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Silicon Hydride Clusters Si_5H_n (n = 3−12) and Their Anions: Structures, Thermochemistry, and Electron Affinities

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The molecular structures, electron affinities, and dissociation energies of the $Si_5H_n/Si_5H_n^-$ ($n = 3-12$) species have been calculated by means of three density functional theory (DFT) methods. The basis set used in this work is of double-ζ plus polarization quality with additional diffuse s- and p-type functions, denoted DZP++. The geometries are fully optimized with each DFT method independently. Three different types of the neutral−anion energy separations presented in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The first Si−H dissociation energies for neutral Si_5H_n and its anion have also been reported.

Introduction

Over the past decade, hydrogenated silicon clusters have attracted a lot of attention because of their intrinsic interest from the point of view of chemical structure and bonding and their importance in the modern industry.[1−10] For instance, although analogous carbon and silicon species are isovalent, the chemical properties of carbon and silicon congeners can be quite different. One of the reasons for these differences is that the relative orbital sizes of the valence s and p orbitals are different for the carbon and silicon atoms; silicon has a larger p orbital than carbon, and carbon has a large s orbital than silicon.[11] On the other hand, the hydrogenated silicon compounds play key roles in the chemical vapor deposition of thin films, photoluminescence of porous silicon, potential fluctuations, and the Staebler−Wronski effect of hydrogenated amorphous silicon (α-Si:H), which is an important but a poorly understood process.[12−27] The knowledge on equilibrium structures, thermochemistry, and electron affinities of silicon hydride clusters is very important for the understanding these process. With this motivation, we have carried out a detailed study of the structures and electron affinities by means of density functional theory (DFT).[28−30]

There have been some previous theoretical and experimental studies on silicon hydrides. Neumark and co-workers[5] reported the photoelectron spectroscopy study of Si_nH^- along with ab initio calculations to aid the assignment. Pak et al.[11] presented the structure and electron affinities of SiH_n and Si_2H_n with density functional theory (DFT). Xu et al.[13] performed studies of the structures and electron affinities of Si_3H_n with DFT methods and concluded that BHLYP provides the most reliable results for Si−Si bond lengths and B3LYP provides the most reliable results for Si−H bond lengths. We recently reported the structures and electron affinities of Si_nH and Si_4H_n, and B3LYP and BPW91 methods are thought to provide the most reliable adiabatic electron affinity by comparison with limited experimental values.[7,20,31] For electron affinities of Si_nH_2 clusters, we have performed theoretical computation, and the results will be published in a future publication.

DFT has evolved into a widely applicable computational technique, while requiring less computational effort than convergent quantum mechanical methods such as coupled cluster theory.[32] Gradient-corrected DFT is effective for predicting the electron affinities of many inorganic species.[32,33] The reliability of the predictions for electron affinities with DFT methods was comprehensively discussed in the 2002 review by Rienstra-Kiracofe et al.[34] They reported that the average deviation from experiment for more than 50 molecules is only 0.15 eV with the DZP++ B3LYP method.

Theoretical Methods

The three different density functionals forms used here are (a) the half-and-half exchange functional[35] with the Lee, Yang, and Parr correlation functional[36] (BHLYP); (b) Becke's three-parameter hybrid exchange functional[37] with the LYP correlation functional (B3LYP); and (c) Becke's 1988 exchange functional[38] with the correlation functional of Perdew and Wang[39] (BPW91).

Restricted methods were used for all closed-shell systems, whereas unrestricted methods were employed for the open-shell species. All the electron affinities and molecular structures have been determined with the Gaussian 98[40] program package. The default numerical integration grid (75 302) of Gaussian 98 was applied.

A standard double-ζ plus polarization (DZP) basis set with the addition of diffuse functions was utilized. The DZ part of the basis set was constructed from the Huzinage−Dunning−Hay[41] set of contracted double-ζ Gaussian functions. The DZP basis was formed by the addition of a set of five d-type polarization functions for Si and a set of p-type polarization functions for H [$\alpha_d(Si) = 0.50$, $\alpha_p(H) = 0.75$]. The DZP basis was augmented with diffuse functions; Si received one additional s-type and one additional set of p-type functions, and H received one additional s-type function. The diffuse function orbital exponents were determined in an "even-tempered sense" as a mathematical extension of the primitive set, according to the formula of Lee and Schaefer[42] [$\alpha_s(Si) = 0.02729$, $\alpha_p(Si) = 0.02500$, $\alpha_s(H) = 0.04415$]. The final contraction scheme for

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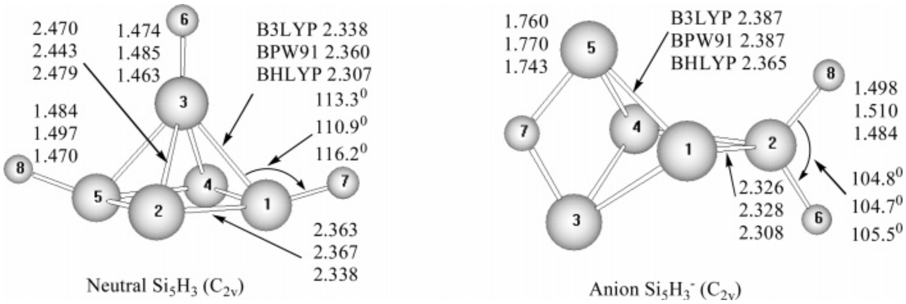


Figure 1. Optimized geometries for neutral Si_5H_3 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 8. All bond distances are in angstroms.

this basis set is Si (12s8p1d/7s5p1d) and H (5s1p/3s1p). This extended basis will be denoted as "DZP++".

All Si_5H_n/$Si_5H_n^-$ ($n = 3-12$) stationary point geometries were analyzed by the evaluation of their harmonic vibrational frequencies at the three different levels of theory.

Results and Discussion

Si_5H_3 and $Si_5H_3^-$. The C_{2v}-symmetry structure of the $^2B_1$ ground state for neutral Si_5H_3 and the C_{2v} symmetry structure of the $^1A_1$ ground state for anion $Si_5H_3^-$ are displayed in Figure 1. The bond length evaluated by all of these methods is also shown in Figure 1. As mention above, the BHLYP method provides the most reliable Si−Si bond length predictions, and the B3LYP method provides the most reliable H−Si bond length predictions.[13] Hence, the most reliable Si−Si bond distances for neutral Si_5H_3 are predicted to be 2.338 Å (BHLYP) for the four equivalent Si−Si bonds, 2.307 Å (BHLYP) for the two equivalent Si_1-Si_3 and Si_3-Si_5 bonds, 2.479 Å (BHLYP) for the two equivalent Si_2-Si_3 and Si_3-Si_4 bonds, 1.474 Å (B3LYP) for Si_3-H_6 bonds, and 1.484 Å (B3LYP) for the two equivalent Si−H bonds.

