# Nonlinear Optics
### of
# Organic Molecules
### and Polymers



Edited by

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*Chapter 14*

# Application of Nonlinear Optics to Passive Optical Limiting

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## CONTENTS

## I. INTRODUCTION

The nonlinear optical (NLO) properties of materials can be used to reduce significantly the transmittance of a device for high inputs. Such a device is called an optical limiter (sometimes referred to as an optical power limiter, OPL). For many applications, including protection of optical sensors from laser-induced damage (LID), it is desirable for an optical limiter to have high linear transmittance. The output of what is often referred to as an ideal optical limiter is shown in Figure 1. The limiter has a high linear transmittance, a variable and potentially low limiting threshold (the input corresponding to the breakpoint in the curve), a fast reponse (e.g., picoseconds or faster), a broadband response (e.g., the entire visible spectrum), and a large dynamic range defined as the ratio of the linear transmittance to the transmittance at the highest possible input (often $10^4$ or greater is desired for sensor protection). In most cases, the limiting does not occur with a sharp threshold as indicated by Figure 1, but changes from high to low transmittance gradually. Some applications need the material to be in thin film form. The best known optical limiting materials are photochromics used in sunglasses which darken in sunlight. This nonlinearity is often due to a chemical reaction induced by light (sometimes in organic dyes) which recovers in the dark due to thermal effects. These materials satisfy many of the criteria mentioned above except they are too slow in response and recovery time for most applications. We concentrate here on nonlinear properties useful for limiting of picosecond to microsecond pulses.

Very little progress has been made at developing such optical limiters in thin film form to limit nanosecond or shorter pulses without an optical system to concentrate the light into the nonlinear material. However, significant progress has been made for applications where the nonlinear optical material can be placed at or near a focal plane. The irradiance or fluence (energy per unit area) at the focal plane can be high enough to give sufficient nonlinear absorption (NLA), nonlinear refraction
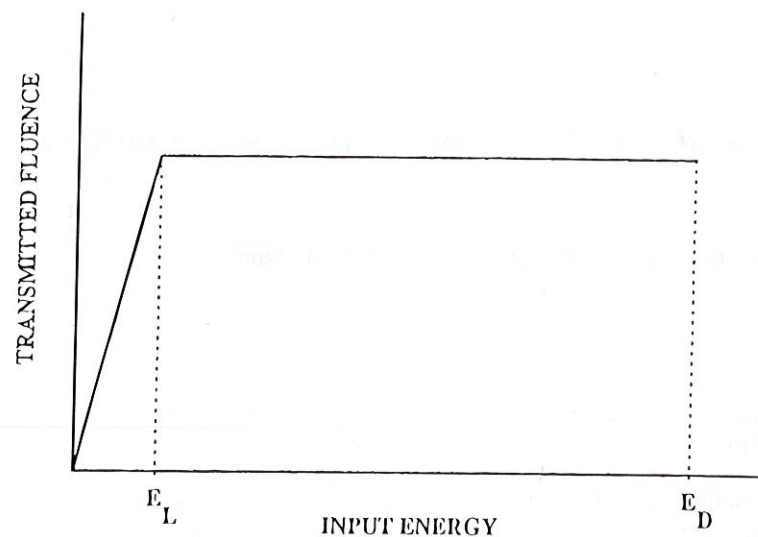
**Figure 1** The output energy, power, or fluence of an ideal optical limiting device as a function of the input energy, power, or fluence. $E_L$ is the energy at which limiting begins and $E_D$ is the energy at which the limiting device damages.

In this chapter we discuss the increasing use of NLO organic materials and carbon derivatives for such sensor protection applications. We begin in Section II with a brief discussion of previous optical limiting research as well as a general overview of the useful nonlinear mechanisms. In Section III we describe some of the physical processes available for limiting with organics. In Section IV we look at the use of materials displaying the ultrafast bound-electronic nonlinearities of two-photon absorption (2PA) of coefficient $\beta$, and nonlinear refraction of coefficient $n_2$. We then discuss in Section V reverse saturable absorbing (RSA) materials which are currently under intensive experimental investigation. These materials are discussed in detail by Perry in Chapter 13. Limiting in liquid crystals is briefly discussed in Section VI and pure carbon compounds, carbon black suspensions, and fullerenes are overviewed in Section VII. We also briefly examine the optical geometry of optical limiting devices used to optimize the dynamic range. Section VIII looks at thick limiters and Section IX shows how tandem limiters can extend the dynamic range of devices. Overall conclusions are given in Section X.

## II. BACKGROUND

We will not give a complete history of optical limiting research, but mention a few experiments, devices, or materials that exemplify the uses and potential uses of organic materials for optical limiting. The first limiter was based on thermal lensing in nitrobenzene. Leite et al.[1] demonstrated a device that used thermal blooming in this liquid which after spatial filtering regulated the output power of a cw Ar+ laser. The principle of this limiting process is shown in Figure 2. In 1983, CS₂ was tested as a limiting
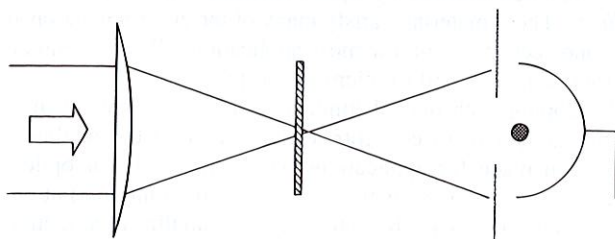


**Figure 2** A schematic of a typical optical

medium for nanosecond pulses.[2] These experiments, using a focused geometry similar to that of Leite et al., showed that the mechanisms that limit the transmission of this device are catastrophic self-focusing, along with absorption and scattering associated with the resulting laser-induced breakdown plasma. The response time of the reorientational nonlinearity responsible for the self-focusing is extremely broadband and has a 2 ps relaxation time.[3] $CS_2$ meets most of the requirements for a useful optical limiting material; however, the critical power ($\approx 8$ kW in the visible) is too high for most applications. Liquid crystals can have refractive nonlinearities orders of magnitude higher than that of $CS_2$, but the response times are correspondingly slower, usually nanoseconds or longer.[4] Some of the largest nonlinearities exhibited to date are in semiconductors.[5] Unfortunately, these extremely large nonlinearities are associated with near band-gap resonance and are maximized in a region of relatively high linear absorption. In addition, solids undergo irreversible optical damage. Even so, effective limiting has been demonstrated in semiconductors using other mechanisms. In 1969 Geusic et al.[6] reported limiting in Si that was attributed to stepwise nonlinear absorption with 1.06 μm radiation. More recently, two-step absorption processes in GaP have been used to produce low threshold limiters.[7] Boggess et al.[8] demonstrated fluence limiting in Si that was due to a combination of two-step nonlinear absorption with a refractive contribution induced by the photoexcitation of free carriers. Power-limiting experiments were conducted by Ralston and Chang[9] in a series of semiconductors such as CdS, GaAs, and CdSe. This was the first reported use of two-photon absorption (2PA), an Im$\{\chi^{(3)}\}$ process, for optical limiting. $\chi^{(3)}$ is the third-order nonlinear optical susceptibility which in this chapter we only use to describe ultrafast responses. Boggess et al.[10] were the first to use the combined effects of 2PA and carrier defocusing to obtain optical limiting. The geometry used was to focus picosecond 1.06-μm pulses onto the surface of a thin sample of GaAs and monitor the fluence by measuring the transmittance of an aperture in an arrangement similar to that shown in Figure 2 except a second collecting lens was inserted prior to the aperture. Such experiments showed that limiting depended on the position of the sample with respect to focus as shown by Miller et al.[1] which eventually led to the development of the Z-scan by Sheik-Bahae et al.[12,13]. Since for thin samples the damage-prone surfaces are subjected to the maximum fluence of the input pulses, the range over which these devices function without incurring damage is low. In 1988, Van Stryland et al.[14,15] demonstrated that if samples of optical thickness much greater than the Rayleigh range are used, the large nonlinearities of the semiconductor can actually be used to self-protect the limiting device from damage. For example, at high inputs, the 2PA-induced carrier self-defocusing occurring prior to focus keeps the fluence below the damage threshold. All these different nonlinearities observed in semiconductors and used for optical limiting have now been observed in organics.[16,17]

