

## MP2 Study on Water Adsorption on Cluster Models of Cu(111)

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Received: August 27, 2003; In Final Form: October 29, 2003

Interaction energies of a water molecule with a model Cu(111) surface were investigated using the cluster model approach and high-level ab initio methods. Potential energy scans were calculated for a Cu<sub>10</sub> model cluster and a water molecule with a second-order Møller–Plesset (MP2) method using a RECP/6-31+G\* basis set and counterpoise correction (CP) for the basis set superposition error (BSSE). Different adsorption sites and water orientations were considered. A full geometry optimization for a water molecule at the on-top adsorption site of the Cu<sub>10</sub> cluster gave 77 degrees for the optimal tilt angle between the water plane and the surface normal, and non-CP interaction energy of −41 kJ/mol. Interaction energies between a Cu<sub>18</sub> model cluster and H<sub>2</sub>O were also calculated at selected points. Without the CP correction, the orientation with hydrogens parallel to the Cu<sub>18</sub> surface was the most favorable with interaction energy of −48 kJ/mol. After CP correction, the interaction was significantly weaker and the orientation with hydrogens toward the surface was the most favorable energetically for the chosen method with a CP-corrected minimum of −16 kJ/mol.

## 1. Introduction

Copper is an important transition metal, with high electrical and thermal conductivity. It is used in many industrial processes, in the pure state as sheets, tubes, rods, and wires, but also as an alloy with other metals. Electrodeposition, a process where metal ions are adsorbed on the metal surface, is used to improve material properties such as electrical conductivity or corrosion protection. Electrodeposition has applications also in the electronics industry, and can be used to form device electrical contacts and connectors.<sup>1,2</sup> A detailed understanding at the atomic level of the electrodeposition mechanism is essential for design, optimization, and control of such processes. We are currently using molecular simulations to study the dynamics and equilibrium properties of aqueous copper solutions near a solid copper surface. Key to such modeling is the interaction energy between the metal surface and the molecules and ions in aqueous media. Here we report the results of a quantum mechanical study on the interaction energy between water molecules with copper clusters representing the metal surface.

Much experimental and theoretical work has been performed on the interaction of water with transition metal surfaces. Metal–molecule interactions are usually viewed as arising from electronic  $\sigma$  donation from the ligand to the metal as well as  $\pi$  back-donation of electrons from the metal to the ligand. The balance between these two effects differs for different types of ligands, and water is an example of a pure  $\sigma$  donor molecule, without the  $\pi$  back-binding.<sup>3–6</sup> Water is also a prototypical hydrogen-bonded system. On the metal surface, water tends to form hydrogen-bonded clusters.<sup>7–9</sup> In the present study, only one water molecule is considered. Quantum chemical methods have their advantages in providing atomic-level understanding of the adsorption mechanism. There have been many studies

on the interaction between a single Cu atom<sup>3–4,10–14</sup> or Cu<sup>+</sup> ion<sup>4,15–22</sup> with a water molecule. When complexes include metallic positive ions, association arises from electrostatic interactions, whereas in complexes with neutral metal atoms the attraction is due primarily to dispersion forces<sup>4,10–11</sup> and nearly all of the interaction comes at the correlation level. A computational method that includes electron correlation is thus necessary for accurate modeling of the Cu–H<sub>2</sub>O system.<sup>4,10,13,21</sup> In addition, the basis set superposition error (BSSE) correction has a strong influence on the interaction energies.<sup>3–4,13</sup> These studies give valuable information about the nature of the Cu–H<sub>2</sub>O interaction, but the interaction of a water molecule with a metallic surface may be quite different. The surface is commonly described using a cluster model, but the cluster size has a strong influence on the adsorption energies obtained for a metal/copper surface.<sup>23–26</sup> Hu and Boyd<sup>23</sup> showed in their DFT study that adsorption energies converge very well when the cluster has more than 18 atoms. They conclude that the atom at the adsorption site should have as many coordination atoms as there are in the real surface environment, and a sufficiently large surface area. Small clusters can give larger or smaller interaction energies than those obtained from larger cluster calculations or experiment, and they may give the wrong order for the cleavage planes.<sup>23</sup> According to Balbuena et al.<sup>24</sup> the ends of the cluster, or low-coordinated atoms tend to concentrate the spin density; atoms having larger coordination numbers tend to have the highest negative charge. Many properties (dissociation energy, HOMO–LUMO gap, ionization potential) have differences between the end atoms and central ones.<sup>24</sup>

The adsorption sites and adsorbate orientations for water on a copper surface have been studied with various experimental and theoretical methods. However, studies using high-level computational methods and a realistic surface model have been very limited. The preferred water geometry and adsorption site calculated with angular-dependent Lennard-Jones potentials by

