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To cite this version:
Patrick Nuernberger, Kevin Lee, Adeline Bonvalet, Thomas Polack, Marten Vos, et al.. Suppression of perturbed free-induction decay and noise in experimental ultrafast pump-probe data. Optics Letters, Optical Society of America, 2009, 34 (20), pp.3226-3228. 10.1364/OL.34.003226 . hal-00818494

HAL Id: hal-00818494
https://hal-polytechnique.archives-ouvertes.fr/hal-00818494
Submitted on 14 May 2014

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Suppression of perturbed free-induction decay and noise in experimental ultrafast pump–probe data

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Received May 15, 2009; accepted September 4, 2009;
published October 15, 2009

We apply a Fourier filtering technique for the global removal of coherent contributions, like perturbed free-induction decay, and noise, to experimental pump–probe spectra. A further filtering scheme gains access to spectra otherwise only recordable by scanning the probe’s center frequency with adjustable spectral resolution. These methods cleanse pump–probe data and allow improved visualization and simpler analysis of the contained dynamics. We demonstrate these filters using visible pump/mid-infrared probe spectroscopy of ligand dissociation in carboxyhemoglobin.

We use femtosecond pulses near 800 nm from a 1 kHz regenerative amplifier. A fraction is split off in front of the compressor, yielding positively chirped pulses (≈120 ps). The other fraction is compressed and used to generate 400 nm pump pulses, which pass a continuously scanning delay stage and are chopped mechanically at 500 Hz, and 5.1 μm probe pulses [10,11]. Pump (pulse energy 0.4 μJ, focal diameter 140 μm) and probe (0.3 μJ, 60 μm) are individually focused and noncollinearly overlapped with parallel polarizations, resulting in an instrument response function (IRF) with a FWHM of 0.17 ps, found with a GaAs wafer. Our sample is 5 mM human hemoglobin in a D$_2$O [pD=7.6] Tris-HCl buffer, reduced with 40 mM dithionite under CO atmosphere, and 100 μm thick between CaF$_2$ windows. It is rotated so that the sample changes every laser shot. The transmitted probe is upconverted with the chirped 800 nm pulse [10,11] and recorded by a spectrometer with a 100×1340 pixel CCD camera. Individual spectra and motor positions are record for each laser shot. The spectra are binned to τ intervals of 30 fs, and a linear fit to the spectral baseline, excluding the absorption region, is subtracted. The average of all pump-blocked spectra serves as reference spectrum $T$ used to convert between Δ$T$ and Δ$A=-\log_{10}(ΔT/T+1)$ after filtering.

Figure 1(a) shows the multiplexed spectrum $ΔT^m(τ,ν)$ obtained with a broadband probe. The pump dissociates the CO ligand from the heme, causing a transient bleaching of the $A_1$ band at $\approx1951$ cm$^{-1}$ ($ν_0=58.5$ THz), which is nearly constant...
during 1 ns [12]. There is also a small bleaching (less than 10% compared to the A1 signal) that is due to the A0 band at ω=1968 cm−1 (59.0 THz). The two structural substates correspond to two orientations of the distal histidine in the heme pocket, giving rise to two distinct absorption bands [13] of the Fe-bound CO.

Due to PFID, the increased transmission at νa does not set in at τ=0, but sets in over 1 ps earlier. Spectral oscillations are clearly visible for negative delays, producing characteristic hyperbolic lines associated with constant ντ values. For τ<0, the differential spectrum has spectral oscillations over the whole probe bandwidth, with a period of 1/τ. Conversely, at a given ν, the pump–probe signal quasi-periodically oscillates at frequency 1/τ as a function of ν.

To suppress the oscillations, the data is transferred to shift space (ν, t) by a 2D Fourier transform,

$$\hat{\Delta T}_m(\nu, t) = \int \int d\nu d\nu \Delta T_m(\tau, \nu) e^{i(2\pi \nu_\tau - 2\pi \nu t)}. \quad (1)$$

This data is multiplied by i[sign(t)+1] to enforce causality and by the complex filter function

$$\hat{f}(\nu, t) = \exp[-|2\pi \nu_\tau|^2/2 + i(2\pi \nu_\tau)/2], \quad (2)$$

motivated by the fact that the spectrotemporal resolution is limited by the probe, which in shift space reads

$$\hat{\Delta}(\nu, t) = \exp\left[\frac{-2(2\pi \nu_\tau^2)\Delta t^2}{16 \ln 2} - \frac{t^2 \ln 2}{\Delta t^2} + \frac{i(2\pi \nu_\tau)}{2}\right]. \quad (3)$$

The 1/e² width of |\hat{\Delta}(\nu, t)| for any transform-limited (TL) pulse of duration Δt lies within the 1/e² width of |\hat{f}(\nu, t)|. Hence, the filter damps away contributions located at |2πνt| > 4 (the filter’s 1/e² limit), as they cannot be due to dynamics probed by any TL pulse in the scanning approach. See [9] for the detailed theory. The filtered data is then Fourier transformed back to (τ, ν) space, and the imaginary part ΔT(τ, ν) is further analyzed. In the filtered data of Fig. 1(b), the oscillations are completely removed. Only a cross-shaped structure remains, owing to PFID contributions that change too slowly with frequency (along τ = 0) or delay (along ν=νa) to be filtered out. Hence, unwanted coherent signals can be considerably suppressed, permitting a more straightforward visualization of the data. Note that neither the IRF nor the actual duration of the probe (which should be nearly TL and not have a very structured spectrum) are explicitly considered for this filtering method.

