Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Appearance of V-encapsulated tetragonal prism motifs in VSi_{10}^- and VSi_{11}^- clusters

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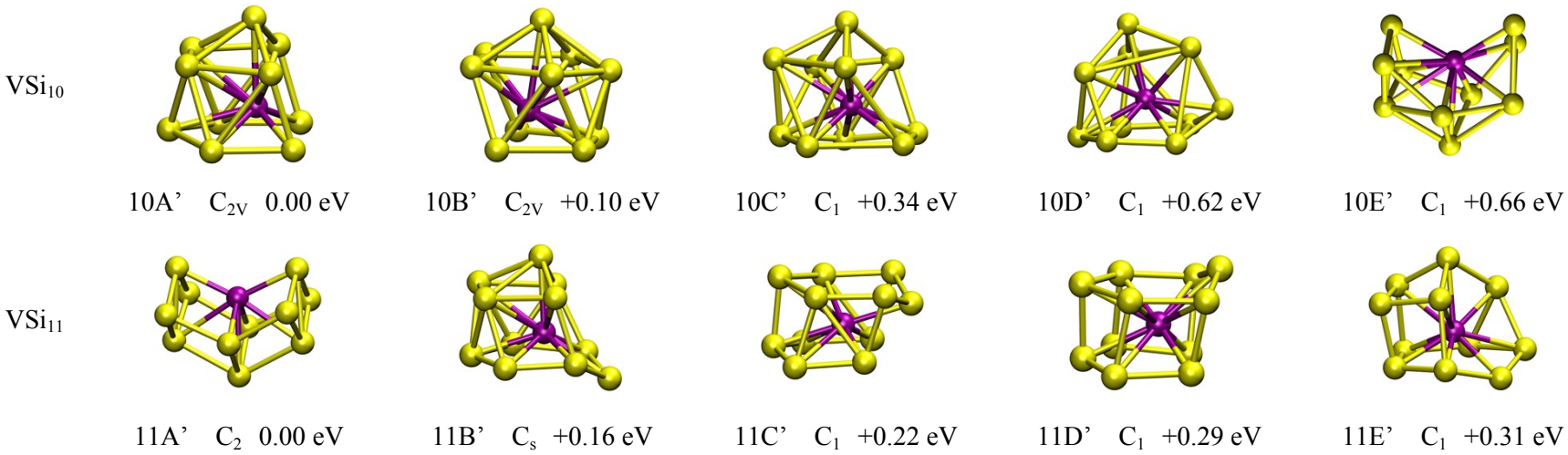
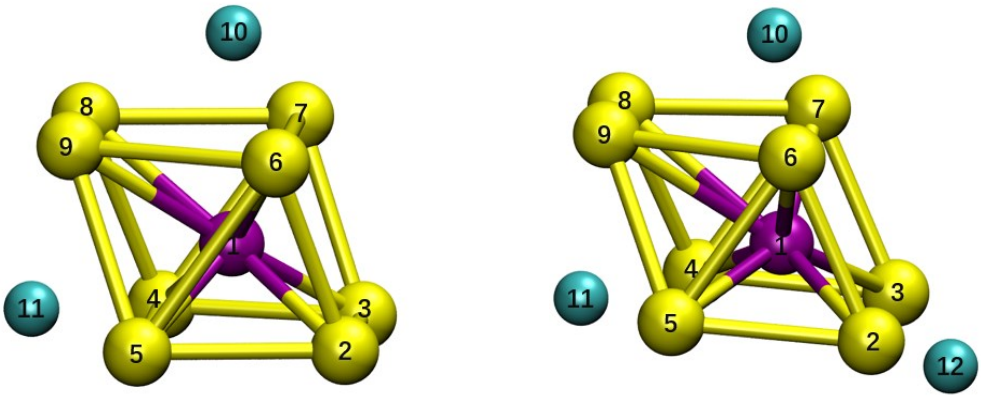


Fig. S1. Typical low-lying isomers neutral VSi_{10} and VSi_{11} clusters, their point group symmetries, and relative energies at the CCSD(T)//aug-cc-pVTZ/V/cc-pVTZ/Si level of theory. The purple and yellow balls stand for the V and Si atoms, respectively.



