MAX IV Beamline Review Report

HIPPIE

March 2020

Review of the HIPPIE beamline at MAX IV Laboratory

March 2020

Jan Knudsen, Mattia Scardamaglia, Joachim Schnadt, Andrey Shavorskiy, Suyun Zhu

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1. Technical Status of HIPPIE

General Introduction

HIPPIE is an undulator-based soft x-ray beamline for ambient pressure x-ray photoelectron spectroscopy (APXPS) on the 3 GeV electron storage ring of the MAX IV Laboratory with a collimated plane grating monochromator (cPGM) design. The beamline provides photon energies between 250 and 2200 eV. HIPPIE is one of two beamlines for APXPS at the MAX IV Laboratory, the other one being the SPECIES beamline on the 1.5 GeV ring.

HIPPIE can supply two branch lines with photons. Switching occurs at the vertically focusing mirror M3. Presently only one branch line is built up completely, with the second being built up until the exit slit of the cPGM. So far there exists no second M3 mirror required in the implemented switching design.

The APXPS end station, based on a Scienta Omicron HiPP-3 analyser, features a highly modular design. The entire sample environment can be exchanged, with the electron energy analyser, beamline entrance and gas system left in place. Two principal sample environments have been implemented so far, one for experiments on liquids, including a liquid jet, and electrochemical samples (dip-and-pull), one with an ambient pressure cell-based dual UHV/AP environment. The latter environment allows for further variation of the sample environment by exchange of the AP cells. The AP cells can be combined *in situ* with equipment for laboratory PM-IRAS measurements.

HIPPIE is one out of approximately 22 synchrotron-based APXPS experiments worldwide, at 15 synchrotron radiation facilities. It is quite unique in its excellent conditions not only for the lower soft x-ray range, but also for the 1000 to 2000 eV range, its modular sample environment capabilities, prime possibilities for gas delivery and gas sampling and combination with other characterisation methods.

1.1. Beamline

1.1.1. Source

Technical characteristics of the insertion device

The photon source of the HIPPIE beamline is an APPLE-II type undulator (EPU53) with a period length of 53 mm, and the total number of periods 70 (the undulator is ca 4 m long). The minimum photon energy is 250 eV and the minimum gap 11 mm. The design of EPU53 is based on glued magnet pairs developed at MAX IV for magnet holders with wedges for both transverse planes. The operational envelopes of the HIPPIE EPU gap versus the phase were defined by the minimum photon energy of 250 eV, i.e. the maximum allowed deposited power on the downstream vacuum chamber at 500 mA beam current. Figure 1 shows the envelope implemented in the control system for the HIPPIE EPU to achieve a photon energy of 250 eV from linear horizontal via circular to linear vertical polarisation with an effective K-value of 3.3.

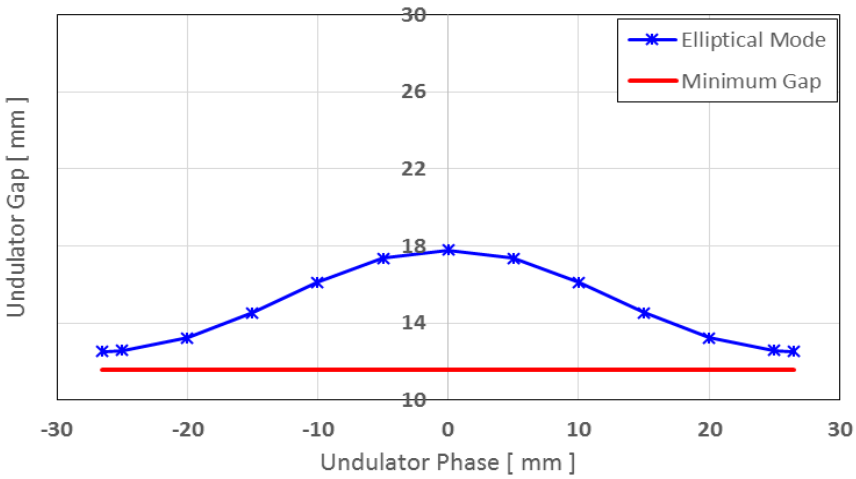

Figure 1. Operational envelope of the HIPPIE EPU53 with 250 eV limit in elliptical mode

As of February 2020, the HIPPIE EPU53 is in standard user-mode for the horizontal polarisation mode. Both elliptical and inclined modes are commissioned and available in the control system. However, the calibration of the polarisation angles in the inclined mode still needs to be performed before giving this functionality to the users. In spring-2020 user run only one group has requested polarisation control – to be able to perform measurements on the liquid microjet in magic angle geometry. The polarisation measurements are scheduled to take place in week 10 of 2020.

Figure 2. HIPPIE EPU-53 spectra at three different gas openings. FE mask opening are: H x V= 1.4 x 1.9 mm2, exit slit 50µm, and all other masks fully open shows undulator spectra for the first harmonic for three different gap settings and 50 µm exit slit. Clearly with current alignment the beamline acceptance is not at optimum – the shape of harmonic is asymmetric and the width – higher than expected. Alignment of both optical elements and the electron beam in the R3 is also scheduled to W10 and Tuesdays following weeks.

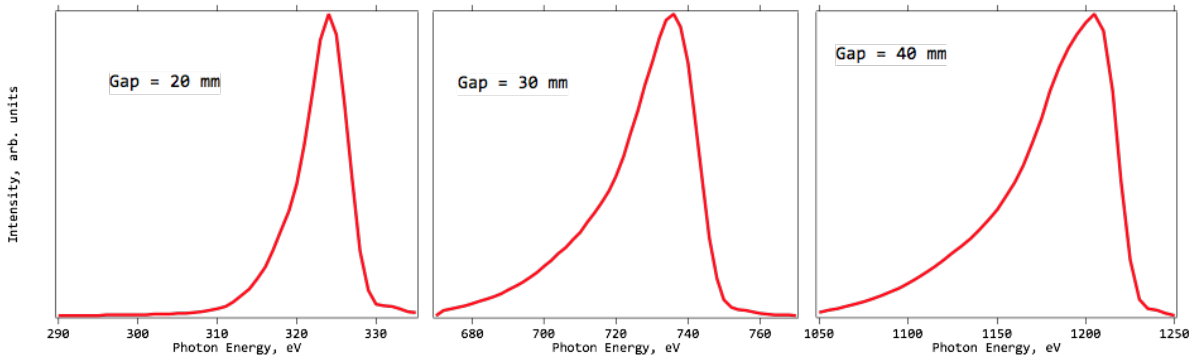

Figure 2. HIPPIE EPU-53 spectra at three different gas openings. FE mask opening are: H x V= 1.4 x 1.9 mm2, exit slit 50µm, and all other masks fully open

1.1.2. Beamline Optics and Diagnostics

Optical design of the beamline

The layout of the HIPPIE beamline is shown in Figure 3. The beamline makes use of a collimated plane grating monochromator (c-PGM) design developed at BESSY. The first optical component is a toroidal mirror (M1) that collimates the beam vertically and focuses the beam horizontally onto the exit silt. The monochromator has a plane mirror (M2) and a plane grating (PG) with 1200 l/mm line density. After the monochromator, a cylindrical mirror (M3) focuses the beam vertically onto the exit silt. A single toroidal mirror (M4) accomplishes the refocusing

for the APXPS branch, located at 49 m from the light source. All mirrors are made of Au-coated silicon. The basic parameters of all optics are shown in Table 1. M1 and M2 are internally cooled, whereas the PG is side cooled via water-cooled blocks, and M3 by simple contact with a cooper brace. M4 receives so little heat that there is no need for cooling.

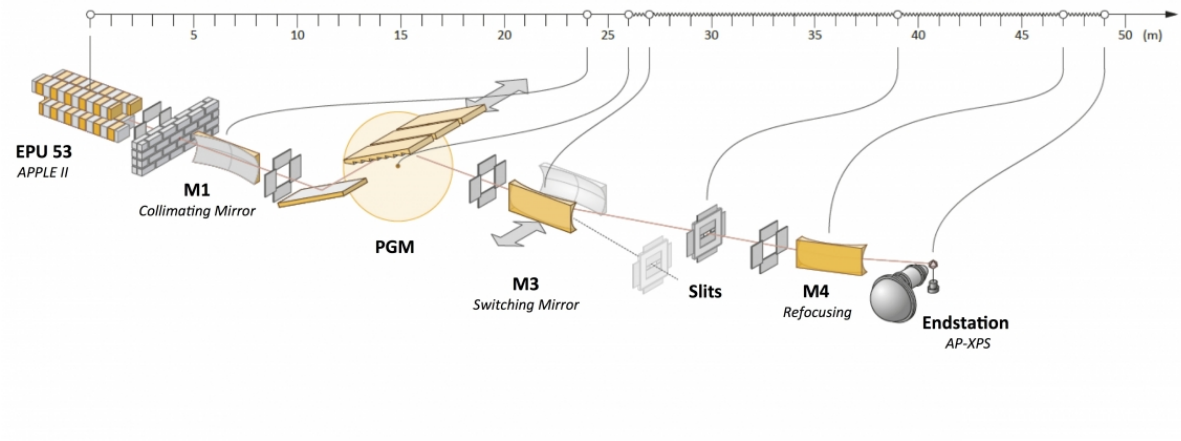

Figure 3. Optical layout of HIPPIE beamline

A novel mirror chamber was designed in collaboration between MAX IV and FMB Berlin. It consists of a vacuum vessel, inside which a mirror is rigidly mounted, and a separate chamber for pumping and beam diagnostics. The movement of the mirror is accomplished by moving the entire vacuum vessel by means of five motors. The M3 and M4 pumping chambers contain single-axis manipulators with a selection of diagnostic tools: an AXUV100 photodiode, a YAG crystal, and a gold mesh for drain current measurement. The X-ray beam entering the monochromator, M3 and M4 can be shaped by four independently moving blades each. The light entering the beamline can also be shaped in the frontend by water-cooled masks. These masks are used primarily to select the central part of the undulator cone and to decrease the heat load on the beamline components.

Table 1. Parameters of the optical components of HIPPIE beamline

Optical element	M1	M2	PG	M3	Exit slit	M4
Shape	toroid	plane[a]	plane[a]	cylinder[b]	rectangle	Toroid
Deflection	hor.	vert.	vert.	Hor.	-	Hor.
Distance(mm)	24000	Var.	26000	27000	39000	47000
Incidencent Angle	1°	0°- 9°	0°- 12°	1.5°		1.5°
Geom. Size (mm)	370×60×60	420×60×60	140×25×45	140×40×40	-	150×40×40
Opt.size (mm)	320×10	370×10	130×10	120×28	Adj.	130×20
Substrt. material	Si	Si	Si	Si	Si	Si
Coating	Au,40±5nm	Au	Au	Au	Au	Au
Roughness(Å)	2.53	2.1	3	1.9	-	3
Slope error(arcsec)	0.17/0.43	0.024/0.05	0.02/0.04	0.07/0.25	-	0.19/2
Entrance arm(mm)	24000			-/∞		8000
Exit arm(mm)	15000/∞			-/12000		2000/2025

Parameters	R=1216580 mm ρ=837.6 mm		Blazed N=1200 l/mm Blaze 1.1°	ρ=628.25 mm ±0.25%	width 5mm height 0...500µm	R=129500.0 mm ±0.5% ρ=84.60 mm ±0.25%
Absorbed power at 263 eV (undulator peak power 4.7 kW)	658 W	170 W	4 W			

1.1.3. Current Performance

Comparison to DDR. Flux, resolution, beam stability, carbon deposition

In this section, we present some performance data for the beamline. Even though the beamline is fully operational, we still continue to improve the beamline alignment and measure the ultimate performance in terms of flux, resolution, beam size, etc. We hope and expect that this will be finalised within the first half of 2020 (a dedicated campaign is planned in week 10 in 2020, and in addition we have the commissioning day if users do not require a bakeout every Tuesday).

The beamline flux (Figure 4. Beamline flux measured before (blue circles) and after (red squares) oxygen cleaning. Measurements have been done with exactly same beamline settings and corrected for 500mA ring current and photodiode size. Black triangles show flux predictions for the same , red squares) was measured using a photodiode (AXUV 1000 from international radiation detections) and corrected for the photodiode's sensitivity and normalised to 500 mA ring current. The exit slit opening was 50 µm which at 1000 eV beamline energy resulted in R= 6000. The result shows that the beamline flux is higher than 10^{12} photons/s up to a photon energy of 2000 eV.

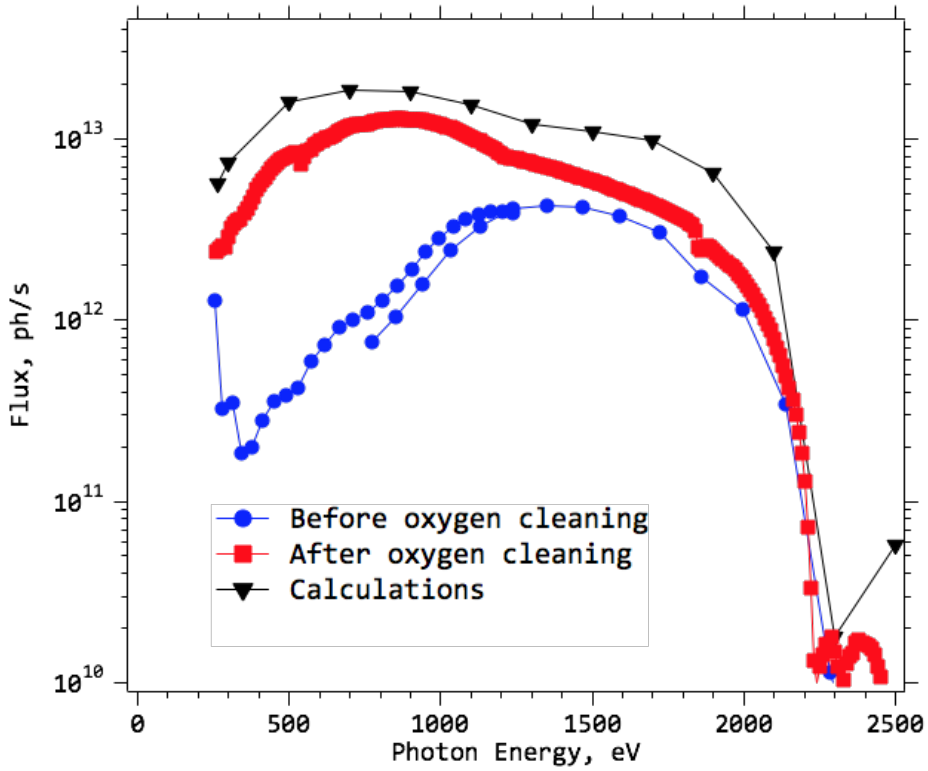

Figure 4. Beamline flux measured before (blue circles) and after (red squares) oxygen cleaning. Measurements have been done with exactly same beamline settings and corrected for 500mA ring current and photodiode size. Black triangles show flux predictions for the same beamline settings

As is visible form the beamline flux curve, the HIPPIE beamline has already experienced a rather dramatic drop in flux below a photon energy of 1200 eV (Figure 4, blue circles). The recent introduction (week 7 of 2020) of ca 1×10^{-6} mbar oxygen into the monochromator and constant exposure since, has drastically reversed the trend: at certain energies the flux has increased 20-fold since the beginning of the treatment, and for all photon energies below 1200 eV a significant amelioration is visible. Also, apparent visible reduction of "carbon stripe" on the mirror surface itself (Figure 5). Hence, the beamline's performance had been impacted by substantial carbon deposits, which are removed by the oxygen treatment. Due to these deposits the final alignment could not previously been finished as well as final measurements of the resolution and beam profile/size could not been performed. However, flux values measured after oxygen cleaning are already close to those calculated for the same beamline settings (Figure 4, black triangles), which indicates the alignment of the beamline if close to its final state. Also, past realignment attempts have not led to noticeable improvement and that the beam shapes measured just before M4 are as expected.

