# Reactions and clustering of water with silica surface

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The interaction between silica surface and water is an important topic in geophysics and materials science, yet little is known about the reaction process. In this study we use first-principles molecular dynamics to simulate the hydrolysis process of silica surface using large cluster models. We find that a single water molecule is stable near the surface but can easily dissociate at three-coordinated silicon atom defect sites in the presence of other water molecules. These extra molecules provide a mechanism for hydrogen transfer from the original water molecule, hence catalyzing the reaction. The two-coordinated silicon atom is inert to the water molecule, and water clusters up to pentamer could be stably adsorbed at this site at room temperature. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1878652]

## I. INTRODUCTION

The interaction between water and solid surfaces is of fundamental interest in materials science and biological systems. Much work has been done to investigate the adsorption of water on metal[1–4] and oxide[5–10] surfaces. It is well established that the adsorption of water can be either molecular or partially dissociative, depending on the water coverage.[1,3,5,7] Due to the competition between the intermolecular hydrogen bonds among water molecules and those formed between the water molecules and a solid surface, water molecules can form layers of ordered structure[3,5,7] or form clusters from monomers to hexamers.[2,4]

Silica ($SiO_2$) is one of the most abundant minerals on the Earth's surface, and is an important technological material. It can be used in a wide variety of applications: high-frequency devices, glass, substrates for silicon in microelectronics, for adhesion polymers, and in oxide multilayers in optics, etc.[11,12] In each of these applications, the role of water and how it changes the properties of silica are important features, and the interaction between silica and water has attracted considerable attention.[13–21] Water weathers and dissolves the Earth's crust silicate mineral. It is present during quartz nucleation, and thus influences its crystal strength and growth rate. Silica glass exhibits static fatigue in humid environments[22] or with the incorporation of small amounts of water into the glass.[23] Silanol groups (Si–O–H) have been detected on silica surfaces by experiments,[13–15] but it is very difficult to deduce how water dissociates on the silica surface and how these silanols are formed[13]

A powerful method for understanding the hydrolysis process is molecular dynamics (MD) simulation. However, to describe the chemical bonds and reaction dynamics accurately this needs to be performed using a quantum-mechanical treatment. Earlier theoretical work has been carried out to investigate the hydrolysis of silica by *ab initio* methods,[16–21] but mainly concentrating on the reaction barriers and pathways. In general, the silica cluster models used

have been crude, and several constraints imposed, making it difficult to establish their relevance to the real silica surface. Our work reported here is the first one that studies the reaction process between silica surface and water by first-principles MD simulations with a large pure silica cluster, and predicts a mechanism for the hydrolysis of silica.

## II. METHODS

The calculations were performed using the linear combination of atomic orbitals (LCAO) basis SIESTA code, implementing the density-functional theory (DFT) within the generalized gradient approximation (GGA).[24] We use the functional of Perdew, Burke, and Ernzerhof (PBE). Core electrons are represented by norm-conserving pseudopotentials using the Troullier–Martins parametrization. The pseudopotential for the silicon atom was generated in the electron configuration $[Ne]3s^2 3p^2$, for oxygen in $[1s^2]2s^2 2p^4$, and for hydrogen in $1s^1$, with the square brackets denoting the core electron configurations. Various basis set configurations were tested, and a good compromise between accuracy and efficiency was found using the double-zeta set with polarization for all the species. For the species in water molecules, triple-zeta set with polariztion is used. For the isolated water molecule we obtain a OH distance of 0.98 Å, and HOH angle of 103.7°. For the water dimer, for the distance between oxygen atoms we obtain 2.88 Å. These numbers are in reasonable agreement with the experimental values of 0.96 Å, 104.5°, and 2.98 Å, respectively.[25] Greater accuracy could be achieved with hybrid functional methods,[26] but it is not crucial for the energetics we will describe below. The adsorption energy $E_{ads}$ is calculated from $E_{ads} = E_w + E_s - E_{w/s}$, where $E_w$, $E_s$, and $E_{w/s}$ are the energies of the isolated water molecule, the substrate, and the combined system, respectively. The Newtonian dynamics is integrated using the velocity Verlet algorithm and a time step of 0.2 fs.

The results described in this paper are based on spin-unpolarized calculations. Because there are some under-coordinated Si and O atoms in the cluster, the ground state of

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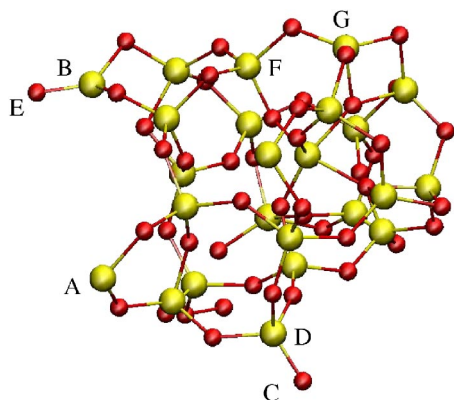FIG. 1. $(SiO_2)_{24}$ silica cluster model used in the simulation. Red and yellow spheres indicate O and Si atoms, respectively.

the cluster could be spin polarized. However, we have tested the results of the hydrolysis processes occurring on the three-coordinated silicon sites by spin-polarized calculations and found that the spin has no influence on the results.

