Z-scan measurement techniques are widely used to characterize the nonlinear absorption strengths of photo-activated materials. A typical technique to find the material two-photon absorption cross-section – an essential parameter of nonlinear materials which is used to predict material behavior in different light conditions – is to fit Z-scan measurements by approximating the results with only two energy levels and a simple analytical formula. However, the accuracy of this standard technique depends on using very low laser energies and thin samples. SimphoSOFT does not have these restrictions.

SimphoSOFT has many benefits for fitting and modeling Z-scan experiments compared to traditional techniques:

- Includes Optimization to fit experimental data.
- No restrictions on energy level diagrams – three or more levels can be modeled.
- Accurate numerical results with no analytical approximations.
- Thin and thick samples simulated and fit.
- Both low and high laser pulse energies easily modeled.
- No time-consuming writing of computer software code.
- Graphical User Interface to simplify the user experience.
- 3D and 2D graphics generated to visualize and interpret results.

This application note shows that when laser energies exceed certain values, SimphoSOFT becomes an essential tool, if not the only one commercially available, to fit unknown two-photon absorption parameters to open-aperture Z-scan measurements as well as being a useful fitting tool for modeling low laser energies. By using SimphoSOFT Z-scan add-on, our customers can

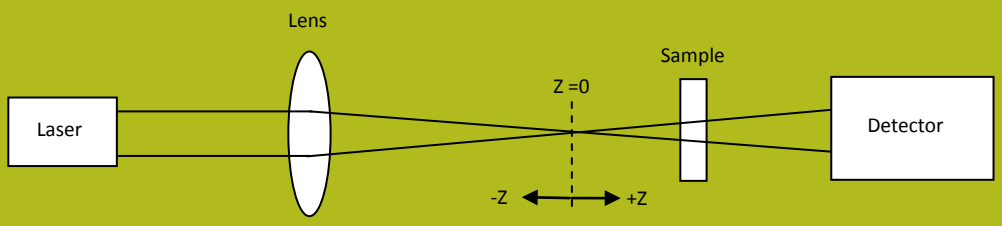
- predict a range of low laser beam energy values for accurate Z-scan measurements within a traditional two-level model,
- run Z-scan fits for high laser beam energy values and more accurate models of three or more energy levels.

Running Z-scan measurements at higher energies is beneficial as it reduces undesirable noise from the signal, which is inevitable at low energies, and is useful for determining additional parameters such as excited state absorption when the energy level diagram has three or more levels.

Z-Scan Fitting and Simulations for Two-Photon Absorption

Open-Aperture Z-scan measurements. The Z-scan measurement technique is a common technique where a single laser beam is tightly focused onto a nonlinear sample medium (References 1 and 2). The laser beam is directed perpendicular to the input plane of the sample. The sample is moved along the z direction (the laser beam direction) in and out of the laser focal point. The transmitted signal goes either directly to a detector (open-aperture Z-scan), as shown in Fig. 1, or through an aperture to a detector (closed-aperture Z-scan). In the case of open-aperture Z-scan, the laser pulse energy can remain constant, but the beam intensity at the sample varies as the sample position is moved in the z-direction due to the changing beam diameter at the sample. The resulting sample transmission is plotted as a function of the sample position – these positions are called z-displacements. With open-aperture Z-scan, one can determine the nonlinear absorption cross-section of the material. For example, one can determine the cross-section for two-photon absorption.

Fig 1. Schematic diagram of an open-aperture Z-scan experiment.



