Tracking Atomic Positions in Molecular Reactions by Picosecond X-ray Scattering at the ESRF

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Introduction

The enormous gain in intensity from undulators has led to an equivalent gain in time resolution and some techniques can now be performed routinely at synchrotrons at a time resolution of 100 picoseconds, a limit set by the X-ray pulse length. In the simplest time-resolved experiment, the evolution of a process is recorded by the detector just as a video camera records a football match. In diffraction and scattering experiments, however, the time-resolution of large-area CCD detectors, which are essential for capturing a large fraction of the signal, is milliseconds at best. This is significantly longer than the fundamental times in physics, chemistry, and



Figure 1: Laue pattern from a Lysozyme recorded with 10^{10} photons from a single pulse from the ESRF. The pattern contains 250 reflections. The pattern is recorded to a resolution of 2.2 Å (W70, ID9, 1994).

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Figure 2: Principle of the pump-probe set-up on ID9B. The high-speed chopper reduces the pulse frequency to 1 kHz, which is also the frequency of the laser. The relative timing of the two beams is measured with a diamond (X-rays) and a GaAs detector (laser/X-ray). The pump-probe delay is changed by moving the laser timing electronically. The laser can be move in time steps down to 10 ps. A multilayer monochromator was recently inserted between the chopper and the diamond detector (not shown).

biology: the femto-, pico-, and nanosecond time scales. The pump-probe method is often used to improve the time resolution in diffraction and scattering experiments at the expense of much longer acquisition times. The samples are usually initiated by short laser pulses and the ensuing structural evolution recorded with "flashes" of X-rays at a given delay. By measuring many delays, the snapshots can be stitched together into a film. The highest time resolution from a synchrotron is obtained when the X-ray flash is generated by a single bunch of electrons. For those experiments that can use the pink beam, Laue diffraction for example, high-quality signals can sometimes be recorded in *one* pulse, as shown in Figure 1.



Figure 3: (a) The blue curve shows the spectrum of the single-harmonic undulator U17 measured with a Si monochromator. The red curve shows the spectrum monochromatized by an Ir multilayer with a 1.6% bandwidth. (b) The temporal pulse profile measured with a streak camera for pulses from the four-bunch mode (10 mA bunch charge) and in the hybrid mode (4 mA bunch charge).



Figure 4: Measured change in scattering from the dissociation of an iodine atom from HgI₂ in methanol. The dissociation was triggered by a 0.1 ps 267 nm laser pulse. The sample was probed 100 ps later by a 100 ps X-ray pulse. The pulse sequence was repeated at 1 kHz. (a) Old data from a 100-second exposure with a monochromatic beam from a Si (111) monochromator. (b) Same curve taken in four seconds with the pink beam from the U17 undulator at 18 keV.

Pump-probe set-up

Beamline ID9 at the ESRF is 50% dedicated to pump-probe experiments and named ID9B. It is being refurbished within the Upgrade Programme to become 100% dedicated to time-resolved work in 2015. A simplified schematic of the pump-probe set-up on ID9B is shown in Figure 2.

ID9 is powered by two in-vacuum undulators, a 17 mm period U17 and a 20 mm period U20. The U17 is single-harmonic with a fundamental at 15 keV with a 2.5–5.0 % bandwidth (bw), depending on the acceptance. The spectrum is shown in Figure 3 together with the temporal profile of pulses from two filling modes of the ring. The U17 is sufficiently monochromatic for SAXS/WAXS from proteins [1]. It is also used for WAXS work on small molecules but the resolution is limited by high-q smearing from the asymmetric spectrum. The U17 spectrum is "semi-Gaussian," which complicates the

conversion from scattering angle 2θ to q, $q = 4\pi \sin(\theta)/\lambda$, where 2θ is the scattering angle, λ the x-ray wavelength. The problem is solved by monochomatizing the U17, while maintaining high flux, with a multilayer as shown by the red curve in Figure 3, which is symmetric.

For the U20 undulator, the fundamental can be varied from 8–16 keV by varying the undulator gap. Higher harmonics are always present so the pink beam is rarely used. With the new multilayer monochromator, these higher harmonics can be used for high-spatial-resolution experiments for the first time, as discussed below.

A unique feature on ID9 is the chopper system that allows controlling the pulse structure on the sample. It can either isolate single 100 ps pulses from suitable timing modes of the ring (4- or 16-bunch mode, etc.), or chop-out pulses of any duration $> 0.2 \ \mu$ s. The high-speed chopper (HSC) is a triangular rotor that rotates

Table 1: Flux numbers for beam configurations on ID9 in 16 bunch mode (5mA per bunch)

15 keV (U17, harm 1)	ph/pulse	25 keV (U20, harm 3)	ph/pulse
Pink, 5% bw	2.7E+09	Pink beam	-
Ru, 3.2% bw	4.3E + 08	Ir 1.6% bw	3.3E+07
Si(111), 0.014% bw	5.9E+06	Si(111) 0.014% bw	8.1E+05

