

Nonlinear Absorption

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Abstract

Nonlinear absorption refers to any effect in which a material's optical transparency depends on the intensity of the illumination. This includes changes in which the transparency increases or decreases. Such processes can occur almost instantaneously as in two-photon absorption, or can accumulate in time as in optically triggered chemical reactions (e.g., the mechanism in many photochromic sunglasses). In general, the magnitude of the nonlinear optical response gets smaller as the response time gets faster. Thus, slow nonlinear optical effects can be observed with sunlight while fast effects require pulsed laser beams. This entry discusses many but by no means all such effects. In general, nonlinear refraction accompanies nonlinear absorption since these processes are intimately connected by causality. Thus, this entry is a companion to the one on nonlinear refraction by M. Sheik-Bahae and M. Hasselbeck. In that entry, the causal relationship is described in more detail.

INTRODUCTION

Nonlinear absorption (NLA) is any process by which light changes the optical absorptive properties of a material. Easily recognizable examples are the photochromic sunglasses, where sunlight makes the transparent glass turn dark, i.e., absorbing. This is a light-induced chemical reaction balance between the thermal process, which creates silver ions, and the light-induced reaction creating absorbing silver particles or as in more modern sunglasses (e.g., photogrey[®]) where ultraviolet (UV) light absorbed by ring-like organic molecules open into more linear molecules that absorb in the visible region. This is an example where the light energy drives a process that makes the material less transparent, i.e., more absorbing. Another example is a nearly instantaneous process referred to as two-photon absorption or 2PA.^[1] There are other processes in which light induces an absorbing material to become transparent. Such a process is often referred to as saturable absorption.^[2] In this brief description of NLA processes, we will outline the most common types of NLA, which are as follows:

Saturable absorption—SA

Two-photon absorption—2PA

Excited-state absorption—ESA

Reverse-saturable absorption—RSA

In general, these processes require the relatively high irradiance levels achieved with laser beams and often times laser pulses. The eyeglass example is unusual in this respect. It is normally the case that the magnitude of the nonlinear response, e.g., darkening of the photochromic glass, depends on the time of response of the material. Thus, the large response of the photochromic sunglasses to the ~ 1 kW/m² irradiance of light outside is accompanied by a very slow response of ~ 1 min. However, the nearly

instantaneous response time of 2PA ($< 10^{-15}$ sec) can require irradiance levels of $\sim 10^{10}$ W/cm².

SATURABLE ABSORPTION

We will begin with SA.^[2] This first requires a fundamental understanding of linear absorption. Fig. 1 shows a fundamental process that occurs in all materials that is referred to as linear absorption or, for our purposes, one-photon absorption.

In this process, a single quantum of energy, $\hbar\omega$ is absorbed, i.e., eliminated, thus promoting the material from a lower energy state, b, to a higher energy state, a. For this to occur, the final state must have an energy $\hbar\omega$, i.e., Planck's constant times the frequency of the incident optical radiation, higher than the lower energy state. Thus, energy is conserved in this "transition." The concept of energy transitions is fundamental to this process. For the sake of clarity, let us assume that we have a gas of atoms of density N (number of atoms per unit volume). The light of irradiance I (power per unit area) is incident on this material. This irradiance is the photon flux, number of photons per second per unit area, times $\hbar\omega$. If N_b is the density of atoms in the lower state and N_a in the upper state ($N = N_b + N_a$) with population difference $\Delta N = N_b - N_a$, then

$$\frac{dI}{dz} = -\alpha I = -\sigma(N_b - N_a)I \equiv -\sigma\Delta N I \quad (1)$$

where z is the depth within the sample, α is the absorption coefficient, and σ is the absorption cross section. In the case of low irradiance, $N_b \cong N$, the system will absorb according to Beer's law, where the solution to this equation gives the characteristic exponential loss with distance $I(z) = I(0) \exp(-\alpha z)$, where $I(0)$ is the incident irradiance (ignoring reflection losses). In order to understand SA, we simply need to realize that as the photon flux increases,

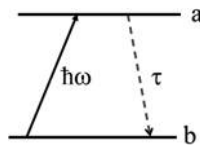


Fig. 1 A two-level atom (ion or schematic of a solid band structure) illustrating a light-induced transition from a state of lower energy, b, to a state of higher energy, a, with a decay time to the lower state of τ . The quantum of energy absorbed in a linear process is $\hbar\omega$.