## III. MODEL

Our chosen method of DFT-MD limits the possible system size to $\approx 100$ atoms, and hence it is crucial to find a sensible approach to scale the realities of the complex silica surface into a such a small model. In order to do this, we use the extensive empirical modeling in Ref. 27 as a basis. The authors considered silica slabs of over 2000 atoms and, after simulated annealing, characterized the density of different types of surface defects. As one would expect some of the surface is occupied by siloxane groups (Si–O–Si) formed by four-coordinated silicon atoms and two-coordinated oxygen atoms—effectively bulklike sites. The rest of the surface is occupied by defects. Such under-coordinated defects are inevitably present on the real silica surface[28,29] and are likely to be the most reactive sites for water. The hydrolysis of the siloxane bond in the absence of defects has been studied extensively previously,[17,18,20] and it has been shown that the high activation energy barrier effectively makes it unlikely in an ambient environment. Hence, our reaction simulations were mainly performed around defect sites.
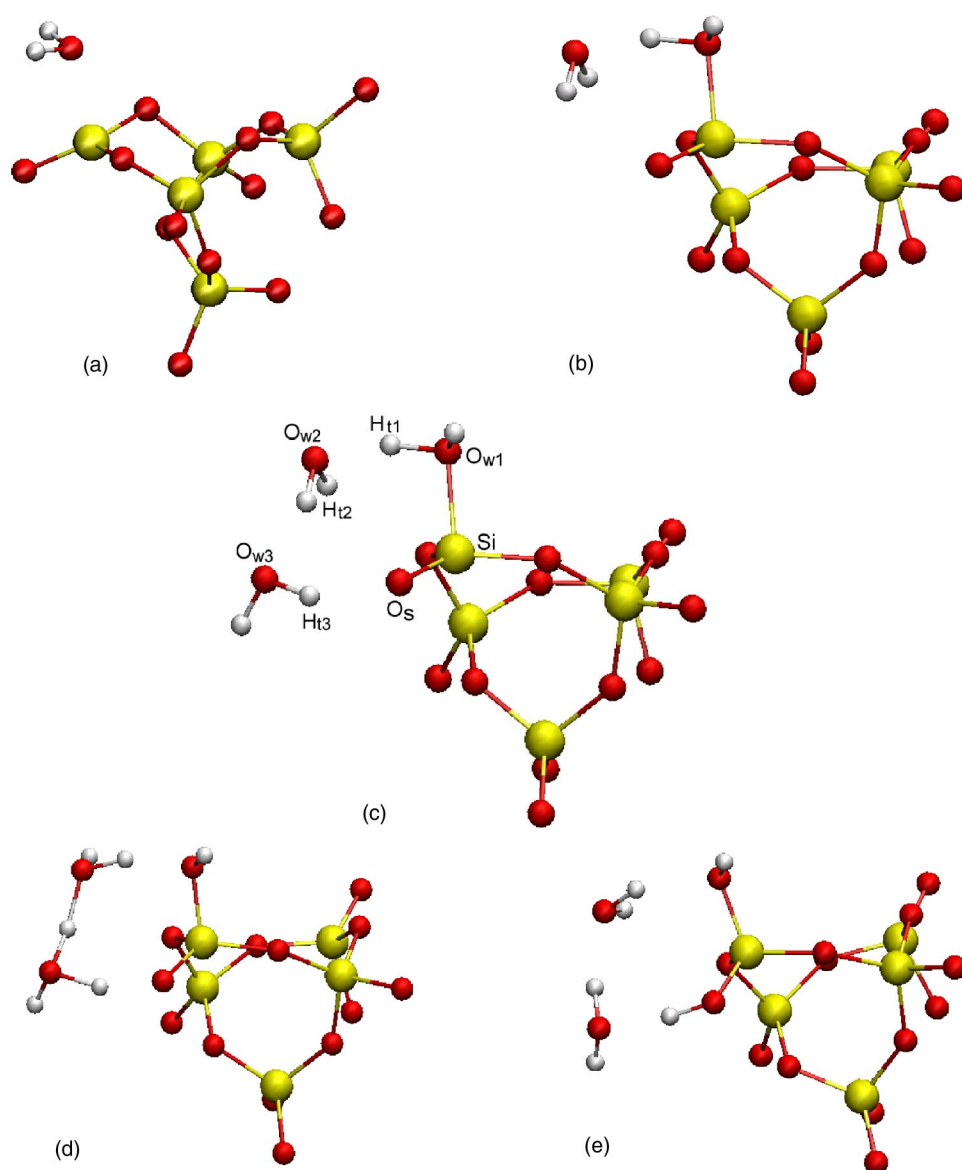


FIG. 2. Hydrolysis process of a three-coordinated silicon atom connected with a one-coordinated oxygen atom $(Q_3^1)$ by water trimer. For clarity, only atoms around the reaction site are shown. Red, yellow, and white spheres indicate O, Si, and H atoms, respectively. (a) A single water molecule is physisorbed on the silicon atom. (b) Two water molecules are adsorbed on the silicon atom. (c) The initial configuration of the system before reaction. (d) and (e) are the structures at 33 fs and 130 fs, respectively.

According to Ref. 27, there are three types of likely defect site on the silica surface: (i) three-coordinated silicon atoms, where one oxygen has a dangling bond. This is denoted as $Q_3^1$ (subscript 3 for connection to three oxygens, superscript 1 for one dangling bond); (ii) three-coordinated silicon atoms, denoted as $Q_3^0$; and (iii) four-coordinated silicon atoms, where one oxygen has a dangling bond. This is denoted as $Q_4^1$. An ideal model system would provide all these defects in a single "piece" of silica but would be large enough to also represent the bulklike structure.

In an attempt to produce this system, we considered several different sizes of silica clusters cut from the perfect $\alpha$-quartz bulk system. Each then underwent simulated annealing at high temperature to find a stable silica cluster model. Note that, due to the nonpolynomial character of the optimization problem via annealing, the structure found may not correspond to the absolute energy minimum, but nevertheless represents one of the most stable possibilities. We found that an annealed $(SiO_2)_{24}$ cluster (see Fig. 1) provided the best combination of defect sites and bulk structure. Specifically, atom $B$ in Fig. 1 is a $Q_3^1$ site and atom $D$ is a $Q_4^1$ site. There is no $Q_3^0$ site on the cluster, but one can be easily created by removing an oxygen atom ($C$) producing a $Q_3^0$ site at atom $D$.

