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> **Abstract:** It was reported that a scanning tunneling microscopy (STM) study observed the adsorption geometry of a water monomer and a tetramer on NaCl(100) film. Based on first-principles density functional theory (DFT), the adsorption behavior of water on the NaCl surface was simulated with CASTEP code. The results showed that the water monomer almost lay on the NaCl(001) surface with one O–H bond tilted slightly downward. This was quite different from the STM observations. In fact, the experimental observation was influenced by the Au(111) substrate, which showed an upright form. A recent report on observations of two-dimensional ice structure on Au(111) substrate verified our simulations. However, the water tetramer formed a stable quadrate structure on the surface, which was consistent with observation. The intermolecular hydrogen bonds present more strength than surface adsorption. The simulations presented a clearer picture than experimental observations.

Keywords: first-principles; density functional theory; water; interface; NaCl

1. Introduction

Although water is one of the most common molecules, study of the anomalous properties of water is still challenging. Many theoretical studies [1–4] and experimental observations [5,6] have focused on the adsorption behavior of water molecules on the surface of transition and heavy metals. Water adsorption on an NaCl surface is also a typical system and is greatly significant to environmental science and biology systems.

Different computational methods have been used to investigate water behavior on an NaCl surface, such as classical molecular dynamics [7], ab initio simulation based on the cluster model [8], and density functional theory (DFT) with local density approximation (LDA) [9].

In laboratory experiments, Bruch et al. studied the adsorption of water on NaCl(001) using helium atom scattering and observed a diffraction pattern [10]. Verdaguer et al. used scanning polarized force microscopy to study the adsorption behavior of water molecules on cleaved NaCl(001) at different relative humidity [11]. Guo et al. used scanning tunneling microscopy (STM) to observe the water monomer and tetramer on an NaCl(001) surface with an Au substrate [12]. According to their report, a water monomer adsorbed on NaCl(001) film shows that the monomer was bonded on top of Na⁺ and aligned with the Na⁺-Cl⁻ direction. However, this may not be the true position of a water monomer adsorbed on a pure NaCl(001) surface. Meyer's simulation showed that water molecules took on almost horizontal adsorption configurations. For theoretical studies, determining whether LDA can correctly describe the adsorption of water molecules at an interface may be key to understanding the interaction between water and NaCl [13]. Yang et al. used the exchange correlation (XC) potential of a general gradient approximation (GGA) to study this issue and concluded that the water monomer dipole plane had a downward-tilted



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). metastable configuration [14]. As the coverage rate of water molecules increases, the interaction between the water molecules is greatly enhanced, and the interaction between the water and NaCl surfaces decreases. Recently, Jiang et al. observed that 2D ice grown on the Au(111) surface corresponds to an interlocked bilayer ice structure consisting of two flat hexagonal water layers. They believed that bilayer hexagonal ice forms on hydrophobic substrate and that there is no hanging hydrogen bond on the surface of bilayer hexagonal ice [15]. Hereinafter, we simulated the monomer and tetramer geometry adsorption on an NaCl surface. The discrepancy between simulation and observation was also discussed.

2. Materials and Methods

The quantum mechanics DFT code CASTEP [16] was used to search the geometry configuration of water adsorption on NaCl. The lattice constants and atomic coordinates of an NaCl unit cell are a = b = c = 5.62 Å and $\alpha = \beta = \gamma = 90^{\circ}$ by default. The NaCl(001) plane was cleaved with a thickness of 6 layers, and a 3 × 3 supercell was then built with a vacuum of 12 Å. The water monomer was built separately and copied to the NaCl surface. The oxygen was set on the top of Na⁺. Considering the possibilities of upright to horizontal geometries, we designed seven different adsorption configurations. Considering that the electron density of this system is almost uniform, the XC functional of the LDA was used for geometric optimization with DFT + D correlations. Since the lattice constants should not be affected by water monomer, the supercell was not optimized. In addition, the inner-layer lattices were not constrained, meaning that the interactions between the water and surface went into three layers.

