Water Adsorption to Crystalline Cu₂O Thin Films: Structural and Vibrational Properties

C. Möller,[†] J. Barreto,[‡] F. Stavale,[‡] H. Tissot,[§] S. Shaikhutdinov,[§][®] H. J. Freund,[§][®] and N. Nilius^{*,†}[®]

[†]Carl von Ossietzky Universität, Institut für Physik, D-26111 Oldenburg, Germany

[‡]Brazilian Center for Research in Physics, Rio de Janeiro, Brazil

[§]Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

ABSTRACT: D₂O adsorption to well-ordered Cu₂O(111) thin films has been explored with scanning tunneling microscopy, thermal desorption and infrared absorption spectroscopy. The molecules bind associatively to the oxide surface, whereby the first D₂O layer experiences slightly stronger adhesion due to interfacial hydrogen bonds. At higher coverage, amorphous solid water (ASW) films condense on the Cu₂O(111) surface, as concluded from a dominant 155 K desorption peak and a broad vibrational band centered at 2540 cm⁻¹. Development of ASW is also observed on bare Au(111), being used as substrate for Cu₂O growth. In contrast to the oxide surface, no binding enhancement is detected for the D₂O monolayer and desorption is accompanied by dewetting and transformation to



crystalline ice. The different binding schemes of water reflect the hydrophilic versus hydrophobic character of $Cu_2O(111)$ and Au(111) supports, respectively.

1. INTRODUCTION

Hydrophilicity and hydrophobicity are fundamental antipodes of water-surface interactions in nature. While water-surface coupling, as mediated by covalent bonding for example, is stronger than intermolecular cohesion in the former case, hydrogen bonding inside the molecular network prevails in the latter.¹ Hydrophobicity often results in the formation of 3D water structures and might be accompanied by a crystallization to ice.^{2,3} Hydrophilic supports, on the other hand, exert a certain template effect on the water molecules and may induce the formation of ordered adsorption patterns. If the surface lattice deviates considerably from the intrinsic dimensions of the hydrogen-bonded network, ordering may be impeded, and water condenses into amorphous films.⁴ The formation of amorphous solid water, termed ASW in the following, also arises from kinetic effects, e.g., if individual molecules are unable to reach their equilibrium arrangement despite a favorable energetic situation. In this case, gentle annealing may induce the ice transition. Hydrophilicity is observed for many oxide surfaces, where both the cationic and anionic surface species are able to attract the water molecules.^{5,6}

The exploration of water crystallization phenomena has a long tradition and started already in the late 1970s.^{7,8} Back then, the sharpening and redshift of characteristic vibrational bands were taken as fingerprints of the transition from ASW to ice. The main vibrational modes, being followed across the ice transition, are the OH stretching, bending and libration modes. Their energetic position is readily detected with Raman and/or Fourier-transformed infrared-reflection absorption spectroscopy (FTIR). Assignment of the bands to specific inter-

intramolecular H₂O vibrations is, however, intricate and the subject of ongoing theoretical efforts.^{9–11} Also the molecular mechanisms behind the crystallization process are still in the focus of research.^{12,13} With the advent of scanning tunneling microscopy (STM), ordering effects in H₂O layers became accessible to real-space experiments.^{2,4} Ordered water structures were found on many metal and oxide supports, such as Pd(100), Ru(0001), FeO_x, and CaO(100).^{14–16} On Pt(111), dewetting phenomena and the development of ice clusters have been detected with molecular resolution, providing evidence for hydrophobic water–support interactions.^{17,18}

In this study, we examine the adsorption of water (D_2O) to crystalline Cu₂O films. Cuprous oxide has recently attracted much attention, because favorable optical properties make it interesting for photocatalytic and photovoltaic applications.¹⁹ In contrast to other photoactive materials, e.g., ZnO and TiO₂, it has a reduced band gap of 2.15 eV and is able to harvest a much larger fraction of the solar radiation on earth. Moreover, its electronic structure makes it suitable for photoinduced water splitting and promotes the hydrogen-evolution reaction. Our group has recently developed a thin-film model system for Cu₂O(111), prepared by reactive Cu deposition on an Au(111) single crystal.²⁰ Its surface shows long-range hexagonal order with 6 Å periodicity and is likely Cu-deficient. STM measurements revealed the development of quasi-amorphous water ad-layers upon D₂O exposure at 90 K and subsequent

