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Introduction

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Author for correspondence:
J. P. Marangos
e-mail: j.marangos@imperial.ac.uk

The measurement of ultrafast electronic and structural dynamics with X-rays

J. P. Marangos

Blackett Laboratory, Imperial College London, South Kensington, London SW7 2AZ, UK

In this theme issue, leading researchers discuss recent work on the measurement of ultrafast electronic and structural dynamics in matter using a new generation of short duration X-ray photon sources. These photon sources, based upon high harmonic generation from lasers and X-ray free-electron lasers, look set to have a high impact on ultrafast science.

This article is part of the theme issue 'Measurement of ultrafast electronic and structural dynamics with X-rays'.

1. Introduction

For many decades, the key to our scientific understanding of matter in various forms, i.e. molecules, polymers, solid materials (metals, semi-conductors, dielectrics) and biomolecules, has been through our ability to determine their atomic scale structure. Indeed, structural biology is driven by the notion that structure and function are tightly connected. This paradigm has proved enormously successful in developing our picture of many phenomena in physics, chemistry and biology. Our scientific understanding of structure was delivered by the capability to use X-ray, neutron and electron diffraction/imaging to determine the atomic scale arrangement of the material. As successful as this picture has been it misses a key part of the story when matter undergoes a change, e.g. when correlated electronic and nuclear motions lead to a chemical reaction or a phase change in a condensed matter system. To measure the ensuing electronic and structural dynamics that can occur over a wide range of time scales, from 10s of attoseconds to many milliseconds, while retaining the high-resolution structural determination over all relevant spatial scales, is a current frontier challenge to our measurement capabilities. It is the emerging possibility

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to use ultrafast pulses of X-rays from new types of laser-based and accelerator-based light sources to achieve this *four-dimensional* imaging that is the focus of the current issue.

2. Basics of ultrafast electronic and structural dynamics

We can think of the microscopic state of a material system in terms of a semi-classical picture by considering the equilibrium positions of the classical atomic nuclei and the quantum wave functions of the electrons. Most of the electrons will be found localized to single atomic sites. A few of the electrons contributed by each atom are more delocalized, the valence electrons, and participate in bonding in a molecule or dielectric or as conductors in a metal or semiconductor. The wave function of these valence electrons determines the electronic properties and bonding of the material. The occupation, energy, symmetry and spatial distribution of the valence electronic states are the key electronic structure properties that we would like to determine for both static and dynamical structures. Likewise, we would like to know the positions and geometrical arrangement of the different atomic nuclei that form the 'static' framework in this picture.

Of course, the atomic nuclei also follow the rules of quantum mechanics. The vibrational (phonon) modes of many structures can be excited at finite temperature and their presence determines the behaviour of the matter at equilibrium. To get an idea of the timescales of typical structural dynamics (e.g. those resulting from a thermally induced chemical reaction), we should think about the timescale of the vibrational (phonon) modes of the atomic nuclei in the structure. These range in oscillation period from picoseconds for a typical pair of heavy weakly bonded atoms, to 25 fs for a typical C–C bond, to ≈11 fs for a C–H bond. It is thus clear that the structural dynamics associated with the motion of atomic nuclei in a thermally induced chemical reaction are from ≈100 fs to 100 ps or longer since the crossing of the potential barrier that initiates a reaction is often a relatively rare event. In this case, the electronic states adjust adiabatically as the structural dynamics proceeds, a picture consistent with the familiar idea of the Born–Oppenheimer separation of electronic from nuclear time scales in molecular physics.

However, there are important classes of chemical and physical changes that can be photo- or electron-triggered, in which case the electronic charge motion can proceed at electronic timescales. Electronic timescales are more typically sub- to a few femtoseconds and strongly non-adiabatic behaviour may dominate the initial dynamics and the subsequent vibronic coupling. Such changes are, for example, important in photo-triggered processes including photosynthesis, photocatalysis, photo-damage of biomolecules and photo-induced phase changes in strongly correlated quantum materials. Therefore, being able to track dynamics down to sub-femtosecond timescales has both fundamental scientific, as well as wide-ranging technological, significance. So far, ultrafast X-ray sources are the sole technology available to us for this purpose.

Pump-probe methods are essential to capture the fastest dynamics as fast enough cameras are not available. In such a method, a short light pulse, typically in the IR-UV optical range but also possibly an X-ray pulse, initiates the event either by direct photoelectronic excitation into an excited intermediate quantum state of the system or by creation of a sudden non-equilibrium state of the ensemble, e.g. by injection of 'hot' non-thermal electrons to activate the reaction. The probing can then take place with a short X-ray pulse using one or other of the established (static) methods but now capable of yielding the time-dependent instantaneous structure, i.e. imaging in *four dimensions* instead of just the usual three spatial dimensions.