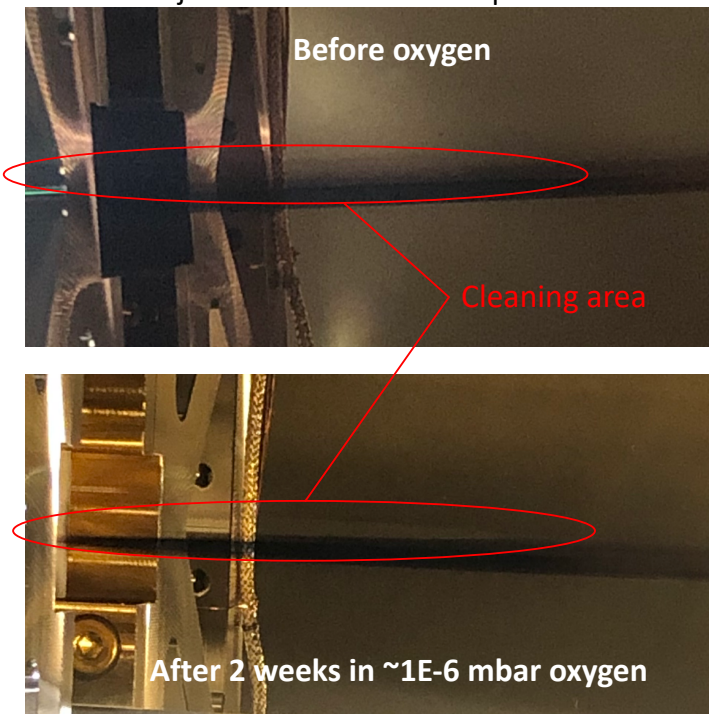

Figure 5. M2 surface before and after oxygen cleaning

The stability of the beam is evaluated from a measurement of the intensity of the photodiode signal (or XPS signal) over time at given energy. An initial grating misalignment led to the loss of beam whenever the beamline energy was changed; this has been corrected since and the beam motion with energy change is negligible now. Nevertheless, the beam is still not stable, which is experienced as a beam loss over time. The reason for this instability is the result of inhomogeneous (in time) heating of M1. Although the mirror is internally cooled, we still observe beam motions, which can be compensated by adjusting the pitch of the mirror. We are confident that this is due to heating of the very compact vacuum vessel in which the mirror block is rigidly fixed to a wall by secondary electrons. The motion of the mirror is then accomplished by moving of the whole chamber. Clearly, even the small deviations of the chamber's temperature could lead to changes in mirror positions without the control system

noticing this. This behaviour has been observed at least at another operational beamline where the same mirror mounting system is used. The beamlines using the system are presently planning a campaign to improve the cooling design (e.g. in front of the mirror surface), but implementation of such solution will require re-mounting of the mirror and bakeout and thus shall be scheduled well in advance. Meanwhile a feedback system has been implemented to constantly adjust M1 pitch to compensate heating instabilities. The feedback system works very well for our users, and with the feedback switched on the beam is sufficient stable for use in the experiments.

1.2. APXPS Endstation

1.2.1. General description and vacuum layout

Prep chamber, Analysis chamber, UFO, storage, electron energy analyser, IRRAS setup, brief discussion of AP cells and modes of operation, proposed, but non-constructed cells

The APXPS end station (Figure 6) was produced by PREVAC sp. z o.o based on tender specifications and in close collaboration with the HIPPIE team. It is designed to allow for different sample environments including both the cell-in-cell and exchangeable-cell concepts. When switching between the two different environments, the beamline entrance and electron energy analyser remain in place, while the sample environments are exchanged. In addition, the end station has a stationary UHV preparation chamber (base pressure 1×10^{-10} mbar), load lock chamber (5×10^{-9} mbar) with a sample storage carousel for six samples and with halogen lamps for quick bakeout, and radial distribution chamber (UFO, 1×10^{-10} mbar) for transfer of samples between the different parts of the system and likewise equipped with a sample storage carousel for six samples. The average time for sample transfer between any two places is less than a minute.

The preparation chamber is a typical surface science preparation vacuum chamber equipped with LEED (OCI BDL800IR-3G), QMS (MKS Microvision 2, up to 200 amu), QCM Balance (Prevac QO 40A1), ion source (Prevac IS 40C1), a range of pumped ports for user equipment such as evaporators and a gas/vapour dosing system for four gases plus a noble gas for sample sputtering. The chamber manipulator is equipped with two slots for sample heating: an e-beam heater (up to 900° C) and a low degassing resistive heater (up to 600° C). In the resistive heater slot, the sample can also be cooled down to -100° C using the liquid nitrogen. Pumping of the preparation chamber is achieved using a turbomolecular (Pfeiffer HiPace 300) and an ion getter pump (Gamma Vacuum TiTan 400L). The in-cell configuration features, in addition to the above-mentioned vacuum vessels, an analysis chamber (1×10^{-10} mbar), AP cell chamber (MP, 1×10^{-9} mbar) and a quadrupole mass spectrometer (QMS, 1×10^{-10} mbar) chamber. All chambers are separated from each other by gate valves. On the MP chamber a manipulator is mounted that carries the AP cell. The AP cell can be exchanged; presently, there exists one setup, the catalysis AP cell setup.

The analysis chamber is a vacuum vessel of similar size as the preparation chamber. It features the same pumping scheme and a UHV manipulator with similar heating and cooling performance. It is connected to the end station gas system. The MP chamber holds the AP cell. It can be separated from the analysis chamber when doing UHV XPS measurements.

The end station is designed to allow measurement of XPS in both UHV and AP conditions. In AP conditions an aperture of 0.3 mm diameter is placed on the analyser entrance. This aperture is not a fixed part of the analyser, but is rather part of the sample environment, which implies that measurements in UHV conditions are performed with a larger analyser opening.

The analysis and MP chambers and the AP cell manipulator are mounted on moveable rails. Using these rails, the entire unit can be removed and substituted by a vacuum chamber-based AP cell setup. At present, one such setup exists: the electrochemical/liquid cell (EC).

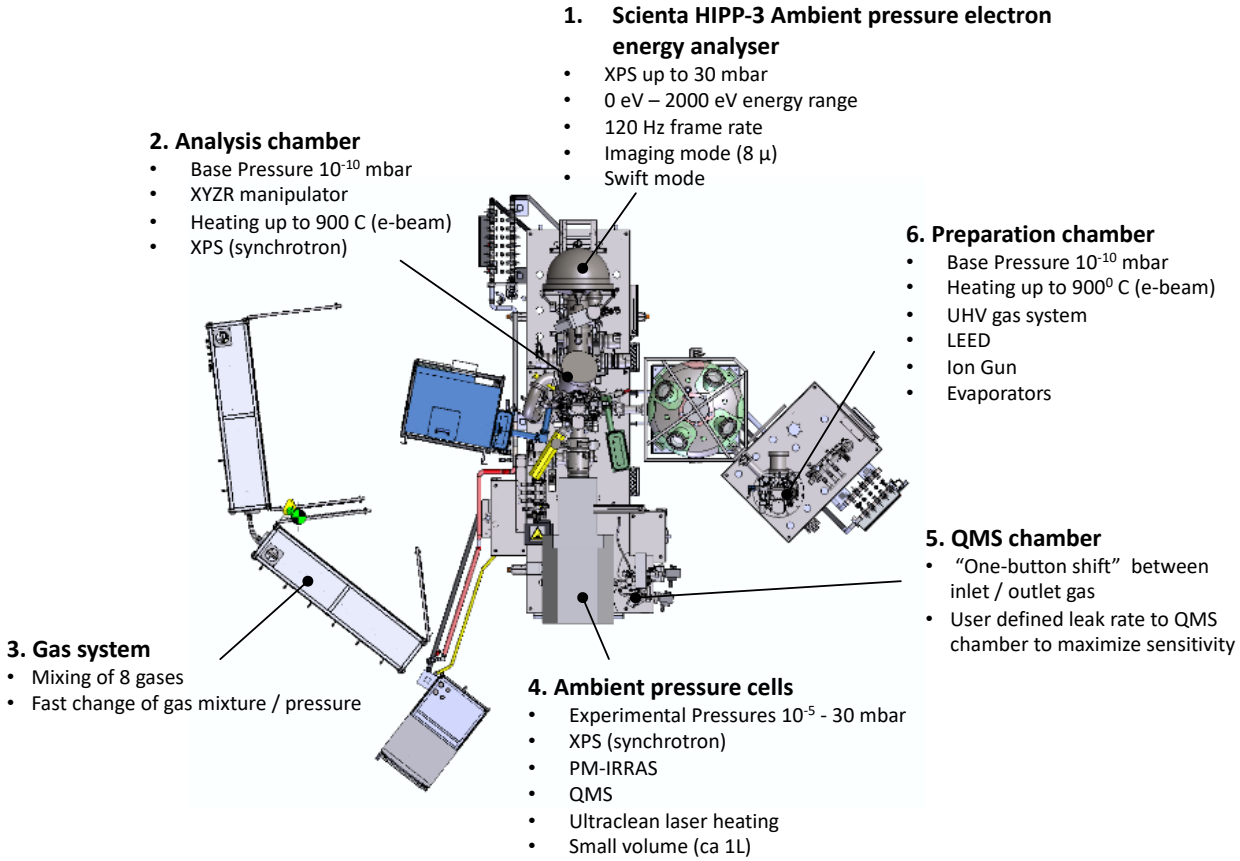

Figure 6. Components of the APXPS Endstation

The Scienta Omicron HiPP-3 electron energy analyser has a differential pumping stage and electrostatic lens system that allows for ambient pressure operation at up to 30 mbar at 0.3 mm nozzle diameter. The analyser is placed horizontally, in the plane of the storage ring and at 55° with respect to the direction of the x-ray beam. The microchannel plate detector can be equipped with two different cameras with either 17 Hz or 120 Hz frame rate, which allows 60 µs and 9 µs time resolution in fixed mode, respectively. The spatial resolution of the analyser was measured to be 8 µm in the spatial detector direction.

The swift acceleration mode of the analyser substantially improves its performance under ambient conditions, especially at low kinetic energies where electron scattering is most prominent.

A Bruker Vertex 70v FTIR spectrometer with all-in-vacuum beam path and polarisation modulation (PM) module can be attached to the catalysis AP cell setup, allowing simultaneous IRRAS and XPS measurements under in situ conditions. The x-ray and infrared beams probe the same spot on the sample. The infrared beam first passes a polarisation modulator (42 kHz PEM (AR-coated) and F350 polariser). Via two gold-covered out-off-axis parabolic (OAP) mirrors the light is transferred into the catalysis AP cell via ZnSe viewports separating the beam path pipes, analysis chamber and catalysis AP cell respectively. The beam illuminates the sample at 7° grazing incidence. After reflection by the sample, the light goes through the same series of infrared light-transmitting viewports. A single OAP mirror is used to reflect the light into the detection module with an MCT detector (medium band, spectral range 12000 –

600 cm^{-1}). The combined wavenumber range of the system is 8000 to 720 cm^{-1} with a standard resolution of 0.4 cm^{-1}.

1.2.2. Catalysis AP Cell and Gas Dosing System

Description of the catalysis AP cell, modes of operation, gas dosing system, QMS

AP Cell

When in use the AP cell is docked onto the electron analyser by a fully automatic docking system. Direct transfer of samples from the UFO chamber is possible without undocking the cell, which makes sample transfer easier for our users. The gate-valve-like locking mechanism allows easy and reliable way for sealing-off the AP cell from the analysis chamber.

While the cell is docked and filled with few millibars of gas, the analysis chamber maintains a pressure in the range of 10^{-5} mbar. Silicon nitride windows of 200 nm thickness are used to separate the AP cell from the analysis chamber while allowing x-rays (either from the beamline or X-ray anode) to enter the cell. The cell also embeds viewports for a camera and a visible light source.

In the Catalysis cell, the sample surface normal is aligned to the analyser axis and sample motion along this axis and in the directions parallel to its surface plane is possible. Sample motion is controlled by closed-loop motors equipped with absolute encoders.

The sample can be directly heated from the back by a fiber-coupled infrared laser emitting 800 nm at a maximum power of 4.3 W. Temperatures up to 600 °C can be obtained in a gaseous atmosphere with few mbars of pressure. The laser-heating is fast and very linear heating rates can be obtained. As the heating is local sample holders degas very little giving our users access to very clean sample environment. Temperatures are measured with thermocouples mounted at the flag-type sample holders. Cooling down to -5°C is possible using ethanol/water mixtures as chilling agent.

The AP cell is the most used cell from our system and within two years it has been performing quite satisfactorily. However, during this time we still experienced the following problems:

- The sample motion has noticeable backlash and cross-talk of x,y,z axes which makes sample scanning difficult. Users have been notified about the issue; however, no significant difficulties have been reported since then.
- Absence of precise positioning of the sample with respect the cone. This was requested from the supplier but failed to provide by PREVAC. Users rely on the analyser count rate, use small step sizes, and use common sense when manipulating sample. However, few sample-cone crashes have still been observed.
- Broken laser due to deposition of material at the window separating the AP cell volume from the fiber. Biannual service of the laser optics is planned to diminish odds of breaking in the future.
- Inefficient and unfriendly software for motion and temperature control. This is the main issue of the CS which is partially resolved by the software written by the team. However due to lack of time/people the team could not be fully engaged in creating all applications at the beamline.

Despite the problems described above the Catalysis AP cell has shown to be robust and efficient in creating condition for variety of (very) different experiments and majority of the users have satisfactory experience with it (see Section 3.2).

Gas dosing

The gas inlet system of the Catalysis Cell contains eight gas lines equipped with individual mass flow controllers (MFCs), gas filters, and cold traps. Liquid vapours can be dosed into the system through an automated leak-valve. This setup allows permanent installation of standard gases such as H_2, O_2, CO, and CO_2, as well as user-defined gases without frequent venting and time-consuming bakeout of the gas lines. The pre-defined gas mixture from the MFCs can be dosed into the AP cell, either directly or via a variable leak valve. This dual type of inlet systems gives users the possibility to dose gas mixtures at any total pressure between 1.0×10^{-8} mbar and 30 mbar. Since the gas system is always pumped by the turbo pump/AP cell the rapid change of the gas composition is possible at any total pressure.
The Catalysis Cell is equipped with two pumping lines with inner diameter of 4 mm and 35 mm. Pumping through both lines can be controlled by butterfly valves, which creates the ability to change the total gas flow in the cell independently of the gas pressure as well as quick evacuation of the cell before e.g. sample retrieval to UHV conditions.
The system has been designed with pneumatic valves at all places where the users need to operate the valves. Therefore, all dosing can be controlled from the control software, which also prevents the users from injecting too much gas into the system etc. At the moment the large complexity of the gas dosing system makes it, however, cumbersome to use for new users and often in case of failures the safety build into the system makes it difficult to "restart". At the beamline we continuously working on improvements of the system. However, the implementation of improvements often gets delayed due to lack of IT/PLC resources.
Further details of the gas delivery system could be found in sections 1.3.1 or Appendix A.

