Transient hydroxyl formation from water on oxygen-covered Au(111)

R. G. Quiller,¹ T. A. Baker,² X. Deng,² M. E. Colling,² B. K. Min,³ and C. M. Friend¹,²,a)

¹School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge, Massachusetts 02138, USA
²Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St., Cambridge, Massachusetts 02138, USA
³Clean Energy Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea

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We present evidence for the formation of transient hydroxyls from the reaction of water with atomic oxygen on Au(111) and investigate the effect of adsorbed oxygen on the hydrogen bonding of water. Water is evolved in peaks at 175 and 195 K in temperature programmed reaction experiments following adsorption of water on oxygen-covered Au(111). The peak at 175 K is ascribed to sublimation of multilayers of water, whereas the peak at 195 K is associated with oxygen-stabilized water or a water-hydroxyl surface complex. Infrared reflection absorption spectra are consistent with the presence of molecular water over the entire range of coverages studied, indicating that isolated stable hydroxyls are not formed. Isotopic exchange of adsorbed H216O with H218O following adsorption and subsequent temperature programed reaction, however, indicates that transient OH species are formed. The extent of oxygen exchange was considerable—up to 70%. The degree of oxygen exchange depends on the initial coverage of oxygen, the surface temperature when preparing oxygen adatoms, and the H216O coverage. The hydroxyls are short-lived, forming and disproportionating multiple times before water desorption during temperature programed reaction. It was also found that chemisorbed oxygen is critical in the formation of hydroxyls and stabilizing water, whereas gold oxide does not contribute to these effects. These results identify transient hydroxyls as species that could play a critical role in oxidative chemical reactions on gold, especially in ambient water vapor. The crystallinity of adsorbed water also depended on the degree of surface ordering and chemical modification based on scanning tunneling microscopy and infrared spectra. These results demonstrate that oxidation of interfaces has a major impact on their interaction with water. © 2008 American Institute of Physics. [DOI: 10.1063/1.2965821]

I. INTRODUCTION

Water plays an important role in a variety of chemical phenomena that occur on metal surfaces including catalytic reactions such as the water-gas shift reaction,¹ hydrocarbon oxidation,² and hydrogenation reactions.³ Understanding the interaction of water with oxygen on metal surfaces, in particular Au, is also of broad fundamental interest because of the possible role of water in liquid phase systems, such as catalysis,⁴ electrochemistry,⁵ and the performance of biointerfaces. For example, molecular dy-
present. Recently, Ojifinni et al.\textsuperscript{17} found that hydroxyls readily form from oxygen-scrambling experiments involving $\text{H}_2\text{^{18}}\text{O}$ on an oxygen-covered Au(111) surface prepared using a rf generator to dose atomic oxygen. Although density functional theory results suggest that two hydroxyls are not thermodynamically stable compared to a water molecule interacting with atomic oxygen on Au(111),\textsuperscript{18} the difference in energies of these states, 0.05 eV, is sufficiently small that rapid and reversible OH formation is expected and favorable even at 45 K.\textsuperscript{17} These calculations did not address the interactions between OH formed from dissociation and neighboring water molecules. Earlier studies using x-ray photoelectron spectroscopy (XPS) did not provide evidence of a stable hydroxyl species when water is adsorbed on oxygen-covered Au(111).\textsuperscript{19} The work described herein investigates conditions necessary for the formation of transient OH species which are most likely stabilized by hydrogen bonding to neighboring water molecules, and illustrates that the surface roughness and the presence of oxygen adatoms affect the intermolecular interactions.

