PHYSICAL REVIEW B **74**, 245409 (2006)

Water adsorption on a NaCl (001) surface: A density functional theory study

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(Received 25 June 2006; revised manuscript received 8 October 2006; published 8 December 2006)

Water adsorption on a NaCl (001) surface has been studied using density functional theory (DFT) with a generalized gradient approximation (GGA). Water monomer is more likely to locate near the top site with its O atom adjacent to Na^+ and its H atoms attracted by the nearest Cl^-. For the most stable configuration, the dipole plane of the water monomer tilts downward to the surface. The adsorption energy ranges from ~0.2 to 0.4 eV/molecule for most typical sites. In the case of small water cluster adsorption (dimers and tetramers), the hydrogen bond and the water-substrate interaction come into play. We found that the hydrogen bond plays an important role in determining water adsorption configuration besides the mechanical and chemical constraints of the substrate. A systematic study of the water overlayer adsorption at higher coverages ranging from 1 monolayer (ML), 1.5 ML, and 1.75 ML to 2 ML on NaCl (001) was also conducted, where we found hydrogen bond patterns with alternating square and pentagonal or hexagonal rings dominate at coverages $\geqslant 1$ ML. The new structural characteristics are due to the compromise of maximizing hydrogen bonding between water molecules and the water-NaCl interaction. The water-substrate interaction is gradually reduced and water-water interaction is increased as the coverage increases. Our results of the energetics and structures have been compared with available experiments.

DOI: 10.1103/PhysRevB.74.245409 PACS number(s): 68.43.Bc, 68.35.−p, 82.20.Wt, 82.30.Rs

I. INTRODUCTION

Water is one of the most important and ubiquitous substances in nature. Of particular interest in science is what happens when water molecules adsorb on the surfaces of certain materials.[1–3] Recent theoretical[4–7] and experimental[8,9] studies have shed new light on the behavior of water molecules on transition and noble metals. On oxides, the partial dissociation of water on MgO (100), first predicted by theory,[10] has been observed experimentally by our group.[11]

Besides metals and oxides, another typical system is water on salt's surfaces, which has a lot of important implications, particularly in environmental sciences and biology. During past decades, a lot of efforts have been made on the study of H_2O adsorption on the most common salt surface, NaCl (001), by various experimental techniques, such as ultraviolet photoelectron spectroscopy, X-ray photoelectron spectroscopy, electron energy-loss spectroscopy,[12,13] and near-edge X-ray-absorption fine structure,[14] for the surface, with or without defects. Bruch *et al.*[15] studied water adsorption on NaCl (001) by helium atom scattering (HAS) and found a (1×1) diffraction pattern, while Fölsch *et al.* suggested a puckered hexagonal bilayer structure in $c(2\times4)$ periodicity on the basis of their low-energy electron diffraction (LEED) analysis.[13] Toennies *et al.* have recently shown that the (1×1) HAS pattern can be transformed to the $c(2\times4)$ structure under electron irradiation.[16] Using infrared spectroscopy, Ewing's group found that water forms a liquidlike thin film onto the surface of NaCl (001) under ambient conditions.[17,18] The scanning polarization force microscopy (SPFM) has recently been used to study the adsorption of water on cleaved NaCl (001) at different relative humidity (RH).[19] However, until now, few experiments are capable of detecting directly the adsorption geometry and adsorption energy of water monomer and dimer on NaCl (001).

On the theoretical side, many approaches, including classical molecular dynamics,[20] semiempirical method,[21] *ab initio* method based on cluster models,[22] and density functional theory (DFT) with local density approximation (LDA),[23] have been used to study the H_2O/NaCl (001). For the optimal adsorption configuration of water monomer on NaCl (001), some predicted an upright-standing dipole plane,[20,22] while the others predicted a nearly flat-lying geometry.[23] However, LDA generally overestimates the binding energies between atoms.[24] In particular, LDA is inadequate in describing hydrogen-bond (H-bond) interaction, which is essential for water-water and water-surface interactions.[10] Therefore it throws doubt on the results of overlayer water adsorption given by LDA.[23] Park *et al.* studied the adsorption of water on NaCl (001) surfaces by density functional calculations and suggested that the (1×1) monolayer structure may transfer to a more stable $c(4\times2)$ structure based on the much larger adsorption energy of the latter.[25] In spite of the previous theoretical efforts,[20–23,25–28] the binding nature of water molecule from first principles, as far as we are aware, remains unexplored. The atomistic mechanism regarding the electron-irradiation-driven transition of (1×1) water pattern to the $c(4\times2)$ structure[16] is still unclear so far. Furthermore, the role of the hydrogen bond in the adsorbed water network and the competition between water-substrate and water-water interactions remain intriguing but elusive problems.

Here we present an extensive and systematic DFT study within the generalized gradient approximation (GGA) framework for water adsorption on NaCl (001). We studied the water monomer, small clusters, and overlayer (at coverages of 1–2 monolayer) adsorption. A monolayer is defined as one H_2O molecule per surface Na-Cl unit, which is abbreviated as 1 ML in the following discussions. For water monomer, we found a series of metastable configurations with a downward-tilted dipole plane, when the O atom moves along the [110] (Na^+-Na^+) direction. Our study shows that the configurations with a nearly flat dipole plane are always more stable than the upright ones. Hydrogen bond and the substrate have significant influence on the formation and adsorption of small water clusters. The role of the H bond is further studied in the adsorption of 1 ML, 1.5 ML, 1.75 ML, and 2 ML water overlayers on NaCl (001). The water-water interactions are greatly enhanced while the water-substrate interactions are reduced with the increase of the water coverage. More interestingly, we found that the 1 ML water structure of one water molecule on the top of each surface Na^+, as assumed previously,[15,25] is not stable in our molecular dynamics studies; instead, we obtained a new ordered water structure at 1 ML, which is composed by alternating square and pentagonal/hexagonal rings of water hydrogen bonds. In addition, by careful comparison with experiments, the (1×1) HAS pattern[15,16] is assigned to 2 ML water overlayers, where each surface Na^+ or Cl^- site adsorbs a water molecule linked by hydrogen bond. The transition between these overlayer structures may take place under experimental conditions. Our results provide a plausible atomistic mechanism for the electron-irradiation transition of water patterns on NaCl (001).[16]

The paper is organized as follows. After this Introduction, we will present the theoretical model and computational details in Sec. II. The Results and Discussion section follows in three different parts: water monomer adsorption to study the nature of water-substrate interaction, water dimer and tetramer adsorption to study the role of the hydrogen bond, and overlayer adsorption to study the competition of the two interactions and to compare our findings with existing experiments. Finally, Sec. IV presents concluding remarks.

