

Adsorption of water on chlorine-terminated Si(111) from first principles: Substrate-induced ordering versus intermolecular interactions

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The adsorption of water molecules on a chlorine terminated Si(111) substrate is used as a model to analyze in detail the interaction between water and a hydrophilic surface by means of *first-principles* calculations. Possible initial adsorption configurations for single water molecules and the potential energy surface are studied. The water monomers are found to adsorb preferably on interstitial sites between surface chlorine atoms. The effect of the substrate on the rotational orientation of the molecule is very small. This is consistent with the computational results for a full termination layer of water on the surface which show that the long-range order of the water layer stems from intermolecular interactions rather than from substrate-induced ordering effects.

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Water plays a crucial role in many scientific fields extending from biology, environmental and atmospheric sciences to technological investigations on corrosion, passivation, and catalysis. Still, many fundamental questions related to dynamical processes in aqueous systems on ultrashort time scales,¹ the impact of hydrogen bonds on the electronic and optical properties of water monomers² or structural and electronic properties of low-dimensional water structures such as clusters³ or thin films⁴ are still open. The adsorption of water on solid surfaces provides a model system to study in detail the interaction between water monomers using sophisticated surface analysis techniques as well as accurate *ab initio* calculations.^{5–8} Recently, the adsorption and crystallization of water on the hydrophilic chlorine terminated Si(111) surface was studied using ultrafast electron crystallography.⁹ A long-range ordered surface ice film could be detected. In the present work we use *first-principles* calculations to determine the respective roles of substrate-molecule and intermolecular interactions for the formation of thin ordered water films on Cl/Si(111).

To this end we use density functional theory (DFT¹⁰), in conjunction with a plane-wave basis set as implemented in the *ab initio* simulation package VASP.¹¹ The electron-electron interaction is described within generalized gradient approximation (GGA) of the exchange-correlation energy.¹² The electron-ion interaction is modeled by the projector augmented wave method,^{13,14} which on the one hand gives access to all-electron wave functions in the atomic core regions, but on the other hand allows for restricting the plane-wave expansion of the wave functions in the present case to a maximum kinetic energy of 30 Ry. The surface is modeled by periodically repeated slabs using supercells containing five bilayers of Si oriented along [111] direction and a vacuum region of similar thickness. One side of the slab is saturated with hydrogen, while the upper layer is terminated with one monolayer of chlorine atoms. The in-plane lattice constant of the Si slab is 5.468 Å. Figure 1 shows the geometry of the slab. Different coverages of water molecules on

this surface were studied using 1×1 , 2×2 , and 4×4 surface periodicities. The respective surface Brillouin zones were sampled with a \mathbf{k} -point density equivalent to a uniform (8,8,1) mesh for the unreconstructed surface. The thickness of the slab as well as the number of \mathbf{k} points were checked carefully for convergence. The saturating hydrogen atoms as well as the bottom bilayer of Si atoms are kept fixed during the calculations. All remaining atoms are fully relaxed until the forces are below 5 meV/Å.

For the geometry of the chlorine terminated Si(111) surface we confirm the early theoretical findings of Bachelet and Schlüter.¹⁵ The chlorine atom preferably sits atop the Si atom of the uppermost surface layer. The distance between the Si and Cl atom is 2.07 Å. This is in excellent agreement with experiment.¹⁶ Single adsorbed water monomers on the chlorine terminated Si surface are modeled using one molecule in a 2×2 surface unit cell. Enlarging the unit cell to 4×4 periodicity changes the adsorption energy by less than 5 meV, indicating that intermolecular interactions are nearly

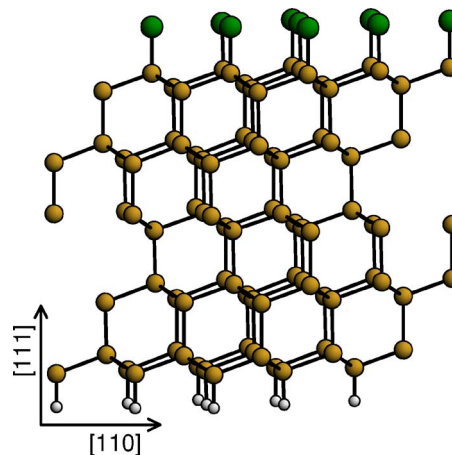


FIG. 1. (Color online) Side view of the used slab geometry; gray/brown (large dark/green, small/white) atoms denote Si (Cl, H) atoms, respectively.

