Multiscale photon-based spectroscopies for *In-Situ* and *In-Operando* in time and energy landscape

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Following catalytic reactions in-situ and in-operando is now the focus of number of dedicated experiments at light sources which have been developed to track the electronic and molecular structural dynamics of catalysts. The challenges for this goal are two fold; first, developing spectroscopic tools in the energy- and time domain are required. The photo-catalytic processes have early dynamics of tens of femtosecond, further reaction takes seconds, minutes and even hours. Second, combination of tools to probe processes not only in solid, but also in solutions and at interfaces. In this special issue we are presenting the recent development at the synchrotron facility BESSY II using photon energy from the infrared and extreme ultra-violet up to soft X-ray regime 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 involved.

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/H_2 and He/H_2/C_3H_4 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 chromatograph.

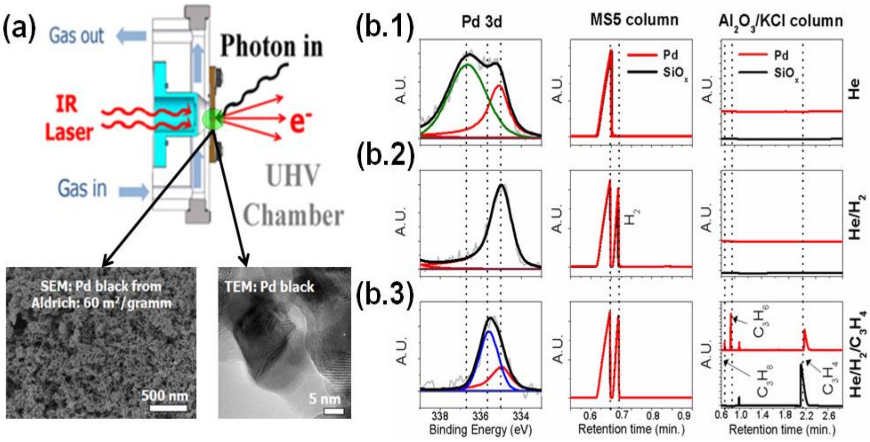


Figure 1: *a) Gas reaction cell and SEM/TEM of Pd catalyst used b) Pd 3d XP spectra and gas chromatography traces using a mol sieve MS5 column and* Al_2O_3*/KCl column: b.1) He, b.2) He/*H_2*, and b.3) He/*H_2*/*C_3H_4 *gas mixtures. Reproduced from [4] with the permission of AIP Publishing*

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 *In-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, oxyhydroxides etc.) containing Fe, Ni, Co, etc. are currently of increasing interest because of their abundancy and stability. X-ray absorption and emission spectroscopy (XAS and XES) are suitable tools for revealing the occupied and unoccupied electronic structure of such materials. Especially investigations at the transition metal L-edges and the oxygen K-edge provide a wealth of information. The challenge in this context is that detailed electronic structure investigations *via* these edges require soft X-rays. 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. ***The research group "Operando Characterization of Solar Fuel Materials" at the BESSY II facility headed by Prof. 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 was developed for XAS measurements in total fluorescence yield (TFY) mode and XES investigations. [5] In this cell the liquid is separated from the vacuum environment via a thin Si_3N_4 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 inserted into the electrolyte. 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 BESSY II TFY-XAS spectra are detected with a GaAsP diode, whereas partial fluorescence yield (PFY) XAS spectra and XES spectra are recorded with a Rowland circle based spectrometer. With this cell the electronic structure changes can be monitored while electrochemically 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 often not possible due to saturation effects, background correlated or relaxation pathway dependent distortions. 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 together with the respective spectrum recorded in transmission mode. It is obvious that transmission and fluorescence spectra strongly deviate. The TFY spectrum cannot be deconvoluted into spectra of different oxidation states. Therefore the team developed specifically for XAS measurements an *in-situ* and *operando* transmission cell shown in figure 2c. [7] This design is a further development of the transmission cell previously presented by Nagasaka *et al.* [8] 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 nm gold film serves 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. This reduces the liquid layer thickness, allowing significant transmission. Transmission spectra are recorded with a GaAsP photodiode behind the membrane sandwich in He-chamber 2. A holder in front of the membrane sandwich in He-chamber 1 can be used to either record additionally TFY spectra with two GaAsP diodes or to manipulate the sample with visible light emitted by 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.

