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Variation of the sign of nonlinear refraction of carbon disulfide in the short-wavelength region

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Abstract: We report the spectral dependence of the nonlinear refractive index (γ) of carbon disulfide (CS_2) in the range of 400–1100 nm in the case of the femtosecond laser pulses. The positive sign of γ dominated in the region between 600 and 1100 nm. At a shorter wavelength (500 nm), we observed the intensity-dependent competition between the fifth-order related self-defocusing and third-order related self-focusing. Further decrease of the wavelength of the probe pulses (400 nm) resulted in domination of the negative nonlinear refraction. The fifth-order nonlinear refractive index of CS_2 at $\lambda = 400$ nm ($\eta = -4\times10^{-22}$ cm^4 W^{-2}) is determined.

1. Introduction

Carbon disulfide (CS_2) is often mentioned as the liquid showing positive nonlinear refractive index (γ). Its value is refereed as 3×10^{-15} cm^2 W^{-1} without elaboration that this parameter was obtained for the specific wavelength and in the case of ultrashort (femtosecond) laser pulses [1–4]. Meanwhile, the reported values of this parameter differ from each other by more than one order of magnitude.

A difference in the reported measurements of the same material is attributed to the application of different conditions of experiments, such as pulse duration, wavelength, repetition rate, and intensity of the probe pulses. The latter characteristic of laser radiation can modify the value of the third-order nonlinear optical parameter γ by adding the higher-order component of the optical nonlinearity. The method of determination also plays important role. Table 1 comprises some of earlier reported results of Z-scan studies of this liquid.

Table 1. Short-list of the measurements of the nonlinear refractive index of CS_2 using pulses of different duration

λ (nm)	Pulse rep. rate (Hz)	Pulse width	γ ($\times10^{-15}$ cm^2 W^{-1})	Reference
770	76×10^6	130fs	2.3	[5]
800	20	110fs	3.1	[3]
800	8×10^7	100fs	12 (fast component)	[6]
800	10	110fs, 75ns	3 (110 fs), 30 (75 ns)	[1]
1200, 600	1000	1ps	12(1200 nm), 24 (600 nm)	[2]
800	10	120 fs	2.1	[7]
532	10	7 ps	8	[8]
700	1000	28 ps	92	[4]
480	1000	100 fs	6	[9]

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This table comprising only a few excerpts of such studies demonstrates both the long-lasting interest to this liquid and the difference in the approaches and results. Still one of important issues, which have rarely been touched, is the spectral dependence of γ. A few studies of this dependence were reported [2,9]. Particularly, the measurements of the nonlinear refractive indexes of CS_2 liquid in the 580–1600 nm wavelength range were analyzed in [2]. They observed a small wavelength dependence of γ in the 1175–1600 nm range with some increase toward the shorter wavelengths (580–800 nm). The wavelength dependence of this parameter (from 390 to 1550 nm) was also studied in [9]. They observed a drop of the nonlinear refractive index starting from $\lambda = 480$ nm. However, no detailed elaboration of this process was presented.

Overall, no reports about the modification of this parameter in the shorter-wavelength region were published. Recently, the spectral properties of γ were analyzed using picosecond pulses [4]. An increase of the nonlinear refractive index of CS_2 at the shorter wavelength region compared with the NIR region (9×10^{-14} cm^2 W^{-1} ($\lambda = 700$ nm) and 4×10^{-14} cm^2 W^{-1} ($\lambda = 1000$ nm), respectively) was followed by a decrease of this parameter at the wavelengths below 600 nm. In [4], the joint influence of the electronic Kerr effect and molecular and orientation Kerr effects leading to the stronger self-interaction compared with the case of ultrashort pulses was analyzed. Those effects originate from the bound-electronic response and three noninstantaneous mechanisms related to the nuclear motions, such as collision, libration, and diffusive reorientation. The combination of those processes leads to a time-dependent third-order response. To exclude the noninstantaneous mechanisms, one can use the probe pulses shorter than the shortest relaxation time for the development of the three nuclear motions, i.e. 1–10 ps. In present paper, we study in detail the variations of γ at different wavelengths of the femtosecond probe pulses and demonstrate the influence of the purely electronic higher-order nonlinear refractive process on the variation of the sign of γ at 400 nm.

