Observation of Three-Photon Enhanced Four-Photon Absorption

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We report the measurement of instantaneous resonant four-photon absorption in the polydiacetylene-PTS [polymer poly(bis para-toluene sulfonate) of 2,4-hexadyine-1,6 diol]. Although normally too weak to be observable, an exact degeneracy between three- and four-photon absorption into the dominant exciton and two-photon states, respectively, resonantly enhances this effect so that it can be measured (four-photon coefficient $\alpha_4 = 0.01\ \mathrm{cm}^5/\mathrm{GW}^3$) at its peak wavelength of 1900 nm. Femtosecond measurements from 1200 to 2200 nm of two- and three-photon absorption, and the nonlinear refractive index coefficient are also reported.

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The investigation of nonlinear optical effects has been a thriving field since its inception in the 1960s when phenomena such as stimulated Raman, self-focusing, second harmonic generation, etc., were first observed and understood [1]. The introduction of concepts such as all-optical switching, bistability, etc., in the 1980s focused attention on the third order susceptibility $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ which gives rise to an intensity-dependent refractive index n_2 and a two-photon absorption (2PA) coefficient α_2 [2]. The n_2 results in an index change proportional to the intensity that leads to intensity controlled interference effects for the all-optical manipulation of signals. Although the additional absorption $\Delta\alpha = \alpha_2 I$ due to 2PA has for many years been considered an undesirable factor because it decreased the throughput of all-optical devices, recently it has been the focus of the search for materials with large α_2 for two-photon microscopy [2,3]. These and other applications continue to keep the investigation of nonlinear refraction and absorption in the forefront of nonlinear optics.

One of the most promising classes of nonlinear materials with large $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$s are polydiacetylenes [4]. They are conjugated polymers in which the p atomic orbitals of mutually bonded carbon atoms delocalize to produce π molecular orbitals parallel to the quasilinear carbon (polymer) chain [5]. The optically induced electron motion is essentially one dimensional and leads to large maximum (on and near resonance) values of both n_2 and α_2 along a single molecular axis, which has been demonstrated experimentally [6,7]. Polydiacetylenes are model third order materials because their nonlinearities are essentially one dimensional; they can be grown in good quality single crystal form and their electronic states have either even (A_g) or odd (B_u) symmetry [5].

Both linear and nonlinear absorption spectroscopy have identified the dominant (strongest oscillator strength) one- and two-photon transitions between the ground ($1A_g$) and the one- ($1B_u$) and two- (mA_g) photon excited states. The values for the maxima of the one- (1PA) and two-photon absorption spectra are $\alpha_1 = 7 \times 10^5\ \mathrm{cm}^{-1}$ (at 620 nm) and $\alpha_2 = 7 \times 10^2$ cm/GW (at 930 nm), respectively, in single crystal PTS [polymer poly(bis para-toluene sulfonate) of 2,4-hexadyine-1,6 diol] [6,7]. These large values suggest the possibility of measuring the next higher order nonlinear absorption, namely, three- (3PA) and four-photon (4PA) absorption. Although high order, multiphoton, band-to-band absorption in semiconductors and ultrafast 3PA involving electronic transitions have been measured in some organic materials before, there has been only one preliminary report of 4PA to two-photon active energy levels [8–10]. Normally 4PA would be very difficult to observe in molecular systems. However, in PTS the transition dipole moments from $1A_g \Rightarrow 1B_u$ and from $1B_u \Rightarrow mA_g$ are very large — over $1e\text{Å}$ ($1.6 \times 10^{-29}\ \mathrm{Q \cdot m}$) [11]. Moreover, there is an accidental degeneracy between 3PA ($3 \times 620 = 1860$ nm) and 4PA ($2 \times 930 = 1860$ nm). This degeneracy provides an enhancement mechanism which might make 4PA large enough to be observed. Indeed, since the intermediate $1B_u$ level is resonant for 3PA, $\Delta\omega = 3\omega - \omega_{01} \to 0$ and the 4PA process becomes dependent on the inverse lifetime of the $1B_u$ state, Γ_1. Formally, then, the enhancement of $\chi^{(7)}(-\omega; \omega, -\omega, \omega, -\omega, \omega, -\omega, \omega)$ can be estimated by $\mathrm{Im}(\chi^{(7)})_{\text{3PA enhanced}} \approx \mathrm{Im}(\chi^{(7)})_{\text{nonresonant}}[\omega_{01}^2/\Gamma_1^2]$ [12]. Previous experiments have shown that Γ_1^{-1} is of the order of 2 psec [13]. Based on these parameters, degeneracy further enhances the 4PA coefficient by about 4–5 orders of magnitude. In this Letter we report femtosecond measurements of both the degenerate nonlinear refraction (n_2) and multiphoton absorption in the range 1200 to 2200 nm. Strong 4PA was observed at 1900 nm.

