

Structure Revealing H/D Exchange with Co-Adsorbed Hydrogen and Water on Gold

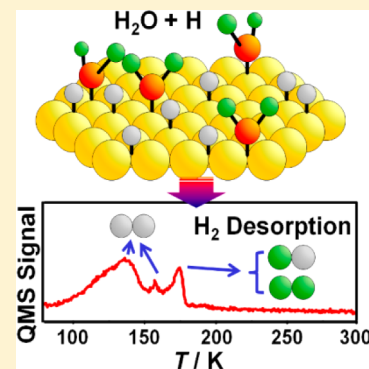
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S Supporting Information

ABSTRACT: A fundamental understanding of the interactions between coadsorbed water and hydrogen on metallic surfaces is critical to many chemical processes including catalysis and electrochemistry. Here, we report on the strong and intricate interactions between coadsorbed H/D and water on the close-packed (111) surface of gold. Deuterium isotopic labeling shows H/D exchange in H–D₂O and D–H₂O systems, indicating water dissociation and suggesting a nonrandom scrambling process by revealing the origin of hydrogen evolution (from surface H atoms or from water molecules) during annealing. In this reaction, the protonation of the H-bonding ice network (i.e., the formation of (H₂O)_nH⁺) is energetically favorable and is responsible for water dissociation. Density functional theory (DFT) modeling suggests that the thermodynamics and structure of the protonated clusters are predominant factors for yielding the traceable H₂ desorption features from the surface interaction with H atoms, providing insights into reaction mechanisms.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



Nanoscale gold-based catalysts have been found to be highly active for a variety of chemical transformations^{1,2} at low temperatures, including selective hydrogenation reactions.^{3,4} However, relevant fundamental, model studies of catalytic hydrogenation chemistry over gold are severely lacking. Model investigations⁵ could provide valuable insights into the reaction mechanisms and catalytic properties of gold^{6,7} and help advance the state of the art. Although there is a large energetic barrier to H₂ dissociation on pristine gold surfaces,^{8,9} it is clear that the metal oxide–gold interface can readily dissociate hydrogen,¹⁰ and hydrogen spillover onto the gold results in a very weakly bound H atom^{9,11} that is quite reactive, leading to the high hydrogenation activity observed at low temperatures in classical catalysis experiments.

Here, we further demonstrate the remarkable surface chemistry of gold^{12,13} via a study involving adsorbed H/D atoms that activate the dissociation of water on a Au(111) sample. Pt surfaces have also shown hydrogenic isotopic exchange via an interaction between adsorbed hydrogen and water;^{14–17} however, here, the Au(111) surface reveals new details regarding the structure of the hydrogen–water overlayer on the surface. Because water and hydrogen are prevalent in the chemistry and physics of many processes,^{18,19} we believe that our studies will be of utility regarding (1) gold-catalyzed chemical reactions involving H and H₂O, such as the water–gas shift reaction,^{20,21} and steam re-forming of hydrocarbons²² and alcohols;²³ (2) applications of gold electrodes in aqueous solutions;²⁴ and (3) the formation of hydronium (H₃O⁺)²⁵ and protonated water clusters [(H₂O)_nH⁺]²⁶ that are associated

with proton transfer and transport in water and which have been studied widely in many fields of chemistry and biology.²⁷

It is well-known that water adsorbs intact on Au(111) and has a small binding energy with the surface.^{28,29} However, in the present work, we observe that coadsorbing H atoms and water molecules on Au(111) reveals newly formed desorption features for both species in temperature-programmed desorption measurements that indicate stronger interactions. Employing an isotopically labeled reaction system, such as D₂O + H or H₂O + D, we have discovered the production of scrambled H₂, HD, and D₂. Our results suggest a reaction of water with H adatoms on Au(111) and further identify the origins of H (from surface H atoms or H₂O molecules) for each H₂ desorption feature in the H + H₂O system. Density functional theory (DFT) calculations are employed to understand the mechanisms; clusters of water play a key role in the reaction with H atoms on the surface. Formation of protonated water (H₂O)_nH⁺ as an intermediate is energetically favorable, and its thermodynamics and structure account for the nonrandom H/D exchange in H–D₂O and D–H₂O systems.