(a) $VSi_{10}^{-/0}$ (b) $VSi_{11}^{-/0}$

Fig. S2. The labeling of (a) $VSi_{10}^{-/0}$ and (b) $VSi_{11}^{-/0}$ clusters. The Si atoms located outside of the tetragonal prism unit are highlighted with cyan color.

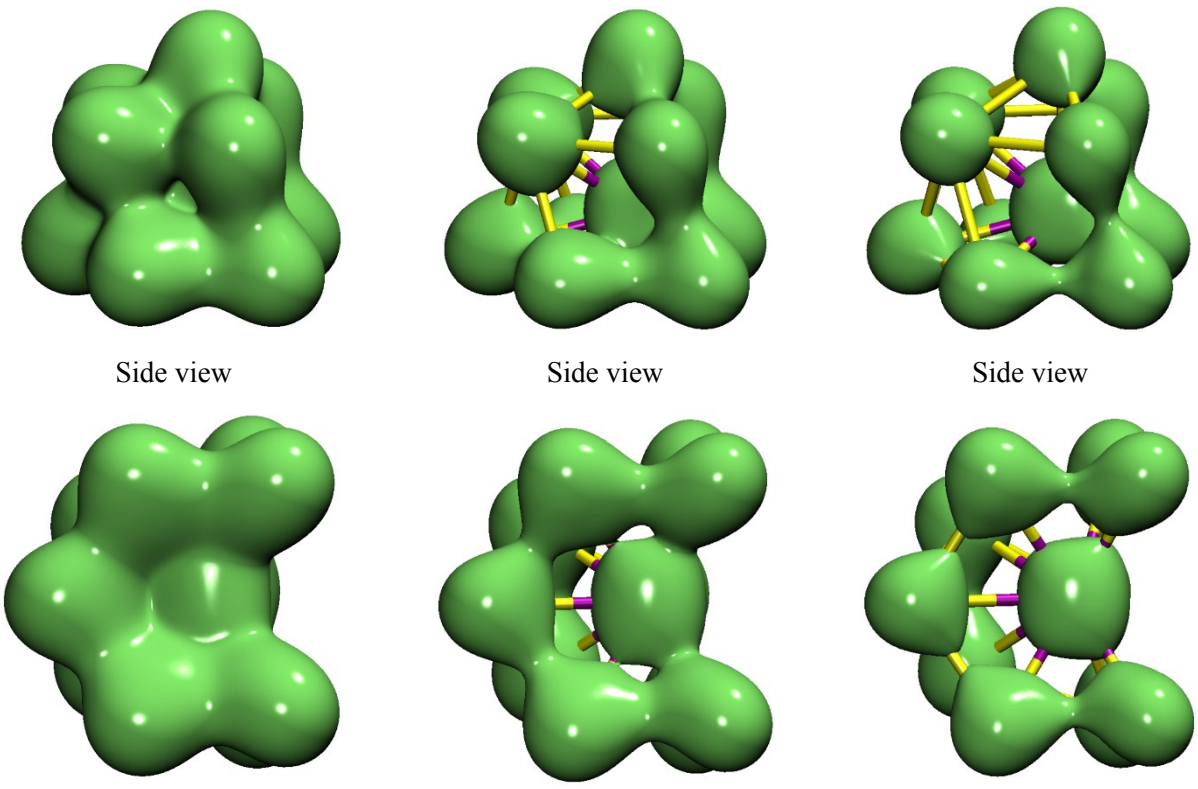
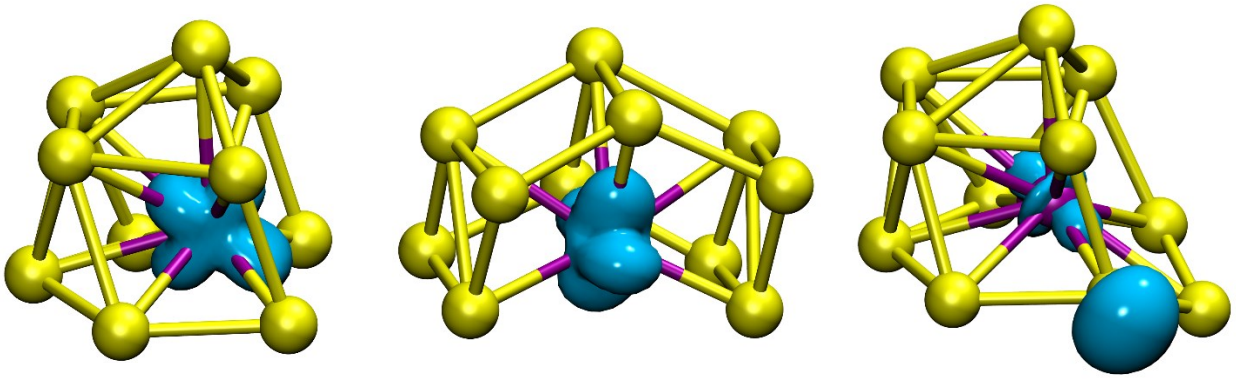


