# Thermally managed eclipse Z-scan

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**Abstract:** We report a new variation of the conventional Z-scan method to characterize the third-order optical nonlinearity of photonic materials. By exploiting the combination of the eclipse Z-scan with a thermal nonlinearity management technique, we demonstrate an improvement in sensitivity and flexibility of the method to simultaneously characterize the thermal and nonthermal nonlinearity of optical materials. The method is demonstrated by measuring the nonlinear refractive index in $CS_2$, $SiO_2$ and $H_2O$, standard materials, and also in a biomaterial, the amino acid Tryptophan in water solution, using a femtosecond Ti-Sapphire laser operating at 76MHz repetition rate.



**OCIS codes:** (190.0190) Nonlinear optics; (190.4720) Optical nonlinearities of condensed matter.

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## 1. Introduction

The field of Nonlinear Optics has provided many techniques to characterize photonic materials, yielding direct information on the nonlinearities and its origin, which have been perfected throughout the years [1-3]. One well established method, known as Z-scan (hereafter called conventional Z-scan), was introduced in 1989 by Sheik-Bahae and co-workers [4]. Since then, several variations of the method have been developed, including improvement of its sensitivity [5], allowing for nondegenerate and time resolved measurements [6-8], anisotropy measurements [9], measurements in reflection mode (reflection Z-scan, appropriate for opaque materials) [10], measurements in slow absorbers using low power cw lasers [11] and time resolved measurements of thermal effects due to one and two photon absorption [12]. More recently, thermally managed Z-scan using high repetition rate lasers have been introduced [13, 14].

The Z-scan technique (and variations) concerns with nonlinearities as fast as the laser pulse and slow contributions. Several physical processes can be involved in the nonlinear response of different materials as crystals, glasses or biomolecules. It is well known that a variety of mechanisms can be related to the molecules nonlinear susceptibilities. Electronic and molecular libration processes contribute to the nonlinear response under fs irradiation while molecular reorientation and redistribution are important concern for ps and longer pulses analyses [15]. Reorientation time of the Tryptophan molecule, for instance, is approximately 30ps [16].

In this paper, we introduce a new combination of the eclipse Z-scan [5] with the thermally managed Z-scan [14], that gains in sensitivity associated with the simultaneous measurement of the thermal and nonthermal contributions to the NL refractive properties of photonic materials, besides the measurement of its NL absorptive properties. To demonstrate the method, we measured both the thermal and nonthermal nonlinearities of liquid $CS_2$, bulk $SiO_2$ and water. We also explored the large sensitivity of the technique by measuring the NL response of a water solution of Tryptophan which presents small NL refractive index and has important biological action.

## 2. Experimental results

The conventional Z-scan method [4] exploits the light-matter interaction so that an incident beam propagating inside a NL medium induces a change in the electromagnetic field phase that gives rise to a front wave distortion of the beam. By measuring the variation of the transmitted beam intensity through a small aperture placed in front of a detector in the far-field region, one can determine the sign and magnitude of the NL refractive index, $n_2 \propto \mathrm{Re}[\chi^{(3)}]$, whilst when the entire light beam passing through the sample is detected, the NL absorption, $\alpha_2 \propto \mathrm{Im}[\chi^{(3)}]$ is obtained. NL coefficients can be determined by measuring the difference between the normalized peak and valley transmittance, $\Delta T_{p-v}$. For small phase distortion, the variation of $\Delta T_{p-v}$ is linear dependent with the on-axis phase shift at the focus, $\Delta\Phi_o$, as given by:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} \left| \Delta\Phi_o \right|, \qquad (1)$$

where S is the aperture transmittance, given by $S = [1-\exp(-2r_a^2/w_a^2)]$, with $w_a$ denoting the beam radius at the aperture and $r_a$ is the aperture radius. The on-axis phase shift is given by $\Delta\Phi_o = kn_2 I_o L_{eff}$ ; where $I_o$ denotes the irradiance of the laser beam within the sample, k is the wave vector and $L_{eff} = (1-e^{-\alpha L})/\alpha$ , with L being the sample length and $\alpha$ the linear absorption coefficient.

