Analyte-induced spectral filtering in femtosecond transient absorption spectroscopy

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ABSTRACT

We discuss the influence of spectral filtering by samples in femtosecond transient absorption measurements. Commercial instruments for transient absorption spectroscopy (TA) have become increasingly available to scientists in recent years and TA is becoming an established technique to measure the dynamics of photoexcited systems. We show that absorption of the excitation pulse by the sample can severely alter the spectrum and consequently the temporal pulse shape. This "spectral self-filtering" effect can lead to systematic errors and misinterpretation of data, most notably in concentration dependent measurements. The combination of narrow absorption peaks in the sample with ultrafast broadband excitation pulses is especially prone to this effect.

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1. Introduction

Since the introduction of commercial femtosecond lasers, transient absorption (TA) spectroscopy has become an established technique that is used by thousands of scientists in almost all fields of natural sciences [1–7]. In recent years commercial TA instruments have made this technique available to researchers with a wide variety of backgrounds other than non-linear optics. In combination with non-collinear parametric amplifiers (NOPAs), sub-30 fs time resolution can be achieved with standard setups. This high time resolution requires sufficient bandwidth in the excitation (pump) pulse. Here we show that the combination of a broadband pump pulse with a narrow ground-state absorption band in the sample can lead to strong distortions in the pump pulse spectrum and alter its time profile. This can lead to systematic errors and misinterpretation of experimental data. Consideration of this effect becomes increasingly important as near-transform-limited pulses on the ten femtosecond timescale with appropriately broad spectra become ever more accessible.

For TA spectroscopy, the pump pulse is typically tuned to overlap with the ground state absorption spectrum of the sample. If the absorbance peak is narrow compared to the pulse spectrum, then spectral components will be removed from the pulse non-uniformly and the frequency spectrum will be altered. Absorption spectra with narrow lines are found in many bio-molecular systems; for example in proteins like rhodopsin that are responsible for vision processes, and in porphyrins involved in photosynthesis [8,9]. Narrow absorption features are also common in photochemical systems like transition metal complexes used for photocatalysis and solar cells [10–14], and have been reported for semiconductor bulk materials and nanostructures as well [15–18]. TA measurements on semiconductors at the band edge are another example affected, since partial pulse overlap with a sharp absorption edge will lead to a similar effect. Sample concentration- and thickness-dependent TA experiments are especially prone to this effect because the time profile of the pulse will depend on the optical density (concentration or thickness) and measurements on different samples cannot easily be compared to each other. Here we demonstrate this effect with a series of measurements involving Zinc-tetraphenylporphyrin (Zn-TPP). Zn-TPP is a prototypical chromophore that has been used in numerous studies ranging from medicinal chemistry [19] to materials science [20].

2. Experimental

The TA setup has been described previously [21]. Briefly, femtosecond pulses are generated in a Ti:sapphire oscillator (Coherent

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Mantis) and amplified in a 10 kHz amplifier (Coherent Legend), resulting in 38 fs pulses centered at 800 nm. The amplifier output is used to pump a home-built NOPA. The near-IR NOPA output is frequency doubled and the resulting pump pulse is centered at 422 nm with a full-width at half maximum (FWHM) of 13 nm. The spectrum of the pulse overlaps almost completely with the Soret absorption band of Zn-TPP (Fig. 3). A white light supercontinuum generated in a 3 mm sapphire window acts as a probe. The probe is compressed using a pair of BK7 prisms. Pump and probe beams are focused to 300 µm and 100 µm diameters at their intersection, respectively. The relative polarization is set at magic angle. The pulse energy of the pump is 200 nJ before incidence on the sample, corresponding to an energy regime in which the sample exhibits a linear transient absorption response. Transient absorption measurements are performed on solutions in 1 mm path length quartz cuvettes. A lock-in amplifier, photo-diode and monochromator are used for single wavelength detection. Cross-correlation measurements are performed using Type-I SHG in a 200 µm thick BBO crystal.

3. Results and discussion

The "spectral self-filtering" effect has been initially observed for a set of TA measurements that were performed on solutions of increasing concentration of Zn-TPP in tetrahydrofuran (THF). These measurements showed an apparent concentration dependence of the excited state relaxation dynamics in the first 100 fs. We studied this compound previously and found a rise time of the TA signal at 520 nm of 120 ± 10 fs after excitation with a pump pulse centered at 420 nm [22]. This process is commonly assigned to relaxation in the S_2 state [23,24]. The rise of the signal appeared to slow down by nearly a factor of two as the concentration was increased by two orders of magnitude. After verifying that concentrations as high as 100 µM were below the point of aggregation of Zn-TPP in THF [25] and that neither demetallated porphyrin nor any other impurities were responsible for the ostensible concentration dependence, we concluded that the effect must be attributed to a change in the instrument response function (IRF) of the instrument.

