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14. ABSTRACT

This report summarizes the status of the apparati which have been created or augmented by equipment purchased under the titled DURIP grant. Initial progress made using these systems in studies of two-photon absorption and optical limiting is also reported. Two new measurement systems have been set up and are operational. These systems are: 1) nanosecond transient absorption spectroscopy, and 2) femtosecond time resolved absorption spectroscopy. The transient spectroscopy systems provide a capability for monitoring the time evolution of transient species over the time scale of ~100 fs to milliseconds, by following absorption bands in the range of ~300 to 1000 nm. Initial results obtained using the new systems described above are presented. 1) The optical limiting properties of a new charge transfer complex (bis-(dibutylamino)stilbene:(2,4,7-trinitrofluoren-9-ylidene)malononitrile; BDAS:TNFDM) are reported. This complex shows a sizeable nonlinear response at 600nm which is dependent on solvent polarity, with the strongest response in toluene solution. 2) the solvent dependence of the nonlinear transmission response of BDAS, which is dominated by two-photon induced excited state absorption (TPESA), is reported. Very large nonlinear absorption coefficients are observed in polar solvents like acetonitrile, alcohols and acetone, up to a factor of 10 larger than that in toluene. This indicates that optimization of the environment can be important for TPESA chromophores like BDAS.

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Summary

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Two new measurement systems have been set up and are operational. These systems are: 1) nanosecond transient absorption spectroscopy, and 2) femtosecond time resolved absorption spectroscopy. The transient spectroscopy systems provide a capability for monitoring the time evolution of transient species over the time scale of ~100 fs to milliseconds, by following absorption bands in the range of ~300 to 1000 nm.

Initial results obtained using the new systems described above are presented. 1) The optical limiting properties of a new charge transfer complex (bis-(dibutylamino)stilbene:(2,4,7-trinitrofluoren-9-ylidene)malononitrile; BDAS:TNFDM) are reported. This complex shows a sizeable nonlinear response at 600nm which is dependent on solvent polarity, with the strongest response in toluene solution. 2) the solvent dependence of the nonlinear transmission response of BDAS, which is dominated by two-photon induced excited state absorption (TPESA), is reported. Very large nonlinear absorption coefficients are observed in polar solvents like acetonitrile, alcohols and acetone, up to a factor of 10 larger than that in toluene. This indicates that optimization of the environment can be important for TPESA chromophores like BDAS.

1 Technical description of instruments

In this section, descriptions of the status of the nanosecond and femtosecond transient spectrometers, and the optical limiting apparatus are given.

1.1 Nanosecond transient absorption spectrometer

The nanosecond time resolved absorption spectrometer is based on a pump-probe geometry in which the pump pulses are derived either from a frequency tripled YAG laser (for experiments at 355nm) or a continuously tunable parametric oscillator which can be tuned over a wide range (460-690 nm and 230-345 nm). The probe pulse is a white light generated from pulsed Xe-Arc lamp (400-900 nm). An experimental set up of the pump-probe measurements is given in Figure 1. In a typical pump-probe experiment the intensity of the light transmitted through the sample is collected by a CCD detector with and without the pump pulse. The difference between the intensities with and without the pump pulse is measured as a function of the delay between the pump and probe pulses. The advantage of having a CCD is enormous as one can measure the absorption

