NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the Air Force Research Laboratory Wright Site (AFRL/WS) Public Affairs Office and is available to the general public, including foreign nationals. Copies may be obtained from the Defense Technical Information Center (DTIC) (http://www.dtic.mil).

AFRL-ML-WP-TP-2007-525 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

*//Signature//       //Signature//
PAUL A. FLEITZ, Ph.D.     MARK S. FORTE, Acting Chief
Program Manager     Hardened Materials Branch
Exploratory Development     Survivability and Sensor Materials Division
Hardened Materials Branch

//Signature//
TIM J. SCHUMACHER, Chief
Survivability and Sensor Materials Division

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government’s approval or disapproval of its ideas or findings.

*Disseminated copies will show “//Signature//” stamped or typed above the signature blocks.*
**REPORT DOCUMENTATION PAGE**

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. **REPORT DATE (DD-MM-YY)**
   - August 2006

2. **REPORT TYPE**
   - Conference Paper Preprint

4. **TITLE AND SUBTITLE**
   - COMBINED NONLINEAR EFFECTS IN TWO-PHOTON ABSORPTION CHROMOPHORES AT HIGH INTENSITIES (PREPRINT)

6. **AUTHOR(S)**
   - Richard L. Sutherland, Daniel G. McLean, and Mark C. Brant (Science Applications International Corporation)
   - Joy E. Rogers (UES, Inc.)
   - Paul A. Fleitz and Augustine M. Urbas (AFRL/MLPJ)

7. **PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**
   - Science Applications International Corporation
   - Dayton, OH 45433
   - Hardened Materials Branch (AFRL/MLPJ)
   - Survivability and Sensor Materials Division
   - Materials and Manufacturing Directorate
   - Wright-Patterson Air Force Base, OH 45433-7750
   - Air Force Materiel Command, United States Air Force

9. **SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
   - Air Force Research Laboratory
   - Materials and Manufacturing Directorate
   - Wright-Patterson Air Force Base, OH 45433-7750
   - Air Force Materiel Command, United States Air Force

12. **DISTRIBUTION/AVAILABILITY STATEMENT**
   - Approved for public release; distribution unlimited.

13. **SUPPLEMENTARY NOTES**
   - Conference paper submitted to the Proceedings of the SPIE Optics and Photonics Conference. The U.S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. PAO Case Number: AFRL/WS 06-1698, 10 Jul 2006.

14. **ABSTRACT**
   - Large two-photon and excited state absorption have been reported in donor-acceptor-substituted pi-conjugated molecules. We have performed detailed nonlinear absorption and photophysical measurements on a system of AFX chromophores and calculate the nonlinear transmission based on an effective three-level model. A numerical model that includes far wing linear absorption has been developed and compared with an analytical three-photon absorption model. The models are in accordance and yield excellent agreement with experimental nonlinear transmission data of 0.02-M AFX solutions up to laser intensities ~ 1GW/cm2. Concentration effects at this intensity become increasingly evident. We have extended our modeling efforts to include some new effects that may be anticipated in this regime, such as stimulated scattering are included. We report on our experimental observations of various materials and discuss results with respect to our extended theoretical models.

15. **SUBJECT TERMS**

16. **SECURITY CLASSIFICATION OF:**
   - a. REPORT Unclassified
   - b. ABSTRACT Unclassified
   - c. THIS PAGE Unclassified

17. **LIMITATION OF ABSTRACT:**
   - SAR

18. **NUMBER OF PAGES**
   - 20

19. **NAME OF RESPONSIBLE PERSON**
   - Paul A. Fleitz

**AFRL-ML-WP-TP-2007-525**
Combined nonlinear effects in two-photon absorption chromophores at high intensities

R. L. Sutherland\textsuperscript{a}, D. G. McLean\textsuperscript{a}, M. C. Brant\textsuperscript{a}, J. E. Rogers\textsuperscript{b}, P. A. Fleitz\textsuperscript{c}, and A. M. Urbas\textsuperscript{c}
\textsuperscript{a}Science Applications International Corporation, Dayton, OH, USA 45431
\textsuperscript{b}UES, Inc., Dayton, OH, USA 45432
\textsuperscript{c}Air Force Research Laboratory Wright-Patterson Air Force Base, OH, USA 45433

ABSTRACT

Large two-photon and excited state absorption have been reported in donor-acceptor-substituted pi-conjugated molecules. We have performed detailed nonlinear absorption and photophysical measurements on a system of AFX chromophores and calculate the nonlinear transmission based on an effective three-level model. A numerical model that includes far wing linear absorption has been developed and compared with an analytical three-photon absorption model. The models are in accordance and yield excellent agreement with experimental nonlinear transmission data for 0.02-M AFX solutions up to laser intensities \textasciitilde 1 GW/cm\textsuperscript{2}. Concentration effects at this intensity become increasingly evident. We have extended our modeling efforts to include some new effects that may be anticipated in this regime, such as stimulated scattering, molecular interactions, and saturation. Effects of chirped pulses and linewidth of the pump laser on stimulated scattering are included. We report on our experimental observations of various materials and discuss results with respect to our extended theoretical models.