## IV. RESULTS

### A. Hydrolysis

#### 1. $Q_3^1$ site

Placing one $H_2O$ molecule near the $Q_3^1$ site (atom $B$ in Fig. 1) induces little change to the silica cluster and the water molecule [Fig. 2(a)]: the water molecule is physisorbed on the $Q_3^1$ site with the adsorption energy of 0.9 eV. The distance between the silicon atom and the oxygen atom of the water molecule (denoted as $O_{w1}$, where $w$ stands for water and 1 for the first water molecule) is 2.01 Å. The notations of the atoms are only shown in Fig. 2(c). The bond length $O_{w1}$–H and the bond angle $\angle HO_{w1}H$ increase slightly to 0.99 Å and 106.4°, respectively. Upon adding another water molecule near the first one [Fig. 2(b)], the silica cluster remains intact. The bond $O_{w1}$–$H_{t1}$ of the first water molecule increases by 0.09 Å and the length of the Si–$O_{w1}$ bond decreases to 1.88 Å. The distance between $O_{w1}$ and $O_{w2}$ is 2.46 Å. The adsorption energy of the second water molecule is 1.0 eV. The large structural changes and the large adsorption energy result from the combination of the hydrogen bond between the water molecules and the interaction between $O_{w1}$ and Si. Due to the hydrogen bond between $O_{w2}$ and $H_{t1}$, the electron density of $O_{w1}$ that contributes to the bond $O_{w1}$–$H_{t1}$ decreases, elongating the $O_{w1}$–$H_{t1}$ bond. This "spare" density is then transferred to the bond between the $O_{w1}$ and Si, which makes the distance between $O_{w1}$ and Si decrease.

The above structures were obtained by optimizing the system with the conjugate-gradient (CG) method only. Finally, a third water molecule is placed at a randomly selected position near the second one, with the initial distances between $O_{w2}$ and $O_{w3}$, and between $O_{w3}$ and $O_s$ ($O_s$, the singly coordinated oxygen on the silica surface) within the range of
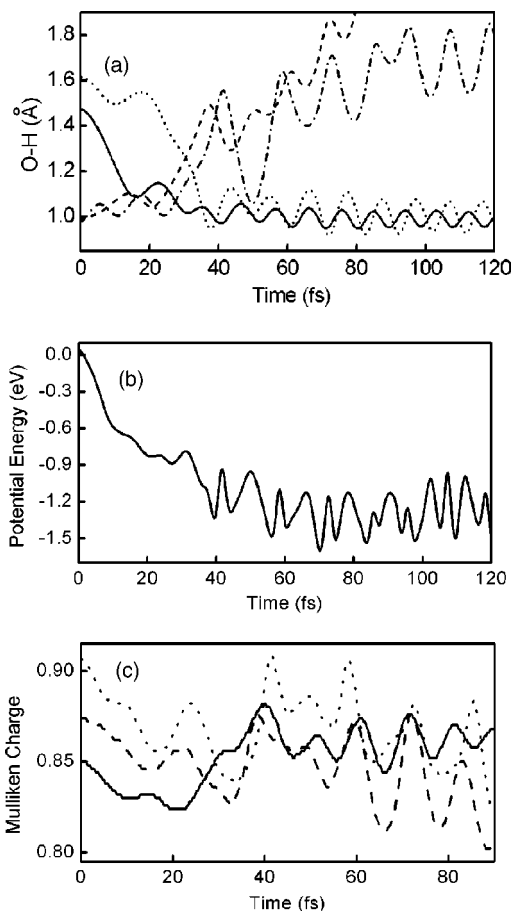


FIG. 3. Some information of the hydrolysis process shown in Fig. 2. (a) The time evolution of the length of bonds $O_{w2}$–$H_{t1}$ (solid), $O_{w2}$–$H_{t2}$ (dash), $O_{w3}$–$H_{t2}$ (dot), and $O_{w3}$–$H_{t3}$ (dash dot). (b) The time evolution of the potential energy of the system. (c) The time evolution of the Mulliken charges of $H_{t1}$ (solid), $H_{t2}$, (dash), and $H_{t3}$ (dot).

2.40–2.70 Å, as shown in Fig. 2(c). No velocity has been assigned to the atoms of the system. Instead of structure optimization, the system was simulated by first-principles molecular dynamics, imposing no constraints. As the initial structure is not a stable state, the forces among the atoms drive the atoms to move, including the Si and O atoms far away from the water molecules. Figures 2(d) and 2(e) show the structures at 33 fs and 130 fs, respectively. In Fig. 2(d), a hydrogen atom $H_{t1}$ ($t$ for transfer, 1 for the first water molecule) has left the first water molecule and bonded with $O_{w2}$. At the same time $H_{t2}$ has left the second water molecule and moved towards $O_{w3}$. The $O_{w3}$–$H_{t3}$ bond has also increased by 0.21 Å, as $H_{t3}$ tends to move towards $O_s$. In Fig. 2(e), this hydrogen transfer process has completed, leaving two water molecules and two silanol groups Si–$O_{w1}$–H and Si–$O_s$–$H_{t3}$. Due to the initial long distance between $H_{t2}$ and $O_s$, such a hydrolysis process through multiple hydrogen transfer could not happen without the participation of the third water molecule. The hydrogen-bonding network formed by the three water molecules plays an important role in this reaction. In fact, structure optimization by CG technique also led to the formation of structure in Fig. 2(e) through hydrogen transfer.