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Figure 5: (a) simulated scattering $q \Delta S(q)$ from CO dissociation in Ru₃ (CO)₁₂. The black curve is from a Si monochromator at 25 keV, the reference spectrum. The red curve is simulated with a 1.6% bw at 25 keV. The blue curve is the U17 spectrum. The U17 curve is fine at low q but above 4 Å⁻¹ the amplitude is lower and the nodal points are shifted. (b) The black curve is measured at 500 ps with a 1.6% bw at 25 keV. The old U17 data with a q_{max} of 8.5 Å⁻¹ is shown in green. Extending q_{max} from 8.5 to 11.5Å⁻¹ is important for "finger-printing" atom-atom changes inside molecules. The red curve is a gas-phase simulation which agrees with that measured for q > 2Å⁻¹ where temperature changes in the solvent can be ignored.

continuously at 1 kHz. The chopping is done by passing the X-rays through two slits on one of the sides of the triangle (see Figure 2). The HSC is preceded by a heat load chopper (HLC) that chops the beam into 50 μ s pulses at 1 kHz in sync with the HSC to reduce the heat load on the optics. The chopper system is reviewed in [2].

The importance of having the highest possible flux in timeresolved experiments should be stressed. In Figure 4, the scattering from a weak monochromatic beam is compared with that from a strong pink beam. The pink beam is 250 times more intense than the monochromatic beam. The exposure times are adjusted to give the same number of incident photons on the sample in the two experiments. The recorded signal is from the UV dissociation of HgI₂:

$$\mathrm{HgI}_2 + \mathrm{h}_{\nu}(267 \mathrm{~nm}) \rightarrow \mathrm{HgI} + \mathrm{I}.$$

The excitation was done with a 100 fs pulse at 267 nm and the delay is 100 ps. The curves are obtained by subtracting the radial curve "*laser off*" from the curve "*laser on*." The negative downturn at low q is caused by

dissociation: the forward scattering is proportional to N^2 , where N is the number of electrons in the molecule. The curve in (a) was exposed 1000 s and the curve in (b) 4 s. The high-q oscillations in (b) are absent in (a). In the monochromatic case, 250 times more sample was needed, which increases the risk of instabilities in the beams, sample, and detector.

The gain in flux from the pink beam comes at a price: the $S(2\theta) \rightarrow S$ (q) conversion is ill defined at high q due to the asymmetry of the spectrum. Which wavelength should be used? The peak of the spectrum or the center-of-mass? Is it possible to correct for absorption in the sample and detector when these functions are energy dependent? To be more specific, the simulated WAXS patterns from CO dissociation in Ru3(CO)₁₂ are shown [4]. Note that the blue U17 curve deviates significantly from the monochromatic ones in red and black above 2 Å⁻¹. Note that the U17 nodal-points shift away from the monochromatic ones above 6 Å⁻¹. The high-q range is very sensitive to structural changes inside molecules, so this shift is dangerous. Note that the 1.6% and 0.014% curves are nearly identical. The good news is that



Figure 6: (a) The ML monochromator in the vacuum vessel in front of the sample. (b) Cooling system and the main actuators mly, mlz, mlr, and mlpitch motors. Moving the vessel with mly, the Ru, Ir, or Si crystals can be moved into the beam. The two substrates rotate together via mlr; their relative angle can be varied by a stepper motor, mlpitch, via a weak flexible link.

high-flux beam from multilayers with symmetric 1-5% bandwidths can be used in WAXS experiments, with 25–75 fold gain in intensity, without significant loss in spatial resolution.

Multilayer monochromator

A first-generation ML monochromator was installed in the optics hutch in 2004. A double-crystal ML stage was attached to the cryogenic monochomator and cooled by liquid nitrogen. This ML stage never worked well due to low-temperature stress from the Cu absorbers and vibrations in the cooling pipes that excited the second crystal. With the installation of the heat load chopper in 2009, a modified ML stage, the in-focus ML monochromator, was installed 1.0 m from the sample. This stage is water cooled. The performance is much superior due to the 1000-times-lower heat load and the shorter distance to the sample.

The new ML monochromator is shown in Figure 6. The first substrate is cooled by spring-loaded Cu absorbers. Both substrates have two coating stripes that can moved into the beam by a horoizontal translation (mly). The first coating is ruthenium with the composition $[Ru/B_4C]_{51}$, which gives a 3.2% bw and iridium, $[Ir/Al_2O_3]_{100}$, with a 1.6% bw. The diffraction is dominated by the high-Z metals and the inter-layer distances are 39.20 Å for Ru and 25.66 Å for Ir. The usable Bragg angles are 0.45–0.90°, which gives 10–20 keV for Ru and 16–30 keV for Ir. The spectrum of Ir at 18 keV is



Figure 7: The new picosecond laser of ID9B. (a) The weak beam from the Micra oscillator enters the stretcher, where the pulse is changed 0.1 ps to 100 ps. The pulse is then passed through a 2 nm bandpass filter and sent to the Ti: Al_2O_3 crystal. In the crystal, the pulse is amplified 10⁶ times, from 4 nJ to 4 mJ, by the evolution pump laser. The pulse is finally compressed to 1.2 ps. (b) Picosecond laser and TOPAS wavelength shifter (300–2000 nm).

