Structures, stabilities, and electronic properties of F-doped Si_n ($n = 1 \sim 12$) clusters: Density functional theory investigation*

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The geometries, stabilities, and electronic properties of FSi_n ($n = 1 \sim 12$) clusters are systematically investigated by using first-principles calculations based on the hybrid density-functional theory at the B3LYP/6-311G level. The geometries are found to undergo a structural change from two-dimensional to three-dimensional structure when the cluster size n equals 3. On the basis of the obtained lowest-energy geometries, the size dependencies of cluster properties, such as averaged binding energy, fragmentation energy, second-order energy difference, HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap and chemical hardness, are discussed. In addition, natural population analysis indicates that the F atom in the most stable FSi_n cluster is recorded as being negative and the charges always transfer from Si atoms to the F atom in the FSi_n clusters.

Keywords: FSi_n cluster, density-functional theory, geometrical structures, electronic properties

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1. Introduction

During the past several decades, small clusters have attracted more attention, because the properties of cluster-based materials can be designed by exploring the enormous variabilities in size, shape, and composition of constituent clusters.[1–3] Silicon is a semiconducting material of considerable importance in the microelectronics industry, device fabrication, and atomic scale engineering. Due to some unusual physical and chemical properties, the Si clusters have been extensively investigated both experimentally and theoretically. Using a magnetic-bottle electron spectrometer, Kishi *et al.*[4] investigated the geometric and electronic structures of silicon–sodium cluster anions, by photoelectron spectroscopy. In order to understand the vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) of V–Si clusters, Xu *et al.*[5] reported on the anion photoelectron spectrum experiments and density functional theory (DFT) calculations of small silicon clusters doped with one and two vanadium atoms. Very recently, they also investigated the electronic and structural properties of $ScSi_n^-$ and $CuSi_n^-$ clusters by using photoelectron spectroscopy combined with the DFT calculations.[6,7] In the theoretical aspect, Ma *et al.*[8] reported on the equilibrium geometries and energetics of cobalt atoms encapsulated in Si_n ($n = 1 \sim 13$) clusters by generalized gradient approximation combined with a genetic algorithm. Guo *et al.*[9] performed theoretical calculations on the total bonding energies, equilibrium geometries, Mulliken populations as well as Hirshfeld charges of $TaSi_n$ ($n = 1 \sim 13$) clusters by a relativistic density functional theory with the generalized gradient approximation available in the Amsterdam density functional program. Based on the Austin Model-1 (AM1) and third parametrization of MNDO (PM3) type semi-empirical molecular orbital methods within the restricted Hartree–Fock (RHF) formalism, Erkoça and Türkerb[10] calculated the energetics and structural stabilities of small Si_mC_n ($m+n = 2 \sim 5$).

However, the discussions mainly focus on the transition metal atom-doped silicon clusters or alkali metal atom-doped silicon clusters; there are very limited reports on halogen F atom-doped silicon clusters. So far as we know, there are only two experimental studies on the geometries and properties of $Si_nF_m^-$[11] and Si_nF^-,[12] which have been reported. Thus, comparing with the availability of experimental data, an adequate analysis of the electronic properties of the silicon–fluorine cluster is still lacking. In this paper, we describe a systematical investigation of the structure and electronic properties of the F-doped silicon clusters. In order to reveal the relative stability of the F-doped silicon cluster and the effect of F doping on the electronic properties of the Si cage, we carry out the theoretical calculations of FSi_n ($n = 1 \sim 12$) clusters and compare the results with those of pure Si_n clusters.

2. Computational method

All optimizations of the FSi_n ($n = 1 \sim 12$) clusters are performed by using density functional theory with the unrestricted B3LYP exchange–correlation potential[13,14] and 6-311G basis set as implemented in the Gaussian 09 pro-

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gram package.[15] The convergence thresholds were set to be 1.5×10^{-5} Hartree/Bohr (1 Hartree = 2 Ry = 27.2114 eV) for the forces, 6.0×10^{-5} Å for the displacement, and 10^{-6} Hartree for the energy change.[16] In searching for the ground state structures, lots of possible initial isomers, which include one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures, have been taken into account in geometry optimization, and all clusters are relaxed fully without any symmetry constraint. Owing to the spin polarization, each initial configuration is optimized at possible spin multiplicities (singlet, triplet, and quintet). Finally all the ground state structures have real vibrational frequencies and therefore correspond to the potential energy minima. In order to test the reliability of the calculation method and basis set used here, we calculate the properties of Si_2 dimer. The results are listed in Table 1. The calculated values of bond length, vibrational frequency, vertical ionization potential, and vertical electron affinity of Si_2 dimer are 2.29 Å, 489.5 cm^{-1}, 8.84 eV, and 2.03 eV respectively, which are in good agreement with the reported theoretical and experimental results.[17–21]

Table 1. Calculated values of bond lengths (r), vibrational frequency (ω), vertical ionization potential (VIP), and vertical electron affinities (VEA) of Si_2 dimer.

