

Multiscale photon-based spectroscopies for In-Situ and In-Operando spamming the water window in time and energy landscape

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The need for watching the catalytic reaction in operation got to be the focus of the light sources where number of dedicated experiments have been developed to track the electronic and molecular structural dynamics in operation. Two major challenges are coming together for this goal; first, is developing spectroscopic tools not only in energy domain but also the time domain. The photo-catalytic processes have early dynamics of 10s of femtosecond, further reaction take further seconds, minutes and even hours. Second, combination of tools to probe processes not only in solid, but also solutions and at interfaces. In this special issue we presenting the recent development at the soft X-ray light source BESSY-II for using photon source from infra-red and the extreme ultra-violet up to the soft X-ray photon for in-situ and in-operando applications addressing these two major challenges. As this work is a contribution of several groups, each section will present the group activities and related team members involving.

I. Bridging the “pressure gap” in photo-electron spectroscopy

The discrepancy between high operation pressures applied in catalysis and low pressures during surface sensitive X-ray characterization is known as the “pressure gap”. To bridge it, new setups and methodologies have been established, such as NAP-XPS (near ambient

pressure X-ray photoelectron spectroscopy), which allows pressures in the mbar range. [1] This technique was extended to higher photoelectron kinetic energies (KE). In combination with a small aperture nozzle, pressures up to 100 mbar [2] to be realized. An alternative approach to reach higher pressures entails the use of an electron transparent graphene membrane to separate sample environments from the vacuum required for operation of the spectrometer. [3] Here, we take advantage of an array of micro holes coated with graphene that solves the mechanical stability problem of free standing graphene covering large open areas while still providing high transmission for low KE electrons. [4] *Team from Fritz Haber headed by Dr. Knop-Gericke* have been able to investigate the local electronic structure of catalysts by means of surface sensitive photoelectron spectroscopy (PES) in the presence of gases at 1 bar (see Figure 1a) while simultaneously monitoring reaction products by mass spectrometry and gas chromatography. The hydrogenation of propyne was studied with this new gas reaction cell. Pd black was drop cast onto the graphene layer. The powder was exposed to a gas stream of He, He/H₂ and He/H₂/C₃H₄ at 1 bar and was heated to 80°C (see Figure 1b). The initial state of the Pd black is characterized by a mixture of Pd metal and Pd oxide. The Pd particles reduce when hydrogen is added to the gas stream, indicated by the disappearance of the Pd oxide peak in the Pd3d core level XP spectrum (Fig. 1b.2). Finally the addition of propyne to the feed induces the formation of a PdC_x compound characterized by a binding energy shift of the Pd3d peak to 335.6 eV (Fig 1b.3). Simultaneously, the formation of hydrogenation products like propane and propene was observed by gas chromatography.

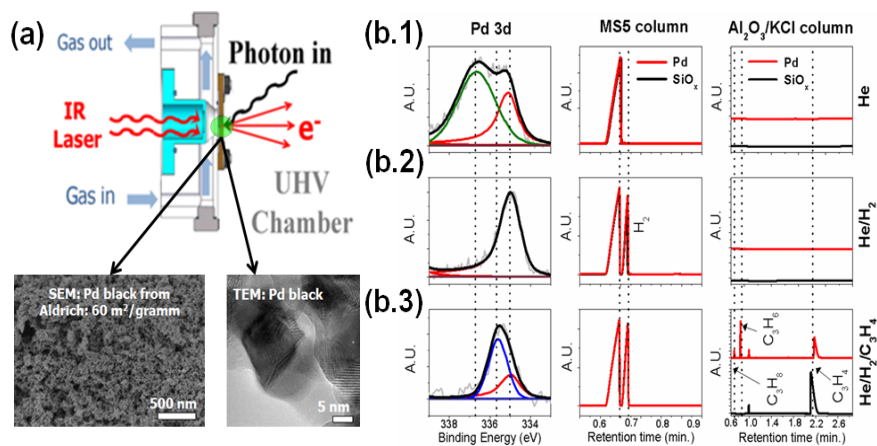


Figure 1: a) Gas reaction cell and SEM/TEM of Pd catalyst used b) Pd 3d XP spectra and gas chromatography traces using a mol sieve MS5 column and Al₂O₃/KCl column: b.1) He, b.2) He/H₂, and b.3) He/H₂/C₃H₄ gas mixtures.

