Journal of **large-scale research** facilities

Journal of large-scale research facilities, 3, A126 (2017) http://dx.doi.org/10.17815/jlsrf-3-89

Published: 04.12.2017

LiquidJet PES: Soft X-ray Photoelectron Spectroscopy from Aqueous Solution end-station at BESSY II

Helmholtz-Zentrum Berlin für Materialien und Energie *

Instrument Scientist:
- Dr. Bernd Winter, Helmholtz-Zentrum Berlin für Materialien und Energie,
  phone: +49 30 8062-15001, email: bernd.winter@helmholtz-berlin.de

Abstract: The LiquidJet PES apparatus is a specialized end-station at the synchrotron radiation facility BESSY II, Berlin, for studying the electronic structure of liquid water, aqueous and non-aqueous solutions with soft X-ray photoelectron spectroscopy. Targets are liquid microjets that are introduced into a vacuum chamber via a $\sim 20\ \mu$m glass capillary.

1 Introduction

Fundamental interactions between solute electronic structure and highly volatile liquid solutions, especially water, which are essentially the key to chemical reactivity, have remained poorly understood. Only with the introduction of the liquid microjet technique, and its first application in conjunction with synchrotron radiation about a decade ago, has liquid-phase photoelectron spectroscopy evolved as a research field.

The LiquidJet PES station presented here has been designed to measure (photo)-electrons from a liquid microjet that is introduced into the main interaction chamber via an 18-25 μm glass capillary, forming a free liquid surface in vacuum. One 1500 l/s turbo pump and several lN_2 cold-traps keep the pressure on the 10^{-4} mbar level under operation conditions. Photoelectrons are detected by a robust and compact SPECS EA10 hemispherical analyzer with a replaceable 100-500 μm skimmer orifice, acting as a pressure barrier between the main chamber and the electron analyzer. The small distance of <0.5 mm between the jet and the orifice assures that detected electrons have not suffered from inelastic scattering with water gas-phase molecules near the jet surface. Typical energy resolutions of the hemispherical energy analyzer are 100 meV at 10 eV pass energy (used for valence photoelectron measurements at

---

* **Cite article as:** Helmholtz-Zentrum Berlin für Materialien und Energie. (2017). LiquidJet PES: Soft X-ray Photoelectron Spectroscopy from Aqueous Solution end-station at BESSY II. *Journal of large-scale research facilities, 3*, A126. http://dx.doi.org/10.17815/jlsrf-3-89

170 – 200 eV photon energy) and $\sim$ 200 meV at 20 eV pass energy (used for core level and resonant photoelectron measurements at higher photon energies up to 1500 eV).

