

Nonlinear spectroscopy: absorption and refraction

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ABSTRACT

We have been developing tools for nonlinear spectroscopy aimed toward the ultimate goal of building a nonlinear spectrophotometer analogous to the ubiquitous linear spectrophotometer where a sample is placed in the instrument, a button is pushed, and the absorption spectrum is obtained sometime later. This paper describes our progress toward this goal, describing many difficulties and complications as well as opportunities. We also show spectroscopic data and analysis of a variety of materials that we have taken with preliminary nonlinear spectroscopic instrumentation we have already developed. One of the more interesting observations obtained along this research path is the realization that linear dispersion theory can also be applied to nonlinear systems when formulated properly such that Kramers-Kronig relations can be used to connect the dispersion of nonlinear refraction to the spectrum of nonlinear absorption. In some circumstances this can be more easily applied to nonlinear systems than to linear systems since the nonlinear absorption spectrum can be limited in wavelength. In addition, we have developed tools that can simultaneously give the spectrum of nonlinear absorption as well as the dispersion of the nonlinear refraction over an octave spectral range from 400nm to 800 nm, the so called White-Light-Continuum Z-scan. Much of the research on nonlinear optical materials has been a collaborative effort requiring the skills and expertise of organic chemists and materials manufacturers. The goals of this part of the research are to determine predictive structure-property relation capabilities. The database needed for this research makes the nonlinear spectrophotometer a necessity.

Keywords: nonlinear optics, nonlinear spectroscopy, nonlinear absorption, nonlinear refraction

1. INTRODUCTION

Here we describe our progress in developing the understanding and methodology for determining the nonlinear absorption spectrum and dispersion of the nonlinear refraction of normally transparent materials close to and off one-photon resonances. Figure 1 gives a good introduction to nonlinear measurements.¹ This shows the reported two-photon absorption (2PA) coefficient, α_2 (often referred to as β), of the semiconductor GaAs (on a semilogarithmic scale) as a function of the year published in the literature. As you will note, α_2 appears to decrease with time! Of course, it is only the experimental methodologies along with the, interpretation that have changed, and the now accepted 2PA coefficient for GaAs is ~ 26 cm/GW (which can change by $\sim 20\%$ depending on crystal orientation). This figure illustrates the difficulty of performing and analyzing nonlinear absorption data. The simplest experiment would appear to be looking at the transmittance as a function of the input irradiance in Watts per cm squared (usually GW/cm²). The first difficulty is to have an accurate knowledge of the irradiance which requires a measurement of the energy (for pulses which are normally needed to obtain the necessary irradiance), the spatial energy distribution, and the temporal distribution. Gaussian spatial profile beams are by far the most convenient to use given their simple propagation properties. However, it can be difficult for many systems, especially broadly tunable optical parametric sources to get high quality Gaussian beams. We do considerable spatial filtering in our experiments for this purpose. The temporal distribution can also be problematic in that pulses may have modulation that is difficult to detect. For ultrashort pulses, autocorrelation methods or "FROG" traces are needed.² Over the years we have built up facilities specifically for NLO characterization that allow broad tunability and a very large range of pulsewidths: tunable femtosecond OPG/A 250 nm -11 μ m; tunable

picosecond OPG/A – 450 nm - 18 μm ; tunable nanosecond OPO – 450 nm – 1.7 μm ; and a line tunable, single longitudinal mode TEM₀₀ CO₂ TEA laser.

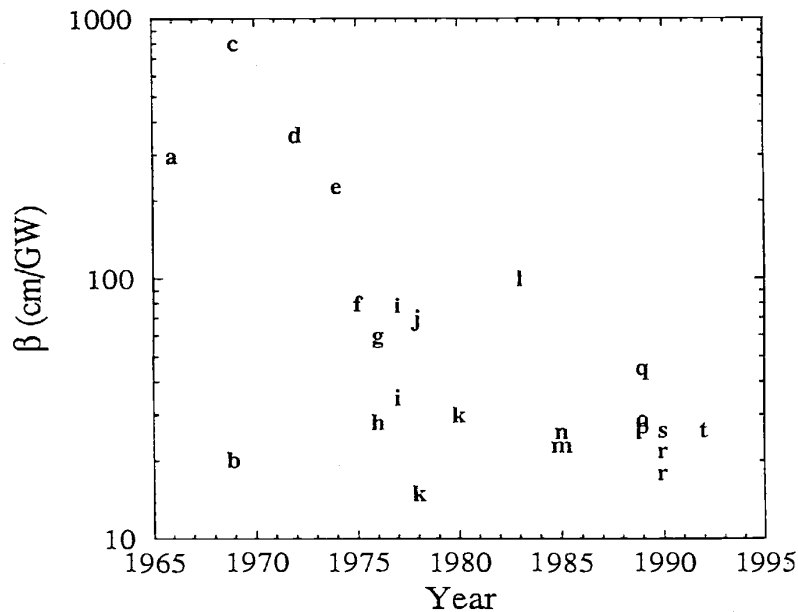


Figure 1. Two-photon absorption coefficient α_2 (here listed as β as is often done in the literature) of GaAs vs. year published. From Ref. [1]¹

Using these facilities we can measure the nonlinear absorption spectrum and nonlinear refraction dispersion and look at the time response using different laser pulsedwidths which allows us to unravel the various physical mechanisms that lead to the NLO response. We will describe some of these processes while we introduce the various measurement techniques.

2. Z-SCAN

We developed the initial Z-scan method in 1989³ while performing optical limiting experiments where we noted that the signal fluence strongly depends on the sample position with respect to focus.³ Thus, scanning the sample through the focus and monitoring the far field transmittance of an aperture gives an accurate measurement of the nonlinear refraction. Figure 2 shows the standard setup along with a typical signal from a sample showing self focusing and no nonlinear absorption. We refer to this as a “Closed-aperture” Z-Scan.⁴ Typically the aperture transmits ~40% in the linear regime which only slightly reduces the sensitivity to nonlinear refraction but averages over the beam imperfections in transverse profile. The sign is determined by whether the peak appears with the sample closest to the lens (self defocusing) or farthest from the lens (self focusing).

There have been a myriad of variations on this simple scheme.⁵⁻¹² Some show better sensitivity, e.g. EZ-scan⁵, and with referencing⁶, some allow non-Gaussian beams using reference materials^{7,8}, etc.; however, we still use the original method with referencing⁶ because of its simplicity of application and simplicity of data analysis. In addition, time resolution can be obtained with 2-color Z-scan methods.⁹⁻¹² If the sample simultaneously shows nonlinear absorption, a Z-scan with the aperture removed can be performed as shown in Fig. 3. This is insensitive to nonlinear refraction as long as the sample is “thin” in the sense of internal self-action, i.e. no spatial beam changes due to linear or nonlinear propagation from the induced phase distortion.¹³

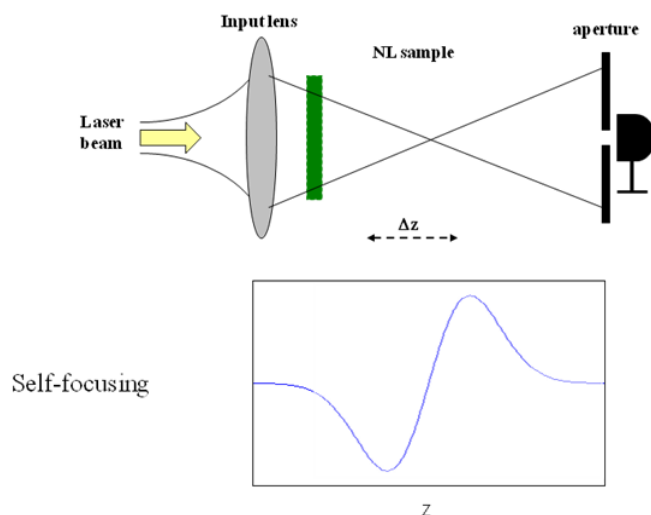


Figure 2 “Closed-aperture” Z-Scan and the resulting signal for a third-order self-focusing nonlinear response.

