Optical Layout and Endstation Concept for the Enhanced Liquid Interface Spectroscopy and Analysis (ELISA) Beamline at BESSY-II

SIMONE VADILONGA, PAUL DUMAS, ULRICH SCHADE, KARSTEN HOLLDACK, KARSTEN HINRICHS, GERVIE REICHARDT, TIMM GERBER, ANTVELLE VOLLMER, JAN PHILIPP HOFMANN, HOLGER OERTEL, BERND RECH, ROBERT SCHLOGL, JENS VIEFHÄUS, AND HENDRIK BLUM

1Helmholtz Zentrum Berlin, Berlin, Germany
2Synchrotron SOLEIL, Gif-sur-Yvette, France
3Leibniz-Institüt für Analytische Wissenschaften–ISAS– e.V, Berlin, Germany
4SPECS Surface NanoAnalysis GmbH, Berlin, Germany
5Technical University of Darmstadt, Darmstadt, Germany
6Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Liquid-vapor and liquid-solid interfaces drive numerous important processes in the environment and technology, such as the sequestration of CO₂ by the oceans, the uptake and release of trace gases by aerosol droplets, the corrosion of metals, and reactions in electrochemical energy conversion and storage devices. Our understanding of the physical and chemical properties of liquid interfaces under realistic environmental and operating conditions on the molecular scale still falls short of what has been achieved for solid-vapor interfaces over the past decades. This limitation hampers the development of, e.g., more precise climate models and electrochemical devices with increased efficiency.

The main reason for this situation is the often greater difficulty in (1) the preparation of liquid interfaces (compared to solids) with controlled properties and (2) their investigation with high interface specificity under realistic conditions. This is partly due to the spatial fluctuations in the position of the interface and the fast diffusion from the interface into the bulk and vice versa (liquid-vapor), as well as the challenge of selectively detecting a signal from a nanometer-wide region that is wedged between two condensed phases (liquid-solid). In addition, traditional (vacuum-based) methods for the preparation of clean surfaces are not applicable for liquid interfaces. The challenge is thus investigating these critical interfaces with increased fidelity while, in parallel, developing new methods for their preparation and interrogation.

The Enhanced Liquid Interface Spectroscopy and Analysis (ELISA) beamline at BESSY-II aims at addressing these scientific and technological challenges through a concept that tailors both beamline optics and endstation infrastructure to the specific requirements of liquid interface science. The beamline combines soft X-ray and infrared (IR) radiation, both originating from the storage ring, which are incident on the sample surface at the same time and the same location. While core-level spectroscopy, in particular ambient pressure X-ray photoelectron spectroscopy (APXPS), provides information on the elemental and chemical composition as well as potential gradients at the interface, reflection-absorption IR spectroscopy (RAIRS) offers complementary information about the orientation and bonding of molecules at the liquid-solid and liquid-vapor interface, expands the pressure range of in situ and operando experiments, and provides an excellent method to monitor possible radiation-induced damage to the interface and surrounding media in X-ray-based spectroscopies.

The advantage of IR radiation from a synchrotron over that originating from a conventional globar source is its high brilliance, which allows matching the IR beam to the same spot size as the X-ray beam, crucial for the correlation of the data obtained by vibrational and X-ray-based methods. There are also opportunities for time-resolved combined soft X-ray and IR measurements, since both originate from the same source and thus have the same time structure. Although the advantages and opportunities of a combined soft X-ray and IR beamline have been recognized over the past decade [1–4], such a beamline has yet to be realized. However, experiments that combine non-synchrotron-based IR, UV-Vis or Raman spectroscopy with scattering and spectroscopy methods based on X-rays from a synchrotron have already been performed in the hard [e.g., 5–10] and soft [11] X-ray regime.

The future ELISA beamline at BESSY-II, which is anticipated to be operational in 2024, will enable combined RAIRS and APXPS experiments with temporal and spatial overlap, covering a wide energy range across two branches, both in the X-ray (30–2500 eV) and IR domain (10–10,000 cm⁻¹). The low energy branch is dedicated to in situ studies of functional interfaces, in particular those with relevance for batteries and (photo)electrochemical devices, and covers the far UV range (including the Li K edge) up to the transition metal L edges. The high energy branch is dedicated to the investigation of liquid-vapor interfaces, for both fast flowing (e.g., jets and droplet trains) and static liquids (e.g., in a Langmuir trough). In the following, we describe the optical layout and endstation concept of the ELISA beamline at BESSY-II.
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Basic design and operation criteria

The main design considerations for the beamline and endstations are: (1) flexible and adaptable sample environments for in situ and operando experiments in diverse fields, spanning from (photo)electrochemistry and catalysis to atmospheric chemistry; (2) optimum use of the available beamtime; (3) flexibility in the combination of IR and X-ray-based experiments; (4) compatibility with experiments using a wide array of solid, liquid, and gaseous samples and reactants, including toxic gases.