In particular very large 2PA coefficients have been reported in polydiacetylenes. For example, Lawrence et al.[1] measured the 2PA spectrum of polydiacetylene paratoluene-sulfonate (PTS) using Z-scan and found a peak near $2\hbar\omega = 2.7$ eV of $\beta \approx 700$ cm/GW. The potential of such materials for sensor protection applications relies on improving their linear transmissive properties, i.e., low linear absorption, low scattering loss, and good index homogeneity. Besides large 2PA which blocks the energy transmission, self-lensing nonlinearities can effectively reduce the fluence transmission in an image plane. If the lensing is due to bound-electronic effects, the response is ultrafast, described by Re$\{\chi^{(3)}\}$, and the index change characterized by $n_2$. At a fixed wavelength in a material it is often the case that both 2PA and $n_2$ effects are present. In fact these nonlinearities are related by causality in a manner analogous to the Kramers-Kronig relations relating the linear index to linear absorption.[19–22] The combination of these nonlinearities can be an effective approach to both reduce the energy transmittance and spread the beam of short pulses at an image plane.[14,15] In addition, 2PA often leads to excited states that can themselves linearly absorb light.[16] This is also usually accompanied by refractive index changes.[17] These nonlinearities are further discussed in Section IV on ultrafast nonlinearities.

Such excited states can also be created by linear absorption which *requires* that the optical limiter have linear loss; however, this type of nonlinearity in organics is one of the most promising for applications in sensor protection. This so-called reverse saturable absorption (RSA) is discussed in Section V.

In principle, 2PA-based limiters and or ultrafast nonlinear refraction ($n_2$)-based limiters offer the

detector damage. Thus the nonlinearity is cumulative, getting larger as the pulse width increases for a fixed irradiance, i.e., longer pulses are effectively limited. These RSA materials are discussed in detail in Chapter 13.

In the next section we discuss these physical processes and their characterization.

## III. PHYSICAL PROCESSES

Researchers often define a change in absorption as $\alpha_2 I$ (or $\beta I$) and a change in index as $n_2 I$ and then quote experimental values of $\alpha_2$ and $n_2$. The numbers quoted can be misleading unless a clear explanation of the underlying physical mechanisms leading to these changes is given. As examples we further examine two-photon absorption (2PA), excited-state absorption (ESA), and thermal refraction, and we discuss how to describe these nonlinearities.

As defined in most nonlinear optics texts the total material polarization, $P$, that drives the wave equation for the electric field, $E$, is (ignoring nonlocality)

$$P(t) = \epsilon_0 \int_{-\infty}^{\infty} \chi^{(1)}(t - t_1)E(t_1)\, dt_1 + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}(t - t_1, t - t_2)E(t_1)E(t_2)\, dt_1\, dt_2$$

$$+ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(3)}(t - t_1, t - t_2, t - t_3)E(t_1)E(t_2)E(t_3)\, dt_1\, dt_2\, dt_3 + \ldots , \tag{1}$$

where $\chi^{(n)}$ is defined as the $n$th order time-dependent response function or time-dependent susceptibility. Thus the nonlinear polarization is electric field dependent. As an example, for harmonic generation (second harmonic from $\chi^{(2)}$ of third from $\chi^{(3)}$ the nonlinearity by necessity follows the field. The only material response capable of this is the bound-electronic response, i.e., the so-called "instantaneous" response.

The 2PA coefficient $\beta$ arises from the imaginary part of the ultrafast third-order nonlinear susceptibility, $\chi^{(3)}$. Similarly the bound-electronic $n_2$ comes from the real part of this susceptibility. We note here that in the literature $n_2$ is used to discuss everything from thermal and reorientational (e.g., for $CS_2$), to changes in index from saturation of absorption to ultrafast $\chi^{(3)}$ nonlinearities. Here we use $n_2$ only to describe the ultrafast index change.

For the bound-electronic response, two optical pulses with the same electric field but different pulsewidths result in the same polarization. This statement is also approximately true if the pulse widths of both pulses are much longer than the material response time contained in the susceptibilities in Equation 1. However, the integrals allow for memory. Thus slower responding materials can have their nonlinear response build up with time. For example, in $CS_2$, the molecules can be reoriented due to the difference in polarizability along the long and short axes of the molecule which changes the macroscopic index as seen by the incoming light. For pulses shorter than the $\simeq$ 2-psreorientational response time this buildup can be measured. Or, for a thermal nonlinearity, the light heats up the material which changes the linear index.

Fourier transformation of Equation 2 results in the usually quoted frequency-dependent susceptibility $\chi^{(n)}(\omega_1, \omega_2 \ldots \omega_n)$. Memory, which was previously explicitly included in the response function, is lost in the dispersion. Thus, irradiance, $I$, and fluence, $F$, dependences are treated equally, which can lead to confusion.

Consider thermal nonlinearities as an example. It is more instructive to account properly for the physics under investigation by quoting the index change ($\Delta n$) with temperature and the temperature change with input power for cw inputs, or fluence, $F$, for pulsed inputs than to quote a $\chi^{(3)}$. The overall index change for a thermal nonlinearity assuming quasi-steady state is

by absorption to have traversed the laser beam and short enough that thermal diffusion can be ignored. For other pulse widths transient effects must be accounted for and the index change will not be proportional to $F$. For example, for tightly focused beams and nanosecond pulses the thermal nonlinearity is transient. Defining a $\chi^{(3)}$ for a process such as thermal refraction can be misleading since the value will depend on the pulse width as well as the focusing geometry.

There exist orders of magnitude differences appearing in the literature for the third-order susceptibility of the same material.[23,24] Many of these discrepancies are due to measurements of different nonlinear processes occurring in the same material under different experimental conditions, e.g., input pulse width.

Such processes as reorientational, electrostrictive, thermal, saturation, and excited-state nonlinearities can also be thought of as two-step processes, or cascaded $\chi^{(1)}$:$\chi^{(1)}$ nonlinearities. For example, for ESA, light first induces a transition to the excited state (an Im$\{\chi^{(1)}\}$ process) and then the excited state absorbs (a second Im$\{\chi^{(1)}\}$ process), i.e., two *linear* absorption processes. This cascading description is useful when the pulse width is shorter than or comparable to the material response time.