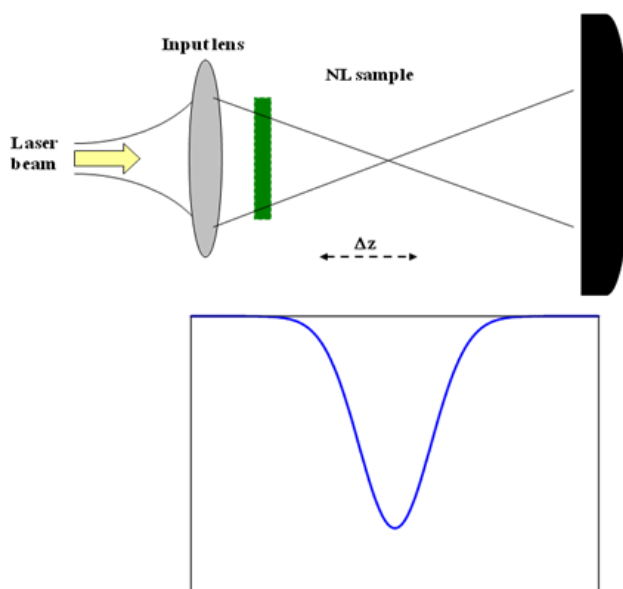


Figure 3. “Open-aperture” Z-Scan and the resulting signal for a third-order nonlinear response.

If both nonlinear absorption and nonlinear refraction are simultaneously present, which is often the case, the closed-aperture Z-scan signal is distorted from that shown in Fig. 2 as shown in the example of Fig. 4. The signal can simply be fit or the closed-aperture Z-scan data can be divided by the normalized open aperture Z-scan data to retrieve a signal that is nearly the same as if there had not been absorption in the first place (assuming that the absorption signal is fairly small). This simplicity of separating absorptive and refractive nonlinearities is one of the attributes that has made Z-scan so popular. In addition it is remarkably sensitive, in particular to induced phase distortion. We have performed Z-scans with sensitivity down to $\lambda/10^3$ (the EZ-scan has shown sensitivity to $\lambda/10^4$).⁵ This interferometric sensitivity at first seems strange for a single beam technique. However, the sample serves as a phase mask and the amplitude distortion appears upon propagation to the far field, i.e. via diffraction. Diffraction is the interference of different portions of the

beam upon propagation. Here think of the high intensity center interfering with the low intensity wings, so that the Z-scan is a single beam interference method. Figure 5 shows a Z-scan of a sample of BaF₂ where the picosecond pulse energy was lowered to show the signal to noise ratio. Here the overall phase distortion is $\sim\lambda/75$ with a signal to noise that would easily allow detection of $\lambda/300$ as shown.

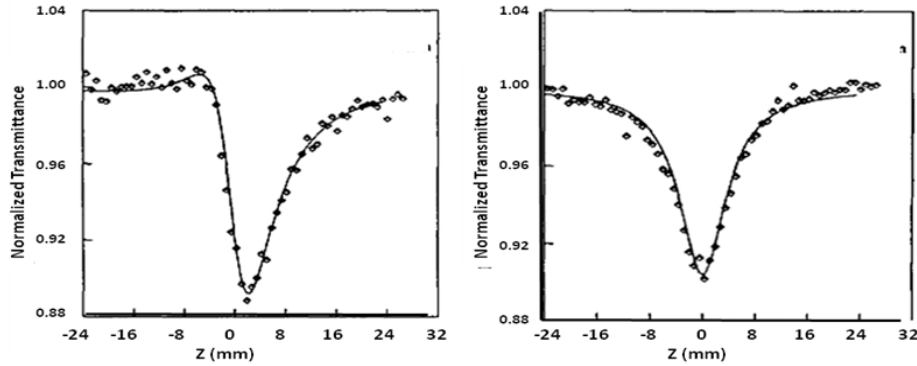
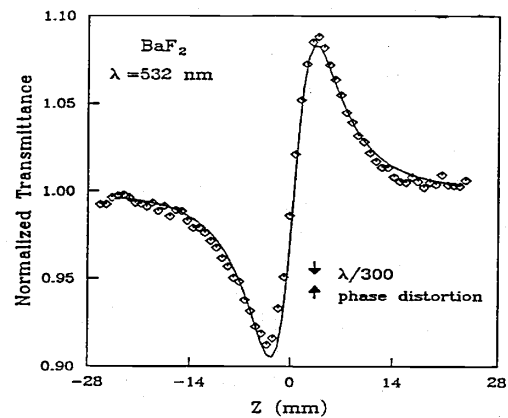


Figure 4. Closed- and open-aperture Z-scan data of ZnSe using picosecond pulses at 532 nm. The solid lines are fits to the data and show that it exhibits both 2PA and free-carrier refraction, FCR. From Ref [4]⁴

Figure 5. Z-scan of BaF₂ at a wavelength of 532nm using ~ 30 ps pulses. The solid line is a fit for a third-order nonlinear refraction. From Ref [4]⁴



While the Z-scan separately yields the sign and magnitude of both nonlinear refraction and nonlinear absorption, it does not give the physical mechanisms behind these nonlinearities, although fits to the data can often tell the order of the nonlinear response (e.g. third order for bound electronic nonlinearities). Other information is needed to elucidate these physical processes which often occur in unison. The temporal dynamics is often key to this understanding. Thus pump-probe methods using short pulses are very useful.^{14,15} We developed a method using a femtosecond pump along with a white-light continuum (WLC) femtosecond probe that allows spectroscopy to be performed. This method was actually motivated by our work on nonlinear Kramers-Kronig (KK) relations for bound electronic nonlinearities.¹⁶⁻¹⁹ What we found was that KK relations could be applied to frequency nondegenerate nonlinear absorption measurements to calculate the dispersion of the nondegenerate nonlinear refraction. We will discuss these relations in Section 5. First we will describe the WLC pump-probe method schematically shown in Fig. 6.²⁰

3. FEMTOSECOND WHITE LIGHT CONTINUUM (WLC) PUMP-PROBE SPECTROSCOPY

As shown in Fig. 6, a femtosecond pump beam prepares the sample to be interrogated by a broad spectrum pulse (WLC) that can be temporally delayed to give the spectral dynamics of the nonlinear absorption response.^{20,21} A WLC reference pulse gives the linear transmittance which can be subtracted from the transmittance of the probe WLC to give the change

in transmittance at all wavelengths as a function of temporal delay. This is a very powerful technique; however, it takes considerable skill to use and analyze data given that there are other ultrafast signals produced besides the nonlinear absorption signal that are described in detail in Ref. [21].²¹ In the end, after the extraneous signals are removed, the data analysis can be fit with a single equation that depends on the chirp of the WLC, and the nonlinear absorption. This has proven particularly useful for both 2PA and ESA and given the temporal resolution, can easily distinguish between these nonlinearities.

