

Initial Stages of Water Adsorption on Au Surfaces

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We report the results of low-temperature ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) measurements examining the initial stages of water adsorption on Au surfaces. Understanding the adsorption of H₂O molecules at electrode surfaces in electrolyte solution is one of the most important issues in elucidating the nature of solid–liquid interfaces. Adsorption of H₂O on metal surfaces has been intensively investigated by means of low-temperature UHV-based experiments.^{1,2} Temperature-programmed desorption spectroscopy (TPD),^{3–5} work function measurements,⁶ and ultraviolet spectroscopy and X-ray photoelectron spectroscopy (UPS and XPS)^{7,8} have combined to provide a macroscopic picture of water adsorption on many metal surfaces. There is considerable evidence¹ that H₂O orders on the (111) planes of Pt and other hydrophilic materials, forming a hexagonal monolayer structure (known as the “bilayer”) essentially equivalent to the basal plane of ice (I_h). For example, recent STM images showed well-ordered H₂O films formed on Pt(111) at 140 K.^{9,10} However, there is less understanding about the initial stages of H₂O film formation on more weakly interacting surfaces such as Au. This lack of understanding is particularly unfortunate given the variety of surface electrochemical studies utilizing Au(111) surfaces.

Before exposure to H₂O, STM images¹¹ of a clean, well-ordered Au(111) surface¹² obtained at 100 K show the characteristic “herringbone” pattern with a corrugation amplitude of 0.02 nm arising from the well-studied ($\sqrt{3} \times 23$) Au(111) surface reconstruction.¹³ Higher resolution images reveal the underlying Au(111) surface structure.

Figure 1A shows a STM image of the reconstructed Au(111)

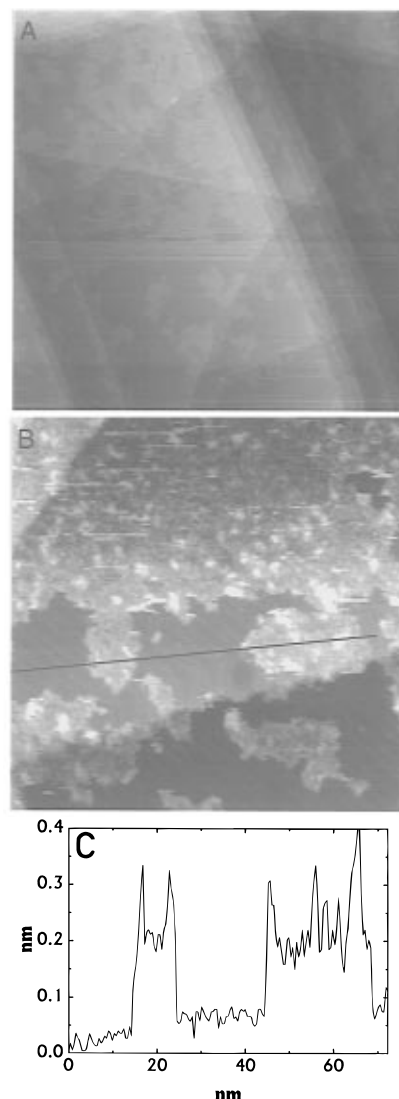


Figure 1. A. The 202 nm \times 202 nm STM image of Au(111) at 100 K following dosing with 1.5×10^{15} molecules/cm² of H₂O. $V_{\text{tip}} = -2.1$ V, $I_{\text{tunnel}} = 0.3$ nA. B. The 78 nm \times 77 nm STM image of the same film at 100 K. $V_{\text{tip}} = -2.1$ V, $I_{\text{tunnel}} = 0.1$ nA. C. Cross-sectional view obtained along dark line shown in Figure 1B showing height of the H₂O islands and clusters.

surface at 100 K after a H₂O exposure¹⁴ of 1.5×10^{15} molecules/cm². Clearly evident in the image are many small islands associated with H₂O exposure, which form on the terraces as well as at step edges. Some of islands are isolated, while others are connected to form larger islands. These islands, surprisingly, evince planar rather than three-dimensional or spherical contours. Although the islands do not exhibit highly dendritic shapes, the island ledges are atomically rough rather than 3-fold symmetric as would be expected for an epitaxial film.

Figure 1B,C shows a close-up STM image taken on another area of the same surface and a corresponding cross-sectional view. The image shows regions of bare reconstructed Au(111), regions of the planar film, and regions where clusters of a few nanometers in diameter are growing atop the film. No clusters are observed to be growing on the bare Au surface. It is noteworthy that the nucleation of H₂O islands does not always start from the elbows of the reconstruction as is found for more strongly interacting adsorbates.¹⁵ In this image, small H₂O

(14) H₂O adsorption was performed by filling the chamber with a H₂O pressure of 1×10^{-9} to 5×10^{-9} mbar while maintaining the sample temperature at 100 K. The STM tip was removed from the sample during water exposure to avoid shadowing effects.

