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Structure, collective hydrogen transfer, and formation of $Si(OH)_4$ in $SiO_2-(H_2O)_n$ clusters

Hai-Ping Cheng[a)]
Department of Physics and Quantum Theory Project, Gainesville, Florida 32605

Robert N. Barnett and Uzi Landman
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332

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SiO_2–water clusters are studied using first-principles Born–Oppenheimer molecular dynamics based on density functional theory and generalized gradient approximations. Systematic investigations of structure and energetics as functions of cluster size demonstrate the roles of water molecules in chemical reactions. The water-assisted formation of a $Si(OH)_4$ molecule from a single SiO_2 molecule is revealed at the atomic level. The dynamics of dissociation of water molecules and formation of Si–OH bonds is investigated via simulations at finite temperature. A complex process that involves double and triple hydrogen atom transfer is discovered to be the reaction path. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473808]

I. INTRODUCTION

The interaction of molecules and water clusters is a subject of general interests in a broad range of modern scientific research.[1–6] Many physical processes in materials science, environmental science, and biological science are influenced by the presence of a small number of water molecules. Clusters that consist of water and solute molecules are ideal model systems for understanding the basic nature of hydrogen bonding, solvation shell structure, proton or hydrogen atom motion, and the interplay between structures and dynamics. In the past decade, a variety of molecule/ion–water aggregates have been studied experimentally[1–3] and theoretically.[4–6]

As an important technological material, amorphous silicon dioxide (silica) has attracted much attention in many research activities. In particular, its interaction with water molecule that has been discussed in geophysics and materials science, has become a new focus recently.[7–15] The so-called hydrolytic weakening effect is believed to be a significant factor that enhances fracture and crack development and propagation in materials under stress.[14,15] It is found that water can reduce the strength of the Si–O bonds in silica.

To understand the hydrolytic weakening, in addition to a clear picture of the mechanical properties of the materials, a precise description of the chemical bonding and reaction dynamics is required. Quantum mechanical studies are necessary to fully understand the exact nature of bonding, bond weakening, and bond-breaking processes. It is equivalently important to investigate the dynamics of the process, which demands molecular dynamics simulations with a quantum description of the electronic structure of the system along the trajectories of the nuclei. The conventional classical molecular dynamics that has been successfully used to simulate material properties is not suitable for studying chemical reactions with high precision.

While multiscale simulation methods for studies of large extended systems are under development,[16] the cluster model is still very useful in the investigation of molecular interactions. For example, in order to describe chemical properties of a surface or the tip of a crack, it is not appropriate to use information that is obtained from crystalline structure. To overcome difficulties that come from the demands of accuracy as well as large dimensionality, several groups[13–15] have recently tried to generate model surface structure from classical molecular dynamics simulations. The structures are then reduced to several model clusters and further optimized via *ab initio* calculations. These models, which reflect local features of silica surface are proposed to be the reactive sites on surface. Quantum mechanical studies of interactions between water and model cluster are performed to study water dissociation processes on SiO_2 surfaces.

Although these studies provide valuable data on individual model systems, the complete physical and chemical picture of the SiO_2–water interaction remains to be explored. In order to fully understand the effects of local structure as well as effect of water, it is a first fundamental step to investigate $(SiO_2)_n$–water clusters in a systematic approach with various size and configurations. These clusters can be used to study the solvent effects or to represent the local structure of amorphous SiO_2. To date, there are no systematic first-principles studies on $(SiO_2)_n$–water interactions that address issues such as the number of water molecules versus the size of SiO_2. Most of the previous *ab initio* studies are limited to one water molecule interacting with a few particular model clusters for SiO_2 surfaces.[14]

In this paper, we report results on $SiO_2-(H_2O)_n$ ($n=1-6$) clusters from first-principles molecular dynamics simulations. This series is the first group in a collection of $(SiO_2)_m(H_2O)_n$ clusters, some of which we intend to use for modeling a silica surface or a crack tip. Note that the empha-

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[a)] Author to whom correspondence should be addressed.

sis of this study is on the solvent effects. Our studies of the second group of $(SiO_2)_n(H_2O)$ clusters will be reported elsewhere.[16] It worth mentioning one more compelling reason for cluster study: The unique physical and chemical properties of materials at small scales such as nanoclusters are clues for discovery of new phenomena. Finite size systems have attracted much attention from scientists in the past 20 years and continue to be an active area in science.