With the increase of laser intensity, the higher-order nonlinear optical refraction can play a growing role in the modification of the effective nonlinear refractive index of CS_2. This effect was reported in the case of longer-wavelength range when the self-defocusing attributed to the fifth-order nonlinearity led to some decrease of the effective nonlinear refractive index [7]. In our study, we report the observation of the prevailing influence of the fifth-order nonlinear optical refractive index on a whole value of nonlinear refraction of carbon disulfide in the short-wavelength region leading to the change of this process from self-focusing (at $\lambda = 500$ nm) to self-defocusing (at $\lambda = 400$ nm).

Earlier, the comparative studies of the third- and fifth-order optical nonlinearities of different materials have demonstrated the importance of the higher-order process on the behavior of the laser beam propagation [10–16]. As mentioned, such process was also reported in carbon disulfide, when the additional component of the nonlinear refractive index increased the self-defocusing at the wavelength of 800 nm [7]. However, though in their case the sign of the fifth-order nonlinear refractive index was negative its influence was not significant. It did not change the whole sign of the self-interaction remaining to be positive. In our case, we demonstrate how the negative sign of the higher-order process can cancel the self-focusing and cause the self-defocusing in CS_2 at the shortest used wavelength close to the absorption band of this liquid.

In this paper, we analyze the dynamics of γ of CS_2 in the short-wavelength region using 150 fs probe pulses (PP). Below we describe the observed decrease of this parameter in the spectral region below $\lambda = 600$ nm and attribute it to the influence of the fifth-order process, which, to the best of our knowledge, has never been reported in this spectral range. We demonstrate that this higher-order process can drastically decrease the effective value of the nonlinear refractive index and even lead to the change of the sign of nonlinear refraction.

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2. Method

In the Z-scan scheme, the 1-mm thick silica glass cell filled with CS_2 (Sigma-Aldrich, ≥99.9%) was moved along the z-axis through the focal point of the focusing lens using a translating stage (Fig. 1(a)). The radiation was focused by a 110 mm focal length lens. The beam waits radius of the focused 800 nm radiation was 15 μm. The Rayleigh length of the focused radiation was 1.2 mm.

