

CryoEXAFS: X-ray absorption spectroscopy station with cryogenic or in-beam operando electrochemistry sample conditions at BESSY II

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Abstract: The Cryo-EXAFS experimental station at beamline KMC-3 is a dedicated experiment to investigate the short-range environment around selected atomic species and redox behavior in condensed matter by X-ray Absorption Spectroscopy with cryogenic or in-beam, operando electrochemistry sample conditions.

1 Introduction

The Cryo-EXAFS X-ray absorption spectroscopy (XAS) station at beamline KMC-3 at BESSY II was developed and is operated in a cooperation treaty between the FU Berlin, FB Physik (Prof. Holger Dau) and the HZB. The endstation is dedicated to XAS in a range of about 3-13 keV and is open for general user proposals since September 2016. To operate the CryoEXAFS station, the other station of the KMC-3 beamline (Helmholtz-Zentrum Berlin für Materialien und Energie, 2017), the KMC-3 XPP station (Helmholtz-Zentrum Berlin für Materialien und Energie, 2016), must be evacuated and the beamline must be extended to include the CryoEXAFS station. For this purpose, the CryoEXAFS station is installed on a moveable table inside of the experimental hutch and can easily be flanged to the KMC-3 beamline. Recent progress in the development of the CryoEXAFS station includes the installation of a 13-element energy-resolving silicon-drift detector (SDD) with rapid data readout (≤ 1 ms) for rapid-scan and time-resolved applications such as in-beam, operando electrochemistry. The KMC-3 CryoEXAFS station offers XAS experiments in a 5-300 K cryogenic

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range (liquid Helium cryostat) as well as under in-beam, operando electrochemistry conditions (materials in solution or deposited on surfaces, for example electrodes). Both setups are installed in parallel to enable a rapid change from cryogenic to in-beam, operando electrochemistry mode (Figure 1). Both experiments at this bending magnet beamline are performed with a widened beam focus (several mm² on the sample) thereby avoiding radiation-induced sample modifications (avoidance of radiation damage).

