A versatile instrument for ambient pressure x-ray photoelectron spectroscopy: The Lund cell approach

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A B S T R A C T

During the past one and a half decades ambient pressure x-ray photoelectron spectroscopy (APXPS) has grown to become a mature technique for the real-time investigation of both solid and liquid surfaces in the presence of a gas or vapour phase. APXPS has been or is being implemented at most major synchrotron radiation facilities and in quite a large number of home laboratories. While most APXPS instruments operate using a standard vacuum chamber as the sample environment, more recently new instruments have been developed which focus on the possibility of custom-designed sample environments with exchangeable ambient pressure cells (AP cells). A particular kind of AP cell solution has been driven by the development of the APXPS instrument for the SPECIES beamline of the MAX IV Laboratory: the solution makes use of a moveable AP cell which for APXPS measurements is docked to the electron energy analyser inside the ultrahigh vacuum instrument. Only the inner volume of the AP cell is filled with gas, while the surrounding vacuum chamber remains under vacuum conditions. The design enables the direct connection of UHV experiments to APXPS experiments, and the swift exchange of AP cells allows different custom-designed sample environments. Moreover, the AP cell design allows the gas-filled inner volume to remain small, which is highly beneficial for experiments in which fast gas exchange is required. Here we report on the design of several AP cells and use a number of cases to exemplify the utility of our approach.

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1. Introduction

The development of experimental and theoretical surface science during the past four to five decades has significantly increased our understanding of the intricate atomic-scale details of surfaces. This, in turn, has improved our ability to control these details and to design improved materials and technologies within e.g. materials science, catalysis, and the solar cell and biosensing domains. In all these areas the interaction of a solid surface with a second phase, gaseous or liquid, plays an important role. The reason for the importance of the interaction is that the presence of this second phase might interfere with the functioning of the material (e.g. water vapour in solar cells). Another reason is that the second phase may play a crucial active role for the function of the surface: for example, in heterogeneous catalysis, thin layer growth, or in sensing applications the gas phase might deliver the reactants or analytes to a surface. However, traditional surface science is mostly carried out in ultrahigh vacuum (UHV) environments and this with good reason: on the one hand it allows keeping surfaces clean for a reasonably long period of time (hours) during which the experiment can be carried out, and on the other hand the use of vacuum, albeit it does not have to be UHV, allows the use of electrons with low kinetic energy as a highly surface sensitive probe.

It has, however, been realised for a long time that the relevance of UHV results to realistic systems may be limited (see e.g. [1–4]). This circumstance has been termed the “pressure gap” which exists alongside the “materials gap” related to the much higher structural complexity of real materials in comparison to the idealised samples of surface science. The pressure gap might cause relevant surface structures to go unrecognised which exist at realistic pressure, but not at UHV pressure as a result of either kinetic hindrances or the lacking gas/liquid phase chemical potential. And even when it is possible to form a particular surface structure in UHV, it remains difficult to predict if it is this surface structure that exists under realistic conditions, in spite of the many advances in theoretical modelling. Also, UHV implies the freezing of dynamics and the absence of the exchange of species between the surface and the second phase. By now it is entirely clear that dynamics can play a decisive role for the chemical properties of a surface [5]. Thus there has been a considerable drive to bridge the pressure gap by adapting surface science techniques to allow exposure of the solid sample to a gas, vapour, or liquid phase (e.g. the reactive medium) during measurement. Among the techniques that have been adapted by instrumental development are infrared spectroscopy, like polarisation-modulated infrared reflection absorption spectroscopy and sum

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frequency generation [6,7], surface x-ray diffraction [8], scanning tunnelling microscopy [9,10], scanning electron microscopy [11], and transmission electron microscopy [12].

