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13. ABSTRACT (Maximum 200 words

We have studied the spectroscopy, kinetics and non-linear characteristics of conjugated organic dyes by means of a new femtosecond transient spectroscopy system that allows us to study ΔA values as small as 0.003. We were able to measure accurately absorption spectra, kinetics and cross-sections of all states, transients and intermediate. These data prove that our materials have the best known RSA characteristics. All the molecules studied were found to have very strong and broad band reversed saturable absorption that collectively covers the optical spectrum relevant to optical limiters. We initiated studies using several molecules dispersed in a polymer matrix and find that as expected they cover the entire visible spectrum. Kinetic studies show that the RSA rate of formation is in the picosecond range and an intense transient absorption band is formed within the excitation pulse (r = 1.6 ps), and decays with a rate of -10^{10} s^{-}. We believe that such very highly absorbing and fast forming intermediate states will provide needed soldier and sensor protection. We were not able to proceed further with the practical devices we were fabricating because of the termination of this project.

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BASIC STUDIES OF NONLINEAR OPTICAL MATERIALS FOR EYE AND SENSOR PROTECTION

I. Abstract:

We have studied the spectroscopy, kinetics and non-linear characteristics of conjugated organic dyes by means of a new femtosecond transient spectroscopy system that allows us to study ΔA values as small as 0.003. We were able to measure accurately absorption spectra, kinetics and cross-sections of all states, transients and intermediate. These data prove that our materials have the best known RSA characteristics. All the molecules studied were found to have very strong and broad band reversed saturable absorption that collectively covers the optical spectrum relevant to optical limiters. We initiated studies using several molecules dispersed in a polymer matrix and find that as expected they cover the entire visible spectrum. Kinetic studies show that that RSA rate of formation is in the picosecond range and an intense transient absorption band is formed within the excitation pulse (r = 1.6 ps), and decays with a rate of -10^{10} s^{-}. We believe that such very highly absorbing and fast forming intermediate states will provide needed soldier and sensor protection. We were not able to proceed further with the practical devices we were fabricating because termination of this project.

II. Accomplishments:

Four papers have been published, which reveal the non-linear and spectroscopic properties of several dyes and other organic molecules and consider them for use as optical limiters . A patent was submitted. A graduate student received the Ph.D. degree. Two undergraduates a graduate and a postdoctoral fellow were involved in this research. Four invited talks were presented. An ACS prize was awarded to one of the investigators.

III. Introduction:

One of the most active areas of nonlinear research is the field of optical limiters[1-4]**.** The important goal of these research studies is the identification of the ultimate nonlinear optical (NLO) material and its utilization for the development of optical limiting devices that shall protect the soldier and sensors from the threat of damaging laser radiation. There are several types of NLO materials that could be utilized for power limiting applications. The most promising type includes compounds with large reversed saturable absorption (RSA)[5-8]**.** It is possible, however, to have materials with these properties and exhibit a 10^4 nonlinear attenuation. When a RSA material is exposed to intense pulsed laser radiation the population of the excited state increases very fast; consequently, if the excited state absorption cross section of the material is much higher than that of the ground state, then the effective absorption between excited states will increase significantly and the material will "limit" the transmission of laser light. For materials to be suitable as media for optical limiting devices, several requirements should be met:(1) in order to attenuate the power of the incoming light to a safe level, the excited state absorption cross section σ_{ex} should be much larger than σ_{gr}, the absorption cross section of the ground state. (2) The materials should have broadband spectral response that covers the entire or a very large segment of the visible region. (3) They should have relatively high transmission at low intensity light levels. (4) The response time should be faster than the exciting laser pulse rise time, but the material should become immediately transparent after the pulse. In order to design materials, which satisfy the above requirements, their nonlinear optical properties, as well as the spectra and kinetics of their intermediate states must be determined. Information concerning the nonlinear optical properties, ultrafast spectra and kinetics can be collected with the Z-scan technique [9-11], a simple method that allows one to measure both the nonlinear refraction and nonlinear absorption coefficients, and by means of ultrafast transient spectroscopy. The results of these measurements make possible the selection of the materials, which are suitable for power limiting applications, and in addition provide guidance for the design and synthesis of new molecules possessing better nonlinear properties.

As an example of this technique we present the experiments performed on several newly materials, which are known to have highly non-linear properties. Their ground state electronic spectra show a very intense absorption bands. For most of the compounds the band maximum which is located in the visible region of the spectrum and shift towards the infrared with increase in conjugation. To optimize the optical limiting effect of these materials we must increase the $\sigma_{ex} / \sigma_{gr}$ cross section ratio. In addition we have studied several organometalic materials consisting of dyes that are stable under strong radiation and have very high non-linear absorption and display some of the largest known RSA behavior. To determine the suitability of these materials for power limiting applications, we measured the transient spectra and kinetics of the intermediate states of these materials, after excitation of their visible absorption band with a picosecond pulse and from these data we have been able to determine the mechanism responsible for the observed optical limiting effects. We observed that all of the molecule presented here, developed a new transient absorption band with λ_{max} between 400- 780 nm, shortly after excitation. The decay lifetime of these excited states were measured and found to vary from 7 to 30 ps depending on the molecule. For some of the molecules we observed a second transient absorption band with λ_{max} between 700-730 nm, whose rise time was the same as a decay of the first transient absorption band. The second band decayed, subsequently, with a lifetime of 15-30 ps. Several azulenic and dye molecules were found to have quite strong reversed saturable absorption in a broad region of the visible spectrum. Therefore these molecules can be used as the active elements of optical limiting devices. The two-dimensional Z-scan method [25-27] was used for the determination of the nonlinear properties of these molecules. This technique allows us to use any arbitrary beam shape and sample thickness, which makes it a perfect diagnostic tool for optical limiters.

IV. Outline of accomplishments:

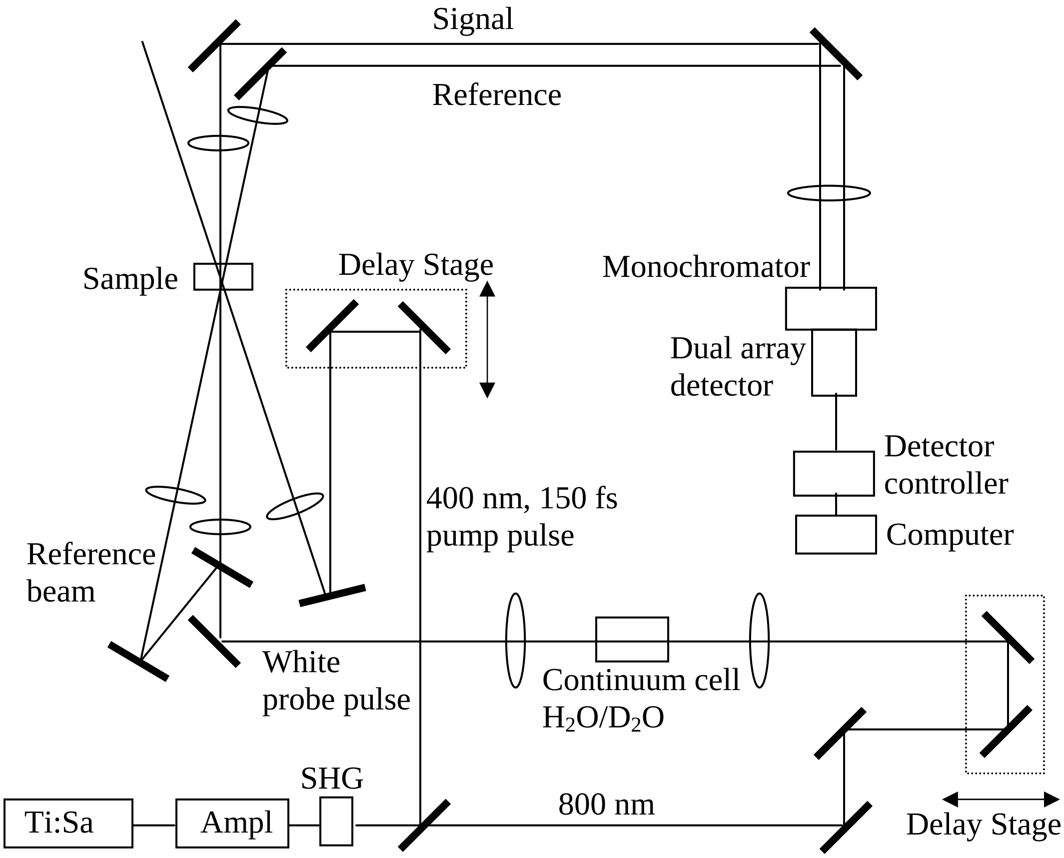
We have disclosed previously , that azulenic and porphyrin molecules have RSA and two photon cross sections with magnitudes that suggest the possibility of utilizing them as candidates for optical limiting devices. Detail description of the experimental system,, the results obtain and analysis of the data is presented in the following sections of this report.

