Preface to Special Topic: The Advent of Ultrafast X-Ray Absorption Spectroscopy

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X-ray sources have undeniably revolutionized science; however, paradoxically, their potential has only been partially exploited thus far. Recent technological advancements have propelled the development of "ultrafast" x-ray sources,[1,2] capable of emitting x-ray pulses lasting femtoseconds or even shorter. These groundbreaking x-ray sources introduce new, previously unexplored avenues for time-resolved experimental techniques, marking a significant leap forward in scientific exploration.

The evolution of ultrafast x-ray sources has been gradual with noticeable acceleration in the past decade. Initially, the predominant method for generating short x-ray pulses, lasting approximately 100 ps, involved operating synchrotrons in single-bunch mode.[3] Subsequently, this approach was refined by implementing a femtosecond (fs) laser to selectively isolate the x-ray emission associated with a fraction of the electron bunch (the "laser-slicing" technique).[4,5] This advancement led to a remarkable reduction in pulse duration to tens of femtoseconds, albeit at the expense of x-ray pulse intensity. In the late nineties, alternative laboratory methods based on high-order harmonics generation (HHG) emerged.[6] The HHG sources utilize table-top laser beams to produce femtosecond or attosecond soft x-ray pulses with photon energies up to hundreds of electron volts (eV) from high-pressure waveguides or gas jets.[7] In the late 2000s, the x-ray free electron laser (FEL) technology became available.[8,9] The technological innovation of FELs has provided access to high peak power, highly coherent, femtosecond soft and hard x-ray pulses with polarization control and narrow bandwidth.[10,11]

However, the development of new ultrafast x-ray sources has not ceased with the availability of FELs. Recent progress in laser-driven plasma acceleration has resulted in compact betatron x-ray sources,[12,13] capable of generating intense, broadband and collimated hard x-ray beams lasting femtoseconds in laboratory settings.[14] Additionally, noteworthy is the conceptual design of a picosecond megahertz (MHz) synchrotron source currently under consideration at Elettra,[15,16] based on the transverse deflecting cavities (TDCs) scheme.[17] This design enables the production of 1–5 ps (FWHM) x-ray pulses from a vertically tilted electron bunch isolated within a "dark gap" of approximately 80 ns from the rest of the bunches accumulated in the synchrotron ring.

The future of ultrafast x-ray sources is poised to be shaped by plasma acceleration technology, offering research institutions the capability to operate cost-effective, space-efficient, intense, tunable, ultrafast x-ray sources.[18] A pivotal player in this technological transition is the EuPRAXIA European project, under way.[19] This ambitious initiative aims to construct the first free electron laser (FEL) facility driven by a compact plasma acceleration source[20] and make it accessible to the broader scientific community. This exciting prospect encourages scientists to expand conventional x-ray techniques into the time domain, providing unprecedented access to ultrafast dynamics of matter constituents, including electrons, atoms, and other relevant quasi-particles such as magnons, polarons, and excitons. Among these techniques, x-ray absorption spectroscopy (XAS) emerges as particularly promising due to its unparalleled chemical selectivity, sensitivity to both electronic and local atomic structures, and remarkable versatility. With the capability to resolve timescales from sub-picoseconds to attoseconds, time-resolved XAS (TR-XAS) represents a unique experimental approach that has recently found application in diverse scientific investigations, unveiling its tremendous potential.

This special topic aims to highlight the significant progress achieved thus far by TR-XAS methods and promote the use of TR-XAS in the scientific community, showcasing selected works recently conducted by expert scholars in the XAS field.

TR-XAS has arisen as a valuable tool for elucidating ultrafast mechanisms underlying specific functionalities in materials. The work presented by Marangos and collaborators[21] demonstrates the application of TR-XAS in soft x-rays to monitor ultrafast processes triggered by the absorption of visible light in organic photovoltaic devices. The sensitivity of TR-XAS to the ultrafast modification of electronic

structures at specific atomic sites enables the detection of excitons and charge transfer dynamics, which are fundamental to material functionality. In this context, TR-XAS can be complemented by other time-resolved core-hole spectroscopies. An illustrative example is provided by the work of Chergui and colleagues,[22] who utilize time-resolved resonant inelastic scattering (TR-RIXS) to unveil an ultrafast ligand-to-metal charge transfer in α-I_2IrO_3.

