Technical Design Proposal for P63/PETRA III

The main application of the new XAFS/XRD beamline at P63 is the investigation of chemical processes under realistic operando conditions with a high temporal resolution on the second time-scale. It will be possible to measure spectroscopy and scattering data almost simultaneously with high quality, which will allow to detect structural phase transitions during reactions, and to gain information on structural changes.

1. Required technical specifications

Since the instrument has a broad application both in techniques as well as in scientific applications, high versatility is required. The energy of the photons has to be tunable over a large energy range without any gaps in the range, which covers the absorption edges of the elements of interest, and the beam profile should not vary significantly over typical energy-scan ranges. This imposes several requirements on the x-ray source, the monochromator, and additional optics like mirrors and lenses.

Special detectors are required for the different techniques, and their requirements are high sensitivity, linearity, and high speed for fast measurements.

Special sample environment is required for different scientific applications, and the control of different parameters has to be implemented in the beamline control software in order to synchronize sample manipulation and data collection.

Data-conversion from raw detector data into data, which can be analyzed with conventional programs, has to be implemented, and a preliminary data-analysis, which helps to select new sample parameters for the following measurements.

1.1. Setup

The properties of the incident x-ray beam have to be adjustable for x-ray absorption spectroscopy (XAS), small angle x-ray scattering (SAXS), and x-ray powder diffraction (XPD). The best solution seems to be a U33-Undulator as the x-ray source, two different monochromators for fast measurements on the sub-second timescale with slightly lower flux and small vertical beam motions, and a second monochromator for slower measurements on the minute-timescale with higher flux and fixed beam position. Focusing optics should be based on mirrors for lower and on x-ray lenses for higher energies.

1.2 Source

The only source of radiation, which can be efficiently used at PETRA III is an undulator. Wigglers and bending magnets have the disadvantage of a large horizontal and vertical divergence, which requires the installation of a collimating mirror upstream of the monochromator. The first optical element can be installed at a distance of about 40 m from the source, which limits the collectable solid angle significantly, which in return reduces the flux on the sample significantly.

Experience at P64 and P65 have demonstrated that it is possible to collect EXAFS up to 25 $Å^{-1}$ with good data-quality within a few minutes. QEXAFS-spectra suffer from spatial

inhomogeneities of the intensity distribution in the incident x-ray beam, however, recent experience and measurements at P64 showed that these inhomogeneities can be reduced by selecting different harmonics and spatial parts of the incident beam.

The low divergence of the undulator beam is perfectly suited for SAXS and XPD measurements.

The U33-undulator covers an energy range starting from 2.2 keV, and it has been used at P64 at energies as high as 48 keV (Eu K-edge). The fundamental and 3rd harmonic have a large overlap, which is essential for EXAFS-measurements of Mn, Fe, and Co, which can be measured with both harmonics. Changing the harmonic during an EXAFS-scan can be avoided, which is important for high data-quality.

1.3 Monochromator

Two different types of monochromator should be installed at the beamline: One monochromator for fast energy scans on the second timescale (QEXAFS), and another for slower scans on the minute timescale with higher stability both in position and flux (fixed-exit double-crystal monochromator).

The QEXAFS-monochromator has to be a channel-cut crystal for stability reasons. Since the beam-position moves slightly vertically for different energies and during an energy scan, a second, fixed-exit double-crystal monochromator should be also installed. Both types of monochromators require different reflections for different energy ranges, since the dimensions of the crystal limit the smallest Bragg angle to approximately 4°. The Si(111) reflection covers an energy range from 4.7 keV to 25 keV, and the Si(311) reflection from 9 keV to 47 keV, which covers most required edges. The fixed-exit monochromator can go down to 3.5 and 6.5 keV, respectively.