For these types of slow cumulative nonlinearities the irradiance (or field) may no longer be the important input parameter. For ESA nonlinearities, 1 GW/cm$^2$ for a picosecond pulse could give the same $\Delta n$ as 1 kW/cm$^2$ for a microsecond pulse. In any case, quoting $\alpha_2$ or $n_2$ without a clear explanation of the physical mechanisms can be misleading. This is particularly true for excited-state nonlinearities.

Both 2PA and ESA are third order in nature, but only 2PA is irradiance dependent. As the intermediate level in the 2PA process becomes resonant, the intermediate level (i.e., first excited state) can have a *real* population as opposed to virtual. This population has a finite lifetime while the nonresonant (virtual) *lifetime* is determined by the uncertainty principle and the energy mismatch between its energy and the input photon energy. Thus, for input pulses shorter than the lifetime of this intermediate state, the nonlinearity will be fluence dependent, i.e., the absorption grows over the duration of the pulse as the excited-state population increases. While this ESA can be considered a resonant 2PA process, a description of the process by $\chi^{(3)}$ is no longer as useful near resonance because of this change to a dependence on the time-integrated irradiance, i.e., the fluence. The ESA terminology and analysis becomes more useful. Therefore, quoting an $\alpha_2$ gives a number that is pulse width specific. A longer pulse would have given a larger $\alpha_2$. The nonlinear absorption is now governed by strictly linear quantities, the ground and ESA cross sections ($\sigma_g$ and $\sigma_e$). The nonlinear response is better described by a sequential Im$\{\chi^{(1)}\}$:Im$\{\chi^{(1)}\}$ process. In particular, for low inputs (where the excited-state population remains much less than the ground-state population) the nonlinear response can be described by[25,26]:

$$\frac{dI}{dz} = -\sigma_g N_g I - \sigma_e N_e I \tag{3}$$

where $N_g + N_e = N$ is the number density of absorbers. The excited-state density is created by linear absorption from the ground state, the generation rate being

$$\frac{dN_e}{dt} = \frac{\sigma_g I}{\hbar \omega} \tag{4}$$

These equations can be combined for $N_g \gg N_e$ to give,

$$\frac{dF}{dz} = -\sigma_g N_g F - \frac{\sigma_e \sigma_g N_g}{2\hbar\omega} F^2 \tag{5}$$

where $\hbar\omega$ is the photon energy. Note the similarity in form to the 2PA equation,

$$\frac{dI}{dz} = -\alpha I - \beta I^2 \tag{6}$$

equation as discussed in Section V, but the ultimate loss for very high inputs is easily determined. It is simply given by the absorption coefficient at saturation ($N_e = N_g$), $\alpha' = (\sigma_g + \sigma_e)N/2$. In practice, the excited electronic state of organics rapidly relaxes to a thermally equilibrated distribution of the rotational-vibrational continuum. This actually simplifies the analysis (except for femtosecond pulses), and, in principle, the absorbers can all be excited, giving a maximum absorption coefficient of $\sigma_e N$ (again assuming $\sigma_e > \sigma_g$). We briefly discuss these processes in Section V and they are discussed in considerable detail in the chapter by Perry.[1]

For optical limiting applications, knowing whether a quoted $\sigma_2$ is due to 2PA or ESA is extremely important. Let's look at an example where, for simplicity, no spatial or temporal integrations are performed. We are given an "$\alpha_2$" in the literature of $\alpha_2 = 100$ cm/GW and a linear absorption coefficient of 0.1 cm$^{-1}$. The measurements were performed with 10 ns laser pulses and the authors quote the energy and irradiance so that we can calculate the fluence and the length. If this is a 2PA coefficient we expect a transmittance of $T_{NL} = 0.83$ at $I = 1$ MW/cm$^2$ where the linear transmittance is $T_L = 0.90$. If on the other hand, the loss is from ESA, with a fluence of $10^{-2}$ J/cm$^2$ we find $\sigma_e = 2.0 \times 10^{-17}$ cm$^2$ assuming $\sigma_g = 1.0 \times 10^{-18}$ cm$^2$, $N_g = 10^{17}$ cm$^{-3}$, and $\hbar\omega = 10^{-19}$ J (i.e., for the above values the losses from 2PA or from ESA are assumed the same). However, if the experiment is repeated for 1-μs pulses with the same irradiance, we would see the same loss for 2PA but low transmittance ($\simeq 0.14$) for ESA since the fluence is now 1 J/cm$^2$. Similarly, if 100-ps pulses are used with the same irradiance, the ESA loss becomes negligible ($F = 10^{-4}$ J/cm$^2$). Simply stated, 2PA is irradiance dependent and ESA is fluence dependent.

From these arguments we see that if we want to perform optical limiting of picosecond pulses, 2PA may be more useful (assuming normal values of $\beta$ from 1–100 cm/GW). If we need to limit longer pulses from nanoseconds to microseconds, ESA may be more useful.

An important note on ESA is that in the above example the largest loss possible is $\alpha$ changing from 0.1 cm$^{-1}$ to 20 times larger or 2 cm$^{-1}$ when all the absorbers are promoted to the excited state. This "saturation" of ESA is much less likely for 2PA (the population of the 2PA excited state would have to become comparable to that of the ground state which would require very large $\beta$'s and high irradiance).

## IV. ULTRAFAST NONLINEARITIES IN ORGANICS

In the last decade, organic materials have emerged as potentially viable media for optical switching and limiting. Many researchers have been involved in the investigation of the nonlinear optical properties of various types of organics.[27–32] It is thought that the number of conjugated bonds (alternating double-single bonds between carbon atoms which leads to large linear oscillator strengths) will lead to large nonlinearities. Because the bonding π-electrons are loosely bound to the individual nuclear sites, their orbitals extend over long distances. Additionally, the joint density of states is raised in going from three to one dimension as in polymers.[33] This is similar to what happens in going from bulk semiconductors to quantum wires. In linear polymeric molecules such as polydiacetylenes, bound-electronic $n_2$'s of 5 × 10$^{-3}$ cm$^2$/GW have been reported by Lawrence et al.[17] and 2PA coefficients of 700 cm/GW have been reported by Lawrence et al.[18]

While for all-optical-switching applications it is desirable to have large $n_2$ but small $\beta$ (see Chapter 12 by Stegeman), for optical limiting it is desirable for both $n_2$ and $\beta$ to be large. The 2PA absorbs energy and, thus, lowers the transmitted energy, while the NLR will spread the beam lowering the transmitted fluence. This has been shown to work well in semiconductors.[14,15,34]

Recently there has been considerable progress in the understanding of the relationship between electronic nonlinearities and the structure of polyene chains with terminal electron donor and acceptor groups. Quantum chemical calculations[35] and experimental measurements of first and second hyperpolarizabilities[36,37] for such systems suggest that the hyperpolariabilities are dependent on the bond length alternation in the conjugated chain, which varies from about 0.11 Å for a neutral polyene to −0.11 Å for a fully polarized (zwitterionic) polyene. Cyanine or cyanine-like molecules are those limiting structures. The structure property trends that emerge from these studies indicate that the second hyperpolarizability, $\gamma$, which is directly related to the ultrafast electronic $n_2$, exhibits three extrema as the

which have optimized positive or negative $\gamma$, for their given length. Molecules with very large negative $\gamma$ may give rise to large negative $n_2$ materials which would exhibit strong ultrafast self-defocusing.