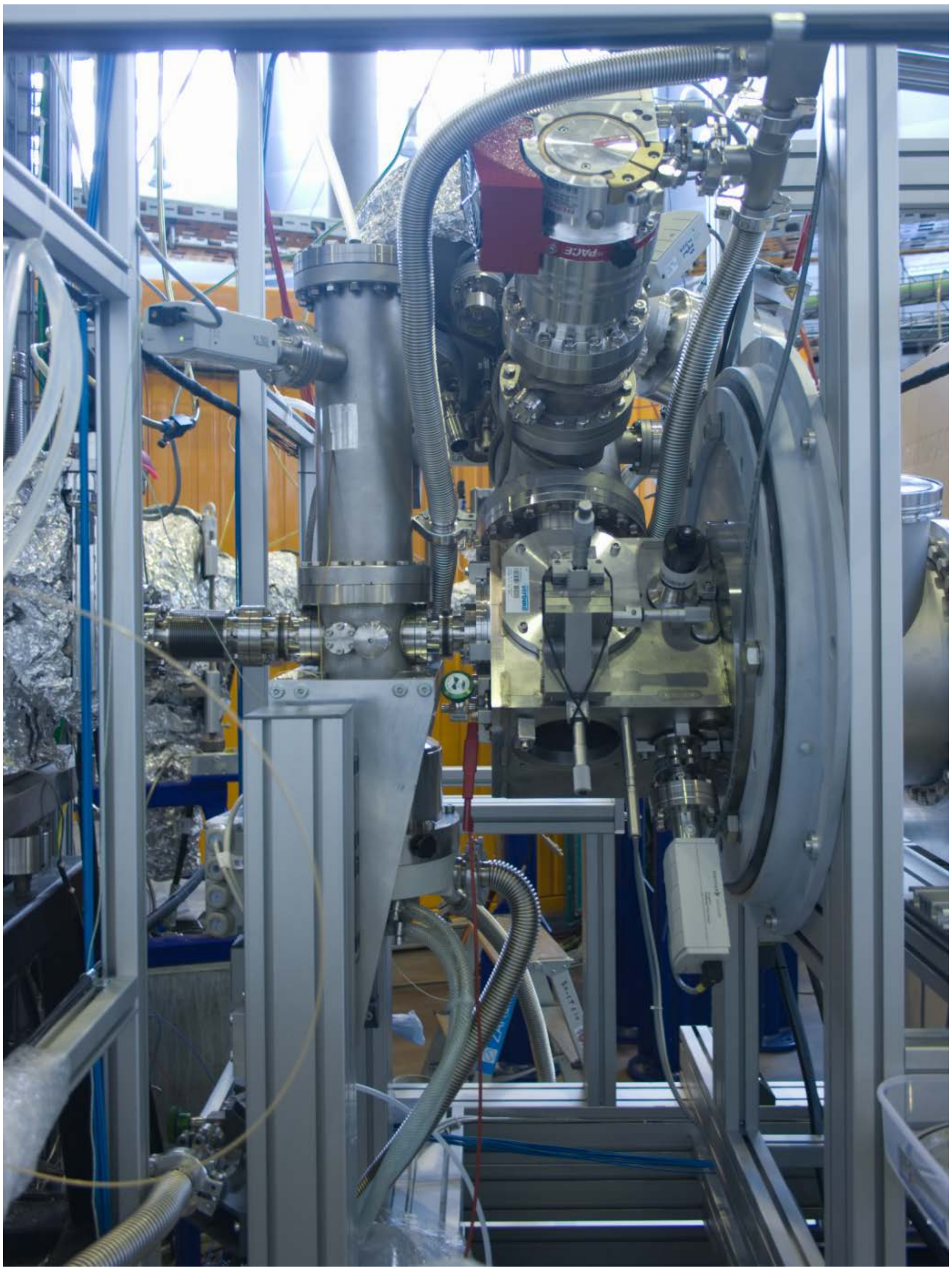

Figure 1: View of the LiquidJet PES endstation. The vacuum chamber is rotatable to measure under different angles between the polarization vector of the incident light and the detector.

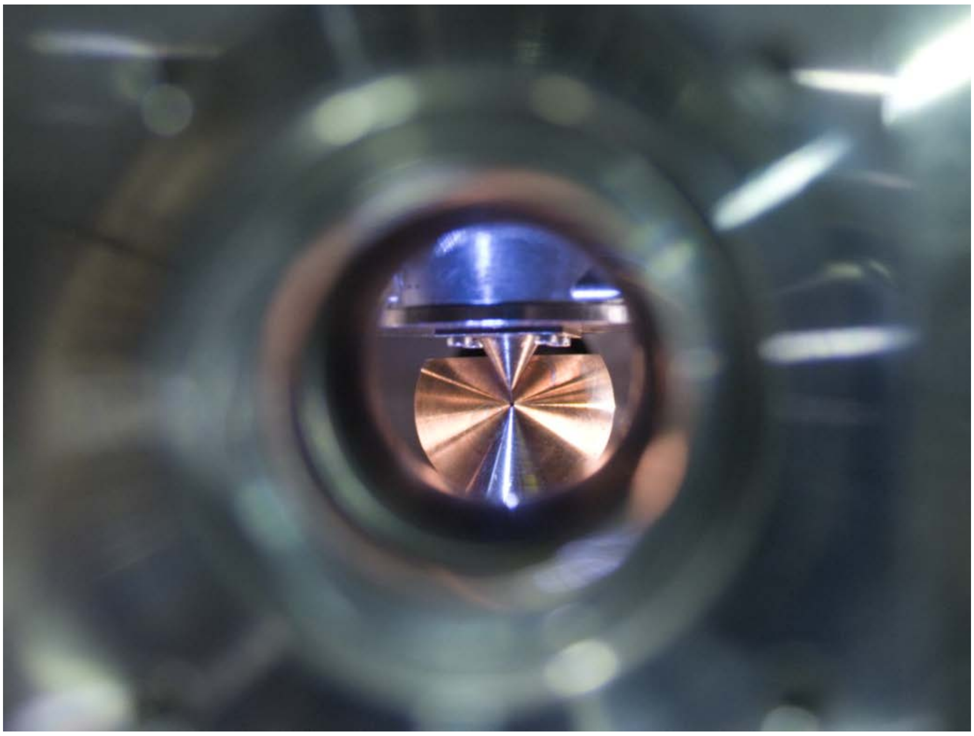

Figure 2: View inside the interaction chamber.