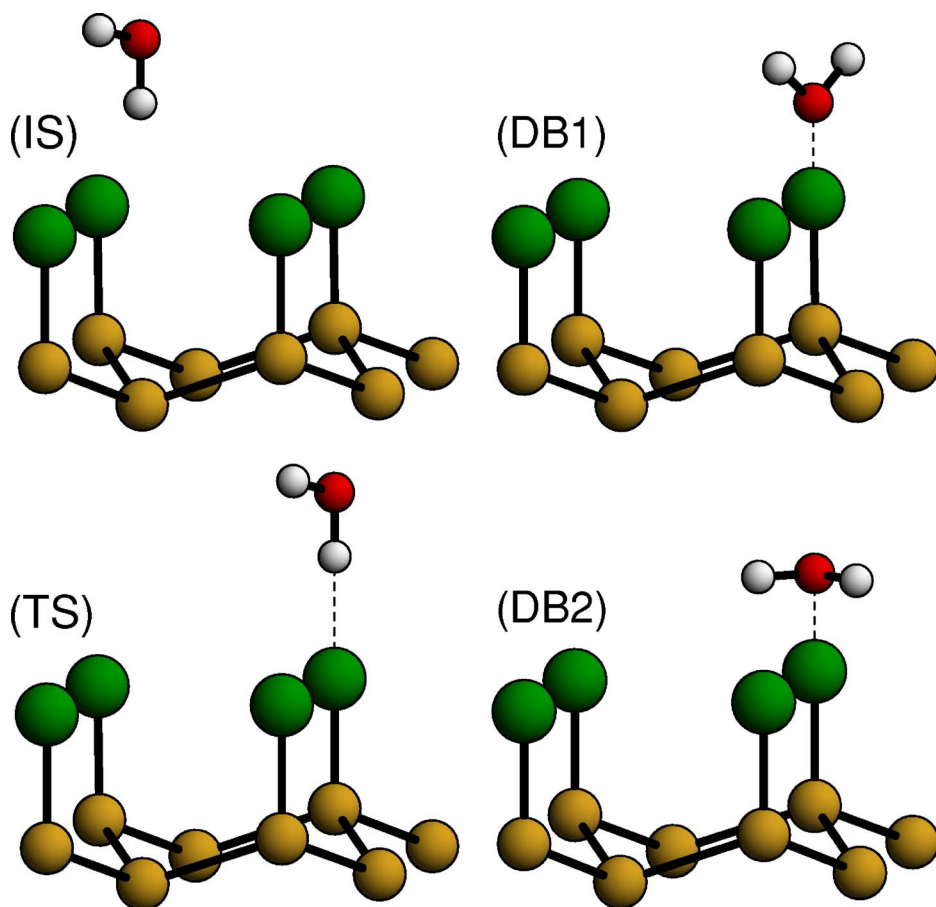


FIG. 2. (Color online) Initial configurations of a water molecule on Cl/Si(111) substrate: (a) IS, (b) TS, (c) DB1, and (d) DB2, gray/brown (large dark/green, small/white, small dark/red) atoms denote Si (Cl, H, O) atoms, respectively.

