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The Quick EXAFS Setup at Beamline P64 at PETRA III for up to 200 Spectra per Second

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Abstract. The layout and the characteristics of the Quick scanning EXAFS (QEXAFS, ref. [1]) setup at beamline P64 at the storage ring PETRA III, DESY, Germany are described. The quickly oscillating cryo-cooled monochromator allows measurements from 4.5 keV to 44 keV with frequencies up to 100 Hz. The effect of tapering of the undulator on spectra as well as the different detection schemes with transmission, reflectivity and fluorescence are discussed. The data acquisition is explained in detail. Reference spectra at different frequencies and examples of time resolved user experiments are shown. The influence of noise and filtering on the spectra is analysed.

BEAMLINE LAYOUT

Beamline P64 at the high brilliance storage ring PETRA III at DESY, Germany, is dedicated to advanced EXAFS techniques. The layout of the beamline is given in Fig. 1. The ring has a circumference of 2.3 km and is operated at 6 GeV with a current of 100 mA in top-up mode. A 60 pole undulator with a magnetic period of 32.9 mm acts as insertion device with horizontal linear polarization. One of the beamline's special features is a dedicated cryo-cooled monochromator with Si(111) and Si(311) channel-cut crystals on an oscillating stage. With a Bragg angle Θ from 4.4° to 30°, an energy range from 4.5 to 44 keV is accessible. Mirrors for horizontal and vertical focusing are available downstream the monochromator, allowing a focal beam size down to 50 µm (v) x 150 µm (h). The first mirror offers five coatings with different geometries for horizontal focusing: Rh, Si, Pt (all flat), Rh and Si (both cylindrical). The second mirror is bendable and allows for vertical focusing with Rh, Pt or Si coatings. In the experimental hutch a photon flux of up to $5x10^{12}$ photons/s/mm^2 is available with the untapered first harmonic of the undulator at a beam size of 1x1 mm^2.

Additionally, a von Hamos type spectrometer and a 100 elements Ge-detector is available for slower detection methods. In addition to the quick EXAFS monochromator, a conventional double crystal monochromator is available. Various carbon filters in the front end can be used to absorb the low energy content if desired.

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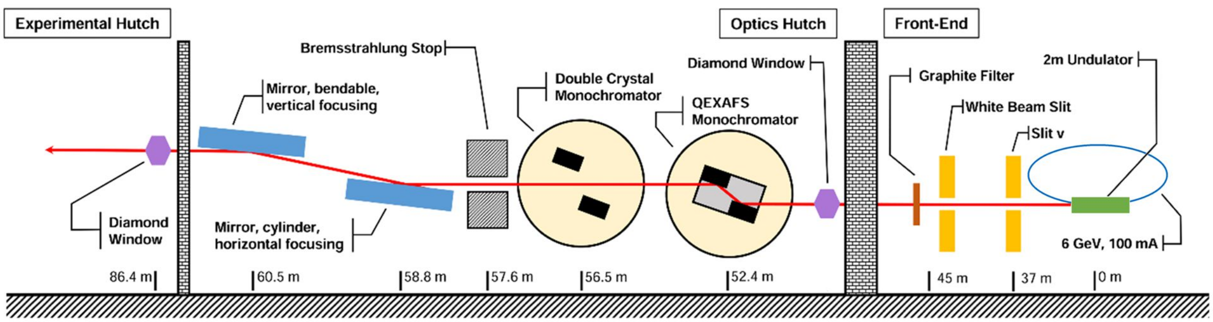

FIGURE ***1:*** Schematic of the beamline layout with important components from the ring to the experimental hutch. The undulator beam passes a primary slit system and optional graphite filters. The quick EXAFS monochromator or a conventional monochromator can be selected. Optional focusing is available with mirrors. The position relative to the undulator is noted below each component.