SimphoSOFT can model open-aperture Z-scan (SimphoSOFT comes with a predefined Z-scan template which sets a Z-scan run: select `File\New` menu item and choose a template with the name af455 Z-scan). In fact, Z-scan is a special case of a series run in SimphoSOFT. As in a series run, during a Z-scan fitting run or a regular Z-scan simulation run, SimphoSOFT calculates the transmittance values corresponding to a set of provided values of a variable parameter. The only difference is that the series variable is assigned indirectly by the following two steps:

- The user provides positive z-displacement values for the distances at which the front of the sample is displaced from the laser focus point (which corresponds to $z=0$).
- The SimphoSOFT Math Kernel will convert the provided values into beam radii values, $W(z)$, and will launch a fitting run or a series run with $W(z)$ as the series variable

The following formula is used for converting z-displacements into $W(z)$ values:

$$W(z) = W(0)\sqrt{1+\left(z/z_0\right)^2}$$

$$z_0 = \frac{\pi W(0)^2}{\lambda}$$

where $W(0)$ is the HW1/e^{2}M radius of the laser beam at the beam focus (i.e., $z = 0$) and λ is the wavelength of the beam in air or vacuum (*Caution*: Note the parameter $W(0)$ is larger by a factor $\sqrt{2}$ than another SimphoSOFT internal parameter, denoted as $R0$ (or R_0) in the program and defined as the HW1/eM radius).

Two-photon absorption (2PA or TPA) *is the simultaneous absorption of two photons in order to excite a molecule from one electronic state (usually the ground state) to a higher energy electronic state. The energy difference between the two states is equal to the sum of the energies of the two photons. Two-photon absorption is a third-order nonlinear process that is several orders of magnitude weaker than linear absorption. Instead of being linear in light intensity, the strength of 2PA depends on the square of the light intensity. Two-photon absorption was predicted by Maria Goeppert-Mayer in 1931 but was not experimentally verified until thirty years later when lasers were invented.*

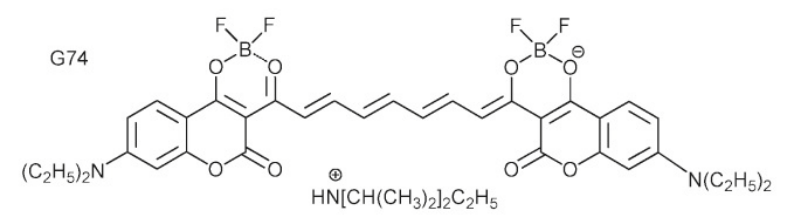
Example simulations

In this application note, we will show two examples of Z-scan simulations. In Example 1, we will use a model with two energy levels and will fit experimental Z-scan data taken at low laser pulse energy in order to determine the 2PA cross-section. In Example 2, we will use a model with three energy levels and we will examine what can happen to Z-scan results at higher pulse energies.

Example 1: Fitting 2PA to Z-scan experimental data

We use Z-scan data for an example organic molecule, G74, and fit the data to obtain the two-photon absorption cross-section. The molecule, G74, is a symmetrical anionic polymethine dye that was studied at the College of Optics and Photonics, University of Central Florida, Orlando, Florida (Reference 3).

Fig 2. Chemical structure of polymethine dye G74.



The data to be fit are shown below (Reference 4) along with the experimental conditions. The laser pulse energy is 39 nJ at 1550 nm.

Fig 3 (a). Z-scan data: sample displacements values (in nm) are in the first column and the corresponding normalized transmission values are in the second column

00000000	0.960047
01000000	0.976298
02000000	0.989328
03000000	0.994437
04000000	0.996669
05000000	0.997802
10000000	0.999427
15000000	0.999743

Fig 3 (b). Experimental parameters.

2PA of G74 in Acetonitrile	
Wavelength	1550nm
Spot size	24um(HW1/e2M)
Pulse width	110fs (FWHM)
Length	1.0mm
Index of refraction	1.34
Conc.	1.7mM=1.024e18 cm^{-3}

Setting up Z-scan fitting in SimphoSOFT

There are two essential CAD panels in SimphoSOFT which should be set for Z-scan simulation. In SimphoSOFT Experimental CAD (E-CAD in short, see Fig. 4(a)), the CAD's workspace should contain a laser beam and a sample. Laser and sample properties listed above should be entered into the appropriate properties dialogs (Right-click over the objects). Material CAD (or, in short, M-CAD, see Fig. 4(b)) should show a simple two-level model with a two-photon absorption transition (labeled S0.1) and a 1 ps long relaxation transition (labeled A1.0).

