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The Silicon Hydride Clusters Si_3H_n ($n \leq 8$) and Their Anions: Structures, Thermochemistry, and Electron Affinities

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The molecular structures, electron affinities, and dissociation energies of the $Si_3H_n/Si_3H_n^-$ ($n \leq 8$) species have been examined using five hybrid and pure 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++. These methods have been carefully calibrated (*Chem. Rev.* **2002**, 102, 231). 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 D_e ($Si_3H_n \rightarrow Si_3H_{n-1}+H$) for the neutral Si_3H_n and D_e ($Si_3H_n^- \rightarrow Si_3H_{n-1}^-+H$) for the anionic $Si_3H_n^-$ species have also been reported. In the prediction of bond lengths, the BHLYP predicts the most reliable Si−Si bond lengths and the B3LYP predicts the most reliable Si−H bond lengths. The most reliable EA_{ad}, obtained at the B3LYP and BPW91 levels of theory, are 2.34 or 2.32 eV (Si_3), 2.56 eV (Si_3H), 1.73 or 1.74 eV (Si_3H_2), 2.46 or 2.45 eV (Si_3H_3), 1.95 or 1.93 eV (Si_3H_4), 2.24 or 2.23 eV (Si_3H_5), 1.41 or 1.30 eV (Si_3H_6), and 2.14 eV (Si_3H_7). For Si_3H_8, there are no reliable EA_{ad} but there are reliable VDE. The values of VDE for Si_3H_8 are 1.03 eV (B3LYP) or 1.10 eV (BPW91). The first dissociation energies ($Si_3H_n \rightarrow Si_3H_{n-1}+H$) predicted by all of these methods are 2.65∼2.74 eV (Si_3H), 2.82∼3.12 eV (Si_3H_2), 2.13∼2.23 eV (Si_3H_3), 2.92∼3.08 eV (Si_3H_4), 2.63∼2.95 eV (Si_3H_5), 3.29∼3.53 eV (Si_3H_6), 2.19∼2.54 eV (Si_3H_7), and 3.45∼3.62 eV (Si_3H_8). For anion clusters ($Si_3H_n^- \rightarrow Si_3H_{n-1}^-+H$), the dissociation energies predicted are 2.89∼2.95 eV (Si_3H^-), 2.01∼2.27 eV ($Si_3H_2^-$), 2.83∼2.96 eV ($Si_3H_3^-$), 2.37∼2.68 eV ($Si_3H_4^-$), 2.96∼3.10 eV ($Si_3H_5^-$), 2.36∼2.74 eV ($Si_3H_6^-$), 3.03∼3.16 eV ($Si_3H_7^-$), and 1.44∼1.54 eV ($Si_3H_8^-$).

Introduction

Over the past decade, clusters of silicon and hydrogen have attracted a lot of attention because of their potential applications in semiconductors and optoelectronics and in surface growth processes and their likely existence in the circumstellar atmospheres of evolved carbon stars.[1−18] The binary clusters of silicon and hydrogen are thought to be present in hydrogenated amorphous silicon (α-Si:H), porous silicon, and silicon surfaces. In addition to the fundamental interest, their study may throw some light on complex phenomena occurring in these systems. Hydrogen plays an important role in these systems in phenomena like photoluminescence of porous silicon, potential fluctuations, and the Staebler-Wronski effect in hydrogenated amorphous silicon (α-Si:H).[19−25] The knowledge on the ground and low-lying electronic states of the neutral and negatively charged silicon hydrides clusters is very important for the understanding of these phenomena.[2,10,20,21] With this motivation, we have carried out a detailed study of structures, thermochemistry, and electron affinities of silicon hydrides clusters Si_3H_n ($n \leq 8$) and their anions using density functional theory (DFT).[26−28]

When predicting molecular energies, structures, and electron affinities, there are many theoretical approaches, but considering both reliability and computational expense, gradient corrected density functional theory is effective for predicting electron affinities of many inorganic species such as the SiH_n/SiH_n^-, $Si_2H_n/Si_2H_n^-$, GeF_n/GeF_n^-, SeF_n/SeF_n^-, and AsF_n/AsF_n^- systems.[8,29−31] The reliability of the predictions for electron affinities with DFT methods was comprehensively discussed in the recent (2002) review of Rienstra-Kiracofe et al.[32] They reviewed the theoretical predictions of electron affinities with six DFT methods (BHLYP, B3LYP, B3P86, BP86, BLYP, and LSDA) and showed that the average deviation from experiment for electron affinities with the B3LYP and BLYP methods is only 0.15 eV for a set of 91 molecules. They also suggested that B3PW91 and BPW91 methods might outperform the B3LYP, BLYP, and BP86 functionals.

The objective of the present study is to systematically apply several contemporary forms of DFT to the determination of the electron affinities and other properties of the Si_3H_n ($n \leq 8$) series. Of specific interest is (a) the comparison of the electron affinities with the limited available experimental results; (b) the relationship between the neutral Si_3H_n ($n \leq 8$) and their anions as measured by the three types of energy separations, for example, the adiabatic electron affinity (EA_{ad}), the vertical electron affinities (EA_{vert}), and the vertical detachment energy of the anion (VDE); (c) the predictions of other properties including dissociation energies; and (d) the comparison of the different DFT methods. We would like to establish reliable theoretical predictions for those silicon hydrides clusters in the

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absence of experimental results and in some cases to challenge existing experiments.

Theoretical Methods

The five different density functionals or hybrid Hartree−Fock/density functional forms used here are (a) Becke's 1988 exchange functional[33] with Lee, Yang, and Parr's correlation functional[34] (BLYP); (b) the half-and-half exchange functional[35] with the LYP correlation functional (BHLYP); (c) Becke's three-parameter hybrid exchange functional[36] with the LYP correlation functional (B3LYP); (d) Becke's 1988 exchange functional with the correlation functional of Perdew and Wang[37] (BPW91); (e) Becke's three-parameter hybrid exchange functional with the correlation functional of Perdew and Wang (B3PW91).

Restricted methods were used for all closed-shell systems, while unrestricted methods were employed for the open-shell species. All the electron affinities and molecular structures have been determined using the Gaussian 98[38] 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[39] 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 [$\alpha_d(\mathrm{Si}) = 0.50$, $\alpha_p(\mathrm{H}) = 0.75$]. 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[40] [$\alpha_s(\mathrm{Si}) = 0.02729$, $\alpha_p(\mathrm{Si}) = 0.02500$, $\alpha_s(\mathrm{H}) = 0.04415$]. The final contraction scheme for this basis set is Si (12s8p1d/7s5p1d) and H (5s1p/3s1p). This extended basis will be denoted as "DZP++".

All $Si_3H_n/Si_3H_n^-$ ($n \leq 8$) stationary point geometries were interrogated by the evaluation of their harmonic vibrational frequencies at the five different levels of theory.

The electron affinities are evaluated as the difference of total energies in the following manner: the adiabatic electron affinity is determined as $\mathrm{EA_{ad}} = \mathrm{E}$ (zero-point corrected neutral) − E (zero-point corrected anion); the vertical electron affinity by $\mathrm{EA_{vert}} = \mathrm{E}$ (optimized neutral) − E (anion at optimized neutral geometry); and the vertical detachment energy of the anion by VDE = E (neutral at optimized anion geometry) − E (optimized anion).

The dissociation energies for $Si_3H_n/Si_3H_n^-$ are determined from differences in total energies in the following manner: the first dissociation energies for the neutrals refer to the reaction $Si_3H_n \rightarrow Si_3H_{n-1} + H$, while the first dissociation energies for the anions refer to the reactions $Si_3H_n^- \rightarrow Si_3H_{n-1}^- + H$.

