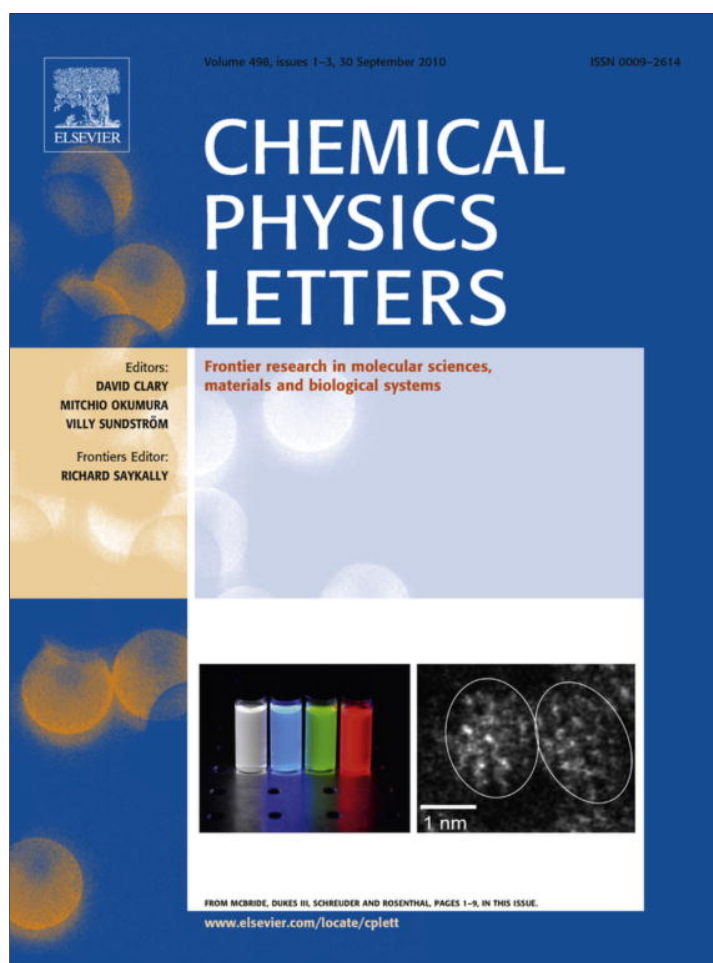


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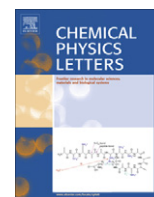
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journal homepage: www.elsevier.com/locate/cplettPhotoelectron spectroscopy and density-functional study of Sc_2Si_n^- ($n = 2-6$) clusters

Hong-Guang Xu, Zeng-Guang Zhang, Yuan Feng, Weijun Zheng*

Beijing National Laboratory for Molecular Science, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

We conducted a photoelectron spectroscopy and density-functional study on Sc_2Si_n^- ($n = 2-6$) clusters. The adiabatic detachment energies of $\text{Sc}_2\text{Si}_{2-6}^-$ were estimated to be 1.42 ± 0.08 , 1.37 ± 0.08 , 1.33 ± 0.08 , 1.9 ± 0.2 , and 2.0 ± 0.2 eV respectively from their photoelectron spectra. Comparison of theoretical and experimental results indicates that each of these clusters has more than one isomer in the experiments. In the most stable structures of $\text{Sc}_2\text{Si}_{3-6}^-$ clusters, the silicon atoms form an n -membered silicon ring, and the two Sc atoms cap to the opposite sides of the ring. The Sc–Sc interaction in Sc_2Si_n^- clusters is very weak comparing to the strong V–V interaction in V_2Si_n^- clusters.

