Characterization of dynamic optical nonlinearities with pulse trains

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We report a simple extension of the Z-scan technique where pulse trains characteristic of a Q-switched and mode-locked Nd:YAG laser are employed to investigate the dynamics of third-order optical nonlinearities. The method allows discriminating between fast and accumulative nonlinearities, and was applied to the investigation of liquid samples, namely chloroform, benzene, and a solution of Disperse Red 1 dye. © 1999 American Institute of Physics.

Nonlinear optical properties of organic materials have been the subject of a large number of theoretical and experimental investigations during the last decade due to the prospect of their use in photonic switching devices.\(^1\text{,}^2\) The operation of such devices is based on the light-induced refractive-index change related to the real part of the third-order nonlinear susceptibility, \(\text{Re}\{n_2(\omega = \omega + \omega - \omega)\}\). Accordingly, the development of new materials with high and fast third-order nonlinearities, and the quest for fundamental understanding about their origin are aspects that have motivated research on organic samples. The origin of the nonlinearity can be related to several different physical processes that can, in principle, be distinguished according to their time response, through the use of different experimental techniques. Among several methods employed for the investigation of third-order nonlinearities, the Z-scan technique stands out due to its high sensibility and experimental simplicity.\(^3\) Its two-beam time-resolved version, introduced by Wang et al.,\(^3\) allowed the measurement of fast processes in a time interval limited by their 43 ps pulse duration, and by the time delay between the pump and probe pulses, on the order of 1 ns. Recently, it was used by Samoc et al.\(^5\) for the study of conjugated polymers in the femtosecond regime. For the investigation of the dynamic optical nonlinearity in the time interval going from about 50 ns to 1 ms, a cw probe beam can be used.\(^6\) In this case, slower processes such as free-carrier diffusion and recombination, and thermal index changes can be monitored. From the operational point of view, since these methods use two collinear beams, there can be problems for a perfect pump–probe modal overlap and the complete separation of the beams after passing through the sample. Besides, they just measure the nonlinearity time evolution after the sample has been excited and not during the excitation process. This means that the nonlinearity buildup in accumulative processes cannot be followed. As an example, Z-scan measurements in polyaniline salts resulted in a refractive nonlinear index of \(n_2 = 5.9 \times 10^{-13} \text{cm}^2/\text{W}\) when 35 ps duration pulses at 527 nm were employed\(^7\) and \(n_2 = -6.4 \times 10^{-12} \text{cm}^2/\text{W}\) for excitation with a complete train of Q-switched and mode-locked laser light at 532 nm.\(^8\) This discrepancy is probably due to an accumulative process and methods to identify it are sought. The subject has been addressed in a recent investigation on the sign of the nonlinear refraction in a chloroaluminum phthalocyanine solution.\(^9\)

First, by using a single 18 ps pulse switched out of the envelope of a Q-switched and mode-locked pulse train, Z-scan measurements provided a positive value for \(n_2\). On the other hand, when all pulses in the pulse train are employed, \(n_2\) has its sign reversed and this is attributed to the heat-induced temperature rise and the population relaxing to triplet states. But again, the nonlinearity buildup in the accumulative processes is not followed and the time evolution is not investigated.

The present work introduces a new approach for the single-beam Z-scan technique, where pulse trains contained in Q-switched and mode-locked lasers can advantageously be used to study dynamic optical nonlinearities in the 10–1000 ns time interval. Similarly to the two-beam Z-scan technique, this method allows us to discriminate between fast and slow nonlinear effects, as we demonstrate in different samples. The experimental setup is the standard for single beam Z-scan measurements.\(^3\) The pump source is the second harmonic of a cw-pumped Q-switched and mode-locked Nd:YAG laser delivering pulses of 70 ps at 532 nm, in pulse trains containing about 20 pulses (separated by 13.2 ns) at a 100 Hz repetition rate. The beam was focused with a lens of focal length \(f = 12\) cm onto the sample placed in a quartz cuvette with a 2 mm path length. The diameter of the laser beam at the focal plane is about 50 \(\mu\)m and the aperture placed at the far-field position has a linear transmittance \(S = 0.05\) for all closed-aperture data given in this letter. We use a fast detector (rise time \(\sim 1\) ns) that provides the signal going to a 400 MHz digital oscilloscope, triggered by a pulse coming from the Q-switch electronic box, and passing through an adjustable delay generator. The averaged signal is fed into a homemade data acquisition system based on a personal computer. When the sample is far from the focal plane, we acquire a pulse train, as shown in the upper inset of Fig. 1 (a box car averager could also be employed to obtain the pulse train, but that would take longer). At this position, no nonlinear effect is expected. The computer finds the position and height of each peak, and the strongest one is arbitrarily labeled ‘‘0.’’ Each peak height is proportional to the corresponding pulse fluence because the detection system has a rise time much slower than the 70 ps pulse duration. By carefully measuring the radius of the laser beam at the focal plane \(w_0\), and the average power of the pulse train, we can determine the absolute value of the pulse fluence. On the other hand, the absolute intensity value can be found by performing Z-scan measurements for each laser pulse in the well-characterized nonlinear material CS\(_2\), as described later.