quenched beyond this coverage. Four different starting configurations are chosen, see Fig. 2. To study bonding via the OH groups of the molecule, i.e., establishing a hydrogen bond to the surface, the molecule is placed atop a Cl atom [top site (TS)] or on an interstitial surface site (IS), one OH group pointing towards the surface, see Figs. 2(a) and 2(b). A possible bonding via the oxygen dangling bonds is probed using configurations where the oxygen atom is placed on top of a Cl surface atom and the OH group either points out of plane (DB1) or in plane (DB2), see Figs. 2(c) and 2(d). The initial geometry of the water molecule is taken to be the calculated gas-phase geometry, with a HOH angle of 104.5° and an OH bond length of 0.985 \AA . The relaxed adsorption configurations and the calculated adsorption energies are given in Fig. 3 and Table I, respectively. The adsorption site IS is energetically most favored. The initial configurations DB1 and DB2 are not favored: DB1 has a positive adsorption energy, i.e., the molecule is repelled from the surface, and DB2 relaxes into a final geometry that closely resembles the IS configuration. However, even in the most favored case the binding energy calculated in DFT-GGA is rather low, only 62 meV per molecule. In both IS and TS the relaxed water molecule structure remains close to the gas phase structure; the OH bond lengths are slightly shortened to 0.975 \AA , the HOH angles are 104.5 and 104.2° , respectively. The distance between the surface Cl atoms and the closest water hydrogen is 2.88 and 3.01 \AA for IS and TS, respectively. This is clearly beyond the sum of the respective covalent radii of hydrogen and chlorine, that amounts to

1.29 \AA , but relatively close to the sum of the respective van der Waals radii, 3.00 \AA (data taken from Ref. 17). Dispersive or van der Waals forces are nonlocal interactions that are not contained in the local description of exchange and correlation energy within the GGA. Therefore the actual adsorption energies might be slightly larger than predicted here.¹⁸ By the same token, the calculated distance between the water molecule and the Cl/Si(111) surface is probably overestimated by a few percent.

Figure 4 shows the potential energy surface (PES) experienced by the water monomer. In order to calculate it, the lateral position of the water oxygen was fixed for a number of sampling points on the surface while its vertical position as well as the other molecular and substrate surface degrees of freedom were free to relax. The PES shows that water favors the interstitial position between the Cl atoms. Although allowed to rotate freely, the water molecule mainly kept its orientation as given in the IS and TS configurations. To estimate the influence of the substrate on the monomer orientation, we rotated both OH groups of the fully relaxed IS molecule around the surface normal, keeping the substrate layers and the water oxygen atom fixed. The change of the adsorption energy relative to the fully relaxed configuration versus the rotation angle is shown in Fig. 5. The plot does not show the threefold symmetry of the clean surface, because the substrate atoms remained fixed during these calculations. The calculated energy difference of 4.5 meV between the most preferred and the most adverse position is

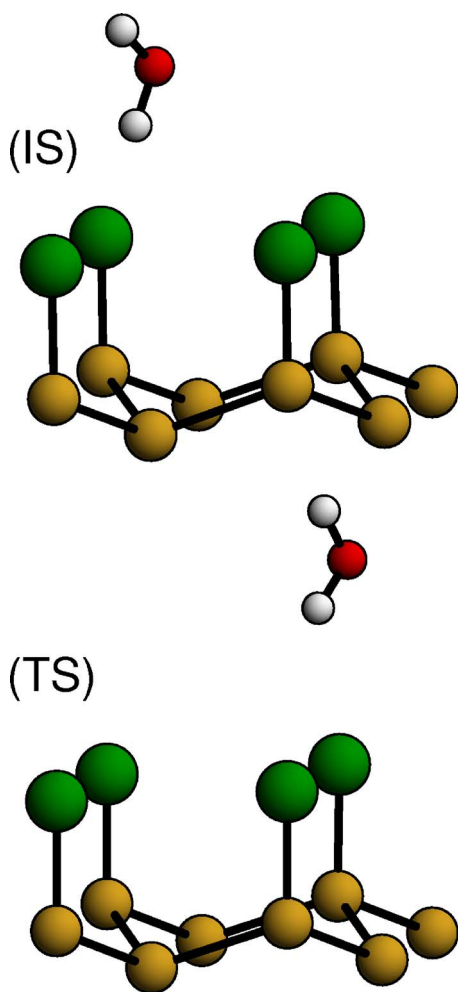


FIG. 3. (Color online) Final geometry of (a) one IS and (b) one TS water molecule in a 2×2 surface cell.

