# First-principles calculations for the adsorption of water molecules on the Cu(100) surface

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First-principles density-functional theory and supercell models are employed to calculate the adsorption of water molecules on the Cu(100) surface. In agreement with the experimental observations, the calculations show that a $H_2O$ molecule prefers to bond at a onefold on-top ($T_1$) surface site with a tilted geometry. At low temperatures, rotational diffusion of the molecular axis of the water molecules around the surface normal is predicted to occur at much higher rates than lateral diffusion of the molecules. In addition, the calculated binding energy of an adsorbed water molecule on the surfaces is significantly smaller than the water sublimation energy, indicating a tendency for the formation of water clusters on the Cu(100) surface.

## I. INTRODUCTION

The adsorption of water on metal surfaces has been extensively studied for many years due to its technological importance and wide academic interest.[1–3] In recent years, there have even been some new experiments on water enhanced surface reactions of environmental importance.[4,5] One of the central issues is the microscopic understanding of the bonding and orientation characteristics of water molecules on the surfaces. While experimental and theoretical investigations have provided unified information about the bonding structure for most water-adsorbed metal surfaces, theoretical results are not always in agreement with the experimental observations. One example is the water-adsorbed Cu(100) surface.[6–13]

Copper is an important material for structural, electrical, and electronics applications. Corrosion of copper, which is a source of significant economic losses and occurs both in aqueous environments[14,15] and atmospheric air,[16,17] depends intimately on water adsorption. Adsorption of water on copper is therefore important, both from technological and basic scientific points of view. The experimental investigations for the adsorption of water on Cu(100) have been done with various techniques including ultraviolet photoemission spectroscopy, Auger electron spectroscopy, electron-energy-loss spectroscopy (EELS), and low-energy electron diffraction (LEED).[6–8,10] Water has been found to adsorb molecularly on the surface at low temperatures ($<150$ K) and to tend to form clusters. Temperature programmed desorption (TPD) measurements have shown that the desorption of water from the surface occurs at a temperature of $\sim 160$–170 K.[9,10] The EELS data of Anderson *et al.* suggested that the water molecule is bonded at the onefold on-top ($T_1$) site with its oxygen end towards the surface and its axis tilted away from the surface normal (at an estimated angle of about 60°).[6,8]

Several groups have performed theoretical calculations for the water-adsorbed Cu(100) surface using cluster models.[11–13] While these investigations have provided useful insight about the interaction between water and the surface, some of the key results are not in agreement with the experimental data. For example, while *ab initio* density-functional cluster calculations showed that the configuration with a tilted water molecule at the $T_1$ site on Cu(100) would be more stable than that with the axis of the water molecule parallel to the surface normal,[11,13] they predicted that the $T_1$ site would not be the energetically most favorable bonding site. Instead, the calculations showed that water would prefer to bond at the twofold bridge ($B_2$) site with its molecular axis parallel to the surface normal.[13] Similarly, semiempirical quantum chemical cluster calculations concluded that the adsorption of a water molecule at a fourfold hollow site $H_4$ would be energetically most favorable.[12] Both results disagree with the experimental data, which suggest a tilted geometry of water at the $T_1$ site on Cu(100).

Here we present results of total-energy density-functional calculations in which supercell models are used to simulate the Cu(100) surface. The atomic and electronic structures of the adsorbed surface, as well as the preferred bonding site and orientation of water molecules, are determined. In agreement with the experimental data, the most stable adsorption site for water molecules chemisorbed on the Cu(100) surface is determined to be the on-top $T_1$ site, and a tilted geometry of water at the on-top site with an angle of approximately 70° away from the surface normal is shown to be energetically favorable. Moreover, rotational diffusion of the water axis around the surface normal is predicted to dominate over lateral diffusion at low temperatures. In addition, the energetics of molecularly adsorbed water on the Cu(100) surface suggests a tendency for the formation of water clusters on the surface.

The remainder of this paper is organized as follows. In Sec. II we describe the computational method and the supercell models that we used. In Sec. III we present and discuss our theoretical results. Finally, in Sec. IV, we summarize the main conclusions obtained from our calculations.