more and more atoms get promoted or “excited” to the upper state and are no longer available to absorb. Therefore, the absorption decreases. This process is countered by relaxation processes, which return the atoms to their lower state. The relative rate of relaxation and excitation determines the amount of saturation. Thus, the absorption coefficient becomes irradiance dependent. Looking at the time rate of change of the population difference in the two-level system of Fig. 1, we find the rate equation

$$\frac{d\Delta N}{dt} = -2 \frac{\sigma(\omega)\Delta N}{\hbar\omega} I + \frac{N - \Delta N}{\tau} \quad (2)$$

where τ is the upper-state lifetime. In the steady state, this gives

$$\Delta N = \frac{N}{1 + ((2\sigma(\omega)\tau)/(\hbar\omega))I} \quad (3)$$

so that

$$\begin{aligned} \frac{dI}{dz} &= - \frac{\sigma N}{1 + ((2\sigma(\omega)\tau)/(\hbar\omega))I} I \\ &= - \frac{\alpha_0}{1 + ((2\sigma(\omega)\tau)/(\hbar\omega))I} I = -\alpha(I,\omega)I \end{aligned} \quad (4)$$

with

$$\alpha(I) = \frac{\alpha_0(\omega)}{1 + (I/I_{Sat}(\omega))} \quad (5)$$

where $\alpha_0(\omega)$ is the low irradiance (linear) absorption coefficient as a function of frequency, and this last equation defines the saturation intensity I_{Sat} .^[2] Thus, for the homogeneously broadened case, we have the result showing I_{Sat} is inversely proportional to the frequency-dependent cross section and lifetime. For an inhomogeneously broadened system, we find,

$$\alpha(I,\omega) = \frac{\alpha_0^{In}(\omega)}{\sqrt{1 + (I/I_{Sat}^{In})}} \quad (6)$$

where the saturation irradiance, I_{Sat}^{In} , is not frequency dependent and the low irradiance absorption coefficient, α_0^{In} , is modified by the inhomogeneous broadening. These are plotted on a semilogarithmic scale in Fig. 2 as a function of the input irradiance. Many different processes determine

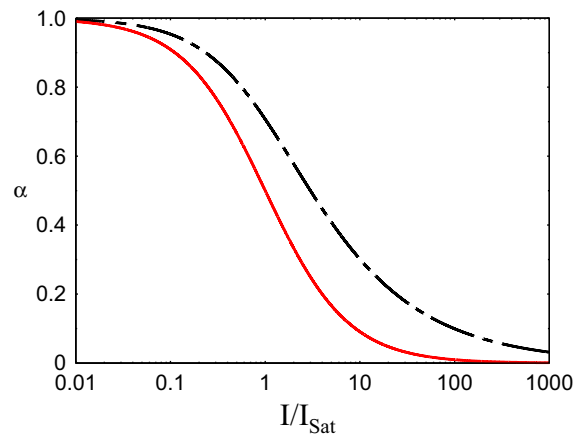


Fig. 2 Absorption coefficient as a function of irradiance, I , in a homogeneously broadened (solid line) and inhomogeneously broadened (dashed line) medium.

the relaxation appearing in the saturation intensity. For example, in a gas, spontaneous emission and collisions deexcite the atoms.

This type of saturation also occurs in gain or lasing media, where the population has been inverted. In this case, the gain is said to saturate, i.e., reduce.

TWO-PHOTON ABSORPTION

Two-photon absorption was first theoretically described by Maria Goepfert-Meyer in 1932,^[1] but first observed by Kaiser and Garrett^[3] in 1961 right after the invention of the laser. In 2PA, two quanta of light are simultaneously absorbed to promote an atom, ion, or solid from a lower energy state to a higher energy state as illustrated in Fig. 3. From a theoretical standpoint, it is necessary to have at least three levels for the system to describe 2PA. For the moment, let us assume the frequency degenerate case where the two photons have equal energy. Here, one photon takes the system to a “virtual” state (dotted line in Fig. 3 with $\hbar\omega_1 = \hbar\omega_2$) and the second photon takes the

