Carbon monoxide adsorption on small Si clusters: a full-potential linear-muffin-tin-orbital

molecular-dynamics study

Carbon monoxide adsorption on small Si clusters: a full-potential linear-muffin-tin-orbital molecular-dynamics study

Bao-xing Li†‡ and Pei-Lin Cao†

† Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou, Zhejiang, 310027, People's Republic of China
‡ Department of Physics, Hangzhou Teachers' College, Hangzhou, Zhejiang, 310012, People's Republic of China

Abstract. Using the full-potential linear-muffin-tin-orbital method, we have performed molecular-dynamics simulations for carbon monoxide (CO) adsorption on Si_{2-7} clusters. The calculations show that the carbon monoxide can be adsorbed tightly on an active site of each small silicon cluster. Their adsorption energies decrease successively and rapidly as the atom number of the silicon clusters increases. Besides the active sites, there are some other sites on which the CO molecule can be very weakly bound as a molecule. When the CO molecule is adsorbed on the active sites, the CO bond length and the structures of the Si clusters will change significantly. Otherwise, the CO molecule remains almost unchanged, and the changes in the structures of the Si clusters resulting from the carbon monoxide molecular adsorption are much less than those caused by H_2O, NH_3, and C_2H_4 adsorptions.

1. Introduction

The properties of silicon clusters have been of considerable interest in physics and chemistry because silicon is an important material in the semiconductor industry. Their reactivity is very different from that of bulk silicon [1]. Many experimental studies of the chemical reactions of silicon clusters with water [2,3], acetylene [2], ethylene [4–9], ammonia [2,10–15], oxygen [2,9,16], and carbon monoxide [1,17] have been performed. Studies of the chemistry reveal that silicon clusters containing up to 70 atoms appear to be much less reactive than bulk silicon surfaces.

The adsorption of simple, diatomic gases on metal surfaces is one of the most widely studied prototype adsorption systems. Experimental results [1,18] show that carbon monoxide often undergoes molecular adsorption on metal surfaces. Jarrold and Bower have studied the reaction between Si_{25}^+ and carbon monoxide in low-energy ion beam experiments [17]. Three product ions are observed: $Si_{24}C^+$, Si_{19}^+, and Si_{15}^+. Jarrold has reported in brief his experimental results in reference [1]: that CO does not react with bulk silicon at room temperature, and that it does not react with the silicon clusters at room temperature either. When the temperature is lowered to 77 K, a series of $Si_n(CO)_m^+$ products are observed. These products arise from molecular adsorption where the carbon monoxide is very weakly bound as a molecule (the binding energies are about 0.1 eV) to the clusters. The low binding energy results in high mobility of the carbon monoxide over the cluster surface. Chamberlain *et al* have investigated

adsorption of CO on Si(100)-(2 × 1) at room temperature [19]. Ultraviolet photoelectron spectroscopy shows molecularly adsorbed CO at the surface. To the best of our knowledge, there have been no other reports involving adsorption of CO on bulk silicon and silicon clusters since 1990.

Some theoretical studies have been performed on the reactivity of silicon clusters. Krack and Jug [20] have studied ammonia adsorption with neutral Si_5 and Si_{10} clusters using a semiempirical molecular orbital (MO) method SINDO1 and the *ab initio* program Gaussian 90. Using the DV-X_α method, our group has studied the nature of NH_3-molecule adsorption and dissociation on neutral Si_{5-7} and Si_{10} clusters [21, 22]. We have also performed full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) studies for NH_3 and H_2O adsorption on Si_{5-7} clusters [23, 24]. However, to the best of our knowledge, there have been no theoretical studies concerning carbon monoxide adsorption on silicon clusters. In providing a deeper and more complete understanding of the physical and chemical properties of silicon clusters, such theoretical study does have scientific importance.

In the present work, we will study carbon monoxide adsorption on neutral Si_{2-7} clusters by the FP-LMTO-MD method. Although experimental attention is focused more on studies of the chemistry of cluster ions or cations, it is appropriate to study the adsorption on the neutral clusters, which is, in many cases, more scientifically interesting in view of the different behaviours of clusters and extended surfaces.

2. Method

The FP-LMTO method [25–28] is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [29]. In this method, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centred at the nuclei and the remaining interstitial region. LMTOs are augmented Hankel functions, and are augmented inside the MT spheres, but not in the interstitial region [30, 31]. In order to derive a force theorem, we attempt to differentiate the LDA Kohn–Sham total energy directly, but the expression derived is extremely complicated. To circumvent this, we chose the Harris energy functional. It has been shown that the Harris energy equals the Kohn–Sham energy at self-consistency [27, 28]. In the LMTO method, one thing that we must do is to calculate the interstitial-potential matrix elements:

$$V_{ij}^I = \int_I \phi_i(x) V_I(x) \phi_j(x) \, dx \tag{1}$$

where I is the interstitial region, V_I is the interstitial potential. In different methods, we handle V_{ij}^I in different ways. In the FP-LMTO method for clusters, Methfessel and Schilfgaarde [27, 28] used non-overlapping MT spheres. They retained non-spherical potential terms inside the MT spheres, but expanded the interstitial potential $V_I(x)$ in a different set of atom-centred Hankel functions. In order to obtain the interstitial-potential matrix elements, we need an accurate representation, valid in the interstitial region, of the product of two Hankel functions centred at the same or at different sites. That is, we require an expansion of the form

