

Two Dimensional Ice Adsorbed on Mica Surface

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First principles molecular dynamics simulations have been performed on water adsorption at the surface of muscovite mica. At monolayer coverage we found water to condense into a fully connected two dimensional hydrogen bond network, which we denote as 2D ice. The structure is stable up to 300 K and it is proposed as a candidate for the solidlike structure recently detected in scanning polarization force microscopy on the hydrated muscovite surface at room temperature [Hu *et al.*, Science **268**, 267 (1995)]. [S0031-9007(97)02856-1]

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The properties of water adsorbed on solid surfaces are of widespread interest for many disciplines, ranging from biology to material science [1]. In particular, the possibility of icelike structure formation in adsorbed water has attracted considerable interest in recent years [1]. Micas are in this respect of special interest since they have been long studied as ecologically acceptable replacements of AgI as ice nucleators in cloud seeding [2,3]. Furthermore a detailed knowledge of water adsorption on mica surface is useful for the understanding of the swelling of clays, a process which plays an important role in many industrial applications such as petroleum engineering and catalysis [4,5].

Recently, an icelike structure stable at room temperature has been reported on the hydrated surface of muscovite mica [6,7]. This evidence comes from scanning polarization force microscopy (SPFM) measurements at finite humidity which have shown that water condenses into solidlike polygonal domains in angular epitaxial relationship with the underlying mica surface [6,7]. The stability of this phase at room temperature is rather unusual since previously reported icelike structures on metals [1] and on insulators [8,9] have been observed in ultrahigh vacuum (UHV) only at low temperatures.

In this Letter we present first principle molecular dynamics (MD) simulations [10,11], of the structural and dynamical properties of water adsorbed on 2M₁-muscovite mica, a 2:1 layered dioctahedral (hydroxy-) aluminosilicate with formula unit KAl₂(Al,Si₃)O₁₀(OH)₂ [12]. Our calculation shows that water at monolayer coverage on muscovite forms an ordered and stable hexagonal network of H bonds where all the water molecules donate two H bonds. This confirms the interpretation of the somewhat indirect structural SPFM data and provides insights into the stability and the detailed structure of the icelike phase.

The surface is modeled by a periodic slab of mica with a 13 Å wide vacuum perpendicular to the plane of cleavage, as measured between the potassium ions. The

intrinsic layering of mica provides a natural choice for the thickness of the slab, which is nine atomic layers thick. The simulation slab is shown in Fig. 1. In the study of the clean surface we considered only one crystallographic unit cell in the surface plane as shown in Fig. 1, while in the study of hydration the simulation cell contained two surface unit cells. In the muscovite structure a

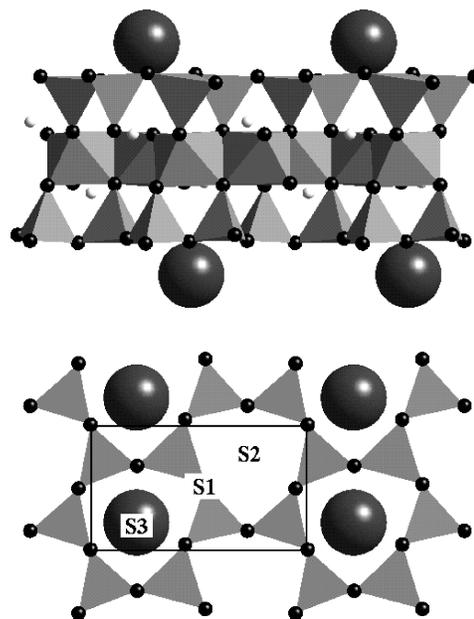


FIG. 1. The relaxed simulation slab shown from the side and from above. Black, white, and gray spheres depict oxygen, hydrogen, and potassium atoms, respectively. The polyhedra contain silicon and aluminum in the center. Two layers of tetrahedra sandwich one octahedral aluminum layer. The surface unit cell is drawn to show the periodicity and as a measure of size. The in-plane lattice constants were fixed to the experimental ones [12] (5.1918 Å × 9.0153 Å). The potassium ions are relaxed towards the surface as compared to the bulk. The simulation cell used in the study of hydration contains two surface unit cells and a total amount of 84 atoms. S1-S3 denote adsorption sites for water molecules.

