Ice Tessellation on a Hydroxylated Silica Surface

Jianjun Yang, Sheng Meng, L. F. Xu, and E. G. Wang*

State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

The adsorption of water on a fully hydroxylated silica surface is studied by using density-functional total-energy and molecular dynamics calculations. The (100) surface of $\beta(\alpha)$-cristobalite covered by geminal hydroxyls has been taken as the substrate. A well-ordered and stable two-dimensional ice with quadrangular and octagonal patterns of hydrogen bond (H-bond) networks — an ice tessellation — is found on the surface for the first time. With the vibrational recognition, the four water molecules in the quadrangle are found to be bonded by strong H bonds while the quadrangles are connected to each other by weak H bonds. This configuration is the most stable, because all the water molecules are fully saturated with H bonds either to each other or to the surface hydroxyl groups.

Understanding the microscopic mechanism of water adsorption on silica has been an active research area over the years because of its technical importance [1]. Existing experimental data on the amorphous hydroxylated surface are often rationalized by modeling the surface as an alternation of patches of the hydroxylated (100) and (111) surfaces of β-cristobalite, which is the crystalline phase of silica with density and refractive index closest to those of amorphous silica [1,2]. Further experiments [3] suggested the existence of local ordering on amorphous silica surfaces. The two main faces can sustain the two types of hydroxyl groups identified experimentally on the amorphous silica surface, namely, the single species typical on the (111) surface and the geminal species typical on the (100) surface. Water adsorbs on these surfaces through hydrogen bonds (H bonds) between water and surface hydroxyls [4–9]. So far the molecular picture for the water adstructures and bonding properties on these surfaces has not been achieved by experiments. Computer simulation based on *ab initio* density-functional theory (DFT) has proven to be a powerful and reliable tool to study water-solid interfaces at the molecular level [10,11]. Several authors studied theoretically the interaction of water with silica hydroxyls using silanol molecules as a cluster model [12,13], which is not sufficient to describe a two-dimensional (2D) surface. A deeper insight into the water on a hydroxylated silica surface is thus desirable.

In this Letter, we present a theoretical study of water adsorption on a hydroxylated β-cristobalite (100) surface based on *ab initio* DFT total-energy and molecular dynamics (MD) calculations. A single H_2O molecule is found to stabilize on the surface by means of two hydrogen bonds, simultaneously acting as both H donor and acceptor. Our most interesting finding is that water forms an ordered 2D quadrangular and octagonal H-bond network, very similar to a floor tessellation on the surface. The vibrational spectrum calculated from MD simulations shows that the four water molecules in the quadrangles are bonded by strong H bonds while, in turn, the

quadrangles are connected to each other by weak H bonds. MD simulations also show that this structure is stable up to room temperature. Our study suggests the existence of a new ice phase not seen in the bulk case.

The calculation has been carried out using the Vienna *ab initio* simulation package, VASP [14]. The generalized gradient approximation [15] is used for the exchange correlation energy. It has been found to yield satisfactory results in recent studies of water molecules on metal [10] and oxide [16] surfaces. Electron-core interactions are described by the Vanderbilt ultrasoft pseudopotential [17]. Kohn-Sham orbits are expanded in plane waves up to a kinetic energy cutoff of 350 eV. The Monkhorst-Pack scheme [18] with $4 \times 4 \times 4$ and $2 \times 2 \times 1$ k points has been used for integration in the bulk and surface Brillouin zone, respectively. The geometry optimization is stopped when energy convergence is less than 0.0001 eV per atom. Within this scheme we find excellent agreement between the theoretical and experimental [19] structural parameters of bulk β-cristobalite (see Table I). To model the surface, we used the slab geometry in a 1×1 surface cell with periodic boundary conditions. The slabs were seven atomic layers thick and are separated by a vacuum of ~ 10 Å width. A theoretical lattice constant 7.21 Å was used throughout this work.