Fig. S3. Constant electronic charge density surfaces of the lowest-lying isomer of VSi_{10}^- anion, with charge density equals (a) 0.04 a.u., (b) 0.055 a.u., and (c) 0.065 a.u., respectively.



(a) VSi_{10} 10A’ (b) VSi_{11} 11A’ (c) VSi_{11} 11B’

Fig. S4. Spin density map of (a) the global minimum isomer 10A′ of VSi_{10} neutral, (b) the global minimum isomer 11A′ and (c) the low-lying isomers 11B′ of VSi_{11} neutrals (isosurface value=0.01).

Table S1. Cartesian coordinates for stable isomers of $VSi_{10}^{-/0}$ clusters.

VSi_{10}^{-}

	10A				**10B**		
	X	Y	Z		X	Y	Z
V	0.00000000	0.00000000	0.40914100	V	0.00000000	0.00000000	0.58708400
Si	0.00000000	1.45985900	2.25026600	Si	-2.05127500	1.30790300	0.31245200
Si	0.00000000	1.21644800	-1.91178600	Si	0.00000000	-2.00424100	1.77552000
Si	0.00000000	-1.21644800	-1.91178600	Si	0.00000000	2.00424100	1.77552000
Si	1.44379100	-1.98054900	0.20831100	Si	0.00000000	2.07372300	-1.02564900
Si	-1.44379100	1.98054900	0.20831100	Si	-1.23055200	0.00000000	-1.85702300
Si	1.44379100	1.98054900	0.20831100	Si	-2.05127500	-1.30790300	0.31245200
Si	0.00000000	-1.45985900	2.25026600	Si	2.05127500	-1.30790300	0.31245200
Si	2.10775400	0.00000000	-1.09118200	Si	0.00000000	-2.07372300	-1.02564900
Si	-2.10775400	0.00000000	-1.09118200	Si	2.05127500	1.30790300	0.31245200
Si	-1.44379100	-1.98054900	0.20831100	Si	1.23055200	0.00000000	-1.85702300
	10C				**10D**		
	X	Y	Z		X	Y	Z
V	-0.09622900	0.13712700	0.00000000	V	0.34140700	-0.05069500	-0.29374800
Si	1.07043800	-2.21846200	0.00000000	Si	-1.36423100	-0.00710700	-2.01191500
Si	1.31687700	0.73403800	1.96800600	Si	2.74784100	0.89058000	0.00104800
Si	-0.65266400	2.22377100	-1.26351900	Si	-1.12946900	2.07537600	-0.85611500
Si	2.39556100	-0.21879800	0.00000000	Si	1.55215500	-2.06566400	0.57966500
Si	-1.06350000	-1.97943800	1.22334800	Si	-0.46252700	0.85001100	2.05313100
Si	-1.06350000	-1.97943800	-1.22334800	Si	2.18050300	-0.98035400	-1.38602500
Si	-1.25466900	0.12761900	-2.13212300	Si	-2.28281400	0.36714200	0.44812800
Si	1.31687700	0.73403800	-1.96800600	Si	0.85704600	2.24640900	0.55047100
Si	-0.65266400	2.22377100	1.26351900	Si	-2.09228500	-1.76896600	-0.45879300
Si	-1.25466900	0.12761900	2.13212300	Si	-0.56710300	-1.52414200	1.56299000
	10E						
	X	Y	Z				
V	-0.12892400	0.38696600	0.00000000				
Si	0.90267200	1.58012300	2.01042600				
Si	0.90267200	1.58012300	-2.01042600				
Si	-1.04420900	0.26865100	2.72238700				
Si	-1.62796000	-1.39227800	1.20003700				
Si	-1.04420900	0.26865100	-2.72238700				
Si	0.48000800	-2.27069200	0.00000000				
Si	0.90267200	-0.91084800	-1.91638300				
Si	0.90267200	-0.91084800	1.91638300				
Si	1.46544400	2.54366600	0.00000000				
Si	-1.62796000	-1.39227800	-1.20003700				

