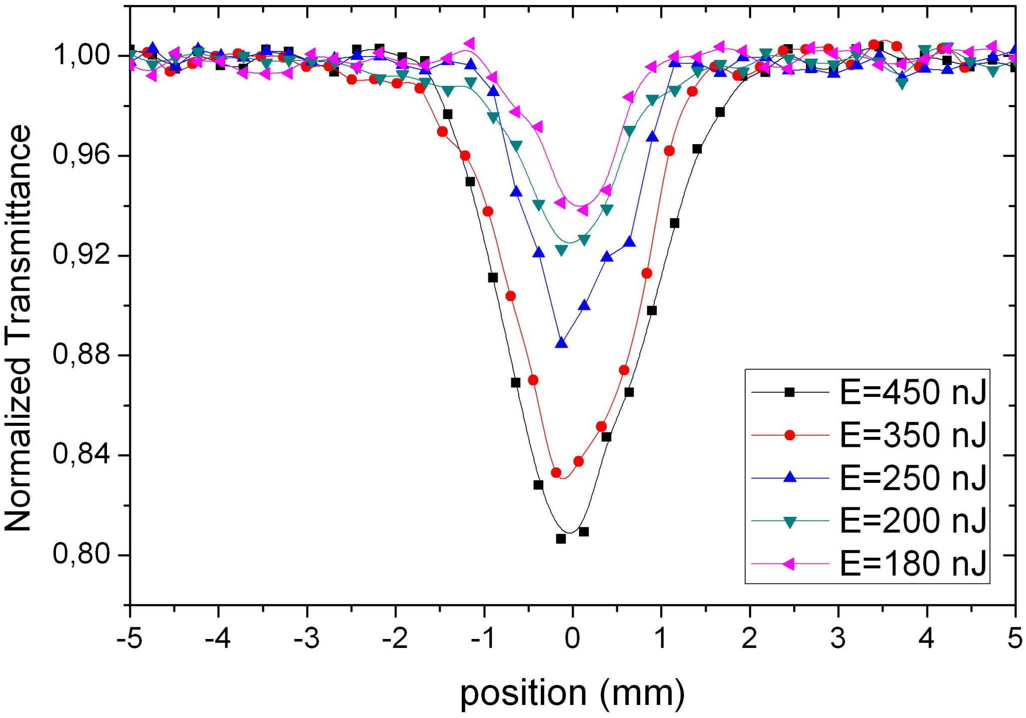

Fig. 2 Open aperture Z-scan measurement: Normalized transmittance for different laser intensities (values correspond to pulse energy before target).

Experimental data and the corresponding fit-curves are shown in Fig. 3. The data are fitted using equation (4) for two-photon absorption and equation (3) for three-photon absorption. The comparison shows, that for CR-39 and the given laser parameter (25fs and intensity range) three photon absorption plays an important role.

From fitting the data for different laser intensities, one could obtain the TPA coefficient. As seen from Table 1, the TPA coefficient would increase with laser intensity. This implies, that the observation in Fig. 3 is correct, that the data can be better fitted under the assumption that three photon absorption dominates. This is not astonishing, since the band gap of CR-39 is 3.8eV [3]. This requires 3 photons of 800nm (1.5eV). In addition, the increase of the absorption maxima with laser intensity in Fig. 2 favor a three photon process: Theory predicts an increase proportional to the laser intensity I for TPA and proportional to I^2 for ThPA. The increase in Fig.2 is slightly more than I^2.

Table. 1. Two-photon absorption for different intensity. As seen the TPA coefficient increases with increasing laser intensity.

Intensity (W/cm^2) $\times 10^{-12}$	2.8	3.6	4	5.24	5.78
TPA coefficient (cm/W) $\times 10^{-12}$	0.84	0.95	1.3	1.36	1.47

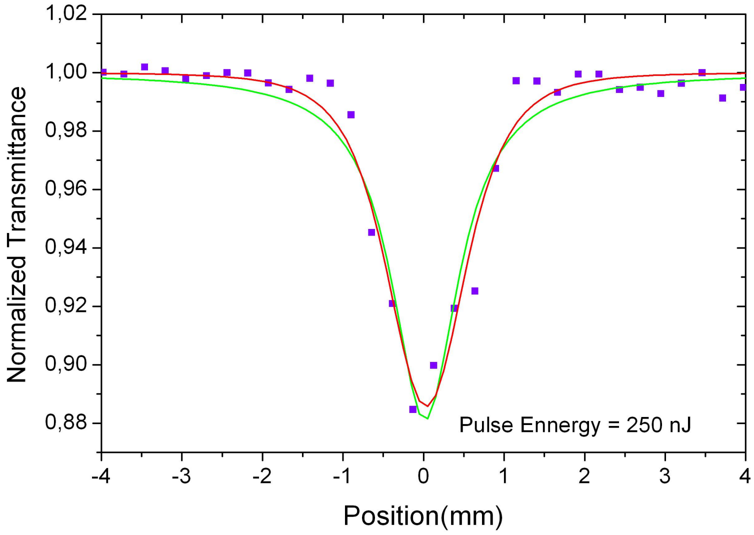

Fig. 3 The measured normalized transmission is fitted with equation (3) (green, TPA) and equation (2) (red, ThPA).