One particular technique which has been adapted to more realistic pressures, and which is truly one of the workhorses of surface science, is x-ray photoelectron spectroscopy (XPS). When the sample is exposed to a gas or vapour during measurement, the technique is termed “ambient pressure x-ray photoelectron spectroscopy” (APXPS), “high pressure x-ray photoelectron spectroscopy” (HPXPS), or “near-ambient pressure x-ray photoelectron spectroscopy” (NAP-XPS). Both UHV-based conventional XPS and APXPS provide not only information on the elemental composition of surfaces, but also on the electronic structure of the surface and, by means of the so-called chemical shift (see e.g. [13]), on the chemical state of the surface atoms.

In XPS electrons with a relatively low kinetic energy of typically up to some hundreds of eV are detected. In this energy range the electron scattering cross section $\sigma$ is high. $\sigma$ governs the electron attenuation according to $e^{-\frac{dp}{\sigma d}}$, where $p$ is the pressure and $d$ the distance travelled in the medium with scattering cross section $\sigma$. Already at a pressure of around $10^{-2}$ mbar the attenuation is so strong that the permissible path length for the electrons in the gas medium, which still allows a measurable signal, is not more than a couple of centimetres (cf. Fig. 1).

At a pressure of 1 mbar this number is further reduced to around a millimetre. The only practically viable solution for XPS experiments with the sample in an ambient atmosphere is to shorten the path in the gas phase, which the photoemitted electrons have to travel through, by apertures and differential pumping schemes. This is indeed the approach that was chosen already for the first instruments designed in the groups of Joyner and Roberts [16] and Grunze [17]. These early instruments used x-ray anodes as light sources, filled in UHV chambers. Typi-}
2. AP cells at the APXPS instrument in Lund

A drawing and a picture of the original AP cell of the instrument in Lund are shown in Fig. 3. The instrument and the AP cell were designed by SPECS Surface Nano Analysis GmbH, Berlin, based on the specifications developed in Lund. The AP cell is mounted on a manipulator with a 450 mm stroke so that it can be moved from a separate AP cell chamber into the analysis chamber and docked to the electron energy analyser. To the right in Fig. 3(a) the front docking part is seen, which also holds the (exchangeable) first aperture. Upon
The sample, mounted on a “flag-style” sample holder, is introduced into the cell through a door, which can be closed and locked using the transfer wobblestick. Gas, delivered by a gas system with facilities for gas cleaning, is introduced into the AP cell through a pipe from the back. Even with a pressure of 10 mbar inside the AP cell the pressure in the analysis chamber remains in the \(10^{-6}\) mbar range, which allows fast return to UHV conditions upon undocking and removal of the AP cell to the AP cell chamber. The AP cell can be operated in quasi-batch mode – since gas flow out of the AP cell always occurs through the nozzle towards the analyser, conditions are not completely static, though – or in flow mode. The last mode is made possible by a gas exhaust line connected to the back of the HP cell and leading to a vacuum pump. This exhaust line is also used to deliver gas to a quadrupole mass spectrometer for analysis, so that reaction studies can be carried out simultaneously with APXPS measurements. Also the gas delivery line has a valve connection to the mass spectrometer so that the gas purity prior to interaction with the sample can be verified. The gas pressure inside the AP cell is measured either using a Pirani gauge on the gas exhaust line or by measurement of the pressure in the prelens pumping stage of the analyser by means of a calibration curve \([26]\).

The z position of the sample inside the cell can be adjusted to match the optimum distance to the aperture of around two aperture diameters. In this version of the AP cell this is done by visual inspection using a zoom camera within line of sight of the sample through a window on the AP cell. The effective positioning resolution of the aperture-sample distance is of the order of around 50 µm. The z motion is made possible by the use of internal bellows. Also lateral movement during measurement is possible, an important feature to avoid the effects of beam damage. Sample heating is achieved by electron bombardment of the wall behind the sample. A prerequisite for this type of heater is that the filament, placed in the volume inside the inner bellows, remains in vacuum. This is achieved, since the volume of the filament is connected directly to the analysis chamber. The sample can also be cooled to moderately low temperature of around 220 to 240 K using liquid nitrogen.

