



From solid–vacuum to solid–gas and solid–liquid interfaces: *In situ* studies of structure and dynamics under relevant conditions

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ABSTRACT

Surface science instrumentation usually requires working under high vacuum. But in many cases the surface reactivity and structure in real environments can be dramatically different from that measured in this pressure range, where traditional atomic scale studies have been carried out. In this paper we briefly describe some techniques that have been improved to work under high pressures of gases or with liquids. Examples of recent research studies on solid–liquid and solid–gas interfaces are shown. The possibility to work with these instruments under realistic conditions to obtain information *in situ* during reactions or processes can have a great impact in heterogeneous catalysis, fuel cells, photovoltaics, batteries, corrosion, biological systems and many other fields.

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1. Introduction

Surface science involves the study of the chemical and physical properties at the interface of two phases and it is a key for important processes such as heterogeneous catalysis, atmospheric science, fuel cells, corrosion, friction, *etc.* During the last years it has been demonstrated that the surface structure and dynamics under relevant conditions can differ from those deduced using traditional high vacuum techniques. This fact can impact our understanding of the behavior of surfaces and has pushed the scientific community to develop new instrumental techniques capable of operating under more realistic conditions. For example in catalytic reactions, which generally take place under higher pressures, it is critical to determine the state of the surface of the catalyst while exposed to reactant gases and products (solid–gas interface). Similarly, the study of wetting, corrosion and tribology, as well as the study of biological samples, needs to be carried out in humid environments (solid–liquid interface). The field of environmental science, including soil contamination and atmospheric chemistry, also requires an atomic and molecular scale understanding of these processes under controlled humidity conditions.

At pressures of 10^{-6} Torr and above the surface of most materials is covered by a dense layer of adsorbed atoms and molecules. With conventional Ultra-High Vacuum (UHV) techniques this high surface coverage of adsorbates can be achieved by lowering the temperature.

But cooling slows down the kinetics leading to thermodynamic equilibrium eventually making it impossible to reach it. Since some processes occur only in regions of the P–T phase diagram that are not accessible with traditional high vacuum and UHV techniques, it is important to develop spectroscopic and microscopic techniques that can operate under relevant environments. Thereby we can obtain detailed knowledge of the atomic scale geometrical and electronic structures of the surfaces and interfaces as close as possible to real operating conditions of pressure and temperature. Photon based techniques like infrared and Raman spectroscopy, and sum-frequency generation among others have been used for this purpose. During the last decade however, some of the traditional surface science techniques that require high or ultra-high vacuum conditions have been improved to go beyond this limitation. As a result new information from relevant systems, in liquid environments and close to atmospheric pressures is now available. In this paper we show some experimental results from surface-sensitive techniques which have been successfully implemented to work under ambient-pressures: photoelectron spectroscopy, X-ray absorption spectroscopy and scanning tunneling microscopy.

2. *In situ* techniques for surface science studies: approach to real conditions

2.1. Ambient-pressure photoelectron spectroscopy (APPES)

One of the most versatile analytical techniques for probing the composition and electronic structure of surfaces is X-ray photoemission

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spectroscopy (XPS). In this technique an impinging X-ray photon excites a core-level electron to high energy states which can then be ejected from the analyte above the vacuum level with a certain kinetic energy (E_k). The kinetic energy of the electron ejected is measured with an electron spectrometer and from it the binding energy (E_B) of the core-level can be calculated using the expression: $E_B = h\nu - E_k - \phi_s$, where $h\nu$ is the X-ray photon energy and ϕ_s the work function of the spectrometer. This technique allows for quantitative analysis of the surface composition and provides information about the chemical state of elements by the detection of “chemical shifts” in the binding energy of the photoelectrons. The X-ray photons can originate from a laboratory-based device, *i.e.* from Mg and Al anodes, which have a fixed energy of 1253.6 eV and 1486.6 eV respectively, or from a synchrotron light source, which has the advantage that the energy can be tuned in a continuous way, its polarization is known and the photon flux is orders of magnitude higher. The interaction of electrons of energies <1500 eV with matter results in an inelastic mean free path in the nm range when traveling in solids or liquids. This is what makes the technique strongly surface-sensitive. Due to the scattering of photoelectrons by gas molecules, along with vacuum requirements for electron multipliers, *etc.*, XPS is conventionally performed under high-vacuum conditions. The introduction of differentially pumped stages made it possible to perform experiments at pressures $>10^{-5}$ Torr. Kai Siegbahn, who pioneered much of this work [1], was awarded the 1981 Nobel Prize in Physics for his contribution to the development of high-resolution electron spectroscopy. To overcome the attenuation of the electrons by the gas phase the sample in the reactor chamber is located close (a few mm) to an aperture, a few tenths of mm in diameter, connected to a differentially pumped stage. The pressure drops by several orders of magnitude within a distance a few times the aperture diameter. This reduces the path length the electrons must travel in the high-pressure region to distances comparable to their mean free path at pressures of a few Torr. To further decrease the pressure in the electron energy analyzer chamber several pumping stages are required. In the first designs using the differential pumping concept and conventional X-ray sources, the photoelectrons emitted were spatially filtered through a series of aligned apertures without further focusing (Fig. 1.A). The introduction of an electron lens system focusing the electrons at the crossover apertures greatly increases the transmission towards the analyzer (Fig. 1.B). This improvement combined with the use of synchrotron X-ray sources, which provide a more intense X-ray beam with a smaller cross-section, allow for using smaller apertures without reducing the solid angle contributions. A thin membrane window separates

the X-ray source from the sample chamber. A detailed description of the history and current development of ambient pressure X-ray photoelectron spectroscopy (AP-XPS) can be found elsewhere [2].

