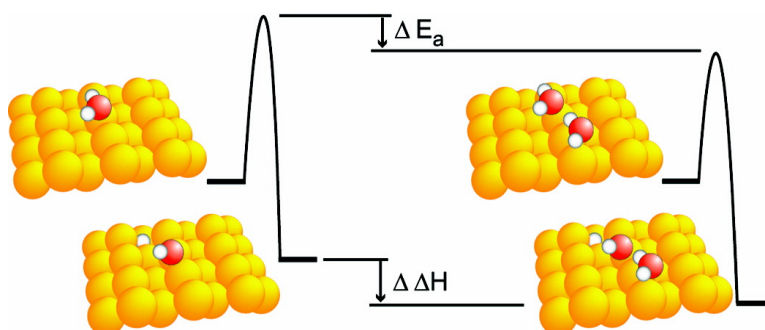Article

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# Autocatalytic Water Dissociation on Cu(110) at Near Ambient Conditions

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**Abstract:** Autocatalytic dissociation of water on the Cu(110) metal surface is demonstrated on the basis of X-ray photoelectron spectroscopy studies carried out in situ under near ambient conditions of water vapor pressure (1 Torr) and temperature (275−520 K). The autocatalytic reaction is explained as the result of the strong hydrogen-bond in the $H_2O$−OH complex of the dissociated final state, which lowers the water dissociation barrier according to the Brønsted−Evans−Polanyi relations. A simple chemical bonding picture is presented which predicts autocatalytic water dissociation to be a general phenomenon on metal surfaces.

## 1. Introduction

Water chemistry on metal surfaces constitutes a fundamental part of chemical processes of great technological and economical importance, such as hydrogen-production through steam reforming (SR), $CH_4 + H_2O \rightarrow CO + 3H_2$, and the water-gas shift (WGS) reaction, $CO + H_2O \rightarrow CO_2 + H_2$, both of which are cornerstones of today's large-scale chemical industry.[1] Other examples of the importance of water−metal chemistry include corrosion and fuel cell technology. Although a correct modeling of elementary surface reactions involving water chemistry at the gas−solid interface should consider earlier reports on hydrogen (H-) bond assisted lowering of the water dissociation barrier from ultrahigh vacuum (UHV) studies[2,3] and theory,[4−10] on both metal[2,4−6] and nonmetal surfaces,[3,7−10] this is very far

from common practice. The effects of lateral and attractive H-bond interactions are today still only partially known, particularly at near ambient and reaction conditions.

On Cu(110), a large variation of the dissociation barrier for water has been observed depending on experimental conditions. From kinetic measurements of the WGS reaction rate at 10 Torr $H_2O$ + 26 Torr CO, 543 K ≤ $T$ ≤ 653 K, Nakamura et al.[11] report a water dissociation barrier of 0.87 eV. A significantly lower dissociation barrier with a value of ∼0.55 eV in the saturated water monolayer was obtained by some of the present authors under UHV conditions and low temperatures.[2] The difference in activation barriers can be explained by two extreme situations for water dissociation, the monomer and the saturated water monolayer.[2] This autocatalytic water dissociation on Cu-(110) is also supported by recent calculations within the framework of density functional theory (DFT).[4]

In order to arrive at a general understanding of the autocatalytic water dissociation, we extend our studies on Cu(110) using synchrotron-based X-ray photoelectron spectroscopy (XPS) to elevated water pressure (1 Torr)[12,13] and temperatures up to ∼520 K, i.e., approaching technologically relevant conditions. Autocatalytic water dissociation is argued to be a general phenomenon on metal surfaces, originating from a strong H-bond between $H_2O$ and OH in the dissociated final state.

## 2. Experimental Section

Experiments were performed in the ambient pressure photoemission spectroscopy (APPES) endstation at the undulator beamline 11.0.2 at

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the Advanced Light Source (Berkeley, CA).[12] The vacuum base pressure in the endstation is about $2 \times 10^{-10}$ Torr. The electron spectrometer is a Specs Phoibos 150 with a custom-designed differentially pumped electron lens. O 1s XPS spectra were recorded at a photon energy of 735 eV and a total energy resolution on the order of 350 meV.

