REPORT DOCUMENTATION PAGE

FORM APPROVED
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 22, 1996	Final Sept 1993 - September 1996

4. TITLE AND SUBTITLE OF REPORT

Experimental Investigation of Optical Nonlinearities in Conjugated Polymers

5. FUNDING NUMBERS

F49620-93-1-0554
61103D
3484/XS

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AFOSR-TR-96
0490

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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Bolling AFB, DC 20332
D. Lee

10. SPONSORING/MONITORING AGENCY REPORT NUMBER:

11. SUPPLEMENTARY NOTES:

12a. DISTRIBUTION AVAILABILITY STATEMENT

UL

12b. DISTRIBUTION CODE

19961015 046

13. ABSTRACT (Maximum 200 words)

This AASERT award has allowed us to extend our research into (1) the third order nonlinearities of conjugated polymers and (2) their applications in nonlinear optics.

THG Spectroscopy of Polymers - The real and imaginary parts of the third order susceptibility $\chi^{(3)}(3\omega)$ were measured by Third Harmonic Generation (THG) over broad spectral ranges with the fundamental wavelength varying from 700 to 2200 nm. Fitting the resulting spectra to 2, 3 or 4 level models, i.e. 2, 3 or 4 electronic states participating in the transitions, identified the number of important states and the oscillator strengths for transitions between them.

Nonlinear Optics of PTS - In our parent grant we had measured the frequency dependence of the complex susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. At high incident intensities, of order of a few GW/cm^2, effectively an intensity-dependent $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ was found in the immediate vicinity of the strong two photon transition from the $1A_g$ to the dominant mA_g state. Our analysis of the functional dependence on the intensity showed that saturation of the population in the two photon state was responsible. The corresponding saturation intensity was found to be 2 GW/cm^2.

14. SUBJECT TERMS			15. NUMBER OF PAGES:
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT: U	18. SECURITY CLASSIFICATION OF THIS PAGE U	19. SECURITY CLASSIFICATION OF ABSTRACT U	20. LIMITATION OF ABSTRACT

AUGMENTATION AWARDS FOR SCIENCE & ENGINEERING RESEARCH TRAINING
(AASERT)
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The department of Defense (DoD) requires certain information to evaluate the effectiveness of the AASERT funds, the Grantee agrees to provide 1) a brief (not to exceed one page) narrative technical report of the research training activities of the AASERT funded student(s) and 2) the information requested below. This information should be provided to the Government's technical point of contact by each annual anniversary of the AASERT award date.

1. Grantee identification data: (R & T and Grant numbers found on Page 1 of Grant)

a. University of Central Florida
University Name

b. F49620-93-1-0554
Grant Number

c. _____
R & T Number

d. George I. Stegeman
P.I. Name

e. From: September 1993 To: September 1996
AASERT Reporting Period

NOTE: Grant to which AASERT award is attached is referred to hereafter as "Parent Agreement."

2. Total funding of the Parent Agreement and the number of full-time equivalent graduate student (FTEGS) supported by the Parent Agreement during the 12-month period prior to the AASERT award date.

a. Funding: $100,000

b. Number FTEGS: 2

3. Total funding of the Parent Agreement and the number o FTEGS supported by the Parent Agreement during the current 12-month reporting period.

a. Funding: $ 148,816 (Account closed)

b. Number FTEGS: 0

4. Total AASERT funding and the number of FTEGS and undergraduate students (UGS) supported by AASERT funds during the current 12-month reporting period.

a. Funding: $ 150,000
b. Number FTEGS: 1
c. Number UGS: 0

VERIFICATION STATEMENT: I hereby verify that all students supported by the AASERT award are U.S. citizens.

Principal Investigator

September 1, 1996
Date

Title of Project: Experimental Investigation of Optical Nonlinearities in Conjugated Polymers

Executive Summary:

This AASERT award has allowed us to extend our research into (1) the third order nonlinearities of conjugated polymers and (2) their applications in nonlinear optics.