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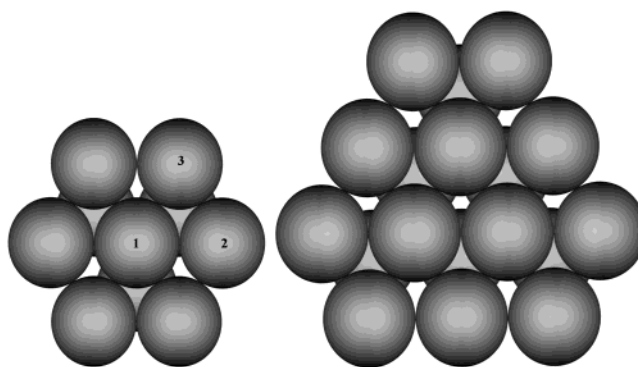
Zu and Philpott<sup>27</sup> was the oxygen toward the surface, at the on-top site (directly on a copper atom). Similar results have been found with a relatively small cluster model ( $\text{Cu}_5$ ) and the SCF-LCAO- $X\alpha$  method. In addition, the molecular plane of the water was found to prefer a tilt of 70 degrees from the normal to the surface.<sup>7</sup> The EELS experiments by Andersson et al.<sup>28</sup> predict also that the  $\text{H}_2\text{O}$  molecule is attracted via the oxygen atom to the Cu(100) surface, and the water axis is tilted from the surface by 60 degrees.<sup>28</sup> Ignaczak et al.<sup>25,29</sup> have studied water interactions with Cu(100) cluster models up to  $\text{Cu}_{12}$  using the B3LYP/LANL1MB/6-31G method. The strongest interactions found were between the oxygen atom and the on-top and bridge sites. Water adsorbed most strongly at the bridge site (between two adjacent copper atoms), with the molecular plane of water perpendicular to the surface. It adsorbed almost as strongly at the on-top site with a tilt angle of 55 degrees. In smaller models, where there are exposed terminal copper atoms, the on-top site was more favorable than the bridge site. The water conformation with hydrogens down was preferred at the 4-fold hollow site, which was the least attractive adsorption site.<sup>25,29</sup> Thiel and Madey<sup>30</sup> report the experimental energy for the molecular adsorption of the water molecule on transition metals to be in the range  $-40$  to  $-65$  kJ/mol. Moreover, they state that in general, according to both experimental and theoretical work, water adsorbs molecularly to most surfaces through the oxygen atom; hydrogen attractions are rare.<sup>30</sup>

The aim of our work was to investigate copper–water interactions in large cluster models with high-level ab initio methods.  $\text{Cu}_{10}$  and  $\text{Cu}_{18}$  cluster models of the (111) cleavage plane and their interactions with water were calculated using MP2/RECP/6-31+G\* with CP correction for BSSE. Different adsorption sites and water orientations were considered.

## 2. Theoretical Methods and Models

**2.1. Methods.** Feller et al.<sup>15</sup> tested different methods and basis sets for  $\text{Cu}^+(\text{H}_2\text{O})_n$  clusters. Results with MP2 and a medium sized basis set were in good agreement with the very larger basis sets and higher level methods (CCSD(T)). These calculations used 6-31+G\* basis set for water and a split valence RECP (relativistic effective core potential) basis set for Cu, augmented with a single set of f-type polarization functions for copper (Dolg et al.<sup>31</sup> [s, p, d] contraction plus an f function ( $\zeta = 2.7$ ) optimized for  $\text{Cu}^+(\text{H}_2\text{O})$ , (8s, 7p, 6d, 1f)  $\rightarrow$  [6s, 5p, 3d, 1f]. The RECP replaces a  $10e^-$  Ne core, leaving 19 active electrons in  $\text{Cu}^{31,32}$ ). We also chose this MP2/RECP/6-31+G\* method for our calculations. MP2 is computationally the simplest way to include correlation,<sup>33</sup> since more accurate methods, like CCSD(T), are currently unattainable for our cluster models. The calculations require substantial CPU time even at the MP2 level with the models used. For example, a single-point calculation with CP correction using a Compaq Alpha ES45 4-processor computer takes from one to two days for  $\text{Cu}_{10}$  and over two weeks for  $\text{Cu}_{18}$ . The Cu atom– $\text{H}_2\text{O}$  complex was calculated also using the CCSD(T) method for comparison purposes. The Wachters<sup>32,34,35</sup> basis set ((14s, 11p, 6d, 3f)  $\rightarrow$  [8s, 6p, 4d, 1f], f exponents from C. W. Bauschlicher et al.<sup>36</sup>) for Cu and the aug-cc-pVDZ basis set for  $\text{H}_2\text{O}$  was used with CCSD(T) method.