Gas probing

The AP cell's inlet and outlet lines as well as the first differential pumping stage of the analyzer are connected to a quadrupole mass spectrometer (Hiden HAL/3F PIC) via a combination of automatic angle and leak valves providing a way for the quick analysis of the gas composition before or after its contact with the sample without creating artificial pressure build-ups and dead volumes in the gas pipes. Thus, within 5 seconds the users can change from probing inlet to outlet composition by the gas spectrometer.

1.2.3. Liquid/EC AP cell

Two cells in one – liquids, EC, microjet
In situ and *operando* experiments with liquids, including electrochemical measurements, are available at HIPPIE in the Liquid/EC AP cell (EC cell). The EC cell is a vacuum vessel with a background pressure of 1×10^{-5} mbar. It has a large loadlock style port (door) for quick access to the chamber's interior for sample loading. The chamber can be backfilled with gases and vapours at pressures up to ~30 mbar (when using a 0.3 mm front cone opening), and the gaseous atmosphere can be heated up to ~90 °C by halogen lamps. A four-axis manipulator (XYZR) can be installed at the top, and a three-axis manipulator (XYZ) with cooling and heating functionality (via liquid coolant media) - from the bottom. Two top manipulators are available: one for liquid jet and one for electrochemistry experiments.

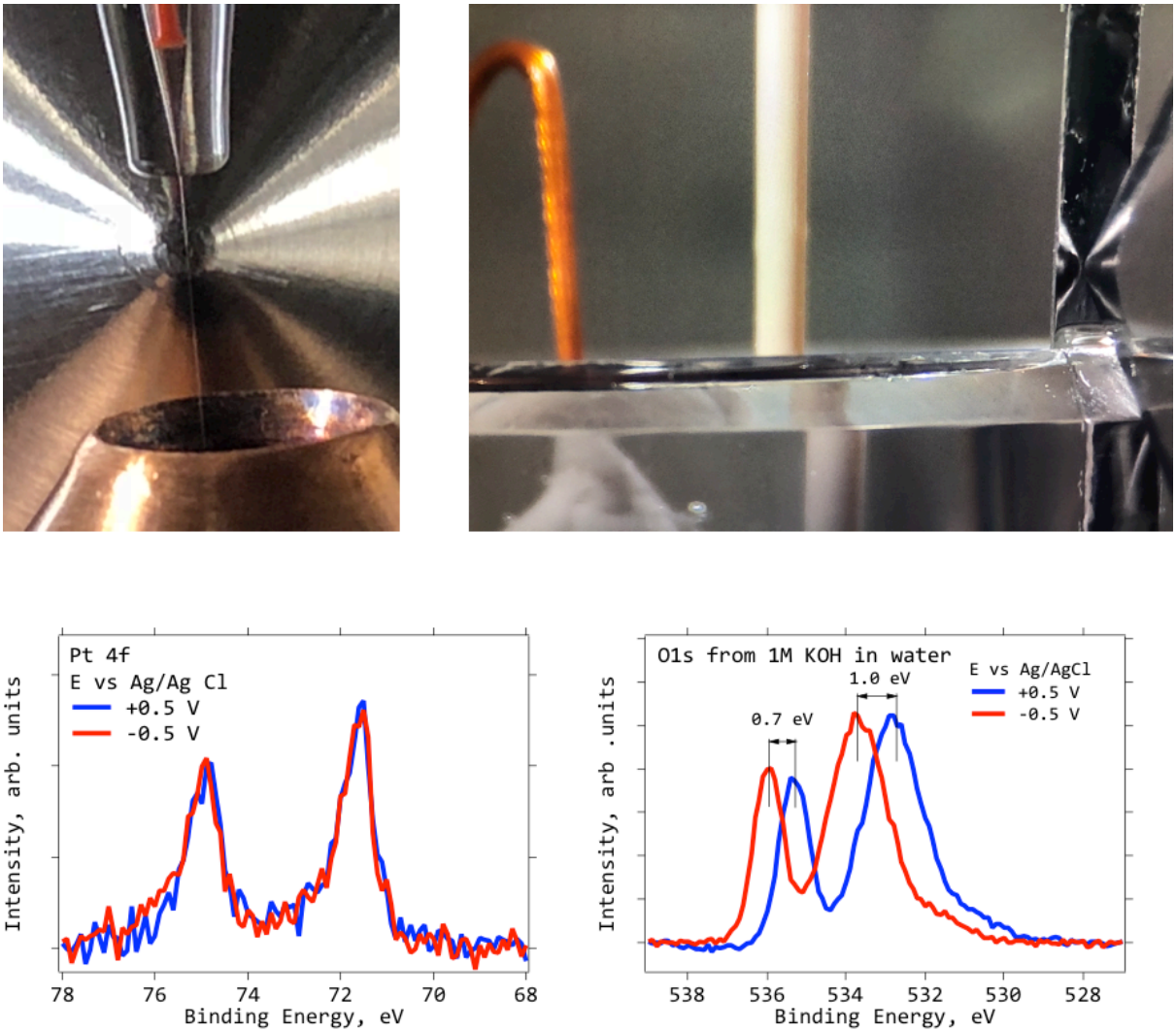

Figure 7. Electrochemical (EC) cell at the HIPPIE beamline. Liquid microjet (top left) emerging from the end of a 20 µm glass nozzle into an opening of a waste container. In the background the analyser cone with 300 µm opening is seen. Dip-and-pull setup (top right) showing sample (working electrode), Ag/AgCl reference, and N-doped diamond counter electrodes from right to left. The sample is in XPS position with the mirror reflection of the analyser cone being visible on the sample's surface. Pt 4f (bottom left) and O 1s (bottom right) XP spectra measured in the setup shown in top right panel at 24 mbar of H_2O and room temperature. Blue (red) curves correspond to +0.5 V (-0.5 V) applied potential. The thickness of the KOH electrolyte layer estimated from the attenuation of Pt signal (the vacuum spectrum is not shown) is ca 20 nm. Each spectrum took ca 3 min to record. hv = 1800 eV, PE = 100 eV, exit slit 100 µm. potentials are with respect to Ag/AgCl reference electrode

The liquid jet manipulator provides the possibility for APXPS measurements of surfaces of liquids as well as the liquid-gas interfaces. The setup (Microliquids) contains a glass nozzle with a 15 or 20 µm opening, connected to an HPLC pump to provide a pressurised liquid flow through the nozzle (Figure 7, top left). A truncated conical copper trap (catcher) with an opening of 8 mm and a volume of 300 ml is mounted on the bottom manipulator. It collects the ejected liquid. The temperature of the collected liquid can be controlled and defines the vapour pressure in the chamber.

The electrochemical top manipulator is equipped with three electrical feedthroughs, where EC electrodes can be mounted, whereas the bottom manipulator is also equipped with two electrical feedthroughs and is designed to hold a container for liquid electrolytes. The system is designed to carry out "dip-and-pull" experiments, in which up to three electrodes can simultaneously be plunged into a liquid electrolyte and retracted to allow for the XPS investigation of the liquid-solid interface at simultaneous control of the sample bias and current via a potentiostat (Figure 7, top right).

The cell is equipped with an enclosure (called “glove box”) to provide an oxygen- and moisture-free atmosphere for sensitive experiments, such as experiments on Li-ion battery materials. The glove box is made from a transparent plastic and contains a load-lock for sample transfer. It can be constantly purged with N_2 or Ar, but does not, however, have a catalyst for active O_2/H_2O removal. So far, the glove box was used during one beamtime where Li-containing materials have been used and demonstrated satisfactory performance. At the moment the box is under repair and upgrade at the supplier but will be available for users within short.

To test the probing depth and the continuity of the potential profile across the thin liquid film, a Pt foil sample and 0.1 M KOH solution were used. Figure 7 shows Pt 4f (bottom left) and O 1s (bottom right) XP spectra recorded after the Pt sample first was immersed and then partially pulled out from the KOH solution. The thickness of the KOH film was estimated by the attenuation of the Pt 4f signal and found to be 20 nm. At this liquid film thickness, it took ca. three minutes to record a single Pt 4f spectrum using electrons of kinetic energy 1626 eV, i.e. at a photon energy of 1800 eV. Previously, the usage of “tender” x-rays (3-6 keV) was considered necessary for probing the solid-liquid interfaces with XPS. To our knowledge, this is the first time that the dip-and-pull method is demonstrated using soft x-rays. The O 1s XP spectrum demonstrates two features with the low binding energy-component corresponding to liquid water and the high binding energy one to gas phase H_2O. Different potentials were applied to the sample with the blue (red) curves, representing spectra recorded at +0.5 V (-0.5 V). Due to the grounding of the sample required for XPS measurements, the Pt spectra overlap. The O 1s spectra, on the other hand, undergo a shift to lower binding energy when the potential is changed from a negative to a positive value: the liquid component shifts by 1.0 eV and the gas phase one by 0.7 eV. The equality of the shift of the liquid component and the difference in applied potentials implies that the potential is carried through the thin film without any losses. The drop occurs at the liquid-solid interface, which is a normal behaviour for such systems.

Figure 8 shows AP-XPS spectra of various elements originating from 5mM sodium dodecyl sulphate jet at few mbar. Clearly one can measure composition of the liquid under equilibrium conditions in HIPPIE’s EC setup.

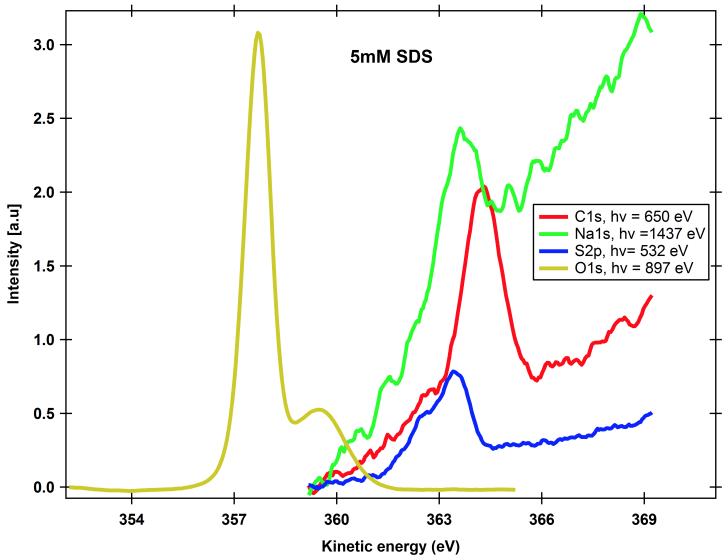

Figure 8. XPS spectra from the liquid jet containing 5mM sodium dodecyl sulphate

1.3. Infrastructure

1.3.1. Safety

General safety, gas system, issues

One of the biggest scientific areas using HIPPIE is chemistry (catalysis, materials, energy, geo-, atmospheric-, etc). All groups of users (general, in-house or collaborations) study chemicals in various states and forms as well as reaction between them. Often these materials contain hazards to either human health or environment. A large group of such materials are gases used to create ambient conditions around the sample, another – samples themselves. Finally, many operations during day-to-day life of the beamline (e.g. spotwelding, gluing x-ray windows, using a soldering iron) can create hazards to health indirectly. The HIPPIE beamline has always been under scrutiny regarding usage of various chemicals and user activities at the beamline were one of the reasons for the formation of MAX IV safety organisation and its ongoing reformation.
To enable safe gas supply to the analysis volume as well as its removal a complex gas delivery system is being built in collaboration with the safety team. Details of the system are presented in Appendix A. In short, the gas delivery system consists of three major parts – (1) gas cabinets where bottles (typically 1-5 L / 200 bar) are permanently installed and main safety components (e.g. shut-off valves, gas sensors, flow indicators) are placed; (2) gas panels where eight individual gas supply/control lines (one from a separate gas bottle) are installed; and (3) experimental cell together with the exhaust lines. The components 2 and 3 are operational and in compliance with safety requirements. The project for installation of gas cabinets is undergoing at the moment. Below are several key features of the gas system allowing safe operation:

- Two fire-proof gas cabinets. One for flammable and one – for oxidising gases
- Automated interlock system (PLC) shutting gas supply on any safety-concerning triggers (e.g. high pressure of gas, gas sensor alarm, ventilation failure alarm)
- Permanently installed bottles to reduce the risks of accidental gas release upon bottle exchange
- Ventilated enclosure for gas panels.
- Fully automatic user control of gas lines (valves, MFCs, etc)
- Limited gas flow (RFO) and pressures inside gas panels – max 1.6 bar (o) which together with a small volume of gas pipes prevents formation of hazardous gas concentrations (toxic, explosive) even in the case of accidental release
- Process gas exhaust directly into ventilation

The user experimental safety is responsibility of mainly the safety team. The team is engaged in the discussion with the users about the samples during weeks or months prior the beamtime typically requesting risk assessment for those chemicals/processes which could create any hazards. The beamline team typically gets involved in the process when an unusual setup or process is proposed.
Users of HIPPIE can apply for access to the chemical and biological laboratories as a part of the general access to MAX IV. At the beamline a sample preparation laboratory (shared with another soft x-ray beamline) exists where mounting or samples and handling of vacuum equipment can be done. In this area it is approved use of a spotwelder, an ultrasonic bath, using a heat gun, a soldering iron and two-component adhesives (the last three are allowed only for beamline personnel).

Beamline personnel has always been and still is heavily involved in various processes concerning safety at the beamline such as writing risk assessments, conducting regular safety checks, participation in general discussions regarding safety at MAX IV. Since no proper safety system and culture existed previously at MAXlab most of the rules, regulations, and requirements had to be created from scratch which required a lot of time and competence, which was not always available in the group. This resulted in the delays of several major projects like gas delivery system or mirror cleaning which in many cases affects day-to-day user operation or the beamline performance. Nevertheless, temporary solutions and workarounds which have been found and agreed allowed user operation of the beamline and successful execution of experiments. At the moment proper risk assessment of the whole beamline is still pending; on the other hand, several critical components of the beamline like the gas system or preparation laboratory are on the track to be properly assessed with the rest of the beamline following them

1.3.2. IT

Hardware and software

Most of the hardware and software components at the HIPPIE beamline and APXPS endstation follow MAX IV standards. This enables quick and efficient problem resolution and high level of support in general, but at a cost of limited functionality, which is the result of accepting general solution rather than finding a specific one best tailored to our needs. Following are the hardware components used at HIPPIE and part of MAX IV standard: IcePAP motion controllers, Allen Bradley PLC, ALBA e-meters, encoders, motors, all IT infrastructure (switches, hubs, PCs, etc). All electrical installations have been performed by MAX IV or have been requested to follow laboratory standards.

