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Two Photon Absorption Spectroscopy of Polydiacetylene PTS

J. M. Leng [a] , Z. V. Vardeny [a] , B. A. Hooper [b] , K. D. Straub [b] , J. M. J. Madey [b] & G. L. Baker [c]

[a] Department of Physics, University of Utah, Salt Lake City, Utah, 84112

[b] Free Electron Laser Laboratory, Duke University, Durham, NC, 27708

[c] Department of Chemistry, Michigan State University, East Lansing, MI, 48824

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TWO PHOTON ABSORPTION SPECTROSCOPY OF POLYDIACETYLENE PTS

J.M. LENG AND Z.V. VARDENY
Department of Physics, University of Utah, Salt Lake City, Utah 84112
B.A. HOOPER, K.D. STRAUB, AND J.M.J. MADEY
Free Electron Laser Laboratory, Duke University, Durham, NC 27708
G.L. BAKER
Department of Chemistry, Michigan State University, East Lansing, MI 48824

Abstract We have studied two photon absorption (TPA) of single crystal polydiacetylene-toluene-sulfonate (PTS) using the Mark III Free Electron Laser (FEL) in the spectrum range of 0.95 - 1.5 μm. We observed two features in the TPA spectrum at two photon energies of 1.85 eV and 2.35 eV, respectively. We discuss the assignment of the two bands in terms of TPA allowed excitons reached by two successive one-photon absorptions.

INTRODUCTION

Polydiacetylene (PDA) is a promising material for all-optic computations because of its unique nonlinear optical properties[1,2]. However, the role of even parity states in the nonlinear optical properties of PDA is unclear and debated over the last decade. Weiser *et al.*[3] discovered in electroreflectance (ER) a feature at 2.45 eV which is hidden in the direct reflectance spectrum, dominated by the 1.95 eV exciton transition. They assigned the 1.95 eV absorption band as the $1B_u$ state and the 2.45 eV spectral feature as the electronic continuum (EC). Similar experiments were performed on another form of PDA (DFMDP) by Tokura *et al.*[4]. Two features were observed in ER at 2.25 eV and 2.85 eV, respectively. These features are blue shifted in PDA-DFMDP with respect to PDA-PTS due to different side groups. Tokura *et al.* however assigned the 2.85 eV feature as the mA_g exciton rather than the EC as in PDA-PTS[3]. Recently several models[5-7] have emerged regarding essential energy states and their roles in

nonlinear optical properties, based on the Peierls-Hubbard Hamiltonian. Among these models, Guo *et al.*[6] predicted that a $2A_g$ and mA_g excitonic states should appear below and above the $1B_u$ state, respectively.

In this work, we report TPA measurements of PDA-PTS using a Mark III free electron laser (FEL). Our results reveal that there are two spectral features in PDA-PTS at 1.85 eV and 2.35 eV, respectively. Two possible assignments of these spectral features are discussed.

EXPERIMENTAL

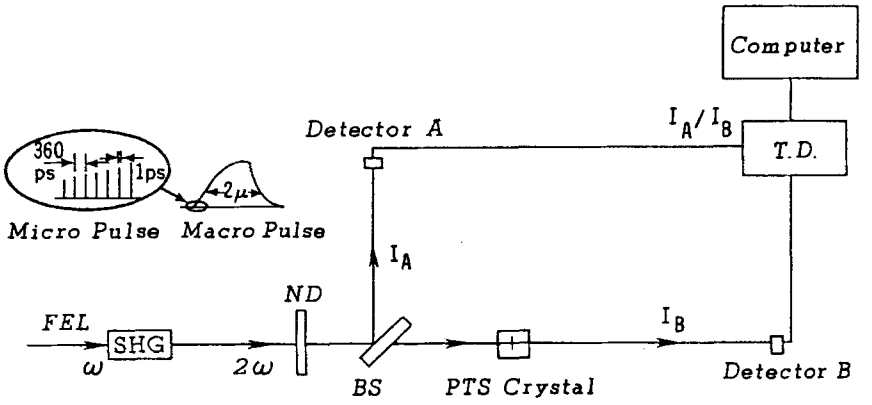

FIGURE 1 Experimental setup of TPA measurements using the FEL.