Keywords: two-photon absorption, excited state absorption, nonlinear transmission, nonlinear scattering

1. INTRODUCTION

Symmetric and asymmetric electron-donor/acceptor-substituted, \pi-conjugated systems are a major class of enhanced two-photon absorption (TPA) materials.\textsuperscript{1,2} The molecular TPA cross section, \(\sigma_2\), is often characterized by nonlinear transmittance (NLT) experiments, both in the nanosecond and femtosecond regimes. However, the nanosecond measurements in these materials typically yield values of \(\sigma_2\) larger by more than two orders of magnitude.\textsuperscript{3,4} Excited state absorption (ESA) has been postulated to play a role in the nanosecond measurements, and for this reason the nonlinear parameters have been called effective TPA cross sections.\textsuperscript{5,6}

TPA followed by ESA was observed as early as 1974, and a value for the product of the ESA cross section and excited state lifetime of the chromophore was estimated based on a rate equation analysis.\textsuperscript{7} Several authors have posited the effects of excited states on nonlinear absorption and refraction, and these effects have been convincingly demonstrated in degenerate four-wave mixing and Z-scan experiments.\textsuperscript{8-11} Evidence of ESA has been demonstrated in NLT and Z-scan measurements of organic materials,\textsuperscript{12,13} and effective (intensity dependent) TPA coefficients have been employed to estimate ESA cross sections.\textsuperscript{5,11,14} However, to our knowledge no one has independently identified and characterized these excited states, then used this information to theoretically predict or model nanosecond NLT measurements. The nature of these excited states is important. For example, properties of the excited singlet state are significant for fluorescence imaging and laser applications, whereas the triplet state plays an important role in photopolymerization and photodynamic therapy. Moreover, the intrinsic (pulse-width independent) value of the TPA cross section \(\sigma_2\) as well as the significance of ESA in comparison to other potential nonlinear mechanisms, such as stimulated scattering, self-focusing/defocusing, and possibly two-step TPA,\textsuperscript{15} need to be elucidated for accurate modeling of nonlinear absorption in the nanosecond regime.\textsuperscript{13} Our goal is to ensure that all of the material parameters necessary to model the NLT are independently characterized. Eliminating these other phenomena as potential sources of NLT simplifies the modeling.

Recently, He et al. reported the observation of stimulated backscattering in a two-photon absorption medium, where the frequency of the stimulated wave was identical to the incident laser frequency (within the resolution of their interferometer), and the small-signal gain was quadratic in the incident laser intensity.\textsuperscript{16,17} They considered a stimulated thermal

---

\textsuperscript{a}sutherlandr@saic.com
Rayleigh scattering model based on TPA-enhanced temperature and density fluctuations, but ruled this out due to (a) the broad linewidth of their pump laser, which would severely reduce the gain of the stimulated wave, and (b) the fact that the peak gain in this theory is for an anti-Stokes-shifted wave, contrary to their experimental results. They concluded that the stimulated wave was due to a Bragg grating formed by the superposition of the incident laser beam and an elastically (Rayleigh) backscattered wave, creating an index grating via a TPA-resonance enhanced nonlinear index coefficient $n_2$, i.e., a Kerr effect. The stimulated backscattered wave is then due to reflection of the laser from this grating.

Two-beam coupling (TBC) has a rich history in nonlinear optics. Early studies established two conditions for one-way energy transfer between two electromagnetic waves in a Kerr medium: 1) the frequencies must be nondegenerate, and 2) the nonlinearity of the medium must have a finite response time. The nonlinear refractive index is usually assumed to obey a simple Debye relaxation model. Energy transfer under these conditions is always from the high frequency beam to the low frequency beam for a positive Kerr nonlinearity. Silberberg and Joseph showed that counter-propagating beams in such a Kerr medium can exhibit optical instabilities and self-oscillation, while Yeh gave an exact solution for energy transfer between two co-propagating beams including the effect of linear absorption. In each of these studies, both beams had non-zero input values.

TBC also describes several stimulated scattering phenomena, such as stimulated Raman (SRS), Brillouin (SBS), and Rayleigh-wing scattering (SRWS). The Stokes (down-shifted frequency) wave in these phenomena arises internally from scattered light and experiences gain at the expense of the incident laser beam. The Stokes frequency shift is a normal mode of the medium (e.g., vibrational) for SRS, an acoustic frequency for SBS, and the inverse reorientation time of an anisotropic molecule for SRWS. SRS, SBS, and SRWS are resonant phenomena, indicating that the nonlinear medium has a finite response time. In each of these stimulated scattering effects the small-signal gain of the Stokes wave is proportional to the laser intensity.

Fig. 1. Chemical structure of AFX molecules used in this study.

The model proposed by He et al. would appear to violate the two conditions previously established for one-way energy transfer by TBC in a Kerr medium. The frequencies are degenerate, and the third order susceptibility related to TPA is due to electronic polarization, which has a virtually instantaneous response for nanosecond laser pulses. Although, under the condition of a TPA resonance, this mechanism may indeed have a finite response time, the intensity dependence of the Kerr effect in TBC is inconsistent with the experimental results reported by He et al.