II. COMPUTATIONAL DETAILS

The calculations are performed within the framework of the DFT with the Vienna *ab initio* simulation package (VASP),[29] which employs a plane-wave basis set and Vanderbilt's ultrasoft pseudopotentials.[30] The generalized gradient approximation by Perdew and Wang (PW91)[31] is used for the exchange-correlation energy. A five-layer slab,[32] separated by a vacuum of 12.66 Å, is used to model the NaCl (001) surface. We use the calculated lattice constant 5.67 Å, which is in good agreement with the experimental value (5.64 Å[33]). Water molecules are put on one side of the slab. For the monomer, dimer and tetramer adsorption, we used a $p(2\sqrt{2}\times2\sqrt{2})$ surface cell of NaCl (001) substrate. For 1 ML, 1.5 ML, and 2 ML water adsorption, a $p(2\sqrt{2}\times2\sqrt{2})$, $p(2\times4)$, and $p(2\sqrt{2}\times2\sqrt{2})$ surface cell is used, respectively. The Monkhorst-Pack scheme,[34] with the origin being at Γ point, has been used for integration in the surface Brillouin zone. We use a $2\times2\times1$ k mesh for the $p(2\sqrt{2}\times2\sqrt{2})$ cell and a $2\times1\times1$ k mesh for the $p(2\times4)$ cell.

Energy cutoff (E_{cut}) for the plane waves is 300 eV. Using E_{cut}=400 eV only results in a minor difference in the total energy on the level of several millielectron volts. The Fermi level is smeared by the Gaussian method with a width of 0.2 eV. This set of parameters assures the total energy converges to a precision of at least 0.5 meV per atom. In structure optimization, the adsorbed water molecules and the top three layers of the substrate NaCl are relaxed simultaneously into their ground state using conjugate gradient technique. The process is stopped when the total energy converges to a precision of 10^{-3} eV.

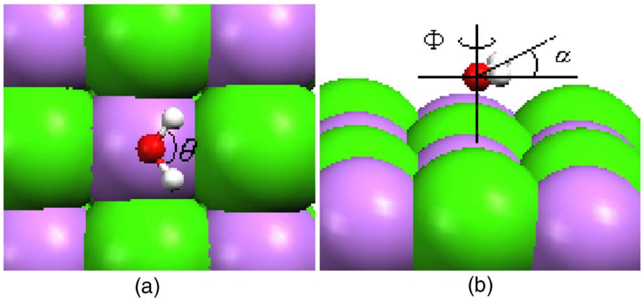

FIG. 1. (Color online) Top (a) and side (b) views of a water monomer on a NaCl (001) surface. The Na^+ and Cl^- ions are represented by purple (smaller) and green (larger) balls, respectively. Water molecules are represented by tiny balls joined by sticks, white for hydrogen and red for oxygen. Similar symbols are applied in the following figures.

In the present case, both the functionals and the lack of a description of van der Waals interaction[35] will affect the energy at least at the millielectron volt level. The calculated binding energies will be presented in a precision of 10 meV.

III. RESULTS AND DISCUSSION

A. Water monomer adsorption

In order to get an insight into the nature of water-substrate interaction, we have carried out an extensive study for the optimal water monomer configuration on various adsorption sites (top, bridge, hollow, and along Na^+-Na^+ axis), covering more than 40 different configurations. The geometric parameters that are used to describe the water monomer on NaCl (001) are shown in Fig. 1. The adsorption energy is obtained by the following formula:

$$E_{ads} = E[(\mathrm{NaCl(001)})_{\mathrm{relaxed}}] + E[(\mathrm{H_2O})_{\mathrm{gas}}] - E[(\mathrm{NaCl(001)} + \mathrm{H_2O})_{\mathrm{relaxed}}]. \quad (1)$$

Here $E[\mathrm{NaCl(001)}+\mathrm{H_2O}]$, $E[\mathrm{NaCl(001)}]$, and $E[\mathrm{H_2O}]$ are the total energies of the adsorption system, the NaCl substrate, and a water molecule (gas phase) after relaxation, respectively.

The structural parameters and adsorption energies of some typical configurations are summarized in Table I. The most stable configuration, with the adsorption energy of 0.40 eV, is shown in Fig. 2. The water molecule lies nearly flat along the Na-Na axis, but with the dipole plane tilting downward slightly. The overall configuration is somewhat similar to the one proposed in Refs. 23 and 25, but with a larger lateral displacement of O atom from the exact top site of Na^+ ion

TABLE I. Adsorption energies (E_{ads}) and optimized structural parameters for water monomer on a NaCl (001) surface. H^1 is the H atom that forms a hydrogen bond with Cl^-, and H^2 is the other H atom. Δ Oxy is the lateral displacement of O away from the precise top site of Na^+ [Fig. 2(a)–Fig. 3(e)] or Cl^- [Fig. 3(f)]. α is the H_2O-NaCl (001) tilt angle, Φ is the angle between [001](Na-Cl) and the projection of the dipole axis onto the (001) plane, and θ is the HOH angle, as depicted in Fig. 1. The units for energy, length, and angle are eV, Å, and degree, respectively.

Configuration	E_{ads}	O-Na	H^1-Cl	Δ Oxy	α	Φ	θ	O-H^1	O-H^2
Fig. 2(a)	0.40	2.385	2.347	1.074	–27	45	104.9	0.980	0.980
Fig. 3(a)	0.33	2.392	3.074	0.182	14	49	105.8	0.975	0.974
Fig. 3(b)	0.37	2.403	2.192	1.048	27	48	104.6	0.987	0.973
Fig. 3(c)	0.30	2.319	2.640	0.452	90	0	108.7	0.977	0.971
Fig. 3(d)	0.34	2.302	2.231	0.831	90	0	109.5	0.983	0.967
Fig. 3(e)	0.28	2.384	3.670	0.000	90	0	106.1	0.970	0.970
Fig. 3(f)	0.17	4.336	2.232	0.013	90	0	104.7	0.982	0.971

($\Delta Oxy = 1.1$ Å, compared to $\Delta Oxy = 0.7$ Å and 0.83 Å in Refs. 23 and 25, respectively) and a larger downward tilted angle ($\alpha \approx -27°$, compared to $\alpha \approx -10°$ and $\alpha \approx -18°$ in Refs. 23 and 25, respectively). The difference may come from the type of exchange-correlation functions (LDA in Ref. 23, PBE-GGA in Ref. 25).

The adsorption involves both the strong O-Na^+ and H-Cl^- attractions. This can be inferred by the distances of O-Na^+ and H-Cl^-, as given in Table I. Our calculation shows that when the distance approaches O-$Na^+ \approx 2.4$ Å (H-$Cl^- \approx 2.2$ Å), a strong O-Na^+ (H-Cl^-) attraction presents. Interestingly, when the water molecule is translated along the Na^+-Na^+ direction ([110]), we obtained a series of metastable configurations with somewhat smaller adsorption energies, among which the same configuration proposed in Ref. 23 is included, with $\alpha \approx -9°$, $\Delta Oxy = 0.76$ Å, and $E_{ads} = 0.39$ eV. When moving away from the most stable site along the Na^+-Na^+ direction, either the O-Na^+ attraction or the H-Cl^- attraction is reduced. The adsorption energy of water monomer as a function of the lateral displacement of O from the top site of the nearest Na^+ is shown in Fig. 2(c). This series metastable (and the most stable) configurations originate from the sp^3 hybridization nature of water molecular orbitals, as displayed in Figs. 2(d)–2(f). The lone pairs of water molecules lie in a plane perpendicular to the dipole plane, thus forming a tetrahedral distribution of electrons around O together with OH bonds [Fig. 2(d)]. Therefore, in order to maximize the interaction between Na^+ and the lone pairs, the dipole plane of the adsorbed water molecule likely adopts a flat-lying or slightly tilted feature [Fig. 2(e)]. Moreover, by considering the attraction between H and Cl^-, the O atom will move away from the top site of Na^+. Finally, the water molecule with a downward-tilted dipole plane reaches the most stable configuration with both strong O-Na^+ and H-Cl^- interactions.