In summary it was shown, that X-ray photoelectron spectra under reactions conditions at 1 bar can be measured simultaneously with the catalytic performance by the application of electron transparent graphene membranes.

II. In-situ and Operando Cells for Soft X-Ray Absorption and Emission Spectroscopy

Optimizing energy materials for complex applications such as water splitting or fuel cells requires a detailed understanding of their electronic structure under realistic working conditions. First row transition metal based materials (oxides, oxihydroxides etc.) containing Fe, Ni, Co, etc. are due to their abundance and stability currently of increasing interest. X-ray absorption and emission spectroscopy (XAS and XES) are suitable tools for revealing the occupied and unoccupied electronic structure of such materials. Challenging in this context is that that detailed electronic structure investigations via the transition metal L-edge require soft X-rays. The same applies to the oxygen K-edge, which is of mayor interest for the study of transition metal oxides or water splitting applications. Bridging the pressure gap between the vacuum conditions required for soft X-ray studies and the liquid electrolyte contained in a water splitting or fuel cell is one of the great challenges in this context. *The research group “Operando Characterization of Solar Fuel Materials” at the BESSYII facility headed by Dr. Lange* are developing in-situ and operando cells for soft X-ray absorption and emission spectroscopy. Two different approaches are followed: the first cell presented in figure 2a is developed for total fluorescence yield based soft XAS and XES. [5] In this cell the liquid is separated from the vacuum environment via a thin Si₃N₄ membrane. This membrane is coated with a thin gold layer (~20 nm), which serves as front contact of a three electrode setup and the catalyst and/or photoabsorber of interest. From the backside of the cell counter and reference electrode are implemented. The solution in the cell can be flown such that electrochemical deposition and investigations with a different electrolyte solution can take place without opening the cell. Implemented into the vacuum environment of the LiXEdrom [6] spectrometer at BESSYII total fluorescence yield spectra are detected with a GaAsP diode, whereas partial fluorescence yield spectra and XES spectra are recorded with a Rowland circle based spectrometer. With this cell the electronic structure changes can be monitored while applying varying voltages to the system. Usually, the changes in applied voltages lead to a change in oxidation state of the investigated transition metal. However, a spectral decomposition of TFY XAS spectra into spectral contributions from different oxidation states is due to saturation effects, background correlated or relaxation pathway dependent distortions often not possible. An example for such a distorted spectrum obtained in TFY mode from the Fe L-edge of a Co_{0.6}Fe_{0.4}O(OH) catalyst is shown in figure 2b and it is obvious that no direct deconvolution into spectra of different oxidation states can be made. Therefore the team developed specifically for XAS measurements an in-situ and operando transmission cell shown in figure

2c. [7] The heart of this cell is a sandwich configuration of two Si_3N_4 membranes, which are separated from each other with a 100 μm PTFE spacer. On the backside membrane a 20 μm gold film serves again as an electrode, on top of which the catalyst and/or photoabsorber of interest are deposited. In the space between the membranes an electrolyte solution can be flown. Close to the Au-coated membrane the reference and counter electrode are placed in the electrolyte. For measurements the He-pressure in the He-chambers 1 and 2 is increased such that the membranes are bent and the spacing between the membranes is reduced until transmission spectra can be obtained with a GaAsP photodiode behind the membrane sandwich. A holder in front of the membrane sandwich can be used to either record additionally TFY spectra with two GaAsP diodes or to apply visible light to the sample with two LEDs. If visible light is applied, a 200 nm Al foil in He-chamber 2 is used to block the visible light from the transmission diode. The advantage of the transmission cell design for the study of solids, liquids and solid/liquid interfaces under operando conditions (applied voltage/light illumination) are: (i) the possibility to measure XAS in transmission and fluorescence mode simultaneously, (ii) fast sample/membrane replacement (less than 5 min due to a systematic reduction of loose parts), (iii) reduced risk of beamline contamination with electrolyte solution due to two protection membranes, and (iv) manipulation of the sample with visible light. For comparison between the transmission and TFY measurements also the transmission spectrum of the $\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}(\text{OH})$ is shown in figure 2b and one can see that this spectrum is not affected by the above mentioned distortions. Complementary to these soft X-ray based approaches also systems for tender and hard X-rays are used and further developed.