The manuscript is organized in the following order: theoretical treatment and simulation details, results, and, finally, discussion and conclusions.

II. METHOD AND SIMULATION

We use Born–Oppenheimer local spin density molecular dynamics (BO-LSD-MD), developed by Barnett and Landman in 1993.[17] The Hamiltonian of a dynamical system is written as

$$H=\sum_I \frac{|\mathbf{P}_I|^2}{2m_I}+\sum_{I>J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}+E_{\mathrm{elec}}(\{\mathbf{R}_I;\mathbf{r}\}), \tag{1}$$

where upper case letters represent nuclear quantities, $\mathbf{r}$ is the position of electrons in real space. E_{elec} is the total electronic energy that consists of the kinetic energy of electrons, electron–electron, and electron–nuclear interactions. In the classical limit, Newtonian dynamics of nuclei in the system is used to obtain trajectories on the ground state potential energy surface, E_{elec} plus the ionic interaction [the second term in Eq. (1)]. The equations of motion for the nuclei are

$$M_I\frac{d\mathbf{R}_I^2}{dt^2}=-\nabla_{\mathbf{R}_I}\sum_{I>J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}-\nabla_{\mathbf{R}_I}E_{\mathrm{elec}}. \tag{2}$$

In BO-LSD-MD, E_{elec} is calculated in the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA). The Kohn–Sham (KS) equations of the systems are solved self-consistently at each time step for a given nuclear configuration. The energy and forces on each nuclear are evaluated once the iteration for solving the KS equation has converged.

The KS wave function is expanded in a plane wave basis set in conjunction with pseudopotential method.[18] Since the plane waves are independent of the positions of the nuclei $\{\mathbf{R}_I\}$, the only nonzero term in the gradient of E_{elec} is from the derivative of the Hamiltonian operator of the electronic system, thus simplifying the calculations of interatomic forces. With cutoff energy being the only parameter, the planewave-pseudopotential approach reduces substantially the complication in testing the quality of the basis set.

BO-LSD-MD is optimized to treat finite size systems such that systems with a net charge, dipole moment or higher order moments can be studied. Two rectangular grids with uniform spacing in each direction are required to expand the wave functions and charge density, respectively. In the dynamical simulations, the size of the grid on which the systems are evolving is chosen large enough to give approximately zero charge density on each of the six surfaces of the rectangular grid. When high accuracy is required in the total energy estimation, the size of the grid as well as the spacing of grid points are chosen to obtain the energy convergence at the desired accuracy.

The details of solving the KS equations are given by Barnett and Landman in Ref. 17. We do not to repeat the description here. It should be mentioned, however, that various techniques, such as charge mixing during the self-consistent iteration, solving for the lowest n eigenstates, prediction of new density using the density at the previous time steps, etc., are applied and fully tested to speed up the calculation.

In this study, the pseudopotential by Troullier and Martin,[18] GGA by Perdew, Burke, and Ernzerhof (PBE),[19] and a cutoff energy of 62 Ry is used. With this combination of pseudopotential, GGA functions, and energy cutoff, the accuracy in binding energy is better than 0.5 kcal/mol for hydrogen bonding in water clusters. The test results on water-water interactions are similar to ones in our previous studies.[5]

Three algorithms for structural optimization are used in our investigation: A modified steepest-decent/conjugated gradient method, simulated annealing, and a mixture of the first two approaches. According to the physical conditions, constraints can be applied to the systems in both optimization procedure and dynamical processes. The Newtonian dynamics is integrated numerically with the Verlet algorithm. A time step of 0.2 fs is used in the simulations.

III. SIMULATION AND RESULTS

We study the size dependence of interactions between SiO_2 and $(H_2O)_n$ $(n=1-6)$ using the BO-LSD-MD method. The first step is to find the ground state structure of both SiO_2 and H_2O molecules. Since the systems are relatively simple, direct minimization is enough for searching the minimum energy structures. The SiO_2 is a linear molecule [Fig. 1(a)] with a Si–O bond length of 2.87 a_o. The water molecule has an O–H bond length of 1.83 a_o and an H–O–H bond angle of 104.3°. These structural parameters are in excellent agreement with experimental data.

