1. INTRODUCTION

The ubiquity of both water and oxide surfaces in the environment ensures that their interactions represent some of the most fundamental chemical reactions occurring in nature. Moreover, water—oxide interactions underpin many areas of science and technology including heterogeneous catalysis, electrochemistry, corrosion processes, and environmental science. Until recently, utilization of the surface science approach to understanding such interactions at the atomic scale, which has yielded tremendous insight for water—metal interactions, has been precluded for many oxides by a lack of basic knowledge about the surface structure. However, where this knowledge is in place, for example, for TiO$_2$(110) and ZnO(1010), water adsorption has been demonstrated to be both molecular and dissociative, with the surface termination and defects such as O vacancies ($V_O$) playing a significant role. In the presence of $V_O$, it is thought that water adsorbs dissociatively according to eq 1, with the water hydroxyl (O$_W$H) filling the vacancy to create a surface hydroxyl (O$_S$H), and the dissociated H atom forming a second O$_S$H with a nearby surface oxygen atom (O$_S$):

$$H_2O_W + V_O + O_S \rightarrow O_SH + O_SH$$  

(Dissociative adsorption in the absence of $V_O$ results in an adsorbed surface hydroxyl (O$_W$H) containing the oxygen atom from the water and an O$_S$H according to eq 2,

$$H_2O_W + O_S \rightarrow O_WH + O_SH$$  

In this article, we report the remarkable observation that water adsorption behavior at the Fe$_3$O$_4$(001) surface under our experimental conditions. We argue that this hitherto unreported adsorption behavior for water occurs because recombinative desorption of water is kinetically hindered by the adsorption geometry. Consequently, alternative reactions between O$_W$H can occur, leading to desorption at room temperature, possibly as H$_2$ and O$_2$.

2. EXPERIMENTAL DETAILS

The experiments described here were performed in two separate ultra high vacuum (UHV) systems. The first system comprises separate vessels for preparation (base pressure = 1 × 10$^{-10}$ mbar) and analysis (base pressure = 5 × 10$^{-12}$ mbar), with capability for low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). The low energy ion scattering (LEIS) measurements were performed in a UHV chamber also equipped for LEED and Auger electron spectroscopy (AES) analysis. The measurements were performed using a synthetic Fe$_3$O$_4$ single crystal that was grown using the floating zone method by Z. Mao and co-workers at Tulane University, New Orleans, LA. The crystal was oriented, cut, and polished by Mateck GmbH. The clean stoichiometric Fe$_3$O$_4$(001) surface was prepared using sputter and anneal cycles. The cycles comprise sputtering with 1 keV Ar$^+$ ions (sample current 1.5 μA) and subsequent annealing at ~1000 K for 1 h in 2 × 10$^{-6}$ mbar O$_2$. A sharp ($\sqrt{2} \times \sqrt{2}$)R45$^\circ$ LEED pattern was observed (not shown) and no contamination was detectable in XPS survey spectra. Deionized H$_2$O was further purified using freeze—pump—thaw cycles and was dosed into either the preparation or analysis vessel of the STM system through high precision leak valves. Isotopically labeled H$_2^{18}$O (Sigma-Aldrich) was purified using a similar freeze—pump—thaw procedure and was dosed directly into the LEIS system also using a high precision leak valve.
STM measurements were carried out using a SPECS Aarhus 150 STM with electrochemically etched W tips. All STM images were taken in the constant-current mode imaging empty states ($V_{\text{sample}} = +0.7$ to $+1.8$ V and $I_{\text{tunnel}}$ from 0.15 to 0.3 nA) at RT. The time between the water dosing and the onset of the STM measurements was typically ca. 15 min. Images acquired thereafter showed no dependence on time with indistinguishable appearance over several hours.

To check that typical components of the residual gas in our UHV chamber do not influence the sample surface, we have independently dosed 100 Langmuir CO, H$_2$, and O$_2$ to the sample surface at room temperature and obtained STM images representative only of the clean Fe$_3$O$_4$(001) surface. Similarly, XPS spectra show no contamination of the surface with C in our detection limit following CO dosing, and following the water dosing experiments described here.

