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M. Cha
University of Central Florida

W. E. Torruellas
University of Central Florida

G. I. Stegeman
University of Central Florida

W. H. G. Horsthuis

G. R. Möhlmann

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M. Cha, W. E. Torruellas, G. I. Stegeman, W. H. G. Horsthuis, G. R. Möhlmann, and J. Meth

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M. Cha, W. E. Torruellas, and G. I. Stegeman
Center for Research and Education in Optics and Lasers (CREOL), University of Central Florida, Orlando, Florida 32826

W. H. G. Horsthuis and G. R. Möhlmann
AKZO Electronic Products, Arnhem, Netherlands

J. Meth
DuPont de Nemours, Experimental Station, Wilmington, Delaware 19898

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The two photon absorption spectrum has been measured in the 780–1600 nm range for a di-alkyl-amino-nitro-stilbene side-chain polymer. A single two photon peak centered at 920 nm is observed with a peak two photon coefficient of 5.5 cm/GW. Bleaching via two photon absorption at this wavelength is investigated by measuring a refractive index change after an intensive exposure. © *1994 American Institute of Physics.*

Charge transfer molecules with large second order nonlinearities are being used for poled polymer electro-optic applications.[1] These molecules usually have a very strong one-photon absorption band associated with a charge transfer state, with a linear absorption peaked at λ_{max} in the 350–600 nm range. When illuminated at a wavelength close to λ_{max}, a trans→cis isomerization can occur reducing not only the linear absorption and refractive index but also the second order nonlinearity. In fact this photobleaching is frequently used for patterning in particular waveguide structures.[2] Typically these polymers are used for applications at wavelengths far from λ_{max} and photobleaching with one photon processes is not normally expected. However, TPA (two photon absorption) processes can also lead to photobleaching, the amount of photobleaching depending on the strength of the TPA coefficient at the device operating wavelength.[3,4] TPA information of DANS (di-alkyl-amino-nitro-stilbene) molecules, intensively developed for electro-optic applications in the form of side-chain polymers, to the best of our knowledge, is missing in the literature.[5] In this letter we report measurements of the TPA coefficient in a DANS side-chain polymer over a large wavelength range spanning possible device application spectral windows from 780 to 1600 nm.

Open aperture *Z*-scan measurements have been performed on device grade thick solid films of DANS side-chain polymer. The DANS samples contained approximately 50% DANS molecules by volume. 300 μm thick samples were prepared by solution casting. Three different laser systems were used in the measurements. The complete experimental layout is shown in Fig. 1. A 76 MHz Kerr lens mode-locked Ti:sapphire laser with 3 ps pulses was used to cover the range from 780 to 965 nm. To avoid damage or flux-dependent effects an acousto-optic modulator combined with an aperture allowed trains of 75–150 pulses to reach the sample at a 10 Hz repetion rate. A 10 Hz, 35 ps Nd:YAG laser was used to gather data at 1064 nm. Finally we used 65 ps pulses from a Nd:YLF pumped OPG&A (Optical Parametric Generator and Amplifier) system operating at 10 Hz which was tuned from 1200 to 1600 nm. A typical *Z*-scan result with the best fit to the data is shown in Fig. 1.

Our results showed no evidence of excited state effects. For example, we found no dependence of the data on the number of pulses used. We also varied the pulse energy for the *Z*-scan measurement and found the TPA coefficient deduced to be independent of pulse energy within our experimental uncertainty. Typical intensity dependence is shown in Fig. 2(a). These results indicate that the multiphoton effects present are only due to TPA.

The measured dispersion of the TPA coefficient α_2 ($\Delta\alpha=\alpha_2 I$, where I is the local intensity) over the primary

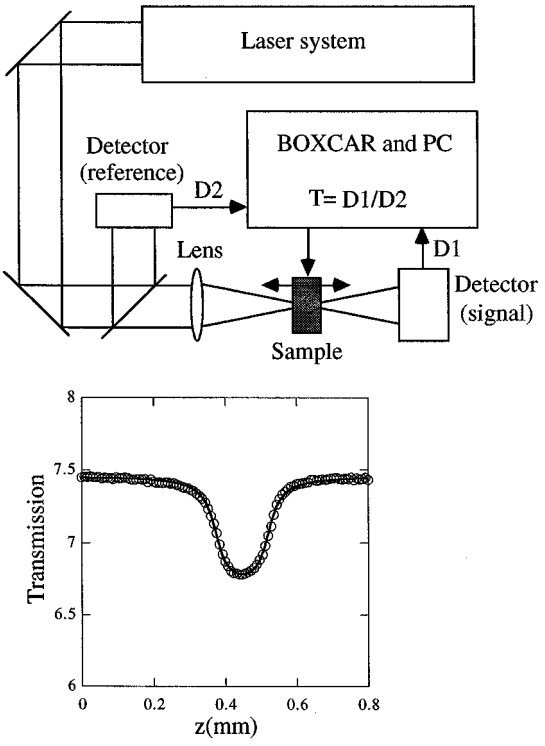

FIG. 1. TPA experimental setup (upper). Laser system is one of the following: Ti:sapphire laser with A/O modulator, *Q*-switched Nd:YAG laser or OPG/OPA. Typical open aperture *Z*-scan data (open circles) with fit (solid line) are also shown (lower). Note that a tight focusing scheme has been used assuming small nonlinear refraction.