V. Experimental System:

We have designed and constructed the new experimental system, proposed in 2000, for the study of the kinetics and mechanism of ultrafast processes responsible for the nonlinear and optical limiting properties of materials, to be used as optical limiters. This system allows us to measure transient absorption spectra and their evolution with 150 fs time resolution and 0.003 optical density. The experimental system is shown, schematically, in figure 1.

The system consist of a diode-pumped Ti:Sapphire tunable laser (Tsunami, Spectra Physics) that generates 800 nm, 150 fs pulses at 80 MHz repetition rate and average power of 600 mW. After amplification the output beam energy increased to 0.8 mJ per pulse at 1000-10 Hz repetition rate and 150 fs pulse duration. After SHG the fundamental and second harmonic beams are split by a dielectric mirror and used as probe and pump beams respectively. The fundamental, 800 nm, beam is directed to the delay stage, which allows us to adjust the delay time between the probe and the pump pulses at the beams intersection inside the sample cell. The fundamental beam then is focused inside the continuum cell, filled with 1:1 mixture of water and deuterated water, to produce white a continuum pulse, that covers the spectral region from 400 to 800 nm. This probe pulse is split by means of 50% beam splitter to two beams. One is focused into the sample cell and referred as signal and the other is the reference beam. The 400 nm pump beam is directed and focused inside the sample cell where it overlaps with the probe signal beam, while the probe reference beam enters the sample cell in the area positioned about 1 cm apart from the signal and pump beams and thus does not intersect with them. The changes in the optical limiter material, induced by the fast pump pulse, affect only the intensity of the signal probe pulse, but not the reference pulse. Both signal and reference beams after passing through the monochromator were focused on dual array detector attached to the monochromator. Each beam impinges on the separate channel and the collected data is send to the computer for processing. This system allows us to measure transient absorption spectra induced by the pump pulse at any preselected time. By changing the time delay between pump and probe pulses we can observe evolution in time of the transient absorption spectra, with resolution corresponding to the pulse duration, i.e. 150 fs. These data make it possible for us to draw important conclusions about the nature of intermediates involved in optical limiting and other nonlinear processes, obtain their absorption spectra and kinetics and determine the mechanism and characteristics of the material studied.

Figure 1. New experimental system for transient absorption spectroscopy and kinetics measurements with 150 fs resolution.



VI. Results and Discussion:

VI-1. 1,1′-Diethyl-2,2′-dicarbocyanine Iodide (DDI).

DDI molecule, which belongs to the class of carbocyanine dyes, shows excellent optical limiter properties. This molecule was studied earlier by means of 2Z-scan technique, where we utilized Nd: YLF picosecond laser, generating SHG 527 nm, 30 ps pulses at 1KHz repetition rate. The absorption spectrum of DDI is shown in figure 2.

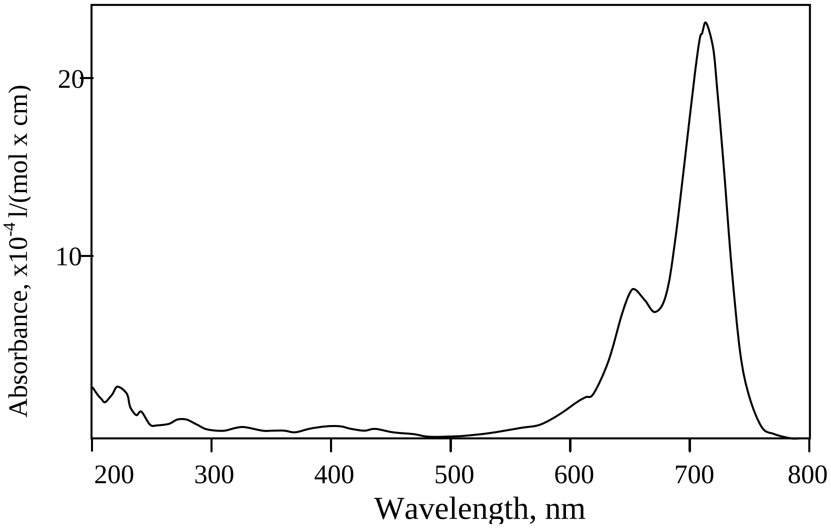


Figure 2. Absorption spectrum of DDI in EtOH

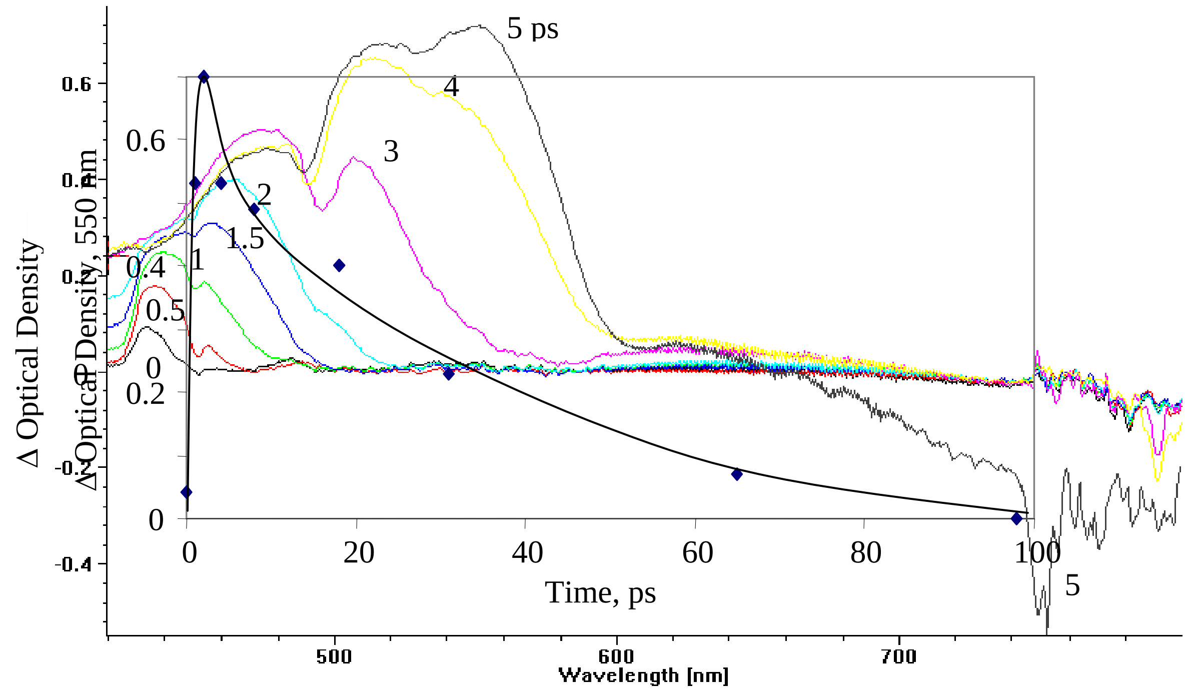
As it is typical for carbocyanine dyes, DDI has strong long wavelength absorption band in the red, 700 nm, region with extinction coefficient $\varepsilon = 2.3 \times 10^5$ and relatively low absorption in the rest of the visible and UV regions, which makes solutions and doped polymer films transparent even at relatively high concentration of the dye. The transients induced by high intensity laser pulses possess much higher absorption crosssection in the visible region than the dye ground state, which causes it to absorb the excitation light and reduce its intensity.