	Si_2		
	Our work	Theor.	Expt.
r/Å	2.29	2.29[a], 2.23[b], 2.28[c]	2.246[d]
ω/cm^{-1}	489.5	494[a], 568[b], 502[c]	511.0[d]
VIP/eV	8.84		8.15[d]
VEA/eV	2.03		2.176±0.002[e]

[a]Ref. [17], [b]Ref. [18], [c]Ref. [19], [d]Ref. [20], [e]Ref. [21].

3. Results and discussion

3.1. Geometry

The optimized geometries of the low-lying isomers of FSi_n ($n = 1 \sim 12$) clusters obtained with DFT calculations are shown in Figs. 1 and 2. According to the relative energies from low to high, the stability orders of each cluster are designated by order of letter, $na > nb > nc$ (n is the number of Si atoms in FSi_n cluster).

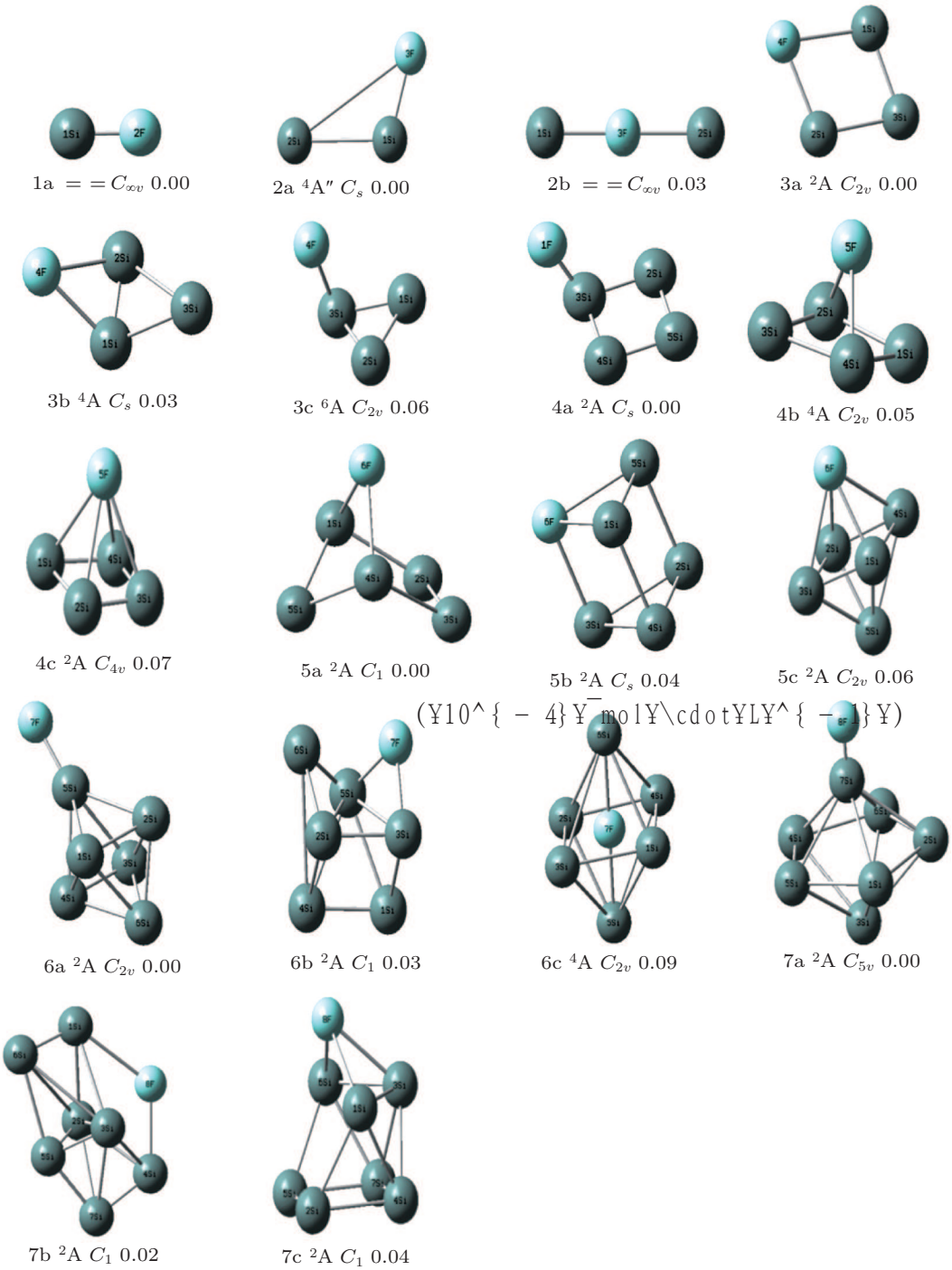
The equilibrium geometry of the FSi cluster with $C_{\infty v}$ symmetry is optimized. The F–Si bond length and averaged bonding energy of FSi dimer are 1.72 Å and 3.08 eV respectively. As shown in Fig. 1, theoretical calculations show that the FSi_2 has two stable isomers 2a and 2b with C_s and $C_{\infty v}$ symmetry respectively. According to the calculated results, it is found that the lowest energy structure 2a is an irregular triangular structure with two F–Si (1.72 Å and 3.44 Å) and Si–Si (2.48 Å). For the bond angles, we obtain the values of 43.2° for Si–F–Si and 28.3°, 108.5° for Si–Si–F. The linear structure 2b with F atom in the middle is the next isomer with 0.03 eV higher in energy than the 2a isomer. For FSi_3, the lowest energy structure 3a (C_{2v}) is a planar rhombus, and the bond angle for Si–F–Si is 85.6°. The butterfly structure 3b (C_s) is the next isomer with 0.03 eV higher in energy than the 3a isomer. The third isomer 3c (C_{2v}) can be regarded as Si trimer capped by one F atom.