Screenshots of SimphoSOFT® E-CAD and M-CAD workspaces with experiment's components and energy level diagram, respectively

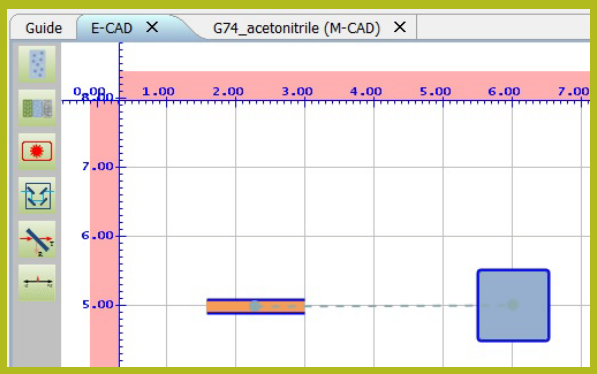


Fig 4 (a). E-CAD: Experimental CAD workspace

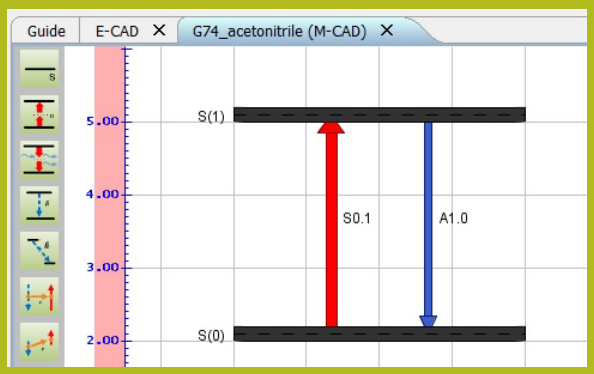


Fig 4 (b). M-CAD: Material CAD workspace with two energy levels

Now we are ready to set Z-scan fitting. In E-CAD, right-click on the sample object (blue rectangle) and select 'Fit Parameter'. An Optimization dialog called 'Optim', see Fig. 5(a), will open. Select the desired 'Fitting Parameter' and fill in the dialog selections labeled 'Lower Limit', 'Upper Limit', 'Starting Value' and 'Tolerance' as in the example below. For 'Experimental Type' in Optim, choose 'Z-Scan'. Insert 'Displacement' values for Z. The 'Displacement' values do not need to be same as the experimental values. The experimental (measured) 'Observed Transmission Data' is imported from a text file, for example 'Z-scan_G74_data_39nJ.txt'. The actual values are shown in Fig. 3 (a). Next go to 'Run Configuration' panel to set up actual run, select 'Parameters' tab (Fig. 5(b)) and set 'Fitting' as a run Type and check the 'Summary Report' box.