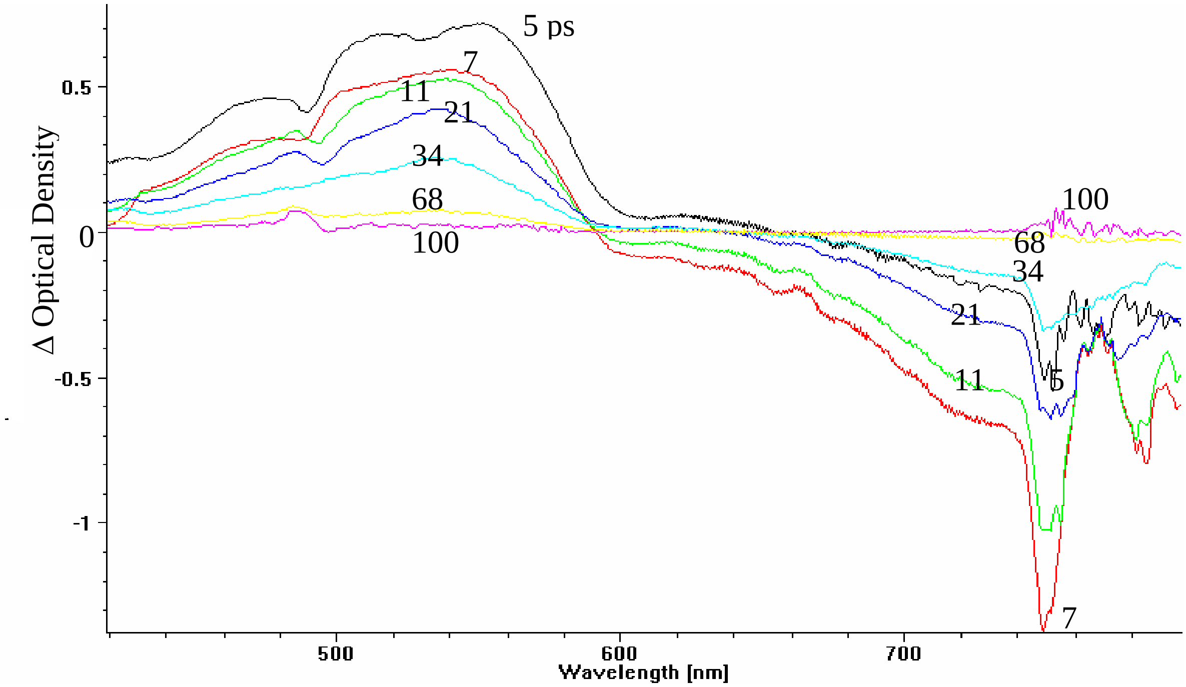
We have studied the transient absorption spectra and kinetics of the intermediates induced by 400 nm, 150 fs laser pulses in DDI solutions in ethanol. Figure 3 shows the differential spectra change after pulse excitation. It is shown that a transient with very intense and broad absorption band appears after excitation of the DDI molecule. This absorption band covers the spectral region from 400 to 600 nm and causes the attenuation of light, which is transmitted by the original, not excited material. As shown in figure 3, the appearance of the absorption band is accompanied by a spectral shift towards the red region of the spectrum.

By independent experiments we have shown that this spectral shift is actually attributed to the dispersion of the white continuum probe pulse. In this case, the blue spectral components of this pulse arrive at the sample later than red components, causing the absorption spectrum at shorter wavelengths first 2 ps to appear earlier than at longer wavelengths. We assume that the observed transient absorption is the S_1 – S_n transition of the electronic excited state of DDI molecule. The kinetics of formation and decay of the transient absorption measured at 550 nm is shown in figure 4.

Figure 3. Transient absorption spectra of DDI.

The rate of formation of time these absorption bands was determined to be about 300 fs, which is comparable with excitation pulse duration, 150 fs. The difference could be explained by broadening of the excitation pulse at the sample cell position due to dispersion of the pulse





accuracy as it passes the various optical elements of the system such as lenses, beam splitters, sample cell, etc. It is also that the possible involvement of other ultrafast processes, such as solvent relaxation and others are involved in some smaller degree. The absorption band induced by light pulse decays with the lifetime of about 30 ps, which corresponds to the lifetime of the S_1 electron excited state of DDI.

Figure 4. Kinetics of the transient absorption measured at 550 nm.

VI-2. Rhodamine 800.

Rhodamine 800 is a laser dye, which also possesses optical limiter properties. Its absorption spectrum, shown in figure 5, has a window in visible region ~350 nm to 580 nm and strong absorption at wavelengths longer than 600 nm such a spectra or doped polymer films will be transparent. We have found, that Rhodamine 800 is also a more stable dye than DDI and other carbocyanine dyes, which undergo partial decomposition under light excitation, especially when, as here, the UV light is applied.

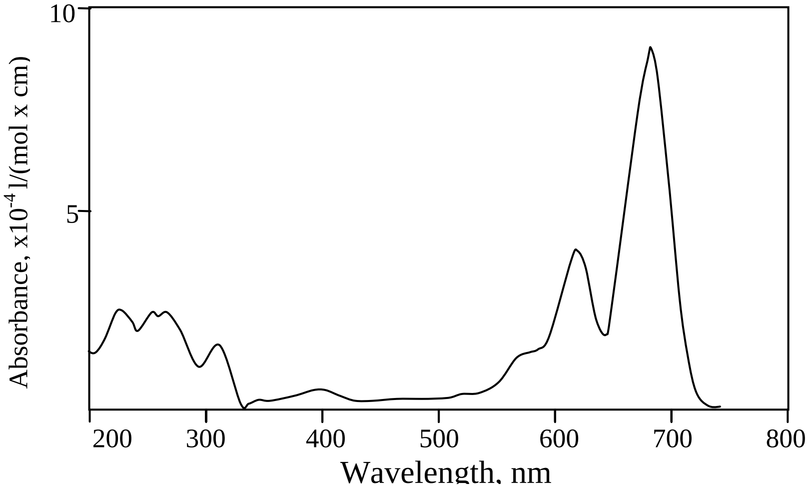


Figure 5. Absorption spectrum of Rhodamine 800 in ethanol.

The transient absorption spectra of Rhodamine 800 solution in ethanol are shown in figure 6. A broad absorption band appears after pulse excitation a 400 nm, and covers the spectral region 400 – 600 nm, which is transparent for the original solution. The formation and decay kinetics are shown in figure 7. The rise time of the transient absorption band follows the excitation pulse duration, then decays with the lifetime of 30 ps. The fast transient, which is assigned to the first electron excited state of the Rhodamine 800 molecule, has a much higher absorption cross-section in 400 – 600 nm spectral region than the ground state. The strong absorption induced by laser pulse at 400 nm makes this molecule suitable for use in optical limiter devices that may attenuate ultrafast, femto- and picosecond, laser pulses.