Results and Discussion

Si_3 and Si_3^-. There are many previous studies on Si_3. Arnold and Neumark,[41] in their ZEKE (zero-electron-kinetic-energy) spectrum of Si_3^-, have assigned to the $^3A_2'$ state of Si_3 because the observed frequencies (337 ± 10 $\mathrm{cm^{-1}}$) has the character of $^3A_2'$ (D_{3h} symmetry). Fournier et al.[42] presented that the ground state of Si_3 is $^3A_2'$ at LSD (local spin density) level of theory. However, the MP4 (fourth-order Møller−Plesset perturbation),[43] CCD+ST (coupled cluster theory with all double substitutions plus single and triple substitutions),[43] CAS SCF/CI (complete active space MC SCF and restricted first-order configuration interaction),[44] ECP (effective core potential),[45] and GVB (generalized valence bond) methods[46] indicated that the ground state of Si_3 is $^1A_1$ with C_{2v} symmetry.

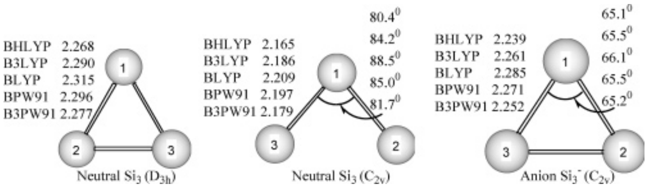

Figure 1. Optimized geometries for neutral Si_3 and anionic Si_3^-. All bond distances are in Å.

Our DFT results are $^1A_1$ state at BLYP level of theory, while other methods are $^3A_2'$ state. BLYP predicts that $^1A_1$ state is more stable than $^3A_2'$ state about 0.09 eV, while B3LYP, BHLYP, BPW91, and B3PW91 indicate that $^3A_2'$ state is more stable than $^1A_1$ state by 0.01, 0.10, 0.05, and 0.12 eV, respectively. The equilibrium geometries of the $^3A_2'$ (D_{3h} symmetry) and $^1A_1$ (C_{2v} symmetry) ground states of neutral Si_3 are given in Figure 1.

The bond length of D_{3h}-symmetry of Si_3 is predicted to be 2.268−2.315 Å. From our previous experience[28−30] and other literature[8,11] and this work (see below Si_3H_8 section), the BHLYP method should give the most reliable bond length (2.268 Å). There are no experimental bond lengths for D_{3h}-symmetry with $^3A_2'$ state, but there are several theoretical values. Raghavachari[43] reported the bond length of $^3A_2'$ state is 2.284 Å at HF/6-31G*. Balasubramanian[44] reported the bond length is 2.30 Å at CAS SCF/CI level. Curtiss et al.[47] reported the bond length is 2.264 Å at MP2/6-31G* level. Fournier et al.[42] reported a theoretical bond length of 2.273 Å. The bond length predicted by MP2/6-31G* is only shorter than BHLYP by about 0.004 Å. For $^1A_1$ (C_{2v} symmetry) state, the bond angle ∠213 of 80.4° evaluated by BHLYP is in agreement with results derived by other authors.[43−47]

For the anionic Si_3^- molecule, Raghavachari and Rohlfing[48] reported in 1991 that $^2A_1$ (C_{2v} symmetry) state is the ground state, which has a theoretical bond length of 2.250 Å, 2.250 Å, and 2.235 Å and a bond angle of 64.8°, 64.8°, and 65.6° at HF/6-31G*, HF/6-31+G*, and MP2/6-31G* level of theory, respectively. Our result is the same as the result of Raghavachari and Rohlfing. The equilibrium geometries of the $^2A_1$ (C_{2v} symmetry) ground states of negatively charged ion of Si_3^- are also shown in Figure 1. As can be seen from Figure 1, the bond distances are predicted to be 2.239−2.285 Å and the bond angle is predicted to be 65.1°∠66.1°. The DZP++ BHLYP bond length, deemed to be the most reliable, is predicted to be 2.239 Å, which is only longer than MP2/6-31G* bond length of 2.235 Å by about 0.004 Å. The bond lengths predicted by the BLYP are the longest. There are no experimental values for comparison.

Our theoretical neutral-anion energy separations for Si_3, as well as experimental electron affinity data, are given in Table 1. The $\mathrm{EA_{ad}}$ for $^3A_2' \leftarrow {}^2A_1$ is predicted to be 2.27 eV (BHLYP), 2.34 eV (B3LYP), 2.14 (BLYP), 2.32 eV (BPW91), and 2.41 eV (B3PW91). The BHLYP, B3LYP, and BPW91 methods give values that are close to the experimental values: 2.29 ± 0.002 eV by Xu et al.[49]or 2.30 ± 0.0 eV by Arnold and Neumark.[41] The $\mathrm{EA_{ad}}$ predicted by BHLYP is a smaller experimental value by about 0.02∼0.03 eV, while the $\mathrm{EA_{ad}}$ predicted by B3LYP and BPW91 is larger than the experimental value by about 0.04∼0.05 eV and 0.02∼0.03 eV, respectively. Curtiss et al.[47] obtained $\mathrm{EA_{ad}} = 2.24$ eV at Gaussian-2 theory, which is also close to the experimental values. The theoretical $\mathrm{EA_{vert}}$ ranges

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_3H_n ($n \leq 8$) Clusters, Presented in eV

compound	method	EA_{ad}	EA_{vert}	VED
$Si_3(^3A_2' \leftarrow {}^2A_1)$	BHLYP	2.27	2.12	2.65
	B3LYP	2.34	2.22	2.66
	BLYP	2.14	2.02	2.43
	BPW91	2.32	2.20	2.71
	B3PW91	2.41	2.29	2.81
	Expt.	2.30 ± 0.0[a]		
		2.29 ± 0.002[b]		
$Si_3H(^2B_2 \leftarrow {}^1A_1)$	BHLYP	2.45	2.39	2.52
	B3LYP	2.56	2.51	2.63
	BLYP	2.37	2.32	2.43
	BPW91	2.56	2.52	2.62
	B3PW91	2.64	2.59	2.70
	Expt.	2.53 ± 0.01[c]		
$Si_3H(^2A' \leftarrow {}^1A_1)$	BHLYP	2.36	2.07	2.52
	B3LYP	2.55	2.17	2.63
	BLYP	2.41	1.97	2.43
	BPW91	2.57	2.16	2.62
	B3PW91	2.60	2.24	2.70
Si_3H_2	BHLYP	1.60	0.26	2.48
	B3LYP	1.73	0.38	2.55
	BLYP	1.59	0.13	2.37
	BPW91	1.74	0.37	2.72
	B3PW91	1.78	0.55	2.71
Si_3H_3	BHLYP	2.33	2.06	2.62
	B3LYP	2.46	2.17	2.71
	BLYP	2.31	1.98	2.53
	BPW91	2.45	2.16	2.71
	B3PW91	2.43	2.23	2.76
$Si_3H_4(^1A' \leftarrow {}^2B_1)$	BHLYP	1.96	1.08	2.09
	B3LYP	1.95	1.04	2.22
	BLYP	1.69	0.78	2.07
	BPW91	1.93	1.13	2.32
	B3PW91	2.07	1.24	2.35
$Si_3H_4(^1A_1 \leftarrow {}^2B_1)$	BHLYP	1.93	0.79	2.09
	B3LYP	1.95	1.00	2.22
	BLYP	1.73	0.91	2.07
	BPW91	1.90	1.11	2.32
	B3PW91	2.02	1.10	2.35
Si_3H_5	BHLYP	2.06	1.71	2.29
	B3LYP	2.24	1.92	2.45
	BLYP	2.10	1.80	2.29
	BPW91	2.23	1.92	2.44
	B3PW91	2.27	1.94	2.49
Si_3H_6	BHLYP	1.27	−0.73	2.14
	B3LYP	1.41	−0.46	2.27
	BLYP	1.33	−0.45	2.10
	BPW91	1.30	−0.44	2.33
	B3PW91	1.32	−0.48	2.39
Si_3H_7	BHLYP	1.89	1.17	2.57
	B3LYP	2.14	1.40	2.82
	BLYP	2.05	1.31	2.71
	BPW91	2.14	1.39	2.84
	B3PW91	2.13	1.39	2.84
Si_3H_8	BHLYP	−0.29	−0.82	0.78
	B3LYP	0.04	−0.55	1.03
	BLYP	0.05	−0.53	0.97
	BPW91	0.14	−0.47	1.10
	B3PW91	0.05	−0.57	1.06

[a] Reference 41. [b] Reference 49. [c] Reference 2.

from 2.02 to 2.29 eV. The range of VDE is from 2.43 to 2.81 eV. Our most reliable result for EA_{vert} is 2.12 (BHLYP) − 2.22 (B3LYP) eV and for VDE is 2.65 (BHLYP) − 2.71 (BPW91) eV. The values of EA_{ad}, EA_{vert}, and VDE are different from each other on account of the large change in geometry between neutral and its anion. The apex bond angles change from 60° in neutral to 65.1°∠66.1° in its anion structures.

