Two-photon spectroscopy and analysis with a white-light continuum probe

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We present a powerful experimental tool and analysis for characterization of two-photon absorption (2PA) spectra. We demonstrate this method with ZnS and then apply it to organic dyes in solution. We also compare the results with those from other methods such as two-photon fluorescence spectroscopy. This femtosecond pump–probe method uses a white-light continuum (WLC) as the probe to produce a nondegenerate 2PA spectrum. The extreme chirp of the WLC requires that transmittance data be collected over a range of temporal delays between pump and probe pulses. These data then need to be corrected for the effects of this chirp as well as for the temporal walk-off of the pulses in the sample that result from the frequency nondegenerate nature of the experiment. We present a simple analytic solution for the transmitted fluence through the sample, which is applicable for most practical cases.   © 2002 Optical Society of America

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The quest for materials that exhibit high nonlinear optical (NLO) absorptivities has increased dramatically over the past several years. Two-photon absorption (2PA) is an object of interest in chemistry, photonics, and biological imaging. Several current and emerging technologies, including optical power limiting, two-photon fluorescence imaging, two-photon photodynamic cancer therapy, and two-photon microfabrication, exploit 2PA.[1]

With the advent of tunable, short-pulse laser sources, many experiments that are of use in NLO materials characterization have become possible. One method of interest is femtosecond pump–probe spectroscopy, in which a broadband, weak, white-light continuum[2] (WLC) pulse is used to probe a medium that has just been subjected to an intense pump pulse. This pump–probe technique yields a frequency nondegenerate NLO absorption spectrum. It could, in principle, be a single-shot technique because the large spectral extent of the probe beam allows for full characterization of the sample. In practice, because of WLC chirp, the temporal delay between pulses must be scanned. An alternative method for obtaining the spectral dependence of the nonlinearity involves the often more time-consuming process of tuning and calibration of the probe and (or) pump pulses at various different wavelengths, e.g., in pump–probe experiments or in degenerate Z scans.[3] Furthermore, one can, under certain conditions, use the nondegenerate NLO spectrum to infer the spectral dependence of the nonlinear refraction through Kramers–Kronig relations.[4]

The WLC probe is chirped because of positive group-velocity dispersion (GVD) of optical elements including the WLC generating element, and therefore the transient spectra suffer from a wavelength-dependent time-delay distortion. To extract the true dynamics, we must vary the relative pump–probe time delay and rescale the data as discussed below. This is important, especially in the case of short-time-scale processes, such as 2PA, in which the nonlinear interaction takes place only during the time overlap of the probe and pump pulses. The information contained in the time-delay measurements is also useful for determining the origin of the nonlinearity, e.g., differentiating between 2PA and long-lived processes such as excited-state absorption.

The nondegenerate character of the experiment also leads to a temporal walk-off between the pump and the probe within the sample that reduces the effective interaction length. This walk-off is due to the group-velocity mismatch in the sample and causes a reduction in the nonlinear signal as the frequency difference between pump and probe increases. Spencer and Shore[5] give a theoretical treatment of the pump–probe interaction in a lossy Kerr medium to describe the cross-phase modulation and chirp imposed on the probe owing to excitation. Ziólek *et al.*[6] show how the real temporal response function of a pump–probe apparatus can be determined if the linear properties of the sample (dispersion of the refractive index) are known. Here we present a general model, including linear and nonlinear effects, of the pump–probe interaction in Kerr media for a 2PA process. Whereas the group-velocity mismatch between pump and probe can significantly reduce the nonlinear signal strength, GVD can have a negligible effect on the probe pulse propagation. An analytic solution of this propagation in Kerr media for the normalized fluence transmittance of the probe can be found in this limit of negligible GVD for the probe. How this can be true for the WLC is described in more detail below. This limit is valid for most practical cases, e.g., a sample thickness L of a few millimeters, and for probe pulses near 100 fs. The normalized fluence transmittance, T, is then given by

$$T(\sigma, \tau_d, W, \rho, \Gamma) = \frac{\exp(-2\sigma)}{W\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left\{-\left(\frac{\tau + \tau_d - \rho}{W}\right)^2\right.$$

$$\left. - \frac{\Gamma\sqrt{\pi}}{\rho}\left[\mathrm{erf}(\tau) - \mathrm{erf}(\tau - \rho)\right]\right\}\mathrm{d}\tau,$$

$$(1)$$

where $\sigma = \alpha L$ (α is the linear absorption coefficient),

$$\rho = \frac{L}{w_p c}\left(n - n_p + \lambda_p \frac{dn}{d\lambda}\bigg|_{\lambda_p} - \lambda \frac{dn}{d\lambda}\bigg|_{\lambda}\right)$$

