Structural and bonding properties of $ScSi_n^-$ ($n = 2 \sim 6$) clusters: photoelectron spectroscopy and density functional calculations*

Xu Hong-Guang(许洪光)[a], Wu Miao-Miao(吴苗苗)[b], Zhang Zeng-Guang(张增光)[a], Sun Qiang(孙 强)[b]†, and Zheng Wei-Jun(郑卫军)[a]‡

[a] *Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing* 100190, *China*

[b] *Department of Advanced Materials and Nanotechnology and Center for Applied Physics and Technology, Peking University, Beijing* 100871, *China*

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Anion ion photoelectron spectroscopy and density functional theory (DFT) are used to investigate the electronic and structural properties of $ScSi_n^-$ ($n = 2 \sim 6$) clusters and their neutrals. We find that the structures of $ScSi_n^-$ are similar to those of Si_{n+1}^-. The most stable isomers of $ScSi_n^-$ cluster anions and their neutrals are similar for n=2, 3 and 5 but different for n=4 and 6, indicating that the charge effect on geometry is size dependent for small scandium–silicon clusters. The low electron binding energy (EBE) tails observed in the spectra of $ScSi_{4,6}^-$ can be explained by the existence of less stable isomers. A comparison between $ScSi_n^-$ and VSi_n^- clusters shows the effects of metal size and electron configuration on cluster geometries.

Keywords: photoelectron, density functional theory, metal-doped silicon clusters

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1. Introduction

Sc-doped fullerene cages possess unique electronic and mechanical properties, which are of wide interest from both scientific and technological points of view.[1−4] Because of the similarities between silicon and carbon elements and the eminence of Si-based devices in the microelectronics industry, particular attention has been paid to Sc-doped silicon clusters. Thus, numerous studies[5−10] have been conducted to unravel the complex structural and electronic properties of Sc-doped silicon clusters using experimental and theoretical methods. Geometries, stabilities, and bonding features of $ScSi_n$ ($n = 1 \sim 6$) have been investigated by Xiao *et al.*[8] using the density functional method. The most stable structures of $ScSi_3$, $ScSi_5$, and $ScSi_6$ are of substitutional types, whereas the most stable structures of ScSi and $ScSi_4$ are of adsorption types. They also found that strong hybridization exists between Sc d and Si orbitals in $ScSi_n$. Koyasu *et al.*[5,6,11] have studied the electronic and geometrical structures of Sc-doped silicon clusters using mass spectrometry, anion photoelectron spectroscopy, and adsorption reactivity towards H_2O. They found that the adiabatic detachment energies (ADEs) of $ScSi_n^-$ ($n = 6 \sim 20$) exhibit local maxima at n=10, 16, probably due to a cooperative effect between their geometric and electronic structures.[6] In particular, $ScSi_{16}^-$ shows pronounced stability and can be considered as a superatom based on a 20-electron rule.[5] Reveles and Khanna[12] examined the stability of $ScSi_n$ ($n = 15 \sim 17$) using first-principles calculations and suggested that the most stable $Sc@Si_{16}^-$ adopts a Frank–Kasper structure with T_d symmetry. Torres *et al.*[7] also provided theoretical support for their findings by performing the calculations through using the density functional theory (DFT) and predicted that the stability of the $ScSi_{16}^-$ cluster is due to the spherical cage-like structure and the l-selection rule of the spherical potential model. Very recently, we investigated silicon

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†Corresponding author. E-mail: sunqiang@pku.edu.cn

‡Corresponding author. E-mail: zhengwj@iccas.ac.cn

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clusters doped with two Sc atoms using photoelectron spectroscopy combined with DFT calculations,[13] and showed that the most stable structures of $Sc_2Si_{3-6}^-$ clusters is an n-membered silicon ring capped by two Sc atoms on the opposite sides of the ring. In order to further explore the properties of small scandium–silicon clusters, we perform the anion photoelectron spectroscopic study of single Sc atom doped small silicon clusters, $ScSi_n^-$ ($n = 2 \sim 6$), combined with DFT calculations in this paper.

2. Experimental and theoretical methods

The experiments were conducted on a home-built apparatus consisting of a linear time-of-flight mass spectrometer and a magnetic bottle photoelectron spectrometer, which has been described elsewhere.[14] Briefly, Sc-doped silicon cluster anions were generated in a laser vaporization source by the laser ablation of a rotating translating disk target (13-mm diameter, Sc/Si mole ratio 1:1) with the second harmonic of a nanosecond Nd:YAG laser. The typical laser power used in this work was $\sim$ 10 mJ/pulse. Helium gas with $\sim$ 4 atm (1 atm=1.01325×10^5 Pa) backing pressure was injected by a pulsed valve into the source to cool the formed clusters. The generated cluster anions were mass-analysed with the linear time-of-flight mass spectrometer. The cluster anions of interest were selected with a mass gate, decelerated by a momentum decelerator before being photodetached by the laser beam from a second Nd:YAG laser (266 nm) or an excimer laser (193 nm). The electrons resulting from photodetachment were energy-analysed by the magnetic-bottle photoelectron spectrometer. The resolution of the magnetic-bottle photoelectron spectrometer was $\sim$ 40 meV at an electron kinetic energy of $\sim$ 1 eV. The photoelectron spectra were calibrated with known spectra of Cu^- and Au^-. In this work, both mass and photoelectron signals were amplified by a broadband amplifier, digitized with a digital card, and monitored with a laboratory computer. The background noise of the photoelectron spectra was subtracted shot by shot.