II. EXPERIMENTAL

Experiments were performed in three separate ultrahigh vacuum chambers with base pressures $<4\times10^{-10}$ torr. One chamber is equipped with a quadrupole mass spectrometer (Pfeiffer Prisma QMS 200), an Auger electron spectrometer (Varian model 981–2607), and low-energy electron diffraction (LEED) optics (Princeton Research Instruments model PRI-179). The second chamber is equipped with a quadrupole mass spectrometer (Pfeiffer Prisma QMS 200), an Auger electron spectrometer (Perkin-Elmer model 15–155), and LEED optics (Physical Electronics model 15–180) and is interfaced with a Fourier transform infrared spectrometer (Thermo Nicolet 670). Scanning tunneling microscopy (STM) experiments were performed in an ultrahigh vacuum chamber with base pressure of $\sim2\times10^{-10}$ torr, with separate compartments for sample preparation and characterization.\textsuperscript{20} The system was equipped with a STM (RHK SPM 100), LEED optics, an Auger electron spectrometer (PRI 179), and a mass spectrometer (Balzers QME 200). The Pt/Ir scanning tip was cleaned in vacuum using field evaporation (300 V, (3.8–4.0) $\times10^{-6}$ A, 15 min) on a separately mounted gold single crystal. Atomically resolved Au(111)-(1 $\times$ 1) was used to calibrate scan dimensions.

The surface of the Au(111) crystal was prepared using the established method\textsuperscript{21,22} of cycles of Ar$^+$ bombardment, followed by annealing at 900 K for 5 min and 700 K for 60 min. This procedure is repeated until no impurities are detected by Auger electron spectroscopy, and satellite spots characteristic of the herringbone reconstruction were obtained in LEED.\textsuperscript{22,23}

Atomic oxygen-covered Au(111) was prepared by exposing the crystal to ozone at 200 K with a direct doser using a method that is previously described.\textsuperscript{20,24} The surface coverage of atomic oxygen was determined by comparing the area of the O$_2$ desorption peak to the area obtained at the saturation coverage ($\sim$1 ML).\textsuperscript{20,24} The roughened Au(111) surface without oxygen was prepared by exposing the 0.2 ML oxygen-covered surface to CO at 200 K using a direct doser with a background pressure rise of $2.5\times10^{-9}$ torr for 10 min. This was sufficient to react away all surface oxygen so that no oxygen would be detected with the mass spectrometer when heated. This procedure is known to preserve the surface’s roughened morphology\textsuperscript{25} and was confirmed using STM.

Distilled H$_2$O and H$_2$\textsuperscript{18}O (Cambridge Isotope Laboratories, 97% atomic purity) were purified using freeze-pump-thaw cycles, and the purity was confirmed using mass spectrometry by condensing multilayers on the crystal and subsequently subliming the multilayer while monitoring with mass spectrometry. During H$_2$\textsuperscript{18}O dosing, the inlet consisted of 80% H$_2$\textsuperscript{18}O and $\sim$20% H$_2$\textsuperscript{16}O, which is accounted for in our analysis. The rise in chamber pressure during directed water dosing was $1\times10^{-10}$ torr; direct dosing exposures were calibrated by comparing desorption spectra from Au(111) following water dosing from a controlled background pressure. The enhancement factor due to direct dosing was estimated to be $\sim150$. All water exposures were performed at a crystal temperature of 145 K, which is below the desorption temperature of molecular water.

Temperature programmed desorption (TPD) data were acquired with a computer-interfaced Pfeiffer Prisma QMS 200 mass spectrometer. The crystal was biased at $\sim70$ V during data collection to prevent any electron-induced reactions from the mass spectrometer’s filament. Temperature was measured using a $K$-type chromel/alumel thermocouple. Resistive heating with a tantalum wire was used to obtain an average heating rate of $\sim2.4$ K/s between 120 and 600 K. In order to deconvolute multiple water desorption peaks, integrated intensities were approximated by subtracting the resulting spectra with a Gaussian function and subsequently integrating the function.

Reflection-absorption infrared spectroscopy (RAIRS) data were recorded using a Thermo Nicolet MCT-A semiconductor photodiode detector. Background spectra were acquired at 120 K after first heating to 600 K to desorb all water and oxygen. Three sets of 600 scans were coadded for each experiment with a resolution of 4 cm$^{-1}$.

III. RESULTS AND DISCUSSION

Water desorbs from the clean Au(111) in a single zero-order peak [Fig. 1(a)].\textsuperscript{26,27} This peak shifts from 167 to 178 K with increasing water exposure\textsuperscript{27,28} in the range studied, 0.3–1.0 L, and shows no distinguishing characteristics separating submonolayer and multilayer coverages.

