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Vanadium-doped small silicon clusters: Photoelectron spectroscopy and density-functional calculations

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ABSTRACT

Vanadium-doped small silicon clusters, VSi_n^- and V_2Si_n^- ($n = 3-6$), have been studied by anion photoelectron spectroscopy. The vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) of these clusters were obtained from their photoelectron spectra. We have also conducted density-functional calculations of VSi_n^- and V_2Si_n^- clusters and determined their structures by comparison of theoretical calculations with experimental results. Our results show that two V atoms in V_2Si_n^- clusters tend to form a strong V–V bond. V_2Si_6^- has D_{3d} symmetry with the six Si atoms forming a chair like six-membered ring similar to the ring in cyclohexane and the two vanadium atoms are joined with a δ bond.

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1. Introduction

Silicon and carbon behave very differently when they are forming clusters although they belong to the same group in the periodic table. Pure silicon clusters tend to form compact three-dimensional geometries via sp^3 hybridization [1,2] while carbon clusters prefer chain, ring, or cage structures through sp^2 hybridization [3,4]. In the last decade, it has been shown by both theory [5–15] and experiments [16–21] that insertion of a transition metal atom into silicon clusters is able to stabilize silicon cage structures. Transition metal-doped silicon clusters have been investigated extensively by many research groups. Beck [22] conducted the first mass spectrometric study of metal-doped silicon cluster cations. Hiura and co-workers [23,24] reported the formation of a series of metal (Hf, Ta, W, Re, Ir, etc.)-containing hydrogenated silicon clusters using an ion trap. Nakajima and co-workers [16,21,25,26] performed mass spectrometry and photoelectron spectroscopy studies of transition metal (Sc, Ti, V, Y, Zr, Nb, Hf) and lanthanide (Lu, Tb, Ho, Ta) containing silicon clusters. Bowen and co-workers [20,27] investigated the photoelectron spectra of CrSi_n^- and EuSi_n^- . Duncan and co-workers [28] studied the photodissociation of MSi_n^+ ($M = \text{Cu, Ag, Cr}$) clusters. In addition to the transition metal-doped silicon clusters, some main group element-doped silicon clusters were also studied. Na_mSi_n^- clusters have been studied by Nakajima and co-workers [29], and Wang and co-workers [30,31]; Bi_2Si_5^- cluster has been investigated by Bowen and co-workers [32].

Most of the previous experimental studies were dedicated to medium-sized metal–silicon clusters (MSi_n , $n > 6$). However, it is

necessary to investigate small metal–silicon clusters in order to obtain more detailed information about the bonding between metal and silicon. Moreover, small metal–silicon clusters might act as building blocks for larger clusters and nanomaterials. Plus, it is important to investigate silicon clusters doped with multiple metal atoms. There have been many theoretical calculations on silicon clusters doped with multiple metal atoms: Kumar and co-workers [33] studied the silicon clusters doped with multiple transition metal atoms ($M = \text{Mn, Fe, Co, Ni}$); Han et al. [34] investigated the stabilities and charge-transfer of Mo_2Si_n clusters systematically with density-functional theory; Khanna and co-workers [35,36] performed theoretical calculations on the geometries and magnetic properties of neutral and anionic M_2Si_n ($M = \text{Cr, Mn, Fe, Co, Ni}$) clusters. Although some main group element-doped silicon clusters, such as Na_mSi_n^- and Bi_2Si_5^- , have been studied experimentally, experimental investigation on silicon clusters doped with multiple transition metal atoms are very rare. In this work, we report anion photoelectron spectroscopy experiments and density-functional calculations of small silicon clusters doped with one and two vanadium atoms, V_mSi_n^- ($m = 1-2$; $n = 3-6$).