2 Instrument application

Typical applications are:

- Systems: organic and inorganic molecules, and nanoparticles in water
- Electronic structure of liquid water and aqueous solution
- Solute and solvent electron binding energies
- Core-level chemical shifts, lowest ionization energies and reorganization energies
- Structure and composition of solution interfacial structure; depth profiles
- Chemical equilibria at the solution surface
- Ultrafast relaxation processes induced by core-level ionization/excitation
- Ultrafast energy and charge transfer in hydrogen-bonded systems
- Resonant and non-resonant autoionization (Auger) electron spectroscopy
- Electron scattering processes in water and in solution
- Angular-resolved PE spectroscopy from aqueous solution

Methods:

- (Resonant and off-resonant) X-ray photoelectron spectroscopy (XPS, RPES)
- Auger-electron X-ray spectroscopy
- Angular resolved photoelectron spectroscopy (ARPES)
- Partial electron yield measurements (PEY-XPS)

3 Technical data

Monochromator	Designed to match layout of few beamlines
Experiment in vacuum	Yes
Temperatur range	275 – 300 K
Detector	SPECS EA 10-MCP hemispherical electron analyzer
Manipulators	xyz manipulators for positioning the liquid jet and the jet- catching reservoir
Microjet Unit	Temperature-stabilized liquid microjet emerging from typically 18-25 micrometer diameter glass capillaries
Special features	Rotatable vacuum chamber to measure under magic angle (54.7°), 90°, and 0° Second port available for additional detectors (e.g. photon spectrometerfor dispersed fluorescence measurements)

