

Structural Evolution of $B_2Si_n^{-/0}$ ($n = 3–12$) Clusters: Size-Selected Anion Photoelectron Spectroscopy and Theoretical Calculations

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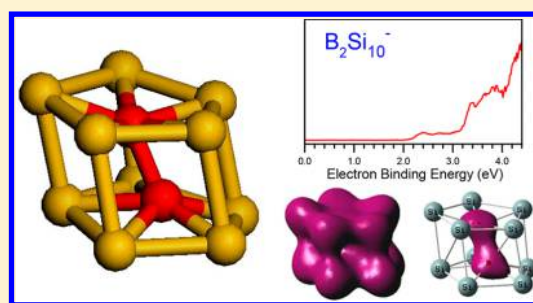
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Supporting Information

ABSTRACT: The structural evolution of $B_2Si_n^{-/0}$ ($n = 3–12$) clusters were investigated by anion photoelectron spectroscopy and *ab initio* calculations. The two B atoms in $B_2Si_{3–12}^{-/0}$ incline to form a B–B bond and more B–Si bonds. The lowest-lying isomers of $B_2Si_3^{-/0}$ have planar structures, while those of $B_2Si_{4–7}^{-/0}$ primarily adopt bowl-shaped based geometries. The two B atoms in $B_2Si_{8–9}^{-/0}$ are not completely encapsulated into the Si_n cages. For $B_2Si_{10}^{-/0}$, the two B atoms are completely encapsulated inside the Si_{10} cage to form a distorted pentagonal prismatic structure. Moreover, $B_2Si_{10}^{-/0}$ exhibits 3D aromaticity and B_2Si_{10} neutral has $\sigma + \pi$ double delocalized bonding patterns. $B_2Si_{11}^-$ anion has an endohedral polyhedral cage-like structure, whereas B_2Si_{11} neutral adopts a bicapped pentagonal prismatic structure with only one interior B atom. The structures of anionic and neutral B_2Si_{12} are endohedral tetracapped tetragonal prisms. It is interesting that two Si_5 five-membered rings are stabilized by two B atoms in $B_2Si_{10}^{-/0}$, while the stabilization of two Si_6 six-membered rings by two B atoms is not observed in $B_2Si_{12}^{-/0}$.



1. INTRODUCTION

Silicon has attracted tremendous attention in the last decades because of its importance in catalyst industry, microelectronics, and spintronics.^{1,2} Boron is an intriguing element in the periodic table that can form diverse geometric structures (planar, tubular, bilayer, and cage-like structures) and can also exhibit different types of bonding characteristics (single, double, and triple bonds) owing to its electron-deficient intrinsic nature.^{3–6} Boron element is one of the most important p-type dopants for crystalline silicon.^{7–10} Boron–silicon compounds have important applications in microelectronics, optoelectronics, and solar cells.^{11–14} First-principles calculations found that silicon-rich B–Si compounds have graphene-like honeycomb structures with the Si atoms preferring sp^2 hybridization and simultaneously possess metallic properties,¹⁵ and boron-doped cubic silicon can exhibit superconducting properties due to the standard phonon-mediated BCS-type mechanism.¹⁶ Owing to the importance of bulk boron–silicon compounds, silicon clusters doped with B atom have attracted great attention.

To date, numerous experimental and theoretical efforts have been devoted to investigate the geometric structures and electronic properties of silicon clusters doped with B atom. The SiB_4 and SiB_6 silicon borides^{17,18} and SiB_n^+ ($n = 1–4$) clusters¹⁹ were investigated by theoretical calculations. The high-spin ground electronic state of BSi dimer has been predicted by

theory²⁰ and confirmed by using the electron spin resonance (ESR) spectroscopy technology.²¹ Density functional theory (DFT) calculations found that small BSi_2 , B_2Si , and B_2Si_2 clusters tend to form ringlike structures with strong π bonding interactions.²² Several experimental and theoretical studies were focused on the thermochemical parameters and growth mechanisms of small silicon clusters doped with a single B atom, and revealed that each BSi_n cluster can be constructed by adding an additional Si atom to smaller BSi_{n-1} cluster.^{23–26} Ngan and Nguyen suggested that B atom doped into Si_8 cluster can form a stable cubic structure with the B atom located at the center.²⁷ Infrared-ultraviolet two-color ionization (IR-UV2CI) spectroscopy and quantum chemical calculations indicated that the most stable isomer of BSi_6 is a distorted pentagonal bipyramid structure with the B atom located at an apex position.²⁸ Recently, anion photoelectron spectroscopy and theoretical investigation on the $B_2Si_6^{-/0/+}$ clusters showed that their lowest-lying isomers all adopt peculiar structures with a Si atom hanging over a distorted bowl-shaped B_2Si_5 framework.²⁹ Anion photoelectron spectroscopy study and DFT calculations on the $B_3Si_{4–10}^-$ clusters found that the three B atoms interact with each other to form a B_3 triangle due to the strong B–B

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bonds, and $B_3Si_9^-$ icosahedron is characterized as a unique superatom cluster with a magic number of 40 skeletal electrons and a closed-shell electronic configuration.³⁰ More recently, the infrared-ultraviolet two-color ionization spectroscopy and quantum chemical calculations of neutral B_2Si_{3-8} clusters revealed that their low-energy isomers all exhibit a B–B bond due to the B–B bond that is stronger than the B–Si and Si–Si bonds.³¹

To provide more useful information regarding the underlying mechanisms of forming new boron–silicon compounds and understand the initial chemical processes in the formation of novel boron–silicon assembled materials, we carried out a joint size-selected anion photoelectron spectroscopy and *ab initio* calculations study on the $B_2Si_n^{-/0}$ ($n = 3-12$) clusters.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Experimental Method. Experiments were performed on a home-built apparatus consisting of a laser vaporization cluster source, a time-of-flight mass spectrometer, and a magnetic-bottle photoelectron spectrometer, which has been described in detail elsewhere.³² Briefly, $B_2Si_n^-$ cluster anions were produced 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 SureliteII-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 cool the laser-ablated plasma and to generate the clusters beam after undergoing a supersonic expansion inside the nozzle. The generated cluster anions were mass-analyzed by the time-of-flight mass spectrometer. The most abundant isotopologues of $B_2Si_{3-12}^-$ cluster anions were each size selected and decelerated before crossing with the laser beam of the fourth-harmonic light (266 nm) pulses from another nanosecond Nd:YAG laser. The resulting photoelectrons were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectra of $B_2Si_{3-12}^{-/0}$ clusters were calibrated with the known spectra of Cu^- and Au^- taken under similar conditions. The resolution of the magnetic-bottle photoelectron spectrometer was about 40 meV for electrons with kinetic energies of 1 eV.