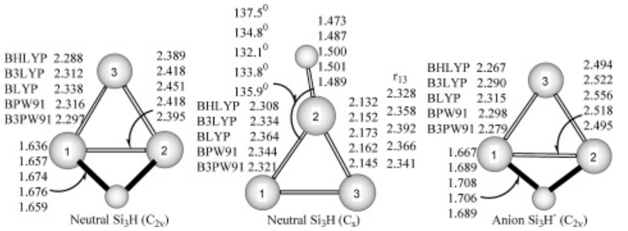

Figure 2. Optimized geometries for neutral Si_3H and anion Si_3H^-. Only silicon atoms are numbered. Black solid line indicates bridged bonding between hydrogen and silicon atom. All bond distances are in Å.

Si_3H and Si_3H^-. There are a few previous studies on the possible structures of the Si_3H cluster. Kalcher and Sax[4] in 1996 performed a detailed CCSD(T) study of Si_3H in several possible geometric arrangements. A C_{2v} with $^2B_2$ state structure was found to be the ground state by these authors. In 1998, Neumark and co-workers[2] also assigned the ground state of neutral Si_3H to be $^2B_2$ by photoelectron spectroscopy experiments and QCISD(T)/6-31G* level of theory. Recently, Balamurugan and Prasad[21] presented ground-state structures for small Si_nH ($2 \leq n \leq 10$) and employed the Car-Parrinello molecular dynamics (CPMD).

Our DFT results are C_{2v} symmetry with $^2B_2$ state (shown in Figure 2) at pure DFT (BLYP and BPW91), while hybrid DFT (BHLYP, B3LYP, and B3PW91) are C_s symmetry with $^2A'$ state (shown in Figure 2). Both $^2B_2$ and $^2A'$ states are very close in energy. For pure DFT, the $^2B_2$ state is more stable than the $^2A'$ state by about 0.03 eV (BLYP) and 0.002 eV (BPW91) in energy. For hybrid DFT, the $^2B_2$ state is less stable than the $^2A'$ state by 0.09 eV (BHLYP), 0.02 eV (B3LYP), and 0.05 eV (B3PW91) in energy, respectively. All of these indicate that the potential energy surface of Si_3H is very flat, many isomeric arrangements are possible, and accurate predictions of equilibrium geometries require advanced quantum mechanical investigations. The BPW91 and BLYP results of the $^2B_2$ state for the ground state of Si_3H perhaps are the most reliable because they are in agreement with CCSD(T) result[4] and QCISD(T)/6-31G* result.[2]

As can be seen from Figure 2, the bond length for C_{2v} symmetry with $^2B_2$ state is predicted to be 2.288−2.338 Å for the two equivalent Si−Si bonds, 2.389−2.451 Å for another Si−Si bond, and 1.636−1.676 Å for the bridged H−Si bond lengths. The BHLYP predicts the most reliable Si−Si bond lengths and the B3LYP predicts the most reliable H−Si bond lengths (see below Si_3H_8 section). Hence, the most reliable Si−Si bond lengths are 2.288 Å and 2.389 Å (BHLYP) and the most reliable Si−H bond lengths are 1.636 Å (B3LYP), which are similar to the CCSD(T) result of Kalcher and Sax:[4] 2.287 Å, 2.365 Å, and 1.624 Å. Xu et al.[2] reported that the QCISD(T)/6-31G* bond lengths are 2.305 Å for the equivalent Si−Si bonds, 2.403 Å for another Si−Si bond, and 1.667 Å for the bridged H−Si bond lengths. There are no experimental data for comparison. For C_s symmetry with $^2A'$ state, the three Si−Si bond lengths predicted by BHLYP are 2.308 Å, 2.328 Å, and 2.132 Å, which are close to the CCSD(T) result of Kalcher and Sax:[4] 2.301 Å, 2.327 Å, and 2.118 Å, respectively. The Si−H bond length evaluated by B3LYP is 1.487 Å.

For anion Si_3H^-, our theoretical predictions show that the structure of ground state has C_{2v} symmetry with $^1A_1$ state. The geometry is displayed in Figure 2. This result is the same as previous studies.[2,4] The bond length for C_{2v} symmetry with $^1A_1$ state is predicted to be 2.267−2.315 Å for the two equivalent Si−Si bonds, 2.494−2.556 Å for another Si−Si bond, and 1.667−1.708 Å for the bridged H−Si bond lengths. The most reliable bond lengths are 2.267 Å (BHLYP) for the two

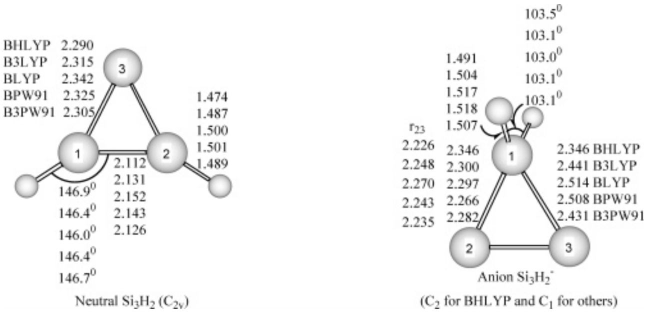

Figure 3. Optimized geometries for neutral Si_3H_2 and anion $Si_3H_2^-$. Only silicon atoms are numbered. All bond distances are in Å.

equivalent Si−Si bonds, 2.494 Å (BHLYP) for anther Si−Si bond, and 1.689 Å (B3LYP) for the bridged H−Si bonds. There are no experimental bond lengths for anion Si_3H^-, but there are several theoretical values. Kalcher and Sax[4] reported the bond lengths are 2.252 Å for the equivalent Si−Si bonds, 2.469 Å for another Si−Si bond, and 1.656 Å for the bridged H−Si bonds at CCSD(T) level of theory. Xu et al.[2] reported that the QCISD(T)/6-31G* bond lengths are 2.284 Å, 2.498 Å, and 1.699 Å, respectively.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_3H ($^2B_2 \leftarrow {}^1A_1$) ranges from 2.37 to 2.64 eV with the five different functionals. Among these, the BHLYP (2.45 eV) value is in agreement with the experimental result (2.53 ± 0.01 eV) given by Xu et al.[2] from their anion photoelectron spectra. Especially, the B3LYP and BPW91 values of 2.56 eV are in excellent agreement with the experiment value of 2.53 ± 0.01 eV.[2] The BHLYP value is smaller than the experimental data by about 0.08 eV. The B3LYP and BPW91 values are only larger than the experimental data about by 0.03 eV. Kalcher and Sax[4] predicted the adiabatic electron affinity for Si_3H to be 2.65 eV at the CCSD(T) level of theory, which is close to the B3PW91 value of 2.64 eV. The EA_{vert} values range from 2.32 to 2.59 eV. The range of VDE is from 2.43 to 2.70 eV.

For Si_3H ($^2A' \leftarrow {}^1A_1$), the theoretical EA_{ad} and EA_{vert} are also computed and listed in Table 1. As can be seen from Table 1, the B3LYP (2.55 eV) and BPW91 (2.57 eV) values for EA_{ad} are in excellent agreement with the experimental result of 2.53 ± 0.01 eV taken from Xu et al.[2] The EA_{vert} values ranges from 2.16 to 2.24 eV. The values of EA_{ad}, EA_{vert}, and VDE for Si_3H ($^2A' \leftarrow {}^1A_1$) are different from each other on account of the large change in geometry between neutral and its anion.

