A full-potential linear-muffin-tin-orbital study of water adsorption on and saturation in small Si clusters

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Abstract. The structure and geometrical parameters for water adsorption on a small-silicon-cluster surface have been studied using the linear-muffin-tin-orbital method. We find that the most favoured adsorption site is the atop site of the capped atom for Si_5, Si_6, and Si_7 clusters. When H_2O adsorbs at such sites, the silicon clusters are elongated in the direction of the axis connecting one capped atom to another capped atom. Also, saturation studies have been performed. Each of these clusters can only adsorb two H_2O molecules at two atop sites of capped atoms. These clusters cannot adsorb any more H_2O molecules.

1. Introduction

The reactivity of silicon clusters containing from two to seventy atoms is very different from that of solid silicon [1]. Many experimental studies of the chemical reactions of silicon clusters with water have been performed. Using Fourier transform mass spectrometry (FTMS), Creasy *et al* [2] have carried out studies of the reactions of water with small-silicon-cluster cations (Si_{1-6}^+). Their results show that reactions with H_2O are not observed for Si_{4-6}^+, implying that the reactions proceed at rates which are less than 10^{-11} to 10^{-12} cm^3 s^{-1}, i.e. it is difficult to get water to react with Si_{4-6}^+ clusters. Ray and Jarrold [3] have studied the reaction between silicon-cluster cations (Si_{10-65}) and water using the injected-ion drift tube technique. Their results show that the only products observed for the reactions between the silicon-cluster cations and water were a series of $Si_n(D_2O)_m^+$ adducts. All of these experimental results corroborate the assertion that silicon clusters are relatively unreactive with water.

Very few theoretical studies have been performed on the reactivity of silicon clusters. Using the semiempirical molecular orbital (MO) method SINDO1 and the *ab initio* program Gaussian 90, Krack and Jug [4] have studied ammonia adsorption with neutral Si_5 and Si_{10} clusters. We have studied the nature of NH_3-molecule adsorption and dissociation on neutral-Si-cluster surfaces by the DV-X_α method [5, 6] and the full-potential linear-muffin-tin-orbital (FP-LMTO) molecular dynamics method [7]. However, as far as we are aware, there have been no theoretical studies of water adsorption on silicon-cluster surfaces. There has been a gulf between experiment and theory. To achieve a deeper understanding of the properties of silicon clusters, such a theoretical study has some scientific importance.

In the present study, the most favoured adsorption site, the geometrical parameters, and the energy of adsorption of water on a neutral-Si_{5-7}-cluster surface are calculated by the FP-LMTO molecular dynamics method. Although many experimental results have been

obtained for water adsorbed by cation clusters, it is appropriate to discuss the results for neutral clusters; this is, in many cases, more scientifically interesting as regards different behaviours of clusters and extended surfaces. We also performed saturation studies. It is important to carry out such studies, because saturation studies can provide valuable information on the number and nature of the reactive sites, and the structure of the products [1].
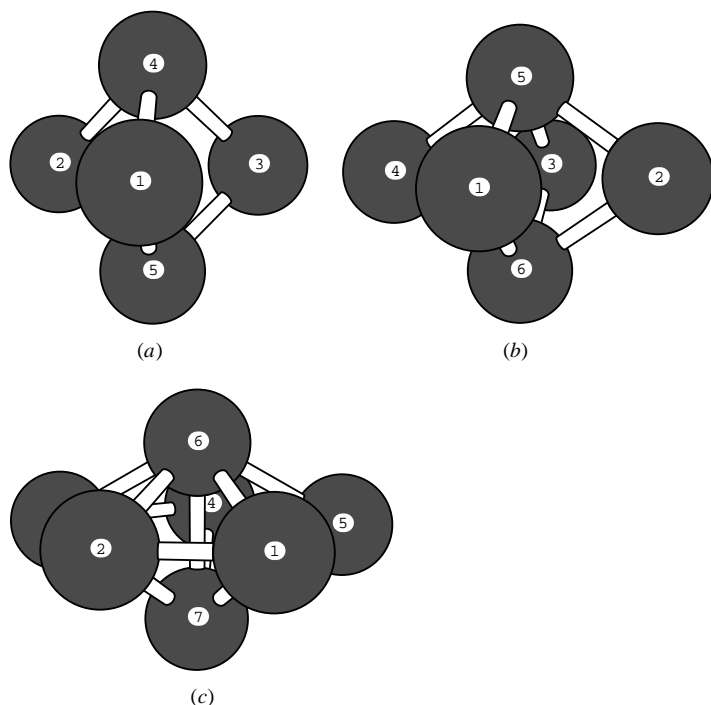