3. RESULTS

A schematic model of the energetically favorable Fe$_3$O$_4$(001) surface, as determined by a density functional theory (DFT) and quantitative low energy electron diffraction (LEED-IV) investigation,$^{15,16}$ is shown in Figure 1a. The surface adopts a ($\sqrt{2} \times \sqrt{2}$)R45$^\circ$ superstructure following a Jahn–Teller distortion, doubling the periodicity along the [110] direction. This structural model corresponds well with STM images,$^{17–19}$ in which undulating anti-phase rows attributable to surface Fe atoms (Fe$_S$) are observed (see Figure 1b). The symmetry reduction results in an inequivalence between the two surface O sites without a subsurface Fe (Fe$_{SUB}$) neighbor; in the bulk, these two O sites are identical. Oxygen atom O$_{NAR}$ is located where the Fe$_S$ rows are relaxed together and O$_{WIDE}$ is located where the undulations render the Fe$_S$ rows further apart.

Exposure of the clean surface to 22.5 Langmuir CO$_2$ at RT results in the appearance of several bright double protrusions located over Fe$_S$ sites (Figure 1c). Identical protrusions were observed as a result of atomic H deposition in a previous study,$^{20}$ and consequently, we attribute them to O$_S$H species (white atom in the model in Figure 1c). STM does not directly image the O$_S$H, but their presence leads to a modification of the density of states (DOS) in the neighboring Fe$_S$ atom pair (colored orange in the model in Figure 1c), enhancing their contrast in STM images.$^{20}$ Adsorbed H atoms relax toward the symmetrically equivalent O$_{NAR}$ atom from the atop site within the surface unit cell, forming a hydrogen bond.$^{20}$ It is important to note that diffusion of this adsorbed H at room temperature occurs only between the two symmetrically equivalent O$_{NAR}$ atoms, as indicated by the dashed black arrows in Figure 1a.

In Figure 2, we show a series of STM images acquired following exposure of the clean Fe$_3$O$_4$(001) surface to water at room temperature, with nominal exposures ranging from 0.045 to 90 L. For the lowest exposures (0.045 and 0.085 L), 0.01 ML O$_S$H is observed (here 1 ML O$_S$H is defined relative to the number of O$_S$ atoms, and is comparable to the saturation coverage achieved through the deposition of atomic H$^{20}$). The O$_S$H are not randomly distributed, but appear as pairs in neighboring unit cells; two such paired O$_S$H are marked in Figure 2 with yellow half circles. Consistent with prior work, we expect the vacancy to be filled by the O$_W$H, with the extra H bound to a nearby O site. Consequently, paired O$_S$H are compatible with the reaction of water with V$_O$ as described by eq 1. Increasing the water exposure by another order of magnitude (to 4.5 L) leads to an increased coverage of 0.013 ML. The surface still exhibits 0.01 ML paired O$_S$H with the difference made up by several isolated O$_S$H species. This suggests that the increase in H coverage above 0.01 ML is not due to the reaction of water with V$_O$ as described by eq 1 but that the additional O$_S$H species stem from dissociative adsorption at regular lattice sites (eq 2). One would then expect O$_W$H in addition to O$_S$H, but interestingly, no feature is observed that could be attributed to such a species. Further increasing the water exposure to 22.5 L leads to an increased O$_S$H coverage (0.044 ML). The majority...
of unit cells are now occupied and it is no longer possible to distinguish paired and isolated O$_{2}$H. For exposures greater than 45 L, the surface is almost saturated (0.0825 ML) with O$_{2}$H; again no other adsorbates are observed. Full saturation at one O$_{2}$H per unit cell equates to one atom per every eight surface O atoms (0.125 ML), apparently such a full coverage is never reached. At saturation, the O$_{2}$H order with the same ($\sqrt{2} \times \sqrt{2}$)R45° periodicity of the underlying substrate, with a coverage of one O$_{2}$H per reconstructed surface unit cell. The LEED pattern observed for all water dosed surfaces demonstrated ($\sqrt{2} \times \sqrt{2}$)R45° periodicity, consistent with the ordered overlayer observed in STM. STM movies acquired at various coverages demonstrate H hopping over narrow sections between the Fe rows, again consistent with adsorption of H at the O$_{\text{NAR}}$ sites. 20

