Near Ambient Pressure XPS at ALBA

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Abstract. The ALBA light source has started to operate this year. One of the seven beamlines built in the first phase is the CIRCE beamline (BL24), with two endstations in different branches, dedicated to Photoemission Electron Microscopy (PEEM) and Near Ambient Pressure Photoelectron spectroscopy (NAPP). In this communication we present the NAPP endstation. A differentially pumped electron energy analyzer allows extending the standard X-ray Photoelectron Spectroscopy (XPS) technique, which traditionally required ultra-high vacuum (UHV) conditions, to sample pressures up to 20 mbar. The surface reactivity and structure in more realistic environments can reveal dramatic differences with respect to the solid-vacuum studies. A novel differentially pumped system for the photon beam entrance and other state-of-the-art instrumentation built by SPECS GmbH (Berlin, Germany) are briefly described.

1. Introduction

ALBA is a third generation synchrotron light source with a 3 GeV low-emittance storage ring. Currently there are seven beamlines with different scientific interests. CIRCE (BL24) is a soft X-ray beamline (hν=100-2000 eV) with two endstations, located in two independent beamline branches, for Photoemission Electron Microscopy (PEEM) and Near Ambient Pressure Photoelectron spectroscopy (NAPP). Both endstations share a helical undulator with tunable polarization and a plane grating monochromator. Using a couple of deflecting mirrors the photon beam direction can be selected to feed the PEEM or the NAPP branch (figure 1.b).

![Figure 1](image-url)

**Figure 1.** Calculated flux (a) and resolution (c) for the NAPP endstation. The flux plot in (a) shows the flux (in photons per second) integrated in the bandwidth selected by the monochromator, which is given in (c). LEG, MEG and HEG labels in the legend correspond to low, medium and high energy grating. (b) Beamline layout of NAPP beamline from different perspectives (top and side view).
X-ray Photoelectron Spectroscopy (XPS) is a technique to probe the chemical composition of material surfaces and the electronic state and environment of their constituents. Due to the short mean free path of photoemitted electrons in gas atmosphere and to vacuum restrictions of the detectors used, XPS has been traditionally performed under high or ultra-high vacuum conditions (HV or UHV). The pressure gap existent between the conditions for relevant processes (catalytic processes, corrosion, gas adsorption, etc) and the conditions required for XPS was partially overcome by Salmeron and Schlögl groups. They developed a differentially pumped electron energy analyzer which allows exposing the sample at pressures up to 20 millibar while the detector is still under HV conditions [1]. The possibility to work under more realistic conditions and get information in situ during reactions or other processes has a great impact in heterogeneous catalysis [2], fuel cells [3], photovoltaics [4], environmental science [5], corrosion [6], biological systems [7] and many other fields.

2. Near Ambient Pressure Photoelectron spectroscopy at ALBA

The NAPP endstation has been designed by SPECS GmbH (Berlin, Germany) in collaboration with ALBA and it has been built by SPECS. It consists of a load lock chamber, a preparation chamber used for sample preparation (cleaning, overlayer deposition, etc) and complementary characterization (e.g. Low Energy Electron Diffraction) and an analysis chamber (AC) for the XPS measurements in UHV or in the presence of different gases with pressures up to 20 mbar (expected count-rate with respect to UHV ~ 0.2%). The analysis chamber has an outer μ-metal shield of 3 mm thickness to minimize the residual magnetic field, avoiding potential artifacts in the photoelectron spectra. The analyzer used is a PHOIBOS 150 NAP, which ensures a pressure difference of $10^{-9}$ between detector and sample (schematics shown in figure 2 with permission from SPECS).

![Figure 2. Cross-section of PHOIBOS 150 NAP analyzer.](image)

A nozzle (figure 2.b) with a sub-millimeter aperture communicates the AC with the analyzer and collects the photoelectrons emitted from the sample. A system with four differentially pumped stages, connected with small apertures in between, creates the pressure difference. An electrostatic lens system focuses the electron beam in each aperture minimizing the signal loss. The sample sits on a platform in the head of a 5 axes manipulator when measuring. This platform can be cooled by a LN$_2$ or an alcohol cooler. Moreover all the sample transfer process can be done in horizontal position, making it possible to work with powdered samples. Different models of sample holders are available: button heater, Peltier cooler and laser heating system. The NAPP includes different state-of-the-art components in its design. In the next subsections we will briefly describe two of them: the photon beam entrance and the laser heating system.