2.2. X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is an element-specific technique used for the study of the electronic and/or local geometric structure of matter [3]. This technique requires a source of tunable X-rays, *i.e.* synchrotron radiation. XAS is usually divided according to two energy regions and referred as (i) X-ray absorption near edge structure (XANES) or near-edge X-ray absorption fine structure (NEXAFS), characterized by fine features near the absorption edge, and (ii) extended X-ray absorption fine structure (EXAFS). NEXAFS or XANES typically includes the energy region from the absorption edge to about 50 eV higher and offer information about the electronic transitions to unoccupied molecular orbitals. EXAFS covers the oscillatory structure extending for hundreds of electron volts above the absorption edge. These oscillations are due to changes in the absorption cross-section with energy caused by interference of the excited photoelectrons scattering from neighboring atoms. The core hole produced by the absorption of the X-ray photon is annihilated by a transition of an electron from an occupied level and this produces the emission of a photon and of secondary electrons. Detection of the secondary electrons is the method called total or partial electron yield, which is surface sensitive. Detection of the photons is called fluorescent yield mode, and provides information from deeper layers in the material.

XAS is widely used for studying environmental and high-pressure phenomena in the hard X-ray regime (typically above 2 keV) because those X-rays can penetrate significant distances through materials. Soft X-rays have the advantage that their energies cover the range of core level binding energies of most important energy related environmental and biological materials, such as C, O, N, Si and many others. However they have short attenuation lengths when interacting with matter, therefore the entire system (sample, detector, etc) must be contained in vacuum. The sample is often inserted directly into vacuum as a solid but in the last years there has been an increasing effort to develop static [4] and dynamic (with flow) [5,6] liquid cells, and gas cells [7,8] which can be used for *in situ* experiments. The detection methods primarily used involve electron and fluorescence yield, but one can use the transmission detection mode for measuring the X-ray intensity after absorption through a liquid thin film [9]. Another approach for studying liquid samples in vacuum environment is to generate a liquid jet. This technology was first introduced by Faubel et al. [10] and then applied to XAS [11] and XPS [12].

2.3. High-Pressure scanning tunneling microscopy (HP-STM)

The introduction of scanning tunneling microscopy (STM) by Binnig and Rohrer [13] marked the beginning of a revolution in surface science, providing for the first time atomic resolution images of surfaces. In a few decades a diverse set of techniques were developed encompassed in what today is called scanning probe microscopy (SPM), with the great advantage of being applicable in different media: vacuum, air, or liquid. In STM a conducting sharp tip is placed within nanometer distance from a conductive sample so that electrons can tunnel between the tip and the sample. The images are obtained by monitoring the tunneling current flowing between tip and surface using a small bias voltage. STM has been applied to the study of heterogeneous catalysis using single crystals as model catalysts. However, most metals are chemically active and react in air to form oxide coatings and contamination layers. Therefore most studies require UHV conditions to ensure sample cleanliness, a limitation known as the “pressure gap” in heterogeneous catalysis due to the

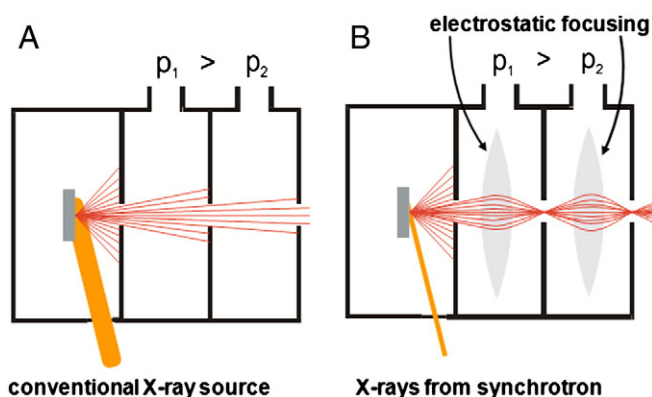


Fig. 1. Schematic designs illustrating the principle of high pressure photoelectron spectroscopy: (A) traditional setup with several differential pumping stages to keep the analyzer under vacuum while the pressure in the sample chamber is in the Torr or higher range. Spatial filtering is obtained by a set of aligned apertures; and (B) improved setup with higher electron collection efficiency using an electrostatic lens system that focuses the electrons in the apertures separating the various chambers. Synchrotron light provides higher photon intensity and variable energy. Reprinted from reference [2] with permission from Elsevier.

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