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. V_mSi_n^- cluster anions were generated in a laser vaporization source by laser ablation of a rotating translating disk target (13 mm diameter, V/Si mole ratio 1:4) with the second harmonic of a nanosecond Nd:YAG laser (Continuum Surelite II-10). This method is relatively lower cost

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for generating metal-doped silicon clusters compared to the dual-laser-vaporization method reported by Nakajima and co-workers [26]. 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 passed a skimmer, drifted into the extraction region of the time-of-flight mass spectrometer, were extracted and accelerated by pulsed voltages applied on the extraction plates. The voltages on the extraction plates were -1500 , -1420 , -1420 , and 0 V, respectively. The spacings between adjacent plates were 30, 10 and 10 mm, respectively. A horizontal deflector, a vertical deflector and two sets of Einzel lens were positioned downstream of the extraction plates in a 3.5 m flight tube. The anions passed through the flight tube and were detected with a MCP (microchannel plates) detector.

The negative photoelectron technique has the following energy-conserving relationship: $h\nu = \text{EKE} + \text{EBE} + \text{NKE}$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, EBE is the electron binding energy and NKE is the neutral recoil kinetic energy which can be ignored because it is below 10^{-4} eV in our experiment according to conservation of momentum. In our experiment, in order to take a photoelectron spectrum, the anions of interest were selected by 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 electrons from photodetachment were energy analyzed by the magnetic-bottle photoelectron spectrometer. The magnetic-bottle photoelectron spectrometer is composed of a permanent magnet located 6 mm below the photodetachment region, a 2.2 m flight tube surround by a solenoid covered with two layers of μ -metal, and a MCP detector. The electric current applied to the solenoid is about 1A, which produces a magnetic field of ~ 10 gauss at the center of the flight tube in our case. The resolution of the magnetic-bottle photoelectron spectrometer was ~ 40 meV at electron kinetic energy of ~ 1 eV. The photoelectron spectra were calibrated with known spectra of Cu^- and Au^- [37,38]. 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.

2.2. Theoretical

The geometry optimization and frequency calculations of VSi_n^- and V_2Si_n^- ($n = 3-6$) were carried out using density-functional theory (DFT) at B3LYP/6-311 + $G(d)$ level. All geometry optimizations were conducted without any symmetry constraint. Harmonic vibrational frequencies were calculated to make sure that the structures corresponded to real local minima. All theoretical calculations in this work were performed with the GAUSSIAN 09 program package [39]. The diagram of the molecular structures and orbitals were made with GAUSSVIEW5.0.8.

3. Experimental results

Fig. 1 shows the photoelectron spectra of VSi_n^- and V_2Si_n^- ($n = 3-6$) recorded with 266 nm (4.661 eV) photons. Each peak of 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 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

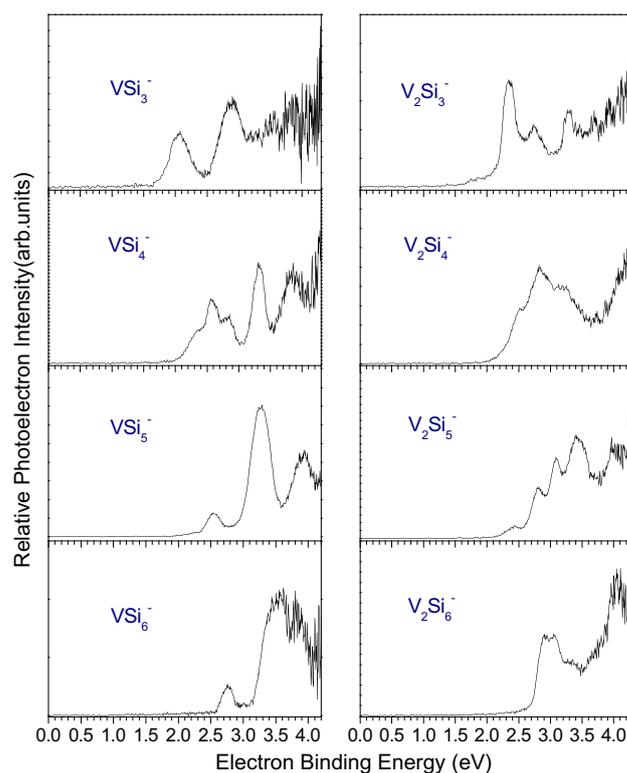


Fig. 1. Photoelectron spectra of VSi_n^- and V_2Si_n^- ($3 \leq n \leq 6$) clusters recorded with 266 nm photons.

