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Citation: The Journal of Chemical Physics **135**, 184305 (2011); doi: 10.1063/1.3660354
View online: http://dx.doi.org/10.1063/1.3660354
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/135/18?ver=pdfcov
Published by the AIP Publishing

Lowest-energy structures and electronic properties of Na-Si binary clusters from *ab initio* global search

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(Received 20 July 2011; accepted 24 October 2011; published online 14 November 2011)

The ground state structures of neutral and anionic clusters of Na_nSi_m ($1 \le n \le 3$, $1 \le m \le 11$) have been determined using genetic algorithm incorporated in first principles total energy code. The size dependence of the structural and electronic properties is discussed in detail. It is found that the lowest-energy structures of Na_nSi_m clusters resemble those of the pure Si clusters. Interestingly, Na atoms in neutral Na_nSi_m clusters are usually well separated by the Si_m skeleton, whereas Na atoms can form Na-Na bonds in some anionic clusters. The ionization potentials, adiabatic electron affinities, and photoelectron spectra are also calculated and the results compare well with the experimental data.
 [doi:10.1063/1.3660354]

I. INTRODUCTION

Silicon is the most important semiconducting element and is the backbone of the modern microelectronics industry, while sodium is a typical simple metal with a nearly free valence electron. In the form of bulk solid, a few Na-Si alloy phases such as NaSi, $NaSi_{14}$, and Na_4Si_{23} have been reported,[1] and recently Na-Si binary phase diagram has been established.[2] In the past nearly 15 years, Na adsorption on Si surfaces has received considerable interest from both fundamental and technological points of view.[3–16] It has been found that the Na adsorption not only modifies the electronic and optical properties of a Si surface,[4–8,16] but it also results in the reconstruction of the surface structures.[3,9,14,15]

In cluster science, elemental clusters of both Si and Na have been the focus of intensive research;[17–20] however, much less attention has been paid to Na-Si mixed clusters. Similar to the case of silicon surfaces, it would be interesting to examine the effects of Na adsorption on the atomic and electronic structures of Si_n clusters. In a series of pioneer experiments, Kishi *et al.*[21,22] detected the geometric and electronic structures of neutral and anionic Na_mSi_n binary clusters up to n = 14 and m = 5 by means of mass spectroscopy, ionization potential, photoelectron spectroscopy, and reactivity with NO molecules. In addition to experiments, they also carried out *ab initio* MP2/6–31G* calculations to compute the ground state configurations and electronic properties of $NaSi_n$ and $NaSi_n^-$ clusters with n = 1–7. Later, Yu *et al.*[23] have performed a detailed study on the ground state structures and electronic states of $NaSi_6^-$ cluster using a combined technique with photoelectron spectroscopy and *ab initio* calculations.

Stimulated by the experimental progress, *ab initio* calculations have been performed by several groups to further explore the geometric and electronic properties of neutral and charged sodium-silicon binary clusters with up to two Na atoms and/or ten Si atoms.[24–29] In an early study by Wei *et al.*,[24] the most stable structures of $NaSi_n$ and $NaSi_n^+$ ($n \le 10$) clusters have been obtained from molecular dynamics simulations within the framework of density functional theory (DFT) and local density approximation (LDA). Li *et al.* optimized the ground state structures of semiconductor-alkali binary anion clusters X_nA^- (X = Ge and Si; A = K, Na, and Li; n = 1–10) using *ab initio* MP2 method and computed their vertical detachment energies (VDE).[25] Using B3LYP/6–31+G(d) method, Sporea *et al.*[26,27] investigated the equilibrium geometries and electronic properties (including adsorption energies, vertical and adiabatic ionization potentials, electric dipole moments, static dipolar polarizabilities, and population analysis) of Na_mSi_n and $NaSi_n^+$ ($n \le 6$, $m \le 2$). Zhao *et al.*[28] explored the equilibrium geometries and electronic properties of neutral Na_mSi_n ($m+n \le 7$) clusters using DFT calculations at the B3LYP/6–311+G(d) level. Lin *et al.*[29] investigated the molecular structures, electron affinities, and dissociation energies of $NaSi_n$ and $NaSi_n^-$ ($n \le 10$) clusters using different DFT methods with DZP++ basis set.

Despite the above efforts, our current theoretical knowledge on Na-Si binary clusters is still rather limited due to the following reasons: (1) the previous studies were usually limited in the very small size range with up to only six to seven silicon atoms; (2) although the experiments of Kishi *et al.* provided data for the binary clusters with up to four Na atoms, most of the *ab initio* calculations included only one Na atom except for the work of Sporea who considered Na_2Si_n clusters up to n = 6; (3) all cluster configurations in those previous works were constructed from some presumed structures and there was no global optimization for the ground state structures of these clusters. The last point is most critical since the potential energy surface (PES) of the clusters (in particular, the binary clusters) is so complicated that it is difficult to

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obtain their global minima and the best is to perform global search in an unbiased way.

To gain deeper insight into the ground state structures, bonding characteristics, and electronic properties of the Na-Si binary cluster system and to compare with more experimental data, in this paper we have systematically searched the lowest-energy structures of neutral and anionic Na_mSi_n ($2 \le n \le 11$, $0 \le m \le 3$) clusters using genetic algorithm (GA) incorporated within an *ab initio* code of the total energy calculation. The electronic properties including ionization potentials and electron affinities of these clusters have been computed and compared with experiments.

II. COMPUTATIONAL METHODS

The unbiased global search of the most stable configurations of Na_mSi_n ($1 \le n \le 11$, $1 \le m \le 3$) clusters was carried out by using GA[30,31] as implemented in the DMol3 program.[33] The DFT calculations were performed with the double numerical basis including *d*-polarization function (DND) and generalized gradient approximation (GGA) with the Perdew-Burke-Enzerhof (PBE) functional.[34] Self-consistent field calculations were done with a convergence criterion of 10^{-6} a.u. on the total energy. Orbital cutoff was set as 7.0 Å, and the cluster geometries were fully optimized without any symmetry constraint. For most situations, the zero point energy (ZPE) was not included in the total energy.