$$\phi_i^* \phi_j = \sum_k C_k^{ij} \chi_k(x) \tag{2}$$

where i and j are abbreviations for νL and $\nu' L'$, respectively, and ϕ_i is a LMTO envelope function centred at site ν with angular momentum L. L is an abbreviation for the angular-momentum quantum numbers (l, m). k stands for $(\nu L\alpha)$, the index α runs over different locations, and the χ_k are functions of the charge-density Hankel function set. C_k^{ij} are expansion coefficients. The interstitial-potential matrix element V_{ij}^I then reduces to a linear combination

of integrals of the functions χ_k times the interstitial potential. Because the interstitial potential itself is also expanded in functions of the same type as χ_k, the desired interstitial integral has now been expressed as a linear combination of integrals of products of pairs of Hankel functions; i.e., the three-centre integral has been reduced to a sum of two-centre integrals. Because the products are smooth functions, the coefficients in equation (2) can be adjusted until the best fit of the values and slopes of the right-hand side to the values and slopes of the products is obtained for all spheres simultaneously by a tabulation technique for the surfaces of the spheres. In the cluster method, the expansion is first calculated for two atoms arranged along the z-axis and the coefficients are tabulated as a function of the interatomic distance. For general geometry, the expansion is obtained by rotating the tabulated fit using the rotation matrices of the spherical harmonics. The tabulated fit is performed by direct numerical integration and can be made as accurate as desired [26]. The exactness of the total energy depends on the approximation one makes for the exchange–correlation part. The LDA exchange–correlation energy is given by

$$E_{xc}[\rho(r)] = \int \rho(r)\epsilon_{xc}[\rho(r)] \, \mathrm{d}^3r \tag{3}$$

where $\epsilon_{xc}[\rho(r)]$ is the LDA exchange–correlation energy density. Inside the muffin-tin spheres, ϵ_{xc} is easily evaluated numerically for each point on the radial mesh. In the interstitial region, we perform the non-linear local operations $\epsilon_{xc}[\rho(r)]$, and fit these to a series of atom-centred, overlapping Hankel functions. The exchange–correlation energy density ϵ_{xc} may thus be expressed in the same way as the charge density. Direct numerical integration on a mesh can be used. The force expression for the FP-LMTO method can be obtained from the Harris energy function [25, 26]. When the optimization of one structure is being carried out, no restriction is imposed. Starting with one geometric configuration, we set up one time step. In each time step, the eigenvalue problem is solved exactly and the output density is admixed with the input density in the usual way. The nuclei are then moved according to the forces using the Verlet algorithm. We then decompose the mixed density, move each partial density along with its atom, and re-overlap at the new geometry. 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 errors in the total energies calculated are less than 0.01 eV. We do not carry out a vibrational frequency analysis of the optimized structure to verify that it represents a local energy minimum. But, to avoid a saddle point on the energy surface, we increase the time step as far as possible in our calculations. In our results, the zero-point vibrational energies are not included.

3. Results and discussion

In this section, we will present the results for carbon monoxide adsorption on small Si_{2-7} clusters. Based on our FP-LMTO-MD study, the ground-state structures of Si_{3-7} clusters are: isosceles triangle (C_{2v}), rhombus (D_{2h}), trigonal bipyramid (D_{3h}), tetragonal bipyramid (D_{4h}), and pentagonal bipyramid (D_{5h}) (see figure 1). This is in good agreement with earlier theoretical results in [32–37]. The ground-state structures of small ($n \leqslant 7$) silicon clusters (except for $n = 5$) have been confirmed by experiments [38]. They are shown in figure 1.

For the carbon monoxide (CO) molecule, our calculated CO bond length is 1.134 Å. This datum is in good agreement with the experimental value: 1.13 Å [39].