Because both gas-phase attenuation and transmission of electrons through the electron optics are energy-dependent processes, particular care needs to be taken for a proper analysis of the data. Quantification of surface coverage is obtained by measuring the relative O 1s and Cu 3p signals for identical electron kinetic energies, obtained by choosing appropriate X-ray excitation energies, and by calibration against the O 1s to Cu 3p ratio obtained for a 0.5 monolayer of atomic O[14,15] [1 monolayer (ML) = $1.09 \times 10^{15}$ atoms cm$^{-2}$ for Cu(110)]. Similarly, through reference measurements of adsorbed, as well as gas-phase, species with well-known C:O ratio, the C 1s to O 1s intensity ratio for identical electron kinetic energies could be established. This was used to determine the level of C-contamination on the surface.

The Cu(110) crystal was cleaned by cycles of Ar$^+$-sputtering and annealing to 850 K until a sharp $1 \times 1$ LEED pattern was observed. The temperature of the sample was monitored by a K-type (chromel−alumel) thermocouple located inside a special pocket of the sample for good thermal contact. The Milli-Q water ($H_2O$, $T = 295$ K) used was cleaned (degassed) by multiple freeze−pump−thaw cycles and finally by distillation right before introduction into the experimental chamber.

The surface cleanliness before water adsorption was $\leq 0.03$ ML O. This remaining small amount is most likely due to a small percentage of highly reactive defects on which $H_2O$ dissociates at $1 \times 10^{-7}$ Torr, the base pressure after evacuation from experiments at 1 Torr $H_2O$. We believe that these small amounts of atomic O are not affecting the results obtained at pressures 7 orders of magnitude higher that produce large amounts of dissociated $H_2O$. Although no C was observed (<0.001 ML) before water adsorption, a small amount was detected after water exposures, reaching $\leq 0.03$ ML in the experiments at 1 Torr $H_2O$. In order to keep C-contamination at this low level, each data point at 1 Torr $H_2O$ was obtained after a cleaning procedure and thus corresponds to an experiment on a freshly prepared clean Cu(110) surface. In all cases, rapid data acquisition was essential. Starting from vacuum ($\sim 10^{-7}$ Torr), a 1 Torr $H_2O$ environment was reached within $\sim$30 s, and acquisition of the O 1s XPS spectrum, with an acquisition time of 60 s, then immediately started.

Regarding the issue of X-ray- and electron-induced water dissociation,[2,16] a comparative ambient pressure XPS study of Cu(111) and Cu-(110),[17] recorded under X-ray irradiation and water pressure conditions identical to those reported here, resulted in no observable dissociation products on the chemically more inert Cu(111) surface unless predosed with atomic O. We take this as proof that possible X-ray- and electron-induced water dissociation, in the gas-phase and at the surface, does *not* influence our results. The Cu(111) results also rule out possible $O_2$-contamination in the water vapor. We also performed blank experiments on Cu(110) to investigate water dissociation in the absence of the X-ray beam. Introducing water up to pressures of 1 Torr was followed by evacuating down to $\sim 1 \times 10^{-7}$ Torr and then recording the spectra. Equally large amounts of water dissociation products were observed as when the X-ray beam was present during water dosing. Water dissociation on Cu(110) at $1 \times 10^{-7}$ Torr was negligible compared to high-pressure exposures. We are therefore confident that our results are not affected by X-ray- or electron-induced dissociation.
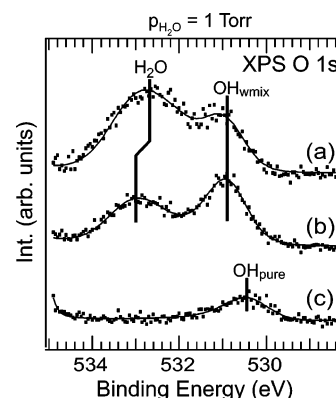
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**Figure 1.** O 1s X-ray photoemission from Cu(110) recorded in the presence of 1 Torr partial pressure of $H_2O$ at: (a) 275 K, (b) 348 K, and (c) 453 K. The two spectral features $OH_{wmix}$ and $OH_{pure}$ correspond to OH-species bonding with $H_2O$ and isolated OH groups, respectively. The spectra are normalized with respect to coverage, and the result of a least-squares peak-fitting procedure after background subtraction is shown as a solid line for each spectrum. The gas-phase peak of $H_2O$ located above 535 eV is not shown.