The initial geometry was obtained by cutting the bulk parallel to the (100) crystallographic plane. To obtain a fully hydroxylated surface we saturated the dangling oxygen bonds with hydrogen atoms on one side of the slab. On the other side, hydrogen atoms passivated the cleaved bonds too, and they, together with the bonded O atoms, were fixed in their optimized positions in the calculation. The optimized orientation of the hydroxyls indicates that two geminal hydroxyl groups do not interact with each other, but they interact vicinally to the neighboring group via an H bond, forming H-bond chains along the [110] direction at the surface, as illustrated in Fig. 1. The H-bond lengths are 1.64–1.69 Å, suggesting a strong H bonding. We obtained the completely hydroxylated (100) surfaces that are covered with geminal and

TABLE I. Calculated and experimental parameters for the bulk structure of β-cristobalite.

	a (Å)	d_{Si-O} (Å)	$\angle OSiO$ (°)	$\angle SiOSi$ (°)
Present work	7.21	1.612	109.4, 110.2	150.9, 178.5
Expt.[a]	7.16	1.611	107.8, 112.8	146.7

[a]Reference [19].

vicinally hydrogen-bonded hydroxyl groups, which is in good agreement with previous theoretical works [5,6].

Single water molecule adsorption on a hydroxylated β-cristobalite (100) surface was investigated. The geometry parameters and adsorption energy are summarized in Table II. The adsorption energy is defined as the total energy of the adsorption systems subtracting those of separate substrates and gaseous water molecules, averaged by the number of adsorbed water molecules. This circumstance strongly favors the H_2O forming two H bonds on the geminal site, as shown in Fig. 2(a), rather than residing on a top site and forming only one H bond (not shown here), where the adsorption energy of the former case is 170 meV larger than that of the latter. We also studied the water monomer adsorption on two nonequivalent surface geminal silanols, which results in only a small energy difference (~6 meV) between them. In the case of two H_2O molecule adsorption, a water dimer forms with each H_2O sitting atop a surface hydroxyl [Fig. 2(b)].

Figure 3 shows the optimized geometry for a water monolayer (ML) adsorption on a hydroxylated β-cristobalite (100) surface. Here the coverage is defined as the ratio of the number of adsorbates to the number of

FIG. 1 (color). Optimized geometry of the hydroxylated β-cristobalite (100) surface shown from the side (a) and from above (b). Only a few atomic layers in the surface are shown and only surface Si, O, and H atoms are shown space filled. Dotted lines indicate H bonds. Oxygen, silicon, and hydrogen atoms are represented by red, gray, and white spheres, respectively. White lines depict the surface cell.

surface hydroxyls. In our case, 1 ML corresponds to four H_2O molecules in the unit cell. Based on the calculation of all possible configurations, we conclude that a 2D fully hydrogen-bonded water network, which is composed of four-membered strongly H-bonded water rings connected to each other by weak H bonds, is formed, as shown in Fig. 3. Such a structure for water with quadrangular and octagonal hydrogen bond patterns has not been reported before in bulk ice, nor on other surfaces. We name this novel ice phase a water tessellation.

In this ice phase, all H_2O molecules lie nearly coplanar on the surface. Two H_2O molecules out of four in the unit cell sit flatly on the surface by accepting an H bond each from surface hydroxyl groups, and each of the rest adsorbed water molecules has one OH pointing perpendicularly down to the surface, donating an H bond. In this way, each H_2O is H bonded to three neighboring molecules and one surface hydroxyl, donating and accepting two protons, respectively [Figs. 3(a) and 3(b)]. Therefore, no free OH sticks out of the surface plane. Consequently, a two-dimensional H-bond network consisting of quadrangular and octagonal rings of water molecules is formed regularly [Fig. 3(c)]. The OO distances inside the water quadrangles are typically 2.82 Å, and between the quadrangles they are 3.16 Å. This indicates a strong H bonding inside the quadrangles and a weak H bonding between them. In Fig. 3(a), a fencelike structure appears in which every two geminal hydroxyls are H bonded with two water molecules atop them, similar to the dimer case. A cage structure — which is composed of three quadrangles of H bonds: one is a water ring plane and the other two are side faces including water and hydroxyls—is also characterized for the tessellation ice [Fig. 3(b)]. The cage serves as a bridge connecting the two adjacent H-bond chains of hydroxyls parallel on the silica surface. The formation of the new ice phase is mainly determined by the requirement of saturating hydrogen bonds among both water molecules and surface hydroxyls, in which a distortion of ideal sp^3 electron hybridization occurs, shown by the angles between H bonds of ca. 90° and 135°, differing from that of an ideal tetrahedron (109.5°).