As will be detailed below, the inner volume of the AP cell, which is on the order of 0.5 l, is small enough to allow complete gas exchange within approximately 15 s. In comparison to the time it takes to completely exchange the gas in a standard vacuum chamber as depicted in Fig. 2(a) this exchange rate is favourable and fully sufficient for many experiments. However, for other experiments it is desirable to obtain even higher exchange rates. In a new AP cell design we have reduced the inner volume of the AP cell (see below) which is beneficial for the rate. AP cells with a much smaller volume on the order of some ml are also conceivable at the expense of the possibility of translating the sample during measurement.

In comparison to the standard way of performing APXPS measurements by backfilling a standard vacuum chamber (Fig. 2(a)), the large wall surface area of the AP cell could potentially lead to increased problems with surface contamination due to exchange of residual contaminants adsorbed on the walls with the gas and then with the sample surface. This effect is, however, counteracted by the much higher turnover of gas flow past both the chamber walls and the sample surface. The flow conditions imply that overall a rather clean situation can be achieved quite easily in the AP cell. Moreover, if contamination issues arise, the compact design of the cell allows a relatively fast bake-out e.g. overnight. In addition, we also found that heating the sample (and sample holder) to \(-600\) K while flushing the AP cell in a high flow of O\(_2\) is a very efficient cleaning procedure. Such flow cleaning of a backfilled APXPS setup is clearly much more difficult than with an AP cell setup.

Since the design of the original AP cell changes and improvements have been implemented in newer versions by SPECS Surface Nano Analysis GmbH \([27]\). Such improvements concern e.g. the here used and other heating schemes and easier assembly of the heating stage. Also, improved schemes of the gas delivery to the sample have been tested and implemented.

A similar AP cell as the original one has recently been designed within a SOLEIL–MAX IV collaboration. This AP cell is shown in Fig. 4. While the basic purpose of this AP cell is essentially the same as that of the original AP cell shown in Fig. 3, several changes have been made to improve gas flow, door mechanism, heating, and pressure measurement.

One major change is that a button heater is used for heating instead of electron bombardment through the wall. This has the advantage that the heating is more local, but cooling of the sample to temperatures below room temperature will not be possible with this design. Another major change is that the pressure is measured directly on the cell volume using a micropirani gauge. This gauge is mounted on the same cone as the windows. The micropirani gauge was chosen here due to its miniature format. In principal, absolute pressure transducers could have been an alternative, since they exist for the pressure range between \(10^{-3}\) to a maximum of 50 to 100 mbar of interest here. However, sufficiently small absolute pressure transducers are not commercially available. This implies that care has to be taken to properly zero the here employed micropirani gauge at regular intervals and to make sure that the correct gas calibration is chosen. In practice, the calibration curves for different gases follow each other well up to ca. 10 mbar, and therefore calibration plays a major role only for higher pressures \([28]\).

In the new AP cell gas is delivered directly to the front of the sample surface through a double cone, which also works as the nozzle towards the electron energy analyser (cf. Fig. 4(d–e)). The two cones of the double cone are separated by a ceramic distance holder with holes all around its perimeter. The gas is delivered from two sides to the holes of the distance holder and then directed towards the samples in the gap between the two cones. Laminar gas flow simulations, the results of which are shown in Fig. 4(e), suggest an efficient gas flow towards the spot from which the photoelectrons are collected, which was one of the aims with the design of the new AP cell \([29]\).

Another aim was to avoid the pitfalls of gas bypasses past the sample, which could result in inaccuracies in the reactivity measurements performed with the mass spectrometer on the exhaust of the AP cell. Such gas bypasses certainly exist in the original AP cell design described above. As the results of the gas flow simulations in Fig. 4(e) show, such bypasses do not play any role here.

From the simulations we find a pressure ratio of 4 between the regions of highest (in front of the sample) and lowest pressure. True dead volumes close to the sample surface could not be identified, although such volumes might exist closer to the exhaust in the back of the AP cell. Such dead volumes would, however, not affect the gas composition and pressure at the sample surface and are also unlikely to have further impact on reactivity measurements.