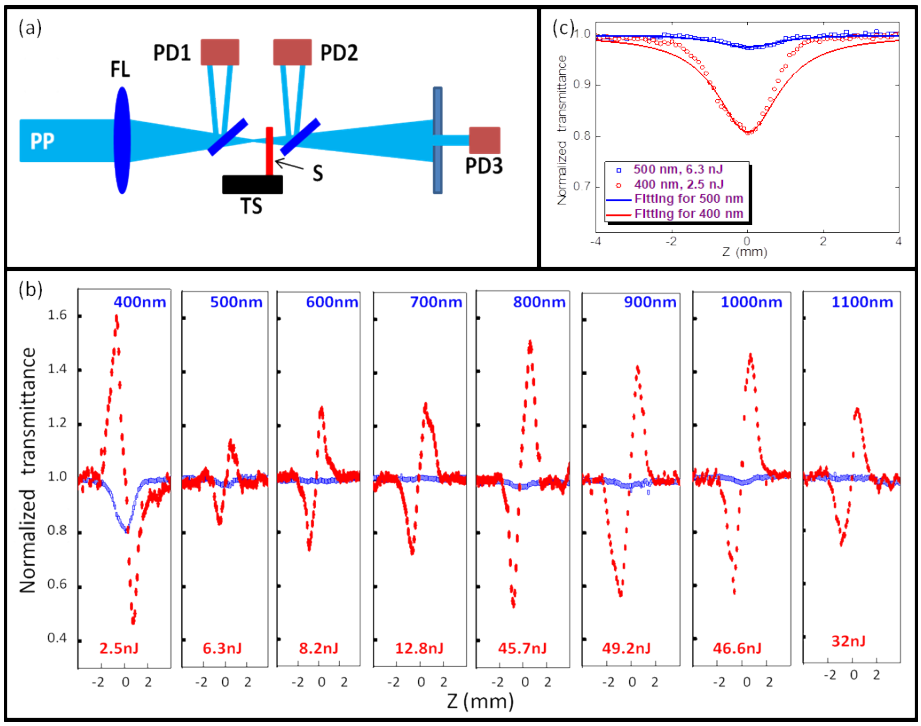

Fig. 1. (a) Z-scan scheme. PP: 150 fs probe pulse; FL: spherical focusing lens; PD1 – PD3: photodiodes determining normalized transmittance (PD1), open-aperture transmittance (PD2), and closed-aperture transmittance (PD3); TS: translating stage; S: sample (1-mm thick silica glass cell filled with carbon disulfide). (b) Closed-aperture (red) and open-aperture (blue) Z-scans of carbon disulfide in the range of 400–1100 nm. The energies of PP are shown beneath the corresponding Z-scans. (c) Open-aperture Z-scans using 400 nm (red empty circles) and 500 nm (blue empty squares). The fittings using Eq. (2) for corresponding experimental data are shown by red and blue solid curves.

The energy of the input laser pulse was measured with a calibrated photodiode (PD1) and registered with a digital voltmeter. To measure closed-aperture (CA) Z-scans, the 1-mm aperture was fixed at a distance of 150 mm from the focal plane behind which the second photodiode (PD3) was located. The ratio of transmitted light through this aperture was $S = 0.02$. The ratio of the transmitted radiation registered by the second photodiode and the incident radiation registered by the first photodiode was taken as the normalized transmittance (T). Away from the focal point, where nonlinear processes do not occur, the normalized transmittance was equal to $T = 1$. The CA scheme allowed determining the sign and value of γ of CS_2. Third photodiode (PD2) measured the whole energy propagated through the cell. The open-aperture (OA) scheme allowed determination of the nonlinear absorption coefficient (β) of the studied liquid.

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The femtosecond laser system consisted of ORPHEUS-HP Optical Parametric Amplifier with PHAROS PH2 Femtosecond Pump laser. The generated pulse width was 150 fs with a 500 kHz pulse repetition rate. The tuning along the 400–1100 nm range was used in the present studies. The temporal characteristics of laser pulses were maintained approximately same over the whole range of spectral variations of the laser output, which was confirmed by autocorrelation measurements of the pulse width.

The following equation [17] was used for fitting the CA Z-scans:

$$T = 1 + \frac{2(-\rho x^2 + 2x - 3\rho)}{(x^2 + 9)(x^2 + 1)}\Delta\Phi_o \tag{1}$$

Here $x = z/z_0$, z_0 is the Rayleigh length of the focused radiation, $z_0 = \pi(w_0)^2/\lambda$, w_0 is the beam waist radius, λ is the wavelength of the probe radiation, $\rho = \beta/2\,k\gamma$, $k = 2\pi/\lambda$, $\Delta\Phi_o = k\gamma I_0 L_{\text{eff}}$, I_0 is the laser radiation intensity in the focal plane, $L_{eff} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective length of the sample, α_0 is the linear absorption coefficient, and L is the thickness of the studied sample.

The OA Z-scans were fitted using the equation [18]

$$T \approx 1 \; - q(x)/2(2)^{1/2}, \tag{2}$$

where $q(x) \quad \beta I_0 L_{\text{eff}} / [1 + x^2]$.

These relations are valid for the case of the week optical nonlinear response. This case was discussed in [18]. Their studies of CS_2 show the variation of the peak-to-valley (ΔT) versus peak laser irradiance. This dependence remained linear up to at least 0.32, without showing any signs to deviate from this dependence at higher intensities of PP. Our experimental measurements were carried out at different laser intensities. The linear dependence of $\Delta\Phi_o$ from laser intensity was used to select data that could be used to acquire Kerr values and indicate at what power the analytical model does not work anymore. No saturation of the nonlinear refraction was observed since $\Delta\Phi_o$ increased linearly with intensity for our experimental conditions. The nonlinear refractive index can then be deduced from the slope of the curves.

Equation (1) adopts the commonly used assumption S << 1, which is our case (S = 0.02). As smaller the S becomes, as smaller the influence of the nonlinear absorption on the CA Z-scan. We used above theoretical equations since for our setup the value of 1-S was equal to 0.98 thus indicating that this parameter gives 1% error to the measurements, which is much smaller than the experimental error induced by other reasons.