1.4 ~~Θ~~Further beamline optics

Mirrors are required to reduce the intensity of higher harmonics, which can disturb the spectra, and to focus the beam if a smaller beamsize is required. The present layout will allow to focusing the beam to dimensions of 50 µm x 150 µm (v x h), and if a smaller focus is required, additional lenses can be installed in the experimental hutch upstream of the sample. A stable focus in the sub-µm scale will not be possible without a significant loss of intensity, and it will require significant investments in the design of the experimental hutch and other experimental configurations (table for experiments, sample environment). This is not part of the baseline configuration but may be added later on.

For ultra-fast time-resolved measurements on the MHz-scale, the timing-mode of PETRA III can be used, and novel data-collection strategies need to be applied.

1.5 Detectors

Conventional ionization gas chambers, filled with N_2, Ar and Kr will be used for measurements in transmission mode. The new version of the automatic ion-chamber filling program will be modified in order to enable automated fast changes of the gases within the beamline control software. The ion-chambers have to be fast for QEXAFS-measurements, and also linear at high flux and small beamsize, which can cause problems with linearity. Additional development on existing ion-chambers is probably required, otherwise, two different types of ion-chambers, which are optimized for fast or for high-flux applications, can be used.

If samples are measured in fluorescence mode, a Passivated Implanted Planar Silicon (PIPS) Detector can be used if the signal is reasonably high. These detectors can be used also

in QEXAFS-mode with scan-times down to 0.1 s. If the concentration is lower, energy-dispersive detectors are required in order to select photons with the energy of the fluorescence line of the element of interest. These detectors are too slow for QEXAFS-measurements even on the second time-scale.

Two different types of energy-dispersive detectors will be required. In the lower energy-range, Silicon Drift Detectors (SDD) with high energy resolution are perfectly suited. At higher energies, Ge-detectors are more advantageous since Si with a thickness of 500 µm becomes transparent for x-rays with an energy above 15 keV. Multi-pixel Ge-detectors have the disadvantage of a rather thick Be-window, which absorbs too many x-rays with an energy below 10 keV.

In addition, for time-dependent measurements, Avalanche Photo-Diodes (APDs) with a reasonable energy resolution and fast detection mode can be used, since they can separate the signal of different electron-bunches in timing mode.

Diffraction and scattering experiments require a large area-detector with small pixel size, high dynamic range, and fast readout. Energy-discrimination will be required in order to reduce background which is caused by fluorescence from elements with an absorption edge with an energy below the energy of the incident photons.

1.6 Sample alignment; grazing incidence capabilities

Positioning stages, goniometers and control devices are required for stable, accurate sample alignment. Cameras, 2D detectors and abilities to perform motor scans and quickly visualize the results are needed to make the sample alignment as quick and easy as possible. It is particularly important for measurements in grazing incidence mode, which are crucial for single-crystal supported samples. The necessity of having an excellent sample stage for high precision sample alignment in x-y-z and the rotation needs to be emphasized for measurements in grazing-incidence mode, as for example for recording X-ray reflectivity curves and for 2D mappings.

1.7 Sample environments and other equipment

An essential element of this beamline should be all necessary infrastructure for *in situ* and *in-operando* investigations of thermal and electrocatalytic processes. This includes: gas lines, mass flow controllers, heaters, temperature controllers, electrolyte pumps, potentiostats and sample cells themselves, with sufficient flexibility that users' own sample cells can also be used, if needed. For *operando* experiments it is essential also to monitor on-line the reaction products via mass spectroscopy and gas liquid/gas chromatography.

Here, the gas distribution system as well as the safety measures should allow operation of the gas phase reactors at up to 100 bar using all types of feed gas to fulfill the requirements of industrial operating conditions. A laser source and solar simulator implemented in the beamline would also enable to follow photocatalysts in pump-and-probe mode.

In addition to the experimental facilities incorporated in the experimental hutch, chemical sample preparation and pre-treatment has to be possible in a safe way in the vicinity to the beamline pointing towards the need of a small chemical laboratory equipped with a fume hood and a vented gas cabinet. The shared chemistry lab in the Paul-Peter Ewald Hall with two fume-hoods needs the capability to prepare and pre-treat samples with all different types of gases under similar conditions as the measurements at the beamline. A small sample preparation lab with a pellet press and a wet bench for preparation and tests of electrochemical cells for measurements right next to the experimental hutch is essential.