MONOCHROMATOR LAYOUT

The monochromator is housed in a vacuum tank (800 mm inner diameter) with a Huber goniometer on the main flange. Inside the goniometer the quick oscillating torque motor is installed and connected to the crystal stage via a fixed axis. The oscillation frequency can be varied from 0.01 Hz up to 100 Hz with an amplitude of up to 4° limited by the torque provided by the motor at high frequencies. Single spectra can be recorded within 5 ms, because two spectra are recorded during one sinusoidal oscillation. The two channel-cut crystals are mounted between three copper cooling blocks which are connected to the cryo-cooler. The crystals are thermally isolated against their mounting frame, which is kept at a constant temperature of about 20°C by regulated heaters.

The magnetic windings of the torque motor are driven by two 2-quadrant power supplies with a voltage of up to 720 V and currents up to 25 A in a star connection scheme. The power supplies generate two 180° phase shifted sine waves with a constant positive offset. The offset creates a near parabolic magnetic background potential, in which the the motor's rotor and thus the crystals can oscillate, driven by the sine wave part. The current sinking capability of the power supplies is especially important to sink induced currents and thereby to reduce the heat generated in the motor, and to prevent electrical resonances. More detailed information on this drive scheme can be found in refs. [2, 3].

UNDULATOR TAPERING

If the undulator is kept at a constant gap the spectral width of a given harmonic is about 100 eV or less only. It is 2 m long with a magnetic period of 32.9 mm. If the undulator is tapered, i.e. the gap is varied by up to 1 mm over its total length, the harmonics are broadened. Tapering the undulator has the highest impact on its harmonics at small gaps. An energy range of about 1000 eV can be obtained with the third and higher harmonics. The first harmonic with its large undulator gap does only allow smaller energy ranges. Therefore, the undulator was designed to reach energies down to the Fe K-edge (7112 eV) on the third harmonic. The highest flux is available at the untapered first harmonic with up to 5×10^{12} photons/s/mm^2. Notably, the second and other even harmonics have a wider spectrum than the odd harmonics but at a lower intensity. However, they are useful when multiple edges are to be measured simultaneously.

DETECTION METHODS

For the detection of incident and transmitted intensities, special fast gridded ionization chambers and fast low noise amplifiers have been developed [4]. Recently a 2-circle goniometer with a linear stage on the Θ axis was installed in the experimental hutch. It allows measurements in reflection mode for surface sensitive experiments, as well as for time-resolved EXAFS measurements combined with X-ray diffraction. The attenuated total reflection at angles around the critical angle is used to vary the penetration depth of the X-rays into the sample between several monolayers and some 10 nm. The reflected intensity is measured with ion chambers mounted on the 2Θ axis. Additionally, a PIPS diode with a fast matched amplifier for fluorescence detection was successfully commissioned, which can be used at all available oscillation frequencies in transmission and reflection mode experiments.

DATA ACQUISITION

The data acquisition is accomplished by a NI PXIe-6366 multifunction I/O module. It comprises an 16 bit analog-digital converter (ADC) module with 8 channels and a sampling rate of up to 2 MS/s/channel as well as a 16 bit digital-analog converter (DAC) module with 2 channels. 4 of the 24 digital I/O ports can be used as 32 bit counters. The amplified signals of the ionization chambers are sampled by the ADCs simultaneously. The angular position of the selected channel-cut crystal is measured with an angular encoder with a theoretical angular resolution of $5x10^{-5}$ degree or $8.7x10^{-4}$ mrad. Each of those angular steps is detected by one of the counters. At each ADC sample the corresponding counter value is recorded to ensure that the measured X-ray intensities are synchronous to the corresponding angular positions. All detector voltages and the counter value are then written to the DAQ PC in continuous file streams. For data analysis the acquired file can be processed with the dedicated analysis software tool JAQ. First, the single file is split into separate spectra at each extremum of the sine like angular signal. In a second step, each of these spectra is calibrated to the edge position of a simultaneously acquired signal of a reference foil. Additionally, JAQ allows filtering in both energy and time domain.

