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Atomic Structure and Bonding of Water Overlayer on Cu(110): The Borderline for Intact and Dissociative Adsorption

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Water overlayer structure on single-crystal surfaces has been a source for long-time debate because of its immense importance in various areas, such as catalysis, corrosion, electrolysis, fuel cells, and biotechnologies.[1,2] Among all controversies, the most intriguing is whether water molecules are intact or dissociated. Recently, the general belief that water adsorbs molecularly and forms intact bilayers resembling bulk ice on precious metal surfaces has encountered great challenges from low energy electron diffraction (LEED),[3] X-ray photoelectron spectroscopy (XPS),[4] and theoretical studies.[5] On the basis of the coplanar geometry in LEED and the density functional theory (DFT) calculation, Feibelman proposed a new structural model in which water binds Ru(0001) through intact and partially dissociated water molecules alternatively.[5] Later studies argue that water dissociation is an activated process and assign the dissociated overlayer due to beam damage.[6] Although water/Ru is still under active debate, there are less studies of water on open surfaces, such as Cu(110), which is believed to be another borderline for water dissociation.[1] On Cu(110), the LEED pattern $c(2 \times 2)$ was commonly observed above a water coverage of 0.15 monolayers (ML) (1 ML refers to one water per surface Cu atom) and was assigned to hydrogen bond network formation[7−10] and/or dissociation by irradiation.[11] Parallel chain structure separated by ∼50 Å and a 2D overlayer have also been observed recently,[11] where water may have different adsorption sites. Contradicting results were reported in recent XPS studies: Ammon et al. found that partial dissociation of D_2O in $c(2 \times 2)$ occurs at 95 K,[10] while Andersson et al. reported no dissociation below 150 K.[12] In addition, the atomic structure of H_2O and the $OH + H_2O$ layer, such as the adsorption site, proton disorder, and water orientation, is far from conclusive in the literature. In this work, by carefully comparing the calculated and measured work function data, energetics, and vibration spectroscopy, we determine explicitly the water structure in $c(2 \times 2)$ on Cu(110) to be the intact water overlayer with a majority component of H-down bilayer in low temperature experiments. Water dissociation is accessible by heating or illumination, resulting in a sensitive change in electron density at the surface and could be monitored by work function measurement. This lays down the foundation of the water structure on an important surface: Cu(110).

Our study is based on state-of-the-art ab initio calculations in the framework of DFT. We use a projector-augmented plane waves method and the PBE exchange-correlation functional as implemented in VASP code.[13] The supercell consists of six layers of Cu atoms in the [110] direction and a vacuum layer exceeding 23 Å. The water molecules are placed on one side of the slab in $c(2 \times 2)$ periodicity. Proton disorder results in only a minor energy difference of <0.02 eV/H_2O. A plane wave cutoff of 400 eV and k-point mesh of $(2 \times 2 \times 1)$ are used. The bottom three layers of Cu substrate are fixed at their respective bulk positions, while all other atoms and water molecules are allowed to fully relax until forces on them are less than 0.05 eV/Å. Reaction barriers are calculated using the nudged elastic band method. The calculated lattice constant of 3.6349 Å for bulk Cu is used, which compares well to the experimental value of 3.6149 Å.

A single water molecule binds on the top site lying flat, with a Cu−O bond length of 2.18 Å and adsorption energy of 0.375 eV. Water diffuses easily along both [110] (barrier: 0.12 eV) and [001] directions (0.23 eV), which favors cluster formation even at low temperature. On the other hand, dissociation of a single H_2O is not possible due to the high barrier of 0.94 eV, though dissociation is exothermic by 0.40 eV. After dissociation, OH relocates to a bridge site with a binding energy of 3.69 eV and H in the groove with an energy of 2.37 eV. The energy gain is enough to break an OH bond with an energy of 5.21 eV. These results clarify earlier speculations of water adsorption on hollow[7] or bridge sites.[8]

At the coverage of 1 ML, water could form an ice bilayer, which is a puckered hexagonal network with one OH in every two waters pointing to (H-down, Figure 1a) or away from the surface (H-up). Once this OH bond breaks, it forms the half-dissociated overlayer as Feibelman proposed (Figure 1c). The dissociated H resides on a 4-fold site in the groove. Our calculation shows that the H-down bilayer is more stable than H-up. However, the adsorption energies of H-down (0.554 eV/H_2O) and H-up bilayers (0.514 eV/H_2O) are both significantly lower than that of the dissociated layer (0.632 eV/H_2O), similar to that on Ru(0001).[5] The vertical OO distance in the half-dissociated layer is 0.10 Å, much smaller than that of H-down (0.38 Å) and H-up (0.76 Å). In addition, top site adsorption is preferred for both H_2O and $OH + H_2O$ layers, which is at least 0.07 eV/H_2O more favorable than the bridge site. This rules out most of the structural models assumed previously.[9,14]

To determine the real structure observed in experiments, we calculated the work function change, $\Delta\Phi$, upon adsorption in Table 1. A decrease of work function for intact adsorption and an increase for the dissociated layer is observed. Compared to experiments,[7−9] this strongly suggests intact adsorption over dissociation. Furthermore, $\Delta\Phi = -0.8$ eV for the H-down bilayer is the closest to the experimental value, indicating the majority of H-down bilayer in the experiment. Because $\Delta\Phi$ is a surface average quantity, we infer that a mixture of H-up:H-down = 1:13 to 1:23 could reproduce experimentally measured values. This idea is verified by $\Delta\Phi$ being equal to the average for a mixed bilayer of H-up:H-down = 1:1 (Table 1).