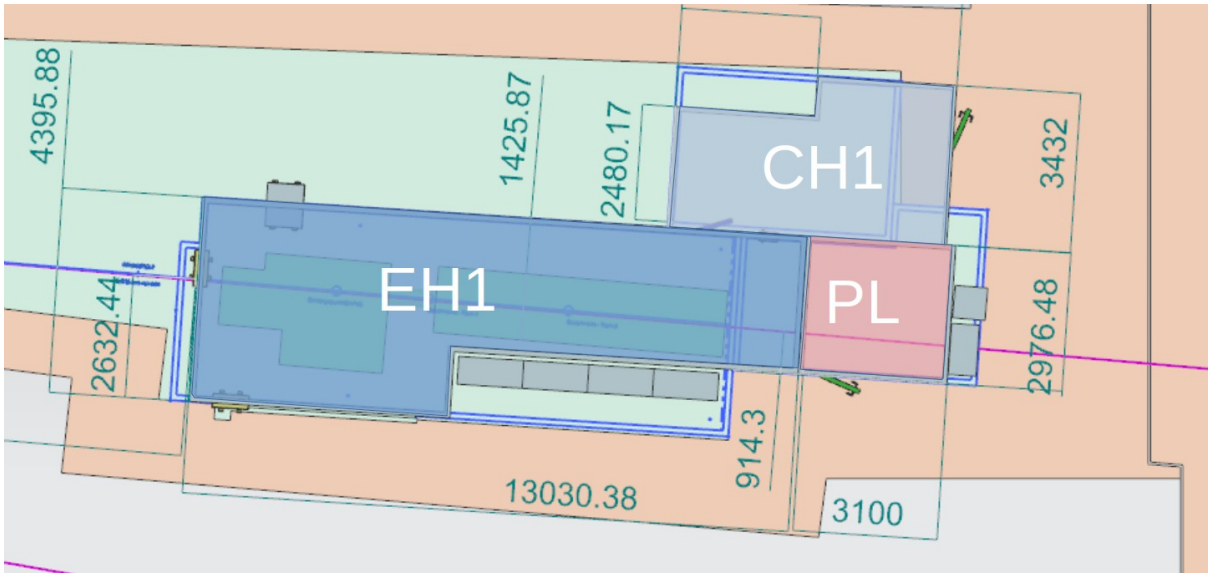

Figure 1: Proposed Hutch-Layout for P63 at PETRA III. The Experimental Hutch (EH1) has a length of 13 m, which is well suited for SAXS with reasonable resolution. The upstream part of the hutch is dedicated to beam-diagnosis instrumentation with ion-chambers, beam-position monitor and slit-system, the experimental table for the sample and required infra-structure for sample manipulation, and the narrower downstream part is dedicated to the SAXS-beamtube and detector. It is also possible to install a high-resolution back-scattering emission spectrometer in the upstream part of the hutch for simultaneous XES and SAXS-measurements at 12.4 keV (1 Å). The sample preparation lab (PL) offers sufficient space for a bench for sample preparation for measurements. Complex sample treatment has to be done in the common chemistry lab in room EG.007. The control hutch (CH1) offers sufficient space for control hardware, computers and monitors. Electronic racks have to be placed at different locations outside the hutches. 4 gas-cabinets (GC) are located outside the hutch at the downstream side. One of these gas-cabinets has to move to a different location for operation at PETRA IV, since some space might be required for a laser-hutch of the XAS/XES-beamline, which is right now located at P64.

1.8 Combination with other techniques

In this beamline, XAS measurements will be complemented with XRD measurements. An existing realization of measurements in QEXAFS mode with quasi-simultaneous acquisition of scattering and diffraction images is available, e.g., at ESRF beamline BM26A[1], or ALBA, NOTOS beamline. The setup at the proposed beamline should allow one to observe changes in the XRD peaks during *in situ* experiment but is not expected to replace "full-scale" high-energy XRD measurements at dedicated beamlines.