Basis set superposition error (BSSE) was corrected by applying the full counterpoise (CP) procedure.<sup>37</sup> BSSE is caused by the use of an incomplete basis set, and leads to an overestimation of the interaction energies. Some Cu atom– $\text{H}_2\text{O}$  studies have shown that this Cu– $\text{H}_2\text{O}$  interaction is sensitive to the BSSE, and needs to be corrected.<sup>3–4,10,13</sup> In many cases,



**Figure 1.** The  $\text{Cu}_{10}$  and  $\text{Cu}_{18}$  models (metallic radii of 1.278 Å were used for copper in the figures).

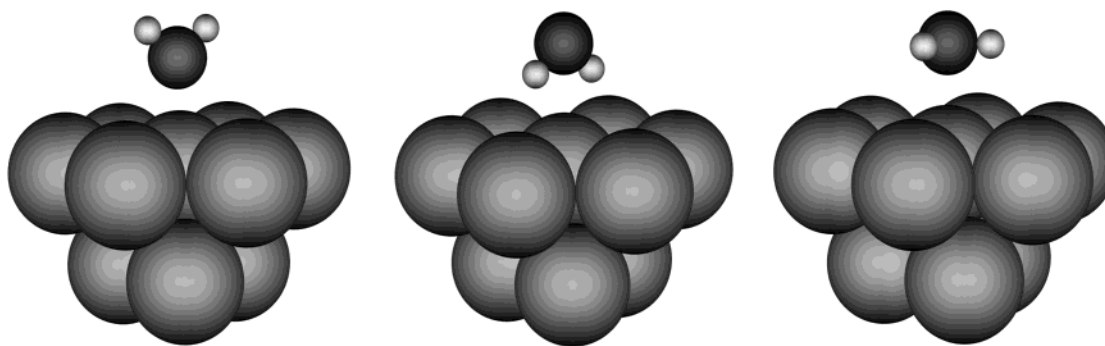
the CP correction has been shown to correct effects of small basis sets on interaction energies.<sup>38</sup> However, in some systems the correction has been reported to lead to too small interaction energies.<sup>15,39–40</sup> The basis set used for  $\text{H}_2\text{O}$  contains diffuse functions on oxygen, to reduce the size of the BSSE, but it is still large and needs to be corrected.<sup>31</sup> Basis sets that could be used without BSSE correction are too large and costly for our models.

All calculations were carried out using the *Gaussian98*<sup>41</sup> program package.

**2.2. Models.** The most studied cleavage planes for copper are the (100),<sup>8,23–24,27,29,42,45</sup> (111),<sup>8,23–24,27</sup> and (110).<sup>8–9,23,27</sup> These planes have different properties. Atomic spacing and the adsorption energies will therefore be different.<sup>23</sup> A surface atom on the (111) plane has nine coordination atoms, six beside and three below, whereas a surface atom on the (100) plane has eight neighbors, four beside and four below. Three different adsorption sites are usually considered: on-top, bridge, and hollow sites. The (111) surface has a 3-fold hollow site, whereas the (100) surface has a 4-fold hollow site.

We chose the most compact Cu(111) cleavage plane because of later practical applications, and we used  $\text{Cu}_{10}$  and  $\text{Cu}_{18}$  clusters to model the surface (Figures 1 and 2). Cluster models are often used to represent a surface when investigating certain phenomena, such as adsorption, where local effects are more important than bulk effects.<sup>24</sup> The cluster models used were constructed using the experimental value for the nearest Cu–Cu distance (2.55616 Å)<sup>43</sup> from the literature. The  $\text{Cu}_{10}$  model has seven atoms in the surface layer, and three in the lower layer (Figure 1). A  $\text{Cu}_{18}$  model (Figure 1) was also used, but only for a smaller number of surface– $\text{H}_2\text{O}$  distances, since it is computationally very expensive. The  $\text{Cu}_{18}$  model contains 12 atoms in the surface layer and six in the lower layer.

Three different adsorption sites on the Cu surface were considered. For adsorption to the on-top site, the oxygen of the water molecule is directly above the central surface copper atom (number 1 in Figure 1). At a bridge adsorption site, the oxygen atom is centered above the contact location between two copper atoms (atoms 1 and 2). At a 3-fold hollow site, the oxygen is centered above a triangle of surface copper atoms (atoms 1, 2, and 3) and directly above a Cu atom in the next layer below the surface. The on-top site at the center of the  $\text{Cu}_{10}$  model has as many neighbors (9) as there are in the bulk surface. However, the bridge and hollow sites are not so sheltered. In the  $\text{Cu}_{18}$  model, the bridge and hollow sites also are sheltered from terminal effects. Three different adsorption orientations for water were used with the three adsorption sites: (1) hydrogens up (away from the surface), (2) hydrogens down (toward the surface), and (3) hydrogens parallel to the surface. In all three



**Figure 2.** The  $\text{Cu}_{10} + \text{H}_2\text{O}$  adsorbed at an on-top site hydrogens-up, -down, and -parallel (left to right).