From the gas flow simulations it is seen that the pressure measured by the micropirani gauge is likely to deviate from the pressure at the sample surface. The pressure ratio of 4 between the regions of highest and lowest pressure gives an upper limit to the deviation and seems acceptable. In particular, the deviation is certainly much better than the deviation obtained when measuring the pressure on volumes far away from the sample surface. Thus the goal is achieved to avoid the problems with large pressure differentials between the location of the sample and that of the gauge.

Recently, there has been a strong drive towards \textit{in situ} studies of electrochemical systems in general and of APXPS studies in particular (see e.g. \([30–34]\)). An AP cell directed at the study of electrochemical samples is presently being developed for the setup at the MAX IV Laboratory, cf. Fig. 5. The concept of this AP cell is intermediate between true \textit{in situ} capability and \textit{of post mortem} experiments: the idea of the AP cell, which will allow standard three-electrode electrochemical experiments, is to use a rotatable sample mounting to switch the solid surface \textit{in situ} from a position in the liquid to APXPS measurement position within the shortest possible time frame. In this setup the liquid is
The design of the two new AP cells demonstrates that the sample environment concept of Fig. 2(b) is well-suited for adaptation to different types of experiments. Further cell developments presently ongoing concern the study of liquids according to the trundle concept of Siegbahn et al. [35] and of sulphiding environments such as H₂S and other sulphur compounds. The latter AP cell is designed according to the scheme presented in Fig. 4, but will be provided with its own gas delivery system to avoid contamination of any ambient pressure parts of the instrument with sulphur.

3. Examples

In this section we will briefly present a number of examples of research carried out using the APXPS instrument in Lund. The examples serve to illustrate some of the advantages of an AP cell concept rather than to present an exhaustive description and analysis of the research projects. Advantages that we will address are the short gas switching times, ease of measurement of reaction products simultaneously with the XP spectra, and the possibility of connecting results from traditional surface science studies to experiments carried out in ambient environments.

3.1. Atomic layer deposition of HfO₂ on InAs(001)

Atomic layer deposition (ALD) is one of the most important methods to achieve a controlled growth of thin films in general [36] and oxides in particular. However, depending on the choice of ALD parameters, the achieved quality of the films may differ greatly in terms of crystallinity, surface roughness, and optical properties [37]. These properties are intimately linked to the atomic-scale structure of the oxide films, which, in turn, is linked to the surface chemistry during growth [37]. Post mortem characterisation by home laboratory and synchrotron-based electron spectroscopy has provided extremely important insight in the mechanisms of ALD (see e.g. [38]). However, post mortem investigations cannot provide a true identification of surface species under growth conditions [37], which makes it difficult to formulate models of the chemical kinetics of the growth process. Moreover, systematic investigation of the role, nature, and surface chemistry of the support and of defects is possible only with difficulty.

APXPS provides the means of studying ALD in real time. Fig. 6 shows results for the ALD of HfO₂ on an InAs(001) surface from tetrakis(dimethylamido)-hafnium (TDMAHf) and water as the metal and oxygen precursors, respectively. Here only data are shown of the first half-cycle, during which the InAs surface, covered with a native surface oxide, was exposed to the metal precursor at a pressure of ~0.01 mbar. Due to the high sticking tendency of the precursor to the walls of the gas pipes, the ampoule with the precursor was mounted as closely as possible to the inlet of the AP cell, and the gas system of the instrument was not used.

While we leave a detailed analysis and discussion to a forthcoming publication (R. Timm, S. Yngman, A. R. Head, M. Hjort, J. Knutsson, J. Knudsen, J. Schnadt, and A. Mikkelsen), we would like to note a couple of points of interest to the present article. First, the comparably small volume of the AP cell allows fast filling and evacuation of the sample.
environment. This is visible from the mass spectrometer signal measured on the exhaust gas from the AP cell in Fig. 6(b). Here the signals for fragments of the precursor are reported. Since the maximum mass-to-charge ratio of the particular spectrometer used is 200 u/e, it was unfortunately impossible to track the signal of the intact precursor. Nevertheless, it can be seen clearly that the targeted pressure is reached within less than 50 s (the variations at t \approx 300 and 500 s are due to manual adjustment of the valve). Later, at t \approx 700 s, full evacuation is reached within approximately 100 s after closing of the valve. The times for filling and evacuation are still relatively long, partly due to slow manual opening of the inlet valve, but in the case of evacuation also due to the sticky nature of the precursor. As will be seen below, even better rates can be achieved with more standard gases. Nevertheless, in comparison to setups, in which standard vacuum chambers are filled, the time for gas switching in the AP cell is short, and could be further shortened by design of a cell with even smaller inner volume.

