Real-time detection of quantum coherences by two-dimensional electronic spectroscopy

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Two-dimensional electronic spectroscopy (2DES) is the "ultimate" time-resolved nonlinear optical experiment, since it provides the maximum amount of information that can be extracted from a system within third-order nonlinear spectroscopy. A 2DES experiment can be schematically described as shown in Fig. 1. The system under study is excited by three ultrashort light pulses, with controllable relative delays τ and T. This pulse sequence builds up a macroscopic nonlinear polarization in the medium that emits a field, following pulse 3 with a delay t. This field is fully measured in amplitude and phase with the help of an additional pulse (pulse 4, known as local oscillator, LO). Finally, by Fourier transforming with respect to τ and t for a fixed value of the "waiting time" T, one derives the 2D spectrum as a function of "excitation frequency" ω_τ and "detection frequency" ω_t. Remarkably, if the excitation pulses are sufficiently short, then the experiment directly measures the third-order nonlinear optical response of the system.

By spreading the information content of the nonlinear signal on two frequency axes, 2DES allows: (i) to remove inhomogeneous broadening and thus measure the homogeneous linewidth of optical transitions, providing direct access to the polarization and to electronic dephasing due to decoherence processes; (ii) to separate, and thus distinguish, contributions to the nonlinear signal that are spectrally overlapped in the 1D experiments; (iii) to overcome the Fourier limit and to obtain simultaneously high temporal and spectral resolution; (iv) to directly observe and quantify couplings between different transitions, which appear as cross peaks in the 2D spectra; (v) to follow in real time, by recording spectra as a function of the waiting time T, the pathways by which the coupled electronic/vibrational dynamics within a complex system evolve after photoexcitation, and to track energy/charge transfer processes.

This presentation will review the experimental techniques currently used to perform 2DES in the visible range and will introduce our approach to 2DES, based on a passive birefringent interferometer for the generation of phase-locked pump pulses [1]. Finally, we will present a few exemplary 2DES results on multi-chromophoric systems and nanostructures [2, 3].

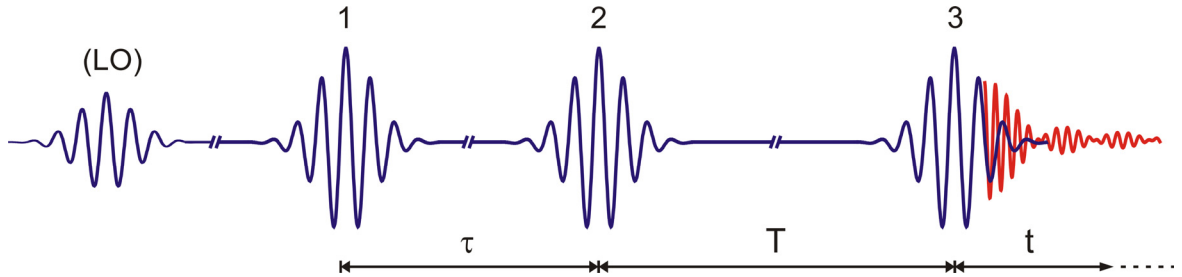

Fig. 1: pulse sequence in a two-dimensional electronic spectroscopy experiment.

Bibliography

[1] D. Brida, C. Manzoni, and G. Cerullo, Opt. Lett. 2012, 37, 3027.
[2] T. Stoll et al., J. Am. Chem. Soc. 2016, 138, 1788.
[3] A. De Sio et al., Nature Commun. 2016, 7, 13742.