As cluster size increases, 3D structures are lowest in energy for FSi_n clusters. From Fig. 1, it is found that the most stable structure (4a) for FSi_4 is the one in which the edge of a C_s rhombus Si_4 is capped by one F atom. The structure of 4b (C_{2v}) isomer is similar to the 4c (C_{4v}) isomer, but the energy of 4b is 0.02 eV lower than that of 4c isomer. For FSi_5, three isomers are presented. The ground state structure 5a with C_1 symmetry is found to be the most stable structure in all isomers. The second isomer 5b (C_s) is a triangular prism. An octahedron with an F atom at the top (5c) is obtained as a low-lying isomer, the energy of 5c is 0.02 eV higher than that of the 5b isomer. In the case of FSi_6 cluster, the isomer 6a with C_{2v} symmetry is of a ground state structure in all isomers, which can be viewed as one F atom capping on the top of the tetragonal bipyramid. The second isomer 6b with C_1 symmetry is reasonably higher in energy (0.03 eV) than 6a isomer. The isomer 6c with C_{2v} symmetry is 0.02 eV higher than the lowest energy structure. The lowest energy structure of FSi_7 cluster is the isomer 7a with C_{5v} symmetry, which can be viewed as one F atom capping the top of the pentagonal bipyramid. The total energy of isomer 7a is 0.02 eV and 0.04 eV lower than those of isomers 7b and 7c respectively.

As for the FSi_8 cluster, the isomer 8a is evaluated to be the ground state structure, which can be regarded as the F atom capping the top of the tetrahedron. The isomer 8b can be viewed as being derived from the isomer 8a. But its energy is 0.02 eV higher than that of the 8a isomer. The isomer 8c with C_1 symmetry is the third most stable structure. For the FSi_9 clusters, three isomers are shown in Fig. 2. The most stable isomer of FSi_9 (9a) may be considered as the addition of an Si atom to face cap isomer 8a. The isomers 9b with C_{2v} symmetry is similar to the isomer 9a, the difference between them is the site of the F atom. Also, its energy is 0.02 eV higher than the lowest energy 9a isomer. The isomer 9c with C_1 symmetry is generated by capping one Si atom on the isomer 8c. Likewise, we identify three low-energy isomers for FSi_{10}, shown in Fig. 2. The isomer 10a with C_s symmetry is of a ground state structure. The isomer 10b with C_s symmetry is expected to be the lowest energy structure. However, its energy is 0.03 eV higher than that of 10a isomer. The isomer 10c with C_1 symmetry can be viewed as one Si atom capping the 9c isomer. As for $n = 11$, three stable structures denoted as 11a, 11b, and 11c are optimized to be the minima at the energy surface. As shown in Fig. 2, the isomer 11a with C_1 symmetry is found to be the most stable structure. The geometry of 11b

isomer is similar to the 11a isomer, but the energy of 11b is 0.01 eV higher than that of 11a. In addition, isomer 11c with C_s symmetry is of the third most stable structure. The three low-energy isomers for FSi_{12} cluster are plotted in Fig. 2. The calculation shows that the isomer 12a with C_{2v} symmetry is of a ground state structure.