Received:November 2, 2017Revised:December 18, 2017Published:January 3, 2018

annealing.²¹ In this work, we complement this information with FTIR and thermal desorption (TDS) data and compare the D_2O adsorption to $Cu_2O(111)$ and Au(111) surfaces. Although water binding is weak in both cases, the character of the emerging water layers is rather different. Whereas Cu_2O features hydrophilic properties, gold acts as a hydrophobic support.

2. EXPERIMENTAL METHODS

The experiments have been carried out in two UHV chambers, equipped with a custom-built Beetle-type STM, TDS, and lowenergy electron diffraction (LEED) in one case, and with a Bruker IFS 66v/S infrared spectrometer, TDS, and LEED in the other. The comparability of sample preparation in both chambers was proven by matching LEED and TDS results, while STM and FTIR were available as complementary methods. Temperature control of the sample during TDS and FTIR measurements was realized by direct current heating in conjunction with LN₂ cooling. The TDS heating rate was set to 3 K/s. The STM images were taken in the constant current mode at 90 K.

Cu₂O films of 3 ML thickness were prepared by Cu deposition from an e-beam evaporator in 5×10^{-6} mbar O₂, followed by 600 K annealing at UHV conditions. The crystallinity of the oxide layer was shown by a sharp (2 × 2) LEED pattern with respect to the Au(111) support.²⁰ The adsorption studies were performed with laboratory grade D₂O, dosed at 90 K onto the surface. In flashing experiments, the sample was heated to a preset temperature and cooled back to 90 K prior to data acquisition. The samples for STM have always been flashed to 150 K to remove water multilayers.

3. RESULTS

3.1. D₂O on Cu₂O(111). Figure 1 displays STM topographic images of the Cu₂O/Au(111) thin film exposed to increasing amounts of water. The hexagonal structure of the oxide surface with 6 Å periodicity is clearly discernible. According to DFT calculations, the bright pattern is produced either by the 4s dangling-bond states of unsaturated Cu_{Cus} ions in the stoichiometric surface, or by upward-buckled O_{cus} ions on Cu-deficient films.²² Our films are likely nonstoichiometric and oxygen-terminated, as $\mathrm{Cu}_{\mathrm{Cus}}$ ions turned out to be thermodynamically unstable in ultrathin films. Further information on the Cu₂O/Au(111) system can be found in earlier publications.^{20,22} At low D₂O coverage, isolated water clusters are observed that nucleate at defect lines and step edges of the Cu₂O surface (Figure 1a). With increasing exposure, they evolve to monolayer-high islands that seem disordered at first glance (Figures 1b,c). Closer inspection reveals, however, a distinct short-range order of the D₂O molecules that follows the hexagonal $\tilde{Cu}_2O(111)$ lattice.²¹ Evidently, the cuprous oxide exerts a weak, yet discernible template effect on the adwater. TDS measurements corroborate our STM data (Figure 1d). At low D_2O exposure, a desorption peak becomes visible at 170 K, originating from the water monolayer seen in STM. At higher dosing, multilayers of ASW condensed on the Cu2O surface give rise to a prominent maximum at 155 K. This lowtemperature desorption is of zero-order and characteristic for physisorbed water.^{1,23}

Further information on the D_2O/Cu_2O adsorption system comes from FTIR. The coverage-dependent spectra in Figure 2a display three maxima, a sharp peak at 2730 cm⁻¹, and two



Figure 1. (a–c) STM topographic images of Cu₂O/Au(111) thin films covered with increasing amounts of D₂O (1.0 V, 10 pA, 25 × 25 nm²). Isolated water clusters, as detected at low coverage (a), evolve to amorphous islands of monolayer height at continued dosing (b,c). (d) Thermal desorption spectra of D₂O bound to thin Cu₂O films (orange) and Au(111) (black). The faint 170 K shoulder in the Cu₂O spectrum arises from interfacial water with slightly enhanced adhesion (broken line).



