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First-principles molecular-dynamics investigation of the hydration mechanisms of the (0001) α-quartz surface†

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Using first-principles molecular dynamics, we investigate the interactions of water with the (0001) α-quartz surface. Both the cleaved (unreconstructed) surface, which presents non-bridging oxygen atoms, and the dense surface, which is characterized by 3-membered and 6 membered-rings with siloxane bonds at the top, are considered. The cleaved surface is found to be very hydrophilic. When a water molecule arrives at the surface, its oxygen atom bonds to an under-coordinated Si atom. One of its hydrogen atoms is then transferred to a neighboring non-bridging oxygen through the formation of a hydrogen bond. When the surface is already partially hydrated, the formation of hydrogen-bond chains is observed between the water molecule and adjacent silanol groups. By contrast, the dense surface is shown to be hydrophobic. Our calculations provide qualitative information on the possible reaction paths for the dehydration mechanisms, and more generally on the interactions of water with amorphous SiO_2 surfaces.

1. Introduction

The interactions of water with silica surfaces play an important role in many advanced technological fields.[1,2] On a freshly formed dehydrated surface, a number of reactive sites (*e.g.* siloxane bonds, non-bridging oxygens) react rapidly with the atmospheric moisture causing the formation of silanol species.[2] The concentration, distribution and nature of silanol groups on the hydrated surface clearly influence the properties relevant for the technological application. To cite just one example, in microelectronics, the wafer-bonding technique is used to produce a buried oxide. A hydrophilic Si wafer pair is adhered together *via* hydrogen bonds of the silanol groups (≡Si–OH) on both surfaces. With the increase of temperature, siloxane bonds (≡Si–O–Si≡) are formed between the two surfaces by dehydration of the silanol groups. Hence, the bonding behavior of silicon wafers largely depends on the quality of the original surfaces and on their dehydration mechanism.

As illustrated by this example, the detailed microscopic knowledge of the hydration/dehydration processes of silica surfaces in contact with water is highly desirable to improve the relevant properties. From this standpoint, first-principles calculations based on the density functional theory (DFT)[3,4] reveal to be a very valuable tool since the local atomic arrangement and even movements (in the case of molecular dynamics) can be simulated with great accuracy.

Such techniques have first been used with cluster models for the silica surfaces. The simplest one consists in a silicic acid monomer (H_4SiO_4) interacting with a water molecule. From this model, it was shown[5] on energy grounds that a 4% expansion of the Si–O bonds of the siloxane was sufficient to allow the hydrolysis reaction:

$$\equiv\text{Si–O–Si}\equiv + H_2O \rightarrow \equiv\text{Si–OH} \cdots \text{HO–Si}\equiv$$

to occur. This led to useful predictions for reaction sites and paths of water–silica interactions. Using more complex cluster models representing defect sites on the amorphous surface, the activation barriers and pathways for hydration reactions were also investigated.[6]

The use of cluster models for SiO_2 systems is very satisfactory to simulate charge transfer effects, which are local in silica, and electronic responses, which are short-ranged. However, the elastic field underneath the surface, which also has a significant effect on the surface reconstruction due to water adsorption, cannot be accounted for with such models. As a result, the activation barriers and reaction energies are generally overestimated.[7]

In order to simulate this elastic field more accurately, a periodic slab can be used to model the surface. Recently, first-principles approaches have been applied to study hydration and dehydration reactions involving 2-membered rings at the (111) β-cristobalite surface as well as for a model amorphous silica surface.[8,9] The dehydration of the (100) β-cristobalite surface, which presents geminal silanols, was also investigated using constrained path first-principles molecular dynamics.[10] It should be mentioned that the periodic slab approach also has an important drawback since it introduces a long-range order at the surface that is not present in amorphous silica. But, it can be systematically improved by increasing the size of the cell.

