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Atomic structure and energetics of adsorbed water on the NaCl(001) surface

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We have studied the structure and energetics of adsorbed water on the NaCl(001) surface using density-functional calculations within the generalized gradient approximation. We predict a new adsorption structure for the $c(4\times2)$ water bilayer which is energetically favored over the previous puckered hexagonal $c(4\times2)$ structure. Our calculations show that the 1×1 monolayer structure (wherein every water molecule binds to each surface cation) is metastable, thereby suggesting that the 1×1 structure would be transformed to the more stable $c(4\times2)$ structure which has an increased H-bond interactions between water molecules.

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The adsorption of water on crystal surfaces has been the subject of numerous studies in the past decade. While extensive investigations of water on the surfaces of metals, semiconductors and oxides have been carried out,[1–5] a determination of the structure of adsorbed water has been often controversial. Especially, the water/NaCl system[6–18] is of particular interest because of a crucial role in various areas such as environmental science and biophysics. The detailed knowledge of the adsorption structure of water on the NaCl surface would provide useful information related to the heterogeneous chemical reactions in the troposphere over oceans.[19,20]

Despite experimental[7,8] and theoretical[9–15] efforts to understand adsorbed water on the NaCl(001) surface, there is a controversy on the structure of the two-dimensional (2-D) phase which is formed before the condensation of three-dimensional phases. Using low energy electron differaction (LEED) analysis together with ultraviolet photoelectron spectroscopy and x-ray photoelectron spectroscopy, Fölsch *et al.*[7] suggested a puckered quasi-hexagonal bilayer structure of $c(4\times2)$ symmetry. Note that in this bilayer structure the arrangement of adsorbed water molecules is similar to that of the ordinary I_h ice bilayer. However, the helium atom scattering (HAS) experiment of Bruch *et al.*[8] showed that the diffraction peaks represent a highly ordered commensurate arrangement of water molecules with the lattice (no additional half or higher order peaks), indicating a well-ordered 1×1 monolayer structure with one water molecule per surface unit cell. These experimental observations of two different structures have stimulated theoretists to determine the adsorption structure of the 2-D water layer on NaCl(001). Classical simulations using model potentials have predicted either 1×1 monolayer or $c(4\times2)$ bilayer structures depending on the calculational methods. A semiempirical calculation[11] and a periodic Hartree–Fock calculation[12] found that the 1×1 structure is slightly more stable than the $c(4\times2)$ structure. The theoretical difficulty in determining water layer structure on NaCl(001) arises from the competing water–water and water–surface interactions, leading to several local minima on the potential energy surface whose energy differences are within a few meV.[12,15]

In this paper, in order to provide an explanation for the controversial issue on the low temperature phase of water on NaCl(001), we study the structure and energetics of water on the NaCl(001) surface using first-principles calculations. We predict a new adsorption structure for the $c(4\times2)$ water bilayer to be energetically favored over the previous puckered hexagonal $c(4\times2)$ structure as well as the 1×1 monolayer. In the new $c(4\times2)$ bilayer structure, the lower-layer water molecules occupy all Na sites (similar to the arrangement of water molecules in the 1×1 monolayer), while the presence of the upper-layer water molecules being bound to Cl sites with hydrogen-surface Cl interaction and H-bonded to neighboring lower-layer molecules. Based on our calculation results, we propose that the metastable 1×1 monolayer structure would be transformed to the $c(4\times2)$ structure, driven by increased H-bond interactions between water molecules.

We perform the total-energy and force calculations using density-functional theory[21] within the generalized-gradient approximation.[22] The Na, Cl, and H (O) atoms are described by norm-conserving[23] (ultrasoft[24]) pseudopotentials. A periodic slab geometry was employed with three NaCl layers and adsorbed water molecules on both sides of the slab.[25] The vacuum spacing between these slabs is about 17 Å. A plane-wave basis set was used with 25 Ry cutoff, and the **k** space integration was done with meshes of 64, 16, and 8 **k** points in the 1×1, 2×2, 4×2 surface Brillouin zones, respectively. For the $c(4\times2)$ structure we employed the equivalent 4×2 cell whose surface area is twice as large as that of the $c(4\times2)$ cell. All the atoms except the center NaCl layer were allowed to relax along the calculated Hellmann–Feynman forces until all the residual force components were less than 1 mRy/bohr. This calculation scheme was successfully applied in our previous studies for water adsorption on several surfaces.[26]