To mimic the STM experimental conditions, we further constructed an Au(111) substrate-based NaCl(001) bilayer surface according to Guo's experiments and repeated the water-adsorption calculation. First of all, the Au(111) plane and the NaCl(001) plane were cleaved separately. Since the lattice constants and atomic coordinates of Au(111) are a = b = 2.884 Å and $\gamma = 120^\circ$, the lattice constants of NaCl(001) and Au(111) are mismatched. Thus, the Au(111) plane was cleaved with a thickness of 2 layers, and a 9 × 8 supercell was built. The lattice constants and atomic coordinates of NaCl $\phi = 23.070349$ Å and $\gamma = 120^\circ$. Then, the lattice constants and atomic coordinates of NaCl were changed to a = 25.133404 Å, b = 22.480 Å and $\gamma = 116.565^\circ$ by justifying the surface vectors. A 2 × 2 supercell was built to match the lattice constants of NaCl(001) and Au(111). After that, the two-film structure was combined with a vacuum of 20 Å. Thus, we simulated the water monomer adsorption configuration on the NaCl–Au surface.

Finally, a water tetramer was constructed and placed on the NaCl surface above four neighbor Na⁺ ions. The geometry optimization was performed with the same parameters mentioned previously.

3. Results and Discussion

3.1. Adsorption of Water Monomer on an NaCl(001) Surface

For the modeling of the adsorption of water molecules on an NaCl(001) surface, we first placed a water molecule at about 2–3 Å above the NaCl(001) surface. The monomer configurations were designed with seven positions from upward to downward. Figure 1 shows the optimized geometries. Comparing the total system energy across these seven results, the structure with the lowest electrostatic potential was that one O–H bond parallel to the Na–Cl bond and the other hydrogen tilted slightly downward, as shown in Figure 1f. Figure 2 shows the energy differences curve and Table 1 presents values with the two H–Cl lengths of these seven configurations.



Figure 1. Seven conformations from (**a**–**g**) of a water monomer on an NaCl(001) surface. The upper picture is the top view and the lower picture is the side view for each optimized model. Conformation f has the lowest system energy. O, H, Cl⁻, and Na⁺ are denoted by red, white, green, and purple spheres, respectively.



Figure 2. Energy differences across seven water monomer conformations. Structure f is the baseline and has the lowest system electrostatic potential.

Models	E (eV)	H ¹ -Cl (Å)	H-Cl (Å)
а	2.365	2.817	3.084
b	3.334	2.281	3.538
с	2.158	3.120	3.372
d	0.587	2.632	2.760
е	2.878	2.839	3.020
f	0	2.443	3.404
g	0.210	3.007	4.124

Table 1. Energy difference (E) and optimized structural parameters of the seven models. The lowest system energy of conformation f was taken as the reference point. The two nearest H–Cl distances are presented for comparison.

Figure 3 shows the configuration of the f model in detail; the water molecule lies almost flat on the NaCl(001) surface, while the dipole plane is tilted slightly downward. In our simulation results, the thickness of NaCl film is 13.346 Å. The distance of O⁻-Na⁺ is 2.255 Å, and the distances of H⁺-Cl⁻ are 2.220 Å and 2.642 Å, respectively, showing a structure in which one O–H bond is almost horizontal and the other is tilted slightly downward. In contrast, Yang's simulation showed that two O–H bonds were inclined downward at the same angle. The adsorptions of this system are derived from the intermolecular electrostatic interaction between polarized water molecules and Na⁺-Cl⁻ ions.

Due to the hybridization of the SP³ orbital of oxygen, the spatial distributions of the electron cloud present a tetrahedral structure along with two O–H bonds. To match the interaction between Na⁺ and the lone pair of oxygen electrons, the most stable configuration is slightly tilted. According to Guo's STM report, the water monomer was upright on the surface [12]. Since they only deposited a few layers of NaCl film, the upright geometry should be a result of repulsive forces from the Au substrate, and the actual interactions were H₂O/NaCl/Au. Thus, the real adsorption geometry configuration on the pure NaCl surface was not what they can see from STM experimental observations. We have discussed this issue with Jiang's team and confirmed this conclusion. Recently, their laboratory first observed two-dimensional ice on Au(111) substrate [15]. The bilayer molecules bonded together to form a two-dimensional film. Each water molecule presents three inner-layer hydrogen bonds and one between-layers hydrogen bond. This phenomenon manifested the strong hydrophobic property of Au.