From Figs. 1 and 2, it is interesting to note that the lowest energy structures of FSi_n clusters favor the planar structures for $n = 1 \sim 3$ and 3D structures for $n = 4 \sim 12$. The ground state structure of FSi_n can be obtained by capping one F atom on the ground state structure of FSi_{n-1} for $n \leq 7$, while the lowest energy structures of FSi_n ($n = 8 \sim 12$) can be seen as one F atom substituting for one Si atom of the most stable structure of the Si_{n+1} cluster. The F atom tends to fall into the Si-framework when $n \geq 8$. This property is similar to those of other doped Si clusters, such as Si_nNa ($n \leq 10$).[22]



(¥10^{-4}¥ mol¥cdot¥L¥^{-1}¥)

Fig. 1. (color online) The lowest-energy and low-lying structures of FSi_n ($n = 1 \sim 7$) clusters. The corresponding symmetries, electronic states, and relative energies to the most stable isomers are presented by the B3LYP calculations.

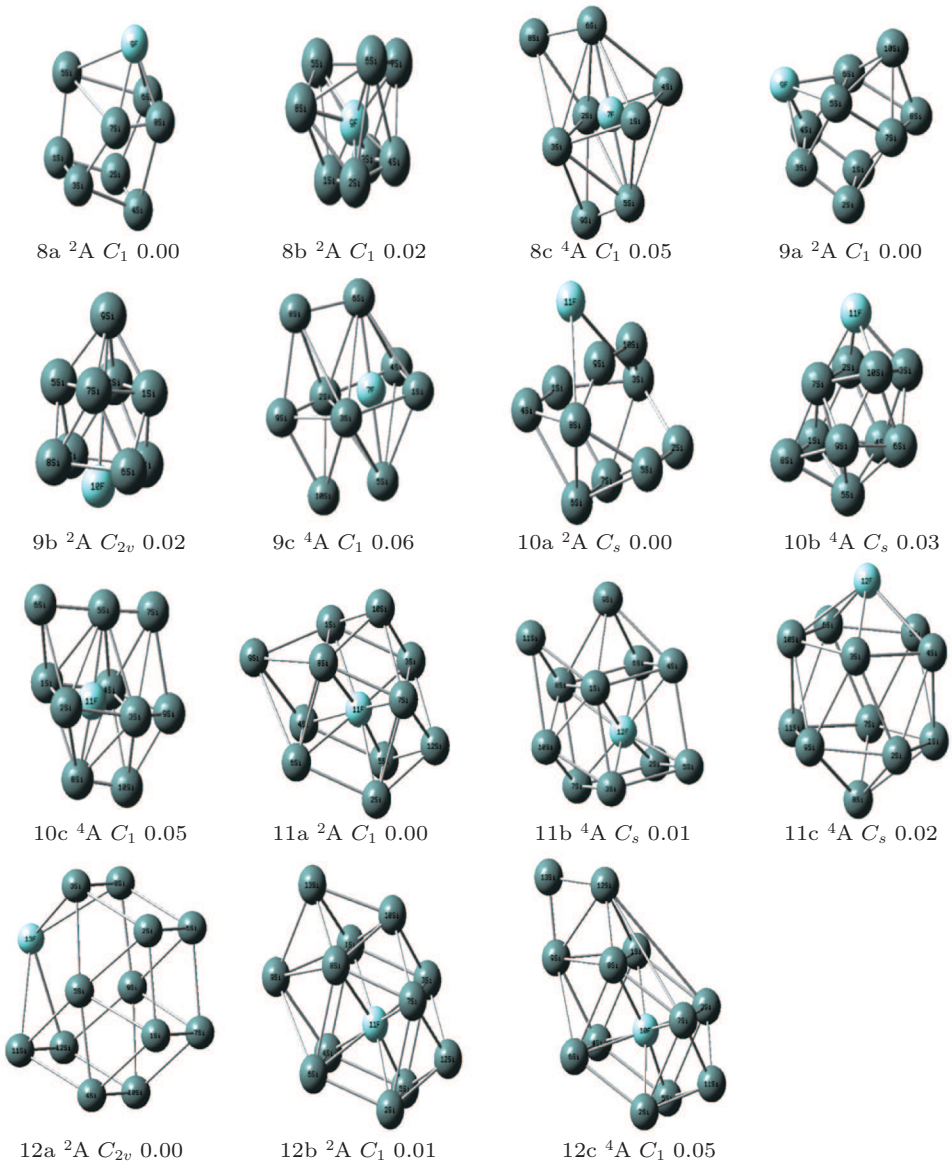


Fig. 2. (color online) The lowest-energy and low-lying structures of FSi_n ($n = 8 \sim 12$) clusters. The corresponding symmetries, electronic states, and relative energies to the most stable isomers are presented by the B3LYP calculations.

