Factors influencing surface carbon contamination in ambient-pressure x-ray photoelectron spectroscopy experiments

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ABSTRACT
Carbon contamination is a notorious issue that has an enormous influence on surface science experiments, especially in near-atmospheric conditions. While it is often mentioned in publications when affecting an experiment’s results, it is more rarely analyzed in detail. We performed ambient-pressure x-ray photoelectron spectroscopy experiments toward examining the build-up of adventitious carbon species (both inorganic and hydrocarbons) on a clean and well-prepared surface using large-scale (50 × 10 mm²) rutile TiO₂(110) single crystals exposed to water vapor and liquid water. Our results highlight how various factors and environmental conditions, such as beam illumination, residual gas pressure and composition, and interaction with liquid water, could play roles in the build-up of carbon on the surface. It became evident that beam-induced effects locally increase the amount of carbon in the irradiated area. Starting conditions that are independent of light irradiation determine the initial overall contamination level. Surprisingly, the rate of beam-induced carbon build-up does not vary significantly for different starting experimental conditions. The introduction of molecular oxygen in the order of 10 mbar allows for fast surface cleaning during x-ray illumination. The surface carbon contamination can be completely removed when the oxygen partial pressure is comparable to the partial pressure of water vapor in the millibar pressure range, as was tested by exposing the TiO₂(110) surface to 15 mbar of water vapor and 15 mbar of molecular O₂ simultaneously. Furthermore, our data support the hypothesis that the progressive removal of carbon species from the chamber walls by competitive adsorption of water molecules takes place following repeated exposure to water vapor. We believe that our findings will be useful for future studies of liquid-solid interfaces using tender x rays, where carbon contamination plays a significant role.

I. INTRODUCTION
Ambient pressure x-ray photoelectron spectroscopy (APXPS) is a powerful chemical analysis technique for surfaces and interfaces under close to operando conditions. It is based on recent technical innovations that lift the pressure limitations of the conventional XPS analysis, traditionally an ultrahigh vacuum (UHV) technique, through the use of differentially pumped electrostatic lens and hemispherical energy analyzer systems. This development has been one of the many branches of photoelectron spectroscopy that has been strongly influenced by Charles S. Fadley. It allows to perform XPS in the presence of a gas atmosphere typically up to a few tens of mbar or to study interfaces between solid surfaces and liquids of sufficiently low vapor pressure when an appropriate experimental approach is taken. In surface science investigations, the results of an experiment depend critically on the conditions of the sample and its environment. The situation is aggravated for studies under near-atmospheric pressures (1–30 mbar), as there is limited control over partial pressures of residual gases or contaminants within liquids that are brought in contact with the sample surface. The build-up of carbon contamination is a typical and well-known effect in APXPS and often
plays a role in surface chemistry when exposed to synchrotron radiation, but this role is rarely discussed in the literature.

Studies have observed how the incident radiation and emitted photoelectrons and secondary electrons decompose precursor molecules (typically CO and hydrocarbons) present in the residual gas even under typical UHV conditions, forming a solid phase that is often termed “adventitious carbon.” Dosing small quantities of O₂ at elevated temperatures is often done to induce the oxidation of these deposited carbon species and to minimize carbon contamination, for example, as maintenance for optical elements in synchrotron beamlines. When working at pressures of a few millibar, this approach is clearly not possible. Most of the current APXPS studies are performed using soft x rays where the strong photon flux on the sample was calibrated with a photodiode (AXUV20HS1) in UHV: at the PHOENIX I beamline, the photon flux is 3.1 × 10¹¹ photons/s at 4000 eV, and at the ISS beamline, the flux is 3.9 × 10¹¹ photons/s at 1000 eV.

II. EXPERIMENTAL SETUP AND METHODOLOGY

All experiments were performed at the Swiss Light Source, using the recently commissioned solid-liquid interface chamber endstation connected either to the PHOENIX I tender x-ray beamline or to the soft x-ray In Situ Spectroscopy (ISS) beamline. A detailed description of the experimental setup is included in Ref. 36; therefore, we only mention experimental details specific to the experiments reported in this paper. The photon flux on the sample was calibrated with a photodiode (AXUV20HS1) in UHV: at the PHOENIX I beamline, the photon flux is 3.1 × 10¹¹ photons/s at 4000 eV, and at the ISS beamline, the flux is 3.9 × 10¹¹ photons/s at 1000 eV.