The techniques used to produce optical quality PTS crystals are well documented [14]. Monomer single crystals are made by controlled evaporation of acetone from saturated solutions of PTS molecules dissolved in acetone. Multiple successive recrystallizations purify the

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crystals until finally they have a light pink hue. The monomer crystals are hand cleaved into platelets 100 to 300 μm thick. Polymerization is performed with controlled heating.

The Z scan was used for the measurements. The sample is moved through the focus of a beam and the transmitted signal is either completely (open aperture) detected or just sampled over a small aperture centered on the beam axis (closed aperture) [15]. Polarization scan in which the sample remains in or near the beam focus and the polarization of the incoming light is changed was used to take advantage of (and verify) the essentially 1D nonlinear response of PTS. The light source is a Spectra-Physics/Positive Light Optical Parametric Generator/Amplifier (OPG/OPA). It produces 20 μJ, 100 fsec pulses at a 1 kHz repetition rate with spectral bandwidths of order 40 nm and peak intensities up to 40 GW/cm^2 incident on the sample. Custom made TE cooled InAs detectors by EG&G with sensitivity out to 2200 nm were used.

For multiphoton absorption, the open aperture scan by itself is not very sensitive to the number of photons, 2,3, or 4, involved in the absorption process, especially when more than one process is active [10]. Shown in Fig. 1 is the intensity dependence of the multiphoton absorption in which all of the other nonlinear coefficients are set to zero. If only one multiphoton absorption process is present, analysis of the Z scans would yield an intensity-independent coefficient for that case. For example, in Fig. 1(a) the fitted values of the α_3 coefficient are not independent of intensity. Similarly, the fit to just α_4 in Fig. 1(b) shows that there is a small admixture of other nonlinear absorption processes involved. However, these intensity dependences can be fit to multiple orders of absorption. Z scans were generated numerically with different admixtures of pairs of nonlinear processes until the intensity dependence in Fig. 1 was reproduced. Examples of the efficacy of this procedure are also shown in Fig. 1. Note that the curves deduced from the experimental data can be reproduced quite accurately, leading to a physically reasonable decomposition into the contributing processes.

Similarly, nonlinear refraction measurements (closed aperture Z scan) were taken as a function of increasing intensity at each wavelength. In all cases, fitting to only the Kerr process, i.e., $\Delta n = n_2 I$, led to n_2s independent of intensity, to within experimental error. The measured wavelength variation, shown in Fig. 2, exhibits a monotonic decrease with increasing wavelength and connects with previous data at 1064 nm [5($\pm$1) $\times 10^{-3}$ cm^2/GW] measured on a sample from a different source [7]. This strong self-focusing, when combined with strong multiphoton absorption, can lead to interpretation errors