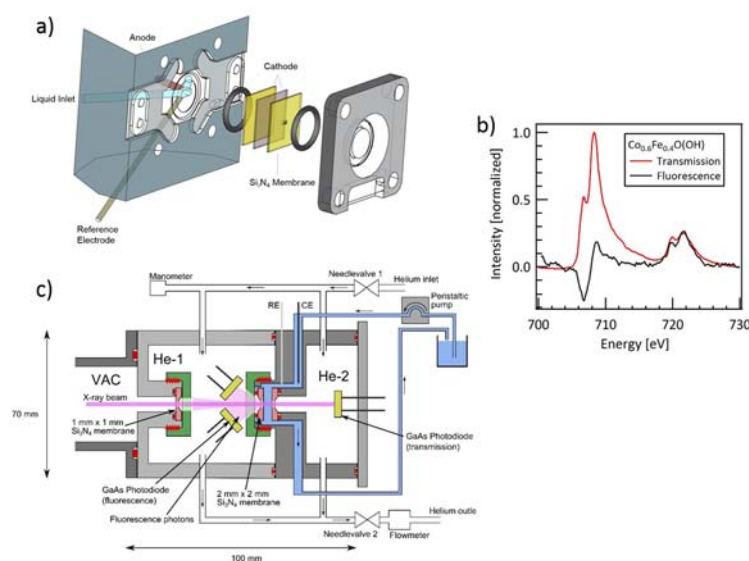


Figure 2: a) Design of the TFY XAS and XES in-situ and operando cell b) comparison of Fe L-edge spectra obtained from a $\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}(\text{OH})$ catalyst c) Design of the transmission XAS in-situ and operando cell

III. Soft X-ray Spectroscopy on Solid/Liquid Interface: A Closer Look on Heterogeneous Catalysis

To perform in operando XAS and resonant inelastic X-ray scattering study of water oxidation catalysts a group headed by **Dr. Xiao** and **Dr. Tisch** in **Dr. Aziz** team use the recently designed electrochemical flow cell by Dr. Lange team [5] (Figure 3.a). The cell allows to perform measurements with soft x-rays on catalyst under working conditions while it is separated from the vacuum by a 100nm thin Si₃N₄ membrane. Using a liquid inlet-outlet system the catalyst can be directly electrodeposited in situ. An energy dispersive detection of the emitted photons will provides information of electronic transitions within the system. To investigate chemical and catalytic reactions of liquids on a surface it is crucial to obtain detailed knowledge about the interfacial region where the reaction is occurring. Therefore, measurement techniques are needed that can unambiguously distinguish between signals stemming from bulk and the solid/liquid interface. For this, the team developed further a liquid flow cell comprising a gold-coated Si₃N₄ membrane that serves as interface to the liquid and as barrier between liquid and vacuum (see figure 3.b). An additional backside electrode allows to bias the system. The molecules at the surface and in the bulk will be studied simultaneously by fluorescence and electron yield. The unique point her is that the XA spectrum based on total electron yield (TEY) signal can directly compared to the XA spectrum from bulk sensitive total fluorescence yield (TFY) and partial florescence yield (PFY) enabling to distinguish between signals from the molecule layer that is directly in contact with the surface and the bulk molecules. Such cell could be implemented in the recently constructed high energy resolution Q-resolved RIXS and angel resolved PES (PEAXIS endstation [8]).

