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Simultaneous determination of nonlinear optical and thermo-optic parameters of liquid samples

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The authors apply the theory of photothermal lens formation and also that of pure optical nonlinearity to account for the phase modulation in a beam as it traverses a nonlinear medium. It is used to simultaneously determine the nonlinear optical refraction and the thermo-optic coefficient. They demonstrate this technique using some metal phthalocyanines dissolved in dimethyl sulfoxide, irradiated by a Q-switched Nd:YAG laser with 10 Hz repetition rate and a pulse width of 8 ns. The mechanism for reverse saturable absorption in these materials is also discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2403185]

The study of nonlinear properties of photonic materials is important because an intense laser beam passing through them produces self-focusing, temporal and spatial self-phase modulations and light induced gratings that cause effects such as hole burning. Thermal effects such as the thermal variation of the refractive index, thermal expansion, and thermally induced stress of photonic materials are also very important. Usually, part of the excited state decay is nonradiative in nature. So the laser heats the sample and an optical path change is established owing to the temperature coefficient of the optical path, ds/dT, which causes the so-called thermal lens (TL).^{1–3} In this letter we demonstrate how these two important properties, viz., nonlinear optical effects and photothermal effects, can be studied using a single experimental technique.

Cobalt and nickel phthalocyanines (CoPc and NiPc), dissolved in dimethyl sulfoxide (DMSO) at a concentration of 0.5 mM, were used for this study. There is no special absorption peak for either of these metal Pc's around 532 nm, which was the excitation wavelength used. The z-scan method to measure the nonlinear absorption β , nonlinear refraction γ , etc., is well documented in literature.⁴⁻⁶ The nonlinear refraction encountered by an intense laser beam as it propagates through a liquid medium can have various physical origins such as electronic, molecular, or thermal.⁷ Under specific experimental conditions, there is the possibility of TL formation which will be reflected in the z-scan signal. A transient TL signal will be formed in liquid samples, in the nanosecond regime,^{1,7,8} which we exploit here to simultaneously determine thermo-optic coefficient, dn/dT, and the nonlinear optical parameters. The experimental arrangement is given elsewhere.⁹ The laser source used was a frequency doubled, Q-switched Nd:YAG (yttrium aluminum garnet) laser with a repetition rate of 10 Hz and pulse duration of 8 ns. A spatial filter was used to limit the beam size, and then it was focused by a short focal length convex lens, producing a Gaussian spot of 15.4 μ m in radius. The corresponding Rayleigh range is 1.4 mm and therefore since the sample was taken in a quartz cuvette of 1 mm path length, it satisfies the thin lens condition. The sample was translated through the focus and the transmitted pulse energy in the presence and also in the absence of a far field aperture was probed by a detector (Rj 735, Laser Probe Inc.) as a function of sample position *z*, obtaining the closed aperture (CA) and open aperture (OA) *z* scans, respectively. The linear transmittance of the far-field aperture, *S*, was fixed to be 0.28 for the CA *z* scan. The thermo-optic coefficient, $dn/dT(K^{-1})$, and some of the nonlinear optical parameters are extracted as follows.

Here we are considering the changes in refractive index due to purely optical nonlinearity and also that due to TL formation. The effect of this nonlinear refractive index is to produce a phase shift, which varies across the beam profile, resulting in transmittance change when viewed through an iris placed at the center of the beam spot in the far field. As mentioned in Ref. 8, the best procedure to extract both these nonlinearities is by a fit of the z-scan signal, taking into account both these effects. This can be done by modifying the on-axis phase shift at focus $\Delta \phi_0$, used in the derivation for far-field transmittance in Ref. 9, by including the phase shift due to transient TL formation. We write this phase shift as

$$\Delta\phi_0 = \Delta\phi_0(\text{opt}) + \Delta\phi_0(\text{ther}), \tag{1}$$

where $\Delta \phi_0$ is related to the total change in nonlinear refraction as

$$\Delta \phi_0 = \frac{2\pi}{\lambda} \Delta n_0 L_{\rm eff}.$$
 (2)

