4-14-2010

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Abstract: We report a novel photoacoustic Z-scan (PAZ-scan) technique that combines the advantages offered by the conventional Z-scan method and the sensitivity of the photoacoustic detection. The sample is scanned through the focused laser beam and the generated photoacoustic signal is recorded using a 10 MHz focused ultrasound transducer. Since the signal strength is directly proportional to the optical absorption, PAZ-scan displays nonlinear behavior depicting the nonlinear optical absorption of the material. Among many advantages, our experiments on mouse blood show that PAZ-scan can potentially be used as a standard technique to calibrate contrast agents used in theranostics in general and photoacoustics in particular.

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1. Introduction

Every real and physical oscillating system exhibits nonlinear response when it is overdriven. In optical systems it occurs when there is sufficiently intense light illumination. The third order optical nonlinearities cover a vast and diverse area in nonlinear optics. The third order nonlinear susceptibility $\chi^{(3)}$ is a complex quantity and its real and imaginary components represent nonlinear refraction and nonlinear absorption, respectively. Measurement of these parameters is important for many practical applications. In recent years, $\chi^{(3)}$ is measured for a wide variety of materials which are potential candidates for photonics, optoelectronics and biomedical applications [1,2]. Several techniques have been proposed to measure these parameters [3–7]. Of them, in view of its simplicity and sensitivity, Z-scan is the most extensively used technique [1,7]. It can be used for measuring both the sign and magnitude of the nonlinear refractive index coefficient n_2 and the magnitude of the nonlinear absorption coefficient β. In the conventional Z-scan experiment (hereafter called Z-scan) the transmittance of a nonlinear medium is recorded by a photodetector while the sample is scanned through (Z-axis) the focused laser beam. This is called an open aperture Z-scan and the plot between z-axis and the normalized transmittance curve depicts only the losses due to the linear and nonlinear absorptions of the sample from which β is calculated. However if the transmitted light is recorded behind an aperture, closed aperture Z-scan, the curve displays both the absorption and scattering. From this n_2 will be obtained. Since the invention of Z-scan several improvements have been demonstrated in order to improve the sensitivity and/or to study a variety of materials. These include the use of non-Gaussian-beam profiles, thick samples, measurements in reflection mode (reflection Z-scan, appropriate for opaque materials) and total beam-profile distortions [8–10]. In spite of these advances, however, it is still not convenient to use the Z-scan technique in certain situations. For example, the excitation laser wavelength has to be off resonance for strongly nonlinear absorption materials so that transmitted optical signal can be measured. Weak nonlinear materials require intense optical beam, often resulting in damage of the material. Also Z-scan cannot be used to study opaque and highly absorptive optical samples, and surface properties of non-transparent materials like semiconductors. This holds true even for frozen aqueous samples where formation of microcrystals and craks lowers the transparency of the sample.

In this paper, we present a novel technique, photoacoustic Z-scan (PAZ-scan), to measure the nonlinear absorption coefficients of a wide variety of materials. It combines the advantages offered by the conventional optical Z-scan technique and the highly sensitive photoacoustic detection. The photoacoustic effect, in which the absorption of light results in the generation of acoustic waves, was first described by Alexander Graham Bell in 1860 [11]. It has been used as a highly-sensitive tool for the measurement of low absorptions and linear absorption coefficients in various forms of materials [12–15]. With advent of state of art high power nanosecond lasers, recently the photoacoustic tomography and microscopy have become popular in medical imaging [16]. In the last two years the photoacoustic effects have also been exploited to study Malus's law and optical beam characterization [17,18]. It is argued that the photoacoustic detection technique allows the investigation of nonstandard and opaque polymeric films, where the analysis of the optical measurements is a difficult task.

In PAZ-scan, like in the Z-scan, the lens is translated in small steps along the (Z-axis, optical axis) so that the test sample is scanned through the focused laser beam. In the Z-scan the transmitted optical signal is recorded at each step. In the PAZ-scan, however, the generated photoacoustic (PA) signal is recorded using a focused ultrasound transducer. The

feasibility of the technique is demonstrated by studying nonlinear absorption behaviors of saturable (SA) and reverse saturable absorbers (RSA). Further the blood sample of mouse was studied which otherwise is not possible with the Z-scan without diluting the blood sample. Our calculations on nonlinear absorption coefficient of the samples using the PAZ-scan curves are in good agreement with those obtained from the Z-scan curves and complement each other. PAZ-scan technique has potential for the characterization of nonlinear optical properties for a wide variety of materials including highly absorbing, non transparent or optically thick samples which can be in a variety of physical forms – thin films, frozen, crystals, powders, and liquids. As the generated acoustic waves are propagated outwards in all directions, PAZ-scan can be easily performed in either transmission or reflection geometry. This enables one to study the surface properties of non-transparent materials and living subjects.

