Synchrotron Radiation in Natural Science **19**, 5-7 (2020)

Laboratory for high energy resolution X-ray spectroscopy at the Institute of Nuclear Physics of the Polish Academy of Sciences

W. Błachucki[1]*, A. Wach[1], J. Czapla-Masztafiak[1], W. Kwiatek[1], J. Szlachetko[1]

[1]*Institute of Nuclear Physics, Polish Academy of Sciences, 31-342 Kraków, Poland*
*e-mail: wojciech.blachucki@ifj.edu.pl, wojciech.kwiatek@ifj.edu.pl, jakub.szlachetko@ifj.edu.pl

DOI:10.36184/SRNS.2020.19.005
Received: 25 March 2020
Published: 13 May 2020
PACS/topics: laboratory X-ray spectroscopy, von Hámos X-ray spectrometer, liquid jet target

The technological progress in the X-ray instrumentation made nowadays possible the development of efficient laboratory X-ray spectroscopy setups. The new excitation sources, optics and detectors allow constructing cost-effective and robust X-ray spectroscopy stations which, unlike large-scale facilities where the access is infrequent and not guaranteed *a priori*, are permanently available enabling the realization of entire research projects as well as giving more flexibility in the preparation of experiments at synchrotrons and X-ray free-electron lasers. At the Institute of Nuclear Physics of the Polish Academy of Sciences a new X-ray laboratory has been opened.

Introduction

The Department of Applied Spectroscopy (NZ53) has been recently established at the Institute of Nuclear Physics of the Polish Academy of Sciences. It covers well-equipped chemistry and biology laboratories, an X-ray laboratory specialized in the application of X-ray absorption and emission spectroscopy (XAS/XES) [1,2], X-ray microscopy and tomography setups as well as a particle-induced X-ray emission (PIXE) facility. The experimental setups and supporting preparation laboratories are commonly employed in research devoted to both fundamental and applied research. Particularly, high energy resolution X-ray spectroscopy methods are a part of the department's in-house activity and are focused on *in-situ* time-resolved X-ray studies on electron dynamics of atoms and molecules and in particular surveying the role of metals in biological complexes, photo-chemical systems and materials important for renewable energy.

X-ray spectroscopy laboratory

The X-ray lab's equipment is split into two independent X-ray hutches (10 m^2 each) located close to each other. The rooms' walls are shielded with a 5 mm-thick lead layer and the access to them is through shielded sliding doors. Each room has a heavy-duty optical table where the experiments are carried out and are well equipped with all the equipment arranged in lab cabinets as well as movable racks which makes the lab works very flexible. The X-ray hutches have interlock safety systems installed which prevent applying a high voltage on the X-ray tubes without prior safety check (confirmed with a badge reader by the room entrance) and disconnects the X-ray tubes' power supplies whenever the door is open while the X-rays are on.

Von Hámos spectrometers

The X-ray equipment allows setting up two in-air crystal X-ray spectrometers in the von Hámos geometry[3] (see Fig. 1). In this geometry the measured X-ray beam first falls on an analyzing crystal which, as described by the Bragg's diffraction law, diffracts at different angles photons of different energies. Thus spatially dispersed radiation beam reaches a positon-sensitive X-ray detector, such as a charge-coupled device (CCD), whereas photons of different energies fall on the detector at different channels or pixels along the dispersion axis. Fig. 1 shows an exemplary arrangement of spectrometers sharing one X-ray source[4]. In this arrangement the unit collinear with the excitation beam captures the radiation exiting the X-ray tube and, with the sample in the beam focal point, the radiation transmitted through it, thus allowing measurement of absorption spectra. Simultaneously, the unit placed aside records spectra of the radiation emitted in fluorescence induced in the sample by the excitation beam.