TR-XAS proves to be a versatile tool suitable for monitoring dynamics in molecular or nanoscale samples, even when diluted in solvents for practical or functional reasons. For instance, Milne *et al.*[23] utilize TR-XAS to investigate the migration of holes in ZnO nanoparticles following exposure to a femtosecond laser pump. Notably, they compare TR-XAS measurements conducted in single-bunch mode at a synchrotron with those obtained at the SACLA FEL. Sokaras and collaborators[24] showcase a sophisticated setup operated at the SSRL synchrotron, coupling the MHz repetition rate of x-rays delivered in single-bunch mode with a recirculating liquid jet sample delivery system. Their study reveals the light-induced excited spin state trapping in a prototypical spin crossover iron aqueous complex on a timescale of hundreds of picoseconds. In another study, Wörner and colleagues[25] employ attosecond transient absorption spectroscopy at the C K-edge to probe the few-femtosecond electronic and structural dynamics in the methane cation driven by the Jahn–Teller effect. This experiment utilizes an HHG table-top apparatus capable of delivering ultrashort soft x-ray pulses ($t < 200$ attoseconds) with a cutoff energy of approximately 400 eV.

The experiments on matter in extreme conditions of temperature and pressure, transiently induced by high peak power optical pumps, necessitate ultrafast methods for monitoring the resulting nonequilibrium samples on the sub-picosecond timescale. TR-XAS proves to be an effective tool for this purpose. In a comprehensive review, Dorchies *et al.*[26] detail their recent TR-XAS single-shot experiments conducted on metals excited to the warm dense matter regime. They demonstrate the utilization of laser–plasma x-ray sources and betatron sources for TR-XAS experiments, showcasing the remarkable potential of femtosecond near-edge soft x-ray absorption spectroscopy. Additionally, Beye and collaborators[27] present an ultrafast XAS experiment on nickel conducted at the EuXFEL. By varying the fluence of the FEL on the sample across the nickel L_3-edge, they induce pronounced changes in the spectra, which reflect the rearrangement of the electronic structure of the sample under extreme conditions.

The interpretation of TR-XAS experiments necessitates robust theoretical calculations capable of providing meaningful insights into the experimental findings. Therefore, the development of efficient and reliable theoretical methods for analyzing TR-XAS spectra is crucial. Penfold and colleagues[28] propose an innovative machine learning approach employing a deep neural network (DNN). Their neural network learns the structure-dependent differences between the higher and lower levels of time-dependent density functional theory (TD-DFT) and, after this learning process, becomes capable of optimizing the spectra obtained through rapid low-level DFT calculations. This approach mitigates computational costs while preserving accuracy in theoretical predictions. Similarly, Coriani and colleagues[29] employ TD-DFT and the coupled cluster singles and doubles method to calculate the TR-XAS of a small BT-1T molecule typically found in organic electronic devices. In this system, XAS variations are expected due to a light-induced charge transfer mechanism. Their findings indicate that changes in XAS after light exposure primarily stem from the rearrangement of electronic populations rather than modifications in atomic structure. This insight not only facilitates a reduction in computational time but also broadens the applicability of the approach to larger molecular systems.

The outstanding papers[21–29] included in this special topic witness the advent of TR-XAS. As we look to the future, the continued evolution of this technique, supported by robust theoretical methods and cutting-edge technologies, promises to unveil even deeper insights into the ultrafast mechanisms governing the properties and functionalities of materials and molecules. Collaborative efforts among researchers and institutions worldwide will be crucial in fully realizing the potential of this powerful technique. The involvement of young researchers embarking on TR-XAS for the first time is particularly essential, as they bring fresh perspectives and innovative approaches that will undoubtedly accelerate progress in this field.

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