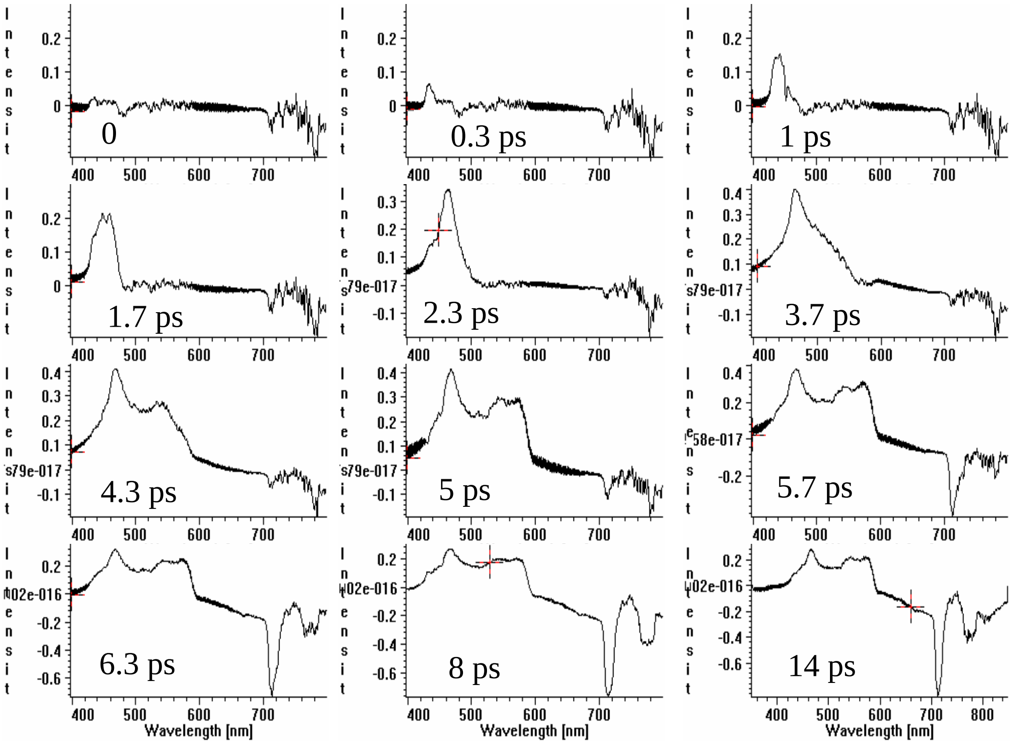


Figure 6. Transient absorption spectra of Rhodamine 800 in ethanol

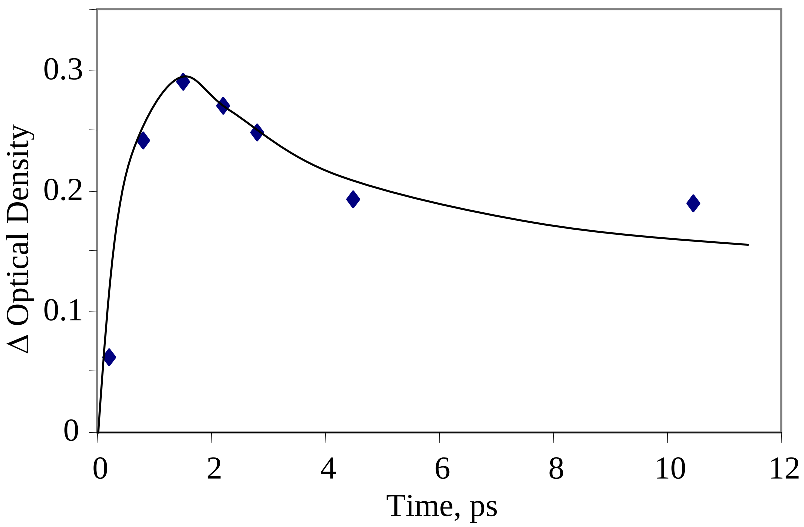


Figure 7. Transient absorption kinetics of Rhodamine 800 in ethanol

Because a practical device preferably should be a solid state system, we conducted experiments on Rhodamine 800 dye, dispersed homogeneously, in PMMA matrices. The solid polymer matrices with embedded Rhodamine 800 dye were prepared by radical polymerization of monomer MMA solutions. Because the dye has very low solubility in nonpolar media, such as MMA, to enhance its solubility, we have used polar plasticizers, including alcohols, acetonitrile and others. Solid polymer blocks were then cut to 1 cm cubes and 1 mm thick slides and therefore polished to optical quality.

Figure 8 shows the transient absorption spectrum of Rhodamine 800 dispersed in a PMMA matrix. The laser pulse induced absorption spectrum appears to be the same shape, width and maxima as the spectrum of this dye in alcohol solutions.

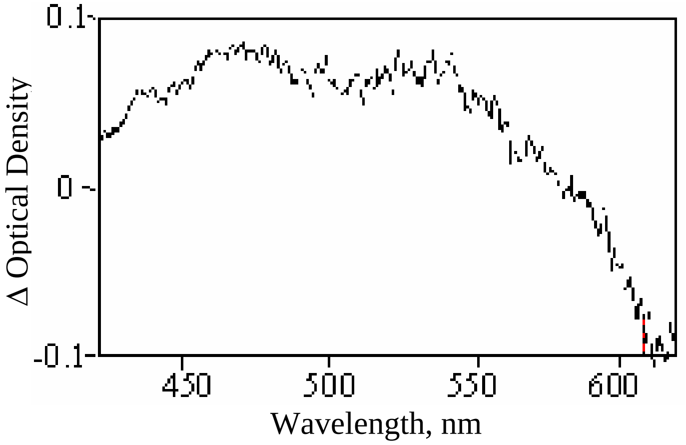


Figure 8. Transient absorption spectrum of Rhodamine 800 in PMMA.

VI-2. Nile Blue.

We have also studied Nile Blue dye as a potential candidate for utilization in optical limiter devices. Nile Blue is an oxazine dye. This class of organic dyes is known for their exceptional resistance to photo and thermal decomposition. As with the other dyes studied, Nile Blue also has strong absorption band in the red region of above 600 nm, and at shorter wavelengths as is shown in figure 9.

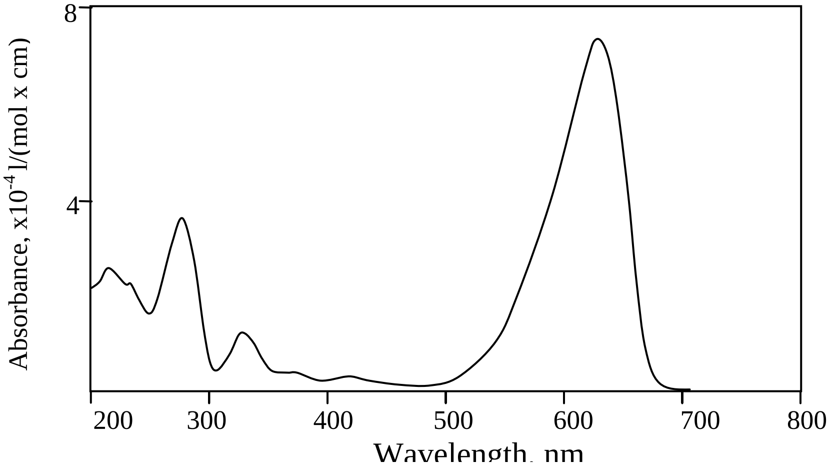


Figure 9. Absorption spectrum of Nile Blue in ethanol.

Excitation of a Nile Blue solution in ethanol at 400 nm, with ps pulse leads to the appearance of our induced transient absorption in the 400 – 550 nm region, where the original material is transparent. The transient absorption spectra and kinetics are shown in figure 10 and 11 respectively. Nile Blue dye shows strong, induced transient absorption after the laser pulse excitation. The formation rate of this transient pulse duration is approximately equal to the pulse duration. This absorption band excitation in intensity to about 65% of its maximum value after 6 ps and then continues to decay with nanosecond rate. The nanosecond rate lifetime of the first electronic is excited state of the Nile Blue oxazine dye. The observed fast component of the decay kinetics may be attributed to the relaxation processes involving higher electron excited states of the dye molecule and solvent orientation. This data suggests that involvement of the high electron in excited states may play an important role in the optical limiting properties of this material.

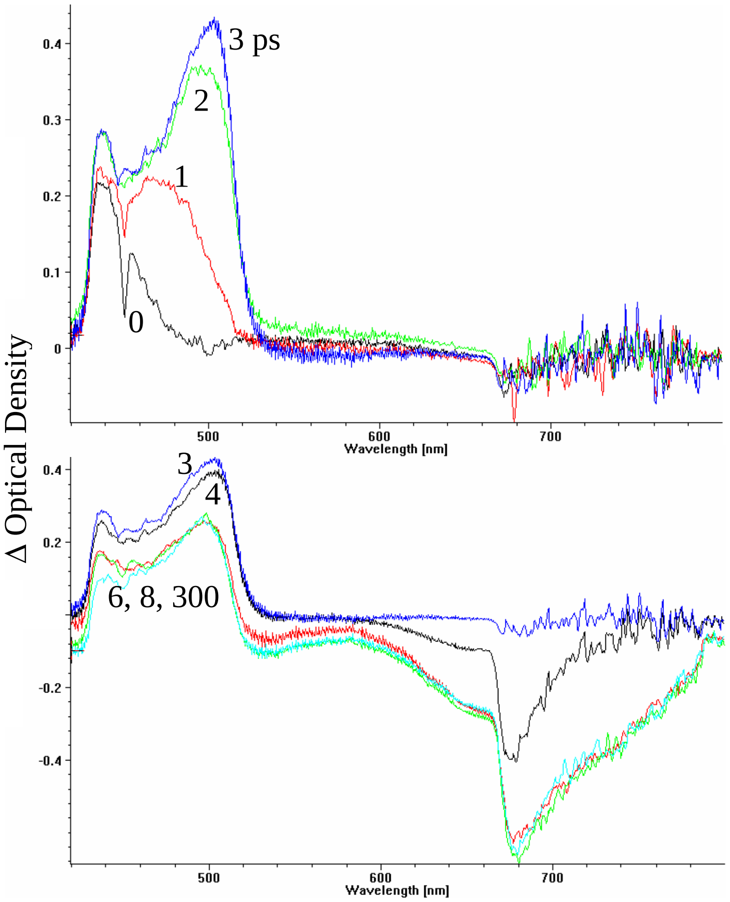


Figure 10. Transient absorption spectra of Nile Blue in ethanol.

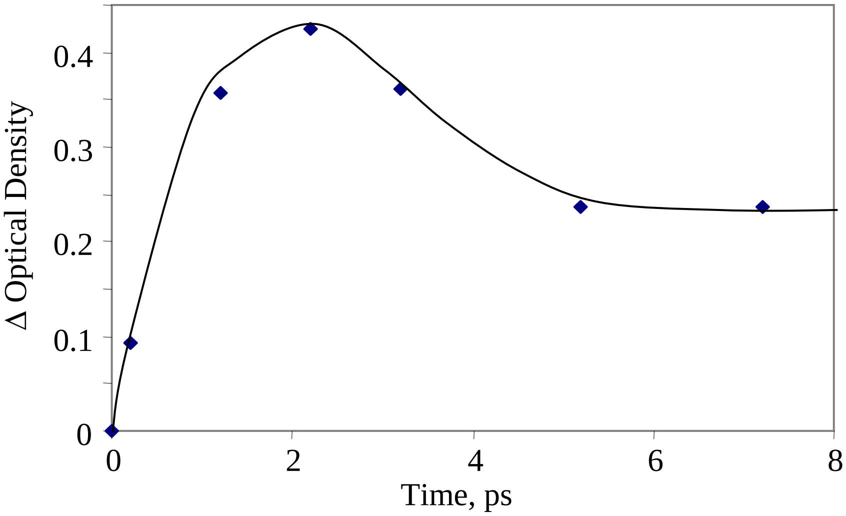


Figure 11. Transient absorption kinetics of Nile Blue in ethanol, λ = 500nm.