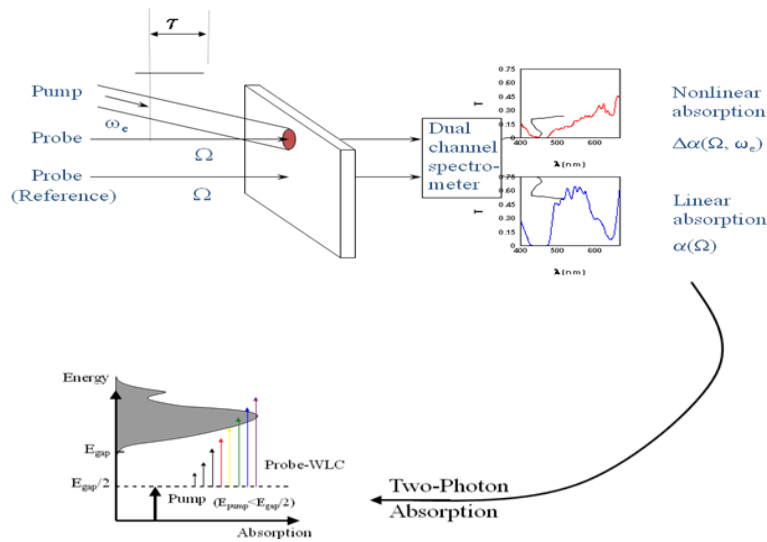


Figure 6. Femtosecond White-Light Continuum pump-probe spectroscopy indicating the example of two-photon absorption for the nonlinear response.

Figure 7 shows data taken on semiconductor (CdSe) quantum dots of two different radii giving their spectrum of nondegenerate 2PA.^{22,23} In addition, the signal taken using two-photon fluorescence (2PF) is shown giving the degenerate 2PA signal. While not discussed in this paper, 2PF is a powerful relative technique for determining 2PA in materials with reasonable fluorescence efficiency.^{24,25}

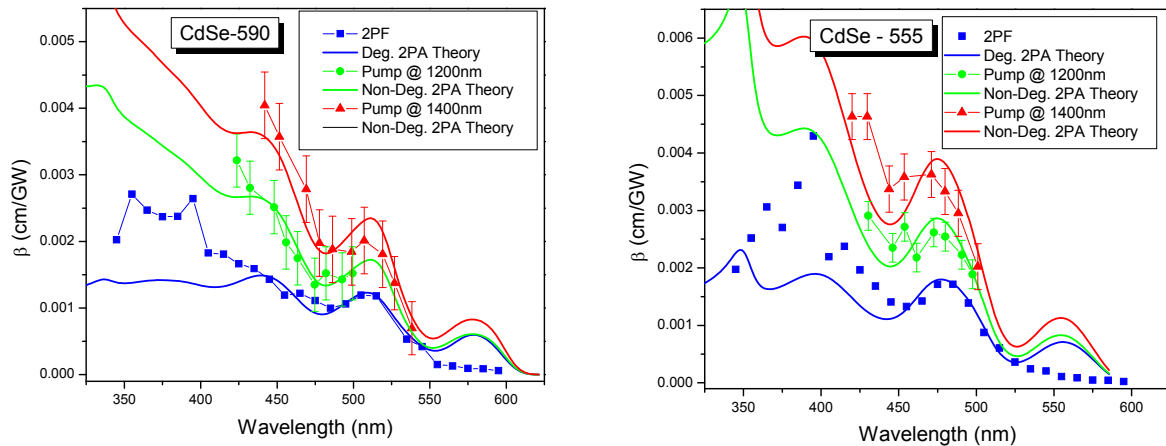


Figure 7. Plot of the 2PA coefficient, α_2 , or here β , as a function of the probe wavelength for a pump at 1400nm along with theoretical fits for CdSe quantum dots.²³ There are two different sizes of quantum dots shown having linear resonance absorption peaks at 590 nm (left) and 555 nm (right). Also shown is the 2PA from referenced two-photon fluorescence, 2PF. From Ref. [23].²³

Note that the nondegenerate signal is always larger which shows what we refer to as intermediate state resonance enhancement (ISRE), i.e. as the photon energies become separated, one of the photons comes closer to single photon resonance which enhances the 2PA signal in accord with theory as shown by the solid lines in Fig. 7.²³

While this pump-probe spectroscopic method is a very fast way to determine the spectrum of frequency nondegenerate nonlinearities while also giving the temporal response, it is often the case that the primary interest for applications is the degenerate nonlinear absorption and refraction. In addition, for the nondegenerate case there is a large number of pump and probe wavelengths to choose and the data acquisition and analysis can become cumbersome. For this reason we developed a complementary technique that allows us to simultaneously determine the spectrum of nonlinear absorption and the dispersion of nonlinear refraction. This is the WLC Z-scan.²⁶⁻²⁸ This method answers the question of how to perform the degenerate spectroscopy rapidly.

4. WLC-Z-SCAN

In this method the WLC^{26,27} is used as the single beam source for Z-scans.²⁸⁻³⁰ Ideally one would want to simply send this WLC through the sample, disperse the light onto a detector array and determine the nonlinear absorption as a function of wavelength. Unfortunately there is a major problem with this, best illustrated with the example of 2PA. Here many different energy photons can be simultaneously absorbed giving a very large nonlinear absorption signal that includes both degenerate 2PA and nondegenerate 2PA as illustrated in Fig. 8. Basically, any pair of photons of frequencies ω_1 and ω_2 where $\hbar\omega_1 + \hbar\omega_2 = E_2 - E_0$ satisfy the 2PA criterion.

Nondegenerate 2PA

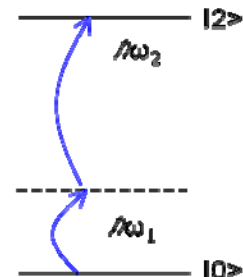


Figure 8. Nondegenerate 2PA process with unequal energy photons $\hbar\omega_1$ and $\hbar\omega_2$.