The adsorption energy of the tessellation ice on β-cristobalite (100) is 712 meV/H_2O, almost the same as that in bulk ice, 720 meV [21]. However, the latter is overtaken by 33 meV, if zero-point energy correction, which can be estimated from our vibration spectrum, is considered (Table II). This indicates the 2D ice is at least as stable as against 3D ice clusters on the surface. There are two types of tessellation ice with different proton orderings. One has anticlockwise dipoles in the water quadrangles (not shown), while the other type does not (as shown in Fig. 3). The former is less stable by 17 meV. We believe both proton orderings are possible. The configuration in which the water quadrangles sit on the same geminal silanols is found to be only ~15 meV energetically less favorable than the one with quadrangles sitting on two vicinal H-bonded hydroxyl groups, as in Fig. 3.
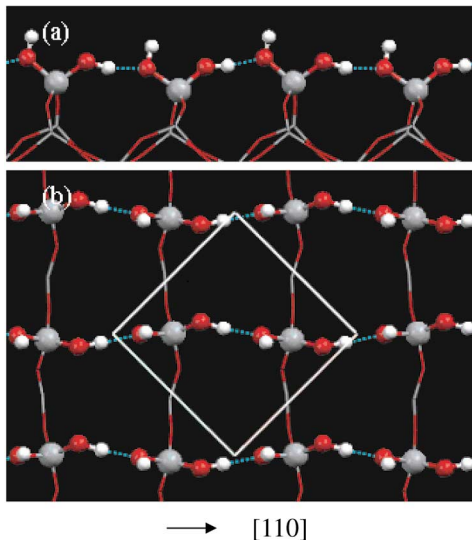
TABLE II. Optimized geometries and adsorption energies for water adsorption on a β-cristobalite (100). O_S-O_w, O_w-O_w are the OO distance between O atoms in surface hydroxyls and in water, and between those in water, respectively. $\angle O_1O_2O_3$ is the typical angle between H bonds. The values in parentheses are the adsorption energy after zero-point energy correction.

	O_S-O_w (Å)	O_w-O_w (Å)	$\angle O_1O_2O_3$ (°)	E_{ads} (meV)
H_2O molecule	2.74, 2.75	$\cdots$	56.3	508
Tessellation ice	2.69, 2.75	2.82, 2.94, 3.16	89.9, 134.6	712 (629)
Ice-Ih (273 K)	$\cdots$	2.76[a]	109.5[a]	720 (596)[b]

[a]Reference [20].
[b]Reference [21].

The feature of the water structure (ice tessellation) is essentially the same for these two possibilities. Adding one more H_2O molecule into the unit cell does not distort this tessellation pattern while it reduces the adsorption energy to 623 meV/H_2O (without zero-point energy correction), further proving the stability of the tessellation ice at comparable coverages. Furthermore, doubling the surface unit cell and increasing the SiO_2 slab to nine atomic layers does not change the results.

The existence of the 2D quadrangular and octagonal ice structure is strongly dependent on the substrate. This is due to the fact that the surface hydroxyl groups, which position the adsorbed H_2O molecules and determine the ice structure, are highly directional. One layer of free-standing tessellation ice, with an adhesion energy of 427 meV, is much less stable than a tetrahedron coordinated ice bilayer in a free space (507 meV) because of the distortion of ideal sp^3 hybridization. Although icelike phases have been identified on several metal surfaces [22] such as Rh(111), Pt(111), and Ru(0001), and on a mica surface as well [11], they are all based on hexagonal H-bond networks, or tetrahedron coordination, similar to bulk ice Ih. 1D quadrangular ice tubes were found to form inside carbon nanotubes due to axial confinement [23]. On a silica surface, for the first time, we predict a stable 2D quadrangular/octagonal ice phase at 1 ML with all OHs saturated with H bonds. Most important, with almost the same surface lattice and hydroxylated character, α-cristobalite (100) surface is also found to form the similar ice tessellation in our calculations.