2.2. Theoretical Method. Theoretical calculations have been conducted using the Gaussian 09 program package.³³ Full structural optimizations and frequency analyses of $B_2Si_n^-$ anions and their neutral counterparts were carried out employing DFT in the context of Beck's three-parameter and Lee–Yang–Parr's gradient-corrected correlation hybrid functional (B3LYP).^{34–37} Pople-type all-electron 6-311+G(d,p) basis sets^{38,39} were used for the B and Si atoms. For both anionic and neutral clusters, no symmetry constraint was imposed during the full geometry optimizations. The initial structures were obtained by putting the B atoms to different adsorption or substitution sites of the low-lying isomers of bare silicon clusters at all possible spin states. Additionally, the crystal structure analysis by particle swarm optimization (CALYPSO) software⁴⁰ was used to search the global minima of $B_2Si_n^-$ anions and their corresponding neutrals. The detailed information on CALYPSO has been described previously.^{40–42} In order to check that the calculated results are independent with the functional and basis set, the $B_2Si_n^-$ anions were also optimized at the PBE0//aug-cc-pVDZ level of theory^{43–45} and displayed in Table S1 (SI). The results obtained from the PBE0

level agree well with those of the B3LYP level. Harmonic vibrational frequency analyses for all clusters were carried out to confirm that the obtained structures were true local minima on the potential energy surfaces. To further evaluate the relative energies of the low-lying isomers, the single-point energies of $B_2Si_{3-12}^{-/0}$ clusters were also calculated by using the more accurate coupled-cluster methods including single, double, and perturbative contributions of connected triple excitations (CCSD(T))^{46,47} based on the geometries optimized at the B3LYP level of theory, in which the augmented correlation-consistent polarized valence triple- ζ (aug-cc-pVTZ) basis sets^{44,45} were used for the B and Si atoms. Zero-point energy (ZPE) corrections obtained from the B3LYP functional were considered in all the calculated energies. Natural population analysis (NPA) was performed to gain insight into the charge distributions of $B_2Si_{3-12}^-$ anions using the Natural Bond Orbital (NBO) version 3.1 programs,^{48–55} as implemented in the Gaussian 09 program package.

3. EXPERIMENTAL RESULTS

Figure 1 shows the photoelectron spectra of $B_2Si_n^-$ ($n = 3-12$) clusters recorded with 266 nm photons. The experimental

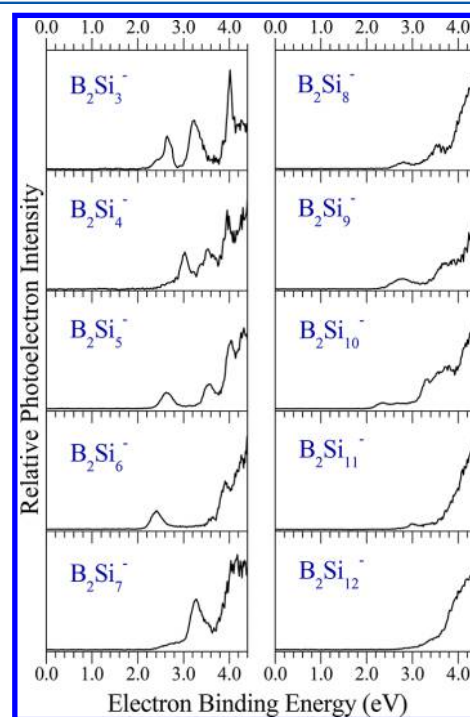


Figure 1. Photoelectron spectra of $B_2Si_n^-$ ($n = 3-12$) clusters recorded with 266 nm photons.

VDEs and ADEs of these clusters measured from their photoelectron spectra are summarized in Table 1. The experimental VDEs of $B_2Si_n^-$ ($n = 3-12$) cluster anions were obtained from the maxima of the first peaks, and the experimental ADEs were assigned by drawing a straight line along the leading edge of the first peaks to intersect with the baseline of the photoelectron spectra, and then the electron binding energy (EBE) values at the intersection points plus the instrumental resolution.

The photoelectron spectrum of $B_2Si_3^-$ reveals a low-intensity shoulder peak at 2.46 eV, followed by four major peaks centered at 2.64, 3.22, 4.02, and 4.3 eV, respectively. In the

Table 1. Relative Energies, Theoretical VDEs and ADEs of the Low-Lying Isomers of $B_2Si_n^-$ ($n = 3-12$) Clusters, and Experimental VDEs and ADEs Estimated from their Photoelectron Spectra^a

Isomer	Sym	ΔE^b (eV)	VDE (eV)		ADE (eV)		isomer	sym	ΔE^b (eV)	VDE (eV)		ADE (eV)			
			theo. ^c	expt. ^d	theo. ^c	expt. ^d				theo. ^c	expt. ^d	theo. ^c	expt. ^d		
$B_2Si_3^-$	3A	C_s	0.00	2.40	2.46	2.33	2.16	$B_2Si_8^-$	8A	C_1	0.00	2.70	2.79	2.39	2.47
	3B	C_2	0.54	2.16		1.74	8B		C_2	0.19	2.70		2.28		
	3C	D_{3h}	1.12	3.36		0.97	8C		C_s	0.23	3.08		2.49		
$B_2Si_4^-$	4A	C_s	0.00	2.87	3.02	2.27	2.71	$B_2Si_9^-$	9A	C_1	0.00	2.96	2.81	2.22	2.21
	4B	C_{2v}	0.06	2.65	2.82	2.49	2.26		9B	C_1	0.04	2.95		2.20	
	4C	C_1	0.28	2.90		2.32	9C		C_1	0.06	3.05		2.17		
	4D	C_1	0.94	2.67		1.87	9D		C_s	0.10	2.76		2.01		
$B_2Si_5^-$	5A	C_s	0.00	2.62	2.62	2.35	2.31	$B_2Si_{10}^-$	10A	C_2	0.00	2.45	2.4	2.14	2.1
	5B	C_2	0.33	2.48		2.08	10B		C_s	0.10	2.63		2.38		
	5C	C_s	0.41	2.45		1.96	10C		C_1	0.12	2.82	2.8	2.33	2.3	
	5D	C_s	0.59	2.22		1.87	10D		C_1	0.48	3.04		2.76		
$B_2Si_6^-$	6A	C_1	0.00	2.28	2.40	1.98	2.12	$B_2Si_{11}^-$	11A	C_1	0.00	3.06	3.0	2.93	2.8
	6B	C_1	0.08	2.32		1.92	11B		C_1	0.10	2.78		2.59		
	6C	C_{2h}	0.31	2.99		2.25	11C		C_1	0.17	3.09		2.42		
	6D	C_2	0.47	2.45		2.01	11D		C_1	0.30	3.15		2.86		
$B_2Si_7^-$	7A	C_1	0.00	3.12	3.27	2.78	2.98	$B_2Si_{12}^-$	12A	C_s	0.00	3.42	3.4	2.65	2.9
	7B	C_1	0.02	2.90	2.98	2.24	2.20		12B	C_1	0.25	2.93		2.54	
	7C	C_1	0.18	2.77		2.18	12C		C_1	0.34	3.05		2.89		
	7D	C_1	0.20	2.97		2.39	12D		C_1	0.36	3.02		2.45		

^aThe isomers labeled in bold are the most probable isomers in the experiments. ^b ΔE values are calculated at the CCSD(T)//aug-cc-pVTZ level of theory. ^cThe ADEs and VDEs are calculated at the B3LYP//6-311+G(d, p) level of theory. ^dThe uncertainties of the experimental VDEs and ADEs for $n = 3-9$ are ± 0.08 eV, and for $n = 10-12$ are ± 0.1 eV.

spectrum of $B_2Si_4^-$, there is a low-intensity shoulder peak at 2.82 eV, followed by four major peaks centered at 3.02, 3.53, 3.96, and 4.3 eV, respectively. The spectrum of $B_2Si_5^-$ displays four major peaks centered at 2.62, 3.57, 4.05, and 4.32 eV, respectively. As for $B_2Si_6^-$, a low-intensity peak at 2.40 eV, a weak shoulder peak at 3.61 eV, a major peak at 3.90 eV, and a high-intensity peak at 4.3 eV can be resolved. $B_2Si_7^-$ has a low-intensity peak at 2.98 eV and two high-intensity broad peaks centered at 3.27 and 4.2 eV.

