

Water adsorption on Si₈₋₁₀ clusters: a full-potential linear-muffin-tin-orbital molecular-dynamics study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 1

(<http://iopscience.iop.org/0953-8984/13/1/301>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 08:16

Please note that [terms and conditions apply](#).

Water adsorption on Si_{8–10} clusters: a full-potential linear-muffin-tin-orbital molecular-dynamics study

Bao-xing Li^{1,2} and Pei-Lin Cao¹

¹ Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou, Zhejiang, 310027, People's Republic of China

² Department of Physics, Hangzhou Teachers' College, Hangzhou, Zhejiang, 310012, People's Republic of China

Received 24 May 2000, in final form 7 November 2000

Abstract

Water molecule (H₂O) adsorption on Si_{8–10} clusters has been studied using the full-potential linear-muffin-tin-orbital method. The calculations show that water molecules can be adsorbed on some sites of the cluster surfaces. Their adsorption energies are situated in the ranges 0.01–0.49 eV for Si₈, 0.14–0.24 eV for Si₉, and 0.15–0.42 eV for Si₁₀. The results suggest that the clusters are relatively unreactive with water. After an H₂O molecule adsorbs on a site, the structures of the silicon cluster and the water molecule change slightly.

1. Introduction

Studies of the structures and the chemical reactions of silicon clusters are of scientific importance. Using the full-potential linear-muffin-tin-orbital method, we have investigated the structures of Si_{*n*} and Ge_{*n*} (*n* = 2–10, 20, and 60) [1–6]. Some ground-state structures have been discovered. As regards the chemical reactivity, it has been found that it is very different from that of bulk silicon [7]. Many experimental studies of the chemical reactions of the silicon clusters with acetylene [8], ethylene [9–14], ammonia [8, 15–20], oxygen [8, 14, 21], carbon monoxide [7, 22], and water [8, 23] have been performed. Studies of the chemistry have revealed that silicon clusters containing up to 70 atoms appear to be much less reactive than bulk silicon surfaces.

Creasy *et al* [8] have carried out studies of the reactions of water with small-silicon-cluster cations (Si_{1–6}⁺) using Fourier transform mass spectrometry (FTMS). Their results show that reactions with H₂O are not observed for Si_{4–6}⁺, implying that the reactions proceed at rates which are less than 10^{–11} to 10^{–12} cm³ s^{–1}, i.e. it is difficult to get water to react with Si_{4–6} clusters. Ray and Jarrold [23] have investigated the reaction between silicon cluster cations Si_{10–65} and water using the injected-in drift tube technique. Their results suggest that the only products observed for the reactions between the silicon cluster cations and water are a series of Si_{*n*}(D₂O)_{*m*}⁺ adducts. These experimental results indicate that the silicon clusters are relatively unreactive with water.

Up to now, few theoretical studies have been performed on the reactivity of the silicon clusters. Krack and Jug [24] have investigated ammonia adsorption with neutral Si₅(D_{3h})

and $\text{Si}_{10}(\text{T}_d)$ clusters using the semiempirical MO method SINDO1 and the *ab initio* program Gaussian 90. We have studied the nature of NH_3 -molecule adsorption and dissociation on neutral silicon cluster surfaces by the DV- X_α method [25, 26] and the full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method [27]. We have also studied the adsorption of H_2O and C_2H_4 on neutral Si_{5-7} cluster surfaces [28, 29] using the FP-LMTO-MD method. Recently, we have investigated carbon monoxide adsorption on Si_n ($n = 2-7$) cluster surfaces [30]. It is found that there is one active site for each small silicon cluster. Their adsorption energies decrease rapidly as the atomic number of the silicon clusters increases.

In the present work, we will study the adsorption of H_2O on neutral Si_{8-10} cluster surfaces by the FP-LMTO-MD method. It is a continuation of our previous paper [28].

2. Method

The FP-LMTO method [32–35] is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [41]. This method expands the electron wave functions in terms of muffin-tin orbitals [42]. Also this method uses a completely general form for the potential and density in which space is divided into nonoverlapping 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 method can be performed are described in references [34, 35].

3. Results and discussions

In this section, we will present the results for the adsorption of H_2O on Si_{8-10} cluster surfaces. On the basis of our FP-LMTO-MD study, the ground-state structures of Si_{8-10} clusters are: bicapped octahedrons (C_{2h} and C_{2v} for Si_8), bicapped pentagonal bipyramid (C_{2v} for Si_9), tetracapped trigonal prism (C_{3v} for Si_{10}) [2, 3, 43, 44], as shown in figure 1. 8(a) (C_{2h}) is a distorted bicapped octahedron, which has been reported previously by some authors [36–40]. Its binding energy is 36.34 eV. Using FP-LMTO-MD, we have obtained another structure, 8(b) (C_{2v}), as stable as 8(a), by capping the adjacent faces in the vertical direction. Its binding energy is also 36.34 eV.