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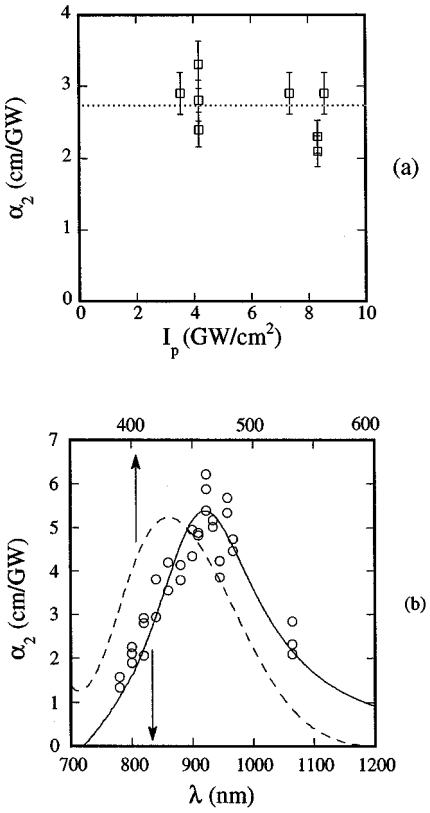

FIG. 2. (a) TPA coefficients vs peak intensity used in the open aperture Z scan at 1064 nm. No significant intensity dependence is observed. (b) Dispersion of TPA coefficient near the TPA resonance. Open circles: α_2 data, solid line: fit from two-level model; dashed line: one photon absorption data for comparison (refers to upper horizontal axis).

spectral region of interest is shown in Fig. 2(b). Note that the maximum coefficient is 5.5 cm/GW. Furthermore, for wavelengths in the range 1200–1600 nm we found the α_2 to be less with 0.1 cm/GW. Hence we conclude that there is only one two photon state which can be accessed over this wavelength range, and such a state or resonance is not accessible by two photons from both telecommunication windows at 1.3 and 1.5 μm. However, in applications which require large powers at wavelengths below 1 μm, TPA induced degradation could become an important concern.[6]

Since the DANS molecule is not centrosymmetric, the wave functions have mixed one and two photon character, and thus the charge transfer band can be accessed by both one and two photon absorption. In terms of a two state model, the degenerate third order susceptibility is given by (in MKS units)[7]

$$\chi^{(3)}(-\omega;\omega,-\omega,\omega) = \frac{N\langle\cos^4\theta\rangle L_3 \mu_{01}^2 \Delta\mu_{01}^2}{3\epsilon_0\hbar^3} \frac{1}{(\Omega-2\omega)(\Omega-\omega)} \times\left(\frac{1}{\Omega-\omega}+\frac{1}{\Omega+\omega}\right)+\text{nonresonant terms.} \quad (1)$$

The complex angular frequency Ω is associated with the excited state defined such that $\Omega = E/\hbar - i\Gamma/2$, where E is the energy difference between the excited state and the ground state, and Γ is the FWHM (full-width at half-maximum) of the Lorentzian lineshape. μ_{01} is the transition dipole moment between the ground and excited state, and $\Delta\mu_{01}$ is the difference in permanent dipole moments between the ground and excited state. N is the molecular density, $\langle\cos^4\theta\rangle$ represents the average of the induced polarization projected onto the molecular axis for one-dimensional molecules and L_3 is the local field correction factor, for example, calculated by the Lorentz local field. The TPA coefficient is related to $\chi^{(3)}$ by the following expression:

$$\alpha_2(\omega) = \frac{3\pi\ \mathrm{Im}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]}{\epsilon_0 c n^2 \lambda}. \quad (2)$$

Using the above Eqs. (1) and (2), our fits to the TPA data produced $\Delta\mu \approx 12$ D, whereas $\mu_{01} \approx 7$ D was obtained from the linear absorption data. In this case dipole–dipole interactions and retardation effects have been neglected.

There is an intriguing red shift in the peak of the TPA coefficient from its expected position. Shown for reference in Fig. 2(b) is the linear absorption spectrum which peaks at 430 nm. As a result one expects the two photon spectrum to peak at 860 nm, not the observed 920 nm. We note that two overlapped peaks were also observed in the THG spectrum of DANS, with one maximum shifted to longer wavelengths from the peak associated with the three photon resonance with the state responsible for the one photon absorption peak.[8] This shift has not been satisfactorily explained to date.