3. Results and discussion

We did not observe any significant Kerr response from the 1-mm thick silica glass cell at the laser intensities ($I_0 = 3\times10^9$ W cm^{-2}) used for the experimental measurements of the studied liquid. The contribution of the two walls of empty cell was small ($\gamma \approx 10^{-16}$ cm^2 W^{-1} at 500 nm and twice smaller at longer wavelengths), once we used larger intensities of laser pulses. The self-focusing induced by the cell was more than one order of magnitude smaller than the one induced by the carbon disulfide. As mentioned, the nonlinear optical response from the empty cell was observed only at relatively high intensities of the femtosecond pulses. At these intensities, a significant involvement of the nonlinear absorption in CS_2 notably varied the pattern of Z-scan curves, which made them difficult to analyze. Because of this we used the small intensities of the probe pulses, which allowed entirely exclude the contribution of the cell's walls to our measurements.

The OA and CA Z-scans of CS_2 using the 150 fs pulses tunable in the range of 400–1100 nm are shown in Fig. 1(b). The energies of used pulses were varied to demonstrate the variations of these scans due to the growing values of the nonlinear refraction and nonlinear absorption in the shorter wavelength region. Correspondingly, the scans in the 400–700 nm range are shown for

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the pulses varying in the range of ~1–10 nJ, while the scans in the 800–1000 nm range are shown for the ~45 nJ pulses. The exact values of the used energies of 150 fs pulses are shown beneath each scan.

The nonlinear absorption (OA Z-scans; Fig. 1(b), blue curves) in the 400–1100 nm spectral region can be attributed to the two different processes. In the case of the longer-wavelength region (800–1100 nm), the main mechanism is the three-photon absorption. This process has been well analyzed in previous studies [3,7,19,20]. It was concluded that the two-photon absorption of CS_2 is negligible in the 800 - 1100 nm region. The wavelength-dependent behavior of a decrease of the transmittance at stronger intensity (i.e. in the focal plane of OA Z-scan scheme) can suggest that three-photon absorption can be considered as a mechanism of this intensity-dependent modulation of transmittance. This is the most probable mechanism of nonlinear absorption in the case of longer wavelength pulses since, at $\lambda \sim 1000$ nm, the probability of two-photon absorption using the intensities of $I_0 = 3\times10^9$ W cm^{-2} applied in present studies is too small. The dominance of three-photon absorption in this spectral region has been reported in a few above-mentioned studies. Overall, the two-photon absorption is not energetically possible in the region of 800–1100 nm. Correspondingly, the Z-scan fitting assumes that this process is poor and the fitting for three-photon absorption is better. Meanwhile, the nonlinear absorption of 500 nm and lower-wavelength PP is attributed to the two-photon process.

While not analyzing the three-photon absorption in-depth and referring to previous studies, we present the fitting of the OA Z-scans in the shorter-wavelength region using small intensities of 150 fs pulses. This process was almost suppressed at 600 nm and appeared at 500 nm while showing strong influence at 400 nm (see OA scans at three left panels of Fig. 1(b)). Two OA Z-scans for the latest two wavelengths are combined in Fig. 1(c). One can see that 400 nm, 2.7 nJ pulses allow observation of a significant valley (ΔT “ 0.2, empty red circles), while 500 nm, 6.3 nJ pulses caused a notably smaller valley (ΔT “ 0.02, empty blue squares). The fittings of these scans using Eq. (2) allowed determining the nonlinear absorption coefficients (7×10^{-10} cm W^{-1} and 5.6×10^{-9} cm W^{-1} for 500 nm and 400 nm PP, respectively) attributed to the two-photon absorption. These values of β are three (in the case of 400 nm PP) to four (in the case of 500 nm PP) times larger than similar parameters reported in [9] in the case of 32 fs PP.

The main contributions to the uncertainty in determination of the nonlinear absorption coefficients and nonlinear refractive indices arose from the power, the pulse duration, and the beam waist radius measurements, laser power fluctuations and uncertainty in the fitting procedure. One can also assume the variations of these parameters for different used wavelengths of the probe radiation. Including all error sources, the uncertainty in the measured values was estimated to be 30%, which is typical for experimental errors during Z-scan measurements.