Figure 3 shows a plot of the average O$_{2}$H coverage in the STM images versus the nominal water dose in Langmuir. The offset of 0.01 ML is due to the O$_{2}$H pairs, which result from filling V$_{\text{O}}$’s by dissociated water. Upon the onset of isolated O$_{2}$H adsorption, the coverage increases approximately linearly with exposure until saturation is observed at 0.0825 ML for exposures in excess of 45 L. The linear dependence of O$_{2}$H coverage on dose indicates that the dissociation of a single molecule is the rate-limiting step in the dissociation of water, at least for partial pressures up to $10^{-5}$ mbar. To check whether reactions between adsorbed H$_{2}$O could be necessary for dissociation, we performed experiments in which the total exposure was kept constant and the partial pressure and exposure time were varied. No discernible variation in the O$_{2}$H coverage was observed.

### 3.2. Low Energy Ion Scattering Studies

The most surprising observation from the STM investigations is the lack of evidence for O$_{\text{NAR}}$ species on the surface. Since STM probes the density of states of the surface and only indirectly the topography, it is possible that the O$_{\text{NAR}}$ may be present on the surface but not visible in the images. Moreover, if the O$_{\text{NAR}}$ species are mobile, it may also be difficult to observe them with STM at RT, although it should be pointed out that measurements on a cooled samples ($T = 250$ K) did not provide any evidence for O$_{\text{NAR}}$ either. Further cooling of the sample is complicated by the onset of molecular water adsorption around 230 K. 22 To further investigate whether the O$_{\text{NAR}}$ was present on the surface, we performed He$^+$ low energy ion scattering (LEIS) experiments using isotopically labeled H$_{2}$^{18}O water. LEIS is a strictly surface sensitive technique and even small amounts of $^{18}$O at the surface can be detected. 21 Figure 4a (top) shows LEIS spectra acquired from the clean Fe$_{3}$O$_{4}$(001) surface and following saturation exposure (225 L) of H$_{2}$^{18}O. The data from these two surfaces are indistinguishable, with peaks due to elastic scattering from Fe and $^{16}$O at 800 and 450 eV, respectively. An $^{18}$O-related peak would be expected to appear at 495 eV, but is not observed.

In contrast, Figure 4b shows three LEIS scans acquired for the clean Fe$_{3}$O$_{4}$(001) surface in a background pressure of $\sim 1 \times 10^{-8}$ mbar H$_{2}$^{18}O. The first scan resembles the data presented in Figure 4a, but during the third and fifth scans, an $^{18}$O peak grows at the expense of the $^{16}$O peak, up to a coverage of $\sim 10\%$ ML. We attribute this behavior to the reaction of the water with surface $^{18}$O...
defects created during bombardment by the 1 keV He⁺ ion beam. Most importantly, however, the data presented in Figure 4b clearly demonstrate that the LEIS technique is sensitive to low concentrations of 18O on the surface.

3.3. STM Studies: Desorption. Both the STM and LEIS studies of the water saturated Fe₃O₄(001) surface indicate that only hydrogenation of lattice oxygen occurs. However, in a prior temperature programmed desorption (TPD) study, it was observed that molecular water desorption occurs at 520 K. To investigate the thermal desorption of the OSH at the atomic scale, we flash-annealed the OSH saturated surface (225 L) to various temperatures in the range of 373-873 K, before cooling the sample as quickly as possible back to room temperature for imaging with STM. Flash anneals up to 500 K do not significantly alter the appearance of the OSH saturated surface. However, annealing to 520 K produces the image presented as Figure 5, which exhibits dark patches covering approximately 3.25% of the surface area. Mostly surrounding the dark patches we observe a small number of remnant OSH species (~0.02 ML), while much of the surface resembles clean Fe₃O₄(001) (Figure 1b). Annealing at temperatures in excess of 550 K results in the disappearance of the dark patches and the recovery of the clean Fe₃O₄(001) surface.