A new water peak, in addition to the peak at $\sim175$ K, is observed at 195 K when Au(111) is oxidized at 200 K and subsequently exposed to water at 145 K [Fig. 1(b)], in agreement with other studies.\textsuperscript{17} The maximum intensity of the 195 K water peak depends on the initial oxygen coverage (Fig. 1, inset). The amount of water in the 195 K peak rises with increasing oxygen coverage, up to $\sim0.2$ ML; thereafter, it decreases as a function of increasing oxygen coverage. At an oxygen coverage of 0.58 ML, there is no discernible water
which we measured to be face matched the \( m/z = 18:17 \) ratio for the water peaks on the oxygen-covered surface. The water peak retention is increased beyond \( 0.6 \text{ L} \), the 195 K peaks saturates and only shows an apparent intensity increased due to the local bonding of oxygen on the surface to 400 K. After oxidation at 200 K, there is a preponderance of small (2–5 nm diameter) Au particles associated with a disordered surface was observed in XPS at low oxygen coverages for ozone decomposition at 200 K, while gold oxide—i.e., an ordered two dimensional (2D) structure—signified by an \( \text{O}(1\,\text{s}) \) binding energy of 530.1 eV is predominant at oxygen coverages \( >0.5 \text{ ML} \) and when ozone is decomposed on the surface at 400 K.

In addition, the morphology of the surfaces created at 200 versus 400 K is substantially different. Oxidation induces release of Au atoms from the surface under all conditions [Figs. 2(a) and 2(b)]. After oxidation at 200 K, there is a preponderance of small (2–5 nm diameter) Au particles [Fig. 2(a)]. A gold oxide phase is associated with the rough morphology, and the development of pits and islands are observed for oxygen coverages approaching 1 ML. Larger particles with regions of atomic-scale order in a rectangular structure are formed upon oxidation at 400 K [Fig. 2(b)]. Similar ordering and the agglomeration of the gold oxide phase is accomplished by annealing low coverages of oxygen on the Au(111) surface to 400 K.

Detailed studies of the water desorption peaks were performed for an oxygen coverage of 0.2 ML after oxidation at 200 K in order to gain more insight into the bonding of water with the oxygen-covered Au [Fig. 1(b)]. The 195 K peak develops first for low water exposure. As the water exposure is increased beyond \( \sim 0.6 \text{ L} \), the 195 K peaks saturates and the 175 K peak begins to appear. Above this exposure, the 175 K peak continues to grow linearly and does not saturate up to the maximum water dose studied, 6.4 L. The 195 K peak retains essentially the same shape for exposures beyond \( \sim 0.6 \text{ L} \) and only shows an apparent intensity increased due to overlap with the trailing edge of the 175 K peak.

The water desorption peak at 195 K has two possible origins. Oxygen might stabilize water molecules on the surface via hydrogen bonding, thereby increasing the strength of interaction and increasing the desorption temperature from \( \sim 175 \) to 195 K. The formation of stable \( \text{H}_2\text{O}–\text{O} \) complexes has previously been proposed to account for this temperature upshift. Water stabilization due to chemisorbed oxygen is

O\(_2\) desorption occurs at 535 K and the amount of oxygen remains the same, regardless of water exposure, confirming that water reversibly desorbs at low temperature without affecting the surface oxygen coverage.

The appearance of the water desorption peak at 195 K associated with the presence of O atoms on the surface depends strongly on the conditions used to oxidize the surface. Specifically, the 195 K water desorption peak was absent when the surface was oxidized at 400 K [Fig. 1(e)]. This is true for all oxygen coverages studied: 0.09, 0.20, 0.38, and 0.81 ML. Furthermore, the 195 K peak is absent for oxygen coverages above 0.53 ML even for oxidation carried out at 200 K.

