Structural evolution and bonding properties of BSi$_n^{-}/0$ ($n = 4$–12) clusters: Size-selected anion photoelectron spectroscopy and theoretical calculations

Sheng-Jie Lu,$^{1,2}$ Xi-Ling Xu,$^{2,3}$ Guo-Jin Cao,$^3$ Hong-Guang Xu,$^{2,a}$ and Wei-Jun Zheng$^{2,4,a}$

$^1$Department of Chemistry and Chemical Engineering, Heze University, Heze, Shandong 274015, China
$^2$Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
$^3$Institute of Molecular Science, Shanxi University, Taiyuan 030006, China
$^4$University of Chinese Academy of Sciences, Beijing 100049, China

(Received 19 August 2018; accepted 15 October 2018; published online 7 November 2018)

Size-selected anion photoelectron spectroscopy and theoretical calculations were used to investigate the structural evolution and bonding properties of BSi$_n^{-}$ ($n = 4$–12) clusters. The results showed that the B atom in BSi$_{4-12}^{-/0}$ prefers to occupy the high coordination sites to form more B–Si bonds. The lowest-lying isomers of BSi$_{4-7}^{-/0}$ primarily adopt bowl-shaped based geometries, while those of BSi$_{8-12}^{-/0}$ are mainly dominated by prismatic based geometries. For anionic clusters, BSi$_{11}^{-}$ is the critical size of the endohedral structure, whereas BSi$_n$ neutrals form the B–endohedral structure at $n = 9$. Interestingly, both anionic and neutral BSi$_{11}$ have a $D_{3h}$ symmetric tricapped tetragonal antiprism structure with the B atom at the center and exhibit 3D aromaticity. The BSi$_{11}^{-}$ anion possesses $\sigma$ plus $\pi$ doubly delocalized bonding characters. The natural population analysis charge distributions on the B atom are related with the structural evolution of BSi$_{n}^{-}$ and the B–Si interactions. Published by AIP Publishing. https://doi.org/10.1063/1.5052559

I. INTRODUCTION

Boron is one of the important p-type dopants in silicon.\textsuperscript{1–4} Boron-silicon compounds have attracted tremendous attention in the last decades owing to their potential applications in microelectronics, optoelectronics, and solar cells.\textsuperscript{5–14} First-principles calculations suggested that the Si atoms in silicon compounds doped with boron can adopt $sp^2$ hybridization to form graphene-like honeycomb structures with metallic properties,\textsuperscript{15} and boron doped cubic silicon can possess superconducting properties owing to the phonon-mediated Bardeen-Cooper-Schrieffer (BCS)-type mechanisms.\textsuperscript{16}

Because of the importance of boron-silicon compounds, silicon clusters doped with single or multiple B atoms have received considerable attention from both experimental and theoretical points of view. The structures and stabilities of SiB$_4$, SiB$_6$, and SiB$_{14}^+$ were studied by several theoretical calculations.\textsuperscript{17–19} Theoretical calculations predicted that the BSi dimer has a high-spin ground electronic state,\textsuperscript{20} which is subsequently confirmed by the electron spin resonance (ESR) spectroscopy.\textsuperscript{21} Density functional theory (DFT) calculations suggested that BSi$_2$, B$_2$Si, and B$_2$Si$_2$ incline to form ring-shaped structures with strong $\pi$ bonding interactions.\textsuperscript{22} The growth mechanisms of small BSi clusters were investigated by time-of-flight mass spectrometry and theoretical calculations.\textsuperscript{23–26} Quantum chemical calculations predicted that BSi$_5^+$ has a stable cubic structure with the B atom at the center\textsuperscript{27} and BSi$_9^-$ and BSi$_{10}^+$ exhibit endohedral structures with spherical aromaticity.\textsuperscript{28} The BSi$_3$ monolayer was predicted to be the c-BSi$_3$ silicene with planar aromatic $D_{6h}$ c-Si$_6$ rings and metallic characters.\textsuperscript{29} BSi$_6$ was identified as a distorted pentagonal bipyramid structure with the B atom located at an apex position by infrared-ultraviolet two-color ionization (IR-UV2CI) spectroscopy and quantum chemical calculations,\textsuperscript{30} while B$_2$Si$_6$-$^{10+}$ were characterized as peculiar structures with a Si atom hanging over a distorted bowl-shaped B$_2$Si$_3$ framework by anion photoelectron spectroscopy and theoretical calculations.\textsuperscript{31} Infrared-ultraviolet two-color ionization spectroscopic studies of neutral B$_2$Si$_3$, SiB$_4$, and anion photoelectron spectroscopic studies of B$_2$Si$_3$, B$_2$Si$_4$, and SiB$_4$ revealed that the two B atoms have strong interactions.\textsuperscript{32–33} Anion photoelectron spectroscopic and theoretical studies of B$_3$Si$_{4-10}^-$ found that the three B atoms incline to form a B$_3$ triangle due to the strong B–B bonds and B$_3$Si$_{10}^-$ is a unique superatom cluster.\textsuperscript{35} Very recently, an \textit{ab initio} study of medium sized boron-doped silicon clusters Si$_n$B$_m$ in $n = 11–13$ and $m = 1–3$ was reported.\textsuperscript{35} To get more detailed information regarding the structural evolution and bonding properties of BSi$_n$ clusters, in this work, we investigated the BSi$_n^{-/0}$ ($n = 4$–12) clusters by using size-selected anion photoelectron spectroscopy and \textit{ab initio} calculations.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Experimental methods