To gain more insight on the interactions of water with amorphous SiO_2 surfaces, the use of the (0001) α-quartz surface as a periodic slab model reveals particularly interesting since it allows us to investigate surface sites that have not been considered so far. Indeed, recent first-principles calculations[11] have demonstrated that the cleaved (unreconstructed) surface presents non-bridging oxygens while the dense surface, which is the most stable, shows 3-membered and 6-membered rings with siloxane bonds. Besides, α-quartz is one of the most abundant minerals at the earth's surface and it is the stable crystalline form of SiO_2 over a broad range of temperatures and pressures, including ambient conditions.

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In this paper, we report on the first-principles molecular-dynamics investigation of the hydration mechanisms of the (0001) α-quartz surface. We study both the cleaved (unreconstructed) and the dense surface. The cleaved surface is found to be very hydrophilic. Our simulations show that a water molecule arriving at the surface is attached through its oxygen atom to an under-coordinated Si atom located underneath. Then, the transfer of one of its hydrogen atoms to a neighboring non-bridging oxygen is mediated by the formation of a hydrogen bond. For already partially hydrated surface, we observe that hydrogen-bond chains form between the water molecule and adjacent silanol groups. By contrast, the hydrophobic character of the dense surface is demonstrated by our calculations.

2. Technical details and models

Preliminary simulations for bulk α-quartz and for an isolated water molecule are performed to serve as references for the absolute surface energy calculations and to fix the initial bond lengths and angles to be used in the actual surface simulations.

We consider a tetragonal unit cell containing a slab of α-quartz and four water molecules. The slab consists of 6 O–Si–O layers along the (0001) direction, with the bottom extremities saturated with hydrogen atoms. The sides of the surface unit cell $a = 9.62$ Å and $b = 8.34$ Å are fixed to the theoretical equilibrium lattice constant of α-quartz.[12] The dimension of the cell in the direction orthogonal to the surface is taken to be $c = 21.17$ Å, allowing for the H_2O molecules to be located more than 7 Å away from the surface (this is far enough to suppress any interaction). Globally, our systems contain 24 Si atoms, 48 O atoms and 16 H atoms. It should also be mentioned that the sides of the surface unit cell are large enough to allow for a separation of at least 4 Å between the water molecules. At this distance, the contribution of long-range electrostatic interactions to the total energy is negligible.

The atomic positions are fully relaxed using the Car–Parrinello method,[13] which provides the electronic structure as well as the forces that act on the ions. Only valence electrons are explicitly considered by means of norm-conserving pseudopotentials[14] to account for the core–valence interactions. The electronic wave functions are expanded into plane waves with a kinetic energy cutoff of 50 Ry, which guarantees the convergence of the total energy, the forces, and the structural properties. Exchange and correlation are included using PW91 approximation for the exchange–correlation energy functional.[15] Gradient corrections are needed for the accurate treatment of hydrogen bonds, and their inclusion leads to successful treatment of, *e.g.* the structure of water[16] and ice[17] and the dissociation energies of small molecules.[18] The Brillouin zone (BZ) is sampled using only the Γ-point in all our calculations. In the minimization process, the atoms of the lowest SiO_2 mono-layer are kept fixed. For the dynamics, the time step was taken to be 0.17 fs.

To model the dry surface, we consider both the cleaved (unreconstructed) and the dense (0001) α-quartz surfaces which present a 1×1 geometry. The structural and electronic properties of these two surfaces have been analyzed in detail in ref. 11. The cleaved surface is characterized by non-bridging oxygen atoms and 3-coordinated silicon atoms at the top, as shown in Fig. 1(a). The dense surface, presented in Fig. 1(b), contains only 4-coordinated Si atoms and 2-coordinated O atoms with no dangling bonds. It presents 3-membered and 6-membered rings with siloxane bonds at the top, as illustrated in Fig. 1(c). The dense surface is the more stable by 0.12 eV Å^{-2}.[11]