Si_3H_2 and $Si_3H_2^-$. The geometries of ground state of neutral Si_3H_2 and its anion $Si_3H_2^-$ are displayed in Figure 3. The ground-state structure of Si_3H_2 (HSiSiSiH) has C_{2v} symmetry with $^1A_1$ state. This result is the same as the previous result examined by Ernst et al.[50] The bond length is predicted to be 2.290−2.342 Å for the two equivalent Si−Si bonds, 2.112−2.152 Å for another Si−Si bond, and 1.474−1.501 Å for the H−Si bond lengths. The BHLYP method, deemed to be the most reliable, predicts the Si−Si bond distances to be 2.290 Å and 2.112 Å, which are similar to the HF (Hartree−Fock) result of Ernst et al.:[50] 2.28 Å and 2.11 Å. The B3LYP method, thought to be the most reliable, predicts the Si−H bond lengths to be 1.487 Å. There are no experimental data for comparison.

The BHLYP predicts that the structure of the ground state of $Si_3H_2^-$ ($SiSiSiH_2^-$) is C_2 symmetry with ^2B state. The bond lengths are evaluated to be 2.346 Å for the bonds of Si_1-Si_2 and Si_1-Si_3, 2.226 Å for the bonds of Si_2-Si_3, and 1.491 Å for bonds of Si_1-H. The B3LYP, BLYP, BPW91, and B3PW91 predict that the structure of the ground state of $Si_3H_2^-$ ($SiSiSiH_2^-$) is C_1 symmetry. The bond lengths are evaluated to be 2.266−2.300 Å for the bonds of Si_1-Si_2, 2.431−2.514 Å for the bonds of Si_1-Si_3, 2.235−2.270 Å for the bonds of Si_2-Si_3, and 1.504−1.518 Å for the bonds of Si−H. The most reliable Si−H bond lengths calculated are 1.504 Å (B3LYP). There are no experimental data for comparison. Compared with neutral HSiSiSiH, the shape of anion $SiSiSiH_2^-$ primary change is intramolecular H-transfer.

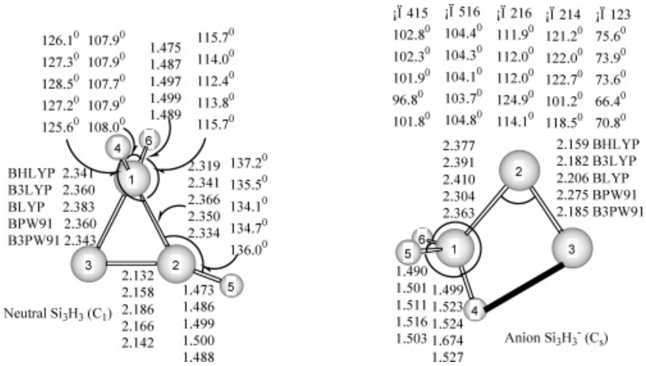

Figure 4. Optimized geometries for neutral Si_3H_3 and anion $Si_3H_3^-$. Silicon atoms are numbered from 1 to 3, and hydrogen atoms are numbered from 4 to 6. Black solid line indicates bridged bonding between hydrogen and silicon atom. All bond distances are in Å.

The theoretical EA_{ad}, EA_{vert}, and VDE are reported in Table 1. The EA_{ad} for Si_3H_2 is predicted to be 1.60 eV (BHLYP), 1.73 eV (B3LYP), 1.59 (BLYP), 1.74 eV (BPW91), and 1.78 eV (B3PW91). The B3LYP predicted EA_{ad} of 1.73 eV is very close to BPW91 EA_{ad} of 1.74 eV. There are no experimental values for comparison. The EA_{vert} is evaluated to be 0.26 eV (BHLYP), 0.38 eV (B3LYP), 0.13 (BLYP), 0.37 eV (BPW91), and 0.55 eV (B3PW91). The VED is estimated to be 2.48 eV (BHLYP), 2.55 eV (B3LYP), 2.37 (BLYP), 2.72 eV (BPW91), and 2.71 eV (B3PW91). Again, the values of EA_{ad}, EA_{vert}, and VDE are different from each other on account of the large change in geometry between neutral and its anion.

Si_3H_3 and $Si_3H_3^-$. The C_1-symmetry structure of the ground state for neutral Si_3H_3 and C_s-symmetry structure of $^1A'$ ground state for anion $Si_3H_3^-$ are shown in Figure 4. For neutral Si_3H_3 ($H_2SiSiSiH$), the bond lengths are predicted to be 2.341−2.383 Å, 2.319−2.366 Å, and 2.132−2.186 Å for the three Si−Si bonds, 1.473−1.500 Å for the H−Si bonds in the SiH group, and 1.475−1.499 Å for the H−Si bonds in the SiH_2 group. The most reliable bond lengths of Si−Si predicted by the BHLYP are 2.341 Å, 2.319 Å, and 2.132 Å, respectively. The most reliable bond lengths of Si−H calculated by B3LYP are 1.486 Å for in the SiH group and 1.487 Å for in the SiH_2 group. There are no experimental values for comparison.

For anion $Si_3H_3^-$ ($H_2SiHSiSi^-$) (see Figure 4), the nonsymmetrical H-bridged bonds are formed between the hydrogen atom numbered 4 and silicon atoms numbered 1 and 3 at BHLYP, B3LYP, BLYP, and B3PW91 levels of theory. At BHLYP, B3LYP, BLYP, and B3PW91 levels of theory, the bond lengths of the nonsymmetrical H-bridged structure of $H_2SiHSiSi^-$ are predicted to be 2.363−2.410 Å for Si_1-Si_2 bonds, 2.159−2.206 Å for Si_2-Si_3 bonds, 1.490−1.511 Å for H_5-Si_1 and H_6-Si_1 bonds, 1.499−1.527 Å for H_4-Si_1 bonds, and 70.8°∠75.6° for SiSiSi bond angle ∠123. The BHLYP Si−Si bond lengths, thought to be the most reliable, are 2.377 Å (Si_1-Si_2) and 2.159 Å (Si_2-Si_3). The B3LYP H−Si bond lengths, deemed to be the most reliable, are 1.501 Å for H_5-Si_1 and H_6-Si_1 bonds and 1.523 Å for H_4-Si_1 bonds. We have not obtained the nonsymmetrical H-bridged structure at BPW91 level of theory. At BPW91 level of theory, the near-symmetrical

H-bridged structure is obtained. The bridged H−Si bond lengths are 1.674 Å (H_4−Si_1) and 1.774 Å (H_4−Si_3). The other bond lengths are predicted to be 2.304 Å for Si_1−Si_2 bonds, 2.275 Å for Si_2−Si_3 bonds, 1.516 Å for H_5−Si_1 and H_6−Si_1 bonds, and 66.4° for SiSiSi bond angle ∠123. At BHLYP, B3LYP, BLYP, and B3PW91 levels of theory, the near-symmetrical H-bridged structure can be obtained, but the near-symmetrical H-bridged structure is less stable than the nonsymmetrical H-bridged structure in energy by about 0.05, 0.02, 0.02, and 0.05 eV, respectively. Compared with neutral $H_2SiSiSiH$, the feature of anion $H_2SiHSiSi^-$ primary change is intramolecular H-transfer. There are no experimental data for comparison.

Our theoretical neutral-anion energy separations for Si_3H_3 are given in Table 1. The range for EA_{ad} is from 2.31 to 2.46 eV. The EA_{vert} ranges from 1.98 to 2.23 eV. The VDE ranges from 2.53 to 2.76 eV. As can be seen from Table 1, the B3LYP EA_{ad} of 2.46 eV, EA_{vert} of 2.17 eV, and VDE of 2.71 eV are very close to the BPW91 values 2.45, 2.16, and 2.71 eV, respectively. There are no experimental values available.