is the temporal walk-off parameter (w_p is the pump pulse width, n is the sample refractive index at wavelength λ, and c is the speed of light), and $\Gamma = L(n/n_p)I_p{}^0\beta$ describes the nonlinearity.[7] Here τ_d is the ratio between the relative time delay and the pump's temporal width (HW1/eM), W is the ratio of probe and pump temporal widths, $I_p{}^0$ is the pump's peak irradiance (in watts per square meter), and β is the nondegenerate 2PA coefficient (in meters per watt). All subscripts p refer to the pump. We use this analytic solution to fit the experimental data at 10-nm increments over the bandwidth of the probe. As stated, Eq. (1) is valid over spectral ranges at which the GVD is negligible; although this is certainly not true for the entire continuum, it is true for portions of the WLC. We verified this through calculations and observations of the WLC chirp by making the optical Kerr effect (OKE) measurements, as described below. Our spectrometer resolution is limited to ~4 nm, but a bandwidth-limited pulse of ~100 fs has a bandwidth of ~5 nm (in the visible range), thus limiting our resolution. The analysis treats the continuum as made up of a group of bandwidth-limited pulses. This works well, but analyzing the pulses as spectrally broader also works up to the point where the GVD becomes important. In our case our analysis is valid for bandwidths of as much as ~15 nm FWHM.

To characterize the WLC we performed an OKE experiment on a thin piece of fused silica, $L = 50$ μm. It is convenient to use OKE in transient spectroscopy because the experimental setups involved are the same except for simple rotations of the pump polarization and probe analyzer.[8] This experiment maps the frequency content of the continuum in the time domain. One more advantage of the method is that, as with white-light interferometry, one can measure the GVD of an unknown sample inserted into the WLC's path. From OKE measurements, with and without the sample in the probe path, the difference in arrival time for a fixed frequency component of the continuum gives the group index of the material. It is necessary to know this value for materials whose dispersion is not yet in any database. Looking at a plot of an OKE signal as a function of wavelength and time shows that for any fixed λ the pulse width is equal to the width of the pulse used for continuum generation, i.e., ~100 fs.[8] The fact that the pump also interacts simultaneously with other spectral components does not influence the interaction with the narrow frequency band.

We measured the spectral energy of the probe to be ~1 nJ/nm, with a chirp of 3.5 fs/nm. For a 5-nm bandwidth this makes the probe ~40 times less intense than the pump, given that the probe is more tightly focused than the pump. This input is too low to lead to nonlinearities by itself, even when nondegenerate 2PA

from other portions of the probe is included; i.e., the 2PA induced by the pump on the probe dominates.

The samples that we used to demonstrate this method were ZnS ($L = 0.84$ nm) and an alkyl-fluorene derivative ($L = 1$ mm) whose molecular structure and synthesis are given in Ref. 9. The ultrafast nonlinear spectroscopy measurements were made with two independently tunable optical parametric sources pumped by a regeneratively amplified 120-fs (FWHM) source at 775 nm. The transmittance of the WLC probe (obtained by focusing of 1–2-μJ, ~100-fs pulses at 1400 nm into a 1.5-mm-thick fused-silica window) was monitored after the pulses passed through a 0.15-m spectrometer. A TE-cooled silicon dual-diode array was used for detection. The excitation was set at a wavelength less than half the bandgap of the sample being studied to avoid degenerate 2PA of the pump.

We obtained the transient absorption spectrum of a 2PA sample by varying the pump–probe delay time in 20-fs increments and monitoring the reduced transmittance for those wavelength for which the probe and the pump overlapped in time. As in the analysis performed on OKE traces, we built the cross-correlation signals, i.e., nonlinear absorption signals at fixed probe wavelengths versus time delay. The amplitudes and widths of these curves depend not only on the strength of the nonlinearity but also on the relative speed of the pulses in the sample. For pulses of significantly different wavelengths, the GVM led to a relatively fast differential speed between pump and probe, resulting in a shortened effective interaction length within the sample; i.e., pulses walk through one another. This walk-off translates to a reduced nonlinear signal strength, which must be accounted for by use of Eq. (1).