Table 1

Experimentally observed VDEs and ADEs from the photoelectron spectra of VSi_n^- and V_2Si_n^- ($n = 3-6$).

Cluster	VDE (eV)	ADE (eV)
VSi_3^-	2.00 (8) ^a	1.79 (8)
VSi_4^-	2.35 (8)	2.10 (8)
VSi_5^-	2.51 (8)	2.38 (8)
VSi_6^-	2.74 (8)	2.64 (8)
V_2Si_3^-	2.34 (8)	2.15 (8)
V_2Si_4^-	2.51 (8)	2.25 (8)
V_2Si_5^-	2.43 (8)	2.24 (8)
V_2Si_6^-	2.90 (8)	2.74 (8)

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

of the value of instrumental resolution to the onset of the first peaks in the spectra. Note the ADEs of the cluster anions can be taken to correspond to the electron affinities (EAs) of the corresponding neutrals.

3.1. Photoelectron spectra of VSi_n^- ($n = 3-6$)

Based on the spectra of VSi_n^- ($n = 3-6$) (Fig. 1), we can see that the electron affinity of the corresponding neutral (VSi_n) increases when the number of silicon atoms increases from 3 to 6. The photoelectron spectrum of VSi_3^- has two major peaks centered at 2.0 and 2.8 eV, and a broadened feature higher than 3.2 eV. In comparison, the electron affinity of VSi_3 is slightly lower than that of pure Si_3 cluster [40]. The spectrum of VSi_4^- has five features centered at 2.35, 2.55, 2.85, 3.31, and 3.8 eV, respectively. Three well-resolved peaks centered at 2.54, 3.27, and 3.94 eV are evident in the spectrum of VSi_5^- . One small peak centered at 2.74 eV and two broad ones at approximately 3.5 and 3.8 eV are observed in the spectrum

of VSi_6^- . The spectrum of VSi_6^- is consistent with that reported by Nakajima and co-workers [16] except the first peak is well resolved in this work.

3.2. Photoelectron spectra of V_2Si_n^- ($n = 3-6$)

As it can be seen from Fig. 1, the electron affinity of V_2Si_n increases when the number of silicon atoms increases from 3 to 6, and the electron affinities of V_2Si_n ($n = 3-6$) are higher than those of VSi_n with the same number of silicon atoms. The spectrum of V_2Si_3^- has three peaks centered at 2.51, 2.84, and 3.20 eV, followed by an unresolved broad feature at higher binding energy. The spectrum of V_2Si_4^- has two broad features, one is over 3.7 eV, and the other is between 2.0 and 3.7 eV. The broad feature between 2.0 and 3.7 eV is composed of three unresolved peaks centered at 2.51, 2.82, 3.17 eV, respectively. The spectrum of V_2Si_5^- contains more than five bands, and the first band centered at 2.29 eV is very weak. The spectrum of V_2Si_6^- exhibits two broad bands at ~ 2.9 and ~ 4.0 eV. The first band at 2.9 eV is split into two peaks.

4. Theoretical results and discussion

The optimized geometries of the low-lying isomers of VSi_n^- and V_2Si_n^- ($n = 3-6$) clusters obtained with DFT calculations are presented in Fig. 2 and 3 with the most stable structures on the left. We have considered many different initial structures and multiplicities. Limited by the space, we only show the low energy isomers here. The relative energies between these isomers as well as the VDEs and ADEs from theoretical calculations are summarized in Table 2. We have also optimized the structures of the neutral clusters using the structures of their corresponding anions as initial structures. We find that the neutral structures vary only slightly from those of their corresponding anions. Based on the energy differences between the neutrals and anions, we calculated