The bond between atoms is closely related to the structure. In order to investigate the combination of various structure parameters and bonds, the average bond length of total, the average bond length of Si–F bond, and the average bond length of Si–Si bond are calculated and the results are shown in Fig. 3. It can be seen that the average bond length of Si–Si is between 2.39 Å and 2.80 Å. The average bond length of Si–Si increases as the number of Si atoms increases but more and more slowly. The average bond length of Si–F increases with size increasing, and it can also be seen that the average bond length of Si–F is greater than that of Si–Si, with one Si atom added to the lowest-energy structure on FSi_{n-1} clusters from $n = 8$. The average bond length increases with size increasing gradually, which means that the chemical activities of FSi_n clusters are enhanced. The average bond length sharply drops down when $n = 11$, which is maybe influenced by the chemical bond type and quantity.

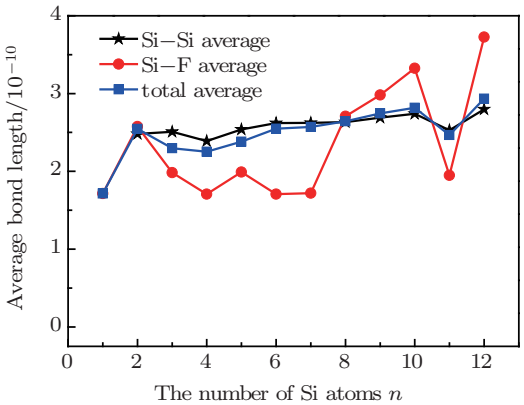


Fig. 3. (color online) Size dependencies of the average bond length for the lowest energy structures of FSi_n ($n = 1 \sim 12$) clusters.

3.2. Relative stabilities

In order to investigate the relative stabilities of the most stable FSi_n ($n = 1 \sim 12$) clusters, we calculate the averaged binding energy E_b, fragmentation energy D, second-order energy difference Δ_2E, and HOMO–LUMO energy gap E_{gap}. The theoretical calculations are summarized in Table 2. Considering the influence of the impurity atom on the pure silicon cluster, we compare the E_b and E_{gap} calculations with the pure Si_{n+1} clusters. The values of E_b for FSi_n and Si_{n+1} cluster can be expressed by the following formula:

$$E_b(Si_{n+1})] = [(n+1)E_k(Si) - E_k(Si_{n+1})]/(n+1), \quad (1)$$

$$E_b(FSi_n)] = [nE_k(Si) + E_k(FSi_n)]/(n+1), \quad (2)$$

where the values of $E_k(Si)$, $E_k(Si_{n+1})$, $E_k(F)$, and $E_k(FSi_n)$ are the total energies of the most stable structures for Si, Si_{n+1}, F, FSi_n clusters, respectively.

Table 2. Calculated values of averaged binding energy (E_b), second-order energy difference (Δ_2E), fragmentation energy (D), and HOMO–LUMO energy gaps (E_{gap}) for the lowest energy structures of FSi_n ($n = 1 \sim 12$) clusters.

Cluster	E_b/eV	Δ_2E/eV	D/eV	E_{gap}/eV
FSi	3.08		6.15 (6.013)[a]	2.01
FSi_2	2.97	–1.16	2.76 (4.777)[b]	1.63
FSi_3	3.21	–0.51	3.92 (5.049)[b]	1.90
FSi_4	3.45	0.93	4.43 (3.920)[b]	2.14
FSi_5	3.46	–1.41	3.49 (3.593)[b]	1.76
FSi_6	3.67	0.93	4.91 (4.409)[b]	1.91
FSi_7	3.70	0.26	3.97 (3.411)[b]	1.79
FSi_8	3.71	–0.13	3.72	1.39
FSi_9	3.72	–0.15	3.84	1.38
FSi_{10}	3.74	–0.02	3.99	1.43
FSi_{11}	3.76	–0.19	4.00	1.26
FSi_{12}	3.80		4.19	1.23

[a]Ref. [23], [b]Ref. [12]