We spent considerable time separating different wavelengths prior to the sample using both prisms to spatially separate the wavelengths as well as using thick, high dispersion glass samples to temporally separate (chirp) the wavelengths.²⁸ These methods showed some success but greatly increased the complexity of the experiment. In the end we use the simple approach of narrow bandpass filters placed in the WLC prior to the sample as shown in Fig. 9.³⁰

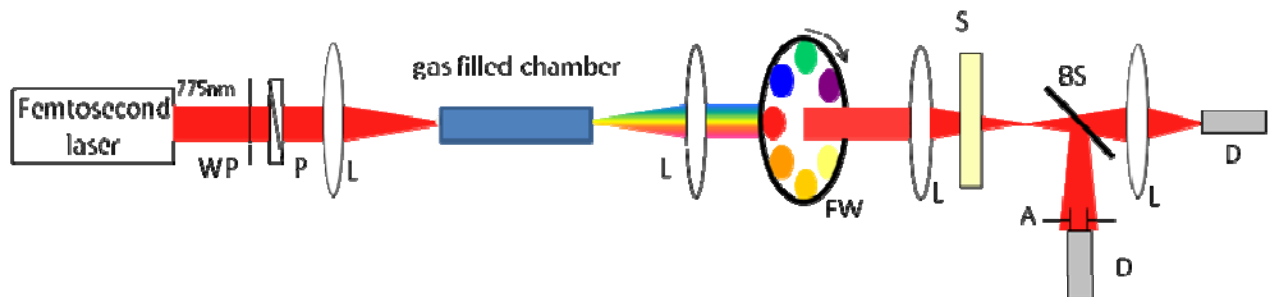


Figure 9. White Light Continuum, WLC Z-scan for simultaneous measurement of the degenerate nonlinear absorption spectrum (e.g. α_2) and dispersion of the nonlinear refraction (e.g. n_2). The spectrally intense WLC is spectrally filtered and used in the standard Z-scan (both closed- and open-aperture). The sample, S (right – yellow), is scanned in Z for each separate narrow bandpass filter on the filter wheel. From Ref. [30]³⁰

These filters, of bandpass $\sim 10\text{nm}$, still support short pulses ($\sim 100\text{fs}$) and eliminate the problem of nondegenerate 2PA. One might ask why this method would be any better than simply tuning the ubiquitous Optical Parametric devices (e.g. OPOscillator or OPAmplifier). The answer is in the experimental time. When an OPA is tuned, the spatial profile will change and possibly the pulsewidth will change as well. Therefore, the device output has to be characterized each time it is tuned. This is a very time-consuming process usually involving spatial filleting to obtain a Gaussian beam as well as knife edge or pinhole beam scans. Thus a single sample can take days to get a spectrum over an octave wavelength range (which also requires changing ancillary frequency mixing attachments to the OPA). In contrast, once the femtosecond WLC has been characterized, the spatial profile at any wavelength along with the temporal pulsewidth at any wavelength is reproducible from day to day and week to week. Thus it can simply be used to measure nonlinear properties without constantly re-measuring the spatial and temporal properties which are shown in Fig. 10. Fortuitously, the output spatial profile is Gaussian for all wavelengths within the octave spectral range from 400nm to 800 nm. The method for producing this high brightness WLC is to weakly focus $\sim 140\text{fs}$ pulses at 775nm from a regeneratively amplified Ti:sapphire laser into a 1.25m long gas-filled cell with Kr gas at 2.5 atm.

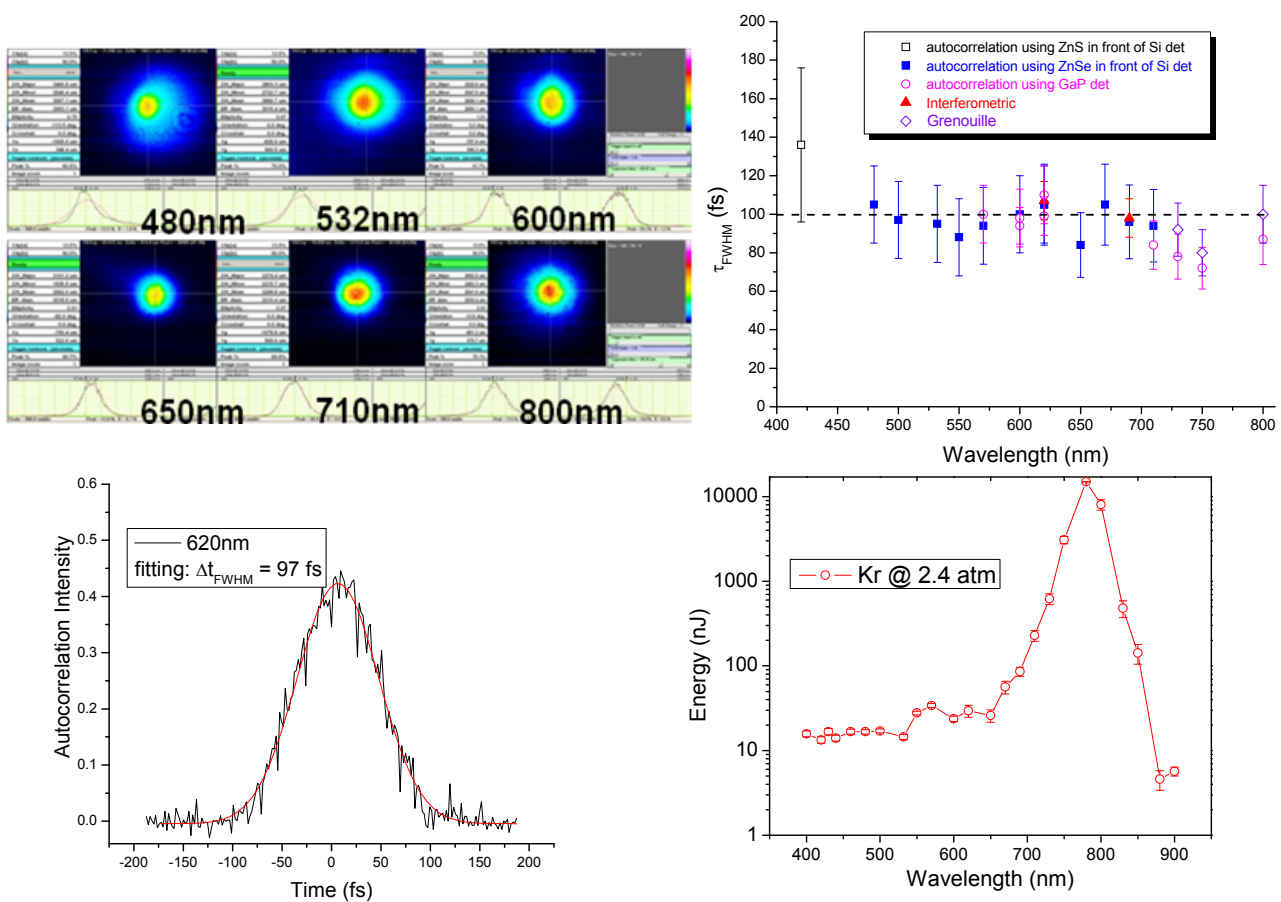


Figure 10. Spatial (upper left), temporal (upper right along with an example of an autocorrelation trace – lower left) and usable energy per pulse (lower right) characteristics of the white-light continuum used for the WLC Z-scan. See Ref. [30]³⁰

Currently, the wavelength range we can cover with this technique is limited to one octave, ranging from 400nm to 800 nm. While there is energy in the continuum past 800nm, the spatial profile breaks into a doughnut pattern past 800nm in agreement with theoretical calculations for a 775nm pump.³¹ We are searching for ways to extend this wavelength coverage. Examples of data using this method are shown in Fig. 11.