VII. Carbocynines

Carbocyanine dyes are probably best known for their use as saturable absorbers in mode-locked laser systems [1-6], because many of these dyes have strong saturable absorption bands attributed to the $S_0 \rightarrow S_1$ transition in the visible and infrared regions. These dyes can be also employed as active media in tunable dye lasers [7-10]. Because of these applications, the chemical and spectroscopic properties of the carbocyanine dyes have been thoroughly studied [11-16]. The main interest of these studies has been on the laser induced saturable absorption of the $S_0 \rightarrow S_1$ band, the lifetime of the S_1 state and fluorescence properties of the dyes. Our research data and those of Ref. 17-19 show that these dyes exhibit strong transient reverse saturable absorption (RSA) shifted to the blue of the $S_0 \rightarrow S_1$ absorption band. This RSA band was attributed to $S_1 \rightarrow S_n$ transient absorption. Recently, molecules with high RSA have been of great interest, because of their potential application in optical power limiting devices. RSA is considered to be one of the most promising mechanisms for optical limiting. For molecules exhibiting high RSA the excited state absorption, $S_1 \rightarrow S_n$ cross section, σ_{ex}, is much larger than σ_{gr} , the $S_0 \rightarrow S_1$ absorption cross section of the ground state. At low intensities the effective absorption, of a medium containing such molecules, is due to ground state absorption. If the medium is exposed to intense laser light, however, the population of the excited state becomes significant, resulting in a dramatic increase in the medium effective absorption, because of the additional $S_1 \rightarrow S_n$ absorption process. Utilizing these properties, it is possible to construct a device, composed of such molecules that is transparent at low light intensities, and becomes opaque at high intensities. In such a molecular system the higher the ratio of the excited to ground state cross sections σ_{ex}/σ_{gr} , the lower the threshold of the nonlinear absorption. However if there are fast processes that deplete the population of the first singlet excited state, S_1, the optical limiting process starts to saturate at a certain intensity, that at higher intensities results in increase in transmission. In the carbocyanine dye HITCI; for example, this effect was explained by the increase of the population of the second singlet state S_2 that has a lifetime comparable with the exciting laser pulse duration [20-21].

There are several classes of compounds that exhibit strong RSA in the visible region, including metallo-porphyrins [22], azulenes [23] and metallo-phthalocyanines [24-25]. Typical cross section ratios σ_{ex}/σ_{gr}, for these molecules, are between 10 and 20. However, recently strong optical limiting has been reported in several carbocyanine dyes [26], with the largest σ_{ex}/σ_{gr} ratio of 200, at 532 nm.

In this report we present the experimental results of our study of six carbocyanine dyes, 1,1′-diethyl-4,4′-carbocyanine iodide (DCI, also known as cryptocyanine), 1,1′-diethyl-2,2′-dicarbocyanine iodide (DDI), 3,3′-diethyl-2,2′-thiadicarbocyanine iodide (DTDCI), 3,3′-diethyl-2,2′-thiatricarbocyanine iodide (DTTCI), 3,3′-diethyl-2,2′-oxatricarbocyanine iodide (DOTCI), and 1,1',3,3,3',3'-hexamethyl-4,5,4',5'-dibenzoindodicarbocyanine (HDIDCI), studied both in solution and in uniformly dispersed polymer matrices, by means of picosecond transient absorption spectroscopy (TAS) and nonlinear transmission (NLT). Linear spectroscopy and kinetics of these dyes have been very well studied. To the best of our knowledge, however, none of these molecules have ever been considered or studied for optical limiting. Our ultrafast TAS experiments reveal that after excitation by a picosecond laser pulse all dyes studied developed a strong RSA band in the 450-600 nm region, attributed to the $S_1 \rightarrow S_n$ transition. In some of the molecules, the population rise time of this band was found to be dependent upon the excitation wavelength. When low energy photons were used for the excitation, the $S_1 \rightarrow S_n$ band appeared within the excitation pulse width. However, in case of high energy photon excitation the development of the $S_1 \rightarrow S_n$ band was slower than the duration of the excitation pulse. This can be explained by the relatively slow decay of one of the high-lying excited electronic states, most likely the S_2 state. Using the experimental data, we have calculated the absorption cross sections of the $S_1 \rightarrow S_n$ transition, and the lifetime of the S_2 state. The cross section ratios σ_{ex}/σ_{gr} were quite large for all of the dyes, with the value of 350 for DTDCI at 470 nm, which is the largest ever reported for a molecule in the visible region. The lifetime of the S_2 state was determined to be 4.3-17.5 ps for DTTCI, DOTCI and DTDCI molecules and less than the pulse duration (<1.4 ps) for DCI, DDI and HDIDCI dyes.

The optical limiting performance of the molecules in solution was also studied by means of picosecond NLT experiments at 527 nm. These experiments showed that these dyes have strong optical limiting. However, in all molecules except DCI a saturation of the optical limiting effect was observed, owing to the relatively long lifetime of the S_2 state. DCI exhibited the best optical limiting performance. For 55% transmitting sample at low intensities, the transmittance dropped to 5% at a 3 J/cm^2 peak fluence. The same optical limiting characteristics were measured when this dye was dispersed in a PHEMA and PMMA copolymer matrix.

VII-1. Ultrafast transient absorption experimental system

The picosecond TAS system used for these experiments has been described elsewhere [23], therefore only a brief description of the system is given here. We employed a picosecond laser system that consists of a mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics) coupled to a regenerative amplifier (Spitfire, Spectra-Physics). The laser system emitted 1.4 ps (FWHM), 798 nm and 700 μJ pulses at 1–0.1 kHz adjustable repetition rate. The output beam was frequency doubled by means of a BBO crystal to 399 nm. The 399 nm beam was separated from the fundamental by a dichroic beam splitter and used for excitation. With this experimental system absorbance changes as small as 5×10^{-3} were resolved. For some of the measurements we employed the fundamental beam for sample excitation instead of the second harmonic. In these experiments we removed the second harmonic BBO crystal and changed the dichroic beam splitter to a 50%, 800 nm dielectric beam splitter. All carbocyanine molecules were Aldrich 98-99% purity and were used without further purification unless stated otherwise. For solvents we used absolute ethanol and HPLC grade methanol and acetonitrile.

VII-2. Nonlinear transmission experimental system

For NLT measurements a cw mode locked Nd: YLF laser coupled to regenerative amplifier was employed. In the experiments described in this paper only the second harmonic, 527 nm, 35 ps (FWHM) pulses were used. A half wave plate, a polarizer and various neutral density filters, adjusted the intensity of the second harmonic. After passing a spatial filter the beam was focused by a 150 mm lens inside a 1 mm quartz cell containing the sample solution. The distribution of the beam before the lens was found to be very close to Gaussian. The size of the spot inside the cell was estimated to be 24 μm (FWHM). The energy of the pulse before and after the sample was monitored by two calibrated photodiodes. Before entering the experimental system, a small part of the beam was separated from the main beam by a glass plate and focused into the first photodiode, which produced a signal proportional to the input pulse energy. The laser beam transmitted by the sample, after passing through a 527 nm interference filter and several optical neutral density filters, was focused onto the second photodiode, which measured the energy of the transmitted pulse. In order to eliminate heating effects, we used single pulse measurements for these NLT experiments. The single pulses were separated from the train by means of a mechanical shutter placed in front of the sample. After each single pulse measurement the sample was moved such that each pulse excited a fresh sample. Usually, we averaged 20 pulses for each measurement. For the NLT experiments we used a 10^{-4}–10 J/cm^2 fluence range.

VII-3. Picosecond transient absorption spectroscopy

It has been emphasized in the introduction, that there have been numerous studies concerned with the spectroscopic properties of carbocyanine dyes. For example, the lifetimes of the S_1 level are well documented for all molecules considered in this paper except HDIDCI and DOTCI. These lifetimes along with other spectroscopic properties of the molecules can be found in Table 1.

Table 1. Spectroscopic properties of carbocyanine molecules in ethanol.