Other configurations, whose adsorption is mainly through O-Na^+ attraction, are shown in Figs. 3(a) and 3(c); the ones through both strong O-Na^+ and H-Cl^- attraction are shown in Figs. 3(b) and 3(d). From Table I, we also found that the strength of O-Na^+ interaction depends not only on the O-Na^+ distance, but also on the orientation of the dipole plane, i.e., the orientation of lone pairs. The configurations with a slightly tilted dipole plane are always energetically more stable than the upright ones, which can also be understood by the sp^3 hybridization of water molecules. This is further evidenced by the charge density difference in Figs. 2(e) and 2(f), where the binding feature between O lone pairs and the ions of NaCl (001) is clearly shown. Therefore we conclude that the water-substrate interaction involves both electrostatic and covalent features.

Furthermore, to discuss the difference of O-Na^+ and H-Cl^- attraction in water monomer adsorption, we compared two typical configurations: Fig. 3(e), upright water on Na^+, which can be regarded as an example of the adsorption through only O-Na^+ interaction, and Fig. 3(f), upright on Cl^- with a H pointing down, where only the H-Cl^- hydrogen bonding is presented. The adsorption energies are 280 meV and 170 meV for the two configurations, respectively (Table I). The strength of O-Na^+ bonding is almost two times larger than the H-Cl^- hydrogen bonding. This leads to the conclusion that O-Na^+ attraction is dominant over the H-Cl^- hydrogen bond, in contrast to the inference in Ref. 23, which assumes that the main contribution to adsorption energy is the H-Cl^- bonds.

The difference between the present calculation and the results in Ref. 23 comes from the different type of exchange-correlation approximation. As mentioned before, LDA overestimates the binding energies of atoms and predicts the wrong bond length (too short) and bond energies (too large) of hydrogen-bonding systems.[10,36,37] Our present lattice constant ($a = 5.67$ Å) is in good agreement with the experimental value ($a = 5.64$ Å,[33] which was the value used in the calculations of Ref. 25), while the result by LDA is $a = 5.45$ Å. Moreover, the results of water monomer adsorption in Ref. 23 are derived from the adsorption of 1 ML water on a small (1×1) surface cell with only a thin two-layer slab by static calculations, which lack sufficient description of a realistic ionic NaCl (001) surface and the Madelung potential introduced by crystal electrostatic field.[38] In contrast, our results generally agree with the corresponding ones of Ref. 25, where a GGA approximation was also used.

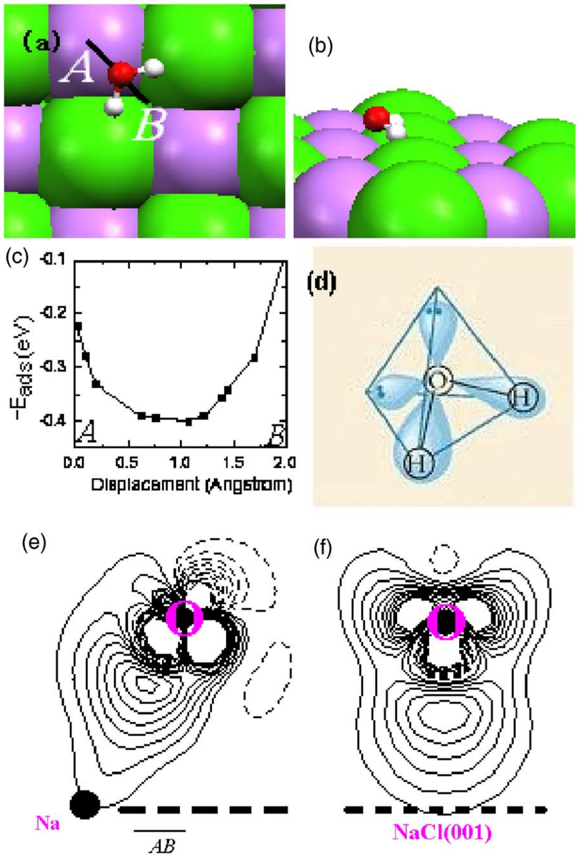

FIG. 2. (Color online) Top (a) and side (b) views of the most stable configuration of water monomer on NaCl (001). (c) Adsorption energy of water monomer vs the displacement of O from the top site of Na^+. (d) The schematic diagram for the sp^3 hybridization of water molecular orbitals. (e) Contour plot of charge density difference ($\Delta\rho$) for the water monomer adsorption on NaCl (001) studied here. $\Delta\rho$ is defined as $\Delta\rho=\rho[H_2O/NaCl(001)]-\rho[NaCl(001)]-\rho[H_2O]$, where $\rho[H_2O/NaCl(001)]$, $\rho[NaCl(001)]$, and $\rho[H_2O]$ are electron densities of the total system, the isolated NaCl (001) surface, and the H_2O molecule in gas phase, respectively. The plane is cut along the [110] direction (line $\overline{AB}$), perpendicular to the surface. (f) Same as (e) but the plane cuts along $[1\bar{1}0]$ and goes through the O atom. The contours have the densities $\Delta\rho=\pm 0.005\times n e/\text{Å}^3$, for $n=1,2,3,4,5,6,7,8,9,10$. Solid line and dashed lines correspond to $\Delta\rho>0$ and $\Delta\rho<0$, respectively.

B. Small water clusters

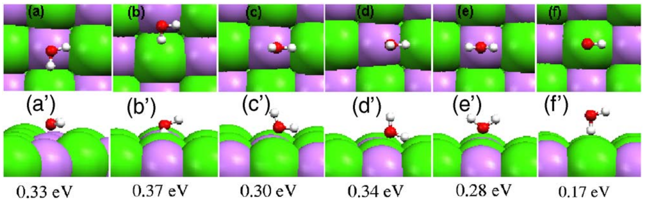

FIG. 3. (Color online) Top (up panel) and side (down panel) views of some typical configurations of water monomer on a NaCl (001) surface. The adsorption energy of each configuration is put below each panel.