We first determine the geometries of a water monomer, dimer, and trimer on NaCl(001) using a 2×2 unit cell. Each optimized structure is shown in Fig. 1. For water monomer we consider two adsorption configurations on top of the Na atom [Fig. 1(a), labeled as type I] and the Cl atom [Fig. 1(b),

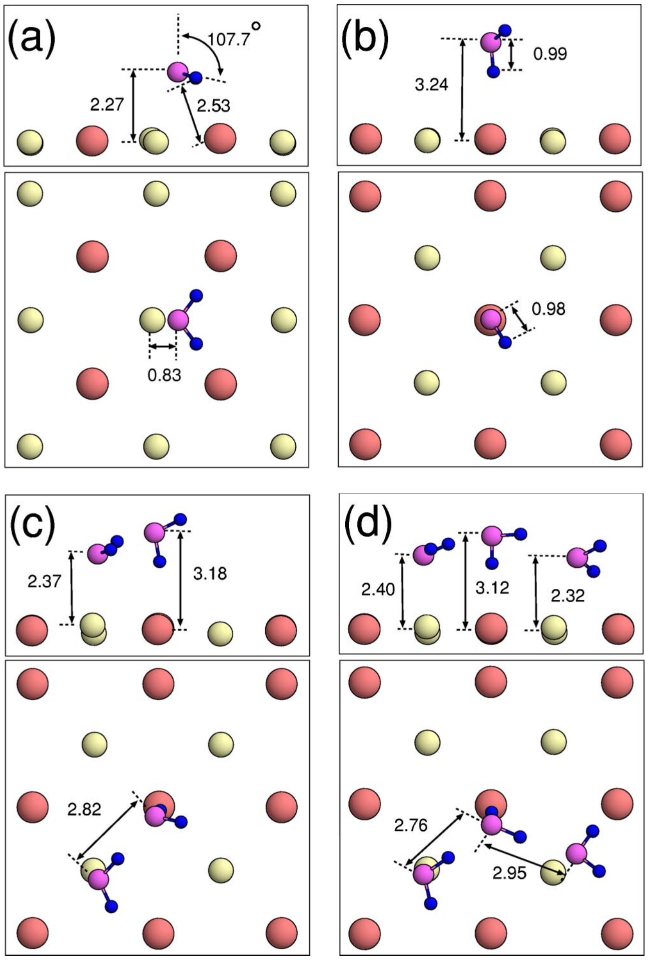

FIG. 1. (Color online) Optimized geometries for (a) a water monomer of type I (above the surface Na atom), (b) water monomer of type II (above the surface Cl atom), (c) a dimer, and (d) a trimer in a (2×2) NaCl(001) surface unit cell. Distances are in Å.

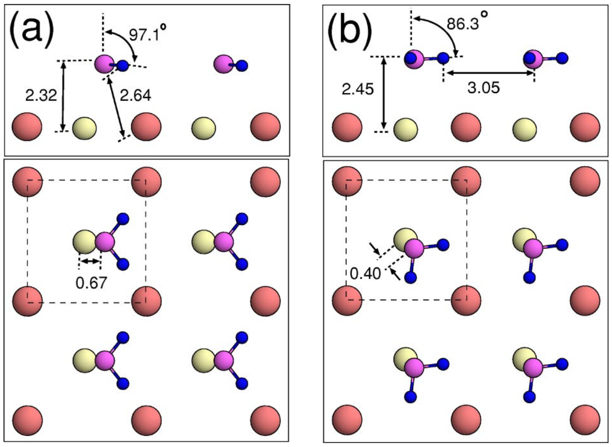

FIG. 2. (Color online) Optimized monolayer geometries in a 1 ×1 surface unit cell with one water in each cell. (a) a (1×1)-A monolayer, suggested by HAS experiment and (b) (1×1)-B, wherein molecular axis is rotated from that of (1×1)-A monolayer along the *z*-axis by 45°. Dashed line squares denote the 1×1 surface unit cell.