Dye	λ_{gr}, nm	σ_{gr}, 10^{-16} cm^2	λ_{ex}, nm	σ_{ex}, 10^{-16} cm^2	σ_{ex}/σ_{gr} at λ_{ex}	τ_2, ps		τ_1, ns
						this paper	Ref.31	
DCI	709	8.60	550	2.1±0.2	51±5	<1.4	n/a	0.075 [a]
DDI	711	8.79	540	4.0±0.5	42±5	<1.4	n/a	0.027 [a]
DTDCI	655	8.52	490	4.7±0.5	152±16	17.5±0.6	18.9±1.1	0.73 [b]
DTTCI	763	8.03	531	8.2±0.7	157±14	4.3±0.4	12.3±1.4	1.28 [b]
DOTCI	687	7.91	490	2.8±0.4	79±11	7.6±0.3	16.2±0.5	n/a
HDIDCI	679	7.27	534	2.9±0.4	23±3	<1.4	n/a	n/a

λ_{gr} – $S_0 \rightarrow S_1$ band maximum absorption wavelength; σ_{gr} – absorption cross section of the $S_0 \rightarrow S_1$ band measured at λ_{gr}; λ_{ex} – $S_1 \rightarrow S_n$ transient band maximum absorption wavelength, σ_{ex} – absorption cross section of the $S_1 \rightarrow S_n$ band measured at λ_{ex}; σ_{ex}/σ_{gr} – excited to ground state absorption cross section ratio measured at λ_{ex}; τ_1 – S_1 state decay time; τ_2 – S_2 state decay time.

[a] Ref. 13.

[b] Ref. 16.

n/a: data not available.

However, there are only few papers published concerning the $S_1 \rightarrow S_n$ RSA band in these dyes [17-19]. In fact, to the best of our knowledge, the $S_1 \rightarrow S_n$ transition cross sections of only DCI and DOTCI molecules have been previously measured [15, 18]. All carbocyanine molecules reported in this paper, have a very strong absorption band in the near infrared region of their ground state electronic spectra (the band maximum cross sections are in the rang of 7.3-8.5x10^{-16} cm^2, see Table 1). This band is attributed to the $S_0 \rightarrow S_1$ transition. The second absorption band, that corresponds to the $S_0 \rightarrow S_2$ transition, is much weaker and is strongly shifted towards the ultraviolet from the $S_0 \rightarrow S_1$ band, forming a wide very low, almost negligible absorption band in the visible part of the spectrum. According to Ref. 17-19, excitation of the carbocyanine molecule by a laser pulse results in formation of a new transient RSA band located in this low ground state absorption spectral window. Therefore we may expect to have very large σ_{ex}/σ_{gr} cross section rations in this region of the spectrum. Taking this into account we employed picosecond TAS for the measurement of the excited state cross sections and the early time kinetics of the carbocyanine molecules.

All molecules studied exhibit the same kinetics after excitation with a picosecond pulse. Therefore, we will only discuss the kinetics of DTTCI molecule dissolved in ethanol, as a representative example. The transient spectra that we measured showed the bleaching of the $S_0 \rightarrow S_1$ band and the appearance of a new transient absorption band, that represents the $S_1 \rightarrow S_n$ transition, with maximum absorption at 531 nm. The initial 15 ps kinetics of the excited DTTCI is shown in Fig.12. We used both the fundamental and the second harmonics for excitation. In both experiments bleaching of the $S_0 \rightarrow S_1$ band is formed within the 1.4 ps excitation pulse. Open circles, in Fig. 12, represent the kinetics of bleaching, after excitation with the 399 nm second harmonic pulse, measured at the maximum of the $S_0 \rightarrow S_1$ band. The formation of the $S_1 \rightarrow S_n$ absorption band was found to be dependent upon the excitation wavelength. If the fundamental 798 nm pumping pulse is used, the $S_1 \rightarrow S_n$ transient absorption band and the $S_0 \rightarrow S_1$ band bleaching appear within the excitation pulse. However, if excitation with the second harmonic 399 nm pulse is used, the formation rate of the $S_1 \rightarrow S_n$ band is slower than the rate measured with the fundamental pumping. The rise time of the formation of this band was measured to be 4.3±0.4 ps. Solid squares and stars, in Fig. 12, represent the kinetics of the $S_1 \rightarrow S_n$ band formation after excitation with the fundamental and second harmonics respectively. It is worth noting that no change in the shape of the $S_1 \rightarrow S_n$ absorption band was observed during its formation, therefore the processes, such as the interband electron relaxation and solvent orientation, are faster than the 1.4 ps resolution of the system. The observed kinetics can be accurately explained by a simple 3 band model (Fig. 13). When pumped by a fundamental 798 nm pulse, molecules are excited directly only onto the first singlet S_1 electronic band. Therefore we observed simultaneous bleaching of the ground state $S_0 \rightarrow S_1$ absorption band and the formation of the $S_1 \rightarrow S_n$ transient absorption band. However, if second harmonic pumping is used, molecules are excited to the second S_2-singlet excited state, which decays to the S_1 state with a 4.3±0.4 ps lifetime. In this case we observe bleaching of the $S_0 \rightarrow S_1$ band with a rising time equal to the 1.4 ps excitation pulse width and the $S_1 \rightarrow S_n$ absorption band growth with a 4.3 ps rate.

All other molecules studied showed the same kinetics with, a variation in the lifetimes of the S_2 state (see Table 1 for details). In DCI, DDI and HDIDCI molecules, the formation times of the $S_1 \rightarrow S_n$ absorption band were the same as the excitation pulse rise time even if the second harmonic excitation was used. Therefore the lifetimes of the S_2 states in these molecules must be shorter than the 1.4 ps resolution time of our experimental system. The fact that the carbocyanine molecules, considered in this paper, have the unusually long S_2 lifetime is also supported by their anomalous blue fluorescence observed by us and other researchers [17, 27-31]. In fact, the lifetimes of the S_2 states in DTDCI, DTTCI, DOTCI and several other related dyes have been recently measured by time-resolved fluorescence single-photon counting [31] (see Table 1). The S_2 lifetime of DTDCI molecule measured by us agrees very well with the lifetime reported in Ref. 31,

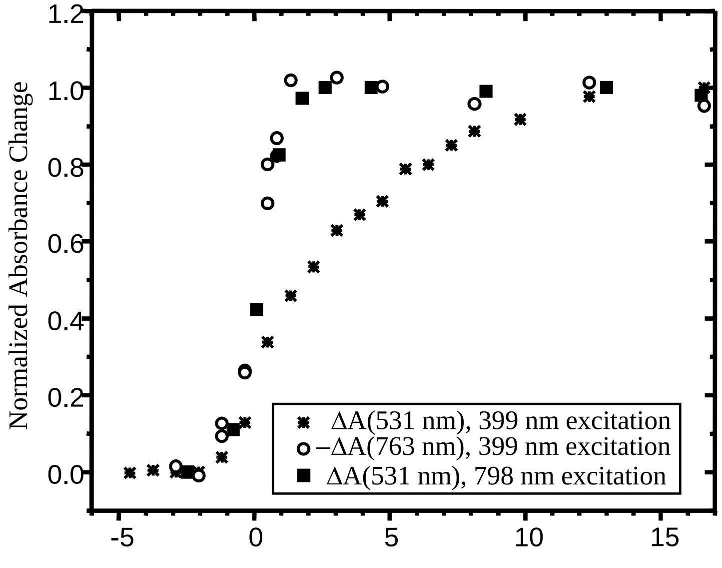


Fig. 12 . DTTCI Kinetics

while for DTTCI and DOTCI we have measured somewhat shorter lifetime values. We believe that our measurements are more reliable because we used 1.4 ps (FWHM) excitation pulses, which were much shorter than the measured lifetimes. This was not the case in the experiments described in Ref. 31, the 50 ps (FWHM) excitation pulses were used to extrapolate to ~15 ps lifetimes

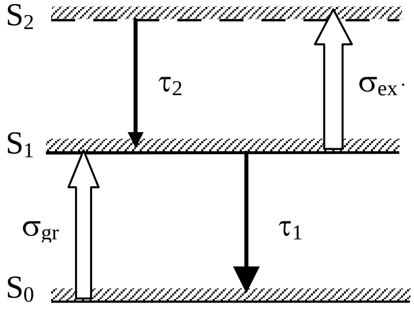


Fig. 13. Schematic energy diagram of DTTCI/ethanol solution.