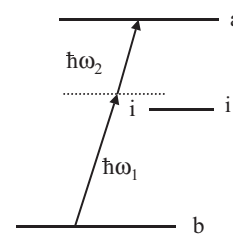


Fig. 3 A three-level atom (ion or schematic of a solid band structure), illustrating a light-induced transition from a state of lower energy, b, to a state of higher energy, a. In this process, two quanta of energy $\hbar\omega_1$ and $\hbar\omega_2$, “photons,” are absorbed.

atom to the final upper state. This virtual state is not a real state and is simply a useful tool for describing the process. In a perturbation theory description, the first photon takes the atom to the intermediate state, i , and the second photon takes the atom to the final state, a . However, in neither of these separate transitions is energy conserved. The difference in energy between $\hbar\omega$ and the energy difference between the levels define simultaneity for the 2PA process. For example, for the first transition, the Heisenberg uncertainty principle specifies that the atom can only exist in the intermediate level for a time equal to \hbar divided by this difference in energy. For most circumstances of interest, this time is the order of fractions of a femtosecond. This simultaneity is the reason why 2PA is referred to as an ultrafast nonlinearity. In the frequency domain, this simultaneity leads to Lorentzian frequency dependences showing the absorption resonances in the simplest model.

Throughout this entry, we use the term “photon” loosely and in a nonrigorous manner. This can be useful, but care must be taken. For example, to see how 2PA leads to an NLA loss, consider the following. We have a stream of photons incident on a 2PA material. For low irradiance, the material does not absorb much. However, as the photon flux increases, i.e., I increases, the probability that two photons are coincident increases, thus increasing the probability that the atom can simultaneously absorb two photons.

The equation governing degenerate 2PA is

$$\frac{dI}{dz} = -\alpha_2 I^2 \quad (7)$$

which has the solution

$$I(z) = \frac{I(0)}{1 + \alpha_2 I(0) z} \quad (8)$$

indicating a less drastic dependence on depth than exponential as shown in Fig. 4.^[4] It is fairly easy to extrapolate

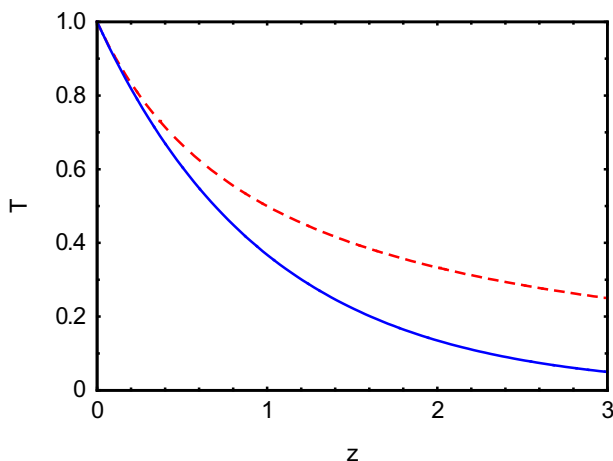


Fig. 4 The depth dependence of losses from linear (solid line) and two-photon absorption (dashed line).

these results to get to equations for higher-order NLA processes of three-photon absorption, etc. A method to write the various orders of nonlinear processes in general was developed in the early 1960s by Bloembergen and coworkers called the nonlinear susceptibility.^[5] See the entry titled *Nonlinear Refraction*, p. 1832 by M. Sheik-Bahae and M. Hasselbeck for more details; however, the absorptive processes are related to the imaginary part of the various nonlinear susceptibilities. The real and imaginary parts of these susceptibilities are related by Kramers–Kronig relations.^[6,7] This is also discussed in the nonlinear refraction entry, where each absorptive process (imaginary part of the susceptibility) results in a change in refractive index (real part of the susceptibility). Both depend on the frequency dependence of the other. This is the primary reason for showing Fig. 3 for the nondegenerate frequency case, since it is the generalized nondegenerate 2PA, which is related to the corresponding ultrafast nonlinear refraction.

For material samples that are sufficiently thick such that the nonlinear refraction can lead to diffraction within the length of the sample, the laser beam shape can change within the sample and, thus, the irradiance can change. This then can increase or decrease the NLA depending on the sign of the nonlinear refraction. Under such circumstances, the NLA gets mixed up with the nonlinear refraction and the full electromagnetic wave equation must be solved rather than the simple irradiance equation (e.g., Eq. 7). Here, we assume thin samples throughout so that this mixing is negligible.