labeled as type II]. We find that type I which has an adsorption energy (E_{ads}) of 330 meV is greatly favored over type II with $E_{\mathrm{ads}}=112$ meV. Here, the adsorption energy is defined as $E_{\mathrm{ads}}=-(E_{\mathrm{tot}}-E_s-nE_{\mathrm{H_2O}})/n$, where E_{tot} is the total energy of the water-adsorbed NaCl(001) system, E_s is the NaCl slab energy, $E_{\mathrm{H_2O}}$ is the isolated water monomer energy, and n is the number of water molecules in a given unit cell. As shown in Fig. 1(a), the O atom of type I is laterally displaced by 0.83 Å from the Na atom and the two H atoms point toward the neigboring Cl atoms. Its water plane containing the two OH bonds is marginally parallel to the surface; the angle of this plane with respect to the normal direction of the surface is 107.7°. On the other hand, the O atom of type II is located just above the Cl atom, where one OH bond points to the Cl atom. For the water dimer we consider a structure composed of one type-I monomer and one type-II monomer [see Fig. 1(c)]. Note that the OH bond of type I points to the O atom of type II, leading to a H-bond between I and II. Owing to the presence of type II which is weakly bound to the Cl atom (despite the H-bond interaction between two water molecules), the adsorption energy of the water dimer is only 328 meV, similar to that of an isolated monomer I (330 meV). On the other hand, we find that the trimer case [Fig. 1(d)] composed of two type-I monomers and one type-II monomer shows much increased adsorption energy (418 meV) due to increased H-bond interactions between water molecules.

Based on the experimental findings, we study the geometry of the 2-D phase of adsorbed water on NaCl(001) within 1×1 and $c(4\times2)$ structures. Our basic idea to search for the possible lowest conformations for water on NaCl(001) is to optimize the two interactions such as the cation–water interaction and H-bonding interaction at the same time. Our low energy geometries are mainly characterized by (i) geometries wherein every molecule is bound to a Na atom and by (ii) geometries wherein a Na-bound molecule is H-bonded to the neighboring molecule on a Cl atom. In the case of (i), various geometries were examined by taking into account of the various OH bond orientation, different surface unit cells, and the H-bonded structure between molecules on Na atoms. We report only several important structures among many local minima that we explored. Figure 2 shows two configurations for the 1×1 water monolayer, i.e., 1×1-A [Fig. 2(a)] and 1×1-B [Fig. 2(b)]. These two structures are almost isoenergetic. The calculated adsorption energies for the 1×1-A and 1×1-B structures are 310 and 318 meV, respectively. Thus, water molecules in these two structures are somewhat weakly bonded to the surface compared with an isolated monomer I ($E_{\mathrm{ads}}=330$ meV). We examine two dominant contributions for water adsorption due to water–surface and water–water interactions. The water–surface ($E_{\mathrm{w-s}}$) interaction is given by $E_{\mathrm{w-s}}=-(E_{\mathrm{tot}}-E_w-E_s)/n$, where E_{w} is calculated by removing the NaCl slab from the optimized water-adsorbed NaCl(001) structure. We obtain the water–water ($E_{\mathrm{w-w}}$) interaction energy by subtracting $nE_{\mathrm{H_2O}}$ from E_w. Our calculated $E_{\mathrm{w-s}}/E_{\mathrm{w-w}}$ for the 1×1-A structure is 302/8 meV, whereas that for the 1×1-B structure is 226/92 meV (see Table I). It is interesting to note that the two contributions $E_{\mathrm{w-s}}$ and $E_{\mathrm{w-w}}$ between the 1×1-A and

TABLE I. Calculated adsorption energies (E_{ads}), water–surface ($E_{\mathrm{w-s}}$ including the surface reconstruction energy E_{con}), and water-water ($E_{\mathrm{w-w}}$) interaction energies (in meV/molecule) for the optimized stuctures of water adsorbed on NaCl(001).