To further understand the experimental results, the geometry optimization and frequency calculations of $ScSi_n^-$ and $ScSi_n$ ($n = 2 \sim 6$) were conducted by using the DFT at B3LYP/6-311+G(d) level with the Gaussian03 program package.[15] All geometry optimizations were performed without any symmetry constraint, and harmonic vibrational frequencies were calculated to verify the dynamic stability of the optimized structures.

3. Experimental results

Figure 1 presents a typical anion mass spectrum of Sc–Si clusters obtained in our experiments. The resolution of the mass spectrometer is about $\sim$ 400, the isotopic peaks of silicon can be well resolved within the scope of our interest. Three major series of cluster anions, Si_n^-, $ScSi_n^-$, and $Sc_2Si_n^-$, are observed. In the spectrum, the relative intensities of Si_n^-, $ScSi_n^-$, and $Sc_2Si_n^-$ clusters are in the order of $Si_n^- > ScSi_n^- > Sc_2Si_n^-$. Due to the oxidation of the silicon and scandium sample or the tiny amount of oxygen in the carrier gas, some small peaks of $ScSiO_n^-$ can also be detected.

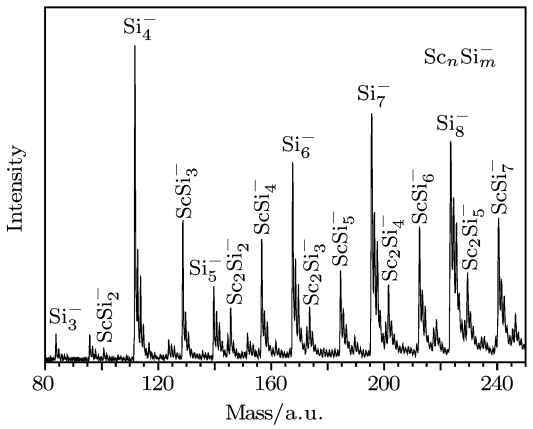


Fig. 1. Typical anion mass spectrum of mixed Sc–Si clusters. The mass unit is in atomic unit (a.u.).

The photoelectron spectra of $ScSi_n^-$ ($n = 2 \sim 6$) recorded with 266-nm and 193-nm photons are shown in Fig. 2. The spectral peaks in the 193-nm spectra are broader than those in the 266-nm spectra since the kinetic energies of the photoelectrons generated by the 193-nm photons are higher than those by the 266-nm photons. The vertical detachment energies (VDEs) and the ADEs of cluster anions estimated from the spectra are listed in Table 1. To account for the broadening of the photoelectron spectrum (PES) peaks due to instrumental resolution, the ADEs are calculated by adding half of the value of instrumental resolution to the onset of the first peaks in the spectra.