For fast electronic processes (response time faster than
the expression nonlinear absorption, as discussed in Ref. 3. However, we consider that excited species are produced through one-photon absorption and that the excited state is characterized by a relaxation time $\tau$, the fraction of molecules pumped to the excited state can be described by means of a rate equation:

$$\frac{d\eta}{dt} = -\frac{\eta}{\tau} + (1 - \eta) W_{up},$$

(2)

where $(1 - \eta)$ is the fraction of molecules remaining in the ground state $W_{up} = \sigma I / h \omega$, $I$ is the light intensity and $\sigma$ is the wavelength dependent one-photon absorption cross section. The solution of Eq. (2) is straightforward and results in:

$$\eta(t) = \frac{\sigma(\omega)}{h \omega} e^{-t/\tau'} \int_{-\infty}^{t} I(t') e^{t'/\tau'} dt',$$

(3)

where $\tau' = \tau(1 + I/I_c)$ and $I_c = h \omega / \sigma$. Since $I$ is proportional to $E^2$, the incoherent term related to the population of excited states contributes to the susceptibility with the same power in the electric field as the instantaneous third-order $\chi^{(3)}$ term. The temporal behavior of $\eta$ depends on the kinetics of formation and relaxation of excited species as the sequence of pulses arrives at the sample. According to the time-averaging arguments of Ref. 3, for a nonlinearity having instantaneous response and decay times relative to the pulse width of the laser, one obtains for a temporally Gaussian pulse: $\langle \Delta n \rangle_j = n Z_{eff} / V^2$, where $I_j$ is the intensity of the pulse with label $j$ and $n_2$ is the nonlinear refractive index associated with the coherent term of Eq. (1). On the other hand, for a cumulative nonlinearity having a decay time much longer than the pulse width, one obtains: $\langle \Delta n \rangle_j = n_{2c} F_j / 2$, where $F_j = I_j(t') dt'$ is the pulse fluence and $n_{2c}$ is accumulated nonlinear index related to the excited state population. However, the cumulative effect and subsequent relaxation of previous pulses has to be taken into account and the complete refractive index change can be written as:

$$\langle \Delta n \rangle_j = \frac{n_{2c} I_j}{V^2} + \frac{n_{2c}}{2} \sum_{i=1}^{N} F_i \exp[-(j-i) \Delta t / \tau],$$

(4)

where $\Delta t$ is the time interval between two consecutive pulses in the train (13.2 ns in our case). This equation can be used to fit the experimental data points and allows the determination of the response time, as well as the nonlinear refractive indices. The physical process governing the nonlinearity origin and relaxation can be quite complex and can change from sample to sample. The theory presented above is oversimplified because it does not take into account more than one relaxation time, and other effects such as thermal index changes, cavitation bubbles, and so on. A thorough analysis of all these effects is out of the scope of the present letter. However, if the accumulative process is proportional to the fluence, extra terms could be added to Eq. (4) in an ad hoc way, but the meaning of the nonlinear index has to be reinterpreted.

In order to demonstrate this method we have used materials with different temporal behaviors, namely chloroform, benzene and a solution of DRI dye dissolved in ethanol (concentration of $0.85 \times 10^{-4}$ mg/cm$^2$, $\alpha = 1.5 \text{ cm}^{-1}$ at 532 nm). For intensity calibration purposes we have used CS$_2$.