The second point of interest is the possibility of following fast processes. In Fig. 6(a) the amplitude of the As 3d signal related to the native oxide (peak at ~44.5 eV in Fig. 6(c)) is plotted as a function of time. Since only the signal at a fixed kinetic energy was sampled, it was possible to follow the process of oxide removal with around 0.1 s time resolution. More information is available from the individual spectra in Fig. 6(c), each of which took around 17 s to obtain. Clearly, the time resolution is sufficient to follow the reduction, and a more thorough analysis reveals a time order of the individual processes which play a role in the reduction as well as the presence of intermediate species (to be published).

3.2. Surface science: CO adsorption on Ir(111)

Understanding the adsorption of molecules on metal surfaces is essential for obtaining an atomic-scale understanding of heterogeneous catalysis. A large number of adsorption structures have been found and characterised from experiments carried out in an UHV environment, i.e. at low temperature and gas pressures below about 10^{-6} mbar. These conditions are, however, far from the ones found in real catalysis, and kinetic barriers or entropy might block the formation of relevant adsorption structures present while the catalytic process is running. In this example we used the APXPS setup in Lund and its capabilities to swiftly change between UHV and near-ambient (mbar) conditions to compare the CO adsorption structure formed on a Ir(111) surface after exposure to 100 L CO at a pressure of 1 \cdot 10^{-6} mbar with the adsorption structure formed after exposing the sample to a CO pressure of 0.6 mbar. The CO adsorption structures and part of the data presented here are discussed in detail in [39,40], and here we will therefore only highlight the most important results.

Fig. 7(a) and (b) shows the C 1s and Ir 4f_{7/2} spectra acquired before gas exposure (bottom), after exposure of the surface to 100 L CO (middle), and finally after exposing the sample to 0.6 mbar of CO (top spectra). Starting with panel (a), the C 1s spectra acquired after exposing an Ir(111) surface to 10^{-6} mbar CO (UHV exposure) and 0.6 mbar (mbar exposure) look almost identical. A single C 1s component is located at 286.2 eV binding energy and we assign this component to CO molecules adsorbed atop Ir surface atoms. In contrast, we observe a clear difference in the corresponding Ir 4f_{7/2} spectra due to different intensities of the Ir_{CO} component originating from Ir surface atoms with CO molecules atop. Also, the reduction in area of the Ir_{surf} component is much larger for Ir(111) exposed to mbar pressures of CO. Using the relative intensities of the surface components (Ir_{surf} and Ir_{CO}) we find a CO coverage of 0.54 monolayer (ML) after UHV CO exposure and 0.79 ML after the 0.6 mbar CO exposure.

Once the 0.79 ML CO adsorption structure is formed it remains stable even if the CO background pressure is removed upon evacuation of the AP cell. We base this conclusion on the observation that both C 1s and Ir 4f_{7/2} spectra are unchanged before and after pumping down (not shown). Also the 0.54 ML CO adsorption structure was found to be stable in UHV conditions. We therefore characterised both adsorption structures both with low energy electron diffraction (LEED) and scanning tunnel microscopy (STM) under UHV conditions (see Fig. 7). This characterisation revealed a (2√3 \times 2√3)-7CO structure with magic (CO)_{7} clusters formed upon CO saturation of the surface in UHV conditions (UHV exposure), and a (3√3 \times 3√3)-19CO structure with magic (CO)_{19} clusters. We note that the theoretical CO coverages of both the (2√3 \times 2√3)-7CO (7/12 ML = 0.58 ML) and the (3√3 \times 3√3)-19CO (19/27 ML = 0.70 ML) structures are consistent with the coverages calculated from the cubic fitting of the Ir 4f_{7/2} spectra.