therefore the upper limit characterizing the substrate-induced corrugation of the angular dependence of the adsorption energy. This clearly indicates that a long-range ordered water adlayer as found experimentally⁹ is due to intermolecular interactions rather than induced by the substrate. Furthermore, these calculations show that the error bar of the calculated PES due to not fully relaxed water molecules is below $\Delta E=5$ meV.

TABLE I. Adsorption energies per water molecule on Cl/Si(111) for different adsorption configurations.

Coverage	Initial geometry	Adsorption energy [meV]
0.25 ML	TS	-26
	IS	-62
	DB1	+14
	DB2	-56
1.00 ML	IS	-118
1.50 ML	Ruan <i>et al.</i> ⁹	-487
2.00 ML	IS+TS	-415

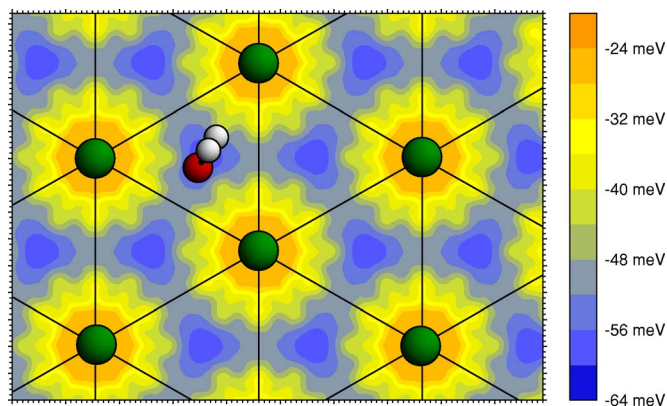


FIG. 4. (Color online) PES for adsorption of water on Cl/Si(111). Cl atoms and relaxed geometry of IS configuration are indicated.

How are the water molecules bonded to the substrate? The final, relaxed configurations assumed by the water monomers on the surface are rather similar in the IS and the TS case, see Fig. 3. The water hydrogen does not point directly to the nearest Cl atom. This, together with the very low adsorption energy, indicates that the water does not form hydrogen bonds with the underlying Cl atoms. The water monomers in the final adsorption configurations are oriented in such a way that the water dipole points nearly parallel to the surface, thus also excluding strong electrostatic interaction between the ad molecules and the substrate.¹⁹ Consistently with the low adsorption energy and the large separation between the water monomers and the substrate, no noticeable bonding/antibonding combinations of the molecular or substrate wave functions—characteristic for covalent bonds—form. The water adsorption does not significantly alter the electronic properties of the surface. In Fig. 6 the surface band structures of the clean Cl/Si(111) surface and of the IS and TS bonding configurations are shown, all in 2×2 surface periodicity. The bands are calculated along the path $\Gamma-M-K-\Gamma$, where $\Gamma=(0,0)$, $M=(\frac{1}{2},0)$, $K=(\frac{2}{3},\frac{1}{3})$. Upon adsorption, no bands show up in the surface band gap. Only a bulk-like valence state is slightly lifted above the projected bulk-band structure near Γ .

