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NONLINEAR OPTICAL CHARACTERIZATION OF ORGANIC MATERIALS

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We report a sensitive single beam technique for measuring both the nonlinear refractive index and nonlinear absorption coefficient for a wide variety of materials. We describe the experiment and present a brief analysis including cases where nonlinear refraction is accompanied by nonlinear absorption. In these experiments the transmittance of a sample is measured through a finite aperture in the *far-field* as the sample is moved along the propagation path (z) of a focused Gaussian beam. The sign and magnitude of the nonlinear refraction are easily deduced from such a transmittance curve (Z-scan). Employing this technique a sensitivity of better than $\lambda/300$ wavefront distortion has been achieved using picosecond frequency doubled Nd:YAG laser pulses. In cases where nonlinear refraction is accompanied by nonlinear absorption, it is possible to separately evaluate the nonlinear refraction as well as the nonlinear absorption by performing a second Z-scan with the aperture removed. We demonstrate this method for a solution of chloro-aluminum-phthalocyanine at 532 nm where excited state absorption is present and the nonlinear refraction is positive.

We have recently developed a sensitive single beam technique for measuring both nonlinear refraction and nonlinear absorption.^{1,2} We refer to this technique as a Z-scan. This method is rapidly gaining use for measuring electronic nonlinearities (eg. n_2) and nonlinear absorption (eg. two-photon absorption coefficients β or excited-state cross sections σ) in materials from semiconductors to glasses to organics. We review this technique and the analysis of Z-scan data to show how nonlinear refraction can be separated from nonlinear absorption. We then apply this technique to a solution of chloro-aluminum-phthalocyanine (CAP) dissolved in methanol which we have previously used for passive optical limiting.³

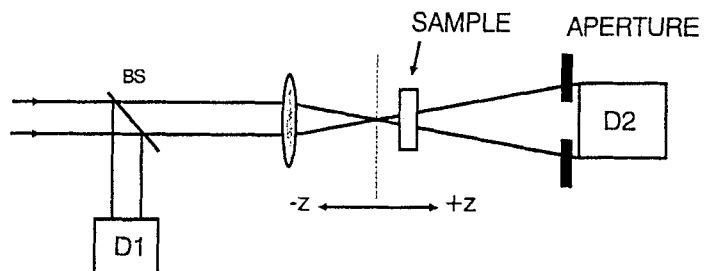


Fig.1 The Z-scan experimental apparatus in which the ratio $D2/D1$ is recorded as a function of the sample position z .

Using a Gaussian laser beam in a tight focus limiting geometry, we measure the transmittance of a nonlinear medium through a finite aperture placed in the far field as a function of the sample position (z) measured with respect to the focal plane as shown in Fig. 1. If only nonlinear refraction is present the following example qualitatively explains how such a trace (Z-scan) yields n_2 . First assume $n_2 < 0$. As the sample is moved toward focus the increased irradiance leads to a negative lensing effect which tends to collimate the beam, thus, increasing the aperture transmittance. With the sample on the $+z$ side of focus, the negative lensing effect tends to augment diffraction and the aperture transmittance is reduced. The approximate null at $z=0$ is analogous to placing a thin lens at focus which results in a minimal far field pattern change. For still larger $+z$ the irradiance is reduced and the transmittance returns to the original linear value. A positive nonlinearity results in the opposite effect, ie. lowered transmittance for the sample at negative z and enhanced transmittance for positive z . We refer to the transmittance change from peak to valley as ΔT_{p-v} . Theoretical Z-scan curves for both positive and negative nonlinear refraction are shown in Fig. 2 for a peak on axis, time averaged phase distortion $\Delta\Phi$ (phase delay or advance) of $\lambda/25$. For example, for an instantaneous positive nonlinearity this phase distortion is given by;

$$\Delta\Phi_0 \approx \frac{2\pi}{\lambda} \Delta n L = \frac{2\pi}{\lambda} \gamma I L = \frac{2\pi}{\lambda} \frac{n_2 E_0^2}{2} L \quad (1)$$

where L is the sample length, I the irradiance (MKS) and E_0 the field (CGS), and γ and n_2 are related by $n_2(\text{esu}) = (cn_0/40\pi)\gamma(\text{m}^2/\text{W})$, where c (m/sec) is the speed of light in vacuum.