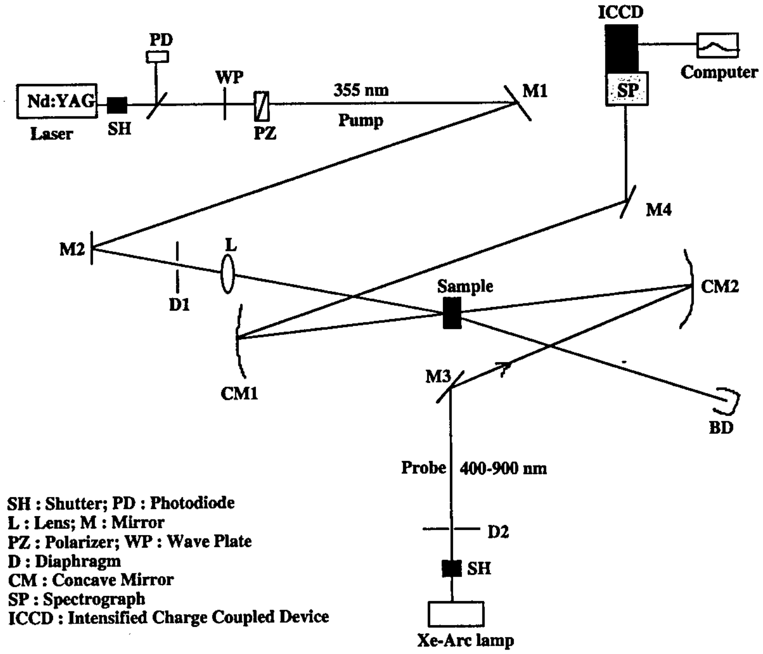


Figure 1. Nanosecond transient absorption spectrometer.

spectrum over a wide range (400-900 nm) simultaneously. In this way one can easily derive the wavelength dependent kinetics of the sample (at various wavelengths) under study in a single measurement instead of measuring the same at various wavelengths individually.

In a typical pump-probe experiment envisaged here, the pump light (5 ns, 355 nm) from a YAG laser is focused weakly onto the sample cell using a lens. The incident power on the sample can be adjusted with the help of the wave plate polarizer combination shown in Figure 1. The probe (white light) pulse from the pulsed lamp (Newport) is focused on the sample using the concave mirror (CM1) as shown in Figure 1. The unabsorbed light coming out of the sample is collected using another concave mirror (CM2) and is then imaged onto the entrance slit of the spectrograph (300 mm focal length, Princeton Instruments) and detected by an intensified charge coupled device (ICCD, 1024 x 256 pixels, Princeton Instruments). One of the important aspect of the time-resolved nanosecond measurements is the synchronization of the laser place with that of the probe pulse and the detector. Currently efforts are under way to synchronize the pump, probe and the CCD detector. This can be achieved by using the pump laser as

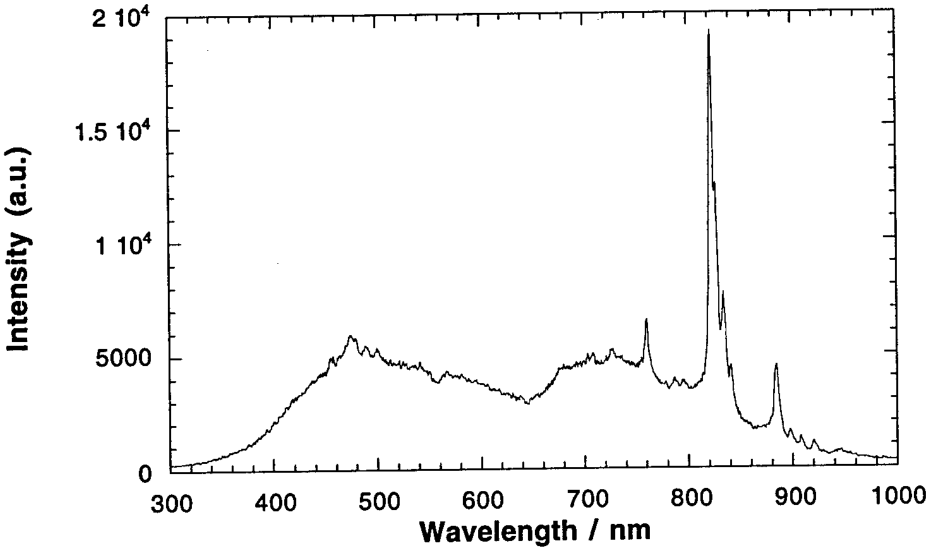


Figure 2. Xenon arc lamp spectrum recorded using the ICCD.

the master to trigger the pulsed lamp and the detector. A timing box is being made to achieve this, which takes into consideration the built-in delays in the detector and the pulsed lamp. The spectrograph has been calibrated by measuring the spectral profiles of the well characterized calibration lamps such as neon, mercury and helium. The spectral profile of the probe light (white light) have been also measured (shown in Figure 2). The time-resolved absorption spectrometer will be used to study the excited absorption spectra and lifetime of the cationic or anionic species produced as a result of photo-excitation of the CT complexes. One example of such an interesting experiment stems from some of the optical limiting experimental results given later in this report.