Control system (CS) at the HIPPIE beamline is Tango with TaurusGUI framework for building GUIs. At the designing phase the beamline was planned to have as much automation of standard routines as possible with only few manual operations. For this purpose, a sophisticated equipment protection system (PLC) was developed to control and protect both the beamline and the endstation vacuum components (valves, gauges, thermocouples, etc) during user operation. A Tango CS then accesses various PLC attributes for both read (e.g. gauge pressure) and write (e.g. open/close valve). Tango CS also allows direct access to electronic equipment over the network for hardware control or data acquisition. Finally, a series of GUIs are built on top of Tango to visualise and enable interaction between the system and the user. Following is the list of major software developments at HIPPIE beamline. It should be noted that many developments implemented at HIPPIE were joint effort of several beamlines implying that either HIPPIE-specific applications have later been implemented at other places or we re-used existing solutions from other beamlines. As in the case of hardware this enables quick implementation and support, but often at cost of functionality and efficiency

- Mirror motion with parasitic movement compensations
- Beamline feedback based on a P (as in PID) controller correcting pitch of M1 to compensate heat-induced mirror motions
- Beamline and endstation synoptics for interacting with beamline/endstation vacuum PLC
- Gas dosing GUI allowing controlled gas supply to the experimental volume
- Motion GUI allowing simple sample motions and storing positions
- Heating GUI allowing sample heating using e-beam or laser heaters

- Cameras (RasPi and Basler)

Hardware installation and commissioning (except certain parts of the endstation delivered by vendors outside of Lund University) are performed by KITS Hardware team. Majority of software development is performed by the KITS Software team. A contact person from the software team is dedicated to communication with HIPPIE beamline. This person discusses current beamline status (once a week), collects new tasks, and follows up on the open tickets. She, however, is not necessarily responsible for actual development or testing. This task is distributed within whole KITS team in non-transparent for beamline way according to the Agile principles. The HIPPIE team is typically engaged in the development of beamline's PLC or CS in following ways:

- Writing PLC functional description
- Writing technical specification for software team
- Developing software.

Software development is clearly one of the most critical resources which HIPPIE always constantly requires. Lack of guaranteed software developer dedicated for the beamline leads to unpredictable availability of this resource and thus difficulty to plan any substantial developments. Although beamline (and APXPS team in general) has internal knowledge and experience with software development, it cannot be fully utilised due to lack of beamline personnel.

2. Project and Operational Status of HIPPIE

2.1. APXPS Team

History of the team. Intro to the team and Species beamline, description of how team works, weekly meetings, todo list, workshops, hippie day

HIPPIE beamline has place for three permanent (two beamline and one instrument scientist) and one temporary (postdoc) positions. At the moment only permanent positions are filled and a postdoc position has been put on hold due to MAX IV budget issues. In addition to permanent staff who is 100% employed by MAX IV, HIPPIE employs 10%-20% of another two positions which are shared with Lund University. Here is the list of current HIPPIE staff:

Jan Knudsen. Ass. Professor, 10% employed by MAX IV (90% at the Division of Synchrotron Radiation Research at LU). Hired in 2012 to work as project manager of HIPPIE project (100%). Budget responsible for the build-up phase, main responsible for the procurement of the beamline and its design. Helped with the initial construction of the beamline and its commissioning. In 2017 he transitioned to LU, but he still keeps connection to HIPPIE where he's mainly doing user support. Furthermore, he helps with the formulating the long-term development strategy. Jan is an expert in surface science and 2D materials and his main focus is currently the development of the APXPS technique for kinetic process of catalytic active surfaces with or without 2D films.

Mattia Scardamaglia. Beamline Scientist 100% employed by MAX IV. Mattia joined HIPPIE in the beginning of 2019 as a postdoc and was promoted to a beamline scientist in the fall of 2019. At the beamline he's responsible for overall beamline performance, performing day-to-day tasks, commissioning new/missing functionalities, establish future functionalities, engaging in collaborations with users, develops a long-term strategy, seek for internal and external funding to support development plans, performing user support, and pursuing own

research agenda. Mattia is an expert in surface science and 2D materials and bases his in-house research on these topics.
Joachim Schnadt. 20% employed by MAX IX (80% at the Department of Physics). With the beamline since making the case for MAX IV and, somewhat later, the very first application for MAX IV beamline funding, including funding for an APXPS beamline. He wrote the application for HIPPIE beamline, took part in the design and initial construction of the beamline and its commissioning. Keeps connection to HIPPIE where he is doing user support. Amongst other things, Joachim develops a programme on atomic layer deposition at HIPPIE at SPECIES, both as his own research topic and in collaborations with users.

Andrey Shavorskiy. Beamline Scientist 100% employed at MAX IV. Andrey joined HIPPIE in 2015. He took part in the endstation beamline construction and commissioning. In 2017 he took a role of a beamline manager (of operations) and in the mid 2019 – manager of the APXPS team. Since the end of 2019 he is also an assistant group manager of the Spectroscopy Group (consisting of RIXS and APXPS teams). At the beamline he is responsible for overall beamline performance, performing day-to-day tasks, commissioning new/missing functionalities, formulate beamline long-term development strategy in collaboration with users, seek for internal and external funding to support development plans, engage in collaborations with users, and user support. Andrey's leading electrochemistry research topic at the beamline mainly through targeted collaboration with specific user groups.

Suyun Zhu. Instrument Scientist 100% employed at MAX IV. He joined HIPPIE in the end of 2014 and took part in the design, construction and commissioning of the beamline. At the moment he's responsible for overall beamline performance, performing day-to-day tasks, development of beamline's new functionalities, and user support.
In past (beginning 2018) HIPPIE employed another person for a postdoc position who unfortunately has left team in a short while (mid 2018).
The situation with staff at HIPPIE is critical. Although current level of personnel allows support of day-to-day operation of the beamline (user support, fixing operational issues) it has become extremely difficult to plan beamline's future developments as well as to focus on operations improvements.
Recently the teams from APXPS endstation of SPECIES and HIPPIE beamline have been merged to form an APXPS team. In addition to the described above HIPPIE personnel the APXPS team includes following members:
Esko Kokkonen. Beamline scientist at the SPECIES beamline. Joined the beamline in 2018 as a postdoc. Took part in beamline and endstation commissioning with first light. In charge of the APXPS branch scientific focus as well as taking part in developing and commissioning new experimental instrumentation for the beamline. Kokkonen engages in external collaborations which extend the capabilities of the endstation through either expanded sample environment parameters or through new developments. Kokkonen uses available in-house research time while also contributing to the external users through collaboration and user-support.

Mikko-Heikki Mikkelä, research engineer, 100% employed by MAX IV. 2013-2015 MAX-lab beamline postdoc at I411 and I3 beamlines. Joined SPECIES in 2015 as research engineer and took part in decommissioning and transfer of the SPECIES beamline to the new MAXIV site. Contributed to build-up and re-commissioning of SPECIES in 2016-2020

Margit Andersson (born Bässler), research engineer 70% employed by Max IV.
1997 - 2000 post doc at Max II building beamline I411 together with Uppsala, Oulu, Linköping and Bergen University. After work in industry at Zeiss Oberkochen metrology optical test

laboratory and parental time, back at beamline I511 HPXPS station in 2012 as part time research engineer supporting users mainly. Break for work in alignment and metrology in 2016 in the Max IV SAM team. Back to Species Rixs and Veritas Rixs in 2019. Since 2020 also at Species APXPS for user support and day-to-day work. Having had the early education in X-ray microscopy at G. Schmahl's synchrotron radiation optics is a deep interest. The post doc building I411 included parts of the optical design work and ray tracing. This together with the beamline commissioning was a work favourite. Concerning experiments expertise is mainly in electron spectroscopy and NEXAFS.

The team was formed in order to gain from synergy of two APXPS groups present at MAX IV. The goal of the team is to support and develop APXPS user and in-house programs as well as to evolve and expand functionalities of the two beamlines in order to keep them state-of-the-art. From 2020 the team has common budget but the members mostly gravitating to their beamlines due to accumulated experience with particular instrumentation. We have, however, already started exchange of the experience by providing user support at different beamlines. The team also meets weekly to discuss ongoing tasks. The last is presented in form of "to-do-list" which contains information about a hundred of ongoing issues at both beamlines. Each issue in this list has a responsible person who proceeds with its execution. The task/issue is typically discussed at the meeting if it needs a special attention such as encountered problems, completion, etc. The meeting is also a forum to discuss past week experience with the users, convey any messages from/to the lab management, and to follow up on IT-related issues via communication with a KITS contact person who attends these meetings as well.

At HIPPIE team we identify following list of technical responsibilities and try to allocate at least two persons in the team who share knowledge about specific area.

Table 2. Beamline responsibilities

PLC (FD, hardware list, communication with PLC group)	Suyun, Andrey
Safety (gases, chemical, machine, electrical, ergonomics, radiation, laser, general)	Andrey, Mattia
Software (defining tech. requirements for KITS, communication with KITS, testing software, GUIs, programming)	Andrey, Suyun
Beamline (beam and hardware alignment, diagnostics, optimisation)	Suyun, Andrey
Endstation UHV equipment (prep and analysis chambers, equipment in UHV chambers: LEED, QMS, QCM, evaporators, etc)	Mattia, Suyun, Jan
Gas delivery system (equipment inside gas cabinets and panels, valves, MFCs, lines to AP cell, inlet line, QMS chamber, outlet line)	Mattia (gas cabinets, panels), Jan (AP cell)
EC cell	Andrey, Mattia
PM-IRRAS	Andrey, Mattia
Bakeout (rewrapping chambers, setting up units, improvements, developing new system)	All
Pumps (TMPs and ACPs, make sure they are running)	Suyun, Andrey
Users (communication, feedback)	Andrey
Beamline PR:	Joachim (conferences, meetings), Andrey (webpage)
Beamline documentation, manuals	Mattia, Andrey

The team organised several workshops in past related to the APXPS program at MAX IV with the major being “a HIPPIE day”, 2019 international APXPS workshop, and branch B exploration workshop. During the “HIPPIE day” all staff of MAX IV was invited to take part in typical day-to-day beamline activities such as sample transfer, dosing gases, XPS measurements, etc. With most of the lab’s staff attending the day it has increased visibility and perceived importance of the beamline operation especially among administration staff as well as members of the groups not often visiting the experimental floor (IT, user office, etc). The branch B exploration workshop was dedicated to the investigation of the possible future development at HIPPIE beamline, in particular construction of the second branch. The results of the workshop could be seen in a later chapter. The annual APXPS workshop is the largest and most important yearly meeting of the scientist in the community and is organised by the teams actively participating in the APXPS research/development typically at the synchrotrons. In 2019, the APXPS team members lead the effort of organising the conference during all stages and successfully run the workshop with more than 100 participants.

2.2. Timeline, Resources, and Budget

2.2.1. Project

Project timeline and budget, delays and issues. Lessons learned

Timeline

The original time plan in the Detailed Design Report (DDR) of 2012 had the goal to start user activities in the end of 2016. At the end of 2014 the following was concluded in the Midway Report (chapter 2.6): “A delayed assembly of the insertion device and a delayed delivery of the end station is not expected to affect the timely completion of the project”. Nonetheless, the first expert users could not be accepted before mid 2017. Table 3 summarises planned and actual timelines for several milestones in the construction project phase

Table 3. Timeline of HIPPIE commissioning

Milestone	DDR	DDR+1.5 yrs	Actual
Beamline Installed and ready for commissioning	Fall 2015	Spring 2017	End of 2016
Beamline Commissioned	Fall 2015 – Spring 2016	Spring 2017 – Summer 2017	March – May 2017
Endstation Commissioned	Summer 2016	Fall 2017	June 2017
PLC migration project			Fall 2017
Expert Users	Fall 2016	Winter 2018	(first) June 2017 (most) Feb-April 2018
General Users			Since May 2018

Analysing the table, a delay of 1.5 yrs from the initial proposal can be noted. When adjusted for this delay (row “DDR+1.5 yrs”) the timeline of the beamline and endstation commissioning was kept according the (adjusted) plan even with addition of resource-heavy PLC migration project. The largest part of the 1.5 yrs delay originates from the delay in installation of the optical components, preparation of the CS, commissioning of the ID and beam delivery to the

beamline. There are, however, several other reasons for smaller delays which have been realised during beamline's installation and commissioning of HIPPIE:

- Different support groups (electricians, vacuum group, alignment, radiation safety etc.) were much less available than anticipated. The initial time plan assumed that the right people would be available for the project when needed; this assumption had been far too optimistic.
- The beamline was understaffed: for a long period of time – essentially during all of the build-up phase – the beamline had only two permanent members of staff.
- There were technical issues with ordered/delivered components and there were issues with the optics. In particular, gold coatings of mirrors were defective and had to be redone (3 months delay). The frontend had been misaligned, and this was detected first after 2 months of attempts to obtain the expected photon flux. Beamline components that had been designed in-house were difficult to align, i.e. both the beamline and MAX IV experienced a steep learning curve on how to design components properly for alignment.
- Lack of general optics knowledge and support staff at MAX IV. The beamline staff members had never commissioned a beamline before, and Rami Sankari, who had designed the beamline optics, had left by the time of the commissioning.

Overall, however, we think the beamline team made a suitable timeplan and kept up with it reasonably well. It was mostly experience with teams outside HIPPIE (both inside and outside MAX IV) which we could not control or influence which caused major delays.

In spite of the delay, HIPPIE was the first soft x-ray beamline to be in operation – something we are very proud about.

Budget

Figure 9 shows the final budget for the beamline project phase.

KAW ÖVERSIKT HIPPIE

Rekvisitionsdatum: 2019-02-19

Kolumn nr	2	3	4	5	6	7	8
HIPPIE	Budget KAW*	Prognos	Avvikelse	Upparbetat 2018-12-31	Rekvirerat 2019-02-19	Rekvirerat ackumulerat	Kvar att rekvirera
Insertion Device	12 000	12 074	-74	12 074	0	8 624	3 376
Front End	4 500	4 418	82	4 418	81	3 156	1 344
Optics	12 600	9 569	3 031	9 569	0	6 835	5 765
Experimental station	19 300	18 724	576	18 724	777	13 374	5 926
Infrastructure	10 500	18 240	-7 740	18 240	291	13 029	-2 529
Personnel cost	8 740	6 309	2 431	6 309	0	4 506	4 234
General cost	1 321	497	824	497	0	355	966
TOTAL	**68 961**	**69 831**	**-870**	**69 831**	**1 149**	**49 879**	**19 082**
- varav medfinansiering	19 961						19 961
- MAX IV medfinansiering			**860**				
BUDGET KAW	**49 000**		**-10**		**1 149**	**49 879**	**-879**

Figure 9. Budget of HIPPIE project

Overall, the beamline project was delivered within budget. Looking at the distribution it is clear that everything except infrastructure is within and below budget.

The reason behind inflated infrastructure costs, we believe are similar to the reasons for the major delay of the beamline delivery – the beamline could control and affect little during

design and decision-making process. For example, much of the infrastructure (electricity, water-cooling, hutches, IT) was designed by (external) consultants without any consideration of cost and benefit. It was seldomly asked whether a commercially available product should be used instead of an in-house development. Many of the solutions implemented at HIPPIE were unnecessarily expensive. No proper centralised project managing structure was in place at the time of building the beamline, so often infrastructure-related decisions were taken by an external consultant with doubtful relation to MAX IV when compared to a contractor.

Changes of scope:

During the project phase the initial project was changed in the following way:

- Originally, our budget and project included an UHV SEM. Early in the project we realised that this would be difficult to afford and instead we decided to implement the PM-IRAS setup.
- Several AP cells and other equipment were cut away due to the high infrastructure cost. This includes: a cell for high temperature materials, a cell for biological samples, and equipment for photocatalysis.
- The liquid and electrochemical cells were merged together into Liquid/EC cell as we are confident that this will be an emerging area.