## 3. Results and Discussion

**3.1. Autocatalytic Water Dissociation: The Observations.** In order to discuss the water chemistry on the Cu(110) surface at near ambient conditions we first identify the species corresponding to the various peaks in the XPS O 1s region. In Figure 1 we show spectra taken in 1 Torr pressure of $H_2O$ at three different temperatures (275, 348 and 453 K). Three different adsorbed species can be distinguished. Molecular $H_2O$ produces a peak in the $532.65 - 533.0$ eV range, depending on the coverage, with the highest binding energy value at the lowest total ($H_2O$ + OH) coverage. Two different types of OH species are observed: one hydrogen-bonding with $H_2O$ ($OH_{wmix}$) with a binding energy at 530.95 eV and another at 530.45 eV which is assigned to a pure OH phase ($OH_{pure}$). All three species compare well with previous measurements of adsorbed $H_2O$ and OH on Cu(110) under ultrahigh vacuum (UHV) and low-temperature conditions.[2,18−20] No statistically significant amounts of atomic O were observed under 1 Torr $H_2O$ in the $275-520$ K range. A more detailed account of our data together with an extensive comparison to previous UHV results is available elsewhere.[21]

The saturation (maximum) coverage of OH on the surface was established to be $0.35 - 0.4$ ML under our experimental conditions. In Figure 2 we show the total OH coverage observed at 1 Torr $H_2O$ as a function of surface temperature. Indicated in the figure is also the temperature ($\sim$430 K) up to which significant amounts of $H_2O$ could be detected by XPS ($\geq 0.03$ ML). We observe that above 380 K the total OH coverage starts to drop significantly below its saturation coverage. This is a result of either kinetic limitations on the rate of OH production (by $H_2O$ dissociation) or a decrease of OH equilibrium coverage. Resolving this issue would have required time-resolved results, i.e., sequential spectra, which unfortunately at 1 Torr was not

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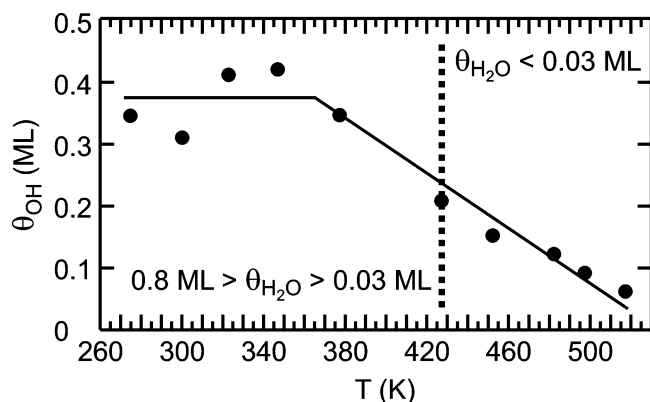
**Figure 2.** Total OH coverage ($\theta_{OH}$) as a function of temperature on Cu-(110). The solid line is shown to emphasize the trend for the observed OH coverage changes. The vertical dashed line marks the highest temperature (428 K) at which molecular water can still be observed by XPS ($\geq 0.03$ ML).

feasible due to increased surface contamination in spectra beyond the first. Irrespective of the actual situation we show that our data, when compared to prior measurements,[2,11] are fully consistent with autocatalytic water dissociation taking place at near ambient conditions.

Based on the total OH coverage after exposure of the sample to 1 Torr $H_2O$ for 60 s (the XPS spectrum acquisition time), the dissociation probability per $H_2O$ collision with the surface ($P_{diss}$) can be calculated. Whether the obtained $P_{diss}$ represents an absolute value or a lower limit depends on whether the observed OH coverage is the result of limitations in the $H_2O$ dissociation rate or simply represents a thermodynamic equilibrium. Either way we find that it does not affect our conclusions.