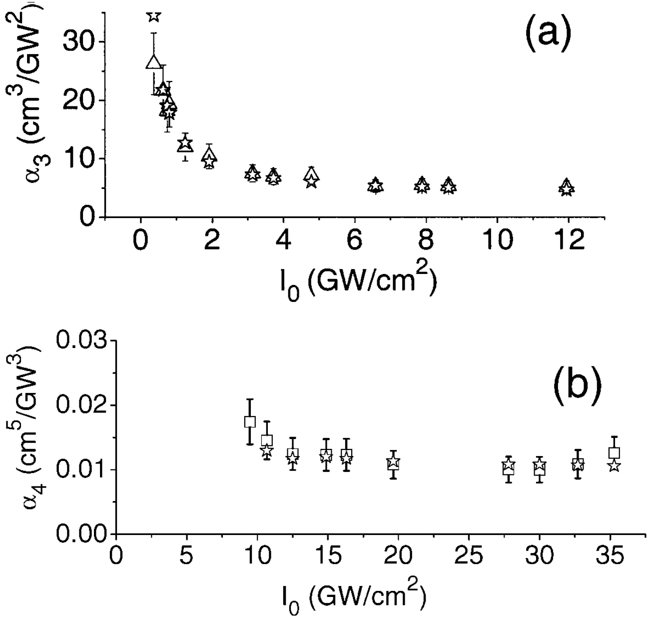

FIG. 1. Two examples of the multiphoton coefficients, calculated fits to the Z scan data when only one multiphoton process is assumed: (a) for α_3 (△) at 1320 nm and (b) for α_4 (□) at 1890 nm. In the second step, Z scan curves were calculated for combinations of two different processes and least-squares fits were performed as for the experimental data. The ratios were adjusted until the calculated data (☆) agreed with the experimental data giving for (a) $\alpha_2 = 6$ cm/GW and $\alpha_3 = 2.7$ cm^3/GW^2 and for (b) $\alpha_3 = 0.03$ cm^3/GW^2 and $\alpha_4 = 0.008$ cm^5/GW^3.

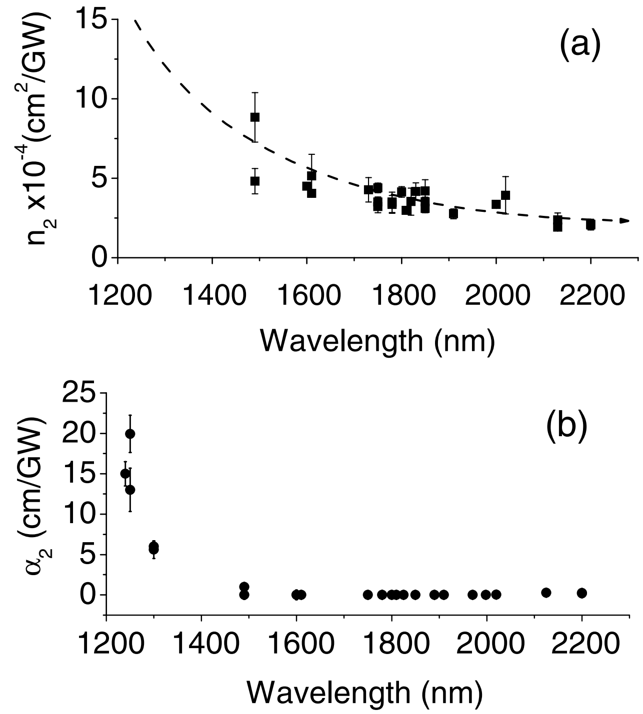

FIG. 2. The wavelength dependence of (a) n_2 deduced from the intensity dependence of the fits to the closed aperture Z scans and (b) α_2 deduced from the intensity dependence of the fits to the open aperture Z scans.

Z scans for samples thicker than 200 μm [16]. Hence samples thinner than 200 μm were used here.

The fitted values of the 2PA (α_2), 3PA (α_3), and 4PA (α_4) coefficients are shown in Figs. 2–4. The 2PA coefficient in Fig. 2(b) decreases monotonically to zero (immeasurably small values), as expected for the tail of the 2PA peak observed previously at 930 nm [7,17]. No evidence was found for the additional 2PA peaks reported at longer wavelengths using 25 psec pulses [7]. However, in that work all maxima due to multiphoton absorption were identified as due to 2PA. Clearly there is a different origin for these other peaks.