## II. METHOD

On the (100) surface of an fcc metal, there are three different symmetric adsorption sites, known as fourfold hollow ($H_4$), twofold bridge ($B_2$), and onefold on-top ($T_1$) sites.[18] We studied the adsorption of water at each of the three bonding sites on Cu(100), and we also investigated the orientation of the water molecule on the surface. The Cu(100) surface was modeled by repeated slabs with seven copper layers separated by a vacuum region equivalent to nine copper layers. Each metal layer in the supercell contained nine Cu atoms (a $3 \times 3$ surface unit cell). Water was adsorbed symmetrically on both sides of the slab. All the Cu atoms were initially located at their bulk positions, with the equilibrium lattice constant of the bulk determined by our calculations. Calculations with a larger supercell containing nine copper layers showed that convergence of the binding energy of a water molecule on the Cu(100) surface for the most stable configuration with respect to the thickness of the slab was to be within 0.02 eV.

The calculations were performed within density-functional theory, using the pseudopotential method and a plane-wave basis set.[19–24] The results reported in this paper were obtained using the Vienna *ab initio* simulation package (VASP).[20–22] The exchange-correlation effects were treated with the generalized gradient-corrected exchange-correlation functionals given by Perdew and co-workers.[25,26] We adopted the Vanderbilt ultrasoft pseudopotentials supplied by Kresse and co-workers.[27,28] A plane-wave energy cutoff of 30 Ry and ten special **k** points in the irreducible part of the two-dimensional Brillouin zone of the $3 \times 3$ surface cell were used for calculating the $H_2O$-adsorbed Cu(100) surface. Test calculations with cutoff energies up to 35 Ry and with different numbers of special **k** points (6 and 10 points) obtained the binding energy of a water molecule on the Cu(100) surface for the most stable configuration within 0.01 eV. Optimization of the atomic structure was performed for each supercell via a conjugate-gradient technique using the total energy and the Hellmann-Feynman forces on the atoms.[19] All the structures were fully relaxed until the forces on all the atoms were less than 0.03 eV/Å. In this sense, the O-H bond length and the H-O-H angle of the $H_2O$ molecule were optimized.

## III. RESULTS AND DISCUSSIONS

We first present the calculated properties for bulk copper and the relaxed clean Cu(100) surface. Calculations for bulk Cu were conducted with 408 special **k** points and a cutoff energy of 30 Ry. The total energy convergence with respect to the cutoff energy (25–40 Ry) and the number of the **k** points (220–570) was within a few tenths of 1 meV per atom. We obtained lattice constants of 3.64 Å for bulk Cu, in good agreement with the experimental value of 3.61 Å.[29]

The properties of the clean Cu(100) surface were calculated using a $1 \times 1$ surface cell and 66 special **k** points in the surface Brillouin zone. All the seven copper layers except for the central one were relaxed. The surface energy of the Cu(100) surface was calculated to be 0.59 eV, and the results

TABLE I. Relaxation of the clean Cu(100) surface. $\Delta d_{ij}$ is the change of the interlayer distance, and $d_0$ is the corresponding distance in the bulk.

|  | $\Delta d_{12}/d_0$ (%) | $\Delta d_{23}/d_0$ (%) | $\Delta d_{34}/d_0$ (%) |
|---|---|---|---|
| This work | −3.4 | +1.5 | +0.2 |
| Experiment[a] | −2.8 | +1.1 | ±0.0 |

[a]Ref 30.

for the surface relaxation are shown in Table I. The surface shows an inward relaxation (approximately 0.03 Å) of the top layer and an outward relaxation (also approximately 0.03 Å) of the second layer. Our results, in good agreement with LEED measurements,[30] show relaxation of the Cu(100) surface with $\Delta d_{12}/d_0 = -3.4\%$ (contraction) and $\Delta d_{23}/d_0 = +1.5\%$ (expansion), where $\Delta d_{12}$ and $\Delta d_{23}$ are the changes in spacing between the top and the second layer and between the second and the third layer, and $d_0$ is the bulk interlayer distance.