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The eclipse Z-scan (EZ-scan) [5] employs a disk in front of the detector (instead of an aperture), such that the eclipsed beam collected by a lens is directed towards the detector. For large disk and small NL phase shift ($\Delta\Phi_o$ <0.2) a linear relationship between $\Delta T_{p-v}$ and $\Delta\Phi_o$ can be written as:

$$\Delta T_{p-v} = 0.68(1-S_d)^{-0.44} \left| \Delta\Phi o \right| , \qquad (2)$$

where $S_d$ is the fraction of the beam blocked by the disk, given by $S_d = [1-\exp(-2r_d / w_d^2)]$, with $r_d$ being the obstacle radius and $w_d$ the beam radius at the disk. From Eqs. (1) and (2), it can be verified that the EZ-scan arrangement can provide ~13 times higher sensitivity than the conventional Z-scan set-up, by substituting the values for $S = 0.01$ and $S_d = 0.99$ and considering the same nonlinear phase shift. These values for S and $S_d$ are experimentally achievable. As $\chi^{(3)}$ can arise from different physical origins, it is important to differentiate among them. For instance, thermal nonlinearities are almost always present in liquids and many glassy materials when excited with cw or quasi-cw (high repetition rate, several MHz) light sources. Generally, to avoid the manifestation of such thermal nonlinearities, low repetition rate single beams are used in the experimental methods, but with high peak power to allow the observation of other nonlinear contributions, particularly those arising from electronic effects. A clever variation of the conventional Z-scan method, which allows differentiating between the thermal and nonthermal nonlinearity, was introduced in Refs. [13,14] even using relatively low peak power with high repetition rate.

We further develop the method of Ref. [13], by combining the EZ-scan with thermal management, as illustrated in Fig. 1.

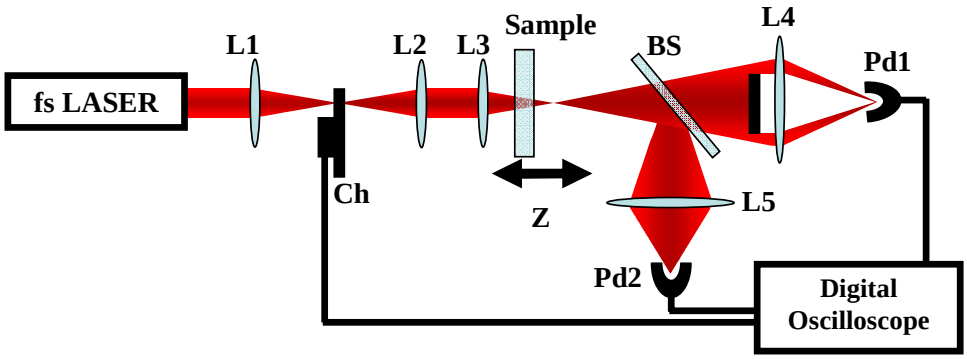


Fig. 1. Experimental set-up for thermally managed eclipse Z-scan. L1 through L5 are convex lens; CH stands for chopper; Pd1 and Pd2 are photodetectors; BS stands for beam splitter.

A Ti-Sapphire laser delivering pulses at 76 MHz, with 150 fs pulse duration and 500 mW average power at 800 nm was used as the light source. A disk with 1.7 cm diameter (corresponding to $S_d = 0.99$) was placed prior to a 10 cm focal distance lens (L4), in order to direct the eclipsed beam to the detector Pd1. The beam directed to detector Pd2 would yield information on nonlinear absorption, which were not detected in the materials studied. A reference arm, first introduced in Ref. 6, and used by other authors afterwards [5], was not necessary due to the laser high amplitude and spatial stability. The chopper is the new element responsible for the thermal management, as described in Ref. [14]. In short, the thermal management method consists in acquiring the time evolution of the Z-scan signal, for the sample placed in the pre-focal and postfocal positions of the sample with respect to lens L3. The time resolution of the system is determined by the chopper opening time, which depends on the finite size of the beam waist on the chopper wheel, which was 18 μs in our experimental set-up. By delaying the photodetector signal acquisition time with respect to t = 0 (determined by the opening time of the chopper) the time evolution of the Z-scan signal at both the pre- and post-focal positions are obtained. The photodetector information is

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processed by a digital scope. A single exponential curve can be use to fit the experimental data and to determine the normalized transmittance at time t = 0, extrapolated from curves similar to Fig. 2(a). From these measurements the EZ-scan curves can be obtained and the contribution of the thermal and nonthermal nonlinearities can be inferred. By extrapolating the time evolution curves for t = 0, we eliminate all contribution from accumulative processes (thermal) in our result. It is important to mention that due to the ultrashort (150fs) pulse width and to the system repetition rate (76 MHz), processes with picoseconds or few nanoseconds response (as reorientation or conformation changes) will not influence the detected signal. Conversely to the conventional Z-scan, in the EZ-scan method a pre-focal peak and a post-focal valley reveal a self-focusing Kerr nonlinearity. It is worth pointing out that conventional Z-scan studies of thermal nonlinearity in photonic materials with high repetition rate pulses (MHz) and with long delay time (controlled by a chopper) were described in Ref. [17], from which only the thermal contribution to the third-order nonlinearity was studied.

Figure 2 shows the results of the thermally managed EZ-scan measurements performed at 800 nm in $CS_2$ (2mm thick cuvette). Figure 2(a) shows the time evolution, with the sample at positions corresponding to the minimum and maximum transmittance. Figure 2(b) shows the Z-scan curves obtained for the different delay.