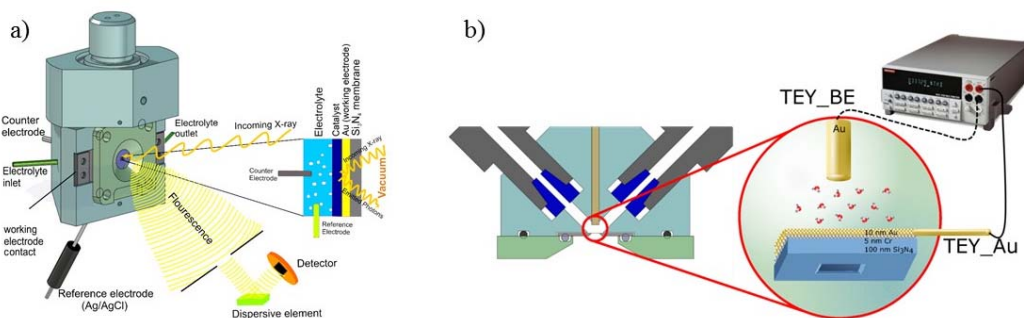


Figure 3: (a) Scheme of the “electrochemical” flow cell. [5] The electrochemical reaction under applied potential and/or light illumination is occurring inside the cell. The catalytic film is accessible from the vacuum side by the X-rays through a 100nm thin Si₃N₄ window. The emitted photons are detected in an energy resolved fashion. (b) Scheme of the “surface interaction” flow cell. The Au coated Si₃N₄ membrane separates the liquid from the vacuum and serves as measuring electrode for total electron yield. Two modes are possible: Measuring the total electron yield on the unbiased Au film (TEY_Au), and measuring the total electron yield under applied potential between the Au film and a backside electrode (TEY_BE).

Carbon nanomaterials, such as nanodiamonds, carbon dots or graphene derivatives are promising materials attracting increasing attention for metal-free photocatalysis. [9] However applying soft X-ray spectroscopy to dispersed carbon nanomaterials is challenging because of the low photon energy required to probe carbon K edge (~285-290 eV). Accordingly, cells like the one described before are not optimum. **Dr. Petit** group in the group of **Dr. Aziz** developing a new flow cell method using holey membrane. By flowing constantly the water in the flow cell, a stable ice layer can form in the holes at the vacuum-liquid interface. The holes size and density has to be optimized to ensure a good stability of the membrane in vacuum while having a good transmission. The liquid samples is flown in the system and XAS in fluorescence yield and XES can be recorded through the ice membrane.

IV. Resonant Auger for the Solid/Aqueous Interface Under Photo-Electrochemical Conditions

Photoelectron and Auger based spectroscopy are ideal tools to track chemical reactions in photo- and electro-chemical processes take place at the interface between solution and the solid catalytic surface, e.g. an electrode in a photo-electrochemical cell (PEC). As depicted in Figure 4, five main principal setups have been demonstrated, some requiring ambient-pressure PE spectroscopy (Figure 4 A - C), others consisting of a miniature cell (flow cell or static; Figure 4 D), and yet another concept is the vacuum liquid microjet. The ambient-pressure (AP) X-ray photoelectron spectroscopy method, AP-XPS, [10,11] refers to the detection of photoelectrons emitted from a thin aqueous-solution film deposited on a solid substrate, equilibrated within a properly adjusted water vapor atmosphere. Films are prepared either by slowly drawing an electrode from a solution beaker (Figure 2A),[3,7] or alternatively, stable aqueous solution films a few nm thick are grown on single crystals at precisely controlled humidity. In addition to the characterization of the immediate solid / solution interface, a combination of X-ray standing-wave fields and ambient-pressure photoemission (SW-AP-XPS; see Figure 4 C) permits measurements of the chemical states of every element within the interfacial region to be resolved vs. depth extending to several nanometers into the film. [12] Methods (A) and (B) have been successfully applied to various electrochemically important solid / solution systems including AP-XPS measurements under applied external electrode bias. [10–12] A potential drawback with method (A) is that the electrolyte films are too thin for carrying out practical electrochemical experiments. [10] One concern is that in the case where chemical reactions involve solutes within the thin solution film, solute replenishing would require long diffusion times from the reservoir to the meniscus films. Such a problem would not occur when using a

liquid cell (ref [3], see Figure 4D) equipped with a graphene or graphene-oxide membrane a few nm thick. It was shown that such membranes are not only sufficiently robust for X-ray PE spectroscopy applications (the interior of the cell can be filled with gas or liquid at atmospheric pressure), they are in particular transparent enough to relatively low-energy electrons, 100 – 1000 eV.