Surprisingly, the ground-state structure for anion $Si_5H_3^-$ takes on a H-bridged bond. Of course, such H-bridged type bonds are thought to be present in α-Si:H and play an important role in explaining the Staebler−Wronski effect.[6,14] The H-bridged bond lengths are evaluated to be 1.743−1.770 Å. The bridged H−Si bond lengths evaluated by the B3LYP method, thought to be the most reliable, are 1.760 Å. The two equivalent bond distances between H-atom and the sp^3-hybridized Si-atom (numbered 2), thought to be the most reliable, are 1.498 Å (B3LYP) which are shorter than the H-bridged bond distances by 0.26 Å. Compared with experimental values, the Si−D (deuterium) bond length is reported to be 1.6 ± 0.2 Å on a Si (100) surface[22] by transmission−ion channeling, the bridged and nonbridged H−Si bond lengths are within the range of experimental error. The most reliable Si−Si bond distances are 2.308 Å (BHLYP) for four equivalent bonds and 2.365 Å (BHLYP) for two equivalent bonds. Compared with the neutral Si_5H_3, the shape of the anion $Si_5H_3^-$ primary change is intramolecular H-transfer. To our knowledge, there are no experimental and theoretical values for comparison.

The theoretical adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE) are listed in Table 1. The evaluated EA_{ad} for Si_5H_3 ranges from 2.63 to 2.83 eV with all three DFT methods. The EA_{vert} values range from1.98 to 2.12 eV. The range of VDE is from 3.17 to 3.82 eV. No experimental dates are available for comparison. It is clear from Table 1 that the EA_{ad}, EA_{vert}, and VDE predicted by B3LYP are close to the values by BPW91. This result is the same as the result presented by Xu et al.[13] and Li et al.[31] It is also clear from Table 1 that the values of EA_{ad}, EA_{vert}, and VDE for Si_5H_3 are different from each other due to the large change in geometry between neutral and its anion.

TABLE 1: The Zero-Point Corrected Adiabatic Electron Affinity (EA_{ad}), the Vertical Electron Affinity (EA_{vert}), and the Vertical Detachment Energy (VDE) for Si_5H_n ($n = 3-12$) Clusters, Presented in electronvolts

compounds	methods	EA_{ad}	EA_{vert}	VDE
Si_5H_3	B3LYP	2.83	2.11	3.17
	BPW91	2.78	2.12	3.21
	BHLYP	2.63	1.98	3.82
Si_5H_4 (C_{2v}-I←C_{2v})	B3LYP	2.14	2.00	2.23
	BPW91	2.20	2.05	2.30
	BHLYP	2.03	1.89	2.11
Si_5H_4 (C_{2v}-II←C_{2v})	B3LYP	2.20	1.09	2.23
	BPW91	2.10	1.16	2.30
	BHLYP	2.31	1.11	2.11
Si_5H_5	B3LYP	2.63	1.93	3.24
	BPW91	2.63	1.93	3.25
	BHLYP	2.44	1.73	3.08
Si_5H_6	B3LYP	1.59	0.96	2.22
	BPW91	1.60	0.97	2.27
	BHLYP	1.51	0.80	2.18
Si_5H_7	B3LYP	2.55	2.05	3.02
	BPW91	2.57	2.04	3.09
	BHLYP	2.33	1.84	2.78
Si_5H_8	B3LYP	0.41	−0.19	2.31
	BPW91	0.45	−0.13	2.00
	BHLYP	0.10	−0.48	2.18
Si_5H_9	B3LYP	2.37	1.62	2.92
	BPW91	2.39	1.63	2.95
	BHLYP	2.11	1.35	2.69
Si_5H_{10}	B3LYP	0.22	−0.36	0.42
	BPW91	0.40	−0.16	0.60
	BHLYP	−0.10	−0.70	0.08
Si_5H_{11}	B3LYP	2.42	1.72	3.07
	BPW91	2.44	1.74	3.11
	BHLYP	2.18	1.47	2.83
Si_5H_{12}	B3LYP	0.30	−0.41	1.45
	BPW91	0.42	−0.37	1.54
	BHLYP	−0.02	−4.81	1.19

Si_5H_4 and $Si_5H_4^-$. Two minima for the neutral Si_5H_4 and one for its anion are shown in Figure 2. At the B3LYP and BHLYP level of theory, the Si_5H_4-I structure with C_{2v} symmetry and $^1A_1$ state is more stable in energy than Si_5H_4-II by 0.09 and 0.31 eV, respectively, whereas the BPW91 functionals predict that the II-type isomer with C_{2v} symmetry and $^1A_1$ is more stable in energy than the I-type by 0.09 eV. In this case, we cannot be sure which structure is more adjacent to the critical points. In fact, the potential energy surface of Si_nH_m is very flat, many isomeric arrangements are possible, and accurate predictions of equilibrium geometries require advanced quantum mechanical investigations. At the MP3/6-311++G** level of theory, it is obtained that the I-type structure is more stable in energy than the II-type by 0.06 eV. Hence, Si_5H_4-I perhaps is the ground-state structure. The most reliable bond lengths for

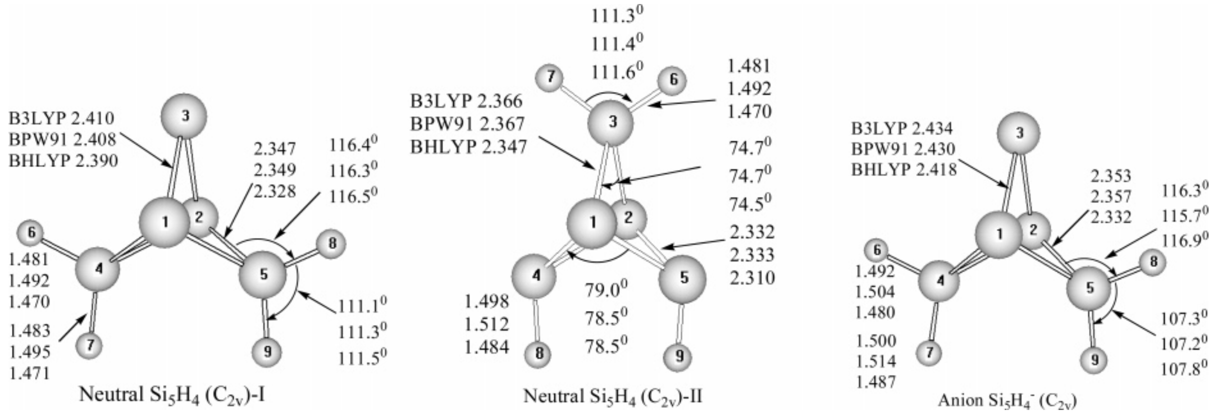


Figure 2. Optimized geometries for neutral Si_5H_4 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 9. All bond distances are in angstroms.