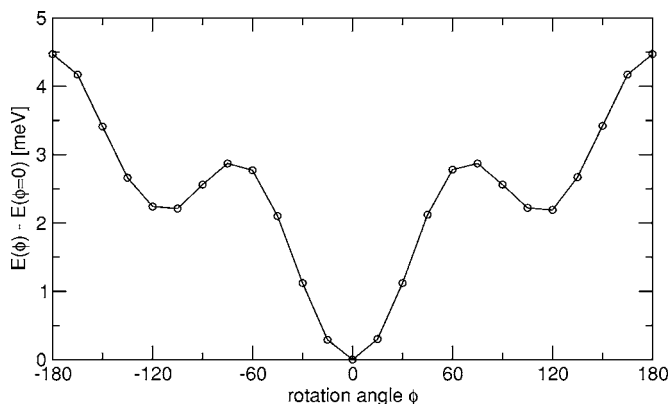


FIG. 5. Binding energy dependence on rotational orientation of single water molecule.

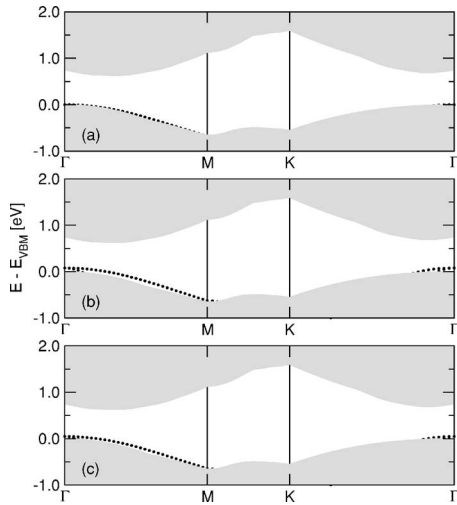


FIG. 6. Surface band structure of (a) clean Cl/Si(111) surface, (b) surface with IS, and (c) with TS water molecule, each in 2×2 surface cell. Energies are normalized to bulk valence band maximum (VBM). Filled circles denote occupied states.

We also investigated the charge redistribution upon water adsorption on Cl/Si(111). In Fig. 7 charge density difference plots show $\Delta\rho(\vec{r})$ near the surface upon adsorption of water in the IS and the TS configuration. It is calculated as

$$\Delta\rho(\vec{r}) = \rho_{\text{slab}+\text{H}_2\text{O}}(\vec{r}) - \rho_{\text{slab}}(\vec{r}) - \rho_{\text{H}_2\text{O}}(\vec{r}), \quad (1)$$

where $\rho_{\text{slab}+\text{H}_2\text{O}}(\vec{r})$, $\rho_{\text{slab}}(\vec{r})$, and $\rho_{\text{H}_2\text{O}}(\vec{r})$ denote the charge densities of the relaxed adsorbed system, the relaxed clean slab, and a relaxed water molecule in gas phase, respectively. In Fig. 7 the two isosurfaces $\Delta\rho(\vec{r}) = \pm 0.01 \text{ e}/\text{\AA}^3$ are shown for the IS and TS configuration. The charge redistribution at the substrate surface is related to the relaxation of the Cl atoms upon adsorption of water. In the case of the IS adsorption configuration, a weak polarization of the adsorbed molecule takes place, probably contributing to the bonding between molecule and substrate. No such effect is noticeable for the TS configuration. Indeed, if we approximate the stabilizing dipole-dipole interaction between the water molecules by an Ewald summation, including appropriate point charges at the positions of the O and H atoms to mimic the water gas-phase dipole moment of 1.85 D, we obtain 11 and 12 meV for the IS and TS configurations, respectively. Thus, the already low adsorption energy of the TS configuration is largely related to the attraction between the admolecules.

We also studied dissociated adsorbate structures, where an OH group and a H atom are placed next to each other on the surface. Two starting configurations D-1 and D-2 are shown in Fig. 8. They are, however, energetically far less favored than the previously discussed structures. Configuration D-1, where a HCl and a HO·Cl complex are assumed to form on the surface, has a positive adsorption energy of +4.88 eV; configuration D-2, where a HCl and a OH·Cl hydrogen bond complex are assumed to form, has a positive adsorption energy of +5.83 eV. Fragmentation of the water monomer costs far more energy than is gained upon bonding the fragments to the surface.

