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Coherent Multidimensional Core Spectroscopy of Molecules with Multiple X-ray pulses

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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. Extensions of these techniques to the x-ray regime 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. We demonstrate how stimulated Raman detection of an X-ray probe may be used to monitor the phase and dynamics of the nonequilibrium valence electronic state wavepacket created by e.g. photoexcitation, photoionization and Auger processes. Spectroscopy of multiplecore excitations provides a new window into electron correlations. Applications will be presented to long-range charge transfer in proteins and to excitation energy transfer in porphyrin arrays. Conical intersections (CoIn) dominate the pathways and outcomes of virtually all photophysical and photochemical molecular processes. Despite extensive experimental and theoretical effort CoIns have not been directly observed yet and the experimental evidence is being inferred from fast reaction rates and some vibrational signatures. Novel ultrafast X ray probes for these processes will be presented. 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. Streaking of time-resolved photoelectron spectroscopy (TRPES) signals offers another powerful window into the joint electronic/vibrational dynamics at concial intersections. 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 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.