Identification and Role of Two-Photon Excited States in a π-Conjugated Polymer

B. Lawrence, W. E. Torruellas, M. Cha, M. L. Sundheimer, and G. I. Stegeman
Center for Research in Electro-Optics and Lasers, University of Central Florida,
12424 Research Parkway, Orlando, Florida 32826

J. Meth
E.I. Dupont de Nemours & Co.,
Central Research and Development Department, Experimental Station,
Wilmington, Delaware 19898

S. Etemad
Bell Communications Research,
Red Bank, New Jersey 07701

G. Baker
Department of Chemistry, Michigan State University,
East Lansing, Michigan 48824

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We have measured the full two-photon absorption (TPA) spectrum in the transparency range of single-crystal polydiacetylene paratoluene-sulfonate (PTS) using z scan. The spectrum consists of three well-defined two-photon excited states superimposed on a continuum of even-parity states. Comparison of the TPA and the one-photon absorption spectra identifies a two-photon accessible state as the lowest excited state of PTS. The accompanying dispersion in the intensity-dependent refractive index coefficient n_2 is also reported.

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Polydiacetylenes (PDA) are wide band semiconductors whose optical properties are dominated by delocalized π electrons confined to move along their one-dimensional conjugated backbone. Identified as ideal quantum wires the study of their electronic structure has been an active research topic in the last two decades for many reasons [1]. For instance, it has been shown that on resonance their optical response differs from that of a 2D semiconductor quantum well, involving strong electron-phonon coupling [2]. Whether the lowest excited state exhibits even or odd symmetry appears to be significant in assessing the role of electron correlations and whether such polymers can luminesce efficiently [3,4]. In addition, the third order optical susceptibility reported in 1976 is still the largest nonresonant nonlinearity known for any material [5]. The origin of such large nonresonant nonlinearities has also been attributed to the presence of one- and two-photon excited states with remarkably large oscillator strengths, the latter are investigated here.

Whereas dispersion of the linear optical constants yields information about the one-photon (odd symmetry) excited states, nonlinear optical (NLO) spectroscopy is needed to identify the two-photon (even symmetry) excited states. Following the pioneering work of Chance and co-workers, on coherent anti-Stokes-Raman spectroscopy (CARS) in soluble polydiacetynes, most of the NLO spectroscopy in such polymeric semiconductors have used third harmonic generation (THG) because of its simplicity [6–9]. However, CARS and THG spectra contain one-, two-, and three-photon resonances and in most cases the latter dominate their spectrum. As a result, identification of two-photon accessible states can be ambiguous. For example, strong two-photon states with energies just above the one-dimensional exciton, labeled E_g, have been inferred from THG in polydiacetylenes and polysilanes (in agreement with two-photon induced fluorescence) [10,11]. By contrast the two-photon-absorption (TPA) spectrum only contains resonances involving one and two photons [12]. Far from one-photon resonances, which is always our case, TPA is only sensitive to states of the same symmetry as the ground state. That is, the TPA spectrum is the natural complement of the one-photon absorption spectrum. Together they can identify the nature of the lowest excited state. But experimental TPA data on π-electron conjugated systems is scarce, mainly because of the complexity of the nonlinear techniques involved, and the multitude of physical processes which can mask and compete with real TPA processes. Two-photon states in finite polyenes have been found below E_g by Kohler, Spangler, and Westerfield [13]. However, in no backbone π-electron conjugated system have any of the NLO measurements been able to clearly observe more than one two-photon state. PTS, poly(2,4-hexadiyne-1,6-diol-bis-p-toluene-sulfonate), has been widely studied because it is available as high quality single crystals. Here we report a complete TPA scan of single-crystal PTS which probes two-photon states from about $0.8E_g$ to $1.6E_g$. A rich spectrum was observed, in-

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cluding three well-defined discrete quantum states and a continuum of two-photon states.

