Ethanol adsorbed on ice: A first-principles study

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Density functional calculations are performed on the adsorption of ethanol molecules on the ice Ih basal plane. Apart from smooth surfaces, also substrate models with vacancies and water admolecules are probed. We find the adsorption energy to increase substantially with the roughness of the ice surface. The adsorption energy is roughly correlated with the number of hydrogen bonds formed between the admolecule and the substrate.

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I. INTRODUCTION

The adsorption of organic molecules found in the upper troposphere such as alcohols, on ice crystallites is assumed to play an important role in the ozone cycle. Upper tropospheric air originating from the warm boundary layer may become highly supersaturated with respect to water, resulting in the formation of a high density of ice particles. This provides surfaces for heterogeneous reactions with trace gases, leading to a repartitioning of different species between the gaseous phase and the solid phase. Experimentally, in addition to smooth surfaces, also substrate models with vacancies and water admolecules are probed. The complexity of the ice surface could be one reason why very different molecular adsorption energies are reported. In the case of ethanol, for example, the experimental values per molecule range from 0.15 eV while the calculations yield 0.28 eV for the liquid-vapor interface and 0.59 eV for the ice surface.

Using the adsorption of ethanol on the ice Ih(0001) as an example, the present DFT study explores the effect of the surface geometry on the adsorption energetics. A rich variety of structures, including models with vacancies and adatoms is used to model the ice surface.

II. COMPUTATIONAL METHODS

The calculations are performed using DFT within the generalized gradient approach (GGA) as implemented in the Vienna ab initio simulation package (VASP). The electron-ion interaction is described by the projector-augmented wave scheme. The electronic wave functions are expanded into plane waves up to a kinetic energy of 30 Ry.

The surface is modeled by periodically repeated slabs. Each supercell consists of four ice bilayers within a (2 × 2) periodicity plus the adsorbed ethanol and (if applicable) water molecules, as well as a vacuum region equivalent to four bilayers (Fig. 1). The three uppermost bilayers as well as the admolecule degrees of freedom are allowed to relax until the forces on the atoms are below 5 meV/Å. The bottom bilayer is kept frozen in bulk geometry. The Brillouin zone integration is restricted to the Γ point. These parameters result in converged geometries and adsorption energies as shown earlier.

FIG. 1. (Color online) Side view of one of the slabs used to model the ice surface. Large (small) circles denote O (H) atoms.
We use the PW91 functional\textsuperscript{25} to describe the electron exchange and correlation energy within the GGA. It describes the hydrogen bonds in solid water (ice Ih) in reasonable agreement with experiment.\textsuperscript{30,31} We find the bulk lattice constant of ice Ih to be underestimated by 0.08 Å and its cohesive energy to be overestimated by 0.12 eV/molecule. While this is larger than the adsorption energy differences for some of the configurations discussed below, the error is systematic and should not affect the trend of the calculated adsorption energies. We mention that the neglect of the dispersion interaction in DFT-GGA is an additional artifact that is expected to impair the accuracy. The resulting error can be expected to be of similar magnitude but different sign than the overbonding of the hydrogen bonds.\textsuperscript{32} Calculations for gas-phase ethanol within a $30 \times 30 \times 30$ Å\textsuperscript{3} supercell are performed to obtain error bars for the numerical description of the admolecule. The structural data obtained from the calculation are very close to the experimental values, as shown in Table I. Bond lengths and bond angles agree within 0.01 Å and 0.5°, respectively.

The ice proton configuration is disordered. We construct the material slab by, first, choosing the hydrogen arrangement at the surface, and then proceed to distribute—obeying the ice rules—the remaining protons in such a way that the cell has a net zero dipole moment. In the following, we discuss results for one and two ethanol molecules within the (2×2) surface periodicity, which we define as half and full monolayer (ML) coverages, respectively.

### TABLE I. Ethanol bonding distances (in Å) calculated within DFT-GGA in comparison with data from Ref. 33.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Present results</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>1.512</td>
<td>1.511</td>
</tr>
<tr>
<td>C-H in CH\textsubscript{3}</td>
<td>1.099</td>
<td>1.090</td>
</tr>
<tr>
<td>C-H in CH\textsubscript{2}</td>
<td>1.106</td>
<td>1.098</td>
</tr>
<tr>
<td>C-O</td>
<td>1.439</td>
<td>1.427</td>
</tr>
<tr>
<td>O-H</td>
<td>0.976</td>
<td>0.971</td>
</tr>
</tbody>
</table>

A large variety of bonding configurations was probed. The (meta)stable configurations for a single ethanol molecule can be classified according to the number of hydrogen atoms from the three nearest water molecules in the uppermost surface layer pointing up to the admolecule. We refer to con-