1.2 Intensity Dependent Transmission Spectrometer

The optical limiting set up shown in Figure 3 is now equipped with new detectors (Large area visible photoreceiver, Model 2031, New Focus) which can be used in three different sensitivity ranges in order to improve the sensitivity of the nonlinear transmission measurements. This system has also now been coupled to an optical parametric oscillator system (MOPO, Spectra-Physics, purchased under a previous DURIP grant), to provide widely tunable wavelength dependent studies. This modified setup has been used to study the solvent dependent optical limiting behavior of organic charge-transfer complexes and 4, 4'-bis(di-n-butylamino)stilbene (BDAS).

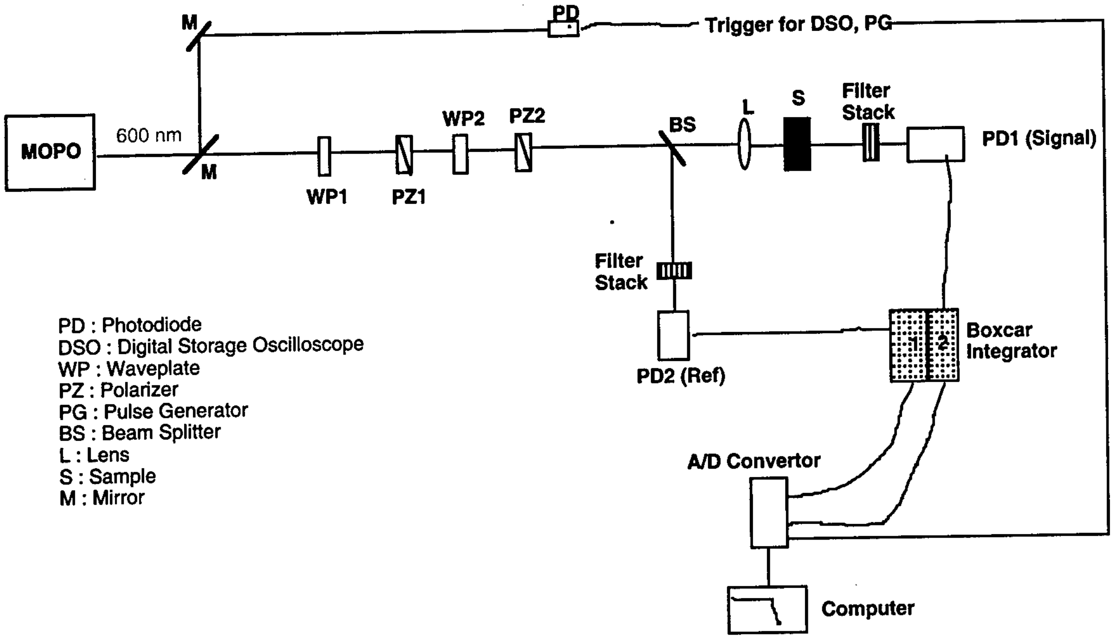


Figure 3. Experimental set up for nonlinear transmission measurements.

1.3 Femtosecond transient absorption set-up

A set-up was built for time-resolved transient-absorption spectroscopy in the ~100 femtosecond to 2 ns time range. While originally planned to be used with picosecond pulses from a dye laser amplifier, the design was recently adapted for use with ~100 fs pulses from our new amplified Ti:sapphire laser system. This allows for a higher time-resolution and much wider wavelength range by using an optical parametric amplifier (OPA). All components used for this set-up, except the laser system, were purchased in the framework of this research project.