2.2.2. Operations

Operational structure, investments

The operational budget for HIPPIE beamline for 2017, 2018, 2019 years was 519 kSEK, 790 kSEK, and 620 kSEK, respectively. The 2020 budget for the whole APXPS team (HIPPIE and SPECIES) is 1040 kSEK. The differences in the budget over last years are due to (a) simultaneous operational and project funding in 2017 and partially 2018, (b) changes in the policy of MAX IV regarding preventive/corrective maintenance, (c) changes in the beamline's needs and MAX IV policy regarding use of consultants. The beamline/team budget consists of two major parts: travel and running budgets. The former is used for travelling to conferences and beamtimes and comprises ~ 25% of overall budget, whereas the latter includes the beamline as well as the endstation components and support for commissioning collaborations. It also includes specific items for service and maintenance which are not covered by any MAX IV agreement. Such agreements cover both corrective and preventive maintenance of all standard vacuum hardware (valves, gauges, fittings and flanges, etc), pumps (TMPs and FVPs), or other standard equipment from a specific supplier. Cost of such maintenance is typically taken outside beamline's budget.

For year 2020 MAX IV introduced new item in the budget: a long-term upkeep investment post larger than 100 kSEK. Cost for each of such items is allocated separately from operational budget, and then amortised over 1-4 years as part of future budgets. HIPPIE obtained the following investment items:

- Clean/spare AP catalysis cell (1.5 MSEK)
- Laser heating in the preparation chamber (250 kSEK)
- O_2 and H_2O detectors for EC cell glove box (120 kSEK)

Development work for these items is planned to start shortly.

Overall, the current level of running budget of HIPPIE beamline/APXPS team is adequate to support operations of beamline(s) and keep its performance at high level. Also, team members have secure funding for traveling e.g. to support their in-house research programs. MAX IV laboratory does not, however, have any internal development programs for new

functionalities/equipment (e.g. second branch or new sample environments) or people. A very poor situation with the research infrastructure support in Sweden makes it also difficult to search for funding for long-term beamline development outside of the lab. Recently MAX IV has started to consolidate projects about next phase beamlines and large developments such as second branches. However, the details of this initiative (e.g. budget, overall timeline, funding sources) are still unclear.
Being an operational beamline HIPPIE cannot rely on getting any resources allocated for projects running by MAX IV central project office (CPO) team and almost all tasks/projects running at HIPPIE need to receive resources through operations. At the moment access to such resources is unpredictable (for example, beamlines at MAX IV do not employ dedicated software engineers) and therefore the timeline of the task execution is unpredictable. The largest needs of the resources are KITS software followed by PLC. Safety is another area where the beamline feels constant pressure but receives little assistance, see the respective chapters for details about IT and Safety. One of the most important reasons for a high resource demand is a high complexity of the setup which require high degree of automation, control, and synchronisation. Another is relatively quick transition of the beamline into an operation phase without proper completion of functionality commissioning. Finally, since HIPPIE is the first soft x-ray beamline of the MAX IV it has often being a driver for the demand for specific solutions (e.g. motion compensation for mirror chambers, beamline energy pseudomotors, heating and motion GUIs) before other beamlines realised the same needs.

2.3. User operation: A week at HIPPIE beamline

Being a beamline in user operation, this task requires the highest focus by the beamline staff. One beamline member, as local contact, follows every month a user's beamtime that typically lasts five days (8 am Wednesday to 8 am Monday). Another beamline staff member is backup. The local contact for each beamtime of the semester is decided as soon as the approves proposals are known. The local contact is responsible for contacting the users before the beamtime, assuring that everything they need is available and in place at their arrival. Duties also include the training and the assistance of the users during their experiment.
To facilitate and to standardise the user support, we have defined a check list that every local contact follows (Appendix B). The procedure begins one month before the beamtime, with the first contact with the users and discussion of the experiment. It should be noted, however, that often the users contact the beamline staff to discuss the experimental feasibility and details well in advance during the writing of the proposal or as soon as they are notified about the beamtime allocation.
The first two days of the week (without synchrotron light) are dedicated to the bakeout (when necessary) and to the installation of user's equipment and gases. On Wednesday, the first day of beamtime, the local contact gives to the users a full overview and training of the beamline (safety, control system and end station) and scientific and technical assistance with the first phases of the user's experiment. During the rest of the week, the local contact is always available and responsible for the on-call service: it covers from 17 to 23 on weekdays and 8-20 during the weekend. Usually, the first two days of the beamtime, the local contact stays with the users until evening, gradually exploring all the features of the end station according to the experimental plan. At the end of the beamtime, there is a discussion with the users about the results obtained and (in case) about the problems and faults they encountered.

The local contact is also responsible for logging the gases used during the beamtime, an important data when it comes to the maintenance of the vacuum pumps, and to handle and keep track of the sample holders.
Following the 2018 user's feedbacks, we have created a user manual (Appendix C) of the beamline where they can find the instruction to use the equipment at the endstation, the description of the most common actions and procedures, as well as a troubleshooting section for the typical problems they can face during a beamtime and how to solve them. We usually send the manual to the users the week before their beamtime. This is helping them operating more independently and, at the same time, is lowering the charge on the beamline staff by reducing the calls for assistance. For the future, we also plan to do some video training and upload them on the website to show the most common action to perform during the beamtime as sample transfer, sample loading through the load lock, approaching the cell to the analyser. We are continuously developing and upgrading the graphical user interfaces for the most used features of the beamline (sample heating, sputtering, gas dosing) in order to make the beamline as much user friendly as possible and, at the same time, integrated into the MAX IV control system.
We have defined a beamline-stability-measurement protocol that consists in measuring the flux and the energy calibration at three different energies prior to each beamtime and comparing it with the results of the previous week in order to individuate quickly eventual loss of intensity or misalignment of the beam.
A typical week at HIPPIE can be described as follow:

- Monday – installation of user's equipment (when needed), bakeout of the vacuum chambers, gas installation.
- Tuesday – First meeting with the users, start sample's mounting and sample's preparation (when needed), stop bake out in the evening. In addition, the light available on Tuesday may be used for beamline internal purposes; if the beam is stable (no other beamline commissioning) can be given already to users from Tuesday afternoon.
- Wednesday/Thursday – The local contact introduces the beamline and the endstation to the users and starts the beamtime with them.
- Friday – in the morning there is the weekly APXPS team meeting.
- Weekend – the local contact is on-call.
- Monday – discussion with the users about the concluded beamtime.

3. Research Programs and Scientific Results

3.1. User Communities

Figure 10 shows the fractions of beamtime that different user communities have had or will have during the coming term at HIPPIE. With almost one quarter of the beamtime, the catalysis community is clearly largest, but not overall dominating. So far, the users can make use of the two implemented AP cell designs described in section 1.2 – the catalysis AP cell, which really functions as a general purpose AP cell, and the liquid/EC AP cell. In addition, we have had several user groups that have made use of the IRRAS setup.

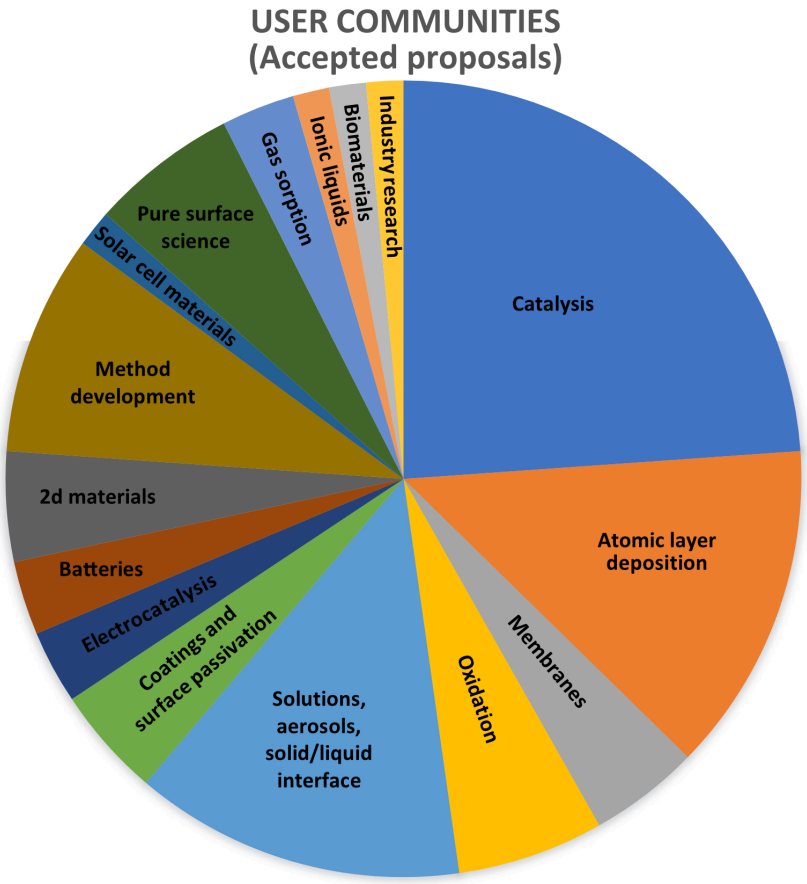

Figure 10. User communities at HIPPIE. The pie chart shows the fractions of the scientific domains with finished/accepted beamtimes at HIPPIE, including both general, in-house and industry users

During the initial five years of operation, 75% of the available beamtime is distributed to general users and 25% to in-house research, including external groups (at Lund University, Uppsala University and KTH) that have been involved in the building-up of the beamline.

General user programme: General users are awarded beamtime in the standard peer-review fashion. As suggested by Figure 10 HIPPIE is being used for research in many different scientific areas. It is clear that a large share of the general users has a surface science background and that they have diversified into different areas. This is visible from a predominance of research on crystalline samples, although we also offer possibilities for research on e.g. catalytic powder samples.

In-house programme: The in-house programme comprises a variety of *method and sample environment developments* for fast measurements, the use of gas pulsing (e.g. for temporal analysis of products in XPS (TAPXPS)), studies of the liquid/solid interface, batteries and electrochemistry, atomic layer and chemical vapour deposition, membranes for gas permeation, the use of standing waves in advanced depth profiling and the simultaneous measurement of APXPS and IRRAS. These developments are driven in *collaborations*: HIPPIE has a long-standing collaboration with the Division of Synchrotron Radiation Research at Lund University (Schnadt, Knudsen) that underlies the entire realisation of HIPPIE. Together with Maria Hahlin at Uppsala University the liquid/EC cell has been designed and set up, with Jonas Weissenrieder at KTH the IRRAS setup and catalysis AP cell have been designed and commissioned, and in collaboration Hendrik Bluhm (FHI Berlin and ALS) and Slavomir Nemsak (ALS) the SWAPPS method has been introduced at HIPPIE. The in-house programme also

serves to *introduce new users*: By definition, all users are new at a new beamline. However, using in-house beamtime efforts have been made to attract users that are not only new, but who do not have any APXPS and/or synchrotron experience. These are user groups from the Department of Chemistry at Oslo University, Department of Solid State Physics at Ghent University and Department of Chemistry at Copenhagen University, Jenny Rissler of RISE. Further collaborations in different areas underly the other in-house projects driven at HIPPIE.

Industry users: Since the start of operations HIPPIE has had 25 shifts of proprietary research. In addition, industry/industrial research institute users have applied for four beamtimes within the general user scheme, without, however, having been awarded beamtime.

3.2. User Statistics

Beamtime and proposal statistics, user feedback, publications

The HIPPIE beamline started user operation since early 2018. We got our first expert users in March 2018 and first general users – in May 2018. Table 4 summarises week distribution for the last 4 user periods between in-house/expert, commissioning, and general user time.

Table 4. Beamtime weeks distribution between commissioning, ih-house, and general users

	2018-I	2018-II – 2019-I	2019-II	2020-I
Commissioning	10	3	2	2
In-house/expert	6	14	5	3
General	5	13	9	10
Total	21	30	16	15
General user share (excluding commissioning)	45%	48%	64%	77%

Large commissioning share in 2018-I round is due to initial 6 weeks of beamline commissioning.

Table 5 shows history of proposal submission and oversubscription rate for same user periods.

Table 5. Proposal statistics

	2018-I	2018-II – 2019-I	2019-II	2020-I
Submitted	41	44	51	28
Accepted	5	13	9	11
Oversubscription	8.2	3.4	5.7	2.5

At the end of each beamtime users can leave feedback regarding 14 various parameters of the beamline, facility, team, infrastructure, and the experiment. The feedback is ranging from 1 (very bad) to 5 (excellent). They can also leave comments about specific experience they got at the beamline/MAX IV. Figure 11 shows distribution of the scores from the feedback forms for all areas. In the Figure we signify three groups of distributions depending on its skew. Black curves signify areas with mostly positive scores (4s and 5s) with the 5s being in majority (excellent on average). Blue curves signify areas with positive scores and 4s being in majority (good on average). Finally, red curves depict areas where substantial amount of satisfactory (3) or even non-satisfactory (1 or 2) scores are observed. In general users have rated quite high MAX IV support infrastructures (UO, web, reception, lunchroom, etc) and beamline support whereas they were less satisfied with the level of IT/software development (control and data acquisition, wi-fi, data access, etc). Figure 12 shows development of scores within time. To get the data represented in the Figure scores sorted by time in ascending order have

been approximated by a linear trend which have then been truncated at time zero. Thus, the Figure represents change in the (average) score since the beginning of user operation. It should be noted that the standard deviation of the score is approx. 1.0 which is larger than observed change. It also should be noted that presence of even single outlier score could substantially alter the trend. Therefore, care should be taken when drawing any conclusion from the Figure 12. Taking into account noticed limitations we noted that following areas have observed improved satisfaction from users since 2018: Beamline experimental control and data processing, endstation and its equipment, and the overall success of the beamtime. Decrease in the technical support satisfaction is due to a single low score from the beamtime in the end of 2019 (outliner score). Decrease in the beamline optic's satisfaction is mainly due to feedback issues which is part of controls area.

