Coherent Ultrafast Multidimensional Spectroscopy of Molecules 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 utilizing the quantum nature of light will be discussed.

Ultrafast nonlinear x-ray spectroscopy is made possible by newly developed free electron laser and high harmonic generation sources. The attosecond duration of X-ray pulses and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal resolution. Stimulated X-ray Raman spectroscopy (SXRS) with sequences of broadband X-ray pulses may be used to probe energy and charge transfer dynamics in molecules and chromophore aggregates such as photosynthetic antennae. In this technique, one X-ray pulse resonant with a selected core transition creates a superposition of valence excited states localized in the vicinity the target atom through a Raman process and its evolution is then probed by another X-ray pulse after some variable time delay. Applications will be presented to long-range charge transfer in proteins and to excitation energy transfer in porphyrin arrays.

Many important photophysical and photochemical molecular processes take place via conical intersections (COIS) where nuclear and electronic degrees of freedom are strongly coupled. 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. An off-resonant composite attosecond and femtosecond probe pulse directly detects electronic coherences that are generated as the system passes through the CI. 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. 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.