A. Structure and energetics

Table I lists energetics of the SiO_2–water clusters as the number of water molecules increases. The hydration energy is calculated via the expression of $\Delta E_n = E[SiO_2(H_2O)_n]-E[SiO_2(H_2O)_{n-1}]-E[H_2O]$. Figures 1(b)–1(g) depict the structure of cluster with 1–6 water molecules.

When one water molecule is attached to SiO_2, the binding energy between the two molecules, or, the solvation energy, is 1.04 eV. Note that this energy is obtained based on a structure in which the water molecule does not disassociate. The water molecule induces a dipole moment in SiO_2 such that the SiO_2 molecule is no longer linear but has a bonding angle of 158.6°. The Si–O bond lengths are 2.88 a_o, an increase of less than 0.4%. The distance between Si and the oxygen molecule in H_2O is 3.64 a_o that indicates that it is much longer that a Si–O single ionic bond [see Fig. 1(b)]. The interaction also modifies the H_2O structure. The

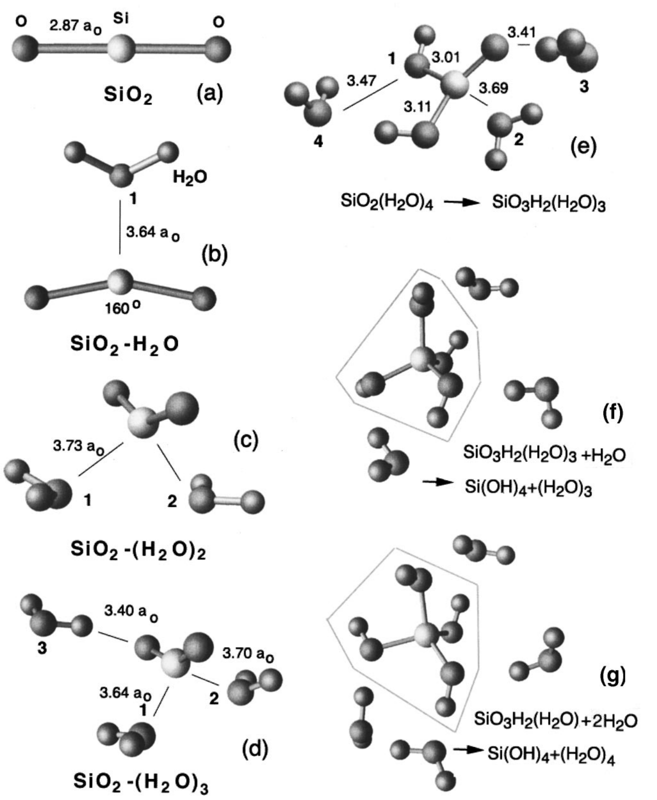

FIG. 1. Solvation and reaction in $SiO_2(H_2O)_n$ ($n=1-6$) clusters. For $n=1-3$, the structures are optimized without breaking a H_2O molecule. For $n=4-6$ one water molecule is dissociated to H and OH that form two single bonds with an oxygen and the silicon in the SiO_2 molecule, respectively.

H–O–H binding angle becomes 111.5°, 7% larger than the angle of an isolated water molecule, and the O–H bond lengths increase 1%.

As the second H_2O is added to the system, the cluster rearranges such that SiO_2 binds the two H_2O symmetrically. The hydration energy is 0.82 eV. The system has C_{2v} symmetry. The distance between Si and the oxygen atoms in the two H_2O molecules are 3.73 a_o slightly longer that the Si–O distance in the SiO_2-H_2O complex. The bond angle of SiO_2 also changes, from 158.6° to 150.3°. The H–O bond length of the H_2O molecules do not change within the accuracy of the calculation. However, the H–O–H angle is now 110.9°, slightly smaller than the one in the complex with one water (111.5°). The structure of the cluster is again based on electrostatic interactions between SiO_2 and two water molecules [Fig. 1(c)].