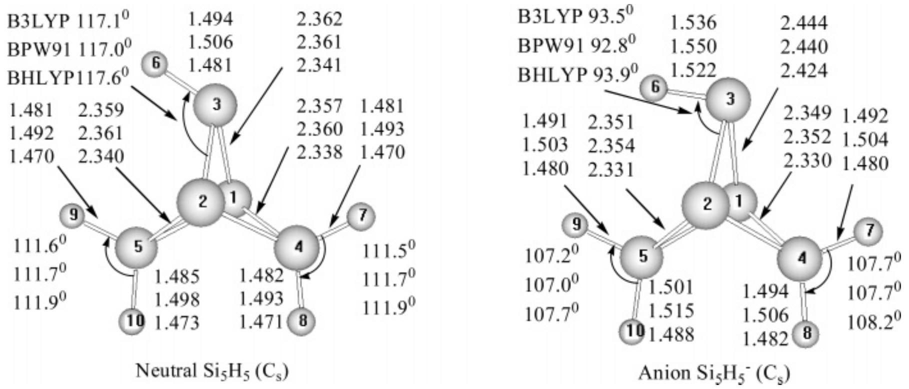


Figure 3. Optimized geometries for neutral Si_5H_5 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 10. All bond distances are in angstroms.

Si_5H_4-I are predicted to be 2.390 Å (BHLYP) for the two equivalent Si−Si bonds, 2.328 Å (BHLYP) for the four equivalent Si−Si bonds, and 1.481 and 1.583 Å (B3LYP) for Si−H bonds in the SiH_2 groups. The HSiH bond angles in the SiH_2 groups are 111.1−111.5°.

For negatively charged ion $Si_5H_4^-$, the ground-state structure displays C_{2v} symmetry with $^2B_2$ state. Compared with neutral Si_5H_4-I, the bond lengths of its anion are lengthened because the additional electron goes into the b_2 orbital, which is antibonding in the plane consisting of nos. 3−5 silicon atoms, causing them to move apart. As can be see from Figure 2, the two equivalent and four equivalent Si−Si bonds have been elongated from neutral structure by 0.028 and 0.004 Å (BHLYP), respectively. The two Si−H bonds in the SiH_2 groups have been lengthened by 0.011 and 0.017 Å (B3LYP). The HSiH bond angles in the SiH_2 groups are 107.2−107.8°. There are no experimental or other theoretical values available.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for the I-type and II-type of Si_5H_4 ranges from 2.03 to 2.20 eV and from 2.10 to 2.31 eV, respectively. The range of EA_{vert} is from 1.89 to 2.05 eV and from 1.09 to 1.16 eV, respectively. The theoretical ranges of VDE for Si_5H_4 are from 2.11 to 2.30 eV by all of these DFT methods. There are no experimental data available.

Si_5H_5 and $Si_5H_5^-$. The geometries of ground state of neutral Si_5H_5 and its anion $Si_5H_5^-$ are displayed in Figure 3. The ground-state structure of Si_5H_5 has C_s symmetry with $^2A'$ state. The most reliable bond lengths are thought to be 2.341 Å (BHLYP) for Si_1−Si_3 and Si_2−Si_3 bonds, 2.338 Å (BHLYP) for Si_1−Si_4 and Si_2−Si_4 bonds, 2.340 Å (BHLYP) for Si_1−Si_5 and Si_2−Si_5 bonds, 1.494 Å (B3LYP) for Si−H bonds in the SiH group, 1.481 and 1.482 Å (B3LYP) for Si−H bonds in the SiH_2 group, and 1.481 and 1.485 Å (B3LYP) for Si−H bonds in the other SiH_2 group, respectively.

For negatively charged ion $Si_5H_5^-$, the ground-state structure displays C_s symmetry with $^1A'$ state. Compared with the ground-state structure of neutral Si_5H_5, the Si−Si bond distances become shorter, and the Si−H bond distances get longer. The most reliable Si−Si bond lengths are deemed to be 2.424 (BHLYP) for Si_1−Si_3 and Si_2−Si_3 bonds, 2.330 (BHLYP) for Si_1−Si_4 and Si_2−Si_4 bonds, and 2.331 Å (BHLYP) for Si_1−Si_5 and Si_2−Si_5 bonds, respectively. The most reliable Si−H bond distances are predicted to be 1.492, and 1.494 Å (B3LYP) in the SiH_2 group and 1.491, 1.501 Å (B3LYP) in another SiH_2 group. There are no experimental data for comparison.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_5H_5 ranges from 2.44 to 2.63 eV. The EA_{vert} values range from 1.73 to 1.93 eV. The range of VDE is from 3.08 to 3.25 eV. Again, the values of EA_{ad}, EA_{vert}, and VDE are different from each other because of the large change in geometry between the neutral and its anion. There are no experimental data available.

Si_5H_6 and $Si_5H_6^-$. The ground-state structure of neutral Si_5H_6 displays D_{3h} symmetry with $^1A_1'$ state and is shown in Figure 4. This result is the same as the previous results obtained by Schleyer et al. and Kitchen et al.[43,44] The most reliable bond lengths are predicted to be 2.336 Å (BHLYP) for the six equivalent Si−Si bonds and 1.481 Å (B3LYP) for Si−H bonds. The HSiH bond angles in the SiH_2 groups are 111.5−111.8°. There are no experimental data for comparison.

For negatively charged ion $Si_5H_6^-$, the ground-state structure also displays D_{3h} symmetry, but the electronic state is $^2A_2''$. Compared with its neutral molecule, the six equivalent Si−Si bonds and Si−H bonds have been elongated from neutral

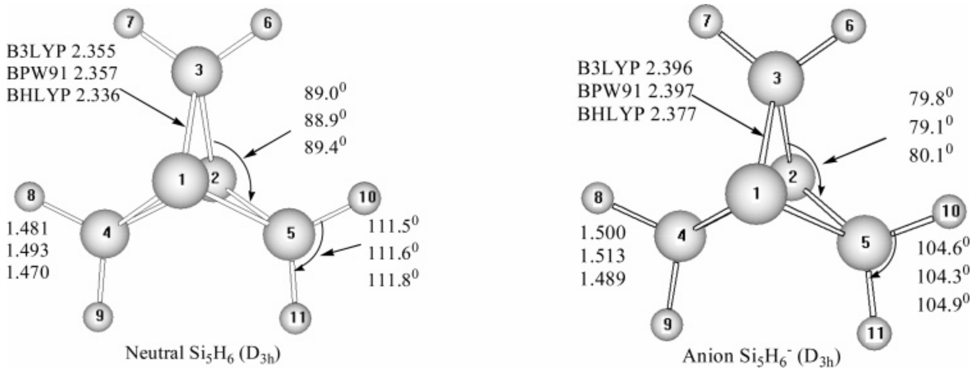


Figure 4. Optimized geometries for neutral Si_5H_6 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 11. All bond distances are in angstroms.