Figure 2. FTIR spectra of D_2O on $Cu_2O/Au(111)$ taken as a function of (a) coverage and (b) temperature. Three water related bands are discernible at 2730 cm⁻¹ (free-OD stretch), 2540 cm⁻¹ (bound-OD stretch), and 1210 cm⁻¹ (D_2O bending). Intensity around 2100 cm⁻¹ results from residual CO bound to the surface.²⁵ (c,d) Identical measurements for D_2O on bare Au(111). Note the sharpening (in b) and the sharpening plus redshift (in d) of the broad 2540 cm⁻¹ band due to structural reorganization in the water ad-layer upon annealing.

broad bands at about 2540 and 1210 cm⁻¹, respectively (Table 1). Whereas the former matches the frequency of the free-OD stretch mode, the latter are typical for bound-OD stretch and D₂O bending modes. The large width of the central peak is caused by the overlap of multiple vibrational bands and

Table	1. C	ompilation	of Freq	uencies	and	Intensities	of	the
Main I	O_2O	Vibrational	l Bands	Detecte	d in	FTIR ⁴		

bound-OD [cm ⁻¹]											
dosage/ temperature	free- OD [cm ⁻¹]	symmetric	asymmetric	$\begin{array}{c} D_2O\\ \text{bending}\\ [\text{cm}^{\text{-1}}] \end{array}$	area ratio free/bound OD						
$Cu_2O(111)$											
0.5 ML, 90 K	2730	2350-2550			0.14						
1.5 ML, 90 K	2730	2540		1210	0.02						
1.5 ML, 140 K	2730	2476	2554	1210	0.015						
1.5 ML, 150 K	2730	2469	2556	1210	0.02						
1.5 ML, 155 K	2730	-		1210	0.09						
Au(111)											
0.5 ML, 90 K	2730	2530		1220	0.03						
3 ML, 90 K	2730	2530		1210	0.02						
3 ML, 140 K	2730	2465	2551	1230	0.007						
3 ML, 150 K	2730	2436	2486	1240	0.009						
Reference 30											
D ₂ O, gas		2672	2788	1178							
D ₂ O, liquid		2407	2476	1206							
a			- · ·								

^{*a*}The area ratio of free and bound-OD peaks is determined by integrating the intensity course between 2710-2740 and 2400-2700 cm⁻¹, respectively.

indicative for various OD-O binding lengths and angles in the amorphous water layer. It therefore corroborates the low structural order of the D₂O monolayer, seen in the STM data before. Moreover, the development of a broad 2540 cm⁻¹ band already at lowest exposure points to the absence of distinct D₂O adsorption sites, in agreement with an oxygen-terminated $Cu_2O(111)$ surface.²⁴ At continued dosing, all three peaks grow in intensity without changing their energy position and width. Apparently, the disordered nature of the interfacial water is maintained in subsequent layers. However, the relative weight of the peaks changes, and in particular the area ratio between free (2730 cm^{-1}) and bound-OD peaks (2540 cm^{-1}) decreases by a factor of 7 when rising the D_2O coverage to 3 ML. No quantitative conclusions can be drawn from this intensity evolution, as both number and orientation of the D₂O species (only perpendicular vibrational components are detected) govern the IR dipole strength. However, a decreasing free-OD peak suggests fewer molecules having an OD bond vibrating freely along the surface normal, which is compatible with a gradual embedding of the initial D₂O molecules into a hydrogen-bonded network. In short, the FTIR spectra reflect the development of an ASW film on the cuprous oxide surface.