Our experiments were performed on a Au(111) single-crystalline surface under ultrahigh vacuum (UHV) conditions (base pressure of 1 × 10^{–10} Torr).^{30–32} We employed a custom-built H-atom generator to populate the surface with a 0.74 relative coverage of adsorbed H-atoms (θ_{H,rel} = 0.74). Subsequent to hydrogen adsorption, a neat molecular beam of

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water vapor was used to deliver 2.68 monolayers (ML) of adsorbed H_2O to the H-precovered surface. Using a quadrupole mass spectrometer (QMS), temperature-programmed desorption (TPD) measurements were then conducted to measure the gas-phase species evolving from the surface and to further identify the surface reaction steps with varying temperatures. RAIRS (reflection–absorption infrared spectroscopy) was also used to study surface reaction intermediates. Prior to every experiment, the sample was cleaned by exposure to NO_2 at 800 K, and the cleanliness was verified by TPD and Auger electron spectroscopy (AES). A detailed description of the experimental apparatus and procedure is included in the Supporting Information.

Figure 1 displays our first indications of the intricate interactions between adsorbed hydrogen and water on gold.

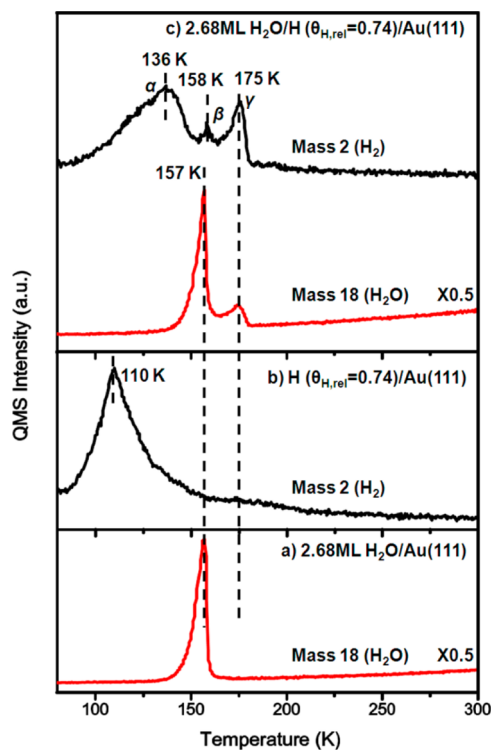


Figure 1. TPD spectra from Au(111) with (a) adsorption of only 2.68 ML of H_2O and (b) adsorption of only H ($\theta_{\text{H,rel}} = 0.74$) and (c) coadsorption of 2.68 ML of H_2O and H ($\theta_{\text{H,rel}} = 0.74$). All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a–c) have the same y-axis scale.

At the outset, it is perhaps instructive to examine the TPD spectra for adsorbed H and H_2O independently, as shown in Figure 1a and b in order to better appreciate the interactions revealed for the coadsorbed system. Figure 1a displays TPD spectra for H_2O from the clean Au(111) surface at a heating rate of 1 K/s. Water desorption has only a single feature on clean Au(111) at 157 K,²⁸ as shown in Figure 1a. Recombinative hydrogen desorption from Au(111) also shows a single feature, peaking at 110 K, as displayed in Figure 1b.

Now turning our attention to TPD spectra regarding the H and H_2O coadsorbed surface as shown in panel c of Figure 1, the measurements exhibit three H_2 desorption features that are denoted as α , β , and γ and are centered at 136, 158, and 175 K, respectively. The α peak is assigned to H atoms recombining

but with a higher temperature compared to that of characteristic H_2 desorption (~ 110 K) from the clean surface, as illustrated in Figure 1b.¹¹ The other two desorption peaks (β , γ) are newly formed and clearly involve the coadsorbed water. On the basis of the integrated TPD area under each peak, we estimate the proportion of the three features to be 83.5, 2.8, and 14.3%, respectively, for the α , β , and γ peaks.

Similarly, water desorption is also strongly affected by adsorbed hydrogen, as shown in Figure 1c with a new feature appearing at a higher temperature, ~ 175 K, aligned with the γ peak in H_2 desorption. It should also be noted that the β peak from H_2 desorption reproducibly appears at a slightly higher temperature (158 K) than the primary water desorption peak at ~ 157 K, as illustrated in Figure 1a and c.