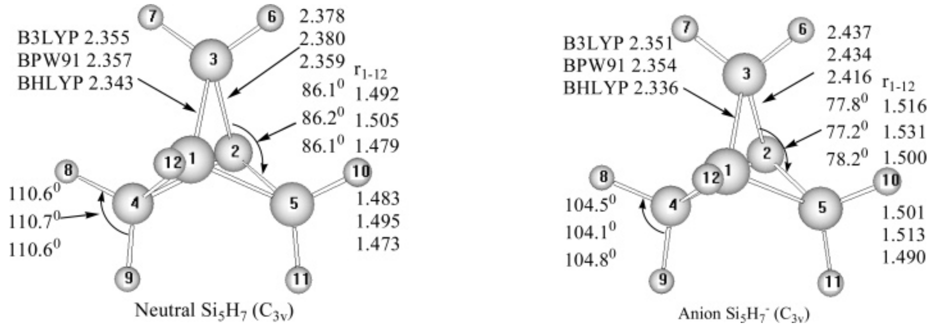


Figure 5. Optimized geometries for neutral Si_5H_7 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 12. All bond distances are in angstroms.

structure by 0.041 and 0.019 Å, respectively. The HSiH bond angles in the SiH_2 groups are 104.3−104.9°, which are smaller than in the neutral structure about 7°.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_5H_6 ranges from 1.51 to 1.60 eV. Swihart[45] reported that the EA_{ad} for Si_5H_6 is 1.54 eV at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. The range of EA_{vert} is from 0.80 to 0.97 eV. The VDE values range from 2.18 to 2.27 eV. As can be seen from Table 1, the BPW91 EA_{ad} value of 1.60 eV is close to the B3LYP EA_{ad} value of 1.59 eV. No experimental values are available.

Si_5H_7 and $Si_5H_7^-$. There are a few previous studies on the structure of Si_5H_7 and its anion. The geometries of the ground state of neutral Si_5H_7 and its anion $Si_5H_7^-$ are displayed in Figure 5. The ground-state structure of Si_5H_7 has C_{3v} symmetry with $^2A_1$ state. The most reliable Si−Si bond lengths are calculated to be 2.343 Å (BHLYP) for Si_1−Si_3, Si_1−Si_4, and Si_1−Si_5 bonds, 2.359 Å (BHLYP) for Si_2−Si_3, Si_2−Si_4, and Si_2−Si_5 bonds. The most reliable Si−H bond lengths are predicted to be 1.492 Å (B3LYP) for Si−H bonds in the SiH groups and 1.483 Å (B3LYP) for Si−H bonds in the SiH_2 groups. The bond angle HSiH in the SiH_2 group is 110.6−110.7°. There are no experimental data available.

For the anionic $Si_5H_7^-$ molecule, the C_{3v}-symmetry structure of the $^1A_1$ ground state is shown in Figure 5. The most reliable prediction of the bond lengths for $Si_5H_7^-$ are 2.336 Å (BHLYP) for the three equivalent Si−Si bonds of the adjacent SiH group, 2.416 Å (BHLYP) for the three equivalent Si−Si bonds apart from the SiH group, 1.516 Å (B3LYP) for Si−H in the SiH group, and 1.501 Å (B3LYP) for Si−H in the SiH_2 group. The bond angle HSiH in the SiH_2 group is 104.1−104.8°. No experimental or additional theoretical data are available for comparison.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The EA_{ad} for Si_5H_7 is predicted to be 2.55 (B3LYP), 2.57 (BPW91), and 2.33 (BHLYP) eV. We note that the EA_{ad} value for Si_5H_7 predicted by Swihart[45] is 2.56 eV at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. The EA_{vert} values range from 1.84 to 2.05 eV. The range of VDE is from 2.78 to 3.09 eV. No experimental values are available.

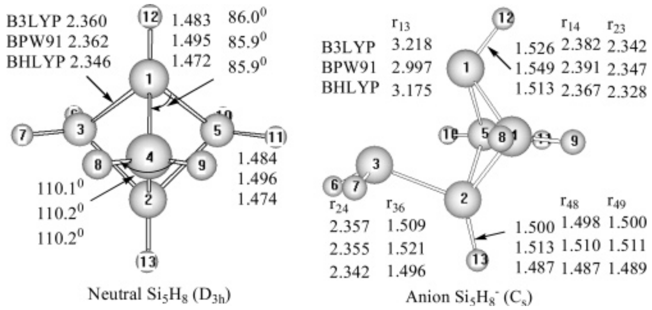
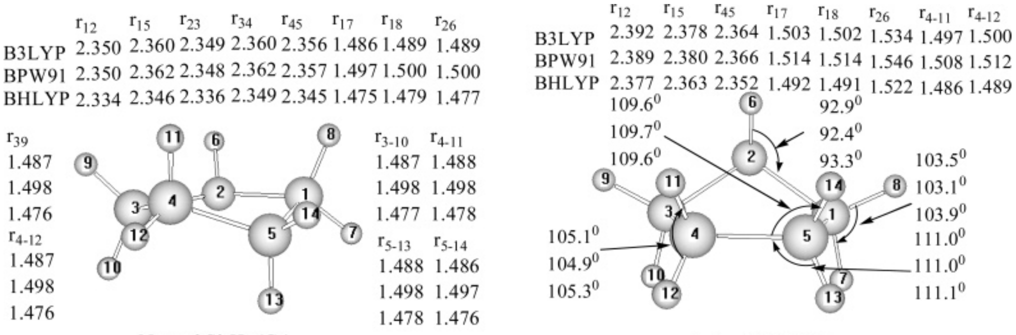


Figure 6. Optimized geometries for neutral Si_5H_8 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 13. All bond distances are in angstroms.

Si_5H_8 and $Si_5H_8^-$. The D_{3h}-symmetry structure of the $^1A_1'$ ground state for neutral Si_5H_8 and the C_s-symmetry structure of the $^2A'$ ground state for $Si_5H_8^-$ are displayed in Figure 6. Our results for the geometry of the ground state of Si_5H_8 are the stereosaturated silanes. The most reliable bond lengths calculated by BHLYP are 2.346 Å for the six equivalent Si−Si bonds. The most reliable bond lengths of Si−H calculated by B3LYP are 1.483 Å in the SiH groups and 1.484 Å in the SiH_2 groups, respectively. The bond angles HSiH in the SiH_2 groups are 110.1−110.2°. No experimental values are available.