In the GA search, a number of initial configurations (16 isomers in this work) were generated from scratch. Any two individuals in this population were then chosen as parents to produce a child cluster via a "cut and splice" crossover operation,[28] followed by an optional mutation operation of 35% probability. Two types of mutations are used in this work: (1) give each atom of a cluster a small random displacement and (2) exchange the atom type of a pair of different types of atoms. The child cluster was then relaxed using DFT optimization. In order to keep the diversity of the populations, the locally stable child was selected to replace one of the individuals if they share the same value of inertia I (the tolerance for the I difference is less than 0.04× atomic number); otherwise (the new structure has an inertia different from all existing isomer), replace the highest energy isomer by the new one. Here the inertia is defined as $I = \sum m_i r_i^2$, where r_i is the distance of the ith atom from cluster center and m_i is the mass of the ith atom. We defined the mass of element Si as 1 and the mass of element sodium as 2. For each cluster size, we performed 1000–3000 GA iterations to ensure that the global minimum on the PES is obtained. The number of GA iteration generally increases with cluster size, and relies on the specific chemical composition of the cluster. The details for the application of GA search in cluster physics can be found in the review articles.[29–31]

III. LOWEST-ENERGY STRUCTURES OF Na_nSi_m CLUSTERS

The lowest-energy structures of neutral and anionic Na_nSi_m clusters ($1 \le m \le 11$, $1 \le n \le 3$) are shown in Figs. 1–11. In the following, we discuss the details of these structures in the sequence of the number m of Si atoms. The Cartesian coordinates of all these lowest-energy structures are available online in the Cambridge Cluster Database.[32]

FIG. 1. The lowest energy structures of neutral Na_nSi and anionic Na_nSi^- clusters ($1 \le n \le 3$). Yellow balls are for silicon and blue balls for sodium atoms.

A. Na_nSi_1 and $Na_nSi_1^-$

From our calculations, the equilibrium bond length of a NaSi dimer (quartet spin state) and $NaSi^-$ anion are 2.724 Å and 2.944 Å, respectively. These are comparable to previous DFT calculations. For example, the Na-Si bond length was calculated to be 2.697 Å, 2.724 Å, 2.72 Å, 2.725 Å, and 2.742 Å in Refs. 21, 26–29, respectively, and for the anion it was calculated to be 2.84 Å[22] and 2.909 Å.[29] With two sodium atoms, the neutral Na_2Si cluster forms a Na-Si–Na chain with the Si atom in the middle (see Fig. 1). Our calculated Na-Si bond length is 2.739 Å and it is close to the value (2.711 Å) obtained by Kishi *et al.*[22] using MP2/6–31G(d) method as well as to the value of 2.70 Å obtained by Sporea *et al.*[27] at the level of B3LYP/6–31+G(d). The Na_2Si^- anion has an isosceles triangle configuration (C_{2v}), with the waist and bottom edge lengths of 2.875 Å and 3.743 Å, respectively. The neutral Na_3Si cluster has a roof shape with C_s symmetry (see Fig. 1), in which two terminals Na atoms are separated by the middle Si-Na dimer and the Na-Si-Na-Na dihedral angle is 145.6°. The same structure was found by Zhao *et al.*[28] For $SiNa_3^-$, the three Na atoms bond with each other and form a triangle. The Si atom sits on the top of the Na_3 triangle base, forming a trigonal pyramid (C_{3v}). This is an interesting case as the number of valence electrons is 8, and it corresponds to electronic shell closure in a spherical Jellium model.

B. Na_nSi_2 and $Na_nSi_2^-$

As shown in Fig. 2, the neutral $NaSi_2$ cluster (with doublet spin state) adopts an isosceles triangle configuration. From our calculations, the Si-Na bond length is 2.922 Å and Si-Si bond length is 2.157 Å. Both the values compare well with the previously reported Si-Na bond lengths of 2.9 Å[27] and 2.905 Å,[29] and Si-Si bond length of 2.124 Å[21] and 2.121 Å.[29] The anionic $NaSi_2^-$ cluster retains the isosceles

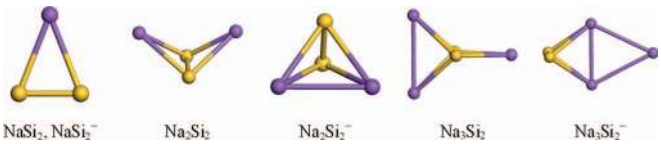

FIG. 2. The lowest energy structures of neutral Na_nSi_2 and anionic $Na_nSi_2^-$ clusters ($1 \le n \le 3$). Yellow (blue) ball represent silicon (sodium) atoms.

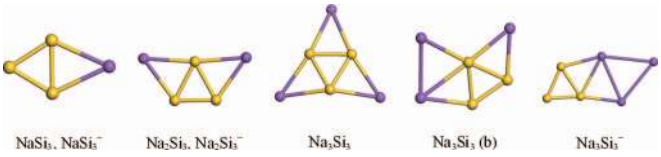

FIG. 3. The lowest energy structures of neutral Na_nSi_3 and anionic $Na_nSi_3^-$ clusters ($1 \le n \le 3$). Na_3Si_3 (b) denotes the most stable structure at room temperature. Yellow (blue) balls represent silicon (sodium) atoms.

triangle, and the Si-Na and Si-Si bond lengths become 2.841 Å and 2.186 Å, respectively, in agreement with the previous results of 2.783 Å and 2.188 Å in Ref. 22.

Similar to Na_3Si, the most stable structure of Na_2Si_2 cluster has a roof shape (see Fig. 2) and the dihedral angle of Na-Si-Si-Na is 106.1°. The calculated Na-Si bond length in Na_2Si_2 is 2.875 Å that is close to the previous values of 2.854 Å[22] and 2.87 Å.[27] Its Si-Si bond length is 2.193 Å from our calculation and 2.19 Å in Ref. 22. Again, analogous to $SiNa_3^-$, the $Na_2Si_2^-$ cluster anion transforms into a trigonal pyramid with Na-Na, Si-Na, and Si-Si bond lengths of 3.422 Å, 3.024 Å, and 2.188 Å, respectively.

The lowest-energy configuration of Na_3Si_2 cluster is an edge-capped distorted tetrahedron with C_{2v} symmetry (see Fig. 2), in which the three Na atoms are separated by the Si_2 dimer. The same structure was reported by Zhao *et al.*[28] Interestingly, the $Na_3Si_2^-$ anion also adopts a C_{2v} configuration as its neutral counterpart; however, the Si_2 dimer goes to a side of the tetrahedron and the three Na form an equilateral triangle.