Complementary to these soft X-ray based approaches also X-ray photoelectron spectroscopy, XES and XAS systems for tender and hard X-rays are used and further developed in the working group.

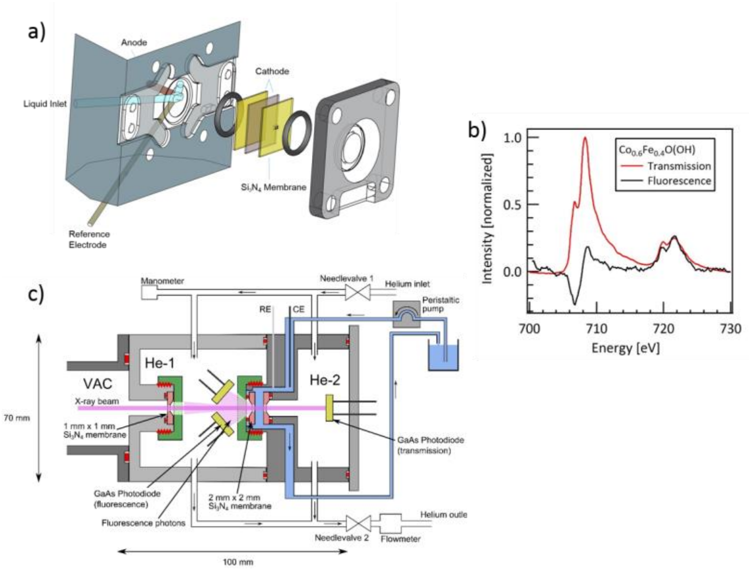


Figure 2: *a) Design of the TFY XAS and XES in-situ and operando cell b) comparison of Fe L-edge spectra obtained from a* $Co_{0.6}Fe_{0.4}O(OH)$ *catalyst c) Design of the transmission XAS in-situ and operando cell*

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

To perform *in operando* studies on water oxidation catalysts a group headed by **Dr. Xiao** and **Dr. Tesch** in the team of **Prof. Aziz** uses the aforementioned electrochemical flow cell [5] in resonant inelastic X-ray scattering (RIXS) mode (Figure 3.a). By detecting emitted photons in an energy resolved fashion detailed information of the occupied valence states - which govern the catalytic reactions - can be obtained. Moreover, this technique provides information about electronic transitions within the system. The knowledge about the occupation of valence states and electronic transitions under catalytic working conditions can facilitate the understanding of the underlying processes in artificial water splitting.

To improve the understanding of chemical and catalytic reactions at a solid/liquid interface, measurement techniques are needed that can unambiguously distinguish between signals stemming from bulk and the interface region. For this, the team developed a liquid flow cell for surface sensitive experiments (see figure 3.b). The Au coated Si3N4 membrane works as surface electrode in combination with a backside electrode to bias the system. The molecules at the surface and in the bulk will be studied simultaneously by fluorescence and electron yield. The XA spectrum based on total electron yield (TEY) signal can be directly compared to the XA spectrum from bulk sensitive TFY and PFY, enabling to distinguish between signals from the molecule layer that is directly in contact with the surface and the bulk molecules. A similar flow cell could be implemented in the recently constructed high energy resolution Q-resolved RIXS and angle-resolved PES endstation (PEAXIS [9]).