We have performed detailed nonlinear absorption and photophysical measurements on a system of AFX chromophores and calculate the nonlinear transmission based on an effective three-level model. A numerical model that includes far wing linear absorption has been developed and compared with an analytical three-photon absorption model. The models are in accordance and yield excellent agreement with experimental nonlinear transmission data for 0.02-M AFX solutions up to laser intensities ~1 GW/cm². Concentration effects at this intensity become increasingly evident. We have extended our modeling efforts to include some new effects that may be anticipated in this regime, such as stimulated scattering, molecular interactions, and saturation. Effects of chirped pulses and linewidth of the pump laser on stimulated scattering are included. We report on our experimental observations of various materials and discuss results with respect to our extended theoretical models.
The chromophores used in this study are part of a class of TPA materials (designated AFX) having a design based on a push-pull charge-transfer model and multidimensional conjugation motif. AF240 is a linear D-π-A chromophore, where the donor (D) is diphenylamino and the acceptor (A) is benzothiazole. AF350 is a three-arm octupolar molecule (D-A3) with a single triarylamino group serving as the electron-rich hub, dialkylfluorenyl bridges, and three π-electron deficient benzothiazoles. AF455 is an A-D3 type octupolar molecule with 1,3,5-triazine as the hub moiety and diphenylamines as the π-electron donating end-groups. These molecules were synthesized and purified in the Polymer Branch of the Air Force Materials Directorate (AFRL/MLBP) as described in References 4, 6, and 22. Solutions of each were prepared in tetrahydrofuran (THF) for both photophysical characterization and NLT experiments. A typical linear absorption spectrum is shown in Fig. 2. The λ_max is in the UV, with absorption band edges ranging from ~ 450 nm to ~ 470 nm. In each case there is very little absorption (σ < 10^{-21} cm², see Fig. 2b) in the 2.5-1.4 eV (500-900 nm) region. The energy difference between the absorption band edge and a laser line at 800 nm is ~ 1.5 eV. The purity should be at least 98% for glassy materials (AF-455) and 99% pure for crystalline compounds (AF-240, 350) based on elemental analysis together with spectroscopic methods and melting point determination. There is only a single peak detected by liquid chromatography for both AF-350 and AF-455. An impurity with a peak in the 500-900 nm range with a peak extinction coefficient of ≥10,000 M⁻¹cm⁻¹ would be observed at a fractional concentration of 10ppm or less. We conclude that it is unlikely that there is significant impurity absorption in the samples.

3. THEORETICAL MODELS

3.1. Effective TPA and 3PA Models

We seek a simple analytical model that can adequately explain and reliably predict, within a reasonable degree of approximation, the nanosecond NLT based on measurable properties of the chromophores and the laser pulse. This model is similar to that used for reverse saturable absorption media, but with TPA from the ground state. We consider ESA from the lowest lying singlet and triplet states. Two-photon-induced ESA is a three-photon process, although three photons are not absorbed simultaneously due to the finite lifetimes of the excited states. It is of interest, nevertheless, to see how useful a three-photon absorption
The (3PA) model is in explaining the data. In the following we present the conditions and approximations for employing such a model.

With the above assumptions, we have for the intensity $I$,

$$\frac{\partial I}{\partial z} = -\left(\beta + \gamma I\right)I^2$$  \hspace{1cm} (1)

where

$$\gamma = \frac{\tau_p \sigma_{\text{eff}} \sigma_3 N}{2\hbar \omega},$$  \hspace{1cm} (2)

$$\sigma_{\text{eff}} = \eta \sigma_{S1} + \left(\frac{1}{2} - \eta\right) \rho_T \sigma_{T1},$$  \hspace{1cm} (3)

and $\beta = \sigma_3 N$ is the TPA coefficient. We have thus modeled the system as a two-photon resonant, three-photon absorption medium, with an effective intermediate state that represents a time-averaged combination of the $S_1$ and $T_1$ states. Several authors have taken the quantity in parentheses in Eq. (1) to represent an effective TPA coefficient $\beta_{\text{eff}}$, from which an effective TPA cross section can be derived. We will consider both effective TPA and 3PA models in analyzing the experimental data. The quantity $\eta$ is the pulse-averaged, relative weight of the $S_1$ state contribution to the effective ESA cross section. When $\tau_p << \tau_S$, $\eta = \frac{1}{2}$ and ESA is essentially from the $S_1$ state only. On the other hand, when $\tau_p >> \tau_S$, $\eta = 0$ and all ESA is effectively from the $T_1$ state. When $\tau_p << \tau_S$, the growth of the $S_1$ population is linear, and the average growth time over a rectangular pulse is just $\tau_p/2$. The maximum relative weight of $\frac{1}{2}$ for either state reflects the fact that in either time regime the growth rate of the respective excited state population (singlet or triplet) is approximately constant. The average population density over the entire pulse is then just one-half of the maximum density obtained at the end of the pulse, $N_{S1,\text{max}} = \phi \tau_p^{-1} N_{T1,\text{max}} = \tau_p \sigma_{S1} N_{\text{peak}}^2 / 2\hbar \omega$. In an intermediate regime where $\tau_T >> \tau_p$ and $\tau_p - \tau_S, \eta < \frac{1}{2}$ means that the $S_1$ population at the end of the pulse is smaller than $N_{S1,\text{max}}$, $N_{S1}^\text{as}$ because of continuous transitions to the $S_0$ and $T_1$ states as $S_1$ is being pumped, analogous to a leaky capacitor.

Equation (1) can be solved analytically, but the resulting expression is transcendental. However, if we take $\beta << \gamma I$, the result reduces to a simple closed form identical to that for three-photon absorption. Assuming now Gaussian spatial and temporal profiles for the incident intensity, we integrate the resulting expression over space and time to obtain the energy transmittance for a sample of thickness $d$:

$$T = \frac{T_0^2}{\sqrt{\pi p_0}} \int_{-\infty}^{+\infty} \ln \left[1 + p_0^2 \exp(-2x^2) + p_0 \exp(-x^2)\right] dx$$  \hspace{1cm} (4)

where $T_0$ is the net linear transmittance from air into the medium due to Fresnel losses only (including all dielectric interfaces), $p_0 = (2\gamma T_0^2 l_0^2 d)^{1/2}$, and $l_0$ is the incident peak, on-axis intensity. The parameters determining $\gamma$ can be found from femtosecond, picosecond, and nanosecond photophysical measurements and standard TPA measurements in the femtosecond regime.