The above example illustrates how traditional surface science adsorption studies can be connected to results obtained in ambient environments. The APXPS setup in Lund is well suited for these types of studies, as it is possible to swiftly change between near-ambient (mbar) and UHV conditions with base pressures of the order of 5 \cdot 10^{-10} mbar when the HP cell is retracted and valved off.

3.3. Intercalation: CO intercalation beneath graphene

In the third example we follow the intercalation of CO molecules beneath Ir(111)-supported graphene with APXPS [39]. We note that CO intercalation under Ir(111)-supported graphene is impossible in UHV conditions, and thus the use of CO pressures in the mbar range is essential for detecting and studying such intercalation.

In Fig. 8(a) and (b) the C 1s and Ir 4f_{7/2} spectra of 0.9 ML graphene/Ir(111) before (bottom) and after (top spectra) ambient pressure CO exposure at 0.1 mbar are compared. During ambient pressure CO exposure the sample temperature was ramped from room temperature to 520 K and back to room temperature again. Simultaneously, both the C 1s and Ir 4f_{7/2} regions were followed in situ with APXPS.
Starting with panel (a), which shows the C 1s spectra acquired before and after ambient pressure CO exposure, CO adsorption at the Ir(111)-graphene interface is signalled by the fingerprint of the CO molecules adsorbed atop Ir atoms (green component C\textsubscript{CO} at 286.2 eV). The graphene C 1s component, which for the pristine graphene film is found at 284.1 eV (CIr), experiences a 0.3 eV downshift upon CO intercalation to give the C1 component (please refer to the caption of Fig. 8 and Refs. [39,41] for the naming of components).

The Ir 4f\textsubscript{7/2} spectrum in Fig. 8(b), with components determined from least-square curve fitting, is almost identical to the top spectrum of Fig. 7(b). This spectrum is assigned to the (3\sqrt{3} x 3\sqrt{3})-19CO structure. Since the graphene film covers 90% of the Ir(111) surface, this implies that the (3\sqrt{3} x 3\sqrt{3})-19CO structure must be formed beneath the graphene layer, i.e. the CO intercalates beneath the graphene.

In Fig. 8(c) the intensities of the C\textsubscript{Ir}, C4, and C\textsubscript{CO} components, determined by least square curve fitting, are plotted as a function of exposure time. During the first 40 min of exposure, when the sample temperature is below 450 K, the CO intercalation rate is slow and almost constant. Above 450 K a significantly higher CO intercalation rate is observed, which suggests that an activation barrier for CO intercalation exists. Interestingly, a similar temperature barrier for oxygen intercalation of Ir(111)-supported graphene at UHV conditions (450 K) was found in a previous study [41]. We therefore speculate that a temperature of 450 K is the temperature needed for unbinding the graphene edges to allow intercalation of large molecules and atoms such as CO and oxygen atoms.

3.4. Catalysis: CO oxidation over Pt(111)

The in situ study of heterogeneous catalysts is a central research field for APXPS, and a large number of studies has been conducted (see for example Refs. [20,23] and references therein). One of the main reasons for this is that chemical characterisation of both the surface adsorbates and the gas composition just above the surface can be probed.
simultaneously by APXPS. This implies that APXPS is an extremely powerful tool to directly correlate reactivity and atomic-scale surface structure. Furthermore, XPS is a standard technique employed for decades in surface science laboratories and at synchrotron facilities, and a large number of adsorbate structures have been characterised by UHV-based XPS.