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1. Introduction

Transition metal-doped silicon clusters have been investigated extensively with experiments [1–10] and theoretical calculations [11–25] since they have potential applications in microelectronics and cluster-assembly materials. Scandium doped silicon clusters have received special attention because scandium is the simplest 3d transition metal. Earlier theoretical calculations conducted by Xiao et al. [26] showed that there is strong hybridization between the Sc d orbitals and Si orbitals in small ScSi_n ($n = 1-6$) clusters and charge transfer proceeds from the Sc atom to the Si framework. Koyasu et al. conducted mass spectrometry, photoelectron spectroscopy and reactivity studies of silicon clusters doped with transition metal atoms [27–29] and found that MSi_{16} ($M = \text{Sc}, \text{Ti}, \text{and V}$) is relatively stable, the vertical detachment energy (VDE) of ScSi_{16}^- (4.25 eV) is high and its pronounced stability is very similar to that of Al_{13}^- , suggesting that ScSi_{16} may be viewed as a superhalogen. Theoretical calculations of Reveles and Khanna [30] confirmed the experimental finding and showed that ScSi_{16}^- has 20 valence electrons around the Sc atom, which might be considered as a nearly free electron gas in the silicon cage. The stability of ScSi_{16}^- is mainly due to the electron counting rules as well as its special geometrical shape. Further theoretical calculations performed by Torres et al. [31] also demonstrated that the near spherical cagelike structure and the l -selection rule of the spherical potential model contribute to the stability of MSi_{16} ($M = \text{Sc}^-, \text{Ti}, \text{and V}^+$) clusters. As for silicon clusters doped with two Sc atoms, the experimental work and theoretical calculations are quite rare except that the reactivities of $\text{Sc}_2\text{Si}_n^{-/0/+}$ ($n = 6-20$) clusters were investigated by Koyasu et al. [28]. In our previous study, we found that the two

V atoms in V_2Si_n^- clusters tend to form a strong V–V bond [32]. It will be interesting to investigate whether similar things will show up in silicon clusters doped with scandium atoms, hence, provide information about the effects of d electrons on the M–M bond in M_2Si_n clusters. In this work, we report a photoelectron spectroscopy and density-functional study of small silicon clusters doped with two scandium atoms, Sc_2Si_n^- ($n = 2-6$).

2. Experimental and theoretical methods

2.1. Experimental

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 [32]. Briefly, Sc_mSi_n^- cluster anions were generated in a laser vaporization source by 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 (Continuum Surelite II-10). The typical laser power used in this work is ~ 10 mJ/pulse. Helium gas with ~ 4 atm backing pressure was injected by a pulsed valve (General Valve Series 9) into the source to cool the formed clusters. The generated cluster anions were mass-analyzed with the linear time-of-flight mass spectrometer. The cluster anions of interest were selected with a mass gate, decelerated by a momentum decelerator, and crossed with the beam of the fourth harmonic (266 nm, 4.661 eV) of a second Nd:YAG laser at the photodetachment region of our apparatus. The resulting electrons from photodetachment were energy-analyzed by the magnetic-bottle photoelectron spectrometer. The resolution of the magnetic-bottle photoelectron spectrometer was ~ 40 meV at electron kinetic energy of ~ 1 eV ($\sim 4\%$ of the electron kinetic energy). The photoelectron spectra were calibrated with known spectra of Cu^- and Au^- . In

* Corresponding author. Fax: +86 10 62563167.

E-mail address: zhengwj@iccas.ac.cn (W. Zheng).

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.

2.2. Theoretical

The geometry optimization and frequency calculations of Sc_2Si_n^- ($n = 2-6$) were conducted using density-functional theory (DFT) at B3LYP/6-311+G(d) level with the GAUSSIAN 03 program package [33]. All geometry optimizations were conducted without any symmetry constraint. Spin doublet and quartet states were considered for each initial structure of Sc_2Si_n^- clusters. Harmonic vibrational frequencies were calculated to make sure that the optimized structures correspond to real local minima. The zero-point vibrational energies (ZPEs) are not considered here since the difference between the ZPEs of the anions and corresponding neutrals are much smaller than the calculation uncertainties, hence, can be cancelled out. The diagram of the molecular structures and orbitals were made with GaussView3.0.