1. THG Spectroscopy of Polymers

The real and imaginary parts of the third order susceptibility $\chi^{(3)}(3\omega)$ were measured by Third Harmonic Generation (THG) over broad spectral ranges with the fundamental wavelength varying from 700 to 2200 nm. Fitting the resulting spectra to 2, 3 or 4 level models, i.e. 2, 3 or 4 electronic states participating in the transitions, identified the number of important states and the oscillator strengths for transitions between them.

THG measurements were performed on PBTV, PBZT and PBTDV 1-dimensional conjugated polymer films. PBTDV is expected to have a larger nonlinearity than PBZT because the conjugation length is longer. But PBTV has only one double C-C bond and its nonlinearity would be expected to be smaller. In fact, the magnitude of $|\chi^{(3)}(3\omega)|$ of PBTDV is very similar to that of PBZT. As expected, PBTV is less nonlinear than the other two. The principal participating states were the ground $1A_g$ state, the one photon allowed $1B_u$ state and the mA_g two photon state.

Sublimated films of 2-dimensional conjugated planar molecules were investigated by THG. Two were planar phthalocyanines, metal-free and copper substituted, and the third was an asymmetric (non-planar) phthalocyanine (subphthalocyanine), employed as a precursor in the synthesis of certain phtalocyanines. A very rich spectrum was observed in each case. For this family of substituted molecules we found that four states contributed to the nonlinearity. They were the ground state, the one photon allowed state and a pair of two photon states.

In a close collaboration with Seth Marder and Mireille Blanchard-Desce, we have investigated the enhancement of the third order nonlinearity by THG when progressively stronger electron acceptor groups are added to one end of a β-carotene molecule. By measuring the spectral dispersion of third harmonic generation, we found a maximum enhancement by a factor of 50 over β-carotene, the parent molecule which itself is considered to be highly nonlinear. We found that the data could be fit to a four level model. Jean-Luc Bredas has successfully modeled our data.

2. Nonlinear Optics of PTS

In our parent grant we had measured the frequency dependence of the complex susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. At high incident intensities, of order of a few GW/cm^2, effectively an intensity-dependent $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ was found in the immediate vicinity of the strong two photon transition from the $1A_g$ to the dominant mA_g state. Our analysis of the functional dependence on the intensity showed that saturation of the population in the two photon state was responsible. The corresponding saturation intensity was found to be 2 GW/cm^2.

Again in the parent grant, we had established that around 1600 nm a negative, ultrafast $\chi^{(5)}$ contributes to the nonlinearity. Combined with a positive value of Real$\{\chi^{(3)}(-\omega;\omega,-\omega,\omega)\}$, theoretical calculations have predicted that stable spatial soliton beams with two transverse dimensions should exist without nonlinear loss. (A spatial soliton is an optical beam which propagates without diffraction in a material: a 2D soliton occurs in a bulk medium.) We are not aware of any other material for which this is possible. In the last few months we have demonstrated experimentally the propagation of 2D spatial solitons.

Detailed Research Achievements:

THG Spectroscopy

The third harmonic spectrum of three phthalocyanines (Pc) was measured over the spectral range 900 → 2000 nm. The material in sublimated film form was supplied by Professor D. Fernando Agullo Lopez of the "Instituto Universitario de Cienca de Materiales "Nicolas Cabrera" of the Universidad Autonoma de Madrid. Investigated were PcH_2, PcCu and asymmetric subPc.

Both the magnitude and phase of $\chi^{(3)}(3\omega)$ were measured. It is clear from the spectra that there are at least three, and possibly four strong resonances contribute. The two strongest are due to the Q- and B-bands, as expected. Therefore there is at least one contributing two photon state, whose resonance is located between the two one photon bands. Based on the phase changes, for PcH_2, there could be at least a pair of two photon states located around 650 and 800 nm. There are also peaks in the THG spectrum of PcCu which correspond to these general locations. Therefore the number of "essential states", 4-5, is clearly larger than for linear molecular systems, polyenes and conjugated polymers.

A disappointing feature is that the magnitude of $\chi^{(3)}$ is much less than for the polyenes (β-carotene) and linear conjugated polymers (poly4-BCMU and polythiophene) that we have studied previously. Also note that substituting the so-called free phtalocyanine PcH_2 with Cu does not enhance the third order response. However, going to an asymmetric structure, with a smaller molecular volume, gives a factor of 5 enhancement.