While the nonlinearities optical properties of organics have been studied for some time, there has not been a great deal of work performed using the ultrafast nonlinearities for optical limiting. However, these ultrafast nonlinearities may offer considerable potential for optical limiting of short pulses, these ultrafast nonlinearities may offer considerable potential. The potential for short pulse protection lies in the claims of (1) large nonlinearities; (2) mechanical, chemical, thermal, and photostabilities; and (3) high optical damage thresholds. In fact, the questions that remain for their application for optical limiting are just those that they are touted for; namely, large nonlinearities, stability, in particular photostability, and high damage threshold. For example, polymethylmethacrylate (PMMA) has a reported damage threshold to 10-ns pulses of $\simeq$2–3 J/cm$^2$.[38] In addition the linear optical quality of many of these materials [e.g., polydiacetylene (PTS)] in solid form exhibits nonuniformities and inhomogeneities that lead to significant scattering. These problems may be extrinsic but need to be solved before organic materials will be widely utilized. Additionally, for optical limiting where broadband operation is needed, the magnitude of the combined nonlinearities of NLA and NLR need to be large over the entire spectral region of concern. These nonlinearities have not in general been measured over sufficiently large spectral ranges to know their applicability. A noted exception is the nonlinear spectrum of PTS as measured by Lawrence et al.[18]

The magnitude of the largest reported 2PA coefficient in organic materials, $\beta \simeq 700$ cm/GW, is in principle large enough to limit the transmittance to levels of 1 μJ output in a 10-ns pulse if used in a "thick" limiter geometry (described in Section VIII). However, this large value is at the peak in the 2PA spectrum and the material, PTS, is one of very few available in millimeter size single crystals. Also it suffers from considerable scattering as well as only linearly transmitting at wavelengths longer than $\simeq$0.7 μm. On the other hand, this large nonlinearity in the near IR shows the potential of organic materials if the several problems mentioned can be overcome. In addition, the large nonlinear refractive index of $\simeq 5 \times 10^{-3}$ cm$^2$/GW ($\simeq 2 \times 10^{-9}$ esu)[17] is capable of producing a significant phase shift for 1-μJ, 10-ns pulses which helps to spread the energy in a focal plane. In fact this magnitude of $n_2$, if broadband, is approximately what is needed to sufficiently limit the fluence of nanosecond pulses acting alone.

However, some organic materials displaying large 2PA also show higher order nonlinearities. These may be associated with excited-state nonlinearities from the 2PA generated excited states. Such higher order nonlinearities were found to be useful for optical limiting in semiconductors[14,15] and hold the potential in organics to give effective optical limiting for nanosecond as well as shorter pulses. We give examples here of two organic materials studied at 532 nm. These nonlinearities were studied in organics as early as 1974 by Kleinschmidt et al.[34] and later by several others.[16,17,40,41]

The materials discussed here are a bisbenzethiozole-substituted thiophene compound (BBTDOT)[40] and a didecyloxy-substitute polyphenyl compound (DDOS).[40] Measurements were performed on samples of BBTDOT and DDOS.[10] The linear absorption for the 2-mm path length spectroscopic cells was too low to measure ($< 2\%$ loss) for both solutions. This is consistent with the maxima in the linear absorption occurring at $\simeq$400 nm for BBTDOT and $\simeq$300 nm for DDOS. Linear spectra for these materials are given in Zhao et al.[40,42] Experiments were performed with 32-ps (FWHM) pulses at 532 nm. These materials have been characterized with degenerate four-wave mixing at 602 nm[40,42] as well as by Z-scan at 532 nm.[10] The nonlinearities observed are analogous to those previously studied in semiconductors.[43,44] As in semiconductors, two-photon absorption (2PA), ultrafast nonlinear refraction (NLR) and excited-state nonlinearities induced by 2PA are observed. The molecular structures of these compounds are shown in Figure 3.

Making measurements of the nonlinear absorption at several input irradiances and defining an effective 2PA coefficient, $\beta_{eff}$, by $dI/dz = -\beta_{eff}I^2$, the plot for BBTDOT of Figure 5a gives a straight line of positive slope. Thus, a higher order effect, such as ESA accessed via 2PA, is contributing to the NLA. The behavior of this material is similar to semiconductors irradiated in the 2PA regime, and hence an analysis similar to that of Said et al.[44] is appropriate. In the case of semiconductors, the NLA is caused by 2PA and by the absorption due to free carriers generated via this 2PA. The propagation
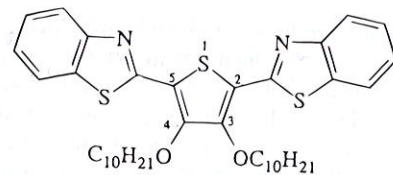
2,5-bis(2-benzothiazoyl)-3,4-didecyloxy-thiophene

(BBTDOT)
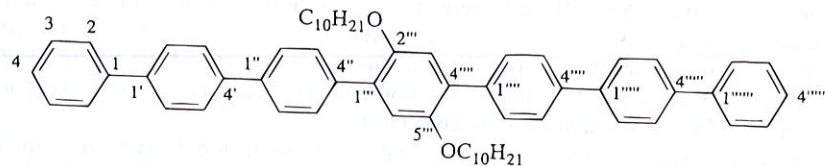
2''',5'''-Didecyloxy-1,1':4',1'':4'',1''':4''',1'''':4'''',1''''':4''''',1'''''''-septiphenyl

(DDOS)

**Figure 3** The chemical structure of BBTDOT and DDOS.

where $\beta$ is the actual 2PA coefficient, $\sigma_a$ is the ESA cross section, and $N_e$ is the density of excited states created by 2PA. The excited-state generation rate is[44,45]

$$\frac{dN_e}{dt} = \frac{\beta I^2}{2\hbar\omega}. \tag{8}$$

where $\hbar\omega$ is the incident photon energy. The data of Figure 4a are described well by Equations 7 and 8, giving a value for $\beta$ and $\sigma_a$. The ESA from the 2PA generated excited states acts as a fifth-order nonlinearity described by a sequential $Im\{\chi^{(3)}\}:Im\{\chi^{(1)}\}$ (2PA followed by linear absorption).[46]

Upon examining the NLR data of BBTDOT at several input irradiance levels, a trend similar to that for the NLA data is seen. The sample exhibits both positive third-order and positive fifth-order contributions to the NLR. The third-order contribution is due to the bound-electronic NLR of coefficient $n_2$, and the fifth-order effect can be described by an index change caused by the production of excited states via 2PA. Hence, the change in the refractive index is

$$\Delta n = (n_2 I + \sigma_r N/k), \tag{9}$$

where $k = 2\pi/\lambda$ and $\sigma_r$ is the excited-state refractive index cross section. Using the same procedure as in the nonlinear absorption case, we plot $\Delta n$ divided by the input irradiance as a function of $I_0$ in Figure 4b,[16,43] Also shown is the total index change before subtraction of the NLR from the cell and solvent.

