ROCK: the new Quick-EXAFS beamline at SOLEIL

V Briois¹, C La Fontaine, S Belin, L Barthe, Th Moreno, V Pinty, A Carcy, R Girardot, E Fonda

Synchrotron SOLEIL, L’Orme des Merisiers, BP 48, Saint-Aubin, 91 192 Gif-sur-Yvette, France

E-mail: briois@synchrotron-soleil.fr

Abstract. ROCK is a new beamline at SOLEIL dedicated to Quick-EXAFS measurements. The optical layout has been optimized to get full advantage of the monochromators, which were designed at SOLEIL and successfully used at SAMBA from 2009 to 2014. ROCK has started user operations since March 2015. It is mainly employed to monitor fast kinetic processes in materials used in catalysis and energy sciences. A review of the ROCK performances and capabilities is presented. The high automation achieved for fast change of monochromators, optimization of mirrors for harmonic rejection and detectors allows the simultaneous operando characterization of different chemical elements present in a material during the same reaction.

1. Introduction
X-ray Absorption Spectroscopy is a well-known technique for in situ characterization of materials such as catalysts and batteries. With the advent of 3rd generation synchrotron radiation facilities allowing a sub-second time resolution in the monitoring of kinetics, the experimentalist can now access to a deeper and more accurate temporal description of the chemical species involved during operative use of these materials. The simultaneous determination of their local order evolution and catalytic or electrochemical properties can be achieved at X-ray Absorption beamlines dedicated to the study of catalysis and materials used for energy storage. The SOLEIL’s ROCK (Rocking Optics for Chemical Kinetics) beamline, recently funded by the French Agence Nationale de la Recherche in the framework of the national “Investissements d’Avenir” program (ANR-10-EQX-45-01), is one of these dedicated infrastructures for the operando characterization of materials by time-resolved Quick-EXAFS.

2. Beamline Design
The SOLEIL’s Quick-EXAFS monochromators installed at ROCK are up-graded versions of the monochromator developed by the Frahm’s group [1], which consists of a channel cut crystal mounted on a cam driven tilt table that oscillates around a selected central Bragg angle, θ, with a user selectable angular amplitude, Δθ. After a joint work between SOLEIL and Frahm’s group for integrating an angular encoder attached to the crystal holder in order to have a direct reading of the crystal position [2], each group worked independently to develop a new flexible monochromator. The SOLEIL’s Quick-EXAFS monochromators, fully described in [3], can oscillate over an angular

¹ To whom any correspondence should be addressed.
amplitude $\Delta \theta$ up to 4°. The Si(111) or Si(220) crystals equipping those monochromators can be remotely selected by the user, allowing to work at energies between 4 and 43 keV. These monochromators were transferred from SAMBA to ROCK in 2014 and are now surrounded by optics designed to obtain the highest flux possible delivered by a SOLEIL’s bending magnet source. The optical setup is designed to follow in operando conditions the reactions of several distinct elements. This “element- or edge-jumping” capability is based on the alternate use of the two Quick-EXAFS monochromators and was already demonstrated at SAMBA to be a powerful skill for unravelling synergetic behaviours between elements during chemical processes [3, 4]. The optical layout of ROCK is shown schematically in Figure 1.

**Figure 1.** Optical layout of the ROCK beamline.

In order to maximize the beamline acceptance defined as 1.5 mrad (H) x 0.22 mrad (V), the first mirror (M1) is installed inside the shield wall of the storage ring at 10.15 m from the bending magnet source ($B = 1.72$ T, $\sigma_x = 60$ µm and $\sigma_z = 24.5$ µm). The beamline is separated from the machine vacuum by a water-cooled 300 µm thick beryllium window. Water-cooled primary horizontal and vertical slits define the X-ray beam before it impinges on the first optic. M1 is a 1.1 meter-long toroidal and cylindrically bendable silicon mirror coated with an Ir layer (50 nm) over a Cr binder layer. The power absorbed by M1 is lower than 100 W allowing the use of In/Ga eutectic cooling channels as heat transmitter to the water-cooling system. M1 deflects upward a horizontally focused beam according to its toroidal shape (fixed sagittal radius = 31.7 mm) with vertical collimation according to its cylindrical shape. Although, the standard working grazing incidence of M1 is 2.25 mrad with a cut-off energy at 37 keV, this angle can be slightly decreased in order to use the beamline up to 43 keV. The curvature of the mirror is adjustable in order to adapt the beam collimation to the machine current (the nominal tangential radius used at 2.25 mrad is 9.02 km).