2.1. Photon Beam Entrance (PBE)

In similar endstations around the world the X-ray beam enters to the AC through a thin membrane ($\text{Si}_3\text{N}_4$, Al, etc). This membrane protects the vacuum in the beamline but at the same time diminishes...
the photon flux and it is a potential source of spectroscopic artifacts due to contamination (e.g. species adsorbed, etc). It can also suffer radiation damage and sudden breakdowns. The NAPP endstation includes a novel PBE with a system of apertures and stages differentially pumped following the same principle applied for the analyzer (figure 3). The PBE of the NAPP has been optimized for alignment, compactness and pumping efficiency. The aperture positions (see numbers 1 to 4 in figure 3.b) are completely adjustable from the outside. The capillary (number 1) has an orifice of 300 µm at the end and the size of the other apertures is 1.5, 2 and 3 mm respectively for apertures 2, 3 and 4 in figure 3.b. This system allows for a pressure difference between the analysis chamber and the beamline of about 9 orders of magnitude. Therefore there is no need of using a membrane for vacuum protection when working at pressures in the millibar range. Nevertheless the system can be implemented to use a membrane in particular cases, for example when using corrosive gases.

![Figure 3](image-url)

**Figure 3.** 3D drawing of the NAPP instrument with (a) the photon beam entrance coupled to the AC, (b) the photon beam entrance in more detail with numbers indicating the position of the different apertures present: 1 (300 µm), 2 (1.5 mm), 3 (2 mm) and 4 (3 mm).

### 2.2. Laser heating system

The NAPP allows sample heating with a typical button heater but also using an IR laser heater with up to 150W power. This laser can heat the sample to temperatures above 1200 °C, both in UHV and at the millibar pressure range. In some particular studies, e.g. catalysis, the possibility to heat the sample avoiding the conventional button heater setup presents many advantages. The hot filament from the button heater is often a good catalyst, therefore it can interfere with the reaction under study. Additionally, with a button heater setup the temperature of the surrounding manipulator parts can increase, while the laser focuses on the sample reducing unwanted heating. The Schlögl group introduced the use of a laser with a wavelength in the IR range, initially with an optical fiber going inside the AC and then shining the laser through a viewport. In the NAPP case, the laser is installed outside the chamber mounted directly on a viewport with a protection cover. The same laser system can be used in different positions of the analysis chamber and in the preparation chamber. To avoid eye laser radiation exiting through the viewports, each of them is equipped with a locked cover connected to an interlock system. Furthermore, there is an IR filter in the viewports (except where the laser can be placed) as secondary protection in case of some unforeseeable failure of the interlock system.

There are four pilot beams for the alignment of the laser beam (figure 4.a). These are low power visible beams that indicate where the heating beam will strike. The beam is made up of a matrix of 19 individual beamlets in a hexagonal array. Twelve diodes make up the outer hexagon with another seven inside (figure 4.c). Both sets of diodes are powered separately therefore their intensity can be adjusted independently. It is possible to provide equal intensity or the outer diodes can be set to be more intense than the inner ones. The latter case is useful in order to homogenize the sample temperature profile in cases where heat losses at the edge of the sample require compensation. With a working distance of about 5 cm, the laser beam diameter at the sample position is 9 mm.
Figure 4. (a) Picture showing the low power visible laser beams for alignment purposes, (b) Ta sample heated at 900 °C in presence of 25 mbar of N₂ (the green colour is due to the viewport filter), (c) drawing of the array of outer and inner laser diodes.

3. Conclusions
The NAPP has been recently installed and it is currently under commissioning. We expect the first users towards the end of this year. The system will be available to perform experiments in sample conditions not accessible to the traditional UHV XPS instrumentation. The possibility to study solid-liquid and solid-gas interfaces in situ under more realistic environments can lead to relevant results in several scientific topics with huge impact for our society. Further implementations in the system are envisaged and will be developed in the future, like a setup to work with liquid jets. This technique can decrease the beam damage by approximately 9 orders of magnitude and spreads the NAPP possibilities, for example to work with organic samples highly sensitive to radiation damage.

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