C. Na_nSi_3 and $Na_nSi_3^-$

Interestingly, all of the neutral and anionic Na_nSi_3 ($n = 1$–3) clusters adopt planar configurations (see Fig. 3). The most stable structures of $NaSi_3$ and $NaSi_3^-$ share the same rhombus shape with some distortion (C_{2v} symmetry). Same structures were suggested previously in Refs. 26–29. From our calculations, the Na-Si bond length is 2.877 Å which is in line with the previous values of 2.88 Å in Ref. 27 and 2.874 Å in Ref. 29. For $NaSi_3^-$, the Na-Si bond length is shortened by

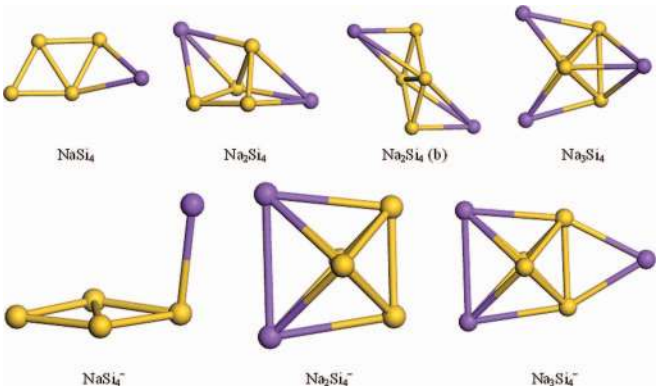

FIG. 4. The lowest energy structures of neutral Na_nSi_4 and anionic $Na_nSi_4^-$ clusters ($1 \le n \le 3$). Na_2Si_4 (b) denotes the most stable structure at room temperature. Yellow (blue) balls represent silicon (sodium) atoms.

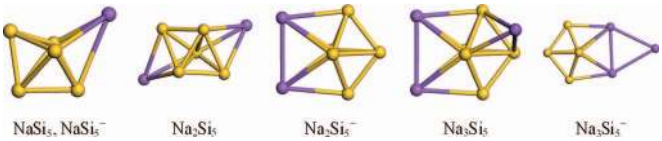

FIG. 5. The lowest energy structures of neutral Na_nSi_5 and anionic $Na_nSi_5^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

0.031 Å, while Si-Si bond length is elongated by 0.143 Å and 0.008 Å with respect to the neutral cluster.

The ground state structure of both Na_2Si_3 and $Na_2Si_3^-$ is a trapezoid with C_{2v} symmetry; this is in agreement with the previous calculations in Refs. 22, 26–28. The Na-Si bond lengths in neutral Na_2Si_3 cluster are 2.814 Å and 2.856 Å from our calculations, which compare well with the previous values of 2.80 Å and 2.84 Å in Ref. 27 and 2.829 Å and 2.842 Å in Ref. 22. The spin state of $Na_2Si_3^-$ is doublet and its Na-Si bond lengths are 2.928 Å and 2.955 Å.

The planar structure of Na_3Si_3 has C_{3v} symmetry; its three Na atoms are symmetrically separated by the central Si_3 triangle tilted with a small off-plane angle. The previous calculations by Zhao *et al.*[28] proposed a different planar configuration for Na_3Si_3 (shown as Na_3Si_3 (b) in Fig. 3). However, we find this isomer to be 0.12 eV less stable than our lowest-energy C_{3v} structure. At room temperature of 298 K, after taking into account the Gibbs free energy calculated from the vibrational frequencies, this isomer predicted by Zhao *et al.* becomes more favorable.

The ground state configuration of $Na_3Si_3^-$ is rather different from Na_3Si_3 and it can be viewed as a planar combination of a Na_3 triangle and a Si_3 triangle. It is noteworthy that the sodium atoms tend to be well separated in the neutral Na_nSi_m clusters, whereas they can stay together in the negatively charged clusters. Natural population analysis (NPA) shows that each Na atom loses about 0.6 e in the neutral Na_3Si_3 cluster. In the anionic $Na_3Si_3^-$ cluster, the on-site charge for the two Na atoms bonded with Si_3 triangle is ∼0.29 e, whereas the Na atom far away from Si carries a negative charge of about −0.35 e. In short, in the anionic Na-Si clusters, there is less Coulomb repulsion between Na atoms with regard to the neutral clusters. In order to further check these results, we performed natural population analysis on NaSi and $NaSi^-$ clusters. For the neutral NaSi cluster, Na atom loses 0.38 electrons, while Si atom gains 0.38 electrons. When the cluster carries a negative charge, the charge distribution on Na atom changes to −0.53 e and Si atom is −0.47 e. In other words, in the anionic clusters, there is less charge transfer from Na atom to Si atom due to the presence of the extra electron. In the larger anionic clusters with

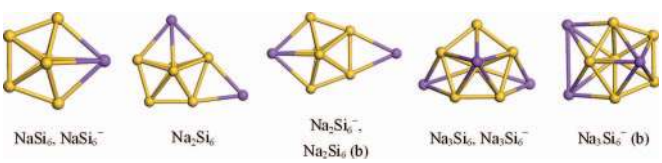

FIG. 6. The lowest energy structures of neutral Na_nSi_6 and anionic $Na_nSi_6^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

FIG. 7. The lowest energy structures of neutral Na_nSi_7 and anionic $Na_nSi_7^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

more than one Na atoms, less Coulomb repulsion between Na atoms with regard to the neutral clusters is anticipated and that has the tendency to favor clustering of Na atoms in some of the cases.

D. Na_nSi_4 and $Na_nSi_4^-$

The most stable structures of both $NaSi_4$ and $NaSi_4^-$ can be considered as a Si_4 rhombus with one Na adatom (see Fig. 4). The Na atom is nearly located within the Si_4 plane in the neutral cluster, and it almost sits perpendicular to Si_4 plane (the angle between the Na-Si bond and the Si_4 basal plane being 83.8°) in the anionic case. Previously, a pyramid-like structure was predicted for $NaSi_4$,[26–29] but it is less stable than our present structure by 0.095 eV. Moreover, the present structure was suggested as a metastable isomer in Ref. 26. Our most stable structure for $NaSi_4^-$ is similar to the one obtained by Lin *et al.*,[29] but it is different from the prediction of a square pyramid by Kishi *et al.*[22]

The neutral Na_2Si_4 cluster adopts a face-capped trigonal bipyramid structure with some distortion, in which two Na atoms are separated by the Si_4 roof. This structure is the same as that obtained in Refs. 27 and 28, but it is different from a bi-capped rhombus structure (C_{2h}) reported in Ref. 26, which is shown as Na_2Si_4 (b) in Fig. 4. After including the Gibbs free energy at room temperature, this C_{2h} isomer becomes more stable than the face-capped trigonal bipyramid by 0.037 eV. For $Na_2Si_4^-$, the two Na and two Si atoms constitute an isosceles trapezoid. The remaining two Si atoms are located above and below the center of the trapezoid, forming a distorted octahedron.