Many years ago Garito predicted that attaching a donor or acceptor group to one end of a symmetric molecule leads to permanent dipole moments and produces electronic states of mixed parity. Consequently this changes the balance between the different contributions to a third order nonlinearity, and adds yet another nonlinear mechanism, due in this case to changes in the dipole moment between the ground and excited states. We have investigated the spectral dependence of $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ for molecules with a sequence of progressively stronger electron acceptors attached to one end of β-carotene, itself a π-conjugated molecule with a large third order nonlinearity.

A three level model produced an excellent fit to the data over the full spectral range investigated, yielding $\Delta\mu_{01}$. The third level is located at energies higher than those probed directly by the experiment and was needed to improve the fit at the shortest wavelengths measured. Both μ_{01} and $\Delta\mu_{01}$ were found to be approximately linear in the peak absorption wavelength which shifted to longer wavelengths with increasing acceptor strength.

We found that increasing the acceptor strength produces huge enhancements in the nonlinearity. There is a 50-fold enhancement over β-carotene, to a value 10^4 times that of fused silica. We found $|\chi^{(3)}(3\omega)|_{max}$ varied approximately as λ^7_{max}. The optimally enhanced values are typical of those associated with the best conjugated polymers. Hence we conclude that this approach could lead to the largest third order nonlinearities yet in organic systems.

Nonlinear Optics of PTS

The second project dealt with the nonlinear optics of PTS and its potential impact on nonlinear optics.

Experimentally we had studied both multiphoton absorption and dispersion in the refractive index in the wavelength range 800 to 1100 nm due to a strong two photon absorption band. The ultrafast nature of the optical response was verified by using lasers with multiple pulse widths of 30 psec, 4 psec and 200 fsec. The data as analyzed in terms of $\Delta n = n_2(I)I$ and $\Delta\alpha = \alpha_2(I)I$, that is

both an intensity-dependent nonlinear refractive index coefficient $n_2(I)$ and two photon absorption coefficient α_2. Clear saturation in both these quantities was observed. This has now been analyzed in terms of a classical model of population saturation for the upper (two photon) state of the transition. The agreement was found to be excellent and has allowed us to deduce the saturation intensity for the two photon state to be of order 2 GW/cm^2. This should be compared to the saturation intensity for the one photon transition from the ground ($1A_g$) state to the first excited ($1B_u$) state of 65 MW/cm^2. The relatively low value of the saturation intensity for the two photon transition is consistent with the huge oscillator strength associated with the two photon transition, the largest known.

Near 1600 nm we had previously found $n_2 = 2.2\text{x}10^{-12}$ cm^2/W and $n_3 = -8\text{x}10^{-22}$ cm^4/W^2 at 1600 nm where the intensity (I) induced index change is $\Delta n = n_2 I + n_3 I^2$. A negative n_3 is usually associated with a nonlinear absorption due to multiphoton absorption effects. However, none was observed at this wavelength in PTS leading us to believe that it's origin is not in a saturation effect but is an ultrafast fifth order nonlinearity, $\chi^{(5)}$. This has important implications for spatial soliton phenomena with a long term goal of implementing NxN reconfigurable interconnects.

Spatial solitons are beams which propagate in a medium without diffraction. Normally spatial solitons beams with two transverse dimensions cannot exist in Kerr nonlinear optical media which obey $\Delta n = n_2 I$. They can however exist in media with saturating nonlinearities, i.e. $\Delta n \Rightarrow$ constant as $I \Rightarrow \infty$ (observed before) or for higher order nonlinearities (never observed before for lack of an appropriate material). For PTS we found numerically that we could generate spatial solitons whose propagation is limited only by linear absorption. Furthermore, we found that at high powers new modulational instabilities should occur. Although such phenomena have been observed in the time domain in one dimension in optical fibers, they have never been observed in two dimensions, or with spatial solitons. Other interesting phenomena such as ring formation (from input Gaussian beams) are predicted to occur after propagation of a few mm.

The generation of 2D spatial solitons was verified by observing the beam width after propagating through a 2 mm single crystal as a function of incident power. At low powers the beam diffracts in space to about twice its 30 μm input size. As the input power is increased, the output beam size collapses to its input size which it then maintains above a threshold intensity. This was actually observed in the laboratory.