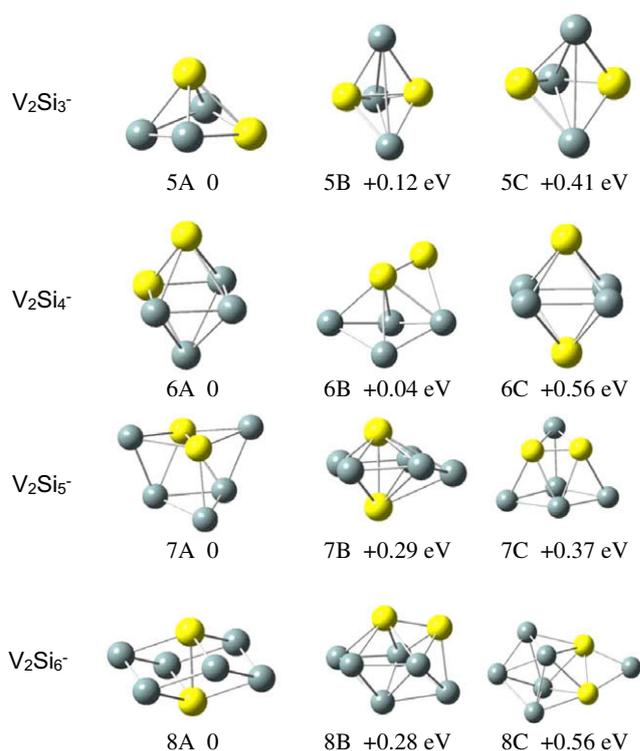


Fig. 3. Optimized geometries of the low-lying isomers of V_2Si_n^- ($n = 3-6$) clusters. The relative energies to the most stable isomers are shown.

the ADEs of these isomers (EAs of the neutrals) and present them in Table 2.

4.1. VSi_n^- ($n = 3-6$)

As shown in Fig. 2, the most stable structures of VSi_n^- ($n = 3-6$) are all three-dimensional structures. We found two isomers for VSi_3^- . The calculated VDEs of both isomers 1A and 1B are in agreement with the experimental measurement. The total energy of isomer 1A is lower than isomer 1B by 0.39 eV, and its theoretical VDE is closer to the experimental value than that of isomer 1B. Thus, isomer 1A is the most likely structure of VSi_3^- in our experiments. Our theoretical calculations show three low-lying isomers for VSi_4^- . They are very close in energy. Among them, isomer 2C is 0.15 eV higher than the most stable isomer (2A). But, its VDE and ADE are more consistent with the experimental values.

For VSi_5^- , the most stable structure (3A) has C_{4v} symmetry. Its VDE and ADE are in agreement with the experiment value. The VDEs of isomers 3B and 3C are in agreement with the experimental value. However, they are relatively high in energy, and their ADEs are far away from the experimental measurement. Thus, isomer 3A probably is what we observed in our experiments. The most stable structure (4A) of VSi_6^- has C_{5v} symmetry. Its energy is much lower than those of isomer 4B and 4C, and its VDE (3.03 eV) is in better agreement with the experiment value (2.74 eV). That indicates isomer 4A is the most likely structure for VSi_6^- .

4.2. V_2Si_n^- ($n = 3-6$)

The first two isomers of V_2Si_3^- are very close in energy with isomer 5B lying only 0.12 eV above isomer 5A. The structure of isomer 5B has D_{3h} symmetry, in which two V atoms are separated by the plane of the silicon trimer. The V–V distance in it is about 2.29 Å, shorter than the V–V distance in metallic vanadium. The calculated