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Figure 8: (a) $C_2H_4I_2$ and two excited-structure candidates, the bridge and the anti-radicals of $C_2H_4I_2$ (b) Measured change in the scattering, laser on minus laser off, is shown on the left in pink. Note how well the bridged candidate fits the experimental data. Fourier transformed data are shown on the right. Note the strong negative peak at 5.0 Å from the destruction of the I-I correlation and the negative peak at 2.2 Å from the change in C-I correlation.

shown in Figure 3. Note the high reflectivity and good matching to the U17 spectrum. The ML and Si fluxes in one pulse are shown in Table 1.

Picosecond laser

The instrumental time resolution in a pump-probe experiment is the convolution of the laser and X-ray pulse lengths and their relative jitter. The jitter of a mode-locked femtosecond laser is very small, < 3 ps (rms), so this term can be neglected. Wavelength tuneable femtosecond lasers have become off-the-shelf items and the first laser systems on ID9 were therefore femtosecond systems. In photochemical reactions, however, the photo-absorbing molecules are highly dilute with typical solute/solvent ratios of 1:1000. For a small $(0.1)^3$ mm sample, $\sim 1 \times 10^{14}$ laser photons are needed to fully excite the sample. If 10¹⁴ photons are squeezed into a 100 fs pulse, multi-photon ionisation might occur from the high intensity, which might lead to unwanted radicals and solvent heating. With a 100 ps X-ray pulse, the laser pulse can be stretched to 50 ps without significant loss of time resolution. The drawback is that the wavelength tuning in a picosecond laser is less efficient, but this problem can be solved by focusing the pulses more tightly. A picosecond laser was installed on ID9 in June 2010. It has a femtosecond mode-locked cavity. The chirpedpulse-amplifier has a mask in the stretcher that, by reducing the bandwidth, makes a 1.2 ps pulse (fwhm) (see Figure 7). The peak intensity in a pulse from the new laser is about 12 times lower than in the old 0.1 ps laser system. The photoproducts from a longer pulse are cleaner, freed from multi-photon processes. The fraction of 2-photon excited molecules scales with the intensity squared, so the 2-photon concentration is $(1/12)^2$ = 0.7% of the 0.1 ps level. The efficiency of the laser excitation is very important for weak signals on a big background. In this weak-signal limit,

the signal-to-noise ratio is proportional to the number of excited solutes. The efficiency of the laser excitation is often more important than the X-ray intensity.

The Micra femtosecond cavity is mode-locked to the ESRF radio frequency (RF) at RF/4 = 88.05 MHz and this reference signal can shift electronically in steps down to 10 ps. The laser/X-ray delay is varied by shifting the laser timing, which has a short-term stability of < 3 ps (rms) but shifts systematically during a fill of the storage ring by up to 10ps.

Iodine dissociation in C₂H₄I₂

To illustrate the power of time-resolved WAXS, we will briefly mention the halogen elimination reaction [5]:

$$C_2H_4I_2 + hv(267~nm) \rightarrow C_2H_4I + I.$$

The C₂H₄I₂ molecules are dissolved in methanol. The reaction is shown in Figure 8. The C-I bond is broken and the radical C₂H₄I. plus an I atom are trapped by the solvent cage. Quantum chemistry predicts two radical structures at low energies: the bridged and the anti-conformers. Before the X-ray experiment, it was impossible to distinguish the two conformers optically. The concentration of C₂H₄I₂ was 60 mM, which corresponds to a solute-solvent ratio of 1:412. The solution was circulated in an open jet at 0.2m/s, which is sufficiently fast to renew the sample in the 1 kHz pump-probe beam. An 18 keV pink beam was made with the U17 at 9 mm gap. The laser wavelength was 267 nm and the pulses stretched to 2 ps in fused silica rods. The WAXS data were recorded on a MARCCD detector and 20 time delays from 0.1 ns to 10 µs were collected. As the X-rays amplify the high-Z elements due to the atomic formfactor, which is proportional to Z² at q = 0 Å⁻¹, the scattering is particularly sensitive to changes in the I-I distance, which is 5.0 Å in the



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parent molecule. Trial structures were calculated by Gaussian for the ground state and two lower energy states of C₂H₄I. The simulations vs experiments are shown in (b). It is clear that the bridged structure agrees with the experimental data. Also in (b), the Fourier transform is informative for this small molecule. Note the two negative peaks in the experimental curve at 2.2 Å and at 5.0 Å. They are from the reduction in C-I and I-I correlations, respectively. The bridged conformer has a single negative peak at 2.2 Å, whereas the anti-structure has two negative peaks from the two C-I distances involved. Subsequently, C₂H₄I does not decay into C₂H₄ + I; rather it reacts in 500 ps with the trapped iodine atom in the cage to form a linear isomer C₂H₄I-I. Note that the simulations and experiments were compared for q > 2.0 Å⁻¹ to avoid the (longer range) thermal signal from the solvent. It is a nice feature in WAXS that the low-q spectrum probes the hydrodynamics of the solvent; i.e., the change in temperature, pressure, and density linked to the cooling of the solutes [6].

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