Based on these criteria, a branched beamline design was chosen, with one branch optimized for valence photoelectron spectroscopy and shallow core-level X-ray absorption spectroscopy, and the second branch for X-rays with energies exceeding 2 keV, and a downward pointing X-ray beam at the sample location for the investigation of static liquid interfaces. While most beamlines feature either horizontal or upward pointing X-rays, downward pointing incident X-rays enable measurements of static liquid-vapor interfaces, but also the preparation of aqueous ice samples with freely adjustable solute concentration and pH. In addition, this geometry might also be favorable for experiments at liquid-solid interfaces, such as in a modified dip-and-pull setup (see Figure 1), as was already demonstrated for ionic liquids in lab-based experiments [12].

Synchrotron-based infrared experiments can be performed in either of the two branches, in parallel with X-ray-based measurements, or with IR in one and X-rays in the other branch. The branched concept is beneficial for the efficient use of available beamtime since the adaptation of the sample environment to a new type of experiment on a given branch can be performed while the other branch is taking beam, thus avoiding unnecessary downtime of the beamline. In the following, the optical layout of the branches will be presented.

General X-ray optical design

Besides optical considerations, the space restrictions at a fully equipped facility like BESSY II were challenging aspects for the optical layout. Under these circumstances, the most suitable location for installation of ELISA was determined to be Section 3 of the storage ring BESSY II [13]. Figure 2 shows the suggested beamline layout.

The source for the X-ray radiation is inside the first dipole bend of Section 3, whereas the IR radiation (not shown) is extracted from the second subsequent dipole of this section. The two branches share the first mirror (M1) and the monochromator, in green in Figure 2. M1 is a toroidal mirror that collimates the X-ray beam vertically and focuses it horizontally on the exit slit of the high energy branch. The vertically collimated beam is guided to a plane grating monochromator with blazed gratings (400 l/mm and 1200 l/mm) of the SX700 type [14]. Additionally, the monochromator will be equipped with a pair of multilayer optics (pre-mirror and grating, which are interchangeable with the standard optics) to increase the reflectivity at higher energies (>2000 eV). The two exit branches are split, making use of two focusing mirrors positioned just after the monochromator. We chose to use two mirrors in independent vacuum chambers instead of a switching mirror unit to increase the separation between the endstations. The final optics design of ELISA is still in progress, as the science case of ELISA would benefit from reaching even higher photon energies. Therefore, we are currently evaluating the optional multi-layer optics for both pre-mirror and grating of the collimated PGM [15, 16], which could have implications on the design parameters of the optical elements relevant for the high-energy branch.

High-energy branch

The first branch (“high energy”) is optimized for energies of 250 eV to at least 2000 eV, and has a downward pointing beam under a total angle of 3 deg. This configuration enables experiments using high kinetic energy electrons at ambient water vapor and trace gas pressures; i.e., total pressures of about 30 mbar, as well as buried liquid-solid interfaces. As mentioned earlier, the downward direction of the beam allows us to probe static (i.e., horizontal) liquid-vapor interfaces, but also special solid-liquid interface configurations; e.g., solid-liquid interfaces prepared using a shallow angle between the sample and the liquid surface.

The high-energy branch optical elements are represented in pink in Figure 2. The first element after the monochromator is a cylindrical mirror (M3 high) under 1.5° incidence angle and deflects the beam towards the right downstream. The light is vertically focused on the exit slit, and refocused by a pair of Kirkpatrick–Baez mirrors.

Figure 1: Some experimental schemes that can be realized using a downward pointing beamline. (a) Measurement of the heterogeneous chemistry of static liquid-vapor interfaces. (b) Investigations of heterogeneous reactions on ice-vapor interfaces, including those of frozen seawater. (c) Measurement of liquid-solid interfaces using a modified meniscus (or dip-and-pull) geometry.
first of these mirrors ($KB_{high}$) reflects the light right downstream with an incident angle of 1.5° and focuses the light horizontally, while the second mirror ($KB_{2high}$) focuses the light vertically and reflects it downwards with an angle of 3°. The focal distance from the center of $KB_{2high}$ is 1.5 m. A pair of KB mirrors was chosen to be able to individually tune the vertical and horizontal focus size and beam position, which is particularly important in APXPS experiments where the entrance aperture of the differentially pumped electrostatic lens systems has a small (~0.2 mm diameter) acceptance area.

