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# Water-silica interaction in clusters

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**Abstract.** The interaction of water with $SiO_2$ is an important problem in geophysics, materials physics, and environmental science. In this paper, we present recent results on studies of $H_2O$-silica clusters from first-principles Born-Oppenheimer molecular dynamics calculations. Bond strength and chemical stability are investigated as a function of cluster size and chemical composition. Both physisorption and chemisorption of water molecules on the clusters are discussed *via* analysis of energetics. Calculations of clusters are compared with the results from extended surfaces. The validity of clusters as models of surfaces is discussed.

**PACS.** 36.40.Jn Reactivity of clusters – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 31.15.Ew Density-functional theory

## 1 Introduction

The interaction of silicon dioxides and water molecules is a subject of interest in modern scientific research [1,2]. The presence of water changes surface properties, induces chemical reactions, and causes bond weakening and breaking. Many physical processes are influenced by interactions with even a small number of water molecules. More recently, because of the rapid development in nanoscale science and its potential application in technology, the interactions of nano-size materials with atmospherical molecules such as water and oxygen have attracted more and more attention. Miniaturization of devices cannot be practical if interactions with environment are not understood. Small systems exhibit properties that can be quite different from the bulk form, and they may interact with other atoms or molecules in distinctive ways. Clusters are often used as model systems for understanding the basic nature of chemical bonding and reaction processes. In the past decade, a variety of molecule/ion-water aggregates have been studied experimentally [3–7] and theoretically [8–10].

Water and silicon dioxides are matters of fundamental importance in human activities. The water-$SiO_2$ interaction is among the most important and difficult problems in materials [1,11] and environmental sciences [2,12]. The phenomenon of so-called hydrolytic weakening was first addressed scientifically in geoscience in the 1960s [13], which stimulated many research activities on the hydrolysis of $SiO_2$, particularly in the areas of mineral, semiconductor, and ceramic sciences. Both experimental [14–20] and computational efforts [21–27] have been made to study the interactions of water with crystalline quartz and amorphous silica. The experiments have generated a large volume of data.

Most of the previous investigations have been aimed at extended systems, and clusters of silica are only used by theorists to represent a piece of bulk matter, which of course is a one of the applications of clusters. While conventional band structure techniques have been employed by other researchers [26] to study water-crystal surface interactions, and new multi-scale simulation methods have been developed by the authors [28,29] to study hydrolysis on amorphous surfaces, clusters remain to be fully understood. There is a huge gap of understanding of systems between the bulk limit and the atomic scale. To understand hydrolytic weakening in nano-size systems, it is necessary to treat clusters as independent physical objects and investigate the size-evolution patterns of silica clusters and their interactions with water. A precise description of energetics and the chemical bonding is required for each cluster. To this end, quantum mechanical studies with large-scale computing are necessary to fully understand the exact nature of bonding, bond weakening, and bond-breaking processes. In this paper we present our recent theoretical results on water-$SiO_2$ cluster interactions. Comparisons of these systems with $SiO_2$ molecules in water clusters, with water-$SiO_2$ surface clusters, as well as with water-$SiO_2$ surfaces, are provided. The manuscript is organized in the following order: theoretical treatment and simulation details, simulation results, and finally discussion and conclusions.

## 2 Theoretical method and simulation details

Born-Oppenheimer local spin density molecular dynamics (BO-LSD-MD), as developed by Barnett and Landman in

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1993 [30], is used to search for the ground state geometry and calculate the energy. In this theoretical framework, the Hamiltonian of a dynamical system is written as

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

where upper case letters represent nuclear quantities, $\mathbf{r}$ is the position of electrons in real space. The total electronic energy $E_{elec}$ consists of the kinetic energy of electrons, electron-electron and electron-nuclear interactions. In the classical limit, Newtonian dynamics of the 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 thus

$$M_I \frac{\mathrm{d}^2\mathbf{R}_I}{\mathrm{d}t^2} = -\nabla_{\mathbf{R}_I} \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \nabla_{\mathbf{R}_I} E_{elec}. \quad (2)$$

In BO-LSD-MD, the term $E_{elec}$ is calculated *via* 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 nucleus are evaluated once the iteration for solving KS equation has converged.