The sample DDOS also shows increasing NLA with increasing $I_0$ as seen in BBTDOT. From the closed aperture Z-scan data for DDOS we determine a negative intercept for a plot of $\Delta n/I_0$ vs. $I_0$ leading to a negative $n_2$ and $\gamma_R$. The slope of this plot is negative, indicating that $\sigma_r$ is also negative for DDOS.
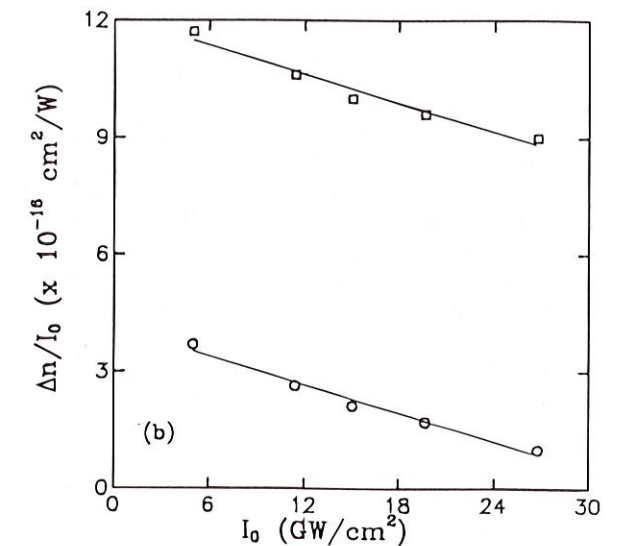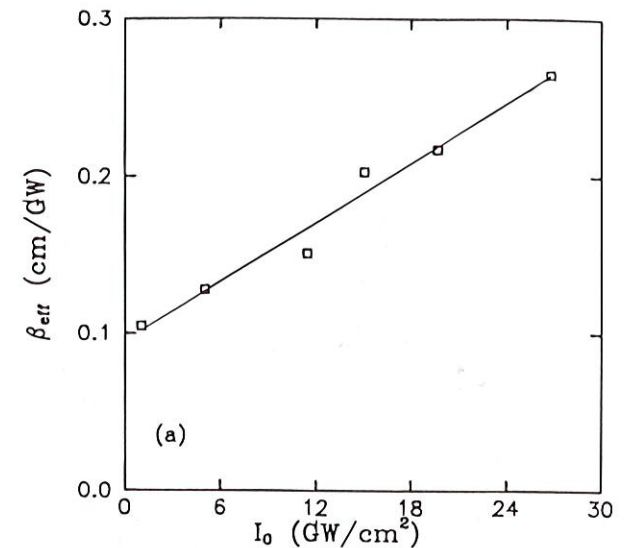


**Figure 4** (a) $\Delta\alpha/I_0 = \beta_{eff}$ vs. $I_0$ for the BBTDOT sample with least-squares fit (solid line). (b) $\Delta n/I_0$ vs. $I_0$ with solvent (squares) and with solvent $n_2$ subtracted (circles) along with fits (solid lines).

## V. REVERSE SATURABLE ABSORBING MATERIALS

Reverse saturable absorbing (RSA) molecules are one of the most promising candidates for use in passive optical limiters.[25–28,38,47] The excited-state absorbtion (ESA) cross section in such materials is larger than that of the ground state, hence the absorption increases with increasing input fluence, $F$ (energy per unit area); thus the name reverse saturable absorber.[48]

The photophysics of these molecules is discussed in detail in Chapter 13. Here we use an oversimplified quasi-three-level model, shown in Figure 5a, to describe the basic physical phenomena. Figure 5b also shows a more realistic five-level model with both singlet and triplet manifolds. We use a ground-state absorption cross section, $\sigma_g$, and an effective excited-state absorption cross section, $\sigma_e$ with no decay to the ground state but extremely fast decay ($r_{32} \simeq 0$) from the uppermost level back to the first excited
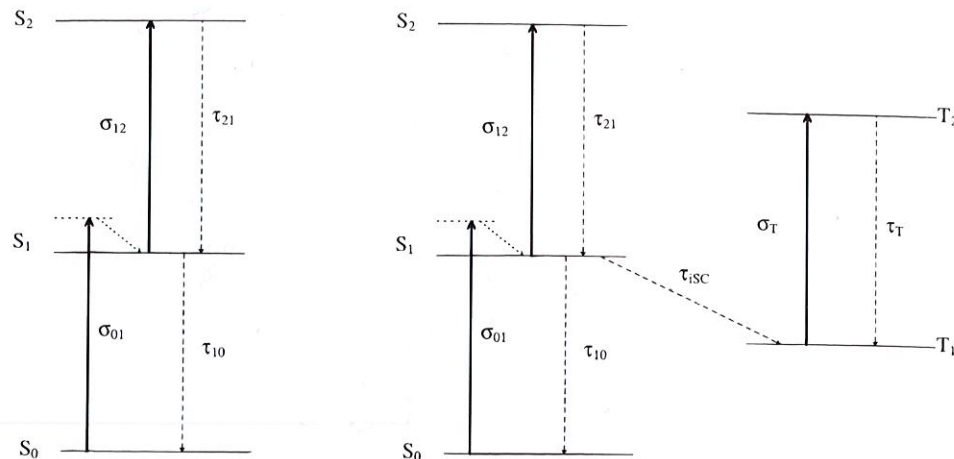
**Figure 5** (a) Simplified three-level structure for RSA molecules along with the more realistic five-level model shown in (b). For the three-level system calculation the lifetimes are taken to be $\tau_{21} = 0$ and $\tau_{10} = \infty$.

As discussed in Section III, for low inputs, the loss from ESA can be described by Equation 5, which is analogous to 2PA except that the loss is to the fluence rather than irradiance. This immediately shows the interest in ESA for optical limiting of long pulses. The nonlinearity grows with fluence and builds up in time. Thus later portions of a pulse are more effectively limited than early portions. Here we give a somewhat more realistic three-level model including ground-state depletion following Miles.[28]

For longer pulses in many systems the first excited state can undergo intersystem crossing to the triplet manifold where the lifetime is long (see Fig. 5b), thus facilitating ground-state depletion. Fortunately the ESA within the triplet manifold can also be larger than the ground-state absorption and in several phthalocyanines has been found to be even larger than the ESA within the singlet manifold. Thus efforts have been undertaken to increase the intersystem crossing rate by heavy atom substitution in the phthalocyanine ring (See Chapter 13).