At ordinary temperature and in normal ambient conditions (not in vacuum), the amorphous SiO_2 surface has a concentration of about 4.5 to 6.2 hydroxyl groups (OH) per nm^2. If we consider the cleaved (0001) α-quartz surface, each Si atom at the surface should bear 2 OH to have its chemical valence satisfied, giving about 10 OH nm^{-2}. We have built a model corresponding to this picture (Fig. 2(a)) by simply saturating the Si atoms at the top of the cleaved surface with the 4 water molecules:

$$=\text{Si–NBO} + H_2O \rightarrow =\text{Si}=(OH)_2$$

in our tetragonal unit cell. We will refer to this structure as the *fully-hydrated surface*.

When the temperature is increased, the number of hydroxyl groups gradually decreases at the surface.[2] It is generally believed that hydroxyl groups condense to form siloxane bonds while a water molecule is removed. If we consider our fully-hydrated surface, we can assume the following dehydration mechanism:

$$=\text{Si}–(OH)_2 + (OH)_2–\text{Si}= \rightarrow =\text{Si(OH)–O–(OH)Si}= + H_2O$$

corresponding to about 5 OH nm^{-2}. The resulting model, depicted in Fig. 2(b), will be referred to as the *semi-hydrated surface*. If dehydration proceeds further, the two remaining OH groups could also condense so that a 2-membered ring (edge-sharing tetrahedra) would form as illustrated in Fig. 2(c). However, a simple atomic relaxation of this surface leads to a completely different structure[11] in which the two oxygens of the two-membered ring prefer to form an O_2 dimer on one of the Si atoms, leaving the other silicon only two-fold coordinated.

We analyzed the relative stability of the different configurations illustrated in Fig. 2. It turns out that the fully-hydrated surface is by 2.9 eV per surface unit cell^{-1} more stable than the semi-hydrated surface which in turn is energetically favored with respect to the surface with the oxygen dimer ($\Delta E \approx 10$ eV per surface unit cell^{-1}). These barriers are too large to allow the simulation of the dehydration reaction paths

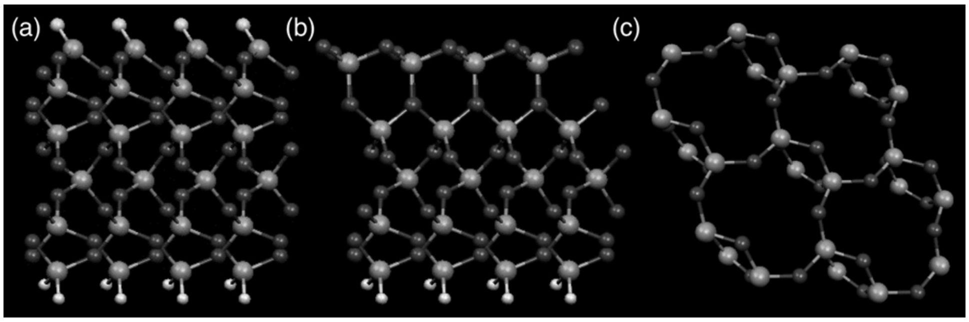

Fig. 1 Ball and stick representation of our periodic slab models. Si, O, and H atoms are represented in light grey, dark grey, and white respectively. (a) Side view of the cleaved surface. The oxygen atoms (in very light grey) are non-bridging and the underlying silicon atoms are 3-coordinated. (b) Side view of the dense surface. This reconstruction presents only 4-coordinated Si and 2-coordinated O with no dangling bonds. (c) Top view of the dense surface, showing the 3-membered and 6-membered rings.