We next study the adsorption of small water clusters on NaCl (001), where hydrogen bonding between water molecules comes into play. Hydrogen bonding is the interaction between a partially positive charged H atom and a nearby partially negative charged X atom ($X=\text{F},\text{Cl},\text{O},\text{N},\ldots$). It is the most important interaction between two water molecules and gives water many unique properties. In a hydrogen-bonded water dimer, the water that provides one H atom is called a *proton donor* and the other is called a *proton acceptor*. A typical distance between the O atoms of a proton donor and a proton acceptor is about 2.95 Å for a free water dimer,[39] with a binding energy of about 0.24 eV. Upon adsorption on a surface, the question arises, what role does the hydrogen bond (H bond) play when a water dimer adsorbs onto the NaCl (001) surface? A number of typical dimer configurations on a NaCl (001) surface are studied, as shown in Fig. 4. The corresponding structural parameters and energies are listed in Table II. The adsorption and interaction energies are calibrated by the following formulas:

$$E_{ads}=\frac{1}{2}\{E([\text{NaCl}(001)]_{relaxed})+2\times[(\text{H}_2\text{O})_{gas}]-E[(\text{NaCl}(001)+dimer)_{relaxed}]\} \tag{2}$$

$$E_{ww}=\frac{1}{2}\{2\times[(\text{H}_2\text{O})_{gas}]-E[dimer]\} \tag{3}$$

$$E_{sw}=E_{ads}-E_{ww}. \tag{4}$$

Here in Eq. (3), $E[dimer]$ is the total energy of the dimer with fixed geometry as that on NaCl (001). Approximately, $2\times E_{ww}$ can be taken as the strength of the H bond ($E_{H\text{-}bond}$) in the adsorbed dimer, and E_{sw} is the strength of water-substrate interaction. In the case of water tetramer adsorption, similar formulas are used.

The most stable dimer on the NaCl surface is shown in Fig. 4(a), where both water molecules lie near Na^+, and the strength of H bond (0.20 eV) is comparable with its free case. Without the restriction of the H bond, or if the two water molecules were relaxed into their respective monomer-like ground state, the corresponding water-substrate interaction energy E_{sw} is 0.40 eV/H_2O, which is 0.09 eV/H_2O larger than the water-substrate interaction in Fig. 4(a). It shows clearly that the H bond affects the adsorption of the water dimer.

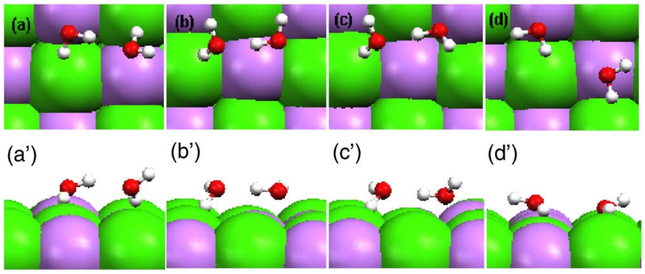

FIG. 4. (Color online) Top (up panel) and side (down panel) views of some calculated water dimers on a NaCl (001) surface.

TABLE II. Energies and structural parameters for two water molecules on the NaCl (001) surface. The adsorption energy E_{ads} (eV/H_2O), the strength of the hydrogen bond between water and water molecules E_{ww} (eV/H_2O), and the interaction energy between the substrate and water molecules E_{sw} (eV/H_2O) are given from left to right. O^D is the O atom in proton donor, H^D is the H atom that forms a hydrogen bond with the other water molecule, O^A is the O atom in proton acceptor, and H^A is the H atom in proton acceptor that forms a hydrogen bond with Cl^-. The distance is given in the unit of Å.

Configuration	E_{ads}	E_{ww}	E_{SW}	O^D-Na	O^A-Na	O^D-O^A	H^D-O^A	H^A-Cl
(a)	0.41	0.10	0.31	2.430	2.917	2.873	1.973	2.218
(b)	0.20	0.09	0.11	3.056	-------	2.758	1.774	2.201
(c)	0.29	0.11	0.18	2.545	-------	2.838	1.848	2.241
(d)	0.35	0.03	0.32	2.440	2.361	3.666	2.962	------

On the other hand, the adsorption configurations of the water dimer will affect the strength of the H bond. Figures 4(b) and 4(c) show the other two water dimer configurations. The main difference between them is the position of proton donors while the proton acceptors are almost the same. The proton donor in Fig. 4(b) lies nearly parallel to the NaCl (001). The projection of O atoms onto the NaCl (001) surface is close to the hollow site, while the HOH plane of the proton donor in Fig. 4(c) forms an angle of ~45° with NaCl (001), and the O atom moves to the nearest Na^+ ion. Based on the O-Na^+ distance and E_{sw} given in Table II, we find that the O-Na^+ attraction in Fig. 4(c) is stronger than that in Fig. 4(b), resulting in an enhanced H bond. This is caused by the electron transfer from the proton donor to the substrate (Fig. 5), which will weaken the O-H bond of the donor water and thus enhance the H bond.

Beside H bonds, the substrate will also affect the formation of water dimers. Figure 4(d) shows the relaxed configuration of two water molecules on NaCl (001) with an initial O-O distance of 3 Å. The O-O distance after relaxation is found to be 3.7 Å, leading to a very weak H bond with a strength of $E_{H\text{-}bond}=0.06$ eV. However, without the substrate, the two free relaxed water molecules will form a strong H bond with $E_{H\text{-}bond}=0.20$ eV. Our calculation also reveals that when the initial O-O distance is larger than 4 Å, whatever the orientation is, only a weak H bond (several tens of millielectron volts) can be formed. In this case, the adsorbed water molecules behave like monomers.

Another typical small water cluster studied here is water tetramer. For the water tetramer adsorption, four water molecules adsorb on adjacent Na^+ and Cl^- alternatively, forming a cyclic, squarelike water ring (Fig. 6). Each water is linked by two hydrogen bonds, serving as both proton donor and proton acceptor; in addition, each water molecule forms a Na-O bond or H-Cl bond with the substrate. Because of the perfect match between the water square and the NaCl (001) surface lattice, and the nearly full saturation of hydrogen bonding between water molecules, we expect that the water tetramer is a very stable and rigid structure on the NaCl (001) surface. Indeed, the calculated adsorption energy of water tetramer is 0.47 eV/H_2O, much larger than the monomer and dimer adsorption. The water-water and substrate-water interaction energy is 0.25 eV/H_2O and 0.22 eV/H_2O, respectively. The former is larger while the latter is smaller than the corresponding values of the most stable dimer adsorption [Fig. 4(a)], a reflection of optimal hydrogen bonding interaction and the presence of H-Cl bonds. We note that the optimal water trimer structure in Ref. 25 has the same geometry as the tetramer here, e.g., a nearly square water ring but with one corner water missing. The large adsorption energy and rigid square ring geometry of the water tetramer make it the most stable water cluster. The square tetramer structure, with some modifications, is one of the fundamental building blocks of the first water overlayer on the surface of NaCl (001), as shown below.