3. Results and discussion

Figure 1 shows the photoelectron spectra of Sc_2Si_n^- ($n = 2-6$) recorded with 266 nm (4.661 eV) photons. Each peak in the photoelectron spectra represents a transition from the ground-state of the anions to the ground or an excited state of their corresponding neutrals. The broad features could be contributed by more than one transition since Sc_2Si_n clusters may have several low-lying states owing to the d electrons and the cluster size. The vertical detachment energies (VDEs) and the adiabatic detachment energies (ADEs) of the cluster anions estimated from the photoelectron spectra are listed in Table 1. To account for the broadening of the PES peaks due to instrumental resolution, the adiabatic detachment energies were calculated by adding half of the value of instrumental resolution to the onset of the first peaks in the spectra. Since some of ScSi_6O^- isotopic peaks overlap with the mass peaks of Sc_2Si_5^- , and those of ScSi_7O^- overlap with the mass peaks of Sc_2Si_6^- , we made effort to minimize the oxygen in our source. We also took the photoelectron spectra of ScSi_6O^- and ScSi_7O^- (Supplementary Material, Fig. S1), and compared them with the spectra of Sc_2Si_n^- ($n = 5$ and 6). We found that the spectra of ScSi_6O^- and ScSi_7O^- are significantly different from those of Sc_2Si_5^- and Sc_2Si_6^- , and the ADEs of ScSi_6O^- and ScSi_7O^- are higher than those of Sc_2Si_5^- and Sc_2Si_6^- . Thus, we could safely rule out the contamination of Sc_2Si_5^- and Sc_2Si_6^- spectra by ScSi_6O^- and ScSi_7O^- impurities.

As seen in Figure 1, the photoelectron spectrum of Sc_2Si_2^- has two major peaks centered at 1.68 and ~ 2.8 eV. The spectrum of Sc_2Si_3^- has three peaks centered at 1.57, 2.28, and 3.12 eV, and a broad shoulder between 2.5 and 3.0 eV, followed by an unresolved broad feature at higher binding energy. Five major peaks are evident in the spectrum of Sc_2Si_4^- , and they are centered at 1.52, 2.28, 2.84, 3.45, and 3.69 eV, respectively. The spectral features of Sc_2Si_5^- and Sc_2Si_6^- are relatively broader than those of $\text{Sc}_2\text{Si}_{2-4}^-$. Therefore, the uncertainties of their VDEs and ADEs determined from the photoelectron spectra are larger than those of $\text{Sc}_2\text{Si}_{2-4}^-$ (Table 1). We can roughly distinguish several features in their spectra. The spectrum of Sc_2Si_5^- contains three broadened features, one is centered at 2.76 eV, and the others are at 3.33 and 3.73 eV, respectively. The spectrum of Sc_2Si_6^- is composed of five peaks centered at 2.33, 2.62, 3.17, ~ 3.5 , and ~ 4.0 eV, respectively.

To investigate the structures and properties of Sc_2Si_n^- ($n = 2-6$), we conducted density-functional calculations on these clusters. The optimized geometries of the low-lying isomers of Sc_2Si_n^-

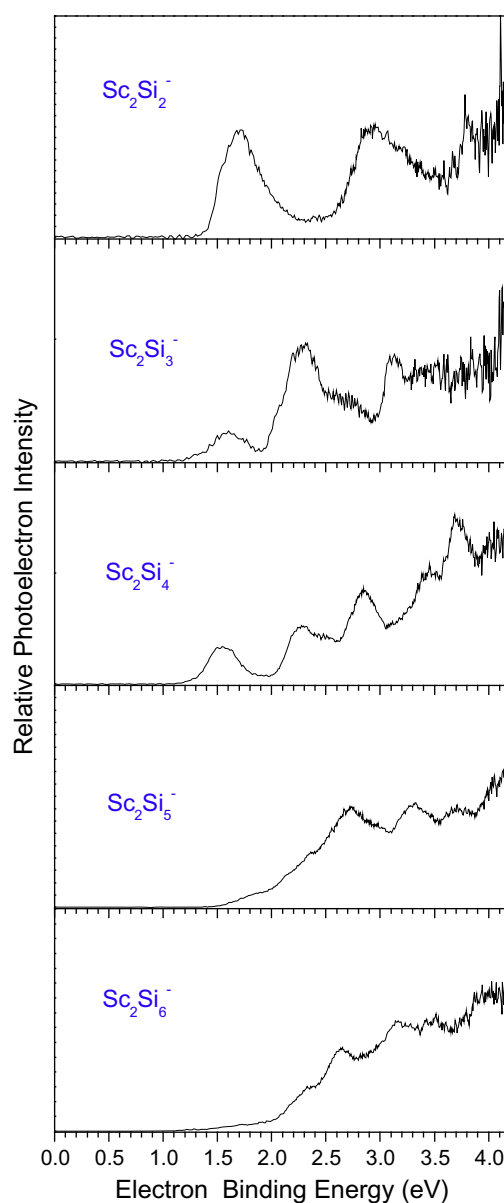


Figure 1. Photoelectron spectra of Sc_2Si_n^- ($n = 2-6$) cluster anions recorded with 266 nm photons.