Considering the facts discussed above, we can obtain a three-photon absorption coefficient α_3 = 1.0±0.3 10^{-24}cm/W^2 from the best fit to the experimental data. This value is more or less independent of laser intensity in the intensity regime investigated.

In Fig. 4 the results for the closed aperture configuration are given. Again the transmission curves have been recorded for different laser intensities. It should be noted, that the intensities are lower than in the open aperture case.

An example is shown in Fig. 5. The lower laser intensities might imply the dominance of TPA over ThPA. On the other hand, the argument concerning the band gap energy would rather imply a three-photon process as well. The fitting of the transmission curves implies that both, TPA as well as ThPA should be considered. In Fig. 5 and 6 this is shown for two laser intensities. The fits for considering only TPA (green, [equation (5)]), merely ThPA (red, [equation (6)]) and both together (blue) are shown.

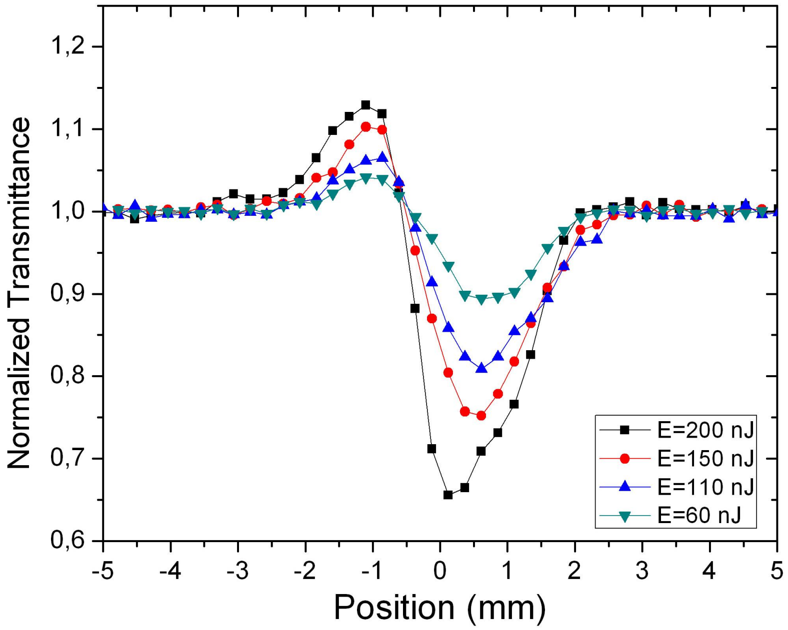

Fig. 4 Transmission curves for the closed aperture configuration for different laser intensities.

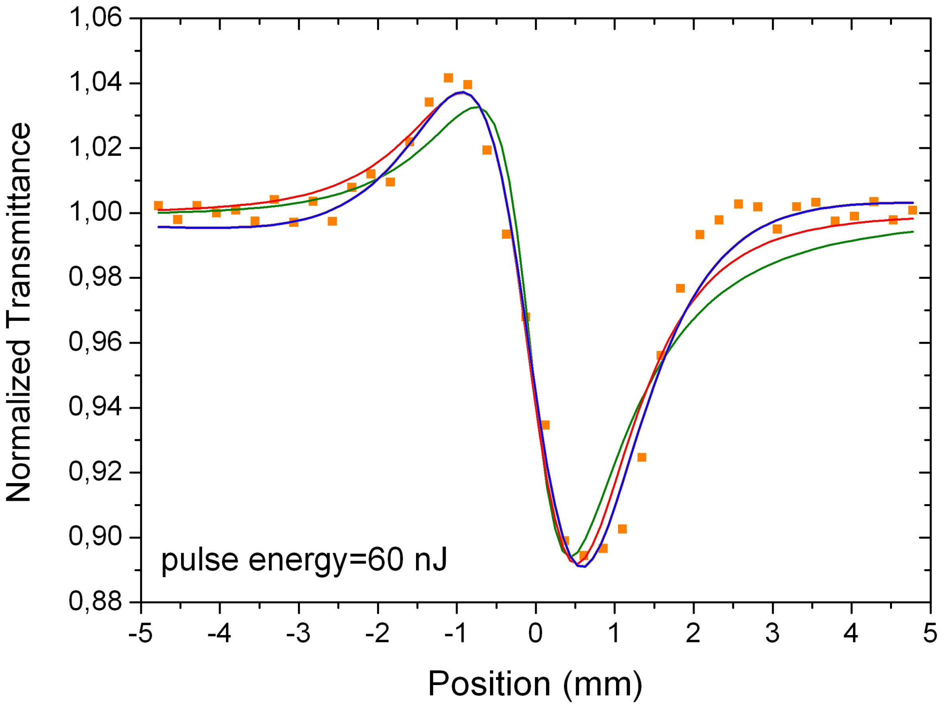

Fig. 5 Fit of the transmission curve in the case of a closed aperture configuration assuming a TPA (green, [equation (5)]), ThPA (red, [equation (6)]) and both together (blue) for a pulse energy of 60nJ.