Figure 1. The geometries of the lowest-energy structures of small silicon clusters. (*a*) Si_5. (*b*) Si_6. (*c*) Si_7. Side atoms: atoms 1–3 for Si_5; atoms 1–4 for Si_6; atoms 1–5 for Si_7. Capped atoms: atoms 4 and 5 for Si_5; atoms 5 and 6 for Si_6; atoms 6 and 7 for Si_7.

2. Models and the method

The most stable structures of Si_{5-7} clusters are the trigonal bipyramid (D_{3h}), the tetragonal bipyramid (D_{4h}), and the pentagonal bipyramid (D_{5h}), according to our accurate FP-LMTO molecular dynamics simulations (see figure 1). This is in good agreement with other theoretical results in [8–13]. According to the number of nearest-neighbour atoms, we can define two kinds of atom in Si_{5-7} (figure 1): capped atoms and side atoms [6]. On the basis of this definition, we try possible adsorption sites: the atop site on the capped atom, the atop site on the side atom, the short-bridge site (between a capped atom and a side atom), the long-bridge site (between a side atom and a side atom), and the surface site (in the space between a side atom, a side atom, and a capped atom). In our calculations, a water molecule will be placed at one such site, and then we start to calculate the adsorption energy and optimized structure by means of molecular dynamics simulations.

    The calculated O–H bond length (0.98 Å) and H–O–H bond angle (103.5°) of free H_2O are adopted to compare with those of H_2O after adsorption (these data are in good
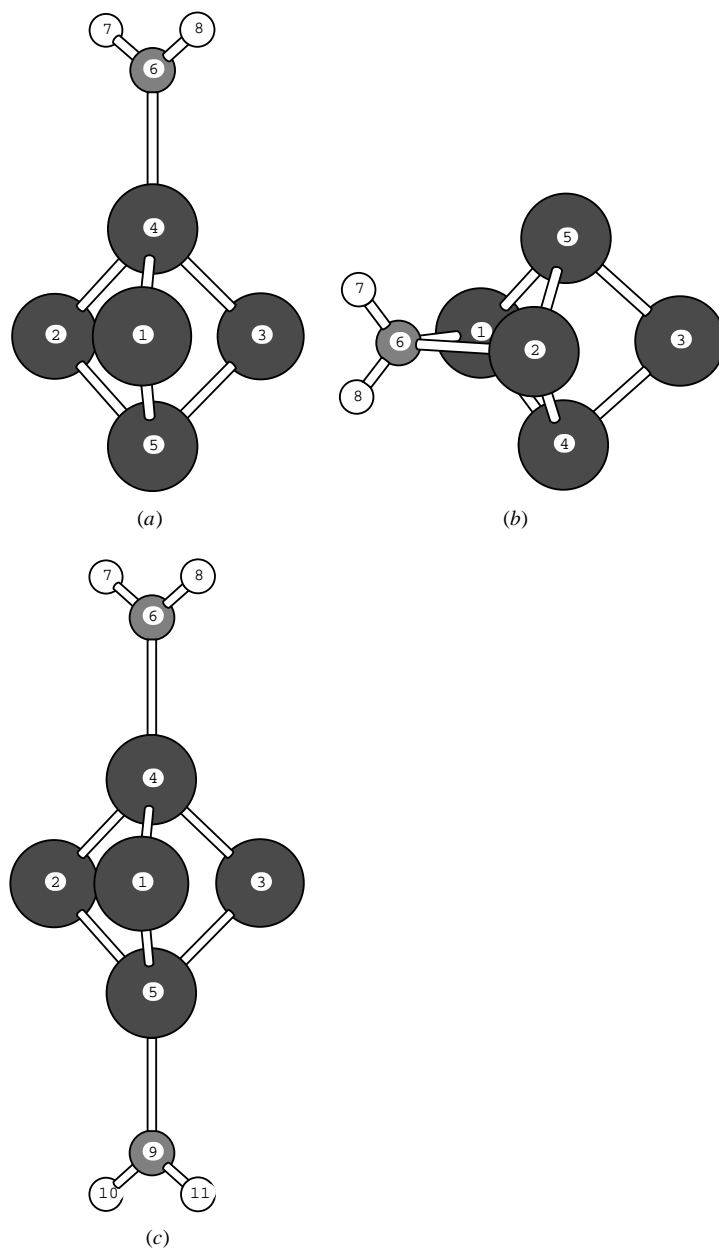
Figure 2. The adsorption and saturation sites for water on the Si$_5$ surface. (*a*) Adsorption at the atop site of capped atom 4. (*b*) Adsorption at the long-bridge site. (*c*) Saturation adsorption.

