

Hydrogen Bonding in Mixed OH + H₂O Overlayers on Pt(111)

C. Clay, S. Haq, and A. Hodgson*

Surface Science Research Centre, The University of Liverpool, Liverpool L69 3BX, United Kingdom

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The stability of OH on Pt(111) has been investigated to determine the role of hydrogen bonding in stabilizing the overlayer. We find that the optimal structure is a mixed (OH + H₂O) phase, confirming recent density-functional theory predictions. The reaction $O + 3H_2O$ forms a hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ -(OH + H₂O) lattice with a weak (3×3) superstructure, caused by ordering of the hydrogen bonds. The mixed overlayer can accommodate a range of H₂O/OH compositions but becomes less stable as the H₂O content is reduced, causing defects in the hydrogen-bonding network that lift the (3×3) superstructure and destabilize the overlayer.

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Despite the importance of the metal surface-water interaction to many areas of science, experimental difficulties in determining the position of the hydrogen atoms have ensured that the structure and composition of these interfaces remain poorly understood [1], stimulating considerable theoretical interest [2–4]. On inert, high coordination transition metal surfaces, water adsorbs intact, forming hydrogen-bonded bilayers whose structure is thought to resemble the buckled “bilayer” of hexagonal ice [5]. Water molecules in the lower half bilayer are bound to the metal and to three neighbors in the upper layer via hydrogen bonds, leaving the upper waters with one unsatisfied hydrogen bond each. Three ordered phases are found on Pt(111). At low coverage islands of a $(\sqrt{37} \times \sqrt{37})R25.3^\circ$ overlayer grow, which then compress laterally to form a $(\sqrt{39} \times \sqrt{39})R16.1^\circ$ phase as the first bilayer saturates [6,7]. The saturation overlayer will grow epitaxially for several layers before the film relaxes to form domains of incommensurate hexagonal bulk ice Ih, oriented to the Pt(111) close packed directions [8]. However, although recent x-ray photoelectron spectroscopy simulations have suggested that H atoms from the upper half of the water bilayer point down towards the Pt surface, weakening the O-H bond and flattening the corrugation of the bilayer [3], the detailed hydrogen-bonding structure is still an open question [9].

Other metal-water structures are possible, particularly on more reactive metals where dissociation may form OH and coadsorbed H. Using density-functional theory (DFT), Feibelman [2] recently postulated that the stable configuration for water on Ru(0001) was as a partially dissociated overlayer containing a hexagonal network of alternating OH and H₂O, with the additional H atoms bound atop uncoordinated Ru atoms or in separate islands. This structure replaces the unsatisfied hydrogen bond of the upper water bilayer with a direct bond between OH and the surface, the overlayer having a $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrangement with OH and H₂O nearly coplanar [2]. Although a LEED-IV analysis favors intact

adsorption on Ru(0001) [10], other calculations have suggested that a similar mixed OH + H₂O overlayer is stable on Pt(111) and can be formed by the reaction of O with water [11]. This reaction was thought to form a pure OH overlayer [12] but Michaelides and Hu [11] proposed that the unusual $O + 2H_2O$ reaction stoichiometry [13] resulted from coadsorption of water in the OH overlayer, rather than dissociation to form coadsorbed OH and H as previously thought [14]. The same overlayer forms as an intermediate in the low temperature oxidation of H₂ on Pt(111) [15], but its structure and composition is not well established.

Here we examine the stability of a mixed OH/H₂O (“OH_x”) layer on Pt(111) as a function of its composition. We find that O reacts with up to four water molecules, depending on the O precoverage. The most stable overlayer is formed by the reaction $O + 3H_2O \rightarrow 2(OH + H_2O)$, adsorption saturating with a total of $2/3$ ML O on the surface to form a hexagonal (3×3) - $3(OH + H_2O)$ overlayer, similar to that predicted by DFT [11,16]. Reducing the water content disorders and destabilizes the overlayer, demonstrating that hydrogen is not adsorbed dissociatively but is incorporated into the overlayer as water, stabilizing the structure by completing the hydrogen-bonding network between OH groups.