Experiments were carried out on a home-built apparatus consisting of a laser vaporization cluster source, a time-of-flight mass spectrometer, and a magnetic-bottle photoelectron...
spectrometer, as described elsewhere.\textsuperscript{36} BSi\textsubscript{n}\textsuperscript{−} cluster anions were generated in the laser vaporization source, in which a rotating and translating disk target compressed from a mixture of boron and silicon powder (B:Si mole ratio 1:1) was ablated by the second harmonic (532 nm) light pulses from a nanosecond Nd:YAG laser (Continuum Surelite II-10). Helium carrier gas with ~0.4 MPa backing pressure was allowed to expand through a pulsed valve (General Valve Series 9) into the source to generate the clusters. The generated cluster anions were mass-analyzed using the time-of-flight mass spectrometer. The most abundant isotopologs in the BSi\textsubscript{n},\textsuperscript{−} clusters were mass-selected and decelerated before being photodetached by the fourth-harmonic light (266 nm) pulses from another Nd:YAG laser. The resulting electrons were energy-analyzed using the magnetic-sector photoelectron spectrometer. Photoelectron spectra of BSi\textsubscript{n},\textsuperscript{−} were calibrated with the spectra of Cu\textsuperscript{−} and Au\textsuperscript{−} taken under similar conditions. Typical instrumental resolution was about 40 meV for electrons with kinetic energies of 1 eV.

B. Theoretical methods

Theoretical calculations have been performed using the Gaussian 09 program package.\textsuperscript{37} Full structural optimizations and frequency analyses of BSi\textsubscript{n},\textsuperscript{−} anions and their neutral counterparts were performed employing density functional theory (DFT) in the context of Beck’s three-parameter and Lee–Yang–Parr’s gradient-corrected hybrid functional (B3LYP).\textsuperscript{38–41} Pople-type all-electron 6-311+G(d) basis sets were used for the B and Si atoms.\textsuperscript{42,43} and no symmetry constraint was imposed during the full geometry optimizations and frequency analyses for both anionic and neutral clusters. The initial structures were obtained by putting the B atom to different adsorption or substitution sites of the low-lying isomers of bare silicon clusters and numerous initial structures reported in the literature were also taken into account at all possible spin states. In addition, the crystal structure analysis by the particle swarm optimization (CALYPSO) program\textsuperscript{44} was used to search the global minima of BSi\textsubscript{n},\textsuperscript{−} anions and their corresponding neutrals. The singlets, triplets, and quintuplets were taken into account for determining the lowest energy spin state for each of the anionic BSi\textsubscript{n},\textsuperscript{−} clusters. As for each of the neutral BSi\textsubscript{n} clusters, the doublets, quartets, and sextets were considered. Harmonic vibrational frequency analyses were carried out to confirm that the obtained structures were true local minima. Perdew-Burke-Ernzerhof (PBE) functional\textsuperscript{45} and HSE06 functional\textsuperscript{46} were used for testing the efficiency of B3LYP functional. The results from the B3LYP functional are in better agreement with the experiments than those of the PBE functional and HSE 06 functional (see Fig. S1 in the supplementary material). Therefore, here we only present the results from the B3LYP functional. To further obtain the more accurate relative energies of the low-lying isomers, the single-point energies of BSi\textsubscript{n},\textsuperscript{−} clusters were calculated by the coupled-cluster methods including single, double, and perturbative contributions of connected triple excitations (CCSD(T))\textsuperscript{47,48} based on the geometries optimized at the B3LYP level, in which the augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) basis sets were both used for the B and Si atoms. Natural population analysis (NPA) was performed to gain insight into the charge distributions of BSi\textsubscript{n},\textsuperscript{−} anions using the Natural Bond Orbital (NBO) version 3.1 programs,\textsuperscript{49–56} as implemented in the Gaussian 09 program package. Theoretical vertical detachment energies (VDEs) were defined as the energy differences between the neutrals and anions both using the anionic geometries. Theoretical adiabatic detachment energies (ADEs) were defined as the energy needed to remove an electron from the anions to states of the corresponding neutrals at their respective equilibrium geometries. Zero-point energy (ZPE) corrections were considered in calculating the relative stabilities and ADEs of these clusters.

III. EXPERIMENTAL RESULTS

The photoelectron spectra of BSi\textsubscript{n},\textsuperscript{−} (n = 4–12) clusters recorded with 266 nm photons are displayed in Fig. 1. The experimental VDEs and ADEs of these clusters measured from their photoelectron spectra are summarized in Table I. Experimental VDEs and ADEs of BSi\textsubscript{n},\textsuperscript{−} (n = 4–12) cluster anions were obtained from the maxima of the first peaks, while experimental ADEs were assigned by drawing a straight line along the leading edge of the first peaks to intersect with the baseline of photoelectron spectra, and then the electron binding energy (EBE) values at the intersection points plus the instrumental resolution.