For the $Si_5H_8^-$ anion, no experimental data are available. As can be seen from Figure 6, silicon atoms 1−3 lie in the same plane, and this cluster has a mirror symmetry about this plane. So the symmetry of $Si_5H_8^-$ is C_s. The distances between numbered 1 and 3 silicon atoms are 2.997−3.175 Å, which indicates that the two silicon atoms are not bonded according



Neutral Si_5H_9 (C_1) Anion $Si_5H_9^-$ (C_s)

Figure 7. Optimized geometries for neutral Si_5H_9 and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 14. All bond distances are in angstroms.

to the rough criterion suggested in the previous study.[46] In other words, the bonds of Si_1-Si_3 broke when the neutral saturated silanes Si_5H_8 obtained one electron. This wound result in unstability of the anionic $Si_5H_8^-$. The bond lengths are shown in Figure 6.

Our theoretical neutral−anion energy separation for Si_5H_8 is given in Table 1. The evaluated EA_{ad} for Si_5H_8 ranges from 0.10 to 0.45 eV with the three different functions. In fact, if the EA_{ad} is small, the VDE may be important. The theoretical ranges of VDE are from 2.00 to 2.31 eV. The ranges of EA_{vert} predicted are from −0.48 to −0.13 eV. At a first approximation, the negative EA_{vert} corresponds to the resonant electron scattering energy.[34,47,48]

Si_5H_9 and $Si_5H_9^-$. The cyclic structure of neutral Si_5H_9 displays C_1 symmetry and is shown in Figure 7. As can be seen from Figure 7, the framework of Si_5 is broken when $n = 9$. All the parameters of the bond lengths for Si_5H_9 are also shown in Figure 7. There are no experiment and other methods data for comparison.

There is no previous study on the structure of the $Si_5H_9^-$ anion. Our theoretical predictions show that the structure of the ground state of $Si_5H_9^-$ is the C_s-symmetry with $^1A'$ state. As can be seen from Figure 7, silicon atoms 1 and 3−5 lie in the same plane and the Si−H bond in the SiH group becomes warped together. Compared with the ground-state structure of neutral Si_5H_9 (C_1 symmetry), the shape of anion $Si_5H_9^-$ become very regular. The calculated bond lengths for $Si_5H_9^-$ are shown in Figure 7.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_5H_9 ranges from 2.11 to 2.39 eV with the three different functionals. Swihart[45] predicted 2.34 eV for Si_5H_9 at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. The EA_{vert} values range from 1.35 to 1.63 eV. The range of VDE is from 2.69 to 2.95 eV. No experimental values are available.

Si_5H_{10} and $Si_5H_{10}^-$. There are many previous studies on cyclopentasilane, Si_5H_{10}, with various methods. And the ground-state structure of cyclopentasilane is both envelope (C_s) and twist (C_2) forms.[49−51] Our DFT results show that the envelope (C_s) and the twist (C_2) structures (shown in Figure 8) have essentially the same energy. Vibrational analysis indicates that the envelope (C_s) structure may be a saddle point (has an imaginary frequency with a″ mode). The a″ imaginary vibrational frequencies of C_s symmetry are $18i$, $19i$, and $14i$ cm^{-1} by the B3LYP, BPW91, and BHLYP methods, respectively. At the BHLYP level of theory, the vibrational frequency of the twist (C_2) structure with ^1A state is real, although the value of 2 cm^{-1} for b mode is small. At the B3LYP and the BPW91 levels of theory, there is an imaginary frequency with b mode to be found for the twist (C_2) structure. The imaginary frequency with b mode for the twist (C_2) structure is $9i$ cm^{-1} at the B3LYP and the BPW91 levels of theory. Following the mode b for the twist (C_2) or the mode a″ for the envelope (C_s), the symmetry collapses to C_1. The smallest vibrational frequency for C_1 is real, but the values of 5 (B3LYP) and 2 (BPW91) cm^{-1} are very small. On the other hand, the C_2-, C_1-, and C_s-symmetry structure have essentially the same energy. Hence, we assign the C_2-symmetry for the ground-state structure of cyclopentasilane. The small imaginary frequencies of $9i$ cm^{-1} at the B3LYP and the BPW91 levels of theory are thought to be an artifact of the numerical integration. The electronic state of the twist structure of cyclopentasilane is ^1A (the electronic state of the envelope structure is $^1A'$).

For the C_2-symmetry structure, the bond lengths are evaluated to be 2.355−2.369 Å for Si_1-Si_2 and Si_2-Si_3 bonds, 2.346−2.360 Å for Si_1-Si_5 and Si_3-Si_4 bonds, and 2.343−2.357 Å for Si_4-Si_5 bonds. At the BHLYP, the B3LYP, and the BPW91 levels of theory, the average Si−Si bond lengths of C_2 symmetry are 2.349, 2.361, and 2.363 Å, respectively. Compared with the experimental value[52] of 2.342(3) Å, the BHLYP result is in excellent agreement with the experimental value. This result has also supported that the BHLYP provides the most reliable results for Si−Si bond lengths. In fact, the average Si−Si bond lengths of C_s symmetry structure are also 2.349 (BHLYP), 2.361 (B3LYP), and 2.363 Å (BPW91), respectively. The most reliable Si−H bond lengths are thought to be about 1.487 Å (B3LYP).

There is no previous study on the structure of the $Si_5H_{10}^-$ anion. Our theoretical calculation shows that the structure of the ground state of $Si_5H_{10}^-$ takes on two minima structures which, C_s symmetry with $^2A'$ state and C_2 symmetry with ^2B state (shown in Figure 8), have the same energy. The Si−Si bond lengths for both the C_s- and the C_2-symmetry structures, thought to be the most reliable, are 2.320 Å (BHLYP). The most reliable Si−H bond distances for the C_2-symmetry structure are thought to be 1.507 Å (B3LYP) for Si_1-H_8 and Si_3-H_{11} bonds, 1.512 Å (B3LYP) for Si_1-H_9 and Si_3-H_{10} bonds, 1.508 Å (B3LYP) for Si_2-H_6 and Si_2-H_7 bonds, 1.516 Å (B3LYP) for Si_4-H_{12} and Si_5-H_{14} bonds, 1.507 Å (B3LYP) for Si_4-H_{13} and Si_5-H_{15} bonds. The most reliable Si−H bond distances for the C_s-symmetry structure are thought to be 1.514 Å (B3LYP) for Si_1-H_8 and Si_3-H_{10} bonds, 1.507 Å (B3LYP) for Si_1-H_9 and Si_3-H_{11} bonds, 1.516 Å (B3LYP) for Si_2-H_6 bonds, 1.507 Å for Si_2-H_7 bonds, 1.510 Å (B3LYP) for Si_4-H_{12} and Si_5-H_{15} bonds, and 1.508 Å (B3LYP) for Si_4-H_{13} and Si_5-H_{14} bonds.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The (−0.10 eV) EA_{ad} of cyclopentasilane predicted by the