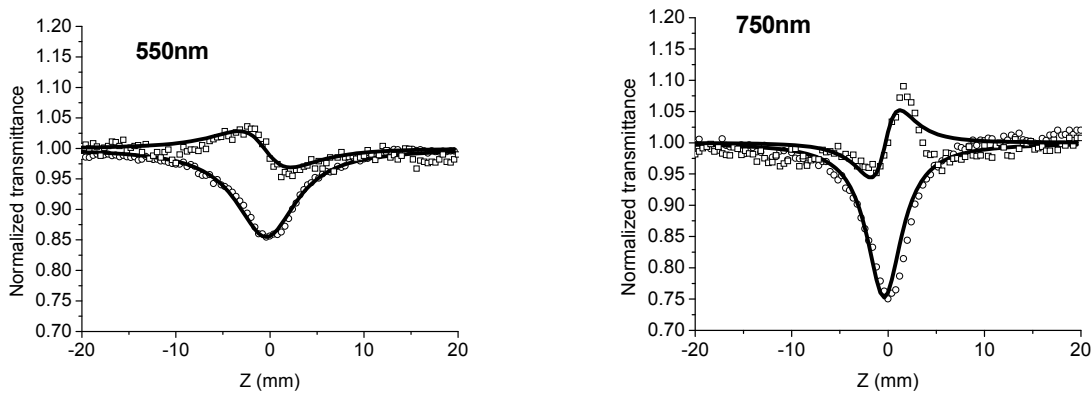


Figure 11. Z-scans (open- and divided) for ZnSe at 550 nm (left) and 750 nm (right) showing the change in sign of the nonlinear refraction from self defocusing (left) to self focusing (right). From Ref. [30]³⁰

Taking data at many wavelengths gives the spectrum of 2PA and dispersion of n_2 shown in Fig. 12.

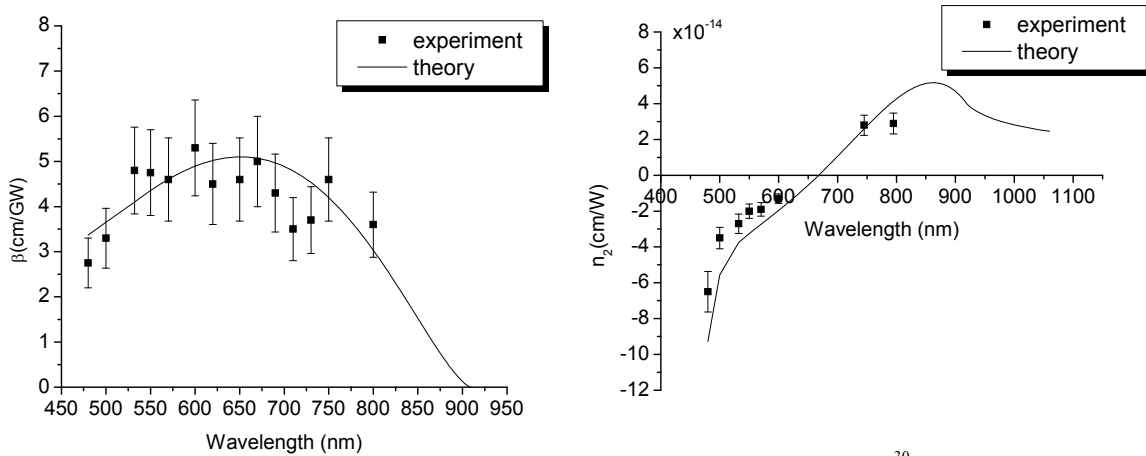


Figure 12. 2PA spectrum of ZnSe (left) along with dispersion of n_2 in ZnSe (right). From Ref. [30]³⁰

Similar data for the semiconductor ZnS are shown in Fig. 13. The solid lines are theory that will be discussed in Section 5 of this paper.

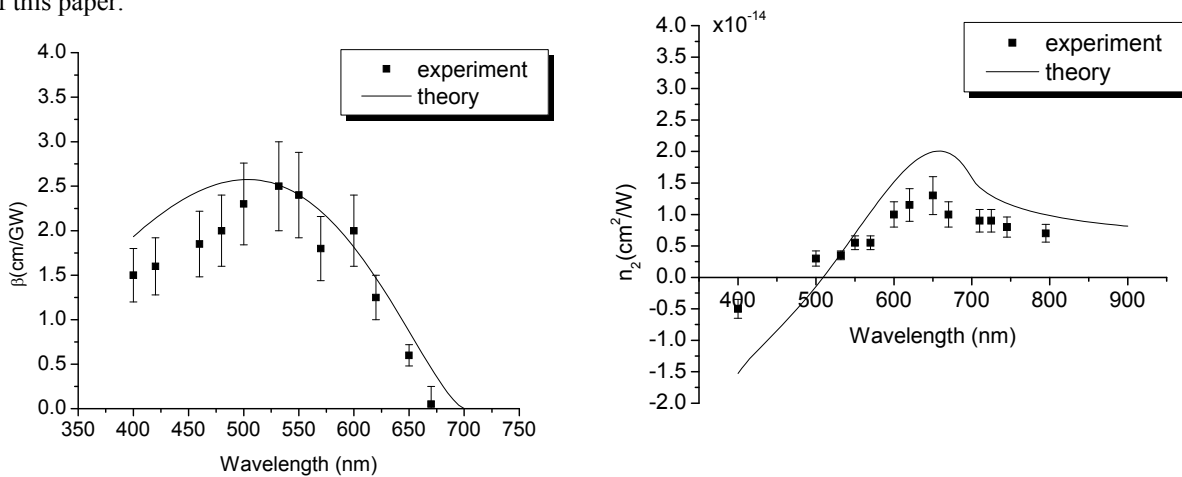


Figure 13. 2PA spectrum of ZnS (left) along with dispersion of n_2 in ZnS (right). From Ref. [30]³⁰