Ab initio MD simulations were performed. Lower energy cutoff of 300 eV for plane waves and time steps of both 0.5 and 1 fs are used. Typically, the system was equilibrated for 1 ps, then constant energy runs were performed for 3–4 ps. Vibrational spectra are obtained by performing Fourier transformation of velocity autocorrelation functions [10]. Figure 4 shows the calculated spectrum for both the ice and surface OH groups at 80 K. The peaks located at the right side ($\geqslant 350$ meV) are OH stretch modes, and those at the left ($\leqslant 100$ meV) are translation and libration modes, while the peaks lying between correspond to Si-O-H bending (139 and 162 meV) and HOH bending (202 meV) modes. It is clearly seen that the OH stretches can be divided into five different modes, identified by their frequencies located at 456, 428, 406, 378, and 347 meV, respectively. They can be compared with the OH stretches in bulk ice (403, 390 meV) and gaseous water (466, 454 meV) [22].

These modes indicate different strengths of the H bonds in the tessellation ice. The more redshifted the OH stretch frequency, the stronger H bonding it forms. Detailed analysis demonstrates that the sharp peak at 456 meV corresponds to the weak H bonds that connect the ice quadrangles, while the 428 and 406 meV modes come from the strong H bonds inside the quadrangles. The OHs that point downward to the surface also give a vibration energy of 406 meV, overlapped with the OH modes in the 2D ice plane. Surface OH groups provide the two lowest modes at 347 and 378 meV. Although the latter is broadened and overlapped with OH stretches in water slightly, a clear separation of OH modes in surface hydroxyls and in ice is seen. Our assignment of these

FIG. 3 (color). The optimized structure of water at 1 ML coverage: (a) side view; (b) top view. For clarity, the top view of the novel 2D ice structure (tessellation ice) without substrate atoms is also shown (c). The H-bond network consists of quadrangles and octagons and no free OH bond sticks out of the 2D ice surface.
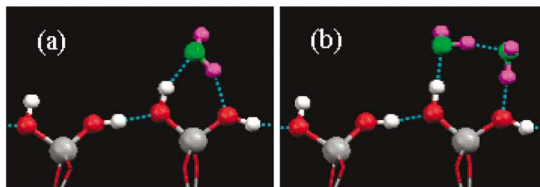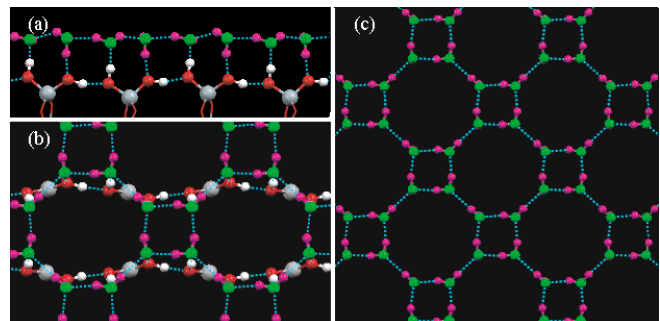

FIG. 2 (color). Atomic structure (side view) for (a) a single water molecule; (b) a water dimer adsorption. Dotted lines indicate hydrogen bonds. O and H in the adsorbed water are colored with green and pink for clarity.
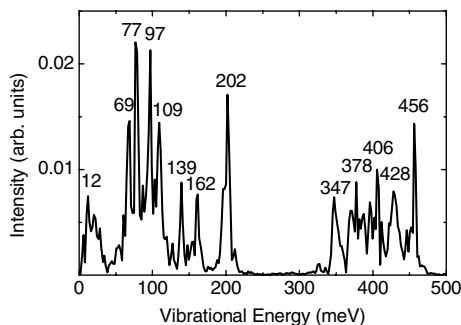
FIG. 4. Vibrational spectrum for tessellation ice and surface hydroxyls from *ab initio* molecular dynamics simulation.

modes can be further verified by the averaged OO distance [from 6000 time steps (3 ps) trajectories] of the corresponding H bonds, with typical values of 3.25, 3.00, and 2.83 Å, respectively, in the 2D ice. Furthermore, our simulation shows the 2D tessellation ice on the silica surface is stable up to room temperature, i.e., 300 K, with all H bonds and their characters sustained. This advantage could provide some potential technical use of the tessellation ice in the future, such as man-made rain seeds.