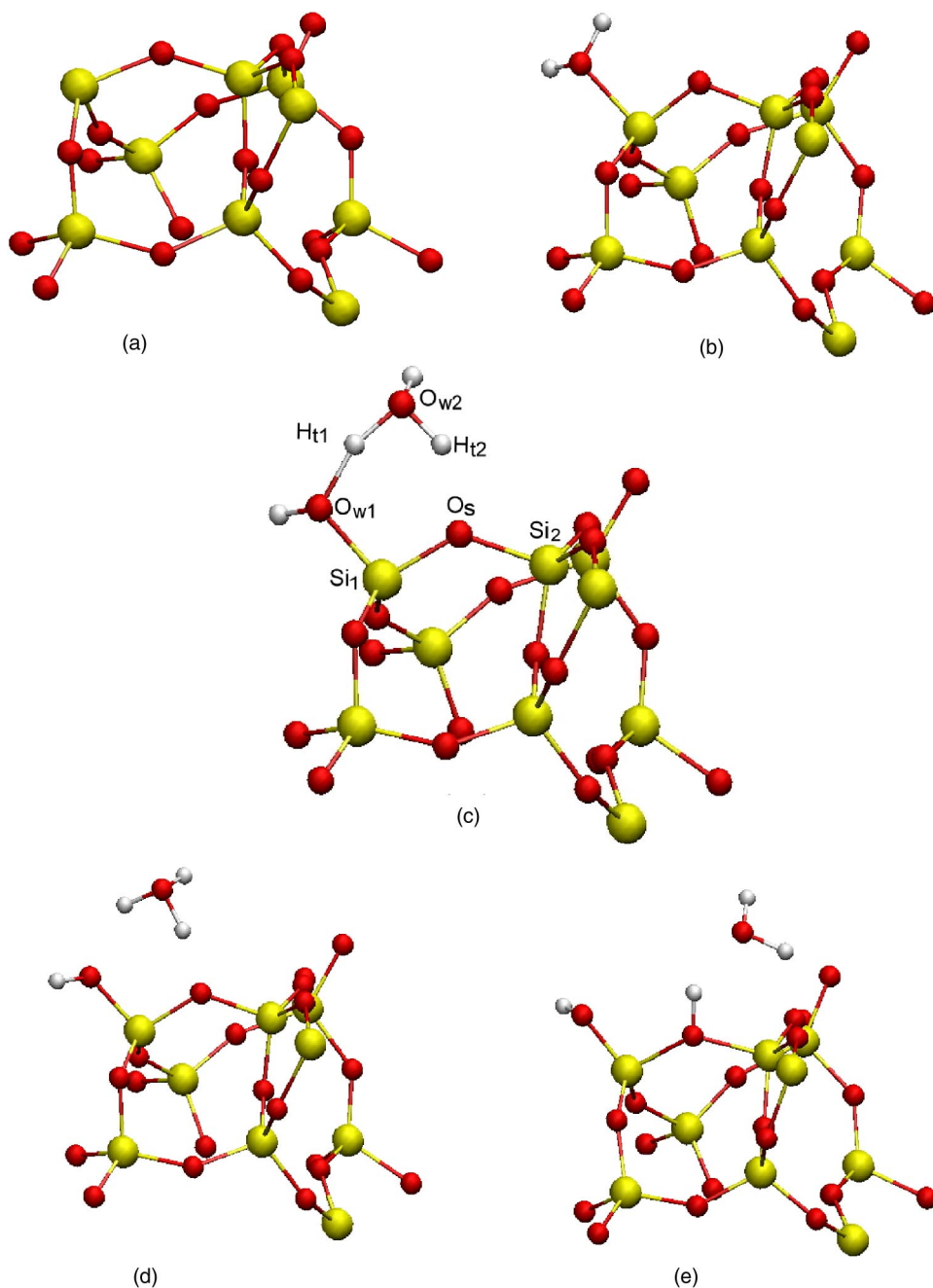Three hydrogen atoms were involved in this hydrogen

FIG. 4. Hydrolysis process of a three-coordinated silicon atom ($Q_3^0$) by water dimer. For clarity, only atoms around the reaction site are shown. Red, yellow, and white spheres indicate O, Si, and H atoms, respectively. The optimizing structures of the $Q_3^0$ site (a) and the structures with one (b) and two (c) water molecules on this site. The structures at 30 fs (d) and 254 fs (e) after heating the structure in (c) to 150 K.

transfer process. We examined the details of this process by the time evolution of the $O_w$–$H_t$ bond length, the potential energy of the system and the Mulliken charges of the transferred hydrogen atoms, as shown in Fig. 3. The transfer of each hydrogen atom is completed within 20 fs. The whole transfer process ends within 40 fs. The time step of the simulation is set to be 0.2 fs, which is small enough so that the total energy of the system could be conserved. The temperature of the system at 0 fs [Fig. 2(c)] is zero. The decrease of the potential energy (about 1.35 eV) within the first 40 fs is due to the evolution of the system from the initial structure in Fig. 2(c) to the structure just after the hydrogen transfers. At the same time, the temperature increases to 130 K at 40 fs, and then fluctuates around 130 K. The fluctuation of the potential energy after 40 fs is due to the oscillation of the system around the ground state. There is no more hydrogen

transfer after 40 fs and Fig. 2(e) is the final structure. The Mulliken charge of the hydrogen atom in an isolated water molecule is 0.88. The time evolution of the Mulliken charges of the hydrogen atoms $H_{t1}$, $H_{t2}$, and $H_{t3}$ in Fig. 3(c) shows that it is the hydrogen atom that is transferred, not just the proton.