One of the goals of present study was the analysis of a flip of CA Z-scan curves (Fig. 1(b)) from being attributed to the self-focusing (for the 600–1100 nm pulses and to some extent for the 500 nm radiation and small intensity of PP) to being attributed to the self-defocusing (for $\lambda = 400$ nm at different intensities of PP and for $\lambda = 500$ nm at high intensities of PP). A change from self-focusing to defocusing can be observed between 500 nm and 400 nm due to the fifth-order nonlinear optical process becomes stronger than the third-order process. Below we analyze this effect in detail by varying the intensity of PP in the intermediate region (500 nm) thus demonstrating the most intriguing modification of the effective nonlinear refractive index due to the competition of two processes, third- and fifth-order nonlinear refractions.

The example of the fitting procedure of CA scans using Eq. (1) is shown in Fig. 2(a) for the 600 nm PP. These measurements were carried out at the intensity $I_0 = 3\times10^9$ W cm^{-2}. The γ deduced from this fitting at the used intensity and wavelength was $(9.5 \pm 2.8)\times10^{-15}$ cm^2 W^{-1}. We also determined the nonlinear refractive index of CS_2 in the longer-wavelength region (900–1100 nm) at a similar intensity of PP. The fitting of each of the CA scans shown in Fig. 1(b) by using Eq. (1) allowed determining the spectral variations of γ. Its value [$(3 \pm 0.9)\times10^{-15}$

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$cm^2\ W^{-1}$] was approximately the same along this spectral range (Fig. 2(b)). A decrease of the wavelength of PP below 900 nm led to the steady growth of γ up to 9.5×10^{-15} $cm^2\ W^{-1}$ at 600 nm. The three-fold increase of laser intensity in the range of 600–1100 nm did not lead to the variation of γ.

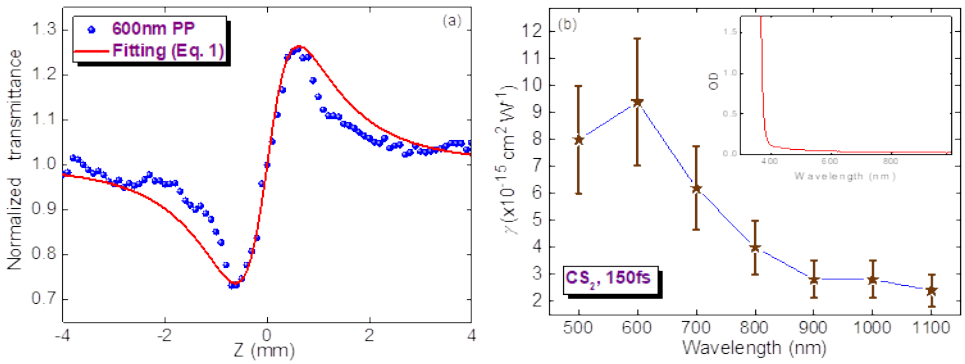

Fig. 2. (a) Closed-aperture Z-scan of CS_2 using 150 fs, 600 nm, 8 nJ pulses (blue diamonds) and the fitting (solid red curve) using Eq. (1). (b) Spectral dependence of the third-order nonlinear refractive index of CS_2 in the case of 150 fs probe pulses. Inset: Spectral distribution of the optical density (OD) of the cell containing carbon disulfide.

A decrease of γ in the case of 500 nm PP ($\gamma = 8\times10^{-15}$ $cm^2\ W^{-1}$, Fig. 2(b)) points out the involvement of the additional process altering this parameter. The addition of the negative component to the value of γ could be attributed to different processes. Below we discuss the involvement of some anticipated processes in the observed decrease of the effective nonlinear refractive index of CS_2 at $\lambda = 500$ nm and further change towards the self-defocusing in the case of 400 nm PP.