The 3PA (α_3) response in Fig. 3 is somewhat surprising. The response around 1800–1900 nm shown in the inset exhibits only a weak enhancement. Also puzzling is the rise in α_3 towards shorter wavelengths from around 1600 nm and extending to the shortest wavelengths studied. Even discounting the data below 1400 nm due to the large error bars caused by the dominance of 2PA, there is definitely a mechanism present with an $\Delta\alpha \propto I^2$ response between 1400 and 1600 nm. This could be the peak previously identified as 2PA at 1400 nm [7]. Furthermore, the 3PA response between 1200 and 1300 nm may be partially associated with another peak reported earlier [7]. However, there is a clear difficulty in assigning the broad but weak shoulder (around 500 nm) in the 1PA to the better defined of these two 3PA peaks [14]. Alternatively, our data could reflect the long wavelength tail of an α_3-like process reported by Kobayashi in the closely related (to PTS) polydiacetylene poly[4,6-dodecadiyn-1,10-diol-bis(n-butoxycarbonylmethylurethane)], which peaks at about 810 nm and monotonically decays towards 1100 nm [13]. He refers to an interexciton interaction (Auger recombination followed by fission) as a probable cause for this $\chi^{(5)}$ effect.

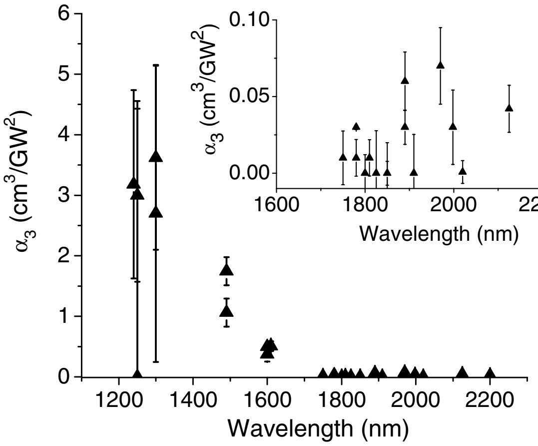

FIG. 3. The wavelength dependence of α_3 deduced from the intensity dependence of the fits to the open aperture Z scans. Inset shows the dispersion of α_3 with an expanded vertical scale for the 1700 to 2200 nm region.

The 4PA spectrum (Fig. 4) is measurable only in the region 1700 to 2200 nm, with a peak at 1900 nm that corresponds closely with the position predicted by the published 2PA spectrum [7,17].

In certain limits, an alternative to a pure α_4 process for an $\Delta\alpha \propto I^3$ response can be 3PA to the $1B_\mathrm{u}$ state followed by excited state absorption (ESA) to mA_g labeled as (3 + 1). Both processes are also resonantly enhanced, and indeed the (3 + 1) process is significant here since the ESA transition dipole moment is comparable to the strongest 1PA from the ground state to $1B_\mathrm{u}$ [11]. The saturation intensity for $1A_g \Rightarrow 1B_u$ has been measured to be 65 MW/cm^2 and, accounting for the factor of 20 difference in the upper state lifetimes for the $1B_\mathrm{u}$ versus mA_g states, we estimate the saturation intensity (I_sat) for the excited state absorption to be of the order of 1–2 GW/cm^2 [6,18]. Thus every electron excited to the $1B_\mathrm{u}$ state by 3PA undergoes an intensity-independent 1PA to mA_g for the intensities necessary to invoke a measurable 3PA response.