At BESSY II, the group of **Dr. Seidel** in the team of **Dr. Aziz** are applying and further developing these PE techniques for the characterization of the electronic-structure interactions at the electrode / solution interface. These activities will be carried out at the newly implemented SOL³PES (angle-resolved AP-XPS) [13] and PEAXIS (q-resolved Resonant Inelastic X-ray scattering combined with angularly-resolved photo-electron spectroscopy) setups. [8]

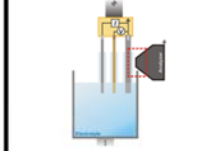
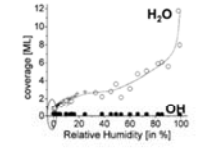
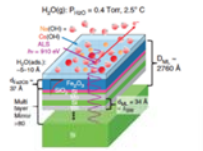
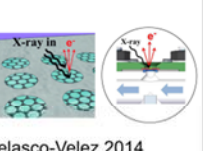
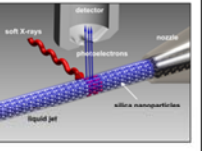
	A	B	C	D	E
Method	AP-XPS (HAP-XPS) 'dip and pull' 	AP-XPS 'water condensation' 	SW-AP-XPS 'standing waves' 	LC-XPS 'liquid cell' 	LJ-XPS 'liquid microjet' 
Parameters & conditions	Liu 2015 Wu 2015 Tender Hard X-rays PE spectroscopy from biased electrode	Wu 2015 Ketteler 2007 Tender X-rays Steady-state PE spectroscopy	Nemsak 2014 Hard X-rays Interfacial atom-specific density profiles	Velasco-Velez 2014 Kolmakov 2011 Soft X-rays PEC operando PE spectroscopy	Brown 2012 Soft X-rays Dissolution (limited by solubility)

Figure 4: Previously demonstrated methods of PE spectroscopy studies at the solid / aqueous interface that can be applied with the SOL³PES setup at BESSY II.

V. Ultrafast XUV Photoelectron Spectroscopy at Liquid Interfaces

The early dynamics of photo-induced chemical reaction for photo-catalysis is generally taking place in 10s of femtosecond, here the synchrotron based techniques cannot track such processes. As an alternative to synchrotron radiation to study such dynamics, we make use of a femtosecond laser based approach and the pump-probe methodology: an ultrashort pump pulse initiates a process and a second time-delayed pulse interrogates the evolution of the excited system. **Dr. Kiyan** group working in **Dr. Aziz** institute have recently completed laser lab ultrashort XUV probe pulses are generated via upconverting the laser frequency in the process of high-order harmonic generation (HHG). [14,15] Combining this tabletop technique with the liquid microjet, they are able to achieve femtosecond temporal resolution to investigate

electronic and structural dynamics of molecular complexes in solutions and at interfaces. (see Figure 5). [16–18] currently the team combining the previously presented cells in the HHG lab to observe the early dynamics of the chemical reactions at the interfaces.

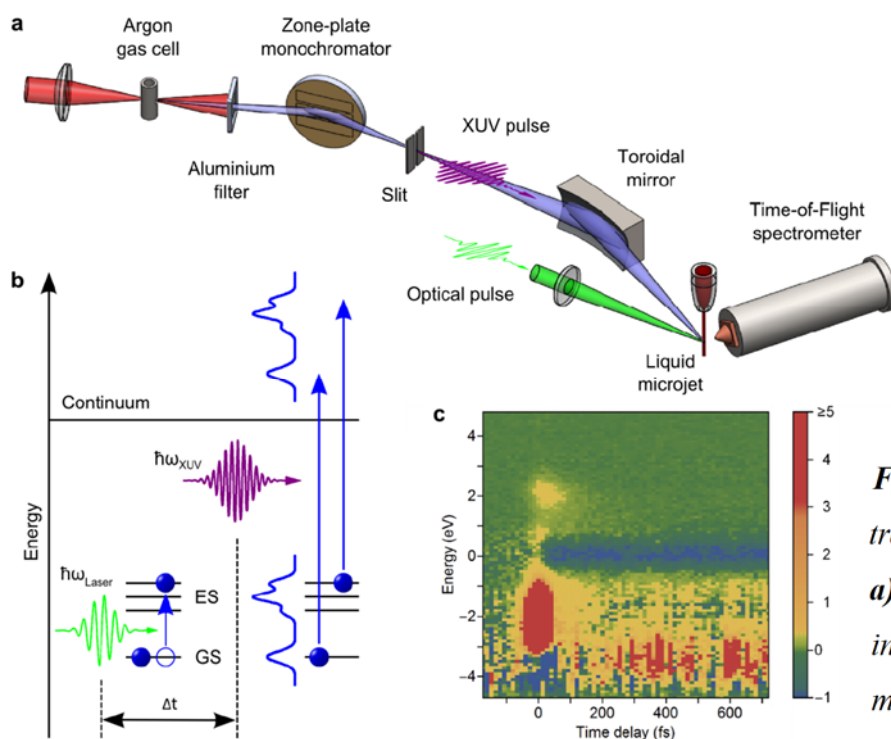


Figure 5: Overview of the transient PES experiment. **a)** Experimental setup including generation and monochromatization of the XUV probe beam and its

