Strongly bonded water monomers on the ice Ih basal plane: Density-functional calculations

C. Thierfelder,* A. Hermann, and P. Schwerdtfeger
Institute of Fundamental Sciences, Massey University, Albany, Auckland, New Zealand

W. G. Schmidt
Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany

The adsorption of water monomers on noncrystallographic sites of the ice Ih basal plane is calculated from *first principles*. The results presented here do not support previous theoretical findings that state molecular adsorption energies in excess of the bulk cohesive energy. Still, due to an enhanced strength of the surface hydrogen bonds compared to the bulk, the admolecules are found to lower the ice surface energy. For the surface structures investigated here, the monomer adsorption energies are found to be rather insensitive with respect to the detailed microscopic structure of the underlying substrate. The latter, however, determines the adsorption-induced changes of the surface dipole layer.

Water is one of the few substances that occurs naturally in all three phases. Its solid phase, ice, appears as an amorphous solid or in more than a dozen of different lattice structures, depending on external pressure and temperature.[1] The flexibility of the hydrogen bond, together with the preferred tetrahedral coordination of water molecules allow for this large variety of solid phases. Under ambient conditions, ice crystallizes in the ice Ih phase. Its bulk properties are rather well understood.[2–4] The oxygen atoms form a regular hexagonal lattice. The two hydrogen atoms belonging to an oxygen atom lie between two of the four oxygen neighbors, obeying the Bernal-Fowler ice rules.[5] The proton configuration is disordered.

In contrast to the bulk material, the ice surface structure is still not really understood. The question of existence of a quasiliquid layer on the ice surface, for instance, dates back to Faraday.[6] Understanding the Ih(0001) basal plane has been the aim of numerous experimental and theoretical investigations, see, e.g., Ref. 7 for a review of early work. More recently, dynamical low-energy electron diffraction (LEED) at $T=90$ K accompanied by Hartree-Fock total energy calculations and semiempirical molecular dynamics (MD) simulations found the Ih(0001) basal plane to be fully bilayer-terminated and unreconstructed.[8,9] Also, helium atom scattering on thick ice layers, grown at $T=125$ K, showed the surface to have 1×1 hexagonal symmetry and to be terminated by a full ice bilayer.[10] X-ray absorption spectroscopy measurements on ice films grown at $T=130,\dots,150$ K, on the other hand, indicate the occurrence of occupied surface sites different from bulk crystallographic positions.[11,12] The reported onset temperatures T_p of surface premelting depend strongly on the respective method and experimental conditions. Surface vibrational spectroscopy studies found $T_p \approx 200$ K.[13] Other experimental studies, however, found T_p as high as $T_p=260$ K.[14] Theoretical studies on the premelting of the surface reported significant surface disordering at $T=230$ K in a semiempirical MD study[15] and at $T=190$ K in a Car-Parrinello MD study.[16] Obviously, the picture of the ice surface structure depending on temperature is far from complete. However, in the low-temperature regime, the assumption of a crystalline surface covered with admolecules seems to be justified.

Recent empirical calculations[17] using the TIP4P potential[18] considered the adsorption, diffusion, and island formation of water admolecules on ice. Surprisingly, for some adsorption configurations it was found that the binding energy of water admolecules exceeds the cohesive energy of the bulk.[17] Motivated by these findings, our paper aims at providing reliable *ab initio* results for the binding of water molecules on the crystalline Ih(0001) surface.

To this end, density-functional theory calculations (DFT) are performed, using a plane-wave basis and the projector augmented wave method (PAW)[19] as implemented in the Vienna *ab initio* simulation package (VASP).[20,21] The exchange-correlation contribution to the total energy is modeled using the generalized gradient approximation (GGA).[22,23] For comparison, some calculations were performed within the local density approximation (LDA).[24] The plane-wave cutoff for the wave-function expansion is 30 Ry. The surface is modeled by periodically repeated slabs. Each slab contains four bilayers of ice within a 2×2 periodicity (see Fig. 1 for the side view). The slabs are separated by a vacuum, equivalent in thickness to four bilayers. Both the number of **k** points and the thickness of the slab and the vacuum were tested for numerical convergence. Somewhat in contrast to the case of bulk calculations, we found the **k**-point sampling to be of minor importance for the calculation of adsorption energies. Upon changing the sampling of the surface Brillouin zone (SBZ) from using the Γ point only to a regular mesh of six **k** points in the irreducible part of the BZ, the calculated adsorption energies change only by a few meV per adsorbate molecule. We use six **k** points for all surface calculations presented below. The adsorption geometries are relaxed until the remaining forces on the atoms are below 5 meV/Å. The oxygen atoms of the bottom bilayer are kept fixed in their ideal bulk positions.

