Coherent Ultrafast Multidimensional Spectroscopy of Molecular Processes With Optical, X-ray, and Quantum Light

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Multidimensional spectroscopy uses sequences of optical pulses to study dynamical processes in complex molecules through correlation plots involving several time delay periods. Recent extensions of these techniques to the x-ray regime as well as by utilizing the quantum nature of light will be discussed. Applications to excitons in aggregates and to trapped ions will be presented.

Strong coupling of molecules to the vacuum field of micro cavities can modify the potential energy surfaces thereby manipulating the photophysical and photochemical reaction pathways. The ultrafast dynamics of molecules confined in optical micro cavities is investigated. The photonic vacuum state of a localized cavity mode can be strongly mixed with the molecular degrees of freedom to create hybrid field-matter states known as polaritons. Simulations of the avoided crossing of sodium iodide in a cavity which incorporate the quantized cavity field into the nuclear wave packet dynamics will be presented. Numerical results show how the branching ratio between the covalent and ionic dissociation channels can be strongly manipulated by the optical cavity.

Many important photophysical and photochemical molecular processes take place via conical intersections (COIS) where nuclear and electronic degrees of freedom become strongly coupled and the adiabatic Born Oppenheimer approximation beaks down. A new technique, TRUE-CARS, Transient Redistribution of Ultrafast Electronic Coherences in Attosecond Raman Signals, is proposed that can detect the passage through a COIS. Short X-ray pulses can directly detect the passage through a CoIn with the adequate temporal and spectral sensitivity. The technique is based on a coherent Raman process that employs a composite femtosecond/attosecond X-ray pulse to directly detect the electronic coherences (rather than populations) that are generated as the system passes through the CoIn.

Signals that utilize the quantum nature of the optical field by varying parameters of the photon wavefunction rather than classical field delays and frequencies will be presented. Entangled photons provide novel nonlinear spectroscopic probes of excitation-energy-transfer and charge-separation processes in chromophore aggregates. The unusual spectral and temporal characteristics of entangled photon pairs combined with interferometric detection make it possible to manipulate and control two photon absorption and Raman signals and extract information not available with classical light.

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