In order to better understand the interaction between water and hydrogen on Au(111), we employed isotopes in the form of deuterium atoms and/or deuterated water to further probe reaction pathways. Figure 2 shows TPD spectra for two

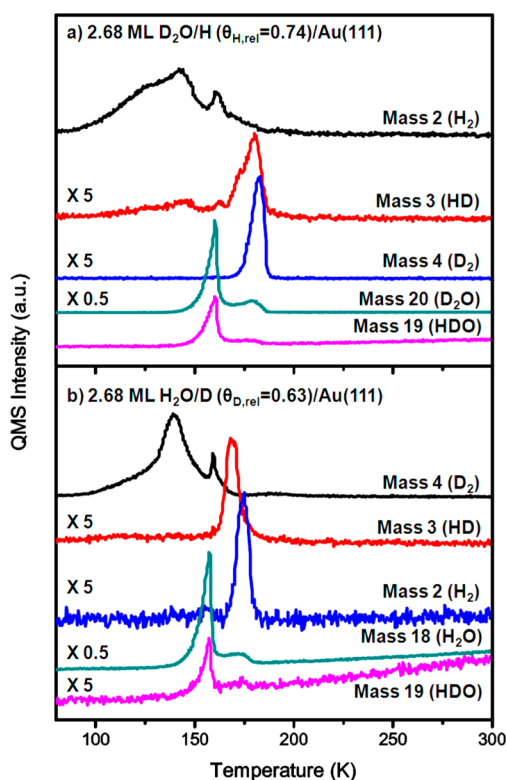


Figure 2. (a) TPD spectra from Au(111) with coadsorption of 2.68 ML of D_2O and H ($\theta_{\text{H,rel}} = 0.74$) and (b) 2.68 ML of H_2O and D ($\theta_{\text{D,rel}} = 0.63$). All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a) and (b) have the same scale on the y-axis.

different experiments, (a) H ($\theta_{\text{H,rel}} = 0.74$) precovered Au(111) with coadsorption of 2.68 ML of D_2O and (b) D ($\theta_{\text{D,rel}} = 0.63$) precovered Au(111) with coadsorption of 2.68 ML of H_2O . Figure 2a indicates that the replacement of D_2O for H_2O on H-precovered Au(111) still produces the two features α and β from H_2 desorption, but the γ desorption features for H_2 are missing at ~ 175 K. Instead, two desorption features have been observed in mass 3 (HD) and mass 4 (D_2) in the temperature range near 175 K; this observation suggests a scrambling reaction between D_2O and H adatoms that induces the production of HD and D_2 on the Au(111) surface. This finding

further indicates that the γ feature in the H_2 thermal desorption spectrum in Figure 1a stems exclusively from a hydrogen-exchange reaction between H and H_2O rather than the recombination of originally adsorbed H atoms. We notice that the desorption of HD and D_2 in Figure 2a yields similar integrated areas, further indicating that $\sim 75\%$ of the hydrogen in the γ peak in Figure 1c is from water. This finding suggests that the yield of exchanged H atoms on the surface is $\sim 10.7\%$ (the γ peak is estimated to contribute 14.3% of H_2 desorption in Figure 1c). However, HD and D_2 have slightly different ionization sensitivities in QMS measurements (leading to some uncertainty here).

In contrast, D_2O desorption shows two features at 160 and 180 K, similar to the observations for H and H_2O coadsorbed on Au(111). The new feature for D_2O at 180 K is at a slightly higher temperature than the similar one from H_2O desorption (175 K), and this feature is likely due to an isotope effect in which the H + D_2O system generates HD and D_2 via breaking of the original O–D bond in D_2O , as discussed in detail later in the paper. The mass 19 signal during TPD represents HDO, which can also be observed in nominally pure D_2O desorption on clean Au(111) and is identified as an impurity. Stronger mass 19 signals have been observed at 160 K during TPD from the H/ D_2O -covered surface; this result is indicative of the production of HDO. This newly formed HDO desorbs at the same temperature as water desorption on clean Au(111), and we believe this isotopic mixing is due to proton transfer in the solid water film.³³

We also studied the Au(111) surface with coadsorbed deuterium and H_2O . Figure 2b shows TPD spectra acquired from 2.68 ML of H_2O adsorbed on D ($\theta_{D,rel} = 0.63$) precovered Au(111). There are significant similarities with the H– D_2O system shown in Figure 2a; (i) H_2O shows a higher-temperature desorption feature at 175 K; (ii) D_2 yields a sharp desorption peak at 160 K; (iii) the production of HD and H_2 has been observed, and the H_2 desorption peak appears at the highest temperature; and (iv) compared to the surface with adsorbed water (H_2O) only, there is an increase in mass 19 (HDO) at 160 K, which is indicative of deuterium transfer in H_2O on Au(111).