C. Water overlayer adsorption

We then extended our study to water overlayer adsorption. In this section, we focus on the competition between water-

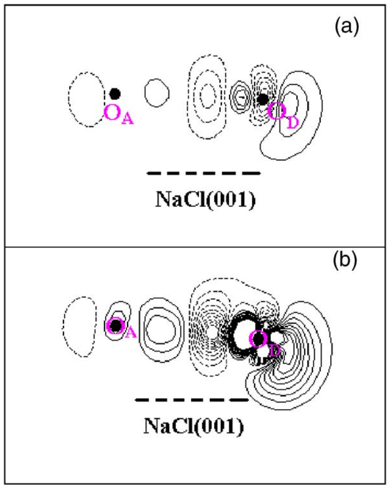

FIG. 5. (Color online) (a) Contour plot of charge density difference ($\Delta\rho$) for one of the water dimers [Fig. 4(b)] adsorption on a NaCl (001) surface. $\Delta\rho$ is defined as $\Delta\rho=\rho[(H_2O)_2/\mathrm{NaCl}(001)]-\rho[(H_2O)_A/\mathrm{NaCl}(001)]-\rho[(H_2O)_D]$, where $\rho[(H_2O)_2/\mathrm{NaCl}(001)]$, $\rho[(H_2O)_A/\mathrm{NaCl}(001)]$, and $\rho[(H_2O)_D]$ are electron densities of the total system, the adsorption of H acceptor on the NaCl (001) surface, and the H-donor H_2O molecule in the gas phase, respectively. The plane is cut along the [010] direction (goes through the O atom of the H donor), perpendicular to the surface. (b) Same as (a) but for another water dimer adsorption on NaCl (001) [Fig. 4(c)]. The O atoms of the H donor and H acceptor are denoted by O_D and O_A, respectively. The contours have the densities $\Delta\rho=\pm 0.005\times ne/\text{Å}^3$, for $n=1,2,3,4,5,6,7,8,9,10$. Solid line and dashed lines correspond to $\Delta\rho>0$ and $\Delta\rho<0$, respectively.

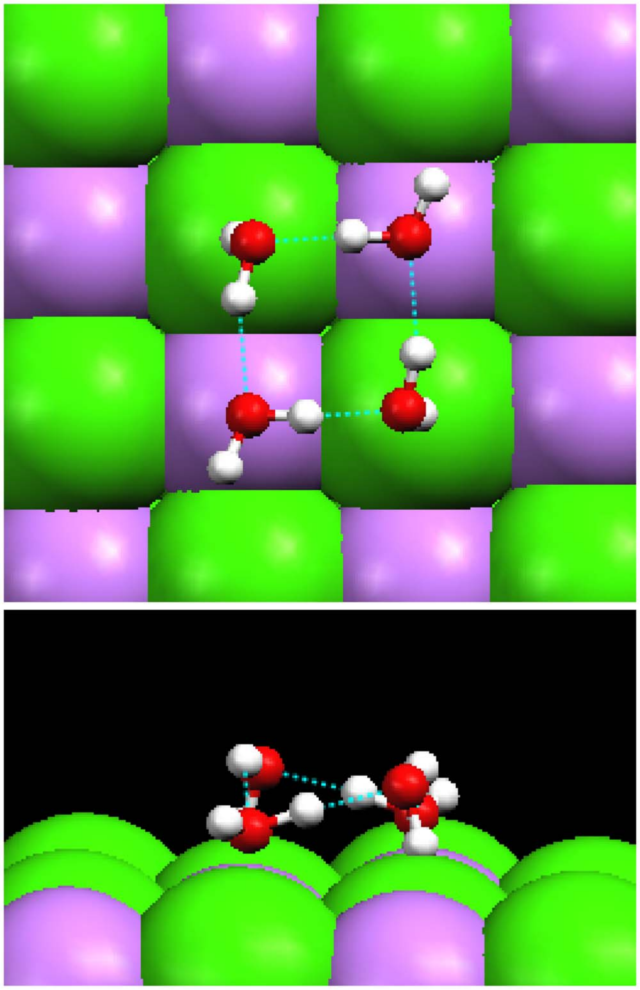

FIG. 6. (Color online) Top (up panel) and side (down panel) views of a water tetramer on a NaCl (001) surface. The hydrogen bonds are denoted by dotted lines.

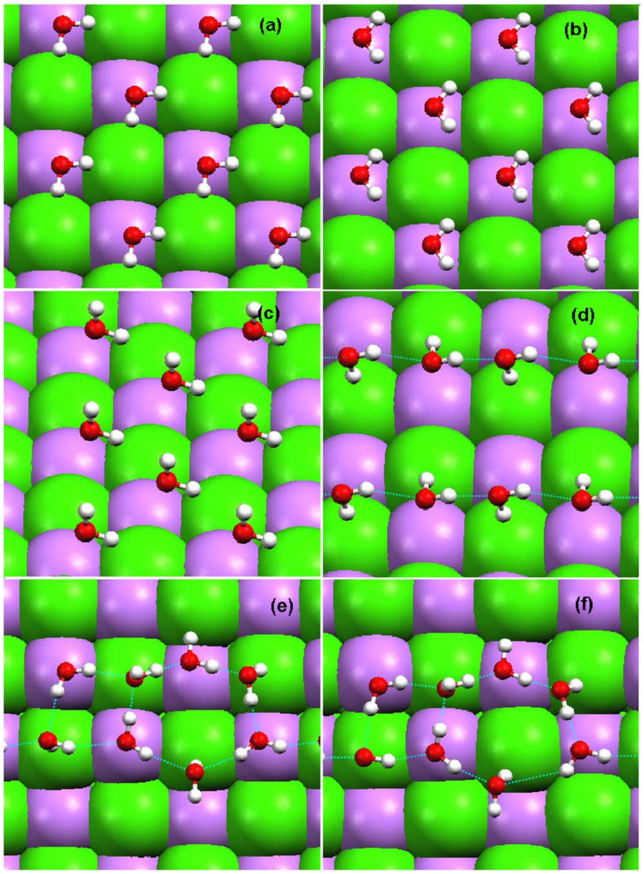

FIG. 7. (Color online) Configurations of 1 ML water adsorption on a NaCl (001) surface. (e) and (f) Results from MD simulations at 80 K of the structure, (d) after equilibration and 2 ps further simulation, respectively. MD simulations on structures (a) and (b) give hydrogen bonding patterns very similar to (e). The hydrogen bonds are denoted by dotted lines.