Si_3H_4 and $Si_3H_4^-$. Two minima for the neutral Si_3H_4 and one for the anionic $Si_3H_4^-$ are shown in Figure 4. For neutral Si_3H_4, the dihydrogen-bridged SiH_2SiSiH_2 structure displays C_{2v} symmetry with $^1A_1$ state. The nonbridged $H_2SiSiSiH_2$ structure has C_s symmetry with $1A'$ state. At BLYP level of theory, the nonbridged $H_2SiSiSiH_2$ isomer is more stable in energy than the dihydrogen-bridged SiH_2SiSiH_2 isomer by about 0.05 eV. At BHLYP, BPW91, and B3PW91 levels of theory, the dihydrogen-bridged SiH_2SiSiH_2 isomer is more stable than the nonbridged isomer $H_2SiSiSiH_2$ in energy by 0.03, 0.03, and 0.06 eV, respectively. At B3LYP level of theory, both SiH_2SiSiH_2 and $H_2SiSiSiH_2$ isomers are almost isoenergetic. The potential energy surface of Si_3H_4 is so flat that we cannot be sure which structures are global minimum and which are local minimum. Accurate predictions of equilibrium structure of Si_3H_4 would require advanced quantum mechanical investigations.

The geometry parameters predicted at all of these DFT levels of theory are also listed in Figure 4. For the nonbridged $H_2SiSiSiH_2$ isomer (C_s symmetry), the most reliable bond lengths are 2.249 Å (BHLYP) for Si_1−Si_2 and Si_1−Si_3 bonds and 1.486 and 1.487 Å for Si−H bonds. The SiSiSi bond angles (∠213) calculated by all of these DFT methods are 68.2−71.6°. For the dihydrogen-bridged SiH_2SiSiH_2 isomer (C_{2v} symmetry), the most reliable bond lengths are deemed to be 2.343 Å (BHLYP) for the Si_1−Si_2 and Si_2−Si_3 bonds, 1.479 Å (B3LYP) for the nonbridged H−Si bonds, and 1.704 Å (B3LYP) for the bridged H−Si bonds. The SiSiSi bond angles (∠123) calculated are 65.6−66.1°. There are no experimental values for comparison.

For the $Si_3H_4^-$ anion, no experimental data are available. Our theoretical predictions show that the nonbridged $H_2SiSiSiH_2^-$ isomer is the ground state with C_{2v} symmetry for its $^2B_1$ state. The Si_1−Si_2 and Si_1−Si_3 bonds have been elongated from the neutral nonbridged $H_2SiSiSiH_2$ isomer (C_s symmetry) by ∼0.14 Å, while the SiSiSi bond angle ∠213 decreases at least by 11°. The DFT SiSiSi bond angles ∠213 range from 57.2° to 57.5° and the HSiH bond angles range from 105.5° to 106.4°. The most reliable bond lengths are predicted to be 2.385 Å (BHLYP) for the Si_1−Si_2 and Si_1−Si_3 bonds and 1.501 Å (B3LYP) for Si−H bonds (see Figure 4).

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_3H_4 ($^1A'$←$^2B_1$) ranges from 1.69 to 2.07 eV with the five different functionals. Among these, the values of 1.93 eV (BPW91), 1.95 eV (B3LYP), and 1.96 eV (BHLYP) are deemed to be the most reliable. The EA_{vert} values range from 0.78 to 1.24 eV. The range of VDE is from 2.07 to 2.35 eV.

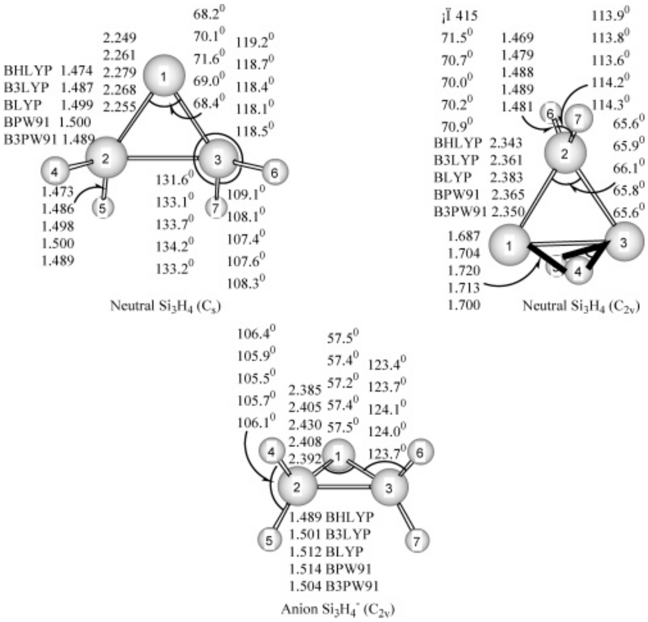

Figure 5. Optimized geometries for neutral Si_3H_4 and anion $Si_3H_4^-$. Silicon atoms are numbered from 1 to 3, and hydrogen atoms are numbered from 4 to 7. Black solid line indicates bridged bonding between hydrogen and silicon atom. All bond distances are in Å.

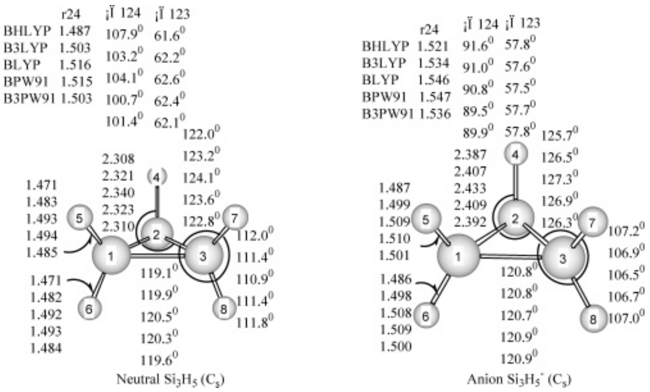

Figure 6. Optimized geometries for neutral Si_3H_5 and anion $Si_3H_5^-$. Silicon atoms are numbered from 1 to 3, and hydrogen atoms are numbered from 4 to 8. All bond distances are in Å.

For Si_3H_4 ($^1A_1$←$^2B_1$), the theoretical EA_{ad} and EA_{vert} are predicted and listed in Table 1. As can be seen from Table 1, the predicted EA_{ad} for Si_3H_4 ($^1A_1$←$^2B_1$) ranges from 1.73 to 2.02 eV. Among these, the values of 1.90 eV (BPW91), 1.93 eV (BHLYP), and 1.95 eV (B3LYP) are similar to the EA_{ad} for Si_3H_4 ($^1A'$←$^2B_1$). The EA_{vert} values ranges from 0.79 to 1.11 eV. Again, the values of EA_{ad}, EA_{vert}, and VDE are different from each other on account of the large change in geometry between neutral and its anion. There are no experimental data available.