agreement with the experimental values: 0.96 Å and 104.5° [14]).

The FP-LMTO method [15–18] is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [19]. This method expands the electron wave functions in terms of muffin-tin orbitals [20]. Also this method uses a completely general form for the potential and density in which space is divided into non-overlapping muffin-tin spheres and the remaining interstitial region (in which the potential is expressed as a

linear combination of Hankel functions), instead of the atomic sphere approximation (ASA). The details of how the molecular dynamics simulation can be performed are described in references [17, 18].

3. Results and discussion

3.1. Adsorption

As a first step, we consider single-molecule adsorption. We will try all of the possible sites, and decide which is the most favoured adsorption site, and also calculate various parameters.

When a water molecule is adsorbed at the atop site of the capped atom of a Si_5 cluster (figure 2(a)), we find some changes in the structures of Si_5 and H_2O. All of these optimized adsorption geometries are shown in table 1. Because of the electron transfer from H_2O to Si_5, the H–O–H bond angle changes to 108.3° upon adsorption, which is 4.8° more than the value for the free H_2O molecule. The Si_5 cluster shows the same tendency as $Si_5 + NH_3$ [7], which is elongated in the direction of the axis connecting capped atoms 4 and 5. However, compared with $Si_5 + NH_3$, Si_5 encounters more difficulty in adsorbing H_2O. The adsorption energy is only 0.30 eV (0.86 eV for NH_3 adsorption). The structure of Si_5 also changes less than that of $Si_5 + NH_3$. The bond length between capped atom 4 and capped atom 5 (d_{4-5}) changes from 2.96 Å to 3.08 Å (3.14 Å for $Si_5 + NH_3$). The bond length between side atom 2 and side atom 3 (d_{2-3}) become shortened, from 3.04 Å to 2.94 Å (2.91 Å for $Si_5 + NH_3$). At the same time, the side atoms move toward the H_2O and away from the opposite capped atom (d_{1-4} changes from 2.29 Å to 2.28 Å, and d_{1-5} changes to 2.31 Å).

We now consider an H_2O molecule at the atop site of a side atom; there is no evidence that Si_5 can adsorb this molecule tightly (the adsorption energy is <0.05 eV). For the short-bridge site and the surface site, the findings are the same. However, Si_5 can adsorb an H_2O molecule on the long-bridge site with adsorption energy 0.20 eV (figure 2(b)).

We can conclude that the atop site of a capped atom is the most favourable for H_2O. According to our previous study [21], side atoms bind to each other via a many-centre bond, and this reduces their numbers of dangling bonds. At the same time, the capped atom binds to three side atoms, and has one dangling bond at its atop site. Thus the H_2O molecule is apt to adsorb at the atop site of the capped atom. On the other hand, a bond between a capped atom and a side atom is stronger than a bond between a side atom and a side atom (a many-centre bond), so H_2O can adsorb at a long-bridge site, but not at a short-bridge site.