### 2. $Q_3^0$ site

We now apply a similar procedure to the $Q_3^0$ defect site (atom $D$ with $C$ removed in Fig. 1) shown in Figs. 4(a). This $Q_3^0$ defect site is obtained by removing the oxygen atom $C$ in Fig. 1 off the cluster, leaving the silicon atom $D$ as a $Q_3^0$ site. The stable structures after adding one and two water molecules are shown in Figs. 4(b) and 4(c), respectively. The notations of the atoms are only shown in Fig. 4(c). In Fig.
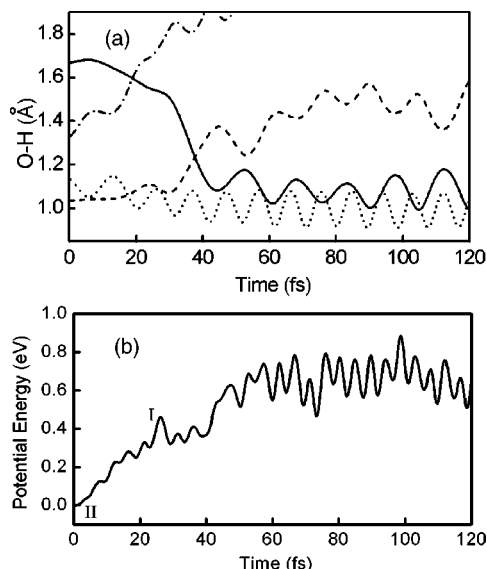
FIG. 5. Some information of the hydrolysis process shown in Fig. 4. (a) The time evolution of the length of bonds $O_{w1}-H_{t1}$ (dash dot), $O_{w2}-H_{t1}$ (dot), $O_{w2}-H_{t2}$ (dash), and $O_s-H_{t2}$ (solid). (b) The time evolution of the potential energy of the system.

4(b), the water molecule pushes the $Si_1$ atom 0.57 Å down. The distance between the oxygen atom $O_{w1}$ of the water molecule and the $Si_1$ atom is 1.87 Å. The bond length $O_{w1}-H$ increases to 0.99 Å, while the bond angle $\angle HO_{w1}H$ increases to 107.8°. The two hydrogen atoms both point away from the silica surface, with the angle between the bond $O_{w1}-Si_1$ and the water molecule plane of 61.5°. The binding energy is 1.9 eV. This large binding energy indicates that the interaction between the water molecule and this defect site is chemisorptive.

The addition of the second water molecule makes the $Si_1-O_{w1}$ bond decrease by 0.14 Å. The hydrogen atom $H_{t1}$ has left $O_{w1}$, with bond lengths $O_{w1}-H_{t1}$ and $O_{w2}-H_{t1}$ equal to 1.33 Å and 1.14 Å, respectively. At the same time, the $O_{w2}-H_{t2}$ bond increases by 0.05 Å. The system now locates at a local minimum energy state. We want to know whether the reaction like that at the $Q_3^1$ site could occur at this site if external influence, such as temperature, is exerted. Cheng et al.[19] have proven that the temperature of 150 K was enough to initialize the reaction between $SiO_2$ and $(H_2O)_n$. So we increase and fix the temperature of the system to 150 K.[30] Figures 4(d) and 4(e) show the structures at 30 fs and 254 fs, respectively. A new water molecule is formed through hydrogen transfer, leaving a silanol bond and a hydrogenated siloxane bond. The transfer of $H_{t2}$ from $O_{w2}$ to $O_s$ is completed within 16 fs [see Fig. 5(a)]. Again, analysis of the Mulliken charges indicate that hydrogen is transferred in atomic form—the Mulliken charge of $H_{t2}$ is about 0.7 after forming a bond with $O_s$.

Figures 3(b) and 5(b) show that the systems encounter energy barriers of 0.1 eV (at around 30 fs) and 0.5 eV [energy difference between points I and II in Fig. 5(b)] during the two reaction processes, respectively. As is well known, unconstrained molecular dynamics can only give an upper boundary for the activation energy barrier, so the exact activation energies needed to promote the reactions may be lower than the values given above. The activation barrier for the hydrolysis of $Q_3^0$ defect site by a single water molecule is calculated to be 0.96 eV,[6] which is much larger than our result, 0.5 eV. The participation of extra water molecules could lower the activation energy.[16–18]

### 3. $Q_4^0$ site

The reactions in the preceding section demonstrate the possibility of hydrogenation of the siloxane oxygen and suggest a mechanism for hydrolysis on the oxygen linking two bulklike $Q_4^0$ sites (in Fig. 1 any four-coordinated silicons bonded to oxygens with no dangling bonds can be considered as $Q_4^0$, e.g., $F$ and $G$). Previous studies have indicated that this hydrogenation weakens the Si–O–Si bridging bonds, and the energy barrier to the reaction for the hydrolysis of the siloxane bond diminishes.[17,18] For the hydrogenated siloxane bond in Fig. 4(e), we expect that the siloxane bond is not difficult to break. Next we consider under what condition the siloxane bond can actually break. Deleting the free water molecule as in Fig. 4(e) and optimizing again the structure, the bond lengths for $Si_1-O_s$ and $Si_2-O_s$ become 1.79 Å and 1.84 Å, respectively. There are two possible ways for an additional water molecule to break the hydrogenated siloxane bond. One is that the water molecule attacks the Si–O bond directly, i.e., the initial bond angle $\angle O_wSiO_s$ is less than 90°. [$O_w$ is the oxygen atom in the attacking water molecule and $O_s$ is the oxygen atom in Fig. 4(c).] The other is that the water molecule interacts with the backbond of the silicon atom, thereby breaking the Si–O bond indirectly, i.e., the initial bond angle $\angle O_wSiO_s$ is greater than 90°. The first route is not favorable for silicon atoms $Si_1$ and $Si_2$ in our silica model. For the second route, adding one water molecule near $Si_2$ as shown in Fig. 6(a), and optimizing the system, leads to an increase in the distance between $Si_2$ and $O_s$ to 2.01 Å, i.e., the $Si_2-O_s$ bond has been broken. The distance between $Si_2$ and $O_{w1}$ is 2.03 Å, so the water molecule was only physisorbed on the silica.

