Modeling of Multidimensional X-ray Probes of Chemical Processes and Dynamics in Molecular Systems

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Introduction. Emerging X-ray free electron laser (XFEL) sources offer new types of probes of matter with unprecedented spatial and temporal resolutions. These experimental advances must be met by robust theoretical and computational tools that provide predictive modeling capacities of the underlying electronic and structural dynamics. The latter will be essential for the design of sophisticated multi-pulse experiments and for their interpretation. The proposed research effort will focus on developing cutting-edge simulation tools for nonlinear multidimensional X-ray/optical spectroscopies and aims to address key questions in "Priority Research Opportunities" 1 (Probing and controlling electron motion within a molecule) and 3 (Capturing rare events and intermediate states in the transformation of matter) as mentioned in the BES Roundtable Report "Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science". XFEL multidimensional nonlinear techniques, which combine sequences of X-ray and possibly optical pulses, provide a unique experimental toolbox for probing the dynamics of core and valence electronic excitations, as well as material structure.

Activity. The proposed effort aims to model the molecular response to X-ray pulse sequences. Novel physical effects that can be measured with available techniques will be predicted, and the experimental toolbox will be extended by designing novel spectroscopic techniques that can reveal fundamental phenomena of coupled nuclear and electronic dynamics. These techniques include multidimensional stimulated Raman signals, three and four-wave mixing, as well as time-resolved X-ray and electron diffraction. The proposed research will be carried out by a multi-disciplinary four-institution research team, which combines academia and national laboratories, and spans the broad and necessary expertise in theoretical spectroscopy, nonlinear optics, quantum chemistry, molecular non-adiabatic dynamics and code development. The research program is delineated into two interconnected thrusts: methodology development (THRUST 1), and application to relevant chemical processes and molecular targets (THRUST 2). Non-adiabatic dynamics will be simulated by a full quantum treatment of the nuclei employing the *Multi Configuration Time Dependent Hartree (MCTDH)* approach. Studies will include electron and energy transfer processes in light harvesting complexes, conical intersection dynamics, photophysics, and relaxation pathways of nucleobases, thionucleobases, DNA, aromaticity and molecular currents, and multiple core excitations in molecules. Coherent control techniques will be used to optimize desired features in signals.
To learn and run MCTDH quantum nuclear dynamics, the candidate will have to work in cooperation with Dr. Fabrizio Santoro, CNR Pisa, spending most of the time there.