Analyte-induced spectral filtering in femtosecond transient absorption spectroscopy

Baxter Abraham^a, Jesus Nieto-Pescador^b, Lars Gundlach^{a,b,*}

^a Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

^b Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

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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

* Corresponding author at: Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA
E-mail address: larsg@udel.edu (L. Gundlach).

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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-TTP (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-TTP 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-TTP 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-TTP solution, possessing an optical density of 1 at 422 nm ($\epsilon = 5.71 \times 10^6 \text{ M}^{-1} \cdot \text{cm}^{-1}$). 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-TTP solution. Fig. 1 shows the rising edge of the TA signal for Zn-TTP 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 pass through Zn-TTP 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-TTP 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-TTP 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-TTP 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-TTP solutions of increasing concentrations together with the spectrum of the Soret band absorption spectrum of Zn-TTP. It can be seen how the sample alters the spectrum by predominantly reducing the intensity at the center wavelength to the point where the central region is completely absorbed and the spectrum shows two peaks at 25 μM concentration.

Fig. 2. The cross-correlation of pump and probe pulses after the pump pulse passes through Zn-TTP solution with increasing concentration.

Fig. 3. Spectrum of the pump pulse after traveling through 1 mm Zn-TTP solution of different concentrations (black solid lines). Soret absorption band of Zn-TTP (red dashed line).

Fig. 4. Comparison of a cross-correlation measured at 25 μM and a cross-correlation reconstructed from the spectrum shown in Fig. 3.

Reconstruction of the cross-correlation by Fourier transformation of the measured spectrum and subsequent convolution with a 20 fs FWHM Gaussian pulse to account for the probe pulse results in a temporal profile that resembles the width and the structure of the measured cross-correlation (Fig. 4).

As mentioned above, this effect can be reduced in a measurement by using thin samples and by placing the region where pump and probe pulse overlap as close to the front surface of the sample as possible. Doing so minimizes absorption of the pump pulse as it travels through the sample prior to the region of spatial overlap with the probe pulse. In addition, a large crossing angle between pump and probe pulse is desirable in reducing the amount of sample penetration prior to their overlap. Using a sample with thickness approaching the order of the interaction volume would be advantageous, such as the thin film produced by a flowing liquid jet [26,27]. The effect of filtering within the sample can be reduced by more than a factor of ten in our setup through careful adjustment of the experiment. Fig. S2 shows measurements on Zn-TTP at concentrations above 50 μM with no distortions due to self-filtering. However, dependence on the alignment makes it difficult to quantify the effect in a real experiment where the exact amount of spectral filtering at the interaction region is unknown and challenging to measure. The effect is therefore difficult to correct mathematically *post hoc*. Our results also suggest that the common practice of deconvoluting time-dependent measurements with a previously measured cross-correlation is not necessarily accurate, as the actual IRF can considerably differ from the cross-correlation measured without the sample.

4. Conclusion

The contribution of a spectral self-filtering effect to the pump pulse within the sample in TA measurements has been investigated. The effect is pronounced in systems where the pump pulse is non-uniformly absorbed by the analyte. Spectral self-filtering is found to alter the temporal profile of the pulse, leading to a reduction in time resolution and thus provides the risk of systematic errors and data misinterpretation. An unaccounted for decrease in the IRF as a result of differences in sample absorbance can easily allow variations in results to be misattributed to changes in excited state dynamics. Experiments focused on concentration dependence are particularly vulnerable to this inconspicuous pulse distortion between samples. Furthermore, a dependence on pulse interaction region indicates that comparison of measurements between different samples requires meticulous alignment and should be taken with care. Recognition of this measurement artifact becomes increasingly relevant as femtosecond TA experiments with resolution limited by pulse bandwidth reach widespread availability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlumin.2017.03.003>.

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