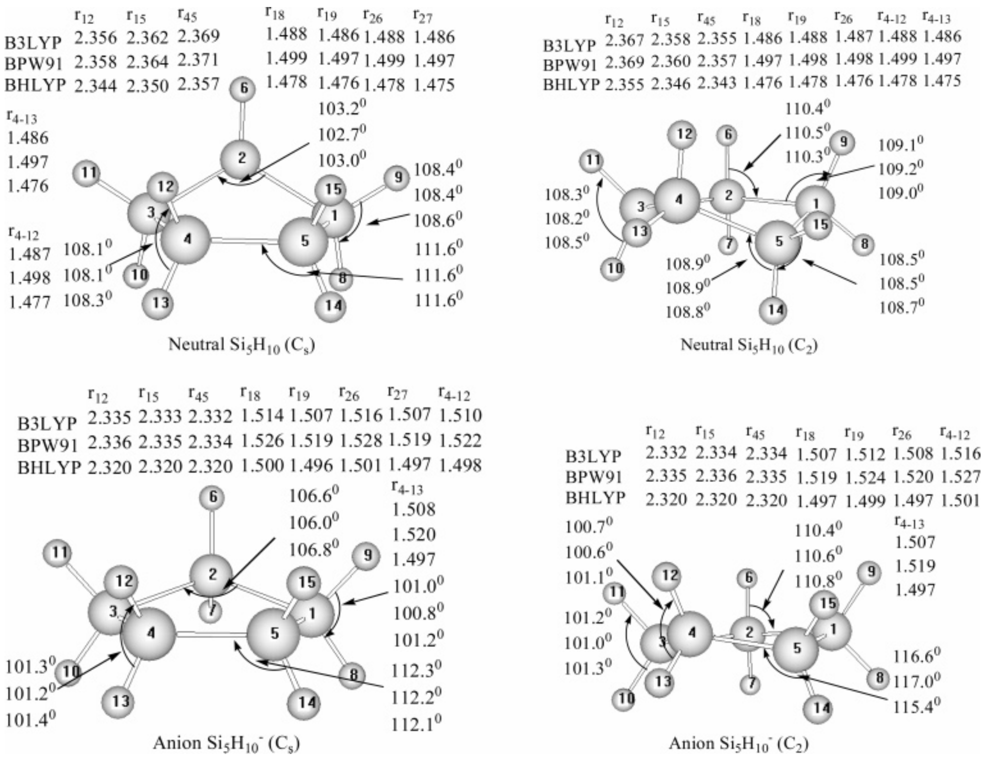


Figure 8. Optimized geometries for neutral Si_5H_{10} and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 15. All bond distances are in angstroms.

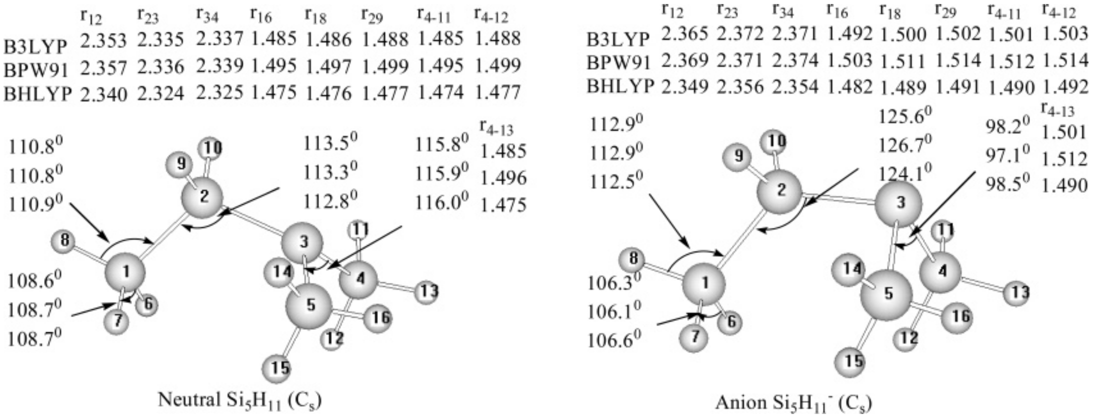
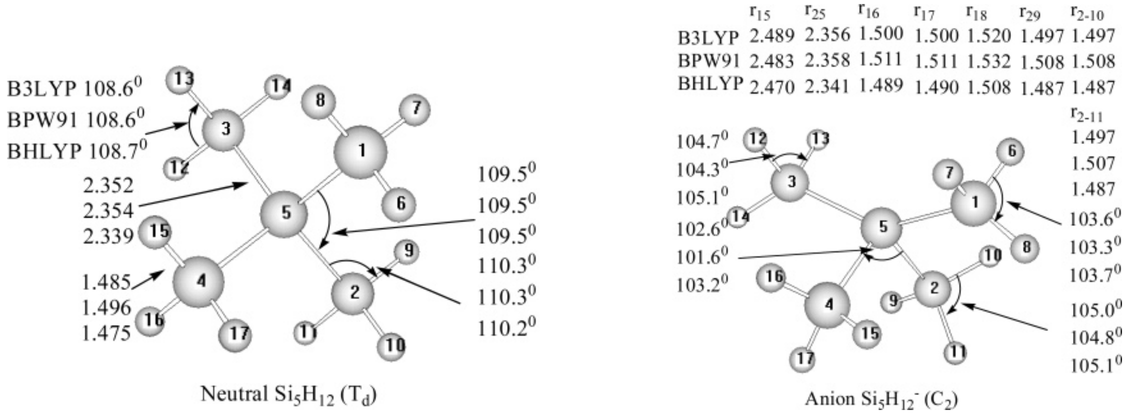


Figure 9. Optimized geometries for neutral Si_5H_{11} and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 16. All bond distances are in angstroms.

BHLYP is negative value. That is, cyclopentasilane does not form a stable anion. At the B3LYP and BPW91 levels of theory, cyclopentasilane possesses very small positive EA_{ad} values of 0.22 (B3LYP) and 0.40 eV (BPW91). The VDE are from 0.08 to 0.60 eV. The range of EA_{vert} predicted by all of these DFT methods is from −0.70 to −0.16 eV. As is the case for Si_5H_8, the negative EA_{vert} corresponds to the resonant electron scattering energy.[34,47,48]

Si_5H_{11} and $Si_5H_{11}^-$. The geometry of the ground state of neutral Si_5H_{11} and its anion are chain structures and displayed in Figure 9. At the BPW91 level of theory, the ground-state structure of Si_5H_{11} is C_s symmetry with $^2A'$ state. At the B3LYP and BHLYP level of theory, there is an imaginary frequency with a″ mode. However, the values of $5i$ (B3LYP) and $1i$ (BHLYP) cm^{-1} are very small. Hence, we assign the C_s-symmetry with $^2A'$ state for the ground-state structure of Si_5H_{11}. The small imaginary frequencies of $5i$ (B3LYP) and $1i$ (BHLYP) cm^{-1} are thought to be an artifact of the numerical integration. There are no experimental data for comparison. The bond lengths, thought to be the most reliable, are 2.340 Å (BHLYP) for Si_1-Si_2 bonds, 2.324 Å (BHLYP) for Si_2-Si_3 bonds, 2.325 Å (BHLYP) for Si_3-Si_4 and Si_3-Si_5 bonds, 1.485 and 1.486 Å (B3LYP) for the Si−H bonds in the SiH_3 group, 1.488 Å (B3LYP) for the Si−H bonds in the SiH_2 group, and 1.485, 1.488, and 1.485 Å (B3LYP) for the Si−H bonds in the two symmetrical SiH_3 groups.