We conducted DFT calculations to uncover the detailed mechanism of the interaction of adsorbed H atoms with water (procedural details are contained in the Supporting Information). The TPD spectra presented in Figures 1 and 2 indicate a specific reaction mechanism, isotopic mixing dictated via overlayer structure. The high-temperature H_2 peak, γ in Figure 1, originates exclusively from the water; however, the two lower-temperature H_2 peaks are derived exclusively from the surface-bound atoms. The fact that the sources of these peaks are related for both surface D/ H_2O as well as surface H/ D_2O indicates that this effect cannot be ascribed entirely to random isotopic scrambling.

We first used DFT to model the behavior of surface-bound H at low temperatures. The three-fold fcc hollow sites are the most favorable adsorption sites for H atoms, as Mavrikakis has reported previously.³⁴ As shown in Figure 3, there is a small barrier for a hydrogen atom to move from a fcc hollow to a hcp hollow. In this manner, the surface-bound atoms may diffuse randomly across the surface at low temperatures. H_2 formation as well as interaction with water, however, requires H atoms to sit atop a surface Au atom. From this position, the reaction for two adjacent top-bound H atoms to form H_2 is barrierless and exothermic by over 0.75 eV (Figure S1, Supporting

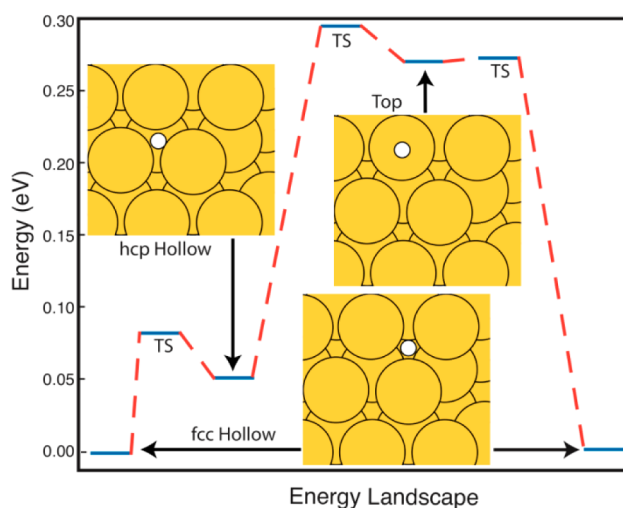


Figure 3. Schematic mechanism of the diffusion of a H atom on Au(111). H atoms adsorb preferentially in the fcc hollow sites. With an energy barrier of ~ 0.30 eV, H atoms are able to move onto a top site.

Information). Thus, the formation of H_2 is not apparent until the temperature is such that the surface-bound protons may diffuse to top sites. This barrier, approximately 0.25 eV from a hcp hollow, represents the energy cost of extracting a surface-bound H atom from the Au(111) surface, and all related processes, such as H_2 formation or the interaction with water, have similar barriers.

In contrast, water is weakly chemisorbed on Au(111) and has little barrier to diffusion. Thus, multiple water molecules move around on the surface until clustering and stabilizing. This phenomenon has been demonstrated by the low surface wettability of Au(111),¹⁸ which is a hydrophobic surface and induces the formation of water clusters with a double-bilayer structure.³⁵ Specifically, water molecules have much stronger H_2O – H_2O interactions than H_2O –surface interactions on Au(111),¹⁸ causing a single desorption feature. On other metal surfaces (such as Ir,³⁶ Pt,³⁷ Ni,³⁸ etc.), there is a discernible transition from the monolayer to the multilayer desorption indicating a stronger interaction between the first layer of water and the surface atoms.

Our DFT calculations for the H_2O + fcc-site H reaction show a 0.29 eV energetic barrier with a 0.22 eV endothermicity. The final H_3O^+ state has three fully equivalent protons and a low barrier for the reverse reaction; therefore, if this reaction were to occur at low temperatures, random isotopic scrambling would occur. The lack of low-temperature scrambling of surface-bound H with water indicates that water molecules form ice before the energetic barrier for surface-bound H to escape the surface can be met. Note that the formation of hydronium has been reported on the H- and water-covered Pt(111) surface by Wagner and co-workers, who detected a H_3O^+ intermediate based on the appearance of a 1150 cm^{-1} loss in high-resolution electron energy loss spectroscopy (HREELS).³⁹