Rutile TiO₂(110) single crystals (floating zone material, one-side polished) with dimensions of 50 × 10 × 1 mm³ size were acquired from SurfaceNet GmbH. Because of the large dimensions, which are needed for dip-and-pull experiments, these samples are denoted as “flag-type” samples throughout the manuscript. They were cleaned by Ar⁺ sputtering with a mean kinetic energy of ~780 eV. The sample was moved every 5 min by 8 mm to achieve uniform Ar⁺ ion bombardment, and subsequently vacuum annealed in a custom-built oven to 550 °C for 30 min (see Figs. 1(a), 1(b), and a detailed description of the oven in Fig. S1). This preparation produced a uniform (1 × 1) surface structure as verified by low-energy electron diffraction (LEED) in the annealed area (see Fig. 1(d)). Other experiments (data shown in Fig. 5 and Figs. S2 and S4) have been performed using a similar 7 × 7 × 0.5 mm² rutile TiO₂(110) single crystal purchased from PI-KEM Ltd.

For dip-and-pull experiments, MilliQ (type 3) water was used as a source and further filtered toward type 1 using a Millipore Direct-Q 3 UV-R system. A significant difference between type 3 and type 1 water is that the former is treated only by reverse osmosis, while the latter undergoes treatment with a high-intensity UV lamp and additional filtering with activated carbon. Such water was outgassed using a single freeze-pump-thaw cycle in a dedicated exsiccator before inserting it into the analysis chamber through a short exposure to air (see SI of Ref. 36 for details). Results shown in Fig. 2 used filtered type 3 water with a resistivity of 18.2 MΩ, using de-ionized water as a source. Experiments at the ISS beamline (data shown in Fig. 5 and Fig. S2) used MilliQ water from the source described above, purified by four freeze-pump-thaw cycles using liquid nitrogen for freezing and a turbomolecular pump for pumping. At ISS, a custom-made round bottom flask connected to a glass-to-metal adapter was used as a water reservoir attached to the analysis chamber via a high-precision leak valve. Oxygen dosing was performed by backfilling the experimental chamber from a miniCan (99.999%, PanGas) using a second high-precision leak valve.

Complementary to standard sputter-anneal cycles, for some experiments the samples have been cleaned ex vacuo using a combination of oxygen, water vapor, and UV irradiation, which has proven to be effective in other efforts to obtain clean surfaces.

LEED images were acquired using a low incident electron beam current of nominally 10 nA to minimize any possible electron-induced processes and then processed with LEEDCal 2013 (Version 4.1) to reduce the distortion induced by the non-spherical field caused by the planar microchannel plates. This is achieved by associating the visible LEED spots to the surface lattice parameters and running an iterative algorithm to compensate for geometric errors, such as radial “pincushion” distortion for MCP-LEED and asymmetrical distortions unique to each instrument.

APXPS data were acquired in a vacuum chamber that was not baked and has a base pressure of 10⁻⁹ mbar. All XPS spectra were acquired with 30° photon incidence and 60° electron emission geometry using linearly polarized light. The electron analyzer (Scienta R4000 HiPp-2) was equipped with an entrance cone aperture diameter of 300 μm and a working distance (l) of 600 μm was used. Unless stated otherwise, all spectra were recorded using 4000 eV photon energy, a pass energy of 100 eV, and analyzer slits nearly fully open (1.5 × 30 mm²). The binding energy (BE) scale was calibrated using a...
polycrystalline gold sample (Au 4f7/2, BE = 84.0 eV). The energy resolution of the Au 4f7/2 peak with the experimental settings given above yielded a full width at half maximum of 0.77 eV when fitted with a GL(70) function. Fitting of spectra has been performed using CasaXPS V.2.3.19 (see fitting details in SI38), while data integration and plot production were done using Igor Pro 6.37; error evaluation is estimated according to Poissonian statistics for peak intensity and background area variation.

The coverage of carbon is referenced with respect to the number of coordinatively unsaturated metal cations on the surface, where 1 monolayer (ML, 5.2 × 10¹⁴ atoms/cm²) corresponds to one carbon atom per surface (1 × 1) unit cell [see Fig. 1(c)]. Cross sections and asymmetry parameters used here have been calculated by Trzhaskovskaya and Yarzhemsky, utilizing the angular cross section for horizontal, linearly polarized light of the following equation:

\[
\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} \left[ 1 + \beta \times P_2(\cos(\theta)) + (\gamma \cos^2(\theta) \sin(\theta) \cos(\varphi)) \right],
\]

(1)

where \(\sigma\) is the cross section, \(\beta\) is a dipole parameter, \(\gamma\) and \(\delta\) are non-dipole parameters, \(P_2\) is the second-order Legendre polynomial, \(\theta\) is the angle between the photoelectron emission direction and the polarization of the incoming photons, and \(\varphi\) is the angle between the photon momentum vector and the plane containing the photoelectron emission direction and photon polarization.