The photoelectron spectrum of BSi\textsubscript{4},\textsuperscript{−} reveals five major peaks at 2.92, 3.30, 3.59, 3.9, and 4.1 eV, respectively. In the spectrum of BSi\textsubscript{5},\textsuperscript{−}, a high-intensity broad peak at 3.58 eV and the onset of a higher EBE peak beyond 4.4 eV can be observed. The spectrum of BSi\textsubscript{6},\textsuperscript{−} displays a low-intensity broad peak at 3.61 eV and a roughly recognized high-intensity

![FIG. 1. Photoelectron spectra of BSi\textsubscript{n},\textsuperscript{−} (n = 4–12) clusters recorded with 266 nm photons.](image)
peak at 4.3 eV. The spectrum of BSi$_n^{-}$ has two narrowly identified overlapping peaks at 3.2 and 3.4 eV, a high-intensity peak at 3.9 eV, and a barely discernible higher EBE peak above 4.4 eV.

Two low-intensity peaks at 3.29 and 3.58 eV, and a high-intensity broad peak at 4.3 eV, can be observed in the spectrum of BSi$_5^{-}$. The spectrum of BSi$_9^{-}$ displays a roughly identified shoulder peak at 3.9 eV. In the spectrum of BSi$_{10}^{-}$, there are two high-intensity peaks at 3.26 and 3.70 eV, followed by two roughly discernible low-intensity peaks at 4.1 and 4.3 eV. The spectrum of BSi$_{11}^{-}$ reveals a low-intensity peak at 3.58 eV and a high-intensity broad peak between 3.8 and 4.3 eV. In the spectrum of BSi$_{12}^{-}$, we can roughly distinguish a low-intensity shoulder peak and a high-intensity broad peak centered at 3.4 and 4.2 eV, respectively.

**IV. THEORETICAL RESULTS**

Figure 2 shows the typical low-lying isomers of BSi$_n^{-}$ (n = 4–12) clusters with the lowest-lying isomers displayed on the left. The most stable isomers of BSi$_n^{-}$ anions are in spin-singlet states. Theoretical VDEs and ADEs of low-lying isomers and their relative energies ($\Delta E$) calculated at the CCSD(T) level are summarized in Table I, and experimental VDEs and ADEs are also included in Table I for comparison. The $\Delta E$ of low-lying isomers calculated at the B3LYP level are summarized in Table S1 of the supplementary material, which are in reasonable agreement with those calculated at the CCSD(T) level. Thus, in this work, we only presented the $\Delta E$ calculated at the CCSD(T) level. Bond lengths of the most stable isomers of BSi$_n^{-}$ (n = 4–12) clusters are listed in Table II. Besides, the photoelectron spectra of the low-lying isomers are simulated based on the generalized Koopmans’ theorem (GKT).$^{37,58}$ The simulated spectra are named as density of states (DOS) spectra, which are shown in Fig. 3, as well as the experimental photoelectron spectra.

BSi$_4^{-}$. For the BSi$_4^{-}$ cluster, the most stable isomer (4A) can be viewed as a distorted bowl-shaped BSi$_4$ structure with C$_{2v}$ symmetry, which is similar with the lowest-lying isomers of BSi$_4^{-}$/$^{0}$ reported in the literature.$^{24,28,32}$ Isomer 4B is a C$_3v$ symmetric trigonal bipyramidal structure with the B atom at the apex position and is slightly higher in energy than isomer 4A by 0.11 eV. The theoretical VDE of isomer 4A (2.74 eV) is in reasonable agreement with the experimental peak at 2.92 eV and that of isomer 4B (3.26 eV) is consistent with the experimental peak at 3.30 eV. The DOS spectrum of isomer 4A can match the experimental peaks at 2.92, 3.59, and 3.9 eV, while that of isomer 4B is in line with the experimental peaks at 3.30 and 4.1 eV. The combination of the DOS spectra of isomers 4A and 4B can well reproduce the peak positions and patterns of the experimental spectrum. Isomer 4C is higher in energy than isomer 4A by 0.20 eV, and its theoretical VDE (2.88 eV) is close to the experimental value (2.92 eV). Isomer 4D is much higher in energy than isomer 4A by 0.47 eV. Therefore, we suggest that isomers 4A and 4B are the most probable structures detected in the experiments and isomer 4C may have minor contribution to the photoelectron spectrum of BSi$_4^{-}$.