**TABLE 1: Interaction Energies and Cu–O Distances for Cu Atom and  $\text{H}_2\text{O}$  Molecule from This Work and from Literature (For H-up orientation the tilt angle for the  $C_s$  symmetrical structure is also presented.)**

water orientation	point group tilt angle <sup>f</sup>	method	$E$ non-CP <sup>e</sup> kJ/mol	$E$ CP <sup>e</sup> kJ/mol	BSSE kJ/mol	$R(\text{Cu}–\text{O})$ Å	ref
H-up	$C_s$ , 55.4	MP2 <sup>a</sup>	−25.93	−8.05	15.40	2.27	This work
H-up	$C_s$ , 55.4	MP2 <sup>b</sup>	−19.30	−9.40	8.90	2.24	This work
H-up	$C_s$ , 55.4	CCSD(T) <sup>b</sup>	−23.40	−12.64	9.75	2.24	This work
H-down	—	MP2 <sup>a</sup>	−2.50	−0.57	1.00	4.45	This work
H-down	—	MP2 <sup>b</sup>	−4.87	−1.81	2.68	4.02	This work
H-down	—	CCSD(T) <sup>b</sup>	−4.92	−1.72	2.82	4.01	This work
one H toward Cu	—	MP2 <sup>a</sup>	−3.22	−0.98	1.65	4.25	This work
H-up	$C_{2v}$	SA CCSD, NR <sup>c</sup>	—	−4.5	—	2.6	12
		SA CCSD, MVD <sup>d</sup>	—	−5.4	—	2.6	12
H-up	$C_{2v}$	CI	—	−34.0	—	2.3	10, 11
H-up	$C_{2v}$	SCF	−3.1	1.8	—	2.8	4
		CI (MP2)	−9.4	—	—	2.3	4
H-up	$C_{2v}$	MP2	−10.6	—	—	2.3	13
		MP4	−17.4	—	—	—	13
		Estimate	−19.3	−14.5	—	—	13
H-up	$C_s$ , 62°	DFT (GC-LDA)	−16.9	−11.6	—	2.3	3
H-up	$C_{2v}$	SCF	−3.3	—	—	2.7	5
H-up	$C_s$ , 67°	SCF-LCAO-Xα	−36.7	—	—	2.0	7

<sup>a</sup> RECP + f for Cu, 6-31+G\* for  $\text{H}_2\text{O}$ . <sup>b</sup> Wachters basis set for Cu, aug-cc-pVDZ for  $\text{H}_2\text{O}$ . <sup>c</sup> Nonrelativistic, <sup>d</sup> Quasirelativistic, includes MVD correction evaluated at the ROHF level. <sup>e</sup> CP = Counterpoise correction <sup>f</sup> Tilt angle = angle between the  $\text{H}_2\text{O}$  plane and the surface normal.

cases, the variable distance  $R$  is the perpendicular distance between the oxygen atom and the adsorption site, taken as the plane of surface copper centers.

### 3. Results and Discussion

**3.1. Cu Atom–Water Interaction.** Energies of the Cu– $\text{H}_2\text{O}$  complex were calculated using the MP2/RECP/6-31+G\* method for reference purposes in three different orientations: (1) H-up with the oxygen toward the Cu atom, (2) H-down with the hydrogens toward the Cu atom, and (3) one hydrogen toward the Cu atom. The geometries of the complexes were optimized, and the interaction energy scans as a function of Cu–O distance, were calculated with the optimal geometries. The geometry changed during optimization of orientation 1 from a planar ( $C_{2v}$ ) to a nonplanar structure ( $C_s$ ). The tilt angle (angle between the  $\text{H}_2\text{O}$  plane and the surface normal) was 55.4° after optimization, which is somewhat smaller than that reported in earlier theoretical studies<sup>3,7</sup> (see Table 1). The binding energies as well as the optimal Cu–O distances are reported in Table 1.

