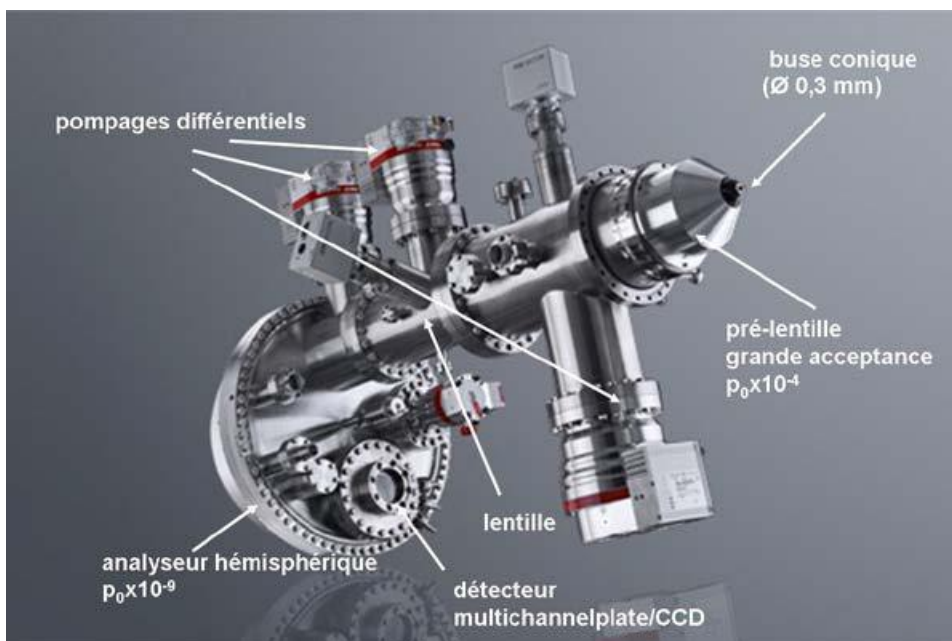


NAP-XPS experimental station : Paris VI University (F. Rochet, JJ Gallet, F. Bournel.)

Since few years ago, photoelectron spectroscopy was a UHV technique operated essentially only in pressure better than 10^{-10} mbar. Because of the relatively low mean free path of the photoelectrons, the electronic, structural and chemical properties could be extracted only if all contaminants were removed from the sample surface. The information which can be extracted from core level binding energy and valence band photoelectron spectroscopy experiments has been determinant from a fundamental and technological point of view when applied to semiconductor physics and in general to surface science. The same tools would be extremely precious also applied to other problems related to surface chemistry, environmental conditions, catalysis where the presence of a gas phase over the surface of the sample cannot be considered as a contaminant and is particularly interesting from a thermodynamic point of view. In these systems, the molecular adsorption can be strongly dependent of pressure and temperature and different from the one observed in UHV conditions.

The main problem is the electron mean free path in the gas phase: 0.04 cm at 1 mbar for 50 eV electrons or 0.4 cm at 1000 eV. For the classic sample analyzer distance of about 15 mm the probability to detect electrons is extremely low. This problem has been overcome by the strategy adopted in the first ambient pressure experiments by ... The sample surface must be very near the electron energy analyzer entrance and the analyzer must be very efficiently differentially pumped. This last request can be particularly well satisfied if the analyzer entrance diameter is very small and near to the surface which corresponds to a small sample area. Several technical solutions are now available: the Near Ambient Pressure spectrometer built by the Specs Company in Berlin is shown below:



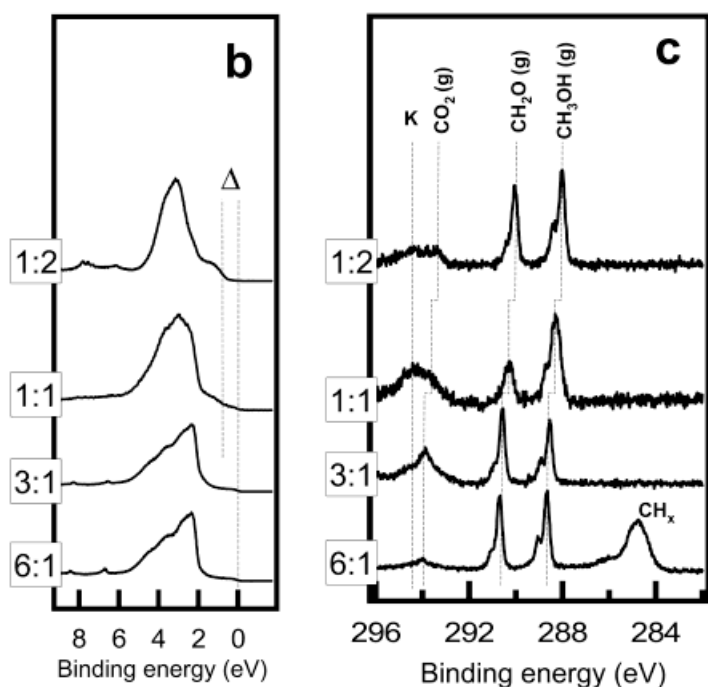
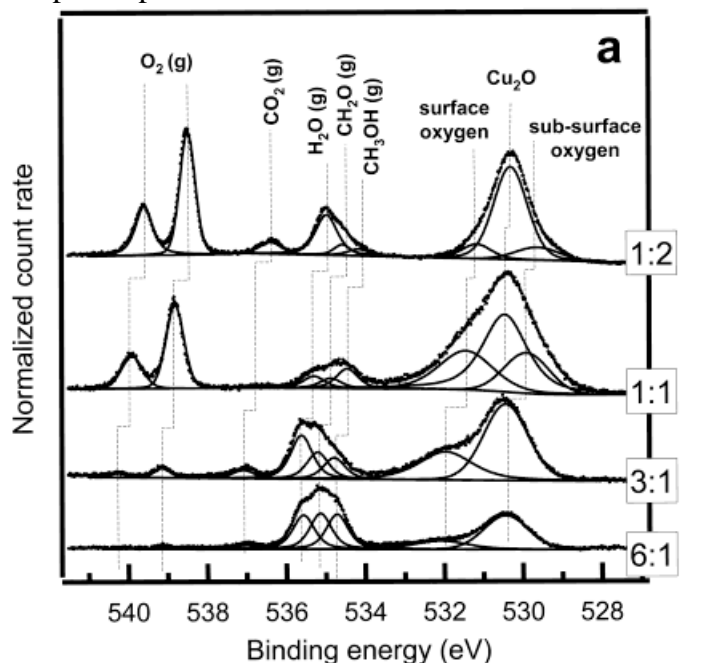
Picture of the PHOIBOS 150 NAP produced by SPECS (Berlin).

For good operating conditions a small focal spot of the x-rays impinging on the sample is indispensable. The 100 microns spot size of the second branch of TEMPO is well adapted to this experimental set up.

NAP-XPS experimental set up are now available in several synchrotron radiation centers (Berkeley, Berlin, Lund) and have been used for many applications: i) environmental

chemistry studies , ii) catalytic reactions iii) surface of liquids and fusion of ice, iv) chemical reactions at surfaces leading to thin film growth. Instrumental details, excellent descriptions of the experimental methods are summarized in several revue articles.

The catalytic reaction of a mixture $\text{CH}_3\text{OH} : \text{O}_2$ at the copper surface [Schlögl, 2004] published in 2004 is an excellent example of the possibilities opened by the NAP XPS. The O 1s spectra presented here:



were measured with 720 eV photon energy (190 eV kinetic energy) in surface sensitive conditions. The contribution from oxygen atoms in different molecules are all well separated by those of the substrate and the surface products can be followed at the same time of the reacting elements. Moreover, the binding energy of the atoms in gas phase depends also on the oxidation state of the surface. The vacuum level, which is the natural energy reference in gas phase experiments is limited by the vacuum level of the spectrometer (which is fixed) and the one of the sample surface which depend on the surface (and depends on the $\text{CH}_3\text{OH}:\text{O}_2$

ratio). With the small value of the mean free path of the photoelectrons it is also possible to disentangle the surface oxygen atoms from the bulk ones.

Another example of NAP-XPS application is the formation of the water / Cu(111) interface at 1.33 mbar and as a function of the temperature between 275 K and 453 K. The O-1s spectra of Anderson and coworkers have shown that water is dissociated to form a OH layer. At the higher temperature only this layer is present. At lower temperature a layer of molecular water is present on the surface and interacts with the OH. The installation of a NAP XPS experimental station on the TEMPO beamline is planned for 2012. The equipment was funded by the "Agence Nationale de la Recherche" (ANR), the "Région Île-de-France" and the "Université Pierre et Marie Curie". It will be under the responsibility of the Group « Functionalized Surfaces » of "Laboratoire de Chimie Physique Matière et Rayonnement".

The set up will be equipped with a UHV preparation chamber to determine the initial and final condition to gas exposure with surface science accuracy. Considering the particular developments realized on the tempo beamline in the time domain, the electron energy analyzer will be equipped with a delay line detector and time resolved experiments in the millisecond range as well as pump probe experiments with laser and synchrotron radiation will be extended to the near ambient pressure region. The experimental station will be opened to the Soleil program committees with first expert users on second trimester 2013.