For H_2O molecules, the calculated O–H bond length (0.97 Å) and H–O–H bond angle (104.39°), which are adopted to compare with those of H_2O after adsorption, are in good agreement with the experimental values: 0.96 Å and 104.50° [31].

In our calculations, we try all of the possible adsorption sites: the atop site on each surface atom, the bridge site between two neighbouring atoms, and the hollow site consisting of three adjacent atoms. After a water molecule is placed at one such site, we start to calculate the adsorption energy and optimized structure by means of molecular-dynamics simulations. After many iterations, the maximum of the forces is less than 0.001 au, and the total energy stays nicely constant because the system stays close to self-consistency (so the forces agree with the energy). The process is stopped when the self-consistency condition is met. The optimized adsorption structures are shown in figure 2 to figure 5. Their adsorption energies are listed in table 1.

3.1. $\text{Si}_8 + \text{H}_2\text{O}$

When a water molecule is adsorbed on the surface of 8(a), its adsorption energy is situated between 0.01 and 0.22 eV. We find that the adsorption results in little change in the structures of the 8(a) and H_2O molecules. After the H_2O is adsorbed on the surface of 8(a), the maximum

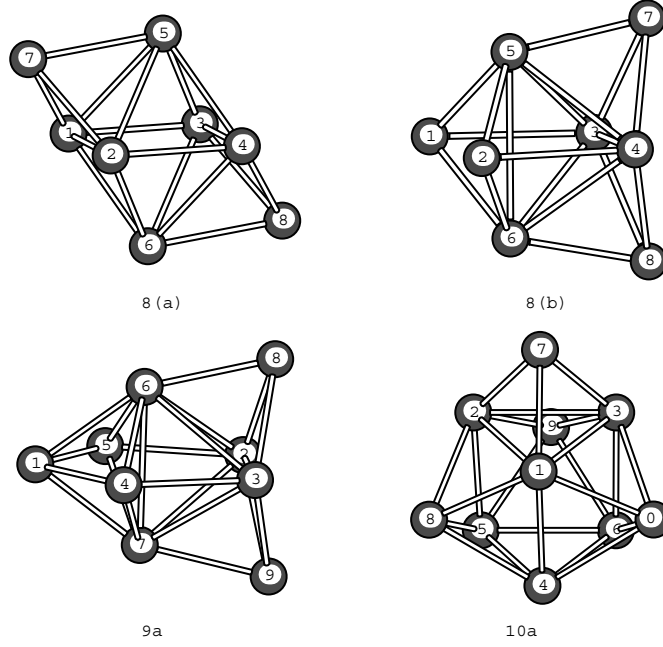


Figure 1. Geometries of the lowest-energy structures of Si₈₋₁₀ clusters. Si₈(a); Si₈(b); Si₉; Si₁₀.

Table 1. Calculated adsorption energies E_a (eV) of water molecules adsorbed on the surfaces of Si₈₋₁₀ clusters.

Si ₈ (a)	8A(a)	8B(a)	8C(a)	8D(a)	8E(a)	—	—	—
E_a	0.22	0.14	0.01	0.14	0.03	—	—	—
Si ₈ (b)	8A(b)	8B(b)	8C(b)	8D(b)	8E(b)	8F(b)	8G(b)	8H(b)
E_a	0.49	0.33	0.20	0.18	0.29	0.16	0.44	0.35
Si ₉	9A	9B	9C	9D	9E	9F	9G	—
E_a	0.24	0.14	0.18	0.14	0.17	0.20	0.17	—
Si ₁₀	10A	10B	10C	10D	10E	10F	10G	—
E_a	0.42	0.27	0.25	0.18	0.15	0.19	0.19	—

of the bond change for the silicon cluster is 0.03 Å, and the maximum changes of the O–H bond and bond angle $\Theta_{\text{H-O-H}}$ are 0.01 Å and 3.15° respectively. Some parameters are listed in table 2.

The most favoured adsorption site for 8(a) is the hollow site of the surface consisting of atoms 3, 4, 5 (or 1, 2, 6), shown as 8A(a). The energy of adsorption on the site is 0.22 eV. The water adsorption does not make the geometry of 8(a) change significantly. But the bond angle $\Theta_{\text{H-O-H}}$ changes from 104.39° to 101.24°, and the bond O–H increases by 0.01 Å compared with 0.97 Å for the free H₂O. It is worth noting that there are three weak O–Si bonds (one bond of 3.14 Å and two identical bonds of 3.34 Å), which make its adsorption energy larger than those for the other sites. In addition, compared with water molecule adsorption on Si₅₋₇ cluster surfaces [28], it is found that two H atoms have moved towards the silicon cluster, and $\Theta_{\text{H-O-H}}$ decreases. This suggests that there is interaction between atoms H and Si. The interaction is favourable for the water adsorption. 8B(a) is obtained by placing an H₂O molecule on the