layer of octahedrally coordinated Al^{3+} ions is sandwiched between tetrahedral silicate layers, with vertices pointing towards the octahedral layer. The buckled basal plane of the tetrahedra form distorted hexagonal rings. Aluminum is randomly substituted for silicon with a ratio of 1:3, and for charge compensation potassium counterions are present at the center of all the hexagonal rings in the bulk. At the surface, half the potassium ions are left after cleavage to preserve electroneutrality, but their positions and distribution have not been experimentally determined. Under the rings and in the junction between the tetrahedral and the octahedral layers, there are hydroxyl groups. Because of the substitution for silicon by aluminum, the ratio of (Si:Al) cations in the rings varies. The surface unit cell shown in Fig. 1 contains one K^+ ion and two hexagonal rings with different Al content, (Si_4Al_2) and (Si_5Al_1).

We adopted an *ab initio* density functional framework in the local density approximation augmented by the generalized gradient correction proposed by Becke [13] for the exchange energy part and by Lee, Yang, and Parr [14] for the correlation part. *Ab initio* norm conserving pseudopotentials have been used. In particular, we treated the semicore $3s$ and $3p$ states of K as valence electrons in order to properly deal with nonlinear-exchange and correlation core effects [15]. The Kohn-Sham orbitals have been expanded in plane waves up to an energy cutoff of 70 Ry. The sampling of the Brillouin zone was restricted to the supercell Γ point. A fictitious electron mass of 800 a.u. and a time step of 0.157 fs have been used in the integration of the equations of motion. Within this scheme we found excellent agreement between the theoretical and experimental structural parameters of bulk muscovite [16]. This scheme has proven also to reproduce the structural and dynamical properties of liquid water [17], ice [18], and ion solvation in small clusters [19–21]. We thus expect this framework to be reliable in describing hydrogen bonds and polarization effects in the rather unusual conditions that are to be found on this surface.

We first studied the structure of the clean surface. We found small changes relative to the ideally terminated bulk geometry. The largest effect is an inward relaxation of K^+ by 0.11 Å. A 5% enhancement of the buckling of the basal oxygen atoms was also observed. The potassium ion is more strongly bound to the (Si_4Al_2) ring than to the (Si_5Al_1) ring by 14 kJ/mol due to lower negative charge of the latter. The competing position for K^+ on top of Al tetrahedra is higher in energy by 84 kJ/mol. The calculated surface energy is $\sim 0.2 \text{ J/m}^2$. Experimental values [22] are as high as $\sim 5 \text{ J/m}^2$; however, it is known that a nonideal distribution of counterions on the real surface can strongly affect the surface energy [23].

We began the study of water adsorption by putting single water molecules on the surface. We found that dissociative adsorption, with a hydroxyl group solvating

the potassium ion and the remaining proton attached to an acid basal oxygen is unfavored with respect to molecular adsorption. We computed the adsorption energy of H_2O in three different adsorption sites, S1-S3 (see Fig. 1), by full structural optimization. In S3 the dipole moment of the water molecule points outwards and the binding energy is 22 kJ/mol, reduced by a factor of ~ 4 from the value of the isolated $\text{K}^+\text{-H}_2\text{O}$ complex due to the presence of the surface. The most favored sites are S1 and S2 with binding energies of 46 and 34 kJ/mol, respectively. The S1 site owes its energy gain to the formation of a straight hydrogen bond with the basal oxygen and to a partial solvation of the potassium ion. In S2 the H_2O dipole points inward and the molecule is centered over the ring of oxygen atoms. H_2O adsorbed on sites S1 and S2 turned out to be stable in an MD run of 0.6 ps at 300 K. Interestingly, in the S2 site the water molecule exhibits large rotational and wagging motions in the ring, which leads to a continuous breaking and forming of hydrogen bonds with the oxygen atoms in the ring. In S1 instead the largest amplitude motion is related to a hindered rotation around the vertical hydrogen bond. We expect these peculiar motions to give rise to identifiable signals in the ir spectrum.