In the optical hutch, M2a and M2b mirrors surround the Quick-EXAFS channel-cut (CC) monochromators. These mirrors are coated with 3 stripes (Pt, Pd and $B_4C$ stripes) used to eliminate the high order harmonics with a rejection coefficient ranging from $10^4$ to $10^8$ depending on the cut-off energy. Additionally, M2a reduces the heat load on the monochromators, keeping the water-cooling solution of these channel-cuts still efficient. The length of both mirrors is 1.1 m. For each mirror, a double axis goniometer ensures the pitch (from 1.75 to 5.2 mrad) and roll adjustments of the mirrors with respect to the incident beam whereas robust motorized translations are used for vertical alignment of the mirror’s center and horizontal stripe exchange. M2a is a flat water-cooled mirror which preserves the beam collimation at the entrance of the monochromator whereas M2b is an adjustable cylindrically bent mirror used to vertically focus the beam at the sample position. M2a and M2b deflect the beam upward and downward, respectively.
Si(111) and Si(220) channel-cuts are installed at a distance of 18.92 and 19.25 m from the source, respectively. As the position of the beam varies vertically depending on the grazing angle used for M2a, two independent 60 mm vertical translations are used to properly align each crystal on the beam. Vertical slits are installed after each optic for cutting diffuse beam while horizontal slits are used after the Quick-EXAFS monochromators in order to cut possible Laue reflections by the channel-cut which may partially overlap the Bragg reflection of interest at the sample position. A SOLEIL’s designed pink screen is installed after M2a in order to visualize the beam deflected by either M1 or M2a while a SOLEIL’s designed monochromatic screen is installed after M2b in order to image the beam coming from the monochromators, which is either by-passed by M2b or deflected by this mirror. X-ray shutters are placed before the shield walls of the storage ring and optical hutch in order to allow the access to the optical and experimental hutch, respectively, while keeping a constant heat load on the optics.

3. Beamline Performances

The calculated and measured fluxes arriving at the sample are shown in Figure 2. The absolute flux was measured using a calibrated silicon photodiode with 450 mA of stored current in the machine whereas the calculations considered perfect optics with the nominal 500 mA current, already achieved at SOLEIL but not yet used for operations. For these reasons, the measured flux is slightly lower than the calculated one. A flux between $10^{11}$ and $10^{12}$ ph/s is achieved over a large energy range, offering the necessary condition to achieve 25 ms of time resolution with convenient signal-to-noise ratio.

![Figure 2: Flux of the monochromatic beam measured at the sample position for a full spot size, plotted as a function of X-ray energies for a beam current of 450 mA. The flux calculated for perfect optics and a beam current of 500 mA is reported for comparison purpose.](attachment:fig2.png)

The beam size achieved in the horizontal direction is invariant with the monochromator in use and depends only on the position of the sample with respect to the M1 focus point, which is located at 32.68 m from the source. At this focus position, the horizontal size of the beam is ca. 380 µm (FWHM). At upstream positions from this focus point, the beam is defocused. Moving the sample from 32.68 to 27 m in the experimental hutch allows for increasing by a factor 10 the horizontal beam size, as shown in Figure 3. The size in the vertical plane is determined by the curvature of the cylindrically bent M2b mirror and can be tuned from defocused to optimized focusing conditions at any sample position in the experimental hutch. A maximum vertical size of ca. 1 mm can be achieved versus ca. 130 µm (FWHM) in optimized vertical focusing condition. The versatility in beam size at the sample position, which can be modified by just moving the sample between 27 and 32.68 m, allows varying the density of photons on the sample while keeping nearly constant the flux and thus the time resolution performance of the beamline. The flexible beam size is important for the study of samples suffering from radiation damage as illustrated in Figure 4 with the decomposition kinetics of a AuCl pellet transformed into Au(0) crystallites under radiation. The lower the photon density, the longer the stability of AuCl.
Mechanically, the channel-cut crystals can oscillate with a frequency up to 30 Hz for small oscillation amplitudes (typically 0.3-0.5°), and is reduced to 20 Hz for larger oscillation amplitudes. Those mechanical characteristics fit well with the acceptable damping of the measured signal observed with increasing oscillation frequencies. As shown in Figure 5, the EXAFS signals recorded for a copper foil over an oscillation amplitude of 2° of the Si(111) channel-cut present only small damping effects for the data recorded at 20 Hz compared to the EXAFS signal recorded step-by-step at the SAMBA beamline. Nevertheless, the inspection of the XANES spectra recorded in the same conditions of wide oscillation amplitude clearly indicates that the intrinsic rise time of detectors and amplifiers is no more adapted, it induces a strong damping in this energy range where fine structures are observed. By reducing the oscillation amplitude to 0.3°, the Quick-XANES spectra recorded at the maximum oscillation frequency (30 Hz) are now well comparable to the step-by-step XANES spectrum. The use of gridded ionization chambers could overcome the observed damping at high oscillation frequency, as recently demonstrated for oscillations at 50 Hz achieved with the newly built direct drive torque motor Quick-EXAFS monochromator developed by the Frahm’s group [5].