NOISE AND DIGITAL FILTERING

With an oscillation frequency of 1 Hz a complete spectrum is recorded in 0.5 s, which is in the order of the acquisition time for just a single data point in a conventional EXAFS scan. It is therefore obvious, that the system is susceptible to noise of any kind. Absorption spectra of a Cu foil recorded at 1 Hz and 10 Hz are shown in Fig. 2. Apparently, the noise is somewhat higher at 10 Hz. However, it is possible to filter the data in the energy domain and if the reaction speed of the experiment allows it, in the time domain as well. The ADC converts the X-ray intensity in each ionization chamber at a fixed sample rate of 2 MHz. Thus the spectra are highly oversampled as it would correspond to an energy spacing in the order of 1 meV between two adjacent data points based on the energy scan rate. This allows for applying averaging filters over some 10 to 100 points. Our data analysis software therefore offers Savitzky-Golay filters. However, reducing the apparent noise in the setup is of utmost importance and crucial to further improve the time resolution or data quality especially for dilute samples.

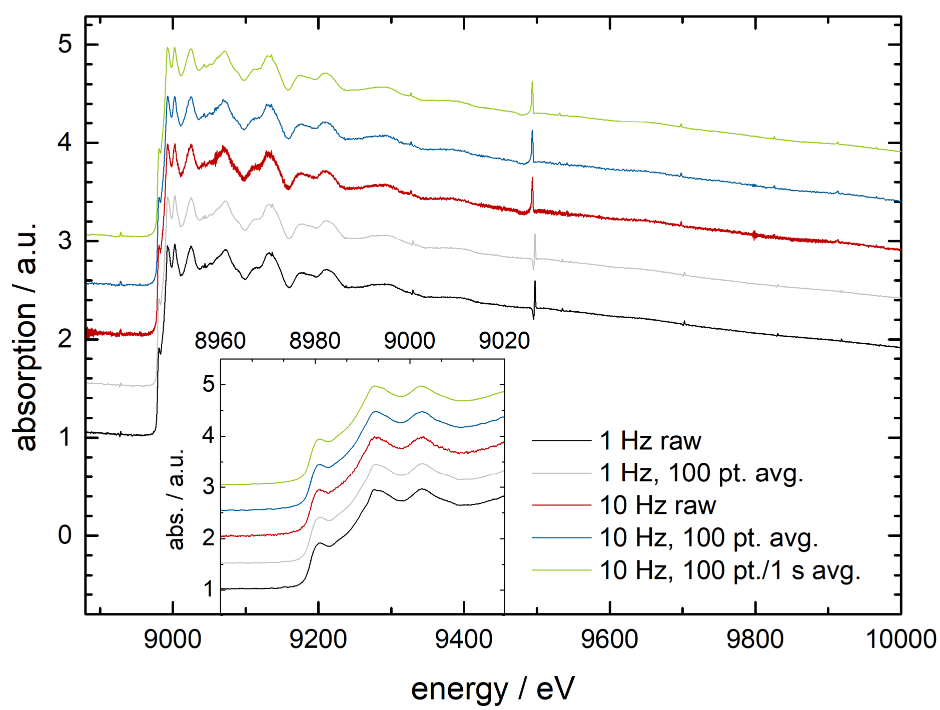

FIGURE 2: Absorption spectra of a Cu foil acquired at 1 Hz and 10 Hz without filtering, with subsequent digital filtering over 100 data points in the energy domain, and averaging over 1 s . The inset shows the absorption edge in detail.

USER EXPERIMENTS

Since its comissioning in 2016, the QEXAFS system was mainly used in transmission mode experiments to observe catalytic reactions in-situ / in-operando like in ref. [5]. The reflectometer was used in studies to investigate the chemical reduction of stainless steel surfaces. In a vacuum cell, samples were heated up to 1100°C and then a gas composition of N_2 with a few ppm of monosilane SiH_4 was introduced. The undulator was tapered to 1 mm on the second harmonic allowing an energy range of about 1600 eV to measure Cr, Mn and Fe in a single energy sweep. Such a wide spectrum is at the limit of what is possible as the maximum oscillation amplitude of 4° is necessary here and the undulator can not provide a broader spectrum at those energies with the given maximum taper. The reflectivity at 1100°C is shown in Fig. 3 starting 60 s after the reducing gas atmosphere was introduced. It can be seen that the reflectivity continuously decreases and that the edge ratios of the three elements vary with time. Both can be attributed to structural and chemical changes in the surface of the heat-treated steel. Further investigations and data analysis are ongoing.