A heat-related appearance of a thermal lens is one of them. We did not use different pulse repetition rates to analyze and exclude the role of accumulative thermal lens formation during these studies since our laser system did not allow the variation of this parameter. Notice that, at $\lambda = 500$ nm, the linear absorption of carbon disulfide is almost insignificant (i.e., the optical density of 1-mm thick cell filled with CS_2 was <0.1, see inset to Fig. 2(b)). Correspondingly, one can exclude this process, at least for the 500 nm PP. The notable absorption in this liquid starts at $\lambda = 380$ nm and then steadily increases at shorter wavelengths. Thus the 400 nm pulses also could not be efficiently absorbed at a 500 kHz repetition rate. Another heat-related process, the dynamic thermal effect appearing during propagation of laser radiation through the medium, is insignificant in the case of femtosecond pulses.

To further prove above assumption, we analyzed the CA Z-scan of the cell filled in with carbon disulfide using the quarter-wave plate placed in front of the focusing lens to determine the role of the heating processes in the formation of the thermal lens leading to the self-defocusing. The application of circularly polarized 800 nm pulses did not cause the appearance of the reverse pattern of the CA curve when peak precedes the valley. At these conditions, the peak and valley almost entirely disappeared from the CA Z-scan. Correspondingly, the thermal lens, which does not depend on the polarization of the heating radiation, was not formed during these experiments using 150 fs, 500 kHz, 800 nm laser pulses. The same conclusion was derived from the similar experiments using 400 nm pulses.

This leaves only the higher-order effect or resonance influence on the γ as those responsible for the observed variation of the effective nonlinear refractive index. The latter processes cannot be realized in this molecule at 500 nm, while the former effect can lead to variations of the effective γ, especially in the region close to the absorption band of this molecule. The negative sign of the

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fifth-order process can cause a decrease in the whole pattern of the self-focusing in this medium. As a consequence of above consideration, the higher-order Kerr effect can be assumed the alone process responsible for the observed self-defocusing of the used 400 nm and, to some extent, 500 nm pulses in the CS_2. This assumption requires additional confirmation by analyzing the variation of the CA Z-scans at different intensities of femtosecond PP.

The negative fifth-order nonlinearity in CS_2 can, to some extent, suppress the valley and peak of normalized transmittance induced by the positive third-order nonlinearity, similarly to the case of pseudoisocyanine dye [11]. As it was mentioned, the conditions when the negative sign of fifth-order nonlinearity decreases the effective nonlinear refraction of CS_2 were analyzed in [7] in the case of 800 nm, 120 fs PP. Notice that a decrease of the effective nonlinear refractive index at this wavelength caused by the involvement of the negative fifth-order nonlinear refractive process was very small. Moreover, they found that the critical intensity of the fifth-order nonlinear process emerging in CS_2 at $\lambda = 800$ nm is 7.5×10^{10} W cm^{-2}.

Earlier, it was suggested that this process can be notably enhanced in the case of femtosecond PP in the vicinity of the absorption band of CS_2 [4]. In our case, we observed that the fifth-order nonlinearity starts to play an important role at $I_0 = 4\times10^9$ W cm^{-2} (in the case of 500 nm PP) and 0.5×10^9 W cm^{-2} (in the case of 400 nm PP).

We performed the intensity-dependent CA measurements at $\lambda = 500$ nm, which demonstrated the unusual asymmetric shape of Z-scans once the intensity of PP exceeded some threshold above which the higher-order process in CS_2 starts prevailing over the lower-order one (4×10^9 W cm^{-2}). Four CA scans presented in Fig. 3 correspond to the following used intensities at the focal plane: (a) 1.5×10^9 W cm^{-2}, (b) 3×10^9 W cm^{-2}, (c) 5×10^9 W cm^{-2}, and (d) 7.5×10^9 W cm^{-2}. In the first two cases (Figs. 3(a) and 3(b)), the usual CA Z-scan shapes corresponding to the positive sign of γ were observed. Meanwhile, one can see that the two-fold growth of laser intensity in the focal plane (i.e. from 1.5×10^9 to 3×10^9 W cm^{-2}) led to relatively insignificant growth of valley-to-peak (ΔT) of CA Z-scan in the latter case ($\Delta T = 0.25$ and $\Delta T = 0.34$, respectively), thus not following the $\Delta T \infty I_0$ rule [18]. Additionally, at $I_0 = 5\times10^9$ W cm^{-2} (Fig. 3(c)), a notable deviation from standard Z-scan shape demonstrating two peaks and two valleys was observed. Further growth of intensity (7.5×10^9 W cm^{-2}, Fig. 3(d)) caused an even larger deviation from the shapes shown in Figs. 3(a) and 3(b).