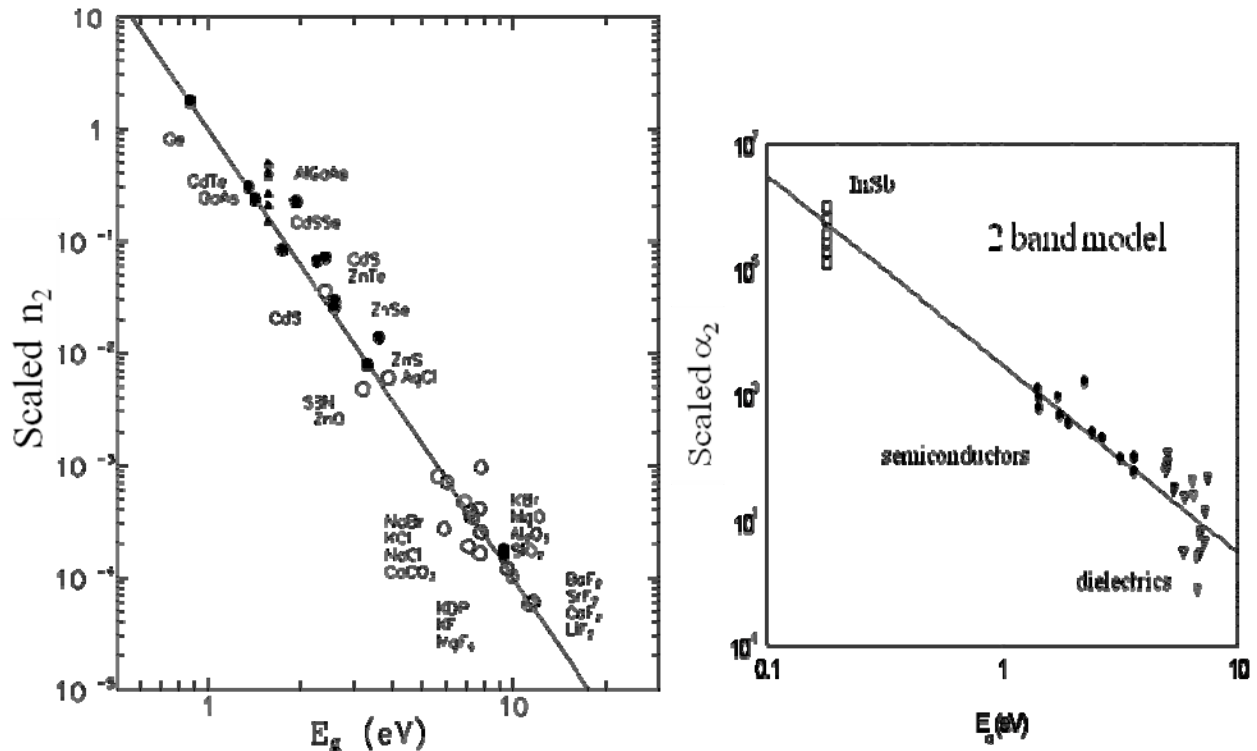


Figure. 14 Left: Bandgap energy dependence of n_2 in many materials. Right: values of α_2 vs. bandgap energy for many materials. Taken from Ref. [18].¹⁸

Performing these experiments and/or similar experiments on a variety of materials and including selected data from the literature (in particular Refs. [32,33]),^{32,33} we can plot the nonlinear refractive index normalized by the universal spectral dependence given by the simple 2-parabolic band model shown in the previous figures by the solid lines.^{18,19,34,35} The result shows the E_g^{-4} bandgap energy dependence of n_2 , see Fig. 14a. Similarly the E_g^{-3} dependence of the 2PA coefficient α_2 is shown in Fig. 14b. The different dependence on bandgap energy compared to 2PA is simply a difference in definition from the nonlinear susceptibility which varies as E_g^{-4} .

5. NONLINEAR KRAMERS-KRONIG RELATIONS

Here we briefly describe the relations connecting the nonlinear refraction shown in Figs. 12, 13 and 14 to the nonlinear absorption. In looking at the dispersion of the nonlinear refraction in Figs. 12 and 13 we see a peak near the 2PA edge followed by a rapidly decreasing n_2 as the photon energy increases turning negative at about 2/3 of the bandgap energy. This is reminiscent of the linear refraction near the one-photon absorption edge which shows a peak index near $\hbar\omega \sim E_g$ which rapidly decreases at higher photon energies where the sample absorbs. Here the linear refractive index is related to the absorption through linear dispersion relations called Kramers-Kronig, KK, relations.³⁶ Since these are linear relations, it was initially controversial to discuss nonlinear KK relations between n_2 and nonlinear absorption; however, it is possible to ‘linearize’ the relations by performing Kramers-Kronig integrals using optical prepared samples where a fixed frequency intense excitation source ‘dresses’ the material (so-called dressed states) and a weak tunable probe beam samples the change in transmittance. In this way the ‘linear’ material is now the sample with the excitation source turned on.

Thus the Kramers-Kronig relation for the nonlinear index becomes: $\Delta n(\omega, \Omega) = \frac{c}{\pi} \text{P} \int_0^\infty \frac{\Delta \alpha(\omega'; \Omega)}{\omega'^2 - \omega^2} d\omega'$ where Ω is the

frequency of the pump beam and appears only as a parameter on both sides of the equation.¹⁶⁻¹⁹ “P” indicates the principal value. The previous difficulties with applying KK relations to ultrafast nonlinearities arose from looking at the

frequency-degenerate nonlinear absorption where pump and probe were at the same frequency; thus the ‘excitation’ wavelength was part of the integrand. This meant that within the integral the pump wavelength was changing and therefore the material changed within the integral clearly violating causality. The change to integrating over the frequency nondegenerate nonlinear absorption removes this difficulty. This was the origin of our interest in pump-probe spectroscopy which ideally matched what was needed for the KK integral. In particular we were now able to relate n_2 to the nondegenerate 2PA spectra but this is only *after* performing the integral by letting $\omega=\Omega$.¹⁸

6. FREE-CARRIER AND EXCITED-STATE ABSORPTION

In order to be sure that the quantities measured in an experiment such as Z-scan, which looks at the degenerate nonlinearities, are due to the ultrafast bound-electronic responses, additional experiments need to be performed. In particular pump-probe experiments as in the example of Fig. 6 are excellent for determining the temporal response. For semiconductors, free carrier absorption (FCA) can be seen for temporal delays long compared to the pulsewidth and for organic dyes, the analog is excited state absorption (ESA).^{37,38} Figure 15 shows an example of pump-probe measurements taken for the dye to the right of the figure.

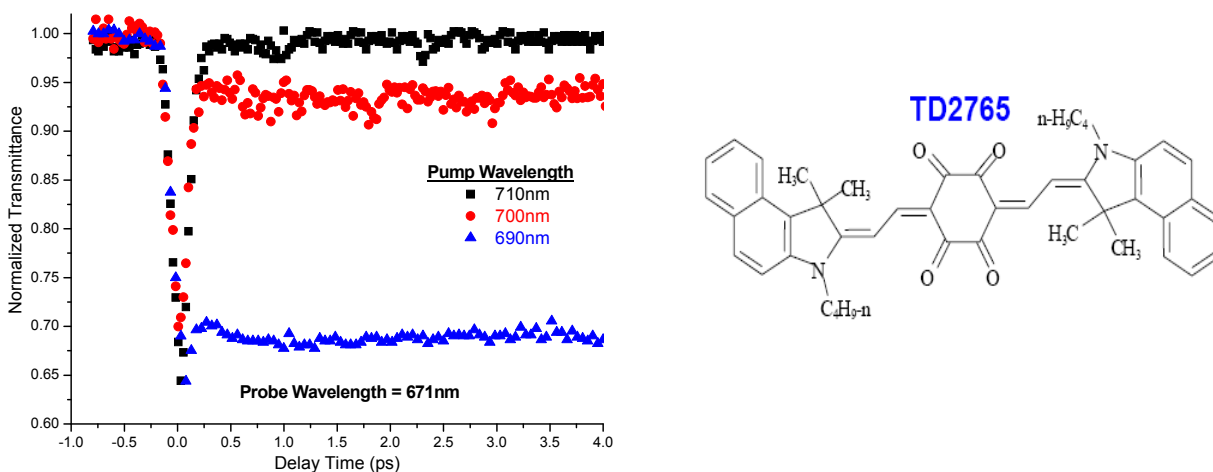


Figure 15. Normalized transmittance as a function of probe temporal delay at 3 different input wavelengths getting closer to the linear absorption edge from 710 nm to 690 nm for the molecule shown to the right. This shows how resonant excitation of excited states grows to nearly dominate the absorption as the wavelength is reduced. From Ref. [39]³⁹

In this case, looking at the spectrum of the material as shown in Fig. 16, we find that these excited states are actually created via linear absorption as opposed to 2PA. This can also be expected due to the fact that we have greatly reduced the possibility of 2PA created ESA by using femtosecond pulse where the ratio of irradiance to energy is large thus few excited states are created via 2PA.