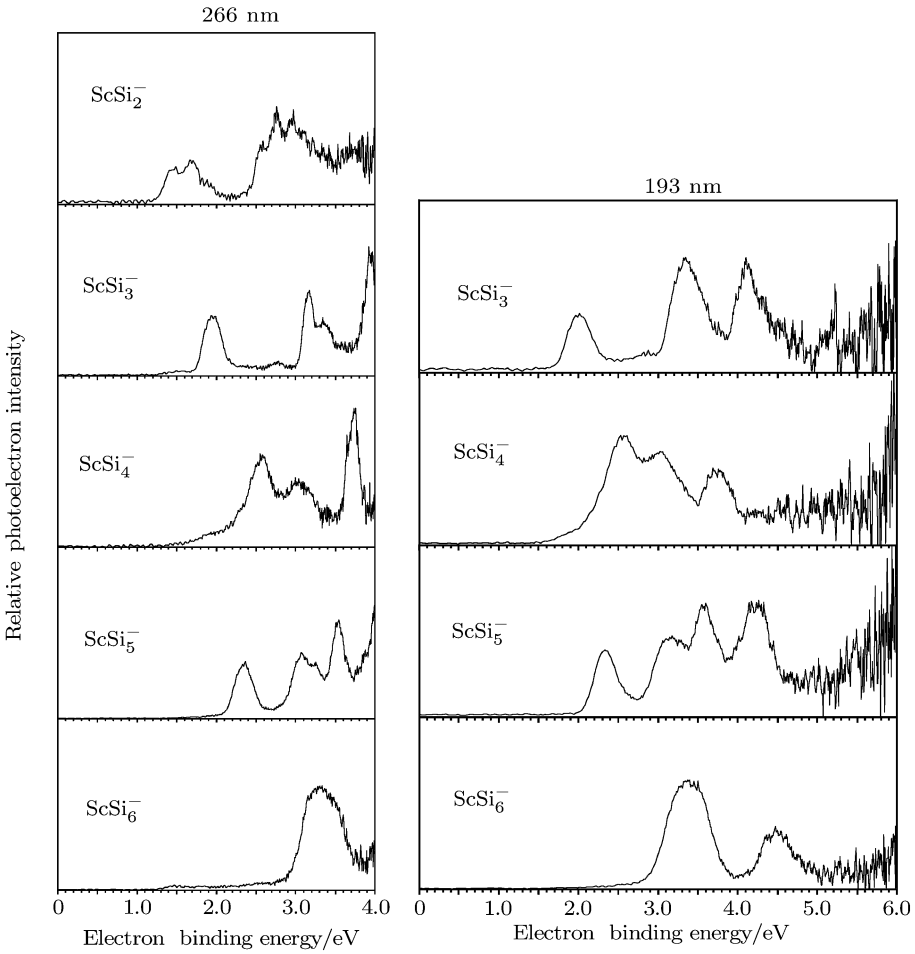


Fig. 2. Photoelectron spectra of $ScSi_n^-$ $(2 \leq n \leq 6)$ cluster anions recorded with 266-nm and 193-nm photons.

Table 1. Measured VDEs and ADEs from the photoelectron spectra of $ScSi_n^-$ $(n = 2 \sim 6)$ clusters. The numbers in parentheses indicate the uncertainties in the last digit.

cluster	VDE/eV	ADE/eV
$ScSi_2^-$	1.44 (8)	1.28 (8)
$ScSi_3^-$	1.95 (8)	1.78 (8)
$ScSi_4^-$	2.57 (8)	2.19 (8)
$ScSi_5^-$	2.35 (8)	2.15 (8)
$ScSi_6^-$	3.28 (8)	2.85 (8)

Due to the low ion intensity of $ScSi_2^-$, only the 266-nm photoelectron spectrum for $ScSi_2^-$ could be recorded. As shown in Fig. 2, the photoelectron spectrum of $ScSi_2^-$ reveals two major bands. The first band is split into two resolved peaks centred at 1.44 eV and 1.69 eV, and the second band is composed of three resolved peaks centred at 2.57, 2.75, and 2.97 eV. There are more unresolved features at an electron binding energy higher than 3 eV due to the overlapping of many electronic states. The ADE of $ScSi_2^-$ is estimated to be 1.28 eV.

The spectrum of $Sc_2Si_3^-$ at 266 nm displays a prominent peak centred at 1.95 eV, followed by a weak peak at 2.76 eV and three strong peaks at 3.17, 3.35, and 3.94 eV. The 193-nm spectrum has a slightly low resolution, thus the details of the features are indistinguishable. The ADE of $Sc_2Si_3^-$ is estimated to be 1.78 eV from the 266-nm spectrum.

Three major peaks centred at 2.57, 3.0 and 3.74 eV are observed in the spectra of $ScSi_4^-$. In addition to the major peaks, we can also observe a weak tail (hot band) in the range of 1.5 eV–2.0 eV. The weak tail may be attributed to the existence of minor isomers. It also indicates that there is a larger geometrical change from the anion to the neutral. We determine the ADE of $ScSi_4^-$ to be 2.19 eV by ignoring the hot band.

In the spectrum of $ScSi_5^-$, we are able to distinguish five peaks centred at 2.35, 3.07, 3.25, 3.53 and 4.2 eV. The peak at 2.35 eV is quite sharp, suggesting that the geometric change between the ground states of $ScSi_5^-$ and $ScSi_5$ is minor. The gap between the first and second peaks is about 0.8 eV. The electron

affinity of $ScSi_5$ is estimated to be 2.15 eV. $ScSi_6^-$ has a strong broad feature centred at 3.28 eV and a slight weak feature centred at 4.47 eV. Note that the photoelectron spectrum of $ScSi_6^-$ at 213-nm photons has been investigated by Koyasu *et al.*,[6] and their measured spectrum is consistent with the results of our work.