($n = 2-6$) clusters obtained with DFT calculations are presented in Figure 2 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 1. The theoretical vertical electron detachment energies (VDEs) were calculated as the energy differences between the anions and neutrals at the geometries of the anions. The theoretical adiabatic electron detachment energies (ADEs) were calculated as the energy differences between the anions and the neutrals relaxed to the nearest local minima from the geometries of the anions. The relaxed neutral structures are similar to those of corresponding anions.

As can be seen from Figure 2, the most stable isomer (1A) of Sc_2Si_2^- is a tetrahedral structure with C_{2v} symmetry in doublet state (2A_1), and the Sc–Sc distance is about 3.04 Å. Isomer 1B has a rhombus structure and is 0.17 eV higher than isomer 1A in total energy. The structure of isomer 1C is similar to that of isomer 1A, however, its Sc–Sc distance (3.51 Å) is much longer than that of isomer 1A, and its energy is about 0.52 eV higher than that of isomer 1A. The calculated VDEs of isomer 1A and 1B are 1.42 and

Table 1
Relative energies of the low energy isomers of Sc_2Si_n^- ($n = 2-6$) as well as their VDEs and ADEs obtained by DFT calculations.

Isomer	$(d_{\text{Sc-Sc}})^a$ (Å)	State	Symmetry	ΔE (eV)	VDE (eV)		ADE (eV)	
					Theoretical	Experimental ^b	Theoretical	Experimental ^b
Sc_2Si_2^-	1A	3.04	2A_1	C_{2v}	0	1.42	1.30	1.42(8)
	1B	2.74	$2B_{3g}$	D_{2h}	0.17	1.78	1.66	
	1C	3.51	4A_1	C_{2v}	0.52	0.88	0.77	
Sc_2Si_3^-	2A	4.16	$^2A_1'$	D_{3h}	0	1.34	1.30	1.37(8)
	2B	2.96	$^2A'$	C_s	0.26	1.64	1.51	
	2C	3.72	2B_2	C_{2v}	0.70	1.52	0.59	
Sc_2Si_4^-	3A	3.73	$^2B_{2u}$	D_{4h}	0	1.76	1.57	1.33(8)
	3B	3.09	2B_2	C_{2v}	0.24	1.42	1.38	
	3C	2.93	2A	C_1	0.55	1.85	1.75	
Sc_2Si_5^-	4A	3.39	2A_1	C_{2v}	0	2.36	2.22	1.9(2)
	4B	3.11	$^2A''$	C_s	0.02	2.00	1.66	
	4C	2.99	$^2A''$	C_s	0.22	1.92	1.80	
	4D	2.74	2B_2	C_{2v}	0.36	2.04	1.82	
Sc_2Si_6^-	5A	3.25	2A_1	C_{2v}	0	2.79	2.10	2.0(2)
	5B	4.22	2A_u	C_i	0.30	2.26	1.83	
	5C	3.07	4A	C_1	0.43	2.34	2.05	
	5D	3.81	2A_1	C_{2v}	0.54	1.45	1.14	

^a $(d_{\text{Sc-Sc}})$, the distance between scandium atoms.

^b Experimental values estimated from the photoelectron spectra in this work.

^c The numbers in parentheses indicate the uncertainties in the last digit.