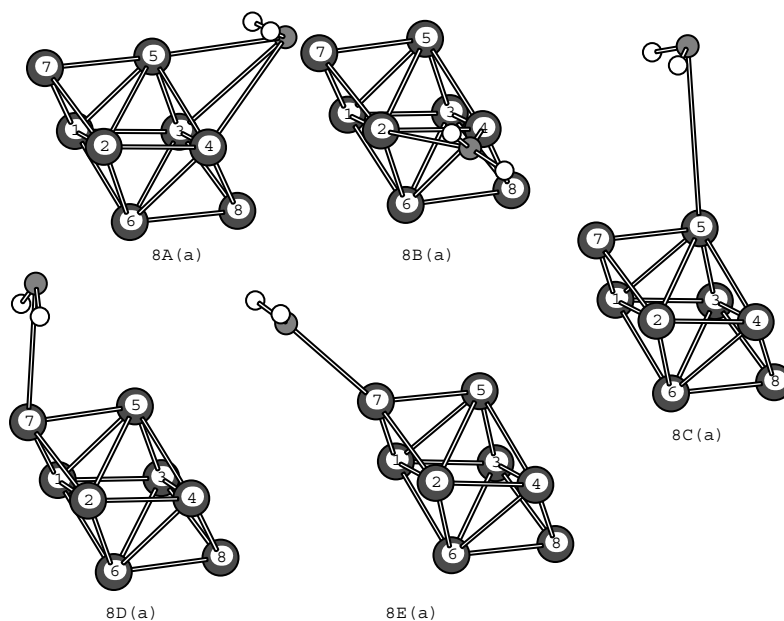


Figure 2. The stable structures of water molecules adsorbed on the five different sites of the $\text{Si}_8(\text{a})$ cluster.

Table 2. Some geometrical parameters (\AA) changed obviously after water molecule adsorption on $\text{Si}_8(\text{a})$ cluster surface. Δ refers to the maximum difference between two corresponding bond lengths of free $\text{Si}_8(\text{a})$ and $\text{Si}_8(\text{a}) + \text{H}_2\text{O}$.

Bond	Free $\text{Si}_8(\text{a})$, H_2O	8A(a)	8B(a)	8C(a)	8D(a)	8E(a)	Δ
d_{15}	2.65	2.64	2.65	2.65	2.66	2.63	0.02
d_{24}	2.45	2.46	2.42	2.44	2.44	2.44	0.03
d_{25}	2.65	2.64	2.64	2.65	2.66	2.63	0.02
$d_{\text{O-Si}}$	—	3.14	3.07	4.28	3.19	2.96	—
$d_{\text{O-Si}}$	—	3.34	—	—	—	—	—
d_{OH}	0.97	0.98	0.98	0.98	0.98	0.98	0.01
$\Theta_{\text{H-O-H}}$	104.39	101.24	104.89	103.65	101.37	104.49	3.15

bridge site of the edge-connecting atoms 2 and 4 (or 1 and 3). It is found that the two H atoms and the silicon cluster are on either side of the O atom and $\Theta_{\text{H-O-H}}$ increases. Increase of $\Theta_{\text{H-O-H}}$ is also caused by the interaction between H and Si atoms. Obviously, when the two H atoms and the Si atoms are on the same side of the O atoms, $\Theta_{\text{H-O-H}}$ decreases. Otherwise, it increases. The adsorption energy of 8C(a) is only 0.01 eV, which is the smallest among the five $\text{H}_2\text{O} + 8(\text{a})$ structures. Its O–Si bond (4.24 \AA) is rather weak. Therefore, the water molecule cannot be adsorbed on the site tightly. 8D(a) and 8E(a) are both obtained by putting an H_2O on the atop site of capping atom 7 (or 8), but their adsorption energies differ significantly. The interaction between H and Si atoms plays an important role for 8D(a), but not for 8E(a).