BSi$_5^{-}$. The most stable isomer (5A) of BSi$_5^{-}$ can be regarded as a Si atom hanging over a distorted bowl-shaped

### Table I. Relative energies, theoretical VDEs and ADEs of the low-lying isomers of BSi$_n^{-}$ (n = 4–12) clusters, as well as the experimental VDEs and ADEs estimated from their photoelectron spectra.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Symmetry</th>
<th>$\Delta E^b$ (eV)</th>
<th>VDE (eV)</th>
<th>ADE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical$^c$</td>
<td>Exp.$^d$</td>
<td>Theoretical$^c$</td>
</tr>
<tr>
<td>BSi$_4^{-}$</td>
<td>4A</td>
<td>C$_{2v}$</td>
<td>0.00</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td>4B</td>
<td>C$_{3v}$</td>
<td>0.11</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>4C</td>
<td>C$_2$</td>
<td>0.20</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td>4D</td>
<td>C$_{2v}$</td>
<td>0.47</td>
<td>3.18</td>
</tr>
<tr>
<td>BSi$_5^{-}$</td>
<td>5A</td>
<td>C$_{4v}$</td>
<td>0.50</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>5B</td>
<td>C$_4$</td>
<td>0.47</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>5C</td>
<td>C$_4$</td>
<td>1.28</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>5D</td>
<td>C$_4$</td>
<td>2.09</td>
<td>2.66</td>
</tr>
<tr>
<td>BSi$_6^{-}$</td>
<td>6A</td>
<td>C$_5$</td>
<td>0.00</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
<td>6B</td>
<td>C$_4$</td>
<td>1.05</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>6C</td>
<td>C$_3$</td>
<td>1.10</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td>6D</td>
<td>C$_4$</td>
<td>1.15</td>
<td>2.87</td>
</tr>
<tr>
<td>BSi$_7^{-}$</td>
<td>7A</td>
<td>C$_4$</td>
<td>0.00</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>7B</td>
<td>C$_4$</td>
<td>0.20</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>7C</td>
<td>C$_1$</td>
<td>0.66</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>7D</td>
<td>C$_4$</td>
<td>0.67</td>
<td>2.32</td>
</tr>
<tr>
<td>BSi$_8^{-}$</td>
<td>8A</td>
<td>C$_2$</td>
<td>0.00</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>8B</td>
<td>C$_4$</td>
<td>0.07</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td>8C</td>
<td>C$_3$</td>
<td>0.13</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>8D</td>
<td>C$_4$</td>
<td>0.17</td>
<td>3.49</td>
</tr>
</tbody>
</table>

$^a$The isomers labeled in bold are the most probable isomers in the experiments.

$^b$The uncertainties of the experimental VDEs and ADEs for n = 4–6, 8, and 10–11 are ±0.08 eV, for n = 7, 9, and 12 are ±0.1 eV.

$^c$The ADEs and VDEs are calculated at the B3LYP/6-311+G(d) level of theory.

$^d$The uncertainties calculated at the CCSD(T)/aug-cc-pVTZ level of theory.
BSi$_4$ framework with $C_{4v}$ symmetry, which is similar with the lowest-lying isomers of BSi$_5$$^−$$^0$ reported in the literature.$^{24,28,32}$ The theoretical VDE of isomer 5A (3.50 eV) is close to the experimental value (3.58 eV), and its DOS spectrum fits the peak positions and patterns of the experimental spectrum very well. The existence of isomers 5B, 5C, and 5D can be ruled out because they are much higher in energy than isomer 5A by at least 0.47 eV. Thus, we suggest isomer 5A to be the most likely structure contributing to the photoelectron spectrum of BSi$_6$$^−$.

**BSi$_6$$^−$.** The most stable isomer (6A) of BSi$_6$$^−$ can be described as a Si atom hanging over a distorted bowl-shaped BSi$_5$ framework with $C_{5v}$ symmetry, similar with the lowest-lying isomers of BSi$_6$$^−$$^0$ reported in the literature.$^{24,28,30,32}$ The theoretical VDE of isomer 6A (3.51 eV) is in reasonable agreement with the experimental value (3.61 eV), and its DOS spectrum can reproduce the peak positions and patterns of the experimental spectrum very well. The existence of isomers 6B, 6C, and 6D can be ruled out because they are much higher in energy than isomer 6A by at least 1.05 eV. Thus, we suggest isomer 6A to be the most likely structure contributing to the photoelectron spectrum of BSi$_6$$^−$.

**BSi$_7$$^−$.** In the lowest-lying isomer (7A) of BSi$_7$$^−$, the B atom and six Si atoms form a Si atom hanging over a bowl-shaped BSi$_5$ structure and then the remaining Si atom caps the Si$_3$ triangular face, which is in line with the lowest-lying isomers of BSi$_7$$^−$$^0$ reported in the literature.$^{28,32}$ The theoretical VDE of isomer 7A (3.07 eV) is in reasonable agreement with the experimental value (3.2 eV), and its DOS spectrum agrees well with the experimental spectrum. The
TABLE II. Bond lengths of the most stable isomers of BSi$_n^{−10}$ (n = 4–12) clusters.