The z-scan technique was used to measure $\alpha_2 \propto \mathrm{Im}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]$ and $n_2 \propto \mathrm{Re}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]$ [14]. The sample was positioned along the axis of a focused high intensity beam so that the focal point could be scanned through the center of the sample. This results in a position-dependent attenuation of the beam which allows the nonlinear loss to be measured when the full transmitted beam is collected. If a small aperture is placed on axis before the detector, the transmission variation with position yields information about both the nonlinear refraction and loss. The methodology and limitations of this technique are well established [14]. The key limitation in our case comes from the optical quality of the sample which can lead to stray scattering and in some cases difficult evaluation of n_2. Using this procedure we are able to monitor higher order contributions to the nonlinear absorption by employing different input energies to obtain a series of z scans. Each set of data provides a different position-dependent scan for a different input energy, and consequently a different input peak intensity at the focal point. Significant nonlinear absorption was found, making detailed analysis necessary. First, it was assumed that $\alpha = \alpha_1 + \alpha_2 I$ and α_2 was evaluated for the open aperture case. Then the closed aperture data was analyzed to yield n_2.

The single-crystal PTS samples were grown from saturated acetone solution and thermally polymerized in vacuum. The platelets varied in thickness from 0.1 to a few millimeters, with several millimeters of cross section. In general the interior of such crystals contains flaws and cracks and it was necessary to search over the surface of many samples to find those with small enough stray scattering to obtain good z-scan data. For such samples, no stray light correction was required or performed. The orientation of the nonlinear axis was verified by monitoring the polarized transmission.

In the inset of Fig. 1 a typical variation in α_2 with input intensity for 65 psec input pulses is shown. These results indicate the existence of higher order nonlinear effects. We therefore write $\alpha = \alpha_1 + \alpha_2 I + \alpha_3 I^2$ where it is explicitly assumed that the higher order effect depends on intensity, and not on pulse energy. This does not exclude the possibility of a two-step process mimicking a TPA resonance, with a relaxation time much shorter than the pulse width. However, the absence of significant pulse width dependence of our results for both single, 2 and 45 psec pulses over the energy range 1.30 to 1.55 eV makes a two-step process less likely there. In this work, the reported α_2 is obtained by extrapolation to zero pulse intensity.

We show the extrapolated values of α_2 versus photon energy in Fig. 1. Superimposed are data obtained from two different samples, taken with three different laser systems. (i) An optical parametric generator (OPG) operating with single 65 psec pulses was used over the energy ranges 0.77 to 1.11 eV, and 1.28 to 1.55 eV. (ii) Single 35 psec pulses were used at 1.17 eV (1064 nm). (iii) Finally, a Ti:sapphire laser operating with 2–4 psec pulses covered the range from 1.30 to 1.55 eV. We observed a rich two-photon spectrum. Three distinct resonances, whose peak values decrease with decreasing photon energy, are clearly observed. The strongest peaks ($\simeq$ 700 cm/GW and 200 cm/GW) identify two-photon states at $\simeq$ 2.7 eV (i.e., about $1.35E_g$) and 2.1 eV (i.e., $1.05E_g$), both lying above the $1B_u$ exciton peak. In addition there is a weaker two-photon state below E_g, clearly centered at 1.8 eV ($0.9E_g$, 30 cm/GW). At 1.6 eV ($0.8E_g$, 5 cm/GW) a weakly defined resonance could be observed. Finally there is a broad two-photon band or "TPA continuum" starting at about 2 eV and increasing in intensity with increasing energy to the highest photon energies measured (1.6 eV).

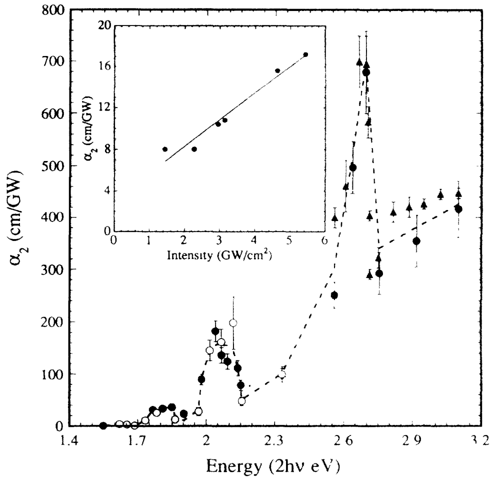

FIG. 1. Two-photon absorption spectrum for PTS single crystals. The empty and filled circles are the data from two different PTS samples. The filled triangles show the results from the 2–4 psec Ti:sapphire laser. The dashed line is a guide to the eye. Note the intensity dependence giving rise to a higher order term in the polarizability shown in the inset at 1530(nm).