To calculate the carbon coverage, a thin film approximation approach is adopted, as the mean free path of the relevant photoelectrons through glassy carbon for photon energies of 4000 eV is approximately 8 nm, according to a TPP-2M model.

The coverage of carbon referenced to the TiO\(_2\) surface unit cell is given by the following equation:

\[
\rho_C / \rho_{Ti} = I_C \lambda_{Ti} \cos(\psi) \frac{(d\sigma_{Ti}/d\Omega)}{(I_{Ti} d_{i}(d\sigma_{C}/d\Omega))},
\]

(2)

Here, \(I_C\) and \(I_{Ti}\) are given by the total integrated counts for each core level, \(\lambda_{Ti}\) is the inelastic mean free path (IMFP) of electrons in the TiO\(_2\)(110) substrate, \(d\sigma_{Ti}/d\Omega\) and \(d\sigma_{C}/d\Omega\) are the differential cross sections, \(\psi\) is the polar emission angle, and \(d_i\) is the interplanar distance for the TiO\(_2\)(110) lattice. An additional attenuation term could
be included to account for attenuation in gas phase water and liquid water; however, due to the high kinetic energy of photoelectrons from C 1s and Ti 2p core levels, we obtain similar values for the respective IMFPs when travelling through gas phase water. Because of this, the gas phase attenuation has only a negligible influence on Eq. (2) since we compare the intensity ratio of two elements.

In the presence of a condensed liquid water layer on the surface (in most cases evaluated to be in the range of a few angstroms), an additional attenuation term is added for the emission from the substrate, with the water layer thickness “d” estimated from the attenuation of the substrate component of the O 1s peak using the following equation:

\[ d = \frac{\lambda_{O \text{water}} \times \cos(\psi) \times \ln (1 + (I_{H_2O} \times \lambda_{O \text{sub}} \times \rho_D)/(I_{O} \times \lambda_{O \text{water}} \times \rho_{H_2O})))}{\lambda_{O \text{water}} - \lambda_{O \text{sub}}} \]  

(3)

Here, \( \lambda_{O \text{water}} \) is the IMFP of electrons passing through liquid water,\(^{46} \lambda_{O \text{sub}} \) is the IMFP of electrons in the TiO_2 substrate, \( \rho_{H_2O} \) is atomic density of oxygen in liquid water compared to the density of O atoms (\( \rho_D \)) in TiO_2, and I represents the intensity of the O 1s peak from liquid water (I_{H_2O}) or TiO_2 (I_{O}). The attenuation due to adventitious carbon is not considered in Eqs. (2) and (3).

III. RESULTS AND DISCUSSION

A. Beam effect on surface carbon contamination

To distinguish beam-induced effects from environmental effects in surface carbon contamination, time-lapsed measurements were performed under fixed experimental conditions and summarized in Fig. 2. Here, a clean TiO_2(110) sample was exposed to 24 mbar of water vapor in equilibrium with a liquid water-filled glass container present inside the chamber. The sample was not dipped into the liquid and the experiment represented the starting conditions of a typical dip-and-pull experiment.\(^7\) The measurement was started immediately after moving a UHV-prepared sample via a UHV transfer chamber to the analysis chamber. After a long measurement sequence in spot “A,” which shows a progressive increase over time in the amount of carbon contaminants, the sample was moved to illuminate spot “B” at a distance (3 mm) greater than the beam size (400 \( \mu \)m). Resuming the measurement on this new area shows a significantly lower amount of carbon, comparable to the beginning of the previous sequence, followed by a similar increase over time.