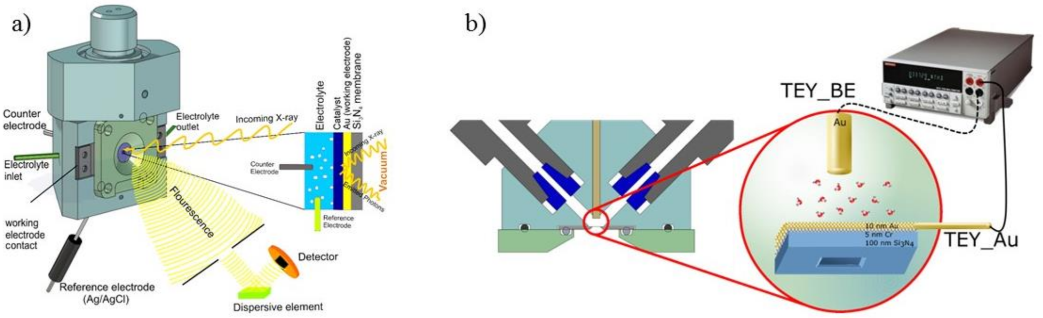


Figure 3:* *(a) *Scheme of the "electrochemical" flow cell. [5] The electrochemical reaction under applied potential and/or light illumination is occurring inside the cell. The emitted photons are detected in an energy resolved fashion.* ***(b)*** *Scheme of the "surface interaction" flow cell. Two modes 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. [10] 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. The group of **Dr. Petit** in the team of **Prof. Aziz** is 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, having a larger X-ray transmission at the carbon K edge than Si_3N_4 membranes. The liquid sample is flown in the system and TFY XAS and XES can be recorded through the ice membrane.

IV. Resonant Auger Spectroscopy 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 that 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, [11,12] 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. [13] Methods (A) and (B) have been successfully applied to various electrochemically important solid / solution systems including AP-XPS measurements under applied external electrode bias. [11–13] A potential drawback with method (A) is that the electrolyte films are too thin for carrying out practical electrochemical experiments. [11] 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 (see section I). 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 **Prof. 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 SOL^{3}PES (angle-resolved AP-XPS) [14] and PEAXIS (q-resolved Resonant Inelastic X-ray scattering combined with angularly-resolved PES) endstations. [9]

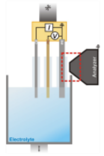
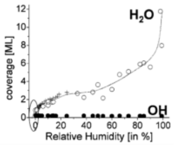
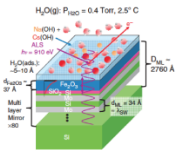
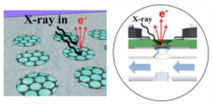
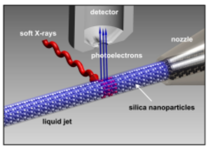
	A	B	C	D	E
Method	AP-XPS (HAP-XPS) 'dip and pull'  Liu 2015 Wu 2015	AP-XPS 'water condensation'  Wu 2015 Ketteler 2007	SW-AP-XPS 'standing waves'  Nemsak 2014	LC-XPS 'liquid cell'  Velasco-Velez 2014 Kolmakov 2011	LJ-XPS 'liquid microjet'  Brown 2012
Parameters & conditions	Tender Hard X-rays PE spectroscopy from biased electrode	Tender X-rays Steady-state PE spectroscopy	Hard X-rays Interfacial atom-specific density profiles	Soft X-rays PEC operando PE spectroscopy	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 SOL^{3}PES 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 tens 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. The group headed by **Dr. Kiyan** as a part of **Prof. Aziz's** institute has recently completed its laser lab in which ultrashort XUV probe pulses are generated via upconverting the laser frequency in the process of high-order harmonic generation (HHG). [15,16] 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). [17–19]

