Study of time and pressure dependent phenomena at the hard x-ray beamline BL9 of DELTA

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Abstract. The beamline BL9 of DELTA (Dortmund ELecTron Accelerator) is a multi-purpose beamline operating in an energy range between 4 and 27 keV. A short overview of the beamline and the experimental endstation is given. Exemplarily three typical applications, namely x-ray diffraction from interfaces, small angle x-ray scattering under high hydrostatic pressure and fast x-ray reflectivity measurements, are discussed in some detail in order to demonstrate the capabilities of the beamline.

1. Introduction

DELTA is a synchrotron radiation source located at TU Dortmund University (Germany). The electron storage ring operates at an electron energy of 1.5 GeV and a maximum current of 130 mA. The typical lifetime at 100 mA is 10 hours. Beside bending magnets, two undulators and one superconducting asymmetric wiggler serve as photon sources for nine beamlines. Several experimental techniques, such as spin resolved photoemission spectroscopy, photoelectron diffraction, x-ray lithography, x-ray fluorescence analysis, x-ray scattering and spectroscopy with hard x-rays are available. Recently a new facility for ultra short pulses in the VUV and terahertz regime started operation [1]. The superconducting asymmetric wiggler with a critical energy $E_c = 7.9$ keV provides x-ray radiation for three hard x-ray beamlines, BL8, BL9, and BL10. The material science beamline BL8 is operated by the Bergische Universität Wuppertal and is dedicated to x-ray absorption spectroscopy experiments [2]. The beamline BL10 is operated by the University of Siegen together with Bergische Universität Wuppertal and is dedicated to x-ray diffraction and x-ray absorption spectroscopy. The multi-purpose beamline BL9 is operated by TU Dortmund University. A Si(311) double crystal monochromator covers an energy range between 4 and 27 keV with an overall energy resolution of $\Delta E/E = 10^{-4}$. The typical photon flux (horizontally focused) at the samples position is $5 \cdot 10^9 \frac{\text{photons}}{\text{mm}^2 \cdot \text{100mA}}$. The experimental endstation of beamline BL9 is equipped with a six circle diffractometer allowing x-ray reflectivity [3], (surface sensitive) x-ray diffraction [4], x-ray standing wave [5] and small angle x-ray scattering (SAXS) experiments [6]. Beside NaI point detectors, a MAR345 image plate with a diameter of 345 mm, and a PILATUS 100k detector with an active area of 83.8 $\times$ 33.4 mm$^2$ and a sensor thickness of 320 $\mu$m are available.
Several sample environments allow a broad spectrum of applications. A closed cycle cryostat (10 K-300 K) and a high temperature furnace (300 K-1000 K) are available to study temperature induced phase transitions in situ. Different pressure cells (0 bar-100 bar gas pressure and 0 bar-5000 bar hydrostatic pressure) can be used to study gas adsorption processes or structural changes of macromolecules under high pressure. Beside this, sample cells for the investigation of solid-liquid interfaces and a Langmuir trough for the investigation of liquid-gas interfaces are available. In the following sections three different applications will be discussed, showing some of the capabilities of the beamline.

2. Mineral formation at the liquid-gas interface

The mineralization of iron compounds at liquid-gas interfaces was investigated by grazing incidence diffraction (GID). In a GID experiment, the incoming x-ray beam hits the surface of the sample under an incidence angle that is smaller than the critical angle of total external reflection, yielding a penetration depth on the order of 5 nm [7]. Thus, the formation of thin crystalline layers at interfaces can be studied.

In order to investigate liquid surfaces at beamline BL9 a 250 mm long Si mirror was installed 2.5 m in front of the six circle diffractometer that bends the incoming x-ray beam down onto the surface of the liquid. Depending on the photon energy incident angles between 0.2° (27 keV) and 0.4° (8 keV) with respect to the surface can be realized. In the center of the diffractometer a Langmuir trough (KSV instruments, 100 × 210 mm² sample surface) was mounted. To detect the scattered radiation in the horizontal plane a supplemental goniometer holding a detector arm was installed. For the detection of scattered radiation the PILATUS 100k detector was mounted on the detector arm. Translation stages allow the variation of the detector height and the distance between detector and sample. A Soller collimator (JJ-XRAY) can be placed between sample and detector yielding a resolution of 0.1°. The mineralization of iron containing compounds at the liquid-gas interface was studied in aqueous 100 mM iron(II) chloride solution. The addition of gaseous ammonia into the sample cell caused a change of the solutions pH value at the liquid-gas interface. This pH change induces the formation of iron containing compounds at the interface. In order to monitor the time evolution of the formation process several diffraction scans were performed. The incidence energy was chosen to 11.5 keV, and the angle of incidence was set to 0.09°. In figure 1, diffraction scans taken at different times are shown. The system shows the formation of crystalline material at the liquid surface. A comparison of the observed Bragg reflections with data from literature reveals the formation of lepidocrocite (FeO(OH)). A peak width analysis indicates a crystal growth starting with a size of (6.4 ± 0.3) nm and ending with (14.4 ± 0.5) nm. Drastic changes are observed in the last scan which can be attributed to the formation of iron chloride hydroxide [8] at the surface going in hand with an immersion of lepidocrocite into the subphase.