Si_3H_5 and $Si_3H_5^-$. The geometries of the ground state of Si_3H_5 and its anion $Si_3H_5^-$ are displayed in Figure 6. The ground-state structure of Si_3H_5, "quasi-cyclic" form, displays C_s symmetry with $^2A'$ state. The bond length is predicted to be 2.308−2.340 Å for the two equivalent Si−Si bonds, 1.487−1.516 Å for the H−Si bonds in the SiH group, and 1.471−1.494 Å for the H−Si bonds in the SiH_2 groups. The SiSiSi bond angle ∠123 calculated is 61.6−62.6° and the HSiH bond angle in the SiH_2 is 110.9−112.0°. There are no experimental

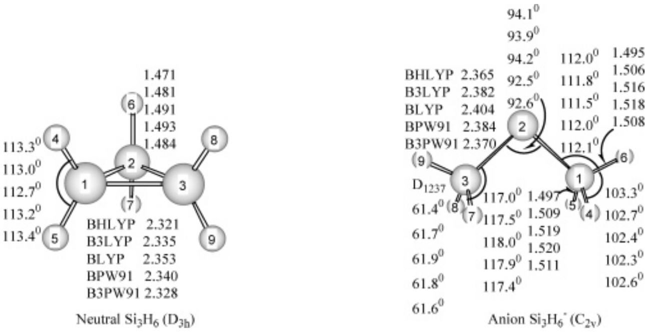

Figure 7. Optimized geometries for neutral Si_3H_6 and anion $Si_3H_6^-$. Silicon atoms are numbered from 1 to 3, and hydrogen atoms are numbered from 4 to 9. All bond distances are in Å. D is dihedral.

data for comparison. The most reliable bond lengths are predicted to be 2.308 Å (BHLYP) for the two equivalent Si−Si bonds, 1.503 Å (B3LYP) for the H−Si bonds in the SiH group, and 1.482 and 1.483 Å (B3LYP) for the H−Si bonds in the SiH_2 groups. The chain structure of trisilaallyl radical has been studied by Coolidge et al.[51]

The ground-state structure of $Si_3H_5^-$ has C_s symmetry with $^1A'$ state. Compared with the neutral Si_3H_5, the two equivalent Si−Si bonds have been elongated from neutral Si_3H_5 structure by 0.08 Å, and the Si−H bonds in the SiH group and SiH_2 groups have been elongated by 0.03 Å and 0.16 Å, respectively, while the SiSiSi bond angle∠123 decreases by 4.5°. The most reliable bond lengths are 2.387 Å (BHLYP) for the two equivalent Si−Si bonds, 1.534 Å (B3LYP) for the Si−H bonds in the SiH group, and 1.498 and 1.499 Å for the Si−H bonds in the SiH_2 group. The chain structure of trisilaallyl anion has been investigated by Korkin et al.[52]

Our theoretical neutral-anion energy separations for Si_3H_5 are given in Table 1. The range for EA_{ad} is from 2.06 to 2.27 eV. Swihart[16] obtained $EA_{ad} = 2.20$ eV using B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) scheme. The EA_{vert} ranges from 1.71 to 1.94 eV. The VDE ranges from 2.29 to 2.49 eV. As can be seen in Table 1, the BHLYP EA_{ad} (2.06 eV) is smaller than the BLYP EA_{ad} (2.10 eV). Again, the B3LYP EA_{ad} (2.24 eV), EA_{vert} (1.92 eV), and VDE (2.29 eV) are close to BPW91 EA_{ad} (2.23 eV), EA_{vert} (1.92 eV), and VDE (2.29 eV). There are no experimental values available.

Si_3H_6 and $Si_3H_6^-$. The geometry of the ground state of neutral Si_3H_6 and its anion $Si_3H_6^-$ are displayed in Figure 7. The ground-state structure of Si_3H_6 has D_{3h} symmetry with $^1A_1'$ state. This result is in accord with the previous result.[6,53] The bond length is predicted to be 2.321−2.353 Å for Si−Si bonds and 1.471−1.493 Å for H−Si bonds. The HSiH bond angles are 112.7−113.4°. To our knowledge, surprisingly, there are no experimental data for cyclotrisilane. The best reliable Si−Si bond lengths are predicted to be 2.321 Å (BHLYP), which are shorter than 2.330 Å of SCF/DZ+d results of Grev and Schaefer[6] by 0.01 Å and shorter than 2.325 Å of HF results of Sax[53] by 0.004 Å. The H−Si bond lengths, thought to be the most reliable, are 1.481 Å (B3LYP), which are longer than 1.466 Å of SCF/DZ+d results[6] by 0.015 Å and longer than 1.472 Å of HF results[53] by 0.01 Å. The geometrical parameters optimized by BHLYP are close to parameters[53] optimized by HF. The DFT/HF hybrid BHLYP functional incorporates the standard Hartree−Fock theory to the greatest degree of all the functionals used in this study.

For negatively charged ion $Si_3H_6^-$, the ground-state structure, $H_3SiSiSiH_3^-$ of chain structure, displays C_{2v} symmetry with $^2B_1$ state. The bond length is predicted to be 2.365−2.404 Å for the Si−Si bonds and 1.495−1.518 Å and 1.497−1.520 Å for the H−Si bonds in the two terminal SiH_3 groups. The SiSiSi bond angles are 92.5−94.2°. The HSiH bond angles in the two terminal SiH_3 groups are 102.3−103.3°. The SiSiH bond angles are 111.5−112.1° (∠216) and 117.0−118.0°. There are no experimental data for comparison. The most reliable bond lengths evaluated are 2.365 Å (BHLYP) for the Si−Si bonds and 1.506 Å and 1.509 Å (B3LYP) for the Si−H bonds.

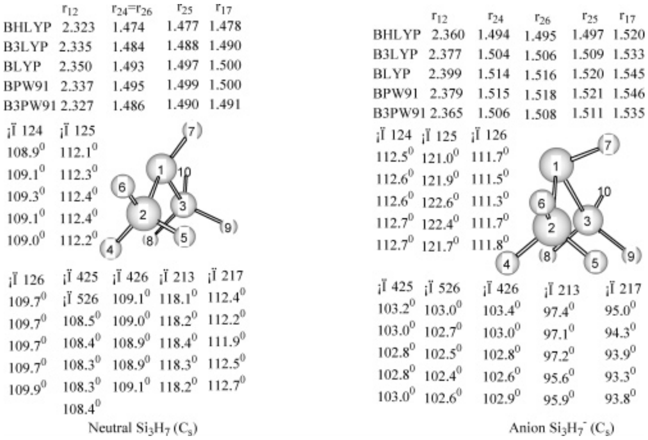

Figure 8. Optimized geometries for neutral Si_3H_7 and anion $Si_3H_7^-$. Silicon atoms are numbered from 1 to 3, and hydrogen atoms are numbered from 4 to 10. All bond distances are in Å.

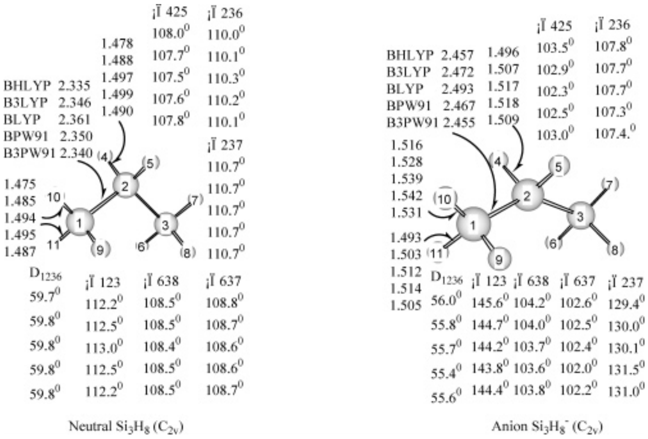

Figure 9. Optimized geometries for neutral Si_3H_8 and anion $Si_3H_8^-$. Silicon atoms are numbered from 1 to 3, and hydrogen atoms are numbered from 4 to 11. All bond distances are in Å.

Our theoretical neutral-anion energy separations for Si_3H_6 are given in Table 1. The range for EA_{ad} is from 1.27 (BHLYP) to 1.41 (B3LYP) eV. The VDE ranges from 2.10 to 2.39 eV. The range of EA_{vert} is from −0.73 eV to −0.44 eV. At a first approximation, the negative EA_{vert} corresponds to the resonant electron scattering energy.[32,54,55] Again, the values of EA_{ad}, EA_{vert}, and VDE are different from each other on account of the large change in geometry between neutral and its anion. There are no experimental data available.