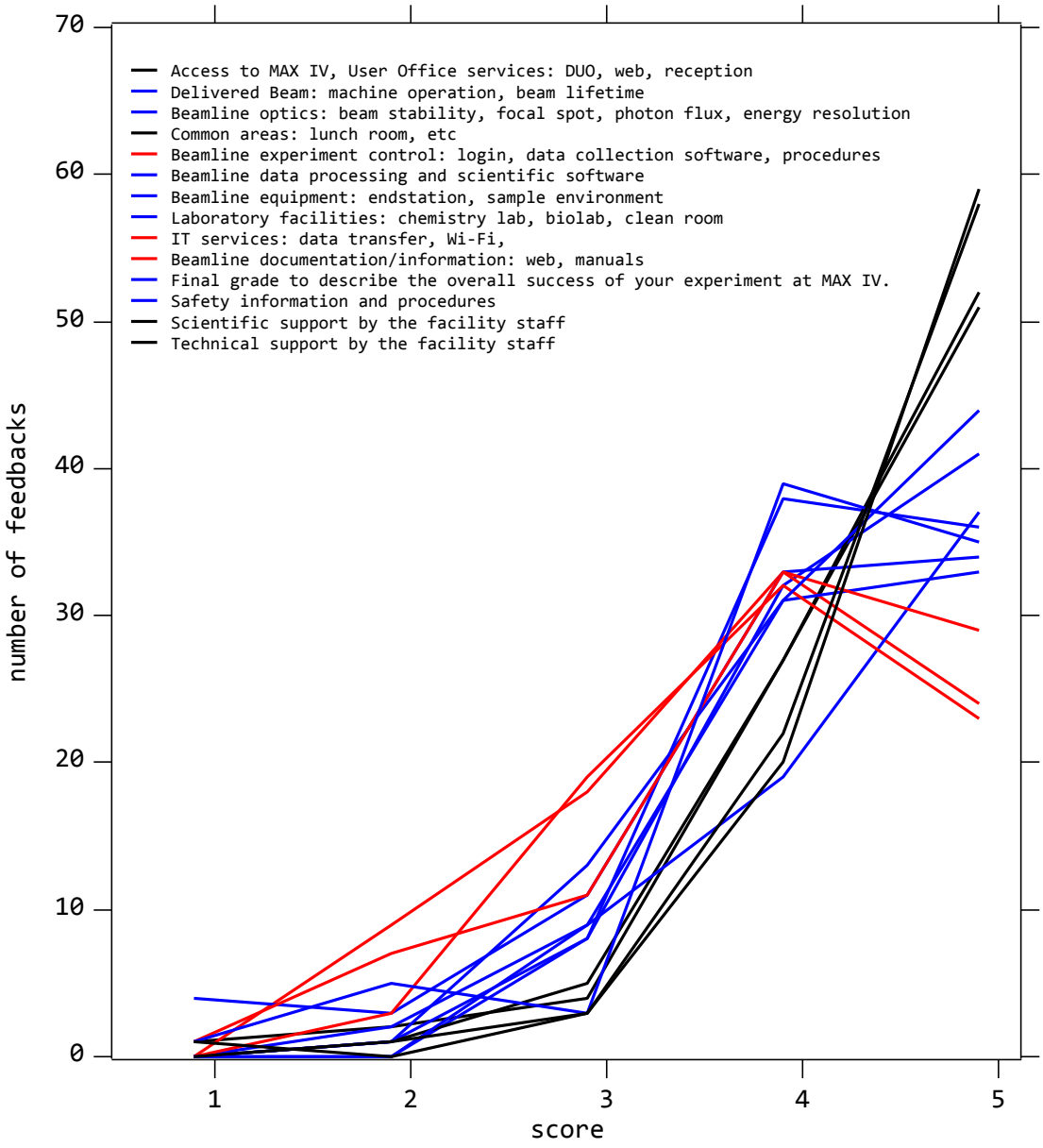

Figure 11. User feedback score distribution

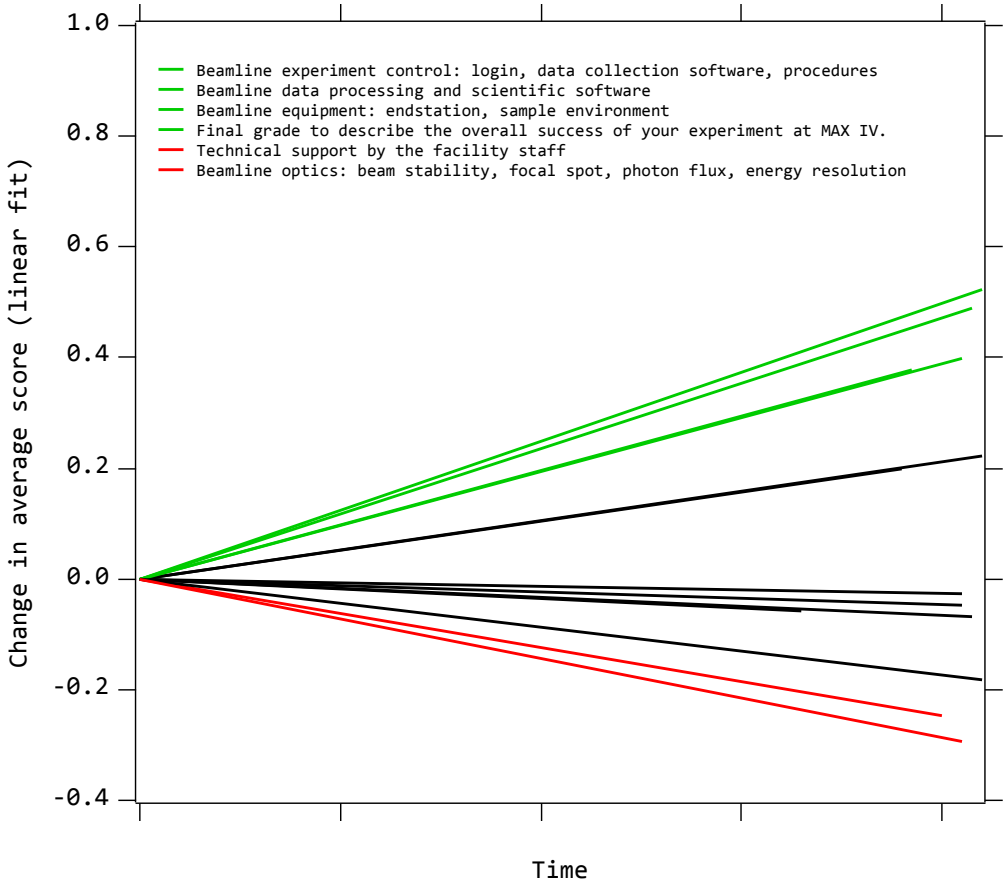

Figure 12. Average user feedback time evolution

At the time of the review seven papers containing data from the HIPPIE beamline have been published/submitted and about 10 are at various stages of data analysis/manuscript writing (according to our users). Below is the list of published and submitted papers:

1. **Redox Properties of Cu2O(100) and (111) Surfaces.** Chunlei Wang, Heloise Tissot, Carlos Escudero, Virginia Pérez-Dieste, Dario Stacchiola, and Jonas Weissenrieder. *The Journal of Physical Chemistry C, 2018 122 (50), 28684-28691.* DOI: 10.1021/acs.jpcc.8b08494
2. **High-Density Isolated Fe1O3 Sites on a Single-Crystal Cu2O(100) Surface.** Chunlei Wang, Heloise Tissot, Joakim Halldin Stenlid, Sarp Kaya, and Jonas Weissenrieder. *The Journal of Physical Chemistry Letters,* **2019** *10,* 7318-7323. DOI: 10.1021/acs.jpclett.9b02979
3. **Pt-Ga Model SCALMS on Modified HOPG: Thermal Behavior and Stability in UHV and Under Near-Ambient Conditions.** Chantal Hohner, Miroslav Kettner, Corinna Stumm, Dominik Blaumeiser, Haiko Wittkämper, Mathias Grabau, Matthias Schwarz, Christian Schuschke, Yaroslava Lykhach, Christian Papp, Hans-Peter Steinrück, Jörg Libuda. *The Journal of Physical Chemistry C,* ***2020*** *124, 2562-2573*. DOI: 10.1021/acs.jpcc.9b10944
4. **Mechanistic insight into carbon-carbon bond formation on cobalt under simulated Fischer-Tropsch synthesis conditions.** C. J. (Kees-Jan) Weststrate, Devyani Sharma, Daniel Garcia Rodriguez, Michael A. Gleeson, Hans O. A. Fredriksson & J. W. (Hans) Niemantsverdriet. *Nature Communications,* ***2020*** *11, 750.* DOI: 10.1038/s41467-020-14613-5

5. **Present and new frontiers in materials research by ambient pressure x-ray photoelectron spectroscopy**. Joachim Schnadt, Jan Knudsen, Niclas Johansson, *Submitted to Journal of Physics: Condensed Matter (2019).*
6. **Inverse single-site Fe1(OH)X/Pt(111) model catalyst for preferential oxidation of CO in H2.** Chunlei Wang, Heloise Tissot, Markus Soldemo, Junling Lu, Jonas Weissenrieder. *Submitted February 2020*
7. **Probing the Galvani potential difference in Li-ion batteries**. Fredrik Lindgren, Ida Källquist, Ming-Tao Lee, Andrey Shavorskiy, Kristina Edström, Håkan Rensmo, Leif Nyholm, Julia Maibach, Maria Hahlin. *Submitted to Nature Communication (February 2020)*

3.3. Users Scientific Results

Reactivity of hydrocarbonaceous adsorbates on highly covered surfaces, a near-ambient pressure study

C.J.(Kees-Jan) Weststrate[1], Devyani Sharma[1,2], Daniel Garcia Rodriguez[1,2], Michael A. Gleeson[2], Hans O.A. Fredriksson[1] & J.W.(Hans) Niemantsverdriet[1,3]
[1]SynCat@DIFFER, Syngaschem BV, Eindhoven, The Netherlands.
[2] Dutch Institute for Fundamental Energy Research (DIFFER), Eindhoven, The Netherlands.
[3] SynCat@Beijing, Synfuels China Technology Co. Ltd., Beijing, China

Fischer-Tropsch synthesis is a well-known reaction that is used on a commercial scale to convert synthesis gas, a mixture of carbon monoxide and hydrogen, into long chain hydrocarbons. Cobalt metal is an active catalyst for this highly complex reaction, and the mechanistic details have been debated for many years. In our work we use a simplified model catalyst, a single crystal surface of cobalt, to get more detailed experimental information about how hydrocarbon species react on the catalyst surface. Since the catalyst under reaction conditions is highly covered it is important to take the influence of a high surface coverage into account.

Ethene was chosen as a simple precursor to generate C_2H_x adsorbates on the cobalt surface to study their reactivity. As a first step the clean Co(0001) sample was exposed to a small dose of ethylene while the sample was held at 313 K. At this temperature ethylene decomposes upon adsorption to form acetylene, C_2H_2 and by keeping the dose low the surface coverage was kept low to allow adsorption of other adsorbates during later stages in the experiment. The lower part of figure 1 shows a heat map of a series of C1s spectra that was recorded, with an interval of ~30 seconds for each spectrum, during exposure to an increasingly high pressure of H_2 up to 10^{-1} mbar, while the top view shows selected spectra at key points. A H^2 pressure of ~10^{-5} mbar would be sufficient to create a high hydrogen coverage at 313 K, but the spectra shape shows that co-adsorbed hydrogen alone does not cause the acetylene to react. After closing the pressure cell the H_2 pressure was further increased to 10^{-2} mbar, and at this point the unexpected appearance of adsorbed CO is evident from the peaks that appear around 285.5 eV in the C1s spectrum. The presence of CO sets off a sequence of reactions where

acetylene is first converted to ethylidyne followed by C-C bond formation via coupling of two ethylidyne species.

The combination of UHV to prepare a well-defined starting point combined with fast measurements of the C1s core level spectrum during exposure to near-ambient pressures allowed us to do an in-situ study of the surface reactivity of hydrocarbonaceous intermediates, on a highly covered surface that mimics the situation under reaction conditions in applied catalysis. By comparing these results with experiments in vacuum without co-adsorbates we demonstrate that the CO molecules are not directly involved in the C-C bond forming reaction but stabilize C_xH_y adsorbates as alkylidyne intermediates that readily react to form new C-C bonds. This makes it likely that the intermediates observed in our model system also participate in the reaction that produces long chains in applied catalysis.

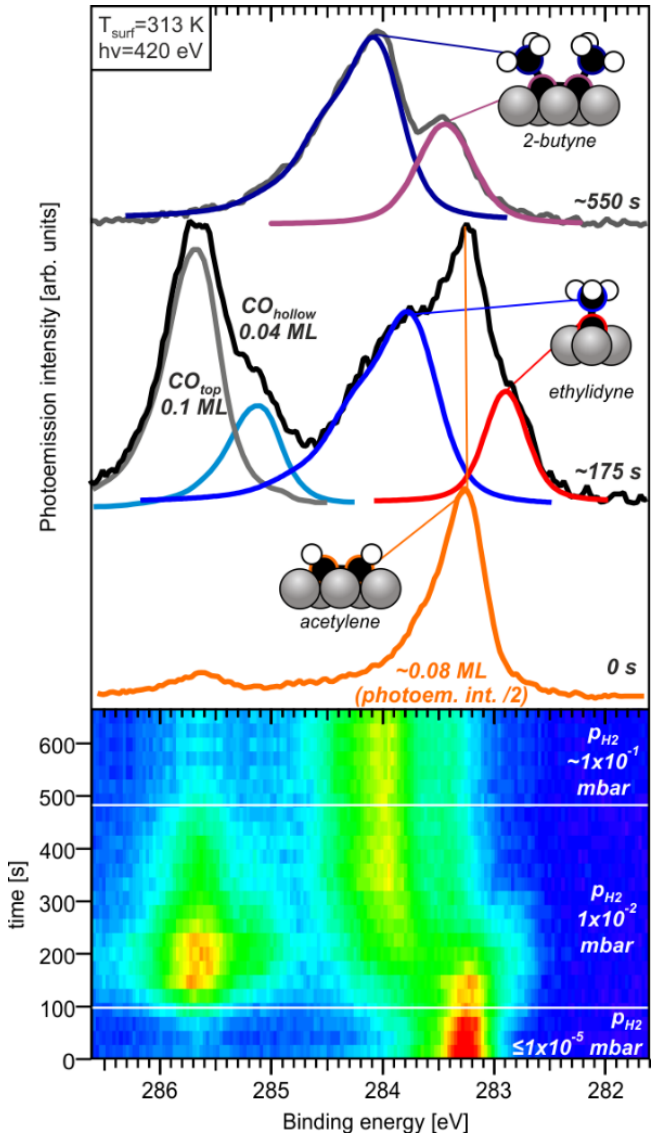

Figure 13. XPS at near-ambient pressures. C1s spectra recorded during exposure of an acetylene-covered Co(0001) surface to increasingly high H_2 pressures at T=313 K. The time evolution of the C1s spectra is shown in the lower panel, whereas the top view shows the spectra at specific stages of the experiment (hv = 420 eV). Note that the signal intensity of the acetylene spectrum in the upper panel was divided by 2 to facilitate comparison

Adsorption of carbon monoxide on a Pt(111) surface at mbar pressures studied by PM-IRRAS and APXPS

Chunlei Wang[1], Heloise Tissot[1], Joakim Halldin Stenlid[2,3], Sarp Kaya[4,5], and Jonas Weissenrieder[1]

[1] Material Physics, School of Engineering Sciences, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[2] Department of Physics, Albanova University Center, Stockholm University, SE-106 91 Stockholm, Sweden

[3] Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[4] Koç University TUPRAS Energy Center, 34450 Istanbul, Turkey

[5] Chemistry Department, Koç University, 34450 Istanbul, Turkey

The *in situ* X-ray photoelectron spectroscopy (XPS) and polarisation-modulated infrared reflection absorption spectroscopy (PM-IRRAS) results were collected using the described above PM-IRRAS setup, with a spectral resolution of 8 cm^{-1}. The Pt(111) crystal was cleaned by a standard sputtering-annealing procedure. Following CO introduction into the analysis chamber the O 1s XP spectra Figure 14a show CO adsorbed in the expected on-top (532.7 eV) and bridge (531 eV) positions of Pt(111) [1,2]. The on-top/bridge O 1s peak intensity ratio was calculated after fitting all of the XP spectra. The evolution of the ratio as a function of CO pressures is shown as insert in Figure 14b (black curve). As expected, the on-top/ bridge intensity ratio increases with CO pressure, which indicates that the surfaceaccommodates an increasing coverage of on-top CO at higher CO pressures. Figure 14b shows the simultaneously collected *in situ* PM-IRA spectra. The indicated peak positions reflect the center of integrated peak area. Two absorption bands are observed at 2095 cm^{-1} and 1854 cm^{-1} at a CO partial pressure of 1.2 x 10^{-8} mbar, consistent with CO adsorption on Pt(111) on-top and bridge sites. [3] The position of the bridge component blue shifts with increasing CO pressure. This blue shift has previously been interpreted as a signature for formation of a compressed high-coverage *c*(4×2) CO layer on the surface and is interpreted as a result of an increased adsorbate-adsorbate repulsion.[4] The formation of the high-coverage CO phase changes the relative coverage of the CO adsorbed in on-top and bridge sites. In the insert of Figure 14b this change in relative coverage is correlated with the IR position of the CO bridge band. At increasing bridge to on-top ratio, a blue shift in CO bridge position is observed. Upon evacuation of the analysis cell, the CO on-top to bridge O 1s intensity ratio decreases slightly due to CO desorption from the surface. The decrease in CO bridge surface coverage is immediately observed in PM-IRAS as a red shift in the CO bridge position.