Screenshots of SimphoSOFT® Optimization dialog and Run Configuration dialogs

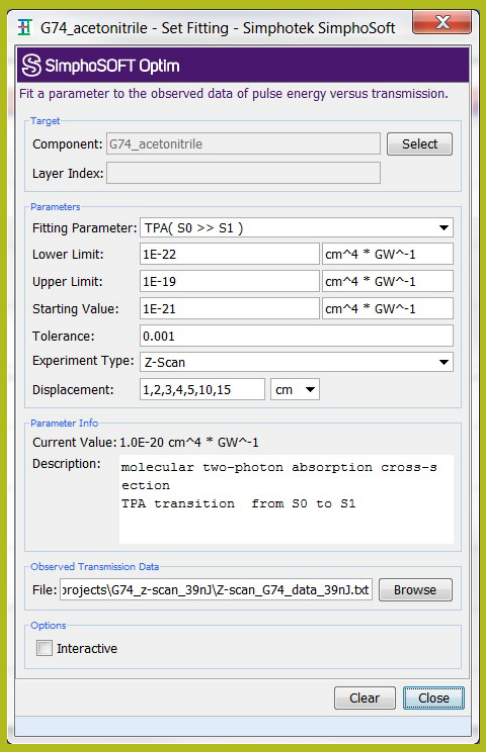


Fig 5 (a). Optimization dialog

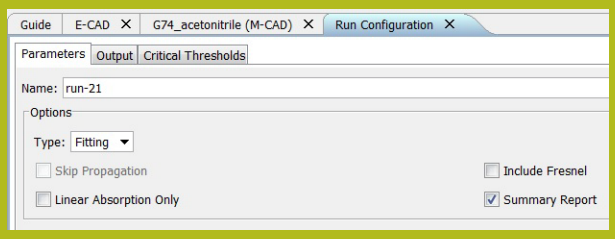


Fig 5 (b). Run Configuration 'Parameters' tab dialog

During the fitting process, SimphoSOFT Optimization uses a least-squares fitting routine to provide the best fit of a chosen parameter in the simulation model to a data set of experimental points. The data set is n points of the form (x_i,y_i) where $i = 0, 1, ..., n\text{-}1$ and where x_i is an independent variable and y_i is a dependent variable. The values of y_i are usually found by doing experiments. For this Z-scan example, x_i is the sample displacement value from the focal point and y_i is the transmission value resulted from this displacement. For a one-parameter least-squares fit using an adjustable parameter, in this case the 2PA cross-section σ_{TPA}, the model function is of the form $f(x_i, \sigma_{TPA})$, where $f(x_i, \sigma_{TPA})$ is a numerical result calculated by SimphoSOFT.

The crucial difference between SimphoSOFT Optimization module and conventional models to fit unknown two-photon absorption cross-sections to Z-scan measurements is that SimphoSOFT model function $f(x, \sigma)$ is not an analytic function (Reference 5), but is found by a more accurate process as a numerical solution of the coupled propagation and rate equations (Reference 6). This allows SimphoSOFT to take into account finer photo-physical processes which are essential at high laser energies for instance.

The optimization process minimizes S (also sometimes called chi-squared, χ^2, using the capital Greek letter chi), which is the sum of the squares of the differences between the experimental transmission values and the calculated transmission values. The value of the sum

$$S = \chi^2 = \sum [y_i - f(x_i, \sigma_{TPA})]^2,$$

is determined by summing over all $i = 0, 1, ..., n\text{-}1$.

The program minimizes χ^2 to determine the best σ_{TPA} and shows the accuracy of the fit for each value tried. A screenshot of an example intermediate fit is shown in Fig. 6. The values of χ^2 for iterations 0-4 are shown in Fig. 6(a). Fig. 6(b) shows a comparison of the iteration-4 fit (iter-4 in blue) – the calculated values – and the experimental values (in orange).

Fig 6 (a). Calculated values of χ^2 are gradually decreasing during iterations 0 - 4

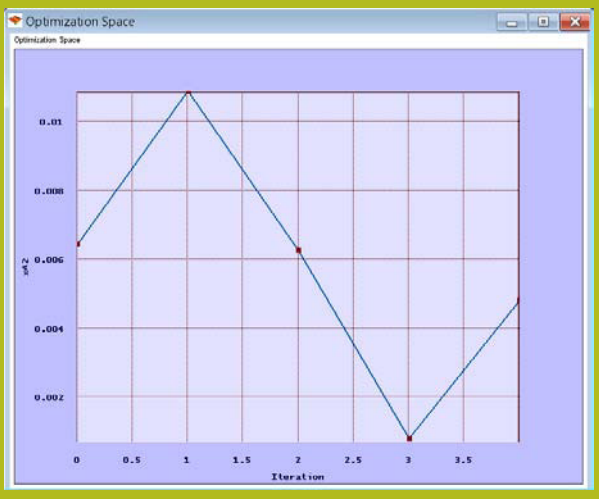
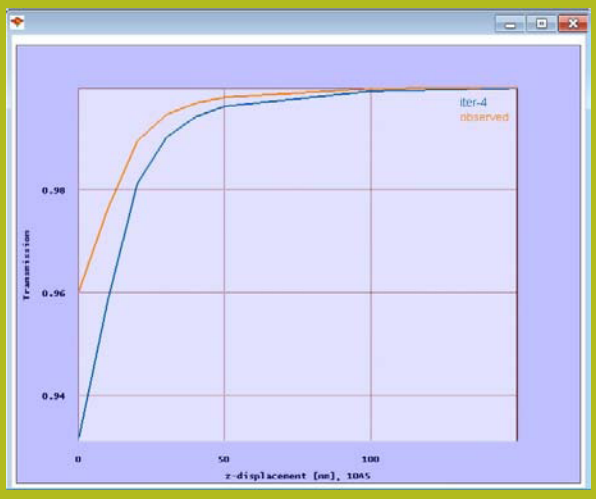


