

SINGLE STATE ABSORPTION SPECTRA OF NOVEL NONLINEAR OPTICAL MATERIALS

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ABSTRACT

During the absorption of a laser pulse of moderate length, the leading edge can experience excited state absorption out of the first singlet state. The measurement of this excited state absorption spectrum can only be accurately probed using short pulse pump-probe techniques. Specifically, we examine the excited state absorption of AF-380 in THF using ultrafast transient white light absorption spectroscopy (TWLA). This material has been the focus of several investigations due to its purported large two-photon absorption cross-section, the discrepancies between long and short pulse measurements, and its use in holographic two-photon induced photopolymerization. It is believed that a substantial excited state absorbance can account for the difference in two-photon cross section measurements. It is also possible that this excited state exhibits coherence for time scales that can affect further absorption of longer pump pulses. We examine the transient absorption of this species, as well as polarization and free carrier effects and discuss the possible implications with regards to measurement techniques.

INTRODUCTION

Recently, we were the first to demonstrate ultrafast holographic two-photon induced photopolymerization (H-TPIP)¹. In one of the systems used to demonstrate this process, a two-photon absorbing dye, denoted AF-380, was a key component. In addition, we have also been working closely with Prasad *et al* to characterize a set of two-photon absorbing chromophores on both the nanosecond and femtosecond time scales^{2,3}. Within this class of chromophores, AF-380 has shown interesting photophysical properties, making it a suitable choice for an in depth spectroscopic investigation. Specifically, our preliminary report indicated that the femtosecond measurement of the intrinsic two-photon absorption cross section was approximately 3×10^{-21} cm⁴/GW. It has since been ascertained that a low cross section, singlet excited state absorption contributed to a lower measurement of the two-photon cross section. Taking this additional absorption process into account has resulted in a correction of the intrinsic two-photon absorption cross section of AF-380 to 8.1×10^{-21} cm⁴/GW. It has also been observed that nanosecond measurement of the two-photon absorption cross section gives a value that is two orders of magnitude higher⁴. This fact suggests that a long-lived state having a high absorption cross section may be contributing to the measurement. Such discrepancies and the complicated excited state dynamics that occur are the subject of this work.

EXPERIMENTAL

Materials

AF-380 represents a multi-dimensional version of a class of linear, asymmetric two-photon chromophores under examination within the Air Force Research Laboratory. These

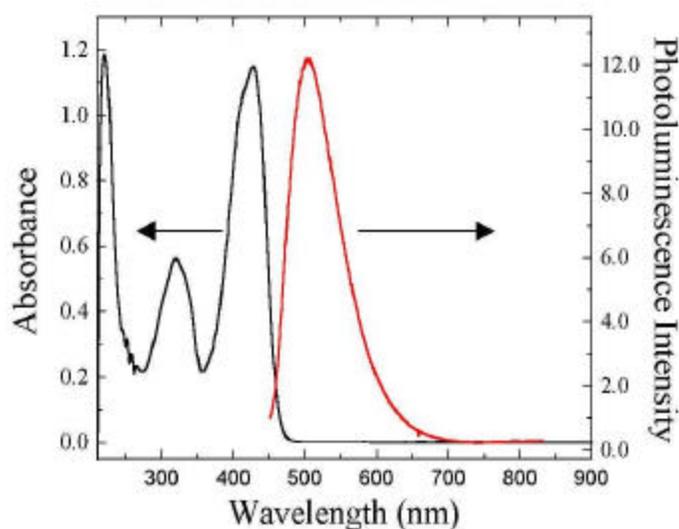


Figure 1 Ground state absorption and linear fluorescence spectra of a 1 mM solution of AF-380 in THF.

measured with 100 fs pulses³. This concern may be mitigated by the broadness of the absorption bands.

For the linear dye analogs, a similarity of absorbance spectral features for a series of dyes with different π -electron accepting species suggested that the excitation was centered on a common subset of the molecules, namely the D- π portion of each molecule. This was further supported through the observed sensitivity of the fluorescence to the nature of the π -electron accepting species. Because AF-380 shares this same D- π portion and has a similar, yet red-shifted, linear absorbance spectrum, the increase in conjugation length may be centered on the multi-dimensional D- π portion of the molecule.