We next studied the interaction of H atoms with water dimers and clusters employing DFT. Protonated water clusters of the form $(H_2O)_nH^+$ are likely to form due to the strong exothermicity of the product state and a large barrier to the reverse reaction. DFT calculations investigated the protonation of a water dimer and a water tetramer as a representative of a

water cluster. Protonation of the dimer is exothermic by 0.27 eV compared to that of the fcc hollow. Importantly, the H-bonded proton of the dimer becomes shared between the two molecules with an equal bond length, as shown in Figure 4. It is

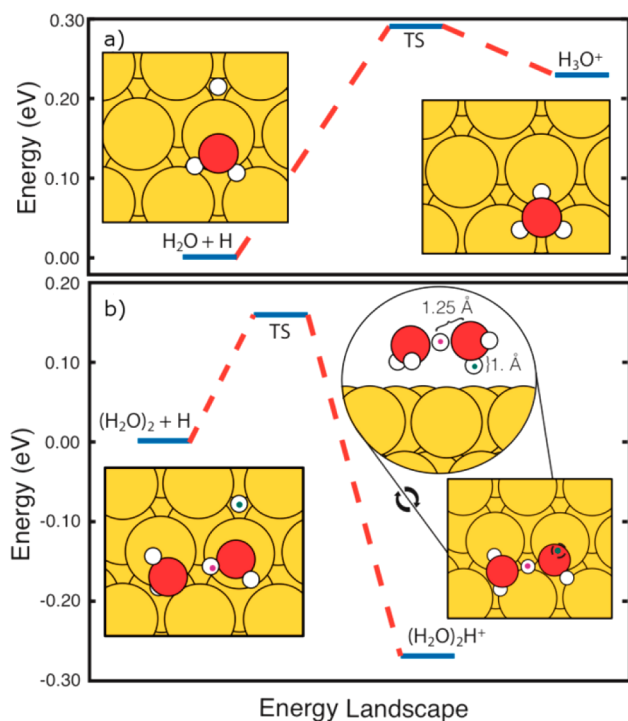


Figure 4. Schematic energy diagram of the interaction of atomic H with a water molecule or a dimer on Au(111). The interaction of atomic H with a single water molecule (a) is endothermic. In contrast, the newly formed bond between a surface H atom (b) and water dimer is strongly exothermic, and the in-network bond lengths.

this stretching mechanism that allows the original water molecule to dissociate; when the dimer breaks apart at higher temperatures, it is the H atom that is originally part of the water molecule that creates the H_2 desorption observed at 175 K in Figure 1c.

When a water tetramer is considered, protonation of the central water molecule is exothermic by 0.93 eV as compared to the fcc hollow, as shown in Figure 5. Thus, when surface-bound H atoms become free to move about the surface, they can either recombine to form H_2 or encounter an undercoordinated water molecule at the edge of an ice cluster and bind irreversibly. Infrared spectroscopy provides evidence for this process. Figure S2 (Supporting Information) shows that the O–D bond stretch (2425 cm^{-1})¹⁸ is observed from the D- and H_2O -covered Au(111) surface upon heating the sample to 110 K and suggests that protonated water is formed. Over the same range of temperatures, D_2 recombinatively desorbs from the surface (Figure 2b), suggesting that D_2 desorption is a competing process with D/H exchange in the D + H_2O system and could further affect the protonation of water clusters. Note that when only the tetramer is considered, as shown in Figure 5, all three of the edge water molecules surrounding the center H_3O -like species are equivalent and equally likely to desorb upon heating. However, for a larger cluster, the other two molecules in the tetramer could be considered as H-bonded to other H_2O molecules in the cluster; therefore, they would be frozen and unable to leave. Thus, with