We now consider an H_2O molecule on the surface of 8(b), when the H_2O molecule is placed on the atop site of the edge atoms 1 (or 2). Its adsorption energy is 0.49 eV, which is the most among the eight $\text{H}_2\text{O} + 8(\text{b})$ structures. The large adsorption energy is at the origin of the strong O–Si bond (2.45 \AA). Its $\Theta_{\text{H-O-H}}$ is 104.10°, which is slightly smaller than that of

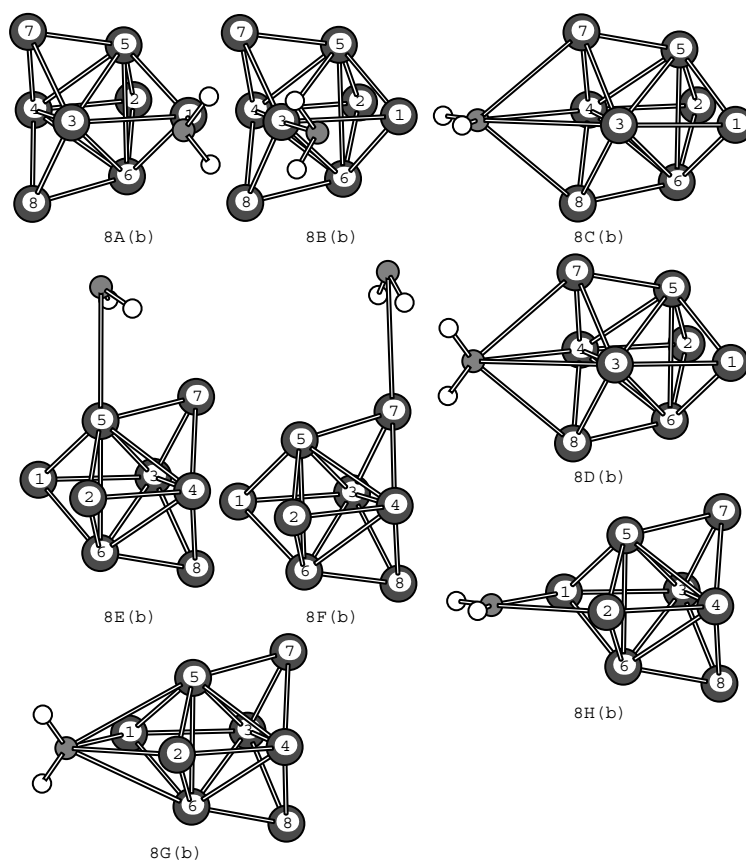


Figure 3. The stable structures of water molecules adsorbed on the eight different sites of the Si₈(b) cluster.

the free H₂O. This suggests that the interaction between H and Si atoms is not strong in 8A(b). 8B(b) can be obtained by placing an H₂O on the atop site of atom 3 (or 4). 8C(b) and 8D(b) are similar. Their adsorption energies are 0.20 eV and 0.18 eV respectively. Four weak O–Si bonds make the H₂O molecule bound on the site. 8E(b) and 8F(b) are obtained by placing an H₂O on the atop sites of the apex atom 5 and the capping atom 7 respectively. The O–Si bond (3.06 Å) in 8E(b) is stronger than that of 8F(b) (3.19 Å). In addition, the $\Theta_{\text{H-O-H}}$ (100.66°) in 8E(b) is slightly smaller than that of 8F(b) (101.00°). Therefore, it is easy to understand that the adsorption energy of 8E(b) is larger than that of 8F(b). 8G(b) and 8H(b) are similar to 8C(b) and 8D(b). But the H₂O is on the bridge site of the edge site connecting atoms 1 and 2. The O–Si bond in 8G(b) is 2.61 Å, which is shorter by 0.106 Å than that of 8H(b). Their two H atoms and Si atoms are on different sides of the atom O. The $\Theta_{\text{H-O-H}}$ (107.24°) in 8G(b) is larger than that of 8H(b) (106.85°). The adsorption energy of 8G(b) is certainly larger than that of 8H(b). Some parameters are listed in table 3.

According to the discussions above, we find that there are three factors affecting the adsorption energies: the strength of the O–Si bond, the interaction between H and Si atoms, and the number of O–Si bonds. The O–Si bond plays the principal role in H₂O adsorption on the silicon clusters. The shorter the O–Si bond is, the larger the adsorption energy is, and the more obvious the structural distortion is. When an H₂O molecule is on a site with higher