Z-scan analysis

A standard Z-scan experiment was performed on the AF-380 chromophore in tetrahydrofuran (THF) to measure the two-photon absorption cross-section. Details of this experiment are described in the literature, therefore no description is given⁶. The experimental parameters for the scan were a beam waist of 80 μm , pulse width of 90 fs, pulse energies between 1–4 μJ , path lengths of 0.2, 0.5 and 1 cm, at a wavelength of 790 nm. The effective two-photon absorption coefficient, β , was measured as function of pulse energy. The data fit to a straight line and the y-intercept at 0 energy reported as the intrinsic value of the two-photon absorption cross section. The slope of the line gives an estimate of the singlet excited state cross section. The fact that the ESA arises from a singlet level is assumed on the basis of time, i.e. the excited state population hasn't had time enough within the pulse width to relax elsewhere.

Transient White Light Absorption Spectroscopy

Details of our transient white light absorption experiment can be found in the literature⁷, therefore a summary is presented here. A femtosecond Ti:Sapphire laser with regenerative amplifier, is used to generate bandwidth limited 90 fs pulses, centered at 790 nm with typical pulse energies between 0.95-1.0 mJ. A pair of phased shutters is used in conjunction with the variable repetition rate of the regenerative amplifier to obtain single pulse events. The pulse is

molecules consist of a π -electron donating and accepting moieties separated by a conjugated aromatic bridge (D- π -A)^{2,3,5}. Due to patent issues, the exact chemical structure can not yet be disclosed. However, in comparison to other dyes that have been previously reported, AF380 has a larger molecular weight, a three-fold increase in linear molar absorption coefficient, and a 30 nm shift in peak linear absorption of the lowest energy transition (see Figure 1). Though the observed red-shifting of the linear absorbance may call into question the direct comparison of the cross-sections measured at 800 nm, AF380 shows nearly an order of magnitude increase in effective two-photon cross section over its linear analog as

split in two by an ultrafast beam splitter. One pulse is used as a pump beam and is propagated down a variable delay line with a total of 5 ns delay. The second pulse is propagated along a fixed delay line and is used to generate a white light supercontinuum in the single filament regime. In this case, the white light generator is a 5 mm flowing water cell. The white light pulse is collimated using a matched lens and propagated through an iris, giving a spot size of 0.5 mm^2 . A small pick off prism is used to select a portion of the probe pulse and send it through a short pass filter with a cut off wavelength of 500 nm. A photodiode and hardware discriminator circuit is used for signal selection. The probe beam is again split into a signal and reference beam and both are imaged through the sample into a spectrometer. A liquid nitrogen CCD array is used for data collection. The ratio of the signal pulse to reference pulse gives the change in absorbance upon excitation.

RESULTS

Shown in Figure 2a is the excited state absorption as a function of probe delay relative to the excitation pulse for the wavelength region of 500 to 650 nm. As can be seen from the cross sectional view in Figure 2b, there are two distinguishing features. The first feature is characterized by a strong rise in the absorption following excitation. A subsequent decrease in absorbance is observed just under 1 ns delay. The second main feature is a slow increase in absorbance out to beyond 4 ns delay. With respect to the dispersion one would expect from discrete states, even molecular states, the fact that this structure seems to be reflected across a wide spectral band ($>150 \text{ nm}$) is interesting, and suggestive of excitation to the continuum.