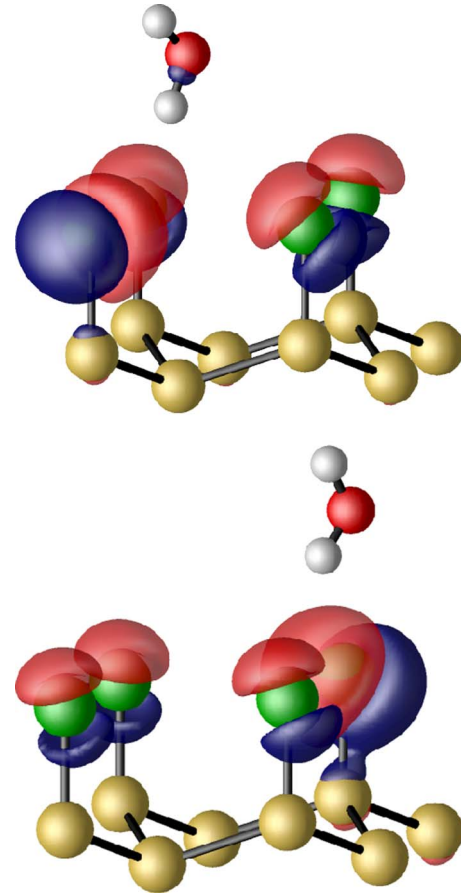


FIG. 7. (Color online) Charge density difference isosurfaces for IS (upper panel) and TS (lower panel) bonding configuration. Light gray/red (dark gray/blue) indicates charge depletion (accumulation). Isosurface value $0.1 \text{ e}/\text{\AA}^3$.

Finally, we investigated the formation of a closed water layer on the surface by increasing the number of water molecules per unit cell. Several configurations were tested: a 1.00 ML coverage structure with one IS water molecule per 1×1 unit cell; a 1.50 ML coverage structure based on experimental findings by Ruan *et al.*;⁹ and a 2.00 ML coverage structure occupying both the TS and IS positions within one surface unit cell. The lower panel of Table I shows the adsorption energies per molecule for these configurations.

In the 1.00 ML case, the Ewald summation described above yields an attractive dipole-dipole interaction energy of 67 meV per molecule, 56 meV more than in the 2×2 cell. Thus, the entire energy gain in the 1.00 ML case is due to the dipolar interaction within the water layer.

The long-range ordered water film found by Ruan *et al.* has a $(\frac{2}{3}\sqrt{3} \times \frac{2}{3}\sqrt{3})R30^\circ$ surface unit cell that contains two water molecules per bilayer.⁹ This corresponds to 1.5 water molecules per Si(111) surface unit cell for one bilayer. We optimized an according structure in a 2×2 surface unit cell (which contains three of the water film's unit cells). See Fig. 9 for the optimized structure. The lower half bilayer molecules occupy every fourth IS and TS site and are bound to the surface. The Cl···H distance is 2.86 Å. The binding energy per water molecule is about 490 meV. This large energy gain is due to the formation of a two-dimensional network of

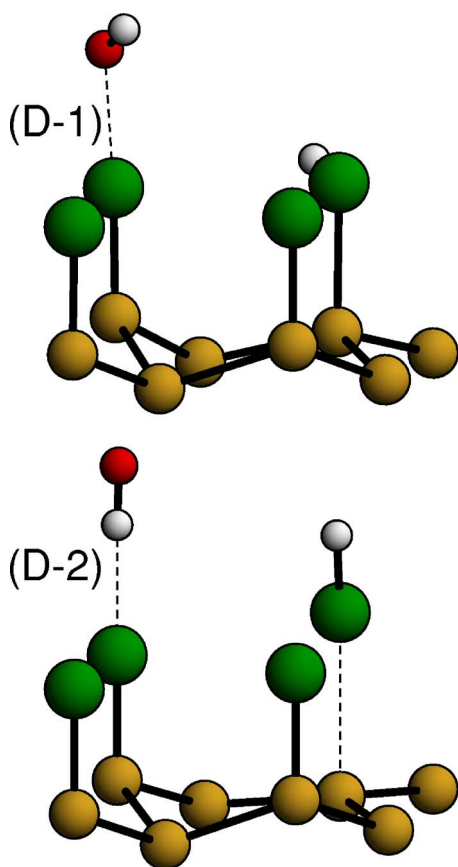


FIG. 8. (Color online) Starting geometries for dissociated adsorbate configurations D-1 and D-2.