Table 1. Water adsorption and saturation geometrical parameters (Å), and adsorption energies (eV), for a Si_6-cluster surface.

	d_{1-2}	d_{1-5}	d_{1-6}	d_{5-6}	O–Si	O–H	θ_{H-O-H}	E_B (eV)
Free Si_6 and H_2O	2.72	2.35	2.35	2.69	—	0.98	103.5°	—
$Si_6 + H_2O$ (capped)	2.70	2.33	2.37	2.74	2.33	0.98	107.4°	0.26
$Si_6 + 2H_2O$	2.67	2.34	2.34	2.79	2.48	0.98	106.1°	0.35

Now we turn to water adsorption for a Si_6 cluster (figure 3 and table 1). Our findings are almost the same for $Si_6 + H_2O$ as for $Si_5 + H_2O$:

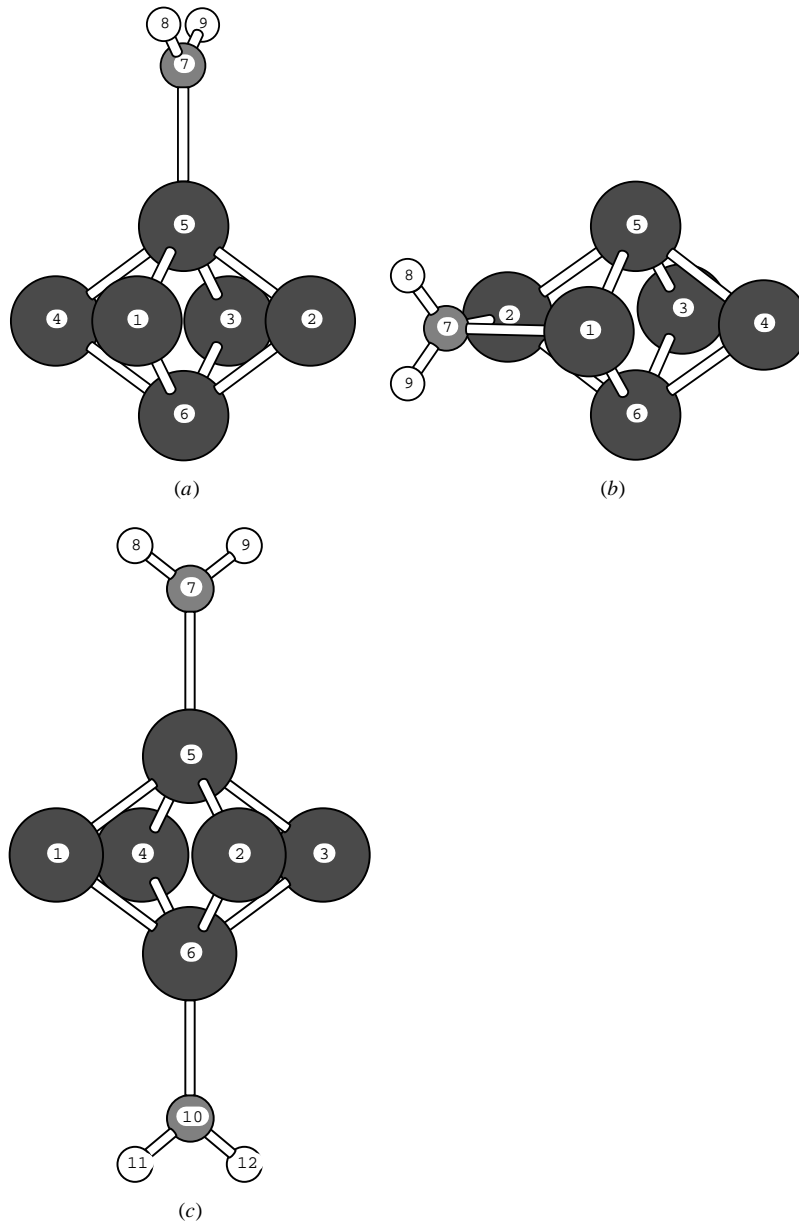(1) the most favoured adsorption site for H_2O is the atop site of the capped atom

Figure 3. The adsorption and saturation sites for water on the Si_6 surface. (*a*) Adsorption at the atop site of capped atom 5. (*b*) Adsorption at the long-bridge site. (*c*) Saturation adsorption.