### 3.2. Numerical ESA Model

The numerical model calculates the spatial, time, and radial dependence of three state populations; all of the transitions between these states; the bimolecular processes of triplet-triplet annihilation, ground state quenching, and oxygen quenching. The radiation transport equation is then,

$$\frac{\partial I}{\partial z} = -\sigma_{S0} N_{S0} I - \sigma_2 N_{S2} I^2 - \sigma_{S1} N_{S1} I - \sigma_{T1} N_{T1} I$$  \hspace{1cm} (5)

The population rate equations are,
\[
\frac{\partial N_{S0}}{\partial t} = -\frac{I}{\hbar\omega} \left( \sigma_{S0} + \frac{\sigma_2}{2} \right) N_{S0} + \left( 1 - \frac{\varphi_T}{\tau_S} \right) N_{S1} + \frac{1}{\tau_T} + \frac{\kappa_{TT}}{2} N_{T1} + \kappa_{ST} N_{S0} + \kappa_{OT} N_O \right) N_{T1} \tag{6a}
\]

\[
\frac{\partial N_{S1}}{\partial t} = \frac{I}{\hbar\omega} \left( \sigma_{S0} + \frac{\sigma_2}{2} \right) N_{S0} - \frac{N_{S1}}{\tau_S} + \frac{\kappa_{TT}}{2} N_{T1} \tag{6b}
\]

\[
\frac{\partial N_{T1}}{\partial t} = \frac{\varphi_T}{\tau_S} N_{S1} - \left( 1 - \frac{\kappa_{TT}}{2} \right) N_{T1} + \kappa_{ST} N_{S0} + \kappa_{OT} N_O \right) N_{T1} \tag{6c}
\]

\[
\frac{\partial N_O}{\partial t} = -\kappa_{OT} N_O N_{T1} + k_O \left( N_0^0 - N_O \right) \tag{6d}
\]

\[
N_{S0} = N - N_{S1} - N_{T1} \tag{6e}
\]

where \(\kappa_{TT}, \kappa_{ST}, \kappa_{OT}, N_O, k_O\) are the triplet-triplet annihilation rate, the ground state self quenching rate of the triplet state, the oxygen quenching rate of the triplet state, the oxygen concentration, and the oxygen singlet state relaxation rate respectively. The rate equations are solved using a stiff Runge-Kutta algorithm supplied in MathCad. This requires the Jacobian to be supplied which was derived. This is solved at every time step. These populations are used to calculate the change in the intensity which is then rescaled assuming Gaussian beam propagation at each z step. A range of input intensities are calculated and used to calculate both the NLT variation and the radial dependence. A Gaussian time profile is used since the measured laser profile nearly matches a Gaussian. The radial and temporal integrations are done to give transmitted pulse energy and compared to the measured data. A normal reflection Fresnel loss is imposed on the incident intensity and again on the output intensity. A refractive index of 1.4535 is used for fused silica at 800 nm and 1.511 for BK7 at 800 nm. The Fresnel reflection at the glass liquid interface is found to be negligible and is not included.

### 3.3. Stimulated Scattering Model

Consider a field with a time dependent amplitude and phase, \(E(t) \sim A(t) \exp[-i\varphi(t)]\). A Taylor series expansion of the phase yields (ignoring a constant term) \(\varphi(t) = \omega t + bt^2 + \ldots\), where \(\omega\) is the central frequency of the wave, and \(b\) is a linear chirp coefficient. For simplicity, I will ignore higher order terms. Co-propagating TBC with chirped pulses has been examined in Kerr media with a finite response time. However, none of these previous studies have considered the interaction of counter-propagating waves through TPA-populated excited states.

Let the total field in a medium of length \(d\) be described by

\[
E(z,t) = A_L(z,t+\tau) \exp\left\{ i[kz - \omega t - b(t+\tau)^2] \right\} + A_S(z,t-\tau) \exp\left\{ i[-kz - \omega t - b(t-\tau)^2] \right\} + c.c.
\]

where \(k = n \omega c, n\) is the linear refractive index, and \(2\tau = 2n(d-z)/c\) is the relative time delay at position \(z\) and time \(t\) between the forward propagating laser wave (L) and the backward propagating scattered wave (S). I assume that the scattered wave originates at \(z = d\) by some elastic scattering process, so \(A_S(z,d+t) = \sqrt{\eta} A_L(d,t)\) where \(\eta\) is a constant \(< 1\). Consequently, the scattered wave has the same spectral composition as the incident laser wave. However, for \(z \neq d\) a lower frequency part of the scattered wave is always interacting with a higher frequency part of the incident wave. The total polarization of the medium is given by

\[
P = e_0 \left( \chi^{(1)}_{\omega} + (N_e/N) \Delta \chi^{(1)}_{\omega} + 3 \chi^{(3)} (E^2) \right) E
\]

where \(\chi^{(n)}\) is the \(n\)-th order susceptibility, and the angular brackets indicate an average over a time longer than an optical period but shorter than \((2b\tau)^{-1}\). We have assumed that TPA produces a single excited state of number density \(N_e \ll N\), the total number density of the nonlinear chromophore. We have also assumed an isotropic medium with linearly polar-
ized light for simplicity, and both $\Delta \chi^{(3)} = \chi^{(3)} - \chi^{(3)}_{g}$ and $\chi^{(3)}$ are complex quantities ($g$ signifies the ground state of the medium). The excited state decays back to the ground state with a time constant $T_e$, so $N_e$ obeys the following kinetic equation:

$$\frac{\partial N_e}{\partial t} = \frac{\sigma_2 N I^2}{2h\omega} - \frac{N_e}{T_e}$$

where $\sigma_2 = \beta/N$ is the TPA cross section ($\beta$ is the TPA coefficient), and $I(z,t) = 2\epsilon_0 nc E^2(z,t)$ is the total intensity. Let the amplitudes be slowly varying in time compared to $T_e$. Equation (9) can then be integrated to yield

$$\frac{N_e}{N} = C_0 + [C_1 \exp[i(2kz - 4b \pi)] + C_2 \exp[i(4kz - 8b \pi)]] + \text{c.c.},$$

where $c_0$ is the free-space permittivity. We will make the assumption that $(4b T_e)^2 << 1$.