	θ(ML)	E_{ads}	$E_{\mathrm{w-s}}$	$E_{\mathrm{w-w}}$
Monomer of type I	0.25	330		
Monomer of type II	0.25	112		
Dimer	0.5	328	247	81
Trimer	0.75	418	231	187
1×1-A monolayer	1	310	302	8
1×1-B monolayer	1	318	226	92
H-down $c(4\times2)$ bilayer	1.5	457	183	274
H-up $c(4\times2)$ bilayer	1.5	427	134	292
H-down $c(4\times2)$ monolayer	1	408	238	171

1×1-B structures differ from each other. The increased $E_{\mathrm{w-w}}$ in the 1×1-B structure is caused by the enhanced hydrogen bonding interaction between water molecules. Note that the H atoms in the 1×1-B structure orient toward the O atoms of the neighboring water molecules with $d_{\mathrm{H-O}}=3.05$ Å [see Fig. 2(b)]. On the other hand, the increased $E_{\mathrm{w-s}}$ in the 1×1-A structure is possibly due to the attractive interaction between the H and Cl atoms. This attraction causes a large lateral displacement of 0.67 Å from the Na atom [see Fig. 2(a)]. Note, however, that this value in the 1×1-A structure is smaller than that (0.83 Å) in a single adsorbed water [Fig. 1(a)], indicating that the attractive interaction in the latter is stronger than in the former.

For the $c(4\times2)$ water bilayer, we consider a new bilayer structure denoted as H-down bilayer [Fig. 3(a)]. Our H-down bilayer structure was modeled within the $c(4\times2)$ unit cell by arranging three water molecules [i.e., two type-I monomers and one type-II monomer, labeled as 1, 4, and 6, respectively, in Fig. 3(a)] plus the trimer of Fig. 1(d). Here, non-H-bonded H atoms of type II (labeled as 5 and 6) point down to the surface. This H-down bilayer ($E_{\mathrm{ads}}=457$ meV) is energetically much more favored over 1×1 monolayer structures ($E_{\mathrm{ads}}=310$ and 318 meV for 1×1-A and 1×1-B, respectively). For comparison with previously proposed $c(4\times2)$ structure,[7] we also determine the $c(4\times2)$ H-up bilayer geometry starting from the puckered hexagonal bilayer structure composed of three water molecules in the lower layer and three water molecules in the upper layer. In our optimized H-up structure [Fig. 3(b)], four water molecules are located above Na atoms, with two additional water molecules (non-H-bonded H atoms direct upward the surface) being located above Cl atoms, similar to that of an earlier theoretical calculation.[15] We find that the H-up structure is less stable than the H-down one by $\Delta E_{\mathrm{ads}}=30$ meV (see Table I).

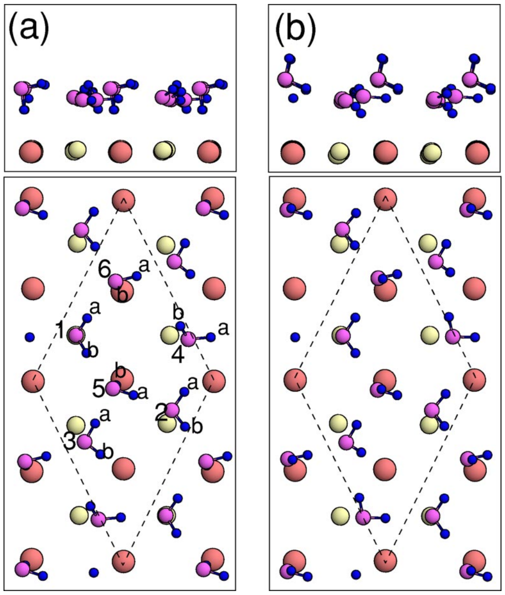

FIG. 3. (Color online) Optimized bilayer geometries in a $c(4\times2)$ surface unit cell with six water molecules in each cell. Dashed line parallelograms denote the $c(4\times2)$ surface unit cell. (a) H-down $c(4\times2)$ bilayer and (b) H-up $c(4\times2)$ bilayer.