In other systems where, for example, longer pulses are used, either FCA (for semiconductors) or ESA (for organic dyes) become significant from the 2PA generated carriers or states. These nonlinearities are analogous and appear identical in pump-probe experiments. By measuring the nonlinear response as a function of input energy, the 2PA generated FCA or ESA can be determined since they are higher order nonlinearities, i.e. $\chi^{(3)}:\chi^{(1)}$, 2PA followed by linear absorption. In a similar way, for example using closed-aperture Z-scans, the Free Carrier Refraction or Excited State Refraction can be determined. Figure 17 shows this method for the semiconductors, GaAs and CdTe.⁴⁰

Figure 16. Linear and 2PA spectra for the molecule shown in Fig. 15. From Ref. [39]³⁹

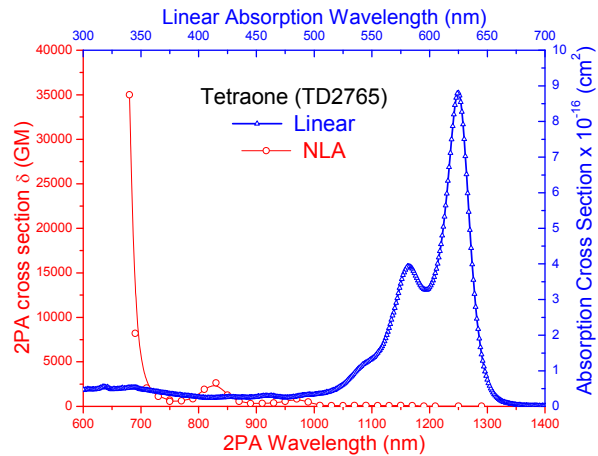
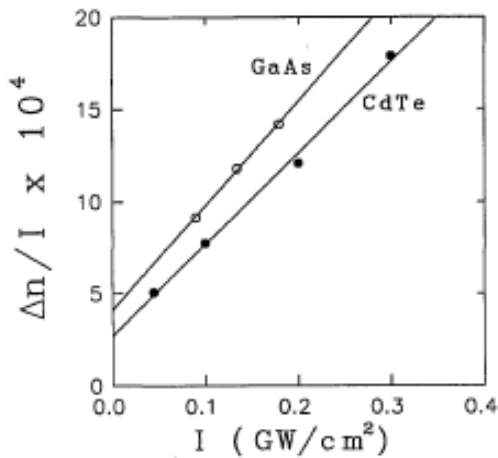


Figure 17. The change in index divided by irradiance as a function of irradiance for GaAs and CdTe as determined by closed-aperture Z-scans at 1.06 μm . This shows self-defocusing from FCR. The slope determines the FCR cross section while the intercept indicates n_2 . From Ref. [40]⁴⁰



While the FCR for semiconductors is always negative (just think of oscillators above the zero frequency resonance), in organic materials the ESR can be either positive or negative depending on which side of resonance wrt the newly created absorbers.

7. OPTICAL LIMITING

We end this article with a straightforward application of these nonlinearities, both nonlinear absorption and refraction, for optical limiting. There are a variety of optical geometries we have investigated utilizing a number of different materials. These geometries are shown in Fig. 18.^{38,41-50}

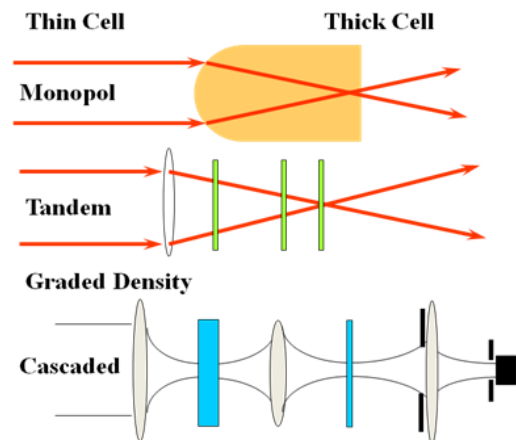
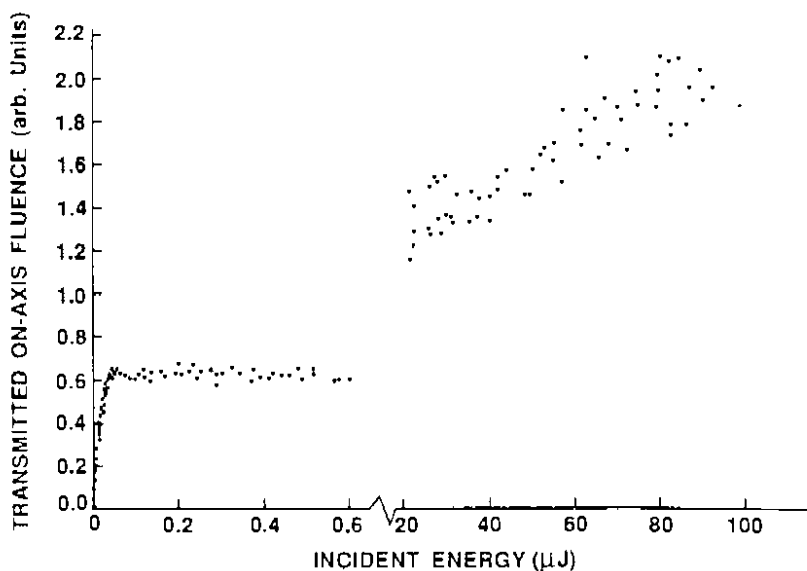


Figure 18. Various geometries used for optical limiting (thin film and thick cell not shown).

In principle, thin films can give the lowest threshold for limiting action to begin with since the irradiance is highest with the sample positioned at focus; however, this geometry will usually have a low dynamic range since the film will undergo irreversible damage. We define the dynamic range (DR) as the ratio of the linear transmittance to the minimum transmittance at the highest possible input prior to damage. In order to extend the dynamic range, various geometries are used. If, for example, the sample does not have appreciable linear loss (e.g. two-photon absorption based) the monolithic optical power limiter geometry (MONOPOL) can be used.^{44,45} In this geometry, the material prior to focus is meant to protect the focus from damage at high irradiance via absorption or self lensing (assuming the self lensing is defocusing). This geometry works well for picosecond pulses in semiconductors (see Fig. 19); however, for longer pulses the thermally-induced self focusing becomes dominant and the sample damages.