A low-intensity broad peak at 2.79 eV and two high-intensity broad peaks centered at 3.57 and 4.3 eV, can be observed in the spectrum of $B_2Si_8^-$. The spectrum of $B_2Si_9^-$ displays a low-intensity broad peak at 2.81 eV, two broad peaks centered at 3.7 and 3.9 eV, and a high-intensity peak above 4.2 eV. In the spectrum of $B_2Si_{10}^-$, there are two low-intensity broad peaks centered at 2.4 and 2.8 eV, followed by three major peaks centered at 3.4, 3.8, and 4.3 eV, respectively. The spectrum of $B_2Si_{11}^-$ reveals a low-intensity peak centered at 3.0 eV, some low-intensity signals between 3.0 and 3.6 eV, and a high-intensity peak above 3.6 eV. In the spectrum of $B_2Si_{12}^-$, a low-intensity shoulder peak centered at 3.4 eV and a high-intensity broad peak above 3.6 eV can be observed.

4. THEORETICAL RESULTS

Typical low-lying isomers of $B_2Si_n^-$ ($n = 3-12$) clusters are presented in Figure 2, in which the lowest-lying isomers are displayed on the left. The theoretical VDEs and ADEs of the low-lying isomers and their relative energies (ΔE) are summarized in Table 1, accompanied by the experimental VDEs and ADEs for comparison. The bond lengths of the most stable isomers of $B_2Si_n^{-/0}$ ($n = 3-12$) clusters are listed in Table 2. Besides, we have simulated the photoelectron spectra of the low-lying isomers based on the generalized Koopmans' theorem (GKT).^{56,57} The simulated spectra are named as

density of states (DOS) spectra for convenience. The DOS spectra and experimental photoelectron spectra are compared in Figure 3.

$B_2Si_3^-$. The most stable isomer (3A) of $B_2Si_3^-$ is a planar structure with the third Si atom interacting with the B1–Si bond of the rhombus framework of $B_2Si_2^-$. The theoretical VDE of isomer 3A (2.40 eV) is very close to the experimental value (2.46 eV) and its DOS spectrum can roughly reproduce the peak positions and patterns of the experimental spectrum, although the intensities of the simulated peaks are slightly different from those of the experimental peaks centered at 2.46 and 4.02 eV. The existence of isomers 3B and 3C can be ruled out because they are much higher in energy than isomer 3A by at least 0.54 eV. Therefore, we suggest that isomer 3A is the most likely structure observed in the experiments.

$B_2Si_4^-$. For $B_2Si_4^-$ cluster, the most stable isomer (4A) can be viewed as a Si atom hanging over a distorted bowl-shaped B_2Si_3 framework. Isomer 4B is nearly isoenergetic with isomer 4A, which is higher in energy than isomer 4A by only 0.06 eV. The theoretical VDE of isomer 4A (2.87 eV) is in reasonable agreement with the experimental peak at 3.02 eV and that of isomer 4B (2.65 eV) is consistent with the low-intensity shoulder peak at 2.82 eV. The DOS spectrum of isomer 4A can match the experimental peaks centered at 3.02, 3.53, and 4.3 eV, while that of isomer 4B is in line with the experimental peaks centered at 2.82 and 3.96 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 0.28 eV. Isomer 4D is much higher in energy than isomer 4A by 0.94 eV. Therefore, we suggest that isomers 4A and 4B are the most probable isomers contributing to the experimental photoelectron spectrum of $B_2Si_4^-$.