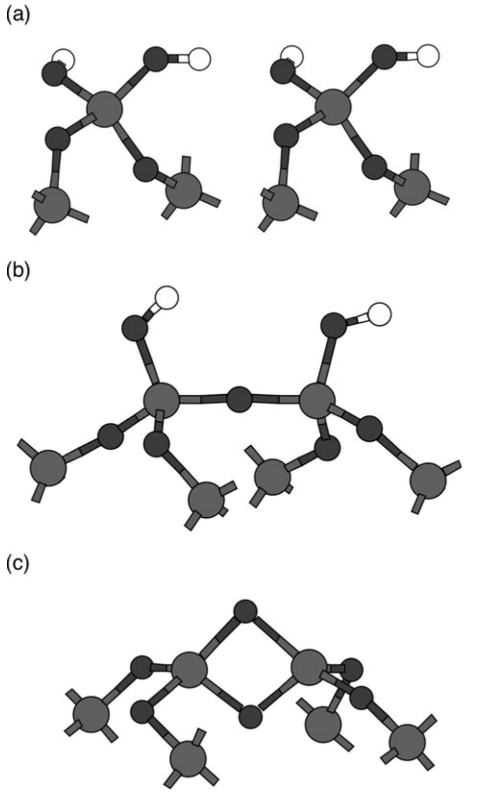

Fig. 2 Dehydration mechanism for the wet (0001) α-quartz surface. The illustration starts with (a) the fully-hydrated surface. Then a water molecule is removed after condensation of two hydroxyl groups to form a siloxane bond leading to (b) the semi-hydrated surface. The mechanism ends by (c) the formation of a 2-membered ring after further condensation of the remaining hydroxyl group and desorption of water. Si, O, and H atoms are represented in light grey, dark grey, and white respectively.

using direct molecular dynamics. Using constrained path dynamics instead might help to overcome this difficulty. However, in order to use such approaches, one must have an idea of a reasonable reaction path.

To gain insight on the hydration mechanisms, we study the hydration of the dry surface which is in principle energetically favored. Indeed, the fully-hydrated surface is by 4.6 and 14.1 eV per surface unit cell^{-1} more stable than the dense surface and the cleaved surface, respectively.

Our simulations consist in throwing the water molecules (one at a time) on the cleaved and dense surfaces, heated at 300 K beforehand, at different velocities (*i.e.* with different kinetic energies). In order to do so, a constant acceleration is given to the atoms of the molecule that is to be thrown. This scheme is thus a second-order change in the molecular dynamics, whereas imposing directly the velocity to the molecule would be a first-order change. Hence, our procedure acts very softly on the dynamics.

It should also be pointed out that due to the amount of CPU time required for each calculation, we cannot afford generating complete statistics taking into account a wide range of trajectories for the water molecules. Therefore, our results should be envisioned from a qualitative standpoint.

3. Hydration of the cleaved surface

We start with the cleaved surface and throw a water molecule with a kinetic energy of 1 eV.[19] When the water approaches the surface, a bond is created between its oxygen atom (O_W) and an underlying silicon with a non-bridging oxygen (NBO_1), as illustrated in Fig. 3(a). The Si_1 atom is 4-coordinated, the O_W is 3-coordinated, while the NBO_1 is still 1-coordinated. The excess hydrogen on O_W does not go immediately on the NBO_1. Instead, a hydrogen bond (dashed line) forms between one of the hydrogen of the water molecule and a neighboring non-bridging oxygen (NBO_2).

In Fig. 3(b), the hydrogen atom oscillates from O_W to NBO_2. After a few oscillations of the hydrogen atom from one oxygen to another, the hydrogen atom remains on NBO_2 so that there are two vicinal silanols at the surface as represented in Fig. 3(c). The first silanol (SIL_1) has a 4-coordinated Si, since NBO_1 is beside the hydroxyl group attached to it, while the newly formed silanol (SIL_2) has a 3-coordinated Si (NBO_2 has been hydrated).

Then, the hydrogen of SIL_2 starts moving toward another neighboring non-bridging oxygen (NBO_3) further away. The hydrogen bond between the oxygen atom SIL_1 and the hydrogen of SIL_2 is broken while a new one forms between SIL_2 and NBO_3, as shown in Fig. 3(d).