To facilitate a well defined change in concentration, we carefully aligned the setup such that we minimize the path length of the pump pulse inside the cuvette before overlapping with the probe pulse. We adjusted the angle between pump and probe pulse to 15° and placed their focal points at the very front of a 1 mm cuvette filled with 17 µM Zn-TPP solution, possessing an optical density of 1 at 422 nm ($\varepsilon = 5.71 \times 10^6$ M^{-1}·cm^{-1}). Next, we placed a second 1 mm cuvette in the path of the pump beam path before the first cuvette and filled it with varying concentrations of Zn-TPP solution. Fig. 1 shows the rising edge of the TA signal for Zn-TPP concentrations ranging from 0 µM to 25 µM. It can clearly be seen that the slope decreases with increase in concentration. The decrease of the signal-to-noise ratio is due to an overall reduction of the signal caused by the decrease in pump energy. A fit of the data shows an apparent increase of the rate constant by a factor of two (Table 1). Global fitting at each probe wavelength employs a sequential-state rate model that has been described in previous work (Ref. [22]). The resulting fit lines are displayed over the experimental data in Fig. S1. The apparent rise time of the TA signal is given by a convolution of the initial excited state absorption dynamics with the Gaussian IRF, which is dependent on the durations of the pulses used in the experiment. These measurements were performed under realistic experimental conditions with a moderately short IRF of 40 fs, and the IRF used for fitting was fixed to 40 fs for all measurements in Fig. 1 to
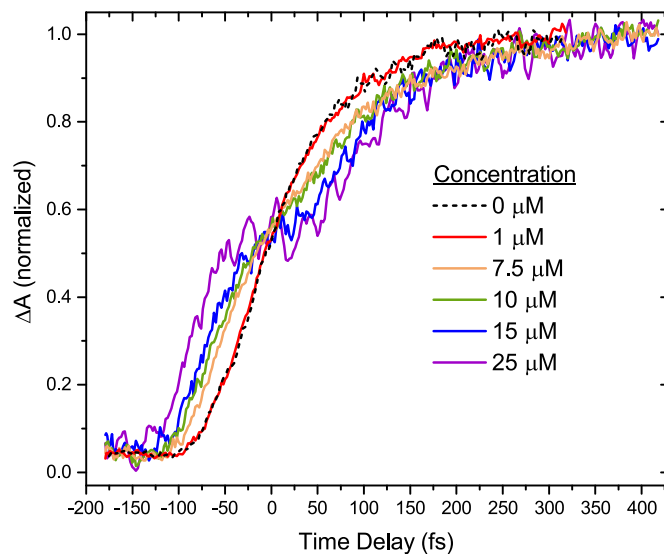
Fig. 1. TA transients at 520 nm probe wavelength. The pump pulses passes through Zn-TPP solutions with increasing concentrations before interacting with the sample. Time constants for the apparent rise time are given in Table 1.

Table 1
FWHM of the Cross-Correlation and TA Rise Times at Different Concentrations.

Zn-TPP Concentration (µM)	Cross-Correlation FWHM (fs)	TA rise time τ_{rise} (fs)
0	40.8	108
1	41.2	113
2.5	42.1	132
5	44.1	151
7.5	44.3	162
10	51.9	186
15	70.3	211
25	73.5	243

demonstrate how spectral filtering can lead to misinterpretation of data. Next we show that the apparent increase in rise time is caused by an increase of the IRF due to spectral self-filtering.

To investigate this effect further we replaced the first cuvette with a BBO crystal in order to measure the cross-correlation between the 422 nm pump and the 520 nm part of the supercontinuum. The second cuvette containing the concentration dependent Zn-TPP solution was kept in the excitation beam before the non-linear crystal. By changing the concentration in the second cuvette, we measured the effect of spectral filtering on the cross-correlation. The results displayed in Fig. 2 reveal that as the concentration of Zn-TPP was increased, the measured cross-correlation increased as well. The cross-correlation trace is strongly distorted and quickly loses its Gaussian shape. The FWHM reported in Table 1 assumes a Gaussian pulse shape and should be taken with care at concentrations higher than 5 µM.

The distortion of the pulse shape in time should be reflected in the spectrum. Fig. 3 shows the spectrum of the 422 nm pump pulse after passing through the cuvette with Zn-TPP solutions of increasing concentrations together with the spectrum of the Soret band absorption spectrum of Zn-TPP. It can be seen how the sample alters the spectrum by predominantly reducing the intensity at the center wavelength to the point were the central region is completely absorbed and the spectrum shows two peaks at 25 µM concentration.