**Low-energy branch**

The second branch (“low energy”) is optimized for energies from 20 eV to more than 1000 eV and is dedicated to valence band and soft X-ray spectroscopy, including X-ray absorption spectroscopy at the Li K-edge. Its optical elements are shown in blue in Figure 2.

The first element after the monochromator is a cylindrical mirror ($M_{3low}$) under 3.5° incidence angle and deflects the beam towards the right downstream (see Figure 2). Such a steep angle was chosen to increase the physical separation of the two branches and also to reduce the contributions of higher orders in the low-energy branch. The light is vertically focused on the exit slit, and refocused by a pair of Kirkpatrick–Baez mirrors. The first mirror ($KB_{1low}$) reflects the light downstream and it focuses the light horizontally, while the second one ($KB_{2low}$) focuses the light vertically and reflects it upwards. The incident angle of the light on both mirrors is 1.5°. The focal distance from the center of $KB_{2low}$ is 1.5 m, as in the high-energy branch.

The beamline design and preliminary simulations show that a photon flux of $\sim 10^{10}$ ph/0.1 A/1 mrad/0.1% BW at a focal size of (h × v)100 × 20 µm² for the high-energy branch, and 200 × 20 µm² for the low-energy branch, can be achieved (see Figure 3). A small vertical focus is particularly important for the high-energy branch in experiments with static liquid, where the X-ray spot will be elongated by a factor of ~20 at a shallow incidence angle of 3 deg.

**Combination of IR and X-ray radiation**

The main considerations for the source of IR radiation for simultaneous measurements with soft X-rays are: (1) broad and continuous

![Figure 2: Principal layout of the optical elements of the ELISA beamline. For details, see text.](image-url)
Figure 3: Calculated photon flux (full line) and bandwidth (dotted line) of the ELISA beamline for the low-energy (blue) and high-energy (red) branch. The values are calculated for a 400 lines/mm grating for the low-energy branch, and a 1200 lines/mm grating for the high-energy branch, for an exit slit height of 50 µm.

Figure 4: Schematic endstation concept for the high-energy branch. Exchangeable sample cells are specifically designed for, e.g., the investigation of static liquid-vapor interfaces; the preparation of jets and droplet trains; the measurement of liquid-solid interfaces; and the investigation of heterogeneous catalysts. The sample cell components are shown in orange. All shared instrumentation is shown in black.
range of wavelengths (from near to far IR) for the investigation of a wide range of samples and phenomena (e.g., vibrational to electronic excitations), including fundamental processes at liquid-solid and liquid-vapor interfaces; (2) spatial overlap of X-ray and IR beam on the sample; (3) simultaneous IR and X-ray-based measurements; (4) spot size as small as possible, on the order of 0.2 mm diameter, to match requirements in combined experiments with X-ray-based spectroscopy; (5) high sensitivity (i.e., low signal-to-noise) for the detection of species at sub-monolayer coverages.

Different IR sources for combined X-ray and IR-based measurements were considered, including a globar (thermal) source, supercontinuum IR laser, difference frequency generation (DFG), external cavity quantum cascade laser, and IR from the storage ring. The IR lasers have a brightness advantage over IR from the storage ring. However, there is a clear advantage in using IR from the storage ring that is due to its broad and continuous range of wavelengths, excellent beam stability and thus high signal-to-noise ratio, and sufficiently high brightness. An additional benefit of synchrotron-based IR is its inherent time structure, which is identical to that of the X-rays, where phase shifts relative to the X-ray pulses can easily be tuned, which opens up opportunities for simultaneous combined IR and X-ray investigations with nanosecond time resolution.

The details of the IR optics layout are currently being developed. The most likely source for IR radiation is dipole 3.2, which is downstream from dipole 3.1, the source for the X-rays. The IR and X-ray radiation will be transported to the endstations in separate beam pipes. Preliminary calculations of the spot size of the IR beam demonstrate that a spatial overlap between the X-ray and IR beam on the sample is achievable.

**Endstation concept for the high-energy branch**

The endstation layout is based on the shared use of major analysis components, such as FTIR and APXPS spectrometers as well as a 2D CCD-detector for X-ray scattering, and the implementation of exchangeable sample chambers that are tailor-made for the specific investigation in question. This is schematically shown in Figure 4. Parts shown in black are shared infrastructure, while the orange elements are components of exchangeable sample chambers. The high-energy branch endstation will feature dedicated sample chambers for (1) fast-flowing liquid samples, such as cylindrical and flat jets as well as droplet trains; (2) static liquids, as for instance in a Langmuir trough; (3) electrochemical experiments, including at solid-liquid interfaces; and (4) heterogeneous catalysis at solid-vapor interfaces. The position of the photoelectron spectrometer is adjustable from vertical to horizontal for optimum measurement conditions for the different sample types.

