Silicon Monohydride Clusters Si_nH ($n = 4-10$) and Their Anions: Structures, Thermochemistry, and Electron Affinities

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Received: December 22, 2004; In Final Form: May 6, 2005

The molecular structures, electron affinities, and dissociation energies of the Si_nH/Si_nH^- ($n = 4-10$) species have been examined via 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++. The geometries are fully optimized with each DFT method independently. The three different types of 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, $D_e(Si_nH \rightarrow Si_n + H)$ for neutral Si_nH and $D_e(Si_nH^- \rightarrow Si_n^- + H)$ for anionic Si_nH^- species, have also been reported. The structures of the ground states of these clusters are traditional H−Si single-bond forms. The ground-state geometries of Si_5H, Si_6H, Si_8H, and Si_9H predicted by the DFT methods are different from previous calculations, such as those obtained by Car−Parrinello molecular dynamics and nonorthogonal tight-binding molecular dynamics schemes. The most reliable EA_{ad} values obtained at the B3LYP level of theory are 2.59 (Si_4H), 2.84 (Si_5H), 2.86 (Si_6H), 3.19 (Si_7H), 3.14 (Si_8H), 3.36 (Si_9H), and 3.56 ($Si_{10}H$) eV. The first dissociation energies ($Si_nH \rightarrow Si_n + H$) predicted by all of these methods are 2.20−2.29 (Si_4H), 2.30−2.83 (Si_5H), 2.12−2.41 (Si_6H), 1.75−2.03 (Si_7H), 2.41−2.72 (Si_8H), 1.86−2.11 (Si_9H), and 1.92−2.27 ($Si_{10}H$) eV. For the negatively charged ion clusters ($Si_nH^- \rightarrow Si_n^- + H$), the dissociation energies predicted are 2.56−2.69 (Si_4H^-), 2.80−3.01 (Si_5H^-), 2.86−3.06 (Si_6H^-), 2.80−3.03 (Si_7H^-), 2.69−2.92 (Si_8H^-), 2.92−3.18 (Si_9H^-), and 2.89−3.25 ($Si_{10}H^-$) eV.

Introduction

During the past decade, silicon hydrides have attracted a lot of attention because of their potential applications in semiconductors, optoelectronics, and surface growth processes and because of their likely existence in the circumstellar atmospheres of evolved carbon stars.[1−18] The binary clusters of silicon and hydrogen 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 poorly understood process.[19−27] Knowledge of the ground and low-lying electronic states of neutral and anionic silicon hydride clusters is very important for understanding these processes. With this motivation, we have carried out a detailed study of the structures, thermochemistry, and electron affinities of silicon monohydride clusters and their anions using density functional theory (DFT).[28−30]

There have been previous theoretical and experimental studies on silicon monohydride clusters. Kalcher and Sax[31,32] performed the studies of Si_2H and its anion with complete active space self-consistent field (CASSCF) geometry optimization followed by a multireference configuration interaction (MRCI) evaluation of the energies and completed Si_3H and its negatively charged ion at the coupled-cluster single double (CCSD) level of theory. Prasad et al.[19−23] predicted the ground-state geometries of small Si_nH ($2 \leq n \leq 10$) clusters using Car−Parrinello molecular dynamics (CPMD), nonorthogonal tight-binding molecular dynamics (NTBMD), and genetic algorithms (GAs) methods. Pak et al.[13] reported the electron affinity of SiH_n and Si_2H_n at the various levels of DFT. Recently, W. G. Xu et al.[2] presented the electron affinity of Si_3H_n at various levels of DFT. C. Xu et al.[8] reported the photoelectron spectroscopy study of Si_nH^- ($n = 2-4$) along with ab initio calculations to aid the assignment.

Many theoretical and experimental studies have predicted that Si_2H and Si_3H are nonclassical H-bridged structures in their ground states.[2,8,13,19−23,31−32] We focused on silicon monohydride clusters Si_nH ($n = 4-10$) in this study and found that they are traditional H−Si single-bond structures in their ground states. This result can be explained. Although hydrogen's valence is 1, it can be bonded with two silicon atoms in the ground state of silicon monohydrides, such as Si_2H and Si_3H, because there is a small charge transfer from the silicon atoms to the hydrogen.[19] Nevertheless, this case only occurred in Si_2H and Si_3H because the ground state of Si_2 and Si_3 has a triplet state,[2,33,34] which makes the charge transfer from the silicon atoms to the hydrogen easy. Conversely, the ground state of Si_n ($n \geq 4$) has a singlet state,[35−37] so the charge transfer is difficult. When hydrogen is bonded with more than two silicon atoms, the Si_nH ($n \geq 4$) is either a saddle point or a local minimal point on the potential energy surface.