The H-up orientation gave the strongest binding energy. This is in agreement with previously reported results calculated with SCF-LCAO-Xα,<sup>7</sup> MP2,<sup>13</sup> CI,<sup>10</sup> CCSD,<sup>12</sup> and DFT<sup>3</sup> methods. The H-down orientation gave the weakest interaction. In the previous studies<sup>3,7,10,13</sup> interactions of Cu atoms with the water hydrogen atoms were found to be only slightly attractive. The Cu–OH<sub>2</sub> interaction energies available in the literature vary depending on the method and the inclusion of the BSSE

correction (Table 1). Our MP2 binding energy with CP correction is close to result of Neogrady et al.,<sup>12</sup> where SA CCSD method with a good basis set and CP correction gave a binding energy of about −5 kJ/mol. Our optimal Cu–O distance is in agreement with previous results with CI, MP2,<sup>4,10–11,13</sup> and DFT<sup>3</sup> study (Table 1).

Orientations 1 and 3 were also calculated using the MP2 optimized geometry and the CCSD(T) method with the Wachters basis set for Cu and the aug-cc-pVDZ basis set for  $\text{H}_2\text{O}$ . MP2 results were also obtained using these same basis sets. The CCSD(T) method gave a somewhat stronger CP corrected attraction for the H-up orientation than the MP2 method (Table 1).

**3.2. Cluster–Water Interaction.** The interaction energy scans for a  $\text{Cu}_{10}$  cluster model with a water molecule were calculated at three adsorption sites (on-top, bridge, and hollow) and three water orientations, H-up, H-down, and H-parallel (tilt angle 0°, 90°, and 180°) to the Cu surface (Table 2 and Figure 2). The  $R$  is the distance between the adsorption site, previously defined, and the water oxygen atom. The results discussed in this section do not include the CP correction.

The on-top site had the strongest attractions, the bridge site somewhat less, and the hollow site had the weakest attractions. At the on-top site of the  $\text{Cu}_{10}$  cluster, the interaction energy for the water hydrogens parallel to the surface was −38.7 kJ/mol. In general, the H-parallel and the H-down orientations were quite similar, but the H-parallel orientation was energetically more favorable at the on-top site, and the H-down orientation was



**TABLE 2: Cu<sub>10</sub> and H<sub>2</sub>O Interaction Energies and Equilibrium Distances**

	<i>E</i> non-CP (kJ/mol)	<i>R</i> <sub>eq</sub> non-CP <sup>a,b</sup> (Å)	<i>E</i> CP (kJ/mol)	<i>R</i> <sub>eq</sub> CP <sup>a,b</sup> (Å)	BSSE (kJ/mol)
On-top					
H-up	-29.83	2.26	6.64	2.8 <sup>c</sup>	28.16
H-down	-35.48	3.07	-12.42	3.62	16.96
H-parallel	-38.72	2.36	-3.36	3.26	18.19
60° tilt angle <sup>d</sup>	-39.10	2.23			
Bridge					
H-up	-23.13	2.34	3.25	2.9 <sup>c</sup>	20.45
H-down	-30.36	3.08	-11.66	3.59	14.25
H-parallel	-29.43	2.58	-7.07	3.31	14.39
Hollow					
H-up	-16.60	2.62	0.87	3.15 <sup>c</sup>	13.66
H-down	-29.20	3.15	-12.20	3.58	13.60
H-parallel	-26.46	2.71	-7.15	3.34	13.49
60° tilt angle <sup>d</sup>	-21.94	2.63	-3.13	3.42	12.01

<sup>a</sup> *R*<sub>eq</sub> is the equilibrium distance between O atom and the adsorption site in question. <sup>b</sup> CP = Counterpoise correction for BSSE. <sup>c</sup> Distance is estimated for calculating the BSSE value at approximately CP equilibrium distance also for the H-up case (which has not a potential well), to allow comparison with other orientations; these estimated distances are also used for Cu<sub>18</sub> model, see Table 3. <sup>d</sup> Tilt angle = angle between the H<sub>2</sub>O plane and the surface normal.

favorable at the hollow site. The H-up orientations were least favorable at every adsorption site.

In addition to the potential energy scans for the three water orientations, the interaction energy and optimal Cu–O distance for a water molecule at the on-top site with tilt angle of 60 degrees was calculated, as suggested by the experimental value for the tilt angle.<sup>28</sup> The interaction energy was somewhat stronger, -39.1 kJ/mol, than for the H-parallel orientation at the on-top site. The optimal distance was 2.25 Å. In addition, a full geometry optimization for a water molecule at the on-top site on the Cu<sub>10</sub> surface was performed. The optimal tilt angle was 77 degrees, and the interaction energy was -41.0 kJ/mol.

Some single-point energies were also calculated for the Cu<sub>18</sub> cluster with a water molecule: H-up, H-down, and H-parallel at the three adsorption sites. The Cu–O distances chosen for these calculations, shown in Table 3, were those obtained for the bottom of the potential wells for the Cu<sub>10</sub>–H<sub>2</sub>O interaction curves. This permits a direct examination of the influence of cluster size.