Nonlinear refractive indices γ and n_4 can be determined from the fits in Fig. 5. Values $\gamma = -5{,}0 \pm 0{,}5 \times 10^{-17}$ cm^2/W and $n_4 = -3.9 \pm 0{,}3 \times 10^{-29}$ cm^2/W^2 are obtained.

Finally, it is interesting to compare the values for α_3 obtained from the open and closed aperture z-scan measurements. As shown above, the value from the fit to the open aperture data resulted in a value $(\alpha_3)_{\text{openAp}} = 1.0 \pm 0.4\ 10^{-24}$cm/W^2. The corresponding value from the closed aperture data was obtained to $(\alpha_3)_{\text{closeAp}} = 1.4 \pm 0.2\ 10^{-24}$cm/W^2. A detailed analysis will be published elsewhere.

We would like to point out, that fits in Figures 5 and 6 basically reflect the fact, that ThPA is the dominant absorption process in CR-39. The best fit shown by the blue curve shows that both the nonlinear refractive indices γ and n_4 have to be taken into account.

4. CONCLUSIONS

We have demonstrated that a Z-scan apparatus based on a low-cost detection system with appropriate software can be used for open- and closed-aperture Z-scan measurements of multi-photon absorption (MPA) cross-sections of solid and liquid samples. Furthermore we have shown, that for 25fsec ultra short laser pulses three-photon absorption (ThPa) will contribute substantially to multi-photon absorption. The appropriate absorption cross-sections and the nonlinear refractive index can be obtained from the experimental transmittance curves. Furthermore, we would like to mention, that ongoing measurements show, that multi-photon absorption can be enhanced pre-irradiating the (solid) sample with ultra-short laser radiation. An important issue, which must be addressed in further investigations, concerns the question, in how far the assumption of only one absorption coefficient is valid. The contributions of several sources of absorption would severely complicate the analysis. Furthermore, the influence of the laser pulse length and intensity are important questions to be addressed.

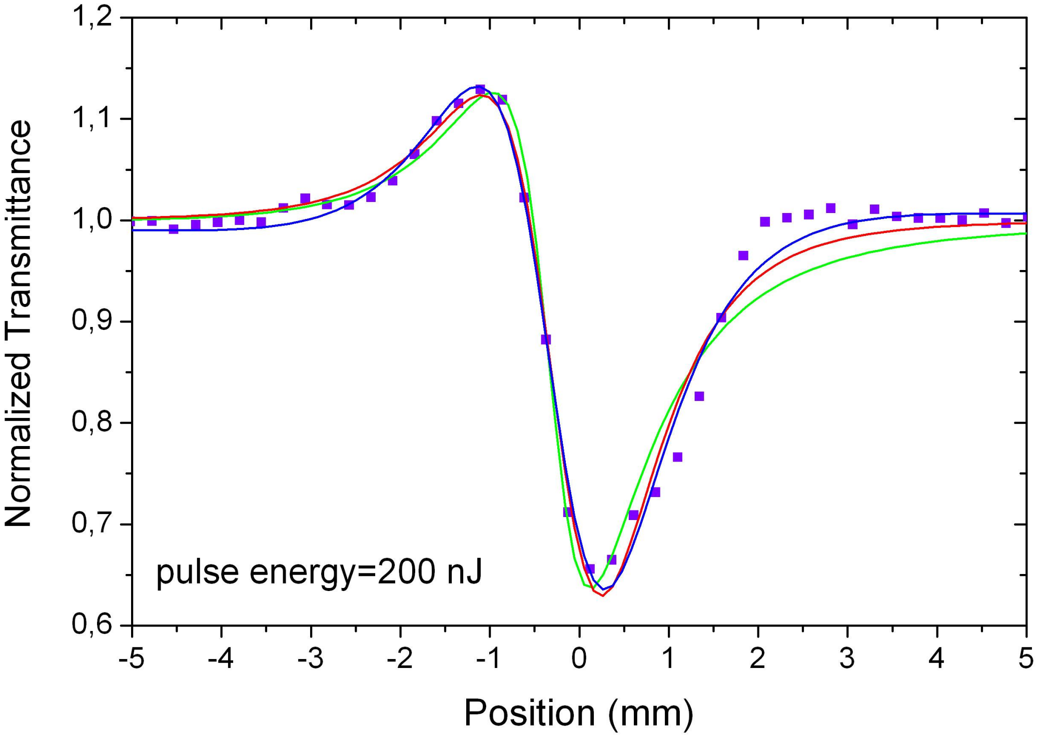

Fig. 6 Fit of the transmission curve in the case of a closed aperture configuration assuming a TPA (green), ThPA (red) and both together (blue) for a pulse energy of 200nJ.

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