Table 1: Technical parameters of the LiquidJet PES endstation

4 Spectra

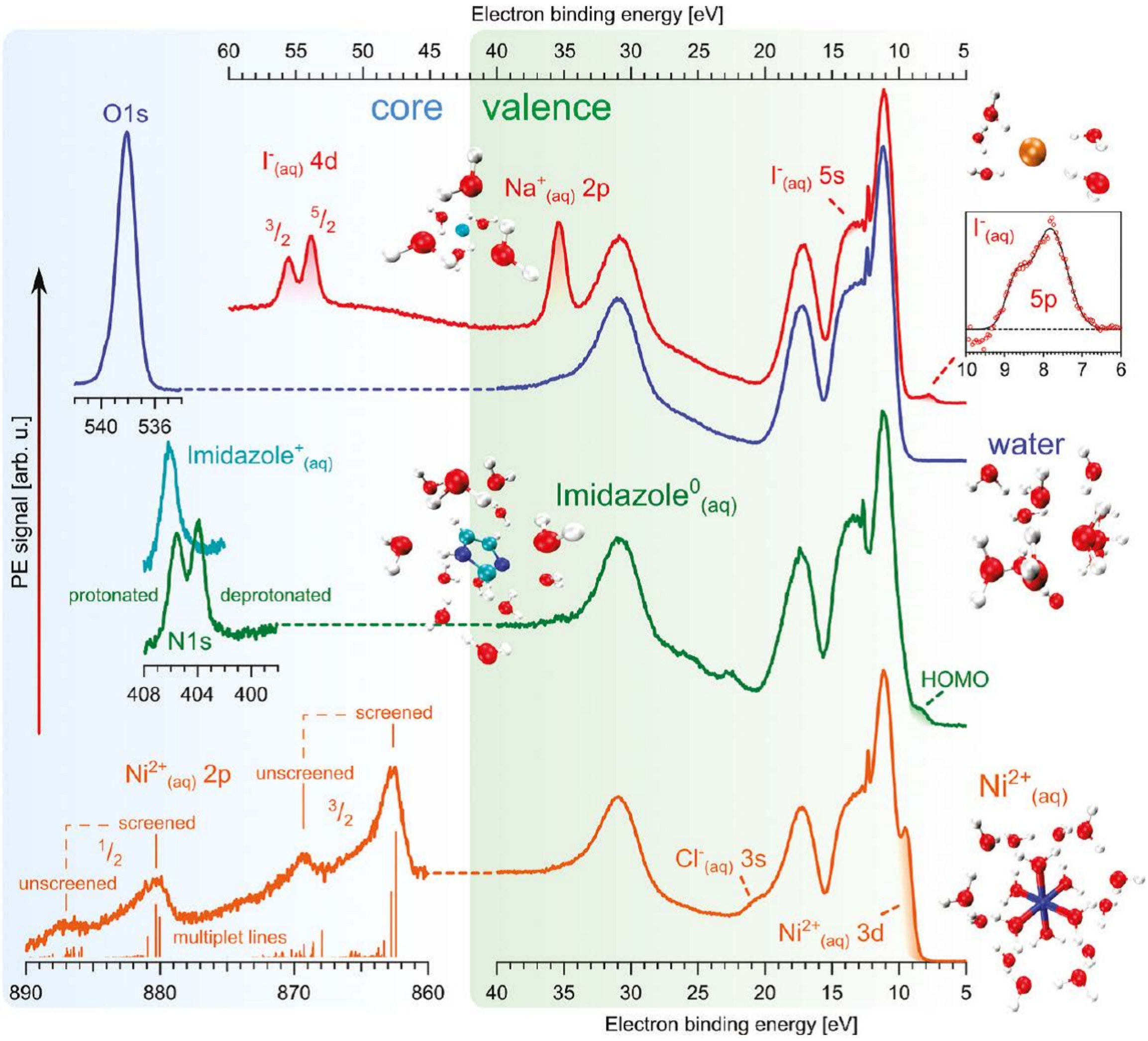

Figure 3: Examples of valence and core-level photoelectron spectra: from neat water (blue, E_{phot} = 200 and 600 eV), from 1 molar NaI aqueous solution (red, E_{phot} = 200 eV), from 1 M imidazole aqueous solution at pH = 10.5 (green, E_{phot} = 200 and 480 eV) and at pH = 2.6 (cyan, E_{phot} = 480 eV), and from 1 M $NiCl_2$ aqueous solution (orange, E_{phot} = 200 and 1000 eV). Important solute peaks are labeled and highlighted.