3. Ultrafast X-ray sources

Time-resolved structural determination is dependent upon the availability of short pulses of X-rays, electrons or neutrons. However, it is only for X-rays that we currently have demonstrated applications of the technology with pulses down to a femtosecond duration or less. Two new classes of ultrafast X-ray photon sources, high-order harmonic generation and X-ray free-electron lasers, have been proven over the last three decades.

High-order nonlinear optical processes, caused by strong-field laser-driven electron acceleration in the vicinity of an atom, were first demonstrated to generate short wavelength light in the late 1980s [1,2], and by 2001, the possibility to use this high harmonic generation (HHG) process for the production of controlled attosecond domain isolated pulses and pulse trains was firmly established [3,4]. Typically, these HHG photon sources have operated in the extreme ultraviolet around 20–100 eV, rather than the X-ray range, but with the availability of new optical parametric-based strong-field laser systems operating at wavelengths from 1.5 to 5 μm, it has been possible to increase the electron acceleration to reach soft X-ray photon energies approaching 1 keV [5–7]. These photon sources, although of low peak power (typically less than 10 kW), have unprecedentedly short pulse duration, with just 50 as being the current record [8]. Moreover, HHG sources have perfect synchronization to other optical pulses driven by the same laser and therefore enable unique possibilities for high-resolution ultrafast studies using photoelectron and X-ray spectroscopy methods.

The second type of new source is the free-electron laser (FEL) [9] and most importantly the SASE (self-amplified spontaneous emission) [10,11] X-ray free-electron lasers (XFEL) that were first demonstrated in 2009 with the switch on of LCLS at Stanford [12] followed soon after by the compact X-ray FEL SACLA in Japan [13]. Earlier, the first VUV SASE free-electron laser [14] had been demonstrated at the Tesla test facility (DESY) that was the forerunner to the very successful VUV/XUV FLASH free-electron laser facility. In this type of source, a linear electron accelerator generates a low emittance, monoenergetic, relativistic electron bunch that is then passed through a series of magnetic undulators in which the radiation emitted causes a microstructuring of the charge density within the electron bunch. This microstructured electron bunch interacting further with the undulator results in the emission of pulses of partially coherent X-rays at the end of a sufficiently long series of undulators [15]. XFEL sources have high peak power (around 100 GW) and a photon energy that, from a single machine, can cover anywhere from 250 eV to 20 keV. Pulse durations of a few femtoseconds were demonstrated almost immediately [16] and now sub-femtosecond operation has been achieved [17]. XFELs have made possible new kinds of time-resolved X-ray diffraction, X-ray coherent diffractive imaging, X-ray photo-/Auger electron spectroscopy and various forms of X-ray spectroscopy including X-ray absorption spectroscopy and resonant inelastic X-ray scattering (RIXS), which are discussed in this issue.

A fuller survey of ultrafast X-ray photon sources and their current status is provided in the review by Schönlein *et al.* [18]. It covers the broad features of each of the technologies, their current status and their potential future capabilities. Recent developments of sub-femtosecond HHG sources in the soft X-ray range are presented in the article by Johnson *et al.* [19], where optimization of X-ray flux is discussed and possible scalings for future laser sources, e.g. at high repetition rate or with a higher power. Various routes to attosecond pulse generation and measurement at XFELS are discussed by Coffee *et al.* [20], including some exciting recent demonstrations of sub-femtosecond operation modes that are already close to user availability.

4. Time-resolved X-ray measurement methods

The short wavelengths of X-ray photons, and the short de Broglie wavelengths of electrons and neutrons of appropriate energy, enable diffraction imaging of matter at the required fine spatial resolution. In the case of X-rays, various types of spectroscopy have been the key to elucidating the accompanying electronic structure. The challenge for time-resolved measurements is to create very short duration structural probes so that this structural information can be sampled at a sufficiently high temporal resolution. As some of the relevant dynamics, e.g. photo-induced charge migration in molecules, occurs on a sub-femtosecond timescale, to accurately record them requires that the probe duration is similarly fast. While some progress has been made recently on short electron pulse generation for ultrafast electron diffraction (UED) [21–23], accessing the sub-10 fs temporal range remains challenging. By contrast, X-ray sources, based on both HHG and XFELs, have already proven themselves capable of operating at these very high temporal

resolutions. Therefore, here we will concentrate upon what X-rays can achieve, while anticipating UED will become a competitive source, at least for diffraction imaging, in the foreseeable future.