As reported in our previous papers, we can define two kinds of atom in the Si_{3-7} structures: apex atoms and side atoms. On the basis of this definition, we try these possible adsorption
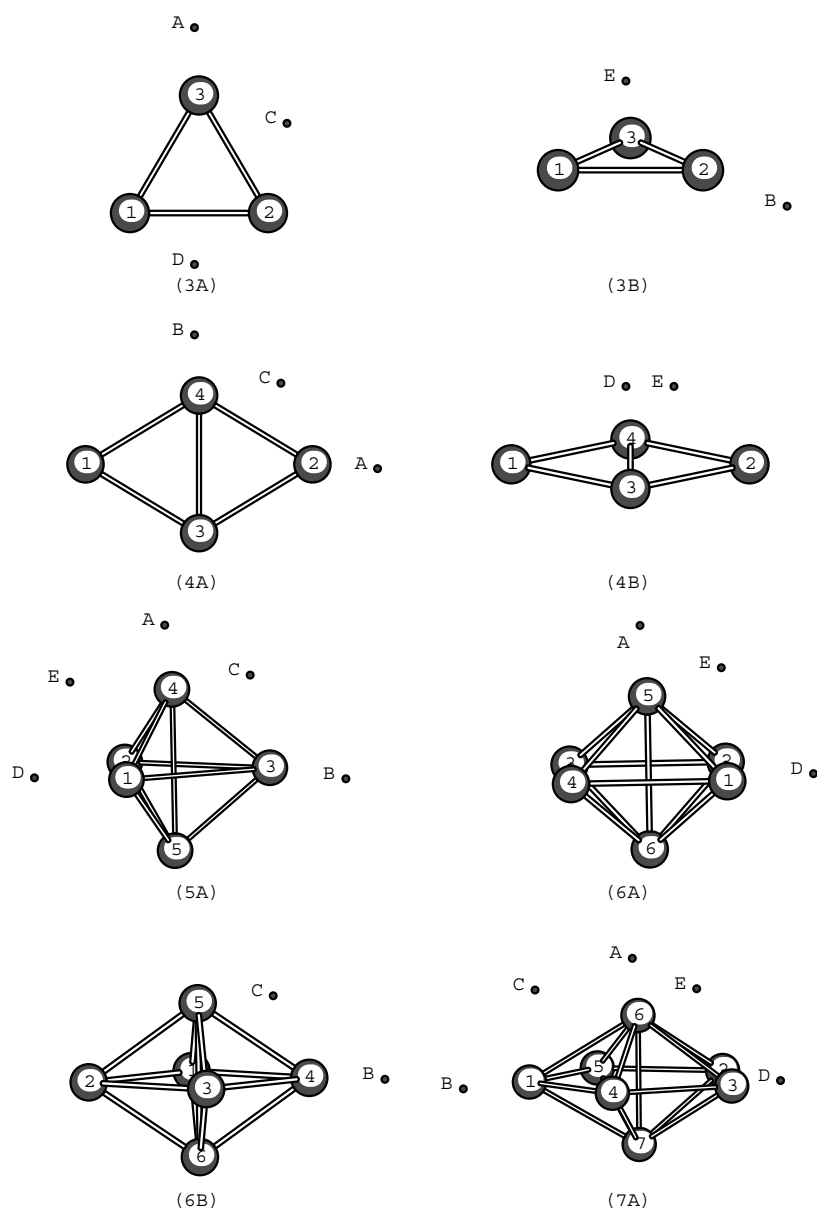
Figure 1. The geometries of the ground-state structures of Si$_{3-7}$ clusters. Si$_3$–Si$_7$ correspond to 3A (or 3B), 4A (or 4B), 5A, 6A (or 6B), and 7A, respectively. Apex atoms: atom 3 for Si$_3$, atoms 1, 2 for Si$_4$, atoms 4, 5 for Si$_5$, atoms 5, 6 for Si$_6$, atoms 6, 7 for Si$_7$. Side atoms: atoms 1, 2 for Si$_3$, atoms 3, 4 for Si$_4$, atoms 1–3 for Si$_5$, atoms 1–4 for Si$_6$, atoms 1–5 for Si$_7$. The small black dots labelled A–E relate to the sites A–E on the silicon clusters.

sites: the atop site on an apex atom (site A), the atop site on a side atom (site B), the short-bridge site (between an apex atom and a side atom, site C), the long-bridge site (between a side atom and another side atom, site D), and the hollow site (in the space between a side atom, another side atom, and an apex atom, site E). The five different sites (site A–site E) are shown as small dark dots in figure 1. In our calculations, a carbon monoxide molecule will be placed on such

a site in three different possible surface orientations: oxygen atom O, or a carbon atom C facing toward it, or the molecular axis parallel to it. Then, we start to calculate the adsorption energy and optimized structure by molecular-dynamics simulations. The optimized adsorption structures are shown in figure 2 to figure 4. Our calculations suggest that the orientation of CO normal to the site toward which the carbon end faces is the correct one. Their adsorption energies are listed in table 1. As might have been expected, the other orientations of the CO molecule make the adsorption energies much smaller.
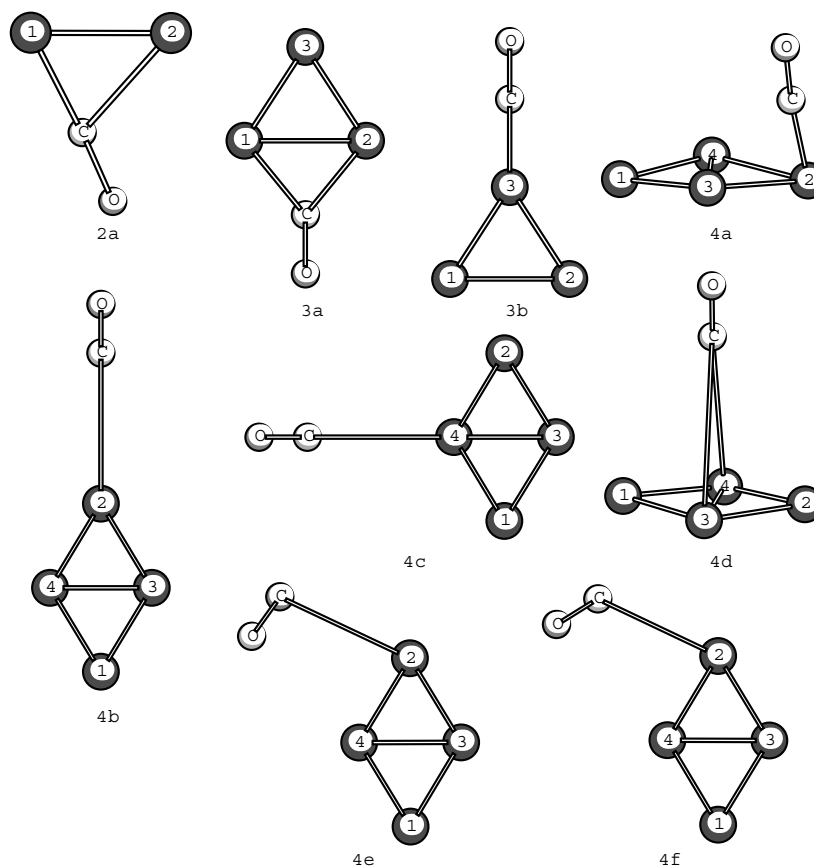