water and water-substrate interactions in water overlayers, with the aim at further exploring the role of the H bond during water adsorption on the NaCl surface. The adsorption energies, water-water interaction, and substrate-water interaction energies are defined by the following formulas:

$$E_{ads} = \frac{1}{n}\{E[(\mathrm{NaCl}(001))_{relaxed}] + n \times E[(\mathrm{H_2O})_{gas}] - E[(\mathrm{NaCl}(001) + \mathrm{H_2O})_{relaxed}]\} \tag{5}$$

$$E_{ww} = \frac{1}{n}\{n \times E[(\mathrm{H_2O})_{gas}] - E[(\mathrm{H_2O})_{network}]\} \tag{6}$$

$$E_{sw} = E_{ads} - E_{ww}, \tag{7}$$

where n is the number of water molecules in the supercell. For 1 ML water adsorption, we first calculated three typical configurations, including two flat-lying ones in Figs. 7(a) and 7(b), and the upright one in Fig. 7(c). All water molecules are located close to $\mathrm{Na^+}$ top sites, as the monomer case. The calculated adsorption energies for these three configurations are 0.39 eV/$\mathrm{H_2O}$, 0.39 eV/$\mathrm{H_2O}$, and 0.35 eV/$\mathrm{H_2O}$, respectively. Similar to the monomer case, the flat-lying configurations are more stable than the upright ones. This result is different from that in Ref. 23, where the order of stability was Fig. 7(a) > Fig. 7(c) > Fig. 7(b). A detailed comparison for the results obtained by LDA[23] and GGA is given in Table III. The water-water interaction in Fig. 7(b) is stronger than those in Figs. 7(a) and 7(c), because each water molecule in Fig. 7(b) is of more favorable orientation to form the H bond with the nearest water molecule. On average, the strength of water-water interaction is around 0.07 eV/$\mathrm{H_2O}$, which is much smaller than water-substrate interaction (~0.34 eV/$\mathrm{H_2O}$).

To explore the role of the H bond, we further constructed a chainlike configuration at a water coverage of 1 ML, shown in Fig. 7(d). The water chains are lined up head-to-tail by H bonds between the neighbor water. Surprisingly, in such a structure, the adsorption energy (0.48 eV/$\mathrm{H_2O}$) is much larger than the ones in Figs. 7(a)–7(c). It implies some more stable water structures may exist at 1 ML adsorption, but these structures are significantly different from the models assumed in previous literature [Figs. 7(a)–7(c)].

TABLE III. Results of LDA (Ref. 23) and GGA (our calculation) for 1 ML water adsorption on NaCl (001) surface. The top three lines are the results of GGA, and the bottom three lines are the results of LDA (Ref. 23). Adsorption energies (E_{ads}), water-water interaction energies (E_{ww}), substrate-water interaction energies (E_{sw}), and structural parameters are presented. The initial configurations used in our structural optimization calculation are the same as the corresponding configurations given in Ref. 23, i.e., (a) to (b)^a, (b) to (a')^a, (c) to (c)^a. Δ Oxy is the lateral displacement of O from the precise top site of Na$^+$. α is the H_2O -NaCl (001) tilt angle, Φ is the angle between [001](Na-Cl) and the projection of the dipole axis onto the (001) plane, and θ is the HOH angle as shown in Fig. 1. Here, the positive value of energies means attraction, and the units for energy, length, and angle are eV, Å, and degree, respectively.

Configuration	E_{ads}	E_{ww}	E_{sw}	O-Na	Δ Oxy	α	Φ	θ
(a) GGA	0.39	0.05	0.34	2.434	0.713	−10	45	103.2
(b) GGA	0.39	0.14	0.25	2.433	0.142	7	0	105.1
(c) GGA	0.35	0.06	0.29	2.360	0.793	90	0	106.6
(b)^a LDA	0.63	0.06	0.57	2.404	0.7	−10	45	105
(a')^a LDA	0.56	0.18	0.38	2.300	0	0	0	105
(c)^a LDA	0.58	0.07	0.51	2.280	0.6	90	0	105

[a] See Fig. 4 and Table II in Ref. 23.

To confirm this, the thermal stability of these configurations was further studied by *ab initio* molecular dynamics simulations at 80 K in a canonical ensemble. Very interestingly, after 2-ps equilibration, the chain structure turned spontaneously to form a network structure of water consisting of alternating squarelike and hexagonal hydrogen bond rings, shown in Fig. 7(e). The stability of this structure is further verified in our molecular dynamics (MD) simulation, which lasted for another 2 ps at 80 K. The final structure shown in Fig. 7(f) preserves the main features of this peculiar 4-6-member ring structure. The energetic parameters of these configurations are given in Table IV. The adsorption energy of the ring structure in Fig. 7(e), 0.52 eV, is much larger than those (1×1) overlayers with energies of 0.39 eV at most in Figs. 7(a)–7(c). This energy gain comes from compromise of optimal H bonding between water molecules and O-Na$^+$ attraction. The water-substrate interaction is slightly reduced, while the water-water interaction is strengthened. To the best of our knowledge, this configuration is far more stable than any previous reported configurations for 1 ML water on NaCl (001). Not surprisingly, our *ab initio* MD simulations on Figs. 7(a) and 7(b) at ~80 K also showed that both configurations evolve into more stable structures with the water molecules connected by hydrogen bonds with similar patterns as in Fig. 7(e) (not shown). In longer MD simulations (~10 ps) at 80 K for Fig. 7(e), distorted square-pentagonal rings are also observed, revealing the flexibility of the water overlayer structures on NaCl at 1 ML, which is unsaturated upon water adsorption. The primitive surface cell of this pattern is $p(2\sqrt{2}\times2\sqrt{2})$ and is $c(4\times4)$ in larger scale. We predict this $c(4\times4)$ structure should be observable in future experiment.

TABLE IV. The surface cells, the number of water molecules contained in each surface cell (N_{H2O}), and adsorption energies E_{ads}, water-water interaction energies E_{ww}, substrate-water interaction energies E_{sw}, for 0.5 ML, 1 ML, 1.5 ML, 1.75 ML, and 2 ML water adsorption on NaCl (001) surface. The unit for energy is eV/H_2O.

Coverage	Surface cell	N_{H2O}	E_{ads}	E_{ww}	E_{sw}
0.5 ML (tetramer)	$p(2\sqrt{2}\times2\sqrt{2})$	4	0.47	0.25	0.22
1 ML (a)	$p(2\sqrt{2}\times2\sqrt{2})$	8	0.39	0.05	0.34
1 ML (b)	$p(2\sqrt{2}\times2\sqrt{2})$	8	0.39	0.14	0.25
1 ML (c)	$p(2\sqrt{2}\times2\sqrt{2})$	8	0.35	0.06	0.29
1 ML (d)	$p(2\sqrt{2}\times2\sqrt{2})$	8	0.48	0.24	0.24
1 ML (e)	$p(2\sqrt{2}\times2\sqrt{2})$	8	0.52	0.32	0.20
1 ML (f)	$p(2\sqrt{2}\times2\sqrt{2})$	8	0.50	0.33	0.17
1.5 ML (a)	$p(2\times4)$	12	0.54	0.37	0.17
1.5 ML (b)	$p(2\times4)$	12	0.57	0.42	0.15
1.75 ML	$p(2\times4)$	14	0.56	0.39	0.17
2 ML	$p(2\sqrt{2}\times2\sqrt{2})$	16	0.56	0.40	0.16

We have also investigated water overlayers at higher coverages, such as 1.5 ML, 1.75 ML, and 2 ML, when more water molecules adsorb on the NaCl (001) surface. The computational details and energies have been summarized in Table IV.