Gases were dosed onto a Pt(111) surface using a molecular beam with a flux of circa 3×10^{-3} ML s⁻¹ to give accurate control over the final surface coverage. The sample could be heated or cooled rapidly in the range 85 to 900 K and overlayers were characterized using reflection absorption infrared spectroscopy (RAIRS) and LEED [7]. A quadrupole mass spectrometer monitored the partial pressure of gases in the chamber during adsorption, and the desorption yield when the crystal was heated in temperature programmed desorption experiments (TPD). LEED patterns for the mixed (OH + H₂O) overlayers were recorded with a beam current ≤ 100 nA and proved more stable to electron damage than pure water layers [7]. The total O coverage of a mixed O + H₂O overlayer is referred to as the OH_x coverage and is given in monolayers (ML), relative to the

density of the Pt(111) surface. Atomic oxygen was adsorbed on the surface by exposing it to an O_2 beam at 90 K and then heating the surface. Oxygen coverages were determined for each experiment by heating the surface to 350 K and exposing it to a beam of CO, which reacts to form CO_2 . The CO_2 desorption signal provided an accurate measure of the relative O coverage and was calibrated relative to the saturated $(2 \times 2)O$ surface with 0.25 ML O coverage. Water doses were determined from the TPD yield and calibrated against the saturation $(\sqrt{39} \times \sqrt{39})R16.1^\circ$ water bilayer [7]. An independent measure of the O and water coverage could be obtained by integrating the H_2O and O_2 adsorption curves [7]; this approach was consistent with the desorption measurements. All experiments were carried out using both D_2O and H_2O but no differences were discernable.

The uptake of water onto a disordered O overlayer was measured at 163 K, where water desorbs slowly from clean Pt(111) terraces (Fig. 1). For initial O coverages below 0.13 ML, the water uptake increases linearly with coverage, with as many as four water molecules adsorbing for each O already on the surface. As the initial O coverage is increased to 0.15 ML, the total OH_x coverage reaches 0.67 ML and the amount of water adsorbed stops increasing, larger O precoverages adsorbing only marginally more water. For a saturation O coverage of 0.25 ML, the surface adsorbs 0.58 ± 0.03 ML of water, giving a saturation OH_x coverage of 0.84 ML and an overall reaction stoichiometry of $(2.3 \pm 0.1)H_2O$ to one O atom. This result is in agreement with previous ^{18}O isotopic exchange experiments [13,14] which reported that the saturation overlayer was formed by the reaction $2H_2O + O$. As water is dosed onto the O/Pt(111) surface a sharp, intense $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern develops even at very low water coverages. Under these conditions, STM results show the $(2 \times 2)O$ overlayer being removed as islands of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase grow [14]. This hexagonal phase was believed to be a $(\sqrt{3} \times \sqrt{3})R30^\circ-2OH$ overlayer, adsorbed atop Pt [17] with incomplete, disordered hydrogen bonds between the OH groups [14]. By

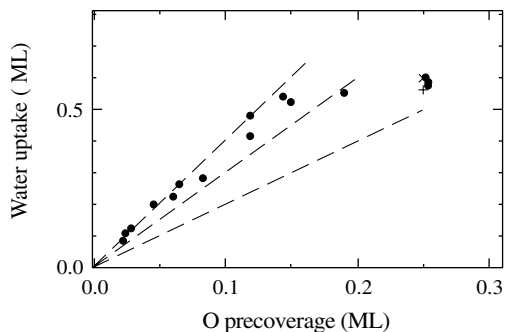


FIG. 1. Uptake of D_2O onto a disordered O overlayer at 163 K as a function of O precoverage. The points (+ [13], \times [14]) show the result of isotope experiments at saturation coverage of 0.25 ML O while the dotted lines show D_2O/O ratios of 4, 3, and 2.

following the LEED patterns during water adsorption, we find that complete removal of ordered $(2 \times 2)O$ islands requires at least two water molecules for every O originally present on the surface. Clearly, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase incorporates considerably more hydrogen than needed to form a pure OH overlayer [12].

Further water adsorption resulted in the appearance of additional LEED spots, forming a (3×3) superstructure. The (3×3) spots were weak but sharp, having a maximum intensity at a total OH_x coverage of 0.67 ML as the surface composition reaches $3H_2O + O$ and disappearing as the water dose is increased towards $4H_2O + O$ or decreased towards a $2H_2O + O$ stoichiometry. The (3×3) structure could also be formed by saturating an O pre-covered surface with water and heating it to allow excess water to desorb. Under similar conditions, STM shows a change in contrast of the hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer to form islands with a (3×3) superstructure, although no (3×3) LEED pattern was observed [14]. Bedurftig *et al.* suggested that the (3×3) phase might result from an ordering of the OH hydrogen bonds to form a cyclic structure, based around the hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ-2OH$ backbone, but this is inconsistent with our observation that the (3×3) structure is formed only as the composition reaches $3H_2O + O$.