In PTS the 1^1B_u exciton peak (linear absorption maximum) occurs at $E_g = 2$ eV, Fig. 2. In the region near and below the optical gap, Fig. 2 compares the two-photon absorption spectrum with the one-photon absorption spectrum reported earlier. The comparison clearly identifies at least two even-parity states well below the odd-parity 1^1B_u state that defines the optical gap at 2 eV. The character of the lowest excited state is significant from a theoretical point of view and has generated a considerable body of theoretical treatments for conjugated polymers in general and PDA's in particular that attempt to explain the NLO spectrum [1,3,13,15–18]. In general polyenes have been chosen in such molecular quantum models as prototype molecular systems because they can be well described by the Pariser-Parr-Pople (PPP) Hamiltonian. Extending

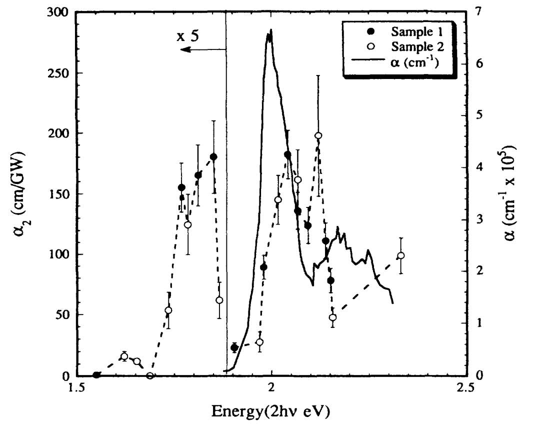

FIG. 2. TPA spectrum for a single crystal PTS near the 1^1B_u exciton peak. The vertical scale is expanded by a factor of 5 below 1.9 eV to make clearer the two resonances at lower energies. The empty and filled circles are the data from two different PTS samples. The dashed line is a guide to the eye; the solid line represents the linear absorption of PTS.

such theories to other conjugated systems like diacetylenes and infinite polymers has proven to be difficult and hence most predictions are based on numerical calculations for finite length molecules whose trends are extrapolated to polymers. However, most of these model calculations are in qualitative agreement with our TPA spectrum; i.e., they predict low lying two-photon excited states below the optical gap and a dominant intense two-photon state above the gap. Clearly the details of our TPA spectrum such as the number of even-parity states below E_g and the presence of intense and well-defined states in other regions of the spectrum together with a broad TPA continuum provide an exciting opportunity for further theoretical consideration. The presence of an even-parity state inside the optical gap is generally interpreted in such theories as a sign of electron correlation effects playing a dominant role in determining the electronic structure of a conjugated polymer. Indeed it seems to be the case for PTS.

The two states lying below E_g are labeled 2^1A_g and 3^1A_g states in reference to polyene models. The 3^1A_g resonance at $0.9E_g$ coincides with a similar peak observed previously by third harmonic generation, verifying the true two-photon nature of this spectral resonance [19]. Two-photon transition matrix elements to both of these covalent gap states are believed to be weak. However, assuming that both the TPA states at $0.9E_g$ and $1.05E_g$ are coupled most strongly to the 1^1B_u state, then the results indicate the dipole transition moment to the $0.9E_g$ state to be at most 3 times weaker than to the $1.05E_g$ state, i.e., not always negligible. In addition the presence of even-parity states below E_g explains the absence of luminescence in PTS. In the presence of strongly allowed transitions between excited states, any excitation above the optical gap will end up in an even-parity state that does not have a dipole allowed pathway to the ground state. As a result, nonradiative transitions are the only means of relaxing the excitation. In high quality PTS crystals, we found any luminescence to have a quantum efficiency less than 10^{-6} [4]. This is to be compared with the high intrinsic luminescence quantum efficiency in PPV which has spurred considerable interest in the scientific community [20].

On the other hand, the TPA resonances are distinct from the TPA "continuum," Fig. 1. Its onset appears to correspond to that of photoconductivity that marks the interband transition to the continuum of delocalized band states [21]. We note that unlike the spectrum of odd-parity states in which a single 1D exciton splits off from the interband continuum, here at least two even-parity states are split off from the continuum. A similar TPA continuum, but without the accompanying TPA resonances, has been observed previously in PTS and was interpreted as arising from defect states [22]. In another single-crystal conjugated polymer, poly(4-BCMU), a broad TPA spectrum with an edge at 2 eV was also observed [23]. We have observed essentially the same spectrum with both 2 and 65 psec pulses. If indeed this broad TPA band is due to defect states their relaxation times must be less than 2 psec. This is unlikely and our results do not support this interpretation of defect states. What makes the rich spectrum of Fig. 1 significant is the observation of the resonant structure together with the continuum of two-photon states in high quality single crystals of PTS.