In this three-level model, the depth, $z$, dependence of the irradiance, $I$, is given by Equation 3, while the rate of change of ground-state population density, $n_g$, is

$$\frac{dn_g}{dt} = -\sigma_g n_g \frac{I}{\hbar\omega} \qquad (10)$$

We now require overall conservation of population density, $N_0$, assuming the uppermost level relaxes instantaneously to the first excited state, i.e., no saturation of the ESA is allowed, and the first excited state does not decay within the time of the input pulse width. This requires

$$N_0 = n_g + n_e \qquad (11)$$

where $n_e$ is the excited-state population density. Defining $F_t = \int_{\infty}^{t} I(t')dt'$, we have

$$n_g = N_0 \exp(-\sigma_g F_t/\hbar\omega) = N_0 e^{-F_t/F_S} \qquad (12)$$

$$\frac{\partial I}{\partial z} = -N_0 I \{\sigma_g e^{-F_t/F_S} + \sigma_e (1 - e^{-F_t/F_S})\} \qquad (14)$$

The term in curly brackets, { }, is the effective absorption cross section as defined by Miles.[28] However, integrating Equation 14 over time from $-\infty$ to $\infty$ to give the fluence change with $z$ yields

$$\frac{\partial F}{\partial z} = -N_0 \left\{ \frac{F_S}{F} (\sigma_e - \sigma_g)[e^{-F/F_S} - 1] + \sigma_e \right\} F = -N_0 \sigma_{eff} F \qquad (15)$$

where the last equality defines the effective absorption cross section, $\sigma_{eff}$. This equation must in general be solved numerically. However, Miles[28] introduced a way to obtain the maximum possible dynamic range for limiting devices based on RSA by keeping the peak fluence constant within a thick nonlinear material at the highest input allowed by the damage threshold of the material. This optimization is obtained by allowing the density of molecules to vary along the propagation direction which requires a solid host material. This allows an analytic solution for the density distribution as well as for the limiting energy.[30,49,50] Allowing the density to vary was originally suggested by McCahon and Tutt.[51]

The effective absorption cross section, $\sigma_{eff}$, defined in Equation 15, grows as a function of the input fluence as shown in Figure 6. Here we take $\sigma_g = 1$, $\sigma_e = 20$ and $F_S = 1$. For low fluence $\sigma_{eff} = 1$, the ground-state cross section, while at very high input fluence $\sigma_{eff} = 20$, the excited-state cross section. Clearly to obtain the most effective limiting (largest overall loss) $F$ must be very much larger than $F_S$ ($F_S = 1$ in Fig. 6). The physical meaning of $F_S$ is that the ground state becomes depleted (i.e., saturated) for $F \gg F_S$. Thus the loss tends to $\partial F/\partial z = -N_0 \sigma_e F$, the maximum possible loss when all the molecules are in the excited state. Therefore, as pointed out by Miles,[28] it is desirable to work in the saturated regime which in turn requires $F_S$ to be small. This also implies that the ground-state absorption cross section should be large, i.e., $F_S = \hbar\omega/\sigma_g$, but still much smaller than that of the excited state. Limitations of the analytic model for optimized RSA limiters can be determined by numerical solutions to the five-level model coupled to the wave equation, as discussed by Hagan et al.[49] and Xia et al.[50]

It is expected that thermal nonlinearities for from a few nanoseconds to longer pulses will play an important role in these and other limiters where absorption is used. For example, for liquid-based
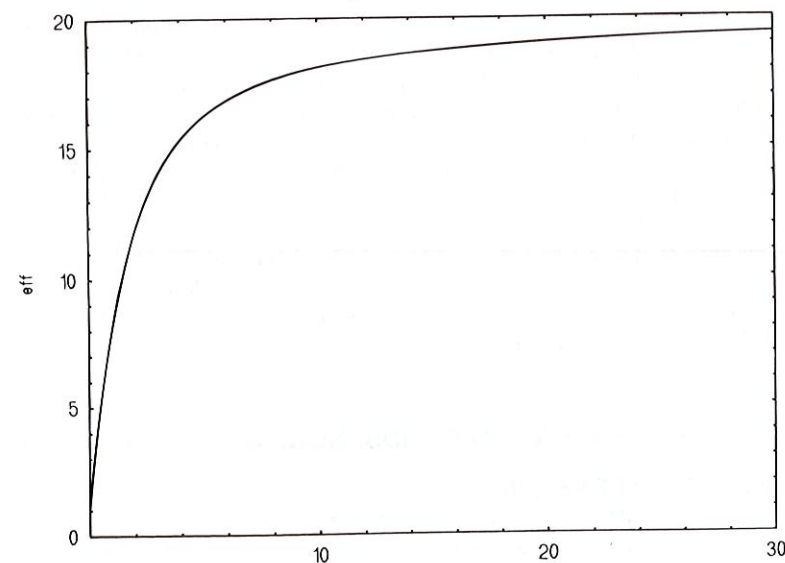
limiters, the index change with increasing temperature results in self-defocusing which spreads the beam. If the thickness of the nonlinear material is long enough for the phase distortion induced by the thermal index change to propagate to change the irradiance distribution within the sample, the fluence limiting process of RSA will be reduced. On the other hand, the fluence may be reduced directly by the self-defocusing at an image plane. Clearly careful design of the limiter will be needed to utilize these effects optimally. This will require computer codes that take into account the full nonlinear propagation as determined by the wave equation as well as accounting for the nonlocal behavior of the thermal as well as excited-state nonlinearities which can diffuse and/or decay in time.[50]

We should also point out that the use of liquid-based vs. solid-state materials for optical limiting leads to considerably different designs. Liquid-based limiters can self-heal after breakdown allowing the absorption and scattering by the breakdown plasma or bubble formation to be utilized in the design of the limiting device. Damage to solid materials is irreversible, and therefore undesirable, so that fluences within the device must be kept below this damage threshold. Thick limiters[14,15,28,51] where the nonlinear material is much thicker than the depth of focus of the input beam, and "tandem" optical limiters[27,28,38,52] with multiple nonlinear elements may allow "self-protection" of the limiter element or elements.

## VI. LIQUID CRYSTALLINE MATERIALS

Liquid crystals are best known for their use in active devices where an electric field aligns the molecules to generate standard liquid crystal displays. Potentially, active limiting devices could be devised using this technology, but the response time would be relatively slow (perhaps as fast as microseconds).

For passive optical limiting several researchers have shown that liquid crystals can give effective limiting.[53–57] However, many liquid crystalline phases may not be suitable for limiting in anything but thin film form due to significant linear scattering. As these material offer the potential for active as well as passive devices they may, in principle, be used for limiting from picoseconds to cw.

Nematic liquid crystals have received the most investigation for passive optical limiting and show the largest nonlinear birefringence.[58–60] Khoo et al.[61] have investigated such liquid crystal response using pulses from picosecond to millisecond duration. They observed a fast component for the NLR which builds up in about 100 ns and a slower component which rises to a maximum in about 10 ms. These effects are attributed to temperature and density changes as described in Khoo and Normandin[62,63]. In addition a very fast component of the NLR was observed due to the bound-electronic response as discussed above in Section IV. As with many other organic materials the large anisotropic molecules have conjugated $p$-orbitals along their length to support charge separation.[25] They can also be reoriented by the applied optical field. This can change the index leading to self-lensing. Liquid crystals can also be used for switching at an interface using total internal reflection geometries.[64]

Soileau et al.[65] investigated the NLO response of liquid crystals in their isotropic phase and found that they can have significant 2PA and used both the 2PA and bound-electronic $n_2$ effects for optical limiting of 30-ps, 532-nm light at energies as low as 0.15 μJ.