To avoid cross-contamination between the different experiments, none of the interior walls of the four sample chambers are shared. This includes the front-end of the electrostatic lens of the photoelectron spectrometer, the SiNx window, window holder and window manipulator for the incident X-rays, as well as the X-ray window and window holder to the CCD detector for X-ray scattering. Avoidance of cross-contamination is especially crucial for investigations of static surfaces in the presence of gas atmospheres. In current systems with exchangeable sample chambers, the beamline and spectrometer parts facing the sample are usually not part of the sample chamber and are thus a source of cross-contamination.

**Endstation concept for the low-energy branch**

Similar to the high-energy branch endstation, the low-energy branch will be equipped with a modular endstation, in which ambient pressure X-ray photoelectron spectroscopy as well as near-edge X-ray absorption fine structure and synchrotron IR reflection absorption spectroscopy can be performed in a space- and time-correlated manner. Exchange of sample environment modules will be possible with limiting cross-contamination between experiments. Initial focus will be on solid-liquid interfaces with relevance to (photo)electrochemical energy conversion and storage with ultra-thin model electrolyte layers and their investigation in the core- and valence-level electronic structure as well as mid-IR vibrational spectroscopy regimes. Because of the low-energy capabilities of the branchline, a differentially pumped X-ray beam entry will be realized enabling X-ray absorption at the Li K-edge; for higher X-ray energies, a gate-valve mounted SiNx window will be used to separate the vacuum in the beamline from the gas atmosphere in the endstation.

There are a number of other pieces of equipment and infrastructure that are required by the various classes of experiments and that can be shared between the user groups for a more cost-effective operation. These include gas handling and analysis, electrochemical characterization tools, solar simulator, ozone/OH radical sources, and laser heating. The entire endstation area will be housed in a hutch to enable safe operation of experiments that involve hazardous gases.

**Conclusions**

The ELISA beamline will combine soft X-rays and IR radiation, both from the synchrotron, with spatial and temporal overlap. The full beamline concept, as partly described here, provides a set of state-of-the-art methods for the preparation and investigation of liquid interfaces. The modular endstation design helps to expedite the development of new concepts for the interrogation of heterogeneous processes at liquid interfaces. It is anticipated that these factors will facilitate interdisciplinary research and result in new approaches for the investigation of the physical chemistry of liquid interfaces.

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**References**

1. A. Marcelli et al., *Anal. Bioanal. Chem.* **397**(6), 2095 (2010). doi:10.1007/s00216-010-3745-1
2. A. Marcelli et al., *J. Synchrotron. Rad.* **19**(6), 892 (2012). doi:10.1107/S0909045512041106
3. M. A. Newton, and W. van Beek, *Chem. Soc. Rev.* **39**(12), 4845 (2010). doi:10.1039/b919689g
4. J. Schnadt et al., *J. Phys.: Condens. Matter.* **32**, 413003 (2020).
5. W. Braset et al., *Science* **267**(5200), 996 (1995). doi:10.1126/science.267.5200.996
6. V. Briois et al., *J. Phys. Chem. A.* **109**(2), 320 (2005). doi:10.1021/jp046691t
7. M. A. Newton et al., *Phys. Chem. Chem. Phys.* **9**(2), 246 (2007). doi:10.1039/B613251K
8. P. Innocenzi et al., *J. Phys. Chem. C.* **111**(14), 5345 (2007). doi:10.1021/jp066566c
9. U. Bentrup et al., *Nucl. Instrum. Methods Phys. Res., Sect. A* **607**, 247 (2009).
10. C. Kongmark et al., *Chem. Commun.* (32), 4850 (2009). doi:10.1039/b007935a
11. A. R. Head et al., *Surf. Sci.* **665**, 51 (2017). doi:10.1016/j.susc.2017.08.009
12. D. Weingarth et al., *Electrochem. Commun.* **13**(6), 619 (2011). doi:10.1016/j.elecom.2011.03.027
13. https://www.helmholtz-berlin.de/user/apply-for-beamtime/infrastructure/index_en.html
14. H. Petersen, *Opt. Comm.* **40**(6), 402 (1982). doi:10.1016/0030-4018(82)90040-2
15. A. Sokolov et al., *Opt. Express* **27**(12), 16833 (2019). doi:10.1364/OE.27.016833
16. R. Follath, *Nucl. Instr. Meth. A* **467–468**, 418 (2001).