The desorption behavior of D_2O has been probed by stepwise annealing the sample to elevated temperature and acquiring FTIR spectra after cooling back to 90 K. A spectral series taken across the D_2O desorption peak is shown in Figure 2b. As expected, the integral intensity decreases steeply above 150 K, the onset temperature of water desorption, and has lost more than 90% of its initial magnitude at 155 K. In addition, the broad band centered at 2540 cm⁻¹ sharpens across the temperature ramp and develops two distinct maxima at 2469 and 2556 cm⁻¹ (Table 1). These modes can be assigned to the lower symmetric and the higher asymmetric OD frequency, as the main sub-bands of the bound-OD stretch vibrations.¹⁰ The sharpening of the bands provides evidence for a partial ordering of the water layer, triggered by a thermally stimulated reorganization of the hydrogen-bonded network.¹³ However, the D₂O does not crystallize upon annealing, as almost no redshift of the vibrational modes is revealed. Such a redshift that might be as large as 100 cm⁻¹ for the bound-OD mode is, however, representative for the ice transition.^{4,12,13} Crystallization of water seems thus impeded on the Cu₂O surface at temperatures below D₂O desorption. Moreover, the area ratio between free- and bound-OD modes increases again, reversing the trend observed upon adsorption (Table 1). Apparently, the residual molecules remain in a 2D network with a finite number of upright OD bonds and do not condense into 3D clusters, as this would cause the peak ratio to decrease in the desorption process.

3.2. D_2O on Au(111). To identify peculiarities in the water adsorption behavior on cuprous oxide, similar data has been acquired on bare Au(111) that serves as substrate for oxide growth. The comparison with Cu₂O spectra is meaningful at this point, as gold exhibits similar coupling strength to water according to TDS (Figure 1d). Also on Au(111), the most prominent TDS peak lies at 155 K and is assigned to ASW desorbing from the surface. However, the faint 170 K shoulder observed for Cu₂O is missing in the gold spectra, as interfacial water does not experience enhanced adhesion to the metal surface.

Despite differences in the TDS data, the FTIR signatures of water bound to $Cu_2O(111)$ and Au(111) surfaces are surprisingly similar (Figure 2). In fact, spectra taken at increasing exposure are nearly indistinguishable. The spectra on gold are governed by a sharp free-OD line at 2730 cm⁻¹ and broad absorption maxima at 2530 and 1210 cm⁻¹, assigned to bound-OD stretch and D_2O bending modes, respectively (Table 1). The large width of the central band indicates low structural order in the water layer again and proves the development of ASW also on Au(111). In contrast to the Cu₂O surface, the area ratio between free and bound-OD stretch vibrations is generally low and does not change during adsorption (Table 1).

Further differences are observed in temperature-controlled FTIR spectra, as shown in Figure 2d. As on Cu₂O, the overall spectral intensity diminishes drastically across the water desorption peak. The process is accompanied by a sharpening of the broad central band that splits into 2436 and 2486 cm⁻¹ modes for the symmetric and asymmetric OD stretch vibrations, respectively. In contrast to the Cu₂O case, the bands undergo a pronounced redshift upon annealing, suggesting that the ad-water not only improves structural order but transforms to crystalline ice. The observed redshift of the bound-OD frequencies results from enhanced inter- with respect to intramolecular coupling in the D₂O network. Another hint for D₂O crystallization on Au(111) at 150 K comes from an almost complete suppression of the free-OD peak, despite large residual intensity in the bound-OD region (Table 1). Evidently, almost all low-coordinated water molecules have disappeared from the surface, as water condenses into large 3D ice clusters with low surface to volume ratio. The different trends in the annealing behavior of ASW on $Cu_2O(111)$ and Au(111) are rationalized in the final paragraph of our paper.

The Journal of Physical Chemistry C

4. DISCUSSION

As presented above, ASW layers develop on both thin-film $Cu_2O(111)$ and metallic Au(111) surfaces upon water dosing at low temperature. In the case of $Cu_2O(111)$, we have recently assigned this behavior to a nonstoichiometric and oxygen-rich surface termination that lacks low-coordinated Cu_{Cus} ions.²¹ The latter would allow for strong covalent bonding of D₂O, whereas only weak hydrogen interactions are present in the absence of Cu_{cus} , ions according to theory.²⁴ In fact, the oxygen-terminated Cu₂O surface is neither able to dissociate incoming water molecules nor to trigger their long-range ordering, in agreement with our experimental results. Also, the 3 Å periodicity of the oxygen sublattice in $Cu_2O(111)$ impedes the formation of a regular hydrogen-bonded network. Molecular interaction lengths in fully relaxed water layers amount to 2.4-2.8 Å; 0.8 Å for the O-D bond inside the molecule and 1.6-2.0 Å for the hydrogen bond to its neighbor.^{2,4} On $Cu_2O(111)$, this spacing needs to be increased by about 20% in order to reach registry at the water-oxide interface. Both factors, the weak adhesion and the unfavorable lattice match are responsible for ASW formation on Cudeficient $Cu_2O(111)$ already in the monolayer limit. Note that water binding to O-terminated cuprous oxide is also compatible with a relatively strong free-OD vibrational band as compared to the one on Au(111) at similar coverage. The respective molecules likely bind in a D-down configuration to the oxide O_{cus} ions and possess an OD bond pointing toward the vacuum, a geometry that was confirmed by DFT calculations.²⁴