Following a procedure directly analogous to that of Yeh and Boyd for non-degenerate TBC, Eqs. (10a)-(10d) are substituted into Eq. (8), and then both Eqs. (7) and (8) are substituted into Maxwell’s wave equation in the slowly varying amplitude approximation. Matching up synchronous terms, the following coupled-wave equations for the laser and backscattered intensities are derived:

$$\frac{dI_L}{dz} = -g(l - z/d) I_L I_S - \gamma_{\text{eff}} (I_L^2 + 3I_S^2 + 6I_L I_S) I_L - \beta(l + 2I_S) I_L$$

$$\frac{dI_S}{dz} = -g(l - z/d) I_L I_S + \gamma_{\text{eff}} (3I_L^2 + 4I_L^2 + 6I_L I_S) I_S + \beta(2I_L + I_S) I_S$$

where $g$ and $\gamma_{\text{eff}}$ are the backward wave gain and effective three-photon absorption (3PA) coefficients, respectively, with

$$g = \frac{8b T_e \omega \Delta \chi^{(3)}_{\text{eff}} d}{c I_{\text{sat}}^2},$$

$$\gamma_{\text{eff}} = \frac{N \Delta \sigma}{l_{\text{sat}}^2},$$

where $\Delta \chi^{(3)} = \text{Re} \left( \Delta \chi^{(3)} \right)$, $\Delta \sigma = \sigma_x - \sigma_y$ is the difference between the linear absorption cross sections of the excited and ground states, and $I_{\text{sat}} = (2\hbar \omega / \sigma_2 T_e)^{1/2}$ is the two-photon saturation intensity. Note that $g = 0$ when $b = 0$ (no chirp). Hence, without chirp there can be no growth of the backward scattered wave. The gain $g$ also carries the sign of $b$ (positive or negative chirp). For a negatively chirped pulse, the scattered wave will be attenuated. For the rest of the paper, we will assume that $b > 0$.

**4. EXPERIMENTAL**

Micromolar solutions were prepared for conventional photophysical measurements (lifetimes, excited state cross sections, and quantum yields). Details of these experiments can be found elsewhere. All solution samples for nanosecond NLT measurements had concentrations of 0.02 M (mol/L) and were placed in 1-mm glass or fused silica cuvettes. Intrinsic $\sigma$ values were obtained from independent femtosecond measurements.
Nanosecond nonlinear transmittance measurements were performed with a Nd:YAG pumped optical parametric oscillator (OPO) tuned from 660 to 880 nm. The pulse was Gaussian shaped with $\tau_L = 3.2$ ns. The beam was focused with an $f = 50$-cm lens into the sample. Over the length of the sample (1 mm) the beam was essentially collimated. The beam shape was slightly elliptical, with a geometric-mean $1/e^2$ radius $w = 18.4 - 18.9 \mu m$, assuming an approximately Gaussian beam shape. The energy was varied, and incident and transmitted energies were measured with energy meters. To rule out the effects of self-focusing/defocusing, a large-area ($\sim 1 \text{ cm}^2$) detector was placed near the exit of the sample to collect all transmitted energy. We also looked for stimulated backscattering by rotating the sample slightly to avoid Fresnel reflected light and measuring 180°-scattered light with an energy meter.

Intermolecular quenching properties were examined. The ground state concentration was varied from 10 $\mu M$ to 20 mM, and the triplet state lifetime measured. At $\sim 10 \mu M$ the lifetime of AF350 was 182 $\mu s$ under deoxygenated conditions, and the lifetime was 96 $\mu s$ at 20 mM. A bimolecular self-quenching rate constant of $2 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ was measured. The NLA experiments were performed under air-saturated conditions, and this small amount of quenching will make no difference since it is in competition with oxygen quenching. Similarly, AF330 run at low and high energy excitation conditions produced no measurable change in the decay rate attributable to triplet-triplet annihilation. This is not unexpected due to the low triplet yield of these materials. Due to the similarity of these materials in structure and known triplet yield, we assume that these intermolecular processes do not play a significant role at this concentration.

### 5. RESULTS AND DISCUSSION

A common method in the literature for screening TPA materials in the nanosecond regime is to fit the NLT data to an effective TPA transmittance (see Eq. (1)) and extract an effective TPA cross section. We show the results of such fits for two series of dipolar (AF240 and AF270), quadrupolar (AF287 and AF295), and octupolar (AF380 and AF350) molecules in Table 1. Another series of chromophores have been measured at a variety of wavelengths, and their effective TPA cross sections are given in Table 2. Such data are useful for observing trends, in molecular structure and spectrally, but do not yield sufficient information to give directions for further improvement. For example, a large effective $\sigma_2$ could be due to a large intrinsic $\sigma_2$, a large singlet and/or triplet cross section, and/or a large triplet yield. Hence, these NLT measurements must be supplemented with photophysical measurements. Both effective 3PA and numerical ESA models may then be applied to ascertain the quality of the model in reproducing the NLT results.