VSi_{10}

□	□	**10A'**	□	□	□	**10B'**	□
□	X	Y	Z	□	X	Y	Z
V	0.00000000	0.00000000	0.58190100	V	0.00000000	0.00000000	0.62045100
Si	0.00000000	1.94140100	2.07143100	Si	0.00000000	2.07469200	1.72724300
Si	1.46178200	2.01891900	0.17081000	Si	-2.04990600	1.34640200	0.31832300
Si	0.00000000	-1.18734100	-1.84468500	Si	2.04990600	-1.34640200	0.31832300
Si	-2.10056600	0.00000000	-1.04635600	Si	0.00000000	-2.06268800	-1.07275400
Si	1.46178200	-2.01891900	0.17081000	Si	2.04990600	1.34640200	0.31832300
Si	0.00000000	1.18734100	-1.84468500	Si	0.00000000	-2.07469200	1.72724300
Si	-1.46178200	2.01891900	0.17081000	Si	1.24770900	0.00000000	-1.80079000
Si	-1.46178200	-2.01891900	0.17081000	Si	0.00000000	2.06268800	-1.07275400
Si	0.00000000	-1.94140100	2.07143100	Si	-2.04990600	-1.34640200	0.31832300
Si	2.10056600	0.00000000	-1.04635600	Si	-1.24770900	0.00000000	-1.80079000
□	□	**10C'**	□	□	□	**10D'**	□
□	X	Y	Z	□	X	Y	Z
V	0.20838000	0.42234200	-0.05443400	V	0.07567200	0.02119000	-0.03633900
Si	1.00967900	-1.52322200	-1.43986900	Si	1.24206500	-1.84402700	-1.19333800
Si	-1.15076900	-0.58517500	-2.01925800	Si	-2.22745700	-0.14979700	-1.15997300
Si	1.89579800	1.92851300	-0.23688200	Si	2.62889900	-0.08969600	-0.46631200
Si	-0.68116500	2.09112800	1.32502100	Si	-0.67016100	2.15755100	1.02747200
Si	-0.77054500	-2.07802600	0.17112300	Si	-1.69687500	-1.30742400	1.21977200
Si	1.12030200	-1.33709000	1.53584000	Si	1.27745300	1.73422000	-1.30682200
Si	2.67389000	-0.36161900	-0.08257700	Si	1.76597200	-0.50775700	1.73957500
Si	-0.94785600	-0.25601500	2.14785300	Si	-1.01699200	-2.16926000	-0.93343200
Si	-1.03642900	1.84277600	-1.44667100	Si	-1.06654800	1.89156600	-1.33709100
Si	-2.45524500	-0.41511700	0.13484700	Si	-0.36067400	0.24981400	2.46985000
□	□	**10E'**	□	□	□	□	□
□	X	Y	Z	□	□	□	□
V	0.25650400	-0.17880900	-0.49877900	□	□	□	□
Si	2.56600900	0.88153300	-0.71627200	□	□	□	□
Si	-0.73468400	-1.79476900	1.11018300	□	□	□	□
Si	-1.53387000	0.54098600	-1.88541400	□	□	□	□
Si	-1.01601000	2.23233700	-0.23547400	□	□	□	□
Si	-2.37738200	-1.44906400	-0.82149100	□	□	□	□
Si	-0.16612900	0.28420800	2.23457000	□	□	□	□
Si	1.74785900	-1.33755600	1.08293000	□	□	□	□
Si	-2.15252400	0.34971500	0.68946900	□	□	□	□
Si	1.09058400	1.85872600	0.82776800	□	□	□	□
Si	2.15474700	-1.27235900	-1.46684500	□	□	□	□