For negatively charged ion $Si_5H_{11}^-$, the ground-state structure displays C_s symmetry with $^1A'$ state. The most reliable bond lengths are predicted to be 2.349 Å (BHLYP) for Si_1-Si_2 bonds, 2.356 Å (BHLYP) for Si_2-Si_3 bonds, and 2.354 Å (BHLYP) for Si_3-Si_4 and Si_3-Si_5 bonds. Compared with the ground-state structure of neutral Si_5H_{11}, the Si−Si bond distances of the anionic $Si_5H_{11}^-$ are lengthened. The most reliable Si−H bond lengths are thought to be 1.492 and 1.500 Å (B3LYP) in the SiH_3 group, 1.502 Å (B3LYP) in the SiH_2 group, and 1.501, 1.503, and 1.501 Å (B3LYP) in the two symmetrical SiH_3



Neutral Si_5H_{12} (T_d)

Anion $Si_5H_{12}^-$ (C_2)

Figure 10. Optimized geometries for neutral Si_5H_{12} and its anion. Silicon atoms are numbered from 1 to 5. And hydrogen atoms are numbered from 6 to 17. All bond distances are in angstroms.

groups. Compared with its neutral structure, the Si−H bonds are also lengthened.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_5H_{11} ranges from 2.18 to 2.44 eV. The EA_{vert} ranges from 1.47 to 1.74 eV. The range of VDE is from 2.83 to 3.11 eV. There are no experimental data for comparison.

Si_5H_{12} and $Si_5H_{12}^-$. There are many previous studies on pentasilane, Si_5H_{12}.[53−56] Our DFT result (displayed in Figure 10) shows that the ground-state structure of Si_5H_{12} is T_d symmetry with $^1A_1$ state. This result agrees with earlier studies.[53,54] All of the SiSiSi bond angles are 109.5°, the HSiH bond angles in the SiH_3 groups are 108.6−108.7°, and the SiSiH bond angles are 110.2−110.3°. The bond lengths, thought to be the most reliable, are 2.339 Å (BHLYP) for Si−Si bonds and 1.485 Å (B3LYP) for Si−H bonds in the four SiH_3 groups.

For negatively charged ion $Si_5H_{12}^-$, the ground-state structure displays C_2 symmetry with ^2A state. The most reliable bond lengths are predicted to be 2.470 Å (BHLYP) for Si_1−Si_5 and Si_3−Si_5 bonds, 2.341 Å (BHLYP) for Si_2−Si_5 and Si_4−Si_5 bonds, 1.500, 1.500, and 1.520 Å (B3LYP) for Si−H bonds in the two SiH_3 groups, and 1.497 Å (B3LYP) for Si−H bonds in the other two SiH_3 groups.

Our theoretical neutral−anion energy separation for Si_5H_{12} are given in Table 1. The EA_{ad} (−0.02 eV) of Si_5H_{12}, calculated by BHLYP, is similar to saturated silanes of SiH_4, Si_2H_6,[11] Si_3H_8,[13] and Si_4H_{10},[31] is negative value. That is Si_5H_{12} does not form a stable anion. The EA_{ad} values of other methods are so small that it cannot be identified by experimental methods. In these cases, the VDE may be important. The range of VDE is from 1.19 to 1.54 eV. For EA_{vert}, Porter et al.[56] reported that the EA_{vert} of Si_5H_{12} is 0.0(1) eV at the diffusion quantum Monte Carlo level of theory. At our DFT levels of theory, the ranges of EA_{vert} are predicted to be from −4.81 to −0.37 eV. As is the case for cyclotrisilane, Si_3H_6,[13] cyclotetrasilane, Si_4H_8,[31] and cyclopentasilane, Si_5H_{10}, the negative EA_{vert} corresponds to the resonant electron scattering energy.[34,47,48]

Dissociation Energies. The first bond dissociation energies for Si_5H_n/$Si_5H_n^-$ (n = 4−12) are given in Table 2 and Table 3. As can be seen from Table 2, for $Si_5H_4 \rightarrow Si_5H_3 + H$, the theoretical dissociation energies range from 2.75 to 3.21 eV. The theoretical results for $Si_5H_5 \rightarrow Si_5H_4 + H$ dissociation energy predicted by all of these DFT methods are in good agreement with each other, and the dissociation energies range from 2.50 to 2.65 eV. For $Si_5H_6 \rightarrow Si_5H_5 + H$ and $Si_5H_7 \rightarrow Si_5H_6 + H$, the ranges of dissociation energies are from 3.48 to 3.69 eV and from 1.78 to 2.14 eV, respectively. For $Si_5H_8 \rightarrow Si_5H_7 + H$, dissociation energies predicted by all of these DFT functionals are in good agreement with each other, and the dissociation energies range from 3.31 to 3.54 eV. The theoretical dissociation energies for $Si_5H_9 \rightarrow Si_5H_8 + H$ and $Si_5H_{10} \rightarrow Si_5H_9 + H$ range from 1.85 to 2.24 eV and from 3.40 to 3.59 eV, respectively. The theoretical results for $Si_5H_{11} \rightarrow Si_5H_{10} + H$ and $Si_5H_{12} \rightarrow Si_5H_{11} + H$ dissociation energy predicted by all of these DFT methods are in good agreement with each other, and the dissociation energies range from 1.09 to 1.31 eV and from 3.42 to 3.60 eV, respectively. The values of Si_5H_7 and Si_5H_{11} indicate that they are less stable.