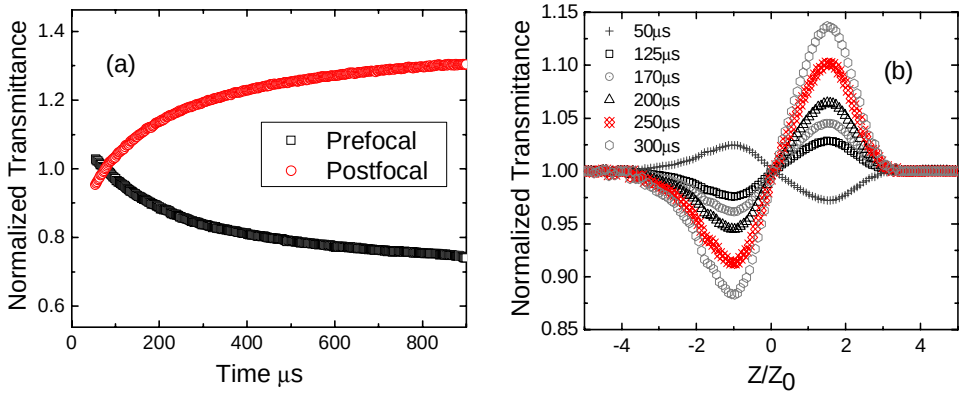


Fig. 2. Thermally managed eclipse Z-scan measurements: (a) time evolution; (b) z-scan signature for $CS_2$.

By extrapolating the time evolution curves for t = 0, the normalized peak-valley transmittance, $\Delta T_{p-v} = 0.27 \pm 0.01$, was obtained for an intensity at the focus of 2.1 GW/cm$^2$. As can be seen, the curves in Fig. 2(a) cross at approximately 80 μs, indicating the dominance of the thermal nonlinearity over the nonthermal contribution after these time delays. A rise or decay time and crossing of the two temporal evolution curves at the pre- and post-focal positions indicate the presence of both nonthermal and thermal nonlinearities; notice that both NL contributions have opposite signs. When a rise or decay time appears without crossing, the signs of the thermal and nonthermal refractive indices are the same or the thermal effect is negligible. Figure 2(a) shows that at times above 80 μs the nonthermal $n_2$ changes to negative indicating the thermal contribution, as already verified in Ref. [14]. This is corroborated by the EZ-scan curves shown in Fig. 2(b).

Figures 3(a) and 3(b) show similar results for the $SiO_2$ sample (1.6 mm thickness) obtained with 2.1 GW/cm$^2$. In this case, due to sample's larger thermal conductivity, a thermal lens contribution is not observed and this fact is directly revealed in the flat curve shown in Fig. 3(a). Similar result has been observed in Ref. [14] for $SiO_2$, but a higher intensity was employed in that work. The signal profile shown in Fig. 3(b) does not change for any temporal delay and $\Delta T_{p-v} = 0.018 \pm 0.002$. The value of $n_2 = (2.1 \pm 0.1) \times 10^{-16}$ cm$^2$/W for $SiO_2$ was determined using $CS_2$ as the reference sample with $n_2 = 2.2 \times 10^{-15}$ cm$^2$/W [18].

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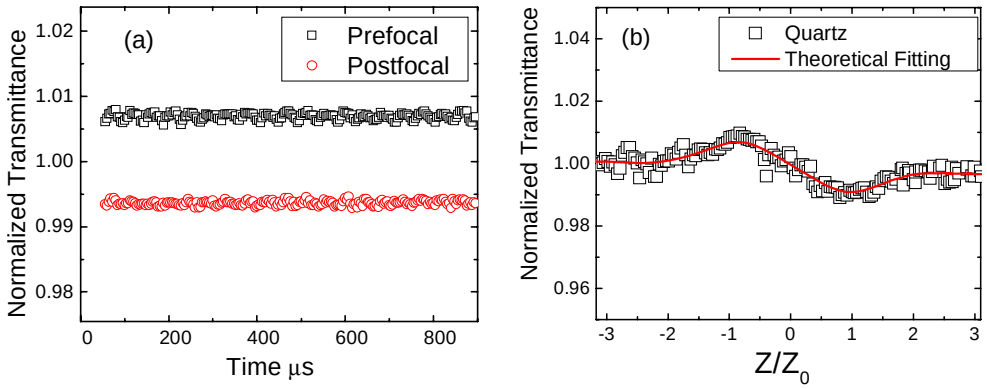


Fig. 3. Thermally managed eclipse Z-scan measurements: (a) time evolution; (b) z-scan signature for quartz.