Previous studies have shown that the morphology of the surface and the local bonding of oxygen depend on the conditions used to prepare the surface. There are at least two distinct oxygen moieties present following ozone decomposition on Au(111) based on XPS [Ref. 20] and high resolution electron energy loss spectroscopy. Min et al. identified these states as chemisorbed oxygen and gold oxide. Chemisorbed oxygen (529.1 eV binding energy) associated with a disordered surface was observed in XPS at low oxygen coverages for ozone decomposition at 200 K, while gold oxide—i.e., an ordered two dimensional (2D) structure—signified by an \( \text{O}(1\,\text{s}) \) binding energy of 530.1 eV is predominant at oxygen coverages \( >0.5 \text{ ML} \) and when ozone is decomposed on the surface at 400 K.

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FIG. 1. TPD spectra obtained after water adsorption on (a) clean Au(111) and Au(111) containing 0.2 ML of oxygen atoms formed by exposure to ozone at (b) 200 K and (c) 400 K. Water exposures were dosed at 145 K and are listed in parentheses. The inset shows the maximum integrated intensity of the 195 K peak as a function of oxygen surface coverage. Water exposures beyond this point were 6.4 L, which was sufficient to saturate the 195 K peak. The solid line is a guide to the eye.
is 0.2 eV stronger than the H2O from the corresponding clean surface or to sublimation of desorption peaks of 30 K or less relative to water desorbing these cases, the presence of oxygen leads to shifts in the experimental studies have found that this type of stabilizing a stabilization of the dissociated state. Similar behavior may hydrogen bond to molecular water, forming stabilized complexes. Theoretical and experimental studies have found that this type of stabilization occurs on Pt(111), where the OH···H2O hydrogen bond is 0.2 eV stronger than the H2O···H2O hydrogen bond, creating a stabilization of the dissociated state. Similar behavior has been reported on Pd(111).

The small difference in the water desorption temperature, ~20 K, for the 195 K state relative to water desorption from clean Au(111) is similar to shifts reported for water interaction via hydrogen bonding to oxygen on several other metal surfaces, such as Ag(110) (Ref. 35) and Cu(110). In these cases, the presence of oxygen leads to shifts in the desorption peaks of 30 K or less relative to water desorbing from the corresponding clean surface or to sublimation of water multilayers. On the other hand, water evolved from OH disproportionation on surfaces including Ag(110), Cu(110), and Pd(100) (Ref. 38) generally exhibits a much larger temperature difference, 55–80 K, from molecular water desorption states.

Isotopic exchange experiments, however, provide unambiguous evidence for the formation of hydroxyl species. Reaction of H218O on Au(111) containing 0.14 ML 18O results in oxygen exchange, in agreement with recent studies by Kim and co-workers. Specifically, 16O2, 18O16O, and 18O2 were detected in a peak at 535 K characteristic of oxygen recombination on Au(111) (Refs. 24 and 39) (Fig. 3). This result unequivocally shows that hydroxyls form, at least transiently, from the reaction of water with oxygen on the surface,

\[
\text{H}_2\text{O}_a + 16\text{O}_a \leftrightarrow 16\text{OH}_a + 18\text{OH}_a \leftrightarrow \text{H}_2\text{O}_a + 18\text{O}_a.
\]

The amount of 18O evolved in the 535 K oxygen peaks versus the initial 18O coverage (Fig. 4) follows the same trend that was found for the maximum integrated area of the 195 K water peak; the amount of 18O evolved as molecular oxygen increases with the initial oxygen coverage up to ~0.2 ML and then decreases with further increases in oxygen coverage. Since only relatively small amounts of 18O evolve for larger oxygen coverages and we found that a negligible amount of 18O evolves when the oxygen-covered surface is prepared at 400 K, this indicates that chemisorbed oxygen, not gold oxide, is the active oxygen moiety for hydroxyl formation.