Figure 4 shows the size dependencies of the averaged binding energy E_b for the lowest energy structures of FSi_n and Si_{n+1} ($n = 1 \sim 12$) clusters. As seen from Fig. 3, the values of E_b for FSi_n and Si_{n+1} clusters show the same growing tendency with cluster size n increasing. The values of E_b for FSi_n and Si_{n+1} clusters increase sharply for small clusters ($n = 1 \sim 6$). For $n > 6$, the values of E_b for FSi_n and Si_{n+1} clusters increase smoothly as the cluster size grows. Both curves exhibit small peaks for Si_{n+1} ($n = 6$ and 9) and FSi_n ($n = 1$ and 12) clusters, indicating an enhanced stability over the adjacent neighboring clusters. Furthermore, the values of E_b for the FSi_n clusters are slightly smaller than those of the pure Si_{n+1} clusters for $n = 2 \sim 12$, which implies that the chemical activities of FSi_n clusters are enhanced by F atom doping.

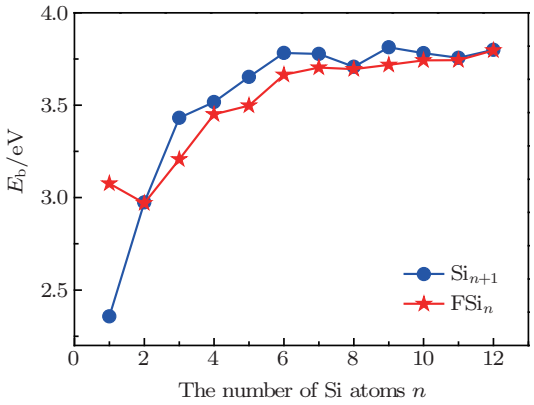


Fig. 4. (color online) Size dependencies of the averaged binding energy E_b for the lowest energy structures of FSi_n ($n = 1 \sim 12$) and Si_{n+1} clusters.

The fragmentation energy D and second-order energy difference Δ_2E are very sensitive quantities that reflect the relative stability of the clusters. In general, the fragmentation energy D and second-order energy difference Δ_2E can be estimated from[24]

$$D(n,n-1) = E_k(FSi_{n-1}) + E_k(Si) - E_k(FSi_n), \quad (3)$$

$$\Delta_2E(FSi_n) = E_k(FSi_{n+1}) + E_k(FSi_{n-1}) - 2E_k(FSi_n), \quad (4)$$

where $E_k(Si)$, $E_k(Sin + 1)$, $E_k(F)$, and $E_k(FSi_n)$ are the total energies of the most stable structures for FSi_{n-1}, Si, FSi_n, FSi_{n+1} clusters, respectively. The size dependence of the fragmentation energy D and the second-order energy difference Δ_2E for the lowest energy structures of FSi_n ($n = 1 \sim 12$) clusters are shown in Fig. 5. From Fig. 5, we can see that the maxima of local fragmentation energy D are found at $n = 4$ and 6, and the Δ_2E for the FSi_n clusters is bigger than for the other neighboring clusters when $n = 4$ and 6. These results mean that there are higher stabilities of FSi_n ($n = 4$, 6) clusters than those of their corresponding neighbors. It is worth pointing out that the relative stability of FSi_6 is the strongest in all the FSi_n ($n = 1 \sim 12$) clusters. Actually, similar results have been reported in $CaSi_6$ and FGe_6 clusters in Refs. [25] and [26].

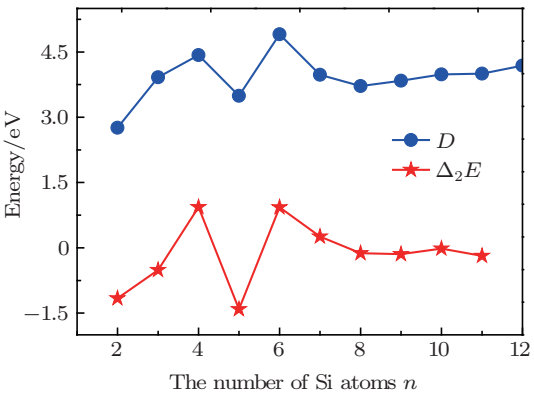


Fig. 5. (color online) Size dependencies of the fragmentation energy D and the second-order energy difference Δ_2E for the lowest energy structures of FSi_n ($n = 1 \sim 12$) clusters.

The energy gap E_{gap} between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is considered to be another powerful parameter that reflects the ability for electrons to jump from the occupied orbital to the unoccupied orbital.[27] A larger E_{gap} corresponds to a closed-shell electronic configuration with higher chemical stability. For the most stable FSi_n clusters, the values of E_{gap} are plotted in Fig. 6. As shown in Fig. 6, the curve of E_{gap} for FSi_n clusters decreases rapidly when the size $n > 6$. Three remarkable peaks at $n = 1$, 4, and 6 for FSi_n clusters are found, which indicate that the FSi, FSi_4, and FSi_6 clusters possess dramatically enhanced chemical stabilities. From Fig. 6, we can also see that the values of E_{gap} of FSi_n clusters are smaller than those of the Si_{n+1} clusters for $n = 2 \sim 12$. This phenomenon means that the doped F atom can enhance the chemical activities of silicon clusters.