In the time scales in which we carried out our experiments, and for the focused beam spot size of 15.4 μ m, the rise time for thermal nonlinearity t_{ther} is of the same order of magnitude as that of the pulse duration (t_p) . The former is governed by acoustic transit time ω_0/v_s , where the sound velocity v_s is nearly 1-5 μ m/ns in most solvents. So the condition t_{ther} $< t_p < t_c$ is satisfied and results in efficient transient TL signal. Here t_c is the characteristic time for TL signal given by $\omega_0^2/4D$, where ω_0 is the beam spot size and D is the diffusivity. Since we are interested in the on-axis index change, we do not consider the effect of diffusion. Under these approximations, the on-axis thermal index variation can be expressed as Δn_0 (ther) = $(\alpha p_0/2\rho_0 c_p)(dn/dT)$.¹⁰ The corresponding value for pure optical nonlinearity is given by $\Delta n_0(\text{opt}) = \gamma I_0$, where the remaining terms are p_0 incident fluence (J cm⁻²), ρ_0 density (g cm⁻³), α linear absorption coefficient (cm⁻¹), c_n specific heat capacity (J g⁻¹ K⁻¹), γ the nonlinear index (cm² W⁻¹), $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective

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FIG. 1. CA z-scan data and theoretical fit for values of γ =8.35 $\times 10^{-5}$ cm²/*GW* and dn/dT=5.02 $\times 10^{-4}$ K⁻¹ at c_p =1.5 J cm⁻³ K⁻¹.

sample path length, and I_0 is the irradiance (W cm⁻²). Since the TL built-up is quasi-instantaneous here, both Δn_0 (ther) and Δn_0 (opt) will contribute to $\Delta \phi_0$ through Eq. (2). This situation is different from the case of cumulative TL effect seen when high repetition rate pulses are used. If the heating effect is cumulative, we need to take into account thermal diffusion which contributes to a slower component to nonlinearity. In such cases one can uncouple the purely optical (fast) and thermal (slow) nonlinearities as done by Haglund et al., where they obtain thermal conductivity and two photon absorption cross sections from a single z-scan signal.¹¹ For 8 ns pulse of 10 Hz repetition rate, conductivity or diffusivity will not significantly affect the propagating pulse. In other words the thermal nonlinearity due to the fast rise time of TL signal is more significant than that due to the decay of the TL.' Since in transient regime, the TL peaks up and distorts $\Delta \phi_0$ while the pulse lasts in the medium, and also since the TL created by one pulse does not affect the subsequent pulses, the problem of uncoupling it from the purely optical nonlinearity becomes less complicated.

Following the method adopted by Weaire *et al.*¹² and Sheik-Bahae *et al.*, we can approximate the normalized transmittance for a Gaussian TEM_{00} beam at the aperture plane as

$$T(z) = 1 - \frac{2\pi}{\lambda} L_{\text{eff}} \left(\frac{\alpha p_0}{2\rho_0 c_p} \frac{dn}{dT} + \gamma I_0 \right) \frac{4x}{(1+x^2)(9+x^2)}, \quad (3)$$

where x is the dimensionless sample position z/z_0 , z_0 being the depth of focus. This expression is used to fit the experimental z-scan signal by treating dn/dT and γ as fit parameters. The detailed curve fitting is done using a trial value for c_p as 1.2 J cm⁻³ K⁻¹ and initial guess values for thermo-optic coefficient and γ were obtained. With these initial values we refine the fit by varying c_p values from 1.2 to 3.0 which is typical for organic solvents and obtain best fit parameters. However, it was sufficient to vary the c_p values from 1.2 to approximately 1.6 after which there was large deviation of the theoretical curve from the experimental one.

The *z*-scan measurements were performed with on-axis peak irradiance I_0 ranging from 0.1 to 0.6 GW/cm². Figure 1 shows an example of the CA *z*-scan trace for CoPc in DMSO at $I_0=0.171$ GW/cm² with theoretical fit using Eq.



FIG. 2. OA z-scan data and theoretical fit.