From our experiments on the clean surface, we know that O vacancies appear as dark spots, and the dark patches are thus attributed to the loss of surface O when the water-exposed, H-covered surface is heated. To verify this, we performed two control experiments. First, the same annealing experiment was performed following adsorption of atomic H instead of water. This experiment resulted in similar dark patches to those shown in Figure 5. Second, the same annealing procedure was performed for the clean Fe₃O₄(001) surface, to no discernible effect.

4. DISCUSSION

The STM data presented in Figures 1 and 2 clearly demonstrate that dissociative water adsorption occurs on the stoichiometric Fe₃O₄(001) surface, in agreement with prior XPS experiments and the predictions of DFT calculations. The surprisingly low saturation coverage observed is linked to the limited availability of O\textsubscript{NAR} sites, which are apparently necessary for the dissociation process. Remarkably, however, both the STM and isotopically labeled LEIS results indicate that O\textsubscript{W}H is not present at the surface at room temperature, as would be expected on the basis of eq 2.

Further evidence for the missing O\textsubscript{W}H comes from the dark patches observed upon thermal desorption of the OSH (Figure 5). Ordinarily, heating an oxide surface with adsorbed dissociated water results in recombinative desorption of H and O\textsubscript{W}H, and the surface returns to its original state. However, since no O\textsubscript{W}H are present at the surface at room temperature, this process cannot occur. As a result, water desorption occurs at 520 K through the abstraction of surface O atoms (Mars–van Krevelen mechanism, see eq 3), resulting in reduction of the surface and the appearance of the dark patches:

\[
\text{O}_\text{S} \text{H} + \text{O}_\text{S} \xrightarrow{\Delta} (\text{H}_2\text{O})_k + \text{O}_\text{S} + \text{V}_\text{O}
\]  

(3)

Each desorbing water molecule removes 2 H atoms from the surface and creates one V\textsubscript{O}. Twice the area covered by the V\textsubscript{O}'s (0.0325 ML in Figure 5) plus the remaining H coverage (0.02 ML) indeed sums to the original H coverage of 0.085 ML. Reduction of iron oxide surfaces has been shown to occur following exposure to CCl₄ and atomic H as observed previously as well as confirmed in our own experiment. To our knowledge, this is the first example of an oxide surface being reduced following exposure to water. However, it should be
noted that the reduced surface is metastable and is reoxidized through O transfer from the bulk above 550 K. In addition, the surface can likely be reoxidized through reaction of water molecules with the oxygen vacancies, creating a hydroxylated surface consistent with eq 1.

Taken together, our results provide compelling evidence that only O\textsubscript{S}H species are present at the surface following dissociative adsorption of water on the Fe\textsubscript{3}O\textsubscript{4}(001) surface at room temperature. But where is the O\textsubscript{W}H?

There are two possibilities; either O\textsubscript{W}H diffuses into the crystal’s bulk or it spontaneously desorbs in some form. Since the Fe\textsubscript{3}O\textsubscript{4} lattice is composed of close-packed O\textsuperscript{2-} ions, diffusion should occur via place exchange, that is, hopping of V\textsubscript{O}’s. Our sample preparation procedure includes significant annealing in O\textsubscript{2}, resulting in an extremely low V\textsubscript{O} density (\sim 0.005 ML at the surface). From our recent work\textsuperscript{30} on the metastable Fe termination of Fe\textsubscript{3}O\textsubscript{4}(001), where significant oxidation of the surface was not observed up to \sim 720 K, we conclude that mobility of O should be rather low at room temperature.

Diffusion into the crystal’s bulk is thus an unlikely explanation for the absence of O\textsubscript{W}H. Moreover, if O\textsubscript{W}H were to diffuse into the immediate subsurface region, we would expect to eventually uncover it during the LEIS measurements when the 1 keV He\textsuperscript{+} beam sputters the surface. We performed extended LEIS measurements of the H\textsubscript{2}{\textsuperscript{18}}O saturated surface and no evidence for subsurface {\textsuperscript{18}}O was observed.