The TPA experimental setup is illustrated in Fig. 1. The FEL macropulse and micropulse durations are of 2 μs and 2 ps, respectively, as is shown in the inset of Fig. 1. The TPA spectrum in the range of 0.95 - 1.5 μm was measured by frequency doubling the fundamental output of the FEL in the wavelength range of 1.9 - 3.0 μm. Two identical gold doped Ge detectors in the optical paths A and B were used to measure the intensity of the laser beam. Path A measures the beam intensity without the sample, whereas path B measures the transmission of the FEL laser beam through the PDA-PTS sample. The PDA-PTS single crystal sample was put in a cryostat in vacuum at room temperature, to avoid photoinduced oxidation. The beam waist at the sample position was about 100 μm and a typical peak intensity on the sample was 10 MW/cm^2. The output from detector A and B were then divided and averaged over 100 macropulses using two transient digitizers. Such an arrangement can effectively eliminate the large fluctuations in a single FEL macropulse.

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Similar TPA measurements, but at a fixed wavelength of 1.06 μm, was also carried out at the Dixon Laser Institute, using a seeded regenerative Nd:YAG laser. The laser had a repetition rate of 1 kHz, average power up to 2 W and pulse duration of ~ 200 ps.

EXPERIMENTAL RESULTS

In Fig. 2 we show a typical TPA data measured with the FEL. For a rectangular shaped laser beam the transmission T in the presence of TPA is related to the transmission T_0 due to nonlinear absorption in the following way[8]:

$$T_0/T = 1+\beta L_{eff} I, \quad (1)$$

here β is the TPA coefficient, L_{eff} is the effective thickness of the sample ($L_{eff} = (1-e^{-\alpha d})/\alpha$), α is the linear absorption coefficient, d is the sample thickness, and I is the intensity of the laser beam on the sample front surface.

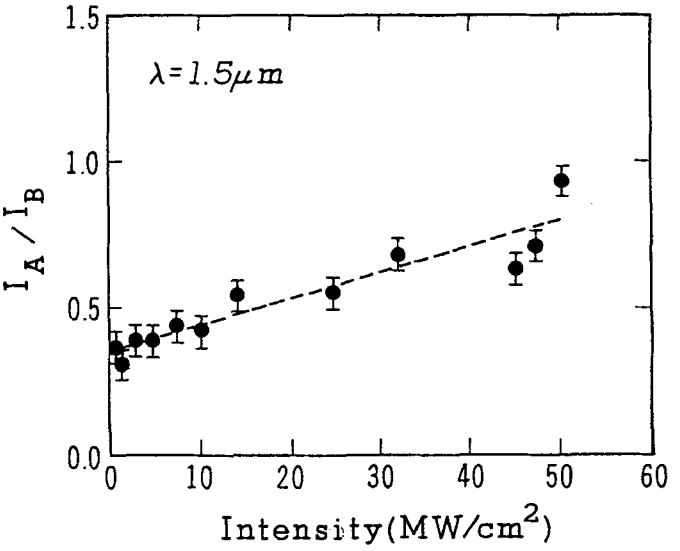

FIGURE 2 Typical TPA measurement with Mark III FEL, I_A and I_B are the laser intensities without the sample and with the sample, respectively (see text).

For a Gaussian shaped laser beam, both in time and space, Eq. (1) is modified as follow[9]

$$T_o / T = 2/(\sqrt{\pi}\beta L_{eff} I)\int_0^{\infty} \ln(1+(\beta L_{eff} I)\exp(-r^2))dr. \quad (2)$$

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Numerical series expansion of Eq. (2) gives

$$T_o/T = 1 + 0.353\ q - 0.0626\ q^2 + 0.0217\ q^3 - 0.00623\ q^4 + 0.00125\ q^5 , \quad (3)$$

where $q = \beta L_{eff} I$. From Eq. (3), it is obvious that for a Gaussian laser beam profile, T_o/T no longer linearly depends on the laser intensity I. Even in the low intensity regime there is a factor of 3 difference between a Gaussian and a rectangular shaped beam.