(3). The values of γ and the thermo-optic coefficient obtained in this case are also shown. The corresponding values for NiPc are 7.78×10^{-5} cm²/GW and 4.86×10^{-4} K⁻¹, respectively. The thermal parameters extracted in both the cases are nearly equal and are close to the dn/dT value of DMSO. Therefore it can be concluded that the small variation of dn/dT value from that of DMSO is due to the presence of impurity, which is the Pc molecule here. The nature of the metallic nuclei in the Pc does not affect the thermal expansion of the solution.

The nature of the OA z-scan traces indicates reverse saturable absorption (RSA) in both the samples. A typical one for NiPc is given in Fig. 2 with theoretical fit using the equation

$$T(z, S=1) = \frac{1}{\sqrt{\pi}q_0(z, 0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z, 0)e^{t^2}]dt, \qquad (4)$$

where $q_0(z,t) = \beta I_0(t) L_{\text{eff}} / (1 + z^2 / z_0)$, β being the nonlinear absorption coefficient.

Within the range of incident fluence used in our experiment, the depth of the valley of the OA *z*-scan traces increases with I_0 , suggesting that there is no saturation of the excited singlet state absorption (ESA), which is the sequential transitions $S_1 \leftarrow S_0$ and $S_n \leftarrow S_1$ that occur in resonance at high fluence. Therefore ESA is one reason for the RSA behavior in OA *z*-scan traces. In Pc's the planar conjugated π electrons have a strong RSA effect. To clearly understand the mechanisms for RSA, we need to solve the coupled rate equations for nonsteady state (time dependent), assuming a five level model for the energy levels (Fig. 3). The set of equations.



FIG. 3. Five level diagram leading to the rate equations (5).

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FIG. 4. Calculated population densities of each state S_0 , S_1 , and T_2 .

$$N_1 + N_2 + N_3 + N_4 + N_5 = N_0, (5a)$$

$$\frac{dN_2}{dt} = \frac{N_3\phi_{32}}{\tau_3} + \frac{N_4}{\tau_4},$$
(5b)

$$\frac{dN_3}{dt} = (N_1 - N_3)\sigma_{13}p - \frac{N_3\phi_{32}}{\tau_3} - \frac{N_3(1 - \phi_{32})}{\tau_3},$$
 (5c)

$$\frac{dN_4}{dt} = (N_2 - N_4)\sigma_T p - \frac{N_4}{\tau_4} + \frac{N_5\phi_{54}}{\tau_5},$$
(5d)

$$\frac{dN_5}{dt} = (N_1 - N_5)\sigma_{15}p - \frac{N_5(1 - \phi_{54})}{\tau_5} - \frac{N_5\phi_{54}}{\tau_5} + (N_3 - N_5)\sigma_{35}p,$$
(5e)

where ϕ 's are the intersystem crossing yields, σ 's are the absorption coefficients, and τ 's are the lifetime of the energy levels.

To solve this, we neglect the intersystem crossing to level T_1 and incorporate the possibility of sequential two photon absorption¹³ and modify the rate equations accordingly, taking into account the rate of change in population as proportional to p^2 (*p* being the fluence) and the nonlinear absorption cross section obtained from the theoretical fit to OA *z*-scan trace. Then the first term on the right hand side of

Eq. (5c) can be neglected, which is due to one photon absorption, and the first term in the Eq. (5e) will be modified as $(N_1-N_5)\beta p^2$. The population dynamics is given in Fig. 4.

It can be assumed that within the duration of the pulse, most of the molecules were excited either through two photon absorption (TPA) or ESA, and hence the population in S_1 and T_1 will be very negligible. So our conclusion is that the OA *z*-scan trace of these metal Pc's can give an effective value of nonlinear absorption β_{eff} , contributed by both ESA and TPA. The calculated values of β_{eff} for cobalt phthalocyanine (CoPc) and nickel phthalocyanine (NiPc) are 5.58 and 6.32 cm/GW, respectively.

In conclusion, we have carried out an experiment to simultaneously determine some of the nonlinear optical parameters and thermo-optic coefficient of a sample in liquid form. This has been demonstrated in metal Pc's dissolved in DMSO using a Nd:YAG laser of 8 ns pulse width and 10 Hz repetition rate. This method can be applied to any nonlinear material with very small linear absorption at the excitation wavelength.

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