In general, the Cu<sub>18</sub> interaction energies were more attractive than those obtained for the Cu<sub>10</sub> model. The attraction enhancement was somewhat greater at the bridge site than at the on-top site. The enhancement was greatest at the hollow site, which is quite exposed in the Cu<sub>10</sub> model. The H-parallel adsorption at the on-top site had the strongest attraction (-48.3 kJ/mol), as was also the case for the Cu<sub>10</sub> model. The H-down orientation was favored at the bridge and hollow sites. In the Cu<sub>10</sub> model the on-top site is situated in the middle of the cluster; in Cu<sub>18</sub> one side of the on-top site has more edge atoms, but the other side remains similar to the Cu<sub>10</sub> cluster. The clear increase in the interaction energy from Cu<sub>10</sub> to Cu<sub>18</sub> cluster size for the on-top site suggests that still larger clusters may be necessary for convergence of the interaction energies to those efficaciously representing adsorption on a metal surface.

Some experimental data of water binding geometry and strength on the Cu(111) surface have been reported. Au et al.<sup>44</sup> estimated -34 kJ/mol for the binding energy of water on the Cu(111) plane, on the basis of X-ray photoelectron spectroscopy. The water was proposed to interact via the oxygen atom, but no tilt angle information was reported.<sup>44</sup>

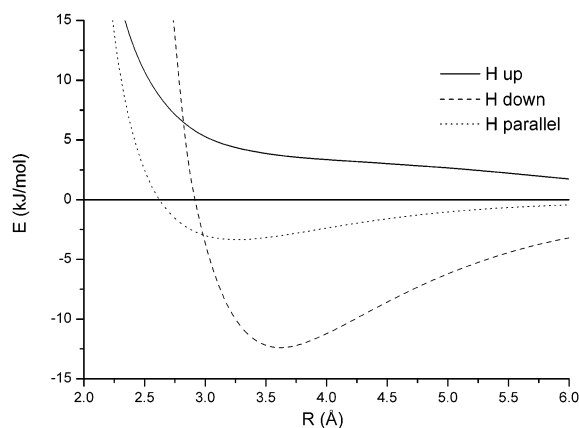
**TABLE 3: Cu<sub>18</sub> and H<sub>2</sub>O Interaction Energies Calculated at Selected Cu–O Distances, the Equilibrium Distances for Cu<sub>10</sub>**

	<i>R</i> (Å)	<i>E</i> non-CP <sup>b</sup> (kJ/mol)	<i>E</i> CP <sup>b</sup> (kJ/mol)	BSSE (kJ/mol)
On-top				
H-up	2.26	-38.32		
H-up	2.80 <sup>a</sup>	-27.44	3.60	31.04
H-down	3.07	-39.23		
H-down	3.62	-34.39	-14.68	19.71
H-parallel	2.36	-48.26		
H-parallel	3.26	-29.38	-7.95	21.43
Bridge				
H-up	2.34	-31.96		
H-up	2.9 <sup>a</sup>	-22.73	4.33	27.06
H-down	3.08	-41.54		
H-down	3.59	-35.38	-15.97	19.41
H-parallel	2.58	-32.79		
H-parallel	3.31	-23.32	-3.90	19.42
Hollow				
H-up	2.62	-25.95		
H-up	3.15 <sup>a</sup>	-15.55	3.31	18.86
H-down	3.15	-42.07		
H-down	3.58	-36.50	-16.57	19.93
H-parallel	2.71	-31.60		
H-parallel	3.34	-22.90	-3.83	19.07

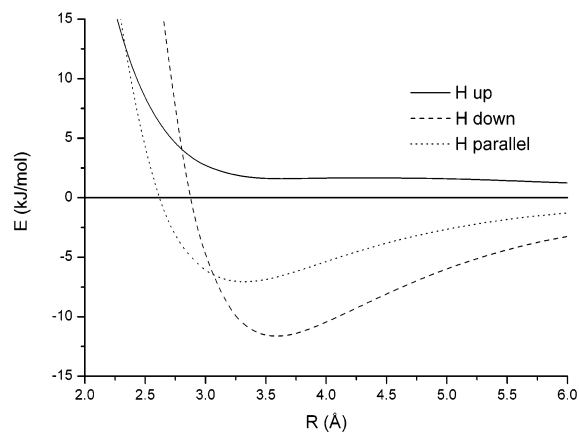
<sup>a</sup> Estimated distance. <sup>b</sup> CP = counterpoise correction for BSSE.