Lists of measured 2PA coefficients in a variety of materials are given in Van Stryland and Chase.^[8] The values of α_2 can be important for a number of applications. It is useful in giving well-behaved mode-locked pulses in solid-state lasers,^[9] serves as a limit on the transparency of materials in the UV for high-power short laser pulses, can cause heating problems in materials, can lead to laser-induced damage,^[10] and imposes limits for all-optical switching devices in, e.g., optical telecommunications.^[11]

EXCITED-STATE ABSORPTION

This discussion of 2PA naturally leads us to a discussion of ESA. As the intermediate state, i , in Fig. 3 becomes nearly resonant with the input light, in this case $\hbar\omega_1$, linear absorption can occur. We will refer to a separate figure for this (Fig. 5).

Now a real transition occurs from state b to state i . In this case, the second photon can come at a later time and excite the system to the upper state a . This is true as long as the second photon comes before the state i decays and, of course, it must conserve energy in the process as well. Now “simultaneity” is no longer required and the process can become much more likely. If the lifetime of state i is

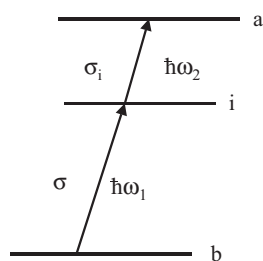


Fig. 5 Energy state diagram for excited-state absorption. The lower state absorption cross section is σ , and the excited-state absorption cross section is σ_i .

τ , and we neglect saturation ($\Delta N \cong N$), then the equations governing the process are^[12]

$$\begin{aligned} \frac{dI}{dz} &= -\sigma NI - \sigma_i N_i I \\ \frac{dN_i}{dt} &= \frac{\sigma NI}{\hbar\omega} - \frac{N_i}{\tau} \end{aligned} \quad (9)$$

These can be integrated over time under the assumption that τ is infinite (i.e., long compared to the input pulsewidth) to give a single equation for the “fluence” F (energy per unit area) as^[12,13]

$$\frac{dF(z)}{dz} = -\sigma NF - \frac{\sigma N \sigma_i}{2\hbar\omega} F^2 \quad (10)$$

Note the striking similarity with the equation for 2PA where F has replaced I here, and α_2 has been replaced by the product of two linear absorption cross sections. The assumption made in writing Eq. 10 is that the lifetime of the intermediate state is very long, i.e., ignoring decay from i to b , which is true as long as the pulsewidth is significantly less than the lifetime—see Xia et al.^[12] The additional assumption is that there is no saturation of the ground-state absorption. Thus, no significant population is excited. This can still describe systems where the excited-state cross section is large compared to that of the lower state, $\sigma_i \gg \sigma$, resulting in RSA.

This name comes from reversing the increasing transmittance of SA to a decreasing transmittance. If we do not ignore saturation, we must carefully solve the problem to determine which process dominates; however, if in Fig. 5, $\sigma_i < \sigma$, the absorption will decrease with increased irradiance. At very high input levels, saturation of both absorption pathways will occur and the absorption will ultimately decrease even for $\sigma_i > \sigma$.^[14] Given this background, we will now give a few specifics for these nonlinearities in selected materials.

SEMICONDUCTORS AND DIELECTRICS

Materials that are well described in the solid state by a single absorption edge or bandgap energy follow a relatively

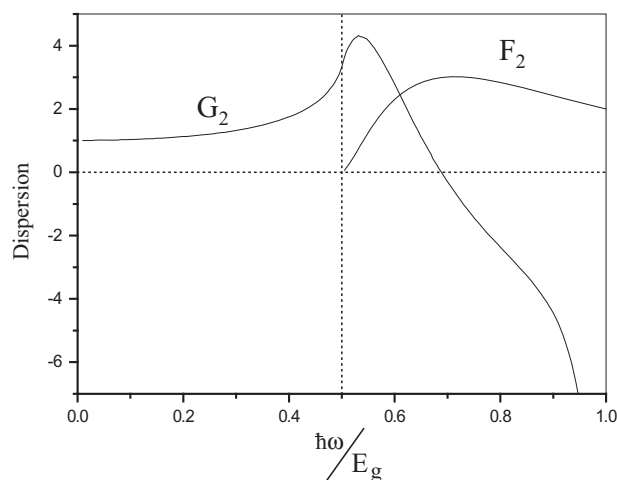


Fig. 6 F_2 shows the frequency dependence of degenerate 2PA in direct-gap semiconductors and dielectrics. G_2 gives the dispersion of the nonlinear refractive index as calculated by Kramers–Kronig relations—see entry by Sheik-Bahae titled *Nonlinear Refraction*, p. 1832. The vertical axis uses arbitrary scaling.