TPA can be a problem near the peak of the two photon resonance. For example, an additional loss of 0.1 cm^{-1} is induced in a channel waveguide of cross section 5 $\mu\mathrm{m}^2$ for a guided wave power of 1 W. Such an input power is typically orders of magnitude larger than that used for electro-optic switching. However, when poled polymers are used for second harmonic generation, maximum input powers of this magnitude can be expected.[9]

Potentially more serious is the cumulative photosensitivity induced by this absorption over the lifetime of a device. Two photons with a sum energy near the main absorption band can also result in photobleaching. In fact, two photon photobleaching in DANS has been observed in experiments aimed at measuring the third order nonlinearity $\chi^{(3)}$ in waveguides.[10] A permanent shift in the optimum coupling angle for grating coupling into slab DANS waveguides was observed after illumination with either ps or ns pulses at 1064 nm. Furthermore, Norwood *et al.* have estimated a lower limit to the expected lifetime of a DANS device due to multiphoton photosensitivity.[3] He assumed that the photobleaching quantum efficiency is the same for one and TPA. From his linear bleaching experiments and his measured upper limit to α_2 of 0.3 cm/GW at 1.3 μm, he estimated a lifetime of 14 years for an input waveguide intensity of 10 $\mathrm{kW/cm}^2$. This corresponds to an input power of approximately 1 mW. At the peak of the TPA in DANS, this lifetime is further reduced by one or two orders of magnitude.

Two photon bleaching can be quantified in terms of a refractive index change (Δn_{TP}) which is proportional to the number of molecules that have undergone the trans→cis isomerization.[2] Assuming that this transition has a constant quantum efficiency with respect to a photoexcited molecule,

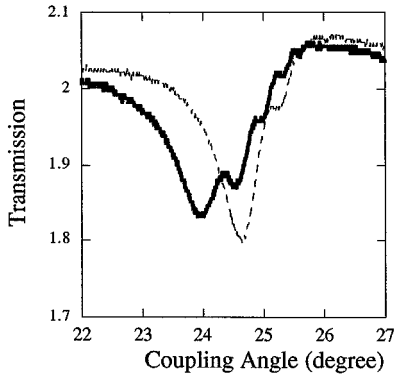

FIG. 3. Waveguide grating coupling dip for the TE_3 mode: partially bleached at 920 nm (solid line) and data for the unexposed area (dashed line).

Δn_{TP} is found to be proportional to P^2t, where P is the input power and t is the accumulated exposure time. Note that two photon bleaching is sensitive not only to the accumulated energy Pt, but also to the peak intensity while single photon bleaching depends on the total energy only.

We performed waveguide coupling experiments to measure an index change after an exposure of our sample. A dye laser pumped by a doubled Nd:YAG laser (injection seeded, Q-switched) was tuned to generate intense 4 ns pulses at 920 nm at a repetion rate of 10 Hz. A 2 μm thick planar waveguide was made by spin coating the DANS side-chain polymer on a fused silica substrate with a pair of coupling gratings. The laser beam was weakly focused onto a small area ($\sim$200 μm in diameter) at the slab waveguide boundary of one of the gratings. The exposure was sustained for 9 h with an input energy of 1.8 mJ/pulse and an estimated intensity of 670 MW/cm^2. A cw diode laser at 780 nm was used to measure the refractive index of the DANS film by the typical grating coupling technique.[11] Although the waveguide supported four TE modes, the TE_3 mode has been chosen because it showed a larger coupling dip than the others. Figure 3 shows the coupling dip close to the grating coupling angle of the TE_3 mode, measured on both the bleached spot and the unexposed area, respectively. From the measured differences in the coupling angles and the previously known data for the unexposed DANS waveguides, we could estimate Δn_{TP} to be -0.005 to -0.01. Based on single photon bleaching experiments, where a cw laser near the absorption peak was used with the peak intensity of 160 mW/cm^2 for 1 h to obtain an index change of -0.027, we obtained a quantum efficiency of 10^{-5} for single photon bleaching.[12] If we assume the same quantum efficiency for one and two photon bleaching, we can estimate $\Delta n_{TP} \sim -0.003$ at 780 nm, in reasonable agreement for this level of approximation with our TPA induced index changes, where any residual one photon induced changes at 920 nm have been neglected. Indeed, the residual one photon absorption at 920 nm is in the order of 1 cm^{-1} which could have contributed an additional index change of -0.002 at 780 nm. Thus a DANS waveguide of cross section 5 μm^2 operating at 920 nm with a cw guided power of 1 mW, and with the estimated TPA induced bleaching quantum efficiency (10^{-5}), will have a lifetime of 7 months, which is significantly shorter than the lifetime at the off-resonant wavelength given by Norwood *et al.*[3]

In conclusion, we report the first TPA spectrum of a DANS side-chain polymer. We believe bleaching through two photon absorption is not a serious problem for DANS based devices operating at 1.3 or 1.5 μm. However, materials with enhanced nonlinearities and λ_{max} close to 600 nm, could suffer from severe degradation when exposed to similar wavelengths.

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