Figure 2. The stable structures of carbon monoxide adsorbed on Si_{2-4} clusters. 2a corresponds to $Si_2 + CO$, 3a and 3b to $Si_3 + CO$, 4a–4f to $Si_4 + CO$.

Table 1. Calculated adsorption energies (eV) of carbon monoxide molecules adsorbed on the Si_{2-7} clusters. 'X' stands for the numbers 2–7.

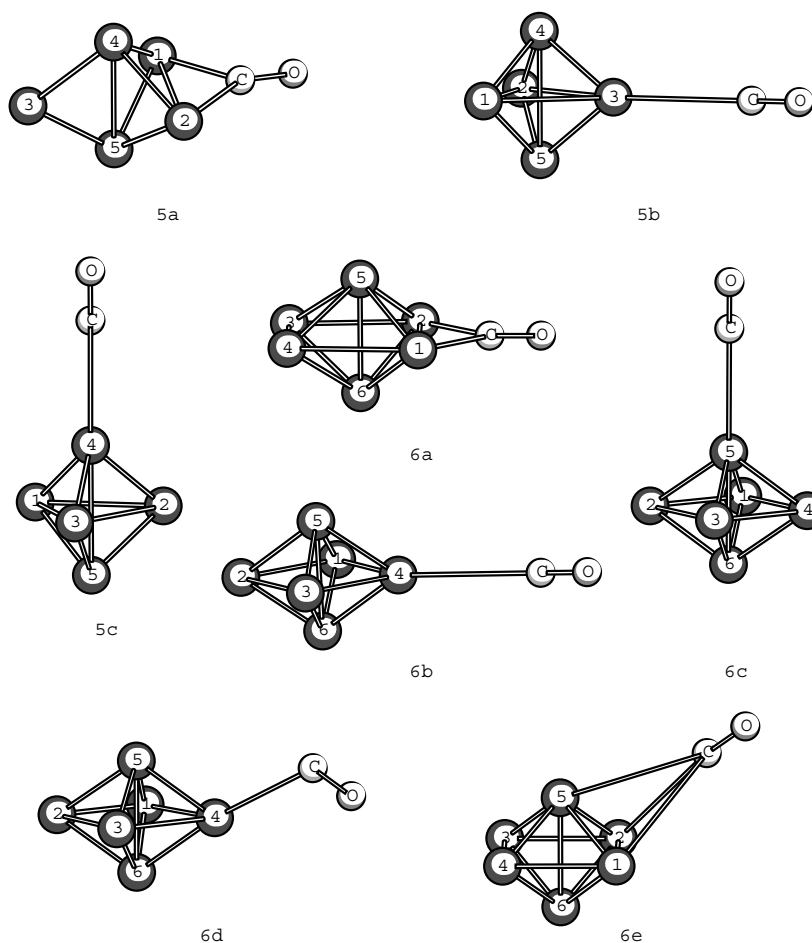| Structure	Xa	Xb	Xc	Xd	Xe	Xf
Si_2	3.641	—	—	—	—	—
Si_3	3.188	1.775	—	—	—	—
Si_4	1.640	⩽0.01	0.017	0.070	0.086	0.106
Si_5	1.321	0.029	0.133	—	—	—
Si_6	0.846	0.019	0.099	0.220	0.096	—
Si_7	0.312	0.024	0.063	0.059	0.265	0.179

Figure 3. The stable structures of carbon monoxide adsorbed on $Si_{5,6}$ clusters. 5a, 5b, and 5c correspond to Si_5 + CO, 6a–6e to Si_6 + CO.

Table 2. Optimized molecular geometrical parameters (Å) for Si_2 clusters, and carbon monoxide adsorption on Si_2 clusters.