**Figure 3.** Versatile beam size as a function of the position in the experimental hutch.

**Figure 4.** Change of decomposition kinetics of a pellet of AuCl with the photon density. The spectra were recorded at the M1 focus point. The speciation curves in the insert compare the decomposition rate at the focus point (open symbols) and at 27 m from the source (closed symbols).

**Figure 5.** Time resolution performances measured on a Cu foil for two oscillation amplitudes. Quick-EXAFS spectra are compared to a step-by-step spectrum (black curve).

4. End Station Facilities
The detectors used for transmission experiments are S-1194 and S-1196 ionization chambers provided by Ohyo Koken Kogyo Co. Ltd. They are installed on the 2.5 m long × 1 m wide motorized
experimental table, which can move along the beam axis from 27 to 34 m from the source. According to the working position of the table, pipes of variable lengths are installed to keep the beam under a primary vacuum in the experimental hutch up to the slits placed in front of the I₀ ionization chamber. Figure 6 displays the experimental table set at the M1 focus position. A wide range of sample environments can be mounted on the motorized sample stage with 60 mm stroke in both x and z directions. ROCK provides to users dedicated cells for heterogeneous catalysis experiments [4] (together with gas delivery system and a mass spectrometer for activity measurement) and for electrochemical cycling of batteries [6]. Sample environment data such as oven temperature or electrochemical conditions can be associated with the Quick-EXAFS data, making easier data analysis and link between local order and applied constraints. Exhaust gas lines are available allowing the safe handling of toxic gases such as H₂S, CO or NO. The beamline also offers the possibility to combine Quick-EXAFS measurements with complementary techniques such as UV-vis. and/or Raman spectroscopies and X-ray Diffraction [4]. Due to the highly demanded “edge jumping” feature offered by ROCK for the *operando* study of bimetallic systems, special supports hosting two identical ionization chambers have been designed at the beamline: each set of ionization chambers is dedicated to one edge, with mixture of gases optimized for the corresponding energy, and is alternatively moved into the beam path (Figure 7).

![Figure 6. Motorized experimental table located at the M1 focus position. Acquisition electronics are loaded in dedicated spaces in and on the experimental table.](image1)

![Figure 7. View of stacked I₁ ionization chambers for “edge jumping” capability.](image2)

### 5. Control System, Data Acquisition and Survey, Automation

The beamline is controlled through the Tango software bus. Electronics and software used to operate data acquisition with the Quick-EXAFS monochromators were developed by the SOLEIL’s Control Command group. When acquisition is started, 5 s double data buffers continuously collect the channels of a 16-bit analog-to-digital converter (ADC), accounting for the ionization chamber currents amplified by fast Keithley 428 current-to-voltage amplifiers. A scaler card collects synchronously the position of the angular encoder at a user-selectable frequency, usually in the range of 250 kHz, this card provide the trigger line to the ADC card. A dedicated software merges the ADC signals and the encoder values in a single binary nexus file. A visualization interface enables the user to look at the evolution of the raw spectra during the course of a kinetic experiment, in a meaningful absorption versus energy plot (Figure 8). The data continuously acquired can be entirely or partly displayed in real-time by this visualisation interface, named QuickExafsViewer. The former operation mode is particularly useful for the staff during the set-up of the beamline and to check the energy calibration while the latter operation mode is well-suited to follow the evolution of kinetics by picking up selected snapshots representative of the reaction. Reference spectra previously recorded and archived can be also loaded in this visualization interface for comparison purposes with the data in acquisition. Automation of data acquisition sequences for “edge jumping” experiments is obtained by using the interactive Python scripting environment (IPython 0.13), which is easily interfaced with the Tango
software bus. The Python shell can then be easily handled by the user to start and stop acquisitions sequences with repeated changes of beamline configuration, including swap of monochromators, change of M2a and M2b stripes, and exchange of ionization chambers, together with suitable reconfiguration of recording parameters. Typical sequences used for edge jumping are 20 to 30 s of data recording with one monochromator and a period of ca. 30 s required to set-up the beamline in the new configuration before recording data for 20 to 30 s with the second monochromator.

6. Conclusion
Fully optimized focusing optics in both horizontal and vertical directions built around the QuickEXAFS monochromators deliver at the sample position a flux ranging between $10^{11}$ and $10^{12}$ ph/s in a large energy range covered by the beamline. At these conditions, 25 ms is a typical achievable time resolution. With such time resolution, users obtain a huge amount of data in a couple of minutes making the common strategy of data evaluation, reduction, and analysis quite inefficient. New tools for data analysis must be proposed to the users to interactively optimize the outcome of an experiment carried out at the beamline. Chemometric tools, such as Multivariate Curve Regression with Alternating Least Square (MCR-ALS) fitting, are emerging as powerful methods for getting more information from XAS spectra of evolving mixtures upon reaction [7]. Therefore, a user-friendly interface is under active development at the beamline to handle this high number of data into normalized matrices of absorption spectra directly suitable as input files for MCR-ALS analysis.

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