simple 2PA dependence. The bandgap energy is $E_g = \hbar\omega_g$, where ω_g defines the frequency above which linear absorption is very strong, $\alpha \approx 10^6 \text{ m}^{-1}$. It has been found experimentally and verified theoretically that for light incident at angular frequency ω , the degenerate 2PA coefficient of Eq. 7 is given by^[15,16]

$$\alpha_2 \cong K \frac{\sqrt{E_p}}{n^2 E_g^3} F_2 \left(\frac{2\hbar\omega}{E_g} \right) \quad (11)$$

where the function $F_2(x) = (x-1)^{3/2}/x^5$ gives the frequency dependence of the 2PA, which turns on for $\hbar\omega > E_g/2$. Here, n is the linear index of refraction at ω , E_p is the Kane energy ($\sim 21 \text{ eV}$ for many materials), and $K \approx 3100$ in units, where $\hbar\omega$ and E_g are in eV and α_2 is in cm/GW . The frequency dependence is shown in Fig. 6.

The simple relation, Eq. 11, holds remarkably well for a variety of materials as shown in Fig. 7, which is a semi-logarithmic plot of the 2PA coefficient, α_2 , vs. bandgap energy, E_g . Here the 2PA coefficient is scaled by the linear index and frequency dependence F_2 , to explicitly show the bandgap dependence.^[6] It has been shown that nondegenerate 2PA (the simultaneous absorption of two photons of different frequencies) can become much larger than in the degenerate case.^[17,18]

ORGANIC MOLECULES

While 2PA is quite well understood in semiconductors and dielectrics, there is yet to be found general scaling rules or structure property relations yielding the magnitude of 2PA for the myriad of organic compounds. However, progress is being made, and strongly conjugated molecules can have

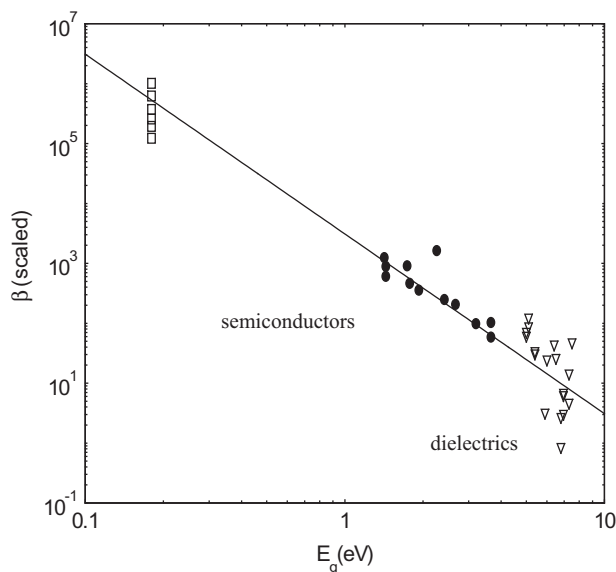


Fig. 7 Scaled α_2 vs. E_g for semiconductors and dielectric materials.

Source: From Van Stryland, Vanherzeele, et al.^[16]

the largest 2PA.^[19,20] Studies have usually been performed on organic dyes and other molecules in solvents because high-quality crystals are limited to a few material systems. In solution, it is convenient to define a 2PA cross section $\sigma^{(2)}$, which gives the intensity dependence per molecule and has units of $\text{cm}^4\text{-sec}/\text{photon-molecule}$. The relation between α_2 and $\sigma^{(2)}$ is $\sigma^{(2)} = \hbar\omega\alpha_2/N$, where N is the number density of molecules in the solution.^[21,22] This definition works well for any species in solution, in a gas, or as a dopant in a solid host as long as the density is low enough that the individual species do not strongly interact. Additionally, rather than a material nonlinear susceptibility, for molecules, it is convenient to define a molecular hyperpolarizability (i.e., nonlinear polarizability).^[23] Two-photon absorption in organic molecules has been exploited for three-dimensional (3-D) microscopic imaging via confocal fluorescence microscopy and 3-D microfabrication by two-photon initiated photopolymerization.^[24,25]