In the study of the hydration process we first performed a run with five water molecules per surface unit cell. From analysis of this run we came to the conclusion that a fully connected network of hydrogen bonded water molecules could be generated by increasing the water coverage. After simulated annealing and geometry optimization at a coverage of six molecules per unit cell we found indeed a fully connected H bonds network over the surface forming a cage around the potassium ions (see Fig. 2). Although in the calculation we used two surface unit cells, the optimized structure showed the same configuration of water molecules in both units. This fact suggests that there is no frustration in the H bonds network. Three molecules in the unit cell out of six are bound directly to basal oxygen atoms at the edges of the empty rings (depicted by O1 in Fig. 2). The oxygen-oxygen distances in the empty rings are such that molecules bonded to basal oxygen atoms can form H bonds across the rings forming a commensurate layer of connected molecules along the groove of empty rings. Partial solvation of potassium further stabilizes hydrogen bonding by forcing a particular orientation of the molecules in the empty groove. The presence of potassium does not interrupt the network in the groove which stretches over the counterions through molecules lying nearly parallel to the surface and fully connected with H bonds. The weak solvation energy of K^+ favors a fully hydrogen bonded network over a full K^+ solvation. Indeed the dipole moment of water molecules around potassium are not directed towards the ion. The arrangement of these molecules is mainly determined by the requirement of saturating hydrogen bonds among

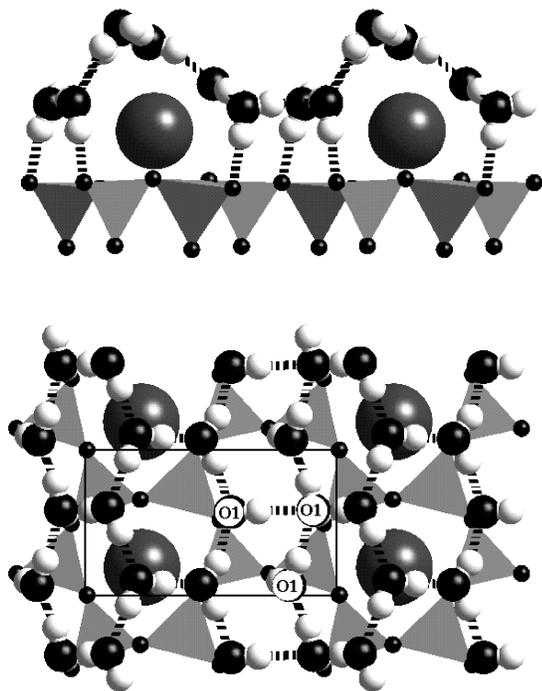


FIG. 2. The optimized structure of water at monolayer coverage. The water molecules and the slab are shown from the side and from above. Dashed lines are hydrogen bonds and the atoms have the same symbols as in Fig. 1. The drawn unit cell of the 2D-ice structure coincides with the unit cell of mica. There are six water molecules per unit cell; half of them (denoted by O1) are closely bound to the surface by donating hydrogen bonds to basal oxygen atoms. The other water molecules solvate the potassium ions, and form bonds to the underlying water molecules and to each other.

them and with the anchoring water molecules in the groove. Although weak, the solvation pulls K^+ out 0.47 \AA from the clean surface equilibrium position. The water molecules are in two planes, they form together a periodic corrugated two dimensional structure that covers the surface. The number of hydrogen bonds per water molecule varies between three and four. The network consists solely of distorted hexagons and no free OH bond sticks out of the surface (see Fig. 3). Thus a free OH high frequency peak is not expected in the ir spectrum. We find it tempting to call this structure 2D ice. (See Fig. 3).