(adsorption energy: 0.26 eV; see figure 3(*a*));

(2) the H–O–H bond angle is bigger than the bond angle of free H_2O because of the electron transmission;

(3) the Si_6 cluster is elongated (all of the changes are the same as those for $Si_6 + H_2O$, although the changes are smaller);

(4) the long-bridge site can adsorb an H_2O molecule (adsorption energy: 0.19 eV; see figure 3(*b*));

(5) the short-bridge site, surface site, and atop site of a side atom cannot adsorb H_2O.

These results are easy to understand, because Si_6, just like Si_5, has many-centre bonds: four side atoms share a four-centre bond [7].

For Si_7 (figure 4 and table 2), we find that the most favoured site is the atop site of the capped atom (adsorption energy: 0.18 eV; see figure 4(*a*)). For such a site, the changes of structure for H_2O and Si_7 are same as those for $Si_5 + H_2O$ and $Si_6 + H_2O$. However, H_2O cannot adsorb on the top of the side atom or at any other sites, even long-bridge sites. Because Si_7 is considered as five tetrahedra sharing a common edge formed by the two capped atoms [8], a side atom binds with all of its neighbouring atoms tightly [7]. This is the main reason that H_2O cannot adsorb at a long-bridge site.
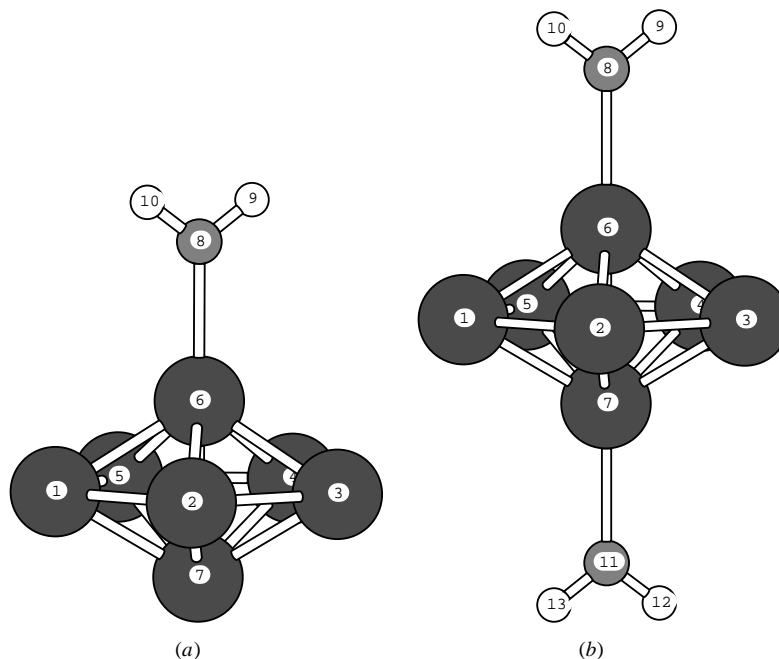

Figure 4. The adsorption and saturation site for water on the Si_7 surface. (*a*) Adsorption at the atop site of capped atom 6. (*b*) Saturation adsorption.