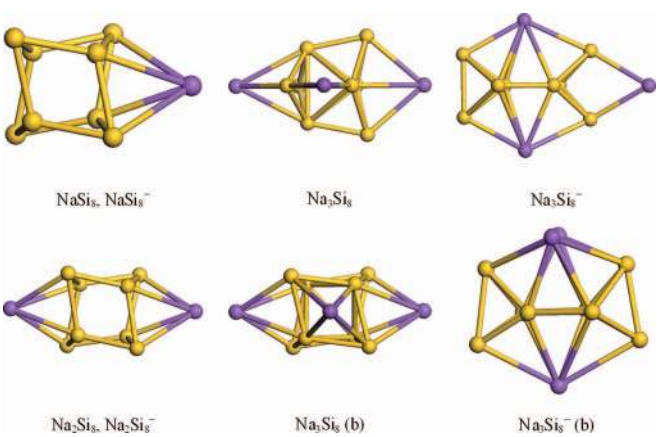

FIG. 8. The lowest energy structures and selected metastable isomers of neutral Na_nSi_8 and anionic $Na_nSi_8^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

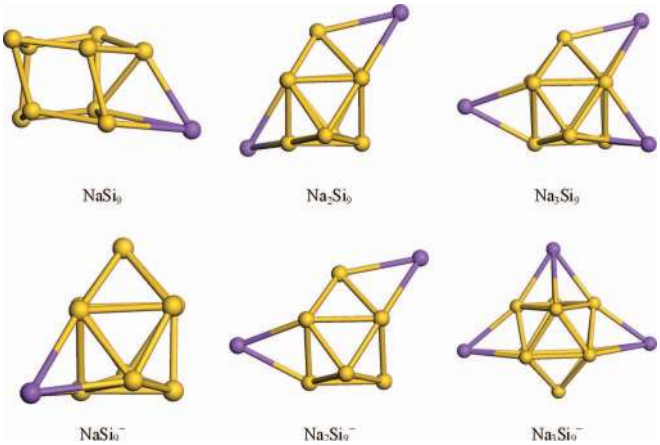

FIG. 9. The lowest energy structures of neutral Na_nSi_9 and anionic $Na_nSi_9^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

In Na_3Si_4, the third Na atom locates on the face of the Na_2Si_4 octahedron, whereas the two original Na atoms break the Na-Na bond and separate. Meanwhile, the third Na in $Na_3Si_4^-$ is edge-capped on the $Na_2Si_4^-$ structure without changing other parts of the configuration. The present structure of Na_3Si_4 is the same as the one reported in Ref. 28.

E. Na_nSi_5 and $Na_nSi_5^-$

As shown in Fig. 5, the lowest-energy structures of $NaSi_5$ and $NaSi_5^-$ are similar with C_s symmetry and both can be viewed as a Si_5 trigonal bipyramid face-capped with one Na. The same configuration was found before.[26,28,29] Similarly, the most stable structures of both Na_2Si_5 and $Na_2Si_5^-$ can be obtained by face-capping a trigonal bipyramid of Si_5 with two Na atoms. In Na_2Si_5 the two Na stay at the opposite faces, while the two Na atoms sit on one side and form a dimer in the case of $Na_2Si_5^-$. Our calculated structure of Na_2Si_5 coincides with the one reported in Ref. 28, but it is slightly different from the C_s structure reported in Ref. 26 in which the two Na atoms are located on different faces of the trigonal bipyramid. The structures of Both Na_3Si_5 and $Na_3Si_5^-$ can

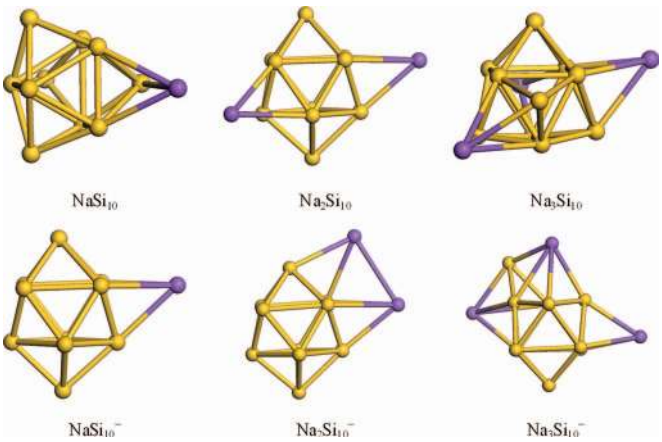

FIG. 10. The lowest energy structures of neutral Na_nSi_{10} and anionic $Na_nSi_{10}^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

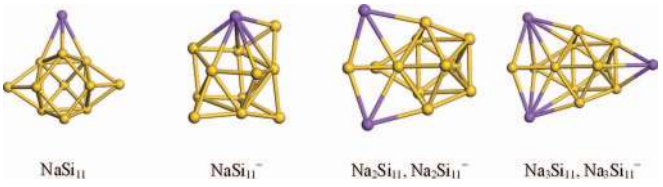

FIG. 11. The lowest energy structures of neutral Na_nSi_{11} and anionic $Na_nSi_{11}^-$ clusters ($1 \le n \le 3$). Yellow (blue) balls represent silicon (sodium) atoms.

be constructed by adding one Na atom on $Na_2Si_5^-$ cluster. In the neutral case, the third Na atom is capped on one of the Si_3 triangular face; while for the latter, the third Na atom is attached to two Na atoms, forming a Na_3 triangle.

F. Na_nSi_6 and $Na_nSi_6^-$

Starting from $NaSi_6$ cluster, the lowest-energy structures are mainly based on those of bare Si clusters and the addition of Na atoms or extra charge does not result in significant change in the cluster configuration. Similar to Si_7 cluster,[35] the structures of $NaSi_6$ and $NaSi_6^-$ are pentagonal bipyramids (see Fig. 6). The same configurations were found for $NaSi_6$ (Refs. 26–29) and $NaSi_6^-$ (Ref. 29) before. Both the ground state structures of Na_2Si_6 and $Na_2Si_6^-$ can be obtained by adding a bridged Na atom, but they are added at different places (see Fig. 6). Previously, it was argued that these two configurations are nearly degenerate with the energy difference of only 0.01 eV;[26] however, our calculations yield a difference of 0.11 eV. Again, the C_s structures of Na_3Si_6 and $Na_3Si_6^-$ are based on the pentagonal bipyramid of Si_7. In this case, one Na atom sits on the top of the bipyramid and the other two Na atoms cap on the two symmetric faces of the pentagonal bipyramid. The isomer of $Na_3Si_6^-$ is 0.021 eV energy higher, and their difference is two Na atoms' arrangement.