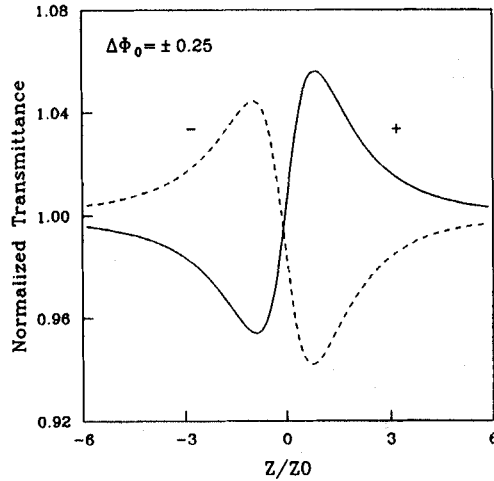


Fig. 2 Theoretical output of a Z-scan for a) negative n_2 and b) for a positive n_2 .

We can define an easily measurable quantity ΔT_{p-v} as the difference between the normalized peak (maximum) and valley (minimum) transmittances. The variation of this quantity as a function of $\Delta\Phi_0$, as calculated for various aperture sizes is found to be almost linearly dependent on $\Delta\Phi_0$. Based on a numerical fitting, the following relationship can be used to determine $\Delta\Phi_0$ from the Z-scan to within a $\pm 2\%$ accuracy;

$$\Delta T_{p-v} \approx 0.406(1-S)^{0.25} |\Delta\Phi_0| \quad \text{for } |\Delta\Phi_0| \leq \pi, \quad (2)$$

where S is the transmittance of the aperture in the linear regime. If our experimental apparatus and data acquisition systems are capable of resolving transmission changes ΔT_{p-v} of $\approx 1\%$, we will be able to measure phase changes corresponding to less than $\lambda/250$ wavefront distortion.

If the aperture is removed (ie. $S=1$ in Eq. 2) the Z-scan is no longer sensitive to nonlinear refraction. A Z-scan then results in no signal unless nonlinear absorption is present in which case a symmetrical curve about the focal position is obtained. If both

nonlinear refraction and nonlinear absorption are present simultaneously, an analysis of the "open" aperture ($S=1$) and "closed" aperture ($S<1$) experiments can be used to separately determine the nonlinear refraction and nonlinear absorption.

The separation and evaluation process is simple: divide the "closed" aperture normalized Z-scan by the one with open aperture. The result is a new Z-scan where ΔT_{p-v} agrees to within $\pm 10\%$ of that obtained from a purely refractive Z-scan. This division process will give a faithful value for n_2 as long as the nonlinear absorption is not dominant. In practice we have found this method to work quite well provided the curve obtained by division looks like Fig. 2 (ie. appears antisymmetric). We have checked it by numerically calculating the results of Z-scans including both nonlinearities.³

We define β as the two-photon absorption (2PA) coefficient and σ as the excited state absorption (ESA) coefficient. For small nonlinear absorption (ie. $\Delta T_{p-v} < 0.1$) the following approximation can be used to determine β or σ from the open aperture Z-scan;

$$\Delta T_{p-v} \approx -\frac{\beta}{2\sqrt{2}} I_0 (1-R) L_{\text{eff}}, \text{ for 2PA,} \quad (3a)$$

$$\Delta T_{p-v} \approx -\frac{\sigma \alpha}{4\hbar\omega} F_0 (1-R) L_{\text{eff}}, \text{ for ESA,} \quad (3b)$$

where $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, with α the linear absorption coefficient.^{4,5} Here I_0 (W/cm^2) is the peak on axis irradiance assuming a temporally and spatially Gaussian shaped pulse, and F_0 (J/cm^2) is the on axis fluence assuming a Gaussian spatial beam. In the case of CAP we found that the nonlinear absorption was due to ESA and not 2PA. We determined this by monitoring the nonlinear absorption for different pulsewidths of 29 ps and 61 ps (FWHM). The same fluence for the different pulsewidths gave the same nonlinear absorption as expected from Eq. 3b for excited state absorption. Equation 3a for 2PA predicts that the same irradiance would give the same absorption.

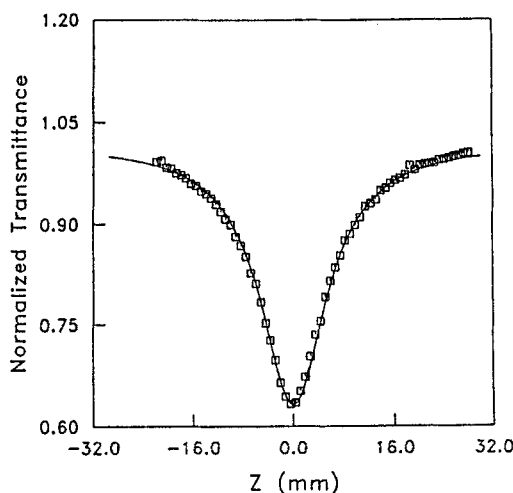


Fig. 3. Open aperture Z-scan on CAP at $3.18 \mu\text{J}$ and theoretical fitting (solid line) with $\sigma=1.8 \times 10^{-17} \text{ cm}^2$ at a concentration of 1.0×10^{-3} moles/liter.