Adding another water molecule near the first one gives the optimized structure shown in Fig. 6(b). One of the hydrogen atoms of the first water molecule has moved toward the second water molecule. The distances between this hydrogen atom and the oxygen atoms of the two water molecules are 1.18 Å and 1.26 Å, respectively. The distance between $Si_2$ and $O_{w1}$ decreases to 1.81 Å, and the distance between $Si_2$ and $O_s$ increases to 2.32 Å. Performing molecular dynamics at 150 K hydrogen transfer occurs. There are two singly coordinated oxygen atoms near the second water molecule, and one of them becomes the acceptor of the extra hydrogen atom. As shown in Fig. 6(c), a stable silanol bond $Si_2-O_{w1}-H$ is finally formed. The whole transfer process is completed in about 350 fs. The most interesting aspect of this hydrolysis process is the breaking of the $Si_2-O_{w1}$ bond by the first water molecule. The occurrence probability of this phenomenon depends on the local atomic structure. For example, the reaction does not happen on the $Si_1$ site. The stable adsorption of the first water molecule on $Si_2$ is the basis for further steps. Furthermore, a nearby undercoordinated oxygen atom or a siloxane oxygen atom is needed as the acceptor of the hydrogen atom.
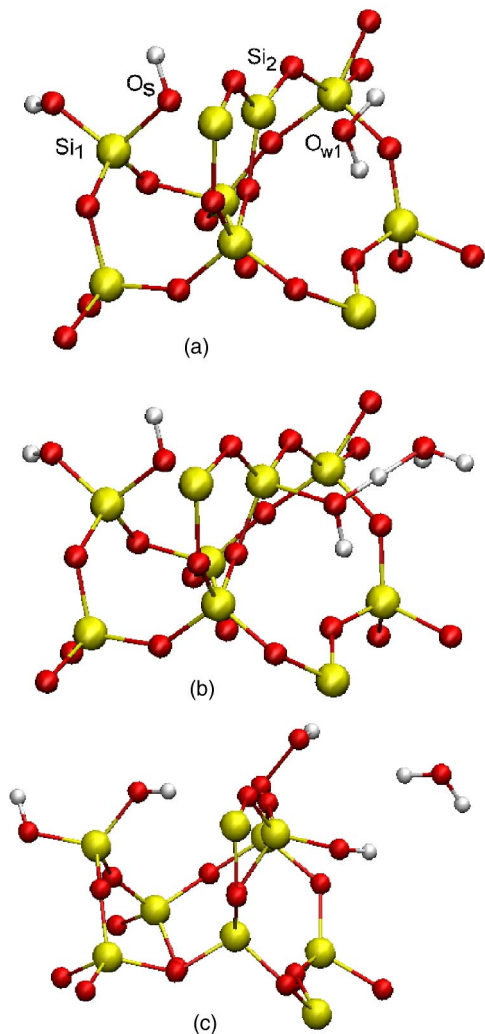
FIG. 6. Hydrolysis process of a protonated Si–O–Si bond by water dimer. For clarity, only atoms around the reaction site are shown. Red, yellow, and white spheres indicate O, Si, and H atoms, respectively. Optimizing structures after adding one (a) and two (b) water molecules around $Si_2$ atom. (c) The structure at 350 fs after heating the system (b) to 150 K.

Due to the initial long distance between the acceptor of the extra hydrogen atom and the second water molecule in Fig. 6(b), a long (~350 fs) relaxation time of the system at 150 K is needed to bring them closer, facilitating the hydrogen transfer. In such a case, addition of more water molecules may facilitate the reaction, provided the water molecules can provide a suitable hydrogen bonding network for the transfer of hydrogen. Figure 7 shows a hydrolysis process with three water molecules, which occurs at the same site as that shown in Fig. 6. However, the acceptor for the extra hydrogen atom is different from that of Fig. 6. We started from the same structure as in Fig. 6(b), and added another water molecule between the second one and another singly coordinated oxygen atom nearby, with the initial distances between adjacent oxygen atoms around 2.40 Å, as shown in Fig. 7(a). The system was first relaxed for 76 fs with direct molecular dynamics and then heated to 150 K. At 8 fs, as shown in Fig. 7(b), one hydrogen atom of the first water molecule is transferred to the second water molecule. At 94 fs, one hydrogen atom of the second water molecule is transfered to the third water molecule, and one hydrogen atom of the third water molecule begins to move toward the singly coordinated oxygen atom, as shown in Fig. 7(c). The whole transfer process is completed at 146 fs, leaving two silanol groups and two free water molecules, as shown in Fig. 7(d).

Although we only show the products at 130 fs, 254 fs, 350 fs, and 140 fs for the four reactions, these products have been verified to be stable for much longer time simulations (up to more than 1 ps). Figures 3(c) and 5(b) also confirm that the reactions really happen and are irreversible.

## B. Clustering

For more inert (with respect to water dissociation) sites on the surface, such as the $Q_4^1$ site and two-coordinated silicons, water molecularly adsorbs to the surface. Hence, it is interesting to explore whether the addition of further water
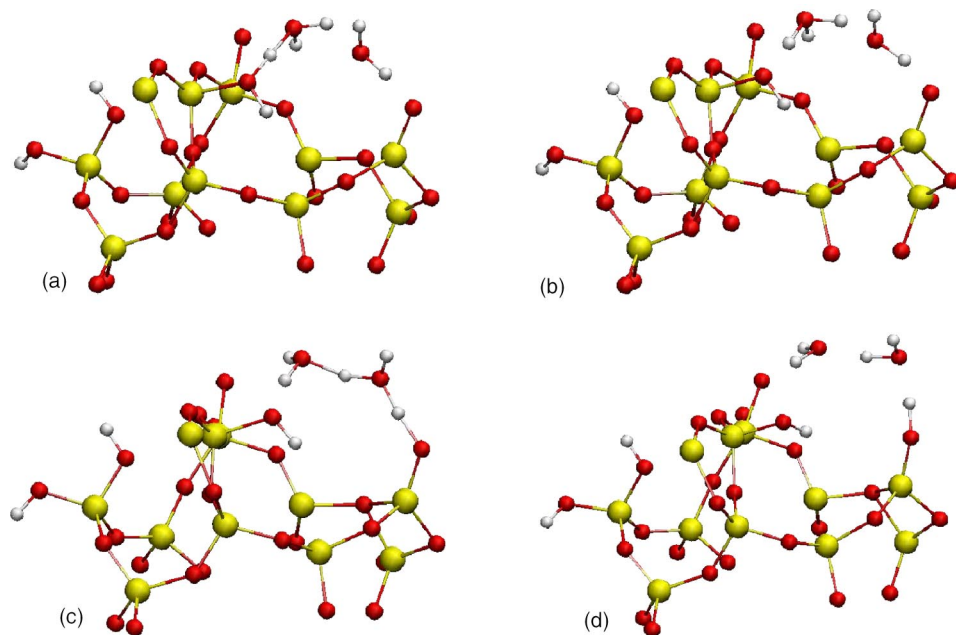