Figure 3. Refined structure of the water monomer on the NaCl(001) surface. Image (**a**) is the top view and (**b**) is the side view.

Subsequently, we simulated the adsorption configuration of water monomer on an NaCl(001)–Au(111) surface. Figure 4 shows the configuration of the H₂O/NaCl/Au model. This result was similar to Guo's experiment observation and confirm the conjecture above. The oxygen was on the top of Na⁺. One O–H bond is almost vertical and the other is almost parallel to the Na⁺-Cl⁻ bond. The distance of H₂O-Na⁺ was changed from 2.255 to 2.469 Å. Comparison of Figures 3 and 4 shows the strong hydrophobic nature of Au.



Figure 4. Refined structure of the water monomer on the NaCl(001) bilayer surface, based on Au(111) substrate. Image (**a**) is the top view and (**b**) is the side view.

We then investigated the water cluster adsorption on the NaCl surface with the same calculation parameters. Four water molecules were placed arbitrarily above four Na⁺ ions to form a square ring. As shown in Figure 5, each water molecule formed two hydrogen bonds as one proton donor and one proton receptor with two adjacent water molecules. Meanwhile, each oxygen atom closed to nearby Na⁺ due to electrostatic interaction. Remarkably, each water molecule had a redundant hydrogen atom facing outward to achieve the tetrahedral configuration, due to the SP³ orbital hybridization of the oxygen atom.



Figure 5. Optimized geometry structure of the water tetramer on the NaCl(001) surface. Image (**a**) is the top view and (**b**) is the side view.

Vitek et al. calculated the geometry structure of water tetramer [17]. Besides the four linked hydrogen bonds' inner four-molecule ring, the arrangement of the four dangling hydrogens is up-down-up-down with respect to the planar square cycle. Yang's simulations of water tetramer adsorption on the NaCl surface showed that the interactions with the interface were stronger, which manifested in two hydrogen atoms tilting downward to Cl⁻ ions. However, the STM observations of Guo et al. showed that the four water molecules took almost the same positions, showing good agreement with our simulations. Therefore, we confirmed that the hydrogen bonding occurred before the adsorption with NaCl, as the hydrogen bonding was stronger than the other inter-molecular interactions.

4. Conclusions

Compared with STM observations, we confirmed that this computational work was more accurate than Yang's work. As they employed a GGA XC functional to calculate the interfacial interactions between water and NaCl, it seemed that the LDA XC functional was more accurate than the GGA in this field. The DFT simulation configurations revealed an optimization scheme for the water wetting on the surface of non-metal substances. Moreover, owing to Jiang's advanced STM technology, we can verify the simulation results with directly experimental observations.

The calculation results present more precise information than the experiment. In the simulation of adsorption of water molecules on the NaCl(001) surface, one water monomer adsorbed on the NaCl(001) surface with one O–H bond parallel to the Na⁺-Cl⁻ bond, while the other hydrogen atom was tilted slightly downward. The water tetramer showed that the hydrogen bonding was stronger than the adsorption energy. Thus, we agree with Yang that the water tetramer is a possible building block for the adsorption of the first water cover layer on an NaCl surface. A new STM report by Jiang et al. observed two-dimensional ice on an Au(111) surface [15]. Also, we simulated the adsorption of water molecules on the NaCl(001)–Au(111) surface. Compared with two results, it showed the hydrophobic nature between water and metal and the strong hydrogen bonding in-

between water molecules. It also verified the monomer and tetramer geometries, both from the simulation and experiments.

Author Contributions: X.-Y.L. and J.-W.C. performed simulations; X.-L.Q., X.-L.Z., X.-H.Y. and X.-C.W. assisted with structural modeling and data processing; X.-Q.Y., Y.-H.L. participated in the discussion of results; Y.W. and P.Z. conducted the project and P.Z. edited the manuscript; all authors gave final approval for publication. All authors have read and agreed to the published version of the manuscript.

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