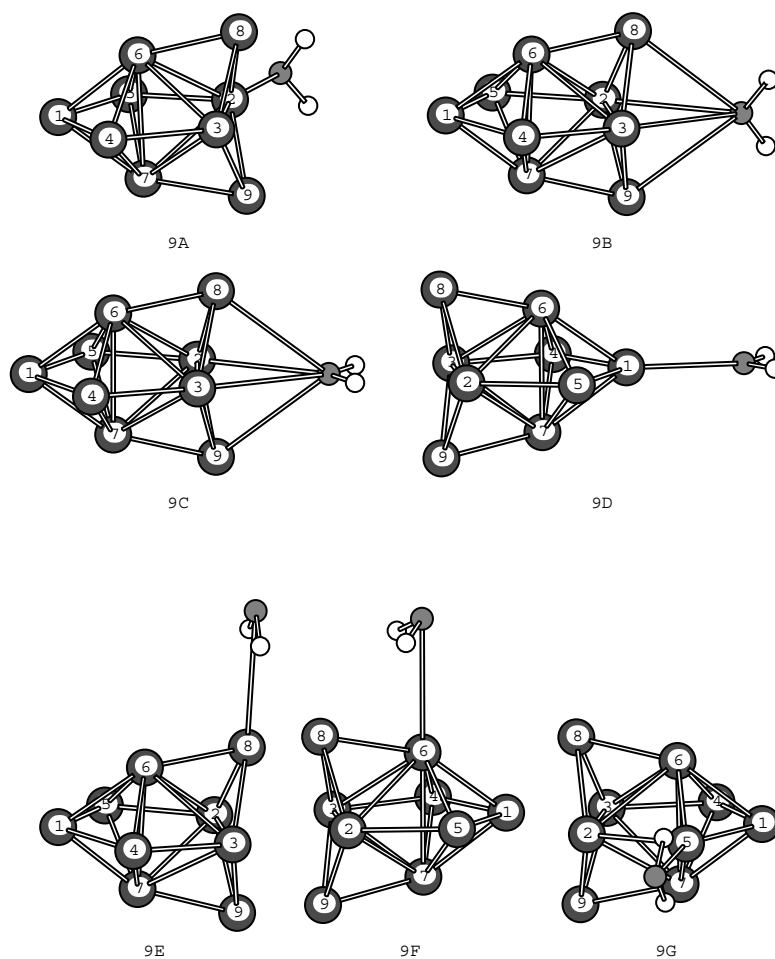


Figure 4. The stable structures of water molecules adsorbed on the seven different sites of the Si_8 cluster.

Table 3. Some geometrical parameters (\AA) changed obviously after water molecule adsorption on $\text{Si}_8(\text{b})$ cluster surface. Δ refers to the maximum difference between two corresponding bond lengths of free $\text{Si}_8(\text{b})$ and $\text{Si}_8(\text{b}) + \text{H}_2\text{O}$.

Bond	Free $\text{Si}_8(\text{b})$, H_2O	8A(b)	8B(b)	8C(b)	8D(b)	8E(b)	8F(b)	8G(b)	8H(b)	Δ
d_{13}	2.67	2.73	2.68	2.67	2.68	2.67	2.68	2.75	2.71	0.08
d_{24}	2.67	2.60	2.57	2.67	2.68	2.67	2.68	2.75	2.71	0.08
d_{56}	3.03	2.99	3.05	3.03	3.01	3.02	3.00	2.95	3.01	0.08
$d_{\text{O-Si}}$	—	2.45	2.50	3.10	3.12	3.06	3.19	2.61	2.72	
$d_{\text{O-Si}}$	—	—	—	3.21	3.22	—	—	3.37	—	
d_{OH}	0.97	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.01
$\Theta_{\text{H-O-H}}$	104.39	104.10	105.01	105.36	105.13	100.66	101.00	107.24	106.85	3.73

symmetry, the interaction between H and Si atoms is small, and two H atoms and the silicon cluster are on different sides of the O atom. Thus the interaction between H and Si atoms makes the $\Theta_{\text{H-O-H}}$ of H_2O increase. But, if the H_2O molecule was on the other sites with

