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New x-ray and extreme ultraviolet (XUV) light sources generated by free electron lasers (FELs) in large accelerator facilities or by tabletop high-harmonic generation (HHG) setups are revolutionizing the study of elementary molecular events with unprecedented temporal (100 as) and spatial (sub-nanometer) resolutions. The x-ray FELs provide hard x-rays (>5 keV) with high flux enabling time-resolved diffraction to measure time-dependent structural changes on tiny crystals. Time-resolved nonlinear x-ray spectroscopy using x-ray pulses or a combination of optical and infrared pulses has now become a reality. These developments offer new insights into time-evolving molecular structures, primary photophysical, photochemical, and biological events, and strongly coupled electronic and nuclear dynamics. A novel time-domain picture of electron correlations is emerging, which will have far reaching implications for the design of new molecules and materials with tailored functionalities. The current state of this field is reminiscent of picosecond optical studies in the 1970s or femtosecond optical studies in the 1980s where rapid development of laser sources enabled novel experiments and spurred theoretical development of time-domain spectroscopy. The papers in this special issue provide a timely overview of state-of-the art experimental and theoretical chemical physics research using XUV and x-ray photons. This special issue should be of interest to experts in this field as well as to newcomers who wish to get familiar with this rapidly evolving field.

The experimental papers include gas phase[1–6] and condensed phase studies[7–12] conducted using table-top sources and user facilities such as synchrotrons and x-ray free electron lasers. Yong *et al.* described how high energy x-ray FEL pulses can monitor the structural changes pertaining to vibrational motion on the highly excited anharmonic surfaces of molecules in the gas phase using x-ray scattering.[1] The coupling of electronic and vibrational coordinates is also probed in the Rydberg states of ammonia by Svoboda *et al.* using photoelectron spectroscopy with VUV pulses generated via higher harmonic generation on the table-top.[3] Indeed, the generation of tailored XUV pulses via HHG is an exciting area of research, and the work by Tross and Trallero-Herrero provides an example of using orbital angular momentum of the driving field to study the process of HHG in molecular nitrogen.[2] As the photon flux of x-ray pulses increases and their pulse length decreases, the study of nonlinear x-ray techniques comes into focus. The papers by Fidler *et al.*[5] and Obaid *et al.*[4] provide examples of moving toward performing multi-pulse x-ray experiments in the gas phase using table-top and XFEL sources, respectively. Niozu *et al.* studied the fundamental intense x-ray free electron laser–matter interaction, which is crucial for the developing new applications of X-FEL pulses.[6] Time-resolved x-ray experiments are sensitive to electronic and atomic structural changes at various length scales in disordered media. March *et al.* described a combined high signal-to-noise x-ray spectroscopy using a third-generation synchrotron source and advanced computational study to model the role of the solvent during a photochemical reaction scheme.[9] Park *et al.* uncovered new chemical intermediates and their structures in a solvent-dependent photo-dissociation reaction using time-resolved x-ray solution scattering at a synchrotron.[8] Femtosecond VUV reflection and absorption using HHG sources are described by Biswas *et al.* and Ash *et al.* to study electron transport coupled with structural changes following photoexcitation in materials and molecules, respectively.[11,12] An example of multi-keV table-top laser-plasma source to study structural changes in the solid state is given by Li *et al.*[10]

New theoretical and computational tools required for the interpretation of x-ray experiments at the microscopic level are described

and applied in several papers in this special issue. The role of coupled electronic and multimode nuclear wavepacket dynamics is explored in the simulation of gas and condensed phase RIXS experiments on methanol by Vaz da Cruz *et al.*[7] The role of coupled electronic states and nuclear wavepacket dynamics and their manifestation in the time-resolved x-ray solution scattering signal are studied by Pápai *et al.*[13] The paper by Simmermacher *et al.* studies the coupling of electronic and nuclear coordinates in the theory of ultrafast x-ray scattering in the gas phase.[14] A theoretical framework for the use of novel photoelectron probes to visualize coupled electronic and nuclear dynamics is provided by Goetz *et al.*[16] and van den Wildenberg *et al.*[15] An accurate description of electronic non-adiabatic effects and spin–orbit couplings is crucial for interpreting ultrafast x-ray spectroscopy and scattering signals of ultrafast photoinduced intersystem crossing and photodissociation of molecular systems. The works by Komarova *et al.*, Wang *et al.*, Tsuru *et al.*, Faber *et al.*, and Valentine *et al.* address this important issue.[17–21] Norrel *et al.* addressed the importance of accurately accounting for solvation effects in interpreting time-resolved XAS and measuring absorption spectra at multiple edges to understand complex photochemical processes in solution.[22] Improved computational techniques (i) for calculating the discrete and continuum absorption cross sections of 1s electrons are proposed by Tenório *et al.* and (ii) for strong field ionization by Hoerner *et al.*[23,24]

Several theoretical papers in this issue propose new experimental observables for studying ultrafast electronic and structural changes.[25–29] Yamazaki *et al.* proposed the use of femtosecond Coulomb explosion imaging to reconstruct structural dynamics of molecules in the gas phase.[26] Inhester *et al.* proposed an attosecond imaging technique to study core-hole wavepacket dynamics in real time.[29] Nenov *et al.* and Zhang *et al.* proposed nonlinear x-ray experiments by calculating two-dimensional coherent x-ray spectroscopy and double core hole valence-to-core x-ray emission spectroscopy.[25,28] Both these studies are motivated by the development of new, coherent, and intense x-ray FEL sources.

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