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Supplementary Materials

Structures and electronic properties of VSi_n^- (n = 14–20) clusters: a combined experimental and density functional theory study

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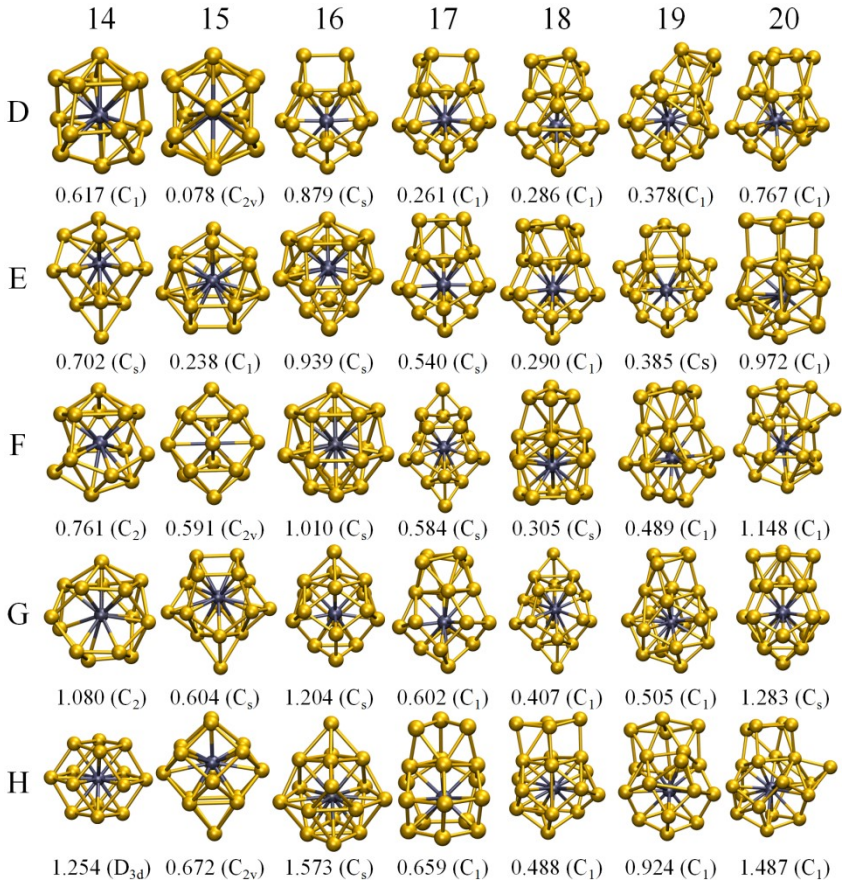

FIG. S1. Low-lying structures of VSi_n^- (*n* = 14–20) clusters at B3P/cc-pVDZ level. For each structure, the total energy difference (eV) and the symmetry with respect to the lowest-energy isomer in main text are given. Grey and golden balls represent V and Si atoms, respectively.