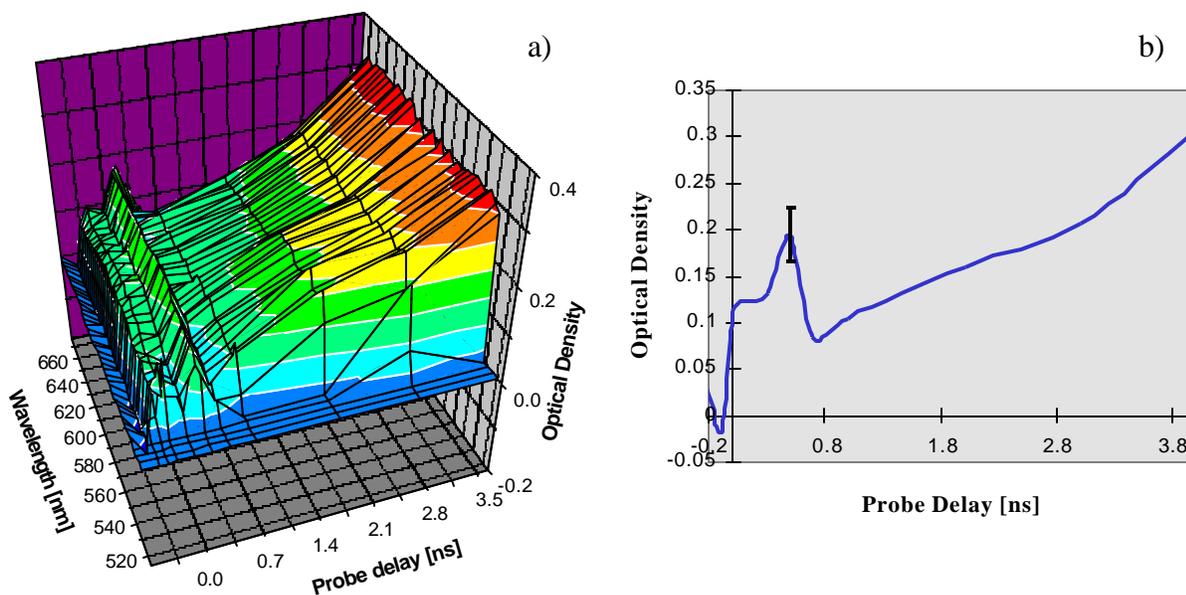


Figure 2 a) Transient white light absorption of AF-380 as a function of time and wavelength. **b)** A single cross section of a) at 600 nm.

Figure 3 shows a polarization dependence of the measured ESA at a 4 ns delay. A linear polarizer was placed within the path of the white light probe and the probe polarization rotated relative to the pump. Note that the zero delay was reset. On the basis that dephasing times of molecular orientation effects are on the order of tens to hundreds of picoseconds, one would expect that at a 4 ns delay, no polarization dependence of the probe should be observed. However, as can be seen from the figure, a slight dependence is measured and fit to a sinusoidal curve (solid line).

As the excited state absorption is dependent on the initial excited state density, a measure of the ESA as a function of intensity should produce a quadratic curve due to the initial two-

photon excitation. Figure 4 illustrates a quadratic dependence at low intensity, denoted by the pure quadratic fit to the low intensity data. However, it can also be seen that at high intensity, a deviation from the pure quadratic occurs. This can be attributed to either a secondary, long-lived absorption contributing to a cumulative effect, or to saturation of the ground state absorption. A simple back of the envelope calculation puts the total photon flux at 0.03 GW/cm² to be $\sim 10^{16}$ cm⁻². As it takes two photons to produce one excited state, this implies at most $\sim 5 \times 10^{15}$ excited states/cm². The molar concentration of the sample was 1 mM, giving approximately 6×10^{16} molecules/cm². Subsequently, at the intensity where a deviation from a quadratic is observed, only 10% of the molecules are in initially in the excited state, far from saturation.

It should also be noted that no permanent photochemical changes were observed in the samples. Linear absorbance spectra before and after testing were carefully compared with no noticeable changes.

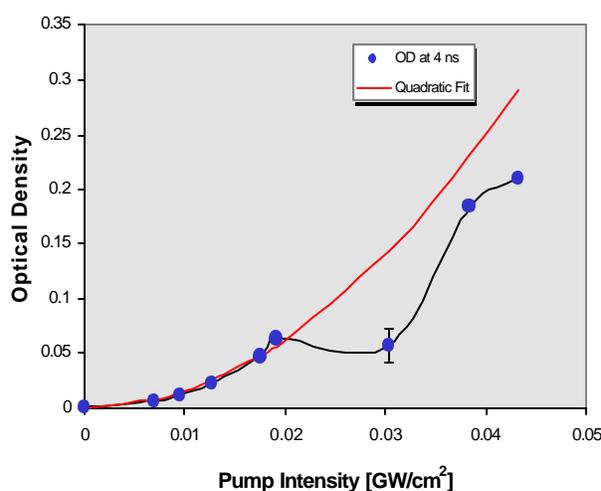


Figure 4 Intensity dependence of ESA at 4 ns delay.