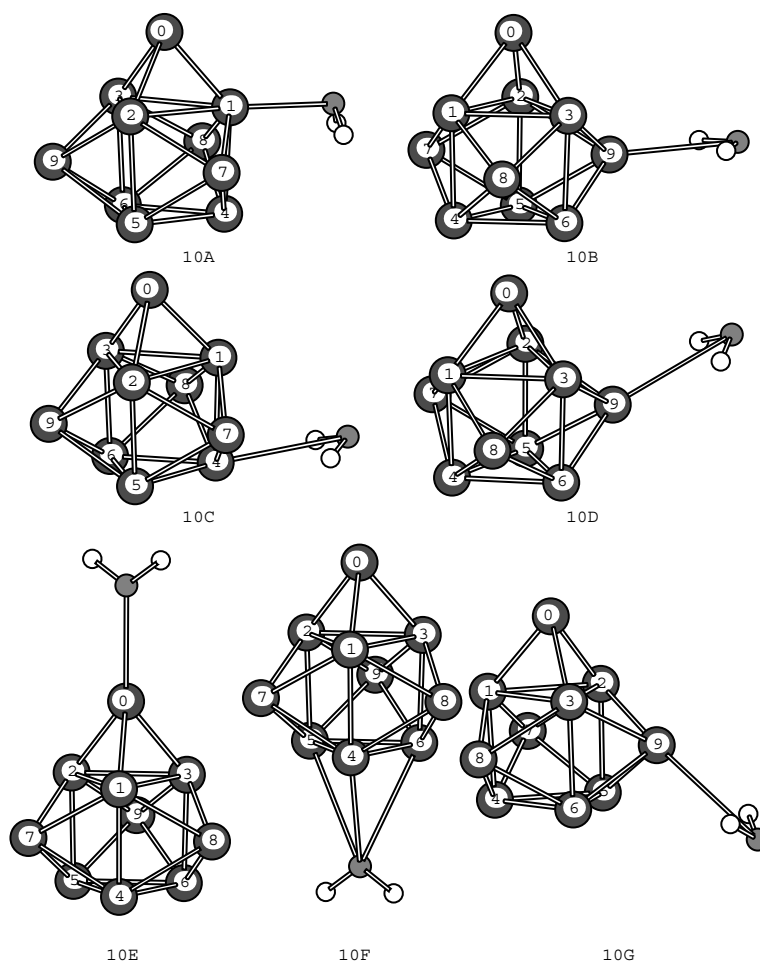


Figure 5. The stable structures of water molecules adsorbed on the seven different sites of the Si₁₀ cluster.

lower symmetry, the two H atoms would move towards the silicon cluster. The interaction between atoms H and Si makes the $\Theta_{\text{H-O-H}}$ of H₂O decrease. The increase of the number of O-Si bonds can also enlarge the adsorption energy, although they may be weak bonds.

3.2. Si₉ + H₂O

Water adsorption on the surface of the Si₉ cluster is similar to that for the Si₈ cluster discussed above. When a water molecule is adsorbed on the surface of a Si₉ cluster, its adsorption energy is situated between 0.24 and 0.14 eV. The adsorption causes the maximum change 0.06 Å of the geometry parameter of the Si₉ cluster and the maximum change 3.96° of the $\Theta_{\text{H-O-H}}$ of H₂O. Some parameters are listed in table 4.

The most favoured adsorption site for Si₉ cluster is the atop site of atom 2 (or 3). The energy of adsorption on the site is 0.24 eV. The water adsorption makes the Si₉ cluster elongate a little in the direction of the water molecule, whereas it becomes shortened in the other two directions. The bond angle $\Theta_{\text{H-O-H}}$ changes from 104.39° to 105.27°, and the bond O-H

Table 4. Some geometrical parameters (Å) changed obviously after water molecule adsorption on Si₉ cluster surface. Δ refers to the maximum difference between two corresponding bond lengths of free Si₉ and Si₉ + H₂O.

Bond	Free Si ₉ , H ₂ O	9A	9B	9C	9D	9E	9F	9G	Δ
d_{15}	2.43	2.37	2.43	2.42	2.41	2.42	2.42	2.41	0.06
d_{26}	2.69	2.75	2.69	2.69	2.68	2.69	2.73	2.69	0.06
d_{27}	2.69	2.75	2.69	2.69	2.68	2.68	2.66	2.69	0.06
d_{O-Si}	—	2.47	3.22	3.21	2.69	3.20	3.08	3.17	
d_{O-Si}	—	—	3.23	3.23	—	—	—	—	
d_{OH}	0.97	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.01
Θ_{H-O-H}	104.39	105.27	104.59	104.85	105.60	100.59	101.17	100.43	3.96

increases by 0.01 Å compared with 0.97 Å for the free H₂O. The changes in structure are similar to those of water adsorbed on Si₅₋₇ cluster surfaces. But Si₅₋₇ clusters have higher symmetry (D_{3h-5h}), in which there are only two kinds of atom: capping atoms and edge atoms, whereas the symmetry of Si₉ is C_s, which makes the cluster have many different kinds of site.

When an H₂O molecule is placed on the bridge site between atom 2 and atom 3, we find that there are two kinds of adsorption structure, in which the planes of H₂O molecules are perpendicular to each other, shown as 9B and 9C in figure 2. The adsorption energy of 9C is slightly larger than that of 9B. The two kinds of O–Si bond in 9B and 9C structures are both longer than 3.2 Å. Although they are long by comparison with that of 9A, four such weak O–Si bonds still cause the water molecule to be adsorbed on the site. The H₂O molecule in 9D is on the atop site of apex atom 1. Its adsorption energy is 0.14 eV, which is the smallest among the seven Si₉ + H₂O structures.

All of the Θ_{H-O-H} in the four structures mentioned above are larger than that of the free H₂O. Their two H atoms and Si atoms are on the two sides of the O atom. But it is found that all Θ_{H-O-H} in 9E, 9F, and 9G are smaller than that of the free H₂O. In the three structures, the two H atoms have moved towards the Si₉ cluster. The O–Si bond in 9E is almost as long as that in 9B and 9C, but the adsorption energy of 9E is larger than that of 9B. This is caused by the interaction between the atoms H and Si.