FIG. 7. Hydrolysis process of a protonated Si–O–Si bond by water trimer. For clarity, only atoms around the reaction site are shown. Red, yellow, and white spheres indicate O, Si, and H atoms, respectively. (a) The initial configuration before reaction. The structures at 8 fs (b), 94 fs (c), and 140 fs (d). After 76 fs, the system was heated to 150 K.
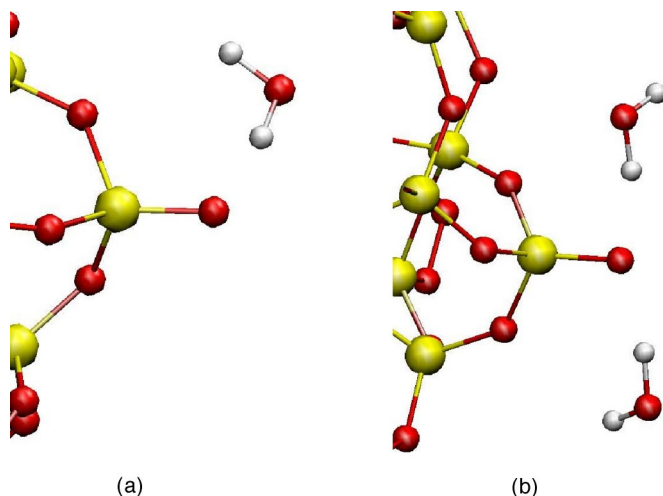
FIG. 8. The one-coordinated oxygen site with the adsorption of one water molecule (a) and two water molecules (b).

molecules will catalyze the reaction (as for three-coordinated silicon), or whether water would cluster at these inert sites.

### 1. $Q_4^1$ site

The adsorption of water molecules on the one-coordinated oxygen $Q_4^1$ site (atom $E$ in Fig. 1) is through the hydrogen bond. Figure 8(a) shows the adsorption of one water molecule on such an oxygen atom, with an adsorption energy of 0.6 eV. The distance between the oxygen atom of the water molecule and the one-coordinated oxygen atom is 2.73 Å. An O–H bond of the water molecule is elongated to 1.01 Å. Addition of a further water molecule results in adsorption either side of the oxygen [see Fig. 8(b)], but no dissociation.

### 2. Two-coordinated silicon

A rarer defect on the silica surface[27] is the two-coordinated silicon atom (atom $A$ in Fig. 1). Based on the results of previous defect sites one would naively expect this defect site to be very reactive, however, extensive simulations show that this site is very inert to the water molecule. In fact, more than on water molecule can adsorb molecularly at the site, forming a stable large water cluster. Figure 9 shows the adsorption structures of water monomer, dimer, trimer, tetramer, and pentamer on the two-coordinated silicon atom. In Table I, we show some structural information for selected water molecules in the water clusters. A water monomer is only physisorbed on the two-coordinated silicon atom, with an adsorption energy of 0.6 eV. The distance between the oxygen atom $O_1$ of the water molecule and the Si atom is 2.47 Å [see Fig. 9(a)]. Adding a second water molecule near the first one, as shown in Fig. 9(b), reduces the distance between the oxygen atom $O_1$ of the first molecule and the Si atom to 2.03 Å. The bond length $O_1-H_1^A$ and the bond angle $\angle H_1^A O_1 H_1^B$ increase to 1.04 Å and 107.5°, respectively. The distance between the oxygen atoms $O_1$ and $O_2$ of the two water molecules is 2.57 Å. The adsorption energy is 0.5 eV.
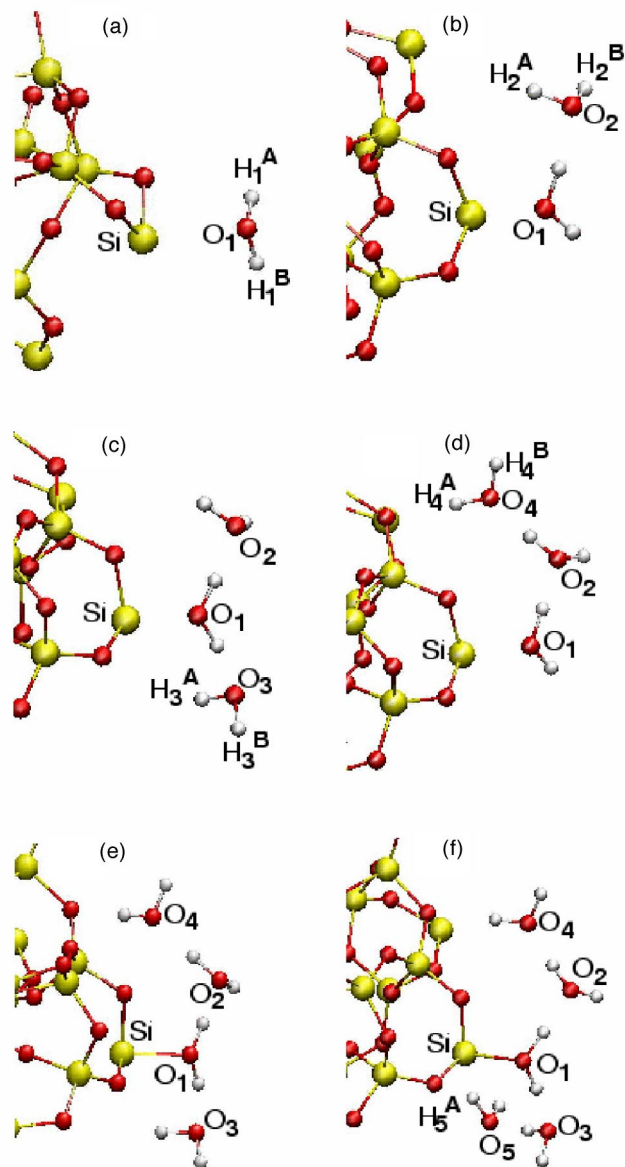


FIG. 9. The two-coordinated silicon site with the adsorption of water monomer (a), dimer (b), trimer (c), (d), tetramer (e), and pentamer (f).