A very simple model is assumed to explain the impact on the measured α_4 of this (3 + 1) process at the intensities used. Assuming both $1B_\mathrm{u}$ and mA_g levels to have an "infinite" lifetime, an electron excited to either one does not have a chance to decay and be reabsorbed. The relevant rate equations for the (3 + 1) process are

$$\Delta N_{1A_\mathrm{g}} = -\frac{N_{1A_\mathrm{g}}}{N_0}\frac{\alpha_3}{3\hbar\omega} I^3 d^3 V dt,$$

$$\Delta N_{1B_\mathrm{u}} = \left[\frac{N_{1A_\mathrm{g}}}{N_0}\frac{\alpha_3}{3\hbar\omega} I^3 - \frac{N_{1B_\mathrm{u}}}{N_0}\frac{\alpha_{ES}}{\hbar\omega} I\right] d^3 V dt,$$

$$\Delta N_{mA_\mathrm{g}} = \frac{N_{1B_\mathrm{u}}}{N_0}\frac{\alpha_{ES}}{\hbar\omega} I d^3 V dt,$$

where the intensity and all the populations N depend on

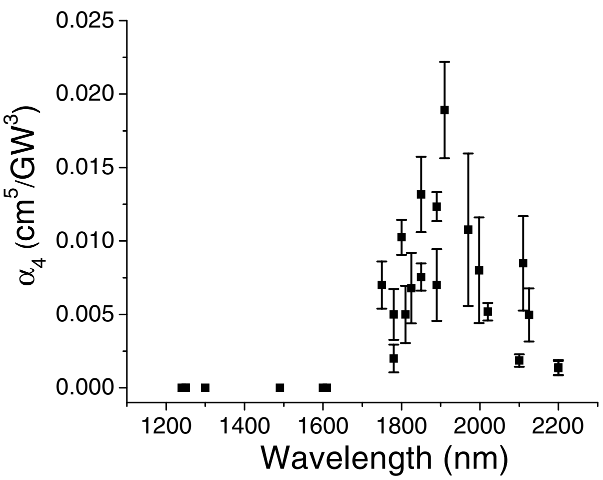

FIG. 4. The wavelength dependence of α_4 deduced from the intensity dependence of the fits to the open aperture Z scans.

the spatial and temporal coordinates, i.e., x, y, z, t, and d^3V is a small volume element. The initial conditions correspond to a nonexcited medium, i.e., $N_{1A_g} = N_0$; $N_{1B_u} = 0$, and $N_{mA_g} = 0$ where N_0 is the initial electron density, and α_{ES} corresponds to the ESA under the assumption that all electrons are in the $1B_u$ state. For $I/I_{sat} \ll 1$, numerical solutions of these equations yield $\Delta\alpha \propto I^3$, but at the $10s$ GW/cm^2 experimental input intensities, $I/I_{sat} \gg 1$ and $\Delta\alpha \propto I^2$ for the $(3+1)$ process, the same intensity dependence as 3PA. Indeed, about 95% to $> 99\%$ of the electrons in the $1B_u$ exciton state undergo 1PA to end up in the mA_g level. In this limit, the contribution of saturated ESA simply increases the (measured) effective $\alpha_{3,\text{effective}}$ to $4/3\alpha_3$. This situation is complicated by the lifetime of the $mA_g \Rightarrow 1B_u$ decay of about 100 fsec, i.e., of the order of the pulse widths used [18]. However, since the $1B_u$ population is replenished by decay from the mA_g state, this is expected to simply enhance the effective three-photon coefficient further, but not to change its intensity dependence. Based on all of these considerations, we therefore conclude that the absorption process observed experimentally as α_4 is instantaneous 4PA, enhanced by the near degeneracy with the three-photon absorption.

In summary, the first measurements of the nonlinear refraction and multiphoton absorption have been made on polydiacetylenes in the 1200 to 2200 nm wavelength range. Detailed data analysis allowed the dispersion of the 2PA, 3PA, 4PA, and n_2 coefficients to be measured. The expected resonances in the 3PA and 4PA coefficients in the 1800 to 1900 nm range were observed. Analysis of the different contributing mechanisms led to the conclusion that the 4PA is 3PA enhanced, the first time that this mechanism has been identified experimentally. However, only order-of-magnitude estimates have been made and there are many theoretical challenges still to be met in understanding the physics of the data reported, especially for interpreting the three-photon absorption data.

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