TABLE I. Hydration energy of $(SiO_2)(H_2O)_n$ cluster, defined as energy increase when add one more water molecule, is estimated by $E[(SiO_2)\times(H_2O)_{n+1}]-E[(SiO_2)(H_2O)_n]-E[H_2O]$, $n=0-5$.

Clusters/energy	Hydration energy (eV)
SiO_2H_2O	1.04
$SiO_2(H_2O)_2$	0.82
$SiO_2(H_2O)_3$	0.42
$SiO_2(H_2O)_4$	2.16
$SiO_2(H_2O)_5$	2.13
$SiO_2(H_2O)_6$	0.44

Next, the third H_2O is attached to the cluster to form $SiO_2-(H_2O)_3$ complex. After we apply a combination of MD simulation (at temperature 100–400 K) and direct minimization, the structure of the complex obtained is shown in Fig. 1(d). The third H_2O is attached to an oxygen atom in SiO_2 with a hydrogen bond of 3.40 a_o between the two molecules. This water molecule modifies the environment of the other two and induces a slight asymmetry. The first two water molecules have a Si–O distance of 3.64 and 3.70 a_o, respectively. The O–Si–O bond angle is 149.1°, only 1° less than for the cluster with two water molecules. The Si–O bond lengths are 2.90 a_o, increasing by 0.02 a_o. The structure of the cluster is stabilized basically by electrostatic interaction and relatively weak hydrogen bonding. The hydration energy is 0.42 eV.

A quite different phenomenon (compared to systems with 1–3 H_2O) is observed when the fourth water molecule is added to the cluster. As we perform the MD simulation at a temperature of 100–400 K, the structure of the system undergoes a major change. A reaction occurs in the cluster that leads to the dissociation of a water molecule. The ground state structure after the reaction depicts a new cluster of $SiO_3H_2-(H_2O)_3$ [see Fig. 1(e)]. The energy gain is 2.16 eV, indicating a chemical binding rather than electrostatic interaction or hydrogen bonding.

The new molecule SiO_3H_2 is solvated by three H_2O with intermolecular distances ranging from 3.41 (O–H) to 3.69 (Si–O), as shown in Fig. 1(e). The two covalent O–H bonds in SiO_3H_2 are 1.87 a_o. The two Si–OH distances are 3.01 and 3.11 a_o, respectively. The remaining Si–O double bond is 2.87 a_o, which is unperturbed from its original length [Fig. 1(a)].

A similar reaction process occurs that leads to dissociation of a second water molecule when a fifth water molecule is added to the cluster. A combination of dynamics simulation, simulated annealing, structure optimization is applied to investigate the states of the cluster. The results suggest that the second dissociation process involve overcoming a barrier of <400 K, similar to the first dissociation process. The binding energy is 2.13 eV, very close to the energy gain as the fourth water is added to the cluster. At the end of the process, a SiO_4H_4 molecule is formed. In Fig. 1(f), the newly formed molecule is circled. Three water molecules remain in the cluster. The four Si–OH bonds are 3.05, 3.10, 3.11, and 3.16 a_o, and the four O–H bonds are 1.87, 1.89, 1.82, and 1.83 a_o, respectively. The slightly asymmetric structure is due to the solvent molecules.

A separated simulation is performed by adding a sixth water molecules to $SiO_2-(H_5O)_5$ before the formation of final product, that is, before the dissociation of a second water molecule. The reaction product $Si(OH)_4$ molecule is again circled in Fig. 1(g). In this case, four water molecules are left in the cluster after the reaction. The four Si–OH bonds are 3.06, 3.07, 3.14, and 3.15 a_o, and the four O–H bonds are 1.88, 1.88, 1.82, and 1.84 a_o, respectively.