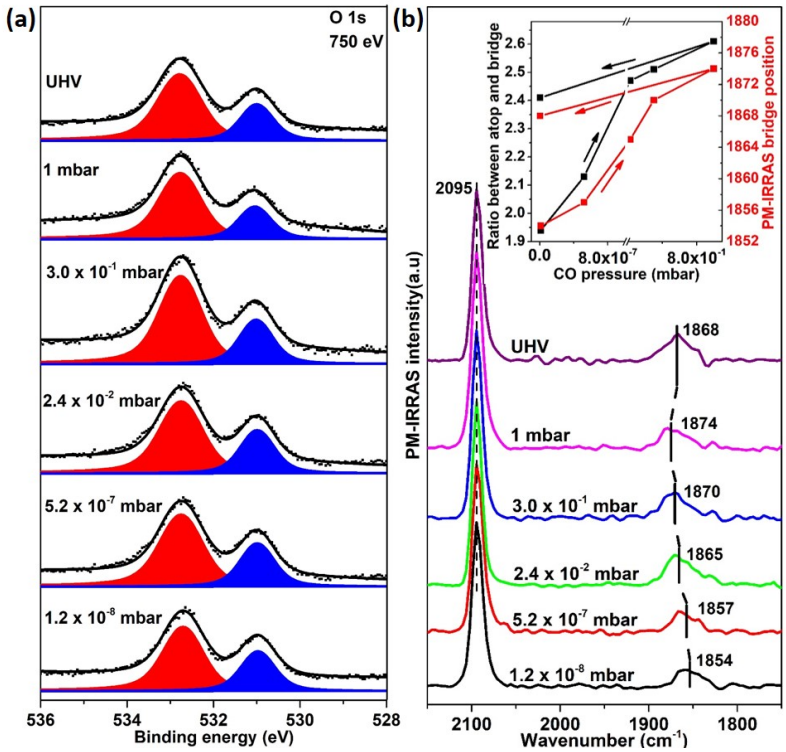

Figure 14. Simultaneous in situ a) O 1s XPS and b) PM-IRAS spectra from Pt(111) as a function of CO pressure. The O 1s spectra were collected at hv = 750 eV. The insert in b) shows the correlation between the ratio the O 1s on-top and bridge peak areas (left axis)

[1] Knudsen, J. , Andersen, J. N. & Schnadt, J.(2016), *Surf. Sci.*, **646**, 160-169

[2] Björneholm, O.; Nilsson, A.; Tillborg, H.; Bennich, P.; Sandell, A.; Hernnäs, B.; Puglia, C.; Mårtensson, N., Overlayer structure from adsorbate and substrate core level binding energy shifts: CO, CCH3 and O on Pt (111). *Surface science* 1994, 315, L983-L989

[3] Crea, F.; De Stefano, C.; Milea, D.; Sammartano, S., Speciation of phytate ion in aqueous solution. Thermodynamic parameters for zinc (II) sequestration at different ionic strengths and temperatures. *Journal of Solution Chemistry* 2009, 38, 115-134

[4] Carrasco, E.; Aumer, A.; Brown, M. A.; Dowler, R.; Palacio, I.; Song, S.; Sterrer, M., Infrared spectra of high coverage CO adsorption structures on Pt (111). *Surface Science* 2010, 604, 1320-1325

3.4. In-house Scientific Results

Retarding Cu oxidation with 2D materials coatings

Mattia Scardamaglia[1], Virginia Boix[2], Giulio D'Acunto[2], Claudia Struzzi[1], Jan Knudsen[1,2], Nicolas Reckinger[3], Xin Chen[4], Abhay Shivayogimath[4], Tim Booth[4]

[1] *MAX IV Laboratory, Lund University, Sweden*

[2] *Division of Synchrotron Radiation Research, Lund University, Sweden*

[3] *Department of Physics, University of Namur, Belgium*

[4] *DTU Physics, Technical University of Denmark, Denmark*

A field where APXPS can show its full potential is the study of metal corrosion. In the experiments presented here, we are studying the protective role that different 2D materials

coatings (graphene and hexagonal boron nitride, grown by collaborators at DTU Physics - Denmark) have towards the oxidation of a copper foil. Being impermeable to liquids and gases and inert to most chemicals, they are very promising candidates. Of strong technological interest is the high-temperature corrosion phenomenon, which is the chemical deterioration of a metal as a result of heating in an aggressive (e.g. oxidizing) environment. This form of corrosion is of particular interest for materials used in car engines, power generation, turbines, or other machinery being exposed to an atmosphere containing corrosive products of combustion at high temperatures.

During the experiments, the ambient pressure cell of HIPPIE beamline is filled with 2 mbar of O_2 gas, then the samples are heated with a constant temperature ramp (6 °C/min). Thanks to the fast acquisition of the ScientaOmicron analyser, we could follow different regions at the same time to understand the dynamics of the process with a temperature resolution of about 1 °C. O 1s core level and Cu LMM Auger line (Figure 15) give important information about the oxidation state of the copper substrate, while C 1s and N 1s, B 1s core levels are fingerprint of the coating layer (graphene and hBN, respectively).

The oxidation of a bare Cu foil starts already at room temperature with the formation of a thin

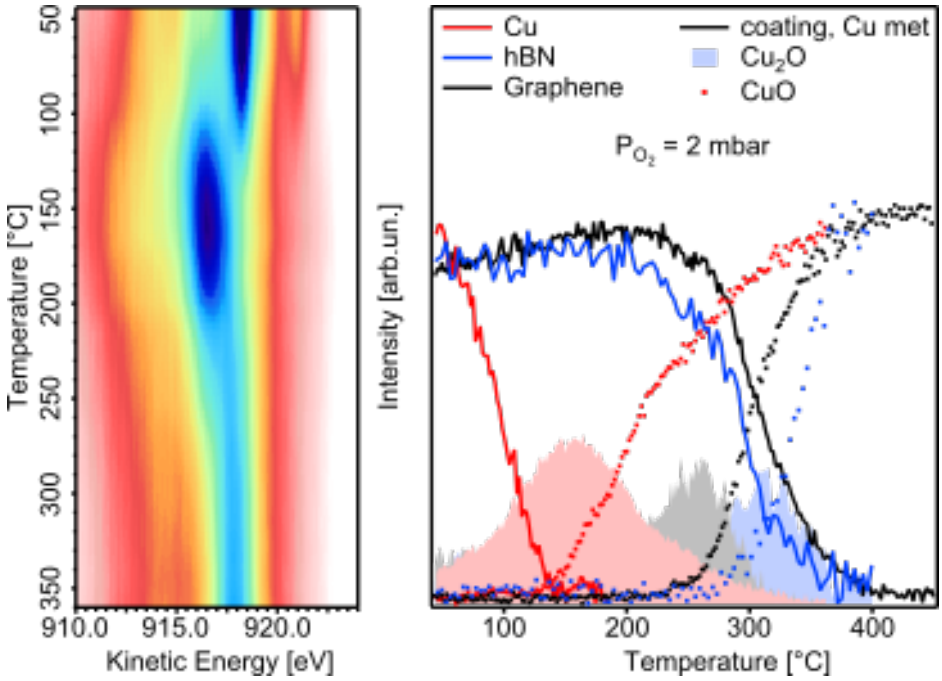

Figure 15. left) Cu LMM image plots measured on Cu foil at 2 mbar O_2 during linear temperature ramp. Right) Intensity line profiles of copper (red), hBN (blue) and graphene (black) measured on the respective coating most significant core level or metal-Cu (full line), and following Cu2O (shaded area) and CuO (dotted line) formation from Cu LMM and O 1s maps

Cu_2O layer which thickness increases with temperature and then starts transforming into CuO from 150 °C. When the copper is covered by 2D monolayers both thresholds are retarded and shifted to higher temperature (Figure 15). In hBN, Cu_2O only forms once the coating is etched away (around 300 °C). In the case of graphene, although the etching occurs at a slightly higher temperature, the formation of Cu_2O starts before (around 250 °C) and coexist with the carbon 2D layer, contrary to the hBN. From a detailed analysis of the C 1s, we found a shift of the peak towards lower binding energy when the Cu_2O formation starts: this is consistent with oxygen intercalation beneath graphene that reduces the interaction with the metallic substrate. The following increase of temperature and consequent formation of CuO are responsible for the graphene etching. The CuO formation is faster on both hBN and graphene

with respect to Cu foil and it starts above 300 °C. The demonstration that graphene and hBN hinder the oxidation of copper in an aggressive environment at high temperatures, shows their great potential as stable protective layers, with only one atom thickness, which retards the formation of copper oxide. Our findings clearly show that the detrimental interaction between oxygen and copper starts when the gas intercalates beneath 2D materials flakes, especially from boundaries and defects; therefore, this is a clear indication that bigger and defect-free flakes provide the best anticorrosive protection.
APXPS technique pushes the limit of standard photoemission spectroscopy, traditionally limited to UHV conditions for fundamental studies, and leads the way toward direct and real time studies of surfaces and interfaces under more realistic working conditions.
This work will continue in the future by studying other corrosive gases (as NO_2) and the effect of different relative humidity level.
Mattia Scardamaglia et al. ACS Appl. Mater. Interfaces 11, 29448−29457 (2019)
Mattia Scardamaglia et al. *in preparation (2020)*

Following the kinetics of confined catalysis under 2D films with ambient pressure x-ray photoelectron spectroscopy

Virginia Boix[1], Tamires Gallo[1], Mattia Scardamaglia[2], Marie Døvre Strømsheim[3], Filippo Cavalca[2], Suyun Zhu[2], Andrey Shavorskiy[2], Joachim Schnadt[1,2,4], Jan Knudsen[1,2]
[1]*Division of Synchrotron Radiation Research, Lund University, Sweden*
[2]*MAX IV Laboratory, Lund University, Lund, Sweden*
[3]*Norwegian University of Science and Technology, Trondheim, Norway*
[4]*NanoLund, Lund University, Lund, Sweden*

Enhanced activity or selectivity of catalytically active metal clusters placed in confined environment such as carbon nanotubes and zeolites have been studied for a variety of systems. The complexity of these confined catalyst materials makes it, however, difficult to achieve an atomic scale understanding of their function. One way to reduce the complexity is to replace the active 3D clusters with active single crystal surfaces and use 2D materials such as graphene (Gr), hexagonal boron nitride (h-BN), silicene etc. to form 2D nano-reactors and then perform the confined chemistry below this cover [1]
Previously, we used x-ray photoelectron spectroscopy (XPS) to study intercalation and reactions below graphene flakes at ultra-high vacuum (UHV) conditions. With those studies, we got an atomistic understanding of the intercalation process of CO, H_2, and O_2 and the corresponding oxidation reactions performed under the Gr flakes at UHV conditions [2].
In this study, we followed the kinetics of a confined reactions under graphene flakes grown on Ir(111) by using short pulses of changing partial pressures to repeatedly intercalate and de-intercalate the Gr flakes while following the process in-situ with ambient pressure XPS (APXPS). Figure 16 show an image plot of C 1s spectra originating from graphene flakes

supported by Ir(111). The image plot was measured with 10 Hz time resolution in snap-shot mode at 370 K in 1 mbar O_2 using a flow of 10 sccm. At these conditions the graphene flakes are intercalated by a p(2×1)-O phase signaled by a graphene component ($C_{O\text{-}int}$) located at 283.6 eV [2]. Two 50 sec pulses of 9:1 sccm H_2:O_2 are subsequently injected into the gas supply and the C 1s signal from graphene signals how hydrogen rapidly react with oxygen under the film to form water under the graphene cover. The water under graphene is signaled by the C 1s graphene component located at 284.4 eV ($C_{OH\text{-}H2O}$) [2]. At the same time another component (C_{Gr}) is observed at the 284.1 eV consistent with pristine graphene. This observation tells us that the water formed under the graphene flakes condense into dense water islands causing the $C_{OH\text{-}H2O}$ component. As oxygen is removed under the graphene flakes by water formation and as the formed water molecules condense we observe also a pristine graphene component C_{Gr}. Figure 16 clearly shows that hydrogen diffusion in under graphene and the subsequent water formation is a fast process. In contrast, the water removal followed by subsequent oxygen intercalation is a slow process that takes minutes most likely because water is a large molecule that is difficult to push out from under the graphene flakes. Altogether, the figure, nicely demonstrates how we can follow the kinetics of surface process below a 2D film in the mbar regime with APXPS, something that to the best of our knowledge never has been done before. In addition, to the work discussed here we studied H_2 as well as CO oxidation at different temperatures both under graphene and h-BN flakes and one article is currently in preparation.

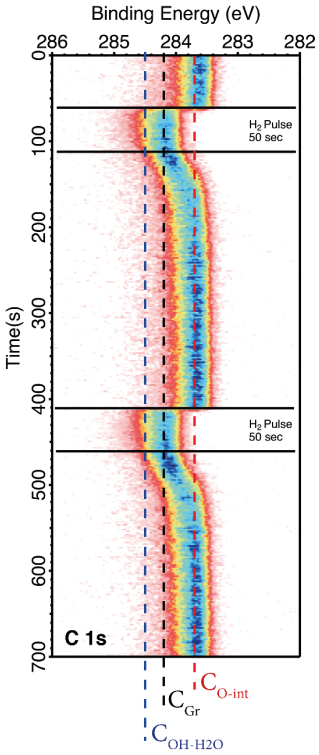

Figure 16. C 1s image plots measured on 0.5 ML graphene flakes on Ir(111) at 370K during two subsequent H2:O2 pulses (9:1 sccm). In between pulses, the sample is kept at an oxygen atmosphere (10 sccm O2). The total pressure is kept at 1 mbar

[1] Q. Fu, X. Bao, Chem. Soc. Rev., 2017, 46, 1842-1874
[2] E. Grånäs, PhD thesis, Lund University 2014

ALD of HfO_2 on InAs: new insight by time-resolved *in situ* studies

Giulio D'Acunto[1], Andrea Troian[1], Esko Kokkonen[2], Sofie Yngman[1], Foqia Rehman[1], Zhihua Yong[1], Joachim Schnadt[1,2] and Rainer Timm[1]

[1]Division of Synchrotron Radiation Research, Department of Physics and NanoLund, Lund University, Lund, Sweden
[2]MAX IV Laboratory, Lund University, Lund, Sweden

Atomic layer deposition (ALD) is a technique that allows the deposition of high-quality ultrathin films of binary materials such as metal oxides and nitrides from cycles of alternate exposure of a support to two different gaseous precursors that react with the support in a self-limiting fashion, at pressures of around 10^{-4} to 100 mbar [1]. One ALD area of interest is the deposition of high-k oxide layers such as HfO_2 on semiconductor supports for device technology. However, the HfO_2 (and other) layers deposited by thermal ALD still suffer from defects and contaminants that result from deficiencies in the deposition process [2]. This calls for a better understanding of the ALD chemistry, and therefore we have developed during recent years an APXPS programme for the investigation of the surface chemistry of ALD [3].