One might argue a mixture of H-up and a half-dissociated layer could also exist. However, it is ruled out by our kinetic considerations. Although energetically favorable, the dissociated layer is blocked at low temperature by a barrier no less than 0.57 eV. Two dissociation pathways are identified, in which the one involving the H residing on the bridge site along [110] in the transition state is preferred (path A, Figure 1a). This barrier agrees with experimental value of 0.53−0.56 eV very well.[12] Additional water lowers

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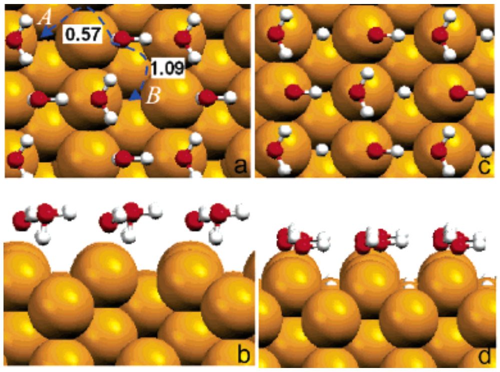

Figure 1. Atomic structure of the intact (a, b) and dissociated water overlayer (c, d) on Cu(110). Shown in both top and side views. Dashed lines and numbers indicate water dissociation pathway and the corresponding energy barrier (in eV).

Table 1. Work Function Change of Various Water Overlayers on Cu(110) Relative to Clean Surface

	H-down	H-up	mix (1:1)	dissociation	expt.[7−9]
$\Delta\Phi$ (eV)	−0.8	−3.6	−2.1	+1.0	−(0.92−1.0)

the dissociation barrier by maintaining specific geometries in the H-bond network that facilitate dissociation.

To understand the bonding nature between water and Cu(110), we plotted the charge density difference in Figure 2. It is clearly shown that the water−Cu interaction involves mainly O lone pairs and Cu p_z states, similar to that on Pt(111).[15] OH interacts with Cu more strongly, resulting in accumulation of a 1π orbital and depletion of Cu d_{z^2} states. This is more prominent in the one-dimensional charge density plot in Figure 2c. Integrating this curve along the surface normal z suggests 0.17e per cell transferred from water to Cu(110) for the H-down bilayer and 0.14e from Cu to adsorbate for the dissociated layer. This explains the opposite sign of $\Delta\Phi$ in Table 1.

Furthermore, the calculated vibration spectrum for the H-down bilayer agrees with experiment excellently (Figure 3). Vibration spectra are calculated through the Fourier transform of the dipole−dipole correlation function along z recorded in 2.5 ps molecular dynamics simulations. Both the peak shapes and positions of libration modes at 94 meV, HOH scissor modes at 195 meV, and OH stretch modes at 406 and 418 meV are in good agreement with experimental vibrations at 93, 200, and 411 meV at 110 K.[9] In contrast, the vibration spectrum for the dissociated overlayer is very different from experiment, for example, the OH stretch at 433 meV and librations at 122 and 111 meV. The Cu−H vibration at 154 meV is also missing. On this basis, we safely exclude the half-dissociated component in the experiment.

Our results are quite similar to that on Ru(0001).[5] Feibelman correctly predicted that half-dissociated water adlayer on Ru(0001) as energetically favorable[5] but ignored kinetic constrains that actually block water dissociation.[6,16] Despite many similarities, there are several important differences between water/Cu(110) and water/Ru(0001). (i) There are isotopic effects in structure and dissociation for water/Ru(0001),[3] while no isotopic effect was reported on Cu(110). (ii) A decease of −0.3 eV in the work function was calculated for the half-dissociated layer on Ru(0001),[5] while it increases by 1.0 eV on Cu(110). This indicates that charge transfer on Cu(110) is more sensitive during water dissociation. (iii) After dissociation, H is held at the center of hexagons and does not form separate H patches on Ru(0001), while on Cu(110), H easily diffuses away in grooves along [110] with a barrier of 0.23 eV. This provides a promising route for H_2 and O_2 separation in the thermal splitting of water.

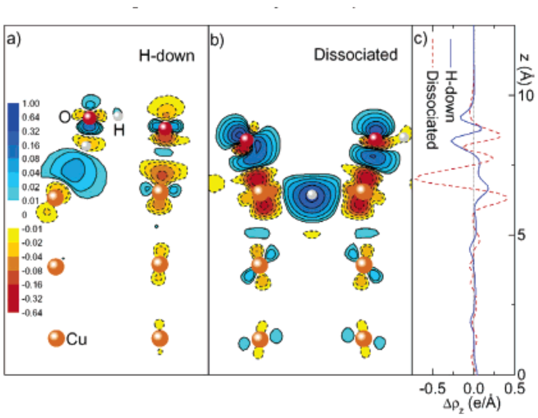

Figure 2. Contour plot of the charge density difference between the total system and that of separate substrate and adsorbate layer upon (a) intact and (b) dissociated water adsorption. Horizontal axis is the [100] direction that goes through O−O, and vertical axis is the surface normal z. (c) Planar averaged charge difference along z for the two structures.

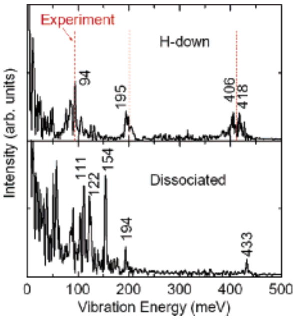

Figure 3. Calculated vibration spectra for the H-down bilayer and half-dissociated overlayer on Cu(110). Dashed lines indicate the experimental peak positions (ref 9).

In conclusion, we provide conclusive evidences for the existence of an intact bilayer on Cu(110) consisting of mainly of H-down bilayer at a temperature <160 K. Our results show that considering DFT energy alone is dangerous in determining water structures in experiment. Much attention has to be paid to the comparisons of different factors, such as work function change, kinetic barriers, and spectroscopic characters.

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