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A beamline for bulk sample X-ray absorption spectroscopy at the high brilliance storage ring PETRA III

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Abstract. P65 is a new X-ray Absorption Fine Structure (XAFS) spectroscopy beamline at the high brilliance storage ring PETRA III in Hamburg, Germany. It is providing a mm sized beam and a monochromatic photon flux of up to 10^{12} s^{-1} at 9 keV. The beamline design is optimised for standard EXAFS measurements under ex- and in-situ conditions. The performance of the beamline is demonstrated using examples from commissioning and the first year of operation.

INTRODUCTION

XAFS spectroscopy is a widespread used analytical method in applied sciences, and XAFS beamlines are installed at storage rings all over the world. Typical applications include in-situ/operando investigations of structure/function relations in catalytic chemistry, energy storage (batteries, H_2-storage etc) and production (solar cells, H_2-production, liquid fuel production), material science, biology (structure around metal centres in proteins) and environmental and geosciences. Most of these applications do not need the high brilliance of todays 3^{rd} generation storage ring sources. Much more important are a stable often mm^2-sized beam, a broad and continuous spectrum for long X-ray photon energy scans, and a moderately high monochromatic photon flux density to avoid radiation damage. A mm sized beam is actually advantagous for many in-situ/operando applications where a gas or fluid stream is lead over catalyst particles. In-situ cells for these experiments require a certain minimum diameter to allow experiments under realistic pressure and flow rate conditions. In many other cases the samples are simply large enough for a mm-sized beam, and there is consequently no need to bear all the experimental complications and the problem of representativity which go hand in hand with small focused beams. Experiments of this type were for many years successfully performed at the bending magnet beamlines at DESY's DORIS III storage ring. P65 was build as part of the PETRA III extension project [1] and is dedicated to fill the gap that was left after the shutdown of the DORIS III storage ring in October 2012. As design goals for P65 were defined:

1. Beamsize: 1 mm * 0.5 mm (h * v)
2. Energy range: Sufficiently large to measure all elements heavier than potassium using either K- or L-edges.
3. Monochromatic photon flux: $>10^{10}$ s^{-1}
4. Use of a water cooled DCM
5. Effective higher harmonics suppression
6. Infrastructure for in-situ experiments

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PETRA III has a circumference of 2.3 km. This large circumference of the PETRA III storage ring and the high e^- energy of 6 GeV exclude the use of radiation from bending magnets and wigglers [6]. Both would provide the required continuous spectrum and a large beamsize, but since the minimum distance between the source and the first optical components is about 40 m, the divergence of these sources is loo large to collect a sufficiently large number of photons for the XAFS experiment. The only remaining option was a short undulator which is requiring synchronised gap scans to tune the energy parallel to the Double Crystal Monochromator (DCM) .

Beamline layout

Figure 1 gives a schematic overview about the beamline layout. The distance between sample and source is 61 m. P65 is using the radiation from a short 11 period undulator with a period length of 32.8 mm and a K_{max} of 2.70 [2]. This undulator has a long overlap of the 1^{st} and 3^{rd} harmonic, so that the entire energy range between 4 keV and 44 keV can be used for long EXAFS scans. The optic design is based on a robust and simple water cooled double crystal monochromator (Si 111 and Si 311). Two plane mirrors in front of the DCM act as low pass filters and decrease the power load on the first DCM crystal. Key parameters are a a working range of 4 keV - 44 keV, a monochromatic photon flux of up to $10^{12}\,s^{-1}$, and an energy resolution ($\Delta E/E$) of $1.4 * 10^{-4}$ (Si 111) and $0.6 * 10^{-4}$ (Si 311). The undulator gap is scanned synchronised with the scan of the DCM. The feedback is realised by a Python script running on the beamline control computer, and the deviations between undulator peak energy and DCM position are <2 eV over the entire scan range of a typical EXAFS scan.