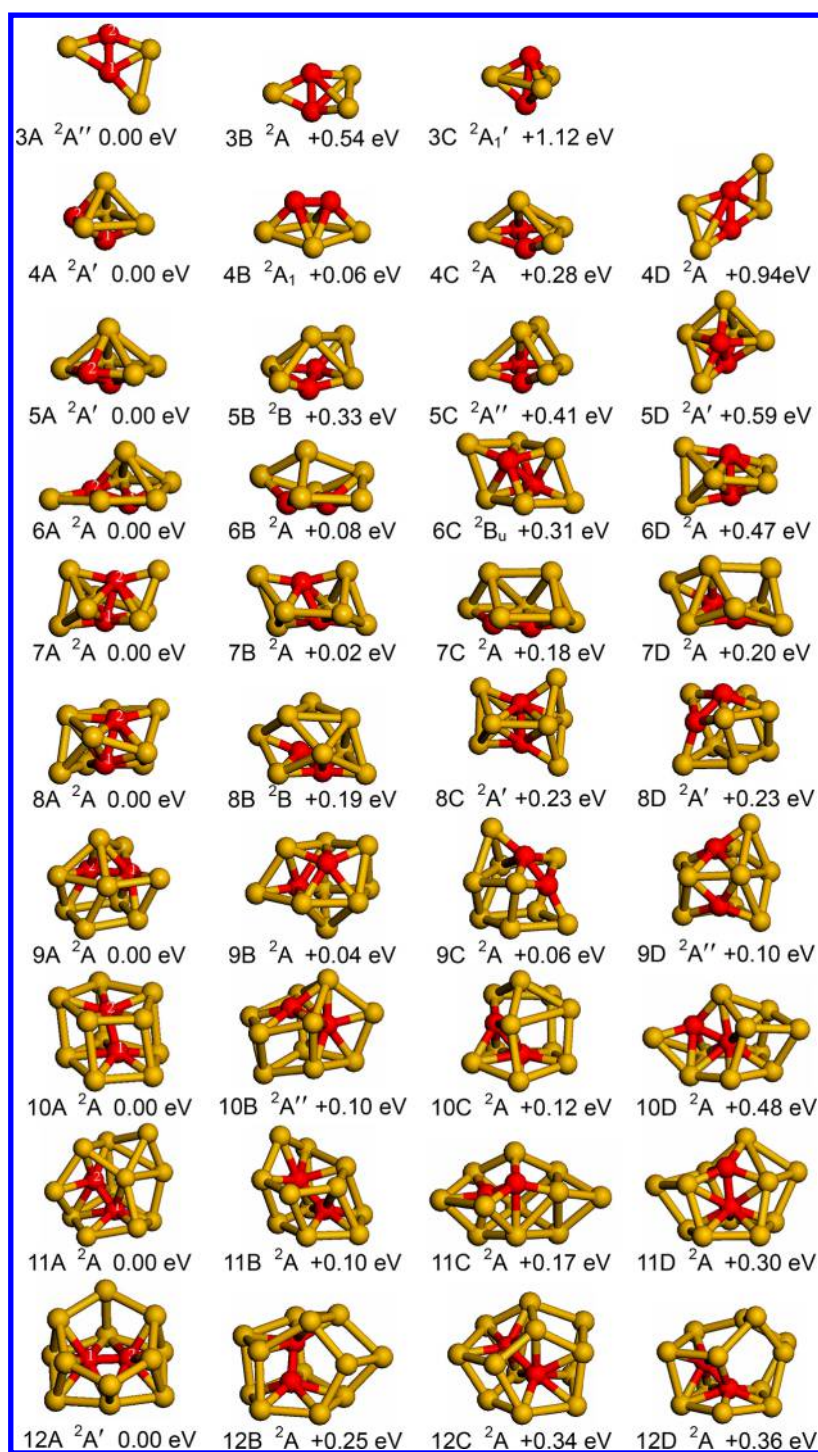


Figure 2. Typical low-lying isomers of anionic $B_2Si_n^-$ ($n = 3-12$) clusters. ΔE values are calculated at the CCSD(T)//aug-cc-pVTZ level of theory. Red and yellow balls stand for the B and Si atoms, respectively.

$B_2Si_5^-$. The most stable isomer (5A) of $B_2Si_5^-$ can be considered as one Si atom located on the top of a distorted bowl-shaped B_2Si_4 framework. The theoretical VDE of isomer 5A (2.62 eV) is equal to the experimental value (2.62 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 excluded because they are much higher in energy than isomer 5A by at least 0.33 eV. Thus, we suggest isomer 5A to be the most probable structure detected in the experiments.

$B_2Si_6^-$. The photoelectron spectrum and low-lying structures of $B_2Si_6^-$ have been investigated in detail previously. The most stable of $B_2Si_6^-$ is found to be a distorted bowl-shaped structure with the sixth Si atom hanging over the B_2Si_5 framework.²⁹ The most stable isomer of $B_2Si_6^-$ (6A) in this work is in agreement with that in previous work. Isomer 6B is also a distorted bowl-shaped structure higher in energy than isomer 6A by only 0.08 eV. Isomer 6B may have minor contribution to the photoelectron spectrum of $B_2Si_6^-$.

Table 2. Bond Lengths of the Most Stable Isomers of $B_2Si_n^{-/0}$ ($n = 3-12$) Clusters

isomer	bond length (Å)	isomer	bond length (Å)
3A	B–B = 1.64	3A'	B–B = 1.63
	B–Si = 1.87–2.05		B–Si = 1.90–2.10
	Si–Si = 2.42		Si–Si = 2.55
4A	B–B = 1.64	4A'	B–B = 1.60
	B–Si = 1.93–2.14		B–Si = 1.97–2.15
	Si–Si = 2.47–2.85		Si–Si = 2.49–2.74
5A	B–B = 1.69	5A'	B–B = 1.66
	B–Si = 1.95–2.24		B–Si = 1.95–2.08
	Si–Si = 2.47–2.63		Si–Si = 2.45–2.77
6A	B–B = 1.68	6A'	B–B = 1.64
	B–Si = 1.97–2.39		B–Si = 1.81–2.24
	Si–Si = 1.98–2.08		Si–Si = 2.32–2.46
7A	B–B = 1.84	7A'	B–B = 1.82
	B–Si = 1.98–2.36		B–Si = 2.08–2.17
	Si–Si = 2.47–2.54		Si–Si = 2.42–2.72
8A	B–B = 1.93	8A'	B–B = 1.81
	B–Si = 2.01–2.15		B–Si = 2.02–2.19
	Si–Si = 2.51–2.79		Si–Si = 2.41–2.72
9A	B–B = 2.08	9A'	B–B = 1.77
	B–Si = 2.02–2.20		B–Si = 2.09–2.30
	Si–Si = 2.39–2.64		Si–Si = 2.47–2.66
10A	B–B = 1.78	10A'	B–B = 1.80
	B–Si = 2.06–2.24		B–Si = 2.14–2.23
	Si–Si = 2.39–2.66		Si–Si = 2.36–2.70
11A	B–B = 1.72	11A'	B–B = 1.75
	B–Si = 2.07–2.20		B–Si = 1.97–2.20
	Si–Si = 2.43–2.70		Si–Si = 2.28–2.83
12A	B–B = 1.75	12A'	B–B = 1.76
	B–Si = 2.10–2.18		B–Si = 2.08–2.25
	Si–Si = 2.35–2.47		Si–Si = 2.38–2.46

$B_2Si_7^-$. In the lowest-lying isomer (7A) of $B_2Si_7^-$, the two B atoms and six Si atoms form a chair-shaped structure with each B atom interacting with four Si atoms, and then the seventh Si atom face-caps the B_2Si_3 rhombus of B_2Si_6 framework. Isomer 7B is slightly higher in energy than isomer 7A by only 0.02 eV. The theoretical VDE of isomer 7A (3.12 eV) is in line with the experimental peak at 3.27 eV and that of isomer 7B (2.90 eV) is consistent with the experimental peak at 2.98 eV. The DOS spectrum of isomer 7A is in reasonable agreement with the experimental peaks centered at 3.27 and 4.2 eV, while that of isomer 7B is consistent with the experimental peaks centered at 2.98 and 4.2 eV. The assembled DOS spectra of isomers 7A and 7B can well reproduce the peak positions and patterns of the experimental spectrum. Isomers 7C and 7D are higher in energy than isomer 7A by 0.18 and 0.20 eV, respectively. Thus, we suggest that isomers 7A and 7B are the most probable structures contributing to the photoelectron spectrum of $B_2Si_7^-$.

$B_2Si_8^-$. The lowest-lying isomer (8A) of $B_2Si_8^-$ can be described as a Si_5 five-membered ring penetrated by the perpendicular B–B axle and the remaining three Si atoms face-capping the bottom of B_2Si_5 framework. The theoretical VDE of isomer 8A (2.70 eV) agrees well with the experimental value (2.79 eV), and its DOS spectrum can well duplicate the spectral features of the experimental spectrum. Isomers 8B, 8C, and 8D are higher in energy than isomer 8A by 0.19, 0.23, and 0.23 eV, respectively. Thus, isomer 8A is suggested to be the most probable structure detected in the experiments.

$B_2Si_9^-$. The most stable isomer (9A) of $B_2Si_9^-$ can be viewed as a Si_8 distorted tetragonal prism crossed horizontally by the two B atoms and the remaining Si atom hanging over the B_2Si_8 framework. Isomers 9B, 9C, and 9D are slightly higher in energy than isomer 9A by 0.04, 0.06, and 0.10 eV, respectively. The theoretical VDEs of isomers 9A, 9B, 9C, and 9D (2.96, 2.95, 3.05, and 2.76 eV) are all in reasonable agreement with the experimental value (2.81 eV). The DOS spectrum of isomer 9A is in line with the experimental peaks centered at 2.81, 3.7, and 4.2 eV, while those of isomers 9B, 9C, and 9D are in reasonable agreement with the experimental peaks centered at 2.81, 3.7, 3.9, and 4.2 eV. The combination of the DOS spectra of isomers 9A, 9B, 9C, and 9D is in line with the peak positions and patterns of the experimental spectrum. Thus, we suggest that isomers 9A, 9B, 9C, and 9D coexist in the experiments. Multiple isomers coexisting in the experiments can explain why the spectral features of $B_2Si_9^-$ are relatively broad.