hydrogen bonds, that is not possible at lower coverages. Every water molecule has three hydrogen bonds to its neighbors, which are slightly unequal: the upper half bilayer molecules donate two hydrogen bonds of length 1.764 Å and

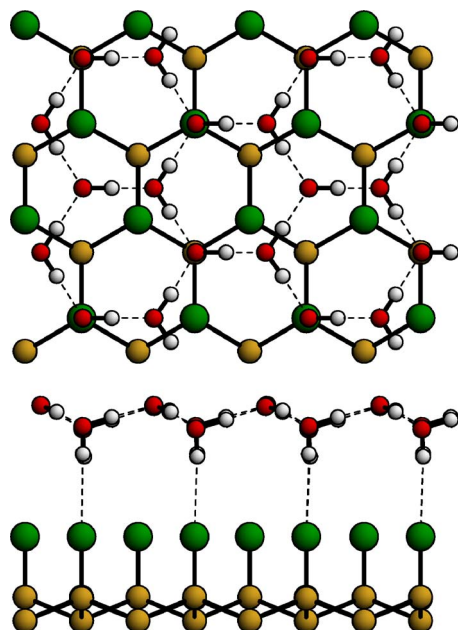


FIG. 9. (Color online) 1.50 ML ice layer, as proposed by Ruan *et al.* (see Ref. 9). Upper panel: top view, lower panel: side view.

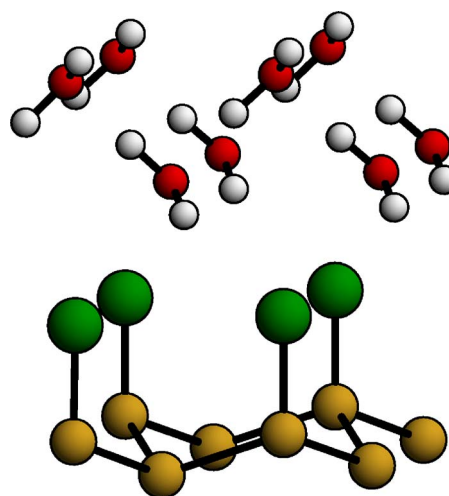


FIG. 10. (Color online) 2.00 ML ice layer, obtained by combining one TS and one IS water molecule in a 1×1 surface cell.

accept one hydrogen bond of length 1.490 Å from the lower half bilayer. Due to their interaction the geometries of the molecules deviate from the gas phase: the surface bound water molecules have OH bond lengths of 0.974 Å (to the surface) and 1.048 Å (to the upper half water molecules) and a HOH angle of 105.0°; the upper water molecules have OH bond lengths of 0.995 Å and a HOH angle of 107.6°. We believe these deviations are a surface effect and that the structure of the water film will be more regular if more than one water bilayer condenses on the surface. The water surface cell lattice constant is 4.465 Å which is very close to the experimental ice *Ih* lattice constant of 4.497 Å.²⁰ This very small mismatch allows for the formation of a relatively strain-free ice-like overlayer on the surface. Is it possible to arrange the water molecules at a higher coverage on the surface?

