Alternative View of Two-Dimensional Spectroscopy

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We show that femtosecond two-dimensional (2D) signals can alternatively be measured and computed as four-wave-mixing signals generated with two femtosecond pulses and two one-sided continuous-wave pulses. This alternative view allows a computationally more efficient evaluation of 2D signals and clarifies the relationship of 2D spectroscopy with other time-domain and mixed time-frequency-domain techniques.

The pulse sequence of a typical 2D experiment is sketched in Fig. 1a. Femtosecond pulses 1, 2 and 3 (arriving at $t = -\tau - T$, $-T$, and 0) generate the third-order laser-induced polarization. The signal is detected through the convolution of this polarization with the local oscillator pulse 4 arriving at $t = t_4$.

We show that the same 2D signals will be measured when the laser fields sketched in Fig. 1b are used. The one-sided continuous-wave (CW) pulses are obtained by one-sided Fourier transformation of the pulses 1 and 4. The femtosecond pulse 1 and the one-sided CW pulse 2 create the doorway state at $t = 0$. The doorway state evolves during the population time T and is detected at $t = T$ by the convolution with the window state, which is created by the femtosecond pulse 3 and the one-sided CW pulse 4. The manipulation of the shape of these pulses allows the optimization of the time and frequency resolution of the 2D spectrum.

This alternative picture of 2D spectroscopy provides insight into the interrelations of 2D spectroscopy with other mixed time-frequency spectroscopic techniques. It reveals that 2D spectroscopy possesses spectral selectivity in the preparation of the doorway and window states, while it provides time resolution for the detection of the wave-packet motion during the interval T. Thanks to this combination of high time and frequency resolution, 2D spectroscopy is one of the most powerful femtosecond four-wave-mixing techniques.

Based on the scheme of Fig. 1b, we have developed a computational method which allows the direct evaluation of cuts of the 2D signal $I(\omega_\tau, \omega_t, T)$ for a specific ω_τ without computation of the third-order polarization on the two-dimensional τ - t grid. This method results in considerable computational savings, as demonstrated by illustrative calculations for several model systems. The method can also be extended towards the simulation of 3D six-wave-mixing signals.

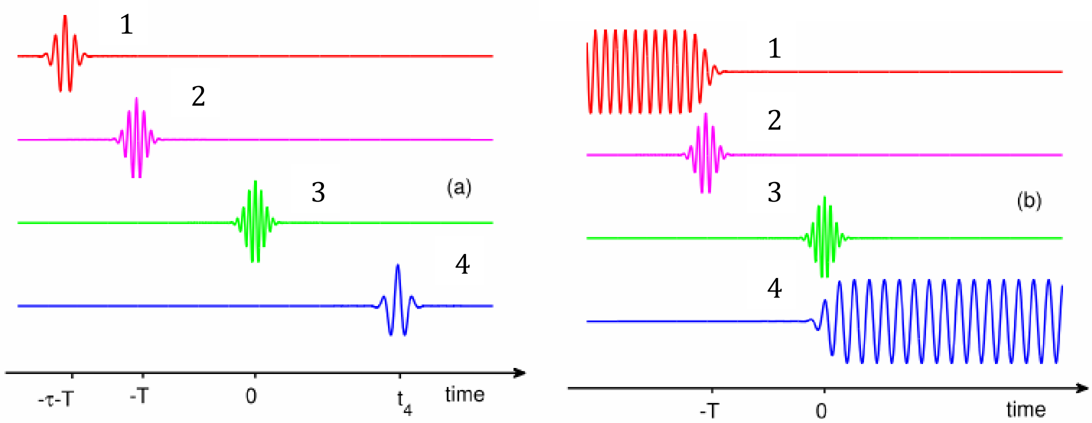

Fig. 1. Sketch of the traditional (a) and alternative (b) scheme for the measurement and simulation of 2D signals.