Structure	d_{12}	Si(1)–C	Si(2)–C	C–O
Free Si_2 and CO	2.182	—	—	1.134
Si_2 + CO	2.220	1.778	2.116	1.191

3.1. Si_{2-4}

The Si–Si bond length in a neutral Si_2 cluster is 2.182 Å. When a CO molecule is adsorbed on it, the Si_2 cluster and the CO molecule both distort obviously in structure. The structure parameters are given in table 2. The Si–Si bond lengthens by 0.038 Å, and the C–O bond increases by 0.057 Å. It is worth noting that our calculated Si–C bond length in the SiC cluster is 1.738 Å. On the other hand, the Si–C bond length in β-SiC crystal is 1.890 Å [40]. For 2a in figure 2, the Si(1)–C bond length is 1.778 Å, which is 0.04 Å longer than the Si–C bond length in a SiC cluster. It is obvious that the 2a structure can be regarded as a mixed structure
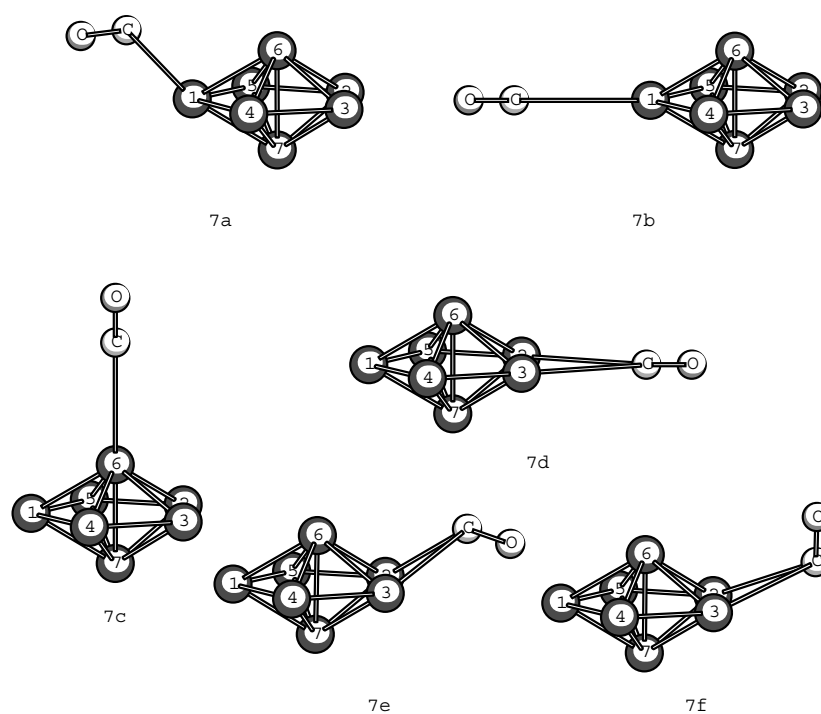
Figure 4. The six stable structures of carbon monoxide adsorbed on Si$_7$ clusters.

consisting of three clusters: Si$_2$, SiC, and CO. In addition, the carbon atom also forms a Si–C bond with another silicon atom (atom 2) in the Si$_2$ cluster. The distortion, mixed structure, and double SiC bonds make its adsorption energy increase to 3.641 eV, which is the highest found among Si$_2$ + CO to Si$_7$ + CO. In fact, the chemisorption results in the distortion in the structure.

These ground-state structures of Si$_{3,4}$ clusters are planar structures. The Si$_3$ cluster can adsorb carbon monoxide molecules on some sites. A CO molecule can be adsorbed on an A site or D site of the Si$_3$ cluster. Our calculations suggest that the D site (3a) is more favoured than the A site (3b). The adsorption energy in 3a is 3.188 eV, which is 1.343 eV larger than that in 3b, with 1.775 eV adsorption energy. According to the structural parameters in table 3, the Si$_3$ cluster and the CO molecule in 3b do not change so much as in 3a. But the Si–C bond length in 3b is 1.779 Å, which approaches the Si–C bond length, 1.738 Å, in the SiC cluster. Although the Si–C bond length in 3a is 0.165 Å larger than that in 3b, the carbon atom C in 3a forms Si–C bonds not only with silicon atom 1, but also with silicon atom 2. The two Si–C bonds make its adsorption energy increase significantly, as for Si$_2$ + CO. The structure for 3a is distorted significantly. Its C–O bond length also increases to 1.191 Å, which is equal to the

Table 3. Optimized molecular geometrical parameters (Å) for Si$_3$ clusters, and carbon monoxide adsorption on Si$_3$ clusters.

Structure	d_{12}	d_{13}	Si–C	C–O
Free Si$_3$ and CO	2.790	2.170	—	1.134
3a + CO	2.466	2.263	1.944	1.191
3b + CO	2.412	2.216	1.779	1.166

C–O bond length in Si_2 + CO. Therefore, the adsorption energy in 3a can be expected to be larger than that in 3b.

The Si_4 cluster can adsorb carbon monoxide molecules on the five possible sites. When a CO molecule is adsorbed on a D site (4d) or E site (4a), the cluster becomes a three-dimensional structure. 4a can be obtained by placing a CO molecule on an E site. In fact, the CO molecule has moved toward the apex atom 2. The carbon atom forms a 1.823 Å Si–C bond with the apex atom. According to table 4, the distortion in 4a is the most among the six Si_4 + CO structures. Its adsorption energy (1.640 eV) is also the largest. 4b and 4c are obtained by placing the CO molecule on the A site and B site, respectively. The distortion in the two structures is not obvious. It is worth noting that the Si–C bond length in 4b or 4c is double that in the SiC cluster, approximately. Therefore, these bonds will be very weak. The adsorption energy in 4b is less than 0.01 eV, and the energy in 4c is 0.017 eV. For convenience of discussion, we still draw the bonds in the figures. The aim is to show that there is an attractive force between them. We can obtain 4d if we put a CO molecule on a D site. Although there seem to be two Si–C bonds in 4d, they are not strong, because their bond lengths are both 3.907 Å, i.e. 2.129 Å longer than those (1.738 Å) in the SiC cluster. So its adsorption energy is also very small. But the two weak Si–C bonds make its adsorption energy increase only slightly compared with those of 4b or 4c. Placing a CO molecule on a C site, we can obtain two stable structures: 4e and 4f. As discussed above, we can also expect the adsorption energy in 4f to be larger than that in 4e in view of their Si–C bond lengths.