An early theoretical study using SCF-LCAO-X $\alpha$  method and a small Cu<sub>5</sub> cluster with a (100) surface gave -36.6 kJ/mol for the binding energy and 2.2 Å for the Cu–O distance for the on-top adsorbed water bonded through the O atom with a tilt angle of 70 degrees.<sup>7</sup> Angular-dependent Lennard-Jones potentials predicted the binding energy for the (111) plane (oxygen toward the surface) to be -38 kJ/mol for the on-top site, -25 kJ/mol for the bridge site, and -24 kJ/mol for the hollow site.<sup>27</sup> A more recent study on water–copper surface interactions by Ignaczak et al.<sup>25,29,45</sup> used B3LYP/LANL1MB/6-31G method. They used a (100) surface on Cu<sub>*n*</sub> clusters with *n* = 2, 4, 5, 9, and 12. The largest cluster, Cu<sub>12</sub> had 6 atoms in the surface layer. The bridge site is closer to the edge of the cluster than the on-top and hollow sites. They found that water oriented with O-down was preferred at the on-top and bridge sites. Water adsorbed at a Cu(100) surface most strongly at the bridge site, perpendicular to the surface (-31.8 kJ/mol 1.9 Å), and almost as strongly at the on-top site with a tilt angle of 55° (-30.8 kJ/mol, 2.3 Å). In models where there are exposed copper atoms, the on-top site was more favorable. However, the H-down orientation was preferred at the 4-fold hollow site (-17.4 kJ/mol), which was the least attractive adsorption site.<sup>29</sup> A potential derived from these quantum calculations suggests a binding energy of -35.5 kJ/mol for the infinite copper surface.<sup>45</sup>

Most previous studies suggest that water adsorbs most strongly at the on-top site in a tilted H-up orientation, or at the bridge site in an H-up orientation. In our study, the non CP values suggest that the on-top site of the Cu<sub>10</sub> or Cu<sub>18</sub> clusters is the most favorable adsorption site, and the H-parallel orientation for water is preferred over the H-up and H-down orientations. The optimal tilt angle at the on-top site of Cu<sub>10</sub> cluster is 77 degrees. Thus, our non-CP results are in agreement with previous experimental<sup>28,44</sup> and other theoretical results<sup>7,25,27,29,44</sup> although the noncorrected interaction energies are likely overestimated due to the BSSE. The BSSE will also be orientation dependent. We also found that the H-down orientation had relatively strong attractions. The small differences in results with other theoretical work may be due to the various computational methods, but also may be affected by the different



**Figure 3.** CP-corrected interaction energy curves for Cu<sub>10</sub> with water adsorbed at an on-top site with hydrogens-up, -down, and -parallel.

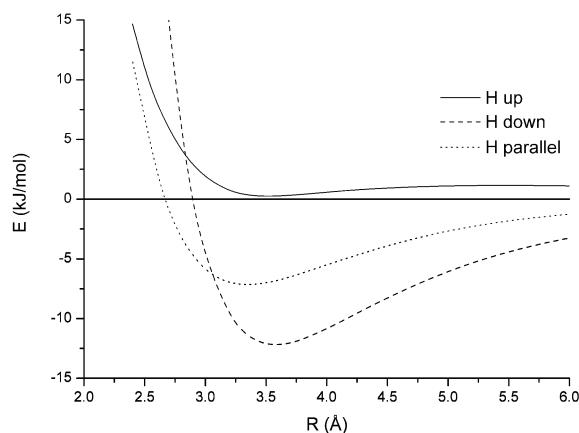


**Figure 4.** CP-corrected interaction energy curves for Cu<sub>10</sub> with water adsorbed at a bridge site with hydrogens-up, -down, and -parallel.

surface cleavage plane, the cluster model size and shape, and the distance of the adsorption site in question from the cluster edge.

**3.3. CP-Corrected Cu Cluster–Water Interaction.** Many studies on the Cu atom–H<sub>2</sub>O interaction have shown that the BSSE needs to be corrected in these kinds of systems.<sup>3–4,10,13</sup> We have used the counterpoise method for correcting the BSSE for our systems. The influence of the BSSE is significant. The noncorrected interaction energy for the Cu<sub>10</sub> cluster with H-up orientation ranged from –17 to –30 kJ/mol, but after CP correction there was no attractive well at any adsorption site (Table 2, Figures 3–5).