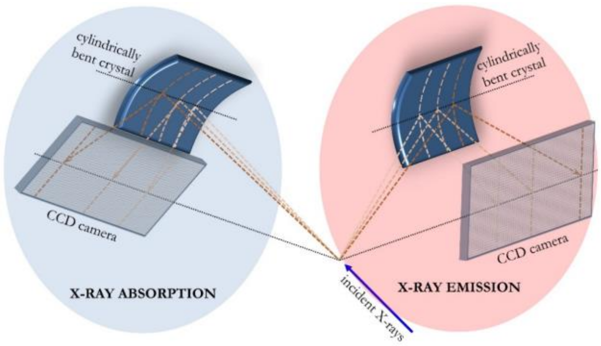

Fig. 1. Scheme of two von Hámos spectrometers sharing the same excitation X-ray source. In this arrangement one spectrometer measures the X-ray absorption spectrum and other measures simultaneously the X-ray emission spectrum.

In the X-ray lab available are 2 X-ray tubes XOS X-Beam Superflux PF, 2 X-ray cameras Andor Newton 920 and a number of different cylindrically bent X-ray crystals. The X-ray tubes are equipped with Mo anodes and polycapillary optics focusing the exit beam to the divergence of about 3°. The sources can operate at the maximum voltage and current of 30 kV and 1 mA, respectively, and are cooled with an integrated fan. The X-ray cameras are based on front-illuminated CCDs composed of 1024 × 256 26 μm-sized pixels. The cameras have 250 μm-thick Be windows and are vacuum sealed which allows cooling the sensors down to -70 °C with the integrated thermoelectric coolers. The use of the front-illuminated type sensor allows for energy discrimination of X-rays falling onto the detector, and thus resolving different diffraction orders given by the X-ray crystal used. The available X-ray crystals' cuts are: Si(111), Si(110), Si(100), Si(310), Si(531). Some of the crystals[5] are bent to a radius of 25cm and others are segmented and glued on a curved frame with the radius of curvature of 25 cm. Each spectrometer can be adjusted to measure radiation in the energy range ~ 5 – 12 keV covering ~ 50 – 200 eV during one measurement at the relative energy resolution of ~ 1 – 2 $\times10^4$.

The available equipment gives large flexibility in the preparation of experiments. For example, the spectrometers can be arranged not only independently, as two separate setups, but can share the same X-ray source, thus allowing simultaneous XAS and XES measurements[4] or two XES measurements in different energy domains (the so-called *two-color mode*). Also, the spectrometers can be oriented horizontally or vertically according to the specific needs of an experiment, as e. g. in XES measurements on liquid jet target the jet wiggling strongly affects the data collected with the horizontally aligned spectrometer but it has no observable effect on the data recorded with the vertical orientation.