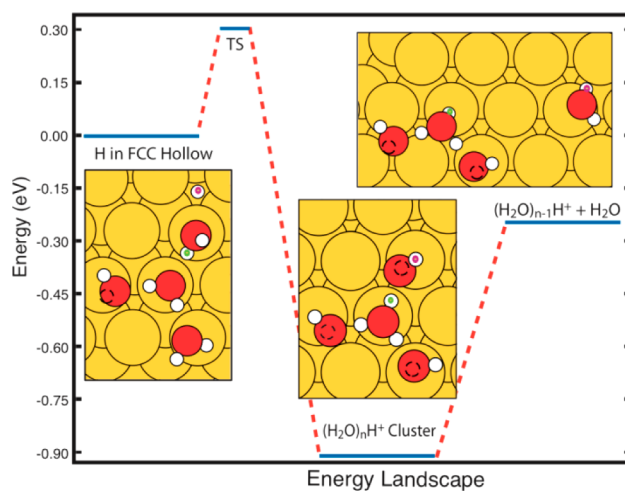


Figure 5. Schematic energy diagram of the interaction of atomic H with a water cluster on Au(111). When atomic H atoms from the surface adsorb to the edge of a water cluster, the interaction is strongly exothermic. Due to the favorable energetics of $(\text{H}_2\text{O})_n\text{H}^+$ clusters as compared to H_3O^+ , when this cluster breaks apart, the original water molecule at the edge dissociates instead of returning the H atom to the surface or creating H_3O^+ .

increased heat applied during TPD, newly formed water molecules (now containing an originally surface-bound atom) located at the edge of the cluster are the most energetically favorable portion to dissociate as the protonated ice cluster breaks apart. The energetic cost of putting the excess proton on the surface or on a single molecule is significantly larger than leaving the excess proton on a cluster of water molecules. In this manner, the edge water molecules dissociate, and isotopic scrambling with surface H(D) occurs.

In TPD measurements of coadsorbed H and H_2O , recombinative H_2 desorption shows two new features (β , γ), and water desorption reveals an additional peak at higher temperature. DFT results show that the $(\text{H}_2\text{O})_n\text{H}^+$ clusters require a higher-energy input to break up than $(\text{H}_2\text{O})_n$ and lead to the new high-temperature desorption feature of water at 175 K. Each water cluster breaks apart into progressively smaller units, and the ultimate effect of the breakup involves cleavage of an O–H (or O–D) bond that was originally part of a water molecule. The H (or D) atom in this bond is ultimately left on the surface as an adatom that can recombine with other H or D on the surface. In experiments involving isotopes, as illustrated in Figure 2, this process can produce scrambled HD and D_2/H_2 (in the H– $\text{D}_2\text{O}/\text{D}$ – H_2O systems).

Thus, our DFT calculations demonstrate the origins of the α , β , and γ peaks. The α peak arises from the surface-bound H atoms that are free to diffuse on the surface and recombine. The hydrophobic Au(111) surface^{40,41} may induce water clustering upon heating, opening up more water-free surface area and increasing the ability of two H adatoms to recombine. However, ultimately, the water clusters lengthen the H atom diffusion distance, leading to the shift in the α peak to higher temperatures with increasing water coverage, as shown in Figure S3 in the Supporting Information. The β peak is the result of surface-bound H whose diffusion is obstructed by large ice clusters and that is not free to recombine until the water clusters begin to break apart at higher temperatures. More specifically, we speculate that the β peak is likely due to a physicochemical process: (i) water adsorbs on the H-

precovered surface and forms clusters covering the H atoms; (ii) the water cluster bottom, which is fully coordinated to other H₂O molecules, has a weaker interaction with H atoms than the edge water molecules; (iii) this interaction inhibits the mobility of H atoms; and (iv) H atoms combine with one another and immediately leave the Au(111) surface once water desorbs at ~ 160 K, leading to a slightly high desorption temperature due to the reaction kinetics. The final peak, γ , consists of protons exclusively from the water and originates from surface-bound H atoms bonding with water molecules at the edges of ice layers to form (H₂O)_nH⁺ clusters that do not break apart until 175 K. This mechanism is consistent with the isotopic results presented in Figure 2, in which isotopic scrambling occurs based on the origin of the species (from the surface or from water). In addition, Figure S3 (Supporting Information) shows that increasing water coverages cause greater desorption features of H₂O and H₂ at 175 K, suggesting that more water clusters form at high coverages and generate a larger number of edge sites to promote the interaction between H and water. These results are in agreement with our DFT calculations that show that water clustering plays a key role in this process.