Excited-state absorption cross sections are important for a number of applications. Specifically, ESA places limits on dye laser and some rare-earth-doped solid-state laser performance. It can also be useful for optical limiting devices where the transmission decreases with increasing input to protect optical components and detectors from damage.^[12,13,26]

The typical molecular-level structure of organic dyes is shown in Fig. 8. Clearly, the ESA can be significantly more complicated than discussed for the three-level system of Fig. 5. However, such systems are easily solved in the rate equation approximation, which is often applicable.^[2] This can even be performed numerically in the transient regime where laser pulses are incident and level lifetimes

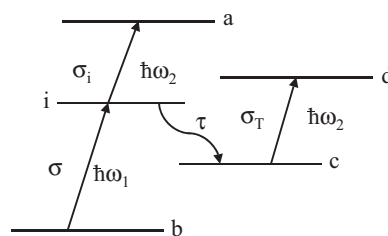


Fig. 8 Schematic of the level structure of common organic dyes showing three singlet levels on the left and two triplet levels on the right with decay from the second singlet level to the lower triplet level called intersystem crossing.

are included.^[27] The nonlinear transmittance can then be calculated from the combination of rate equations and equations analogous to the equation second of Eq. 9. These dyes can be used for lasers where ESA is a problem and for optical limiting devices where ESA is useful. Typical values of ESA cross sections range from 10^{-20} cm^2 for good laser dyes to 10^{-15} cm^2 for good optical limiting dyes.

METHODS OF MEASUREMENT

A variety of techniques has been developed for the determination of nonlinear coefficients. These can be classified into two types. For example, for 2PA, the first type involves direct measurement of transmittance changes caused by 2PA (this includes the now-popular Z-scan^[28] discussed below), while the second involves sensing of the energy deposited in a material by 2PA, e.g., sensing induced temperature changes,^[29] fluorescence (e.g., two-photon fluorescence^[30]), or acoustic signals.^[31]

Simple transmission experiments involving the measurement of transmittance as a function of incident irradiance may be used.^[4] For example, it is simple to show from Eq. 7 that a plot of inverse transmittance (energy input divided by energy transmitted for pulsed sources) as a function of irradiance gives a straight line of slope proportional to α_2 (see entry on *Nonlinear Refraction*, p. 1832, by Sheik-Bahae et al.^[28]).

Perhaps, the most common form of transmission measurements is the Z-scan.^[28] As shown in Fig. 9, this

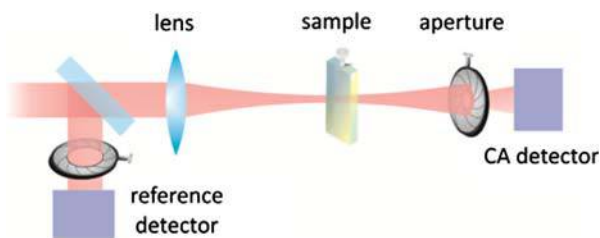


Fig. 9 Schematic of Z-scan experimental method for measurement of NLA and nonlinear refraction (NLR).

technique, first reported in 1989,^[32] monitors the transmittance as a function of the position of a sample with respect to the focal position of a lens. Thus, the irradiance is changed while the energy input is held constant. If all of the transmitted energy is collected, this is an “open-aperture” Z-scan, which is insensitive to nonlinear refraction. However, if an aperture is placed in the far field, the so-called “closed aperture” Z-scan, its transmittance depends on the nonlinear refraction. By performing both open- and closed-aperture Z-scans, the nonlinear absorption and refraction can be separately determined along with their signs.^[32] This technique turns out to be simple to analyze if Gaussian spatial profile beams are used and is absolutely calibrated if the energy, focal spot size, and pulsewidth are known. This has led to its popularity with over 4000 citations to date. However, since it is sensitive to all nonlinear absorption and refractive processes, and does not provide the temporal dependence, it does not uniquely determine the physical processes involved. A combination of Z-scan (perhaps using both linear and circular polarization) and excitation-probe data (discussed below), which can give the temporal dependence as well as polarization dependence, is sometimes sufficient to determine the physical processes involved. A typical Z-scan is shown in Fig. 10.