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10.1021/jp0441543 CCC: $30.25

When predicting molecular energies, structures, and electron affinities, many theoretical approaches are possible, but when both reliability and computational expense are considered, gradient-corrected DFT is effective for predicting the electron affinities of many inorganic species such as the SiH_n/SiH_n^-, $Si_2H_n/Si_2H_n^-$, $Si_3H_n/Si_3H_n^-$, GeF_n/GeF_n^-, SeF_n/SeF_n^-, and AsF_n/AsF_n^- systems.[8,2,38−40] The reliability of the predictions for electron affinities with DFT methods was comprehensively discussed in the recent (2002) review of Rienstra-Kiracofe et al.[41] 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 was 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.

Theoretical Methods

The five different density functionals or hybrid Hartree−Fock/density functional forms used here are (a) Becke's 1988 exchange functional[42] with Lee, Yang, and Parr's correlation functional[43] (BLYP); (b) the half-and-half exchange functional[44] with the LYP correlation functional (BHLYP); (c) Becke's three-parameter hybrid exchange functional[45] with the LYP correlation functional (B3LYP); (d) Becke's 1988 exchange functional with the correlation functional of Perdew and Wang[46] (BPW91); and (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, whereas unrestricted methods were employed for the open-shell species. All the electron affinities and molecular structures have been determined with the Gaussian 98[47] 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[48] 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[49] [$\alpha_s(Si) = 0.02729$, $\alpha_p(Si) = 0.02500$, $\alpha_s(H) = 0.04415$]. 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_nH ($n = 4-10$) stationary point geometries were analyzed by the evaluation of their harmonic vibrational frequencies at the five different levels of theory.

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

The dissociation energies for Si_nH/Si_nH^- were determined from differences in total energies in the following manner: the first dissociation energies for the neutrals refer to the reaction $Si_nH \rightarrow Si_n + H$, whereas the first dissociation energies for the anions refer to the reaction $Si_nH^- \rightarrow Si_n^- + H$.

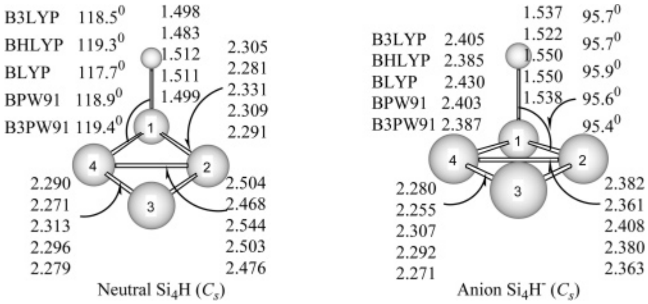


Figure 1. The optimized geometries for neutral Si_4H and its anion Si_4H^-. Only silicon atoms are numbered. Bond lengths and bond angles are in angstroms and degrees, respectively.

Results and Discussion

Si_4H and Si_4H^-. There are a few previous studies on the possible structures of the Si_4H cluster. In 1998, Neumark and co-workers[8] assigned the $^2A'$ state as the ground state of neutral Si_4H by photoelectron spectroscopy experiments and MP2/6-31G* level of theory. Recently, Prasad et al.[19−23] presented the groud-state structures for small Si_nH ($2 \leq n \leq 10$) using the CPMD, NTBMD, and GAs methods.

Our DFT results show a C_s symmetry with a $^2A'$ state (shown in Figure 1) for the ground state of neutral Si_4H. This result is the same as the previous result obtained by Neumark et al.[8] and Prasad et al.[19−23] The bond length evaluated by all of these methods is shown in Figure 1. The BHLYP functional provides the most reliable Si−Si bond length predictions, and the B3LYP functional provides the most reliable H−Si bond length predictions.[2] Hence, the most reliable Si−Si bond length calculations are 2.281 Å (BHLYP) for the two equivalent Si−Si bonds of the adjacent hydrogen atom and 2.271 Å (BHLYP) for the two equivalent Si−Si bonds of the nonadjacent hydrogen atom, and the most reliable Si−H bond length calculation is 1.498 Å (B3LYP), all of which are similar to the MP2/6-31G* results of Neumark et al.[8] (2.313, 2.263, and 1.500 Å, respectively) and shorter than the NTBMD and GAs results of Prasad et al.[21,22] Prasad et al. reported that the NTBMD bond lengths are 2.370, 2.345, and 1.532 Å, and that the GAs bond lengths are 2.360, 2.339, and 1.533 Å, respectively. No experimental data are available for comparison.