The KS wave functions are expanded in a plane wave basis set in conjunction with the pseudo-potential method [31]. Since the plane waves are independent of the positions of the nuclei [30], the only non-zero 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 the upper cut-off 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 [30]. We do not to repeat the description here. It should be mentioned, however, that various optimization techniques, such as charge mixing during the self-consistent iteration, solving for the lowest $N$ eigenstates, prediction of the new density using the density of several previous time steps, etc., are applied and fully tested to speed up the calculation.

In this study, the pseudo-potential by Troullier and Martin [31], the GGA by Perdew, Burk, and Ernzerhof [32], and a cut-off energy of 62 Ry are used. With this combination of pseudo-potential, GGA functions, and energy cut-off, 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 [9].

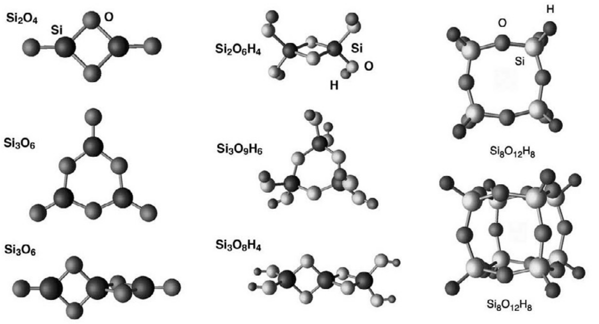

**Fig. 1.** Silica clusters, with and without hydrogen termination. The right-hand column shows two different views of the cluster $Si_8O_{12}H_8$, which is one of the so-called POSS molecules.

Three algorithms for structural optimization are used in our investigation: a modified steepest-descent combined with the conjugated gradient method, simulated annealing, and a mixture of the first two approaches. According to the physical conditions, constraints can be applied to the system in both the 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.

## 3 Simulation results

Small silica clusters can have a variety of chemical forms. A general expression can be written as $Si_nO_mH_l$, in which the $H_l$ are hydrogen atoms that terminate dangling bonds. Clusters without H atoms can also be found in vacuum. Using the BO-LSD-MD method, we study the size dependence of interactions between water and $(SiO_2)_nO_mH_{2m}$ clusters with $n$ = 1, 2, 3, and $m$ = 0, 2, 3, as well as $Si_8O_{12}H_8$. This last molecule belongs to a family of polyhedral oligomeric silsesquioxane (POSS) molecules, which are stable chemical entities. The first step of our study 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. $SiO_2$ is a linear molecule, with a Si–O bond length of $2.87a_0$. The water molecule has O–H bond length of $1.83a_0$, a H–O–H bond angle of 104.3°, and a dipole moment of 1.7 debye. These structural parameters and dipole moment are in excellent agreement with experimental data. A set of silica-based clusters is prepared in their ground state *via* simulation. Figure 1 shows various forms of silica clusters. Silica cluster often form ring-like or chain-like patterns. In case of clusters with H atoms, the number of O atoms is not always twice as many as Si atoms.

We study the cohesive energy, defined as

$$E_c = (E_{cluster} - E_{atom} - E_{\mathrm{OH}})/N, \quad (3)$$

**Table 1.** Cluster cohesive energy $E_c$ and hydration energy $E_{hyd}$ in eV. Groups A and B represent pure and H-terminated clusters, respectively. The two numbers in parentheses in the last column are energy for dissociated water states; strictly speaking, they are not hydration energy but reaction energy.