On the basis of its composition, the STM results [14] and DFT calculations [11,16] there appear to be two possibilities for the (3×3) structure, either (i) it consists of a $(2OH + H)$ overlayer with OH adsorbed in a hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ-2OH$ arrangement and H adsorbed on Pt, or (ii) the overlayer is an $(OH + H_2O)$ structure with the additional hydrogen completing the hydrogen-bonding network. In order to distinguish between these possibilities, we investigated how the stability of the OH_x overlayer changes as its composition is varied.

Whereas water desorbs intact from Pt(111) between 150 and 170 K [7], OH_x overlayers formed by the O/water reaction are more stable, water desorbing near 200 K as the overlayer decomposes leaving the excess O on the surface. Figure 2(a) shows the desorption of water from a Pt(111) surface dosed with increasing O coverages and then saturated with D_2O at 163 K. For 0.12 ML of O or less, the surface shows a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern and has regions of bare Pt. As well as the main desorption peak near 200 K, the desorption profile also shows a small peak near 170 K which disappears as the water coverage is reduced to $3H_2O/O$ or less (Fig. 1). This feature reduces in importance as the surface coverage is increased, suggesting that it is caused by stabilization of water at the edges of islands and by slow loss of excess water from the OH_x overlayer onto Pt(111) terraces. When the initial coverage of O is increased such that the total OH_x coverage exceeds 0.67 ML, the entire overlayer is destabilized (irrespective of its exact H content), the desorption peak shifting ~ 6 K to lower temperature for a saturation coverage of 0.84 ML OH_x . STM images [14] show formation of thick domain walls with a (1×1) arrangement, consistent with DFT

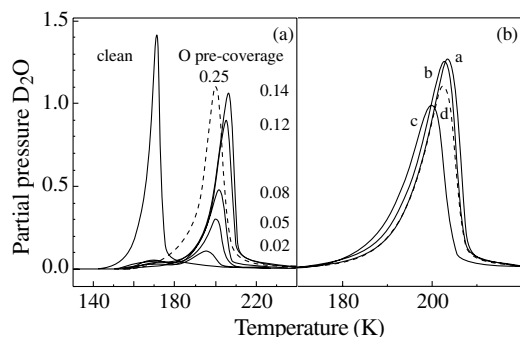


FIG. 2. (a) Desorption of D_2O following adsorption at 163 K onto Pt(111) precovered with 0.02 to 0.25 ML of oxygen. The peak near 170 K shows desorption of a D_2O ($\sqrt{39} \times \sqrt{39}$) $R16.1^\circ$ bilayer from clean Pt(111). (b) The solid lines (a)–(c) show the desorption rate from overlayers with a constant initial OD_x coverage of 0.55 ML and a D_2O/O ratio of 3.0, 2.6, and 1.8, respectively. The dotted line (d) shows the desorption trace for a second overlayer with the same D_2O dose as (c) but a D_2O/O ratio of 3.0. Heating rate of 0.95 K s^{-1} .

calculations which found that OH formed a less stable (1×1) arrangement at high coverage [11].

The effect of the hydrogen content on the stability of the overlayer can be demonstrated by comparing thermal decomposition of overlayers formed with a different ratio of water to O but the same total OH_x coverage [Fig. 2]. As the water content is reduced below $3H_2O/O$, the water desorption curve shifts to lower temperature (traces a–c), indicating destabilization of the overlayer by $\sim 3 \text{ K}$ when the H_2O/O ratio drops to 2. A lower decomposition temperature for overlayers containing less than $3H_2O/O$ can also be seen when the dose of water is kept constant and the initial O coverage varied [compare traces c and d, Fig. 2(b)], resulting in the same total H_2O desorption yield but a different composition and initial coverage of OH_x . This behavior is repeated at all coverages from 0.1 to 0.67 ML OH_x , indicating that the stability of the overlayer depends on the water content, rather than the details of the coverage and island size. When the water dose is increased above $3H_2O/O$, water desorption occurs near 170 K, before reverting to the same curve at higher temperatures once the excess water has been lost [Fig. 2(a)].