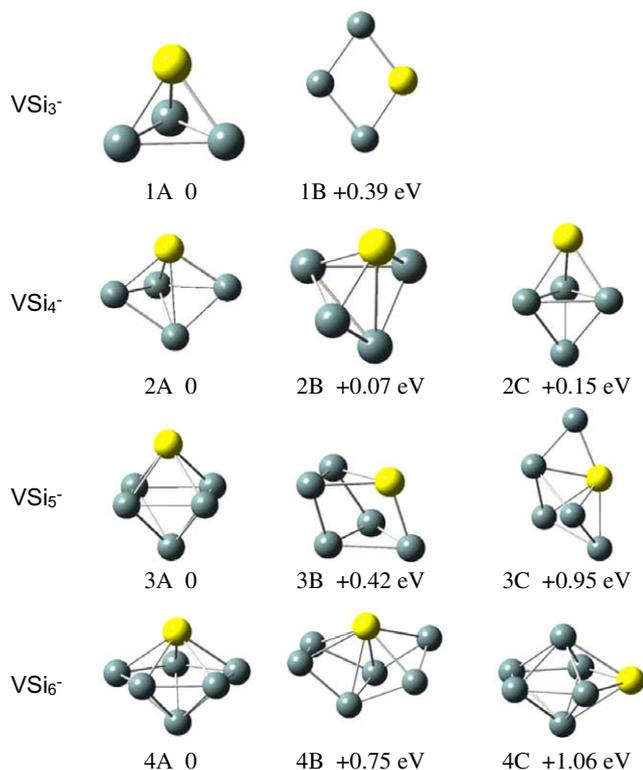


Fig. 2. Optimized geometries of the low-lying isomers of VSi_n^- ($n = 3-6$) clusters. The relative energies to the most stable isomers are shown.

Table 2Relative energies of the low energy isomers of VSi_n^- and V_2Si_n^- ($n = 3-6$) as well as their VDEs and ADEs obtained by DFT calculations.

Isomer		$\langle d_{\text{V-V}} \rangle^a$ (Å)	State	Symmetry	ΔE (eV)	VDE (eV)		ADE (eV)	
						Theo.	Exp.	Theo.	Exp.
VSi_3^-	1A		1A_1	C_{3v}	0	1.98	2.0	1.85	1.79
	1B		$^3A'$	C_s	0.39	2.08		1.91	
VSi_4^-	2A		3A_2	C_{2v}	0	1.95		1.90	
	2B		$^1A'$	C_s	0.07	2.35		1.82	
	2C		$^3A'$	C_s	0.15	2.30	2.35	2.18	2.10
VSi_5^-	3A		1A_1	C_{4v}	0	2.46	2.51	2.38	2.38
	3B		3A	C_1	0.42	2.45		1.81	
	3C		$^1A'$	C_s	0.95	2.47		1.85	
VSi_6^-	4A		3A_2	C_{5v}	0	3.03	2.74	2.84	2.64
	4B		1A	C_2	0.75	3.11		2.62	
	4C		3B_2	C_{2v}	1.06	1.64		1.54	
V_2Si_3^-	5A	2.42	$^4A'$	C_s	0	1.64		1.58	
	5B	2.29	$^2A'_1$	D_{3h}	0.12	2.58	2.34	2.02	2.15
	5C	3.17	4B_2	C_{2v}	0.41	1.68		1.65	
V_2Si_4^-	6A	2.30	$^4A'$	C_s	0	2.30	2.51	2.21	2.25
	6B	1.95	2A	C_1	0.04	2.13		1.70	
	6C	3.33	$^4A_{2g}$	D_{4h}	0.56	1.64		1.49	
V_2Si_5^-	7A	2.11	$^2A'$	C_s	0	2.43	2.43	2.18	2.24
	7B	2.48	$^4A'$	C_s	0.29	2.71		2.58	
	7C	1.91	$^2A''$	C_s	0.37	2.41		2.09	
V_2Si_6^-	8A	2.29	$^2A_{1g}$	D_{3d}	0	2.72	2.90	2.66	2.74
	8B	1.83	$^2A'$	C_s	0.28	2.32		2.26	
	8C	4.19	$^2A'$	C_s	0.56	5.41		4.77	

^a $\langle d_{\text{V-V}} \rangle$, the distance between vanadium atoms.

VDE of isomer 5B is about 2.58 eV, which is in reasonable agreement with the experimental measurement (2.34 eV) at this theoretical level. Therefore, we suggest that isomer 5B is the most likely isomer in our experiments. The existence of isomer 5A and 5C can be excluded since their VDEs are much lower than the experimental value.