Table II shows the calculated binding energies of a water molecule in the different configurations of the $H_2O$-adsorbed Cu(100) surface. The most stable configuration, shown in Fig. 1(a), is that with a tilted water molecule at the on-top $T_1$ site (tilted-$T_1$ configuration). The water molecule is bonded to the surface with the oxygen end toward a surface Cu atom and the molecular axis tilted away from the surface normal at an angle of 73°. The binding energy of a water molecule in this configuration is calculated to be 0.25 eV. Three metastable configurations (local energy minima) were determined from our calculations: a water molecule with its axis parallel to the surface normal at the $T_1$ [Fig. 1(b)], $B_2$ [Fig. 1(c)], and $H_4$ [Fig. 1(d)] sites, respectively. The binding energies of a water molecule in these metastable configurations are smaller by 0.08–0.21 eV than that in the tilted-$T_1$ configuration. We also optimized the structures of the tilted-$B_2$ and tilted-$H_4$ configurations (a tilted water molecule at the $B_2$ and $H_4$ sites, respectively), and found that neither was a local energy minimum. In fact, the tilted water molecule in such configurations was found to relax eventually to a nearby $T_1$ site with a tilted geometry, that is, the tilted-$T_1$ configuration [Fig. 1(a)]. We therefore conclude that water adsorbed on the Cu(100) surface prefers the $T_1$ site with its axis tilted away from the surface normal. This conclusion is in agreement with the experimental observations.

Previous theoretical studies employing cluster models also determined the preferred bonding sites of water on the Cu(100) surface, as mentioned in Sec. I. *Ab initio* DFT calculations using a 13-atom cluster for the Cu(100) surface showed that water would prefer to bond at the $B_2$ site with its

TABLE II. The binding energies (in units of eV) of the water molecule adsorbed in the different configurations on the Cu(100) surface. $\psi$ is the angle between the surface normal and the axis of the molecular water.

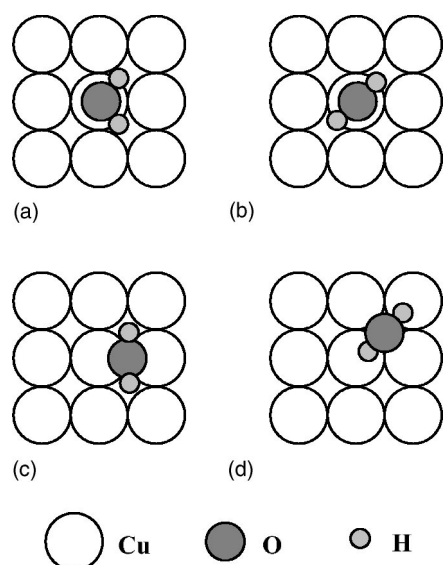| $T_1$ ($\psi$=73°) | $T_1$ ($\psi$=0°) | $B_2$ ($\psi$=0°) | $H_4$ ($\psi$=0°) |
|---|---|---|---|
| 0.25 | 0.17 | 0.14 | 0.04 |

FIG. 1. Schematics of the minimum-energy structures (top view) corresponding to the configurations with a water molecule at (a) the $T_1$ site (with a tilted geometry), (b) the $T_1$ site (without a tilted geometry), (c) the $B_2$ site (without a tilted geometry), and (d) the $H_4$ site (without a tilted geometry) on the Cu(100) surface.
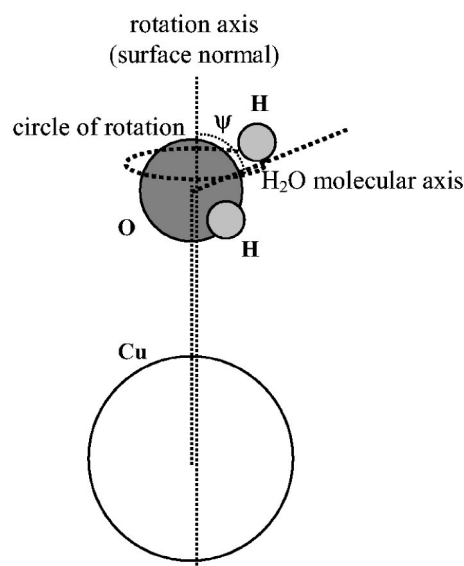


FIG. 2. Schematics of the rotation of the water molecule around the surface normal in the tilted $T_1$ configuration on the Cu(100) surface. Note that the O-Cu connecting line is slightly off (by approximately 0.03 Å) the rotation axis and rotates around it.

