Two-dimensional electronic spectroscopy from the visible to the XUV

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Nuclear Magnetic Resonance (NMR) is a diagnostic technique that has revolutionized structural biology, allowing to determine complex molecular structures with high spatial resolution. In two-dimensional (2D) NMR the signal is recorded as a function of two time variables and the data are Fourier transformed twice to yield a spectrum which is a function of two frequency variables. A wealth of novel information on molecular structure and dynamics can be obtained by extrapolating these 2D techniques to the optical frequency domain, using ultrashort light pulses. 2D spectroscopy is the "ultimate" third-order nonlinear 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.

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 linewidths of optical transitions, enabling to single out the individual levels in strongly congested spectra; (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 excited states, which appear as cross peaks in the 2D spectra, and thus to obtain structural information on the relative spatial arrangement of the chromophores; (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/UV range, present a few exemplary results and finally discuss the prospects of extending 2D techniques to the XUV range, exploiting radiation emitted by the free electron laser.