The value of the light induced refractive index change can be found by assuming two possible contributions for the nonlinear process: one arising from fast electronic effects and another from slower cumulative processes related to the population of the excited state. In this case, we can expand the polarization according to:

$$P = \chi_s^{(1)} E + \chi_s^{(3)} EEE + \eta \chi_e^{(1)} - \chi_e^{(1)} E + \ldots,$$

(1)

FIG. 1. Pulse train envelope for a DR1 solution when the sample is far from the focal plane (open circles), near the transmittance peak (triangles), and valley (squares) of the Z-scan measurement. The upper inset shows details of pulse train, where adjacent pulses are separated by 13.2 ns. The lower inset depicts the Z-scan signature of pulse “0,” and indicates the positions where the pulse trains were acquired.
which is a well-characterized fast medium presenting a nonlinear refractive index of $n_2 = 3 \times 10^{-14} \text{cm}^2/\text{W}$. We measured a $Z$-scan curve for each peak, used the value of $\Delta T_{\text{pe}}$, to obtain $\phi_{\text{NL}}$, which gives $\Delta n = n_2 I$. Once $n_2$ is known, we obtained $I$ from the measured value of $\Delta n$. The DR1 dye is an azo compound with a $-\text{N} = \text{N}(-\text{azo})$ group in its structure, which allows a trans-cis photoisomerization process that has been considered to be employed in molecular devices for optical memory and optical storage. In our case, we are just interested in the origin of the third-order nonlinearity related to the resonant process. Chloroform and benzene were investigated previously with optical Kerr gate experiments and present nonlinearities 20 and three times smaller than CS$_2$, respectively.

Figure 2 presents refractive index changes obtained with the $Z$-scan technique with pulse trains for the samples studied. For chloroform, $\Delta n$ follows the $Q$-switch envelope, indicating a fast noncumulative effect. The data shown in Fig. 2(a) were obtained with an average power $\bar{P} = 4.4 \text{ mW}$ and an intensity $I^{(0)} = 13 \text{ GW/cm}^2$ for peak "0," calibrated with the CS$_2$ sample. By fitting the data with the first term in Eq. (4) we found $n_2$ to be positive and equal to $1.2 \times 10^{-15} \text{cm}^2/\text{W}$, which is about 25 times smaller than for CS$_2$, in good agreement with the ratio 1:20 reported in Ref. 12.

The behavior of the refractive index change of benzene depicted in Fig. 2(b) clearly shows the coexistence of a fast process and an accumulative effect with reversed sign. At the beginning of the pulse train, $\Delta n$ has the tendency of following the $Q$-switch envelope, but after a few pulses, the negative cumulative effect overcomes the fast one. This measurement was carried out with $\bar{P} = 2.8 \text{ mW}$ and $I^{(0)} = 8.3 \text{ GW/cm}^2$. The dashed line represents the fitting to Eq. (4) with the adjusted parameters $n_2 = 4.5 \times 10^{-15} \text{cm}^2/\text{W}$, which is about two times smaller than the value reported in Ref. 12, $n_{2c} = 1.1 \times 10^{-5} \text{cm}^2/\text{J}$ and $\tau' = 500 \text{ ns}$. Since the sample is transparent, the cumulative term in Eq. (4) has to be reinterpreted. One could think that the excited state could be populated by means of a two-photon absorption process, but in this case the effect is proportional to $\int J^2(t') dt'$ and this intensity dependence does not fit our experimental data. Our interpretation for the cumulative term is that it is related to laser-induced cavitation bubbles. By using a cw probe beam we verified that the cumulative negative effect lasts for about 50 $\mu$s, which is typical for the bubble lifetime. Since this effect is very sensitive to the presence of impurities in the focal volume, we were able to even observe the same effect in aged samples of CS$_2$.

Finally, Fig. 2(c) represents the light-induced refractive index change for the DR 1 solution obtained with $\bar{P} = 0.1 \text{ mW}$ and $I^{(0)} = 0.3 \text{ GW/cm}^2$. In this case, the cumulative nonlinearity has the same sign as the fast electronic effect and the two contributions add up. The fitting to Eq. (4) given by the solid line provides the following values: $n_2 = -1.8 \times 10^{-14} \text{cm}^2/\text{W}$, $n_{2c} = -5.4 \times 10^{-4} \text{cm}^2/\text{J}$, and $\tau' = 800 \text{ ns}$. The sign of $n_2$ is in agreement with recent results of Ref. 14 and is explained with a two-level model where the excitation wavelength falls below the resonance frequency (470 nm). The relaxation time is characteristic of azo compounds like DR1 and is related to the photoisomerization mechanism. It is possible that the accumulative effect observed has a thermal origin related to the heat released during the photoisomerization process. But in this case, we measure the thermal lens buildup and not its diffusion.

In conclusion, we have introduced a new approach for the single-beam $Z$-scan technique that allows the discrimination between cumulative and noncumulative processes. The measurement employs pulse trains to map the nonlinearity time evolution along a $Q$-switch envelope and can also be applied to others techniques such as optical Kerr gate experiments.

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\begin{enumerate}
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