ESRF	**Experiment title:** High-Pressure XPS at 1 bar: photo-electron collection at the micrometer scale	**Experiment number**: HC1754
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Report:

The ability to obtain spectroscopic information at the nanometer scale could lead to a breakthrough in the understanding of catalysis. Of particular interest is the local chemical state of catalysts *during* operation. Synchrotron X-ray scanning tunneling microscopy (SXSTM) may be able to provide such information. In vacuum conditions, it was shown that nanometer resolution can be achieved. In our experiment, we have explored the effects of a gas environment on the signals obtained using SXSTM, and the possibility to use the technique for X-ray photo-electron spectroscopy (XPS) and surface sensitive X-ray absorption spetroscopy (XAS).

In SXSTM, a scanning tunneling microscope (STM) is used to collect an X-ray induced current through the STM tip. When in vacuum, and with the tip out of tunneling contact, the current measured on the tip consists solely of primary photo-electrons, auger electrons and secondary electrons. When the tip is brought into tunneling contact, the tunneling current also contributes to the signal. It was found that the magnitude of the tunneling current is influenced by X-ray induced processes. Because this effect has a very short-range dependence on the local concentration of X-ray absorbing atoms, spatially resolved X-ray absorption spectra with a resolution as small as 2 nm can be obtained[1].

In order to perform X-ray absorption measurements in tunneling contact, the conventional tunneling current needs to be separated from the X-ray-induced current. This can be accomplished using a beam chopper and lock-in amplifier based filtering scheme. In order to

minimize the primary, auger and secondary electron contribution to the X-ray current channel, the STM tip is coated with an insulator except for the last 1 µm.
In our experiment, we used SiO_2 coated Mo tips, with which we recorded XAS spectra of Pt(111) in various gasses, with the tip out of tunneling contact. A good signal-to-noise quality could be obtained in all gasses (see figure 1), even for recording times of only a few minutes. We found that the signal is amplified in a gas environment with respect to the signal in vacuum. This can be explained by several mechanisms based on the charging of the tip isolation and the ionization of the gas phase. First, charging of the tip isolation is much more dynamic in a gas environment than it is in vacuum, causing a capacitive coupling current to the tip core. Second, the highly energetic Auger electrons emitted from the sample will cause gas ionization[2]. Charging of the tip isolation and other insulators in the reactor creates an electric field gradient towards tip and sample, that separates the ions and electrons formed in the ionization processes. This causes an additional current. Indeed, when a potential was applied to the sample with respect to the the tip, a strong increase in current was observed. As such a tip-sample bias is required for generating the retarding field in XPS measurements, we found that this is not a viable method.
In SXSTM measurements, the gas induced additional currents are a dominating and undesirable background. From the understanding gained in our experiments, one can design modifications that overcome this problem. We intend to use an additional thick conductive coating on the STM tip, which will disable charging of the tip coating and eleminates capacitive coupling to other insulators in the reactor. Furthermore, it can absorb a large fraction of the Auger electrons, thus minimizing the ionization current.

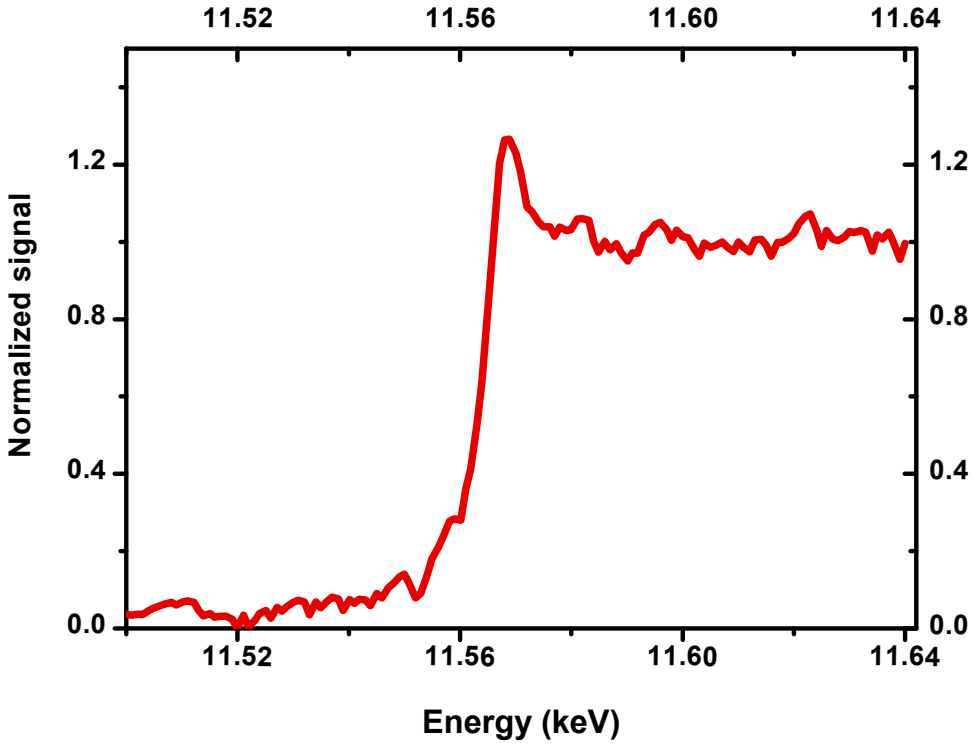

Figure 1: XAS spectrum of Pt(111) in 1bar H_2, recorded using an SiO_2 insulated Mo STM tip

[1] N. Shirato *et al., Nano Letters* 14, 11, 6499-6504, **2014**
[2] S.L.M Schroeder *et al., Surface Science Letters* 324, L371-L377, **1995**