2. Experimental results and discussion

The schematic of the PAZ-scan experimental setup is shown in Fig. 1. The light source is a frequency doubled Nd:YAG laser (Minilite II, Continuum) producing 532 nm laser pulses of 3 ns pulse width (δt). It is focused with a 20 cm focal length lens. The lens is mounted on a translation stage and is moved in small steps such that the focal region (on either side of the focal point) of the beam scans the sample along the z direction. Although the sample is fixed and the lens is the one that is moved, for consistency and simplicity, hereafter we refer that the sample is moved towards the focus. The nonlinear absorbing medium is placed in a 1 mm glass cuvette and is mounted in a cell that contains water for ultrasound coupling. As the laser pulse is incident on the sample, some of the energy delivered is absorbed and converted into heat. This produces pressure transients and thus wideband ultrasonic emission. The ultrasonic waves (PA signal) are then detected using a 10 MHz focused water immersion transducer (Olympus NDT Inc., 1.27 cm diameter and 2.54 cm focal length). The transducer is mounted on a XYZ translation stage and was adjusted so that the nonlinear absorbing sample is at its focal plane throughout the experiment. For correlation and comparison, we also performed Z-scan studies. The light transmitted through the sample is measured by a photo detector.
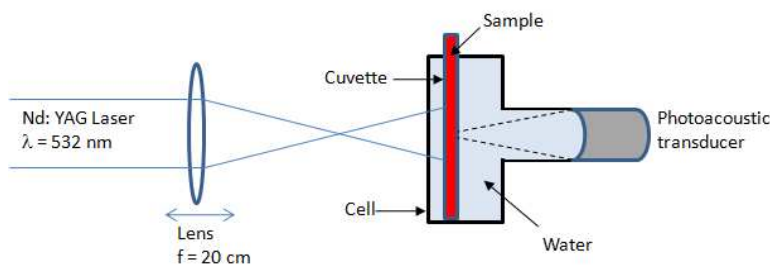

Fig. 1. Schematic of the PAZ-scan setup

Photons incident on an absorbing material will transfer electrons from the ground state to an upper energy state, thereby depleting the ground state population. For RSA materials, the absorption cross-section of the excited state is larger than that of the ground state at the high intensities causing decrease in the transmitted optical signal and increase in the PA signal, as shown in Fig. 2. Similarly for SA materials, the absorption cross section of the excited state is smaller than that of the ground state at high light intensities leading to increase in the transmitted optical signal and decrease in the PA signal, as shown in Fig. 3. These results show that PAZ-scan can also be used to differentiate SA and RSA.

The open aperture Z-scan of copper pthalocyanine (CuPc) in Chloroform solution is shown in Fig. 2(a). Being an RSA material, the transmittance is decreased as the sample is moved towards the focus (Z = 0). The curve is symmetric at Z = 0, means similar observations can be made on either side of the focused Gaussian beam. The absorption coefficient for an RSA material is defined as

$$\mu_{RSA} = \alpha_{0RSA} + \beta I \qquad (1)$$

where α_{0RSA} is the linear absorption coefficient, and β is the excited state absorption or two-photon absorption coefficient. Solid line in the Fig. 2(a) is the best fit to the experimental data obtained using the relation [6]

$$T = \left(\exp(-\alpha_{0RSA}L) / \sqrt{\pi}q_0 \right) \int_{-\infty}^{+\infty} \ln\left[\sqrt{1 + q_0 \ \exp(-t^2)} \right] dt \qquad (2)$$