Table S2. Cartesian coordinates for stable isomers of $VSi_{11}^{-/0}$ clusters.

VSi_{11}^-

		11A				**11B**	
	X	Y	Z		X	Y	Z
V	0.00000000	0.00000000	0.39106300	V	-0.47717800	0.22484200	0.00000000
Si	0.00000000	1.21009800	-2.18697300	Si	-2.03682700	-1.58705500	0.00000000
Si	2.04999600	0.00000000	-1.20778200	Si	1.59240200	1.64822000	0.00000000
Si	1.27931500	2.11904900	-0.18569700	Si	1.77828100	-0.74718600	1.21343100
Si	-1.27931500	-2.11904900	-0.18569700	Si	-0.70406000	2.55881000	-1.14743100
Si	0.00000000	-2.05961000	1.95147800	Si	-0.55685700	-1.52971100	2.02632900
Si	-1.27931500	2.11904900	-0.18569700	Si	-0.55685700	-1.52971100	-2.02632900
Si	-2.04999600	0.00000000	-1.20778200	Si	0.39132800	-2.49369600	0.00000000
Si	0.00000000	2.05961000	1.95147800	Si	-0.70406000	2.55881000	1.14743100
Si	0.00000000	-1.21009800	-2.18697300	Si	-0.09884900	0.74966100	2.51023900
Si	0.00000000	0.00000000	2.98688000	Si	1.77828100	-0.74718600	-1.21343100
Si	1.27931500	-2.11904900	-0.18569700	Si	-0.09884900	0.74966100	-2.51023900
		11C				**11D**	
	X	Y	Z		X	Y	Z
V	-0.06956500	0.08767500	-0.54335700	V	0.27180900	0.11220300	-0.07165700
Si	-1.38872500	-2.13189900	-0.31523500	Si	-1.40646000	0.24711700	-1.91352300
Si	2.36002800	-0.56259700	0.75337400	Si	-2.59129800	-0.08059400	0.11883700
Si	-2.30749300	-0.16034100	-1.45440800	Si	2.82837000	0.63249500	0.32684100
Si	1.93685800	-0.59890500	-1.71571500	Si	-0.76075400	2.29747600	-0.75150300
Si	0.15564600	2.65281800	-0.06995200	Si	-0.75779900	-0.77164100	2.05425000
Si	0.71949600	1.12295100	1.78941600	Si	2.06317900	-1.54072900	-0.74138700
Si	1.05917100	-2.37362200	-0.15833300	Si	-1.58180700	1.52666100	1.57622200
Si	-2.07602600	1.84528200	-0.23018600	Si	1.55849500	2.27077000	-0.55482000
Si	-0.12692500	-1.09414400	1.84964700	Si	-1.41285900	-2.10542700	0.17760500
Si	-2.42717800	-0.34450000	1.00157000	Si	1.64970800	-0.92057000	1.68635700
Si	2.20943300	1.50092000	-0.55752000	Si	-0.03531900	-1.73989100	-1.86115600
		11E					
	X	Y	Z				
V	0.00000000	0.00000000	0.53848000				
Si	-1.52643400	-1.46345200	1.67277200				
Si	0.00000000	0.00000000	-2.15143400				
Si	1.43733800	1.85159300	-0.91486800				
Si	1.30904400	-1.58134400	-0.83022500				
Si	-1.43733800	-1.85159300	-0.91486800				
Si	1.52643400	1.46345200	1.67277200				
Si	2.71745000	0.12181400	0.16805100				
Si	-1.30904400	1.58134400	-0.83022500				
Si	0.00000000	-3.06386500	0.53766500				
Si	-2.71745000	-0.12181400	0.16805100				
Si	0.00000000	3.06386500	0.53766500				