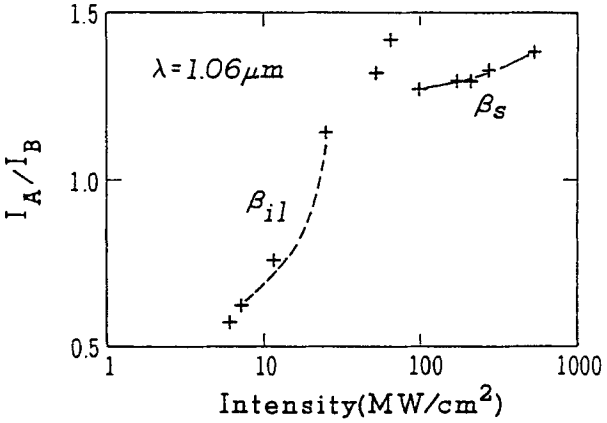

FIGURE 3 Typical TPA measurements at 1.06 μm using Nd:YAG laser.

In Fig. 3 we show a typical TPA measurement at 1.06 μm using the regenerative Nd:YAG laser. It is apparent that the slope which from Eq. (1), should have been proportional to the TPA coefficient β, strongly depends on the laser intensity. A value β_s at saturation was evaluated to be 15 cm/GW at I > 100 MW/cm^2, whereas for I < 30 MW/cm^2, β_{il} was calculated to be 4000 cm/GW. To understand these results, we checked two possibilities. Firstly, heating may affect the slopes of I_A/I_B (Fig. 3) with increasing laser intensity I. A comparative study using the same average power at 1.06 μm, but without the seeding from the YAG laser was done with laser pulse of 200 ns. This experiment did not yield any TPA (increase in T_o/T), indicating that the T_o/T data obtained by using the seeded YAG laser is indeed due to electronic TPA. The other possibility for the change in slopes in Fig. 3 is resonant enhancement of a midgap one-photon absorption. To check this possibility, photothermal deflection measurements to obtain the subgap absorption coefficient α were carried out on a virgin PTS single crystal. The absorption coefficient was low and did not show midgap states. The TPA of this virgin sample showed a value β_o of ~15 cm/GW at 1.06 μm, identical to β_s measured before at saturation illumination conditions. Next the sample

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was treated with an illumination dose of 30 minutes from a Nd:YAG laser with a peak power intensity of 5 GW/cm^2 and then we again measure α by the photothermal deflection technique. we found on this sample that the absorption coefficient within the gap increased by about two orders of magnitude. We then measure TPA on this sample; the resultant β was like β_{II} in Fig. 3. We therefore established in PTS a correlation between the midgap absorption and the resonant enhancement of the TPA coefficient β.

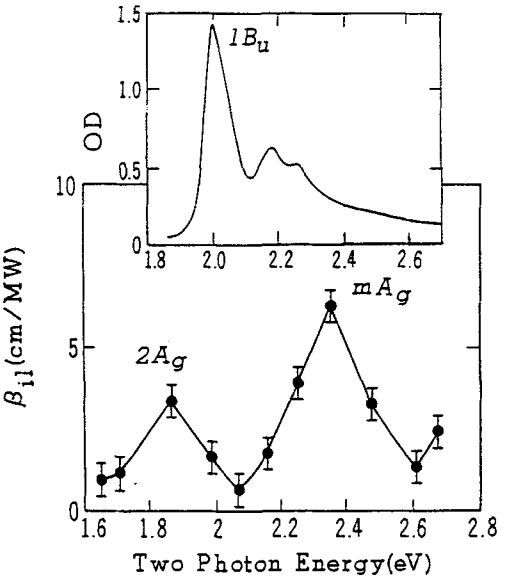

FIGURE 4 TPA spectrum of a PDA-PTS single crystal using Mark III FEL. For comparison we show in the inset a typical absorption spectrum.