Fig 6 (b). Comparison of the iteration-4 fit (blue) and the experimental values (orange)



The final fit at the end of the simulation run is shown in Fig. 7. The value of χ^2 has stabilized near zero after about 8 iterations, see Fig. 7(a). Fig. 7(b) indicates that the calculated transmission values for iteration 13 (iter-13) and the experimental transmission values (in orange) become essentially the same.

Fig 7 (a). Successful convergence of the fit error χ^2 to zero after 14 iterations

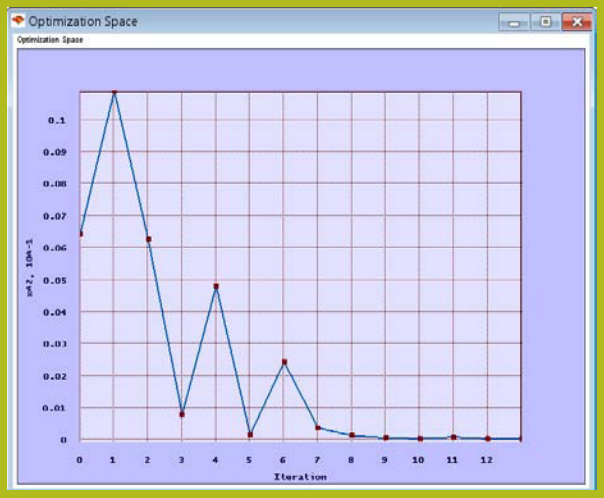
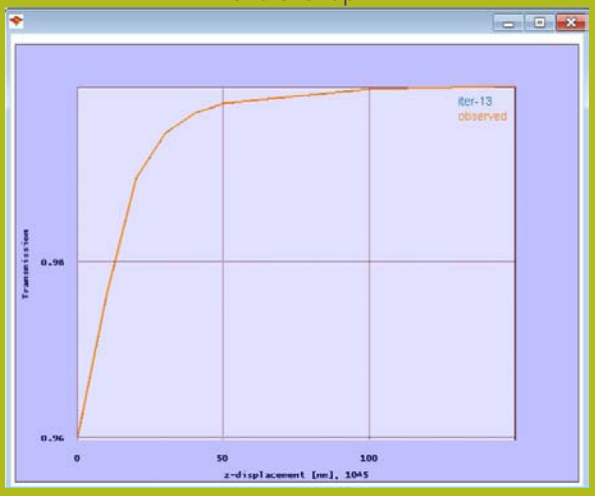


Fig 7 (b). At the last iteration, the fit (blue) and the experimental values (orange) are essentially identical and overlap



At the end of the fitting simulation, the SimphoSOFT presents a summary of the fitting iterations, see Fig. 8.

Fig 8. Summary of fitting results.