<table>
<thead>
<tr>
<th>Isomer (anions)</th>
<th>Bond length (Å)</th>
<th>Isomer (neutrals)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A B–Si = 1.95–2.00</td>
<td>4A′ B–Si = 1.95</td>
<td>5A B–Si = 1.98</td>
<td>5A′ B–Si = 1.96–2.04</td>
</tr>
<tr>
<td>Si–Si = 2.49</td>
<td>Si–Si = 2.53</td>
<td>Si–Si = 2.49–2.58</td>
<td>Si–Si = 2.38–2.77</td>
</tr>
<tr>
<td>6A B–Si = 2.10</td>
<td>6A′ B–Si = 2.08–2.10</td>
<td>7A B–Si = 2.16–2.14</td>
<td>7A′ B–Si = 2.03–2.10</td>
</tr>
<tr>
<td>Si–Si = 2.39–2.66</td>
<td>Si–Si = 2.30–2.78</td>
<td>Si–Si = 2.30–2.65</td>
<td>Si–Si = 2.39–2.62</td>
</tr>
<tr>
<td>8A B–Si = 2.17–2.27</td>
<td>8A′ B–Si = 2.17–2.29</td>
<td>9A B–Si = 2.00–2.07</td>
<td>9A′ B–Si = 2.16–2.33</td>
</tr>
<tr>
<td>Si–Si = 2.30–2.59</td>
<td>Si–Si = 2.37–2.59</td>
<td>Si–Si = 2.44–2.65</td>
<td>Si–Si = 2.42–2.76</td>
</tr>
<tr>
<td>10A B–Si = 2.02–2.15</td>
<td>10A′ B–Si = 2.12–2.26</td>
<td>11A B–Si = 2.16–2.28</td>
<td>11A′ B–Si = 2.15–2.24</td>
</tr>
<tr>
<td>Si–Si = 2.38–2.63</td>
<td>Si–Si = 2.38–2.62</td>
<td>Si–Si = 2.42–2.55</td>
<td>Si–Si = 2.45–2.56</td>
</tr>
<tr>
<td>12A B–Si = 2.06–2.17</td>
<td>12A′ B–Si = 2.12–2.28</td>
<td>Si–Si = 2.33–2.59</td>
<td>Si–Si = 2.35–2.60</td>
</tr>
</tbody>
</table>

Theoretical VDE of isomer 7B (2.90 eV) is much smaller than the experimental value, and isomers 7C and 7D are much higher in energy than isomer 7A by at least 0.66 eV. Therefore, isomer 7A is suggested to be the most likely structure detected in the experiments.

**BSi$_8^{−10}$**. The lowest-lying isomer (8A) of BSi$_8^{−10}$ adopts a C$_{3v}$ symmetric tetragonal antiprism or boat-shaped structure with the B atom at the center and the opening of cage remains unclosed. The theoretical VDEs of isomers 8A and 8B (3.18 and 3.08 eV) are both in reasonable agreement with the experimental value (3.29 eV) and isomer 8B is higher in energy than isomer 8A by only 0.07 eV. The combination of the DOS spectra of isomers 8A and 8B is in line with the peak positions and patterns of the experimental spectrum. Isomers 8C and 8D are higher in energy than isomer 8A by 0.13 and 0.17 eV, respectively. Thus, we suggest that isomers 8A and 8B are the most likely structures detected in the experiments. It is worth mentioning that isomer 8A is different from the lowest-lying isomer of BSi$_8^{−}$ reported in the literature, which is higher in energy than isomer 8A by 0.24 eV, calculated at the CCSD(T) level of theory. Isomer 8C resembles well with the cubic structure of BSi$_8^{+}$.27

**BSi$_9^{−10}$**. The most stable isomer (9A) of BSi$_9^{−10}$ can be viewed as the B atom substituting the vertex Si atom of Si$_10^{0}$ bicapped tetragonal antiprism. Isomer 9B adopts a D$_{3h}$ symmetric capped tetragonal antiprism or boat-shaped structure with the B atom at the center, which can also be obtained by an additional Si atom capping the top of isomer 8A. Isomers 9A and 9B are in reasonable agreement with the low-lying isomers of BSi$_9^{0}$ obtained at the B3LYP level by Tam et al.28 The theoretical VDE of isomer 9A (3.96 eV) is close to the experimental value (3.9 eV), and its DOS spectrum is in reasonable agreement with the experimental spectrum. The theoretical VDE of isomer 9B (3.47 eV) is much smaller than the experimental value, and isomers 9C and 9D are much higher in energy than isomer 9A by at least 0.49 eV. Therefore, isomer 9A is suggested to be the most likely structure contributing to the photoelectron spectrum of BSi$_{10}^{−10}$.