Although the anomalous blue fluorescence emitted by the molecules studied, in this paper, has been observed previously, to the best of our knowledge, the blue fluorescence quantum yield in only DCI has been reported. Using a conventional spectrofluorophotometer (Shimadzu RF5000U) we recorded the blue fluorescence spectra from all molecules dissolved in methanol and acetonitrile except DDI. In addition we have measured the blue fluorescence in DODCI/methanol solution, the quantum yield of which is known [30, 31], and coumarin 151/acetonitrile (Φ_{fl}=0.92 [32]) and Dimethyl-POPOP/cyclohexane (Φ_{fl}=0.93 [33]), which were used as the standards. We found that the fluorescence spectrum shape was independent of the excitation wavelength and that the fluorescence excitation spectrum coincided with the absorption spectrum in all carbocyanine molecules except HDIDCI. Therefore the observed blue fluorescence in these molecules is not induced by impurities, while in HDIDCI it most likely is due to impurities. In order to prove this we have recrystallized HDIDCI and DODCI in methanol. The intensity of the blue fluorescence of a recrystallized HDIDCI sample was 3 times less than the intensity of the original, non-recrystallized, sample fluorescence at the same concentration and conditions, while the DODCI blue fluorescence intensity remained the same. These experiments show that the observed blue fluorescence in the HDIDCI solution is emitted by impurities rather than by HDIDCI molecules. The blue fluorescence in DODCI and most likely in all other dyes studied may be attributed to the dye molecules. It is reasonable to assume that the origin of the blue fluorescence in carbocyanine dyes is the second singlet excited state S_2 of these dyes [17, 27-31]. Table 2 summarizes the calculated absolute fluorescence quantum yields, Φ_{fl}. The maximum quantum yield of $6.9\text{x}10^{-4}$ was determined for DODCI/methanol solution. This value is lower by a factor of two than the quantum yield of $14.4\text{x}10^{-4}$ in the same sample calculated from the data reported in Refs. 30-31 (For these calculations we used the absolute blue fluorescence quantum yield in DODCI/ethanol solution [31] and the relative quantum yield of the same dye dissolved in methanol [30].) This discrepancy maybe due to the prolong purification of our sample. In DCI/methanol solution we obtained $\Phi_{fl}=1.4\text{x}10^{-4}$, which is in close agreement with the previously measured value of $0.9\text{x}10^{-4}$ in DCI/ethanol [29]. Table 2 also includes the natural lifetimes $\tau_n=\tau_2/\Phi_{fl}$ calculated from the S_2 state decay time τ_2 measured by picosecond TAS and the fluorescence quantum yields Φ_{fl} in methanol. The calculated τ_n values vary from 17 to 60 ns. Note, that τ_2 and Φ_{fl} were measured in two different solvents: ethanol and methanol respectively. However, because these solvents are very similar we expect the error in τ_n to be rather small.

Table 2. Anomalous fluorescence properties of carbocyanine dyes.

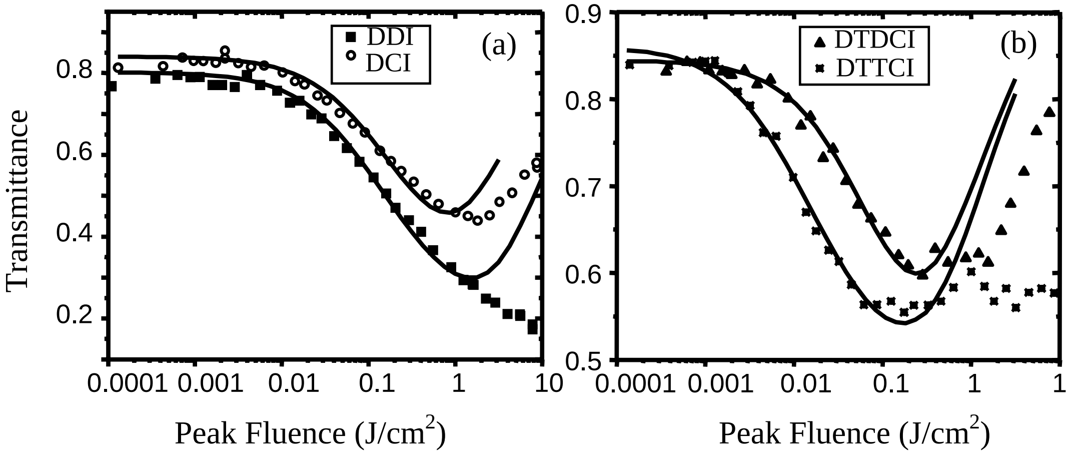
Dye	λ_{fl}, nm (in MeOH)	Φ_{fl}, x10^{-4}		τ_n, ns (in MeOH)
		in ACN	in MeOH	
DCI	460	1.4	1.4	n/a
DTDCI	435	1.9	2.9	60.3
DTTCI	495	1.0	0.9	47.8
DODCI	390	n/a	6.9	n/a
DOTCI	450	2.7	4.5	16.9

λ_{fl} – S_2 state maximum fluorescence wavelength; Φ_{fl} – S_2 state fluorescence quantum yield; τ_n – natural lifetime; MeOH – methanol; ACN – acetonitrile.
n/a: data not available

We have also measured the cross sections of the $S_1 \rightarrow S_n$ transition. In order to perform these measurements, the system was calibrated with a chloranil/acetonitrile solution, the transient cross section of which is well known [34-35]. The cross sections measured at the maximum absorption of the $S_1 \rightarrow S_n$ band, for the molecules studied, in addition to the kinetics and spectroscopic data are listed in Table 1. The $S_1 \rightarrow S_n$ transition cross sections vary from 2.1±0.2x10^{-16} cm^2 for DDI molecule to 8.2±0.7x10^{-16} cm^2 for DTTCI. The latter has one of the largest excited state cross sections ever reported, it is equal, within experimental error, to the cross section of the ground state spectrum measured at the maximum of the $S_0 \rightarrow S_1$ band, which is also considered to be very large even for a ground cross section. To the best of our knowledge, the RSA cross sections of only two of the molecules (DCI and DOTCI) studied here have been reported before. Galanin and Chizhikova [18] have reported the cross section value of ~1.5x10^{-16} cm^2 at 550 nm for DCI molecule in ethanol solution, which is in fair agreement with 2.1±0.2x10^{-16} cm^2 measured by us. The cross section of 0.619x10^{-16} cm^2 at 532 nm obtained for DOTCI/ethanol solution, by the intensity dependent photoquenching technique [15], disagrees with the 1.9±0.3x10^{-16} cm^2 measured by us. We believe, however, that the method we employed for the determination of the cross section is more reliable than the one used in Ref. 15. The highest excited to ground state cross section ratios σ_{ex}/σ_{gr} measured at the RSA band maximum were found in DTDCI and DTTCI molecules, they equal to 152±16 at 490 nm and 157±14 at 531 nm respectively. Although these values are considered to be quite high, even higher cross section ratios can be found at the off-maximum wavelengths. For example, σ_{ex}/σ_{gr} is equal to 234 at 480 nm (σ_{ex}=4.4±0.5x10^{-16} cm^2) and to 350 at 470 nm (σ_{ex}=3.8±0.4x10^{-16} cm^2) in DTDCI molecules, which are the highest cross section ratios ever reported.

VII-4. Nonlinear transmission:

In order to measure the optical limiting effect in the carbocyanine molecules studied, we have performed NLT experiments with 35 ps (FWHM) 527 nm single laser pulses. For ethanol



solutions in a 1 mm optical path length cell the dye concentration was adjusted to 80-85% transmittance at low 527 nm intensities. The dependence of the transmittance, T, on the laser excitation pulse peak fluence is shown in Fig.14. All of the molecules showed optical limiting behavior, namely decrease in transmittance with increase in the input laser pulse fluence. However, in all molecules, except DCI, a saturation of the optical limiting effect was observed at the peak fluences of 0.07-1 J/cm^2, with subsequent increase in transmittance at higher fluences. The same behavior was also reported in HITCI carbocyanine molecule [20], the chemical structure of which is very close to that of the molecules reported in this paper. It was assumed that the high population of the long lived S2 singlet state caused the saturation effect. This assumption was also supported by cross-polarized time-resolved excitation-probe measurements [21].

Fig. 14. Transmittance vs. input peak fluence for a) DCI and DDI, b) DTDCI and DTTCI, c) DOTCI and HDIDCI dissolved in ethanol.