![FIG. 2. (Color online) Adsorption configurations of α, β, and vacancy type in side (left) and top (right) views.](195426-2)
TABLE II. Adsorption energies and bond lengths for the configurations shown in Fig. 2. $d$(OH) is the bond length of OH group of the adsorbed ethanol, $d'$(OH) the bond length of water OH group, $d$(H–O) the distance(s) between the hydrogen atom(s) of the adsorbate and the oxygen atom(s) of the substrate, and $d$(O–H) the distance(s) between the oxygen atom of the adsorbate and the hydrogen atom(s) of the substrate.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Adsorption energy (eV)</th>
<th>$d$(OH) (Å)</th>
<th>$d'$(OH) (Å)</th>
<th>$d$(H–O) (Å)</th>
<th>$d$(O–H) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.360</td>
<td>0.97</td>
<td>0.99</td>
<td>2.48</td>
<td>1.83</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.570</td>
<td>0.98</td>
<td>1.00</td>
<td>1.85</td>
<td>1.78</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.552</td>
<td>0.99</td>
<td>0.98</td>
<td>1.85</td>
<td>1.93</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>0.554</td>
<td>0.99</td>
<td>0.98</td>
<td>1.83</td>
<td>1.92</td>
</tr>
</tbody>
</table>

configurations where one hydrogen points up as $\alpha$ structures. Two possible adsorption geometries $\alpha_1$ and $\alpha_2$ are shown in Fig. 2. They differ with respect to the orientation of the OH group of the admolecule. In $\alpha_1$, the ethanol OH group points upward and the water surface OH group of the surface rotates about 6.3° toward the admolecule, thus establishing a hydrogen bond. The binding energy of 0.36 eV is the minimum energy gain found in this study (cf. Table II). The internal relaxation of the admolecule is small. Only the HOC angle is squeezed about 0.7° compared to the gas-phase geometry. The uppermost substrate molecules move upward by less than 0.1 Å.

The admolecule is positioned with the OH group pointing toward the surface in the $\alpha_2$ case. The ethanol donates one hydrogen bond to the substrate. Another hydrogen bond is formed by the water OH group pointing upward. The lengths of the donated and accepted hydrogen bonds, $d$(H–O) and $d$(O–H), respectively, are 1.78 and 1.85 Å. The respective hydrogen bond angles are 11.0° and 12.1°. These values are well within the common geometrical boundaries for hydrogen bonds. The formation of two rather than one hydrogen bond leads to an $\alpha_2$ adsorption energy of 0.57 eV. This is 58% larger than for $\alpha_1$. The fact that the adsorption energy does not double upon the formation of two hydrogen bonds is related to the molecular strain involved. The HCOH torsion angle of the admolecule changes by about 36.3° compared to gas-phase ethanol, corresponding to a strain energy of about 0.6 eV according to our calculations.

Adsorption configurations where two hydrogens point up from the uppermost ice layer are referred to as $\beta$ configurations (see Fig. 2). The $\beta_1$ and $\beta_2$ configurations differ by the lateral position of the adsorbate. In both cases, the admolecule preserves its gas-phase structure and donates a single hydrogen bond to the substrate and accepts two weaker bonds from the surface molecules. The binding energies are, in both cases, about 0.55 eV and thus very close to the $\alpha_2$ binding site. The hydrogen bonds formed are of similar length for $\beta_1$ and $\beta_2$: $d$(H–O) is around 1.84 Å and $d$(O–H) is about 1.92 Å. The associated bond angles vary between 11.5° and 16.6°. For $\beta_1$ the largest of the three bonds is 2.20 Å, with an angle of 27.3°, whereas in $\beta_2$, it is 2.37 Å and 35.5°.

The adsorption configurations $\alpha_2$, $\beta_1$, and $\beta_2$ are very different, but lead to similar adsorption energies (see Table II). This can be explained by the formation of two short (1.9 Å) and one fairly long (≥2.2 Å) hydrogen bond. The value of the adsorption energy of about 0.6 eV agrees nicely with the experimental and theoretical data of Peybernes et al. In all these configurations, the ethanol OH group points toward the ice surface. The energy gain for the $\alpha_1$ structure is considerably smaller, due to the formation of only one hydrogen bond.

Earlier theoretical studies highlight the importance of vacancies for the adsorption of organic molecules. We probed the adsorption of ethanol on a surface where one water molecule with an upward pointing hydrogen atom is missing, or, in other words, a water-ethanol substitution. Thereby, the ethanol OH group replaces the water oxygen and hydrogen atoms, and the methyl group points upwards. Three hydrogen bonds are established, as for the original surface water molecule. One might, thus, expect an adsorption energy comparable to the binding energy of the water molecule, which is 1.04 eV. In fact, the ethanol adsorption energy for the vacancy amounts to 1.07 eV, i.e., the water-ethanol substitution is slightly preferred.

For ethanol coverages of 1 ML, we found several stable configurations denoted by $\eta$. Their adsorption energies and the molecular distances are listed in Table III. The configuration $\eta_1$ consists of two ethanol molecules in $\alpha_1$ positions. Their interaction is weak, therefore there is nearly no energy gain compared to two single $\alpha_1$ adsorption geometries. The largest binding energy is found for $\eta_1$ (shown in Fig. 3). Here, one of the ethanol molecules is located at an $\alpha_2$ position. The second one establishes two hydrogen bonds to the surface with bond lengths of 1.73 and 2.75 Å. The two ethanol OH groups are very close and form another hydrogen bond with a bond length of 1.78 Å, rendering this structure particularly favorable.