Based on the decrease in the observed ESA, we assume that N_2 has little or no ESA. Such a state may be representative of an intramolecular transitional state during which the two-photon excitation from the pump pulse redistributes itself from the D- π portion of the molecule towards the acceptor regions. This picture is supported by quantum molecular calculations of the excited state electron density^{5,8}. The upper level N_4 is considered to be the continuum and can be populated from either N_1 or N_3 . The reason for this assumption is based on energy conservation of the photons involved in the ESA measurement. Specifically with respect to N_1 , two photons of wavelength 800 nm, followed by a photon within the measured probe wavelengths, namely 500 nm to 650 nm. This is equivalent to a single photon absorption event from the ground state of wavelength 250 nm at the low energy end, well within the continuum absorption band. A similar argument holds for the N_3 to N_4 absorption based on the fluorescence energies in Figure 1. The absorption cross section

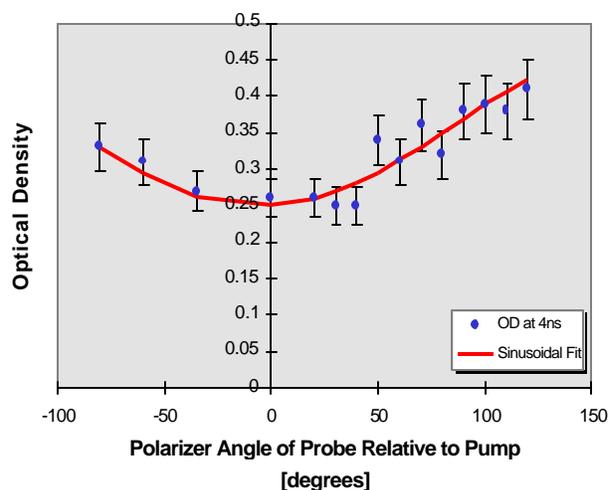


Figure 3 Polarization dependence of the excited state absorption at 4 ns delay.

DISCUSSION

In order to understand the dynamics of the system, we have formulated a simple 5 level rate model based on the above observations. A representative energy level diagram of the model is shown in Figure 5. The energy levels have the following characteristics. N_1 is the first excited state reached through a two-photon absorption process at 790 nm. N_2 is assumed to be an intermediate state between the first excited state and the fluorescing level N_3 associated with the linear fluorescence band illustrated in Figure 1. Based on the decrease in the

from level I to level J are given by $\sigma_{I,J}$. Similarly for the relaxation rates, $k_{I,J}$, of I to J. Ultrafast Z-scan measurements and fluorescence lifetime measurements give the values of the two-photon absorption cross section, σ_{TPA} , the first singlet excited state absorption cross section, $\sigma_{1,4}$, and the fluorescence lifetime of N_3 , $1/k_{3,0}$ to be $8.1 \times 10^{-21} \text{ cm}^4/\text{GW}$, $2 \times 10^{-17} \text{ cm}^2$, and 2.9 ns respectively. This leaves five free parameters. One may argue that if N_4 is truly in the continuum, then the relaxation rates to N_1 and N_3 are proportional to the energy gap between them. Due to the width of these bands, it is not unreasonable to assume that the relaxation rates to each of these levels from N_4 are very similar. We also note that previous authors have observed long-lived free carrier formation of similar triaryl amines, normally on the millisecond time scale and some as long as hours^{9,10}. Therefore, a reasonable estimate of the lifetime of the N_4 state could be at least milliseconds. Ideally one would like to use the transient white light data to fit the remaining parameters, however, there are too many to be convincingly quantitative. The model does, however, qualitatively reproduce the structure of the transient absorption measurement as shown in Figure 6, using moderate values of the remaining ESA cross section (of order 10^{-17} cm^2), and relaxation rates into and out of N_2 based on the white light data (hundreds of picoseconds to order nanosecond).

The idea of a long-lived free carrier population fits well with the observation from Figure 2 of a broad spectral transient, reminiscent of free carrier absorption. It should be noted that if the free carrier population is long-lived, it should necessarily contribute to the loss of an incident wave either through an increase in reflection or free carrier absorption (scattering). Certainly this is true in the case of semiconductors, and is not unreasonable to assume so here. In such a case, a slowing of the repetition rate of the TWLA experiment should reduce the contribution to the absorption of the probe by allowing sufficient time for recombination. We did perform such an experiment and found that the overall absorbance level decreased, as the repetition rate was decreased, while simultaneously preserving the same two transient features pointed out earlier. One might also suspect that if the free carrier population became large enough and lived for milliseconds, that it might manifest itself as a deviation from the quadratic power law of the absorbance mentioned above by effectively trapping population.