As a further application to exploit the large sensitivity of the method, results for a biomaterial, the amino acid Tryptophan ($C_{11}H_{12}N_2O_2$) in water (pH 5.5, concentration: 55 mM) were obtained as shown in Figs. 4 and 5. Tryptophan is a precursor for serotonin (a neurotransmitter), melatonin (a neurohormone), and niacin, and has been considered as a possible cause of schizophrenia in people who cannot metabolize it properly. This amino acid cannot be synthesized by living organisms, including humans, and therefore must be part of its diet. It is recognized that exploitation of nonlinear optical techniques provide important information for clinical diagnoses [19], and to understand molecular mechanism of diseases. Using the same intensities as before, the values of $n_2$ of water and Tryptophan in water were obtained, showing the small thermal contribution for the nonlinearity in this spectro-temporal excitation regime. For water, the experimental data was just above the noise, but the nonthermal result obtained, $n_2 = (1.6 \pm 0.5) \times 10^{-16}$ cm$^2$/W, still agrees with the literature value [20]. The EZ-scan curves for water and the Tryptophan water solution, at t = 0, extrapolated from the data in Fig. 4, are shown in Figs. 5(a) and 5(b). The measured value of the nonthermal NL refractive index of Tryptophan in aqueous solution was $(8.7 \pm 0.2) \times 10^{-16}$ cm$^2$/W, with a positive (self-focusing) nonlinearity. It is worth mentioning that, for the same peak power and detection system as employed here, using conventional Z-scan or other technique, such as four wave mixing or Kerr gate, the data obtained here would be below the noise limit and would not be detectable. Thanks to the high repetition rate used, and the avoidance of thermal effects, the nonthermal nonlinearity could be measured. Further results of the NL optical characterization and applications of this biological medium will be published elsewhere.

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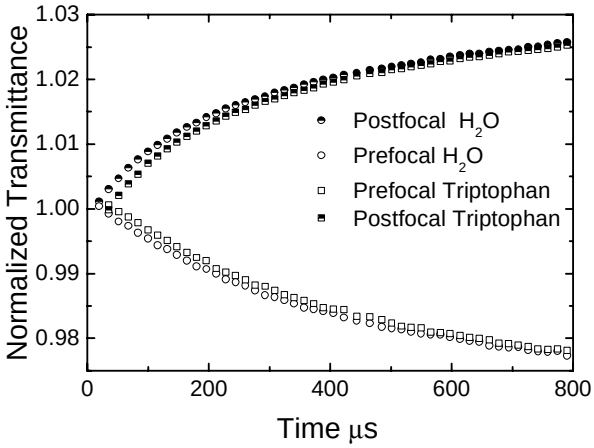


Fig. 4. Time evolution for $H_2O$ and Tryptophan solution.

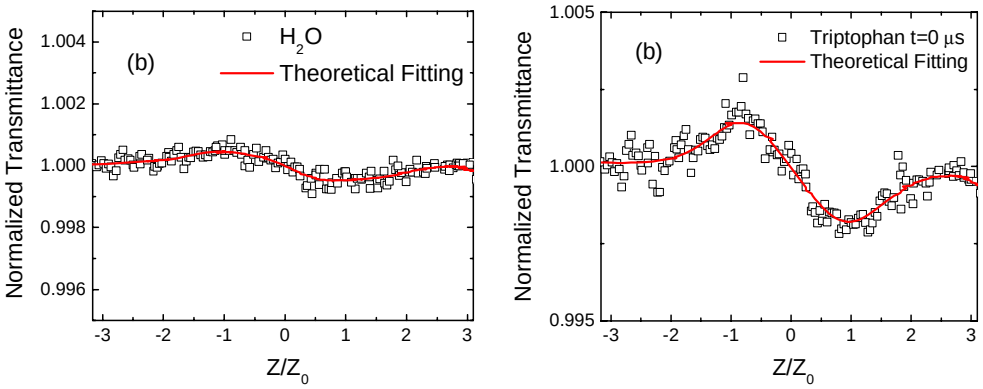


Fig. 5. Thermally managed eclipse Z-scan measurements in water and Tryptophan solution: (a). z-scan signature for $H_2O$; and (b). z-scan signature for Tryptophan solution for t = 0, both extrapolated from t>0 from Fig. 4.

## 3. Conclusion

In summary, we have introduced a novel variation of the Z-scan method, named the *thermally managed eclipse Z-scan*, which allows for improved sensitivity for measurements of the third-order susceptibility of photonics and biophotonics materials using relatively low laser intensities, enabling the distinction between thermal and nonthermal contribution to the nonlinearity. The method was demonstrated using known NL optical materials, such as $CS_2$ and $SiO_2$. The high sensitivity of the method is demonstrated by measuring the NL refractive index of water and Tryptophan in water using a 76 MHz repetition rate Ti-Sapphire laser delivering 150 fs pulses, otherwise not measurable by conventional Z-scan for the peak powers and low energy pulses employed here. Further applications of this method for characterization of nanostructured materials as well as other biomaterials are envisaged.

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