Based on the $c(4\times2)$ structure suggested by Fölsch *et al.*,[13] we calculated two configurations for 1.5 ML water adsorption in a $p(2\times4)$ surface cell, whose primitive cell is $p(2\times4)$ and $c(2\times4)$, respectively (Fig. 8). After structural optimization, the $p(2\times4)$ unit cell in Fig. 8(a) actually consists of six different hexagonal hydrogen bond rings, while the $c(2\times4)$ unit cell in Fig. 8(b) consists of three different hexagonal hydrogen bond rings. The $p(2\times4)$ water network forms a trilayer structure in surface normal direction with $Z_{\text{O-NaCl(001)}}\approx2.5$ Å, 2.9 Å, and 3.8 Å, respectively. On the other hand, the $c(2\times4)$ water network forms a bilayer structure in surface normal direction with $Z_{\text{O-NaCl(001)}}\approx2.6$ Å and 2.9 Å, respectively. The $c(2\times4)$ structure is slightly preferred over the $p(2\times4)$ one based on their difference in adsorption energy (~0.03 eV/H_2O).

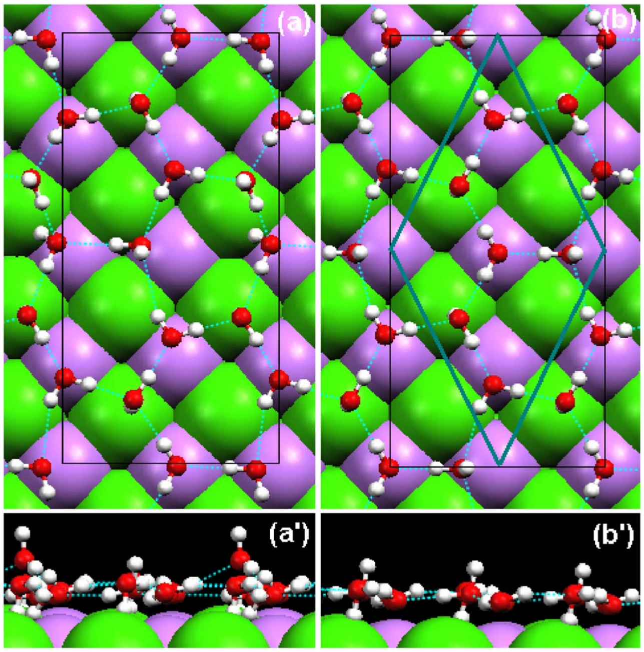

FIG. 8. (Color online) Top (up panel) and side (down panel) views for 1.5 ML water adsorption on a NaCl (001) surface. (a) and (a′): $p(2\times4)$ water structure; (b) and (b′) $c(2\times4)$ water structure.

The 1.75 ML water adsorption configuration is constructed from the $c(2\times4)$ structure, where two more water molecules are added in the unit cell, shown in Fig. 9. After structural relaxation, some hydrogen bonds shown in Fig. 8(b) are broken, while some new hydrogen bonds are built up between the newly added water molecules and the other water. The adsorption energy is 0.56 eV/H_2O, very close to the 1.5 ML overlayer in the same $c(2\times4)$ pattern.

For 2 ML water adsorption, all water molecules take the top positions of either Na^+ or Cl^-, and then form a bilayer structure after optimization, as shown in Fig. 10. The height of the bilayer water film is $Z_{\text{O-NaCl(001)}}\approx2.5$ Å and 3.1 Å for the water molecules atop Na^+ and Cl^-, respectively. The local geometry resembles that of water tetramer very much: Each water molecule has three hydrogen bonds with neighboring water molecules, and the fourth bonds with Na^+ when adsorbed on the Na^+ top site or another hydrogen bond with Cl^- when adsorbed on top of Cl^-. Therefore all the electron lone pairs of water molecules are saturated by hydrogen bonds and/or O-Na^+ bonds. The energies are $E_{ads}=0.56$ eV/H_2O, $E_{ww}=0.40$ eV/H_2O, and $E_{sw}=0.16$ eV/H_2O. Comparing the results of 2 ML water on NaCl (001) with the experimental results for the observed (1×1) HAS pattern by Bruch *et al.*,[15] we find that the adsorption energies are almost the same (0.56 eV/H_2O vs 0.6 eV/H_2O). As the positions of Na^+ and Cl^- ions are equivalent on NaCl (001), a similar diffraction pattern will be obtained if HAS is applied to study the 2 ML water configuration in Fig. 10. In contrast to the (1×1) 1 ML model proposed in Ref. 15, the 2 ML adsorption shown in Fig. 10 will be a more suitable model for the experimental observations, considering the large energy difference of (1×1) 1 ML overlayer [Figs. 7(a)–7(c)] and the 2 ML overlayer. Moreover, it is expected that the adsorption energies will decrease above 2 ML as all water molecules are saturated by hydrogen bonds at 2 ML. Interestingly, we note here that the 2 ML geometry with alternating O-down (on Na^+) and H-down (on Cl^-) water molecules is similar to what is observed on Pt(111).[9] Both water patterns are flat with H atoms pointing downward though the building block is different—square rings reported here vs hexagons in Ref. 9.

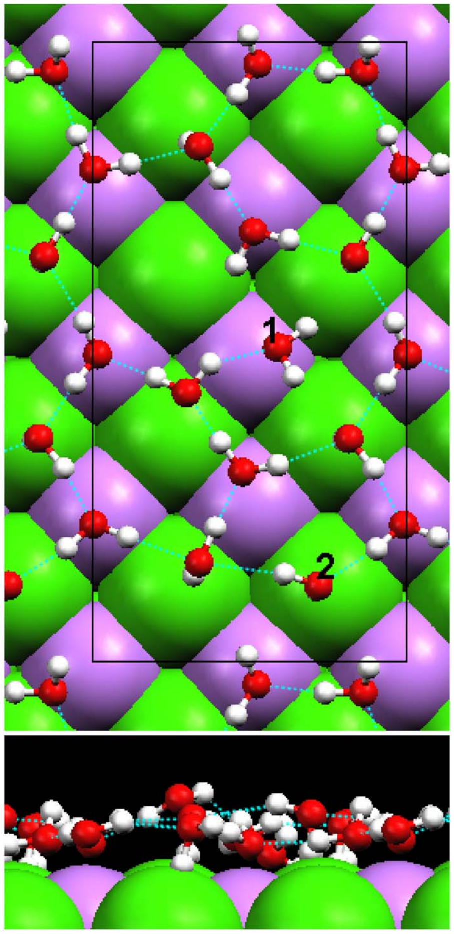

FIG. 9. (Color online) Same as Fig. 8 but for 1.75 ML water adsorption on NaCl (001). Compared to Fig. 8(b), two more water molecules (labeled 1 and 2) are added.