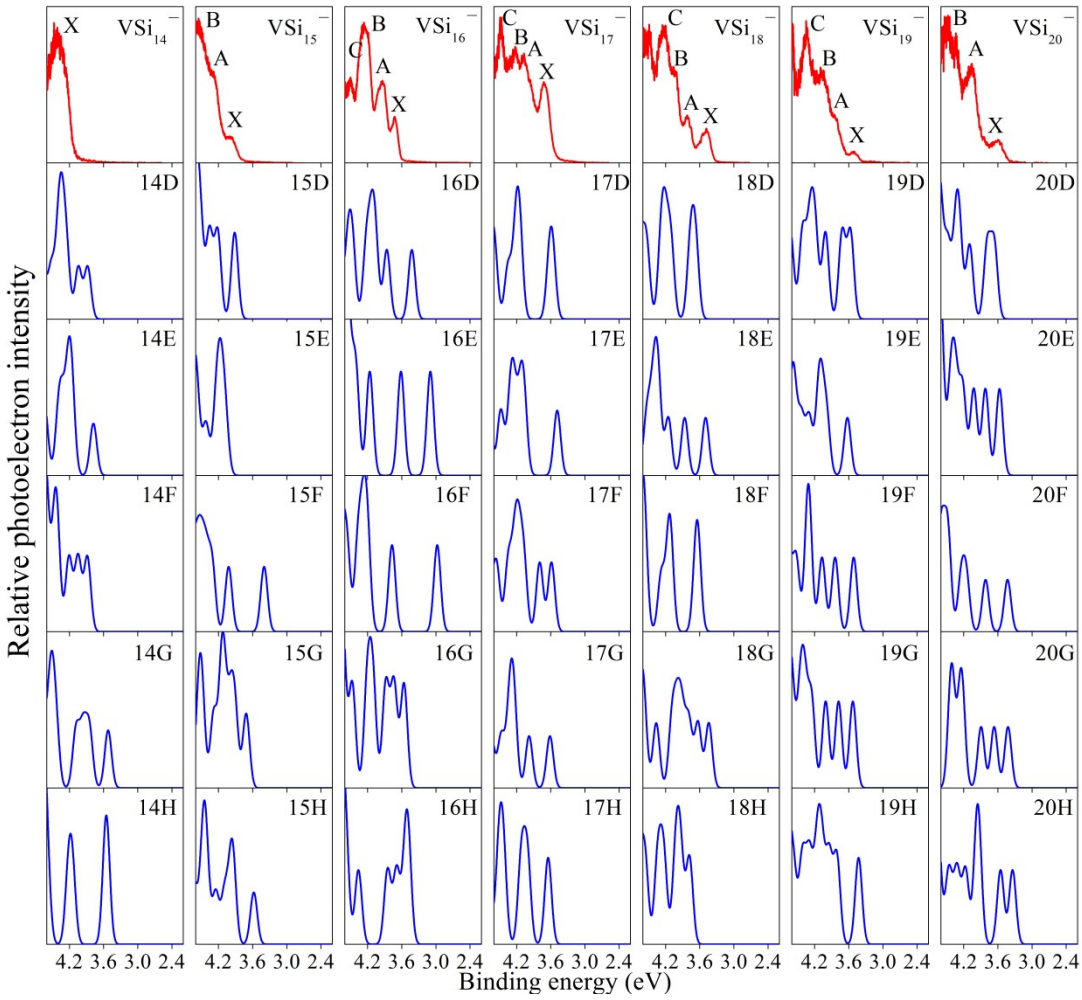

FIG. S2. Uppermost panels: experimental PES spectra of cold VSi_n^- (*n* = 14–20), measured at a photon energy of 5.0 eV. Lower panels: theoretical PES spectra, calculated by density functional theory at the B3P/aug-cc-pVDZ level for the structures shown in Fig. S1.

Tests of functional and basis set

The performances of the functionals PBE, BLYP, BP86, PBE0, M06, M06-2X, and B3P with basis sets (aug-cc-pVDZ and def2-TZVPD) were also assessed by calculating the standard deviation (SD) of the differences between the calculated and measured VDEs where the SD is defined by the following formula:

$$SD = \sqrt{\frac{1}{7}\sum_{n=14}^{20}\left[Theo_{VDE}(n) - Expt_{VDE}(n)\right]^2} \qquad (1)$$

Here, $Theo_{VDE(n)}$ and the $Expt_{VDE(n)}$ are the calculated and experimental measured VDEs for size n, respectively.

As shown in Tables S1 and S2, for the VSi_n^- (n = 14–20) clusters, the aug-cc-pVDZ basis set is more suitable than def2-TZVPD for VSi_n^- (n = 14–20) clusters, and the B3P/aug-cc-pVDZ is the most proper scheme to be used for calculating the electronic structure of VSi_n^- (n = 14–20) due to the minimum discrepancies with the experimental measured ones. Therefore, the B3P/aug-cc-pVDZ scheme was adopted to calculate the relative energies and photoelectron spectra of VSi_n^- (n = 14–20) clusters.

The experimental photoelectron spectra of the VSi_n^- (n = 14–20) clusters were also used as references to evaluate the validity of the functionals and basis sets. In order to facilitate the comparison, the measured spectra and the simulated ones were integrated Figures S3 and S4.