Water adsorption to closed-packed Au(111), on the other hand, is entirely governed by physisorptive interaction schemes, mostly van-der-Waals coupling. Main reasons are the high electronegativity and the delocalized electronic structure of gold that repels the water-oxygen and inhibits formation of localized bonds to the D₂O molecules. As a consequence, Au(111) promotes the formation of ASW, although crystalline water structures have been found on more electropositive *d*metals, e.g., Ru(0001) and Cu(111).² Also, the low area ratio between free and bound-OD stretch vibrations observed for Au(111) is compatible with a mainly physisorptive interaction scheme, in which the molecules lie flat in order to maximize their van-der-Waals bonding.

Although formation of ASW has been found on both $Cu_2O(111)$ and Au(111), the water desorption behavior is distinctively different on the two supports. While on the oxide film, the water layer only partially reorganizes upon annealing, dewetting and crystallization is observed on gold. The latter conclusion is drawn from the sharpening and redshift of vibrational bands in the bound-OD region (2530 cm^{-1}), but can be derived also from real-space STM data. A respective image is depicted in Figure 3 and shows a mixed Cu₂O-Au(111) surface after water adsorption and annealing close to the desorption temperature. The bare Au(111), clearly recognizable by the herringbone reconstruction, holds only few 3D ice clusters that typically attach to the elbows of the reconstruction (Figure 3, inset).²⁶ Conversely, the neighboring Cu₂O regions are still covered by ASW and show no signs of dewetting and crystallization. Note that STM is unable to resolve the small structural changes in the ASW films during annealing, even if those are obvious in the FTIR data.

The pronounced difference in water desorption can be boiled down to the hydrophilic versus hydrophobic nature of the two model systems. Despite weak overall adhesion, $Cu_2O(111)$



Figure 3. STM image of D_2O bound to $Cu_2O-Au(111)$ after flashing to 155 K (1 V, 10 pA, 150 × 150 nm²). While the D_2O monolayer remains intact on the oxide surface, dewetting and formation of 3D ice clusters occurs on the metal. The inset shows preferential D_2O nucleation at elbows of the Au herringbone reconstruction (35 × 35 nm²).

shows clear signs of hydrophilicity as the water remains bound to the surface up to the desorption temperature. Au(111), on the other hand, is hydrophobic, as actual water desorption is preceded by a dewetting step. While the hydrophilicity of $Cu_2O(111)$ arises from hydrogen bonding between the surface-oxygen and the water-hydrogen, the hydrophobicity of Au(111) mainly relates to repulsive forces between water-oxygen and the electronegative gold. Similar differences have been observed for other systems,²⁷ e.g., bare versus mica-covered Pt(111),⁴ and stoichiometric versus hydroxylated MgO.²⁸ Whereas oxygenterminated surfaces often feature hydrophilic properties,²⁹ most metals are hydrophobic and promote the formation of 3D ice clusters.^{3,18}

5. CONCLUSIONS

The adsorption behavior of D_2O to $Cu_2O(111)$ and metallic Au(111) has been compared at the molecular level. Layers of ASW develop on both surfaces at 90 K, as demonstrated by characteristic FTIR spectra and STM data. For the D₂O/Cu₂O system, a high-temperature shoulder in TDS reflects the formation of interfacial water with enhanced adhesion. This layer is unable to undergo structural ordering upon annealing even close to the desorption temperature of 170 K. By contrast, the ASW on Au(111) dewets and condenses into ice clusters from which desorption takes place. The deviating desorption schemes reflect the hydrophilic versus hydrophobic nature of oxide and metal surfaces, respectively, whereby the hydrophilicity of Cu₂O(111) arises from an efficient hydrogen bonding of water to the surface O ions. Further experiments will explore whether water binding to cuprous oxide can be tailored by preparing Cu-rich instead of O-rich surface terminations. In this case, much higher desorption temperatures and the development of crystalline water layers would be expected.