3. High pressure SAXS

In a SAXS experiment, the scattered radiation is detected under small angles 2θ, giving access to the structure of nanometer sized systems. Typical sample systems are solutions or crystals of macromolecules such as proteins, long-chained hydrocarbons, or polymers. The application of high hydrostatic pressure was used to study structural changes of soft matter systems. For instance, the unfolding of proteins and its dependence on mutations can be studied as well as the influence of pressure on the protein-protein interaction in aqueous solutions imitating in vivo systems [9, 10]. Furthermore, the phase diagram of lipid bilayers which serve as model for membranes as present in organisms, especially in the deep sea, can be explored using high pressures [11]. Beside this, high pressure is also of technological interest, for instance in high pressure food processing, e.g. conservation.
In order to study the sample response on high hydrostatic pressure, a high pressure cell is available at beamline BL9. The reversible pressure induced phase transformation of triglycerides was investigated in a pressure range between 1 bar and 4 kbar. A commercially available peanut was used as sample. Figure 2 shows the corresponding SAXS data. At 4 kbar pressure strong Bragg reflections become visible, which shift to slightly lower Bragg angles when the pressure is decreased to 2 kbar. Turning back to 1 bar restores the initial state. The appearance of the Bragg reflection can be explained by the pressure induced crystallization of the triglycerides within the nut, which can form triclinic crystals with a long lattice spacing in one direction [12]. In our case a long spacing of 5.9 nm is observed at 4 kbar and 6.1 nm at 2 kbar, which indicates a compression of the unit cell with rising pressure.

4. Fast x-ray reflectivity

In an x-ray reflectivity (XRR) experiment, the intensity of a reflected x-ray beam is measured as a function of the wave vector transfer perpendicular to the sample’s surface \( q_z = (4 \cdot \pi / \lambda) \sin(\theta) \), with the wavelength \( \lambda \) and the scattering angle \( \theta \). From reflectivity data one obtains the laterally averaged electron density profile of the sample [13]. The analysis of x-ray reflectivity data is usually performed applying the well-known Parratt algorithm [14], yielding parameters such as electron density contrast \( \Delta \rho \), the interfacial roughness \( \sigma \), and layer thickness \( d \). However, many interesting systems show time dependent structural changes. For example, the adsorption of proteins at solid-liquid interfaces takes place at timescales \( \tau \) between seconds and several minutes. Thus, the analysis of the in situ adsorption process by x-ray reflectivity measurements is a non-trivial task because the time of an x-ray reflectivity measurement is on the order of several minutes. Consequently the analysis of time dependent reflectivity data applying a static model of the electron density fails. The reduction of measuring time \( T \) so that \( T \ll \tau \) can solve this problem. However, this is not always possible due to several reasons, like motor positioning times, data statistics, etc. In order to analyse time dependent x-ray reflectivity data (here the adsorption of lysozyme at the solid-liquid interface) we constructed an x-ray reflectivity set-up at beamline BL9 that allows to record a full reflectivity within 55 seconds. For this purpose the PILATUS 100k detector was mounted on a fixed sample stage 1 m behind the sample cell. During a reflectivity scan two slit systems between sample and detector are moved in \( 2\theta \) simultaneously to \( \theta \) guiding the specularly reflected x-ray beam on the detector and minimizing scattering background. Thus, the reflectivity scan is recorded on one detector image. As the time constant of the adsorption process is about several minutes, a series of pictures will be recorded. However, due to the ongoing adsorption of lysozyme during a single XRR scan a
static electron density is still not fully appropriate for modeling the XRR data. Thus, a time dependent electron density $\rho(t)$ was introduced depending on $q_z$. The evolution of $\rho(t)$ is shown in the inset of figure 3 for each reflectivity curve. The resulting XRR curves are presented in figure 3. In order to compare the simulations with XRR data the adsorption of lysozyme was studied using a lysozyme concentration of 0.1 mg/ml and a photon energy of 27 keV [3]. The measurements are shown in figure 3 and exhibit a good qualitative agreement with the simulated curves.

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