G. Na_nSi_7 and $Na_nSi_7^-$

The ground state C_{2v} structure of $NaSi_7$ can be achieved by edge-capping a Na atom to the pentagonal bipyramid of Si_7 cluster. However, with one extra charge, the anionic $NaSi_7^-$ cluster undergoes significant structural change and transforms into a two-interlinked tetrahedral configuration. These two structures were previously proposed by Kishi *et al.*[21] and Lin *et al.*,[29] whereas Kishi *et al.* did not observe structural reconstruction for $NaSi_7^-$.[22] Na_2Si_7 and $Na_2Si_7^-$ share the same C_s configuration, which can be constructed from the most stable structure of bare Si_6 cluster (i.e., a face-capped trigonal bipyramid)[35] with one edge-capped Si atom and two symmetrically side-capped Na atoms (see Fig. 7). Addition of one more Na atom on the face of Si_4 rhombus of Na_2Si_7 configuration leads to the most stable structure of Na_3Si_7. Surprisingly, the anion $Na_3Si_7^-$ cluster adopts a completely different configuration (see Fig. 7) in which the three Na atoms constitute a triangle and six Si atoms separate into two parts: one with four Si atoms and another with two. Within the size range considered, this is the only structure that Si atoms are separated.

H. Na_nSi_8 and $Na_nSi_8^-$

It has been known that bare Si_8 cluster possesses a tetra-capped tetrahedron configuration.[35] According to our calculations, the structures of all $Na_nSi_8^-$ clusters except for $Na_3Si_8^-$ can be obtained by face-capping a certain number of Na atoms on the tetra-capped tetrahedron of Si_8 (see Fig. 8). The same configuration was reported for $NaSi_8$ and $NaSi_8^-$ previously by Lin *et al.*[29] In the D_{2d} configuration of Na_2Si_8 and $Na_2Si_8^-$, the two Na atoms locate on the two sides of Si_8, while in Na_3Si_8 cluster, the third Na atom sits in the middle. There are two nearly degenerate isomers for Na_3Si_8, that is, the third Na edge-capped on Si_8 (C_s) is more stable than the situation of face-capped Na (Na_3Si_8 (b) in Fig. 8, C_2 symmetry) by 0.001 eV. The structure of $Na_3Si_8^-$ differs significantly from those of other clusters. It consists of two Si_4 tetrahedra connected by two middle Na atoms and three Si-Si bonds; the third Na atom is edge-capped to one of the Si_4 tetrahedra. A similar structure in which the third Na atom sits in the middle ($Na_3Si_8^-$ (b) in Fig. 8) is only 0.002 eV less stable than the ground state one.

I. Na_nSi_9 and $Na_nSi_9^-$

The lowest-energy structure of $NaSi_9$ can be constructed from a distorted pentagonal bipyramid of Si_7 by capping two Si atoms and one Na atom. This structure is the same as that in Ref. 29. With one extra charge, the anionic $NaSi_9^-$ adopts a different configuration with C_s symmetry, which is obtained by adding one Na atom on a triangle face of tricapped trigonal prism of a bare Si_9 cluster. This configuration is more stable than the cage structure proposed in Ref. 29 by 0.181 eV. Adding a sodium atom on the top of the trigonal prism leads to another metastable isomer of $NaSi_9^-$, which was also considered by Lin *et al.*[29] and it is 0.154 eV higher in energy than the lowest-energy one. The ground state structures of both Na_2Si_9 and $Na_2Si_9^-$ are obtained by adding one Na atom on the structure of $NaSi_9^-$, whereas the detailed arrangements of these two Na atoms are different in the neutral and anionic clusters (see Fig. 9). The lowest-energy structures of Na_3Si_9 (C_s) and $Na_3Si_9^-$ (C_{2v}) are based on tricapped trigonal prism of Si_9 which is capped by three Na atoms in different ways (see Fig. 9). Except for $NaSi_9$, all other five structures share the same Si_9 skeleton.

J. Na_nSi_{10} and $Na_nSi_{10}^-$

The bare Si_{10} cluster is known to adopt a tetracapped trigonal prism configuration, while the bicapped square antiprism is a metastable isomer.[35,36] From our GA search, the structures of neutral and anionic Na_nSi_{10} clusters are based on one of these two Si_{10} skeletons. Among them, $NaSi_{10}$ and Na_3Si_{10} can be obtained by capping one or three Na atoms on the tetra-capped trigonal prism of Si_{10}. On the other hand, capping one to three Na atoms of the bicapped square antiprism of Si_{10}

TABLE I. The IP and AEA of Na_nSi_m (n = 1–3, m = 1–11) clusters. The experimental values from Refs. 21 and 22 are given in parentheses for comparison.