We confirmed good filtering with simulated data: a homogeneously broadened four-level system with two levels, both in an electronic ground and excited state described by Bloch equations; and pulse durations 120 fs, i.e., IRF FWHM 0.17 ps, T =1.15 ps, T =40 fs, and infinite population lifetimes. Pump and probe intensities are adjusted to allow a comparison of simulation and experiment (Fig. 1), which agree excellently even though neither inhomogeneity, the weak A0 absorption, the finite sample thickness, nor XPM are considered.

If spectral features do not all start at the same delay (e.g., in coherent control with complex pump pulses), PFID cannot be simply ignored by cutting negative delays and can obscure interesting data. To demonstrate this, we simulated a simple scenario with an adjacent absorption line instantaneously bleached 4 ps after the first (Fig. 2). Perturbations

![Image](https://example.com/image.png)

Fig. 1. (Color online) Left, application of the Fourier filtering technique to experimental data (top row) and simulated data (bottom row). (a) 400 nm pump/5.1 μm probe spectrally resolved ΔT(τ, ν) data of HbCO; (b) filtered data ΔT(τ, ν) using filter (2) as described in the text; (c) filtered data using Eq. (3) as filter to emulate ΔT(τ, ν) that would be obtained in the scanning approach with a 600 fs probe pulse. The evolution of ΔT(τ, ν) for probe durations from 300 fs to 2 ps is available as a movie (Media 1). (d)–(f) Simulations corresponding to (a)–(c). Right, transient absorption signals at (g) 59.6 THz, (h) 59.0 THz (A0 band), and (i) 58.5 THz (A1 band) before (dots) and after (line) the filtering procedure; (g) and (h) are vertically offset by 2.4 and 1.2 mOD for clarity. In (h), the standard deviation before (σ) and after (σ) filtering is given for the indicated interval 0.5 ps < τ<6 ps; (i) includes a fit (dashed line) to a single exponential convolved with the IRF. The arrows mark a small coherent spike that is also reduced after filtering.
to the signal of the first line are mostly removed by filtering, which also qualitatively reveals the step at 4 ps owing to a population contribution from the adjacent line.

We further demonstrate another useful filter technique with our experimental data—a pump–probe spectrum $\Delta T_t(\tau, \nu)$ obtained with the scanning method can also be calculated from $\Delta T_m(\tau, \nu)$, provided the latter is measured with a short-enough probe pulse [9]. We achieve this with the same procedure, but with (3) rather than (2) as the filter. Figure 1(c) has results for $\Delta t = 600$ fs. The oscillations are entirely removed, whereas the spectral resolution is degraded owing to the time-bandwidth product of the emulated probe. The asymmetry in Fig. 1(c) is due to the $A_p$ band. The advantage of this method is that it combines the short acquisition time of multiplexing with a produced pump–probe spectrum whose interpretation is straightforward. Despite a compromise between time and frequency resolutions, these parameters can be set after the experiment, as demonstrated in Media 1. Note that the relation between $\Delta T_t$ and $\Delta T_m$ resembles that between pulse representations in optics, like the Husimi and Wigner distributions (e.g., [14]); the first is a 2D convolution of the second with, e.g., a Gaussian function. Interestingly, the Husimi (as $\Delta T_t$) is more intuitive than the Wigner (as $\Delta T_m$), at the cost of the spectrotemporal resolution. In a way, the filtered function $\Delta T_t$ is the best attempt to combine the advantages of both.

While the filtering is done in $\Delta T_t$, an analysis of molecular properties is performed in $\Delta A$, to avoid effects from the probe’s spectral intensity. As an example, three traces are shown in Figs. 1(g)–1(i). On resonance [Fig. 1(i)], the PFID leads to an exponential decay for $\tau < 0$ [2, 4]. A fit yields a constant of 1.15 ps, which would correspond to a Lorentzian of 9.2 cm$^{-1}$ FWHM (reported inhomogeneous linewidth 8 cm$^{-1}$ [15], Gaussian fit to our data 8.3 cm$^{-1}$). After filtering, the transient absorption at $\nu_s$ is more intuitive—only a small feature from the cross-shaped PFID remainder can be observed before the almost unaffected population signal sets in at $\tau = 0$. This is also the case for the signals at $\nu \neq \nu_s$ [Figs. 1(g) and 1(h)]: the expected oscillations for $\tau < 0$ have disappeared after filtering.

When multiplied with the filter function, components of $\Delta T_m(\nu, \tau, t)$ far from the shift space axes are efficiently damped, as is white noise spanning the entire shift space. This efficient noise reduction is evident in Fig. 1(h), where the standard deviation of the $A_0$ population signal decreases by 70%. Finally, a reduction of the coherent spike can be clearly observed as well (arrows in Fig. 1).

In conclusion, the use of femtosecond pulses, which are shorter than the characteristic dephasing times of the system under study, leads to oscillations in pump–probe spectra that may obscure the analysis and extraction of characteristic dynamics. With a simple and general Fourier filtering scheme that is independent of the actual pulse durations, we demonstrated that these coherent signals can be mostly removed. Also, experimental noise is efficiently reduced, while the population dynamics remain virtually unaltered. In a different scheme with the field representation as the filter, scanning approach spectra with adjustable spectral resolution can be obtained from a single spectrally resolved measurement. The versatile pump–probe data procured with the different filters can be used to better visualize and more easily analyze the underlying molecular processes, which is especially beneficial for complex systems where an adequate theoretical model is not available.

We thank Agence Nationale de la Recherche (ANR-BLAN-0286) and Deutsche Akademie der Naturforscher Leopoldina (BMBF-LPDS 2009-6) for support.

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