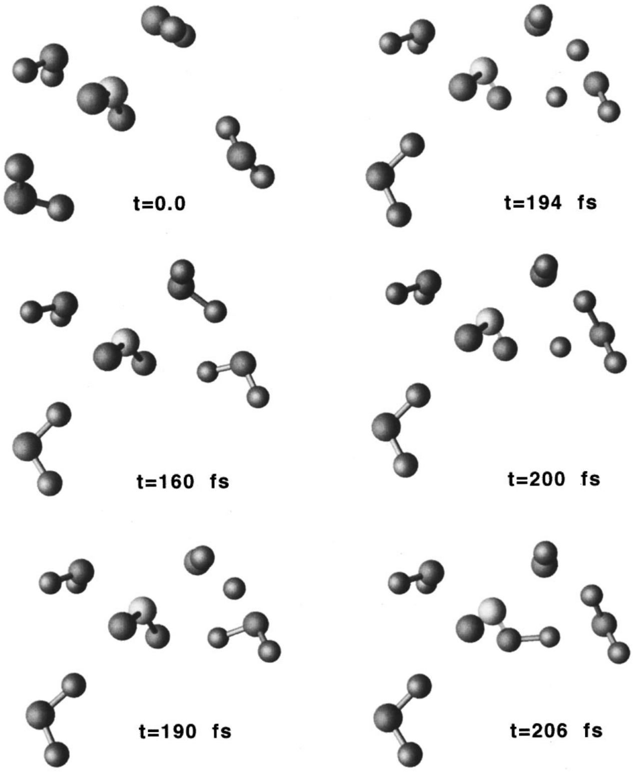

FIG. 2. Double H-atom transfer in a $SiO_2(H_2O)_4$ cluster. The trajectory is obtained via BO-LSD-MD (GGA) on-the-fly simulation. Note that the dissociation of a water molecule requires more than one H_2O. Two water molecules are directly involved in H transfer process and all four H_2O molecules are necessary for reaction to occur at the given energy.

B. Dynamics, energy landscape, and reaction pathway

One of the important findings from our study is the dynamic pathway of the chemical reaction that occurs in the complex of the SiO_2 plus 4-water cluster. Figure 2 demonstrates a sequence of snapshots of the reaction. At $t=0.0$, the fourth H_2O molecule is added to the $SiO_2-(H_2O)_3$ cluster.

The simulation begins with a steepest decent process to bring the cluster to its local minimum energy structure ($t=100$ fs). Next, the system is heated to 150 K and direct MD is performed. The added water molecule moves towards the center of the cluster. All molecules in the system undergo a collective reorientation. The system overcomes a small energy barrier of 0.27 eV as seen in Fig. 3. The potential energy decreases nearly monotonically on the other side of the barrier. Consequently, the system gains kinetic energy that leads a temperature approximately 600 K. At $t=160$ fs, all the molecules in the clusters have reoriented. Only 30 fs later a hydrogen atom from one of the water molecule breaks off and moves towards another water (see Fig. 3 at $t=190$ fs, H_2O molecules on the right-hand side). Instantly ($t=194$ fs), a hydrogen atom in the second water molecule breaks a OH bond and moves in the direction of the oxygen atom in the SiO_2 molecule. This process is completed at $t=260$ fs and produces a new solute species of SiO_3H_2. One of the two Si═O double bonds in SiO_2 is now replaced by two Si–OH single bonds. Three H_2O molecules are present.

After 260 fs, we perform simulated annealing to locate the minimum energy state of the system after this reaction. Figure 3 depicts the potential energy in the annealing process.

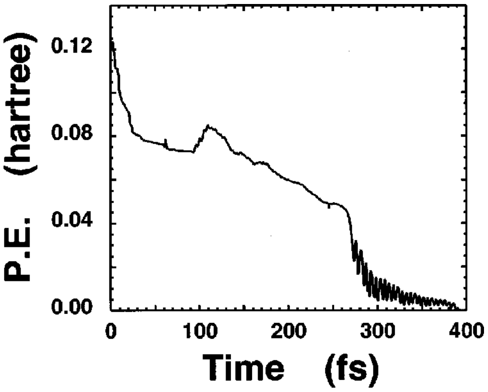

FIG. 3. Potential energy curve as a function of time as reaction take place in a $SiO_2(H_2O)_4$ cluster.