Stabilization of the overlayer at a composition $3H_2O + O$ is consistent with all of the hydrogen being incorporated into an ordered (3×3) - $3(OH + H_2O)$ overlayer, forming a fully hydrogen-bonded network of OH and H_2O . If, in contrast, H was adsorbed directly on the Pt(111) surface to form a $(2OH + H)$ overlayer, we would expect the opposite effect; increasing the hydrogen coverage would increase the rate of $OH + H$ recombination and destabilize the overlayer. This is exactly what is seen when islands of the OH_x structure are exposed to H, formed by H_2 dissociation on Pt terraces. The H reacts immediately with the OH_x overlayer to form water, which desorbs at temperatures well below the OH_x decomposition tem-

perature. This is in agreement with previous observations of the $O + H_2$ reaction [18], which indicate that the OH_x structure is not stable to reaction with adsorbed H. Several other observations support the conclusion that no H is adsorbed on the surface. No H_2 (or D_2) desorption was observed from decomposition of water/O overlayers, irrespective of their composition, whereas H_2 is formed on other surfaces where water dissociation occurs [19]. Finally, formation of a $(2OH + H)$ overlayer cannot explain the (3×3) structure, whereas this periodicity arises naturally from formation of an ordered $(OH + H_2O)$ overlayer (Fig. 3) as we discuss below.

The stability of the $2/3 \text{ ML}$ mixed $(OH + H_2O)$ phase supports DFT calculations which identify this structure as the stable overlayer on Pt(111) [11,16]. Recently, Karlberg *et al.* [16] calculated structures, vibrational spectra, and simulated STM images for $(OH + H_2O)$ overlayers using DFT. They were unable to distinguish the mixed and dissociative cases on the basis of the STM simulations, but concluded that the mixed phase was more stable by 1.4 eV per $(OH + H_2O)$ unit. Stable structures were found using a $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell, which has oriented domains of $(OH + H_2O)$, and a (3×3) structure with water ordered into rings (Fig. 3). We find that the (3×3) LEED spots have a similar intensity irrespective of whether H_2O or D_2O is dosed, despite the reduced zero point motion of D compared to H. This indicates that, although weak, the (3×3) periodicity originates from O scattering, rather than direct scattering from H/D, and is consistent with a small shift in the position of the O atoms in the two types of hexagonal $(OH + H_2O)$ rings (Fig. 3) depending on whether water has both H atoms in the ring or not. This distortion may be induced by a slight difference in the hydrogen-bond length of $(OH-OH_2)$ compared to $(HO-HOH)$, associated with the differing ability of OH and H_2O to accept a proton [11].

Unlike the (3×3) phase, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure appears to be stable over a range of different H_2O/OH ratios. During water adsorption at 163 K, the LEED spots from $(2 \times 2)O$ islands only disappear completely when sufficient water has reacted to reach a composition $H_2O/OH \geq 0.5$, the $\sqrt{3}$ pattern then persisting up to $H_2O/OH \sim 1.5$ at saturation. When a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer is heated to desorb water, the $(2 \times 2)O$ LEED pattern reappears only once the H_2O/OH ratio has dropped to ~ 0.2 .

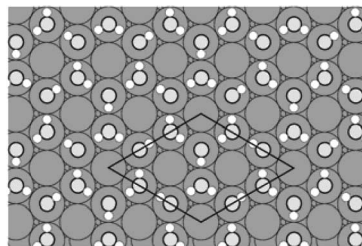


FIG. 3. Schematic showing the proposed structure of the ordered (3×3) - $3(OH + H_2O)$ overlayer [16].