Si_3H_7 and $Si_3H_7^-$. The geometry of the ground state of neutral Si_3H_7 and its anion $Si_3H_7^-$ are chain structures and displayed in Figure 8. The ground-state structure of Si_3H_7 is C_s symmetry with $^2A'$ state. The bond length is predicted to be 2.323−2.350 Å for Si−Si bonds, 1.478−1.500 Å for the H−Si bonds in the central SiH group, and 1.474−1.495 Å and 1.477−1.499 Å for the H−Si bonds in the two terminal SiH_3 groups. The SiSiSi bond angles are 118.1−118.4°. There are no experimental data for comparison. The bond lengths, thought to be the most reliable, are 2.323 Å (BHLYP) for the Si−Si bonds, 1.490 Å (B3LYP) for the H−Si bonds in the central SiH group, and 1.484 Å and 1.488 Å for the H−Si bonds in the terminal SiH_3 groups.

For negatively charged ion $Si_3H_7^-$, the ground-state structure displays C_s symmetry with $^1A'$ state. The bond length is predicted to be 2.360−2.399 Å for the Si−Si bonds, 1.520−1.546 Å for the H−Si bonds in the central SiH group, and 1.494−1.515 Å, 1.495−1.518 Å, and 1.497−1.521 Å for the H−Si bonds in the two terminal SiH_3 groups. The SiSiSi bond angles are 95.6−97.4°. The most reliable Si−Si bond lengths are thought to be 2.360 Å (BHLYP), which are longer than the neutral Si_3H_7 bonds by 0.037 Å but shorter than the anion $Si_3H_6^-$ bonds by 0.005 Å. The most reliable H−Si bond lengths are deemed to be 1.533 Å (B3LYP) in the central SiH group and 1.504, 1.506, and 1.509 Å (B3LYP) in the terminal SiH_3 groups. The SiSiSi bond angles of anion $Si_3H_7^-$ are smaller than the SiSiSi bond angle of neutral Si_3H_7 by 21° but larger than the SiSiSi bond angle of anion $Si_3H_6^-$ by 3.3°. There are no experimental data for comparison.

Our theoretical neutral-anion energy separations for Si_3H_7 are given in Table 1. The range for EA_{ad} is from 1.89 to 2.14 eV. Swihart[16] reported $EA_{ad} = 2.12$ eV. The EA_{vert} ranges from 1.17 to 1.40 eV. The VDE ranges from 2.39 to 2.84 eV. Again, the B3LYP EA_{ad} of 2.14 eV, EA_{vert} of 1.40 eV, and VDE of 2.82 eV is very close to the BPW91 value 2.14, 1.39, and 2.84 eV, respectively. There are no experimental values available.

Si_3H_8 and $Si_3H_8^-$. The ground-state structure of neutral trisilane Si_3H_8 and its anion $Si_3H_8^-$ are chain structures and displayed in Figure 8. The ground-state structure of trisilane is C_{2v} symmetry with $^1A_1$ state. This result agrees with earlier theoretical studies.[6,56,57] The bond length is predicted to be 2.335−2.361 Å for the Si−Si bonds, 1.478−1.499 Å for the H−Si bonds in the central SiH_2 group, and 1.475−1.495 Å for the H−Si bonds in the two terminal SiH_3 groups. Among these, the BHLYP values of 2.335 Å for the Si−Si bonds are in excellent agreement with experimental (gas-phase electron diffraction) data of 2.332 Å obtained by Haaland et al.[58] The error is only 0.003 Å. The B3LYP values of 1.488 Å for the H−Si bonds in the central SiH_2 group and values of 1.485 Å for the H−Si bonds in the two terminal SiH_3 groups are in excellent agreement with experimental values[58] of 1.486 Å and 1.483 Å, respectively. The errors are only 0.002 Å.

On the other hand, the Si−Si bond length for disilane Si_2H_6 are predicted by BHLYP and B3LYP methods with DZP++ basis sets to be 2.332 Å and 2.343 Å, respectively.[8] Compared with the experimental value[59] of 2.327 ± 0.005 Å, the BHLYP value of 2.332 Å is within the range of experimental errors. The Si−H bond length for disilane is predicted by BHLYP and B3LYP methods to be 1.475 Å and 1.485 Å, respectively.[8] The B3LYP result of 1.485 Å is in excellent agreement with the experimental value[59] of 1.482 Å. The error is only 0.003 Å. Hence, we conclude that DFT theory combined with DZP++ basis sets provides reliable results for the geometries of silicon hydrides clusters. Specially, the BHLYP provides the most reliable results for Si−Si bond lengths and the B3LYP provides the most reliable results for Si−H bond lengths.

The values calculated for the SiSiSi bond angle are 112.2−113.0°, which are close to earlier theoretical values of 112.1° [6] and 110.2°.[56,57] The values calculated for the HSiH bond angle in the central SiH_2 group are 107.5−108.0°, which are close to earlier theoretical values of 107.9° [6] and 108.2° [56] and 107.8°.[57] The HSiH bond angles in the terminal SiH_3 groups are predicted to be 108.4−108.8°. The values calculated for the SiSiH (∠236) bond angle are 110.0−110.3°, which are close to earlier theoretical values of 109.9° [6] and 109.7° [56] and 112.9°.[57] The 110.7° values calculated for the SiSiH (∠237) bond angle agree with previous studies data of 110.8° [6] and 111.3° [56] and 112.9°.[57]

TABLE 2: Dissociation Energies (D_e) for the Neutral Si_3H_n ($n = 1−8$) Are in eV[c]

dissociation	BHLYP	B3LYP	BLYP	BPW91	B3PW91
$Si_3H \rightarrow Si_3 + H$[a]	2.72	2.74	2.69	2.65	2.70
$Si_3H_2 \rightarrow Si_3H + H$	3.12	2.98	2.82	2.83	2.99
$Si_3H_3 \rightarrow Si_3H_2 + H$	2.23	2.22	2.15	2.13	2.20
$Si_3H_4 \rightarrow Si_3H_3 + H$[b]	3.08	3.06	2.98	2.92	3.00
$Si_3H_5 \rightarrow Si_3H_4 + H$	2.95	2.81	2.67	2.63	2.78
$Si_3H_6 \rightarrow Si_3H_5 + H$	3.53	3.47	3.34	3.29	3.42
$Si_3H_7 \rightarrow Si_3H_6 + H$	2.54	2.45	2.39	2.19	2.30
$Si_3H_8 \rightarrow Si_3H_7 + H$	3.62	3.61	3.54	3.45	3.53

[a] The energies of ground state for Si_3H are the C_{2v}-symmetry structure for all of these DFT methods. [b] The energies of ground state for Si_3H_4 are the C_{2v}-symmetry structure for all of these DFT methods. [c] Values are corrected with zero-point vibrational energies.

For negatively charged ion $Si_3H_8^-$, the ground-state structure displays C_{2v} symmetry with $^2A_1$ state. The bond length is predicted to be 2.455−2.493 Å for the Si−Si bonds, 1.496−1.515 Å for H−Si bonds in the central SiH_2 group, and 1.493−1.514 Å and 1.516−1.542 Å for the H−Si bonds in the two terminal SiH_3 groups. Among these, the most reliable bond distances are thought to be 2.457 Å (BHLYP) for the Si−Si bonds, 1.507 Å (B3LYP) for the H−Si bonds in the central SiH_2 group, and 1.503 Å and 1.528 Å for the H−Si bonds in the terminal SiH_3 groups. The SiSiSi bond angles calculated are 143.8−145.6°, which are larger than the SiSiSi bond angles in neutral trisilane by about 32°. The HSiH bond angle in central SiH_2 group is predicted to be 102.3−103.5°, which is shorter than in neutral by 5°. 107.3−107.8° and 129.4−131.5° values are calculated for the HSiSi bond angles of the terminal hydrogen atoms and 102.2−102.6° and 103.6−104.2° are found for the HSiH bond angles in the terminal SiH_3 groups.