The optical layout is shown in Figure 4. A first laser pulse (pump) is used to excite the sample (e.g. in a 1 mm path length cuvette). In the simplest case, this can for instance be a 400 nm beam obtained by second harmonic generation (SHG) of the output of the Ti:sapphire laser amplifier (Spectra-Physics Spitfire). A second pulse (probe) is used to probe the absorption spectrum of the sample as a function of delay between both pulses.

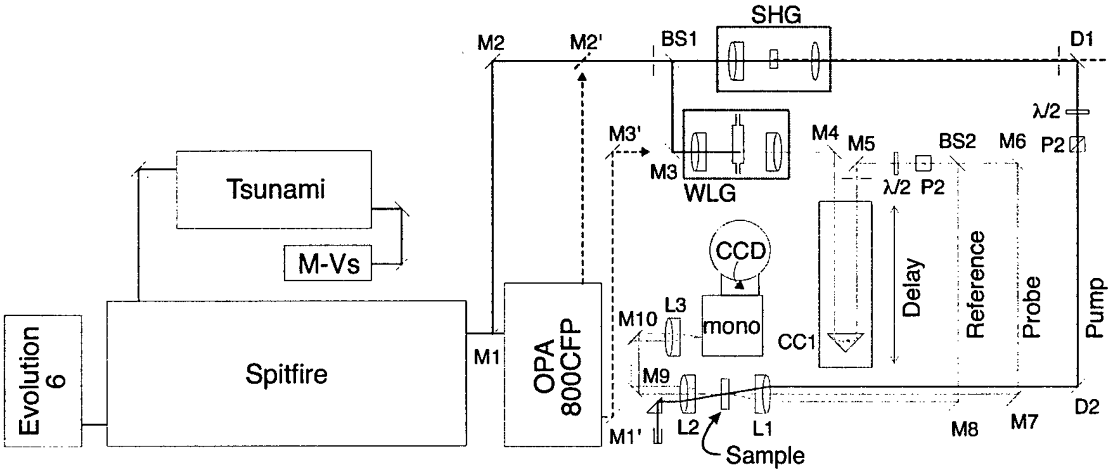


Figure 4. Schematic layout of the femtosecond time-resolved transient absorption set-up. See text for explanation of symbols.

This probe pulse is a white light continuum obtained by white light generation (WLG) using a fraction of the fundamental 800 nm output from the amplifier. The white light probe beam is delayed relative to the pump beam using a precision translation stage with a travel of 12" (Newport PM500-12LW.100), allowing for maximum delay of ~2 ns. Then, the white-light beam is split by beamsplitter BS2 into the actual "probe" beam and a "reference" beam. The probe beam is aligned parallel to the pump beam with mirror M7 and focussed on the same spot in the sample as the pump beam. The reference beam is tilted slightly in the vertical plane by mirror M8 and thus focussed on a different spot of the sample. After traversing the sample, the pump beam is blocked and residual pump light removed by filters (spectral and/or polarization; not shown in figure). Finally, both probe and reference beams are focussed onto two different spots of the vertical entrance slit of a monochromator (ARC SpectraPro-150) and the two resulting spectra imaged on a two-dimensional CCD detector (Princeton Instruments LN/CCD-1100). In this way, two spectra are recorded simultaneously, one (probe) of the white light pulse transmitted by the sample after excitation, and the other (reference) of the sample in the absence of a pump beam. Thus, dividing the probe spectrum by the reference spectrum, small changes in the absorption spectrum induced by the pump pulse can be monitored. To ensure that the pump and probe pulses are synchronized when the translation stage is near its minimum delay, the position of optics M5 through M6 (and/or optics D1 through D2) is adjusted. Two half-wave plate (λ/2) and polarizer (P1, P2) combinations are used to control the intensity and polarization of the pump and probe beams.

As we want to examine dynamics after one-photon as well as after two-photon excitation, the fundamental 800nm output of the amplifier may also be used directly as an excitation source, or depending on the system under study, any output wavelength of the OPA (Spectra-Physics OPA-800CFP) may be used to provide ~100 fs excitation pulses in the range of 300-3000 nm. In case the OPA output is used as a pump beam (mirror M2' used instead of M1 and M2), the residual 800nm pump beam is taken from the OPA via mirrors M1' and M3' to the white-light generator (M3 removed).