molecular axis normal to the surface.[13] Semiempirical quantum chemical cluster calculations with a nine-atom cluster predicted that the binding energy of a water molecule at the $H_4$ site was significantly larger than at the $T_1$ site (by approximately 0.7 eV).[12] These theoretical conclusions are inconsistent with both our *ab initio* supercell calculations and the experimental data. The main problem is that the previous calculations were limited to small clusters, containing only up to 13 metal atoms. In contrast to semiconductors, metals are often poorly represented by small clusters.[2,31–39] Large clusters or extended surface models are usually needed to simulate real metal surfaces in order to achieve good convergence in calculations.

It interesting to note that the variation of the total energies for the tilted-$T_1$ configurations with the rotation of the water molecule around the surface normal (shown in Fig. 2)

The obtained structural parameters of the optimized geometry for the tilted-$T_1$ configuration show that the water molecule keeps essentially the same shape upon adsorption on the surface with the equilibrium O-H bond length (0.98 Å) and H-O-H angle (105.6°) slightly larger than those of a free molecule: 0.97 eV and 105.3°, respectively, determined from our calculations.[40] The experimental values[41] of the O-H bond length and H-O-H bond angle for an isolated water molecule are 0.96 Å and 104.5°, respectively. After the adsorption of a water molecule, the surface Cu atom that is bonded to oxygen is observed to shift its position up along the surface normal (by 0.08 Å) and also to have a slight in-plane shift of 0.02 Å along the direction against the $H_2O$ molecular axis. The distance between the oxygen and its bonded surface copper atom is 0.28 Å. The structural changes reflect the fact that there is a considerable (though weak) interaction between the adsorbed water molecule and the Cu(100) surface.

was determined to be less than 0.02 eV. The activation energy for rotation is thus about 0.08 eV smaller than the lateral diffusion barrier for a water molecule on the Cu(100) surface, which was estimated to be approximately 0.1 eV (with $T_1$-$B_2$-$T_1$ taken as the diffusion pathway). While there so far have been no experimental efforts to observe such rotational diffusion, these energetic considerations suggest that it should occur at much lower temperatures than lateral diffusion. Lateral diffusion at elevated temperatures has been experimentally observed for single water molecules initially adsorbed at low temperatures of about 20 K.[6] The occurrence of the rotation of the water molecule around a stiff axis on the surface is a consequence of the fact that the bonding of water with the Cu(100) surface is dominated by the oxygen lone-pair electronic orbital (see below).

Reliable theoretical values for the water sublimation energy have been obtained with *ab initio* DFT calculations.[42,43] Hamann obtained a value of 0.66 eV for the $H_2O$ ice sublimation energy,[42] while Feibelman,[43] using the same computation package VASP as we employed, obtained values of 0.67−0.72 eV for the $D_2O$ ice sublimation energy. Our calculated binding energy (0.25 eV) of $H_2O$ on Cu(100) is thus significantly smaller than the water sublimation energy. Therefore, water molecules apparently tend to form icelike clusters on the Cu(100) surface. This could occur even at low water coverages when high temperatures make the water molecules diffuse on the surface. Experimental measurements have demonstrated that water clusters were indeed formed on the Cu(100) surface.[6–8,10] In particular, only one peak was observed at a temperature of approximately 160 K in the TPD spectrum of $H_2O$ on Cu(100), indistinguishable from the ice sublimation peak.[9,10]