Figure 6 shows a schematic model of the energetically favorable adsorption geometry for two dissociated water molecules (one molecule per surface unit cell) on the Fe\textsubscript{3}O\textsubscript{4}(001) surface, as determined by recent DFT calculations.\textsuperscript{24,25} The O\textsubscript{W}H species are predicted to occupy sites atop the Fe\textsubscript{5} row and the O\textsubscript{S}H occupy O\textsuperscript{NAR} sites on the opposite sides of the unit cell. In this adsorption geometry, the separation between O\textsubscript{S}H and O\textsubscript{W}H on the surface is large (4.6 Å), which likely represents a significant barrier to recombination. Furthermore, the O\textsubscript{S}H forms an H bond to the neighboring O\textsuperscript{NAR} atom,\textsuperscript{26} further strengthening its bond to the surface. Since recombinitive desorption does not occur at room temperature, we can estimate that the resulting barrier to recombination is at least 18.1 kcal/mol.\textsuperscript{31} Consequently, an alternative process must lead to desorption of O\textsubscript{W}H from the surface. From our experiments, we cannot rule out that the O\textsubscript{W}H radical simply leaves the surface, but we are not aware of any precedent for OH radical desorption from a surface in the absence of photons or other ionizing radiation.\textsuperscript{32,33} Alternatively, two O\textsubscript{W}H may come together to react together forming a third species that is not bound to the surface at room temperature. While Figure 6 demonstrates how the H—O\textsubscript{W}H reaction may be suppressed by the adsorption geometry, facile diffusion of the O\textsubscript{W}H species along the Fe\textsubscript{5} rows could facilitate O\textsubscript{W}H—O\textsubscript{W}H reactions and a significant reaction rate realized through an increase in the preexponential factor, that is, frequent attempts at a reaction.

The reaction of two O\textsubscript{W}H could conceivably result in H\textsubscript{2} plus O\textsubscript{2}, O\textsubscript{2} plus two adsorbed O\textsubscript{S}H, H\textsubscript{2}O plus an adsorbed O atom since it is an LEIS or STM. Moreover, we consider production of H\textsubscript{2}O\textsubscript{2} to be unlikely since it is a less energetically favorable product than H\textsubscript{2} and O\textsubscript{2}. As mentioned above, we have found that neither O\textsubscript{2} nor H\textsubscript{2} to the Fe\textsubscript{5}O\textsubscript{4}(001) surface at room temperature, which suggests that both species would desorb immediately upon formation in the current experiments. However, as the expected amounts are small (total of <0.04 ML over an extended time period in a high water background), they cannot be detected with our experimental setup. Irrespective of the actual reaction products, however, our results suggest that water is split upon reaction with the Fe\textsubscript{5}O\textsubscript{4}(001) surface at room temperature.

5. CONCLUSIONS

In summary, we describe a hitherto unreported adsorption behavior for water, in which dissociative adsorption at room temperature results only in the hydrogenation of the oxygen lattice. Heating of the hydrogenated surface leads to extraction of lattice oxygen atoms to form water; thus, water exposure leads to the reduction of Fe\textsubscript{3}O\textsubscript{4}(001) under UHV conditions. We attribute this surprising behavior to reactive desorption of O\textsubscript{W}H species at room temperature, effectively splitting water at room temperature. This unusual reaction process may occur because the energetically favorable adsorption geometry for dissociated water on Fe\textsubscript{3}O\textsubscript{4}(001) favorably hinders recombinative desorption, but facilities O\textsubscript{W}H—O\textsubscript{W}H interactions.

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Figure 6. Schematic model showing the adsorption geometry predicted in recent DFT calculations,\textsuperscript{24,25} in which the O\textsubscript{S}H and O\textsubscript{W}H species are separated by 4.6 Å. The O\textsubscript{W}H species are situated on the Fe\textsubscript{5} atoms (yellow). Facile diffusion along the Fe\textsubscript{5} atom row (gray arrow) could lead to reactions between O\textsubscript{W}H species, and subsequent desorption if the products are not bound to the surface at room temperature (e.g., H\textsubscript{2} and O\textsubscript{2}, or O\textsubscript{2}, leaving two adsorbed H atoms).
(31) Value calculated using Arrhenius kinetics assuming a low reaction rate (0.1/s), a preexponential factor of 10^{13}/s, and a temperature of 292 K.