MAR15-2014-020453

Abstract for an Invited Paper
for the MAR15 Meeting of
the American Physical Society

Ultrafast 2D Fluorescence Spectroscopy using Spectrally Entangled Photon Pairs

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We propose entangled photon-pair two-dimensional fluorescence spectroscopy (EPP-2DFS) to probe the nonlinear electronic response of molecular systems. [1] The method, inspired by results in [2], uses a technique from quantum optics—a separated two-photon (Franson) interferometer, which generates time-delayed packets of time-frequency-entangled photon pairs. This interferometer is incorporated into the framework of a fluorescence-detected 2D optical spectroscopic experiment [3]. The continuous stream of entangled photons are phase-modulated in the interferometer, and used to excite a two-photon-absorbing sample, whose excited-state population is selectively detected by simultaneously monitoring the sample fluorescence and the transmitted exciting fields. In comparison to standard 'classical' 2DFS techniques using coherent laser pulses and standard pulse-scanning sequences, advantages of this scheme include the suppression of uncorrelated background signals, the suppression of diagonal 2D spectral features, the enhancement and narrowing of off -diagonal spectral cross-peaks that contain information about electronic coupling, and the possibility for enhancement of simultaneous time-and-frequency resolution, including spectral selectivity within an inhomogeneously broadened distribution. These effects arise from the properties of parametric down-conversion light source, which effectively creates a different interaction-scanning protocol than in standard laser-pulse scanning. We numerically simulate the EPP-2DFS observable for the case of an electronically coupled molecular dimer. The EPP-2DFS spectrum is greatly simplified in comparison to its standard classical 2D counterpart. Our results indicate that EPP-2DFS can provide previously unattainable resolution to extract model Hamiltonian parameters from electronically coupled molecular dimers.

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