The calculated electronic density of states (DOS) for the clean and the $H_2O$-adsorbed Cu(100) surfaces are shown in Fig. 3. The main changes of the DOS upon the adsorption of
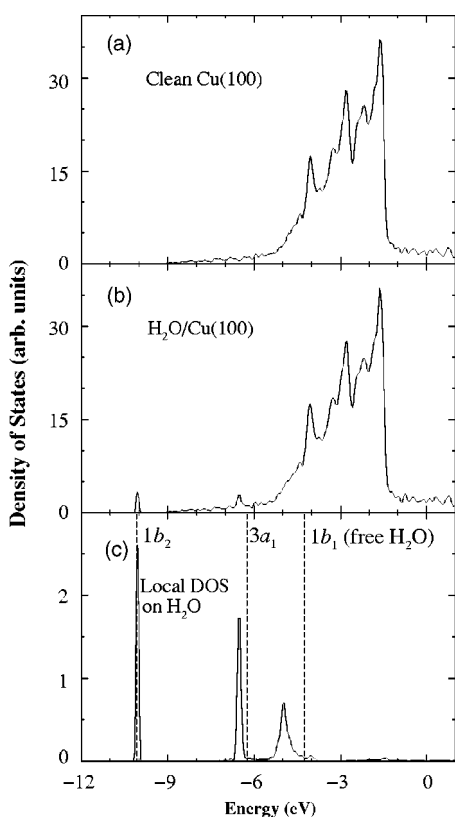
FIG. 3. Total density of states (DOS) for the clean (a) and the water-adsorbed (b) Cu(100) surfaces and local DOS on the water molecule (c) for the water-adsorbed Cu(100) surface. The Fermi level is at 0 eV. The calculated energy levels for the molecular orbitals of a free water molecule are also indicated in (c).

water are found to be in the energy region lower than about 4 eV below the Fermi level on the DOS curve. Two new peaks [Fig. 3(b)], located at $-10.07$ and $-6.52$ eV relative to the Fermi level, respectively, are clearly observed. The curve for the projected density of states (projected or local DOS) onto the water molecule [Fig. 3(c)] indicates that these two peaks correspond to the water $1b_2$ and $3a_1$ states. The highest-energy electronic state of water, that is, the $1b_1$ molecular orbital, is buried in the substrate energy band and hardly observed in the total DOS curve. However, the local DOS curve shows that its peak is located at $-4.97$ eV relative to the Fermi level [Fig. 3(c)]. Upon adsorption, the $1b_1$ and $3a_1$ orbitals of the water molecule are observed to shift down in energy by 0.72 eV and 0.29 eV, respectively, while the $1b_2$ orbital remains almost unchanged in energy level. The $1b_1$ state is also seen to be more delocalized when water

is adsorbed on the surface. These results suggest that water is bonded to the surface via the $1b_1$ state (with some contributions from the $3a_1$ state). The $1b_1$ state is primarily of oxygen $2p$ lone-pair character, and a small charge transfer from water to the copper surface is thus mostly from the oxygen $2p$ state (water is known as a Lewis base). Such a charge transfer and the resulting bonding between the $1b_1$ state and the surface would be facilitated when the $2p$ orbital is perpendicular to the surface and toward a surface atom. Therefore, a water molecule would prefer to bond via oxygen at the on-top $T_1$ site on the Cu(100) surface. Moreover, the molecular axis of water would be tilted away from the surface normal since the $1b_1$ orbital and the O-H bonding orbitals in water tend to form a quasitetrahedral geometry. Thus, the tilted-$T_1$ configuration represents the most stable structure for the water-adsorbed Cu(100) surface. In addition, rotation of the water axis around the surface normal has essentially no effects on the bonding between the $1b_1$ orbital and the surface, resulting in an very small energy cost for such a rotation. These qualitative conclusions, based on the DOS and electronic structures, are in excellent agreement with the quantitative results of the energetics discussed above.

## IV. CONCLUSIONS

The theoretical approach of supercell models combined with first-principles total-energy DFT pseudopotential methods has reproduced experimental measurements of the preferred adsorption geometry for the water-adsorbed Cu(100) surface. Very small differences in total energies among configurations with different orientations and bonding sites of the water molecule have been distinguished. It is shown that the on-top $T_1$ configuration is the most stable structure for the $H_2O$-adsorbed Cu(100) surface, and the water molecule is shown to be tilted with its axis approximately 70° away from the surface normal. The calculations also predict that rotational diffusion of the water axis around the surface normal would occur at low temperatures. In addition, water molecules are likely to form icelike clusters on the Cu(100) surface at high coverages or at high temperatures.

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⁴⁰The results for a water molecule before adsorption (free $H_2O$) were obtained by employing a supercell with the same size as that for the $H_2O/Cu(100)$ surface. Test calculations showed that the supercell was sufficiently large to provide convergent data for a free $H_2O$ molecule.

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