Theory and Simulation of Multidimensional X-ray Probes of Molecular Processes

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Introduction. Emerging X-ray free electron laser (XFEL) sources offer unique probes of matter with unprecedented spatial and temporal resolutions. XFEL-based 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 molecular structure. These experimental advances provide unparalleled insights into the motions of electrons and nuclei, charge and energy transfer in molecular systems and must be combined with predictive theoretical methodologies and computational tools to shed light onto the underlying electronic and structural dynamics and for the simulation and interpretation of the relevant X-ray signals. The proposed research effort focuses on the development of cutting-edge simulation tools for nonlinear multidimensional X-ray/optical spectroscopies and their application to molecular systems aiming to fundamental chemical dynamics. Our proposal addresses 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*". The proposed effort will extend time-resolved methodologies widely used in the visible and the infrared regimes to tackle the molecular response in the X-ray regime. These include multidimensional stimulated Raman signals, three- and four-wave mixing, as well as time-resolved X-ray and electron diffraction, X-ray sum-frequency generation, time-, frequency-, and wavevector-resolved diffraction, novel chiral signals with circularly polarized X-ray pulses, and quantum phase-sensitive imaging using entangled X-ray photons.

Activity. This project aims to streamline the modeling, simulation, and prediction of XFEL-based multidimensional spectroscopies, providing insights into fundamental ultrafast molecular processes and guiding the design of new XFEL experiments. 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. It is delineated into three interconnected thrusts: methodology and protocol development (THRUST 1), design of novel nonlinear X ray signals (THRUST 2), and applications of these methods to a broad range of molecular systems and chemical processes (THRUST 3). Experimental probes at XFEL facilities will be planned. Methodology developments and simulations will be carried out and deployed via open-source codes (NWChem, OpenMolcas, NEXMD and SPECTRON) and made available to XFEL facility users, both experimentalists and theorists. To learn and run MCTDH quantum nuclear dynamics, the candidate will have to work in cooperation with Dr. Fabrizio Santoro, CNR Pisa, possibly spending part of the time there.