Also reports by Yuan et al.[66] show nonlinearities in the liquid crystal CB-15 that change considerably as the input pulse width is varied from cw to picoseconds. One possible interpretation consistent with the current data is that the nonlinear response is a combination of 2PA and excited-state nonlinearities as observed in BBTDOT and DDOS discussed in Section IV.

## VII. PURE CARBON COMPOUNDS: NONLINEAR SCATTERING

### A. CARBON BLACK SUSPENSIONS

Carbon black suspensions (CBS) as used for optical limiting are dilute colloidal suspensions of carbon black in a liquid using a surfactant, e.g., ethanol or water plus surfactant. This is one of the most

The mechanism for limiting is a combination of processes including avalanche ionization and bubble formation, both of which lead to enhanced optical scattering of the input beam. The observed nonlinear scattering results in limiting the transmitted beam fluence. The mechanism using water as the dispersant goes as follows.[68] The tiny suspended carbon particles are rapidly heated by strong linear absorption giving rise to thermionic emission, which in the presence of the strong electric field leads to avalanche ionization. The resulting microplasmas then rapidly expand into the surrounding liquid and strongly scatter the incident light for the duration of the plasma ($\simeq 10^2$ ns). Subsequently at incident energies above the threshold for obtaining a clamped output, the heating leads to bubble formation and further scattering lasting for microseconds. These conclusions imply that the limiting is broadband and fluence rather than irradiance dependent, both of which agree with observations. In addition, since the carbon particles are ionized during the process (and vaporized), the suspension must be replenished after each laser exposure, again as observed. The mechanism in other solvents having a smaller latent heat of fusion may be somewhat different. Fein et al.[70] report bubble formation prior to the avalanche ionization when solvents such as toluene or ethyl-ether are used. In either case, however, the material is vaporized after irradiation and must be replenished. This is considered a drawback for applications of this material.

Another idea for utilizing bubble formation in the suspensions is to use the index change at an interface between glass and CBS.[71] For the interface tilted at an angle such that the vapor glass interface results in total internal reflection, the transmittance switches to zero.

Experiments performed to confirm the NLO mechanisms include optical limiting as a function of pulse width (from 30 ps to 30 ns), focal spot size, limiting experiments of carbon deposited on glass substrates, simultaneous monitoring of transmittance, absorption and scattering (nonlinear scattering dominates for inputs near threshold), several nonlinear refraction experiments (showing that it is not a significant contributor to the limiting), time-resolved transmittance measurements using both a single beam and a pulse-probe technique, time-resolved emission spectra measurements where ionized carbon lines were observed, and angular distribution measurements of the side scattered light for different fluences which show rapid growth of scattering centers with increasing fluence.[68] These experiments confirmed the fluence dependence and physical description of the process.

The power needed to initiate limiting in CBS with $\simeq 10$ ns pulses of $\simeq 10^2$ W peak power (energy of $\simeq 1$ μJ) is compared to $\simeq 8$ kW for $CS_2$ in the visible. The onset of limiting is nearly independent of the concentration of carbon black particles. However, samples with a higher concentration of particles, and in turn lower transmittance for low input light levels, block the output light more effectively at higher incident fluences than samples with a low concentration of carbon particles.

The process involved in CBS is what is commonly referred to as laser-induced damage, and CBS has a very low damage threshold. This understanding of the limiting mechanisms also tells us that we will not be able to lower significantly (i.e., 10×) the limiting threshold or increase the bandwidth. The reasons are that the carbon is "black" and therefore broadband and highly absorbing. To lower the threshold we must either increase the absorption (we cannot significantly do this) or lower the ionization threshold. Flooding the suspension with ionizing radiation may lower this ionization threshold. At the moment a carbon black suspension is one of the most effective optical limiting materials available for nanosecond laser pulses.

It has been argued that limiters based on CBS will be very inefficient for wide field of view systems since the Mie scattering for the large induced scatterers is concentrated in the forward direction and the detector system will collect this light. However, experiments have shown good optical limiting even with relatively small $f$-number systems.[68] Damage to the detector element is fluence dependent and even though the light is scattered in the forward direction and still may be detected, it may be spread over a larger area (similar to the operation of refractive limiters). This is because CBS is usually used in a "thick" sample geometry (see Section VIII) and when limiting initiates, the plasmas or bubbles are formed near the focal point; however, well above threshold these scattering centers are produced prior to the focal plane so that the forward scattering is not imaged onto the detector.

### B. FULLERENES, $C_{60}$

by Brandelik et al.[72] using Z-scan also indicated that nonlinear refraction was present in toluene solutions probably due to thermal lensing in the tight focusing geometry. While the RSA process in the visible is not as effective as several of the organometalics discussed in Section V, this material is still being studied for its limiting properties in the near IR (around 760 nm) where the peak of the excited-state absorption occurs. Unfortunately, this is a region of very small linear absorption making it difficult to saturate the transition and thereby fully utilize the RSA.

## VIII. THICK SAMPLE LIMITING

The experiments performed to characterize CBS showed the fluence dependence of its NLO response. However, limiting experiments do not always follow such a fluence dependence for a variety of reasons. Characterization experiments are usually performed on samples whose thickness is both less than the depth of focus (or Rayleigh range) and less than the distance required for nonlinearly induced phase distortions to propagate to produce irradiance variations. Under such circumstances the sample is considered "thin" and the beam's spatial profile can be easily determined throughout the thickness of the sample. In particular the NLO wave equation can be separated into an equation describing the magnitude of the irradiance (field envelope) and an equation describing the phase as given in Section IV (see Equations 7 and 9). Samples that do not satisfy the thin sample criteria are considered "thick" and the wave equation must usually be numerically integrated to find the output irradiance and phase. However, if the nonlinearity is dominated by losses, either absorbing or scattering, we can determine the expected dependence of output on increasing input.

We find that the fundamental fluence dependence of limiting in CBS or RSA dyes manifests itself quite differently in the thick sample geometry. This is analogous to the irradiance-dependent two-photon absorption (2PA) appearing as a power dependence in tight focusing geometries as described below.[68]

In the case of 2PA the irradiance change $dI$ with depth in the sample $dz$ is

$$\frac{dI}{I} = -\beta I dz \tag{16}$$

where $\beta$ is the 2PA coefficient, giving the change in transmittance as approximately

$$\Delta T = \frac{\Delta I}{I} = -\beta I L_{eff} \tag{17}$$

where $L_{eff}$ is the effective interaction length. For a "thin" cell, $L_{eff} = L$, the sample thickness (assuming negligible linear loss). For a thick cell, the depth of focus ($Z_0$) of the lens determines the approximate range over which the nonlinear interaction occurs and is given by

$$Z_0 = \frac{\pi \omega_0^2}{\lambda} \tag{18}$$

where $\omega_0$ is the beam radius at the focus of the lens ($HW1/e^2M$). The area of the beam is given by

$$A = \frac{\pi \omega_0^2}{2} \tag{19}$$

From Equation 16 the transmission change is proportional to the product of the irradiance times the

Now the nonlinear change in transmittance appears power dependent and is independent of the beam size at focus. That is, $\Delta T$ is independent of the focal length of the input lens of $f$/number. For refractive nonlinearities a similar argument shows that the overall phase shift obtained from $d\phi/dz = kn_2 I$ is $\Delta \phi \propto kn_2 Power/\lambda$.