**BSi$_{10}^{−10}$**. The most stable isomer (10A) of BSi$_{10}^{−10}$ can be regarded as a Si$_4$ rhombus hanging over the bowl-shaped BSi$_4$ structure with the remaining Si atom capping the BSi$_3$ rhombic face, which is in reasonable agreement with the lowest-lying isomer of BSi$_{10}^{−10}$ obtained at the G4 approach by Tam et al.28 In isomer 10B, the B atom is encapsulated into the Si$_{10}^{0}$ pentagonal prismatic cage, which is stabilized by two B atoms in our previous studies of B$_2$Si$_{10}^{n}$ $^{−10}$ 33. It is interesting that, in this work, two Si$_5$ five-membered rings can be stabilized by only one B atom. The theoretical VDEs of isomers 10A and 10B (3.18 and 3.40 eV) are both in reasonable agreement with the experimental value (3.26 eV). The DOS spectrum of isomer 10A is in line with the experimental peak at 3.26 eV, while that of isomer 10B is consistent with the experimental peaks at 3.70, 4.1, and 4.3 eV. The combination of the DOS spectra of isomers 10A and 10B resembles well with the peak positions and patterns of the experimental spectrum. Isomers 10C and 10D are much higher in energy than isomer 10A by 0.19 eV. Therefore, isomers 10A and 10B are suggested to be the most probable structures contributing to the photoelectron spectrum of BSi$_{10}^{−10}$.

**BSi$_{11}^{−10}$**. The lowest-lying isomer (11A) of BSi$_{11}^{−}$ adopts a $D_{3h}$ symmetric tricapped tetragonal antiprism with the B atom at the center. Isomer 11A can also be obtained by three additional Si atoms face-capping the tetragonal antiprism structure of BSi$_8^{−}$. Isomer 11B is nearly isoenergetic with isomer 11A, which is higher in energy than isomer 11A by only 0.08 eV. The theoretical VDEs of isomers 11A and 11B (3.48 and 3.48 eV) are both in reasonable agreement with the experimental value (3.58 eV). The combination of the DOS spectra of isomers 11A and 11B can well reproduce the peak positions and patterns of the experimental spectrum. Isomers 11C and 11D are much higher in energy than isomer 11A by at least 0.40 eV. Therefore, we suggest that isomers 11A and 11B are the most probable isomers contributing to the photoelectron spectrum of BSi$_{11}^{−}$.

**BSi$_{12}^{−10}$**. The lowest-lying isomer (12A) of BSi$_{12}^{−10}$ can be described as four additional Si atoms face-capping the Si$_8$ tetragonal prism with the B atom at the center. The theoretical VDE of isomer 12A (3.43 eV) is very close to the experimental value (3.4 eV), and its DOS spectrum fits the peak positions and patterns of the experimental spectrum very well. The theoretical VDEs of isomers 12B, 12C, and 12D (3.12, 2.86, and 2.92 eV) are much smaller than the experimental value, indicating that their existence in the cluster beams can be ruled out. Therefore, we suggest that isomer 12A is the most probable structure observed in the experiments.

**BSi$_n^{(n = 4–12)}$ Neutrals.** The geometric structures of BSi$_n^{(n = 4–12)}$ neutrals were also optimized at the B3LYP level and displayed in Fig. 4. The most stable isomers of BSi$_n^{(n = 4–12)}$ neutrals are in spin doublet states. We found that the most stable isomers of BSi$_n^{(n = 9, 10, and 12)}$ neutrals have different geometric structures with their corresponding anions, whereas those of the remaining neutral clusters are similar to their corresponding anions with the bond lengths being slightly different, as shown in Table II. The lowest-lying isomer (9A′)
of BSi$_9$ is a capped tetragonal antiprism with the B atom at the center, analogous to isomer 9B of BSi$_{9}^-$, that (10A') of BSi$_{10}$ is a pentagonal prismatic structure with the B atom at the center, similar to isomer 10B of BSi$_{10}^-$, and that (12A') of BSi$_{12}$ resembles with isomer 12D of BSi$_{12}^-$. As for BSi$_n$ neutrals, the critical size of the forming B-endohedral structure is $n = 9$, whereas BSi$_{11}^-$ is the critical size of the endohedral structure for BSi$_n^-$ anions. These indicate that the structural evolution between BSi$_n$ neutrals and anions is different. We would like to point out that the most stable structure (8A') of BSi$_8$ is different from that reported by Tam et al.$^{28}$ The most stable structure of BSi$_9$ in the literature is similar to the isomer 8B' in this work, which is slightly higher in energy than isomer 8A' by 0.07 eV, calculated at the CCSD(T) level.
V. DISCUSSION