(a) Time-resolved X-ray diffraction

X-rays may interact with matter via either elastic or inelastic scattering (the latter is discussed with X-ray spectroscopy in the next section). Thomson (Compton) scattering from the large number of electrons localized to the atomic sites dominates the elastic scattering signal compared to the elastic scattering from the smaller number of less localized valence electrons. If the scattering is from a periodic structure, e.g. a crystal lattice, constructive interference between the scattered X-ray waves leads to strong peaks at certain angles (Bragg peaks) [24] that give the reciprocal space information from which the lattice structure can be retrieved. High brightness X-rays, such as those available from an X-ray FEL, enable structural retrieval from serial exposures of nanocrystals with atomic resolution. This has proven of significant value as many proteins can only be crystallized readily to form nanoscopic, rather than macroscopic, crystals [25]. Even in a non-periodic structure, the X-ray scattering signal for spatially coherent X-rays can give a complex diffraction pattern from which the structure can be retrieved using powerful algorithms that numerically solve the phase problem by applying various physical constraints in an iterative retrieval procedure [26,27]. This coherent diffraction imaging procedure is well suited to the high brightness partially coherent X-rays from XFELs, and the concept of 'diffract-before-destroy' for imaging non-periodic structures has been used to gain nanometer, but so far not atomic, resolution in a variety of biological [28] and non-biological [29] nanoscale structures. The possibilities for determining static structures by this method is being actively pursued at all of the XFELs currently operating and progress is constantly being reported, but further discussion of this topic is outside the scope of this issue.

The X-ray pulses from XFELs have a very short duration, as well as a very high brightness, and so if they are applied time synchronized with another interaction that can initiate structural change then time-resolved X-ray diffraction becomes possible. A number of recent experiments illustrating this possibility have been carried out at the LCLS and SACLA X-ray FELs. The brightness is high enough to capture structural changes in an ensemble of gas phase small molecules [30] and these measurements have revealed photochemical structural changes that occur over a few 100s of femtoseconds, as is described in the article by Ware *et al.* [31]. Structural changes of much larger photoactive protein molecules, in a nanocrystalline form, have also been studied [32], and this is addressed in the article by Hutchison *et al.* [33]. Optical and terahertz fields can be used to induce non-equilibrium phases in strongly correlated quantum condensed phase materials with new emergent properties and the accompanying structural change has been captured by time-resolved X-ray diffraction [34]; this topic is described in the article by Buzzi *et al.* [35].

For these studies, unless picosecond resolution is sufficient, considerable technical effort must be applied to establish the relative timing of X-ray and optical pulses that have an intrinsic temporal jitter of up to several hundred femtoseconds. This goal has been achieved through the development of a number of so-called time-tools [36,37] that can resort the pulse timing to a fidelity of better than 20 fs. Future machines with lower intrinsic jitter and higher resolution time-tools are under development [38,39], which are discussed by Coffee *et al.* [20], and they are anticipated for widespread future use that will improve the achievable resolution to close to 1 fs. This timing technology is also vital for the time-resolved X-ray spectroscopy techniques that we now turn to.

(b) Time-resolved X-ray spectroscopy

Inelastic X-ray interactions can also be enormously powerful and measurement of these interactions via various channels is the basis of a variety of well established X-ray spectroscopies: X-ray photoelectron spectroscopy, Auger electron spectroscopy, X-ray absorption spectroscopy

and X-ray photoemission spectroscopies such as Resonant Inelastic X-ray Scattering (RIXS). With X-ray FEL pulses or HHG sources, these X-ray spectroscopy tools can be made time-resolved with temporal resolution in the femtosecond and, in the future, even the sub-femtosecond range.

Photoelectron emission results when an X-ray photon is absorbed by the target and gives up all of its energy to the excitation of a bound electron either from the valence states or from the inner shell states. If X-rays of well-defined energy are used, the energy analysis of the photoelectrons from the valence and inner shells gives direct information on the binding energies of these states. Angularly resolved measurements of the photoelectrons can give additional detailed information on state symmetries. This technique has been widely exploited to investigate the chemical state of materials and in this form is often termed Electron Spectroscopy for Chemical Analysis (ESCA) following developments by Siegbahn *et al*. [40] that led to his Physics Nobel Prize in 1981. Ionization of an inner shell electron can lead to an unstable electronic hole that can undergo decay through electron–electron correlation with the emission of further Auger electrons [41]. Auger electrons carry information on the energy levels of the involved ionic forms and are used for probing the electronic structure of surfaces in the context of electron microscopy. Streaking in a laser field of atomic photoelectrons and Auger electrons has been used to resolve temporal delays in emissions from different states with as little as a few tens of attosecond difference [42].