Below we briefly discuss our observations in the frames of the published comparative studies of the third-order and fifth-order nonlinear optical effects. In general, at low input irradiance, the change of the nonlinear refractive index is contributed to mainly by the third-order effect. But at high input intensity, it may also be contributed by a fifth-order effect. It was suggested that, if two-photon absorption is the only mechanism for generating excited-state populations, and if the loss of the excited-state populations through recombination and diffusion is neglected because these processes occur on time scales longer than the used femtosecond pulses, the excited-state refractive index could be expected to be proportional to a temporal integrate of $(I_o)^2$, resulting in an effective fifth-order nonlinearity [10]. Notice that, in most of the materials, two-photon absorption is the main mechanism for nonlinear absorption. Other mechanisms like three-photon absorption, saturable absorption, and reverse saturable absorption are generally less effective compared with the two-photon absorption.

Our studies suggest that the signs of the third- and fifth-order refraction are opposite. The fifth-order contribution to the nonlinear refractive index is usually determined by the two-photon absorption-generated excited-state refractive cross section. Thus a negative fifth-order effect can be due to a change in γ caused by the production of two-photon absorption-generated excited states.

In [12], the method that allows estimation of the third- and fifth-order nonlinear refraction coefficients of materials by use of the top-hat-beam Z-scan technique was described. This method is applicable when the third- and fifth-order nonlinearities have the same or opposite signs.

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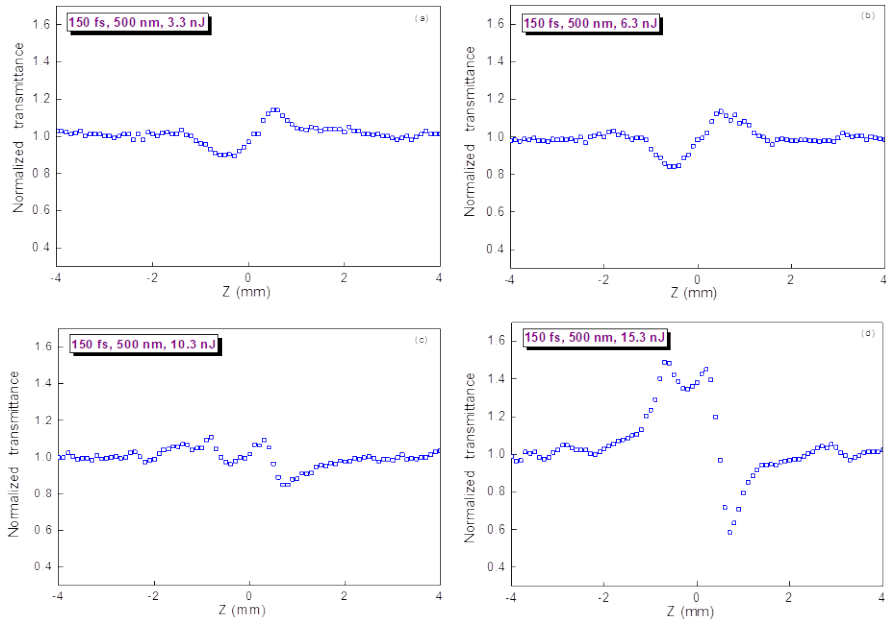

Fig. 3. Closed-aperture Z-scans of carbon disulfide at different energies of 500 nm pulses (see text).

However, it was pointed out that method is available for calculating the third-order nonlinear refraction coefficient but is not suitable for evaluating the fifth-order nonlinear refraction coefficient. The conditions in which the third- and fifth-order nonlinear refractions have opposite signs were also analyzed in [13]. Their theoretical calculations have demonstrated that the two-photon absorption effect shows that not only the peak was suppressed but the valley was also enhanced simultaneously, and the dual peak—valley configuration can degenerate into the single peak—valley configuration. Our observations (see Figs. 3(c) and 3(d)) are similar with their assumptions.