| | Cluster | $E_c$ (eV) | $E_{hyd}$ (eV) |
|---|---|---|---|
| A | $SiO_2$ | 6.07 | 1.04 |
| | $(SiO_2)_2$ | 6.67 | 0.90 |
| | $(SiO_2)_3$, ring | 6.92 | 0.95 |
| | $(SiO_2)_3$, chain | 7.02 | 0.90 |
| B | $Si_2O_6H_4$ | 5.40 | 0.51 (1.50) |
| | $Si_3O_9H_6$ | 5.59 | 0.25 (0.08) |
| | $Si_3O_8H_4$ | 6.00 | 0.26 |
| | $Si_8O_{12}H_8$ | 5.91 | 0.02 |

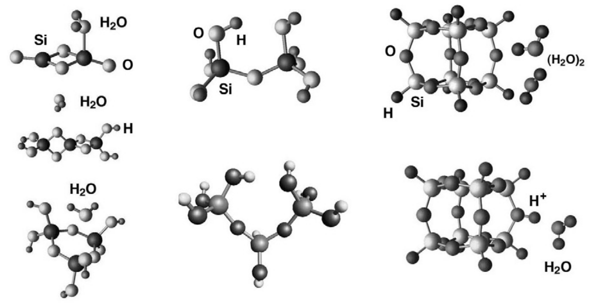

**Fig. 2.** Representative water-silica complexes: the left column is a group in which the $H_2O$ molecule does not dissociate; the bond between $H_2O$ and $Si_2O_4$ (upper left corner) represents a relatively strong interaction, $E_{hyd} \sim 1$ eV. The middle column contains two clusters in which the water does dissociate. The right column depicts an $H_2O$ dimer and $H_3O^+$ interacting with a POSS molecule.

in which $E_{cluster}$ is the calculated energy of a cluster, $E_{atom}$ is the energy of isolated atoms, $E_{OH}$ is the energy of O–H group in its relaxed state, and $N$ is the total number of Si and O atoms. This $E_c$ describes the Si–O bond strength in the clusters. The hydration energy is the binding energy between a cluster and an additional water molecule. Table 1 lists the $E_c$ and first hydration energy of the clusters. Figure 2 illustrates examples of cluster-water complex.

In addition to the data listed in Table 1, water dimer $(H_2O)_2$– and hydronium ion $(H_3O)^+$–$Si_8O_{12}H_8$ binding energies are also calculated. The results indicate a zero binding energy between the dimer (within our accuracy) and the POSS molecule, and 1.7 eV of energy between the ion and the molecule. In former case, the two water molecule form a dimer with a binding energy between two waters similar to the isolated state (∼ 5 kcal/mol). In later case, the $H_3O^+$ transfers a proton to the molecule.

The cohesive energies in Table 1 indicate an increasing $E_c$ as the size increases, a common behavior shared by many clusters. This trend can be seen most clearly in the clusters with no hydrogen termination. It is also evident from the second half of Table 1 that H termination weakens the Si–O bond strength in the clusters. It should be noted that clusters in the middle column of Figure 1 are the clusters from the left column in Figure 1 plus two or three dissociated water molecules, related by the reaction processes

$$Si_2O_6H_4 \leftrightarrow (SiO_2)_2 + 2(H_2O), \qquad (4)$$
$$Si_3O_9H_6 \leftrightarrow (SiO_2)_3 \text{ (ring)} + 3(H_2O), \qquad (5)$$
$$Si_3O_8H_4 \leftrightarrow (SiO_2)_3 \text{ (chain)} + 2(H_2O). \qquad (6)$$

The energy gain in dissociating the water molecules in the three processes is 5.69, 9.19, and 5.78 eV, respectively, corresponding to the nearly constant 2.85, 3.06 and 2.89 eV per water molecule. The cluster $Si_3O_8H_4$ has higher $E_c$ than the other clusters with H termination because of the relatively larger number of Si and O atoms compared to the number of H atoms, a ratio of 11:4. In terms of $SiO_2$ to water molecules, this ratio is 3:2, while the other two systems have ratios of 1:1. For the POSS molecule the ratio Si+O:H is 10:4. The cohesive energies indicate a very strong hydrolytic weakening effect at small cluster size. Nevertheless, even with this weakening, the cohesive energy does increase as the size of the system increases.