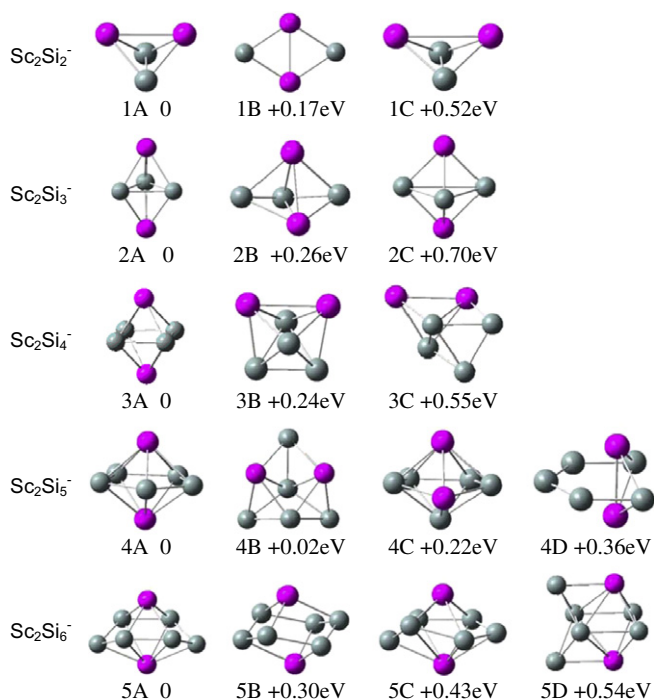


Figure 2. Optimized geometries for the low-lying isomers of Sc_2Si_n^- ($n = 2-6$) clusters. The relative energies to the most stable isomers are shown. The dark cyan and pink spheres stand for Si and Sc atoms, respectively.

1.78 eV respectively. Those values are close to the experimental measurement (1.68 eV). The calculated VDE of isomer 1C is ~ 0.88 eV, which is much lower than our experimental measurement. Thus, the existence of isomer 1C in the experiments can be ruled out. Isomers 1A and 1B probably are what we observed in the experiments.

The most stable structure of Sc_2Si_3^- (isomer 2A) is a D_{3h} symmetric trigonal bipyramid with the two scandium atoms capping on the opposite sides of the plane formed by the three silicon atoms, and the calculated Sc–Sc distance in it is about 4.16 Å. Isomer 2B is about 0.26 eV higher than isomer 2A in energy. The theoretical VDE of isomer 2A is about 1.34 eV, and that of isomer 2B is

about 1.64 eV, both in agreement with the experimental measurement (1.57 eV). Isomer 2C is a trigonal bipyramid with C_{2v} symmetry. Its theoretical VDE (1.52 eV) is very close to the experimental measurement (1.57 eV), however, it is less stable than isomer 2A by about 0.70 eV. Hence, the existence of isomer 2C in our experiments can be excluded. Isomers 2A and 2B probably are the experimentally observed isomers for Sc_2Si_3^- .

The calculations predict isomer 3A as the most stable structure for Sc_2Si_4^- . It has D_{4h} symmetry with the two scandium atoms locating on the opposite sides of the silicon square. The structure of isomer 3B is a bicapped tetrahedron (C_{2v}). It is only 0.24 eV higher than isomer 3A in total energy. The theoretical VDEs and ADEs of isomers 3A and 3B are all in reasonable agreement with the experimental measurements. The total energy of isomer 3C are higher than isomer 3A by 0.55 eV, and its VDE (1.85 eV) and ADE (1.75 eV) deviate more from the experimental measurements than those of isomer 3A and 3B.

The most stable structure of Sc_2Si_5^- (4A) is a distorted pentagonal bipyramid with C_{2v} symmetry. The two scandium atoms also occupy the opposite sides of the five-membered silicon ring. The calculated VDE of isomer 4A (2.36 eV) is consistent with the experimental value (2.37 eV). Therefore, isomer 4A probably is the major product in the experiments. Isomers 4B, 4C and 4D are close to isomer 4A in energy. Their VDEs are relatively lower than the experimental value. As it can be seen from the photoelectron spectrum in Figure 1, there are many unresolved features on the low EBE side in the Sc_2Si_5^- spectrum. These features probably are due to the existence of other low-lying isomers such as isomers 4B, 4C, and 4D in the experiments.

Our calculations found that the most stable structure of Sc_2Si_6^- (5A) has C_{2v} symmetry with the two scandium atoms locating on the opposite sides of the boat-style ring formed by the six silicon atoms. Isomer 5B is 0.30 eV higher than isomer 5A in energy. It has a structure with the six silicon atoms forming a chair-style ring and each scandium atom bonds to three silicon atoms. This structure resembles the most stable structure of V_2Si_6^- [32] except that the Sc–Sc distance (4.22 Å) is much longer than the V–V distance. The structure of isomer 5C is only slightly different from those of isomer 5A and 5B. It is 0.43 eV higher than isomer 5A in energy. Isomer 5D can be considered as Sc_2Si_4^- octahedral structure (3A) capped by two silicon atoms. The calculated VDEs of the isomer 5A, 5B and 5C are 2.79, 2.26, and 2.34 eV, respectively. They are

in reasonable agreement with the experimental measurement. The VDE (1.45 eV) and ADE (1.14 eV) of isomer 5D are much lower than that of the experimental measurements (2.33 and 2.0 eV). Hence, isomer 5D probably had not been produced in the experiments. Again, the broadening of the Sc_2Si_6^- spectral features in the experiments (Fig. 1) probably can be ascribed to the existence of multiple isomers such as 4A, 4B and 4C.