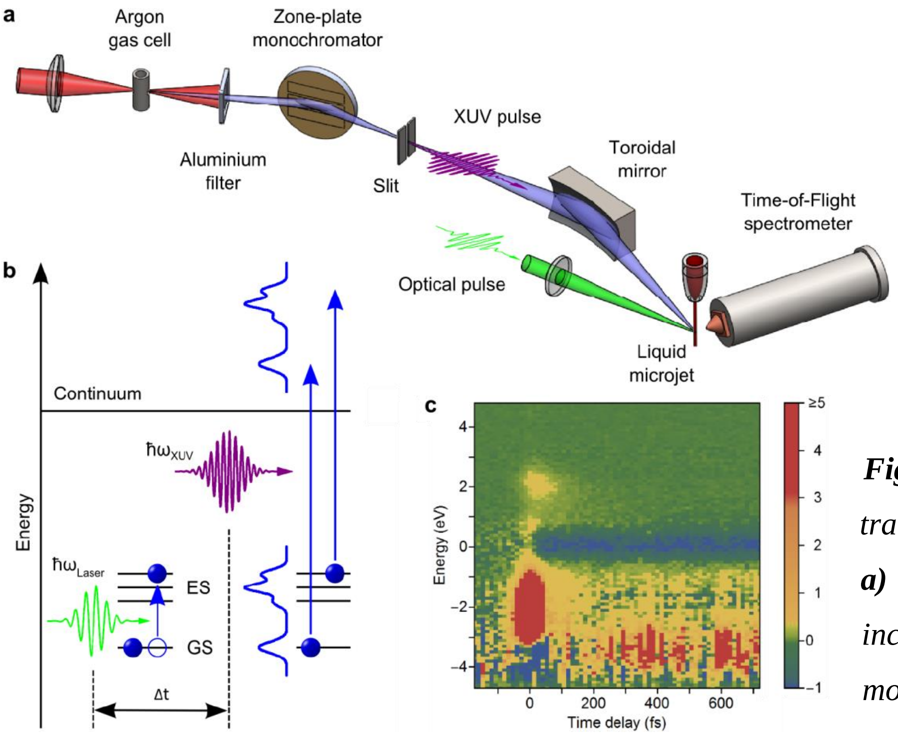


***Figure 5:** Overview of the transient PES experiment. **a)** Experimental setup including generation and monochromatization of the XUV probe beam and its delivery optics, laser pump beam, time-of-flight electron spectrometer, and liquid micro-jet. **b)** Illustration of the principle of transient 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. Infrared Spectroscopy for *In-Situ* and *In-Operando*

The pioneering work of O’Regan and Grätzel on dye-sensitized solar cells (DSSCs) [20] opened the pathway for the reliable solar energy conversion solely based on molecular components. Motivated by the high surface sensitivity of Attenuated Total Reflectance (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. The group of **Dr. Schade** and **Dr. Puskar** in **Prof. Aziz’s team** are currently developing several experiments that will be performed in a 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 [21]. 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.

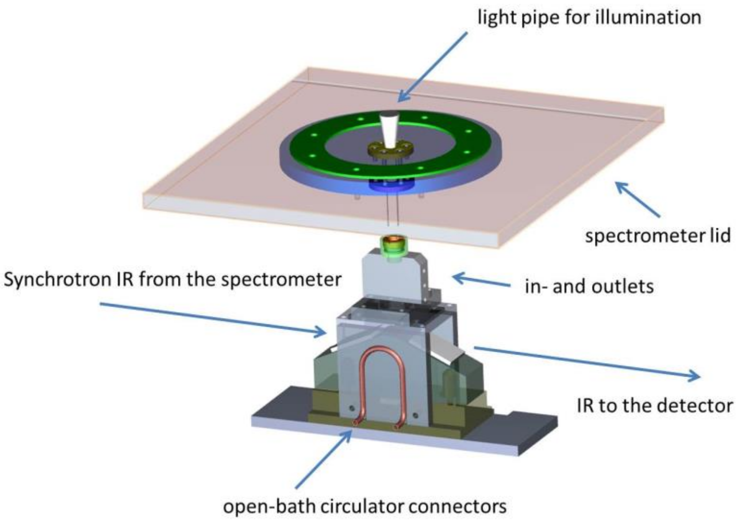


Figure 6: *Schematic overview of the ATR operando cell. Not shown are the polarizer and the photoelastic modulator which are also housed in the spectrometer compartment.*

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