As can be seen in Table 3, for $Si_5H_4^- \rightarrow Si_5H_3^- + H$, the theoretical dissociation energies range from 2.17 to 2.61 eV. For $Si_5H_5^- \rightarrow Si_5H_4^- + H$ and $Si_5H_6^- \rightarrow Si_5H_5^- + H$, dissociation energies predicted by all of these DFT methods are in good agreement with each other and the ranges of dissociation energies are from 2.93 to 3.08 eV and from 2.45 to 2.76 eV, respectively. The theoretical results for $Si_5H_7^- \rightarrow Si_5H_6^- + H$ dissociation energy predicted by all of these DFT functionals are in good agreement with each other, and the dissociation energies range from 2.75 to 2.96 eV. The theoretical

TABLE 2: Dissociation Energy (D_e, eV) for the Neutral Si_5H_n (n = 4−12)[a]

dissociation	B3LYP	BPW91	BHLYP
$Si_5H_4 \rightarrow Si_5H_3 + H^b$	3.12	2.75	3.21
$Si_5H_5 \rightarrow Si_5H_4 + H^b$	2.58	2.50	2.65
$Si_5H_6 \rightarrow Si_5H_5 + H$	3.66	3.48	3.69
$Si_5H_7 \rightarrow Si_5H_6 + H$	1.95	1.78	2.14
$Si_5H_8 \rightarrow Si_5H_7 + H$	3.49	3.31	3.54
$Si_5H_9 \rightarrow Si_5H_8 + H$	2.19	1.85	2.24
$Si_5H_{10} \rightarrow Si_5H_9 + H$	3.58	3.40	3.59
$Si_5H_{11} \rightarrow Si_5H_{10} + H$	1.31	1.09	1.31
$Si_5H_{12} \rightarrow Si_5H_{11} + H$	3.58	3.42	3.60

[a] Values are corrected with zero-point vibrational energies. [b] The energies of the ground state for Si_5H_4 are the I-type structure with the C_{2v} symmetry for all of these DFT methods.

TABLE 3: Dissociation Energy (D_e, eV) for the Anion $Si_5H_n^-$ (n = 4−12)[a]

dissociation	B3LYP	BPW91	BHLYP
$Si_5H_4^- \rightarrow Si_5H_3^- + H$	2.43	2.17	2.61
$Si_5H_5^- \rightarrow Si_5H_4^- + H$	3.08	2.93	3.07
$Si_5H_6^- \rightarrow Si_5H_5^- + H$	2.62	2.45	2.76
$Si_5H_7^- \rightarrow Si_5H_6^- + H$	2.90	2.75	2.96
$Si_5H_8^- \rightarrow Si_5H_7^- + H$	1.35	1.19	1.32
$Si_5H_9^- \rightarrow Si_5H_8^- + H$	4.14	3.79	4.24
$Si_5H_{10}^- \rightarrow Si_5H_9^- + H$	1.44	1.41	1.38
$Si_5H_{11}^- \rightarrow Si_5H_{10}^- + H$	3.50	3.13	3.58
$Si_5H_{12}^- \rightarrow Si_5H_{11}^- + H$	1.46	1.40	1.40

[a] Values are corrected with zero-point vibrational energies.

dissociation energies for $Si_5H_8^- \rightarrow Si_5H_7^- + H$ range from 1.19 to 1.35 eV and from 3.79 to 4.24 eV for $Si_5H_9^- \rightarrow Si_5H_8^- + H$. For $Si_5H_{10}^- \rightarrow Si_5H_9^- + H$, the theoretical dissociation energies range from 1.38 to 1.44 eV. For $Si_5H_{11}^- \rightarrow Si_5H_{10}^- + H$, the range is from 3.13 to 3.58 eV. For $Si_5H_{12}^- \rightarrow Si_5H_{11}^- + H$, the theoretical dissociation energies range from 1.40 to 1.46 eV. These smaller values indicate that $Si_5H_8^-$, $Si_5H_{10}^-$, and $Si_5H_{12}^-$ are less stable.

Table 2 and Table 3 show that the dissociation energies for $Si_5H_n \rightarrow Si_5H_{n-1} + H$ and $Si_5H_{n-1}^- \rightarrow Si_5H_{n-2}^- + H$ are larger when n is an even number and are smaller when n is an odd number. With even n, Si_5H_n and $Si_5H_{n-1}^-$ have a closed-shell electronic structure and so are more stable. In contrast, the products Si_5H_{n-1}, $Si_5H_{n-2}^-$, and H are both open-shell systems, so the analogous dissociation energies would be larger. For odd n, the situation is the opposite, and the dissociation energies are smaller.

To our knowledge, there are no experimental or theoretical data regarding dissociation for these systems. Our results may thus provide a reference for further study.

Conclusion

The present work provides a systematic study of the silicon hydrides clusters Si_5H_n ($n = 3-12$) with the three carefully selected DFT methods. The ground-state structure and geometric parameters are reported. The BHLYP method may provide the most reliable Si−Si bond lengths and the B3LYP may provide the most reliable Si−H bond lengths. The adiabatic EAs predicted by the B3LYP and the BPW91 methods are reliable.[7,13,33] The EAs are predicted by the B3LYP or BPW91 method to be 2.83 or 2.78 eV (Si_5H_3), 2.14 (2.20) or 2.20 (2.10) eV (Si_5H_4), 2.63 eV (Si_5H_5), 1.59 or 1.60 eV (Si_5H_6), 2.55 or 2.57 eV (Si_5H_7), 0.41 or 0.45 eV (Si_5H_8), 2.37 or 2.39 eV (Si_5H_9), 0.22 or 0.40 eV (Si_5H_{10}), 2.42 or 2.44 eV (Si_5H_{11}), and 0.30 or 0.42 eV (Si_5H_{12}).

For the neutral Si_5H_n ($n = 4-12$), the BHLYP method yields the largest dissociation energies and the BPW91 method yields the least dissociation energies. The first dissociation energies ($Si_5H_n \rightarrow Si_5H_{n-1} + H$) predicted by all of these methods are 2.75−3.21 eV (Si_5H_4), 2.50−2.65 eV (Si_5H_5), 3.48−3.69 eV (Si_5H_6), 1.78−2.14 eV (Si_5H_7), 3.31−3.54 eV (Si_5H_8), 1.85−2.24 eV (Si_5H_9), 3.40−3.59 eV (Si_5H_{10}), 1.09−1.31 eV (Si_5H_{11}), and 3.42−3.60 eV (Si_5H_{12}). For anion clusters ($Si_5H_n^- \rightarrow Si_5H_{n-1}^- + H$), the dissociation energies predicted are 2.17−2.61 eV ($Si_5H_4^-$), 2.93−3.08 eV ($Si_5H_5^-$), 2.45−2.76 eV ($Si_5H_6^-$), 2.75−2.96 eV ($Si_5H_7^-$), 1.19−1.35 eV ($Si_5H_8^-$), 3.79−4.24 eV ($Si_5H_9^-$), 1.38−1.44 eV ($Si_5H_{10}^-$), 3.13−3.58 eV ($Si_5H_{11}^-$), and 1.40−1.46 eV ($Si_5H_{12}^-$).

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Supporting Information Available: Tables showing the frequencies of the Si_5H_n ($n = 3-12$) and their anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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