Our calculations found two nearly degenerate isomers for V_2Si_4^- , isomer 6A and 6B. The energy separation between these two isomers is only 0.04 eV. Isomer 6A has C_s symmetry, and its calculated VDE is about 2.30 eV, which is consistent with our experimental value 2.51 eV. The V–V distance in isomer 6A is about 2.30 Å. Isomer 6C has D_{4h} symmetry with two V atoms separated by the plane formed by the four silicon atoms. The V–V distance in isomer 6C is about 3.33 Å. The VDE of isomer 6B is predicted to be 2.13 eV and that of isomer 6C is predicted to be 1.64 eV. These numbers are much lower than our experimental value. Therefore, the existence of isomer 6B and 6C in our experiments can be ruled out.

The most stable structure of V_2Si_5^- is found to be isomer 7A. The calculated VDE of isomer 7A is about 2.43 eV, in agreement with the experimental measurement (2.43 eV). In the structure of isomer 7B, the Si atoms form a five-membered ring, and the V atoms stay on opposite sides of the ring with the V–V bond perpendicular to the ring. The total energy of isomer 7B is 0.29 eV higher than isomer 7A, and the predicted VDE (2.71 eV) of isomer 7B is little higher than the experimental value. The VDE of isomer 7C predicted by theoretical calculations is about 2.41 eV, very close to the experimental value. The total energy of isomer 7C is about 0.37 eV higher than the most stable isomer (7A). We think the chance of the existence of isomers 7B and 7C in our experiments is low. However, their existence cannot be ruled out.

The most stable structure of V_2Si_6^- , isomer 8A, has D_{3d} symmetry whereas six Si atoms form a chair style ring structure similar to the ring in cyclohexane, and each V atom bonds to three Si atoms in the ring. The calculated VDE is about 2.72 eV, which is consistent with the experimental value (2.90 eV) at this theoretical level. The total energy of isomer 8B and 8C are 0.28 and 0.56 eV higher

than isomer 8A, respectively, and their theoretical VDEs are very different from our experimental result. Thus, isomer 8A probably is the only one observed in our experiments.

We find that the two V atoms in V_2Si_n^- clusters tend to form a V–V bond, similar to the theoretical results of T_2Si_n ($T = \text{Fe}, \text{Co}, \text{Ni}$, $n = 1-8$) calculated by Khanna and co-workers [35]. The V–V distance in V_2Si_n^- clusters is between 2.11 and 2.42 Å, which is longer than the V–V distance of 1.77 Å in the vanadium dimer (V_2) [41] but shorter than the nearest neighbor distance of 2.62 Å in metallic vanadium [42]. This indicates that there is a strong interaction between the vanadium atoms in V_2Si_n^- clusters. Based on the strong bond between vanadium atoms, we suggest that, when the number of silicon atom increases, it might be possible to form endohedral $\text{V}_2@Si_n$ clusters. This is in agreement with the theoretical prediction of V–V distance (1.97 Å) in V_2Si_{18} by Andriotis et al. [43]. Janssens et al. [44] found that the fraction of argon complexes formed for V_2Si_n^+ dropped abruptly at $n = 17-18$, which might be the experimental evidence for the formation of endohedral $\text{V}_2@Si_n^+$ at larger cluster size.

It is interesting to compare the structures of V_mSi_n^- clusters with those of Na_mSi_n^- clusters which were reported by Nakajima and co-workers [29]. NaSi_3^- prefers a planar structure and the sodium atom interacts with only two silicon atoms inside NaSi_3^- , while VSi_3^- has a tetrahedral structure and the V atom interacts with all three silicon atoms. The V atoms in VSi_{3-6}^- form bonds with more than two Si atoms, while the Na atom tends to attach to the vertex or edge of silicon clusters and therefore forms only one or two Na–Si bonds. As for V_2Si_n^- , the V atoms are bonded together. In Na_2Si_n^- , however, those two sodium atoms are separated by silicon atoms. The significant differences between the structures of V–Si clusters and Na–Si clusters indicate that the 3d electrons of V atom play important roles in the formation of bonds in V–Si clusters.