Table 2. Water adsorption and saturation geometrical parameters (Å), and adsorption energies (eV), for a Si_7-cluster surface.

	d_{1-2}	d_{1-6}	d_{1-7}	d_{6-7}	O–Si	O–H	θ_{H-O-H}	E_B (eV)
Free Si_7 and H_2O	2.47	2.45	2.45	2.49	—	0.98	103.5°	—
$Si_7 + H_2O$ (capped)	2.46	2.41	2.48	2.54	2.40	0.98	106.8°	0.19
$Si_7 + 2H_2O$	2.45	2.44	2.44	2.56	2.55	0.98	105.5°	0.23

As mentioned above, all Si_{5-7} clusters can adsorb H_2O molecules with very low adsorption energy ($\leqslant 0.30$ eV). We think that Si_{5-7}-cation clusters encounter more difficulty in getting electrons from H_2O molecules; hence the adsorption energy will be smaller than that of neutral clusters, i.e. cation clusters will find it more difficult to adsorb H_2O. From

experimental results [2], we know that reactions with H_2O are not observed for Si_{5-7}-cation clusters, implying that they react with rates which are less than 10^{-10} to 10^{-11} cm^3 s^{-1}. This supports our view that Si_{5-7}-cation clusters find it difficult to adsorb H_2O.

3.2. Saturation

In the preceding section, we investigated the single-molecule adsorption of H_2O. Now we turn to the saturation study, i.e. to deciding on the maximum number of H_2O molecules which Si_{5-7} clusters can adsorb.

Table 3. Water adsorption and saturation geometrical parameters (Å), and adsorption energies (eV), for a Si_5-cluster surface.

	d_{1-2}	d_{1-4}	d_{1-5}	d_{4-5}	O–Si	O–H	θ_{H-O-H}	E_B (eV)
Free Si_5 and H_2O	3.04	2.29	2.29	2.96	—	0.98	103.5°	—
$Si_5 + H_2O$ (capped)	2.94	2.28	2.31	3.08	2.26	0.98	108.3°	0.30
$Si_5 + 2H_2O$	2.91	2.28	2.28	3.10	2.41	0.98	106.6°	0.45

After Si_5 has adsorbed an H_2O molecule at the atop site of the capped atom (atom 4), we put another H_2O molecule at the opposite site: the atop site on the capped atom 5 (figure 2(c)). The total adsorption energy is 0.45 eV—an increase of 0.15 eV on the single-H_2O-molecule adsorption energy (table 3). The strength of the bond between Si and O decreases. So the H–O–H bond angle (106.6°) becomes smaller than the single-molecule-adsorption bond angle (108.3°), and the length of the bond between Si and O is 2.41 Å, which is greater than the value of 2.26 Å for $Si_5 + H_2O$. The Si_5 cluster is more elongated: d_{4-5} is now 3.10 Å. The length of the bond between side atom 1 and side atom 2 (d_{1-2}) becomes shorter, decreasing from 2.94 Å to 2.91 Å.

However, from our further investigation, we found that we cannot put any more H_2O molecules at any possible adsorption sites of Si_5. So the maximum number of adsorbed H_2O molecules for a Si_5 cluster is two.

For $Si_6 + 2H_2O$, similar results have been obtained (figure 3(c)). We do not repeat them here. However, the increase of the adsorption energy is small: 0.09 eV (table 1). Si_6 cannot adsorb any more NH_3 molecules. It is difficult to say whether Si_7 can adsorb a second H_2O molecule (figure 4(b)), because the increase of the adsorption energy is only 0.04 eV. However, we provide all of the parameters in table 2.

4. Summary

We have studied H_2O adsorption and saturation for Si_{5-7} clusters. Our calculations show that the atop site of the capped atom is the most favoured site for Si_5, Si_6, and Si_7 clusters. When H_2O is adsorbed at such a site, the silicon clusters are elongated in the direction of the axis connecting a capped atom to a capped atom. Si_5 and Si_6 clusters can adsorb H_2O at long-bridge sites, although the adsorption energies are smaller. They cannot adsorb H_2O at other sites. But the Si_7 cluster cannot even adsorb H_2O at a long-bridge site. These results can be understood on the basis of the facts that Si_5 and Si_6 clusters form many-centre bonds, while Si_7 has a different bonding character.

For saturation adsorption, all of these clusters can only adsorb two H_2O molecules at two atop sites of capped atoms (for Si_7, it is difficult to say whether it can adsorb the second

H_2O molecule, because the adsorption energy increase is only 0.04 eV). None of them can adsorb any more H_2O molecules.

Acknowledgments

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