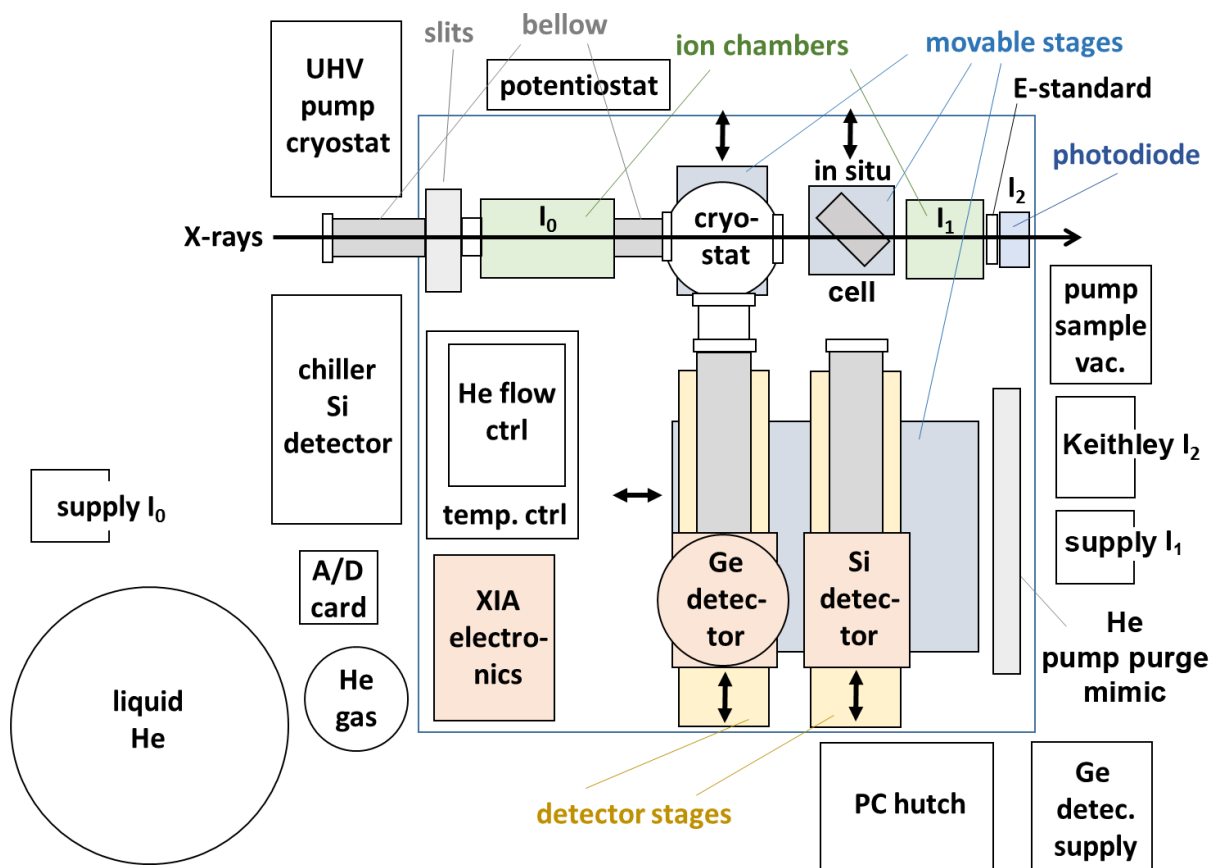
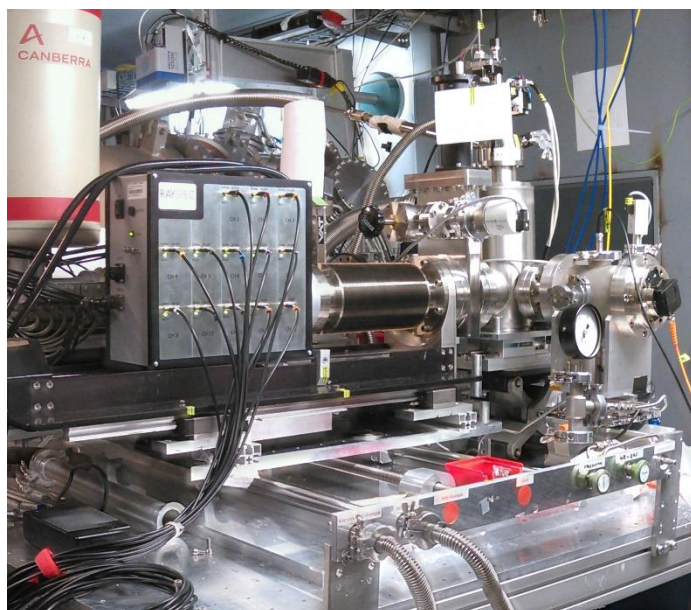


Figure 1: Scheme of the experimental setup for XAS at KMC-3 (CryoEXAFS) with cryogenic or in-situ (operando) ambient-temperature sample condition. Two energy-resolving 13-element fluorescence detectors (Ge and Si) can be used alternatively and facilitate switching between both types of experiments without rearrangements of the experimental set-up.

The general station setup (Table 1) includes a liquid-helium cryostat (Oxford, ca. 5-300 K), detectors (ion chambers, photodiodes) for transmission-mode XAS, as well as two retractable large-area energy-resolving detectors (liquid-nitrogen-cooled window-less 13-element Ge, Canberra; air/water-cooled Be-window 13-element Si-drift SSD, Rayspec) for fluorescence-mode XAS (up to ca. 400 kcps), which are operated via XIA DXP electronics and can be flanged to the cryostat for in-vacuum operation to yield maximum count rates (Figure 2a). Motorized y/z sample positioning is available for samples in the cryostat as well as in the in-beam, operando electrochemistry sample cells. Fast data acquisition/transfer hard- and software facilitates relatively rapid EXAFS scans, e.g. in ca. 3.0 min to $k = 12 \text{ \AA}^{-1}$, as well as fluorescence data

acquisition (e.g. at fixed energy) with the energy-resolving detectors with 1 ms per point or less for superior signal contrast in time-resolved applications. Typical applications for the cryogenic set-up are XAS experiments on biological materials (metalloproteins), (diluted) chemical solution samples, and solid-state materials. For the in-situ setup, sample cells and a potentiostat for in-beam electrochemistry are available and typical applications are XAS experiments on electrode-deposited metal catalyst films in contact with electrolyte at room temperature (Figure 2b).

a)



b)