4. Theoretical results and discussion

The optimized geometries of the low-lying isomers of $ScSi_n^-$ and $ScSi_n$ ($n = 2 \sim 6$) clusters obtained with DFT calculations are presented in Figs. 3 and 4 with the most stable structures on the left. The relative energies between these isomers as well as their VDEs and ADEs from theoretical calculations are summarized in Table 2. The structures of $ScSi_n$ ($n = 1 \sim 6$) neutrals have been reported by Xiao *et al.*[8] The most stable structures of $ScSi_n$ ($n = 2 \sim 6$) neutral found by our calculations are consistent with their results. Figure 3 shows the first report on the structures of $ScSi_n^-$ ($n = 2 \sim 6$) cluster anions. We find that the most stable isomers of $ScSi_{2,3,5}^-$ clusters have structures similar to the neutral structures while the most stable isomers of $ScSi_4^-$ and $ScSi_6^-$ have structures different from those of $ScSi_4$ and $ScSi_6$ neutral clusters.

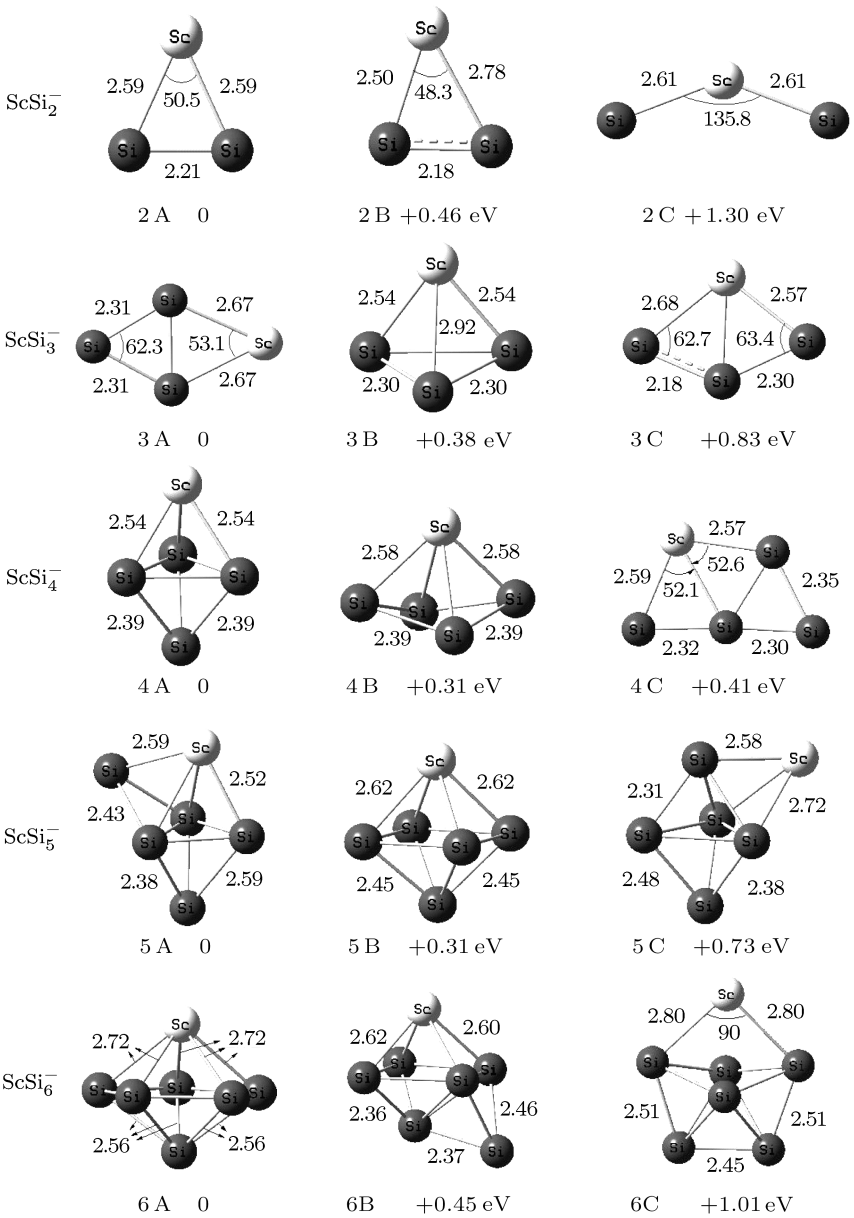


Fig. 3. Optimized geometries of the low-lying isomers of $ScSi_n^-$ ($n = 2 \sim 6$) clusters, and relative energies to the most stable isomers.