$B_2Si_{10}^-$. As the ground state structure of $B_2Si_{10}^-$, isomer 10A is found to be a C_2 symmetric distorted pentagonal prism with the two B atoms sandwiched by two Si_5 rings and each B atom interacting with a Si_5 ring. The theoretical VDE of isomer 10A (2.45 eV) is very close to the experimental peak at 2.4 eV and those of isomers 10B and 10C (2.63 and 2.82 eV) are in reasonable agreement with the experimental peak at 2.8 eV. Isomers 10B and 10C are slightly higher in energy than isomer 10A by 0.10 and 0.12 eV, respectively. The DOS spectrum of isomer 10A is in line with the experimental peaks centered at 2.4, 3.4, and 4.3 eV, while those of isomers 10B and 10C are consistent with the experimental peaks centered at 2.8 and 3.8 eV. The combination of the DOS spectra of isomers 10A, 10B, and 10C is in reasonable agreement with the peak positions and patterns of the experimental spectrum. Isomer 10D is much higher in energy than isomer 10A by 0.48 eV, indicating that it cannot be detected in the experiments. Therefore, isomers 10A, 10B, and 10C are suggested to be the most probable structures contributing to the photoelectron spectrum of $B_2Si_{10}^-$.

$B_2Si_{11}^-$. The global minimum (11A) of $B_2Si_{11}^-$ is an endohedral structure, which can be described as three Si atoms face-capping the top of a pair of BSi_5 six-membered rings shared with a Si–Si bond. The theoretical VDE of isomer 11A (3.06 eV) agrees well with the experimental value (3.0 eV), and its DOS spectrum fits the peak positions and patterns of the experimental spectrum very well. The theoretical VDEs of isomers 11B and 11C (2.78 and 3.09 eV) are both in reasonable agreement with the experimental value, and they are slightly higher in energy than isomer 11A by 0.10 and 0.17 eV. Isomer 11D is unlikely to be detected in the experiments because it is much higher in energy than isomer 11A by 0.30 eV. Thus, we suggest that isomer 11A is the most probable structure observed in the experiments, and isomers 11B and 11C might have minor contribution to the photoelectron spectrum of $B_2Si_{11}^-$.

$B_2Si_{12}^-$. In the lowest-lying isomer (12A) of $B_2Si_{12}^-$, eight Si atoms form a tetragonal prism with the two B atoms encapsulated into the cage and the rest of four Si atoms are grouped into two Si_2 units to face-cap the B_2Si_8 framework from the opposite vertical sides of the B–B bond axis. The theoretical VDE of isomer 12A (3.42 eV) is in reasonable agreement with the low-intensity shoulder peak (3.4 eV), and its DOS spectrum also resembles the experimental spectrum. Isomer 12B is unlikely to exist in the experiments because its theoretical VDE (2.93 eV) is much smaller than the experimental value. The existence of isomers 12C and 12D

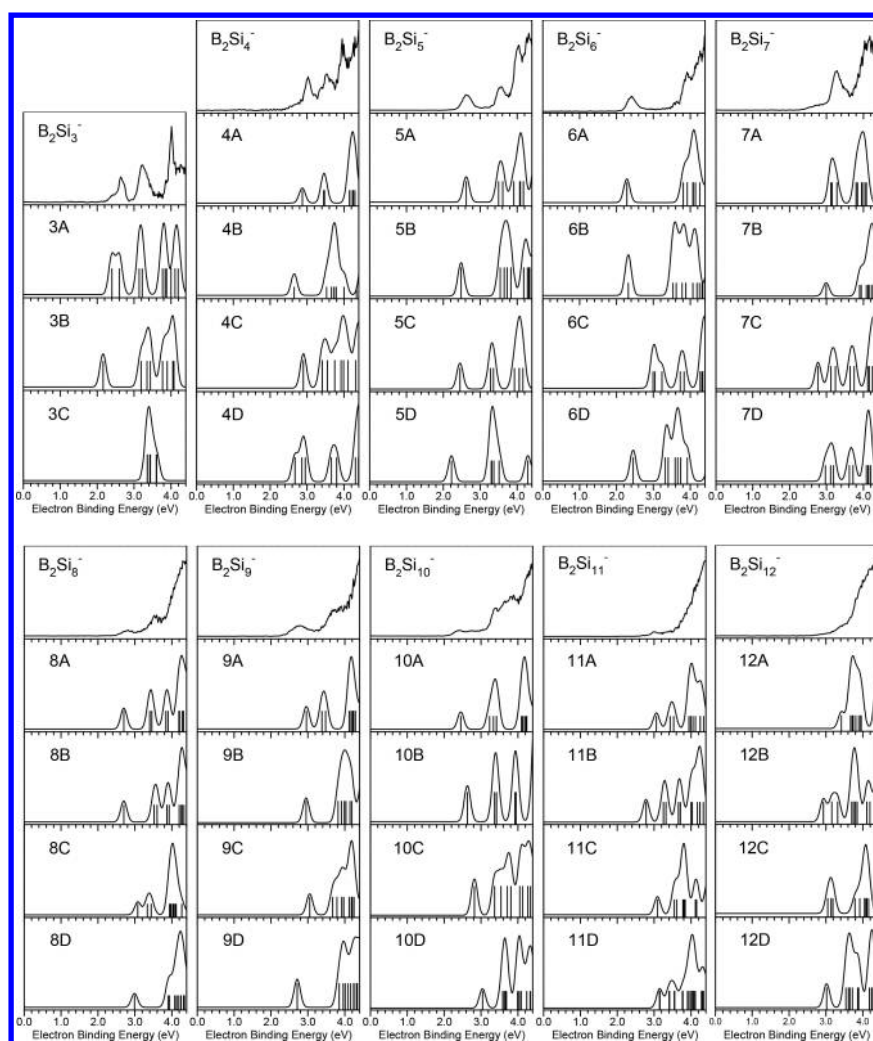


Figure 3. Comparison between the experimental photoelectron spectra and the simulated DOS spectra of the low-lying isomers of $B_2Si_n^-$ ($n = 3-12$) clusters. Simulated spectra were obtained by fitting the distribution of the transition lines with unit area Gaussian functions of 0.20 eV full widths at half-maximum.

can be excluded because they are much higher in energy than isomer 12A by at least 0.34 eV. Therefore, we suggest isomer 12A to be the most likely structure contributing to the photoelectron spectrum of $B_2Si_{12}^{-/0}$.