The open aperture Z-scan, along with a numerical fit, is shown in Fig. 3 for an input energy of $3.2 \mu\text{J}$ at 532 nm using $\approx 27 \text{ ps}$ (FWHM) pulses. Note that for Fig. 3 the $\Delta T > 0.1$ and Eq. 3b is not applicable.² The parameters used are $w_0=28 \mu\text{m}$ ($\text{HW1}/e^2\text{M}$), $R=0.05$, $L=0.2 \text{ cm}$, $\alpha=1.42 \text{ cm}^{-1}$ (or 1390 cm^{-1} per mole per liter) as determined from the 68% measured linear transmittance for a concentration of 1.02×10^{-3} moles per liter. This numerical fit gives a value for σ of $\sigma \approx 1.8 \times 10^{-17} \text{ cm}^2$.

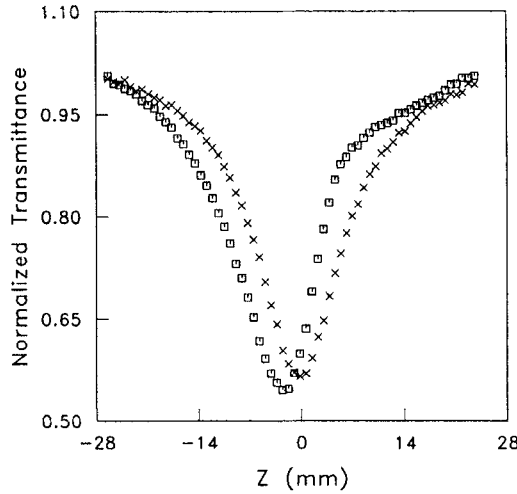


Fig. 4. Open aperture Z-scan (cross) and closed aperture Z-scan (square) results for CAP presented as the normalized transmittance versus z position [mm].

Figure 4 shows both the open and closed aperture ($S=0.4$) Z-scan results for CAP for an input energy of $4.8 \mu\text{J}$. Figure 5 shows the results of dividing the closed aperture Z-scan by the open aperture Z-scan, thus, giving the nonlinear refractive contribution. The value obtained for n_2 is, $n_2 \approx 2.1 \times 10^{-12}$ esu. We found, however, that this nonlinear refraction is associated with the real excitation of the singlet state and is, therefore, also fluence dependent. Thus, this nonlinear refraction is not a true $\chi^{(3)}$ effect but is associated with a sequential $\chi^{(1)}:\chi^{(1)}$ process.

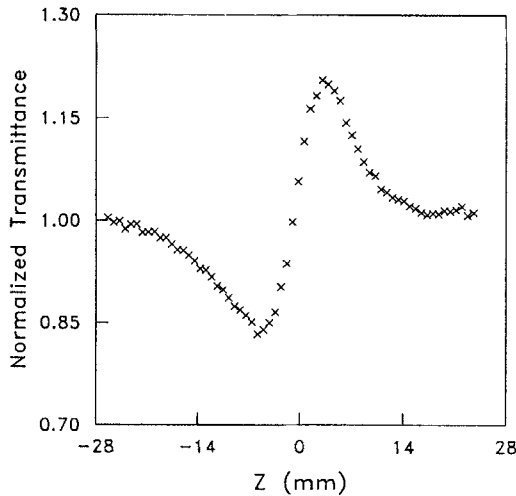


Fig. 5 The results of the division of the curves in Fig. 4 (ie. closed aperture results divided by open aperture results).

In conclusion we have demonstrated a simple sensitive single beam technique for measuring both nonlinear absorption and nonlinear refraction. The sign of the nonlinear refraction is also obtained. We give simple relations that allow the refractive index to be obtained directly from the Z-scan data without resorting to computer fits. We have applied

this technique to several materials displaying a variety of nonlinearities on different time scales. Here we have presented data on chloro-aluminum-phthalocyanine that gives the excited state absorption cross section and the nonlinear refractive index, all for 0.53 μm picosecond pulses. It is expected that this method will be a valuable tool for experimenters searching for highly nonlinear materials.

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