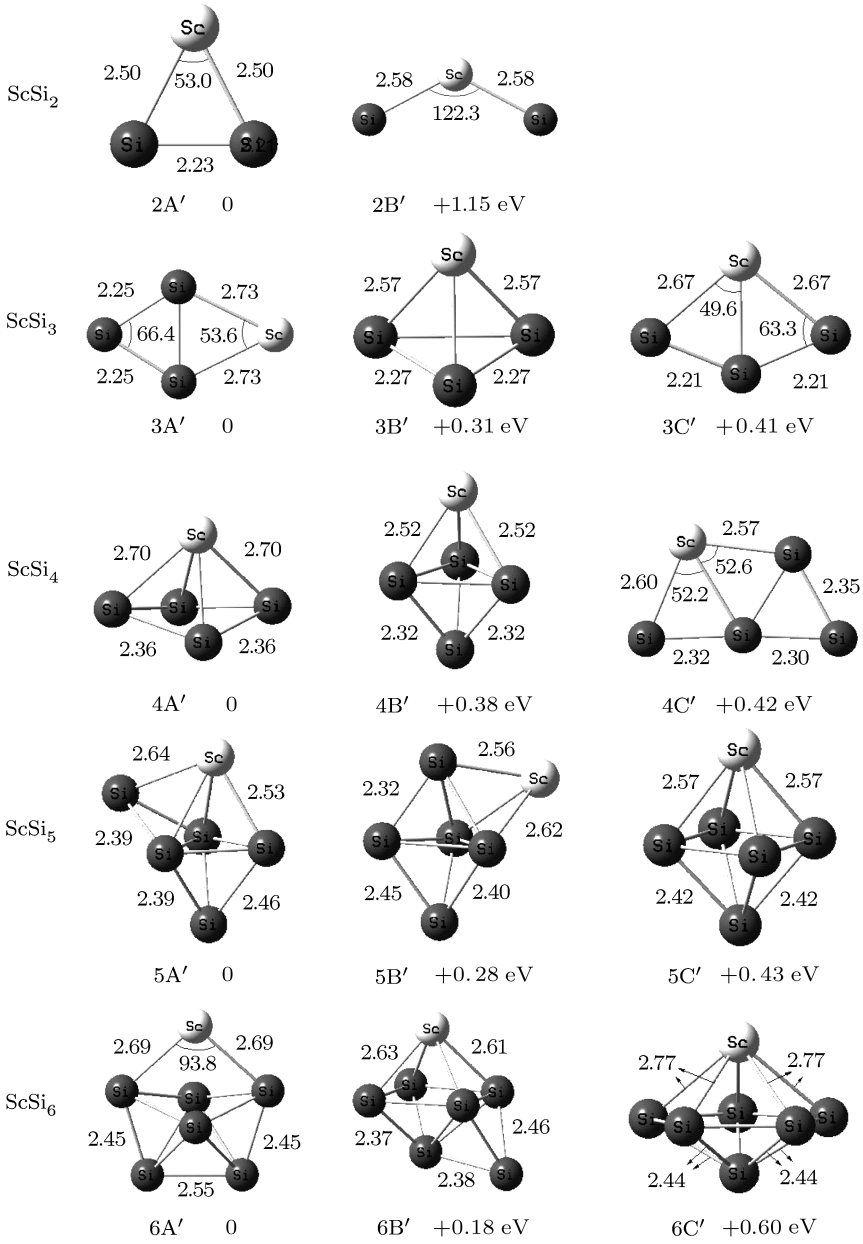


Fig. 4. Optimized geometries of the low-lying isomers of neutral $ScSi_n$ ($n = 2 \sim 6$) clusters, and relative energies to the most stable isomers.

(i) $ScSi_2^-$

As shown in Fig. 3, theoretical calculations show that $ScSi_2^-$ has three stable isomers 2A, 2B, and 2C with C_{2v}, C_s, and C_{2v} symmetry. The total energies of isomers 2B and 2C are 0.46 eV and 1.30 eV higher than that of isomer 2A, respectively. The calculated VDE and ADE for isomer 2A are 1.46 eV and 1.41 eV, respectively, which are in agreement with the experimental measurements (1.44 eV and 1.28 eV). The calculated VDEs and ADEs of isomers 2B and 2C deviate from the experimental measurements. Therefore, isomer 2A is the most likely structure for $ScSi_2^-$.

(ii) $ScSi_3^-$

The most stable structure of $ScSi_3^-$ is a planar kite structure with C_{2v} symmetry. The second stable isomer 3B has a tetrahedron structure. Isomers 3B and 3C are 0.38 eV and 0.83 eV higher in energy than isomer 3A, respectively, so they are less stable than the isomer 3A. The calculated VDEs of both isomer 3A (1.91 eV) and isomer 3B (1.86 eV) are close to the experimental value (1.95 eV), indicating that the existence of isomers 3A and 3B is possible in our experiments, while isomer 3C can be ruled out because its VDE (1.53 eV) is much lower than the experimental value (1.95 eV).