For fluence-dependent nonlinearities the argument follows the same lines and results in an energy-dependent nonlinearity independent of focusing for a thick sample. The above analysis is approximate, and combinations of nonlinear mechanisms can be responsible for limiting in different NLO materials leading to more complicated dependencies. Also at very high inputs the approximation breaks down.

The above analysis gives an idea of how thick sample geometries can give results considerably different from the usual thin sample limits that are normally discussed. As previously stated there are often multiple nonlinear mechanisms present in a given material and predicting the outcome of an experiment, or interpreting experimental results in a thick sample geometry can become difficult. With the rapid increase in computer speed, numerical calculations will become more helpful in the future. An approximate method for characterizing simple nonlinearities in thick media is given in Sheik-Bahae et al.[80]

## IX. TANDEM DEVICES

In addition to a low threshold and high linear transmittance, a practical limiting device must itself maintain a high resistance to irreversible laser damage. This increases the problems in making a practical device, because tightly focusing onto the nonlinear material to reduce the limiting threshold may cause a corresponding decrease in the damage threshold. Nonlinear materials in liquid form have the ability to self-heal, so the damage threshold is set by the windows of the cell containing the liquid. For collimated beams, even liquid limiter cells suffer from permanent optical damage at input fluences about an order of magnitude larger than the limiting threshold. Practical devices require a damage threshold several orders of magnitude larger.

While "thick" sample limiters, discussed in Section VIII, have been shown to self-protect,[14,15] they can suffer from reduced linear transmittance due to their considerable thickness. A similar, but more versatile implementation of self-protecting devices is to place two or more limiting elements in tandem in the optical path.[27,28,49,50,52] The limit of the tandem device for a large number of elements gives the distributed limiter.[28,49,56] A geometry with just two elements is shown schematically in Figure 7, where element 1, the "primary limiter," is placed at or near focus, while element 2, the "protector," is placed in front of the primary at a region of lower irradiance.[27] The basic concept is that the primary limiter provides a low limiting threshold while the protector prevents optical damage to the primary limiter. The damage energy threshold of the system is thus determined by the damage threshold of the protector which occurs at a much higher input energy than the primary by itself. This is because it is positioned far from the focus, where the fluence is lower. The dynamic range of a tandem device of this type, based solely on reverse saturable absorbing materials, can be approximately given by the product of the dynamic ranges of the individual elements.[27] As pointed out by Miles,[28] allowing the primary limiter to be positioned away from the waist allows the multiple element tandem device to be designed for a given maximum input energy. A tandem device is more versatile than the thick limiter, as it gives more freedom to optimize the geometry and allows the use of different materials to play the role of limiting and protecting elements. However, such versatility creates a vast parameter space that must be explored in order to optimize devices of this type. In addition to the choice of materials combinations, one must



INPUT        OUTPUT
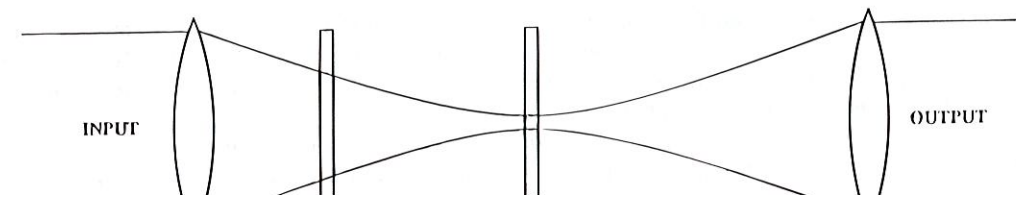
also consider geometric variables such as the number of elements, their relative positions, their thicknesses and, in the case of solutions or suspensions, their concentrations. Nevertheless, using a few simple rules for RSA dyes, researchers have done preliminary optimization which has resulted in the current state-of-the-art in nanosecond limiters.[27,38,52] For other nonlinear processes where nonlinear refraction is present the design of tandem devices becomes quite complicated as propagation between elements can drastically alter the focusing conditions.[49,50]

## X. CONCLUSIONS

Organic materials and carbon compounds have considerable promise as the nonlinear element or elements in practical optical limiting devices where an intermediate focal plane is present. Limiting of pulses from femtoseconds to cw is possible, but different nonlinear materials and processes may be needed for different pulse width regimes. For a recent review of nonlinear optical responses of organic materials the reader is referred to Bredas et al.[81] The reader is referred to Tutt and Boggess[82] and Hermann[83] for recent review articles on limiting mechanisms and materials. Carbon black suspensions are currently the best studied materials for nanosecond inputs and under certain criteria give the "best" limiting performance, e.g., broadest wavelength range, neutral density in appearance (no color distortion). However, the limited output is not low enough for some applications, and the fact that the suspension must be replenished is considered to be a drawback. For the important application of protecting sensors from damage by pulses of $\simeq 1$ ns to 1 $\mu$s duration, reverse saturable absorbing organic dyes appear to have the greatest potential, although recent reports of limiting in some inorganic clusters appear interesting.[84,85] In RSA materials there is a very severe trade-off between the performance of the limiter and the allowable linear transmittance. However, the compromise between these should allow useful devices to operate with tolerable linear transmittance (i.e., $\simeq 70$). The remaining questions for these materials, as well as other types of materials, are the spectral width over which they will protect sensors, the spectral window over which they can have high linear transmittance, and their environmental stability. It may be possible to expand the spectral range of optical limiting by using a combination of different RSA dyes. Also for these and other materials the role of thermal nonlinear refraction is not fully understood. For example, this nonlinearity may reduce the effectiveness of RSA or, perhaps with proper design, help the overall limiting of the transmitted fluence (i.e., spread the beam in the focal plane). This is still a very active area of research both in terms of materials development as well as optimization of use and spectroscopic characterization.

Organic materials, in various forms, are the least well understood nonlinear optical materials. On the other hand, they also offer great potential since organic chemistry has a long history of being able to engineer a material for a specific application. As the materials are not yet well characterized or understood, this research is still in its infancy. A close working relation between materials synthesis, characterization, and modeling will be essential for advances in this field.

Work at utilizing multiple nonlinear responses in combination such as 2PA plus ESA plus thermal lensing may be fruitful. This may allow covering a range of pulse widths. The combination of nonlinearities in thick media or tandem limiters is difficult to model and can require supercomputer codes. The output of these codes along with further experimentation is needed to determine the ultimate usefullness of organics for sensor protection applications.

A nonlinear mechanism used for optical limiting not discussed in this chapter where organics may play a role in the future is photorefraction. Development of organic photorefractive materials is currently a very active research area.[86,87] The potential for optical limiting is to use these new materials in, for example, beam fanning limiters[88] or photorefractive excisors.[89-91]

A final point regarding limiters based on nonlinear refraction or using nonlinear refraction for part of the limiting effect is that the apertures used in experiments performed to study these materials are

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