AUTHOR INFORMATION

Corresponding Author

*E-mail: niklas.nilius@uni-oldenburg.de; phone +49-441-798-3152.

ORCID 💿

S. Shaikhutdinov: 0000-0001-9612-9949

H. J. Freund: 0000-0001-5188-852X

N. Nilius: 0000-0003-0264-120X

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for financial support via the DFG grant 'Photocatalytic processes probed at the atomic scale'. F.S. thanks the FAPERJ and the CNPq for financial support.

REFERENCES

(1) Henderson, M. A. Interaction of Water with Solid Surfaces: Fundamental Aspects. *Surf. Sci. Rep.* **2002**, *46*, 1–308.

(2) Hodgson, A.; Haq, S. Water Adsorption and the Wetting of Metal Surfaces. *Surf. Sci. Rep.* **2009**, *64*, 381–451.

(3) Carrasco, J.; Santra, B.; Klimes, J.; Michaelides, A. To Wet or Not to Wet? Dispersion Forces Tip the Balance for Water Ice on Metals. *Phys. Rev. Lett.* **2011**, *106*, 026101.

(4) Verdaguer, A.; Sacha, G. M.; Bluhm, H.; Salmeron, M. Molecular Structure of Water at Interfaces: Wetting at the Nanometer Scale. *Chem. Rev.* **2006**, *106*, 1478–1510.

(5) Cappus, D.; Xu, C.; Ehrlich, D.; Dillmann, B.; Ventrice, C.A.; Al Shamery, K.; Kuhlenbeck, H.; Freund, H.-J. Hydroxyl Groups on Oxide Surfaces: NiO(100), NiO(111) and $Cr_2O_3(111)$. *Chem. Phys.* **1993**, 177, 533–546.

(6) Mirabella, F.; Zaki, E.; Ivars-Barcelo, F.; Li, X.; Paier, J.; Sauer, J.; Shaikhutdinov, S.; Freund, H.-J. Cooperative Formation of Long-Range Ordering in Water Ad-Layers on $Fe_3O_4(111)$. *Angew. Chem., Int. Ed.* **2018**, DOI: 10.1002/anie.201711890.

(7) Hagen, W.; Tielens, A. G.; Greenberg, J. M. The Infrared Spectra of Amorphous Solid Water and Ice Ic between 10 and 140 K. *Chem. Phys.* **1981**, *56*, 367–379.

(8) Sivakumar, T. C.; Schuh, D.; Sceats, M. G.; Rice, S. A. The 2500–4000 cm⁻¹ Raman and Infrared Spectra of Low Density Amorphous Solid Water and Polycrystalline Ice I. *Chem. Phys. Lett.* **1977**, *48*, 212–218.

(9) Buch, V.; Devlin, J. P. A New Interpretation of the OH-Stretch Spectrum of Ice. J. Chem. Phys. **1999**, 110, 3437–3443.

(10) Li, F.; Skinner, J. L. Infrared and Raman Line Shapes for Ice Ih. II. H₂O and D₂O. *J. Chem. Phys.* **2010**, *133*, 244504.

(11) Bakker, H. J.; Skinner, J. L. Vibrational Spectroscopy as a Probe of Structure and Dynamics in Liquid Water. *Chem. Rev.* **2010**, *110*, 1498–1517.

(12) Backus, E. H. G.; Grecea, M. L.; Kleyn, A. W.; Bonn, M. Surface Crystallization of Amorphous Solid Water. *Phys. Rev. Lett.* **2004**, *92*, 236101.

(13) Shephard, J. J.; Evans, J. S. O.; Salzmann, C. G. Structural Relaxation of Low-Density Amorphous Ice upon Thermal Annealing. *J. Phys. Chem. Lett.* **2013**, *4*, 3672–3676.