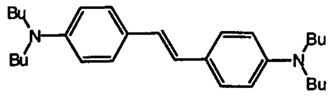
As discussed in section 2.1, various materials/geometries were tested for the white-light generation. In this application, the intensity of the white light continuum is not critical however. The continuum only needs to be stable, and most importantly, cover a wide spectral range. Because low powers can be used, optical damage thresholds are not an issue and both water or sapphire can be used. Still, the widest and smoothest spectrum is obtained with a 1cm pathlength water cell. In cases where a smooth spectrum in the region of 800 nm is critical, the white light generation can also be achieved using the second harmonic (400 nm) of the amplifier output.

2 Results

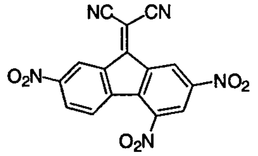
2.1 *Optical Limiting Studies: Charge-Transfer Complexes and Solvent Dependence of Two-Photon Induced Excited State Absorption*

2.1.1 Optical Limiting Studies on BDAS:TNFDM CT Complex

The optical limiting properties of a donor (BDAS) / acceptor (TNFDM) charge transfer (CT) complex (structures shown below) have been studied.



BDAS



TNFDM

The normalized absorption spectra of the BDAS:TNFDM CT complex formed between BDAS and TNFDM in toluene (Tol), tetrahydrofuran (THF), acetone (ACE) and acetonitrile (AN) is shown in Figure 5a. The absorption maximum (λ_{max}) of the complex in various solvents show a hypsochromic shift as the solvent polarity is increased (λ_{max} in different solvents: toluene: 682 nm; THF: 652 nm; acetone: 641 nm; acetonitrile: 640 nm). This implies that the complex in toluene is highly delocalized with nearly equal charge sharing and in more polar solvents is more ionic in character. In the case of acetonitrile it appears that the spectrum also shows a small contribution from the BDAS cation absorption around 600 nm, indicating that a small fraction of molecules has

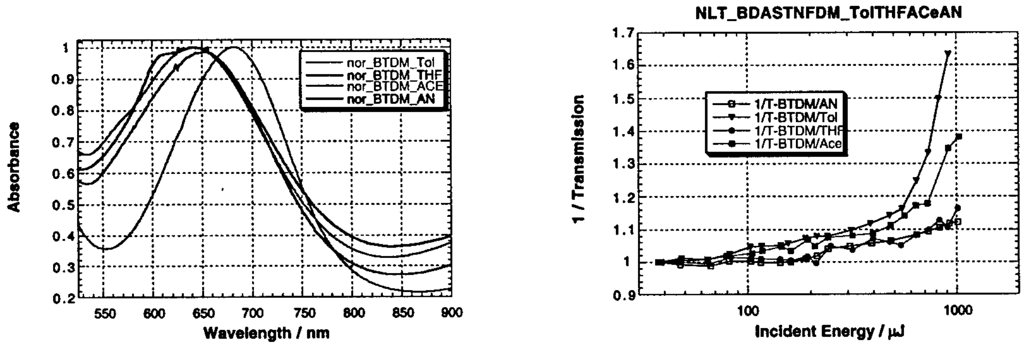


Figure 5.(a) Left: Absorption spectra of CT complex in different solvents. (b) Right: Nonlinear transmission data at 600 nm for CT complex in different solvents.

undergone oxidation. The solvent dependent NLT data for the BDAS:TNFDM CT complex are shown in Figure 5b. The normalized optical limiting (OL) behavior of the CT complex appears stronger in toluene compared to the more polar solvents, and follows the trend

- OL response : Toluene > Acetone > THF, AN

In general the OL response of the CT complex will depend upon the following factors; the equilibrium constant, extinction coefficient and yield of ion formation as a result of photo-excitation of the CT complex.