Even a simple XUV pump—optical probe measurement of the photofragment ion yield from a biomolecule, using a HHG-isolated attosecond XUV pulse, can already return critical information on electronic migration in suddenly ionized cation states [43]; this type of measurement is discussed by Trabattoni *et al.* [44]. Using time-resolved X-ray Auger and absorption spectroscopy probing of optically excited molecules at an XFEL, it has been shown possible to track mechanisms of radiation damage in biomolecules [45] and this work is described in the article by Wolf *et al.* [46]. Also, using XUV-isolated attosecond pulses and pulse trains from HHG, it has recently been shown that the release of the photoelectron wavepacket into a continuum dressed by a synchronized optical field (RABBIT or streaking method) can give access to subtle photoelectron emission phase shifts (delays) that were hitherto inaccessible [47]; this type of measurement is discussed in the article by the group of L'Huillier [48].

Resonant ionization close to an absorption edge of a particular atom, corresponding to a transition from an inner shell state to an unoccupied valence or low-lying continuum state, is a powerful way to learn about the electronic structure in the vicinity of that atom. The cross-section for photoabsorption at different X-ray energies can be determined from absorption or electron yield measurements in a condensed phase or gaseous system to reveal the details of the unoccupied and partially occupied valence and low continuum states near the ionization threshold. This method of X-ray absorption near edge structure (XANES) is widely used to establish critical local electronic structure information [49]. Further into the continuum, the absorption modulations are termed extended X-ray absorption fine structure, which has been used for many years to establish local bond lengths around a specific atomic site [50]. Recently, there has been significant progress in the use of ultrafast pulses from HHG that have been applied to time-resolved X-ray absorption spectroscopy of photochemical processes in gas phase molecules and photophysical processes in condensed phase systems, including probing at the C K edge [51,52]; for more on this topic, see the review by Geneaux *et al.* [53]. Time-resolved X-ray absorption and RIXS using X-ray FELs has now become a proven technique for photochemistry studies [54], as is discussed in the review by Wernet [55].

X-ray photon emission measurement methods are now being used in time-resolved mode using X-ray FELs. An example is resonant inelastic X-ray scattering (RIXS), in which a core excited intermediate state then relaxes to one or other of the neutral valence states by the emission of a photon, and the energy and direction (momentum transfer) of the emitted photons are measured using an angularly resolving X-ray spectrometer. In the language of nonlinear optics, this process is termed spontaneous Raman emission (in contrast to the stimulated Raman processes discussed in the next section). The energy levels of the occupied and partially occupied states can be registered from this signal as well as the existence of the low energy collective excitation modes and their momenta. This provides a powerful way to probe low energy (eV to meV) excitation

modes (such as phonons and magnons) in a condensed phase material. Time-resolved RIXS studies have proved valuable in elucidating the nature of excitations in photoexcited correlated materials [56]; for a discussion, see the article by Cao *et al.* [57].

(c) Nonlinear X-ray spectroscopy

In so much as RIXS and other photon in/photon out methods using spontaneous emission are two-photon in nature, they can be regarded as examples of a nonlinear X-ray interaction. The spontaneous emission, however, is into unoccupied field modes and so is not controlled by the applied X-ray fields. High brightness X-ray sources provide new opportunities for controlled nonlinear X-ray processes. An example is stimulated X-ray Raman demonstrated by Rohringer *et al.* [58,59] and reviewed by this author here. High brightness, high repetition rate, X-ray FELs open the possibility for nonlinear X-ray spectroscopy with entirely new capabilities. An early proposal in this direction is the possibility for impulsive X-ray electronic Raman to create and probe atomically localized valence electronic excitation and so to track ultrafast electronic coupling through a molecule even on attosecond timescales [60]. Another new concept is for nonlinear X-ray diffraction involving a two-photon, optical and X-ray photon, scattering into an X-ray mode that can be heterodyne detected against an applied X-ray field in the same mode. This method is predicted to have the potential to image the charge density evolution of excited electronic states [61] and is described here in the article by Cho *et al.* [62].

5. Conclusion

In this volume, we present a collection of reviews and research papers covering the various ultrafast X-ray photon sources and the new methods enabled by them. The authors have endeavoured to make their articles as clear and accessible to the non-specialist as the material permits. In this way, we hope this volume will have a multi-disciplinary appeal. Of course, much excellent work has been omitted as space limits do not permit a fully comprehensive survey of the topic; the reader is directed to a recent review for some further examples [63]. Hopefully, the current collection of articles will prove stimulating to the reader. The prospects for these methods look really exciting as, although they are still in their infancy, they are already having an incisive impact on our understanding of ultrafast electronic and structural dynamics across a variety of physical, chemical and biological systems. With rapid advances in both HHG sources (e.g. increased photon energy, higher repetition rate and higher average power) and X-ray FELs (e.g. shorter pulses, higher repetition rates, average powers exceeding those of any other X-ray source and more facilities becoming available), the field looks set for a rapid growth in applications with widespread scientific impact over the coming decades.

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