The description of hydrogen bonds is sensitive with respect to the exchange-correlation functional used.[3] Using the PW91 (Ref. 22) and PBE (Ref. 23) functionals, Hamann[3] obtained results for the sublimation energy, equilibrium volume, and bulk modulus in very good agreement with experi-
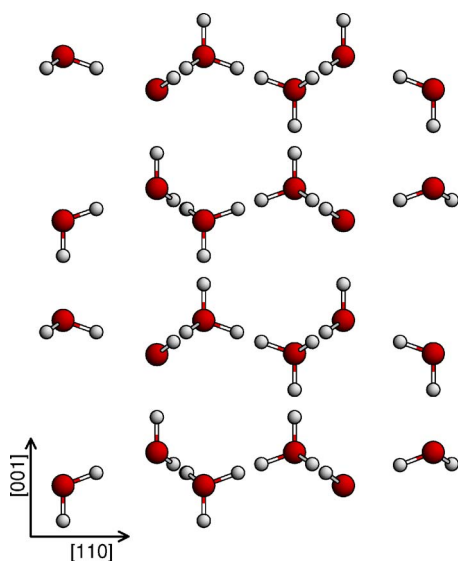
FIG. 1. (Color online) Side view of one of the used ice cells. Red (white) circles denote O (H) atoms.

ment. We performed bulk ice calculations using the unit cell of Ref. 3 together with 12 special **k** points in the irreducible part of the BZ. These calculations result in an ice cohesive energy of 0.70 eV for the PW91 functional, somewhat below the experimental value of 0.58 eV per molecule,[25] (see Fig. 2). The present result exceeds the value of 0.55 eV calculated in Ref. 3, but agrees with other recent calculations.[26,27] The PW91 equilibrium lattice constant 4.418 Å is about 1.8% smaller than the experimental value of 4.497 Å.[28] Because the PBE and PW91 functionals lead to almost the same results, PW91 is used throughout the rest of this work. The contribution of lattice vibrations to the sublimation energy of the crystal was estimated, using monochromatic and Debye approximations for the intramolecular and rotational (translational) vibrations, respectively. These sum up to 88 meV per molecule, in excellent agreement with the experimental result of 90 meV.[25]

To assess the influence of the proton disorder on the total energy of the slab describing the surface (Fig. 1), different
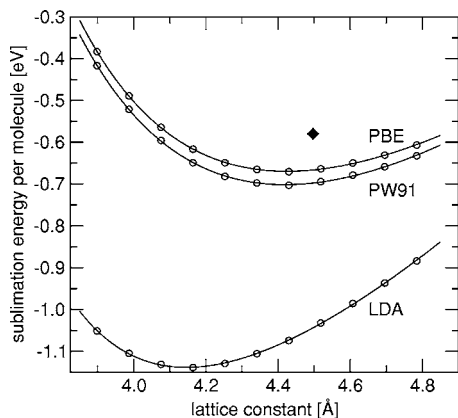

FIG. 2. Cohesive energy per water monomer in ice Ih for different XC functionals. Data are fitted using the Murnaghan equation of state. The experimental values (Ref. 25 and 28) are indicated by the diamond.
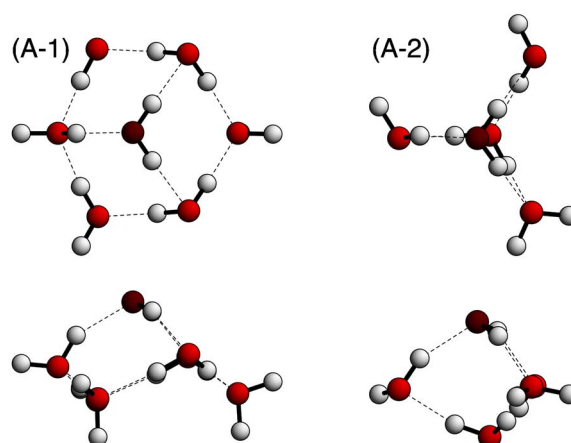