Cluster	IP (eV)	AEA (eV)
NaSi	6.452(5.97 – 6.42)	0.964
$NaSi_2$	7.122(>6.42)	1.483
$NaSi_3$	6.843(>6.42)	1.717
$NaSi_4$	6.102(5.91 – 6.42)	1.571(1.30 ± 0.05)
$NaSi_5$	7.007(>6.42)	2.299(2.45 ± 0.05)
$NaSi_6$	6.637(5.99 – 6.42)	1.913(1.90 ± 0.06)
$NaSi_7$	5.854(5.45 ± 0.06)	1.901(1.94 ± 0.04)
$NaSi_8$	6.993(>6.42)	2.704(2.44 ± 0.13)
$NaSi_9$	6.442(>6.42)	2.706(2.66 ± 0.08)
$NaSi_{10}$	6.174(5.77 ± 0.02)	2.578(2.57 ± 0.22)
$NaSi_{11}$	6.371(5.99 – 6.42)	2.697(2.59 ± 0.25)
Na_2Si	5.029	0.748
Na_2Si_2	5.818(5.60 ± 0.02)	0.647
Na_2Si_3	5.869(5.51 ± 0.07)	0.751
Na_2Si_4	5.964(5.42 ± 0.02)	1.386
Na_2Si_4 b	5.499(5.42 ± 0.02)	1.386
Na_2Si_5	6.249(5.85 ± 0.07)	1.217(1.35 ± 0.05)
Na_2Si_6	5.617(5.37 ± 0.02)	1.137(1.46 ± 0.03)
Na_2Si_6 b	5.788(5.37 ± 0.02)	1.435(1.46 ± 0.03)
Na_2Si_7	6.031(5.99 – 6.42)	1.343(1.61 ± 0.09)
Na_2Si_8	6.214(5.77 ± 0.02)	1.579(1.06 ± 0.04)
Na_2Si_9	6.271(5.99–6.42)	2.018(1.85 ± 0.05)
Na_2Si_{10}	6.219(5.99–6.42)	1.503(1.78 ± 0.02)
Na_2Si_{11}	6.095(5.99–6.42)	2.309
Na_3Si	4.874	0.865
Na_3Si_2	4.121	1.040
Na_3Si_3	3.632(4.58 ± 0.02)	1.061
Na_3Si_3(b)	4.480(4.58 ± 0.02)	1.231
Na_3Si_4	5.316(5.01 ± 0.05)	1.142
Na_3Si_5	4.713(4.5 ± 0.02)	1.551(2.2 ± 0.04)
Na_3Si_6	5.580(5.23 ± 0.06)	1.633(1.51 ± 0.05)
$Na_3Si_6^-$(b)		1.681(1.51 ± 0.05)
Na_3Si_7	4.830(4.7 ± 0.02)	1.958(2.41 ± 0.31)
Na_3Si_8	4.751(4.47 ± 0.04)	1.483(2.02 ± 0.14)
Na_3Si_8(b)	4.853(4.47 ± 0.04)	1.661(2.02 ± 0.14)
$Na_3Si_8^-$(b)		1.581(2.02 ± 0.14)
Na_3Si_9	5.582(5.85 ± 0.06)	2.093(2.02 ± 0.14)
Na_3Si_{10}	4.955(4.67 ± 0.04)	1.700(1.95 ± 0.13)
Na_3Si_{11}	5.574(5.45)	1.987

leads to the most stable configurations of $NaSi_{10}^-$, Na_2Si_{10}, $Na_2Si_{10}^-$, and $Na_3Si_{10}^-$. It is noteworthy that one of the top Si atoms in the bicapped square antiprism skeleton of $Na_3Si_{10}^-$ is replaced by a Na atom. Our theoretical prediction for the most stable structures of $NaSi_{10}$ and $NaSi_{10}^-$ agree with previous calculations by Lin *et al.*[29]

K. Na_nSi_{11} and $Na_nSi_{11}^-$

The bare Si_{11} cluster is known to adopt the distorted pentacapped trigonal prism configuration.[36] Capping one Na atom on this Si_{11} skeleton leads to the most stable structure of $NaSi_{11}$. However, the structure of anionic $NaSi_{11}^-$ is significantly different. It is formed by a $NaSi_8$ cage face-capped with three Si atoms (see Fig. 11). For the other four clusters (Na_2Si_{11}, $Na_2Si_{11}^-$, Na_3Si_{11}, and $Na_3Si_{11}^-$), the lowest-energy configurations share the same Si_9 skeleton of tricapped trigonal prism. Moreover, the neutral and anionic clusters with two or three Na atoms have the same structure. Previously, there was no theoretical study on Na_nSi_{11} clusters and the sizes beyond.

IV. SIZE-DEPENDENT ELECTRONIC PROPERTIES

To further explore the electronic properties of Na_nSi_m clusters, the vertical ionization energies (IPs) and adiabatic electron affinities (AEAs) of neutral Na_nSi_m clusters ($1 \le n \le 3$, $1 \le m \le 11$) are calculated. Our theoretical results are summarized in Table I, along with the experimental data by Kishi *et al.*[21,22] for comparison. Figure 12 plots the ionization energies of $NaSi_n$, Na_2Si_n, and Na_3Si_n clusters as a function of the cluster size n. Here, the theoretical IP values for Na_3Si_3 and Na_2Si_4 were calculated using their most stable structures at room temperature, i.e., the isomers (b). Generally speaking, the agreement between theory and experiment is reasonable, and it is better for the $NaSi_n$ and Na_3Si_n clusters.

For the IPs of $NaSi_n$ clusters, both our first-principles calculations and experiments reveal that there are two peaks at n = 5 and 8 and three valleys at n = 4, 7, and 10, which may be related to the relative stability of pure Si_n clusters. It is well known that Si_4, Si_7, and Si_{10} are relatively stable.[35] Thus, the additional valence electron donated by the extra Na atom could be easily ionized, resulting in low IP values. For

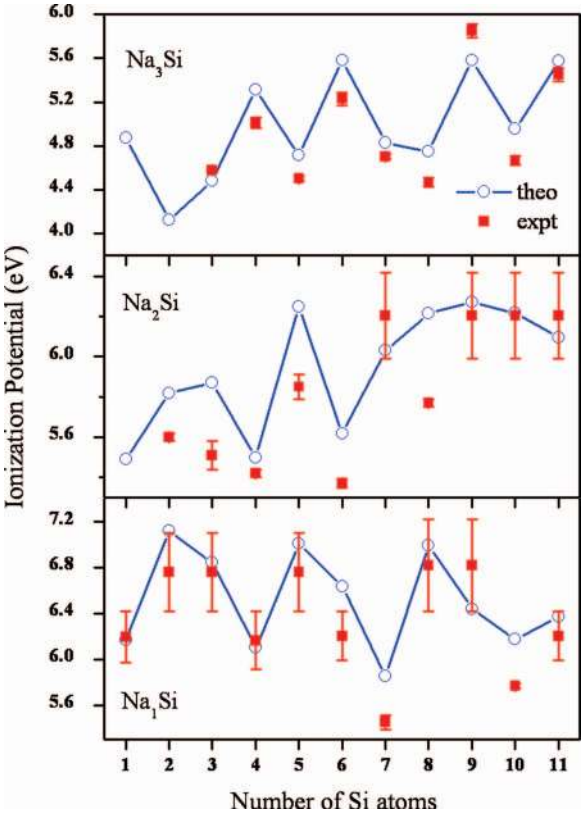

FIG. 12. Vertical ionization potentials of $NaSi_n$, Na_2Si_n, and Na_3Si_n clusters ($1 \le n \le 3$). Red squares with error bar are experimental data by Kishi *et al.*;[21] blue circles connected by solid line are our theoretical values.