The m/z = 20 (parent ion for H218O) to m/z = 18 (parent ion for H18O) ratio for each of the water desorption peaks when H218O is condensed on 16O-covered Au(111) shows that the water formed from the disproportionation of hydroxyls containing oxygen originating from the surface is evolved in both the 175 and 195 K peaks [Fig. 5(a)]. The ratios of H218O:H216O are 2.3:1 ± 0.2 (Ref. 40) and 2.1:1 ± 0.2 for the 175 and 195 K water peaks, respectively.
when 1.0 L of a mixture of H$_2^{18}$O and H$_2^{16}$O is condensed on 0.14 ML $^{16}$O-covered Au(111). The ratio of H$_2^{18}$O:H$_2^{16}$O in water itself is $\approx$ 4:1 as determined by condensation on and subsequent desorption from clean Au(111) [Fig. 5(b)]; therefore, it is evident that there is an increased amount of H$_2^{16}$O in both water peaks for the oxygen-covered surface. The difference in the evolved H$_2^{18}$O:H$_2^{16}$O ratio from the ratio in the water inlet is less pronounced with increasing exposure. For example, for an exposure of 2.4 L on 0.14 ML $^{16}$O-covered Au(111), the ratios are 3.0 $\pm$ 0.2 and 2.4 $\pm$ 0.2 for the 175 and 195 K peaks, respectively. These data strongly indicate that there is rapid formation of OH from water and vice versa, leading to isotopic mixing between condensed water and surface oxygen. This is in agreement with Ojifinni et al.\textsuperscript{17} who explained their observation of water containing oxygen originating from the surface by the rapid surface diffusion of OH for temperatures above 75 K.

Conclusive evidence that the surface hydroxyls are transient or form stabilized water-hydroxyl complexes comes from analyzing the percentage of $^{18}$O in the oxygen peaks evolving at 535 K [Fig. 6]. If the adsorbed oxygen quantitatively reacts with the water, equal amounts of $^{18}$OH and $^{16}$OH would be formed on the surface and, accordingly, the percent of $^{18}$O in the adsorbed oxygen remaining after hydroxyl disproportionation can be as high as 50% if we assume that the hydroxyls disproportionate randomly and if all of the surface oxygen is chemisorbed. (Isotope effects for the recombination of $^{18}$OH vs $^{16}$OH should be negligible.) The percentage of $^{18}$O evolving as molecular oxygen was calculated after reacting an excess of H$_2^{18}$O (2.4 L) with oxygen-covered surfaces with varying oxygen coverages prepared at 200 K. The amounts of $^{18}$O evolving in molecular oxygen during heating were as high as 70%, which approached the maximum possible exchange, 80%, which corresponds to exchange of all surface oxygen based on the ratio of H$_2^{18}$O to H$_2^{16}$O in the doser. This indicates that OH formation and disproportionation must be occurring on the surface multiple times, with an average of at least three exchange events occurring for a given oxygen species (determined by assuming disproportionation occurs randomly, all surface $^{16}$O is reactive at coverages $<0.2$ ML, and a fraction of $^{16}$O based on XPS $1s$ peak intensities\textsuperscript{20} is reactive for larger coverages). Additionally, this confirms that the 195 K water desorption peak is not due to simple disproportionation of isolated OH; rather it is due to oxygen-stabilized water or a water-hydroxyl surface complex.

![FIG. 4. The relative amount of $^{18}$O in the oxygen peaks that evolve during TPD vs initial $^{16}$O coverage when the $^{16}$O-covered surface is exposed to 2.4 L of a mixture of H$_2^{18}$O and H$_2^{16}$O (4:1 ratio, respectively) at 145 K. The $^{16}$O-covered surface was prepared at 200 K. The solid line is a guide to the eye.](image1)

![FIG. 5. TPD spectra for 1.0 L of a mixture of H$_2^{18}$O and H$_2^{16}$O (4:1 ratio, respectively) condensed on (a) oxygen-covered Au(111) ($\theta_{O}=0.14$ ML) and (b) clean Au(111) at 145 K. The oxygen-covered surface was prepared at 200 K. The ratio of $m/z=20$ to $m/z=18$ in (a) was 2.3 for the 175 K peak and 2.1 for the 195 K peak. The ratio of $m/z=20$ to $m/z=18$ for the 175 K peak in (b) was 4.0.](image2)