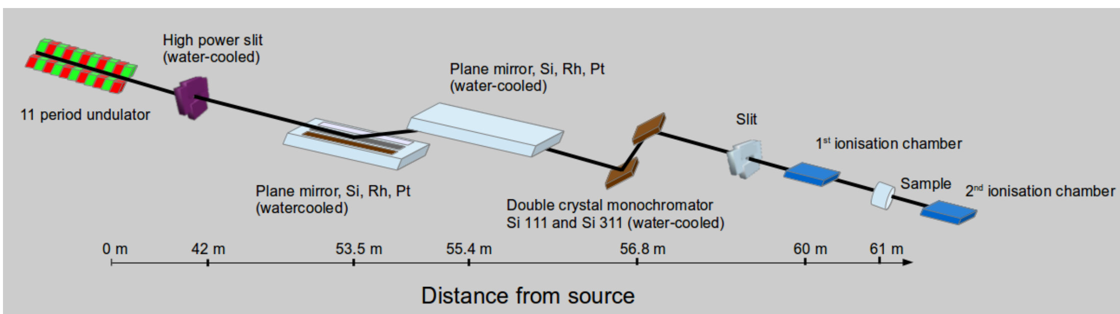

FIGURE 1: Schematic drawing of the beamline

Beamline optics

Main components of the beamline optic are two plane mirrors and a water cooled double crystal monochromator which was originally designed for bending magnet beamlines [3]. Each mirror has three different optical surfaces (Si, Rh and Pt), and the angle of incidence is variable between 1.8 mrad and 4 mrad. Using the different stripes and angles of incidence an effective higher harmonics suppression and high reflectivity is achieved over the entire working range of the beamline. The mirrors are mounted in front of the DCM, and together with a set of water cooled glassy carbon filters with a thickness of 1 mm - 6 mm they form a band path filter to reduce the heat load on the 1^{st} DCM crystal. This set-up combined with the short undulator enables the use of a water cooled DCM at an undulator beamline instead of the usually used cryogenically cooled devices. The distance between DCM and sample position is only approx. 5 m, thus minimising the effect of small instabilities in the DCM on the position of the beam on the sample. The rocking curve in figure 2 demonstrates the performance of the DCM and the absence of heat load effects. The DCM's θ-axis is equipped with an angle encoder system that provides excellent reproducibilty of the energy axis. Figure 3 is depicting the edge region of 15 consecutive EXAFS scans over the Cu K-edge: The deviation of the position of the peak in the edge K-edge of Cu^0 is <0.1 eV.

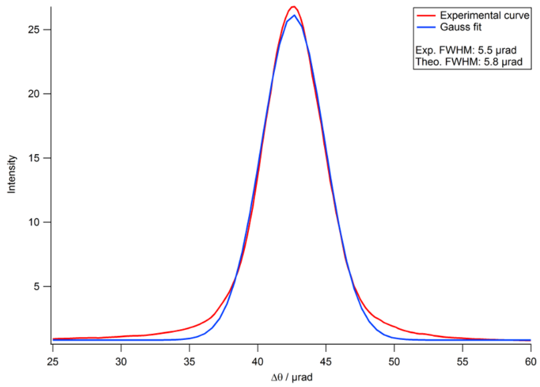

FIGURE 2: Measured Si 311 DCM rocking curve (red) and Gauss fit (blue), E_{DCM}=26508.5 eV, E_{Und}=26275 eV, the theoretical width was calculated using the xrt code [4]

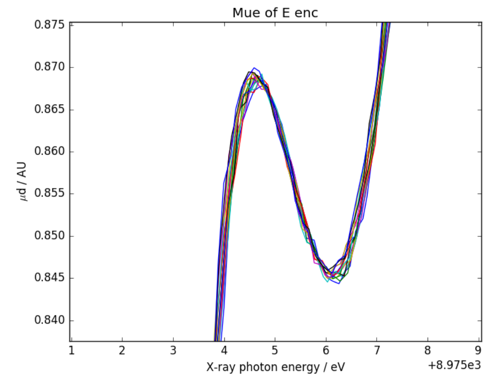

FIGURE 3: Reproducibility of edge position shown is the edge region of 15 continouly measured EXAFS spectra of a Cu foil, encoder based energy scale