The hydration energy of the clusters is an important and interesting quantity. Here, we refer hydration energy to states in which a water molecule is not dissociated. For pure $SiO_2$ clusters, this energy is around 1 eV (0.89–1.04). The nature of the interaction is primarily electrostatic. The permanent dipole of water induces a dipole in $SiO_2$ cluster to form dipole-dipole interaction. In the $SiO_2$–$H_2O$ complex, the $SiO_2$ is no longer linear [27]. For hydrogen terminated clusters, the interaction is much weaker than the pure silica clusters, $\leq 0.5$ eV. The POSS molecule has practically zero binding energy to water, which reflects the hydrophobic nature of the species. The water dissociation energies are also computed for $Si_2O_6H_4$ and $Si_3O_9H_6$. For the two-member ring, $Si_2O_6H_4$, this energy is higher than the hydration energy. The dissociation is a preferred state. However, for the three-member ring, $Si_3O_9H_6$, the situation reverses. This peculiar behavior of silica has also been observed on surfaces: the surface can have both hydrophilic and hydrophobic sites, and the surface properties can also vary upon heat treatment. Finally, the interaction of hydronium ion $H_3O^+$–POSS is strong as expected. Our calculation indicates that the POSS molecule has higher proton affinity than does the water molecule. The proton transfer occurs spontaneously as the ion approaches the molecule. The energy gain 1.7 eV includes protonation energy and hydration energy (the $H_3O^+$ loses a $H^+$ and become a $H_2O$ attached to the POSS molecule).

## 4 Are clusters good models for surfaces?

The clusters under investigation demonstrate properties that are also observed in surface studies. Like bulk matter, silica clusters have various stable forms, which originate from the nature of the mixed ionic-covalent interaction. Bond weakening and bond-breaking are observed both in clusters and on surfaces. Like the surface, some clusters are hydrophobic and some hydrophilic. The bond breaking and water dissociation seen in the two-member rings $Si_2O_6H_4$ and $Si_3O_8H_4$ are also observed in our surface calculations [29]. However, one should not be misled that in general, the clusters are good models for silica surfaces. The hydrated two-member ring in the middle of the left-hand column of Figure 2 is significantly different from the state of a two-member ring on the surface under water attack. This remains true even when the extracted cluster contains a substantial portion of surface [29]. The different response of clusters and surfaces to water attack comes from the long range interaction and surface geometric confinement. Therefore, when using clusters as model for surfaces, serious precaution has to be taken into consideration.

## 5 Conclusions

Our studies demonstrate trends of cohesive energies in the $SiO_2$ clusters, the energetics of hydrogen terminated silica clusters as a result of water dissociation, and water molecule-cluster interactions. The high accuracy and efficiency Born-Oppenheimer molecular dynamics method in the framework of DFT-GGA allows an accurate description of the energetics of a system in its ground state and isomer states, as well as in any configuration during a dynamical process. The results demonstrate a monotonic increase of the cohesive energy as a function of cluster size for pure cluster. Competing mechanism such as the substantial weakening of bond strength due to the presence of H atoms, introduces a second parameter, the ratio between $SiO_2$ and $H_2O$, as the second dimension in the energy trend. The energy gain in water dissociation and formation of H terminated clusters ranges 2.85–3.06 eV, 0.8–0.9 eV higher than the water dissociation energy during formation of $Si(OH)_4$ in a water cluster, which is a reaction between a single $SiO_2$ and two $H_2O$ molecules. Our calculations also reveal a complex behavior of silica clusters under the influence of water molecules. Different silica clusters respond to water differently, ranging from strongly hydrophilic to completely hydrophobic. We also observe significant differences between the interactions of water and hydronium ions with POSS molecules. These results have advanced one small step forward in understanding the interaction between water and silicon dioxide.

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