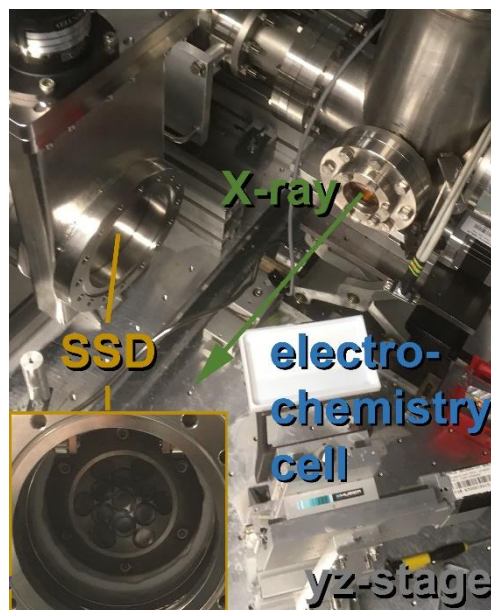


Figure 2: KMC-3 CryoEXAFS experimental station a) with cryogenic condition utilizing the 13-element Si-drift SSD (Rayspec) that is flanged to the cryostat, the same SSD is used in b) to acquire data using an electrochemical cell, the I1 ion chamber and I2 photodiode have been removed for this purpose. Using the yz-stage, the electrochemical cell can be aligned with the X-ray beam. See also Figure 1.

2 Instrument application

- In-situ characterization of materials under catalysis conditions with low-temperature data collection (freeze-quench approach, Klingan et al., 2018; Pasquini et al, 2019, Bergmann et al., 2020; Smith et al, 2017)
- Operando XAS on films for water oxidation reaction (OER) under electrochemistry conditions at room temperature (Smith et al., 2017; González-Flores et al, 2018)
- XAS on dilute-solution (1 mM) protein samples at cryogenic conditions (Reschke et al., 2019)
- Rapid-scan EXAFS (redox transitions and catalytic processes during cyclic voltammetry)
- EXAFS as a function of chemical composition and/or temperature dependent EXAFS (Kesavan et al., 2020)

3 Technical data

(a) XAS experiments at cryogenic (cryostat) or operando (electrochemistry) conditions can be performed in parallel using two energy-resolving detectors. (b) Rapid data readout/transfer (e.g. via fiber optics) facilitates X-ray fluorescence data acquisition with the energy-resolving multielement detectors with 1 ms or less per data point in time-resolved applications for superior fluorescence signal contrast. (c) Relatively rapid scan capabilities (continuous monochromator scans in a few minutes) enable time-resolved XANES/EXAFS experiments, e.g., in operando approaches. (d) Variable beam focusing allows adaptation to different sample cell dimensions of the user groups. (e) Permanent potentiostat facilities and available sample cells can be used for electrochemistry. (f) Well-adapted (in-house) software tools are available for online rapid data processing and evaluation during the measurements. (g) Further upgrades will increase the user friendliness, rapid-scan speed, accessible low-energy range, fluorescence data quality, and combination of techniques (laser excitation, electrochemistry) for superior cryo- and operando-XAS experiments: (i) closed-cycle LHe-cryostat (delivered in February 2020) for increased user friendliness and saving of He (no more need for He dewar in the hutch and its exchange). (ii) Faster detector electronics (XIA Falcon, delivered in January 2020) for saturation-free handling of ca. 10-fold increased maximal count rates (~ 4 Mcps) in fluorescence-mode XAS with the energy-resolving detectors. (iii) Ion chambers for 2-4 keV operation (to be installed in 2020) for extension of the lower-energy range in XAS to the monochromator limit. (iv) For faster XAS measurements, the hardware trigger modus is tested, where measurements are triggered directly from the encoder signal using a digital signal level converter Zebra (Quantum Detectors) purchased in 2020. (v) Pulsed OPO-laser (purchased in 2020) for excitation of samples in the beam to facilitate new operando experiments.

Temperature range	5 - 300 K
Pressure Range	The cryogenic setup is in vacuum with the sample in He gas environment. The in-beam, operando electrochemistry setup is under atmospheric conditions.
Detector	13-element detectors (Ge and Si) with XIA electronics, 3 ionization chambers, Si-PIN photodiodes, scintillation (photomultiplier) detector
Manipulators	Cryogenic and in-situ setup: y,z
Sample holder compatibility	For details, contact the station manager.
Monochromator	Si (111)
Energy range	3 - 13 keV (extension to 2 keV in progress)

Table 1: Specification of the Station.

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