In the temperature range $470 - 520$ K, the water coverage is well below our detection limit (i.e., $\ll 0.03$ ML). Under these conditions we find $P_{diss}$ to be $\geq 0.5 - 0.2 \times 10^{-8}$. These results compare very well with Nakamura et al.[11] who established, under low water coverage conditions, $P_{diss}$ to be $\geq 0.5 \times 10^{-8}$ at 473 K. Equally good agreement is deduced from the obtained WGS data in the same study by Nakamura et al. (Figure 2 in ref 11); extrapolation down to the $470-520$ K range indicates a $P_{diss}$ of $1-5 \times 10^{-8}$. Our results in the $470-520$ K range ($P_{diss} \geq 0.5 \times 10^{-8}$) are hence in good agreement with the different values extrapolated from Nakamura et al.[11] data ($P_{diss}$ $0.5 - 5 \times 10^{-8}$) even though there are considerable differences in reaction conditions and in the way $P_{diss}$ is extracted. The agreement indicates that possible contaminants in our system (e.g., CO and $H_2$) have only a small impact on our results.

In the temperature regime $275 - 380$ K water is observed in large quantities on the surface ($0.8 - 0.2$ ML). Under these conditions we determine $P_{diss}$ to be $\geq 1.5 \times 10^{-8}$, a value several orders of magnitude greater than expected as discussed below. From measurements near 285 K and exposures to $1 \times 10^{-2}$ and 0.1 Torr, $P_{diss}$ was established to be as high as $1 - 5 \times 10^{-7}$. $P_{diss}$ could possibly be higher in 1 Torr at this temperature. Specifically, the determination of $P_{diss}$ at 0.1 Torr was obtained by $\sim 5$ s exposure at 285 K without X-rays present, followed by evacuation to $1 \times 10^{-7}$ Torr and recording of the XPS

spectra, which confirmed an $OH_{pure}$ coverage of 0.2 ML.[22] Three similar blank experiments at 1 Torr in the $285-305$ K range gave rise to a $P_{diss}$-value equal to, or greater than, $0.25 - 1 \times 10^{-7}$. The range given is due to uncertainties in gas-exposure times and because OH was produced to saturation (0.4 ML) during these $H_2O$ exposures, i.e., no further OH formation possible beyond that point, the "or greater than" follows logically.

From extrapolation of the previously obtained low water coverage WGS data[11] down to 275 K a $P_{diss}$ of about $5 \times 10^{-12}$ is expected, however we obtain a several orders of magnitude higher $P_{diss}$ ($\geq 1.5 \times 10^{-8}$) under 1 Torr $H_2O$. The value could possibly be larger than $5 \times 10^{-7}$ based on the $P_{diss}$ obtained at the lower pressure of 0.1 Torr. Our finding that at lower temperatures, corresponding to high water coverage, the $H_2O$ dissociation rate is much faster than expected based on measurements obtained at higher temperatures, i.e., low water coverage, is fully consistent with autocatalytic water dissociation taking place at near ambient conditions.

**3.2. Autocatalytic Water Dissociation: The Origin.** So far we have shown that the barrier (rate) to $H_2O$ dissociation on Cu(110) depends strongly on whether $H_2O$ is in monomeric form or H-bonding with other water molecules. Although a faster $H_2O$ dissociation rate is expected at elevated temperatures this may be more than offset by the concomitant decrease in the concentration of $H_2O-H_2O$ bonded species due to the lower $H_2O$ coverage. In the following we discuss the driving force behind the autocatalytic water dissociation on Cu(110).

