

## Preface to the Special Issue of Topics in Catalysis on Ambient Pressure X-ray Photoelectron Spectroscopy

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This Special Issue of Topics in Catalysis focuses on the application of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) for the investigation of heterogeneous interfaces. The topics of the papers included in this issue range from heterogeneous catalysis, including electrocatalysis, to the chemistry of interfaces in the environment, to solid/liquid and liquid/vapor interfaces. This broad array of applications reflects the utility of APXPS for investigations in a wide range of disciplines. The first APXPS instrument was conceived and installed by the Siegbahn group in Uppsala in the early 1970s and applied in particular to the investigation of concentration gradients across liquid/vapor interfaces, a topic that is as important nowadays as it was then. Several other APXPS instruments were installed over the following decades: At Cardiff at the end of the 1970s, at Novosibirsk in the mid-1980s, and at Orono/ME at the end of the 1980s. All of these instruments used laboratory sources for the incident X-rays, and a set of differentially pumped apertures to separate the high pressure in the sample compartment from the vacuum in the electron analyzer, to minimize the path length of the electrons through the high pressure region and prevent arcing due to large potential differences in the electron analyzer at elevated pressure. The design of a differentially-pumped lens system at Berkeley Lab in the late 1990s helped to overcome the trade-off between efficient differential pumping using small apertures and high-throughput electron detection by placing electrostatic lenses between the differentially-pumped apertures, which

increased the solid angle of electron collection in APXPS and thus the pressure limit from previously 1 mbar by at least an order of magnitude. The first two instruments at the Advanced Light Source in Berkeley and at BESSY in Berlin that used this design produced the vast majority of APXPS publications that appeared in the first decade of the twentieth century. At the end of that decade commercial APXPS instruments became available, many of which were installed at other 3rd generation synchrotron sources around the world. At the time of writing 11 synchrotrons either have already operating instruments or are in the process of installing them. The availability of instruments at synchrotrons has dramatically increased access to APXPS measurements for researchers from a wide range of disciplines, including heterogeneous catalysis, geosciences, atmospheric science and electrochemistry. Recently, a growing number of laboratory-based instruments have been installed; these instruments greatly benefit from the availability of small-spot, monochromatized X-ray anode sources. Future growth in the number of APXPS instruments is expected to be mainly due to the installation of additional laboratory-based instruments as opposed to those at synchrotrons.

While the growth of the APXPS community and the breadth in the application of the technique over the past 15 years has been an important contribution to the development of new tools for the *operando* investigation of interfaces, there are many open problems that need to be addressed by the APXPS community over the coming years. Chief among these is the preparation of surfaces and interfaces with the same control over impurity levels and crystallography as one is used to from ultra-high vacuum-based surface science investigations. Sample preparation is in particular challenging for liquids with high vapor pressures, where exact control of the thermodynamic

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conditions in the sample compartment needs to be achieved lest the sample will either grow or evaporate. Preparing ultraclean liquid interfaces is also being complicated by the possible segregation of even small amounts of impurity species in the stock solution to the interfaces, aided by the high diffusion rates in most liquids. Liquid microjets can overcome these problems but are probably not a viable method for the investigation of heterogeneous chemical reactions at the gas/liquid interface due to the short interaction time between gas phase species and the liquid. Microjets provide, on the other hand, an excellent way to probe the partitioning of solutes from the bulk to the interface. The recent renewed interest in electrochemical systems has put the spotlight on the preparation of liquid/solid interfaces, which permit detecting electrons from the narrow interfacial region, either through a thin (<20–30 nm) liquid film or an ultrathin solid substrate in contact with the bulk solution, ideally under full electrochemical control. The particular advantage of APXPS for the investigation of electrochemical systems lies in its capability to simultaneously determine the chemical composition of the interface and the electrical potentials, using charged particles (i.e., the photoelectrons) as non-contact probes for changes of, e.g., the position of the Fermi or vacuum level. The combination of APXPS with the simultaneous determination of system performance, such as the yield, conversion and selectivity in a catalytic reaction through measurement of the gas phase composition, or cyclic voltammetry in the case of APXPS measurement of electrochemical reactions, adds invaluable information for the correct interpretation of the interface chemistry investigations and affords the cross-correlation of the APXPS results with those obtained in other *operando* experiments. Simultaneous APXPS and interface-

sensitive vibrational spectroscopy (e.g., polarization modulation infrared spectroscopy, optical sum-frequency generation), while technically demanding, will provide for a more complete characterization of the interface chemistry and also allow for improved detection of X-ray beam induced changes to the surface chemistry, a problem that is unfortunately all-too-often being neglected but needs to be addressed in each X-ray based measurement. Efforts to combine ambient pressure vibrational and core-level spectroscopy in one experimental setup for simultaneous measurements are underway in several laboratories and should come to fruition over the next years. Another challenge is the increase in spatial resolution in APXPS experiments. In particular studies of reactions at surfaces would greatly benefit from this development, as small number of isolated “hot spots” can potentially dominate the overall reaction rate at an interface and are in general not readily detectable in experiments that average over extended interface regions. Spatial resolution can be achieved by either focusing the incident X-rays in a scanning microscope, or by full-field approaches, for instance in a (still hypothetical) ambient pressure photoelectron emission microscope (PEEM). Finally, the quest for ever higher pressures in APXPS experiments will most likely lead to routine experiments at atmospheric pressures (about ten times the current maximum pressure achieved). This will require either entrance apertures to the differentially pumped lens system of the order of only a few micrometers, which in turn will reduce the sample-aperture distance to the same order of magnitude and thus severely reduce the scattering of photoelectrons by the gas phase, or detection of the photoelectrons through ultrathin ( $\sim$ nm) membranes. Either approach is challenging but technically feasible.