To illustrate the fitting procedure, in Fig. 1 we show the cross-correlation signals obtained in ZnS ($E_g = 3.54$ eV) at probe wavelengths of 480, 532, and 580 nm with $\lambda_p = 750$ nm. The energy for the pump was 5 μJ, and the beam width was 500 μm (HW1/e^2M). Experimental data were fitted to Eq. (1), yielding β.
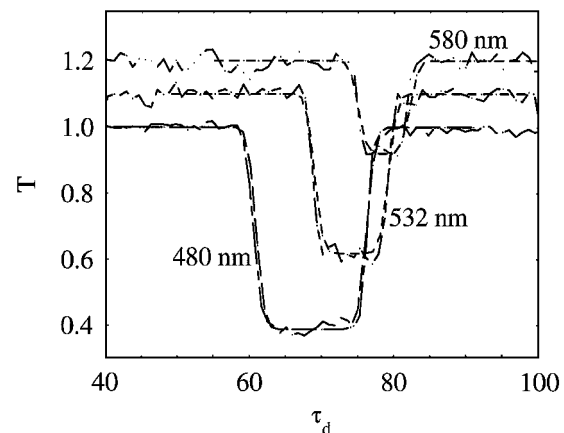

Fig. 1. Normalized probe fluence transmittance T at $\lambda = 480, 532, 580$ nm in ZnS. Solid curves, fits of experimental data (dashed curves) with Eq. (1); the corresponding material and nonlinearity parameters are given in the text. Curves are vertically offset for ease of viewing.
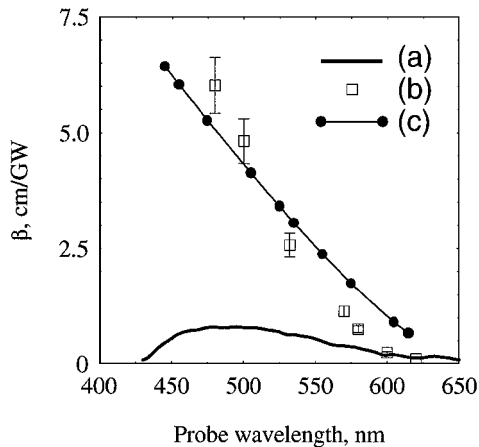
Fig. 2. Nondegenerate 2PA coefficient, β, of ZnS versus probe wavelength: (a) WLC spectral measurement, pump–probe walk-off not included; (b) WLC spectral measurement with walk-off correction; (c) theoretical model for ZnS, $E_g = 3.54$ eV. Experimental parameters are $L = 0.84$ mm, $w_p = 72$ fs (HW1/eM), $W = 0.85$, $\lambda_p = 0.75$ μm.
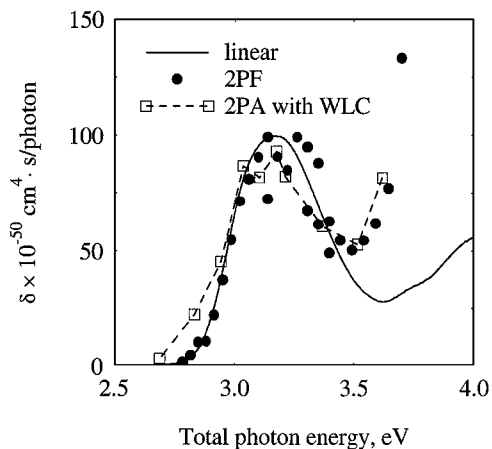

Fig. 3. Nondegenerate cross section δ (open squares) and degenerate 2PA cross sections from 2PF (filled circles) versus photon energy (pump + pump, solid curve) vertically scaled linear absorption spectrum.

The walk-off parameter was calculated from Sellmeier's equation. The material (ρ) and nonlinearity (Γ) parameters that correspond to the wavelengths in Fig. 1 were 16.4 and 4.5 at 480 nm, 9.9 and 1.9 at 532 nm, and 6.2 and 0.6 at 580 nm. We note that temporal walk-off can also be a fitting parameter for unknown samples, where the starting values in the process are those obtained in the OKE experiment. The results for β (centimeters per gigawatt) in ZnS, along with the theoretical prediction of Ref. 10, are shown in Fig. 2, illustrating the large correction required for accounting for GVM at wavelengths far from that of the pump.

An alternative to the pump–probe method presented in this Letter, which works well for fluorescing samples, is two-photon fluorescence spectroscopy. The results are calibrated against a well-known reference standard, e.g., fluorescein.[11] Figure 3 shows the results of our nondegenerate measurement for which we used the WLC probe ($\lambda_p = 1.2$ μm) along with the degenerate 2PA spectrum obtained as described above for our organic dye solution. The linear absorption spectrum of our sample is shown for reference. Agreement of the two methods with the linear spectrum is expected for an asymmetric molecular structure with a large dipole moment.[12]

The WLC pump–probe method of materials characterization presented here is particularly advantageous for rapidly building a database of spectra of organic dyes applicable in the investigation of structure–property relations. The nondegenerate nonlinear absorption spectrum is also of use in predicting the dispersion of the ultrafast nonlinear refraction.[4]

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