Besides, in order to evaluate the influences of diffuse functions on the clusters structure determination, we have calculated the root mean square deviations (RMSD) of structures which are yielded by using basis sets with (aug-cc-pVDZ and def2-TZVPD) and without diffuse functions (cc-pVDZ and def2-TZVP) for the three isomers of 14A, 14B and 14C of VSi_{14}^-. The RMSD is defined by the following formula:

$$RMSD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\left(x_i - x_i'\right)^2 + \left(y_i - y_i'\right)^2 + \left(y_i - y_i'\right)^2\right]} \qquad (2)$$

where x_i, y_i, and z_i are the coordinates of the ith atom in the optimized structure by original basis set, while x_i', y_i', and z_i' are the coordinates of the i^{th} atom in the optimized structure by diffuse basis set, respectively.

The results (Table S3) indicate that diffuse functions have little effect on the structure determination.

Table S1. The experimentally (Expt.) measured VDEs and those theoretical predicted ones when using seven different functionals for the structures which are optimized at the def2-TZVP level and calculated at def2-TZVPD level. All energies are given in eV. The uncertainties of the experimental VDEs are shown in the parentheses.

n	PBE	BLYP	BP86	PBE0	M06	M06-2X	B3P	Expt.
14	4.06	3.78	4.19	4.25	4.11	4.22	4.30	4.35(3)
15	3.92	3.66	3.97	4.00	3.71	3.90	4.08	4.00(3)
16	3.54	3.27	3.60	3.56	3.49	3.47	3.63	3.73(3)
17	3.52	3.28	3.58	3.56	3.48	3.57	3.63	3.70(3)
18	3.30	3.13	3.38	3.23	3.24	3.25	3.34	3.48(3)
19	3.28	3.08	3.35	3.32	3.14	3.28	3.41	3.50(3)
20	3.40	3.13	3.46	3.38	3.39	3.39	3.47	3.55(3)
SD	0.194	0.432	0.119	0.161	0.256	0.185	0.091	

Table S2. The experimentally (Expt.) measured VDEs and those theoretical predicted ones when using seven different functionals for the structures which are optimized at the cc-pVDZ level and calculated at aug-cc-pVDZ level. All energies are given in eV. The uncertainties of the experimental VDEs are shown in the parentheses.

n	PBE	BLYP	BP86	PBE0	M06	M06-2X	B3P	Expt.
14	4.06	3.77	4.12	4.20	4.17	4.19	4.26	4.35(3)
15	3.90	3.66	3.98	4.03	3.77	3.88	4.08	4.00(3)
16	3.55	3.27	3.61	3.55	3.52	3.45	3.63	3.73(3)
17	3.53	3.31	3.61	3.58	3.60	3.60	3.67	3.70(3)
18	3.35	3.19	3.45	3.29	3.37	3.31	3.42	3.48(3)
19	3.30	3.13	3.39	3.36	3.30	3.26	3.47	3.50(3)
20	3.42	3.17	3.49	3.40	3.50	3.40	3.50	3.55(3)
SD	0.181	0.411	0.115	0.146	0.166	0.184	0.068	

Table S3. The root mean square deviations (RMSD) for the three isomers of VSi_{14}^- between the structures which are optimized by using the cc-pVDZ (B1) and def2-TZVP (B3) as well as those by using cc-pVDZ (aug-cc-pVDZ, B2) and def2-TZVPD, B4).

		RMSD (Å)			
		B1	B2	B3	B4
14A	BP86	0.0005	0	0.0003	0
	PBE0	0.0005	0	0.0006	0
	B3P	0.0005	0	0.0004	0
14B	BP86	0.0004	0	0.0003	0
	PBE0	0.0005	0	0.0002	0
	B3P	0.0004	0	0.0001	0
14C	BP86	0.0005	0	0.0004	0
	PBE0	0.0007	0	0.0006	0
	B3P	0.0003	0	0.0004	0

Fig. S3. Photoelectron spectra of cold (T = 10 K) VSi_n^- (*n*= 14-20) cluster anions, measured at a photon energy of 5.0 eV (black lines), in comparison with the simulated photoelectron spectra for the lowest energy structure found at a given functional (red lines) with the def2-TZVPD basis set.

Fig. S4. Photoelectron spectra of cold (T = 10 K) VSi_n^- (n= 14-20) cluster anions, measured at a photon energy of 5.0 eV (black lines), in comparison with the simulated photoelectron spectra for the lowest energy structure found at a given functional (red lines) with the aug-cc-pVDZ basis set.