Over all, we found that the most stable structures of Sc_2Si_n^- differ from those of silicon clusters doped with a single scandium atom, ScSi_n ($n = 2-6$). Theoretical calculations conducted by Xiao et al. [26] showed that the structures of ScSi_n ($n = 2-6$) remain the frame of ground-state or low-lying isomers of Si_{n+1} nearly unchanged with the Sc atom occupying various substitution sites or capping on surface sites. Our calculations show that the most stable isomer of Sc_2Si_2^- has a tetrahedral structure, different from the planar structure of ScSi_3^- or Si_4^- . In the most stable structures of Sc_2Si_n^- clusters with $n = 3-6$, the silicon atoms form an n -membered silicon ring, and the two Sc atoms are capping on the opposite sides of the silicon ring. These structures do not resemble those of ScSi_{n+1}^- or Si_{n+2}^- clusters. The three-dimensional compact framework of pure silicon has been altered since the silicon sp^3 hybridization are weakened by the scandium atoms.

In the most stable structures of Sc_2Si_n^- ($n = 2-6$) clusters, the two scandium atoms tend to bond to the silicon atoms instead of interacting with each other. The Sc–Si distance is in the range of 2.52–2.74 Å, and the Si–Si distance is between 2.30 and 2.54 Å. The Sc–Si interaction is slightly weaker than the Si–Si interaction. That is in agreement with Xiao's calculations [26]. The Sc–Sc distances in the most stable isomers of Sc_2Si_n^- ($n = 2-6$) are between 3.04 and 4.16 Å, much longer than the Sc–Si and Si–Si distances. The Sc–Sc distances in the most stable isomers of Sc_2Si_n^- ($n = 2-6$) are also longer than the Sc–Sc distance in neutral scandium dimer (2.68 Å) [34], and even longer than the Sc–Sc distance in metallic scandium (3.205 Å) [35] except for isomer 1A of Sc_2Si_2^- . The lengthened Sc–Sc distance in these structures indicates that the interaction between the two scandium atoms is relatively weak, in contrast to the short V–V distance and strong V–V interaction in V_2Si_n^- ($n = 2-6$) clusters [32]. It indicates that the number

of 3d electrons has a strong effect on the bond formation of transition metal-doped silicon clusters. It is worth mentioning that the VDEs of Sc_2Si_n^- ($n = 3-6$) are in the range of 1.53–2.3 eV, lower than those of V_2Si_n^- ($n = 3-6$) (2.34–2.90 eV) [32] at the same size.

To further investigate the chemical bonding in Sc_2Si_n^- clusters, we conducted a molecular orbital analysis for these clusters. The molecular orbital diagrams of the most stable isomers of Sc_2Si_n^- ($n = 2-6$) clusters are shown in Figure 3. The most stable isomers all have one unpaired electron. For Sc_2Si_2^- (isomer 1A), the HOMO involves the $3p_z$ of the Si atoms and the $3p_x$ and $3d_{z^2}$ of the Sc atoms. The HOMO-1 is due to the interaction between the $3p_x$ of Si atoms with the $3d_{yz}$ of Sc atoms. The HOMO-2 and HOMO-4 are mostly from the $3p_x$, $3p_y$, and $3p_z$ of Si atoms as well as the $3p_x$, $3d_{xy}$, and $3d_{xz}$ of Sc atoms. As for Sc_2Si_3^- (isomer 2A), the HOMO mainly involves $3p_x$ of Si atoms plus $3p_z$ and $4s$ of Sc atoms. The molecular orbitals from HOMO-1 to HOMO-4 all have 3p components of Si atoms and 3d components of Sc atoms. The HOMO of Sc_2Si_4^- is mainly composed by the $3p_z$ of Si atoms as well as the $3d_{x^2-y^2}$ of Sc atoms, that of Sc_2Si_5^- by $3p_z$ of Si atoms plus $3d_{x^2-y^2}$ of Sc atoms, and that of Sc_2Si_6^- by Si $3p_x$ and $3p_y$ along with Sc $3d_{x^2-y^2}$ and $3d_z^2$. These molecular orbitals indicate that spd hybridization occurs between the scandium and silicon atoms, but there is little hybridization between the two scandium atoms. That is consistent with the lengthened Sc–Sc distance in the Sc_2Si_n^- ($n = 2-6$) clusters and confirms that the Sc–Sc interaction in Sc_2Si_n^- clusters is very weak. Theoretical calculations of ScSi_n clusters by Xiao et al. [26] have shown that the 3d orbitals of Sc have strong hybridization with the 3s and 3p orbitals of the Si atoms. Our results of Sc_2Si_n^- ($n = 3-6$) clusters are in agreement with their findings.