FIG. 3. (Color online) A type site: one proton up. Relaxed geometries in position A-1 (left) and position A-2 (right); top views (above) and side views (below). The dark red atom denotes the O atom of the adsorbate molecule.

configurations were calculated. The total energy was found to vary less than 5 meV for the different structures. This confirms earlier force-field results for bulk ice cells.[26] The proton disorder *within* the slab is therefore not expected to affect the binding energy of an admolecule significantly. We construct the slab cells by first choosing the hydrogen arrangement at the surface and then proceed to distribute— obeying the ice rules—the remaining protons. The cells are set up to have a net zero dipole moment.

First, the adsorption of single monomers on the full-bilayer terminated surface is studied. Out of the many adsorption sites possible, we focus on the most favored structures considered in Ref. 17. The possible binding sites are classified by the orientation of the three nearest water molecules in the uppermost surface layer. Four arrangements are possible. The first one (A) has one hydrogen atom pointing up. The possible adsorption configurations A-1 and A-2 are shown in Fig. 3. They differ with respect to the lateral position of the admonomer. In both cases, the adsorbed molecules behave similarly: They rotate toward the surface and establish hydrogen bonds with the substrate oxygens. The nearest upward-pointing OH group on the surface rotates towards the admolecule to form a third hydrogen bond. The rotation is restricted by the hydrogen bonds with the other substrate molecules.

The binding energy of the adsorbate in A-1 is 0.58 eV, about 82% of the bulk cohesive energy (cf. Table I). This is in clear contrast to the TIP4P calculations that find the surface bonding stronger than in the bulk.[17] Still, the adsorption energy calculated here is larger than possibly expected, given that only three hydrogen bonds to the substrate are formed, compared to four in the bulk case. However, already for liquid water it was recently argued that undercoordinated water monomers tend to enhance the existing hydrogen bonds compared to the bulk configuration.[29] In the present case, the admolecule does not have a regular crystal position and the uppermost substrate molecules also relax from their ideal bulk positions. The internal relaxation of the admolecule is small, only the OH bond is slightly stretched compared to the

TABLE I. Adsorption energies and geometries for the configurations shown in Figs. 3–5. d(OH) is the bond length(s) of adsorbate OH group(s) involved in bonding, d(OH·O) the hydrogen bond length(s) to the substrate, and d'(O·HO) the distance from adsorbing oxygen to upward pointing OH group(s).

| Geometry	Adsorption energy (eV)	d(OH) (Å)	d(OH·O) (Å)	d'(O·HO) (Å)
A-1	0.575	0.99	2.04	1.78
		0.99	2.06	
A-2	0.552	0.98	2.25	1.82
		0.98	2.05	
B-1	0.548	1.00	1.79	1.94
				2.60
B-2	0.550	1.00	1.81	2.07
				2.26
Bridge	0.576	1.01	1.68	1.69
		1.01	1.68	

FIG. 4. (Color online) B type site: two protons up. Relaxed geometries in position B-1 (left) and position B-2 (right); top view (above) and side view (below).

gas-phase geometry. The uppermost substrate molecules move up by up to 0.3 Å. This decreases the OH·O hydrogen bond lengths, which vary from 1.78 to 2.06 Å. However, they are still remarkably larger than the bulk value of 1.69 Å. The HOO hydrogen bond angles vary from 12.9° to 18.4°. These values are well within common geometrical boundaries for hydrogen bonds.[29,30] To estimate the influence of the substrate relaxation on the binding energy, an A-1 geometry with frozen substrate was calculated. Its binding energy of 0.44 eV shows that the substrate relaxation accounts for 0.14 eV of the total adsorption energy.

The A-2 adsorption energy is 0.55 eV, about 79% of the bulk cohesive energy. The adsorbing molecule donates two hydrogen bonds to the substrate atoms and accepts one hydrogen bond from the upward-pointing OH group. The substrate atoms participating in the bonding shift slightly towards the adsorbate. The H-donating molecule moves most, about 0.3 Å. The admolecule nearly preserves its gas-phase structure: The OH bonds are slightly stretched to 0.98 Å; the HOH angle decreases to 103.8°. The OH·O distances and HOO angles of the three hydrogen bonds vary between 1.82 and 2.25 Å, and 13.3° and 18.9°, respectively.