In Fig. 3(e), the hydrogen atom oscillates from NBO_2 to NBO_3. After a few oscillations of the hydrogen atom from one oxygen to another, the hydrogen atom remains on NBO_3: SIL_2 has been dehydrated back into NBO_3 while NBO_3 has been hydrated into SIL_3, as depicted in Fig. 3(f). At the end, the two silanols on the surface SIL_1 and SIL_3 are isolated from one another.

In order to analyze how the hydration proceeds further when the surface is already partially hydrated, we consider a cleaved surface in which two NBO's have already been hydrated, giving approximately 5 OH nm^{-2}. Hence, there remains two non-bridging oxygens in our unit cell. The surface is heated to 300 K, and a water molecule is thrown with a kinetic energy of 1 eV.

The process at the atomic scale is illustrated in Fig. 4. First, the water molecule is captured by the surface through the formation of an hydrogen bond between one hydrogen of the water molecule and a non-bridging oxygen (NBO_1) of the surface, as shown in Fig. 4(a). Then, the water molecule orients in such a way that its oxygen atom (O_W) gets bonded to a silicon with a non-bridging oxygen (NBO_2), as illustrated in Fig. 4(b). At this stage, the silicon is 4-coordinated as illustrated, O_W is 3-coordinated, while the NBO_2 is still 1-coordinated. The excess hydrogen on O_W does not go immediately on the NBO_2. Instead, as presented in Fig. 4(c), it creates a hydrogen bond with the oxygen of a neighboring silanol (SIL_3). In turn, this oxygen is quasi 3-coordinated and hence one of its hydrogen starts bonding with another adjacent non-bridging oxygen (NBO_4). In fact, a whole chain of hydrogen bonds is formed starting from O_W and ending with NBO_4 (at the lower right corner in the figure). After a few oscillations of the hydrogen atoms from one oxygen to another, the protons finally settle in such a way that NBO_4 has turned into an hydroxyl group as depicted by the hydrolysis reaction above and shown in part (d) of Fig. 4. It remains uncertain whether the formation of a hydrogen-bond chain is the real physical mechanism for the transfer of the excess H from O_W to the non-bridging oxygen, or if this is an artifact due to the periodic boundary conditions.

The remaining isolated water molecule has also been thrown on the surface which had only one NBO left and 7.5 OH nm^{-2}. This simulation also ends with the hydrolysis of the silicon with the NBO and again the formation of hydrogen-bond chains is observed, confirming the role of adjacent hydroxyl groups. The creation of these chains might be a interesting reaction path to consider for the simulation of dehydration within constrained path dynamics.

4. Hydration of the dense surface

It is generally believed that water molecules are adsorbed only on the hydrated silica surface and not on the siloxane surface which is essentially hydrophobic. However, hydration must

