Ultrafast X-ray science: structural transients in solution

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We discuss two techniques of ultrafast X-ray science implemented at synchrotrons with application to the study of the real-time dynamics of chemical systems in solution. Time-resolved X-ray scattering and absorption offer complementary ways to study geometrical structural changes in a wide variety of systems. We present a few examples that demonstrate their ability to obtain structural information on timescales ranging from milliseconds down to hundreds of femtoseconds.

Keywords: Absorption; Dynamics; Pump probe; SAXS; Scattering; Structure; Synchrotron; Time-resolved; Ultrafast; X-ray; XAS

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1. Introduction

Chemical reactions and the structure of molecules lie at the heart of chemistry. The nature of the bonds that hold atoms together is a key question for any attempt to understand the detailed properties of a compound. At their most fundamental level, chemical reactions involve the breaking, creation and evolution of interatomic bonds. A complete grasp of these inherently dynamic phenomena requires methods to measure the time-dependent properties of bonds and their associated atomic structures.

As a way to characterize time-averaged structures, X-ray based methods have proved enormously successful in application to chemical systems. X-ray diffraction has had a particularly strong effect on structural biology, with the most famous example being the solution of the structure of DNA [1]. While a structural solution via diffraction currently requires that the molecule of interest be incorporated into a crystal, even for the disordered arrangements of solution-phase molecules, incoherent X-ray scattering gives highly useful information on geometrical structure.

Spectroscopic methods at X-ray wavelengths have also given vital insights into time-averaged structures, both geometric and electronic. Since the binding energies of the atomic-like core electrons correspond to the energy of photons in the X-ray range, X-ray spectroscopy offers a unique way to probe the local environment of specific elements. By measuring the absorption over a wide range of X-ray photon energies just above a transition of an atomic core level to the electronic continuum, it is possible to use the wavelike properties of the ejected photoelectron to probe the immediate geometrical structure surrounding a specific kind of atom in a molecule. Known as X-ray absorption fine structure (XAFS), such measurements can extract local bond distances and angles. Through analysis of the absorption closer to an atomic transition, it is also possible to extract information on the oxidation state of an element and the energies of unoccupied electronic orbitals. In addition to X-ray absorption spectroscopy (XAS), other techniques (e.g., X-ray emission spectroscopy) offer additional details about binding energies and electronic correlations [2–4].

The desire to study the dynamics of geometric and electronic structure using these techniques has stimulated a great deal of technical innovation over the past few years. Although laser-generated plasma and high-harmonic X-ray sources have had and continue to play an important role in the general development of time-resolved X-ray science, the high stability, brightness and spectral tunability of synchrotron-based sources have also led to significant contributions [5,6]. The inherently pulsed time structure of synchrotrons makes them a convenient source for X-ray studies with 100-ps resolution. Recently, new methods have been developed to offer time resolution as good as 140 fs at synchrotrons by using the

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fs-laser slicing technique [7–9]. Although these gains in time resolution come at a severe cost in the number of X-ray photons available, they have already demonstrated how it is possible to extract information on transient changes in chemical bonds that is otherwise unavailable [10].

This contribution is intended to be only a brief introduction to the subject, and, as a result, it is not a comprehensive overview of even the most recent work in this area. The emphasis here is to introduce the basic ideas and to give some relevant examples to help illustrate these concepts.

2. Time-resolved X-ray techniques at synchrotrons

A synchrotron creates X-rays by circulating relativistic electrons around a storage ring, using strong magnetic fields to focus and to steer the electrons on a closed path. Whenever these magnetic fields change the direction of the electron beam, the electrons radiate a broad spectrum of X-rays. At third-generation synchrotron sources, this X-ray radiation is optimized at certain locations with special magnetic structures, known as wigglers and undulators, that produce extremely bright X-rays from multiple sequential bendings of the electron beam [11].

Electrons in the storage ring maintain their energy by interacting with a sequence of radiofrequency (RF) cavities placed within the ring. The periodicity of the RF field causes the electrons to bunch together temporally, essentially dividing the possible instantaneous positions of the electrons into a discrete number of ''buckets.'' The diagram of the storage ring on the left side of Fig. 1 shows the electron bunches pictorially for a bucket ''filling pattern'' similar to one commonly used at the Swiss Light Source (SLS) in Villigen, Switzerland. Fig. 1 shows each bucket containing electrons as a line, with a length proportional to the number of electrons. At the SLS, the 500 MHz RF cavities cause the buckets to be separated at 2-ns time intervals, corresponding to a spatial separation between buckets of about 60 cm. Since the circumference of the SLS is 288 m, there are 480 ''buckets'' available for electrons in the ring. Not every bucket must contain electrons, and, for many facilities, it is advantageous to maintain one or more ''gaps'' of sequential unfilled buckets to avoid losses in the stored current due to positively-charged ions that are attracted to the electron beam. For time-resolved experiments, it is often convenient to inject a large number of electrons into a single bucket within such a gap, making it easier to isolate the X-rays emitted from one packet of electrons. Several synchrotrons periodically offer special bunch-filling patterns, where the number and spacing of filled bunches is tailored to the needs of a particular experiment.

The temporal duration of the electrons in a bucket depends in general on the parameters of the storage ring and the amount of current within the bucket, but it is typically of the order of 100 ps full-width-at-half-maximum (FWHM) for normal operation at most facilities. There have been some recent developments in commissioning a mode of operation at several facilities known as ''low-α mode'' that can bring this down to the order of 10 ps for much reduced values of stored current [12]. Another way to obtain shorter pulses includes so-called ''crab cavities'' that introduce a transverse deflection of the bunch that serves to compress the pulse for a short section of the storage ring [13]. To get even shorter

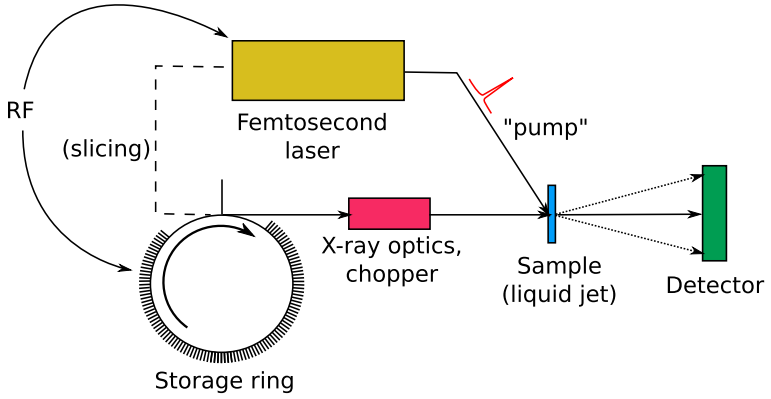

Figure 1. A generic synchrotron ultrafast pump-probe beam-line. A radiofrequency (RF) clock determines the pulse timing of both the storage ring and an optical laser system. An optical or infrared ''pump'' pulse generated by the laser system triggers some reproducible dynamics in a liquid-phase sample. To probe the dynamics of the sample at particular times after the excitation, short pulses of X-rays generated by acceleration of the electrons in the storage ring are directed onto the sample. The X-rays scattered and/or transmitted by the sample are then measured with an appropriate X-ray detector. For fs slicing beam-lines, the X-ray pulse used is created by the interaction of a portion of the optical laser output with the electrons of the storage ring (see Sub-section 2.2 and Fig. 2). The details of the set-up (e.g., the X-ray optics) vary considerably among different facilities and on the specific X-ray probe technique to be applied.