3.3. Si₁₀ + H₂O

For Si₁₀, the most favoured adsorption sites for Si₁₀ are the atop sites of the three atoms 1, 2, and 3, which are equipollent because of the C_{3v} symmetry of Si₁₀. The adsorption energy of 10A is 0.42 eV. The O–Si bond length is 2.36 Å, which is the shortest among all the seven Si₁₀ + H₂O structures. It is found from table 5 that the structural distortion of 10A is also the greatest. But the bond angle Θ_{H-O-H} in 10A increases by only 0.45° relatively to that of the free H₂O molecule because of the fact that the plane of H₂O is almost parallel with the symmetrical axis of the silicon cluster. Another structure similar to 10A is 10C. Placing an H₂O molecule on the atop sites of the three apex atoms in an equilateral triangle consisting of atoms 4, 5, and 6, we can obtain 10C. The O–Si bond is 0.74 Å longer than that of 10A. Its adsorption energy is 0.25 eV, which is 0.17 eV less than that of 10A. Water molecules can be adsorbed on the atop sites of three equipollent atoms 7, 8 and 9 in three ways, which correspond to 10B, 10D, and 10G, as shown figure 5. Placing an H₂O molecule, in which the two H atoms are in the other direction to the O atom relatively to the Si₁₀ cluster, just on the atop site of atom 7, 8, or 9, the structural optimization finds its stable form to be 10B. It is found that the two H atoms have moved towards the Si₁₀ cluster. The bond angle Θ_{H-O-H} decreases

Table 5. Some geometrical parameters (Å) changed obviously after water molecule adsorption on Si₁₀ cluster surface. Δ refers to the maximum difference between two corresponding bond lengths of free Si₁₀ and Si₁₀ + H₂O.

Bond	Free Si ₁₀ , H ₂ O	10A	10B	10C	10D	10E	10F	10G	Δ
d_{12}, d_{13}	2.67	2.73	2.65	2.66	2.66	2.62	2.66	2.65	0.06
d_{23}	2.67	2.60	2.66	2.65	2.65	2.67	2.66	2.68	0.07
d_{47}, d_{48}	2.52	2.48	2.46	2.46	2.48	2.46	2.46	2.45	0.07
d_{SiO}	—	2.36	3.18	3.09	3.16	2.66	3.10	3.14	
d_{OH}	0.97	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.01
$\Theta_{\text{H-O-H}}$	104.39	104.84	100.48	101.23	100.80	105.75	104.93	101.07	3.91

by 3.91°. Its adsorption energy is 0.27 eV. If we place an H₂O molecule on the bridge site of the edge going from atom 2 to atom 3, or the hollow site consisting of three neighbouring atoms 2, 3, and 9, the stable form is 10D, in which the H₂O has moved towards the atop site of atom 9. But this is different from 10B. Another structure similar to 10D is 10G, which is formed by placing an H₂O molecule on the bridge site of the edge going from atom 5 to atom 6, or the hollow site consisting of the three neighbouring atoms 5, 6, and 9.

The last two Si₁₀ + H₂O structures are 10E and 10F. The two H atoms and the Si cluster are on different sides of the O atom in the two structures, which is different from the case for the five structures mentioned above. The H₂O of 10E is on the atop site of the apex atom 0, whereas the H₂O of 10F is on the hollow site of the bottom surface. The O–Si bond (3.10 Å) in 10F is not so strong as that (2.66 Å) in 10E, but three such weak O–Si bonds make the adsorption energy of 10F larger than that of 10E.

4. Conclusions

We have studied the water molecule adsorption on Si₉₋₁₀ clusters by the full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. Our results show that:

- (1) An H₂O molecule can be adsorbed on several sites on the surfaces of Si₈₋₁₀ clusters. The maximum adsorption energy is 0.49 eV, which suggests that Si₈₋₁₀ clusters are relatively unreactive with water.
- (2) Relatively low symmetry causes Si₈₋₁₀ clusters to have many more different adsorption sites than Si₅₋₇ clusters. Therefore, the configuration of water adsorption on the Si₈₋₁₀ cluster surfaces becomes more complicated than that for Si₅₋₇ clusters. When the water molecule is adsorbed on some special sites with higher symmetry, the orientation of the H₂O molecule is similar to that in Si₅₋₇ + H₂O; that is, the two H atoms and the silicon cluster are on different sides of the O atom, and $\Theta_{\text{H-O-H}}$ will increase. But when the water molecule is on the other sites, the two H atoms will move towards the silicon cluster.
- (3) The principal factor affecting adsorption energy is the O–Si bond strength. The interaction between H and Si atoms and the number of O–Si bonds also have influences on the adsorption energy.

Acknowledgments

This work was supported by the National Natural Science Foundation of China.