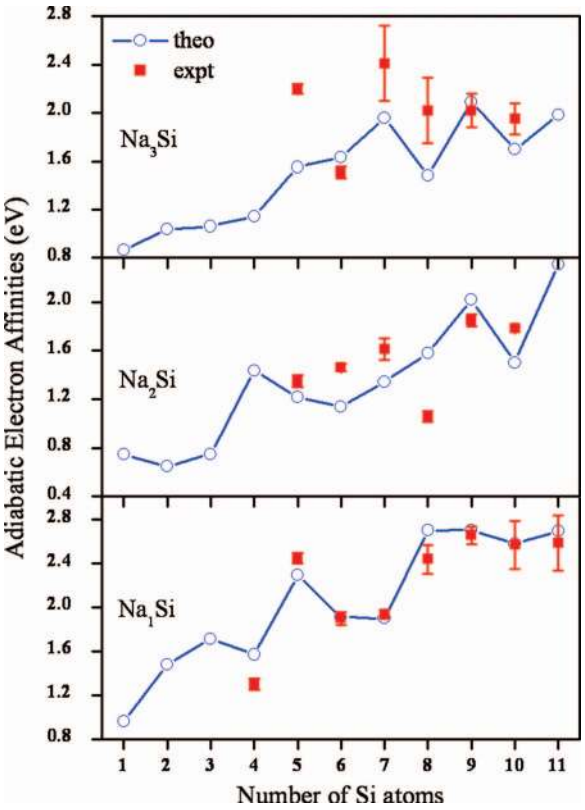

FIG. 13. Adiabatic electron affinities of $NaSi_n$, Na_2Si_n, and Na_3Si_n clusters ($n \leq 11$). Red squares with error bar are experimental data by Kishi *et al.*;[22] blue circles connected by solid line are our theoretical values.

Na_2Si_n, our theoretical IP values are usually higher than the corresponding experiment data. Our calculations successfully reproduced the minimum at $n = 6$, but failed to describe the detailed size-dependent variation of IP data. Both theoretical and experimental IPs of Na_3Si_n clusters exhibit oscillations, with valleys at $n = 3$, 5, 7, 8, and 10 and peaks at $n = 4$, 6, and 9.

Figure 13 displays the adiabatic electron affinities of $NaSi_n$, Na_2Si_n, and Na_3Si_n clusters. Our theoretical calculations roughly agree with the experimental data,[22] especially for $NaSi_n$. For all of the Na_mSi_n clusters with three choice of m, the AEAs generally grow with cluster size n except for several local minima (e.g., $n = 4$, 6, and 7 for $NaSi_n$, $n = 6$ and 10 for Na_2Si_n, and $n = 8$ for Na_3Si_n). For both IPs and AEAs, the discrepancy between theory and experiment might be partially explained by the temperature effect, that is, our theoretical prediction is made for the lowest-energy structures at zero temperature, while cluster beam experiments have been carried out with finite temperature at which some other low-lying isomer may become more favorable. For example, the IPs calculated using zero-temperature structures for Na_3Si_3 and Na_2Si_4 do not agree with experiment. However, for some clusters, inclusion of temperature effect via Gibbs free energy does not improve the agreement with experiments for IP or AEA. Thus, the remaining discrepancy between theoretical and experimental results (especially AEA) might also be attributed to the methodology (usage of DMol3 program, DND basis set, and GGA-PBE functional).

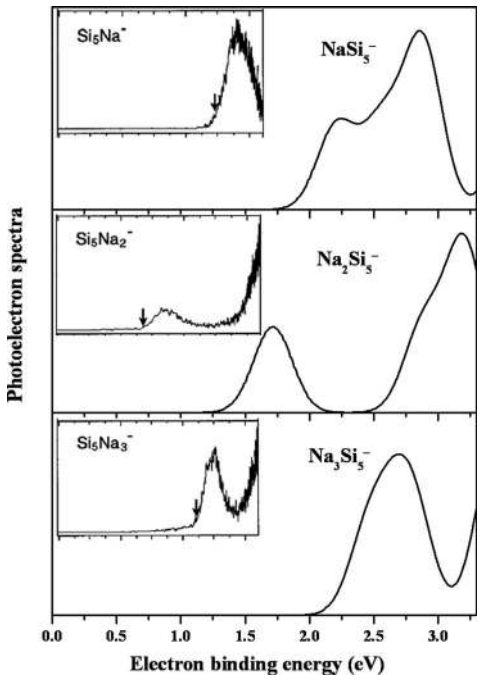

FIG. 14. Simulated photoelectron spectra of $Na_nSi_5^-$ clusters ($n = 1$–3). The experimental photoelectron spectra, taken from Ref. 22, are shown in inset using the same energy scale (from 0.0 to 3.25 eV).

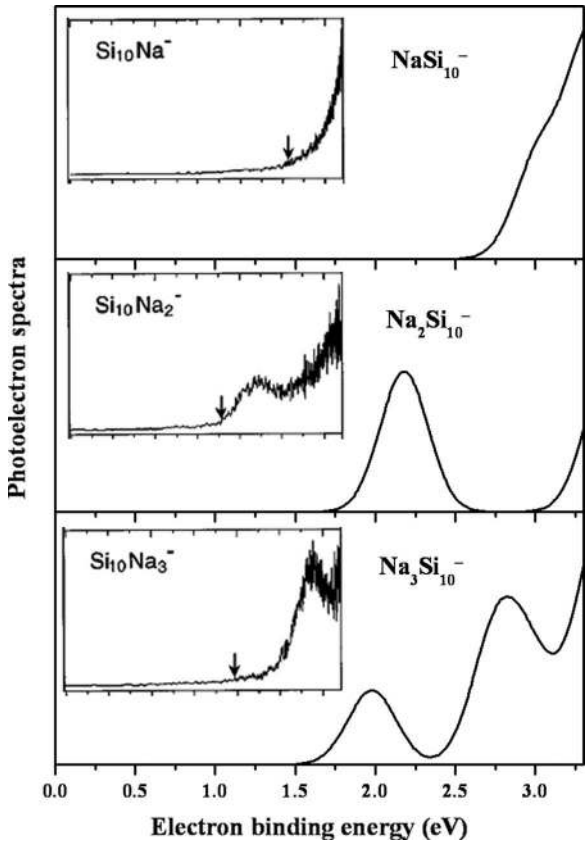

FIG. 15. Simulated photoelectron spectra of $Na_nSi_{10}^-$ clusters ($n = 1$–3). The experimental photoelectron spectra, taken from Ref. 22, are shown in inset using the same energy scale (from 0.0 to 3.25 eV).