In order to understand the bonding in V–Si clusters, we analyzed their molecular orbitals. Indeed, the molecular orbitals show that both 3d and 4s orbitals are involved in the formation of bonds between vanadium and silicon atoms. The structure and molecular

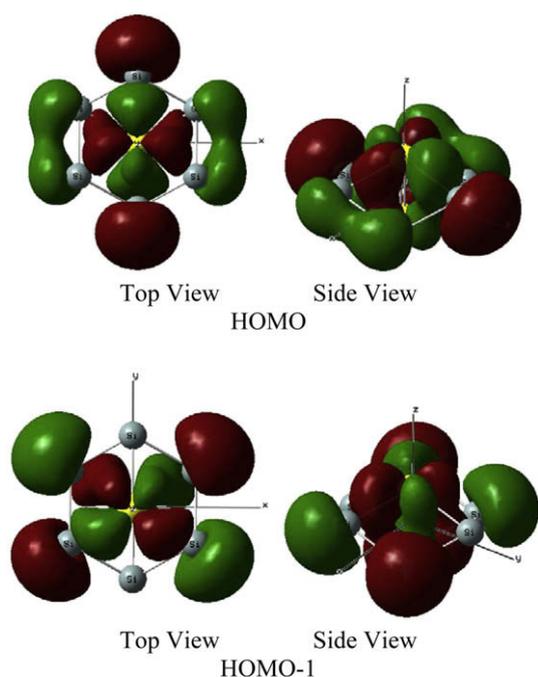


Fig. 4. HOMO and HOMO-1 of $V_2Si_6^-$ viewed from different angles.

orbitals of $V_2Si_6^-$ are especially interesting. As mentioned earlier, the most stable structure of $V_2Si_6^-$ has D_{3d} symmetry whereas six Si atoms form a chair style ring. The HOMO of $V_2Si_6^-$ is mainly composed of the $3d_{x^2-y^2}$ of orbitals two vanadium atoms plus some 3s and 3p components from the silicon atoms, the HOMO-1 composed of the $3d_{xy}$ of two vanadium atoms orbitals. Fig. 4 displays the $V_2Si_6^-$'s HOMO and HOMO-1 with more details. A closer look at the HOMO and HOMO-1 shows that the $3d_{x^2-y^2}$ orbitals of the two vanadium atoms overlap to form a V–V δ bond and the $3d_{xy}$ orbitals also overlap to form another V–V δ bond. Since the HOMO is occupied by only one electron, there are one and half δ bonds between the vanadium atoms in $V_2Si_6^-$ anion. The structure of neutral V_2Si_6 is similar to the $V_2Si_6^-$ anion except that the V–V distance in V_2Si_6 neutral is about 2.36, 0.07 Å longer than that in $V_2Si_6^-$. The HOMO of $V_2Si_6^-$ anion is empty after the electron is removed, and it becomes the lowest unoccupied molecular orbital (LUMO) of V_2Si_6 neutral. Thus, the LUMO and HOMO of V_2Si_6 neutral correspond to HOMO and HOMO-1 of $V_2Si_6^-$, respectively. This indicates that the V–V interaction in V_2Si_6 neutral is weaker than that in $V_2Si_6^-$. It is worth mentioning that the V–V distance in V_2Si_6 neutral is still shorter than that in metallic vanadium.

5. Conclusions

We generated vanadium-doped silicon clusters by laser ablation of a V/Si mixture target. The cluster anions were mass-analyzed with a time-of-flight mass spectrometer. The photoelectron spectra of VSi_n^- and $V_2Si_n^-$ ($n = 3-6$) cluster anions were measured with a magnetic-bottle photoelectron spectrometer. DFT calculations were used to elucidate their structures and electronic properties. The most possible structures of these clusters were identified by comparing the calculated VDEs to the experimental results. We find that the most possible isomers of $V_mSi_n^-$ clusters prefer to adopt three-dimensional structures. The V atom in VSi_{3-6}^- clusters interacts with more than two silicon atoms. There is strong V–V

interaction in dual-vanadium-doped silicon clusters, indicating that it might be possible to form endohedral $V_2@Si_n$ clusters.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.01.050.

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