In the 2.00 ML case, that has 1×1 surface periodicity, the binding energy decreases relative to the 1.50 ML case to about 415 meV per molecule. The relaxed structure resembles one-dimensional water chains along the surface (1, 0) direction, see Fig. 10, where every second molecule is bound to the surface in a TS-like position. However, the coverage is too high to arrange all molecules in a two-dimensional network. We use this computationally easily accessible structure to study the contributions to the binding energy in greater detail. The hydrogen bond network is responsible for a large part of the binding energy. This is confirmed by a separate calculation, where only the water layer is contained in the (same) supercell. The binding energy calculated for this constrained water film is 363 meV per molecule. This is very close to the energy of two single hydrogen bonds in an ice crystal, which is about 350 meV within DFT-GGA.²¹ Thus, ice-like hydrogen bonds stabilize the water bilayer. If we subtract the hydrogen-bond energy from the adsorption energy of the 2.00 ML film on Cl/Si(111), we obtain 52 meV per molecule. This is roughly the adsorption energy of single molecules in IS configuration (or the adsorption energy of the 1.00 ML film reduced by the dipolar interaction energy). In Fig. 11 we show the calculated energy change upon changing the vertical distance between

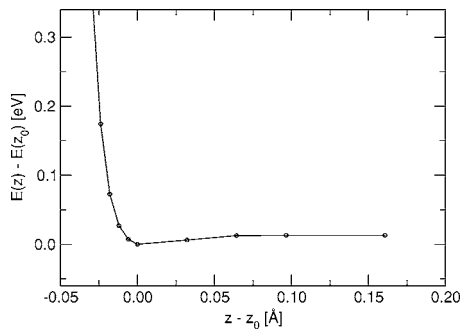


FIG. 11. Energy change upon shifting ice 2.00 ML in z direction; z_0 denotes equilibrium distance from the surface.

the frozen water film (2.00 ML) and the frozen substrate. Consistently with the previous discussion, we find the energy minimum for the equilibrium distance to be very shallow.

The surface band structures of the higher coverage configurations are compiled in Fig. 12. There, the clean surface as well as the 1 and 2 ML cases are plotted, in 1×1 surface periodicity. In the 1 ML case, see Fig. 12(b), one occupied bulk-like state is lifted near Γ , and a weakly dispersive water localized band shows up near K . In the 2 ML case, see Fig. 12(c), several low-lying surface bands occur, again near the K point. In both cases, the fundamental surface band gap shrinks slightly.

In conclusion, we investigated the adsorption of water on the Cl/Si(111) surface by means of *first-principles* DFT-GGA calculations. The potential energy surface for the adsorption of water monomers shows shallow minima at interstitial positions between the Cl atoms. Several bonding configurations were studied in detail and the formation of a closed water film was investigated. The calculations show that very weak, polarization-induced substrate-water interac-

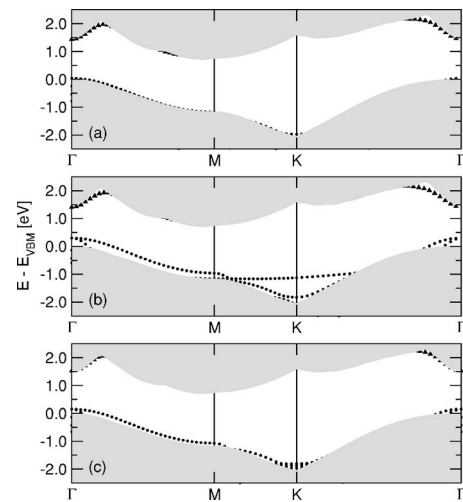


FIG. 12. Surface band structure of (a) clean Cl/Si(111) surface, (b) surface with IS, and (c) with IS and TS water molecules, each in 1×1 surface cell. Energies are normalized to bulk valence band maximum (VBM). Filled circles (triangles) denote occupied (unoccupied) states.

tions occur, that are one order of magnitude smaller than the hydrogen-bond related interactions within the water film. No tendency for dissociation of the water monomers was found. The calculations suggest that the substrate modifies rather than induces the order of the water film. Thus, an ordered water film is favored that maximizes the number of hydrogen bonds in the adsorbate layer.

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