Considering the water monomer adsorption energy, i.e., in our case the desorption barrier $E_{des}$, which has been calculated to 0.38 eV on Cu(110)[4] we find that there are remarkably large amounts of water adsorbed on the Cu(110) surface under our experimental conditions, e.g., 0.04 ML at a temperature of 428 K under 1 Torr $H_2O$. Simple adsorption−desorption equilibrium kinetic considerations[21] show that the monomer adsorption energy is much too low to lead to the observed quantities of adsorbed $H_2O$. Likewise, the $E_{des}$ for water from a pure water monolayer is only about 0.52 eV.[2] Although higher than in the monomer case, this value is still too low to explain the large amounts of water on the Cu(110) surface. In order to account for the observed large quantities of water on Cu(110) we need to add an attractive interaction for water at the surface of approximately 0.2 eV above that provided by the $H_2O-H_2O$ interaction. This extra stabilization of water at the surface can only be provided by existing OH groups,[21] with which $H_2O$ forms a stable $H_2O$(donor)-OH(acceptor) complex (see section 3.3).

Based on the insight from our experiments that the $H_2O-$ OH bond is stronger than the $H_2O-H_2O$ bond on Cu(110),[21] we regard the stability of the $H_2O-OH$ complex as the driving force for the observed lowering of the $H_2O$ dissociation barrier. Considering water dimer (trimer) formation at the surface, possibly facilitated by high $H_2O$ concentrations around already present OH, H-bonding configurations which result in a stabilization of OH after $H_2O$ dissociation by accepting one

(22) Disproportionation of this $OH_{pure}$ species was also studied.[21] XPS binding energies and 2:1 ratio between initial $OH_{pure}$ and final atomic O fully matched prior UHV work[11,18−20] while the conversion rate was much slower, likely due to residual $H_2O$ ($10^{-7}$ Torr range)[21] driving the reverse reaction and a possible poisoning effect by slower desorbing $H_{ads}$[23] generated from initial $H_2O \rightarrow OH_{ads} + H_{ads}$.

(two) H-bonds from $H_2O$ are possible. The stronger $H_2O-OH$ bond (final state) compared to the $H_2O-H_2O$ bond (initial state) should lead, following Brønsted-Evans-Polanyi relations[24,25] for water dissociation[26] and the effect of a considerable decrease in reaction enthalpy ($\Delta H$), to a significantly lower activation barrier (i.e., faster rate) for dissociation in, e.g., a water dimer compared to a monomer on Cu(110).

**3.3. Autocatalytic Water Dissociation: Metal Surfaces in General.** We propose that the enhanced stability of the $H_2O-OH$ complex over $H_2O-H_2O$ observed on Cu(110) is a general phenomenon on metal surfaces, and that this provides a general mechanism for water dissociation.

This can be understood by the fact that the metal-OH bond is strong and of mainly ionic character.[27] The large electron affinity of OH gives rise to a near-closed-shell electronic structure,[27] with significant $OH^-$ character, while $H_2O$ donates electron density to the metal substrate.[28,29] Moderate strength H-bonds, such as $H_2O-OH$ (and $H_2O-H_2O$), are predominantly of electrostatic nature.[30] Hence, on metal surfaces $H_2O$ ($\delta^+$) has enhanced ability to donate H-bonds and OH ($\delta^-$) is of Brønsted base character, i.e., a better H-bond acceptor but worse H-bond donor toward $H_2O$ than $H_2O$ is to itself. The strong H-bond at metal surfaces is therefore the $H_2O$(donor)-OH-(acceptor) bond while the reverse situation yields a very weak bond. This is analogous to the situation of $OH^-$ in solution[31] and consistent with theoretical results for OH donor−acceptor properties toward $H_2O$ on Pt(111)[29,32] and Rh(111).[33] Based on our simple chemical bonding model, we propose that such stronger $H_2O$(donor)-OH(acceptor) H-bond interactions compared to $H_2O-H_2O$ applies to other metal surfaces as well.