The equilibrium constant and molar extinction coefficients of the CT complexes estimated using Benesi-Hildebrand approach reveal the following trend (increasing order):

- Equilibrium constant : THF < Acetone < Toluene < AN;
- Molar extinction coefficient : AN < Acetone < Toluene < THF

These trends follow the opposite order than the OL response indicating that either the extinction coefficient or the yield are less favorable in the more polar solvents. One would expect the yield of ion formation to be greater in a more polar solvent, so we believe the spectral factors may be critical here. These issues will be pursued further using the transient absorption systems established under this grant.

2.1.2 Solvent Effect on NLT of BDAS

The effect of solvent polarity on the nonlinear transmission behavior of BDAS has been studied. Although a large amount of work has been done on BDAS, detailed studies on the solvent effect on NLT, absorption and fluorescence properties have not yet been carried out. So we decided to conduct a thorough study of the solvent effects. We chose a variety of solvents ranging from Toluene, 1,4-Dioxane, CCl_4, THF, Acetone, MeOH, Acetonitrile, DMF and DMSO. These solvents were chosen to cover the range of dielectric constants varying from 2.2 to 46.9 (DMSO).

Absorption Spectroscopy: The Absorption maximum of BDAS in the above mentioned solvents are given in Table 1. There is a slight bathochromic shift with increasing solvent polarity.

Fluorescence Spectroscopy: The fluorescence maximum also shifts to the red as the polarity of the solvent is increased. The maximum shift observed was 12 nm when the solvent is changed from toluene to DMSO. The 12 nm shift is indicative of the fact that there is not much of a structural change when going from ground to the first excited state.

2.1.3 NLT measurements of BDAS in various solvents at 600 nm

The intensity dependent transmission response of BDAS in various solvents is given in Figure 6. The concentration of BDAS in each of the solvents is 0.01 M. As a check, The absorption spectra measured before and after the OL measurements remained the same indicating there was no photo-induced effects. It can be easily seen from the figure that BDAS in CCl_4, THF and DMF exhibit the largest OL response and also that the response in these solvents is comparable. It is interesting to note that OL response of BDAS in MeOH is rather strong even at a very low concentration of 0.001 M(not shown in the figure). However the solubility of BDAS in MeOH is quite limited with 0.001M being near saturation. The observed response (1/T vs incident energy) can be fit very well with a combined two and three photon absorption function. The fit with just a two photon model function is very poor, which is not surprising as we have established this in several cases earlier. For the other solvents studied, the OL response decreased in the order, AN > Ace > Tol > DMSO > Dioxane. The strong response in DMF is consistent with the response of other very polar solvents although other factors must be involved since CCl_4 and THF solvents also give strong responses even though they are nonpolar or moderate polarity, respectively.

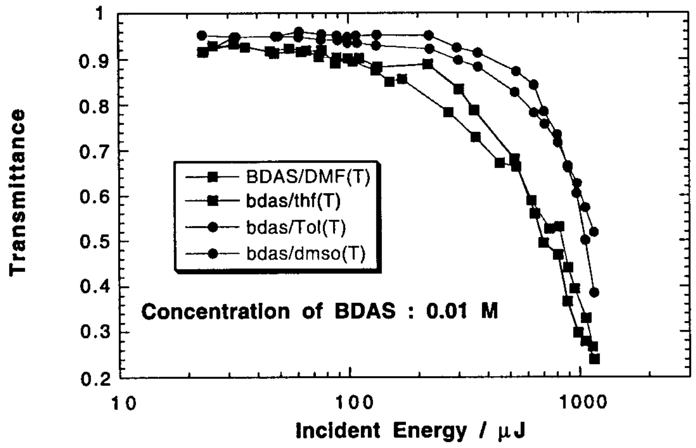


Figure 6. Nonlinear transmission characteristics of BDAS in various solvents at 600 nm.