B_2Si_n ($n = 3-12$) Neutrals. Additionally, we also optimized the geometric structures of neutral B_2Si_n ($n = 3-12$) clusters at the B3LYP level of theory and displayed them in Figure 4. It can be seen from Figure 4 that the most stable isomers of neutral B_2Si_n ($n = 5, 7, 9$, and 11) clusters have different geometric structures with their anionic counterparts, whereas those of the remaining neutral clusters are similar to their corresponding anions. The lowest-lying isomer (5A') of B_2Si_5 is analogous to isomer 5B of $B_2Si_5^-$, while that (7A') of B_2Si_7 can be viewed as two additional Si atoms face-capping the bottom left of B_2Si_5 bowl-shaped framework. The most stable isomer of B_2Si_9 (9A') can be regarded as adding three additional Si atoms to cap the bottom of B_2Si_6 bowl-shaped framework. In the ground state structure of neutral B_2Si_{11} (11A'), one B atom and nine additional Si atoms constitute a distorted pentagonal prism, in which the other B atom is encapsulated into the cage, and the remaining two Si atoms face-cap the top of BSi_9 pentagonal prism. We would like to point out that the lowest-lying isomers of B_2Si_n ($n = 3-8$) neutral clusters are very

similar to those characterized by the infrared-ultraviolet two-color ionization spectroscopy and quantum chemical calculations in the literature.³¹

5. DISCUSSION

The evolution of the experimental and theoretical VDEs of $B_2Si_n^-$ ($n = 3-12$) versus the number of Si atoms is shown in Figure 5. It can be seen that the theoretical VDEs are in reasonable agreement with the experimental VDEs with average derivations of ~ 0.08 eV. Figures 2 and 4 show that the two B atoms in $B_2Si_n^{-/0}$ prefer to occupy the high coordination sites to form more B–Si bonds, which is more likely due to the existence of unfilled p orbitals in the B atom. The two B atoms in $B_2Si_{3-12}^{-/0}$ tend to interact with each other to form a B–B bond, which is in agreement with the infrared-ultraviolet two-color ionization spectroscopy and theoretical investigations of B_2Si_{3-8} .³¹ Likewise, two TM atoms also incline to form a strong metal–metal bond found in $T_2Si_{1-8}^{-/0}$ ($T = V, Fe, Co$, and Ni)^{32,58} and $M_2Si_{3-12}^{-/0}$ ($M = Nb, Ta, Mo$, and W).^{42,59} As we can see from Table 2, the B–B bond lengths in $B_2Si_{3-6}^{-/0}$ are between 1.60 and 1.69 Å, which are slightly longer than the B–B bond length of 1.60 Å in the boron dimer (B_2),⁶⁰ but shorter than the typical B–B single bond length of 1.71 Å.^{61,62} This

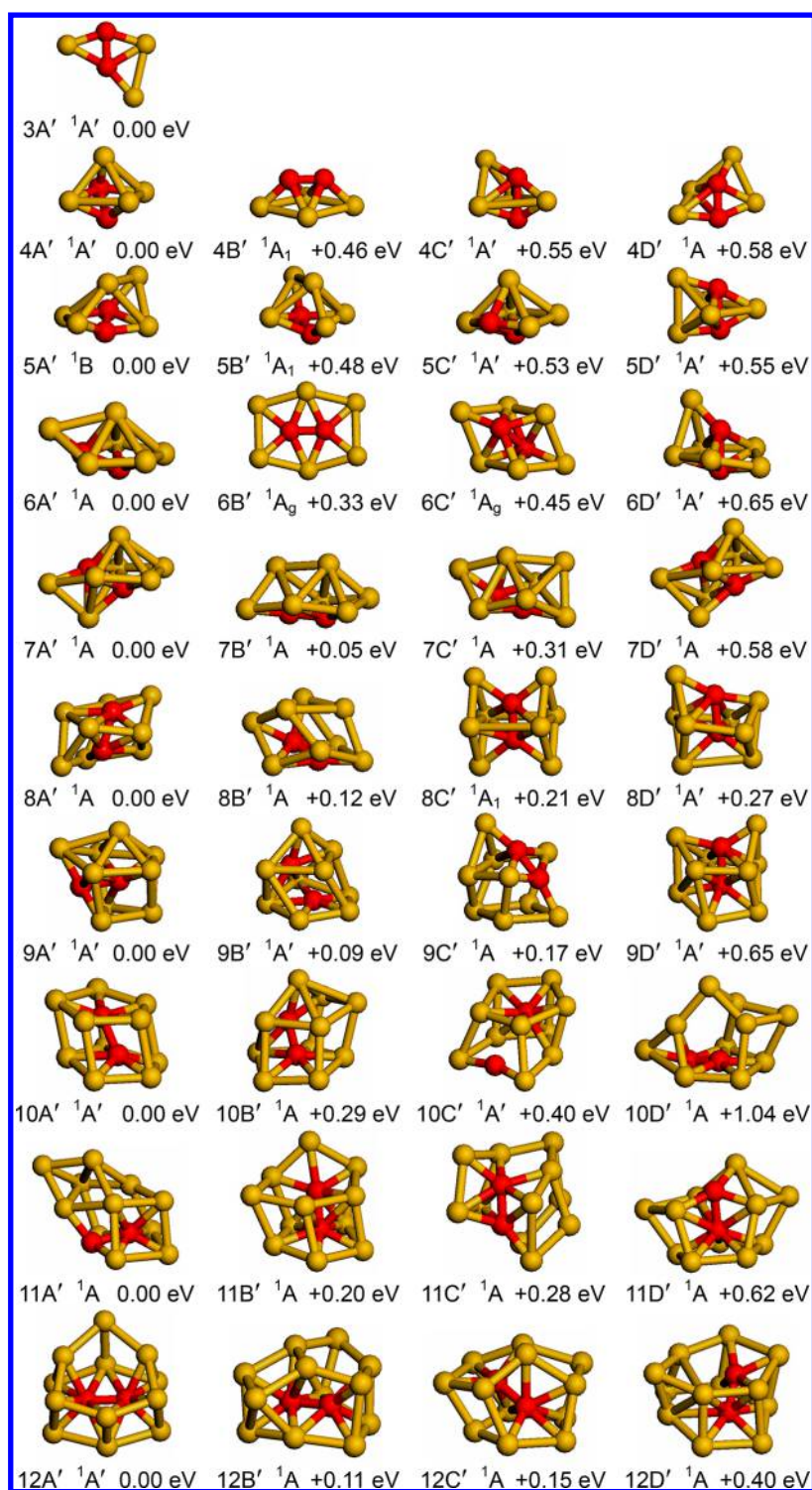


Figure 4. Typical low-lying isomers of neutral B_2Si_n ($n = 3-12$) clusters. ΔE values are calculated at the CCSD(T)//aug-cc-pVTZ level of theory. Red and yellow balls stand for the B and Si atoms, respectively.

suggests that the interactions between the two B atoms in $B_2Si_{3-6}^{-/0}$ are comparable to the typical B–B single bond. However, the B–B bond lengths in $B_2Si_{7-12}^{-/0}$ range from 1.72 to 2.08 Å, which are elongated as compared to those in $B_2Si_{3-6}^{-/0}$ and are longer than the typical B–B single bond length of 1.71 Å, indicating that the B–B bonds in $B_2Si_{7-12}^{-/0}$ should be slightly weaker than the typical B–B single bond. It seems that the interactions between the B and Si atoms weaken the B–B bonds with the increasing number of Si atoms. In

addition, we calculated the Wiberg bond orders of the chemical bonds in $B_2Si_{3-12}^{-/0}$. The calculations showed that the B–B Wiberg bond orders in $B_2Si_{3-6}^{-/0}$ are in the range of 0.90 to 1.24, implying that the interactions between the two B atoms are very close to the typical B–B single bond, which is consistent with the short B–B bond lengths (1.60–1.69 Å) in $B_2Si_{3-6}^{-/0}$. As for $B_2Si_{7-12}^{-/0}$, the B–B Wiberg bond orders are between 0.46 and 0.72, suggesting that the interactions between