Event Log | Schematic | run-31 summary | run-32 summary

```
Summary report: ==========================
Optimization run (# iterations: 14).
Optimal value for sgmTPA: 3.4486250839365575e-020 [cm^4 GW^-1]

Iterations:
00. 1e-022              (err= 0.0039351342554696895)    range[1e-022,9.9999999999999998e-020]
01. 9.9999999999999998e-020             (err= 0.0070047681082988644)    range[1e-022,9.9999999999999998e-020]
02. 9.9999999999999991e-022             (err= 0.0038299179173381659)    range[1e-022,9.9999999999999998e-020]
03. 3.8814634000000003e-020             (err= 0.00047384379152900l3)    range[1e-022,9.9999999999999998e-020]
04. 6.2185363509556003e-020             (err= 0.0030273435854464015)    range[1e-022,9.9999999999999998e-020]
05. 3.3619269314280422e-020             (err= 0.00010443214331198888)   range[1e-022,9.9999999999999998e-020]
06. 9.6007075681127542e-021             (err= 0.0028311969938634254)    range[1e-022,9.9999999999999998e-020]
07. 3.0591612344181817e-020             (err= 0.00044327596760398064)   range[1e-022,9.9999999999999998e-020]
08. 3.4619613778067119e-020             (err= 7.2222244825263333e-006)  range[1e-022,9.9999999999999998e-020]
09. 3.6221968872157937e-020             (err= 0.00018576167641503236)   range[1e-022,9.9999999999999998e-020]
10. 3.4725677360241845e-020             (err= 1.9051902380671597e-005)  range[1e-022,9.9999999999999998e-020]
11. 3.4377015829329311e-020             (err= 1.9841924774758695e-005)  range[1e-022,9.9999999999999998e-020]
12. 3.4553761785112102e-020             (err= 1.6624939989754821e-006)  range[1e-022,9.9999999999999998e-020]
13. 3.4486250839365575e-020             (err= 7.6546219500428503e-006)  range[1e-022,9.9999999999999998e-020]
```

SimphoSOFT Optimization determined the best fit for σ_{TPA} = 3.449 × 10^{-20} cm^4/GW, where a gigawatt (GW) is a gigajoule per second (GJ/s). Other ways to express σ_{TPA} are as δ_{2PA} in units of Goeppert-Mayer (GM) (after its discoverer, Maria Goeppert-Mayer), where GM is 10^{-50} cm^4 s/photon or in terms of β, where β is cm/GW. The factors for converting the SimphoSOFT units to the other units are shown below.

SimphoSOFT TPA units	Multiply by	To convert to other units
σ_{TPA} in cm^4/GW	[(Energy/photon)(10^{50})] or [(hc/λ)(10^{50})]	δ_{2PA} in GM (10^{-50} cm^4 s/photon)
σ_{TPA} in cm^4/GW	Molecular concentration N_0 in molecules/cm^3	β in cm/GW

The energy per photon is hc/λ, where h is Planck's constant and c is the speed of light. The resulting energy per photon in terms of gigajoules, GJ/photon, and wavelength, λ, is given by:

$$E[in\ \text{GJ/photon}] = hc/\lambda = \frac{1989\ \times\ 10^{-28}[in\ \text{nm\ GJ/photon}]}{\lambda[in\ \text{nm}]}$$

At 1550 nm, the energy/photon is 1.283 $\times 10^{-28}$ GJ/photon. The molecular concentration N_0 for this example is 1.024 $\times 10^{18}$ molecules/cm^3.

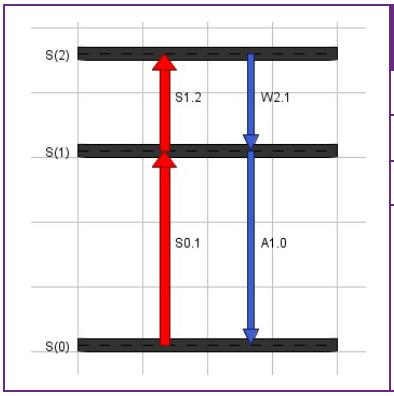
Doing the conversions to the δ_{2PA} and β units gives the following results:

δ_{2PA} = 443 GM
β = 0.034 cm/GW

The value of δ_{2PA} = 443 GM is consistent with published results obtained at the University of Central Florida (Reference 1).

Example 2: Simulating a three-level Z-scan model with both 2PA and ESA

In Example 2, we do Z-scan simulations both at low pulse energy (39 nJ) and high pulse energy (5 µJ) and show that the shape of the Z-scan plot changes dramatically. We modify the simple two-level model shown in Example 1 by adding a third energy level. For the S(0) to S(1) transition, we use the σ_{TPA} value determined in Example 1. Single-photon excited-state absorption (ESA) can occur from state S(1) to state S(2) and electrons can subsequently relax from state S(2) to state S(1). The simulation parameters are shown below.