To summarize, we investigated the structures and properties of Sc_2Si_n^- ($n = 2-6$) clusters with the combination of anion photoelectron spectrometric experiments and density-functional calculations. Comparison of experimental results and theoretical calculations implies that each of the Sc_2Si_n^- ($n = 2-6$) clusters could have more than one isomers existing in our experiments. We find that the most stable isomers of Sc_2Si_n^- clusters prefer to adopt three-dimensional structures and the Sc–Sc distance in

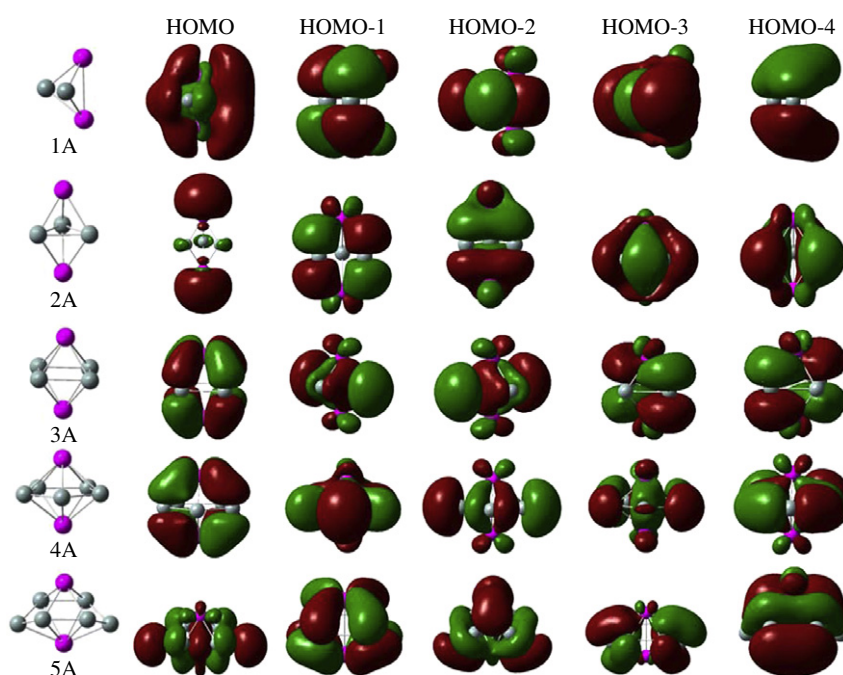


Figure 3. Molecular orbitals of the most stable isomers of Sc_2Si_n^- ($n = 2-6$) clusters.

Sc_2Si_n^- clusters is longer compare to the V–V distance in V_2Si_n^- clusters. The molecular orbital analysis shows that *spd* hybridization occurs between the scandium and silicon atoms, but there is little hybridization between the two scandium atoms. The Sc–Sc interaction in Sc_2Si_n^- clusters is quite weak, in contrast to the strong V–V interaction in V_2Si_n^- clusters, indicating that the number of *d* electrons affects the properties of transition metal-doped silicon clusters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2010.08.027](https://doi.org/10.1016/j.cplett.2010.08.027).