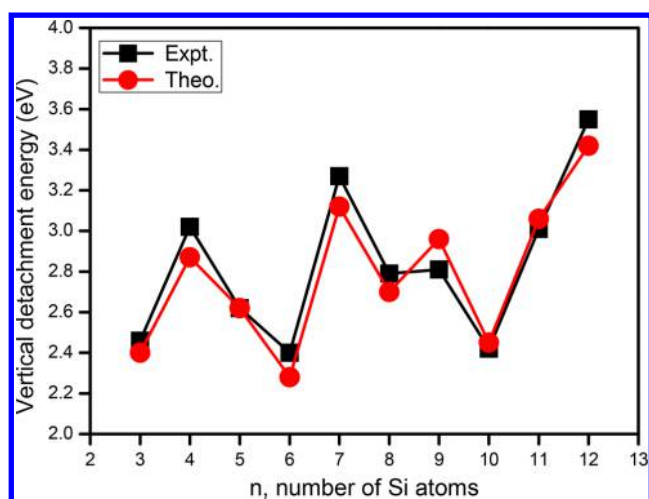


Figure 5. Experimental and theoretical VDEs of $B_2Si_n^-$ ($n = 3-12$) clusters versus n , the number of Si atoms.

the two B atoms are slightly weaker than the typical B–B single bond.

To explore the effective atomic charges distribution of $B_2Si_n^-$ ($n = 3-12$) clusters, we carried out natural population analysis (NPA) on the most stable structures and presented the results in Figure 6. The NPA charges on the two B atoms of $B_2Si_{3-12}^-$

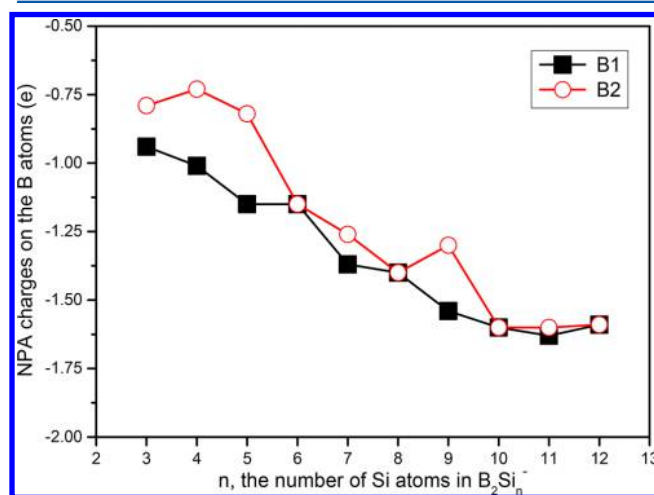


Figure 6. NPA charges on the B atoms of the most stable isomers of $B_2Si_n^-$ ($n = 3-12$) clusters.

are found to be all negative values varying from $-0.70 e$ to $-1.70 e$. It indicates that some electrons of the Si_n frameworks are transferred to the two B atoms, which is more likely due to the stronger Pauling electronegativity ($\chi = 2.04$) of B atom as compared to that ($\chi = 1.90$) of Si atom.⁶³ In addition, we found that the NPA charges on the two B atoms of $B_2Si_{3-12}^-$ gradually increase with the increasing number of Si atoms. Especially, the NPA charges on the two B atoms increase significantly at $n = 10-12$, probably related to the formation of double B atoms endohedral structures at these cluster sizes. It is also worth mentioning that, for the cluster sizes of $n = 3-5, 7$, and 9 , the B2 atom carries fewer negative charges than the B1 atom. That is because the B1 atom interacts with more Si atoms than the B2 atom does in these cluster sizes. As for the other clusters, the B1 and B2 atoms interact with nearly the same number of Si atoms, therefore the NPA charges on the two B atoms are

very similar. Overall, the NPA charge distributions on the B1 and B2 atoms are strongly correlated with the structural evolution of $B_2Si_n^-$ and their interactions with the Si atoms.

The previous photoelectron spectroscopy and photoelectron imaging experiments combined with theoretical calculations suggested that the ground-state structures of Si_3^{2-} , Si_5^- , and Si_5 clusters are trigonal bipyramid with D_{3h} symmetry, and Si_5 five-membered ring geometric structure is not stable.⁶⁴⁻⁶⁶ Interestingly, here, we found that the Si_5 five-membered rings can be stabilized by the B atoms, thus, 10 Si atoms are able to form two Si_5 rings to encapsulate the B atoms in $B_2Si_{10}^{-/0}$. It is also interesting to note that two Si_6 six-membered rings can sandwich a transition metal atom such as Cr, V, or Nb, to form a hexagonal prism or distorted hexagonal prism structures.⁶⁷⁻⁶⁹ Although two Si_5 five-membered rings are able to sandwich a B_2 unit in $B_2Si_{10}^{-/0}$, the sandwich of B_2 by two Si_6 six-membered rings in $B_2Si_{12}^{-/0}$ is not stable. This indicates that the B_2 unit is capable to stabilize the Si_5 rings rather than the Si_6 rings. Figure 5 shows that the theoretical and experimental VDEs of $B_2Si_{10}^-$ are significantly lower than those of its neighboring clusters $B_2Si_{7-9}^-$ and $B_2Si_{11-12}^-$. The drop of the VDE at $n = 10$ may be associated with the special structure of $B_2Si_{10}^-$.

To give insight into the chemical bonding in B_2Si_{10} neutral, the constant electronic charge densities of the most stable isomer of B_2Si_{10} ($10A'$) were analyzed and displayed in Figure 7. We can see from Figure 7, for constant charge density surface of 0.04 au, the electronic charges are distributed uniformly over the B–B, B–Si, and Si–Si bonds, while those at the center of each Si_4 rhombus are very low. For constant charge density surface of 0.06 au, the electronic charges are mainly on the B–B and B–Si bonds. For constant charge density surface of 0.08 au, the electronic charges are mainly observed on the B–B bond. These results indicate that the interactions between the atoms are in the order of $B-B > B-Si > Si-Si$. The strong interaction between the two B atoms is in good agreement with the calculated B–B Wiberg bond order (0.77) and B–B bond length (1.80 Å) in B_2Si_{10} . This is also consistent with the result of the strong V–V interactions and the short V–V bond distance (2.31 Å) revealed in our previous investigation of $V_2Si_{20}^{-/0}$, which is smallest fullerene-like silicon cage structure with a V_2 unit encapsulated inside the cage.⁷⁰ It seems that strong M–M bond ($M = \text{metal or nonmetal atom}$) and short M–M bond distance are essential conditions for forming a stable Si_n cage with a M_2 unit at the center, which can be contributed to design new building blocks used for producing novel cluster-assembled nanomaterials.