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- (11) Experiments were performed in an Omicron UHV system (base pressure $<2.0 \times 10^{-10}$ mbar) equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and an Omicron variable-temperature STM. The STM tip was prepared by electrochemical etching of a tungsten wire at 15–20 V ac in a 1 M KOH solution. The bias voltage is that of the tip referred to the sample. The tips were further treated in UHV by applying a high bias voltage (10 V) for several scan lines while scanning on sample areas different from those studied. STM images were recorded at 100 K in height mode.
- (12) Au(111) surfaces were obtained as Au films deposited on borosilicate glass (Dirk Schröer, Inc., Berlin). The samples were prepared in UHV by cycles of ion sputtering (1 keV , $P_{\text{N}_2} = 2 \times 10^{-8}$ mbar) and annealing at temperatures where the sample started to glow. This procedure produced a clean and atomically flat Au(111) surface as checked by AES and STM. Only one heating–sputtering cycle was necessary for routine cleaning. The samples were cooled to 100 K by a cryostat filled with liquid helium.
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islands are seen sitting on the paired reconstruction rows. The row directions of the reconstruction, although hidden as they pass under the islands, do not appear to be altered by the presence of the H₂O layer. This observation implies that the Au(111) surface remains reconstructed and that, consequently, the strength of the interaction between H₂O and Au is weak.

The cross-sectional view (Figure 1C) clearly shows that the H₂O islands do not have atomically flat surfaces. The height of the planar film is about 0.15 nm above the Au surface, while the cluster reaches to 0.45 nm. The measured 0.15 nm thickness of the film agrees well with that expected for the thickness of a monolayer H₂O film for the tunneling conditions used (ca. 0.1–0.15 nm depending on orientation).¹⁰ Since we do not observe any well-ordered atomic structures on the H₂O islands—but can obtain atomic resolution from the bare Au surface—these images suggest that the first layer of the H₂O film forms an amorphous phase. Similar results were obtained on an Au(100) surface.¹⁶

The amorphous first layer structure for H₂O observed here on Au(111) (and Au(100))¹⁶ is consistent with information obtained from LEED measurements on surfaces other than Au, for which this structural information is not available. TPD curves from H₂O on Au(111)³ are very similar to those obtained for H₂O on Ag^{17–20} and Cu^{21,22} surfaces in that they exhibit only one desorption peak. In agreement with our STM results, the results from LEED studies for H₂O on Ag^{17–20} and Cu^{21,23} suggest that thin films grown on these substrates are also amorphous. In contrast, at least two peaks are observed in TPD from Pt(111) and Rh(001) which have stronger H₂O–metal interactions.¹ These substrates evince ordered H₂O monolayers.^{9,24} On Pt(111), H₂O forms quasi-one-dimensional chains of molecules at the upper side of step edges;⁹ these were never seen on Au(111) or Au(100)—another indication that the H₂O–Au interaction is much weaker than that found for Pt.

The STM data provide considerable insight into the likely molecular mechanism of growth of H₂O on Au surfaces at low temperatures. Of interest is the appearance of H₂O clusters only atop the amorphous film and not on the bare Au(111) surface. This observation suggests that the amorphous film is a necessary precursor to H₂O multilayer formation. The growth process can be depicted as involving at least two steps: (1) formation of planar, amorphous H₂O films followed by (2) attachment of three-dimensional H₂O clusters atop this film. The STM

observations indicate that the planar film formed in the first step does not thicken beyond a monolayer. Although the TPD data for H₂O on Au(111) show a single desorption peak,³ our results suggest that the H₂O molecules are adsorbed on Au in at least two states at submonolayer coverages. Thus, desorption-focussed TPD results may not adequately describe the growth process. The STM results presented here further suggest that individual H₂O admolecules are highly mobile on bare Au(111) and Au(100) while the mobility of admolecules is suppressed not only at the island ledges but also on top of the planar film.

Our model is anticipated by a vibrational spectroscopic study²⁵ of H₂O on Cu(111) which suggested the formation of metastable water species (“wetting species”²⁶) which at least partially wets the surface. In accord with this inference, the planar H₂O films obtained in our observations show direct evidence of a “wetting species”. A similar proposal has been made for H₂O films grown on organic monolayers.^{27,28} We note that annealing H₂O films grown on these and other surfaces at between 120 and 160 K leads to the formation of crystalline ice;²⁹ annealing was not attempted in the present study. However, our study disagrees with recent interpretations of TPD data⁵ which suggested that the growth of H₂O on Au(111) occurs only through the formation of three-dimensional nanoclusters; while clusters may form following annealing at ca. 140 K, the observation of clusters only atop the planar film indicates the importance of the film in the growth of multilayer H₂O in the low-temperature regime.

Using a low-temperature STM, we have observed the initial stages of H₂O adsorption on a Au(111) surface. We show that H₂O first adsorbs on Au as a planar, amorphous, monolayer-high film. We do not observe H₂O cluster formation on the bare metal. Rather, the subsequent growth of H₂O clusters occurs atop this film. This study shows that, even for a weakly interacting surface such as Au, a ‘wetting species’ is a necessary precursor to the formation of H₂O multilayers. Examination of the way adsorbates and annealing alter the H₂O structure is work in progress.

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