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Third-order optical nonlinearities of oligomers, dendrimers and polymers derived from solution Z-scan studies

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Abstract

Z-scan measurements provide a simple way of determining and comparing the third-order nonlinear properties of chemical compounds, especially if measurements can be done on solutions in common solvents. We discuss advantages of the solution Z-scan technique, e.g. the possibility of in situ studies of electrochemical switching of third-order nonlinearity, and problems encountered on the interpretation of the results, such as those due to thermal nonlinearity and solvent effects.

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1. Z-scan in solutions: common ambiguities

The introduction of the Z-scan technique [1] for the determination of third-order optical nonlinearities has brought a flurry of activity to the field of third-order NLO materials. The implementation of the technique and the analysis of the results being rather simple, Z-scan has been used in numerous NLO investigations. We review here some of our results obtained in the implementation of

the technique where the investigated samples are solutions in common solvents.

1.1. Contribution of cell walls

We find that solution Z-scan can be a reliable technique for the determination of third-order NLO properties if adequate care is taken to avoid some common ambiguities. One of them is due to the fact that the measured nonlinear effects involve the contributions from the solute as well as those from the solvent and from walls of the cell in which the solutions are placed. This depends, among others, on the choice of the Rayleigh length of the beam. The choice of experimental parameters can be made either to include or exclude the

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contributions from the cell walls. Our usual choice is a 1 mm path length cell with 1 mm thick glass walls. The Rayleigh length: $z_R = \pi w_0^2 / \lambda$, where w_0 is the Gaussian beam waist and λ is the wavelength, can thus be taken to be $z_R > 3$ mm (which corresponds to $w_0 > 30$ μm for $\lambda = 0.8$ μm). This results in the Z-scans being carried out essentially in the “thin sample” limit and the effective nonlinear phase shift consisting of the sum of all the contributions (glass walls, the solvent and the solute). In practice, a cell with walls made of glass, for which we estimate $n_2 = 4.5 \times 10^{-16}$ cm^2/W , is used for measurements of effects in common solvents (chloroform, tetrahydrofuran, dichloromethane, dimethylsulfoxide) for which the nonlinear index (at 800 nm with 100 fs pulses) is of the order of 1×10^{-15} cm^2/W . Therefore, the total nonlinear phase shift measured in the cell containing a solvent can amount to roughly twice that of the solvent alone. On the other hand, choosing $z_R < 1$ mm one can perform measurements in the “thick sample” regime where the amplitude of the Z-scan signal can be taken as a measure of the nonlinearity of the solution, when compared to a signal from a 1 mm silica plate. The shape of the signal is, however, modified and, in particular, the peak-to-valley distance in a Z-scan is no longer related to z_R but rather to the sample thickness.

1.2. Thermal effects

The most critical, but often neglected issue is that of avoiding the contributions from nonlinear processes other than the instantaneous electronic nonlinearity (e.g. thermal nonlinearity, excited state nonlinearity, molecular reorientations, nonlinear scattering etc.), especially if relatively long light pulses or high repetition rates are used. Routine measurements involve n_2 values of the order of 10^{-15} cm^2/W , and thus one needs to make sure that other processes do not generate effective nonlinearities of similar or greater magnitude. As mentioned in [2], the thermal nonlinearity is sometimes conveniently viewed in terms of its frequency components and using Eqs. (4) and (5) from that paper one finds that, under steady state, the frequency components of the effective n_2 are given by

$$n_{2,\text{eff}}(\omega, s) = \left[\left(\frac{\partial n}{\partial T} \right)_V - \frac{n^2 - 1}{2n} \beta \right] \frac{\alpha}{i\omega c_p \rho + s^2 \kappa}$$

where ω is the frequency and s is the spatial frequency of illumination, β is the volume expansion coefficient, α is the absorption coefficient, c_p is the specific heat, ρ is the density and κ is the heat conductivity coefficient. The terms in the square brackets are the thermochromic and volume expansion components of the thermal changes of the refractive index. With short laser pulses the solution does not have enough time to expand within a single laser pulse duration and the effective n_2 is then given only by the thermochromic contribution, thus $n_2 \approx (dn/dT)_V \alpha t_p / (c_p \rho)$. With typical parameters for organic solvents (the thermochromic part of dn/dT is usually much smaller than the expansion coefficient, which is $\beta \approx 10^{-3}$ K^{-1} , $\alpha \approx 1$ cm^{-1} , $t_p \approx 10^{-13}$ s, $c_p \approx 2$ J/g K, $\rho \approx 1$ g/cm³) the thermochromic part of the nonlinearity is generally negligible unless strongly absorbing solutions are being measured. However, the thermal nonlinearity can easily become dominating if the repetition rate of the pulses, ω_{rep} , becomes comparable with $s^2 \kappa / c_p \rho$. The temperature change and associated refractive index changes may then persist for time comparable to that between the pulses. With the effective nonlinearity essentially due to the thermal volume expansion, typically $dn/dT \approx \beta \approx 10^{-3}$ K^{-1} . We note that, at the continuous illumination, the effective nonlinearity is $n_2 = \beta \alpha / s^2 \kappa$ which is on the order of 10^{-5} cm^2/W for $\alpha = 1$ cm^{-1} and a Gaussian spot size as used in our measurements (taking $s = 1/w_0$). Thus, a duty cycle of 10^{-11} or less is needed to avoid contamination of results by thermal effects. For 10^{-13} s pulses both the above considerations for the repetition rate limit it to about 100 Hz. Most of our studies have been performed at the repetition rate of 30 Hz and with the effective absorption coefficient (including nonlinear absorption) being appropriately low.