VSi_{11}

		11A'				**11B'**	
	X	Y	Z		X	Y	Z
V	0.00000000	0.00000000	0.59586100	V	-0.33982100	0.12763100	0.00000000
Si	-2.97312600	-0.28163600	0.41436400	Si	-2.69270300	1.51478500	0.00000000
Si	-1.63062100	-1.66173100	-0.95744400	Si	-0.84720400	-1.97446500	1.24701700
Si	2.97312600	0.28163600	0.41436400	Si	-0.84720400	-1.97446500	-1.24701700
Si	-1.41322000	-1.62005300	1.63010800	Si	1.04055100	-0.64632600	-2.07206200
Si	0.00000000	2.90514600	0.25327100	Si	1.04055100	-0.64632600	2.07206200
Si	-1.52704200	1.27326400	-0.74352800	Si	-0.63038900	2.57716800	0.00000000
Si	0.00000000	-2.90514600	0.25327100	Si	1.04055100	1.69852700	1.49119700
Si	0.00000000	0.00000000	-2.17245600	Si	2.43661300	0.28843300	0.00000000
Si	1.41322000	1.62005300	1.63010800	Si	1.04055100	1.69852700	-1.49119700
Si	1.63062100	1.66173100	-0.95744400	Si	-2.69967100	-0.79799300	0.00000000
Si	1.52704200	-1.27326400	-0.74352800	Si	1.67662900	-1.94754300	0.00000000
		11C'				**11D'**	
	X	Y	Z		X	Y	Z
V	0.00025900	0.07776500	-0.27923300	V	-0.01451400	0.17201900	0.21128200
Si	2.22700500	-1.66585800	-0.84623700	Si	-1.79925600	0.57281400	1.73293400
Si	0.00121700	-2.40769900	-0.30911200	Si	2.26082100	-1.44246100	0.71019900
Si	-2.00475300	-0.28814600	1.19748200	Si	0.05236600	2.61578100	-0.65342100
Si	2.00541100	-0.28862300	1.19771800	Si	1.80057300	-0.36803500	-1.41024800
Si	2.17933300	1.97327400	0.59501400	Si	2.19919800	1.76592800	-0.33508600
Si	-2.18134300	1.97267200	0.59270200	Si	0.16739100	-2.42848400	0.33205800
Si	-0.00082100	2.49780600	-0.25009700	Si	-2.15192300	1.89409800	-0.25835000
Si	-2.10555900	0.62225600	-1.38112200	Si	1.75689200	0.65325500	1.76829000
Si	-0.00063100	-1.50047500	1.88762700	Si	-1.98553400	-1.67755600	0.86936500
Si	-2.22518000	-1.66814600	-0.84451200	Si	-0.18630100	-1.55604800	-1.91715700
Si	2.10489600	0.62518200	-1.38072500	Si	-2.09038200	-0.31189600	-1.18569000
		11E'					
	X	Y	Z				
V	-0.26340400	0.10795400	-0.00294500				
Si	-1.60906800	-1.33156600	1.42934700				
Si	-1.80605200	-1.42431300	-1.14532300				
Si	1.37906700	1.26900300	1.63187200				
Si	0.48046900	2.55162600	-0.30991800				
Si	1.51304900	-2.00025200	-0.03285300				
Si	0.35745100	-1.35046600	-2.09478300				
Si	-2.97027500	0.24838900	0.24998600				
Si	0.73381800	-1.08880600	2.05542700				
Si	1.40919200	0.80012900	-1.71287300				
Si	-1.77364200	2.12985800	-0.16797500				
Si	2.71872700	0.01904400	0.10193200				

Table S3. The natural electron configuration of the low-lying isomers of $VSi_{10}^{-/0}$ and $VSi11^{-/0}$ clusters at the B3LYP/6-311+G* level of theory.