The experimental and theoretical VDEs of the most stable isomers of BSi$_n$($n = 4$–$12$) versus the number of Si atoms are shown in Fig. 5. One can see that the calculated VDEs are in good agreement with the experimental VDEs with average derivations of $\sim 0.09$ eV, indicating that the theoretical methods used in this work are reliable. It is found that the B atom in BSi$_n$($n = 0$) prefers to occupy the high coordination sites to form more B–Si bonds. For BSi$_{4–7}$($n = 0$), the dominant geometries are bowl-shaped structures, whereas BSi$_{8–12}$($n = 0$) primarily adopt prismatic based geometries. It appears that the changes of the photoelectron spectra of BSi$_{4–12}$($n = 0$) are related to their structural evolution. As shown in Fig. 5, the VDEs...
of BSi$_5^-$ and BSi$_6^-$ are larger than those of the neighbor cluster sizes, which is more likely attributed to BSi$_5^-$ and BSi$_6^-$ having more highly symmetrical bowl-shaped structures. Also, BSi$_{11}^-$ has larger VDEs than the neighbor cluster sizes because it adopts a $D_{3h}$ symmetric tricapped tetragonal antiprism with the B atom at the center. It is worth noting that BSi$_9^-$ has the maximum VDE among the BSi$_n^-$ clusters, which is probably due to its special electronic structure. The total number of effective valence electrons of BSi$_9^-$ adds up to 40 electrons including 3 valence electrons of B atom, 36 valence electrons of nine Si atoms, and the excess electron. Therefore, BSi$_9^-$ has a shell-closing electronic structure and can be termed as a superatom according to the jellium model ($1S^21P^61D_{10}^22S^21F_{14}^22P^6$), which was first proposed by Martins et al. and verified experimentally by Knight et al. The special electronic structure and superatom feature of BSi$_9^-$ were also revealed in previous work. Interestingly, our photoelectron experimental data show that the BSi$_9^-$ cluster has a large VDE of 3.9 eV, which is slightly higher than the electronic affinities (EAs) of the Cl atom (3.61 eV) and Al$_{13}^-$ (3.57 eV). Thus, BSi$_9^-$ can be viewed as a superhalogen anion, similar to Al$_{13}^-$ and AuGe$_{12}^-$, and may have potential applications as building blocks for novel nanostructured materials. Our calculations found that the most stable structure of neutral BSi$_9$ is an endohedral structure with the B atom at the center, different from that of BSi$_9^-$. This finding is in agreement with the previously theoretical results of BSi$_9$. Another possible reason for the high VDE of BSi$_9^-$ is that the neutral structure corresponding to the most stable anionic structure is very high in energy. Indeed, our calculations show that the neutral structure (9D' in Fig. 4) similar to 9A is higher in energy than the most stable neutral structure by 0.18 eV, calculated at the CCSD(T) level. This indicates that the excess electron has an obvious effect on the structures of BSi$_9^-$ anion and BSi$_9$ neutral. In addition, the BSi$_9^-$ cluster implies that the species with a large VDE do not always mean that they adopt a highly symmetric structure because the special electronic structure has also significant influence on the VDE value. The opposite could be true that the species with a highly symmetric structure not always have a large VDE. This conclusion can be supported by the case of BSi$_8^-$ cluster, in which it adopts a $C_{2v}$ symmetric tetragonal antiprism but has a lower VDE value (3.29 eV) in comparison with that (3.9 eV) of BSi$_9^-$. To probe the effective atomic charge distributions of BSi$_n^-$ (n = 4–12) anions, we performed natural population analysis (NPA) on the most stable structures and showed them in Fig. 6. The NPA charges on the B atom of BSi$_{14-12}^-$ are all negative values in the range of $-(1.29-2.05)e$, indicating that some electrons are transferred from the Si$_n$ frameworks to the B atom, more likely due to the stronger Pauling electronegativity ($\chi = 2.04$) of the B atom than that ($\chi = 1.90$) of the Si atom. Especially, the NPA charges on the B atom increase significantly at n = 8 and 11, probably related to the formation of B atom half-endohedral or endohedral structures with a high symmetry at these cluster sizes. It is also worth mentioning that, for the cluster sizes of n = 4–7 and 9–10, the NPA charges...
on the B atom are similar and carry fewer negative charges, which is probably because the B atom in BSi$_{4-7,9-10}$ interacts with nearly same fewer number of Si atoms, as compared to the B atom in BSi$_{8-11}$.$^{-12}$ In summary, the NPA charge distributions on the B atom are correlated with the structural evolution of BSi$_{n^-}$ and the interactions with the Si atoms.

To gain insight into the chemical bonding in BSi$_{n^-}$ clusters, the constant electronic charge densities of the most stable isomer of BSi$_{11^-}$ ($11A$) were analyzed and are shown in Fig. 7. One can see from Fig. 7, for constant charge density surface of 0.04 a.u., the electronic charges are distributed uniformly over the B–Si and Si–Si bonds with those at the center of each Si$_4$ rhombus being very low. For a constant charge density surface of 0.06 a.u., the electronic charges are mainly observed on the B–Si bonds. For a constant charge density surface of 0.08 a.u., the electronic charges are focused on the B atom. These results imply that the interactions between the atoms are in the order of B–Si $> $ Si–Si, which can partly explain why the B atom can be encapsulated into the Si$_{11}$ cage to form a trigonal antiprism.