In order to obtain the physical parameters of these molecules from the experimental data, we have calculated the propagation of a laser pulse through the sample numerically. Assuming a three level model (Fig. 13) we can write the following rate equations:

$$dN_0/dt = -N_0\sigma_{gr}(I/h\nu) + N_1/\tau_1\,, \tag{1}$$
$$dN_1/dt = N_0\sigma_{gr}(I/h\nu) - N_1/\tau_1 - N_1\sigma_{ex}(I/h\nu) + N_2/\tau_2\,, \tag{2}$$
$$dN_2/dt = N_1\sigma_{ex}(I/h\nu) - N_2/\tau_2\,, \tag{3}$$
$$dI/dt = -I(N_0\sigma_{gr} + N_1\sigma_{ex})\,, \tag{4}$$

Where N_i is the population of the S_i state (i = 0, 1, 2); σ_{gr} and σ_{ex} are the cross sections of the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transitions respectively; I is the irradiance; $h\nu$ is the photon energy; τ_i is the lifetime of the S_i state. These rate equations were solved numerically using the computational technique introduced by Hughes [36], which overcomes the "stiffness" problem for high irradiances with a major speed-up in computation time in comparison to traditional numerical methods. Using this technique in conjunction with nonlinear fitting we obtained the transmittance curves depicted in solid lines in Fig. 14. In these calculations, for the S_1 state lifetimes, τ_1, for DCI, DDI, DTDCI and DTTCI molecules, we used the literature accepted values listed in Table 1. Because τ_1 are not available for DOTCI and HDIDCI, we have used the value of τ_1=1.5 ns. Even though the correct values for τ_1 in these molecules may be quite different, the choice of τ_1 will not alter the calculations, even if τ_1 is much longer than the 35 ps laser pulse duration. This condition was checked experimentally during the ultrafast TAS experiments (see the previous section). We did not observe any decay of the $S_1 \rightarrow S_2$ transient absorption band in DOTCI and HDIDCI molecules between 0-200 ps delays used, therefore τ_1 is longer than hundreds of picoseconds. We would like to note that only experimental data for fluences below 1 J/cm^2 were used for fitting, because it was not possible to get acceptable fitting at higher intensities. The poor fitting of the model calculations and the experimental data at fluences higher than 1 J/cm^2, most likely, indicates the presence of other nonlinear effects such as self-focusing, self-phase modulation, Raman scattering, stimulated emission etc., which may alter the transmittance at these fluences. This conclusion is also supported by the recent study of the application of the NLT method to two-photon absorption cross section measurements, which demonstrated that without consideration of other nonlinear effects this method might result in erroneous data [37]. Table 3 compares the parameters of the molecules obtained from fitting with the ones measured by TAS experiments, described in the previous section.

Table 3. Excited state to ground state absorption cross section ratios σ_{ex}/σ_{gr}, at 527 nm, and lifetimes of the S_2 state τ_2 of carbocyanine molecules in ethanol measured by ps TAS and NLT methods.

Dye	σ_{ex}/σ_{gr}		τ_2, ps	
	TAS	NLT	TAS	NLT
DCI	93±10	75.4±7.7	<1.4	2.8±0.4
DDI	67±8	24.1±2.5	<1.4	1.7±0.3
DTDCI	10.8±1.1	9.0±0.8	17.5±0.6	2.2±0.3
DTTCI	163±15	168±21	4.3±0.4	7.9±0.6
DOTCI	15.0±2.2	16.3±2.1	7.6±0.3	4.5±0.6
HDIDCI	29±4	30.8±2.9	<1.4	1.6±0.2

According to Table 3, the excited to ground state cross section ratios σ_{ex}/σ_{gr} measured by NLT agreed very well with the ones obtained by TAS for all molecules except DDI, for which this ratio is approximately two times lower. We have only qualitative agreement for the S_2 state decay times τ_2 in DDI, DTTCI, DITCI and HDIDCI, and considerable deviation in τ_2 for DCI and DTDCI. Since the term N_2/τ_2 in Eqs. (2)-(3), that is responsible for the decay of the S_2 state, contributes to the sample transmittance only at relatively high fluences, the poor correlation of the τ_2 values obtained by NLT and TAS, is probably also due to the contribution of other nonlinear effects competing with RSA. We believe that TAS, under our experimental conditions, provides much more reliable data than NLT, because our fluences and sample concentrations were much lower and thus the nonlinear processes mentioned above were much weaker.

Fig. 14 shows that the strongest optical limiting effect was observed in DCI/ethanol solution. Although this molecule does not have the highest excited to ground states cross section ratio, σ_{ex}/σ_{gr}=93 at 527 nm, the relaxation of the S_2 state into the S_1 state is very fast (τ_2 < 1.4 ps). Therefore, no saturation of the transmittance was observed at the fluences used in these experiments. The original transmittance of ~80% at low fluences dropped to ~18% when the fluence became 10 J/cm^2, the maximum fluence used. Since practical optical limiting devices would most likely be solid, we prepared solid plastic samples uniformly dispersed with DCI. The NLT experiment for these solid samples showed the same optical limiting characteristics as exhibited by the liquid samples. The dependence of the transmittance on the input peak fluence, in 0.7 mm copolymer (PHEMA and PMMA) film containing DCI, is shown in Fig. 15.

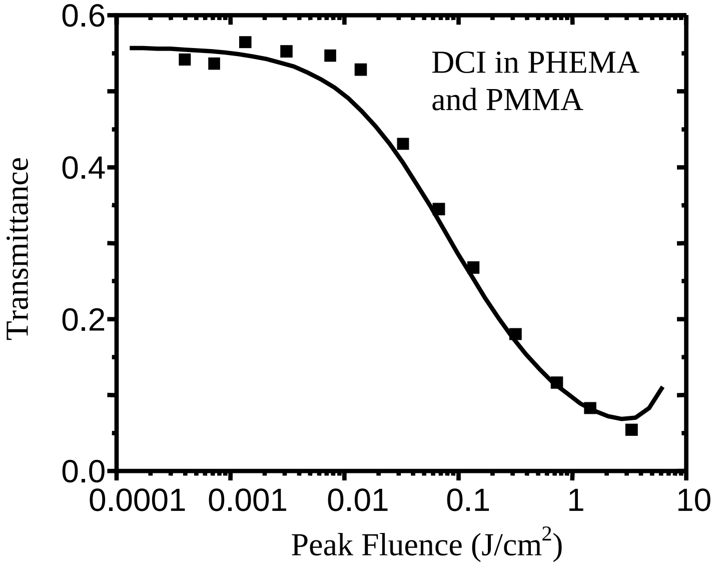


Fig. 15. Transmittance vs. input peak fluence for DCI embedded in copolymer PHEMA and PMMA.

At low fluences the sample has a ~55% transmittance, which drops to ~5% when the 3 J/cm^2 fluence is used. The theoretical curve, shown as a solid line in Fig. 15, calculated by employing the same parameters used for the liquid sample, agrees very well with the experimental data. All polymer/dye experiments were performed immediately after the preparation of the sample. The spectrum of the DCI dye imbedded in polymer was found to be very similar to the spectrum of DCI/ethanol solution. However, a substantial increase in linear absorption in the vicinity of 527 nm was observed a few days after the sample was prepared, even though the sample was kept in the dark. The cause of this absorption increase is not completely known, and we intend to study this effect in the near future.

VIII. Facilities

A new subpicosecond, 100 fs laser facility has been built which allows us the study liquid or solid materials from CW to 100x10^{-15} seconds.

IX. Conclusion:

We have studied the nonlinear absorption and ultrafast kinetics, of several azulenes and laser radiation resistance dyes dissolved in organic solvents and also dispersed in polymer matrices, by means of ultrafast transient absorption and non-linear transmission. All dyes exhibit strong RSA in the 450-600 nm region with very large excited to ground state absorption cross section ratios. One of them was found to have a ratio of 350 which is the largest ever reported. In DTDCI, DTTCI and DOTCI anomalously long, 4.3-17.5 ps, S_2 decay lifetimes were observed. All molecules have shown strong optical limiting properties. As expected, because of the considerably long S_2 state lifetime, a saturation of the optical limiting effect was observed in all molecules except DCI, whose lifetime was shorter than 1.4 ps. The fluorescence quantum yields of the S_2 state were also measured in all molecules, several of these materials are studied further, in the solid state in order to understand their relevant properties in the solid state. These studies are of paramount importance for their application in optical limiting devices.

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Facilities

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Non-Linear Optics and Applications to Computer Storage and Optical Limiters. CSU- Fullerton, 2002

Non-Linear Processes and Devices, Tokyo, Japan 2002

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Alexander Dvornikov, Ph.D., part-time assistant researcher
Yongchao Liang, Ph.D. student, degree awarded
Dmitri A. Oulianov, Ph.D. student, degree awarded
Peter M. Rentzepis, Professor/Principal Investigator

Recognitions:

ACS Tolman Award (P. M. Rentzepis)
The Glen Seaborg National Fellowship (D. Oulianov)

Degrees awarded.

Dmitri A. Oulianov Ph.D.
Yongchao Liang Ph.D.

Patents:

No Patents were applied for during this period.

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