where q_0 is given by $\beta I_0 L_{eff}$. I_0 is the on-axis peak intensity, and L_{eff} is given by $[1-\exp(-\alpha_{0RSA}L)]/\alpha_{0RSA}$. By fitting the experimental data to the Eq. (2), the best-fit two-photon absorption coefficient β was calculated to be 3.976×10^{-9} m/W at $I_0 = 6.1 \times 10^{11}$ W/m^2 where the linear absorption coefficient (α_{0RSA}) was measured to be ~ 1950 m^{-1} using Beer-Lambert's law at low input powers.
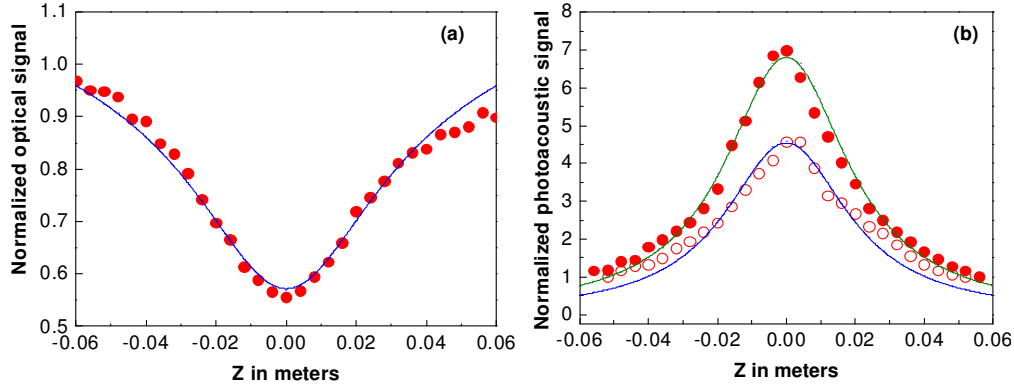

Fig. 2. (a) Conventional Z-scan signal of CuPc solution. Solid lines are the theoretical fit to the experimental data. The on-axis peak intensity $I_0 = 6.1 \times 10^{11}$ W/m^2 and the best fit β value is 3.976×10^{-9} m/W. (b) PAZ-scan curves for the same solution for $I_0 = 8.54 \times 10^{11}$ W/m^2 (open circles) and 1.28×10^{12} W/m^2 (closed circles). The corresponding β values are 5.765×10^{-9} m/W and 9.013×10^{-9} m/W respectively. Y-axis data is normalized to the far field signal.

Figure 2(b) shows the PAZ-scan for the same CuPc solution for two different input laser powers. Similar to the Z-scan, the PA signal is normalized to its far filed value. The PA signal generated due to the irradiation of the laser pulse can be expressed as [19]

$$p(z) = \Gamma \mu_a I(z) \qquad (3)$$

where μ_a is the optical absorption coefficient of the sample, Γ is Grüneisen parameter and $I(z)$ is the incident laser fluence. In the present case, as the photoacoustic transients are produced due to the interaction between the incident laser fluence and the nonlinear absorbing medium, we replaced μ_a to include the nonlinear absorption coefficient. The experimental data fits, as shown in Fig. 2(b), to the Eq. (3) for the values $\beta = 5.765 \times 10^{-9}$ m/W, $I_0 = 8.54 \times 10^{11}$ W/m^2 (open circles) and 9.013×10^{-9} m/W, $I_0 = 1.28 \times 10^{12}$ W/m^2 (closed circles). These values are comparable to that of Z-scan values and others found in the literature. In the fitting we used $\Gamma = 0.11$ for water and also the attenuation of the acoustic waves in water (traveling from the source to the transducer) is taken into the account.

For RSA materials at resonance, the Z-scan yields low transmitted light (hence low SNR) due to strong absorption. However, the SNR in the PAZ-scan is high due to the increase in the PA signal with absorption. Also, from Fig. 2(b) it is noticeable that the difference between the far field and near field values is much larger in the case of PA signal. These findings suggest that the PAZ-scan is more sensitive than the optical Z-scan in characterizing nonlinear optical absorption of the RSA materials.

Similar complimentary behavior between the Z-scan and PAZ-scan is also observed for saturable absorbers. Figure 3(a) shows the open aperture Z-scan of the Disperse Red. The optical absorption saturates beyond certain input intensities. Hence the normalized transmitted signal increases as the sample approaches the focus. The transmission of a two level saturable absorber at steady state, in the homogeneously broadened case, is given by [6]

$$T = \exp(-\alpha_{0SA}L)\exp\left[\left(I_o/I_s\right)(1-T)\right] \tag{4}$$

where α_{0SA} is the linear absorption coefficient, and I_s is the intensity at which absorption saturates. The α_{0SA} is 1966 m^{-1} and the best fit value for $I_s = 7.346 \times 10^{13}$ W/m^2. In the case of PAZ-scan, due to the decrease in the absorption (as a result of saturation) at higher intensities for the SA materials, the PA signal decreases. The nonlinear absorption coefficient of a SA can be written as [6]