Another possible adsorption site (B) has two hydrogen atoms pointing up in the uppermost ice layer. The relaxed adsorption configurations B-1 and B-2 are shown in Fig. 4. Again, they differ with respect to the lateral position of the adsorbate. In both cases, the admolecule donates a single hydrogen bond to the substrate and accepts two weaker bonds from the surface molecules. Its OH group is elongated to 1.00 Å; the OH·O distance is about 1.80 Å. However, finite HOO angles of 11.0° and 10.6° remain for B-1 and B-2, respectively. The two upward-pointing OH groups on the surface rotate towards the adsorbing molecule's oxygen to form weaker hydrogen bonds. The binding energies are in both cases about 0.55 eV and thus very close to the A-2 binding site. For B-1 we determine a substrate relaxation
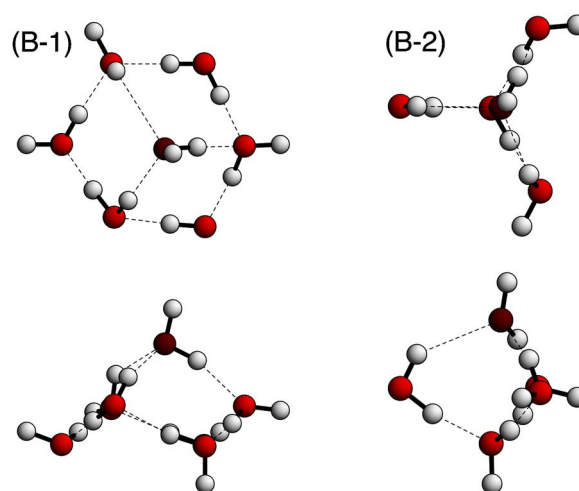
contribution of about 0.17 eV to the total adsorption energy. This is slightly larger than in the A site, because the rotation of *two* surface OH groups towards the adsorbate yields a higher gain in binding energy.

Interestingly, although the adsorption sites are clearly different, the calculated adsorption energies are rather similar, with only a slight preference for the A-1 site. However, if we compare the geometrical properties of the hydrogen bonds formed (see Table I), we find that all bonding situations are rather similar. One rather short hydrogen bond (bond length 1.8 Å) and two longer hydrogen bonds (longer than 2.0 Å) form. The longer bonds are in addition more distorted than the short bonds. This holds for all investigated adsorption sites. Thus, the direct vicinity of the adsorbing molecule is not as important for the adsorption energy as might be expected. Instead, a variety of adsorption sites offer similar possibilities for the water molecule to establish hydrogen bonds. The contributions of zero-point vibrations are therefore expected to be similar in all studied cases. Furthermore, they are expected to be smaller than the bulk value of 88 meV per molecule.

There are two more adsorption sites conceivable: One with three and one with zero protons pointing up at the surface. Within a 2×2 surface periodicity, however, no corresponding slabs can be set up that obey both the ice rules and have a net zero dipole moment. Because the surface periodicity of 4×2 that is compatible with these requirements is presently too large for our computational resources, we cannot consider these structures. In any event, the adsorption of water monomers on sites with three or zero protons pointing up was previously found to be far less favored than in A or B configurations.[17]

The relation between the adsorption energy of an admolecule and the surface formation energy per surface molecule determines the formation of either flat or rough surfaces. We find that depending on the specific geometry the adsorption of water monomers lowers the surface formation energy—compared to the ideal termination—slightly, by up to 0.03 eV. The DFT calculations thus predict a weak tendency to surface roughening.
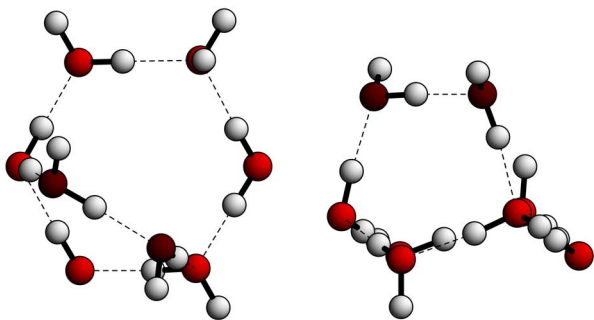
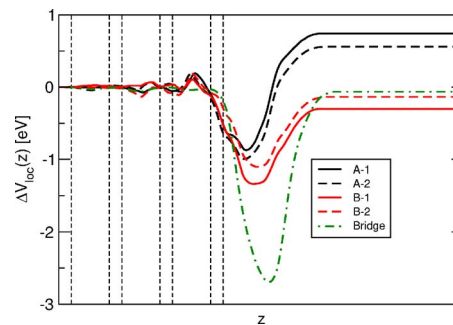FIG. 5. (Color online) Bridge configuration. (a): top view; (b): side view.