To further investigate the chemical bonding properties of BSi$_{11^-}$, the molecular orbitals of the most stable isomer ($11A, ^1A_1'$) were analyzed by using the natural atomic orbital method$^{30-72}$ and displayed in Fig. 8. The LUMO is primarily constructed by the $3p$ orbitals of Si atoms. The HOMOs are all doubly occupied, and the LUMO is higher in energy than the HOMO by 3.27 eV, although the previous investigations have revealed that the HOMO-LUMO gap calculated with the B3LYP functional is more overestimate than that obtained from the other functional (BP86) by $\sim$1.00 eV.$^{67-69}$ This indicates that the BSi$_{11^-}$ anion has a shell-closed electronic structure with a large HOMO-LUMO gap. The HOMO is a Si–Si $\sigma$ orbital with bonding characters, mainly composed by the $3p$ orbitals of Si atoms. The HOMO-1 is degenerate in energy with the HOMO and is also a Si–Si $\sigma$ orbital with bonding characters, which has components from the $3p$ orbitals of Si atoms. Likewise, the HOMO-2 is a Si–Si $\sigma$ orbital with bonding characters, consisting of the $3p$ orbitals of Si atoms. However, the HOMO-3 is found to possess $\sigma$ plus $\pi$ double bonding characters, which involves the $2p$ orbital of the B atom and the $3s$ and $3p$ orbitals of Si atoms. Overall, these molecular orbitals suggest that the BSi$_{11^-}$ anion possesses $\sigma$ plus $\pi$ double bonding characters [further identified by the Adaptive Natural Density Partitioning (AdNDP) analysis of BSi$_{11^-}$, see Fig. S2 in the supplementary material], which play vital roles in the enhanced stability of $D_{3h}$ symmetric trigonal antiprism. From the diagrams of the occupied molecular orbitals, one can see that there are small overlaps between the $2p$ orbitals of the B atom and $3s3p$ orbitals of Si atoms, confirming that the B–Si interactions are not so strong, being in reasonable agreement with the calculated Wiberg bond orders (0.48–0.61) of B–Si in BSi$_{11^-}$.

Three-dimensional (3D) aromaticity due to electron delocalization can remarkably enhance the chemical stability of a molecular cluster. The negative value of nucleus-independent chemical shift (NICS) can be used to probe the 3D aromaticity for various cage structures and the more negative NICS values represent the stronger aromaticity.$^{73,74}$ We calculated the NICS values of the most stable isomers of both BSi$_{11^-}$ anion and BSi$_{11}$ neutral at the B3LYP/6-311+G(d) level within the Gaussian 09 program package. The NICS(0) and NICS(1) refer to the NICS values calculated at the cage centers and at points 1 Å above the cage centers, respectively. The calculations show that the NICS(0) and NICS(1) values of the BSi$_{11^-}$...
anion are $-141.6$ and $-61.6$ ppm, respectively, while those of $\text{BSi}_{11}^{-}$ are $-52.1$ and $-39.5$ ppm, respectively. These large negative NICS values indicate that both $\text{BSi}_{11}^{-}$ anion and $\text{BSi}_{11}^{-}$ neutral exhibit significant 3D aromaticity.

VI. CONCLUSIONS

The structural evolution and bonding properties of B atom doped silicon clusters, $\text{BSi}_{n}^-\pi^0$ ($n = 4$–12), were investigated by size-selected anion photoelectron spectroscopy combined with theoretical calculations. The B atom in $\text{BSi}_{12}^-\pi^0$ inclines to occupy the high coordination sites to interact with more Si atoms. The lowest-lying isomers of $\text{BSi}_{12}^-\pi^0$ are dominated by bowl-shaped based structures, while those of $\text{BSi}_{8}^-\pi^0$ primarily adopt prismatic based geometries. $\text{BSi}_{11}^{-}$ is the critical size of the forming B-endohedral structure for anionic clusters, whereas the B-endohedral structure appears at $n \geq 9$ for neutral clusters. Interestingly, $\text{BSi}_{11}^{-}$ have $D_{3h}$ symmetric tricapped tetragonal antiprism structures with the B atom at the center and exhibit significant three-dimensional aromaticity. Moreover, $\text{BSi}_{11}^{-}$ has $\sigma$ plus $\pi$ doubly delocalized bonding characters. The NPA charge distributions on the B atom are associated with the structural evolution of $\text{BSi}_{n}^-\pi^0$ and the interactions with the Si atoms. The results might be useful for giving insight into the microscopic mechanisms of forming new boron-silicon compounds and for the development of novel boron-silicon based functional nanomaterials.

SUPPLEMENTARY MATERIAL

See supplementary material for the Cartesian coordinates of the low-lying isomers of $\text{BSi}_{n}^-\pi^0$ ($n = 4$–12) clusters, the relative energies of low-lying isomers calculated at the B3LYP level, comparing the experimental VDEs to those of the lowest energy structures of $\text{BSi}_{n}^-\pi^0$ ($n = 4$–12) clusters calculated by different functionals, and the Adaptive Natural Density Partitioning (AdNDP) analysis of $\text{BSi}_{11}^{-}$.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21273246 and 21103202), the Chinese Academy of Sciences (Grant No. QYZDB-SSW-SLH024), the Natural Science Foundation of Shandong Province, China (Grant No. ZR2018BB040), Open Funds of Beijing National Laboratory for Molecular Sciences (Grant No. BNLMS201804), and research start-up funds (Doctoral Science Foundation) of Heze University. The theoretical calculations are performed on the China Scientific Computing Grid (ScGrid) of the Supercomputing Center, Computer Network Information Center of the Chinese Academy of Sciences.