From level(s):	To level(s):	Cross-section:	Relaxation time:
0	1	3.499×10^{-20} cm^4 GW^{-1}	
1	2	1.0×10^{-18} cm^2	
2	1		1 ps (non-radiative)
1	0		1 ps (radiative)

Laser beam properties	
Beam energy	39 nJ or 5 µJ
Beam radius (HW1/e^{2}M)	24 µm
Pulse FWHM	110 fs
Wavelength	1550 nm

Z-scan for low pulse energy of 39 nJ

For a pulse energy of 39 nJ, which is the energy used for the Z-scan fit in Example 1, the population densities of energy levels S(0), S(1) and S(2) are only slightly perturbed, see Fig. 9 (a). Most electrons remain in the ground state S(0) during the time of the pulse. There are only a few electrons in the first excited state S(1) and essentially zero electrons in the second excited state S(2). For 39 nJ, the resulting Z-scan simulation for the 3-level model, shown in Fig. 9 (b), is essentially unchanged from Z-scan simulations for the two-level model (not shown).

Fig 9 (a). The populations of the three states during the time of the 39nJ laser pulse (tau = 0 is the center of the pulse in time)

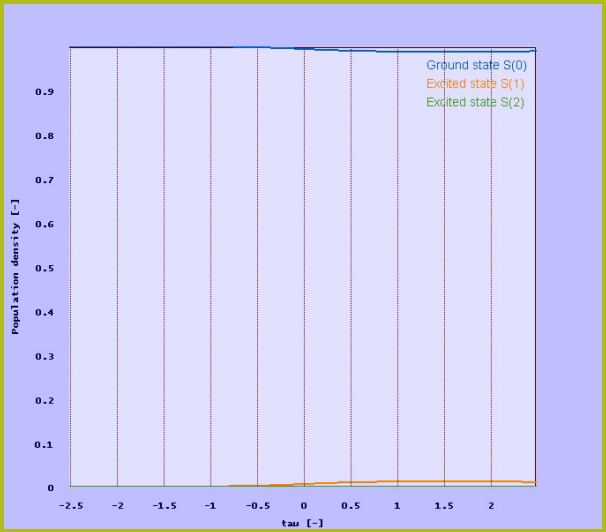
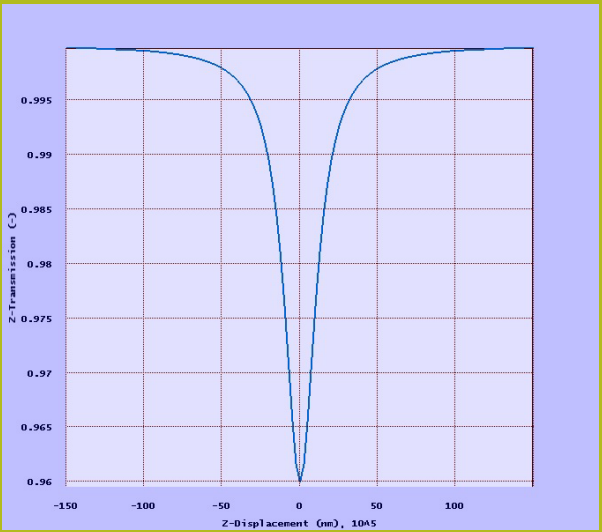


Fig 9 (b). The corresponding Z-scan plot



Z-scan for high pulse energy of 5 µJ

Looking at the populations of the three energy levels during the time of a 5 µJ pulse, shown in Fig. 10 (a), one can observe that the ground state is depleted and electrons initially go mainly to state S(1) during the leading edge of the pulse. By the time the center of the pulse (tau = 0 on the plot) passes through the material, most of the electrons are pumped from an excited state S(1) to the second excited state S(2).