Because of the small size of the simulation cell we were forced to arrange the potassium ions in an ordered fashion [Fig. 1(a)], thus favoring an ordered arrangement of the water molecules. In reality, although the exact position of the potassium ions on the dry surface is not known [24], we expect their distribution to be influenced by the underlying random distribution of Al impurities. The energetic cost of moving a K^+ ion from an Al rich to an Al poor adsorption site (14 kJ/mol) is smaller than a typical hydrogen bond energy, thus we expect that the presence of the water layer might induce some ordering in the K^+ ion arrangement. Furthermore the 2D-ice-like

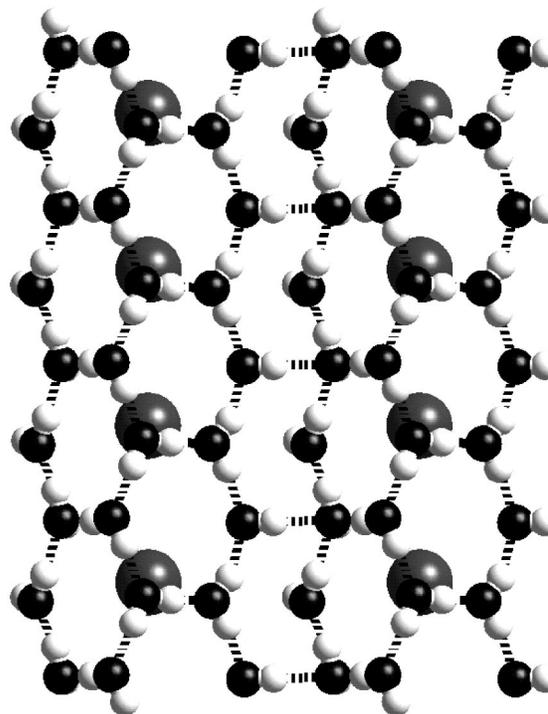


FIG. 3. Top view of the 2D-ice structure. For the sake of clarity several unit cells are reproduced and only the K^+ ions of the underlying surface are shown. The H-bonds network consists of distorted hexagons.

network is determined by the anchoring S1 sites, which is not related to the K^+ ion arrangement. Therefore we expect that the network could maintain its fully connected topology even in the presence of defects in the K^+ arrangement with limited energetic cost.

The adsorption energy per molecule in the 2D ice is 49 kJ/mol , corresponding to roughly 2–3 H bonds per molecule. The adsorption energy of water on mica is comparable to the estimated adsorption energy of water on the surface of metals such as Re, Rh, and Ru [1], where icelike structures have been identified at low temperatures in UHV. The 2D ice is stable up to 300 K in the simulation 2 ps long, and shows librational motions with breaking and reforming of the hydrogen bonds and no molecular diffusion. Therefore we propose that our structure can be identified with the solidlike phase detected in SPFM measurements up to room temperature.

In the SPFM experiments [6,7], the imaging of the sample is a result of the inhomogeneities in the surface polarization. A change in the polarization forces, corresponding to an increase of the dielectric constant by a factor 10–15 has been observed upon hydration. However, this huge difference in polarizability disappears when ac voltage with frequency above 1 MHz is used to monitor the mica surface. Because of this low frequency the difference in polarizability of hydrated and clean surfaces has been attributed to an enhancement of counterions ionic mobility upon hydration. We have calculated the dielectric

constants of the clean and hydrated slab of mica by fully relaxing the ions in an external electric field. The ratio of the dielectric constants [25] of the hydrated and clean slabs is ~ 2 . Hence our result is consistent with the conclusion that the contrast in SPFM is due to change in ionic mobility upon hydration and that the static polarizability of the water structure alone is not sufficient to explain the experimentally observed large increase in polarization upon hydration. The SPFM has not enough lateral resolution to identify the microscopic structure of the icelike film. Therefore a closer comparison of our proposed structure with experimental SPFM data available is not possible.

The stability of the 2D-ice structure on mica at finite humidity and room temperature [6,7] is probably due to high barriers for water diffusion at the surface produced by the very sharp adsorption sites on basal oxygen atoms. This has to be contrasted with the lower barriers for water diffusion expected at metal surfaces [1]. On metals the adsorption occurs mainly via electron donation to regions of low electron density. The nearly homogeneous distribution of electron density on metals provides many adsorption sites very close in energy with low energy barriers between them. Moreover while on metal surfaces the proposed bilayer structure of the icelike phase is simply a bilayer of hexagonal ice [1], on mica the 2D ice differs totally in character from ordinary ice.

In conclusion, we have shown that on muscovite an ordered array of water molecules with new properties is stable. It would be extremely interesting to check experimentally the behavior of this system for different counterions. This, in the lack of a more direct experimental probe, could help confirm the picture put forward here.

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