In the example described in the following we tested the capabilities of the APXPS setup in Lund by studying the oxidation of carbon monoxide over a Pt(111) sample in oxidising conditions. The mixing ratio of O$_2$ and CO was 9:1 and the total pressure 0.15 mbar. While we increased the sample temperature we simultaneously measured O 1s spectra and recorded the quadrupole mass spectrometer (QMS) signal at the outlet from the AP cell. The QMS signal is plotted in Fig. 9(a) and selected spectra are shown in Fig. 9(b). Starting at a temperature of 450 K, we observe four O 1s components, which can be assigned to gas phase O$_2$ (537.4 eV and 538.5 eV) and CO molecules adsorbed in bridge (531.0 eV) and atop (532.6 eV) surface sites, respectively.

![Fig. 8.](a) C 1s and (b) Ir 4f$_{7/2}$ before (bottom) and after (top) 0.1 mbar CO exposure. The sample temperature was ramped from room temperature to 520 K and back to room temperature during CO exposure (see panel (c)). (c) Sample temperature and intensities of the C$_4$ (assigned to C atoms in non-intercalated graphene), C$_{Ir}$ (assigned to C atoms in graphene intercalated by CO), and C$_{CO}$ (assigned to C atoms in the CO molecules) components determined by curve fitting the C 1s spectra as a function of time.

![Fig. 9.](a) CO, O$_2$, and CO$_2$ QMS signals acquired on a Pt(111) surface exposed to 9:1 O$_2$:CO mixture at 0.15 mbar while heating the crystal from 450 to 535 K. (b) O 1s spectra acquired simultaneously with the QMS data. The time at which the spectra were recorded is marked with 1, 2, and 3 in panel (a) and the same labels are used in (b). (c) Illustration of the fast gas exchange in the AP cell measured with the QMS at the exhaust line from the cell while closing the H$_2$ flow controller (see text for details).
The small shoulder at around 538 eV binding energy observed for a temperature of 450 K (not fitted) originates from CO in the gas phase. Under these conditions no or only very little CO$_2$ production is observed in the QMS signal: CO covers the entire surface and blocks dissociative adsorption of oxygen, which is an essential requirement for efficient CO oxidation. The QMS and O 1s data in Fig. 9(a) and (b) demonstrate clearly that this inactive phase persists up to a temperature of 515 K.

At a temperature of 535 K the O 1s spectrum changes drastically. Now the components assigned to adsorbed CO have disappeared completely, and a new component assigned to atomic oxygen has clearly that this inactive phase persists up to a temperature of 515 K.

As a last point we highlight that the conversion of the FeO(111) to FeO$_2$(111) layer contains additional lattice O in between the Fe lattice and the Pt(111) substrate [46]. As the trilayer FeO$_2$(111) film was found to be highly active for the oxidation of CO at low temperature this film has been studied extensively.

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3.5. In situ oxidation: oxidation of FeO(111) to FeO$_2$(111)

The last example concerns the in situ APXPS monitoring of the oxidation of an ultrathin Pt(111)-supported FeO(111) film to FeO$_2$(111). A detailed discussion of our APXPS data has been published recently in Ref. [43]; here a brief summary will be given.

The ultrathin FeO(111) bilayer film consists of a hexagonal Fe lattice sandwiched between a hexagonal O lattice and the Pt(111) substrate. The film was first reported by Vurens et al. [44] in 1988, and its structure is discussed thoroughly in Ref. [45]. Recently, it has been found that the film can be converted to a trilayer FeO$_2$(111) film at oxygen pressures in the mbar regime. Compared to the bilayer FeO(111) film this trilayer FeO$_2$(111) layer contains additional lattice O in between the Fe lattice and the Pt(111) substrate [46]. As the trilayer FeO$_2$(111) film was found to be highly active for the oxidation of CO at low temperature this film has been studied extensively.