Figure 17 shows APXPS data obtained during the exposure of an InAs(100) support to tetrakis(dimethylamido) hafnium (TDAMHf), i.e. during the very first half-cycle of HfO_2 ALD. The data provide unique insight in the surface chemical processes that occur during the initial interaction of TDMAHf with the InAs(100) surface. The removal of the oxide (with concomitant lineshape changes in the In 3d and As 3d core level spectra) can be correlated with the development of the Hf 4f intensity. The shift in the latter, initially down in energy and later up in energy can be related to the details of the interaction of the TDMAHf precursor with the surface: The interaction is characterised by initial molecular adsorption, that goes along with the formation of a bond between the complex and surface via a ligand. First later, when the Hf 4f binding energy moves upwards, the bond between the Hf ion and ligand is broken to result in the formation of a Hf-surface bond. From a detailed analysis of the In 3d spectra, it becomes clear that an oxygen binding layer remains between the surface and adsorbed complex fragment.

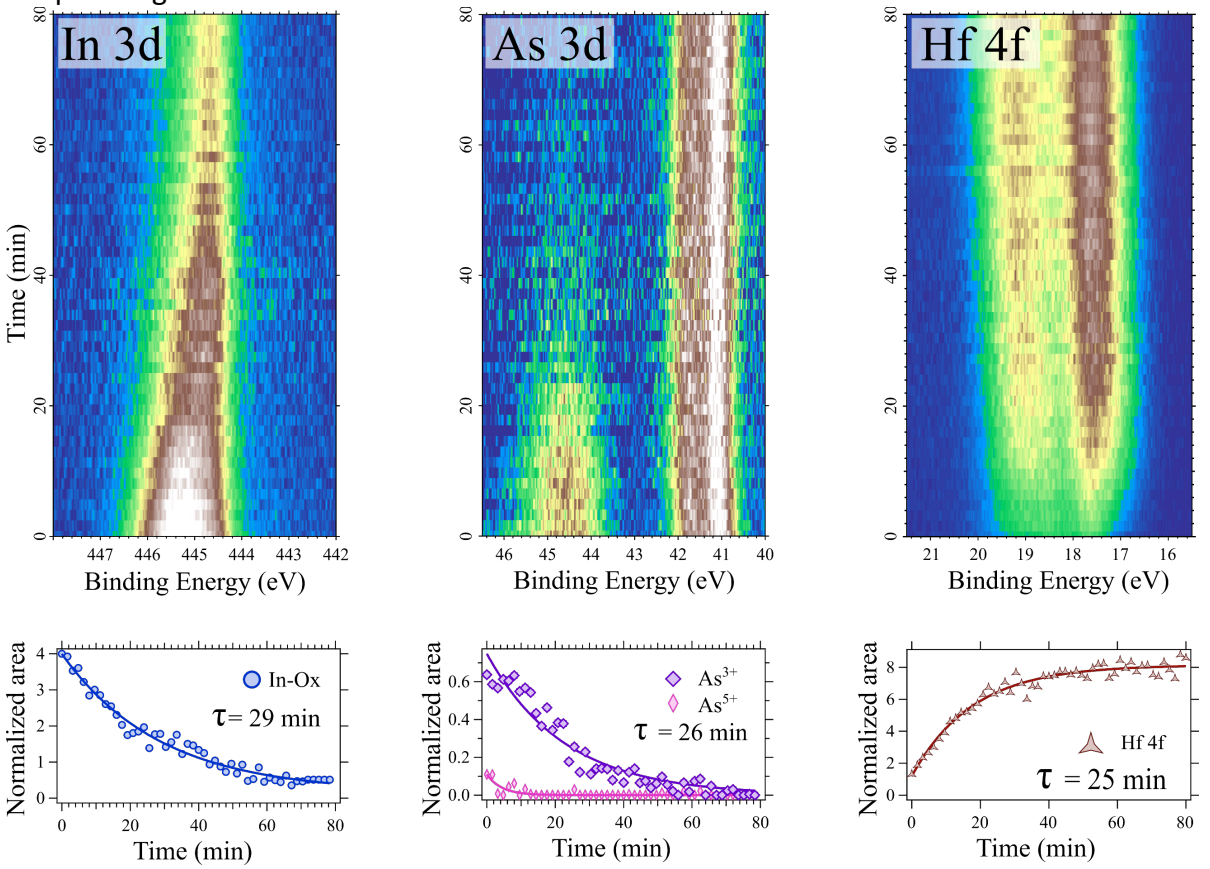

Figure 17. Time-resolvedAPXPS data measured during the exposure of InAs(100) to TDAMHf at~10-4mbar.The top row shows the In3d, As 3d (with the oxide peak at around 44.5 eV and the bulk peak at around 41.5 eV) and Hf 4f data recorded quasi-simultaneously in fixed mode at frequency of around 0.1 Hz. The bottom row shows an evaluation of the development of the different intensities and their exponential time constants. For the As 3d core level the line can be analysed by curve fitting in terms of the As3+and As5+oxide components

The recording of time-resolved APXP spectra during ALD, at the same pressures as used in conventional ALD reactors, are made possible by the excellent photon flux at the HIPPIE beamline. The TDMAHf process is relatively slow, but from similar investigations we have seen that it is possible to characterise other ALD surface chemistries with much higher frame rates.

[1] V. Miikkulainen et al., J. Appl. Phys. 113 (2013) 021301
[2] F. Zaera, Coord. Chem. Rev. 257 (2013) 3177

[3] A. R. Head et al., J. Phys. Chem. C 120 (2016) 243; R. Timm et al., Nature Commun. 9 (2018) 1412; A. R. Head et al., J. Vac. Sci. Technol. A 36 (2018) 02D405; P. Shayesteh, PhD thesis (2019) Lund University

4. Future developments

To keep the beamline at the forefront of the scientific and instrumental development the HIPPIE team is continuously improving current functionalities as well as developing new ones. Thus, for example, we have used the high acquisition rate of the electron detector in order to measure time-resolved (sub 100 ms) XPS. This in combination with rapid and periodic changes in the sample temperature (via pulsing the laser power) or gas phase composition (via pulsing gas flow rates) allowed us to look at the transient changes of the chemical states of both gas phase and sample's surface. The beamline team together with collaborators from FHI (H. Bluhm) and Frei University (T. Risse) recently started developing a setup for studies of sub-surface catalysis on metallic membranes. There is currently a RAC proposal awaiting decision on Feb 29, which could substantially contribute both people and investments in the instrumentation at the beamline if positively evaluated. Another metallic membrane project (however for gas separation purpose) is currently driven by a group of users (H. Venvik, NTNU) with beamline providing technical support. The Atomic Layer Deposition project which proceeds simultaneously at both SPECIES and HIPPIE beamlines by several groups involves both scientific developments as well as technical - a new in situ AP cell dedicated for ALD has just been successfuly tested at SPECIES and will be available for general users in an ongoing call. The AP Standing Wave Photoemission Spectroscopy (SWAPPS) has recently been introduced at HIPPIE in an EC cell. It particularly benefited from the high brightness of the MAX IV ring and the small beam divergence. The time necessary to record a rocking curve decreased substantially compared to other APXPS systems. A High-Pressure Reactor is one of the initially proposed functionalities designed for offline catalytic measurements at pressures close to 1 bar. The reactor is awaiting resources from MAX IV for commissioning. A new catalysis AP cell funded by MAX IV will include multiple functionalities such as a spare catalysis cell with extra-clean environment, high-T (>1000 C), multi-gas and multi-liquid dosing. The sample heater in the Prep chamber will be replaced with a laser to allow fully-automatic sample cleaning (sputtering/annealing cycles) as well as high preparation temperatures. An EC cell based on FHI design and a 1 bar catalysis cell are described in details in sections below.

4.1. B-branch

HIPPIE beamline was originally designed with two branches. Branch B is built up the exit slit and requires M3 switching mirror, M4 refocusing mirror and the endstation to be operational. As described above, the currently operating branchline is dedicated to APXPS and has two available AP cells (catalysis and liquid/electrochemistry). The exchange of these cells takes approximately 3 to 5 days and requires the participation of all beamline personnel. This constrains substantially the user scheduling without loss of beamtime for the exchange process. On the other hand, when in operation, each cell is available for use for 120 hrs in a row (5 days x 24 hrs). This creates extreme demand to the user groups in terms of available personnel to be able to use efficiently all available time. It also implies that scheduling shorter beamtimes (2-3 days) is difficult due to necessity for bakeout between switches.

Having reached almost 2 years of operation, the second branch project is now the most important future long-term development.
To understand the needs and the research interests of the Swedish scientific community, we hold on December the 10th 2019 a workshop at MAX IV with prominent scientists within the fields of chemistry and physics from major Swedish universities to discuss with them about the possibilities for instrumentation and techniques at the branch B of HIPPIE beamline.
During this workshop, their proposals and the ones from the APXPS team (composed by the personnel of HIPPIE and SPECIES beamlines) has been presented, discussed and ranked.
After discussion, four out of eight different proposals were chosen as possible future technical solution at the B-branch:

- "1 bar" cell: ultra-small cell compatible with the existing UHV system which will open new possibilities in catalysis for system operating at real conditions.
- HAXPES analyser (capable of measuring KE up to at least 6 keV) will create the possibility to roll-in the endstation once an open port at the hard X-ray beamlines become available.
- Relocation of the existing Liquid/EC cell which will require only an electron energy analyser and will remove tension from the scheduling of the beamtimes on such a high demand technique.
- Complementary techniques such as a preparation chamber, lab hard x-ray source, X-ray detector (for XAS, elastic scattering, or RIXS), time resolution ability.

These proposals largely overlap, a common ground behind this choice is the existing team knowledge and experience and the very high demand for both existing cells. The availability of a second branch at HIPPIE, with the separation of the two setups would allow a substantial increase in the efficiency of their use. When both cells are permanently fixed it becomes much easier to maintain them and perform small improvement projects. It will also allow two-shift-a-day scheduling which would enable shorter beamtimes currently not possible at HIPPIE. In turn, this would increase number of user throughput and thus number of publications. Finally, the setup at branch B will also create possibility to use it as a test setup (on- and off-line) for some high-risk experiments without sacrificing user time at the catalysis AP cell.
At the moment APXPS team is waiting for an official letter of support from the community of users and will join MAX IV process for consolidated funding application for new phase beamlines in the end of 2020

4.2. 1 bar cell

The APXPS community is expanding very fast and the technique is also continuously developing. One the of trend is to keep increasing the pressure of operation around the sample area; there are several reports in the literature already showing different approaches to rise the sample area pressure from (near) ambition pressure (dozens of mbar) to real atmospheric pressure (1 bar).
In collaboration with Axel Knop-Gericke's group (Fritz-Haber-Institute, Germany), HIPPIE team is currently designing two cells allowing users to approach atmospheric pressure XPS. The basic principle is to use a photoelectron transparent membrane (SiN grid with µm-sized holes covered by graphene) in the gas cell to separate the atmospheric pressure inside the cell from the vacuum on the outside and to maintain UHV conditions in the analyser (shown in Figure 18).
The first cell is based on FHI designed electrochemistry cell: a PEEK vessel allows flowing very small amount electrolyte through it, working electrode direct mounted on the membrane,

reference electrode and counter are mounted from side and rear. The second one is designed for catalysis user community: a flag style sample station is mounted on a piezo motion stage sitting in a small vessel, the vessel is isolated from outside UHV vacuum chamber via the membrane, a camera is used to measure sample-membrane distance, sample can be heated up 600 °C by a IR laser from backwards. Both cell schemes are shown in Figure 19. Left) EC cell scheme. Right) catalysis cell scheme.. Both cells are under design and construction period, they will be ready in the end of May, and one-week beamtime in June is booked for testing. If things work well, those cells will be offered to the users from the autumn 2020 call for proposals.

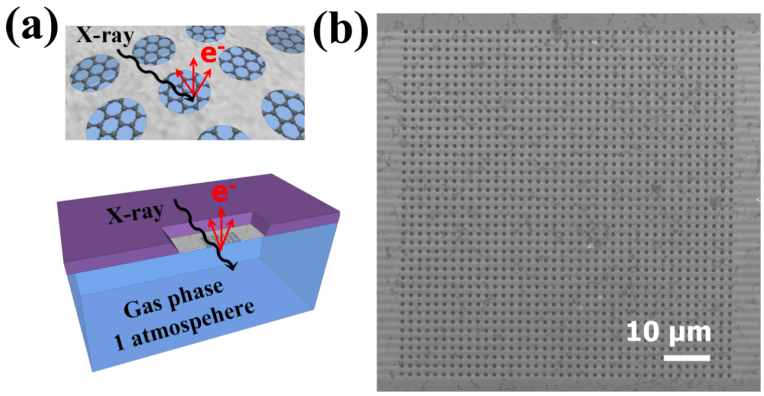

Figure 18. Membrane sketch. (b) SEM image of the holes array (80 µm×80 µm array with one 1 µm diameter holes) fully coated by a bi-layer graphene (BLG). [1]

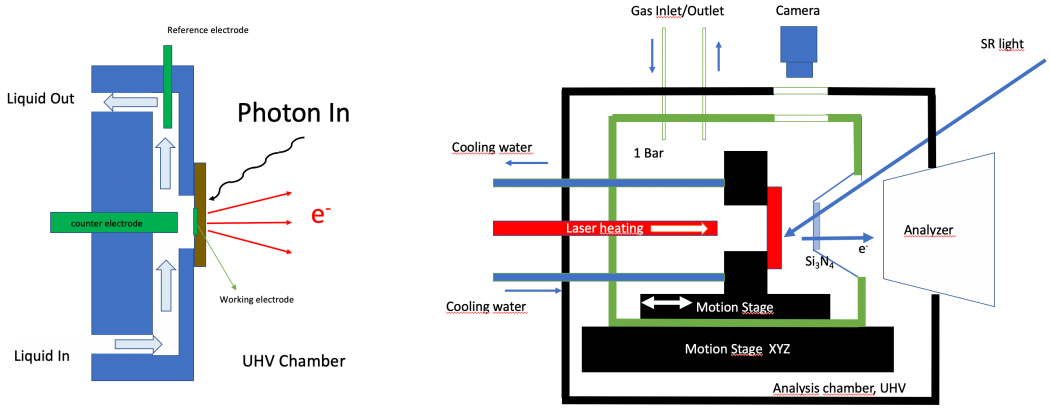

Figure 19. Left) EC cell scheme. Right) catalysis cell scheme.