TABLE II. Calculated O–H bond lengths and O–Na and H–Cl distances (in Å) for the H-down $c(4\times2)$ water bilayer adsorbed on the NaCl(001) surface.[a]

Molecule	O-Na[b]	O-H_a	O-H_b	H_b-Cl
1	2.533	0.997*	0.996*	
2	2.506	0.992	1.007*	
3	2.593	1.010*	0.997	2.318
4	2.513	0.999	0.986	
5		1.000*	1.008	2.073
6		1.001*	1.009	2.061

[a] An asterisk (*) denotes the OH bond involved in H-bond between water molecules in the lower and upper layer. The O–H bond length for an isolated water monomer in the gas phase is 0.984 Å.

[b] For the water monomer of type I in Fig. 1(a); the O–Na distance is 2.415 Å.

Both H-up and H-down structures are highly distorted from the puckered hexagonal network of water molecules[7] due to considerable surface–water interactions as discussed below. In the case of the H-up structure, the vertical distance (0.91 Å) between the oxygen atoms in the lower and upper layers is similar to that in the crystalline ices (0.96 Å), while the H-down structure shows a reduced vertical spacing (0.49 Å), thus forming a less puckered layer. This reduction implies a different nature of water–surface interaction, compared to that of the usual bilayer case wherein the molecules in the upper layer interact mainly with the molecules in the lower layer, rather than with the surface. We find that $E_{\mathrm{w-s}}$ (183 meV) [$E_{\mathrm{w-w}}$(274 meV)] for the H-down structure is larger (smaller) than 134 (292) meV for the H-up one, indicating that the reduced vertical spacing in the H-down structure is possibly due to a more favorable water–surface interaction.

The calculated O–H bond lengths of six adsorbed water molecules [denoted as 1–6 in Fig. 3(a)] in the H-down bilayer are listed in Table II. Molecules 1 and 2 adsorbing nearly parallel to the surface are H-bonded to the neighboring water molecules; H_{3b} points toward a neighboring surface Cl atom and its elongated OH bond length indicates an attraction with the surface Cl atom; only H_{4b} which is not involved in the H-bonding shows a negligible OH bond elongation (see Table II). However, these molecules 1–4 have a common feature that each molecule is bound to each surface Na atom, forming a lower water layer corresponding to 1 ML coverage. Molecules 5 and 6 are bound to surface Cl atoms, with elongated OH bonds due to H-bonding to the neighboring lower-layer molecules. It is worthy to note that the OH bonds interacting with surface Cl atoms are greatly lengthened by a strong OH$\cdots$Cl attraction. This attraction is greater than that in the corresponding isolated molecule case [Fig. 1(b)] because the enhanced polarizability in a 2-D H-bonded network enhances the negative charge of the O atom and the positive charge of the H atom, which have been generally found in H-bond relay systems.[27] Therefore, these Cl-site-bound water molecules reduce vertical spacing between the two layers, and they play a key role to form a 2-D water layer by facilitating a direct interaction with the surface as well as the lateral interaction between absorbates.

In summary, we have performed first-principles calculations for the structural and bonding properties of water adsorbed on the NaCl(001) surface. Compared with the previously proposed $c(4\times2)$ structure which shows puckered hexagonal bilayer geometry, we found a more stabilized $c(4\times2)$ structure with an enhanced water–surface interaction. This new predicted $c(4\times2)$ structure which has a coverage of $\theta=1.5$ ML is more stable than the 1×1 structure (with $\theta=1$ ML) by 139 meV in adsorption energy. Noting that water adsorption on top of the Na atom is strongly favored over the Cl site, we tentatively explain that, at low coverages below 1 ML, water molecules preferably occupy Na sites to form the 1×1 structure, but, as the coverage increases above 1 ML, water molecules can easily occupy Cl sites to form the $c(4\times2)$ structure. However, even before the completion of a water monolayer with the 1×1 structure, the presence of 4×2 domains may be possible because of its increased H-bond interactions between water molecules. In this sense, we believe that previous experiments observed the 1×1 or the $c(4\times2)$ structure because of different water coverages/sample preparation.

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