delivery optics, laser pump beam, time-of-flight electron spectrometer, and liquid micro-jet. **b)** Illustration of the principle of transient PES: the optical pump pulse transfers a portion of the electron population from the initial ground state (GS) to an excited state (ES) of the molecular complex; applied at a variable time delay, the XUV probe pulse maps the electronic spectrum of bound states (blue curve) to the kinetic energy spectrum of photoelectrons. **c)** Example of an 2D color map of the background-subtracted transient signal obtained for 50 mM aqueous solution of $[Fe(bpy)_3]Cl_2$.

VI. Infra-Red Spectroscopy for In-Situ and In-Operando

The pioneering work of O'Regan and Grätzel on dye-sensitized solar cells (DSSCs) [19] opened the pathway for the reliable solar energy conversion solely based on molecular components. Motivated by the high surface sensitivity of ATR infrared spectroscopy and, even though challenging, the possibility to detect monolayer deposits we are adapting this technique

to investigate the anchoring and the regeneration process of dye molecules on metal oxide nanoparticles and to identify intermediate species during the catalytic photo cycle. **Dr. Schade** and **Dr. Pusker** in **Dr. Aziz team** challenging currently several experiments that will be performed in dedicated ATR-based operando spectro-electrochemical cell (see Figure 6) which operates in the vacuum environment of a Bruker Vertex spectrometer at the IRIS beamline [20]. Several ATR crystals (ZnSe, Ge, Si) are available for the cell and allow for measurements from the far to the mid infrared spectral range. The ATR crystals are coated with a nominal 10 nm thick layer of Au to establish an electrode. The cell can be operated in a temperature range between -10 and 90° C controlled by means of an open-bath circulator. All internal materials have been chosen to stand extreme pH-value situations. The cell has several ports as in- and outlets for electrolytes or atmospheres, for accommodating electrodes, counter electrodes and pH and temperature probes. DC and AC radiation of about 10 W (365 nm, 460 nm and 623 nm) can be guided into the cell via a light pipe. Especially for the intermediate states we expect a very low spectral signature. This makes the use of stabile high brilliant linearly polarized synchrotron radiation mandatory for our experiments. In order to increase the sensitivity and to minimize the influence of drifts over time of the set-up a polarization modulation technique similar to reflection anisotropy spectroscopy (RAS) will be employed by making use out of the difference between the p- and s-polarized ATR spectra.

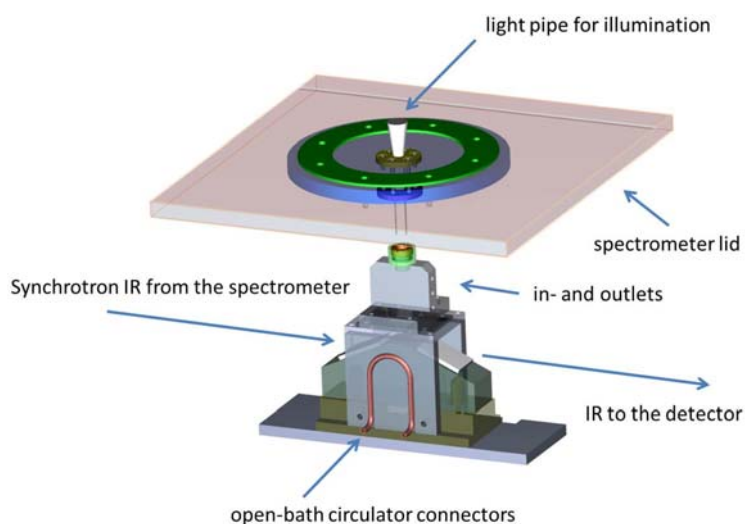


Figure 6: Schematic overview of the ATR operando cell. Not shown are the polarizer and the photoelastic modulator which are also housed in the spectrometer compartment.

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