Table 2. Relative energies of the low energy isomers of $ScSi_n^-$ ($n = 2 \sim 6$) clusters as well as their VDEs and ADEs obtained by DFT calculations.

isomer		state	sym.	ΔE/eV	VDE/eV		ADE/eV		
					theor.[a]	expt.	theor.[a]	theor.[b]	expt.
$ScSi_2^-$	2A	$^3B_1$	C_{2v}	0	1.46	1.44	1.41	1.182	1.28
	2B	$^1A'$	C_s	0.46	1.11		0.95		
	2C	$^5A_1$	C_{2v}	1.30	2.69		1.26		
$ScSi_3^-$	3A	$^3B_1$	C_{2v}	0	1.91	1.95	1.88	1.697	1.78
	3B	$^1A'$	C_s	0.38	1.86		1.80		
	3C	$^1A'$	C_s	0.83	1.53		1.46		
$ScSi_4^-$	4A	$^1A_1$	C_{3v}	0	2.58	2.57	2.50		2.19
	4B	$^1A_1$	C_{2v}	0.31	1.97		1.81	1.812	
	4C	$^1A'$	C_s	0.41	2.17		2.13		
$ScSi_5^-$	5A	$^1A'$	C_s	0	2.18	2.35	2.09	2.087	2.15
	5B	$^1A_1$	C_{4v}	0.31	2.54		2.21		
	5C	$^1A'$	C_s	0.73	1.76		1.63		
$ScSi_6^-$	6A	$^1A_1$	C_{5v}	0	3.31	3.28	3.04		2.85
	6B	$^1A'$	C_s	0.45	2.24		2.18		
	6C	$^1B_1$	C_{2v}	1.01	1.55		1.43	1.649	

[a] Theoretical calculations of this work.

[b] Theoretical AEAs of the neutrals in Ref. [8], which might be slightly different from the ADEs in this work due to the geometry differences between the anions and neutrals.

(iii) $ScSi_4^-$

The first two isomers of $ScSi_4^-$, 4A and 4B, each have a trigonal bipyramid structure. Isomer 4A has C_{3v} symmetry with the Sc atom capped on the tetrahedron formed by the four silicon atoms. Isomer 4B has C_{2v} symmetry, and it may be considered as the Sc atom above the bended tetragon composed of four silicon atoms. Isomer 4C has a W-shaped planar structure. The energies of isomers 4B and 4C are 0.31 eV and 0.41 eV higher than that of isomer 4A, respectively. The VDE of isomer 4A is calculated to be 2.58 eV, which is in agreement with the experimental value (2.57 eV). The calculated VDEs of isomer 4B (1.97 eV) and 4C (2.17 eV) are much lower than the experiment measurement. The most stable structure of $ScSi_4^-$ anion (4A) is different from that of $ScSi_4$ neutral. Instead, the geometry of isomer 4B of $ScSi_4^-$ anion is similar to the ground state structure of $ScSi_4$ neutral found by our calculations (Fig. 4 (4A′)) and Xiao *et al.*[8] where they found that the AEA of neutral $ScSi_4$ is about 1.812 eV that is close to the ADE (1.81 eV) of isomer 4B. We suggest that isomer 4A is the dominating species observed in our experiments but a small amount of isomer 4B might also contribute to the weak tail in the spectrum in the range of 1.5 eV–2.0 eV.

(iv) $ScSi_5^-$

The most stable isomer of $ScSi_5^-$ (5A) may be considered as the addition of an Si atom to face cap isomer 4A, the trigonal bipyramid structure of $ScSi_4^-$. The second isomer 5B has a tetragonal bipyramidal structure with C_{4v} symmetry. Isomer 5C is formed by capping the Si_5 trigonal bipyramid with an Sc atom. Isomer 5C probably does not contribute to the experimental photoelectron spectrum of $ScSi_5^-$ since it is 0.73 eV higher in energy than isomer 5A, it is less stable than the isomer 5A and its theoretical VDE (1.76 eV) is much lower than the experimental value (2.35 eV). The VDEs of isomers 5A (2.18 eV) and 5B (2.54 eV) are both close to the experimental measurement (2.35 eV). Since isomer 5B is 0.3 eV higher in energy than isomer 5A, the isomer 5A might be the most possible isomer detected in the experiments. However, the existence of isomer 5B cannot be excluded.

(v) $ScSi_6^-$

The most stable isomer of $ScSi_6^-$ (6A) has a pentagonal bipyramid structure with C_{5v} symmetry. This is a close-packed compressed structure with the apex atoms (Sc and Si) only ~ 3.22 Å (1 Å=0.1 nm) apart in between. The total energy of isomer 6A is 0.45 eV and 1.01 eV lower than those of isomers 6B and 6C respectively. The calculated VDE and ADE of isomer 6A are 3.31 eV and 3.04 eV, respectively, which are consistent with the experimental measurements (3.28 eV and 2.85 eV). Hence, the existence of isomer 6A in our experiments can be confirmed. Isomer