#### Table 1. Effective TPA Cross Sections of a Series of AFX Chromophores

<table>
<thead>
<tr>
<th>Material</th>
<th>File</th>
<th>Eff $\sigma_2$ $(10^{-20} \text{cm}^4/\text{GW})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF240</td>
<td>NLA 130</td>
<td>50</td>
</tr>
<tr>
<td>AF287</td>
<td>NLA 134</td>
<td>99</td>
</tr>
<tr>
<td>AF380</td>
<td>NLA 131</td>
<td>114</td>
</tr>
<tr>
<td>AF270</td>
<td>NLA 132</td>
<td>29</td>
</tr>
<tr>
<td>AF295</td>
<td>NLA 136</td>
<td>78</td>
</tr>
<tr>
<td>AF350</td>
<td>NLA 137</td>
<td>139</td>
</tr>
</tbody>
</table>
Results of NLT measurements for 0.02-M solutions of AF455, AF350, and AF240 in THF are given in Figs. 3-5, respectively. Using sets of intrinsic $\sigma_2$ values, we calculated the NLT for each material and compare these calculations to the data in Figs. 3-5. Only experimental data were used in the calculations; there were no adjustable parameters.

In Fig. 3 there is good agreement between theory and experiment when the value of $\sigma_2 = 0.51 \times 10^{-20}$ cm$^4$/GW is used. This value was obtained in a femtosecond NLT experiment$^{30}$ for a 0.02-M solution of AF455 in THF, identical to the sample studied here. Although the wavelength used in that experiment was 790 nm, the TPA spectrum$^4$ indicates that $\sigma_2$ does not differ significantly at 800 nm, considering the experimental uncertainty of ±15%.

Figure 3 also compares the transmittance in AF455 calculated for two-photon induced ESA (effective 3PA analytical model) with that due to TPA alone (numerical), and reverse saturable absorption (RSA) which includes the ground state absorption and excited state absorption. Obviously, ESA is the dominant loss mechanism. The inclusion of ground state absorption gives rise to significant nonlinear absorption and fits the data more closely in the region near < 10 $\mu$J where these models are the most reliable.

---

Table 2. Spectral Effective TPA Cross Sections for Four Chromophores

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>File</th>
<th>Eff $\sigma_2$ (10$^{-20}$ cm$^4$/GW)</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF445</td>
<td>NLA0841</td>
<td>44</td>
<td>660</td>
</tr>
<tr>
<td></td>
<td>NLA0771</td>
<td>103</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>NLA0804</td>
<td>29</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>NLA0816</td>
<td>8</td>
<td>880</td>
</tr>
<tr>
<td>E1-BTF</td>
<td>NLA0842</td>
<td>195</td>
<td>660</td>
</tr>
<tr>
<td></td>
<td>NLA0756</td>
<td>145</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>NLA0801</td>
<td>80</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>NLA0817</td>
<td>0</td>
<td>880</td>
</tr>
<tr>
<td>AF380-118</td>
<td>NLA0847</td>
<td>67</td>
<td>660</td>
</tr>
<tr>
<td></td>
<td>NLA0761</td>
<td>117</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>NLA0807</td>
<td>69</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>NLA0822</td>
<td>100</td>
<td>880</td>
</tr>
<tr>
<td>IR-2</td>
<td>NLA0850</td>
<td>114</td>
<td>660</td>
</tr>
<tr>
<td></td>
<td>NLA0776</td>
<td>98</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>NLA0809</td>
<td>103</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>NLA0825</td>
<td>185</td>
<td>880</td>
</tr>
</tbody>
</table>

---

Fig. 3. Experimental (circles) and theoretical (curves) nanosecond nonlinear transmittance as a function of laser pulse energy for a 0.02-M THF solution of AF455 at 800 nm. The curves are for the analytical effective three-photon absorption model, the numerical model with only TPA driving excitation, with only the ground state driving excitation (labeled RSA) and for the complete system.
We note for all materials that there is some departure of experiment from theory in the low energy regime (~ 10 \mu J). It is interesting that an effective TPA theory fits the data better in this regime, indicating that some mechanism that has a quadratic intensity dependence may be at play. He et al.\textsuperscript{17} have observed this kind of dependence and have verified in their case that this is due to a stimulated scattering phenomenon. We consider this next.

Let us examine Eqs. (11a) and (11b) in the case when \( I_0 \ll I_L \approx \text{constant} \). It can be seen that the backward stimulated wave will experience exponential growth when

\[
I_L > 2\beta / (\Delta t_0 - 3y_{eff})
\]

This defines the threshold condition for stimulated backscattering when there is no linear absorption. From Eq. (11b), the small signal gain \( G \), given in terms of \( \Delta I_s = I_s(0) - I_s(d) \), is

\[
G = \Delta I_s/I_s(d) \sim I_L^2
\]

for input intensities where the gain dominates TPA. Also, the reflectance of the scattered wave is defined by

\[
R = I_s(0)/I_L(0),
\]

and the change \( \Delta R = \Delta I_s/I_s \sim I_s(d)/I_L \sim GI_s(d)/I_L \). These results are in agreement with the data presented by He et al. for the measured small-signal gain and reflectance in a 0.01-M solution of PRL 802 in THF.\textsuperscript{17}