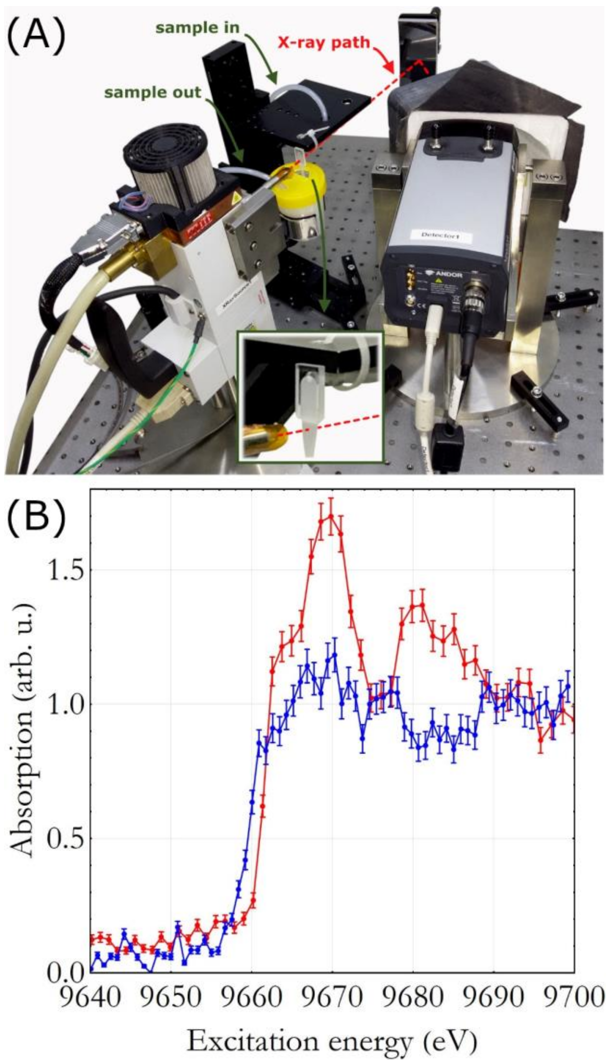

Fig. 2. (A) View on the experimental setup used. The X-ray tube was operated at the voltage of 30 kV and the current of 0.9 mA. (B) The Zn *K*-edge XAS spectra measured for the ZnO aqueous solution in the form of a jet (red) and for a Zn metal foil (blue).

Liquid jet sample delivery system

One of the recent activities in the lab has been the development of a liquid jet sample delivery system Fig. 2(A). We connected a plastic nozzle to a micro-gear pump through a supply tube. The liquid after exiting the nozzle flew through the X-ray beam and was collected by a catcher and sucked back to the circuit through another tube. The nozzle was fixed to a platform equipped with two linear stepper motors capable of positioning the target spot with micrometer precision. The jet was irradiated horizontally in its middle and vertically just below the nozzle's exit. Lead shielding was applied to the detector to diminish the contribution of the scattered photons to the recorded signal.

We tested the jet sample system during Zn *K*-edge XAS measurement on 1 M aqueous solution of ZnO nanoparticles with the jet thickness of 0.5 mm. The measured spectrum is shown in Fig. 2(B). Because of the sharing of valence Zn electrons to the bonding with O, Zn oxidation state increases and in consequence the *K*-edge binding is increased resulting in the shift of Zn *K*-edge XAS spectrum towards higher energy as compared to the spectrum measured for Zn metal. The stronger white line in the ZnO spectrum reflects the higher unoccupancy of the Zn valence states due to chemical bonding.

Summary

Laboratory for X-ray spectroscopy is available at the Institute of Nuclear Physics of the Polish Academy of Sciences. It serves in applied X-ray absorption and X-ray emission measurements on complex samples both in chemistry and biology. The lab is used in the realization of entire research projects and also provides an excellent workspace for the preparation of experiments at synchrotrons and X-ray free-electron lasers.

Acknowledgements: This work was supported by the National Science Centre (Poland) under grant numbers 2017/27/B/ST2/01890, 2016/21/D/ST4/00378, 2019/03/X/ST3/00035, and 2019/03/X/ST2/00949.

References

1. Yano, J. & Yachandra, V. K. X-ray absorption spectroscopy. *Photosynth. Res.* **102**, 241–254 (2009).
2. Bergmann, U. & Glatzel, P. X-ray emission spectroscopy. *Photosynth. Res.* **102**, 255–266 (2009).
3. v. Hámos, L. Röntgenspektroskopie und Abbildung mittels gekrümmter Kristallreflektoren. *Naturwissenschaften* **20**, 705–706 (1932).
4. Błachucki, W., Czapla-Masztafiak, J., Sá, J. & Szlachetko, J. A laboratory-based double X-ray spectrometer for simultaneous X-ray emission and X-ray absorption studies. *J. Anal. At. Spectrom.* **34**, 1409–1415 (2019).
5. Szlachetko, J. *et al.* A von Hamos x-ray spectrometer based on a segmented-type diffraction crystal for single-shot x-ray emission spectroscopy and time-resolved resonant inelastic x-ray scattering studies. *Rev. Sci. Instrum.* **83**, 103105 (2012).