![FIG. 6. Percentage of $^{18}$O evolved in the oxygen peaks vs oxygen coverage when a mixture of H$_2^{18}$O and H$_2^{16}$O (4:1 ratio, respectively) is condensed on $^{16}$O-covered Au(111). The oxygen-covered surface was prepared at 200 K. 2.4 L of the water mixture was exposed to the surface at 145 K.](image3)
RAIRS studies were performed in order to identify and probe the surface species present and their intermolecular interactions when water is adsorbed on the clean and oxygen-covered surface. The HOH bending mode at 1653 cm$^{-1}$ and the OH stretch of bulk ice at 3365 cm$^{-1}$ with a smaller peak at 3456 cm$^{-1}$ were observed following adsorption of water on clean Au(111) (Ref. 28) [(Fig. 7(a)]. The shape of the bulk ice OH stretch is a characteristic of crystalline ice, which was expected based on our water adsorption temperature, 145 K, in accordance with Wang et al., who characterized water on Au(111) using infrared spectroscopy and found that amorphous ice films deposited at 86 K underwent an amorphous-to-crystalline phase transition at $\sim$120 K, which was evident in the shape of the bulk ice OH stretch. The complex shape of this mode is attributed to multiple factors including intermolecular interactions, bond length distribution, and vibrational lifetime. In our work, water was adsorbed well above the amorphous-to-crystalline phase transition but in contrast to previous observations, a small nonhydrogen bonded “free” OH stretch at 3691 cm$^{-1}$ was also observed in our spectra. This stretching mode increased slightly in magnitude with water coverage but remained small. The observation of this feature was not previously reported under these conditions.

When oxygen was preadsorbed on the surface, the HOH bending mode, the bulk ice OH stretch, and the free OH stretch were again observed for all coverages investigated, indicating the presence of molecular water (Fig. 7(b)). The primary differences in the spectra for water adsorption on the clean Au(111) surface and on the oxygen precovered surface are the shape of the bulk ice OH stretch and the intensity of the free OH stretch, which is enhanced for the oxygen-covered surface. Notably, an asymmetric peak at 3400 cm$^{-1}$ for the oxygen-covered surface replaces the peaks at 3365 and 3456 cm$^{-1}$ for the bulk ice OH stretch on clean Au(111). The shape of the bulk ice OH stretch and the presence of the free OH stretch are characteristics of amorphous ice and indicate an effect on the long-range intermolecular coupling forces. The overall shift to higher frequency of the bulk ice OH stretch is indicative of longer O–O bond distances, suggesting water’s interaction with surface oxygen results in weaker H$_2$O⋅⋅⋅H$_2$O hydrogen bonding. The enhanced free OH stretch seen in RAIRS can be attributed to nonhydrogen bonded OH groups dangling into vacuum.

These effects are primarily attributed to the presence of surface oxygen not the moity of the oxygen or the roughening of the Au(111) surface due to ozone decomposition and the release of Au atoms from the surface. When water is condensed on the Au(111) surface with a low coverage, <0.3 ML, of oxygen that was annealed to 400 K for 5 min, which results in an ordered 2D surface gold oxide, the infrared spectra are qualitatively very similar to spectra associated with the surface without annealing (Fig. 8); the nature of the bulk ice OH stretch is amorphous and a strong “free OH” stretch is present. When water is exposed to the roughened
is due to linear adsorption of residual CO on the crystal while cooling the pressure rise of $1/\text{H}_2\text{O}$. Gas external to the ultrahigh vacuum chamber due to vapor phase water constant height mode subsequently cooling to 120 K. The baseline was corrected. The feature in background spectrum was acquired after flashing the sample to 600 K and Au infrared spectrum for 2.2 L water condensed at 145 K on the roughened surface without oxygen. The spectrum was acquired at 120 K. The exposure to CO $= 85$ mV and $I = 0.79$ nA. All STM scans were obtained at 200 K in flat lying geometry of the water-hydroxyl mixed phase. Our results suggest a possible water-hydroxyl surface complex analogous to the water-hydroxyl mixed phase on Pt(111). On Pt(111), OH will decompose with a low activation energy via $2\text{OH}_{\text{ads}} \rightarrow \text{O}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$ unless stabilized by water. The optimum stoichiometry for the mixed phase is 2:1 for water and atomic oxygen, respectively, corresponding to saturation of a Pt(111)-(2 × 2)-O surface with water. LEED-IV structure analysis showed the resulting overlayer consists of hexagonal rings of hydrogen bonded oxygen atoms. The stabilization of the mixed phase is manifested as an increase in the desorption temperature of water by 40 K when compared to water on the bare surface. In accordance with our infrared spectra, no vibrational modes corresponding to hydroxyls are observed. In fact, the saturated mixed phase on Pt(111) does not have measurable adsorption in the bulk ice OH stretch, the free OH stretch, or the H$_2$O bending mode; this is a result of the flat lying geometry of the water-hydroxyl mixed phase.