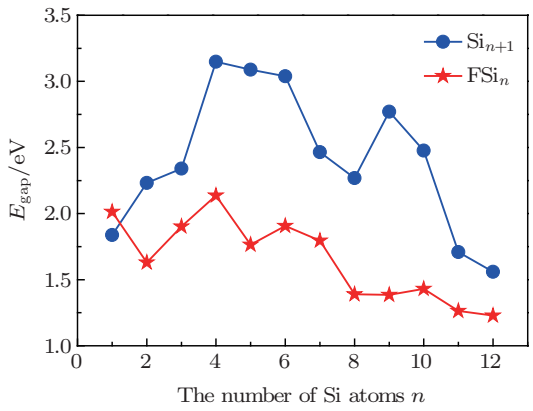


Fig. 6. (color online) Size dependencies of the HOMO–LUMO energy gap E_{gap} for the lowest energy structures of FSi_n ($n = 1 \sim 12$) and Si_{n+1} clusters.

3.3. Electronic properties

The vertical ionization potential (VIP) and vertical electron affinity (VEA) are the most important properties reflecting the size-dependent relationship of electronic structure in cluster physics.[28,29] The VIP of the cluster refers to the binding energy of a neutral cluster losing an electron, a higher value of VIP corresponds to a cluster with higher stability.[30] The VEA reflects the binding energy of a neutral cluster obtaining an electron, which is equal to the total energy difference between the neutral and the anionic cluster. The VIP and VEA are obtained from[31,32]

$$\mathrm{VIP} = E_{(\text{cation at optimized neutral geometry})} - E_{(\text{optimized neutral})}, \quad (5)$$

$$\mathrm{VEA} = E_{(\text{optimized neutral})} - E_{(\text{anion at optimized neutral geometry})}. \quad (6)$$

Next, we calculate the values of VIP and VEA of FSi_n and Si_{n+1} clusters. The calculated results are listed in Table 3. From Table 3, the values of VIP have a decreasing tendency with n increasing. The values of VIP for FSi_n clusters are between 6.86 eV and 8.68 eV, which means that the δ bonds have very strong interaction in clusters. In addition, the values of VIP for the doped FSi_n clusters are lower than those for the equivalent Si_{n+1} clusters, which suggests that doped impurity atoms reduce the stability of host clusters. On the contrary, the values of VEA have a growing trend as a whole with size increasing. It is obvious that the value of VEA increases from 0.74 eV of FSi cluster to 3.29 eV of FSi_7 cluster. So $n = 7$ is the local maximum, which indicates that the chemical activity of FSi_7 cluster is higher than those of neighboring clusters.

Table 3. Values of vertical ionization potential (VIP) and vertical electron affinity (VEA) of the lowest energy Si_{n+1} ($n = 1 \sim 12$) and FSi_n ($n = 1 \sim 12$) clusters; natural population and natural electron configurations of F atom in the lowest energy structures of FSi_n ($n = 1 \sim 12$) clusters.

Cluster	FSi_n		Si_{n+1}		Natural population	Natural electron configuration	
	VIP / eV	VEA / eV	VIP / eV	VEA/ eV		2s	2p
FSi	7.94	0.74 (0.81±0.02)[a]	8.84	2.03	–0.648	1.96	5.69
FSi_2	8.52	1.83 (1.99±0.28)[a]	8.04	1.98	–0.630	1.94	5.68
FSi_3	8.21	2.22 (2.23±0.07)[a]	8.12	2.08	–0.626	1.94	5.69
FSi_4	8.17	2.53 (3.07±0.4)[a]	8.27	1.45	–0.599	1.92	5.68
FSi_5	8.00	2.77 (2.57±0.18)[a]	8.03	1.56	–0.640	1.93	5.71
FSi_6	8.16	2.80 (2.83±0.19)[a]	8.21	1.90	–0.590	1.90	5.68
FSi_7	8.68	3.29 (3.43±0.18)[a]	7.34	1.86	–0.597	1.90	5.69
FSi_8	7.02	2.57 (2.88±0.17)[a]	7.62	2.43	–0.608	1.90	5.70
FSi_9	7.06	2.75 (3.33±0.15)[a]	7.92	2.30	–0.652	1.93	5.72
FSi_{10}	6.94	2.70 (3.74±0.23)[a]	7.35	2.12	–0.617	1.91	5.71
FSi_{11}	7.11	3.17 (2.99±0.19)[a]	7.13	2.89	–0.643	1.91	5.73
FSi_{12}	6.86	2.99	7.03	2.95	–0.642	1.92	5.72