1.3. Possible solvent effects

We have compared results of NLO parameters obtained from solution Z-scan with those obtained by the degenerate four-wave mixing technique on films of many soluble conjugated polymers [3–5].

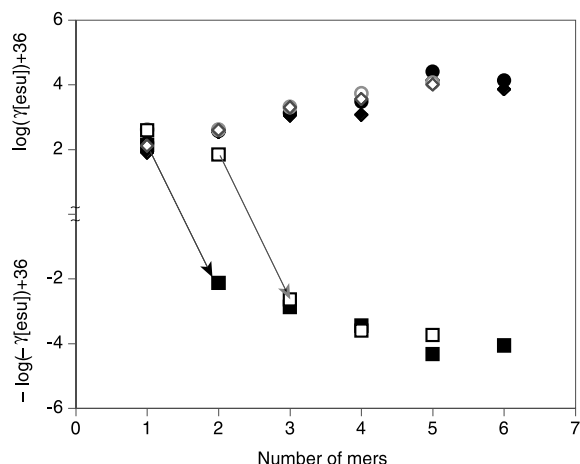


Fig. 1. Results of Z-scan measurements (800 nm, 100 fs pulses) of γ_{real} , γ_{imag} and $|\gamma|$ on a series of soluble phenylenevinylene oligomers $[\text{RO}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4-(\text{C}_6\text{H}_4-\text{C}_2\text{H}_4)_{n-1}-\text{C}_6\text{H}_4-\text{OR}]$ in two different solvents. Open symbols: measurements in THF, filled symbols: measurements in chloroform. Real parts of γ : squares, imaginary parts of γ : diamonds, $|\gamma|$: circles. Note that the change of sign of the real part of γ (indicated by arrows) occurs at smaller number of units in chloroform than in THF.

In general, the results are in reasonable agreement suggesting little effect of the environment on the NLO properties. However, while determining γ_{real}

and γ_{imag} of oligovanilines [6] and oligophenylenevinyls (Fig. 1) [7] we did find substantial shifts in the nonlinear optical properties that were apparently due to the solvents being used. This is in contrast to rather small solvent effects (a few nm shifts) on the absorption spectra of these compounds. At present it is not certain whether the changes in the NLO properties can be interpreted in terms of solvent-induced effects or if there are other experimental factors to be considered.

2. Advantages of solution Z-scan: in situ measurements of electrochemical switching

We have used solution Z-scan to perform systematic studies of cubic nonlinearities of various organometallic compounds with a goal of establishing structure–property relations. The usual difficulty in these studies is the limited solubility of the investigated molecules. This restricts the choice of solvents and limits the accuracy of the determination of γ of the solute. Among the many structures investigated, dendrimeric forms of organometallic acetylides have been found an exciting subject of studies [8,9]. They possess sizable cubic nonlinear-

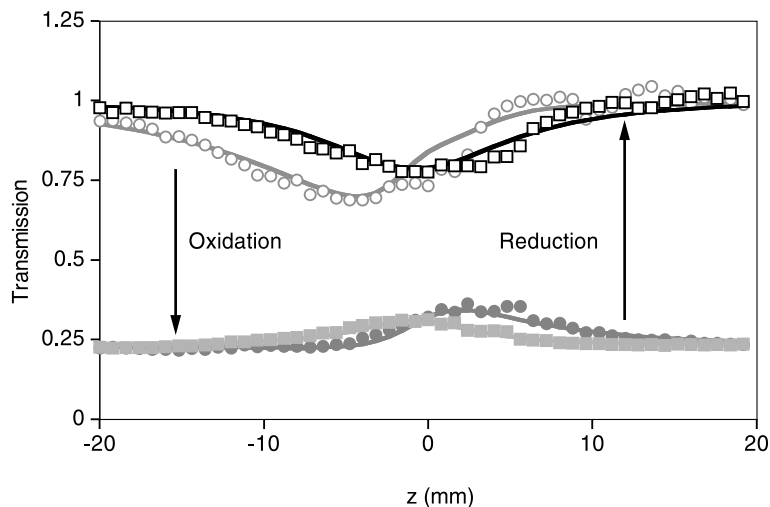


Fig. 2. Closed and open aperture Z-scan traces (800 nm, 100 fs pulses) for the neutral and oxidized forms of an organometallic dendrimer (0.18% solution in dichloromethane). Closed aperture (\circ) and open aperture (\square) scans for the neutral form show two-photon absorption whereas closed aperture (\bullet) and open aperture (\blacksquare) scans for the oxidized form show absorption saturation. The calculated hyperpolarizability values, in 10^{-36} esu, are: reduced form: $\gamma_{\text{real}} = -330 \pm 100$, $\gamma_{\text{imag}} = 2200 \pm 500$; oxidized form: $\gamma_{\text{real}} = 13500 \pm 3000$, $\gamma_{\text{imag}} = -4700 \pm 500$.

ities of both refractive and absorptive type and may also be of interest because of a new phenomenon of electrochemical switching of the cubic nonlinearity. We find that the linear and nonlinear optical properties of some of these compounds can be reversibly switched by electron transfer from an electrode. As an example, switching between nonlinear absorption and absorption saturation was experimentally observed, using an electrochemical Z-scan cell, with femtosecond pulses at 800 nm (Fig. 2) (cf. [10]). In the example shown here, an organometallic dendrimer can be (reversibly) switched from being a two-photon absorber with a negative real part of γ to being a saturable absorber with a positive real part of γ .

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