We used the Multiwfn program (3.41 package)⁷¹ and VMD program⁷² to analyze the bonding properties of B_2Si_{10} neutral by means of the Adaptive Natural Density Partitioning (AdNDP) method⁷³ at the B3LYP//6-311+G(d,p) level of theory, and displayed them in Figure 8. B_2Si_{10} neutral ($10A'$) has 46 valence electrons including six valence electrons of the two B atoms and 40 valence electrons of the 10 Si atoms, which are spread over the 23 delocalized valence MOs with approximate “s” and “p” symmetry. These MOs are composed of 15 $2c-2e$ Si–Si σ bonds (electronic occupation (ON) is equal to $1.85-1.97$ lel), four $3c-2e$ BSi_2 σ bonds (electronic occupation (ON) is equal to 1.90 lel), two $4c-2e$ BSi_3 σ bonds (electronic occupation (ON) is equal to 1.90 lel), and two $6c-2e$ BSi_5 $\sigma + \pi$ bonds (ON = 1.91 lel). These suggest that B_2Si_{10} neutral has σ plus π double delocalized bonding patterns, which can effectively compensate for the intrinsic electron-deficiency of B atom. As a result, a pair of Si_5 five-membered rings can be

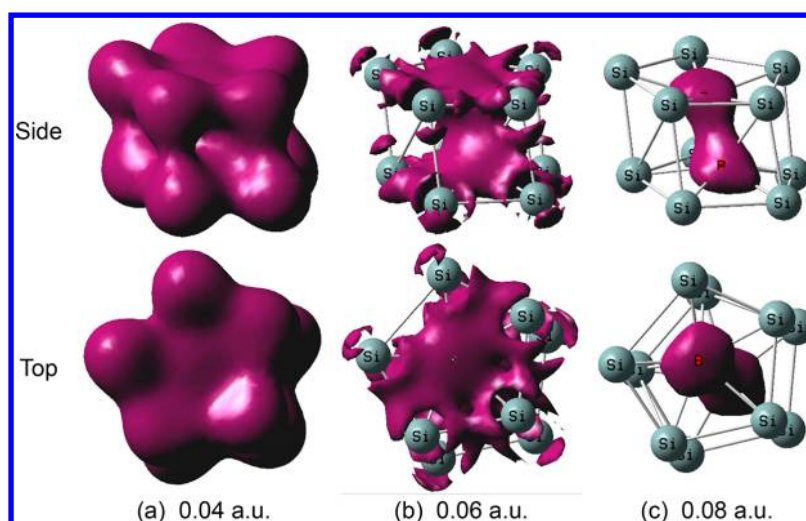


Figure 7. Constant electronic charge density surfaces of B_2Si_{10} neutral. (a) Charge density equals 0.04 au. (b) Charge density equals 0.06 au. (c) Charge density equals 0.08 au.

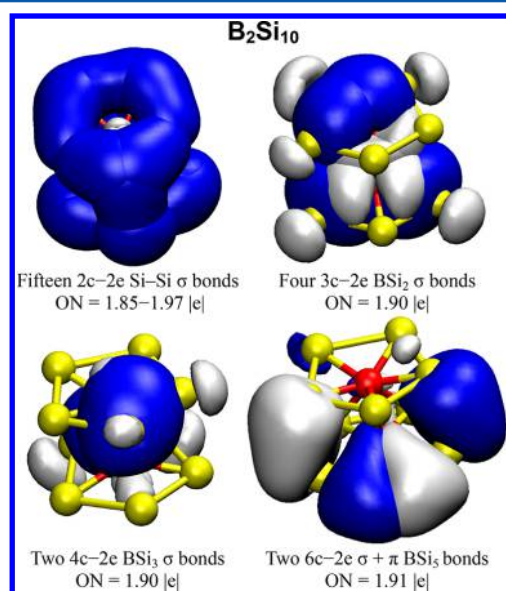


Figure 8. Adaptive density partitioning (AdNDP) bonding patterns (isosurface value = 0.02) of the most stable isomer of B_2Si_{10} neutral obtained at the B3LYP//6-311+G(d,p) level of theory. (ON = electronic occupation). Red and yellow balls stand for the B and Si atoms, respectively.

stabilized by the two B atoms and 10 Si atoms are able to encapsulate a B_2 unit in B_2Si_{10} neutral.

It is well-known that three-dimensional (3D) aromaticity arising from electron delocalization is an important factor contributing to the chemical stability for a molecular cluster. The negative value of nucleus-independent chemical shift (NICS) can be used to probe the 3D aromaticity for various cage structures.^{74,75} Generally, the more negative the NICS values, the stronger the aromaticity. We calculated the NICS values of the most stable isomers of both $B_2Si_{10}^-$ anion and B_2Si_{10} neutral at the B3LYP//6-311+G(d,p) level of theory within the Gaussian 09 program package. The calculations show that both $B_2Si_{10}^-$ anion and B_2Si_{10} neutral have highly negative NICS values, -61.7 and -54.8 ppm, at the cages centers, respectively, and their NICS values computed at points 1 Å above the cages centers are -56.0 and -54.0 ppm,

respectively. These large negative NICS values indicate that both $B_2Si_{10}^-$ anion and B_2Si_{10} neutral exhibit a significant aromaticity, which can partly explain why $B_2Si_{10}^-$ anion and B_2Si_{10} neutral are highly stable.

6. CONCLUSIONS

We conducted a combined size-selected anion photoelectron spectroscopy and theoretical study on the structural evolution of double B atoms doped silicon clusters, $B_2Si_n^{-/0}$ ($n = 3-12$). The results showed that the two B atoms in $B_2Si_{3-12}^{-/0}$ form a B-B bond and occupy the high coordination sites to interact with more Si atoms. The lowest-lying isomers of $B_2Si_{3-7}^{-/0}$ have planar structures, while those of $B_2Si_{4-7}^{-/0}$ are dominated by bowl-shaped based structures. At $n = 8-9$, the two B atoms start to be encapsulated into the Si_n cages. Especially interesting, $B_2Si_{10}^{-/0}$ have distorted pentagonal prismatic structures with the two B atoms sandwiched by two Si_5 rings. Moreover, $B_2Si_{10}^{-/0}$ exhibits three-dimensional aromaticity and B_2Si_{10} neutral has σ plus π double delocalized bonding patterns. $B_2Si_{11}^-$ anion adopts a polyhedral cage-like structure with a B_2 unit encapsulated inside the cage, whereas B_2Si_{11} neutral has a bicapped pentagonal prismatic structure with only one interior B atom. Both anionic and neutral B_2Si_{12} are tetracapped tetragonal prisms with a B_2 unit encapsulated into the cage. The results may be useful for understanding the formation mechanisms of boron-silicon compounds and the development of novel boron-silicon-based materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b10906.

The bond lengths and bond angles of $B_2Si_{10}^-$ anion and B_2Si_{10} neutral, and the Cartesian coordinates of the low-lying isomers of $B_2Si_n^{-/0}$ ($n = 3-12$) clusters (PDF)

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Notes

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