Table 4. Optimized molecular geometrical parameters (Å) for Si_4 clusters, and carbon monoxide adsorption on Si_4 clusters.

Structure	d_{13}	d_{14}	d_{23}	d_{24}	d_{34}	Si–C	C–O
Free Si_4 and CO	2.308	2.308	2.308	2.308	3.391	—	1.134
4a + CO	2.254	2.254	2.414	2.414	2.366	1.823	1.166
4b + CO	2.303	2.303	2.303	2.303	2.385	3.532	1.134
4c + CO	2.308	2.394	2.308	2.394	2.391	3.431	1.134
4d + CO	2.301	2.301	2.301	2.301	2.388	3.907	1.133
4e + CO	2.302	2.305	2.300	2.308	2.388	3.376	1.136
4f + CO	2.307	2.302	2.312	2.303	2.386	3.117	1.137

3.2. Si_5

Si_5 clusters can adsorb carbon monoxide molecules on three sites: the atop site on an apex atom (A site), the atop site on a side atom (B site), and the long-bridge site (D site). Figure 3 shows the final adsorption structures. The calculated structural parameters are given in table 5.

From table 5, we can conclude that the most favoured site for carbon monoxide adsorption is the long-bridge site (D site, 5a), and the adsorption energy is 1.321 eV. The carbon monoxide cannot adsorb on a C site or E site. If we place a CO molecule on the two sites, it is very unstable. Their final stable structures are both the same as 5a. The adsorption energies for the A site (5c) and B site (5b) are 0.133 eV and 0.029 eV, respectively. The CO adsorption on the two sites does not make the structure of the Si_5 cluster change significantly. But for the D site (5a), the situation is very different. Upon adsorption, the C–O bond length stretches from 1.134 Å to 1.174 Å (table 5). The Si–C bond length is 2.054 Å. The structure of the Si_5 cluster distorts significantly. In fact, the Si_5 cluster has reconstructed. Upon carbon monoxide adsorption, the cluster is shortened in the direction of the axis of atom 4 and 5 ($d_{45} = 2.754$ Å, compared to the initial value: 2.967 Å). d_{12} changes from 3.041 Å to 2.697 Å, but d_{13} (=d_{23})

Table 5. Optimized molecular geometrical parameters (Å) for Si_5 clusters, and carbon monoxide adsorption on Si_5 clusters.

Structure	Free Si_5 and CO	5a + CO	5b + CO	5c + CO
d_{12}	3.041	2.697	3.025	3.001
d_{13} or d_{23}	3.041	—	3.042	3.001
d_{14} or d_{24}	2.297	2.304	2.291	2.292
d_{15} or d_{25}	2.297	2.304	2.291	2.294
d_{34}	2.297	2.354	2.290	2.292
d_{35}	2.297	2.354	2.290	2.294
d_{45}	2.967	2.754	2.950	3.006
Si–C	—	2.054	3.297	2.882
C–O	1.134	1.174	1.133	1.133

has broken. Obviously, the two stronger Si–C bonds make the Si_5 cluster distort. As we had expected, the adsorption energy for 5a is much larger than that for 5b or 5c.

3.3. Si_6

The possible sites for carbon monoxide adsorption on Si_6 clusters are shown in figure 3, and all the structural parameters are given in table 6. The most favoured site is the long-bridge site (D site; 6a in figure 3), with adsorption energy 0.846 eV (table 6). Upon adsorption, two Si–C bonds with length 2.098 Å have formed, but they are not so strong as the double Si–C bonds in 5a. The structural changes of the Si_6 cluster are somewhat similar to those of Si_5 + CO. But they are not so significant as for Si_5. Here we do not repeat the analysis.

We also find that the Si_6 cluster can adsorb carbon monoxide molecules on four other possible sites. But all the adsorption energies are small. The adsorption energies are 0.099 eV (A site, 6c), 0.019 eV (B site, 6b), 0.220 eV (C site, 6d) and 0.096 eV (E site, 6e), respectively.

Table 6. Optimized molecular geometrical parameters (Å) for Si_6 clusters, and carbon monoxide adsorption on Si_6 clusters.