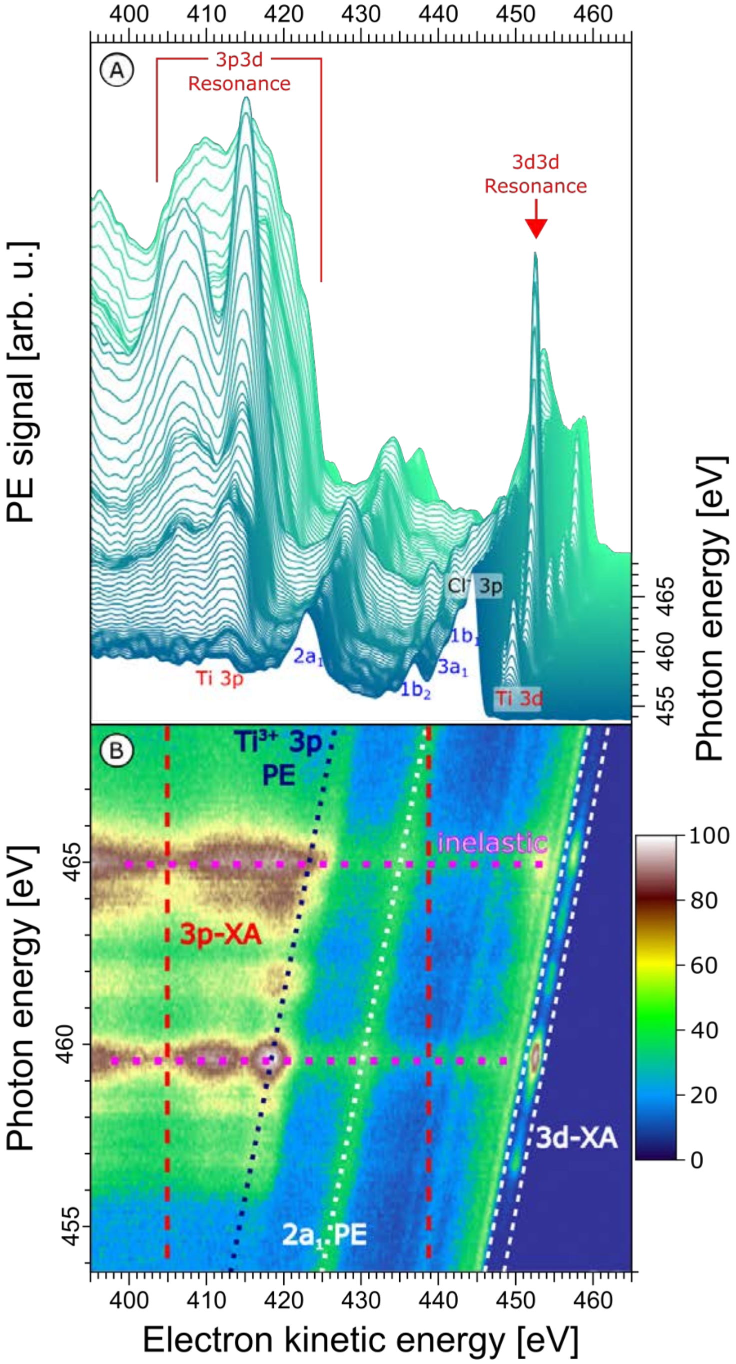

Figure 4: Example for an RPES measurement: Resonant spectra from a 0.8 M TiCl$_3$ aqueous solution are obtained when sweeping the photon energy across the Ti^{3}+ L$_{2,3}$ XA edges. Auger-electron emission ranges corresponding to 2p-3p3d and 2p-3d3d are labeled. 3p-XA and 3d-XA are abbreviations used in labelling the corresponding PEY-XA spectra. Figure **(A)** is a waterfall-spectrum representation, showing the electron distribution curves measured as a function of electron kinetic energy. In **(B)** the same data is presented as a contour map (photon energy *versus* kinetic energy of the electrons, and electron signal is presented by color; intensity increases in the order of blue, green, yellow, brown, and white.

References

Brown, M. A., Redondo, A. B., Sterrer, M., Winter, B., Pacchioni, G., Abbas, Z., & van Bokhoven, J. A. (2013). Measure of Surface Potential at the Aqueous-Oxide Nanoparticle Interface by XPS from a Liquid Microjet. *Nano Letters*, *13*(11), 5403-5407. http://dx.doi.org/10.1021/nl402957y

Margarella, A. M., Perrine, K. A., Lewis, T., Faubel, M., Winter, B., & Hemminger, J. C. (2013). Dissociation of sulfuric acid in aqueous solution: determination of the ohotoelectron spectral fingerprints of H_2SO_4, $HSO_4{}^-$, and $SO_4{}^{2-}$in Water. *The Journal of Physical Chemistry C*, *117*(16), 8131-8137. http://dx.doi.org/10.1021/jp308090k

Pluhařová, E., Schroeder, C., Seidel, R., Bradforth, S. E., Winter, B., Faubel, M., … Jungwirth, P. (2013). Unexpectedly Small Effect of the DNA Environment on Vertical Ionization Energies of Aqueous Nucleobases. *The Journal of Physical Chemistry Letters*, *4*(21), 3766-3769. http://dx.doi.org/10.1021/jz402106h

Seidel, R., Atak, K., Thürmer, S., Aziz, E. F., & Winter, B. (2015). Ti^{3+} Aqueous Solution: Hybridization and Electronic Relaxation Probed by State-Dependent Electron Spectroscopy. *The Journal of Physical Chemistry B*, *119*(33), 10607-10615. http://dx.doi.org/10.1021/acs.jpcb.5b03337

Thürmer, S., Ončák, M., Ottosson, R., N. Seidel, Hergenhahn, U., Bradforth, S. E., Slavíček, P., & Winter, B. (2013). On the nature and origin of dicationic, charge-separated species formed in liquid water on X-ray irradiation. *Nature Chemistry*, *5*, 590-596. http://dx.doi.org/10.1038/nchem.1680

Thürmer, S., Seidel, R., Faubel, M., Eberhardt, W., Hemminger, J. C., Bradforth, S. E., & Winter, B. (2013). Photoelectron Angular Distributions from Liquid Water: Effects of Electron Scattering. *Phys. Rev. Lett.*, *111*, 173005. http://dx.doi.org/10.1103/PhysRevLett.111.173005

Thürmer, S., Unger, I., Slavíček, P., & Winter, B. (2013). Relaxation of Electronically Excited Hydrogen Peroxide in Liquid Water: Insights from Auger-Electron Emission. *The Journal of Physical Chemistry C*, *117*(43), 22268-22275. http://dx.doi.org/10.1021/jp401569w