(14) Maier, S.; Lechner, B. J.; Somorjai, G. A.; Salmeron, M. Growth and Structure of the First Layers of Ice on Ru(0001) and Pt(111). *J. Am. Chem. Soc.* **2016**, *138*, 3145–3151.

(15) Parkinson, G. S. Iron Oxide Surfaces. Surf. Sci. Rep. 2016, 71, 272–365.

(16) Zhao, X.; Shao, X.; Fujimori, Y.; Bhattacharya, S.; Ghiringhelli, L. M.; Freund, H. J.; Sterrer, M.; Nilius, N.; Levchenko, S. V. Formation of Water Chains on CaO(001): What Drives the 1D Growth? J. Phys. Chem. Lett. **2015**, *6*, 1204–1208.

(17) Morgenstern, M.; Müller, J.; Michely, T.; Comsa, G. The Ice Bilayer on Pt(111): Nucleation, Structure and Melting. *Z. Phys. Chem.* **1997**, *198*, 43–72.

(18) Michaelides, A.; Morgenstern, K. Ice Nanoclusters at Hydrophobic Metal Surfaces. *Nat. Mater.* 2007, *6*, 597–601.

(19) Meyer, B. K.; Polity, A.; Reppin, D.; Becker, M.; Hering, P.; Klar, P. J.; Sander, T.; Reindl, C.; Benz, J.; Eickhoff, M.; et al. Binary Copper Oxide Semiconductors: From Materials towards Devices. *Phys. Status Solidi B* **2012**, *249*, 1487–1509. (20) Sträter, H.; Fedderwitz, H.; Groß, B.; Nilius, N. Growth and Surface Properties of Cuprous Oxide Films on Au(111). *J. Phys. Chem.* C 2015, *119*, 5975–5981.

(21) Möller, C.; Nilius, N. Water Adsorption on Cu₂O(111) Surfaces: A STM Study. J. Phys. Chem. C 2017, 121, 20877–20881.

(22) Nilius, N.; Fedderwitz, H.; Groß, B.; Goniakowski, J.; Noguera, C. Incorrect DFT- GGA Predictions of the Stability of Non-Stoichiometric/Polar Dielectric Surfaces. *Phys. Chem. Chem. Phys.* **2016**, *18*, 6729–6733.

(23) Henderson, M. An HREELS and TPD Study of Water on $TiO_2(110)$: The Extent of Molecular versus Dissociative Adsorption. Surf. Sci. **1996**, 355, 151–166.

(24) Riplinger, C.; Carter, E. A. Cooperative Effects in Water Binding to Cuprous Oxide Surfaces. J. Phys. Chem. C 2015, 119, 9311–9323.

(25) The FTIR feature at ~ 2120 cm⁻¹ is assigned to CO adsorption from the rest gas. CO quickly populates suitable binding sites on Cu₂O and therefore contributes already to reference spectra of the bare sample. Upon water exposure, D₂O replaces the weakly bound CO and respective bands show up as negative absorption.

(26) Gawronski, H.; Morgenstern, K.; Rieder, K. H. Electronic Excitation of Ice Monomers on Au(111) by Scanning Tunneling Microscopy: Vibrational Spectra and Induced Processes. *Eur. Phys. J. D* 2005, 35, 349–353.

(27) Dohnálek, Z.; Ciolli, R. L.; Kimmel, G. a.; Stevenson, K. P.; Smith, R. S.; Kay, B. D. Substrate Induced Crystallization of Amorphous Solid Water at Low Temperatures. *J. Chem. Phys.* **1999**, *110*, 5489.

(28) Fujimori, Y.; Zhao, X.; Shao, X.; Levchenko, S. V.; Nilius, N.; Sterrer, M.; Freund, H. J. Interaction of Water with the CaO(001) Surface. J. Phys. Chem. C 2016, 120, 5565–5576.

(29) Henderson, M.; Chambers, S. HREELS, TPD and XPS Study of the Interaction of Water with the $Cr_2O_3(001)$ Surface. *Surf. Sci.* 2000, 449, 135–150.

(30) Pang, X. F. Water: Molecular Structure and Properties, World Scientific: Hackensack, NJ, 2014.