The NLT measurements were repeated at a BDAS concentration of 0.1 M in four solvents, CCl_4, Toluene, THF and DMF at 600 nm (Figure 7). With the exception of BDAS in CCl_4, which again gave a very large response, the OL response of BDAS in THF, DMF and Toluene was quite good and comparable in all the three solvents. Figure 7 shows also the 2 and 3 photon absorption model fit to the observed data. The fitting function used is given below;

$$1/T = 1 + \beta L I_0 + (\gamma/\beta)\, I_0 \ln(1+\beta L I_0) \qquad (1)$$

Where β is the two-photon absorption coefficient, γ is the three photon absorption coefficient, I_0 is the intensity of the laser pulses and L is the path length of the sample. The two (δ) and three (γ) photon absorption coefficients of BDAS in various solvents are given in Table 1. δ was obtained by fitting the inverse of transmission (1/T) against intensity of the laser at low input fluences and γ was obtained by fitting 1/T against intensity of the laser at high input fluences.

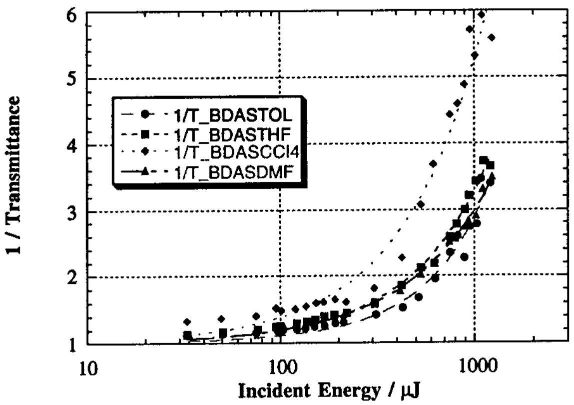


Figure 7. Optical limiting response of BDAS in various solvents at 600 nm. The lines represent the two and three photon absorption model fit to the observed data.

The good OL response of BDAS in the above mentioned solvents is interesting as the nature of these three solvents are entirely different; for example, Toluene is a non-polar solvent, THF is an electron donating solvent (with a dielectric constant of 7.4 and

DMF is a polar aprotic solvent with a dielectric constant of 36.7 and efficient H-bond accepting capability). One possible explanation for the observed effect in THF may be due to the fact that the BDAS cation formed as a result of two photon absorption is well stabilized in THF. It will be interesting to see the solvent effect on the two photon absorption cross-section itself, which is important to predict the mechanism of optical limiting of BDAS in various solvents. Further insight into these observations can be obtained from nanosecond transient absorption spectral studies and also from a better understanding of the ground state structure of BDAS in the three solvents (from FT-IR studies). Also the OL response of BDAS in Toluene, THF and DMF seem to reach a saturation point at the maximum incident energy used in the measurements. Although the response of BDAS in CCl_4 is good it is not well understood. We do observe evidence for the BDAS cation formation as some precipitation occurs in the solution of BDAS in CCl_4 with time. Photochemical oxidation of dyes in the presence of halogenated solvents is well known and could well be involved here. It is worth noting that BDAS in other chlorinated solvents such as $CHCl_3$ and CH_2Cl_2 forms its cation readily, as it can be seen from the immediate color change to blue or green and a huge absorption band near 600 nm.

Table 1 . Absorption, Fluorescence Maxima, Effective Two-photon (δ) and Three photon (γ) Absorption Coefficients of BDAS in various solvents

Solvent	ε^a	λ^A_{max}	λ^F_{max}	δ^b (10^{-48})	γ^c (10^{-74})
CyHx	2.02	369		3.97	8.42
1,4-Dioxane	2.22	374	439	8.3	7.85
CCl_4	2.24			5.94	11.02
Toluene	2.38	375	438.3	2.76	4.73
THF	7.52	374	439.8	6.18	3.98
BzOH	13.1			4.0	
Acetone	21.01	375	441.0	1.02	15.31
EtOH	25.03	371		3.2	28.70
BN	25.9			7.02	
MeOH	33.0	371	442	1.36	48.36
AN	36.64	375	446.0	1.74	21.21
DMF	38.25	378	449.0	5.87	3.27
DMSO	47.24	381	455.0	0.78	6.96

[a] ε (dielectric constant) : from David R. Lide, Handbook of Organic Solvents, CRC Press, 1995. [b] δ in (cm^4/Photon.Molecule) ; [c] γ in (cm^{6}s^2/photon.molecule).