6B may be considered as isomer 5B capped with a silicon atom. The structure of isomer 6C may be considered as one of silicon atom in the Si_7 pentagonal bipyramid, replaced by an Sc atom. The energies of isomer 6B and 6C are 0.45 eV and 1.01 eV higher than that of isomer 6A, respectively, indicating these that two isomers are more unstable compared with isomer 6A. The calculated VDEs of isomer 6B (2.24 eV) and 6C (1.55 eV) are much lower than the experimental value. Note that the ground state geometry of $ScSi_6^-$ is different from that of $ScSi_6$ neutral. Both our calculations and Xiao *et al.*'s [8] show that the most stable structure of $ScSi_6$ neutral (Fig. 4(6A′)) is similar to that of the third isomer of $ScSi_6^-$ (Fig. 3(6C)). The calculated EA of 6A′ by Xiao *et al.*[8] is close to the ADE of 6C in this work. That explains why the EA of $ScSi_6$ does not match the major PES peak observed in the experiment. However, in the 266-nm spectrum of $ScSi_6^-$, there are some very weak signals spreading out from 1.40 eV to 2.90 eV. That is due probably to the existence of a small number of isomers such as isomers 6B and 6C. They are less populated since they are more unstable than isomer 6A.

The ground state geometric differences between $ScSi_{4,6}^-$ clusters and their neutrals found by our calculations are consistent with the low EBE tails observed in the spectra of $ScSi_4^-$ and $ScSi_6^-$. Ohara *et al.*[16] conducted photoelectron spectroscopy studies of $TbSi_n^-$ ($n = 6 \sim 16$). They also found that $TbSi_6^-$ has a relatively high VDE but there is a small tail beside the low EBE side of the main peak. Grubisic *et al.*[17] reported the photoelectron spectra of $LnSi_n$ ($n = 3 \sim 13$; Ln=Ho, Gd, Pr, Sm, Eu, Yb) and found similar tails in the spectra of $HoSi_6^-$, $GdSi_6^-$ and $PrSi_6^-$. However, they suggested that the low EBE tail is an integral part of the electronic structure of $LnSi_n$ instead of that originating from impurities, or isomers, or hot bands. Our theoretical calculations disagree with their conclusions. We suggest that the similar tails observed in the spectra of MSi_6^- systems by Ohara *et al.*[16] and Grubisic *et al.*[17] are due to the existence of less stable isomers. It is true, as suggested by Grubisic *et al.*,[17] that the less stable isomers observed in the experiments correspond to the most stable isomers of the neutrals.

The ground-state structures of Si_n^- ($n = 3 \sim 7$) have been investigated by experiments[18,19] and theoretical calculations[20,21] in detail. A comparison between Si_n^- ($n = 3 \sim 7$) and $ScSi_n^-$ ($n = 2 \sim 6$) shows that the most stable structure of the $ScSi_n^-$ cluster is similar to that of Si_{n+1}^- except that the structure of $ScSi_n^-$ has lower symmetry. For example, the structure of $ScSi_2^-$ is similar to that of Si_3^-. They both have C_{2v} symmetry trigonal structure. The structures of both $ScSi_3^-$ and Si_4^- are planar. $ScSi_4^-$ and Si_5^- each have a trigonal bipyramidal structure. Si_6^- has two nearly degenerated structures, a face-capped trigonal bipyramidal (C_{2v}) structure and a tetragonal bipramid (D_{4h}) structure, to which the isomers of $ScSi_5^-$ are similar. The lowest energy structures of $ScSi_6^-$ and Si_7^- each are pentagonal bipyramid. Thus, the most stable structures of $ScSi_n^-$ ($n = 2 \sim 6$) may be considered as one of the silicon atom in the silicon clusters, substituted by an Sc atom followed by a slight change in the Sc–Si bond length. This result is in agreement with the findings of Xiao *et al.*[8] It is also interesting to compare the structure of $ScSi_n^-$ with that of $Sc_2Si_{n-1}^-$. Our previous studies showed that the most stable structure of $Sc_2Si_2^-$ is a C_{2v} tetrahedron structure and that of $Sc_2Si_4^-$ has a D_{4h} tetragonal bipyramidal structure. The ground state structures of $ScSi_3^-$ and $ScSi_5^-$ are different from those of $Sc_2Si_2^-$ and $Sc_2Si_4^-$. But the trigonal bipyramid structure of $ScSi_4^-$ and the pentagonal bipyramid structure of $ScSi_6^-$ are similar to those of $Sc_2Si_3^-$ and $Sc_2Si_5^-$, respectively.

We have investigated the structures of VSi_n^- ($n = 3 \sim 6$) previously.[14] The most stable structures of $ScSi_6^-$ and VSi_6^- are similar, while those of $ScSi_{3-5}^-$ and VSi_{3-5}^- are different. The most stable isomer of VSi_3^- is of tetrahedron while that of $ScSi_3^-$ has a planar kite structure. The lowest isomer of $VSi_{4,5}^-$ is similar to the second isomer of $ScSi_{4,5}^-$. In $ScSi_n^-$ clusters, the Sc–Si bond lengths are in a range of 2.52 Å–2.73 Å, longer than the Si–Si bond lengths (2.21 Å–2.56 Å). This is different from the case of VSi_n^- clusters, where the V–Si bond lengths are in a range of 2.26 Å–2.55 Å, the Si–Si bond lengths are between 2.38 Å and 2.59 Å. In most cases, the V–Si bonds are slightly shorter than the Si–Si bond. Briefly, the bond strength is of the order of Sc–Si<Si–Si<V–Si.