Structure	Free Si_6 and CO	6a + CO	6b + CO	6c + CO	6d + CO	6e + CO
d_{12}	2.718	2.693	2.745	2.710	2.636	2.711
d_{14}	2.718	2.994	2.697	2.710	2.805	2.727
d_{15}	2.346	2.327	2.345	2.347	2.360	2.344
d_{16}	2.346	2.327	2.345	2.354	2.351	2.350
d_{14}	2.718	2.994	2.697	2.710	2.805	2.727
d_{23}	2.718	2.994	2.745	2.710	2.636	2.727
d_{25}	2.346	2.327	2.343	2.347	2.359	2.344
d_{26}	2.346	2.327	2.343	2.354	2.362	2.350
d_{34}	2.718	2.351	2.697	2.710	2.805	2.714
d_{35}	2.346	2.426	2.345	2.347	2.360	2.349
d_{36}	2.346	2.426	2.345	2.354	2.351	2.348
d_{45}	2.346	2.426	2.353	2.347	2.325	2.349
d_{46}	2.346	2.426	2.353	2.354	2.347	2.348
d_{56}	2.692	2.680	2.686	2.720	2.701	2.693
Si(1)–C	—	2.098				3.539
Si(5)–C	—	2.098				3.542
Si–C	—		3.487	3.001	2.704	
C–O	1.134	1.172	1.134	1.133	1.144	1.134

3.4. Si$_7$

Carbon monoxide can be adsorbed on all five possible adsorption sites of the Si$_7$ cluster. The final structures are shown in figure 4, and the structural parameters are given in table 7. The Si$_7$ cluster does not change so significantly as the five silicon clusters discussed above. The most favoured site is the short-bridge site (C site, 7a), with adsorption energy 0.312 eV. When a CO molecule is adsorbed, the Si$_7$ cluster is elongated slightly in the direction of the axis of apex atoms 6 and 7. d_{67} changes from 2.491 Å to 2.511 Å. Its Si–C bond length is 2.393 Å, indicating that it is not so strong as the Si–C bond in 6a. The structures in 7b (B site), 7c (A site) and 7d (D site) change very slightly according to table 7. Their corresponding adsorption energies are 0.024 eV, 0.063 eV, and 0.059 eV, respectively. Placing a CO molecule on the E site in two different orientations: the CO molecular axis parallel and normal to the surface, we can obtain 7e and 7f with energies 0.265 eV and 0.179 eV, respectively. As discussed above, the adsorption energy in 7e is certainly more stable than that in 7f.

Table 7. Optimized molecular geometrical parameters (Å) for Si$_7$ clusters, and carbon monoxide adsorption on Si$_7$ clusters.

Structure	Free Si$_7$ and CO	7a + CO	7b + CO	7c + CO	7d + CO	7e + CO	7f + CO
d_{14}	2.473	2.459	2.472	2.467	2.480	2.483	2.479
d_{15}	2.473	2.459	2.472	2.467	2.480	2.483	2.479
d_{16}	2.445	2.445	2.445	2.435	2.444	2.443	2.443
d_{17}	2.445	2.481	2.445	2.453	2.444	2.421	2.441
d_{23}	2.473	2.467	2.469	2.467	2.463	2.435	2.462
d_{25}	2.473	2.481	2.476	2.467	2.467	2.470	2.471
d_{26} or d_{36}	2.445	2.442	2.445	2.435	2.446	2.433	2.444
d_{27}	2.445	2.428	2.445	2.453	2.446	2.469	2.450
d_{34}	2.473	2.481	2.476	2.467	2.467	2.470	2.471
d_{37}	2.445	2.428	2.445	2.453	2.446	2.469	2.450
d_{46} or d_{56}	2.445	2.447	2.442	2.435	2.441	2.452	2.442
d_{47} or d_{57}	2.445	2.455	2.442	2.453	2.441	2.436	2.444
d_{67}	2.491	2.511	2.487	2.505	2.486	2.505	2.491
Si–C	—	2.393	3.404	3.091	3.351	2.769	3.033
C–O	1.134	1.148	1.134	1.133	1.135	1.145	1.141

According to our calculations above, there is an active site for every cluster. The adsorption energy for the active site decreases successively and rapidly as the atom number of the silicon cluster increases, as shown in figure 5. If we extrapolate the characteristics of the adsorption energy (E_a) versus the atom number of the silicon cluster (n) to larger silicon clusters, it is reasonable to expect to find that carbon monoxide is very weakly bound on the larger silicon clusters as a molecule.

4. Conclusions

We have studied carbon monoxide adsorption on Si$_{2-7}$ clusters by the full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. On the basis of our calculations, we can draw the following conclusions:

- Firstly, there is an active site on each cluster of Si$_2$ to Si$_7$. The CO adsorption energy for this site is much larger than that for other sites; the reconstruction of the cluster upon CO adsorption on this site is much more substantial than that for other sites.
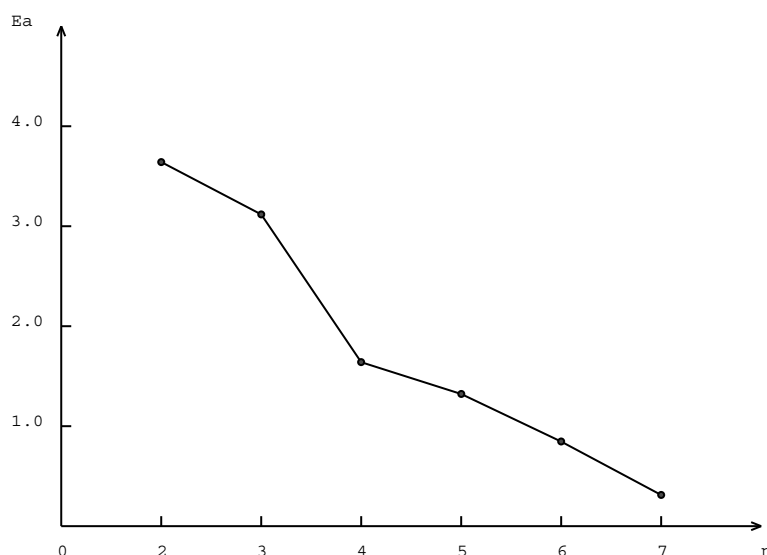
Figure 5. The carbon monoxide adsorption energy E_a (eV) versus the atom number of the silicon clusters, n.