Our theoretical neutral-anion energy separations for trisilane are given in Table 1. The EA_{ad} (−0.29 eV) of trisilane predicted by BHLYP, similar to saturated silanes of SiH_4 and Si_2H_6,[8] is negative value. That is, trisilane does not form stable anion. At B3LYP, BLYP, and B3PW91 levels of theory, trisilane possess very small positive EA_{ad} values of 0.04, 0.05, and 0.05 eV, respectively. In fact, the EA_{ad} is so small that it cannot be identified by experimental methods. The BPW91 predicted the EA_{ad} to be 0.14 eV, which also is smaller. In these cases, the VDE may be important. The theoretical ranges of VDE for trisilane are from 0.78 to 1.10 eV. There are no experimental values available. The ranges of EA_{vert} predicted by all of these DFT methods are from −0.82 to −0.47 eV. As is the case for cyclotrisilane Si_3H_6, the negative EA_{vert} corresponds to the resonant electron scattering energy.[32,54,55]

Dissociation Energies. The first bond dissociation energies for $Si_3H_n/Si_3H_n^-$ ($n = 1−8$) are given in Table 2 and Table 3. As can be seen from Table 2, the theoretical results for $Si_3H \rightarrow Si_3+H$ dissociation energy predicted by all of these DFT functionals are in good agreement with each other, and the dissociation energies range from 2.65 to 2.74 eV. For $Si_3H_2 \rightarrow Si_3H+H$, the theoretical dissociation energies range from 2.82 to 3.12 eV. For $Si_3H_3 \rightarrow Si_3H_2+H$ and $Si_3H_4 \rightarrow Si_3H_3+H$, dissociation energies predicted by all of these DFT methods are in good agreement with each other; the ranges of dissociation energies are from 2.13 to 2.23 eV and from 2.92 to 3.08 eV, respectively. For $Si_3H_5 \rightarrow Si_3H_4+H$, the dissociation energies range from 2.63 to 2.95 eV. The theoretical dissociation energies for $Si_3H_6 \rightarrow Si_3H_5+H$ and $Si_3H_7 \rightarrow Si_3H_6+H$ range from

TABLE 3: Dissociation Energies (D_e) for the Anion $Si_3H_n^-$ (n = 1−8) Are in eV[a]

dissociation	BHLYP	B3LYP	BLYP	BPW91	B3PW91
$Si_3H^- \rightarrow Si_3^- + H$	2.89	2.95	2.92	2.89	2.92
$Si_3H_2^- \rightarrow Si_3H^- + H$	2.27	2.15	2.03	2.01	2.13
$Si_3H_3^- \rightarrow Si_3H_2^- + H$	2.96	2.95	2.88	2.83	2.85
$Si_3H_4^- \rightarrow Si_3H_3^- + H$	2.68	2.55	2.40	2.37	2.59
$Si_3H_5^- \rightarrow Si_3H_4^- + H$	3.08	3.10	3.04	2.96	3.03
$Si_3H_6^- \rightarrow Si_3H_5^- + H$	2.74	2.64	2.56	2.36	2.47
$Si_3H_7^- \rightarrow Si_3H_6^- + H$	3.16	3.17	3.11	3.03	3.10
$Si_3H_8^- \rightarrow Si_3H_7^- + H$	1.44	1.52	1.54	1.45	1.45

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

3.29 to 3.53 eV and from 2.19 to 2.54 eV, respectively. For $Si_3H_8 \rightarrow Si_3H_7 + H$, the theoretical dissociation energies range from 3.45 to 3.62 eV.

As can be seen in Table 3, the theoretical results for $Si_3H^- \rightarrow Si_3^- + H$ dissociation energy predicted by all of these DFT functionals are in good agreement with each other; the dissociation energies range from 2.89 to 2.95 eV. For $Si_3H_2^- \rightarrow Si_3H^- + H$, the theoretical dissociation energies range from 2.01 to 2.27 eV. For $Si_3H_3^- \rightarrow Si_3H_2^- + H$, dissociation energies predicted by all of these DFT methods are in good agreement with each other; the ranges of dissociation energies are from 2.83 to 2.96 eV. For $Si_3H_4^- \rightarrow Si_3H_3^- + H$, the range is from 2.37 to 2.68 eV. For $Si_3H_5^- \rightarrow Si_3H_4^- + H$, the dissociation energies predicted by all of these DFT schemes are in good agreement with each other and the ranges are from 2.96 to 3.08 eV. The theoretical dissociation energies for $Si_3H_6^- \rightarrow Si_3H_5^- + H$ range from 2.36 to 2.74 eV and from 3.03 to 3.17 eV for $Si_3H_7^- \rightarrow Si_3H_6^- + H$. For $Si_3H_8^- \rightarrow Si_3H_7^- + H$, the theoretical dissociation energies range from 1.44 to 1.54 eV. These smaller values indicate that $Si_3H_8^-$ is less stable.

Tables 2 and 3 also show that the dissociation energies for $Si_3H_n \rightarrow Si_3H_{n-1} + H$ and $Si_3H_{n-1}^- \rightarrow Si_3H_{n-2}^- + H$ are larger when n is an even number and are smaller when n is an odd number. This zig-zap phenomenon may be readily explained. With even n, Si_3H_n and $Si_3H_{n-1}^-$ have a closed-shell electronic structure and so are more stable. In contrast, the products Si_3H_{n-1}, $Si_3H_{n-2}^-$, and H are both open-shell systems, so the analogous dissociation energies would be larger. With 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.

Conclusions

The present work provides a systematic study of the silicon hydrides clusters Si_3H_n ($n \leq 8$) with five carefully selected DFT methods. In the prediction of bond lengths, the five methods consistently follow the order: BLYP > BPW91 > B3LYP > B3PW91 > BHLYP for Si−Si bonds and BPW91 > BLYP > B3PW91 > B3LYP > BHLYP for Si−H bonds. The BHLYP method may provide the most reliable Si−Si bond lengths and the B3LYP may provide the most reliable Si−H bond lengths. Compared with the limited experimental EA_{ad} values, the average absolute errors for all five DFT methods are 0.06 (BHLYP), 0.03 (B3LYP), 0.16 (BLYP), 0.03 (BPW91), and 0.11 (B3PW91) eV. The B3LYP and BPW91 methods are the most reliable. The adiabatic EAs are predicted by the B3LYP or BPW91 method to be 2.34 or 2.32 eV (Si_3), 2.56 eV (Si_3H), 1.73 or 1.74 eV (Si_3H_2), 2.46 or 2.45 eV (Si_3H_3), 1.95 or 1.93 eV (Si_3H_4), 2.24 or 2.23 eV (Si_3H_5), 1.41 or 1.30 eV (Si_3H_6), and 2.14 eV (Si_3H_7). For Si_3H_8, there are no reliable EA_{ad} but there are reliable VDE. The values of VDE for Si_3H_8 are 1.03 eV (B3LYP) or 1.10 eV (BPW91).

Unlike unitary clusters, such as Si_n and As_n,[60] the BHLYP method yields the least dissociation energies. For binary clusters of neutral Si_3H_n, the BHLYP method yields the largest dissociation energies. The first dissociation energies ($Si_3H_n \rightarrow Si_3H_{n-1} + H$) predicted by all of these methods are 2.65∼2.74 eV (Si_3H), 2.82∼3.12 eV (Si_3H_2), 2.13∼2.23 eV (Si_3H_3), 2.92∼3.08 eV (Si_3H_4), 2.63∼2.95 eV (Si_3H_5), 3.29∼3.53 eV (Si_3H_6), 2.19∼2.54 eV (Si_3H_7), and 3.45∼3.62 eV (Si_3H_8). For anion clusters ($Si_3H_n^- \rightarrow Si_3H_{n-1}^- + H$), the dissociation energies predicted are 2.89∼2.95 eV (Si_3H^-), 2.01∼2.27 eV ($Si_3H_2^-$), 2.83∼2.96 eV ($Si_3H_3^-$), 2.37∼2.68 eV ($Si_3H_4^-$), 2.96∼3.10 eV ($Si_3H_5^-$), 2.36∼2.74 eV ($Si_3H_6^-$), 3.03∼3.16 eV ($Si_3H_7^-$), and 1.44∼1.54 eV ($Si_3H_8^-$).

We hope that the present theoretical predictions will provide strong motivation for further experimental studies of these important silicon hydrides clusters and their anions.

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