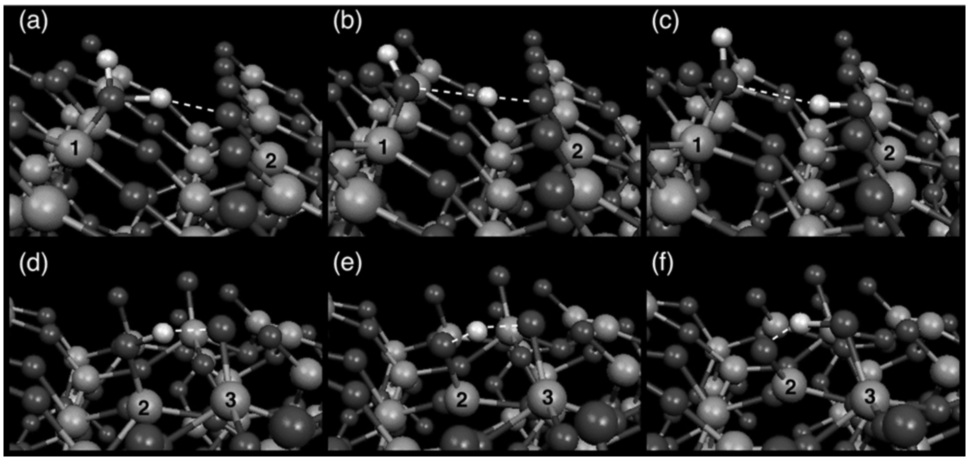

Fig. 3 Hydration mechanism for the cleaved surface. Different side views of the surface corresponding to the principal steps of the process (see discussion in the text) are presented. Si, O, and H atoms are represented in light grey, dark grey, and white respectively. The labels on the Si atoms refer to the indices used in the text.

involve adsorption of water as a first step, so that water is probably chemisorbed by opening up strained siloxane bonds initially and forming silanol groups, then it is adsorbed on the latter rather than on the siloxane surface. Further hydration occurs only on siloxane oxygen sites adjacent to a silanol site, so that the hydrated areas grow in patches as hydration proceeds along the boundary between the hydrated and siloxane regions.

We test various velocities for the water molecule corresponding respectively to kinetic energies of 0.1, 1, 10, 15, and 20 eV. Each time, the H_2O molecule bounces on the surface. Hence, we decide to perform static calculations to determine the potential barrier for the adsorption of the molecule on the surface. The water molecule is positioned at various distances from the surface (as determined by the distance between its center of mass and the upper plane of oxygens). The total energy is then calculated with the oxygen of the molecule kept fixed while the hydrogens are allowed to relax. The result of these calculations are reproduced in Fig. 5.

Another picture of this barrier can be obtained by plotting the minimal distance from the surface, reached by the water molecule for various throwing energies. Indeed, if we consider a purely elastic collision, the molecule will bounce when the repulsive energy equals its kinetic energy. These distances have also been reported in Fig. 5. In both the static and the dynamic calculations, the data roughly exhibit an exponential behavior (see interpolations on the figure). Moreover, there is a quite good agreement between the two results given the fact that in the static calculations the hydrogens are allowed to fully relax for each distance and that in the dynamic calculation we consider a purely elastic collision. The exponential behavior suggests that there exists a minimal distance under which the water molecule can not go.

This tends to confirm that surfaces formed by siloxane are essentially hydrophobic.[2] Moreover, there is no contradiction with previous *ab initio* calculations,[5] since in the dense surface, the Si–O bonds are not strained with respect to the bulk.[11] And thus, the hydrolysis reaction of the siloxane is not energetically favored. Indeed, we found that the dense surface in which we would have forced this reaction to occur for a siloxane bond between two Si of the outer layer [see Fig. 6(a)], is 4.69 eV per surface unit cell^{-1} higher in energy. The hydrophobic character of the dense surface is further confirmed by the fact that by heating this latter surface up to 300 K, we observe the dehydration (*i.e.* the desorption of the water molecule) after 300 fs, as illustrated in Fig. 6. The dehydration process happens as follows: (b) a hydrogen bond forms between the hydrogen of the first hydroxyl group and the oxygen of the second one,