References

- [1] Li B X, Qiu M and Cao P L 1999 *Phys. Lett. A* **256** 386
- [2] Li B X, Jiang M and Cao P L 2000 *Phys. Status Solidi b* **218** 399
- [3] Li B X, Cao P L and Que D L 2000 *Phys. Rev. B* **61** 1685
- [4] Li B X, Jiang M and Cao P L 1999 *J. Phys.: Condens. Matter* **11** 8817
- [5] Li B X and Cao P L 2000 *Phys. Rev. A* **62** 3201
- [6] Li B X and Cao P L 2000 *Phys. Status Solidi b* **219** 253
- [7] Jarrold M F 1991 *Science* **252** 1085
- [8] Creasy W R, O'Keefe A and McDonald J R 1987 *J. Phys. Chem.* **91** 2848
- [9] Jarrold M F and Bower J E 1989 *Z. Phys. D* **12** 551
- [10] Jarrold M F, Bower J E and Creegan K 1989 *J. Chem. Phys.* **90** 3615
- [11] Chelikowsky J R and Phillips J C 1989 *Phys. Rev. Lett.* **63** 1653
- [12] Creegan K and Jarrold M F 1990 *J. Am. Chem. Soc.* **112** 3768
- [13] Anderson L R, Maruyama S and Smalley R E 1991 *Chem. Phys. Lett.* **176** 348
- [14] Jarrold M F and Bower J E 1992 *J. Chem. Phys.* **96** 9180
- [15] Elkind L, Alford J M, Weiss F D, Laaksonen R T and Smalley R E 1987 *J. Chem. Phys.* **87** 2397
- [16] Alford J M and Smalley R E 1989 *Mater. Res. Soc. Symp. Proc.* **131** 3
- [17] Maruyama S, Anderson L R and Smalley R E 1990 *J. Chem. Phys.* **93** 5349
- [18] Alford M, Laaksonen R T and Smalley R E 1991 *J. Chem. Phys.* **94** 2618
- [19] Ray U and Jarrold M F 1990 *J. Chem. Phys.* **93** 5709
- [20] Jarrold M F, Ijiri Y and Ray U 1991 *J. Chem. Phys.* **94** 3607
- [21] Jarrold M F, Ray U and Creegan K M 1990 *J. Chem. Phys.* **93** 224
- [22] Jarrold M F and Bower J E 1989 *J. Am. Chem. Soc.* **111** 1979
- [23] Ray U and Jarrold M F 1990 *J. Chem. Phys.* **94** 2631
- [24] Krack M and Jug K 1995 *Chem. Phys.* **192** 127
- [25] Qiu M, Lee L Q, Cao P L and Que D L 1997 *J. Phys.: Condens. Matter* **9** 6543
- [26] Qiu M, Cao P L and Que D L 1998 *Surf. Sci.* **395** 260
- [27] Qiu M, Zhou Xu-Yan, Jiang M, Cao P L and Zeng Z 1998 *Phys. Lett. A* **245** 430
- [28] Qiu M, Zhou Xu-Yan, Jiang M and Cao P L 1998 *J. Phys.: Condens. Matter* **10** 7743
- [29] Qiu M, Jiang M, Zhao Y J and Cao P L 1999 *J. Chem. Phys.* **110** 10738
- [30] Li B X and Cao P L 2000 *J. Phys.: Condens. Matter* **12** 8357
- [31] Lide D R (ed) 1993–1994 *CRC Handbook of Chemistry and Physics* 74th edn (Boca Raton, FL: Chemical Rubber Company Press)
- [32] Methfessel M 1988 *Phys. Rev. B* **38** 1537
- [33] Methfessel M, Rodriguez C O and Andersen O K 1989 *Phys. Rev. B* **40** 2009
- [34] Methfessel M and Schilfgaard M V 1993 *Int. J. Mod. Phys. B* **7** 262
- [35] Methfessel M and Schilfgaard M V 1993 *Phys. Rev. B* **48** 4937
- [36] Raghavachari K and Rohlfing C M 1988 *J. Chem. Phys.* **89** 2219
- [37] Rohlfing C M and Raghavachari K 1990 *Chem. Phys. Lett.* **167** 559
- [38] Fournier R, Sinnott S B and DePristo A E 1992 *J. Chem. Phys.* **97** 4149
- [39] Andreoni W and Pastore G 1990 *Phys. Rev. B* **41** 10243
- [40] Andreoni W 1991 *Z. Phys. D* **19** 31
- [41] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
- [42] Andersen O K 1975 *Phys. Rev. B* **12** 3060
- [43] Liu B, Lu Z Y, Pan B, Wang C Z, Ho K M, Shvartsburg A A and Jarrold M F 1998 *J. Chem. Phys.* **109** 9401
- [44] Ho K M, Shvartsburg A A, Pan B, Lu Z Y, Wang C Z, Wacker J G, Fye J L and Jarrold M F 1998 *Nature* **392** 582