In experiments, the observed OH modes at 412–440 meV in the infrared absorption spectra for amorphous water/silica interface [1] are in the same range as our calculations. Interestingly, the five bands located at 465, 453, 422, 412, and 385 meV, when the surface OHs are H bonded with amino groups at the silica surface [24], are also close to those in our spectrum. Drost-Hansen summarized the experimental evidence for an ordered water structure induced by hydrogen bonding at the silica/water interface [25]. These may imply that small domains of the tessellation ice could exist in those experiments. For direct observation, we would expect a LEED or helium atom scattering measurement of this ice tessellation on the (100) surface of $\beta(\alpha)$-cristobalite films in the future, where long-range ordering does exist.

In conclusion, we have studied water adsorption on fully hydroxylated crystalline silica surfaces. Our results predict a novel, well-defined, and stable (up to room temperature) ice phase on the hydroxylated β-cristobalite (100) surface. The structure is well characterized by the quadrangular and octagonal patterns of H-bond networks, with all OH groups in water and surface hydroxyls saturated by H bonds. This newly described ice phase, called ice tessellation, provides us with new opportunities to obtain a deeper understanding of water-water and water-surface interactions at the molecular level, and possibly fruitful technical applications in the future.

*Corresponding author.
Email address: egwang@aphy.iphy.ac.cn

[1] *The Chemistry of Silica*, edited by R. K. Iler (Wiley, New York, 1979); *The Surface Properties of Silica*, edited by A. P. Legrand (Wiley, New York, 1998).
[2] I. S. Chuang and G. E. Maciel, J. Phys. Chem. B **101**, 3052 (1997).
[3] *The Colloid Chemistry of Silica*, edited by H. E. Bergna, Advances in Chemistry Vol. 234 (American Chemical Society, Washington, DC, 1994), Chap. 10, and references therein.
[4] D. Ceresoli *et al.*, Phys. Rev. Lett. **84**, 3887 (2000).
[5] S. Iarlori *et al.*, J. Phys. Chem. B **105**, 8007 (2001).
[6] F. Vigné-Maeder and P. Sautet, J. Phys. Chem. B **101**, 8197 (1997).
[7] K. Klier, J. H. Shen, and A. C. Zettlemoyer, J. Phys. Chem. **77**, 1458 (1973).
[8] D. R. Kinney, I. S. Chuang, and G. E. Maciel, J. Am. Chem. Soc. **115**, 6786 (1993).
[9] W. Hertl and M. L. Hair, Nature (London) **223**, 1150 (1969).
[10] Sheng Meng *et al.*, Phys. Rev. Lett. **89**, 176104 (2002); **91**, 059602 (2003).
[11] M. Odelius, M. Bernasconi, and M. Parrinello, Phys. Rev. Lett. **78**, 2855 (1997).
[12] A. G. Pelmenschikov, G. Morosi, and A. Gamba, J. Phys. Chem. A **101**, 1178 (1997).
[13] A. M. Ferrari, P. Ugliengo, and E. Garrone, J. Phys. Chem. **97**, 2671 (1993).
[14] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[15] Y. Wang and J. P. Perdew, Phys. Rev. B **44**, 13 298 (1991).
[16] A. Vittadini *et al.*, Phys. Rev. Lett. **81**, 2954 (1998).
[17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[18] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[19] A. F. Wright and A. J. Leadbetter, Philos. Mag. **31**, 1391 (1975).
[20] *The Structure and Properties of Water*, edited by D. Eisenberg and W. Kauzmann (Oxford University, New York, 1969).
[21] P. J. Feibelman, Phys. Rev. B **67**, 035420 (2003).
[22] P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7**, 211 (1987); M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002).
[23] K. Koga *et al.*, Nature (London) **412**, 802 (2001).
[24] N. W. Cant and L. H. Little, Can. J. Chem. **43**, 1252 (1965).
[25] W. Drost-Hansen, J. Colloid Interface Sci. **58**, 251 (1977).