As a final note, it is desirable to use this model to explain some of the discrepancies between the nanosecond and femtosecond measurements of the two-photon absorption cross section. In contrast to the femtosecond measurement of the two-photon absorption cross section reported above, Joshi *et al* have reported a nanosecond measurement of AF-380's two-photon absorption cross section to be $920 \times 10^{-21} \text{ cm}^4/\text{GW}$. If we use this rate model to predict the transmittance of a pump pulse at 800 nm

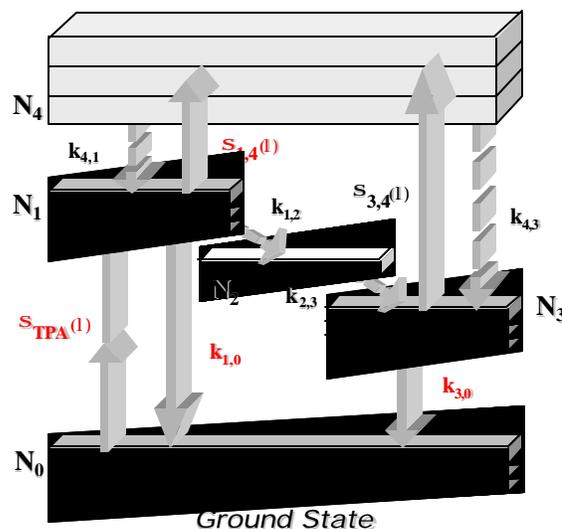


Figure 5 Rate model describing excited state dynamics of AF-380. Solid arrows indicate radiative transitions, while dashed arrows indicate nonradiative transitions.

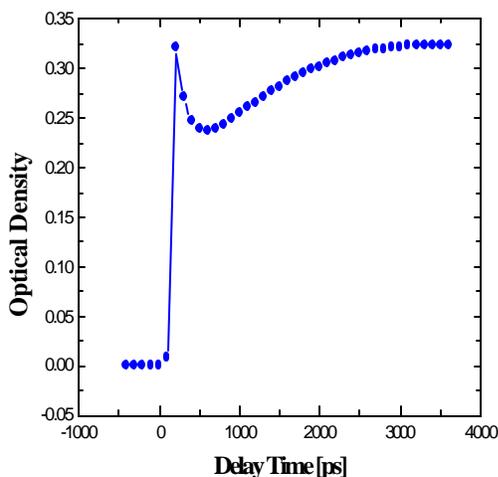


Figure 6 Model prediction of transient absorption experiment.

only (i.e. turn the probe off), assuming that the dispersion in the ESA cross sections is negligible, we find that the difference in the *measured* two-photon cross section can be readily explained. The model predicts that a transmission measurement of the two-photon absorption cross section for an 8 ns pulsewidth of energy 4 mJ would be $\sim 200 \times 10^{-21} \text{ cm}^4/\text{GW}$, while a 90 fs pulse of energy 230 μJ would give $\sim 9 \times 10^{-21} \text{ cm}^4/\text{GW}$ in comparison to the actual cross section used of $8.1 \times 10^{-21} \text{ cm}^4/\text{GW}$. These values were chosen on the basis of typical experimental conditions.

CONCLUSIONS

We have measured the transient absorption of a two-photon absorbing chromophore AF-380, and have constructed a simple rate model to analyze the observed behavior. In so doing we have presented evidence for an intermediate state between the initial two-photon excited state and the one-photon fluorescing level, possible related to excited state redistribution of the electron density and an associated conformational change predicted by quantum molecular calculations. We have also seen evidence of excitation to a free carrier region having a long lifetime (recombination time) and contributing to the overall excited state absorption. This model also predicts a two order of magnitude difference in the effective two-photon absorption cross section as seen by experiment. While this picture appears to explain several key features of the excited state dynamics, there still remains both a question regarding polarization effects in the nanosecond time scale, and the necessity of quantifying some of the remaining free parameters of the model. One experiment currently being planned is a two-photon photoconductivity experiment to try and measure the free carrier population and lifetime.

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