Cluster	Isomer[a]	Atoms[b]	NPA charges	Natural electron configuration on atoms
VSi_{10}^-	**10A**	V1	-2.73	$4s^{0.45}3d^{6.98}4p^{0.15}5s^{0.01}4d^{0.14}5p^{0.01}$
		Si2(3)	0.29	$3s^{1.60}3p^{2.07}4s^{0.01}3d^{0.01}4p^{0.02}$
		Si4(5,6,7)	0.23	$3s^{1.58}3p^{2.15}3d^{0.01}4p^{0.02}$
		Si8(9)	0.12	$3s^{1.55}3p^{2.28}3d^{0.02}4p^{0.02}$
		Si10(11)	-0.01	$3s^{1.54}3p^{2.43}3d^{0.02}4p^{0.02}$
VSi_{11}^-	**11A**	V1	-2.05	$4s^{0.37}3d^{6.33}4p^{0.12}5s^{0.01}4d^{0.21}5p^{0.01}$
		Si2(3)	0.05	$3s^{1.53}3p^{2.38}3d^{0.02}4p^{0.02}$
		Si4(5,6,7)	0.15	$3s^{1.52}3p^{2.28}3d^{0.02}4p^{0.02}$
		Si8(9)	0.08	$3s^{1.57}3p^{2.31}3d^{0.02}4p^{0.03}$
		Si10(11)	0.01	$3s^{1.53}3p^{2.42}3d^{0.02}4p^{0.02}$
		Si12	0.16	$3s^{1.51}3p^{2.30}4s^{0.01}3d^{0.01}4p^{0.02}$
VSi_{10}	**10A′**	V1	-1.94	$4s^{0.44}3d^{6.12}4p^{0.15}5s^{0.01}4d^{0.22}5p^{0.01}$
		Si2(3)	0.32	$3s^{1.60}3p^{2.04}4s^{0.01}3d^{0.02}4p^{0.03}$
		Si4(5,6,7)	0.22	$3s^{1.54}3p^{2.20}3d^{0.02}4p^{0.02}$
		Si8(9)	0.14	$3s^{1.52}3p^{2.30}3d^{0.02}4p^{0.02}$
		Si10(11)	0.08	$3s^{1.56}3p^{2.31}3d^{0.02}4p^{0.02}$
VSi_{11}	**11B′**	V1	-2.19	$4s^{0.39}3d^{6.42}4p^{0.15}5s^{0.01}4d^{0.20}5p^{0.01}$
		Si2	0.12	$3s^{1.37}3p^{2.47}3d^{0.02}4p^{0.02}$
		Si3	0.14	$3s^{1.53}3p^{2.28}3d^{0.02}4p^{0.02}$
		Si4(7)	0.28	$3s^{1.54}3p^{2.13}3d^{0.02}4p^{0.02}$
		Si5(6)	0.28	$3s^{1.51}3p^{2.17}3d^{0.02}4p^{0.02}$
		Si8	0.23	$3s^{1.63}3p^{2.10}3d^{0.02}4p^{0.03}$
		Si9(10,11)	0.08	$3s^{1.52}3p^{2.35}3d^{0.02}4p^{0.02}$
		Si12	0.32	$3s^{1.58}3p^{2.07}4s^{0.01}3d^{0.01}4p^{0.01}$

[a] For comparison, the isomer **11B′** of neutral VSi_{11} cluster is given here.

[b] The atom numbering is given in Fig. S2.