The initial carbon coverage is quite significant, as there are over ten carbon atoms per (1 x 1) unit cell of the TiO_2(110) surface, which corresponds to about 2 monolayers of condensed graphitic carbon. It should be noted that these spectra were acquired after installing a new component (a gate valve placed between the chamber and the turbomolecular pump) onto the transfer chamber that was used as a buffer chamber when transferring samples from the UHV preparation chamber to the analysis chamber with liquid water inside (25 mbar). While this component was clean based on UHV standards, it was never previously exposed to water vapor dosed under vacuum conditions. We speculate that this can contribute to high initial carbon contamination. Another possible cause might be the use of MilliQ water that was not treated with UV light (see Sec. II for details). Other well-known sources of contamination, such as from gas-phase water reacting with a hot filament,\(^7\) can be excluded in the used setup.\(^{40} \)

B. Pressure effect on surface contamination

To investigate the effect of sample environment and history, we monitored the amount of carbon on the surface after exposure to different environmental conditions. As a starting point, a sample underwent the same UHV preparation procedure each time. For most of the measurements, the chamber walls had already been exposed to water vapor for 3 days and had thus been effectively “rinsed” (see below for a further discussion of this effect). In these experiments, we used Type 1 milliQ water that was properly filtered and UV-treated, as opposed to the experiment presented in Fig. 2. The results are summarized in Fig. 3 where the initial contamination level correlates strongly with the environmental conditions. Higher water vapor pressures lead to higher initial levels of carbon contamination, and considerably higher contamination is observed for a dipped surface compared to a sample exposed only to water vapor. In addition to the immediate carbon build-up, the carbon signal increases further over time. This behavior is generally observed for solid/liquid interface experiments using the dip-and-pull method and APXPS.\(^8\) Considering also the results...
shown in Fig. 2, we attribute the additional carbon build-up to synchrotron beam-induced effects.

Maintaining weak and constant pumping balanced by continuous liquid evaporation (resulting in a pressure of 14 mbar) creates a dynamic condition for the water vapor present in the chamber, which was able to significantly reduce the amount of initial carbon, even for a sample immersed in liquid water (first data points in the green and blue curves in Fig. 3). This is attributed to continued pumping of carbon-containing molecules in the gas phase resulting from adventitious carbon displaced from the chamber walls by the water vapor.

Finally, the "history" of the vacuum chamber appears to be a significant factor. "Rinsing" the chamber walls by repeated exposure to water vapor over an extended period of time (3 days) while still pumping seems to reduce the carbon presence in the environment. The detected amount of contamination is visibly lower than upon introduction of the sample into the chamber right after HV conditions have been established after nitrogen venting. This is demonstrated in Fig. 3 by comparing data points for the rinsed chamber (pink) and the nonrinsed chamber (brown), measured at an equilibrium water vapor pressure of 24 mbar under otherwise identical conditions.

C. Effect of oxygen presence during APXPS experiments

The effect of adding molecular oxygen to an environment otherwise in equilibrium with liquid water was also investigated. On a TiO$_2$(110) surface previously contaminated with carbon, no signal above the noise level was detected in the C 1s region once 15 mbar of O$_2$ was added to a partial pressure of 15 mbar H$_2$O (total pressure of 30 mbar) [see Figs. S1(a) and S1(b)].

While it is not possible to observe the effects of oxygen at partial pressures far below the millibar range during in situ experiments in the presence of liquid water, being limited by the resolutions of the pressure gauge in the chamber and of a quadrupole...
mass spectrometer sampling gas within the differential pumping stages of the analyzer, it is possible to observe such effects when adding oxygen at partial pressures comparable to water vapor pressure. This experiment is shown in Fig. 4: after reaching an oxygen partial pressure of few millibars, it was possible to observe a transient phase consisting of only a few energy scans of the analyzer, leading from a significantly contaminated surface to one comparable to the initial contamination observed for a similar total water vapor pressure. This suggests that maintaining a limited oxygen partial pressure during APXPS measurements can assist in reducing or preventing the build-up of carbon over the duration of the measurement.

This cleaning effect seems to be due to a combined effect of oxygen partial pressure and x-ray irradiation. After observing a completely clean surface from the addition of 15 mbar O$_2$ to 15 mbar H$_2$O (see Fig. S1(b)), the oxygen partial pressure was reduced to below the detection limit of the quadrupole mass spectrometer located in the second differentially pumped stage of the electron analyzer. When moving the sample to a new, non-irradiated spot (distance > 1 mm), the C 1s region showed a similar intensity to the one observed before dosing oxygen (see Fig. S1(c)).

A similar experiment was performed at lower pressures by simultaneously co-dosing 1 mbar H$_2$O and 1 mbar O$_2$ at the In Situ Spectroscopy beamline of the Swiss Light Source at a lower photon energy (1000 eV), using the same analysis chamber as in the previous experiments. The design of this experiment is shown schematically in Fig. 5(b).