The two ethanol molecules of $\eta_2$ and $\eta_4$ are positioned according to either $\alpha_2$, $\beta_1$, or $\beta_2$. The distances between the ethanol OH groups (cf. Table III) are too large to allow for hydrogen bond formation. Therefore, the adsorption energy corresponds roughly to those of the single configurations.
Previous work indicates a tendency of surface roughening for ice. Therefore, we also consider the possibility that both ethanol and water molecules are adsorbed on the surface. The corresponding γ structures are listed in Table IV. The structures can be classified according to the intermolecular interactions. If the adsorption sites of the water molecule and the ethanol molecule are well separated, the binding energy is the sum of the binding energies of the two single sites. If the admolecules are bonded to each other, the adsorption energy is clearly increased. The geometrical structures of latter configurations are similar to the water monomer bridges formed on ice surfaces. The bridge is formed via three hydrogen bonds between the water molecule on the one side and the ethanol hydroxide group on the other side (see Fig. 4). With an adsorption energy (for both ethanol and the water dimer) of about 1.2 eV and hydrogen bond lengths of about 1.75 Å, these structures are indeed comparable to the adsorption of two water molecules in the bridge configuration. As in the previous cases, the molecular adsorption is dominated by the ethanol OH group. The most favorable configuration is denoted γ8 and shown in Fig. 4. Here, the adsorption energy of ethanol and the water monomer sum up to about 1.3 eV. This is due to the formation of a weak fourth hydrogen bond with the surface with a length of 1.98 Å. The geometry of the water-ethanol dimer on the ice surface is similar to the free dimer. This holds also for the d1 bond length of 1.72 Å. The d2 length amounts to 2.37 Å, i.e., it is too long to qualify as a hydrogen bond. This is related to the stability of the bridge structure. At least two hydrogen bonds of the bridge configuration have to be deformed to shorten d2. However, the rotation of the ethanol molecule around the O-H axes of the OH group is such as to minimize d2.

We also investigated the adsorption of ethanol on an existing water-bridge configuration. We found that it is energetically favorable for the ethanol molecule to form the configuration shown in Fig. 5. The ethanol adsorption energy for this site is 0.84 eV, i.e., the maximum value found in this study apart from the vacancy adsorption case. The distances between the ethanol molecule and the closest water admolecules are 1.76 and 3.12 Å i.e., they are almost identical to the previous case. The previous discussion shows that the adsorption energy strongly depends on the adsorption configuration, which itself depends on the bonding sites available at the ice surface. Generally, the adsorption is more favorable at rough surfaces, which indicates that the adsorption of ethanol on ice samples will depend on their history, i.e., preparation conditions. In order to see if this can be verified experimentally, we calculate the vibrational modes and frequencies of gas-phase and surface-adsorbed ethanol molecules for two prototypical configurations, d2 and vacancy. Thereby, we use the geometries of the water-ethanol dimer on the ice surface.

### Table IV. Adsorption energies and distances for the coadsorption of ethanol and water monomers. The distance between admolecule OH group oxygens is given by d(OH·OH).

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Adsorption energy (eV)</th>
<th>d(OH·OH) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noninteracting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ3</td>
<td>0.50</td>
<td>4.81</td>
</tr>
<tr>
<td>γ4</td>
<td>0.54</td>
<td>3.54</td>
</tr>
<tr>
<td>Interacting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ1</td>
<td>0.60</td>
<td>2.72</td>
</tr>
<tr>
<td>γ2</td>
<td>0.63</td>
<td>2.77</td>
</tr>
<tr>
<td>γ5</td>
<td>0.61</td>
<td>3.40</td>
</tr>
<tr>
<td>γ6</td>
<td>0.74</td>
<td>2.72</td>
</tr>
</tbody>
</table>

![Figure 3](image3.png)  
**FIG. 3.** (Color online) Top view of the γ7 ethanol dimer adsorption structure.

![Figure 4](image4.png)  
**FIG. 4.** (Color online) Side view of the γ8 adsorption configuration of one ethanol and one water molecule.

![Figure 5](image5.png)  
**FIG. 5.** (Color online) Top view of the ethanol adsorption using an existing water-bridge structure for bonding.
The adsorption of ethanol on the ice Ih basal plane occurs through the formation of hydrogen bonds mainly involving the molecular hydroxide group. The adsorption energy difference between different structures can roughly be explained by the number of hydrogen bonds formed between admolecules and substrate, but is also affected by strain. DFT-GGA calculations predict, nearly irrespective of the coverage and in good agreement with recent experiments and molecular dynamics studies, an adsorption energy of about 0.6 eV for smooth ice surfaces. An increase of the adsorption energy to about 0.7 and 0.8 eV, however, results in scenarios where the coadsorption with water monomers and water dimers, respectively, is considered. The largest adsorption energy of more than 1 eV is predicted for ethanol adsorption in a vacancy site. These results show that the ethanol adsorption process will strongly depend on the microscopic structure of the ice sample. Given that the ethanol-ice interaction is mainly governed by the molecular OH group, we expect our results to widely hold also for larger alcohols.

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