There is also a variety of excitation-probe methods where a laser pulse is used to prepare the sample and a second laser pulse probes the altered material. These can give nondegenerate 2PA coefficients if the pump and probe are at different frequencies or ESA spectra if the probe is tuned. Additionally, different polarization combinations can be used, which is helpful in differentiating different nonlinear processes by their different symmetries. The advent of femtosecond sources has allowed white-light continuum generation so the probe can contain a broad spectrum, thus rapidly yielding NLA spectra.^[17,29–31]

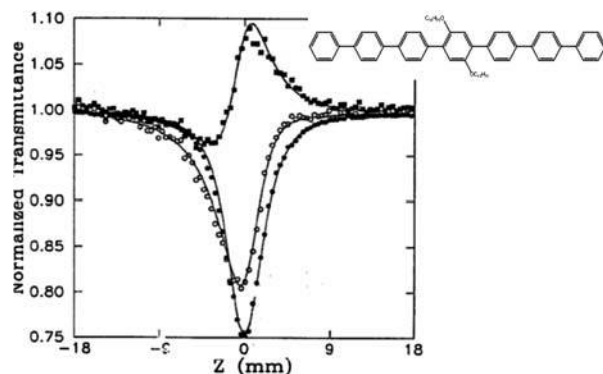


Fig. 10 Open (open circles), closed (closed circles), and divided (closed squares) Z-scan data of an organic molecule, bisbenzothiozole-substituted thiophene compound (BBTDOT). The solid lines are fits to the data. The nonlinearities present in the fit are complicated, including both bound-electronic and excited-state nonlinearities as discussed in the reference.

Source: From Said, Wamsley, et al.^[33]

Other techniques include measuring the energy absorbed directly by monitoring the heat or acoustic wave generated by a laser pulse. All these methods and others, both direct and indirect, usually rely on pulsed laser sources. Advances in parametric devices have greatly increased the frequency range over which these experiments can be performed so that the database of NLA constants is rapidly increasing. Unfortunately, the literature is often filled with conflicting results on the same material. This can occur when the interpretation of the nonlinear response is confused and different pulsewidths are used to make the measurement. For example, if a material exhibits 2PA but in the excited state it can also linearly absorb (as in Fig. 3 but with an additional higher lying level), short pulses will give the correct value of α_2 while longer pulses of the same irradiance will create more excited states to linearly absorb, and the overall absorption will be larger than for 2PA alone. This could lead to overestimation of the 2PA unless the ESA is properly accounted for.

Perhaps, the most common indirect method for measuring NLA is the two-photon fluorescence technique.^[30] Here, the fluorescence from states populated by 2PA is measured vs. excitation wavelength to obtain the degenerate 2PA spectrum. This, however is a relative rather than absolute method and is only useful for materials that have relatively high fluorescence yield. Photoacoustic and calorimetric methods directly measure energy that is deposited in the material. The photoacoustic^[31] or optoacoustic method monitors the sound produced by pulsed sources. This is accomplished by placing a microphone near the sample; however, the acoustic impedance from the sample to air to the microphone can limit the sensitivity. Placing a piezoelectric transducer directly on the sample can sometimes lead to improvements in signal-to-noise ratio for pulsed laser sources. However, building acoustic resonant cavities and using a laser repetition rate at the acoustic resonance can also increase the signal-to-noise ratio. In laser calorimetry, a thermocouple or thermistor is attached to the sample giving a direct read of the sample's temperature.^[29] By monitoring this as a function of time after a repetitively pulsed laser is turned on, the power absorbed can be determined knowing the specific heat of the sample. In this case, it is good to use small (low mass) samples and carefully thermally isolate the sample. Sometimes, vacuum chambers are used to increase the sensitivity.

CONCLUSION

We have discussed the major types of NLA processes in this brief entry. However, changes in the optical properties of materials that lead to changes in transparency are widely variable and we cannot discuss or know all of them. The literature is filled with examples of measurements. In many cases, the underlying physical reasons for the NLA are not well understood. Often, many different experiments

are needed to unravel the mechanisms. Care should always be taken in relying on numerical values of constants such as 2PA coefficients quoted in the literature.

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