There are two possible positions to place a third water molecule to form a water trimer, as the structures shown in Figs. 9(c) and 9(d) demonstrate. Placing one water molecule near the hydrogen atom $H_1^B$, forms a symmetric water trimer. The distance between the oxygen atom $O_1$ and the Si atom further decreases to 1.94 Å. The adsorption energy is 0.6 eV and the distance between the oxygen atoms $O_1$ and $O_3$ is 2.66 Å. In the structure shown in Fig. 9(d), the bond length $O_1-H_1^A$ increases to 1.08 Å. The distances between the oxygen atoms $O_1$ and $O_2$, $O_2$ and $O_4$ are 2.53 Å and 2.67 Å respectively, and the adsorption energy is 0.9 eV. The water tetramer could be obtained by adding one water molecule to the systems shown in Figs. 9(c) and 9(d), and one such structure is shown in Fig. 9(e). Adding the fifth water molecule, produces a water pentamer on the silica surface, as shown in Fig. 9(f). The adsorption energy of this water molecule is

TABLE I. Information of the structures shown in Fig. 9.

| | Si$-$O$_1$ | (H$_2$O)$_1$ | | | (H$_2$O)$_2$ | | (H$_2$O)$_3$ | |
|---|---|---|---|---|---|---|---|---|
| | | O$_1$$-$H$_1^A$ | O$_1$$-$H$_1^B$ | $\angle$H$_1^A$O$_1$H$_1^B$ | O$_2$$-$H$_2^A$ | $\angle$H$_2^A$O$_2$H$_2^B$ | O$_3$$-$H$_3^A$ | $\angle$H$_3^A$O$_3$H$_3^B$ |
| A | 2.47 | 0.99 | 0.98 | 104.8 | | | | |
| B | 2.03 | 1.04 | 0.99 | 107.5 | 0.99 | 104.5 | | |
| C | 1.94 | 1.03 | 1.02 | 107.9 | 0.99 | 104.5 | 0.99 | 104.6 |
| D | 1.97 | 1.08 | 0.98 | 107.1 | 1.02 | 104.9 | | |
| E | 1.92 | 1.06 | 1.01 | 108.6 | 1.02 | 104.9 | 0.99 | 104.4 |
| F | 1.89 | 1.06 | 1.04 | 109.5 | 1.02 | 105.1 | 1.02 | 106.0 |

0.8 eV. The length of the Si$-$O$_1$ bond is 1.89 Å, and the average distance between the oxygen atoms of the adjacent water molecules is 2.62 Å.

The hydrogen atom H$_4^A$ of the fourth water molecule is close to the silica surface, at a distance 2.12 Å to one oxygen atom on the silica model, which is within the range of the hydrogen bond. The bond length O$_4$$-$H$_4^A$ is elongated to 1.00 Å by this hydrogen bond. The distance between the hydrogen atom H$_5^A$ of the fifth water molecule to the two-coordinated silicon atom Si is 2.60 Å, and the electrostatic interaction imposed by the silicon atom reduces the bond O$_5$$-$H$_5^A$ to 1.00 Å.

The water pentamer is adsorbed on the silica surface through both electrostatic interactions and hydrogen bonding. We have checked the stability of this water pentamer: the system is relaxed at 400 K for 2 ps, during which time the water cluster neither dissociates nor leaves the silica cluster. We have tried to add more water molecules to the water pentamer, such as placing water molecules above the oxygen atom O$_1$ of the first water molecule or near the hydrogen atoms H$_2^B$, H$_3^B$, but they are not stable on the water pentamer and relaxation at room temperature will make them desorb quickly.

## V. DISCUSSION

We have simulated water hydrolysis and clustering on various characteristic defect sites on the silica surface. We have shown that the two-coordinated silicon atom is inert to water molecules, and large water clusters (up to pentamers) could be stably adsorbed at this site at room temperature.

Hydrolysis reactions at the three-coordinated silicon atoms proceed with very small barriers provided several water molecules are present. However, the reaction near the four-coordinated silicon atom depends on the local structure, including the existence of an available acceptor for the extra hydrogen atom and suitable hydrogen bonding network linking the acceptor and the reactive site. It has been observed that the addition of extra water molecules can reduce the activation energy of the hydrolysis reaction on silica models.[16,18,29] We show that this is due to water stabilizing the transition states through hydrogen bonding and participating in hydrogen transfer. The extra water molecules act as catalysts. The suggested mechanism agrees with the extra water-catalyzed hydrolysis observed in first-principles MD studies for the Al$_2$O$_3$ (Refs. 8 and 9) and TiO$_2$ (Ref. 10) surfaces, and for the two-membered ring on the silica

surface.[21] However, the easiness of the reactions at these sites absolutely does not mean that silica could dissolve quickly in pure water at normal conditions. In fact, the dissolution of silica is very slow.[31] The defect sites would be the first to be hydrolyzed and dissolve because of the low activation energy. As the surface fraction of these sites decreases, the reaction will concentrate on the non-defect sites where the activation energy is high, and the reaction rate will also decrease greatly. Furthermore, it has been proposed that a "self-healing" effect of silanol groups might also lower the dissolution rate of silica.[32]

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