FIG. 6. (Color online) Averaged and smoothed potential differences with respect to the clean surface (see text), plotted along the surface normal. Dashed vertical lines indicate the substrate ice layers.

We also investigate one adsorption configuration for higher coverage, two molecules arranged in the 2×2 surface cell as suggested in Ref. 31. The relaxed geometry is shown in Fig. 5. The calculated adsorption energy for this configuration is 0.58 eV per molecule and thus nearly equal to the most preferred single admolecule configuration A-1. Again, we have a slight overbinding compared to the bulk cohesive energy: with three newly established bonds we have an energy of 0.38 eV per bond, compared to 0.35 eV in bulk ice. The two admolecules relax into a structure similar to the gas-phase water dimer,[32] but slightly contracted. This dimer-like structure allows us to establish rather unstrained hydrogen bonds to the substrate. Indeed, all adsorption-induced hydrogen bonds have a bond length of about 1.69 Å, close to the bulk value. The relaxation of the substrate molecules is small, with shifts of 0.10 Å and 0.19 Å. However, these relaxations lead to the enhanced binding energy per bond when compared to the bulk.

A further increase of adsorbate coverage should result in the formation of the next half bilayer on the surface. However, our calculations show that this is not a stable configuration; the uppermost half bilayer tends to separate from the underlying bulk. This result is in agreement with experimental findings.[10]

Generally, adatoms or adsorbed molecules may cause or modify a surface dipole layer. This allows us to determine the initial-state contributions to the ionization energy[33,34] that can be considered to dominate in the cases of doped semiconductors. For molecular crystals, in addition, final-state effects may be important for the total ionization energy. Still, changes of the surface dipole layer will also in this case largely determine the changes of the ionization energy. Therefore we study the influence of admolecules on the variation of the local effective potential $V_{loc}(\vec{r})$ across the surface region. It is given in DFT-GGA as

$$V_{loc}(\vec{r}) = V_{loc}^{PS}(\vec{r}) + V_h(\vec{r}) + V_{xc}(\vec{r}), \tag{1}$$

where $V_{loc}^{PS}(\vec{r})$, $V_h(\vec{r})$, and $V_{xc}(\vec{r})$ are the local part of the pseudopotential, the Hartree and the exchange-correlation

energy, respectively. Laterally averaging $V_{loc}(\vec{r})$ yields the in-plane averaged potential $V_{loc}(z)$. By subtracting the potential $V_{loc}^0(z)$ of the free surface

$$\Delta V_{loc}(z) = V_{loc}(z) - V_{loc}^0(z), \tag{2}$$

the influence of the adsorbate on the local potential is obtained. In Fig. 6, $\Delta V_{loc}(z)$ is plotted for all investigated configurations along the surface normal z. Here the potential is also smoothed along z over the width of one ice bilayer. In all cases, the adsorbed molecules change the electrostatic potential near the surface and to some extent in the slab. However, only in the A sites a significant increase of the surface dipole layer (indicative for an increase of the ionization energy or photoelectric threshold) of more than 0.5 eV is observed. This contrasts with the far larger changes of the ionization energy calculated for molecular adsorption on semiconductor surfaces (see, e.g., Ref. 35).

In summary, the adsorption of water monomers on the ice Ih basal plane is found to be energetically very favorable. In contrast to earlier empirical calculations, however, we do not find adsorption energies in excess of the bulk cohesive energy. Still, due to an energy gain per hydrogen bond larger than in the bulk, the adsorption of admolecules lowers the surface energy. This is expected to favor the formation of rough surface structures which may be suitable to explain recent experimental findings of an abundance of isotropically distributed OH groups that terminate the crystalline ice.[31] The adsorption of water monomers has little impact on the surface dipole layer.

*Electronic address: c.thierfelder@massey.ac.nz

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