Under conditions where the nonlinear absorption terms (\( \beta \) and \( y_{eff} \)) can be ignored, Eqs. (11a) and (11b) can be solved analytically. The result can be expressed as

\[
\eta_0 = \frac{R((1-R)(1-R+3\eta_0)+2\eta_0)^{1/2}}{(1+\eta_0^{1/2})^{3/2}}
\]

where \( \eta_0 = I_s(d)/I_L(0) \), and

\[
\Gamma = \frac{1}{2}(1-R)^2 g_{eff}^2(0)\, d
\]

Note that in general \( \eta_0 \neq \eta \), although when the gain is sufficiently small \( \eta_0 \approx \eta \). Also, when the gain is not too large so that \( 1-R \gg \eta_0 \), Eq. (14) can be simplified to the following approximation:

\[
\eta_0 \approx \frac{R(1-R)}{(1+R)^2 \exp(\Gamma)}
\]

It is interesting to compare this result to the case of SBS, for which the denominator of Eq. (16) becomes \( \exp(\Gamma) \). Thus, in the case of negligible loss by absorption, the backscattered reflectance as a function of incident laser intensity will look similar to the Brillouin reflectance. A plot
of the reflectance given by Eq. (16) for a constant input $I_0(d)/I_0(0)$, over a range of $\Gamma$ where the approximation is valid, is shown in Fig. 6.

Numerical solutions of Eqs. (11a) and (11b) are also given in Fig. 6. These illustrate the agreement of the approximation given by Eq. (16) with the exact result, and the effect of including the nonlinear absorption terms. Figure 7 gives $I_d(0)$ as a function of $I_0(0)$. Parameters have been adjusted to yield results close to the experimental data of He et al.\textsuperscript{16,17} The coefficients used for the solid curve in Fig. 7 are $\beta = 9.46$ cm/GW (the value quoted in Ref. 17), $\eta = 0.04$, $g = 1800$ cm$^3$/GW$^2$, and $\gamma_{\text{eff}} = 120$ cm$^3$/GW$^2$, with $d = 1$ cm. In Fig. 8 the corresponding plot for the laser transmittance is given. Here the transmittance is the ratio of output power to input power. To compute this, we assumed a Gaussian dependence for the input intensity and then integrated the output intensity over the area of the cylindrically symmetric beam. The result is compared with what would be expected for pure TPA (no TBC or ESA). The departure from pure TPA in this case is due primarily to energy transfer from the laser to the backscattered beam. Figure 7 also shows a somewhat different result (dashed curve) yielding comparable backscattered intensity. Often the effective TPA cross section measured in the nanosecond regime is a factor $\sim 100$ larger than the intrinsic cross section (usually measured in the femtosecond regime).\textsuperscript{31} Thus, for these calculations we chose $\beta = 0.09$ cm/GW. The other parameters are $\eta = 0.02$, $g = 2860$ cm$^3$/GW$^2$, and $\gamma_{\text{eff}} = 300$ cm$^3$/GW$^2$. TPA is low in this case, but the loss due to ESA significantly slows down the growth of the backscattered wave at higher intensities.

To get an order of magnitude of the numbers involved, consider the experiment of He et al.\textsuperscript{16,17} and the results shown in Figs. 7 and 8 for $\beta = 9.46$ cm/GW. For a laser wavelength of 532 nm and $T_e \sim 1$ ns,\textsuperscript{31} $I_{\text{sat}} \sim 700$ MW/cm$^2$. For a severely chirped pulse the laser linewidth is $\Delta \nu_0 \sim 2 \pi \tau_0$, where $\tau_0$ is the laser pulse width. For $\Delta \nu_0/2\pi \sim 24$ GHz (0.8 cm$^{-1}$), $\tau_0 \sim 10$ ns, and $N = 6 \times 10^{18}$ cm$^{-3}$ (0.01-M concentration), Eqs. (12) and (13) yield $\Delta x_{\text{R}}^{(1)} \sim 4 \times 10^{-3}$ and $\Delta \sigma \sim 1 \times 10^{-17}$ cm$^2$. We note that this numerical example overestimates the approximation made earlier for which $(4b/\epsilon T_0)^2$ is small compared to 1. To account for deviations due to this, the gain and ESA terms in Eqs. (11a) and (11b) would need to be modified by the inclusion of the factor $[1 + (4b/\epsilon T_0)^2]^{-1}$. For example, in the negligible nonlinear absorption case, Eq. (16) would be multiplied by a factor $\ln(1 + \alpha)/\alpha$, where $\alpha = (4bT_0/\epsilon c)^2$, which is $\sim -1$ for $\alpha << 1$. In the present numerical example, this factor is $\sim 0.5$. Consequently, the estimates for $\Delta x_{\text{R}}^{(1)}$ and $\Delta \sigma$ should be increased by a factor $\sim 2$. These values yield approximate agreement with photophysical measurements, and thus suggests that this stimulated scattering with a quadratic intensity dependence may be contributing to the overall shape of the NLT curve.

![Fig. 6](image_url)

**Fig. 6.** Backscattered reflectance as a function of exponential gain factor for various values of nonlinear absorption coefficients. $I_0(d)/I_0(0) = 10^2$ in all cases. Circles give values for $R$ calculated by the approximation in Eq. (10).
Notice that $\Re(\chi^{(3)})$, or $n_2$, does not appear in the gain coefficient of Eq. (12). The reason for this is that $\chi^{(3)}$ was assumed to have an instantaneous response [$\operatorname{Im}(\chi^{(3)}) \propto \beta$]. There is no two-beam coupling in a Kerr medium with an instantaneous response.\textsuperscript{20,21} It is possible however, under TPA resonant conditions, that $n_2$ could have a finite response time (i.e., $\chi^{(3)}$ is complex with a finite damping coefficient\textsuperscript{21}). However, if this is included in the development of the coupled-wave intensity equations, it would lead to a term in the gain $G$ that is proportional to $I_1$, not $I_1^2$, which would be inconsistent with the experimental results of He et al.\textsuperscript{17} It is also quite likely that the Kerr refractive term would be much smaller than the term proportional to $\Delta\chi_R^{(1)}$.