Publications:

1. W.E. Torruellas, M. Cha, G.I. Stegeman, J.A. Osaheni and S.A. Jenekhe, "Third Order Nonlinear Optical Spectroscopy and Two Photon States in Rigid-Rod Benzobisthiazole Polymers", J. Nonlinear Opt., **12**, 193-202 (1995)
2. M.A. Diaz-Garcia, F. Aguillo-Lopez, W.E. Torruellas, B.L. Lawrence and G.I. Stegeman, "Identification of Two-Photon States in Phthalocyanines by Third Harmonic Generation Spectroscopy", Chem. Phys. Lett., **235**, 535-540 (1995).
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4. E.M. Wright, B.L. Lawrence , W.E. Torruellas and G.I. Stegeman, "Stable self-trapping and ring formation in PTS", Opt. Lett., **20**, 2481-3 (1995)
5. G.I. Stegeman, M. Cha, B.L. Lawrence and W.E. Torruellas, "Two photon processes in organic molecules and polymers", book chapter in NATO ASI Workshop on "Photoactive Organic

Materials: Science and Applications", edited by F. Kajzar, V.M. Agranovich and C.Y.-C. Lee, (Kluwer Academic Publishers, Dordrecht, 1996), pp 75-108

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8. G.I. Stegeman, "Applications of Third Order Nonlinear Optics in Organic Materials", book chapter in Nonlinear Optics of Organic Molecular and Polymeric Materials, editors H.S. Nalwa and S. Miyata, CRC Press, in press

9. W.E. Torruellas, B.L. Lawrence, G.I. Stegeman and G. Baker, "Two-Photon Saturation in the Bandgap of a Molecular Quantum Wire", Opt. Lett., in press

10. D. Beljonne, J. Cornil, Z. Shuai, J.L. Bredas, F. Rohlfing, D.D.C. Bradley, V. Ricci, W.E. Torruellas and G.I. Stegeman, "Towards a general model for the description of the third-order optical nonlinearities in conjugated systems:Application to the β-carotene molecule", Phys. Rev. B, submitted

11. W. Torruellas, B. Lawrence and G. I. Stegeman, "Self-focusing and two-dimensional spatial solitons in PTS", Electron. Lett., submitted

12. S. Marder, B.L. Lawrence, W.E. Torruellas, V. Ricci, G.I. Stegeman, S. Gilmour and M. Blanchard-Desce, "Molecular asymmetrization: A route to enhanced third order optical nonlinearities", Science, being prepared by S. Marder

Conference Presentations (* denotes invited)

1.* "Nonlinear Optical Materials and the Experimental Realization of Spatial Solitons", Workshop on Nonlinear Optical Phenomena and Applications, Kaziemerz Poland, September 1996

2.* "All-Optical Materials and Their Applications to Communications", CRL International Symposium on Advanced Technologies in Optical Communication and Sensing", invited, Tokyo, March 1996

3.* "Recent Advances in the Design and Use of the Real and Imaginary Third Order Optical Nonlinearities of Organic Dyes", (given by Seth Marder), ICONO'3, Marco Island, December 1996.

4. B.L. Lawrence, W.E. Torruellas and G.I. Stegeman, "Solitary waves and ring formation in polydiacetylene paratoluene sulfonate", contributed paper, Technical Digest of the Topical Meeting on Nonlinear Guided Wave Phenomena and Their Applications, Cambridge, August 1996, paper SuD5

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6. B.L. Lawrence, W.E. Torruellas, G.I. Stegeman and E.M. Wright, "Stable self-trapping in polydiacetylene paratoluene sulfonate", ACS National Meeting, Symposium on Organic Thin films for Photonics Applications, Orlando, August 1996, Tuesday August 27 1996, 3:00 pm

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9. V. Ricci, W.E. Torruellas, G.I. Stegeman, S. Gilmour, S. Marder, and M. Blanchard-Desce, "Large enhancement in the third order response of asymmetric β-carotenoids", Technical Digest of the topical Meeting on Organic Thin films for Photonics Applications", Portland, September 1995, pp46-48
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