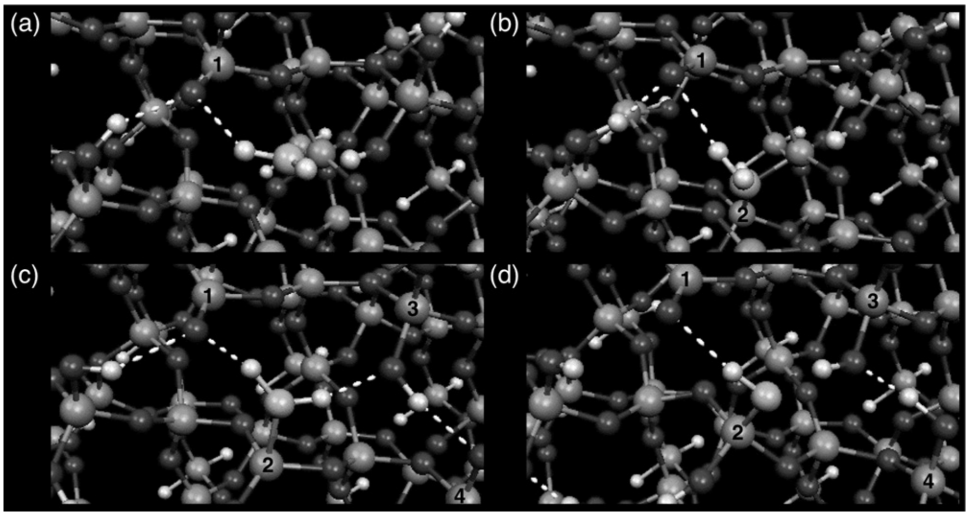

Fig. 4 Hydration mechanism for a partially hydrated surface. Different top views of the surface corresponding to the principal steps of the process (see discussion in the text) are presented. Si, O, and H atoms are represented in light grey, dark grey (except for the oxygen of the water molecule that is in very light grey), and white respectively. The labels on the Si atoms refer to the indices used in the text.

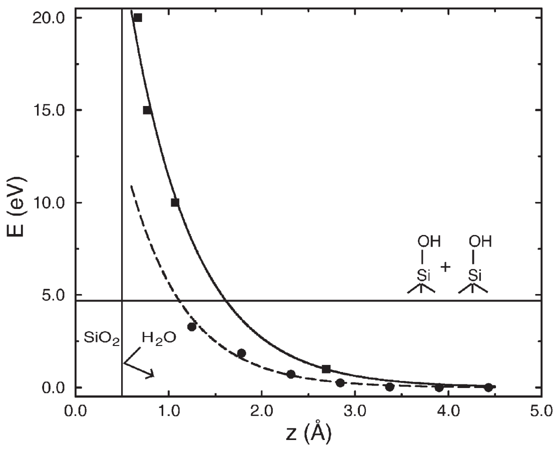

Fig. 5 Repulsive potential (*E* expressed in eV) for the absorption of a water molecule on the dense surface as a function of the distance (*z* in Å) of the center of mass with respect to upper plane of oxygens of the structure. The reference energy is taken to be that of the dense surface with the water molecule more than 7 Å away. A horizontal line at 4.69 eV represents the energy of the structure that would be obtained after the hydrolysis of a siloxane by the water molecule: $\equiv\text{Si–O–Si}\equiv + H_2O \rightarrow \equiv\text{Si–OH}\cdots\text{HO–Si}\equiv$. The open circles indicate the energies determined by static calculations for various distances. The filled squares show the minimal distance reached during the dynamic runs when the molecule was thrown with a kinetic energy of 1, 10, 15, and 20 eV. In both cases, the data roughly present an exponential behavior as suggested by the interpolations (dashed and solid lines for static and dynamic calculations, respectively). Finally, the probable asymptote for the barrier is drawn indicating that the hydrolysis does not occur.

(c) that hydrogen oscillates between the two oxygen atoms, and (d) the water molecule desorbs and a siloxane bond is created.

5. Conclusions

To summarize, we have presented theoretical results related to the interaction of the (0001) α-quartz surface with water. Our preliminary calculations have shown that the energy barriers that are involved in the dehydration of the fully-hydrated surface are too high to try to follow the reaction paths by direct molecular dynamics technique, suggesting that constrained path dynamics should be used instead.

In order to gain insight on the possible reaction paths, we have turned to the study of hydration which is found to be energetically favored in principle. We have performed molecular dynamics simulating the projection water molecules on various surfaces.