The central feature of this theory is contained in the term $4b\tau\tau_e = \Delta\omega T_e$, where $\Delta\omega = 4b\tau$ represents the instantaneous difference in the frequency between the forward and backward propagating waves at position $z$ in the medium. $\Delta\omega$ varies continuously from 0 at $z = d$ to a maximum of $4\hbar n/c$ at $z = 0$. The interference of the forward and backward propagating waves sets up an interference pattern that is traveling to the left if $b > 0$. This intensity pattern forms a population grating via TPA, which lags behind the interference pattern due to the finite response time $T_e$. By examining Eqs. (10c),
the gain is related to the imaginary part of the nonlinear susceptibility, which vanishes when the difference between 
the field. The rate of energy transfer per unit volume to or from an electric field E by a polarization P is 
$2\text{Re}[\alpha|E|P]\text{exp}(i\Delta\phi)$, which is 0 if $\Delta\phi = 0$. Thus, although backscattering by an unchirped wave could also lead to a 
population grating, the grating would not transfer energy to the scattered wave because the field and polarization would 
be in phase. There would thus be no increase in the index modulation as the incident intensity increases and no expo-
nential growth of the scattered wave, i.e., no stimulated scattering. This has an analogy in SBS and SRS. In both cases,
the gain is related to the imaginary part of the nonlinear susceptibility, which vanishes when the difference between 
the laser and scattered wave frequencies shrinks to zero. In addition, the scattered wave in the present theory is attenuated 
for a negative chirp, analogous to the attenuation of the anti-Stokes wave in SBS and SRS.

It should be noted at this stage that linear chirp is not a unique requirement for the energy transfer between incident la-
er and elastically backscattered waves. Higher order chirp terms in the nonlinear time dependent phase have been ignored 
for simplicity but will make additional contributions to the beam coupling. Another potential mechanism involves 
multimode beams. In this case, though, the spectral nature of the backscattered beam will not match that of the incident 
beam. Take the simple case where the incident laser wave consists of two modes: $\omega_1$ and $\omega_1 = \omega_2 + \delta\omega > \omega_1$ ($\delta\omega << \omega_1$). Employing the mechanism involving a TPA-populated excited state described above, there will be energy transfer from 
the $\omega_1$ mode of the incident laser beam to the $\omega_2$ mode of the backscattered beam. Likewise, the $\omega_2$ mode of the back-
scattered wave will yield its energy to the $\omega_1$ mode of the laser wave. The backscattered wave will thus be single-mode 
and its spectrum conspicuously different from the incident laser. However, if the modes in the incident laser beam are 
equally chirped, both modes of the backscattered wave will be amplified, but not equally. When the laser linewidth is 
determined primarily by the linear chirp ($2\beta \omega \gg \delta\omega$), the spectrum of the backscattered wave will superficially resemble 
that of the incident laser, but the energy distribution amongst the modes will differ. This will generally be the case 
also when the number of modes is greater than two. Scattering due to multimode effects have not been studied to any 
large extent. We plan to further examine this both theoretically and experimentally.

6. CONCLUSIONS

In summary, we have measured the excited state properties of donor-acceptor push-pull charge-transfer chromophores 
and modeled the nanosecond NLT as an effective three-photon absorption process combined with stimulated scattering 
at high intensities. All model parameters, including intrinsic TPA cross sections, have been measured independently, 
and the model agrees very well with much of the experimental data for those values of femtosecond TPA cross sections 
that were measured under conditions similar to those of our experiments. A numerical calculation that includes the 
ground state absorption gives significantly better fit to the NLT data. These calculations have no adjustable parameters.
A careful examination of linear absorption data gives evidence for a two-step TPA via the Lorentzian tail between the 
$S_0$ and $S_1$ states. We conclude that the dominant contribution to the nonlinear transmission in these chromophores in 
the nanosecond regime is ESA from both singlet and triplet states. TPA does not contribute significantly to the transmitt-
tance loss, but is key to pumping the excited states. We expect that this is true for a large variety of these types of chrom-
ophores. We have also presented a model of two-beam coupling in a nonlinear absorption medium whereby energy is 
transferred from an incident laser beam to an elastically backscattered beam. In the mechanism proposed, the incident 
laser has a nonlinear time dependent phase and populates an excited state of the medium by two-photon absorption. The 
incident and backscattered waves superpose to form an interference pattern, leading to the formation of a Bragg grating. 
The Bragg grating consists of an index modulation resulting from a modulation of the excited state population. This 
grating is out of phase with the interference pattern which forms it due to the finite lifetime of the two-photon-populated 
excited state and the frequency chirp of the two waves. Energy flows one-way from the higher frequency part to the 
lower frequency part of the coupled waves. Complete energy conversion to the backscattered wave is prohibited, how-
ever, in part because of loss due to two-photon and excited state absorption. Nevertheless, the power spectrum of the 
backscattered wave can be nearly identical to that of the incident wave. This mechanism may be at work and explain the 
NLT curves at lower intensities near energies of 10 $\mu$J.
ACKNOWLEDGEMENTS

We gratefully acknowledge the Air Force Office of Scientific Research (AFOSR/NL) for their support of this work, as well as support from AFRL/ML.

REFERENCES