Besides the results presented here for autocatalytic water dissociation on Cu(110), previous theoretical work has come to the same results for the $H_2O + O$ reaction on Pt(111)[6] and $H_2O$ on Ru(001);[5] in all three cases the water dissociation barrier is lowered by $0.2 - 0.4$ eV.[2,4−6] The theoretical findings on Pt(111) and Ru(001) are in line with thermal desorption spectroscopy (TDS) studies of water from these surfaces under UHV conditions. Significantly higher water desorption temperatures from these surfaces are observed when OH groups are present,[16,34−36] demonstrating the greater H-bond stability of $H_2O-OH$ compared to $H_2O-H_2O$ also on these metal surfaces. At present, the full range of examples on the greater H-bond stability of $H_2O-OH$ compared to $H_2O-H_2O$ on metal surfaces from TDS studies under UHV conditions include Pt(111),[34] Ru-(001),[35,36] Pd(111),[37] Rh(111),[38] Ag(110),[39,40] Ni(110)[41] and Cu-

(110).[42,43] From near ambient XPS studies the stability of the $H_2O-OH$ complex has also recently been demonstrated for the Cu(111) surface.[17] All of these results, consistent with the chemical bonding picture presented, strongly suggest autocatalytic water dissociation to be a general phenomenon on metal surfaces.

In closing, we emphasize that the H-bonding configuration of the dissociating water molecule is expected to strongly affect the dissociation barrier to $OH_{ads} + H_{ads}$. Here we give a general description of the (initial state) configurations proposed to be mainly responsible for the autocatalytic water dissociation.

The water molecule can be involved in one, two or three H-bonds with other waters at the metal surface. For a reaction enthalpy lowering to occur compared to the monomer case, and hence a dissociation barrier lowering (i.e., autocatalysis), the total H-bond strength in the final state must be higher than in the initial state. Based on our simple chemical bonding model this means that the number of $H_2O$(donor)-OH(acceptor) (OH-(donor)-$H_2O$(acceptor)) bonds in the final state should be maximized (minimized) because these bonds are significantly stronger (weaker) than $H_2O-H_2O$. This favors initial state configurations where the dissociating water accepts two (one) H-bonds in case of a trimer (dimer) water cluster. Furthermore, because OH can only donate one H-bond, by excluding cases where the dissociating water donates two H-bonds to other waters in the initial state, the complete loss of a $H_2O-H_2O$ H-bond can be avoided.

In summary, the initial state configurations responsible for autocatalytic water dissociation at metal surfaces are expected to be those where the dissociating molecule accepts as many (and donates as few) H-bonds from (to) other water molecules as possible. This is consistent with the finding that the lowest dissociation barrier to $OH_{ads} + H_{ads}$ in the saturated water monolayer on Cu(110)[4] and Ru(001)[5] is that for a H-down configuration, accepting two and donating only one H-bond to water in the initial state.

We acknowledge that effects beyond what can be investigated experimentally, could also contribute to autocatalysis. From DFT calculations, Michaelides[44] has shown the tendency for H-bond acceptor water molecules not to bind to the metal surface in smaller water clusters. If this acceptor-water dissociates into $OH_{ads} + H_{ads}$, the fact that it did not bind to the metal in the initial state means there will be a relative increase in adsorbate−substrate bonding, compared to the monomer case, upon dissociation. This may contribute to an enthalpy lowering, as discussed earlier.[5] If the effect exists, it should still follow along the lines we have already outlined regarding most plausible initial states giving rise to the autocatalytic water dissociation.

## 4. Conclusions

We have shown the autocatalytic role of water in water dissociation on Cu(110) under near ambient water pressures by means of *in-situ* XPS. Under the conditions explored the water dissociation rate decreases with increasing temperature, i.e., with

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decreasing water coverage. We argue that the greater stability of the $H_2O-OH$ final state complex compared to the $H_2O-H_2O$ in the initial state provides the driving force for the autocatalytic water dissociation, in accordance with the Brønsted-Evans-Polanyi relations. The initial state configurations expected to be mainly responsible for autocatalytic water dissociation at metal surfaces are those where the dissociating water molecule accepts as many (and donates as few) H-bonds from (to) other waters as possible.

The results show that the inclusion of H-bonding effects is crucial for a complete understanding of the observed water chemistry and this is likely to be true in general for surface chemical kinetics in systems with adsorbates capable of H-bond formation.

**Supporting Information Available:** Complete ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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