This process involves a double hydrogen atom transfer (Fig. 3) and the assistance of all for water molecules. A low energy barrier of the order of the thermal energy is required for the reaction to occur, which is different from clusters of fewer water molecules. Note also that the process is extremely fast, taking 100 fs from a local minimum energy structure prior to the reaction.

To break the second Si═O bond, two simulations are performed by adding one and two water molecules to the cluster, respectively. Figure 4 depicts the potential energy landscape along the pathway towards the formation of the $Si(OH)_4$ molecule for the first simulation. The cluster configurations at various points on the energy curve are illustrated. Similar to Fig. 2, the reaction involves a double proton transfer followed by the formation of a Si–OH bond when the O atom in the Si═O bond captures a H atom relayed between two H_2O. The energy landscape and pathway of the second simulation is demonstrated in Fig. 5. In this case, three H_2O molecules participate in the relay to deliver a H atom to the O atom in a Si═O bond. A triple H atom transfer is observed.

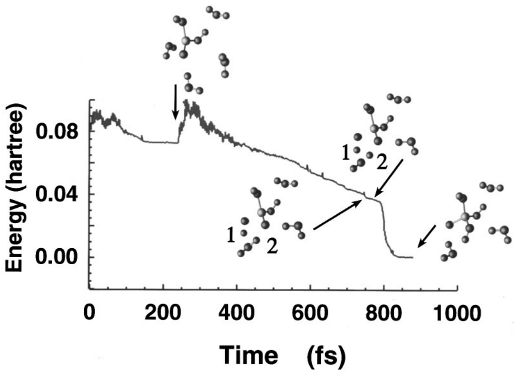

FIG. 4. Energy landscape and reaction pathway to form a $Si(OH)_4$ molecule. Double H-atom transfer is observed. The numbers 1 and 2 in the figure indicate the two H atoms.

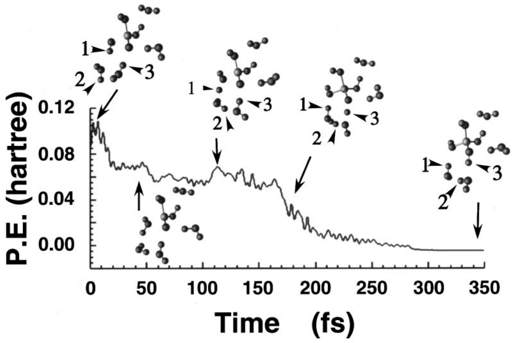

FIG. 5. Energy landscape and reaction pathway to form a $Si(OH)_4$ molecule. Triple H-atom transfer is observed. The numbers 1, 2, and 3 in the figure indicate the three H atoms.

IV. CONCLUSIONS

Our studies demonstrate the important role of water molecules that leads to the formation of $Si(OH)_4$ molecule through the detailed analysis of the structure and dynamics of SiO_2–water clusters. The on-the-fly Born–Oppenheimer molecular dynamics method in the framework of DFT-GGA allows an accurate description of the energetics of the system in its ground state and isomer states, as well as in any configuration during a dynamical process. It provides a powerful tool to observe phenomena that are yet difficult to determine in experiments. The results of our simulation suggest that when 1–3 water molecules interact with a SiO_2 molecule, the molecules are chemically stable at the thermal energy scale. The hydration energy/molecule decreases as the number of water molecules increases from 1 to 3, which is a typical trend in ion/molecule solvation processes. This stability is destroyed when more water molecules are added to the cluster. A fast reaction is observed at the thermal energy regime that leads to the breaking of a Si═O double bond and formation of two Si–O single bonds. A double hydrogen atom transfer process is observed in a $Si-(H_2O)_4$ cluster. The breaking of the second Si═O bond involves a double H transfer in a $Si-(H_2O)_5$ or a triple H atom transfer in a $Si-(H_2O)_6$ cluster. These characteristics reflect the collective nature of the motion of hydrogen in the system. Our study provides a clear picture of the breaking of two Si═O double bonds and the formation of four Si–OH single bonds, as well as a complete description of the dynamical pathway of the reactions between the solute and solvent molecules. Further studies are underway to investigate the water–$(SiO_2)_nH_m$ interaction as a function of n and m, as well as the nature of bond weakening and bond breaking of a single Si–O bond.

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