- Secondly, the stronger the Si–C bond, the more significant the change in structure, and the larger the carbon monoxide adsorption energy. The formation of the two strong Si–C bonds can enlarge the adsorption energy obviously.
- Thirdly, the carbon monoxide adsorption energy decreases successively and rapidly as the atom number for the silicon cluster increases. For the larger silicon clusters, we can expect carbon monoxide to be very weakly bound on the surfaces as a molecule.

Acknowledgments

References

[1] Jarrold M F 1991 *Science* **252** 1085
[2] Creasy W R, O'Keefe A and McDonald J R 1987 *J. Phys. Chem.* **91** 2848
[3] Ray U and Jarrold M F 1990 *J. Chem. Phys.* **94** 2631
[4] Jarrold M F and Bower J E 1989 *Z. Phys.* D **12** 551
[5] Jarrold M F, Bower J E and Creegan K 1989 *J. Chem. Phys.* **90** 3615
[6] Chelikowsky J R and Phillips J C 1989 *Phys. Rev. Lett.* **63** 1653
[7] Creegan K and Jarrold M F 1990 *J. Am. Chem. Soc.* **112** 3768
[8] Anderson L R, Maruyama S and Smalley R E 1991 *Chem. Phys. Lett.* **176** 348
[9] Jarrold M F and Bower J E 1992 *J. Chem. Phys.* **96** 9180
[10] Elkind L, Alford J M, Weiss F D, Laaksonen R T and Smalley R E 1987 *J. Chem. Phys.* **87** 2397
[11] Alford J M and Smalley R E 1989 *Mater. Res. Soc. Symp. Proc.* **131** 3
[12] Maruyama S, Anderson L R and Smalley R E 1990 *J. Chem. Phys.* **93** 5349
[13] Alford M, Laaksonen R T and Smalley R E 1991 *J. Chem. Phys.* **94** 2618
[14] Ray U and Jarrold M F 1990 *J. Chem. Phys.* **93** 5709
[15] Jarrold M F, Ijiri Y and Ray U 1991 *J. Chem. Phys.* **94** 3607

[16] Jarrold M F, Ray U and Creegan K M 1990 *J. Chem. Phys.* **93** 224
[17] Jarrold M F and Bower J E 1989 *J. Am. Chem. Soc.* **111** 1979
[18] Rhodin Th N and Ertl G (ed) 1979 *The Nature of the Surface Chemical Bond* (Amsterdam: North-Holland) p 205
[19] Chamberlain J P, Clemons J L, Pounds A J and Gillis H P 1994 *Surf. Sci.* **301** 105
[20] Krack M and Jug K 1995 *Chem. Phys.* **192** 127
[21] Qiu M, Lee L Q, Cao P L and Que D L 1997 *J. Phys.: Condens. Matter* **9** 6543
[22] Qiu M, Cao P L and Que D L 1998 *Surf. Sci.* **395** 260
[23] Qiu M, Zhou Xu-Yan, Jiang M, Cao P L and Zeng Z 1998 *Phys. Lett.* A **245** 430
[24] Qiu M, Zhou Xu-Yan, Jiang M and Cao P L 1998 *J. Phys.: Condens. Matter* **10** 7743
[25] Methfessel M 1988 *Phys. Rev.* B **38** 1537
[26] Methfessel M, Rodriguez C O and Andersen O K 1989 *Phys. Rev.* B **40** 2009
[27] Methfessel M and Schilfgaarde M V 1993 *Int. J. Mod. Phys.* B **7** 262
[28] Methfessel M and Schilfgaarde M V 1993 *Phys. Rev.* B **48** 4937
[29] Kohn W and Sham L J 1965 *Phys. Rev.* B **140** A1133
[30] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[31] Springborg M and Anderson O K 1987 *J. Chem. Phys.* **87** 7125
[32] Raghavachari K 1990 *Phase Transitions* **24–26** 61
[33] Raghavachari K and Logovinsky V 1985 *Phys. Rev. Lett.* **55** 2853
[34] Jing X, Troullier N, Cean D, Binggeli N, Chelikowsky J R, Wu K and Saad Y 1994 *Phys. Rev.* B **50** 12 234
[35] Binggeli N and Chelikowsky J R 1994 *Phys. Rev.* B **50** 11 764
[36] Menon M and Subbaswamy K R 1993 *Phys. Rev.* B **47** 12 754
[37] Ordejon P, Lebedenko D and Menon M 1994 *Phys. Rev.* B **50** 5645
[38] 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
[39] Anderson A B and Hoffmann R 1974 *J. Chem. Phys.* **60** 4271
[40] Cao P L and Zhou R H 1993 *J. Phys.: Condens. Matter* **5** 2887