For the cleaved surface as well as for an already partially hydrated surface, the hydrolysis of silicon atoms with non-bridging oxygen was observed. In the former case, the process ends up with two isolated silanols on the surface after the transfer of the excess oxygen from the water molecule to neighboring non-bridging oxygens through the formation of hydrogen bonds. In the latter case, we find that the adjacent silanol groups play an important role in the hydration mechanism, by the formation of hydrogen-bond chains. This might be a possible reaction path to consider for the simulation of dehydration within constrained path dynamics.

By contrast, our study of the hydration of the dense surface demonstrated the hydrophobic character of the siloxane bonds. We explained that this is not in contradiction to previous *ab initio* calculations demonstrating that a 4% expansion of the Si–O bonds in siloxane was sufficient on energy grounds to allow its hydrolysis. Indeed, in the dense surface, the Si–O bonds are not strained with respect to the bulk (as shown in the study of the dry surface), so that the hydrolysis reaction of the siloxane is not energetically favored.

To complete the study, it would be interesting to make a similar computation with the semi-hydrated surface to investigate what happens to its siloxane bonds and see if the hydroxyl groups that are present at this surface allow the hydrolysis of these bonds that were shown to be hydrophobic at the dense surface. The simulation of the hydration of other surfaces such as the VAP surface[11] could provide valuable information on the hydration mechanism of amorphous surfaces.

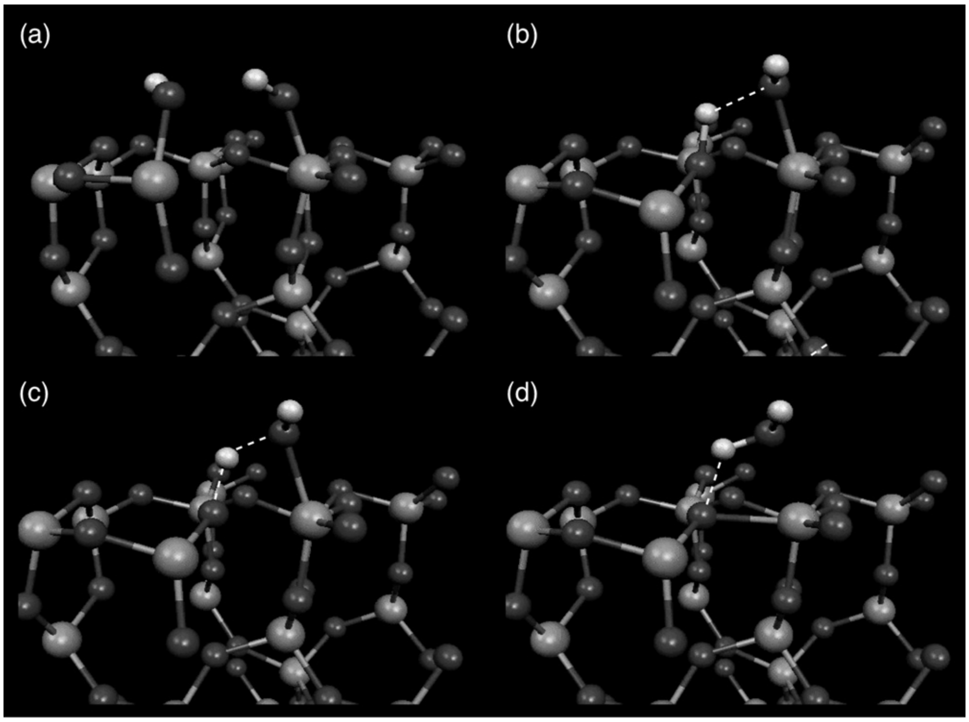

Fig. 6 Dehydration mechanism for a dense surface with a hydrated siloxane bond. Different side views of the surface corresponding to the principal steps of the process (see discussion in the text) are presented. Si, O, and H atoms are represented in light grey, dark grey, and white respectively.

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19 The kinetic energy of 1 eV is not representative of the Maxwell–Boltzmann distribution at 300 K. This high value has been chosen to increase the frequency of the various events that may take place at the surface, allowing us to simulate them in a reasonable amount of CPU time.