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Probing Electronic Excitations in Molecules by Coherent Multidimensional UV and X Ray Spectroscopy

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Two-dimensional ultraviolet (2DUV) spectra of protein backbone (far UV) and side chains (near UV) provide new insights into the protein structures, dynamics and functions. Simulated chirality-induced 2DUV spectra reveal characteristic patterns of protein secondary structures and allow monitoring the aggregation mechanism of amyloid fibrils and predicting the aggregation propensity of peptides. Time-domain experiments that employ sequences of attosecond x-ray pulses in order to probe electronic and nuclear dynamics in molecules are made possible by newly developed bright coherent ultrafast sources of soft and hard x-rays. By creating multiple core holes at selected atoms and controlled times it should be possible to study the dynamics and correlations of valence electrons as they respond to these perturbations. The stimulated x-ray Raman spectrum of *trans*-N-methylacetamide and Cysteine at the Nitrogen, Sulfur and the Oxygen K-edges in response to two soft x-ray pulses is calculated by treating the core excitations at the Hartree–Fock static-exchange level (STEX) level. The signal is interpreted in terms of the dynamics of valence electronic wave packets prepared and detected in the vicinity of (either the nitrogen or the oxygen) atom. The evolving electronic charge density and as electronic coherences are visualized using a basis set of time-dependent natural orbitals. Effects of orbital relaxation upon core excitations are resolved. A two-dimensional extension of the technique that involves a sequence of three resonant Raman pulses will be presented. Extensions to multidimensional spectroscopy with photoelectron detection are proposed.