Linear absorption, self-Kerr nonlinearity, fifth-order nonlinearity and cross-Kerr nonlinearity of quantum dots were investigated in [16]. By using the probability amplitude method, general analytic expression of linear and nonlinear susceptibility of the probe field in quantum dots was obtained. Additionally, the evolution of the intensity and the phase of a beam propagating in a nonlinear isotropic medium exhibiting third- and fifth-order characteristics were calculated in [14]. The analytical relations allowed fitting the experimental data using the recently introduced D4r-Z-scan method. Carbon disulfide was tested at 532 and 1,064 nm in the picosecond regime deducing nonlinear coefficients related to the third- and fifth-order optical susceptibilities. Particularly, in the case of 532 nm radiation, the fifth-order nonlinear refractive index of carbon disulfide measured by picosecond pulses was positive and determined to be $\eta = 1.2\times10^{-24}$ cm^4 W^{-2}. The positive sign of this parameter was assumed to be due to the influence of the molecular reorientation of CS_2 in the case of relatively long probe pulses.

When the third-order and fifth-order nonlinear refraction effects coexist, the total normalized transmittance is not simply derived from the linear superposition of the contributions of pure third-order and fifth-order nonlinear refractions, but it contains the coupling term in the presence of the simultaneous third- and fifth-order effects [21]. It is hard to calculate the fifth-order nonlinear refractive index at above-described conditions (i.e. at $\lambda = 500$ nm and relatively high

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intensity) without knowing this term. Because of this we determined η at $\lambda = 400$ nm when the self-defocusing was significantly stronger than the self-focusing.

The effective nonlinear refractive index at $\lambda = 400$ nm (left panel of Fig. 1(b)) was calculated to be $\gamma_{\text{eff}} = -3\times10^{-13}$ cm^2 W^{-1}. This measurement was performed at $I_0 = 7\times10^8$ W cm^{-2}. The corresponding fifth-order nonlinear refractive index at this wavelength was determined to be $\eta = \gamma_{\text{eff}} / I_0 = -4\times10^{-22}$ cm^4 W^{-2} assuming a relatively small value of the γ attributed to the purely third-order process.

In [7], the third-order nonlinear refractive index $\gamma = 2.1\times10^{-15}$ cm^2 W^{-1} and the fifth-order nonlinear refractive index $\eta = -2\times10^{-27}$ cm^4 W^{-2} of CS_2 at the wavelength of 800 nm were reported in the case of femtosecond PP. The former value is close, with a factor of 2, to our measurements obtained at this wavelength ($\gamma = 4\times10^{-15}$ cm^2 W^{-1}). As for the difference in five orders of magnitude for the η measured at 800 and 400 nm, one can attribute it to the anticipated significant growth of the higher-order nonlinearities in the vicinity of the absorption band in the short-wavelength region.

A detailed research on CS_2 absorption spectrum at small densities shows that it has an absorption peak around 320 nm at room temperature [22]. The theoretical study has shown that this absorption band corresponds to the transition from the ground state A_1 ($\sum_g^+$) to the excited state B_1 ($\sum_u^+$) that has a theoretical energy difference of 34 600 cm^{-1} and an experimental value of 30 900 cm^{-1} [23]. This indicates that observed nonlinear absorption around 800–1100 nm can be satisfied by three-photon absorption.

4. Conclusions

We have analyzed the dynamics of the nonlinear refractive index of CS_2 in the short-wavelength region using 150 fs pulses. We have described the observed decrease of this parameter in the spectral region shorter than 600 nm and attributed it to the influence of the fifth-order process. It was demonstrated that this higher-order process can drastically decrease γ and even lead to the change of the sign of this process. We have also shown that the positive sign of γ dominating in the region between 600 and 1100 nm becomes intensity-dependent at a shorter wavelength (500 nm) due to the competition between the fifth-order induced self-defocusing and third-order induced self-focusing. Further decrease of the wavelength of the probe pulses (400 nm) resulted in domination of the negative nonlinear refraction even at small intensities of the probe pulses. The fifth-order nonlinear refractive index of CS_2 at $\lambda = 400$ nm ($\eta = -4\times10^{-22}$ cm^4 W^{-2}) was determined. Our spectral- and intensity-dependent measurements allowed us to define the region where the higher-order nonlinearity of CS_2 starts playing the dominant role in the nonlinear refraction of femtosecond pulses.

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Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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