CP-corrected interactions for the H-down and H-parallel orientations were reduced to between one-tenth to one-third of the noncorrected values. The equilibrium distances shifted to larger *R* values (about 0.5 Å) with CP correction, consistent with weakening of the attractions. The H-down orientations were favored at all adsorption sites; the on-top and hollow sites had the strongest attractions. The H-parallel interactions were weaker, but still attractive. In the H-parallel orientation the bridge and hollow sites had the strongest attractions. The most favorable combination of adsorption site and water geometry in the Cu<sub>10</sub> model was thus the on-top or hollow site, with hydrogen atoms down, producing an interaction energy of –12 kJ/mol. The corresponding equilibrium distance *R*<sub>eq</sub>(O–X) was 3.6 Å, which corresponds to a distance 3.1 Å between the hydrogen atom and the adsorption site. At the on-top site with tilt angle of 60 degrees the interaction was still repulsive, but at the hollow site with tilt angle of 60 degrees, there was an attractive interaction of –3.1 kJ/mol at the distance of 3.4 Å.



**Figure 5.** CP-corrected interaction energy curves for Cu<sub>10</sub> with water adsorbed at a hollow site with hydrogens-up, -down, and -parallel.

For the Cu<sub>18</sub> cluster, there is no attraction after CP correction for the H-up orientation. H-down adsorption at the hollow site, in the middle of the cluster, had the strongest binding, –16.6 kJ/mol, after CP correction in the Cu<sub>18</sub> model.

The magnitude of the BSSE calculated with the CP method was large. However, the BSSE curves, for both the subsystems as well as for the supersystem, were consistent, and they all followed similar trends as a function of distance. In addition, the magnitude of the BSSE was quite stable, and the influence of the BSSE correction on the interaction energy was thus predictable. For the H-up orientation at the on-top and bridge sites, where the atoms are closest to each other, the BSSE was largest, around 30 kJ/mol for the Cu<sub>18</sub> cluster, whereas with other orientations and adsorption sites for the Cu<sub>18</sub> cluster it was around 20 kJ/mol. This is consistent with the assumption that shared basis sets in the supermolecular approach would have the largest impact at close proximity. Rappé and Bernstein<sup>38</sup> showed that for a water dimer the CP-corrected interaction energy at the MP2 level is very similar with different basis sets, although the magnitude of BSSE decreases with large basis sets.

Our CP-corrected results indicate that the interaction between the Cu(111) surface and a water molecule is weak, and no classic coordination bonding occurs. The interaction is of magnitude of hydrogen bonding for a water dimer,<sup>38,46,47</sup> and differences between the water orientations is small. It can thus be concluded that the Cu(111)–H<sub>2</sub>O interaction is not strongly orientation dependent. The CP-corrected results suggest that the H-down is the most favorable water orientation, contrary to the non CP-corrected results. The CP-corrected interaction energies we obtained are also relatively small. In surface studies, the influence of the CP correction has led to different interpretations of results, even some speculation that the CP method over-corrects for the BSSE.<sup>48</sup> The final conclusions about the most favorable water orientation and adsorption energy remains qualitative due to the uncertainty of the CP correction. Certainly the cluster model and its size are issues with regard to modeling an extended surface in which polarization and dispersion effects may be significantly affected by the cluster termination.

#### 4. Summary

Ab initio MP2 calculations were performed for a water molecule interacting with a Cu atom and two different sized Cu clusters representing the (111) Cu surface. A split valence RECP basis set was used for copper and a 6-31+G\* basis set was used for the water molecule. Counterpoise corrections for the BSSE were applied. The interaction between a single copper

atom and a water molecule was calculated as a reference. After counterpoise correction the interaction energy was  $-8.1$  kJ/mol for the structure oxygen toward the Cu atom with tilt angle of  $55.4^\circ$ . Cluster models for  $\text{Cu}_{10}$  and  $\text{Cu}_{18}$  were used to examine the water interaction with a Cu(111) surface. Without the CP correction, the favored water orientation was the H-parallel (tilt angle  $90^\circ$ ) at the on-top site with interaction energy of  $-48$  kJ/mol for the  $\text{Cu}_{18}$  cluster, and  $-39$  kJ/mol for the  $\text{Cu}_{10}$  cluster. Full geometry optimization for the water at the on-top site of  $\text{Cu}_{10}$  gave a noncorrected interaction energy of  $-41.0$  kJ/mol with tilt angle of  $77$  degrees $^\circ$ . The influence of the counterpoise correction on the interaction energy was significant. With the larger cluster model,  $\text{Cu}_{18}$ , the favored CP corrected interaction energy was around  $-16$  kJ/mol with hydrogens oriented toward the copper surface. With hydrogens parallel to the surface the attraction was somewhat less, and with hydrogens up the interaction with the surface was repulsive. CP-corrected binding energies with the  $\text{Cu}_{10}$  model were all smaller in some degree, at most  $-12$  kJ/mol, with hydrogens down.

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