

Broadband Two-dimensional Electronic Spectroscopy with a Birefringent Interferometer

Giulio Cerullo

Dipartimento di Fisica, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy
giulio.cerullo@polimi.it

A wealth of novel information on molecular structure and dynamics can be obtained by extrapolating 2D techniques, commonly used in NMR, to the optical domain [1]. 2D spectroscopy is the “ultimate” ultrafast optical experiment, since it provides the maximum amount of information that can be extracted from a system within third-order nonlinear spectroscopy. The first applications were with IR pulses, resonant with vibrational transitions. Recently, 2D optical techniques have been extended to the visible and UV ranges, targeting electronic transitions. 2D electronic spectroscopy (2DES) allows fundamentally new insights into the structure and dynamics of multi-chromophore systems, measuring how the electronic states of molecules within a complex interact with one another and transfer electronic excitations [2]. By spreading the information content of the nonlinear signal on two frequency axes, 2DES allows: (i) to measure the homogeneous linewidths of optical transitions, enabling to single out the individual levels in strongly congested spectra; (ii) to separate 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 excited states, which appear as cross peaks in the 2D spectra; (v) to follow in real time the pathways by which the coupled electronic/nuclear dynamics within a complex multi-chromophoric systems 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 we will present our approach to 2DES, based on a passive birefringent interferometer for the generation of phase-locked pump pulses [3]. We will present a few exemplary results on multi-chromophoric systems and nanostructures [4-6] and finally discuss the prospects of extending 2D techniques to the UV range, of interest for biomolecules such as DNA and proteins.

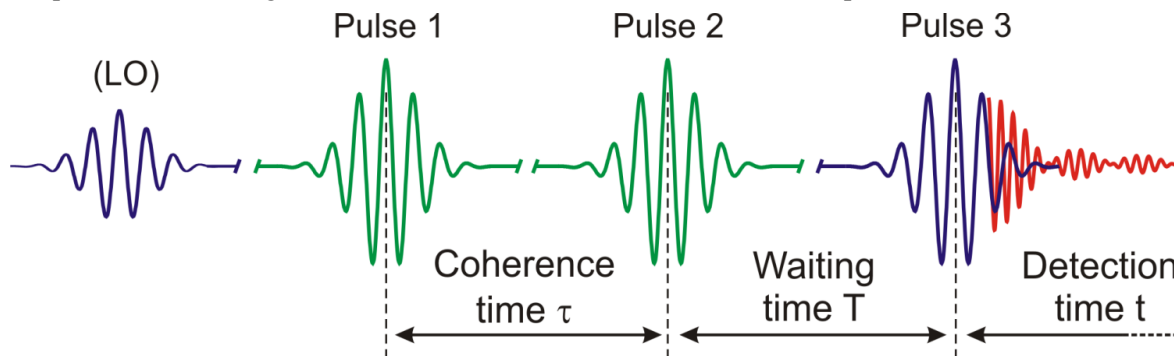


Figure 1 Scheme of pulse sequence used in a 2DES experiment. LO: local oscillator.

References

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