Experimental station

Central part of the experimental station is an optical table with a size of 1.2 m * 2.5 m. Three ionisation chambers are used as detetors for sample and reference sample in transmisison experiments. Optionally a 7 pixel high purity germanium (HPGe) detector, a silicon drift detector (SDD) or a large Si Diode are available for fluorescence yield XAFS. Standard sample environments include a sample changer for measurements at room temperature and a He-cryostat for measurements at temperatures between 4 K and 300 K. Optional is the use of an oven for experiments above room temperature. The sample chamber between 1^{st} and 2^{nd} ionisation chamber can easily be removed, giving plenty of space for user provided sample environments like special ovens and in-situ cells for experiments with gases or liquids. The experimental hutch is equipped with extensive infrastructure for the work with all kinds of toxic, flammable and oxidising gases for in-situ/operando experiments.

Results

The beamline is operated in two modi, first a "classical" step wise scan mode in which the registration of a single spectrum in transmission mode takes about 10 min. The second and preferred modus operandi is the synchronised continuous scan of DCM and undulator which is routinely used for transmission and total fluorescence yield detected XAFS spectra using only ionisation chambers and optional a large Si-diode as detectors. Synchronised scans are performed by scannning the Bragg axis of the DCM with constant velocity and adjusting the speed of the undulator gap scan on the fly, so that the difference between the DCM and the undulator energy is never larger than 2 eV. In this mode, the registration of a single EXAFS spectrum takes about 2 min - 3, min. Energy-dispersive detectors like the SDD or the 7 pixel HPGe detector are only useable in step scan mode. Figure 4 depicts the Ce K-edge (40443 eV) EXAFS of a very homogeneous CeO_2 powder sample. It was measured using the Si 311 DCM in step scan mode, two Pt-mirrors and ionisation chambers as detector. EXAFS are clearly visible up to 22.5 Å.

Figure 5 shows a comparison of EXAFS spectra of a Cu foil taken in step- and continous scan mode. While the continuous scan was finished in 120 s, the step wise scan took a total scan time of approx. 600 s of which the major part was deadtime caused by the alternating start/stops of the DCM. Nevertheless, the quality of both spectra is comparable.

Outlook / PETRA IV

The planned upgrade of the PETRA III storage ring into a diffraction limited source of synchrotron radiation (PETRA IV) offers exciting new possibilities for many experimental methods, mainly for those methods that make use of the coherent part of the X-ray beam. The applications of XAFS spectroscopy for which P65 was designed are not

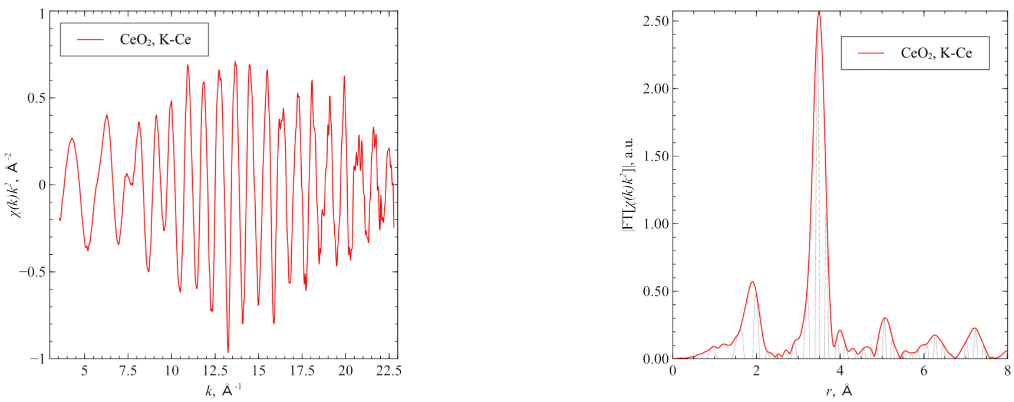

FIGURE 4: Ce K-edge EXAFS (left) and Fourier transformed EXAFS spectrum of a CeO_2 powder sample. Measured at room temperature using the Si 311 DCM and Pt mirrors.

