

# First Principles Simulations of Ice Surfaces

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The surface of hexagonal ice Ih is investigated from *first principles* density functional calculations. Surface formation energies for several low-index surfaces are calculated. The formation of the Ih(0001) basal plane appears most favored. Therefore, the adsorption of water monomers on non-crystallographic sites of this plane is studied. Contrary to previous theoretical findings we do not find molecular adsorption energies larger than the bulk cohesive energy. However, the admolecules lower the ice surface energy due to stronger hydrogen bond formation. The monomer adsorption energies are found to be rather insensitive with respect to the detailed microscopic structure of the underlying substrate.

## 1 Motivation

The surface structure of crystalline ice is not really understood. Depending on temperature, a quasiliquid layer on top of the crystalline bulk seems to form. The question of its existence dates back to Faraday [1]. This being answered positively today, however, there is more uncertainty about the onset temperature  $T_p$  of the surface pre-melting process. For a review of early work on the ice Ih(0001) basal plane, see, e.g., [2]. In recent years, combined experimental and theoretical works have found the ice Ih(0001) surface to be fully bilayer-terminated and unreconstructed at  $T = 90$  K [3, 4], and  $T = 125$  K [5], found occupied surface sites different from bulk crystallographic positions at  $T = 130 \dots 150$  K [6, 7], and report onset temperatures  $T_p$  of  $T_p \approx 200$  K [8],  $T_p \geq 260$  K [9],  $T_p = 230$  K [10], and  $T = 190$  K [11]. It seems that in a certain low-temperature regime, the assumption of a crystalline surface covered with admolecules should be justified.

Recent empirical calculations [12] using the TIP4P potential [13] surprisingly found for some adsorption configurations that the binding energy of water admolecules exceeds the cohesive energy of the bulk [12]. Motivated by these findings, our work aims at providing reliable *ab-initio* results for the binding

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| Surface<br>orientation | Surface formation energy |                     |
|------------------------|--------------------------|---------------------|
|                        | [eV/molecule]            | [J/m <sup>2</sup> ] |
| [0001]                 | 0.141                    | 0.134               |
| [10 $\bar{1}$ 0]       | 0.211                    | 0.245               |
| [11 $\bar{2}$ 0]       | 0.194                    | 0.195               |

Table 1: Ice Ih: Formation energies of different low-index surfaces.

of water molecules on the crystalline Ih(0001) surface. Furthermore, we study different low-index surfaces of ice Ih with respect to their formation energies.

## 2 Methodology

We perform density-functional theory calculations (DFT), using a plane-wave basis and the projector augmented wave method (PAW) [14] as implemented in the Vienna Ab initio Simulation Package (VASP) [15, 16]. See [17] for numerical details. The surface is modelled by periodically repeated slabs: each slab contains four bilayers of ice within a  $2 \times 2$  surface periodicity; adjacent slabs are separated by vacuum, equivalent in thickness to four bilayers. The oxygen atoms of the bottom bilayer are kept fixed in their ideal bulk positions, all other atomic positions are optimized.

## 3 Results

We study the surface formation energies of the following crystalline faces of hexagonal ice Ih: the basal plane [0001], the prism face [10 $\bar{1}$ 0], and the secondary prism face [11 $\bar{2}$ 0]. The basal plane formation is by far favored, see Table 1.

We now calculate the adsorption of water monomers on the ice Ih basal plane. See Fig. 1 for the investigated adsorption sites. The respective adsorption sites are rather similar in energy, with A-1 geometry in favor with  $E = 0.58$  eV per molecule, and the other geometries all gaining  $E = 0.55$  eV per molecule. The final adsorption geometries are rather similar with respect to the hydrogen bonds established between substrate and adsorbate.

## 4 Conclusions

We find that the underlying substrate determines the adsorption energy of ad-molecules of water mainly by its ability to establish hydrogen bonds to the adsorbate. The detailed geometry of the substrate under the adsorption site is not very important. Further, the adsorption energy on one of the investigated sites is slightly higher than the binding energy of a crystallographic site. Thus, the formation of rough ice surfaces should be slightly favored over closed bilayer surface terminations. However, we do not find surface energies in excess of the bulk binding energy, in contrast to previous results [12].

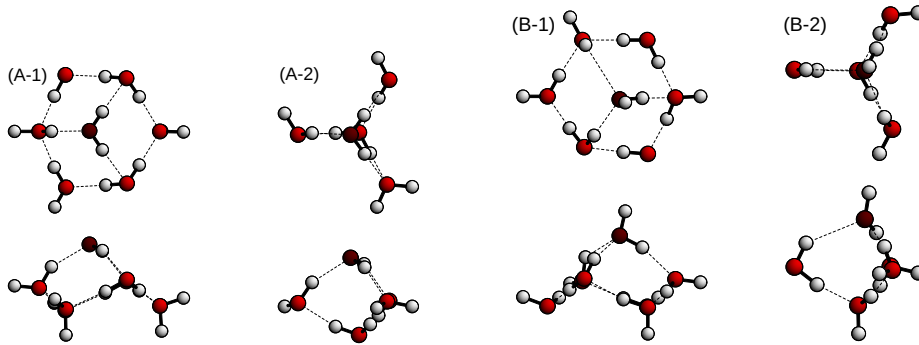


Figure 1: From left to right: A type site (one proton up), geometries A-1 and A-2; B type site (two protons up), geometries B-1 and B-2. Upper panel: top view; lower panel: side view.

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