Using the closed aperture z scan it was also possible to measure n_2 for photon energies below 1.2 eV ($\lambda \geq$ 1064 nm). For shorter wavelengths, nonlinear absorption dominates the measurements. The results, extrapolated to the limit $I \rightarrow 0$ are shown in Fig. 3. First we note that the error bars reflect the difficulty of the experiments due to the dominance of two-photon absorption over most of the measured spectral region. Nevertheless, dispersion in

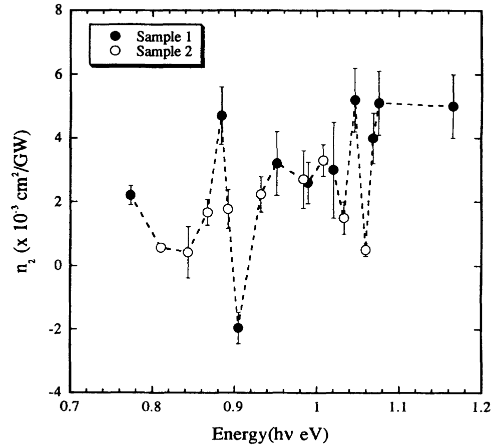

FIG. 3. The dispersion of the refractive nonlinear coefficient n_2 for PTS single crystals. The dashed line is a guide to the eye.

n_2 was found, specifically near the location of the two-photon resonances and particularly near the two-photon band at $0.9E_g$. We note that the sign of n_2 is positive. It is known that near the one-photon resonance at E_g, n_2 is negative, due to saturable absorption and the dynamic Stark shift of the singlet exciton. As the photon energy decreases through two-photon resonances, they give positive contributions to n_2. Our data indicate that the sign of n_2 has changed due to the strong two-photon continuous band and also due to the strong resonance at $1.35E_g$. The latter is in agreement with the predictions of the Kramers-Kronig calculations [24]. In addition, using THG, Sauteret and co-workers have inferred nonresonant nonlinearities of 2×10^{-12} cm^2/W for n_2, the intensity-dependent refractive index coefficient [5]. Our measurements prove that their THG measurement was indeed far from any resonance and is in good agreement with our results.

Finally, over the full spectral region studied we found contributions from higher order processes. These were manifested by nonzero α_3 and n_3. A similar effect has already been reported in photoconductivity and degenerate four-wave-mixing measurements at 1064 nm [25,26]. Such terms can arise from many effects, including excited state absorption subsequent to two-photon absorption, or true higher order effects such as $\chi^{(5)}(-\omega;\omega,-\omega,\omega,-\omega)$ which give $n_3 \propto \mathrm{Re}[\chi^{(5)}(-\omega;\omega,-\omega,\omega,-\omega)]$ and $\alpha_3 \propto \mathrm{Im}[\chi^{(5)}(-\omega;\omega,-\omega,\omega,-\omega)]$. For excited state absorption, the values of n_3 and α_3 would depend on the pulse width, or repetition rate. For the peak at 1.35 eV we found that α_3 was independent of laser parameters, implying that here we are dealing with a true fifth order process, or one whose response time is faster than 2 psec and therefore mimics a two-photon transition. The energy dispersions in α_3 and n_3 will be discussed elsewhere.

In conclusion, we report the first measurement of the TPA spectrum in PDA-PTS clearly identifying strong two-photon resonances. In the important range from below $0.7E_g$ to $1.6E_g$ the TPA spectrum shows four well-defined two-photon accessible states superimposed on a continuum of even-parity states. Comparison of one- and two-photon absorption spectra identifies the lowest excited state as an even-parity state. Since no dipole allowed transition is possible from such even symmetry state back to the ground state, this result explains the absence of intrinsic luminescence in polydiacetylenes. In parallel, we have also measured the intensity dependence of the index of refraction n_2 in the off-resonance regime.

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