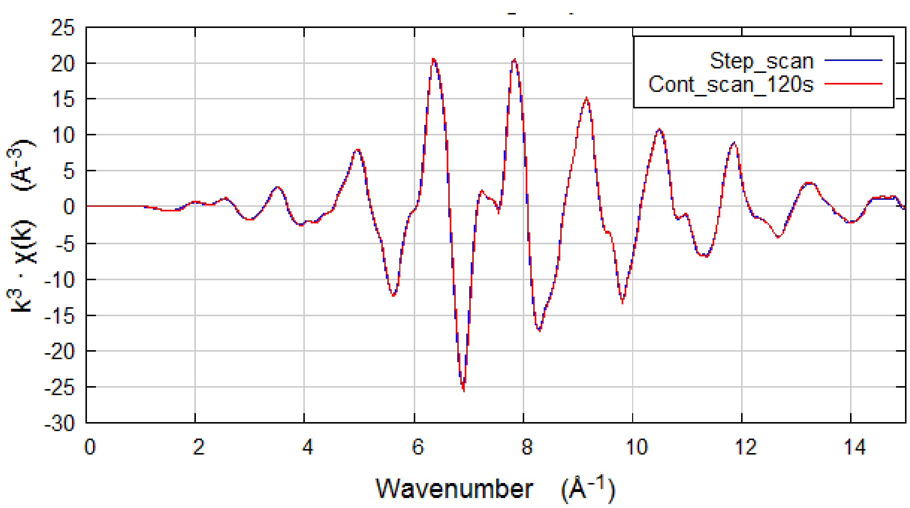

FIGURE 5: Cu K-edge EXAFS measured in step and continuous scan mode. Both spectra were measured at room temperature using the Si 111 DCM and two Si mirrors. Step scan about 600 s, continuous scan 120 s

among these methods, and in fact the conditions for standard XAFS experiments might become worse at a source with 10 pmrad emittance, because the artefacts which are caused by the partially coherent radiation of the undulator source at present day machines will be even more pronounced. We did therefore start to evaluate the experimental conditions at a beamline like P65 installed at PETRA IV by raytracing calculations. The calculations were done using the xrt 1.2.4 code and preliminary machine parameter. The latter will change in detail until a potential upgrade is taking place but the general outcome of the simulations will still be valid. [4]. Parameters for the ray-tracing were:

- Emittance: Horizontal = vertical = 10 pmrad
- Undulator: 61 periods, λ= 32.8 mm, K_{max} 2.8, gap_{min}: 9.5 mm
- DCM: Si 111/311
- Mirrors: Flat, Si/Si, 2 mrad @ 9000 eV

Figure 6 shows the simulated footprint of the direct undulator beam on a slit 45 m away from the source without any optical element before this slit. The only visible difference between the two beamlines is that the footprint of the PETRA IV undulator is slightly smaller in the horizontal direction than the one from the PETRA III undulator. That means that essentially the conditions for a P65 like beamline would not change significantly after a potential move to PETRA IV.

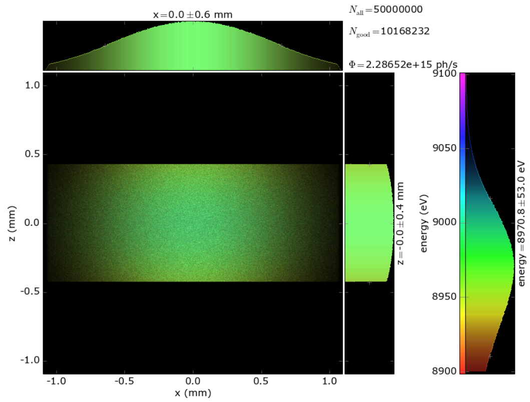

FIGURE 6: Footprint of the direct undulator beam (tuned to 9000 eV, 3rd harmonic) on a screen @ 45 m, beam limited by slit: 2 mm * 0.8 mm (h * v) @ 42 m, PETRA III left, PETRA IV right

The result is in accordance with an earlier study by Susini et al. about optics development for beamlines at the planned upgraded ESRF storage ring which had already shown that the heat load on the optical components is not significantly higher at an ultra low emittance storage ring [5] The main challenge for the beamline optics will be the preservation of the coherence properties of the beam, something that is obviously of no interest for standard XAFS applications.

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