In order to obtain a general picture of the energetics of the water adsorption on NaCl (001), the tendency of water-substrate interactions E_{sw} vs the coverage of water molecules is shown in Fig. 11(a) and the water-water interactions E_{ww} in Fig. 11(b). For 1 ML and 1.5 ML adsorption, the values of E_{sw} and E_{ww} are taken from the most stable configuration [Figs. 7(e) and 8(b)]. At coverage lower than 1.5 ML, one can see E_{sw} goes down while E_{ww} goes up as the coverage increases. By forming hydrogen bonds with their neighbors, the water-water interaction is greatly enhanced, and the water-substrate interactions are reduced at the same time. From 1.5 ML to 2 ML, the adsorption energy shows small fluctuations and keeps nearly constant (Table IV). The increase of water coverage adds to the number of hydrogen bonds as well as the repulsion between water molecules. This

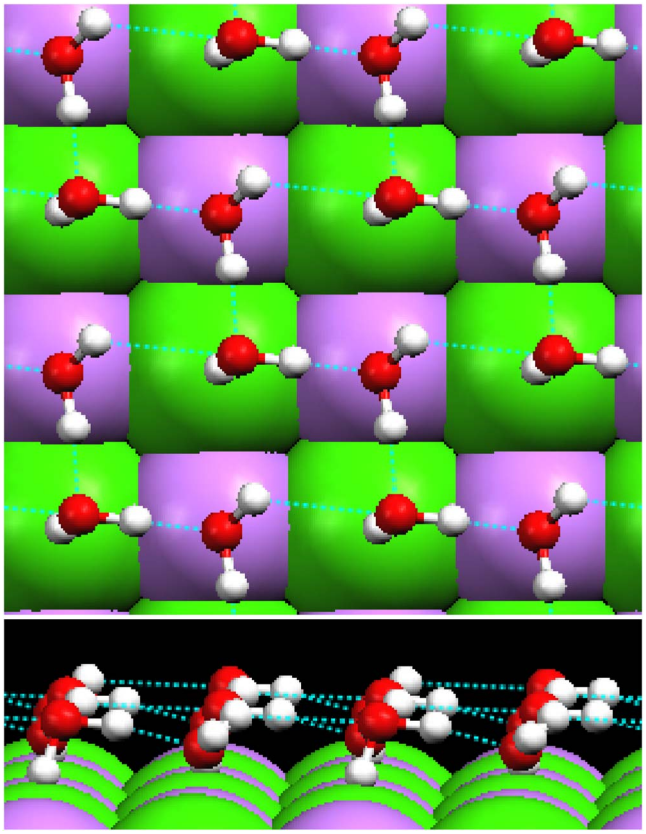

FIG. 10. (Color online) Same as Fig. 8 but for 2 ML water adsorption on NaCl (001).

result implies that from 1.5 ML to 2 ML water adsorption, the stabilities of the configurations are almost the same. This might be the reason why in some experiments a $c(4\times2)$ pattern is observed,[13] while in some other experiments a (1×1) pattern is presented[15] (2 ML in our case). It may just come from the different water coverage deposition on the NaCl (001). The two types of structures, almost energetically degenerate and both thermodynamically stable, may switch to each other under certain experimental conditions (coverage changes, temperature increase, etc.), though currently the kinetic barrier for this transition is unknown and is under further exploration. Nevertheless, our model provides a more plausible atomistic mechanism for the electron-irradiation-driven pattern transition of water layer on NaCl (001).[16] The electron radiation (~90 eV) damage on the (1×1) HAS pattern will possibly cause the desorption of some water molecules, which lowers the water coverage; thus, the water molecules reorganize from the (1×1) pattern (2 ML) to form the $c(4\times2)$ (1.5 ML) structure.

From Table IV and Fig. 11(b), one finds out the adsorption energy has the same increase/decrease tendency as the water-water interaction energy E_{ww}, showing again the role of water-water interaction. At coverage $\geqslant$0.5 ML, E_{ww} is always larger than E_{sw}, indicating that the NaCl (001) surface behaves more like a hydrophobic surface. This result gives evidence at the molecular level to understand why pure NaCl crystals do not tend to adsorb water and deliquesce in the air when the relative humidity (RH) <75% at room temperature.[17]

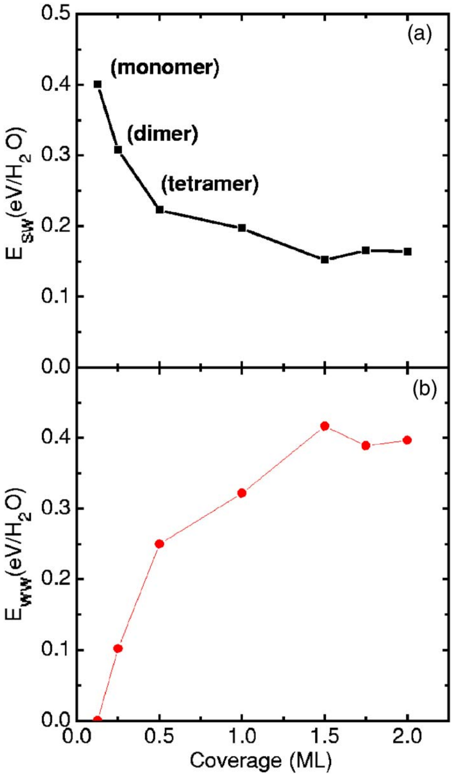

FIG. 11. (Color online) The substrate-water (a) and water-water (b) interactions as a function of water coverage on NaCl (001) surface.

IV. CONCLUSIONS

To summarize, *ab initio* DFT calculations were carried out to study the adsorption of water monomers, dimers, tetramers, and overlayers on NaCl (001) surfaces. In general, water monomers choose to lie on the NaCl (001) surface with a downward-tilted dipole plane, where the O atoms sit near Na$^+$ while the H atoms form H bonds with neighbor Cl$^-$. The sp^3 hybridization of water molecular orbitals can help to understand this result. Moreover, the adsorption of water molecules is neither a pure electrostatic nor a pure covalent interaction but involves both characteristics. The O-Na$^+$ interactions are stronger than H-Cl$^-$ interactions and contribute to the major part of adsorption energies.

Hydrogen bond plays an important role on the adsorption configurations of water dimers on NaCl (001). On the other hand, the substrate restricts the formation of the water dimer and affects the strength of the hydrogen bond. Water tetramer shows qualitatively the same trend. Based on the largest adsorption energy and the strongest geometry rigidity, water tetramer is proposed as one of the possible building blocks for the first overlayer adsorption.

Overlayer water adsorption has been also studied. Beyond 0.5 ML coverage, the water-water interaction becomes stronger than the water-substrate interaction. By MD simulations at 80 K, a new structure consisting of 4-6-water rings for 1 ML has been found to be the most stable. In the cases of 1.5 ML, 1.75 ML, and 2 ML, the adsorption energy of the water network shows minor dependence on water coverage but the same fluctuation tendency with the water-water interaction. We have also found that a 2 ML adsorption model is more suitable for the explanation of the experimental observations by Bruch *et al.*[15]

ACKNOWLEDGMENT

The work was partly supported by the NSF and MOST of China, and U.S. NSF (Grant Nos. DMR-0306239 and DMR-0325218). E.G.W. acknowledges Angelos Michaelides and Matthias Scheffler for many helpful discussions.

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