Fig. 10(a) shows an image plot of the O 1s spectra acquired while heating the FeO(111) film to 500 K in 0.6 mbar O$_2$. Selected spectra extracted from the image plot are shown in Fig. 10(b). Starting with the spectra acquired at 300 K, the doublet from the O$_2$ molecules in the gas phase is observed near 538 eV, while the component due to oxygen in the FeO(111) film is observed at 529.4 eV (component I in Fig. 10). Upon heating this component decreases and three new components (II–IV) are observed. We assign these components to hydroxyl groups at the surface of the FeO$_2$(111) layer (component II), O atoms sandwiched between the Fe lattice and the Pt(111) substrate (III), and O atoms at the surface of the FeO$_2$(111) film [43]. In Fig. 10(c) the relative coverage of the surface components (FeO(111) and FeO$_2$(111) with and without hydrogen attached; components determined from a least square curve fitting analysis) is plotted as function of temperature. Clearly, the hydroxylation of the film coincides with the conversion of FeO(111) to FeO$_2$(111), i.e. the FeO$_2$(111) film is extremely active for water dissociation. In contrast, the bilayer FeO(111) film is extremely inert with respect to water dissociation [43].

As a last point we highlight that the conversion of the FeO(111) to FeO$_2$(111) also is signalled by the binding-energy shift of the gas phase O$_2$ doublet. As the work functions of the FeO(111) film and that of the hydroxylated FeO$_2$(111) film are different from each other the vacuum level above the sample surface is different. This change leads to a shift of the gas phase O$_2$ doublet as evident in the image plot of Fig. 10(a). The gas phase O$_2$ molecules located between the sample surface and the grounded aperture sense, however, only a reduced potential difference. As a result the work function induced binding energy shift of the O$_2$ molecules is smaller than the real work function change. For a detailed and quantitative discussion of the work function shifts obtained from the binding energy position of the O$_2$ doublet we refer to Refs. [43,47].

4. Discussion and conclusions

We have presented the Lund approach to APXPS, which is based on the use of retractable AP cells in an UHV environment. The approach allows both UHV XPS and APXPS experiments on the very same sample and thus enables a direct linkage to the enormous pool of previous – and future – UHV surface science results and knowledge and extends it to the domain of realistic pressures. Of course, this linkage can also be achieved e.g. by separate experiments in UHV and in realistic
pressure or by the use of a vacuum suitcase for transfer of a sample between different experiment stations. The combined approach removes, however, possible ambiguities and doubts about the state of the sample, which typically result from separate UHV and ambient pressure studies or from the not precisely defined pressure during transfer from a vacuum suitcase to the experimental chamber. Highly favourable is also the fact that the inner volume of the AP cells is limited, which allows much easier and faster gas exchange compared to filling of a standard vacuum chamber. Moreover, the ratio of product to reactant gas volume is much higher in such a small volume. This is of importance e.g. in catalysis studies and facilitates the measurement of mass spectra with the quadrupole mass spectrometer connected to the outlet of the AP cell. Finally, the approach allows the exchange of sample environment by exchange of the APXPS instrument. This renders possible sample environments which are custom-designed to the purpose of the experiment, such as e.g. the study of liquids, electrochemical environments, or catalytic samples.

We have exemplified the above points with results obtained at the Lund APXPS instrument and the presentation of new AP cell designs for these instruments. The choice of examples has illustrated the role that APXPS continues and will continue to play for the traditional domains of APXPS — catalysis and oxidation. At the same time a development has started in which APXPS finds more and more application to research areas quite separate from these traditional domains of surface science. Our example concerns Atomic layer deposition in catalysis studies and facilitates the measurement of mass spectra with the quadrupole mass spectrometer connected to the outlet of the AP cell. Finally, the ratio of product to reactant gas volume is much easier and faster gas exchange compared to the use of other real-time investigation techniques.

The here presented instrumental approach is closely related to a similar approach recently implemented on other APXPS instruments. In this case also custom-designed AP cells are being used, but they are mounted directly on the electron energy analyser without surrounding UHV chamber. While this implementation of APXPS does not allow the comparative study of a sample both under UHV and ambient pressure conditions, it has the advantage that bulkier experiments and sample environments can be implemented in comparison to what is possible at our setup. One prime example is a liquid jet in equilibrium with a surrounding vapour phase. Yet other experiments will best be performed in the more traditional approach to APXPS in which a standard vacuum chamber is filled with a gas atmosphere. Hence, the different approaches to APXPS complement each other in an excellent manner.

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