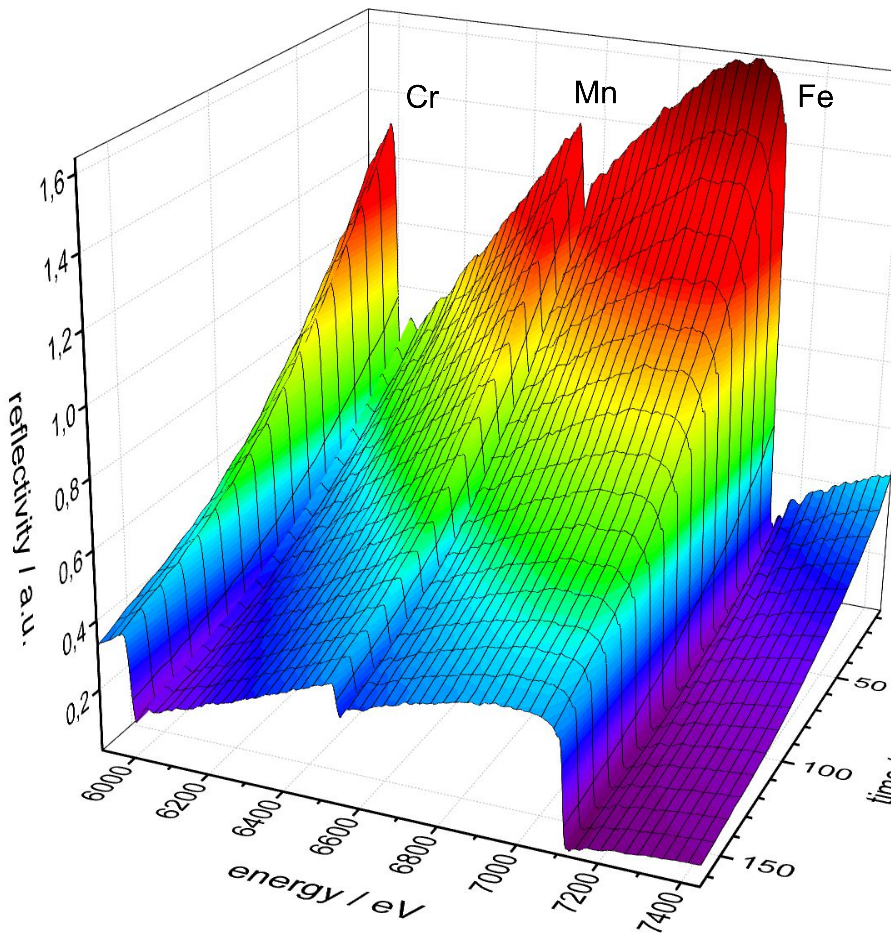

FIGURE 3: Reflectivity spectra recorded at 1 Hz including the Cr, Mn and Fe K-edges of a polished 1.4305 stainless steel sample at 1100°C starting 60 s after the reducing gas atmosphere was introduced in the chamber.

CONCLUSIONS

The quick EXAFS system at beamline P64 allows to collect absorption spectra with acquisition rates of up to 200 spectra per second. X-ray energies between 4.5 kev to 44 keV are available with a photon flux of up to $5x10^{12}$ photons/s/mm^2. To measure full EXAFS spectra covering several 100 eV in QEXAFS mode, tapering the undulator is crucial. For detection gridded ionization chambers and fast amplifiers have been developed. Since the QEXAFS system is susceptible to noise digital filtering in both, the energy- and time-domain is useful to improve the data quality. The beamline is in user operation since spring 2017 and offers detection in transmission, reflection and fluorescence mode. Several user beamtimes investigating different scientific questions have been successfully conducted. Optimization is still ongoing and the QEXAFS setup is open for beamtime applications.

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