Kinetic isotope effects (KIEs) have been studied by comparing coadsorption of H and H₂O to a fully deuterated reaction system. Coadsorption of 2.68 of ML D₂O and D ($\theta_{D,rel} = 0.63$) on Au(111) yields TPD spectra, shown in Figure 6a, that show several characteristic properties of the interaction between hydrogen and water. The D₂ desorption contains three features corresponding to the peaks α , β , and γ in Figure 1c,

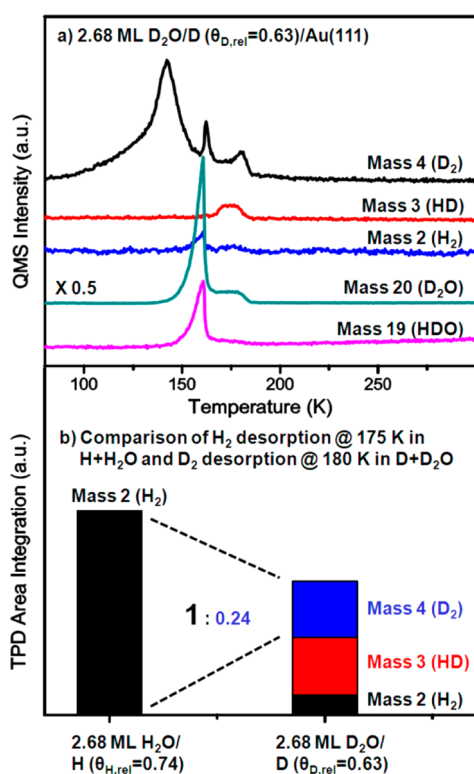


Figure 6. (a) TPD spectra from Au(111) with coadsorption of 2.68 ML of D₂O and D ($\theta_{D,rel} = 0.63$). (b) Integrated TPD areas from H₂ desorption at 175 K in H + H₂O and D₂ (also including HD and H₂) desorption at 180 K in D + D₂O. All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a) and (b) have the same scale on the y-axis.

and D₂O similarly shows a new high-temperature desorption feature. We also observed desorption of HD (mass 3) and H₂ (mass 2) in a temperature range of 175–180 K. These features likely result from the surface-mediated interaction between H–D₂O or D–H₂O because D₂O and D₂ have a considerable amount of HDO (19%) and HD (7%) impurities, respectively, as indicated by multiple control experiments via TPD and FTIR measurements (Figures S4–S6, Supporting Information).

In order to identify the effect of deuterium on the reaction between hydrogen and water, we integrated the desorption features of D₂, HD, and H₂ that peak at 175–180 K and show the results in Figure 6b with a comparison to the reaction of H with H₂O. Note that we normalized the difference between H and D coverages by assuming a proportional relationship between coverages and areas under the γ feature in H₂/D₂ desorption. The integrated areas indicate that the interaction between H and H₂O generates a significantly larger amount of H₂ than the desorption of D₂ from the D–D₂O reaction by a factor of ~ 4 . This result suggests a primary KIE for this surface reaction. In addition, we note that the sum of D₂, HD, and H₂ from D–D₂O is still smaller than H₂ desorption in the case of H + H₂O, as shown in Figure 6b. This observation is a further demonstration of the KIE influence, which is likely due to the elementary steps of water protonation and subsequent decomposition of (H₂O)_nH⁺.

In summary, hydrogen and water have a strong interaction that results in nonrandom isotopic scrambling on the Au(111) surface at low temperature (< 175 K) under UHV conditions. Coadsorbed H and H₂O lead to a new feature appearing at ~ 175 K in the water desorption spectra, which is in contrast to the characteristic desorption peak on clean Au(111) at 160 K. Furthermore, two new features have been observed in H₂ desorption (at 160 and 175 K), as well as a shift in the characteristic H₂ recombination desorption feature to higher temperatures. We used two reactant combinations, H₂O + D and D₂O + H, to study these phenomena and show production of HD, HDO, and H₂(D₂) via a mixing reaction based on the overlayer structure of isotopically labeled water and hydrogen. This study provides evidence that the hydrogen evolving at 175 K from the H- and H₂O-coadsorbed surface is exclusively from bond breaking in water rather than surface-bound H₂ recombinative desorption. RAIRS spectroscopy and DFT calculations predict that protonated water clusters (H₂O)_nH⁺ are intermediates, which dissociate at higher temperature to cause the appearance of new desorption features for water and H₂. Purely deuterated reactants D and D₂O have been employed in this reaction and show a lower reactivity, indicative of a primary KIE.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental and computational procedures, reflection absorption infrared spectroscopy measurements from Au(111) with coadsorption of D₂O and H, and TPD spectra of H₂ and H₂O from H-precovered Au(111) with coadsorption of a variety of H₂O coverages, TPD and FTIR results for D and D₂O on clean Au(111). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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