Similarly, a water-hydroxyl mixed phase was recently reported on Pd(111) from the reaction of chemisorbed oxygen and water with nearly identical behavior to the Pt(111) surface. Clay et al. found that the most stable water-hydroxyl mixed phase contained 0.67 ML of oxygen formed via $3\text{H}_2\text{O} + \text{O} \rightarrow 2\text{H}_2\text{O} + \text{OH}$ and had $(3 \times \sqrt{3})\text{R}30^\circ$ periodicity. Stabilization of the mixed phase was evident by OH recombinating and water desorbing at a temperature 20 K higher than the desorption temperature of pure water on Pd(111).

Our work clearly indicates that the behavior of water at Au interfaces is affected by oxidation and roughness. It was determined that hydrogen bonding of water to oxygen adatoms results in short-lived OH species, which interact with
IV. CONCLUSION

The interaction of water with atomic oxygen on Au(111) was investigated using TPD and RAIRS. The reaction of H$_2^{18}$O with surface $^{16}$O resulting in oxygen exchange conclusively showed that hydroxyls are formed. The extent of exchange, which was up to 70%, indicated that the hydroxyls interacting with water are transient, forming and dispropor- tionating multiple times on the surface. Water containing exchanged oxygen was present in both the 175 K water peak and the 195 K water desorption peaks. These results are corroborating evidence that the 195 K water desorption peak is not due to the disproportionation of isolated stable hydroxyls but rather oxygen-stabilized water or a water-hydroxyl surface complex.

RAIRS spectra further support the transient nature of the hydroxyls, indicating that molecular water is present on the surface for all water exposures investigated, possibly hydrogen bonded to hydroxyl species and suppressing their OH stretch. RAIRS and STM also characterized the effect of preadsorbed oxygen and surface roughening on water’s intermolecular interactions. The presence of chemisorbed oxygen and gold oxide each resulted in a change in shape from crystalline to amorphous for the bulk ice OH stretch, and a substantial enhancement of the free OH stretch signaling a reduction in the number of OH bonds contributing to hydrogen bonding. Surface roughening had a much less significant effect on hydrogen bonding but did alter the shape of the bulk ice OH stretch, and the presence of the free OH stretch indicated contributions from water molecules that were not fully coordinated.

In conjunction with previous XPS studies, it is concluded that chemisorbed oxygen plays a key role in water’s interaction with Au(111). It was found that chemisorbed oxygen is responsible for transient hydroxyl formation and for the stabilization of water during TPD, while gold oxide, which is prevalent at high oxygen coverages and is associated with the ordered surface formed by annealing at 400 K, does not contribute to these effects. These results help identify transient hydroxyls as possibly playing an important role in oxidation reactions on gold in the presence of oxygen and water. It suggests that both water and hydroxyls must be considered in e.g., CO oxidation on Au(111) but it does not answer previous mass balance concerns regarding hydrogen when CO oxidation on oxygen-covered Au(111) is enhanced by water.

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Error estimated from the expected error due to integrated intensity calculations primarily attributed to the data sampling rate.