This suggests that, once the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure has formed, the ordering of the OH_x phase can survive with relatively little water present. Since the (3×3) overlayer shares the same O backbone as the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure [14], we propose that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase forms over a range of different $\text{H}_2\text{O}/\text{OH}$ ratios and is stable to defects induced by exchange of H_2O for OH , or vice versa. Incorporating additional water into the (3×3) - $(\text{OH} + \text{H}_2\text{O})$ overlayer replaces an OH with a water molecule, destroying the (3×3) LEED superstructure. At low coverages some of this water is probably adsorbed at the edge of OH_x islands, but up to 25% more H_2O than OH can be present in the structure even when the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer is complete. Although the additional water is less stable than in the ideal (3×3) - $3(\text{OH} + \text{H}_2\text{O})$ structure, it is stabilized compared to water on bare Pt(111) or to water adsorption on top of OH_x islands. When insufficient H_2O is present to complete the (3×3) - $3(\text{OH} + \text{H}_2\text{O})$ overlayer, substitution of OH for H_2O will leave a missing hydrogen bond. This creates a defect in the hexagonal $(\text{OH} + \text{H}_2\text{O})$ lattice which relaxes the (3×3) superstructure induced by ordering of the hydrogen bonds. Since H exchange is expected to have a very low barrier (less than 10 meV [11]), these defects are likely to be mobile, resulting in a hexagonal OH_x lattice with disordered hydrogen bonds.

Additional evidence to support the disordered nature of hydrogen bonding in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure comes from the linewidth of RAIRS peaks for the $\text{OH}_x(\text{OD}_x)$ overlayers (Fig. 4). These spectra are dominated by a single intense band near $1016(764) \text{ cm}^{-1}$ which is assigned on the basis of the DFT results to an out-of-plane bend of $(\text{OH} + \text{H}_2\text{O})$ [11,16]. Unlike water overlayers, the flat lying $(\text{OH} + \text{H}_2\text{O})$ overlayer does not show significant absorption in either the OH stretching or the H_2O bending region, and it is for this reason that it has previously been assumed to be a pure OH phase [12,14]. This band is broad for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer, typically approximately $130(70) \text{ cm}^{-1}$, but sharpens to $35(12) \text{ cm}^{-1}$ as the composition is changed to form the (3×3) - $3(\text{OH} + \text{H}_2\text{O})$ overlayer and the hydrogen-bonding network becomes complete. This spectrum also shows weak modes at 830, 914, and 3475 cm^{-1} , consistent with the EELS data [14] and with the modes predicted for an $(\text{OH} + \text{H}_2\text{O})$ overlayer [11,16], whereas these peaks are broad and barely visible in the RAIRS spectrum of $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer. When the OH_x coverage is increased beyond $2/3 \text{ ML}$, the OH bend splits into two components, consistent with the presence of compressed regions with a $(1 \times 1) \text{ OH}_x$ structure in addition to the hexagonal $(\text{OH} + \text{H}_2\text{O})$ overlayer.

We conclude that reaction of adsorbed O with water produces a mixed $(\text{OH}/\text{H}_2\text{O})$ overlayer on Pt(111), stabilized by hydrogen bonding between OH and H_2O . As the $\text{OH}/\text{H}_2\text{O}$ coverages become equal, the hydrogen-bonding network is completed and the overlayer orders to form a (3×3) - $3(\text{OH} + \text{H}_2\text{O})$ phase, which has sharp IR bands

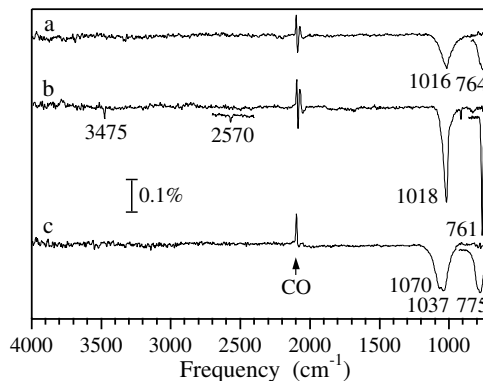


FIG. 4. RAIR spectrum of (a) $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer formed at low $\text{H}_2\text{O}/\text{O}$ doses, (b) ordered (3×3) - $3(\text{OH} + \text{H}_2\text{O})$ overlayer. (c) Saturation dose (0.59 ML) of water on 0.25 ML O. Insets show D_2O .

and is particularly stable to decomposition. The hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ \text{ OH}_x$ structure survives over a range of $\text{H}_2\text{O}/\text{OH}$ ratios, although with a reduced stability as the number of missing hydrogen bonds increases. These results are consistent with calculations which predict that mixed $(\text{OH} + \text{H}_2\text{O})$ overlayers will be stable on metal surfaces [2,11,16].

*Author to whom correspondence should be addressed.

Electronic address: ahodgson@liv.ac.uk

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