5. Conclusions

$ScSi_n^-$ cluster anions are generated by laser vaporization and detected with a time-of-flight mass spectrometer. The photoelectron spectra of $ScSi_n^-$

($n = 2 \sim 6$) clusters are measured at 266 nm and 193-nm photon energies. The structures of $ScSi_{2-6}^{-}$ ($n = 2 \sim 6$) are determined by comparing photoelectron spectral data with density functional calculations. We have found that the most stable structures of $Sc_2Si_n^{-}$ may be considered as one of the silicon atom in the silicon clusters, substituted by an Sc atom followed by a slight change in the bond length. Comparing $ScSi_n^{-}$ clusters with VSi_n^{-} clusters, we have shown that the Sc–Si bond is longer than the V–Si bond due to the different atomic sizes and different electron configurations. We have also found that the most stable structures of $ScSi_{4,6}^{-}$ cluster anions differ from those of $ScSi_{4,6}$ neutrals, suggesting that the effect of charge on geometry is size-dependent. The low EBE tails observed in the spectra of $ScSi_{4,6}^{-}$ are due to the existence of less stable isomers.

References

[1] Yamamoto E, Tansho M, Tomiyama T, Shinohara H, Kawahara H and Kobayashi Y 1996 *J. Am. Chem. Soc.* **118** 2293

[2] Takata M, Nishibori E, Umeda B, Sakata M, Yamamoto E and Shinohara H 1997 *Phys. Rev. Lett.* **78** 3330

[3] Yamazaki Y, Nakajima K, Wakahara T, Tsuchiya T, Ishitsuka M O, Maeda Y, Akasaka T, Waelchli M, Mizorogi N and Nagase S 2008 *Angew. Chem. Int. Ed.* **47** 7905

[4] Ito Y, Fujita W, Okazaki T, Sugai T, Awaga K, Nishibori E, Takata M, Sakata M and Shinohara H 2007 *Chem. Phys. Chem.* **8** 1019

[5] Koyasu K, Akutsu M, Mitsui M and Nakajima A 2005 *J. Am. Chem. Soc.* **127** 4998

[6] Koyasu K, Atobe J, Furuse S and Nakajima A 2008 *J. Chem. Phys.* **129** 214301

[7] Torres M B, Fernandez E M and Balbas L C 2007 *Phys. Rev.* B **75** 205425

[8] Xiao C Y, Abraham A, Quinn R, Hagelberg F and Lester W A 2002 *J. Phys. Chem.* A **106** 11380

[9] He J G, Wu K C, Liu C P and Sa R J 2009 *Chem. Phys. Lett.* **483** 30

[10] Wang J, Ma Q M, Xu R P, Liu Y and Li Y C 2009 *Phys. Lett.* A **373** 2869

[11] Koyasu K, Atobe J, Akutsu M, Mitsui M and Nakajima A 2007 *J. Phys. Chem.* A **111** 42

[12] Reveles J U and Khanna S N 2006 *Phys. Rev.* B **74** 035435

[13] Xu H G, Zhang Z G, Feng Y and Zheng W J 2010 *Chem. Phys. Lett.* **498** 22

[14] Xu H G, Zhang Z G, Feng Y, Yuan J Y, Zhao Y C and Zheng W J 2010 *Chem. Phys. Lett.* **487** 204

[15] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Zakrzewski V G, Montgomery J A, Jr, Stratmann R E, Burant J C, Dapprich S, Millam J M, Daniels A D, Kudin K N, Strain M C, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson G A, Ayala P Y, Cui Q, Morokuma K, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Cioslowski J, Ortiz J V, Baboul A G, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W J B, Chen W W M W, Andres J L G C, Head-Gordon M, Replogle E S and Pople J A *Gaussian 03* Gaussian Inc. Pittsburgh, PA

[16] Ohara M, Miyajima K, Pramann A, Nakajima A and Kaya K 2002 *J. Phys. Chem.* A **106** 3702

[17] Grubisic A, Ko Y J, Wang H P and Bowen K H 2009 *J. Am. Chem. Soc.* **131** 10783

[18] Xu C S, Taylor T R, Burton G R and Neumark D M 1998 *J. Chem. Phys.* **108** 1395

[19] Peppernick S J, Gunaratne K D D, Sayres S G and Castleman A W 2010 *J. Chem. Phys.* **132** 13

[20] Raghavachari K and Rohlfing C M 1991 *J. Chem. Phys.* **94** 3670

[21] Zubarev D Y, Boldyrev A I, Li X, Cui L F and Wang L S 2005 *J. Phys. Chem.* A **109** 11385