References

- [1] H. Hiura, T. Miyazaki, T. Kanayama, Phys. Rev. Lett. 86 (2001) 1733.
- [2] W. Zheng, J.M. Nilles, D. Radisic, K.H. Bowen, J. Chem. Phys. 122 (2005) 071101.
- [3] J.B. Jaeger, T.D. Jaeger, M.A. Duncan, J. Phys. Chem. A 110 (2006) 9310.
- [4] S. Neukermans, X. Wang, N. Veldeman, E. Janssens, R.E. Silverans, P. Lievens, Int. J. Mass Spectrom. 252 (2006) 145.
- [5] E. Janssens, P. Gruene, G. Meijer, L. Woste, P. Lievens, A. Fielicke, Phys. Rev. Lett. 99 (2007) 063401.
- [6] S. Furuse, K. Koyasu, J. Atobe, A. Nakajima, J. Chem. Phys. 129 (2008) 064311.
- [7] P. Gruene, A. Fielicke, G. Meijer, E. Janssens, V.T. Ngan, M.T. Nguyen, P. Lievens, ChemPhysChem 9 (2008) 703.
- [8] A. Grubisic, H. Wang, Y.J. Ko, K.H. Bowen, J. Chem. Phys. 129 (2008) 054302.
- [9] J.T. Lau et al., Phys. Rev. A 79 (2009) 053201.
- [10] A. Grubisic, Y.J. Ko, H.P. Wang, K.H. Bowen, J. Am. Chem. Soc. 131 (2009) 10783.
- [11] A.N. Andriotis, G. Mpourmpakis, G.E. Froudakis, M. Menon, New J. Phys. 4 (2002) 78.
- [12] G. Mpourmpakis, G.E. Froudakis, A.N. Andriotis, M. Menon, J. Chem. Phys. 119 (2003) 7498.
- [13] A.K. Singh, T.M. Briere, V. Kumar, Y. Kawazoe, Phys. Rev. Lett. 91 (2003) 146802.
- [14] P. Guo, Z.Y. Ren, F. Wang, J. Bian, J.G. Han, G.H. Wang, J. Chem. Phys. 121 (2004) 12265.
- [15] A. Negishi, N. Kariya, K. Sugawara, I. Arai, H. Hiura, T. Kanayama, Chem. Phys. Lett. 388 (2004) 463.
- [16] J. Wang, J.G. Han, J. Chem. Phys. 123 (2005) 064306.
- [17] E.N. Koukaras, C.S. Garoufalidis, A.D. Zdetsis, Phys. Rev. B 73 (2006) 235417.
- [18] H.K. Yuan, H. Chen, A.S. Ahmed, J.F. Zhang, Phys. Rev. B 74 (2006) 144434.
- [19] J.G. Han, R.N. Zhao, Y.H. Duan, J. Phys. Chem. A 111 (2007) 2148.
- [20] Y. Ito et al., ChemPhysChem 8 (2007) 1019.
- [21] L.J. Guo, G.F. Zhao, Y.Z. Gu, X. Liu, Z. Zeng, Phys. Rev. B 77 (2008) 195417.
- [22] L.Z. Kong, J.R. Chelikowsky, Phys. Rev. B 77 (2008) 073401.
- [23] R. Robles, S.N. Khanna, A.W. Castleman, Phys. Rev. B 77 (2008) 235441.
- [24] J. Wang, J.H. Liu, J. Phys. Chem. A 112 (2008) 4562.
- [25] A.P. Yang, Z.Y. Ren, P. Guo, G.H. Wang, J. Mol. Struct.: THEOCHEM 856 (2008) 88.
- [26] C.Y. Xiao, A. Abraham, R. Quinn, F. Hagelberg, W.A. Lester, J. Phys. Chem. A 106 (2002) 11380.
- [27] K. Koyasu, M. Akutsu, M. Mitsui, A. Nakajima, J. Am. Chem. Soc. 127 (2005) 4998.
- [28] M. Akutsu, K. Koyasu, J. Atobe, K. Miyajima, M. Mitsui, A. Nakajima, J. Phys. Chem. A 111 (2007) 573.
- [29] K. Koyasu, J. Atobe, S. Furuse, A. Nakajima, J. Chem. Phys. 129 (2008) 214301.
- [30] J.U. Reveles, S.N. Khanna, Phys. Rev. B 74 (2006) 035435.
- [31] M.B. Torres, E.M. Fernandez, L.C. Balbas, Phys. Rev. B 75 (2007) 205425.
- [32] H.-G. Xu, Z.-G. Zhang, Y. Feng, J.Y. Yuan, Y.C. Zhao, W.J. Zheng, Chem. Phys. Lett. 487 (2010) 204.
- [33] M.J. Frisch et al., GAUSSIAN 03, Gaussian Inc., Pittsburgh, PA, 2003.
- [34] L.B. Knight, A.J. McKinley, R.M. Babb, D.W. Hill, M.D. Morse, J. Chem. Phys. 99 (1993) 7376.
- [35] R.W.G. Wyckoff, Crystal Structures, Interscience, New York, 1963.