[a]Ref. [11]

Chemical hardness η is established as an electronic quantity. In many cases, chemical hardness η may be used to characterize the relative stability of molecules and aggregate through the principle of maximum hardness (PMH) proposed by Pearson[33] So it is important to discuss the chemical hardness of the cluster. On the basis of a finite-difference approx-

imation and the famous Koopmans theorem,[34] the chemical hardness η is expressed as[35]

$$\eta = (\text{VIP - VEA})/2. \tag{7}$$

In Table 3, we list the calculated results of the chemical hardness η for FSi_n and Si_{n+1} ($n = 1 \sim 12$) clusters. The relationship of η vs n is plotted in Fig. 7. From Fig. 7, it can be seen that the values of η for the doped system show a downward trend as cluster size increases. Particularly, the FSi cluster has the largest chemical hardness of 3.60 eV, which indicates that the cluster is extremely inert and may be useful to fabricate the cluster-assembled nanomaterials.[17] Furthermore, for the pure silicon cluster, it keeps a high hardness in comparison with the FSi_n clusters at $n > 3$. This phenomenon shows that the doped F atom can reduce the chemical hardness of Si_{n+1} cluster, which is in accordance with the previous analysis based on the averaged binding energy E_b.

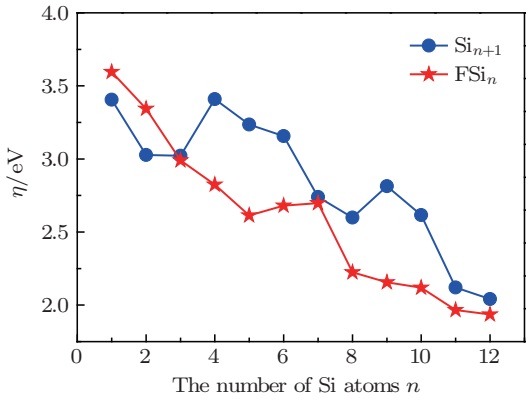


Fig. 7. (color online) Size dependencies of the chemical hardness η for the lowest energy structures of FSi_n ($n = 1 \sim 12$) and Si_{n+1} clusters.

In order to understand the internal charge transfer, we investigate the natural populations (NP) and natural electron configurations (NEC) of the F atom in the lowest energy FSi_n ($n = 1 \sim 12$) clusters. For free Si and F atom, the configurations of valence electrons are $3s^2 3p^2$ and $2s^2 2p^5$ respectively. Here, the charges of 2s and 2p orbitals for the F atom in FSi_n cluster are listed in Table 3. From Table 3, it can be found that the 2s orbital of F atom loses 0.04–0.10 electrons; on the contrary, the 2p orbital of F atom obtains 0.68–0.73 electrons. The NP values for the F atom in the most stable FSi_n isomers are negative ($-0.652e$–$0.590e$). These results indicate that the charges in the most stable FSi_n clusters transfer from Si atoms and 2s orbital of the F atom to 2p orbital of the F atom, namely, the F atom acts as an electron acceptor. This phenomenon is in agreement with the conclusion that the value of electronegativity for the F atom ($\chi_p = 3.98$, $\chi_s = 4.19$) is higher than that of the Si atom ($\chi_p = 1.90$, $\chi_s = 1.92$).[36]

4. Conclusions

The geometrical structures, stabilities, and electronic properties of FSi_n ($n = 1 \sim 12$) clusters are systematically investigated by using the density functional theory at B3LYP/6-311G level. All calculated results can be summarized as follows.

(i) The lowest energy structures of FSi_n clusters favor the planar structures for $n = 1 \sim 3$ and 3D structures for $n = 4 \sim 12$.

(ii) The doping F atom in the FSi_n enhances the chemical activity of the silicon framework, that is to say, the doped impurity atoms reduce the stability of pure Si_{n+1} clusters.

(iii) The HOMO–LUMO gaps of FSi_n clusters are found to be significantly smaller than those of the corresponding Si_{n+1} clusters when $n = 2 \sim 12$, and generally decrease with size increasing. This phenomenon indicates that the metallic characteristics of FSi_n clusters can be enhanced by the F doping.

(iv) Natural population analysis shows that the charges always transfer from Si atoms to F atom in all investigated FSi_n clusters.

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