TABLE II. Binding energies (BEs) of neutral and anionic Na_nSi_m clusters (n = 1–3, m = 1–11).

Cluster	BE of neutral (eV/atom)	BE of anion (eV/atom)
NaSi	0.585	1.067
$NaSi_2$	1.701	2.204
$NaSi_3$	2.189	2.618
$NaSi_4$	2.51	2.831
$NaSi_5$	2.787	3.17
$NaSi_6$	2.927	3.201
$NaSi_7$	3.004	3.241
$NaSi_8$	3.046	3.346
$NaSi_9$	3.116	3.386
$NaSi_{10}$	3.227	3.461
$NaSi_{11}$	3.203	3.427
Na_2Si	0.82	1.069
Na_2Si_2	1.738	1.9
Na_2Si_3	2.131	2.278
Na_2Si_4	2.32	2.551
Na_2Si_5	2.678	2.852
Na_2Si_6	2.747	2.89
Na_2Si_7	2.832	2.981
Na_2Si_8	2.940	3.098
Na_2Si_9	3.02	3.204
Na_2Si_{10}	3.107	3.232
Na_2Si_{11}	3.101	3.279
Na_3Si	0.911	1.127
Na_3Si_2	1.532	1.740
Na_3Si_3	1.896	2.073
Na_3Si_4	2.203	2.367
Na_3Si_5	2.439	2.633
Na_3Si_6	2.538	2.719
Na_3Si_7	2.642	2.838
Na_3Si_8	2.769	2.904
Na_3Si_9	2.902	3.077
Na_3Si_{10}	2.937	3.068
Na_3Si_{11}	3.004	3.146

To further compare with experimental results,[22] we simulated the photoelectron spectra (PES) of the anionic $Na_mSi_n^-$ clusters from their electronic density of states using the theoretical approach described in Ref. 37. As two representatives, the PES of anionic $Na_nSi_5^-$ and $Na_nSi_{10}^-$ clusters (n = 1–3) are compared with experimental curves[22] in Figs. 14 and 15, respectively. Qualitatively, our theoretical simulation reproduces the features of experimental PES. For example, the first PES peak of $Na_2Si_{10}^-$ is located at about 2.2 eV from experiment (Fig. 15), while our first-principles calculations predict a peak value of 2.18 eV. Similar agreement is found for other $Na_mSi_n^-$ clusters, which demonstrates the validity of our theoretical calculations. Note that some low-intensity peaks are not distinctly shown in experimental spectra (e.g., the first peak in the PES of $Na_3Si_{10}^-$) due to limitation of experimental resolution.

We also calculated the binding energy of Na_nSi_m ($1 \le n \le 3$, $1 \le m \le 11$) neutral and anionic clusters. The results are listed in Table II. It is noteworthy that the binding energy and IP have a decreasing trend with an increase in the number of Na atoms, though for Na_2Si_n in the larger size range the IP tends to have similar values as for $NaSi_n$.

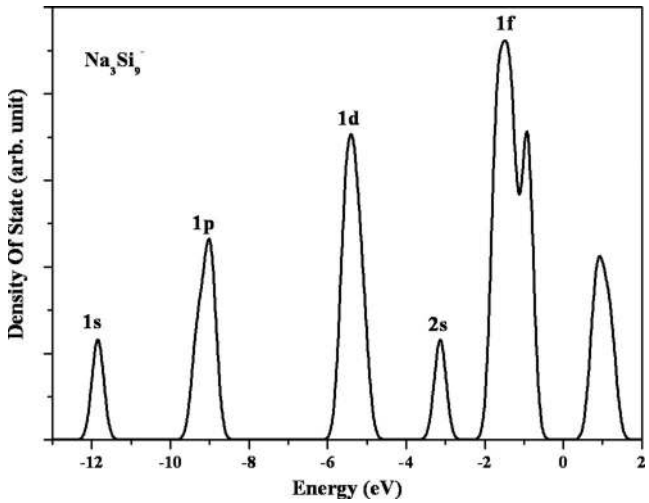

FIG. 16. Electron density of states of the $Na_3Si_9^-$ cluster (with Gaussian broadening of 0.15 eV). The electronic shells (1*s*, 1*p*, 1*d*, etc.) are labeled.

We also find that there are some correlation between the cluster stability and the number of valence electrons. For example, the $Na_3Si_9^-$ cluster possesses a relatively large binding energy of 3.077 eV/atom and a largest AEA of 2.093 eV among $Na_3Si_n^-$, corresponding to high stability. This may be related to its forty valence electrons, which is a close-shell magic number predicted by the jellium model. The electronic states of the $Na_3Si_9^-$ cluster are plotted in Fig. 16. Clearly, the molecular orbitals of valence electrons can be identified into groups that correspond to the discrete 1*s*, 1*p*, 1*d*, 2*s*, 1*f* shells, as predicted by the jellium model. The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap (1.694 eV) of this anionic cluster is also appreciable.

V. CONCLUSION

To summarize, unbiased searches using genetic algorithm incorporated within a first-principles approach were performed to obtain the lowest-energy configurations of neutral and anionic clusters of Na_nSi_m ($1 \le n \le 3$, $1 \le m \le 11$). Generally speaking, the ground state structures and geometry parameters from our theoretical calculations broadly agree with previous first-principles results wherever available, but the present work covers a broader range of cluster sizes. For Na_3Si_3 and $NaSi_9^-$, we have obtained two new lowest-energy structures that are improvements over previous theoretical predictions. For neutral Na-Si clusters, Na atoms prefer to be separated from each other by the Si skeleton; however, in anionic clusters Na atoms can stay together and form Na-Na bonds. For smaller Na_nSi_m and $Na_nSi_m^-$ clusters, the lowest-energy structures are sensitive to both Na-Si stoichiometry and charge state. For larger Na_nSi_m clusters with $m > 7$, addition of one Na atom or one extra charge would not result in significant change in the ground state structure. The electronic properties, including vertical ionization energies, adiabatic electron affinities, and photoelectron spectra, have been computed and compared with experimental

data. The satisfactory agreement between experiment and theory indicates the validity of our simulations.

ACKNOWLEDGMENT

This work was supported by the Fundamental Research Funds for the Central Universities of China (No. DUT10ZD211) and the National Natural Science Foundation of China (No. 11134005).

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