Figure 19. Nonlinear transmittance of a ZnSe MONOPOL limiter for picosecond input pulses at 532 nm. From Ref. [45]⁴⁵



For NLO materials that have linear loss, a judicious choice of sample placement in the tandem geometry can work well.^{38,46,47} Here, each element further toward the focusing lens protects the next element farther away. In the limit of an infinite number of elements, this becomes the “graded density limiter” (not shown).^{38,48} Here we show results for the cascaded geometry limiter which has shown by far the best limiting dynamic range of any of the geometries used to date.^{49,50} This geometry allows for multiple foci of arbitrary focusing geometries and mixing of different materials at the different focal positions. In this example we just use two. The specific elements used for the first such limiter are a phthalocyanine which provides the low limiting threshold via reverse saturable absorption with a CS₂ filled cell at the first focus.⁴⁹ The CS₂ operates by catastrophic self focusing to create a plasma and bubbles that absorb and scatter the light and protect the second focus from damaging inputs. The input/output characteristics are shown in Fig. 20 where encircled energy is that energy falling within a 1.5 mrad cone. The encircled energy is important since it is often the fluence that damages the detector element so that the focusability is of interest. This limiter works extremely well in the visible but since the phthalocyanine dye absorbs some wavelengths in this range the transmittance is colored. By replacing the phthalocyanine with a carbon black suspension (CBS), basically diluted india ink,⁵¹ the limiter becomes grey and works reasonably well throughout the visible for encircled energy as shown in Fig. 21.⁵⁰

Figure 20. Energy output vs input for the cascaded limiter of Fig. 19 showing a DR of at least 37,000 since no damage occurred up to the maximum available input energy of 58 mJ. Output encircled energy vs input energy. The overall linear transmittance of the device is $\sim 30\%$. From Ref. [49]⁴⁹

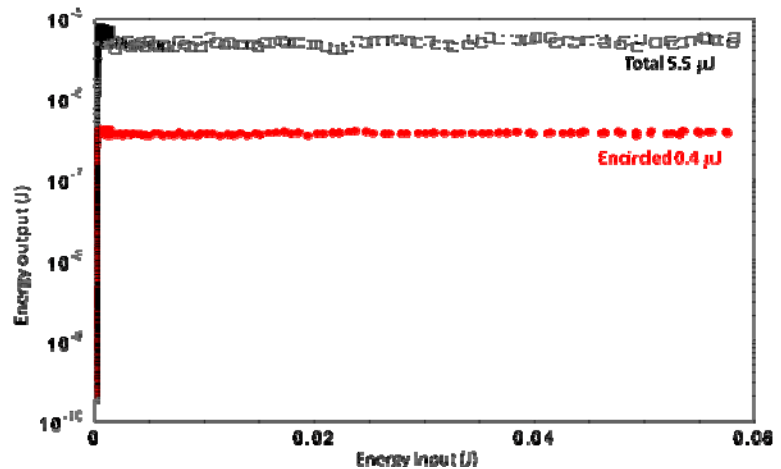
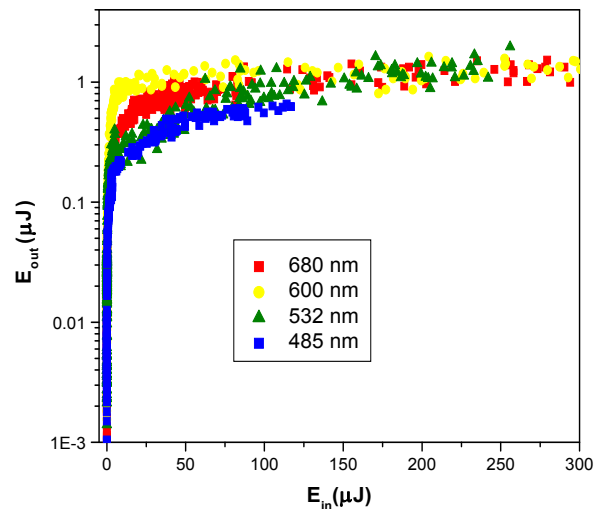


Figure 21. Encircled energy transmitted vs input energy for the cascaded limiter of Fig. 18 with CS₂ in the first cell and CBS in the second cell. The overall transmittance (both photopic and scotopic) is $\sim 30\%$. From Ref. [50]⁵⁰



8. CONCLUSION

In summary, we are utilizing a variety of characterization methods to accurately measure the nonlinear optical properties of many different materials from semiconductors to dielectrics to organics with the goal of building a reliable database from which theories can be tested. The ultimate goals here are to develop predictive capabilities. We have already been successful with predicting the ultrafast NLO properties of semiconductors. We and our colleagues are also making good progress toward building structure-property relations for organic molecules as well. However, more highly nonlinear materials are needed for many of the applications such as optical switching needed for devices. Multidisciplinary collaborations between physicists, chemists, materials scientists and optical scientists are key to these advances.

9. ACKNOWLEDGEMENTS

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Nonlinear spectroscopy: absorption and refraction

[7504-64]

Questions and Answers

Q. By doing the very fast measurement, you do indeed decouple thermal effects on the index, correct?

A. Yes. Obviously thermal is a problem if you are running at a high repetition rate. So, with the femtosecond lasers with the amplified systems we are running at about a kilohertz and with a kilohertz, we can actually run that rep rate down. Sometimes we'll actually check it. We'll run at a kilohertz and then drop it down to 200 Hz, and if there's no difference, we'll know that there's no thermal. But you still have to be careful. You still have to be careful.

Q. One other comment. I don't know how reasonable this is but I know people are thinking about building these electro-optic Fabry-Perot etalons, that you can tune by putting a field across over a different wavelength band. I don't know how large those bandwidths are these days, but I think I've seen about 50 nm. I don't know whether that would help with your filter wheel arrangement or not.

A. 50 nm? This is good, but I need about 800 nm.

Q. In one of your last slides, you mentioned several coherent pathways in the excitation. Is it possible to distinguish them by shaping the excitation pulses, such that one pathway is favored over another.

A. I wouldn't know how. I mean, they're all occurring simultaneously. There's no time ordering in the different processes. If you think of a way to do it, it would be neat to separate those. I wouldn't know how.

Q. It would depend on some properties of these virtual states that they probe.

A. That's right. Yes.

Q. Since you have to put all this intensity in in order to measure these nonlinear coefficients, don't you have a problem with transient defects forming in the material and affecting the measurement through linear absorption?

A. So making defects?

Q. Yes. The laser beam itself generates transient defects.

A. Well, transient defects are actually what we're interested in. That's one of the things we want. The transient defects are, for example, excited states. These may be considered transient defects. We look at those excited states. So by doing multiple experiments (we never rely on a single experiment to determine what the physical processes going on are) so indeed, we are interested in different processes. Certainly in organic materials, sometimes we not only make defects but we break the molecule up into multiple pieces. So, we have to watch all of those things. So, from the standpoint of laser induced damage, defects that we make, for example, sometimes people do z-scans and you end up with a permanent lens in the sample, so you have to understand what the permanent lens is caused by. So the answer is yes. By going to very short pulses with very low energies, we are able often times with the femtosecond pulses look at just the bound electronic processes with none of those other processes going on. When you go to picosecond or longer times, you make more and more of those defects.