$$\mu_{SA} = \frac{\alpha_{0SA}}{1 + \dfrac{I}{I_S}} \tag{5}$$

Several PAZ-scans were performed by varying the input intensities and are shown in Fig. 3(b). The best fit values of saturation intensities are 5.1×10^{12} W/m^2 [for open circles in Fig. 3(b)] and 1.25×10^{13} W/m^2 (closed circles). Throughout these fits, same Γ and the attenuation coefficients values are used.
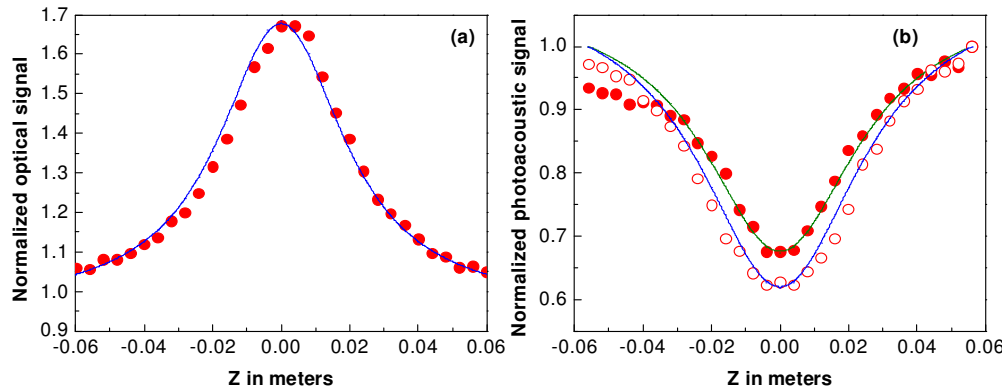

Fig. 3. (a) Conventional Z-scan signal of Azo-red solution (saturable absorber) for the input energy of 78 µJ. (b) PAZ-scan curves for the same solution for 28 µJ (open circles) and 42 µJ (closed circles). Solid lines are the theoretical fit to the experimental data. Y-axis data is normalized to the far field signal.

To demonstrate the potential of the PAZ-scan for characterizing the linear and nonlinear absorption coefficients of contrast agents used in biomedicine in general and photoacoustic imaging in particular, we studied the nonlinear optical absorption behavior of mouse blood. Figure 4 shows its saturable absorption behavior. The best fit saturation intensity is 2.25×10^{13} W/m^2. Due to the strong absorption and opacity of the blood, we could not measure the linear absorption coefficient using Beer-Lambert's law at low input powers. So we used the average of the absorption coefficients in the linear regime of the curve. The obtained value is ~1400 m^{-1} and the accepted value of absorption coefficient of whole blood at 532 nm (~1200 m^{-1}). We believe that highly absorbing medium and the large path length could be the reasons for non-symmetric nature of the PAZ-scan curve. This study suggests that PAZ-scan can characterize the nonlinear optical absorption coefficients of contrast agents used in theranostics. Similarly, Photoacoustic molecular contrast agents are used for disease localization and early detection [20]. Development of the contrast agents is fast advancing

area of research and PAZ-scan can be used as a standard technique to evaluate the performance of these contrast agents before they are used for tomography.
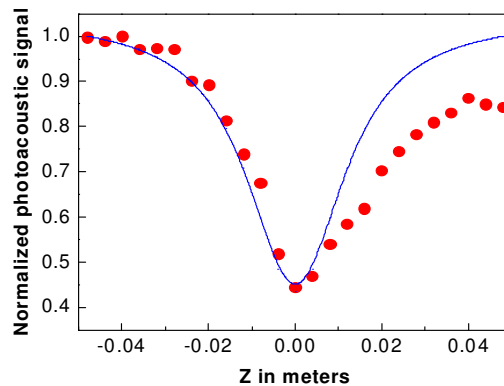

Fig. 4. PAZ-scan of mouse blood demonstrating the saturable absorption behavior.

3. Conclusion

In conclusion, this report demonstrates that PAZ-scan has great potential in characterizing the nonlinear optical absorption coefficient of weak, opaque, highly absorptive, staturable and reverse saturable absorber materials. The nonlinear absorption properties of saturable and reverse saturable absorber materials are studied by translating the sample through the focused laser beam and recording the generated PA signal. As the generated acoustic waves are propagated outwards in all directions, PAZ-scan can be used in either transmission or reflection geometry. This enables us to study the surface properties of non-transparent materials. As photoacoustic signals are time resolved, it is possible to study the nonlinear optical characteristics of thick samples. We believe that PAZ-scan will be a valuable tool for material characterization and may find applications in the fields of chemistry, physics, material science, biomedical, and manufacturing. For example, PAZ-scan technique can be employed in optical-resolution photoacoustic microscopy, where optical focus in biological tissue is maintained due to limited scattering of light in shallow depths (< 1 mm) of living subjects [21]. This facilitates calculation of linear and nonlinear absorption coefficients of endogenous (oxy and deoxgy hemoglobin, water, and melanin) and exogenous photoacoustic contrast agents in living subjects.

Acknowledgements