In contrast to the low-energy 39 nJ simulation, there is a large distortion in Z-scan simulation results for high laser energies. For the highest incident pulse intensity [corresponds to displacement z = 0 on Fig. 10 (b)], the sample has bleached and the transmission at z = 0 is higher than at z = 2 mm (20 $\times 10^5$ nm on the plot) where the radius of the beam is larger and the incident pulse energy is lower.

Fig 10 (a). The populations of the three states during the time of the 5 μJ laser pulse (tau = 0 is the center of the pulse in time)

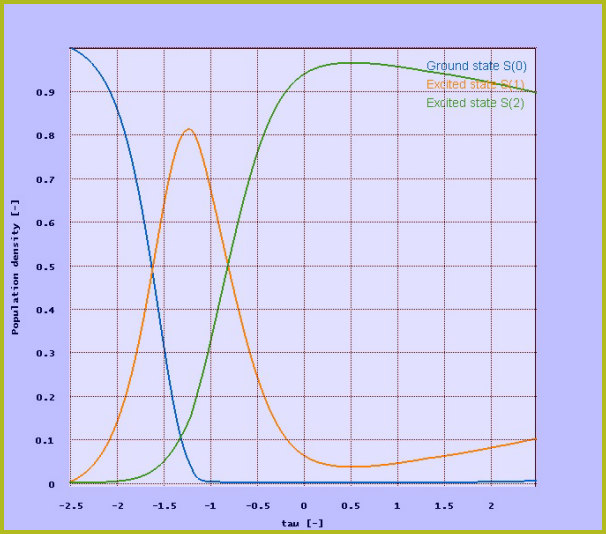
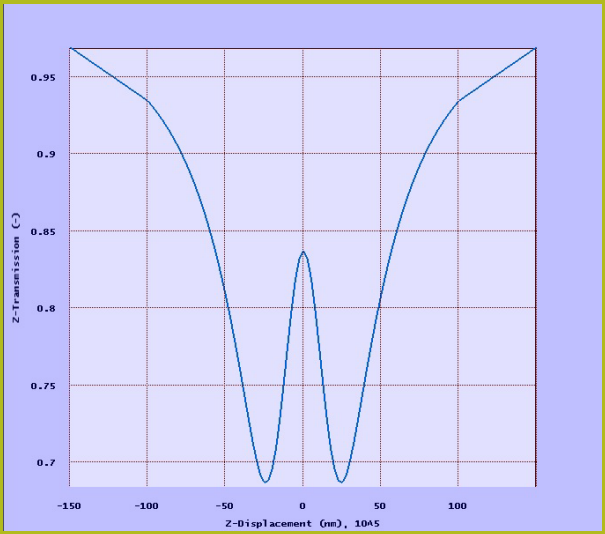


Fig 10 (b). The corresponding Z-scan plot



These simulations illustrate that experimenters need to be careful in choosing the right laser energy for their Z-scan measurements. A simple two-level model for σ_{TPA} is accurate only when pulse energies are not exceeding a certain threshold, unique for every type of material, so that the upper energy levels are only slightly populated. At higher pulse energies, other processes such as ESA can occur and must be accounted for to obtain accurate results.

Thus, SimphoSOFT Z-scan add-on is essential in two cases. First, user can pre-screen Z-scan measurement by analyzing the population density dynamics with SimphoSOFT to see if the chosen energy values are low enough for Z-scan fitting based on simple two-level approximations. Second, in case the chosen values are relatively high, SimphoSOFT can accurately fit the multi-photon absorption cross-section as, contrary to the conventional simple absorption models, it considers higher excited states during calculations which are essential for high energies. SimphoSOFT provides enough graphical output to be used for Z-scan analysis and Z-scan fits for both low and high laser energy inputs.

References:
(1) Sheik-Bahae, M. et al, IEEE Journal of Quantum Electronics, 26(4), 760-769 (1990).
(2) Van Stryland, E. W. & Sheik-Bahae, M., Characterization Techniques and Tabulations for Organic Nonlinear Materials, M. G. Kuzyk, & C. W. Dirk, Eds., 655-692, Marcel Dekker, Inc. (1998)
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