Following UHV preparation and the transfer of the sample to the HV analysis chamber (P < 4.2 × 10$^{-7}$ mbar), the quantification of the C 1s core-level spectra revealed that the initial carbon coverage was 1.7 ML as measured on spot “1” of the sample surface [black spectrum in Fig. 5(a)]. The high base pressure was a result of continuous exposure of the chamber to water vapor (up to 24 mbar) for two consecutive days before these measurements. After exposure to 2 mbar of water vapor for a total time of 15 min (without irradiation), HV conditions were restored (P < 2.6 × 10$^{-8}$ mbar). In spot “2,” the carbon coverage increased to 2.5 ML as a result of this exposure [blue spectrum in Fig. 5(a)]. Then, spot “1” was irradiated with a synchrotron beam for 1 h while the chamber was backfilled with 1 mbar H$_2$O and 1 mbar O$_2$, to allow for possible beam-induced cleaning. In the end, HV was restored (P < 5 × 10$^{-9}$ mbar) and both spots “1” and “2” were measured again. Clearly, on spot “1,” the effect of beam-induced cleaning became apparent [green spectrum in Fig. 5(a)] as the carbon coverage is reduced from 1.7 to 1.2 ML, while on spot “2,” it has further increased to 2.8 ML.

A similar experiment was performed also at 14 mbar H$_2$O plus 14 mbar O$_2$ (total pressure of 28 mbar), again with soft x-ray illumination (1000 eV, data in Fig. S5). The results are consistent with the 1 mbar exposure shown in Fig. 5, where in contrast to what is observed when using tender x rays [see Fig. S1(b)], the carbon contamination is not completely removed.

D. In situ versus ex situ sample preparation

The method of preparation for a sample will undoubtedly have an influence on the surface conditions. This could be particularly important when comparing in situ and ex situ preparations. As an alternative method to the standard sputter-anneal cycles for surface cleaning, ex situ irradiation of TiO$_2$(110) with UV light was performed in the presence of de-ionized water and a slight oxygen flow. This method was observed to produce clean surfaces and to achieve a superhydrophilic TiO$_2$(110) surface as verified by visual inspection of the water contact angle in air. Using this method, a sample was prepared and transferred through air to the experimental chamber, which was pumped to HV before performing XPS measurements. The time of exposure to air was less than half an hour.

The results in Fig. 6 show that there is no significant difference in terms of carbon contamination between in situ and ex situ preparations (4.4 vs 4.2 ML). The comparison of LEED patterns for the two preparations (see Fig. S4) finds them identical and leads to the same conclusion. We note, however, that the ex situ UV-irradiated sample had been previously prepared by means of UHV sputter-anneal cycles before exposure to air. The UV irradiation under humid and oxygen-rich condition on a previously cleaned TiO$_2$(110) surface resulted mainly in the removal of carbon contamination on an otherwise well-defined surface.

The similar level of contamination observed after the two different cleaning procedures could be attributed to a very thin coating of clean water formed on the titanium dioxide surface during ozone cleaning, associated with superhydrophilicity exhibited by clean TiO$_2$. We speculate that this thin water film protects the surface from air-induced contamination during transfer to the UHV chamber. It is known that even at very low relative humidity, a monolayer of water forms on clean TiO$_2$(110). Once the sample is reintroduced into the UHV system, this liquid layer is quickly desorbed, leaving a relatively clean surface behind.

IV. DISCUSSION

The removal of organic contaminants from a TiO$_2$(110) surface was studied by Zubkov et al., finding the need for exposure to both oxygen and water vapor to achieve a clean, hydrophilic surface. It was also found that the UV irradiation time needed to achieve a clean surface depended on the amount of contaminants. However, this view may be too simple based on the recent studies of clean TiO$_2$(110) exposed to ultrapure water, when no hydroxyl formation of oxidized carbonaceous species that are often inherently hydrophilic. The discrepancy might be caused by the formation of oxidized carbonaceous species that are often inherently hydrophilic.