In Fig. 4 we show the TPA spectrum of PDA-PTS from 1.6 to 2.7 eV obtained with the Mark III FEL. The data were taken on a laser illuminated sample. The FEL laser intensity was on the order of 10 MW/cm^2. For comparison the linear absorption spectrum of PTS is shown as an inset in Fig. 4; the $1B_u$ exciton is at 1.97 eV with phonon sidebands at 2.15 and 2.25 eV, respectively. In contrast, the TPA spectrum, has two peaks, one at 1.85 eV and the other at 2.35 eV.

DISCUSSION

We offer two possible explanations for our observed TPA spectrum (Fig. 4). In the first explanation we assume that the observed bands are due to TPA into otherwise

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forbidden A_g states. In this case, the lower energy state, below the $1B_u$ exciton level, is certainly the first forbidden excited state ($2A_g$). This assignment is consistent with the fact that PDA-PTS does not show photoluminescence. Since optical transitions from this $2A_g$ state to the ground state is dipole forbidden, we suggest that photoexcited excitons would decay into the ground state predominately via nonradiative channels involving the lower $2A_g$ state. The higher energy band observed in our TPA measurement is very close to the 2.45 eV spectral feature observed in the ER measurements by Weiser *et al.*[3]. This is in good agreement with the predictions by Abe[5], namely that an A_g state should be close to the EC. We therefore assign the 2.35 eV band in Fig. 4 as the mA_g state.

In the second explanation we assume that the observed TPA spectrum is due to two successive one-photon absorptions via the midgap states. We can then explain the nonlinear susceptibility $\chi^{(3)}$ $(-\omega;\omega,\omega,-\omega)$ enhancement by three orders of magnitude due to the midgap states. Nunzi and Charra[10] have observed such a photoinduced midgap state which lives for several hundreds of ps when pumping at wavelength of 1.06 μm with a 33 ps pump laser. Kim *et al.*[11] also observed a long-lived (on the order of minutes) midgap photoinduced absorption at 0.43 eV which they assign as bipolaron transitions. We therefore assign the 1.85 eV peak as transitions by two successive one-photon absorptions into $2A_g^*$ state of the excited polymer, via the midgap state (of B_u character). Similarly, the 2.35 eV peak is assigned as transitions into a mA_g^* exciton of the excited polymer, via the midgap state.

To help identifying the A_g^* states in the spectrum we have used other spectroscopies. For example, the excitation spectrum[9] of the photoinduced triplet transition at 1.35 eV of PDA-PTS single crystal shows that the quantum efficiency of the triplet excitons starts to increase at 2.15 eV. This threshold of triplet exciton generation can be interpreted in terms of fission of the ionic type mA_g exciton, as discussed by Leng *et al.*[12] in poly(*p*-phenylenevinylene). Then the redshift of mA_g^* exciton of the excited polymer PDA-PTS with respect to mA_g exciton of the pristine polymer by 0.2 eV suggests that a relaxation process occurs at the midgap state after the first photon absorption. Similarly, the $2A_g$ exciton of the pristine polymer PDA-PTS should be at1.65 eV. We note that, by taking account of the relaxation energy of the midgap state for 0.2 eV, our results are in good agreement with Stegeman *et al.*'s TPA results on PDA-PTS[13]. We also note that the observed A_g states in PTS are close in energy to Guo *et al.*'s theoretical predictions[6].

CONCLUSIONS

In conclusion, we have studied TPA in PDA-PTS single crystal in the two photon energy range of 1.65 - 2.7 eV using Mark III FEL. We observed two absorption bands at 1.85 eV and 2.35 eV, respectively. Two alternative assignments are discussed. The FEL 2 μs pulse duration and enhanced midgap absorption favor the second explanation, namely that the 1.85 eV and 2.35 eV bands in the spectrum correspond to $2A_g^*$ and mA_g^* excitons respectively, reached by two successive one-photon absorption processes perhaps involving some relaxation in between.

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