Nevertheless, collection of diffraction patterns or scattering profiles during XANES measurements will be useful as the anomalous X-ray diffraction pattern and SAXS curves would give valuable information with respect to alloy formation, segregation, de-alloying, or the formation of core-shell structures. Regarding technical implementation, we propose to use a beam-stop diode in front of the 2D detector for transmission XAS/XRD experiments of high-loading samples, as it is implemented at the SAXSMAT-beamline P62 at PETRA III.

In addition, having capabilities for UV/vis, Raman and/or FTIR spectroscopy measurements combined with the X-ray techniques will complement the insights with respect to adsorbates and will open up the *operando* investigation of an even broader field of materials. In such combined studies, it would be possible to investigate how the carbon support of the nanoparticles catalysts change and, e.g., follow the coke formation on the catalysts under (electro)chemical reaction conditions by applying *operando* Raman

[1] Nikitenko et al, J. Synchrotron Rad. (2008). 15, 632–640

spectroscopy. Using *operando* FTIR spectroscopy, the adsorption of probe molecules, e.g., NO/CO on (supported) nanoparticles and reaction intermediates could be followed. Understanding the relation between adsorbates, structural properties, morphology and the chemical state of the catalyst using combined X-ray techniques is essential for catalysis and material research.

1.9 Imaging/2D mapping

An attractive feature of this beamline should be the ability to perform 2D XAS mapping of the sample, to detect, e.g., differences in oxidation state (edge step positions) across the sample as it has been done in a few pioneering experiments at P64 in recent years. Two different approaches can be employed here: micro-focusing QEXAFS, where a micro-focused beam is scanned across the sample, or 2D full-field imaging, which employs a 2D detector. 2D full-field imaging allows one to collect images faster and also tends to be more stable. Spatial resolution in this case is limited by the detector resolution. A successful example of spatially-resolved studies of a catalyst using 2D full-field imaging can be found in Ref.[2] The problem with this approach, however, that it cannot be easily combined with measurements in fluorescence mode, which, as mentioned above, are essential for investigations of realistic catalysts, especially those in an electrochemical environment.

Micro-focusing QEXAFS-based 2D mapping thus seems to be better suited for this purpose. In principle, it can also provide higher spatial resolution. The stability of the beam position during the QEXAFS scan, however, will be the critical feature that will ultimately determine the resolution. **While this method has been applied for studies of environmental and biological samples, its applications for catalytically-relevant systems seem to be rare so far. Thus it could be an interesting, unique feature of this beamline.** Another challenge and opportunity is to **combine spatially-resolved measurements with temporarily-resolved measurements**, to obtain truly unique information about the *in situ* evolution of catalyst material.

1.10 Software and data analysis

An important issue for detailed time-resolved or spatially resolved XAS measurements is the ability to quickly and systematically process hundreds and thousands of spectra. Conventional approaches for data alignment and processing (that rely for example on ATHENA and ARTEMIS software) are inadequate in this case. It is important therefore that the beamline is equipped with the proper software for basic analysis of the obtained results. In order to understand structural changes during the reaction in order to determine the next process parameters, automated tools like principle component analysis or multivariate curve resolution-alternating least squares should be implemented. Evolutionary algorithms and neural networks should help to interpret the data in a faster and more efficient way and to gain structural information simultaneously. For the multi-modal approach with different techniques, which will provide complementary information, more advanced tools will be developed.

1.11 Capabilities for future industrial users as collaboration partners to MPG scientists

[2] Alizadehfanaloo et al, *Journal of synchrotron radiation 28(5), 1518 - 1527 (2021)*

In the long term, it is expected that industrial users in the area of Catalysis would be attracted to this MPG beamline through collaborations with MPG scientists. Therefore, it would be important if aspects like **automation, high-throughput measurements, data extraction and reduction** would be considered from the beginning. We would aim for a **user-friendly beamline software** because this will also help the scientific community to significantly improve the experiment efficiency, data quality, safety and in the end the scientific insights gained by the experiments.