In our experiments, we can observe the role of oxygen in a water vapor environment toward reducing the amount of surface carbon under x-ray illumination. As the data shown in Fig. 4 and Fig. S1 differ based on the pressure of oxygen in the chamber, it follows that the relative abundance of O$_2$ and H$_2$O in the gas phase sets the limit for the carbon-removing processes. The incident radiation then appears responsible for both a build-up of carbon over time, from the decomposition of residual carbon species originating from the gas phase, and its removal in the presence of water and oxygen by the creation of active oxygen radical species, as determined in Fig. 5.
While the environmental conditions in the experiments shown in Figs. S1 and S5 are nominally identical, the difference in beam energy might play a key role. In vacuum, the beam fluxes for the PHOENIX I and In Situ Spectroscopy beamlines are comparable, but the transmission of photons at these pressures depends on the photon energy. In 30 mbar water vapor, the transmission for 4 keV photons is approximately 96% over a distance of 20 cm, while it is only 36% at 1 keV, with stronger attenuation for longer distances. This will result in a significantly lower flux of x rays impinging on the surface and thus in fewer secondary electrons. The generation of oxygen radicals in the gas phase in close proximity to the surface will then be significantly reduced.

Using the more bulk sensitive x rays, the presence of 30 mbar of the gas phase leads to a lower sensitivity for low levels of carbon contamination. We estimate that for the given background noise in Fig. S1(b) any coverage below 2 ML would not be visible, for a region measurement lasting approximately half an hour.

Another possibility is that the number of secondary electrons resulting from the higher energetic photoelectrons leads to a more efficient oxygen radical formation and thus removal of carbon from the surface. In this case, one should expect a difference in the reaction pathway between UV and x-ray illumination. While UV light will create ozone by photolysis of oxygen, the cleaning effect that follows x-ray irradiation will likely come from the extracted photoelectrons and secondary electrons entering the gas phase.

Since tender x rays can excite higher energy photoelectrons compared to soft x rays, it could reasonably lead to a higher number of energetic secondary electrons originating from ionization cascades moving into the gas phase and the liquid phase, similarly to what happens in gas cascade amplification known in the field of environmental scanning electron microscopy.

In the absence of gas phase oxygen, the dissociation of water under x-ray illumination appears to not provide any significant cleaning effect: this can be attributed to the high reactivity of ozone and oxygen radicals with the adventitious contamination’s double and triple C—C bonds.

Experiments with pure water previously performed by Balajka et al. demonstrated that clean TiO$_2$(110) can be exposed to liquid...
water with no carbon contamination present on the surface.57
Their experiment was done in a compact chamber with a small overall volume and an internal surface area. A later paper from the same group highlights that several water vapor exposures/re-evacuations need to be performed to minimize the amount of contamination from the chamber walls.50 Our experiments appear in agreement with this latest publication, as keeping the chamber under limited, constant pumping during or after exposure to water vapor did reduce the observed amount of carbon on the surface as shown in Fig. 3. The effectiveness of this procedure could be greatly enhanced if clean and outgassed liquid water could be introduced without breaking vacuum, e.g., via a load lock.

V. SUMMARY AND CONCLUSIONS

Measurements have been conducted to isolate factors that determine the level of carbon contamination as seen in ambient-pressure XPS experiments. Environmental conditions were systematically varied, such as water vapor pressure, gas composition, exposure time to x rays and photon energy, and a pretreatment of the experimental chamber involving repeated interaction of water vapor with the internal surfaces.

We observed how higher water vapor pressures correlate to a higher level of surface contamination with adventitious carbon, originating either from the water or being displaced from internal chamber walls. Similarly, dipping into outgassed liquid water leads to a higher level of contamination compared to simply exposing the sample to water vapor. This contamination can be reduced by keeping the system in a dynamic equilibrium, providing a small pumping speed compensated by liquid water evaporation. By doing so, the surfaces inside the chamber are “rinsed,” which allows to remove the displaced carbon from the chamber.

X-ray illumination has a significant impact on the build-up of carbon over time, while the initial level of contamination is determined by the environmental conditions. This impact of beam-induced carbon build-up can be minimized by periodically moving the sample to illuminate a fresh surface area.

It is also possible to introduce molecular oxygen to remove surface carbon under x-ray illumination if the sample is not sensitive to oxidizing conditions. The effectiveness of the process seems strongly related to the impinging photon energy, photon fluence, and ambient gas pressure, while the kinetics of the process appear fast for XPS data acquisition timescales (as in Fig. 4).

These experiments, while not spanning all the possible environmental and experimental conditions, can provide some insight into processes that can influence near-atmospheric pressure experiments and suggest mitigation scenarios for some of these phenomena.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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