For the anionic Si_4H^- molecule, Xu et al.[8] reported that the $^1A'$ (C_s symmetry) state is the ground state, which has theoretical bond lengths of 2.391, 2.274, and 1.535 Å at the MP2/6-31G* level of theory. Our DFT result is the same as the result of Xu et al.[8] The equilibrium geometries of the $^1A'$ (C_s symmetry) ground states of negatively charged ions of Si_4H^- are also shown in Figure 1. The DZP++ BHLYP bond lengths of Si−Si, deemed to be the most reliable, are predicted to be 2.385 and 2.255 Å, which is shorter than the MP2/6-31G* Si−Si bond lengths by 0.006 and 0.019 Å, respectively. The DZP++ B3LYP bond length of H−Si, thought to be the most reliable, is predicted to be 1.522 Å, which is shorter than the MP2/6-31G* H−Si bond length by 0.013 Å. No experimental values are available.

Our theoretical neutral-anion energy separation for Si_4H, as well as experimental electron affinity data, is given in Table 1. The EA_{ad} is predicted to be 2.59 (B3LYP), 2.48 (BHLYP), 2.39 (BLYP), 2.58 (BPW91), and 2.65 (B3PW91) eV. The B3LYP, BPW91, and B3PW91 methods provide values that are close to the experimental value of 2.68 ± 0.01 eV by Xu et al.[8] The

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_nH (n = 4−10)[a]

species	method	EA_{ad}	EA_{vert}	VDE
Si_4H	B3LYP	2.59	2.17	2.95
	BHLYP	2.48	2.02	2.86
	BLYP	2.39	1.99	2.75
	BPW91	2.58	2.17	2.94
	B3PW91	2.65	2.22	3.02
	experiment	2.68 ± 0.01[b]		
$Si_5H[^2B_2 \leftarrow {}^1A_1\,(C_{2v})]$	B3LYP	2.84	2.49	3.13
	BHLYP	2.80	2.46	3.08
	BLYP	2.59	2.24	2.90
	BPW91	2.83	2.48	3.14
	B3PW91	2.95	2.60	3.24
$Si_5H[^2B_2 \leftarrow {}^1A_1\,(C_{3v})]$	B3LYP	2.86	2.49	3.30
	BHLYP	2.73	2.46	3.85
	BLYP	2.69	2.24	3.11
	BPW91	2.84	2.48	3.33
	B3PW91	2.90	2.60	3.40
Si_6H	B3LYP	2.86	2.40	3.26
	BHLYP	2.81	2.37	3.20
	BLYP	2.63	2.17	3.28
	BPW91	2.83	2.36	3.49
	B3PW91	2.94	2.48	3.34
Si_7H	B3LYP	3.19	2.71	3.64
	BHLYP	3.08	2.59	3.56
	BLYP	2.99	2.53	3.53
	BPW91	3.12	2.65	3.68
	B3PW91	3.21	2.72	3.68
Si_8H	B3LYP	3.14	2.87	3.56
	BHLYP	3.11	2.80	4.13
	BLYP	2.89	2.63	3.27
	BPW91	3.13	2.87	3.51
	B3PW91	3.26	2.98	3.67
Si_9H	B3LYP	3.36	2.77	3.73
	BHLYP	3.39	2.76	3.70
	BLYP	3.05	2.57	3.38
	BPW91	3.34	2.75	3.78
	B3PW91	3.51	2.82	3.79
$Si_{10}H$	B3LYP	3.56	2.87	3.96
	BHLYP	3.51	2.83	4.04
	BLYP	3.32	2.66	3.72
	BPW91	3.43	2.78	3.99
	B3PW91	3.55	2.88	4.10

[a] Presented in eV. [b] Ref 8.

theoretical EA_{vert} ranges from 1.99 to 2.22 eV. The range of VDE is from 2.75 to 3.02 eV. The values of EA_{ad}, EA_{vert}, and VDE are different from each other on account of the large change in geometry between the neutral cluster and its anion. For example, the bond angle ∠HSiSi is 23° less in the Si_4H^- anion than it is in neutral Si_4H.

Si_5H and Si_5H^-. Two minima structures for anionic Si_5H^- and one for the neutral Si_5H are shown in Figure 2. For neutral Si_5H, the structure of the ground state (shown in Figure 2a) displays C_{2v} symmetry with $^2B_2$ electronic state at all five DFT methods. This result is different from the previous result reported by Prasad et al.[19−23] They reported that the structure of the ground state of Si_5H is the nonclassical H-bridged structure (shown in Figure 2b) at the CPMD,[19,20] NTBMD,[21] and GAs[22,23] levels of theory. The structure of Figure 2b also has C_{2v} symmetry with a $^2B_1$ or $^2A_1$ electronic state. The structure with the $^2B_1$ state (Figure 2b) is less stable in energy than that with the $^2B_2$ state (Figure 2a) by approximately 0.45 (B3LYP), 0.57(BHLYP), 0.36 (BLYP), 0.38 (BPW91), and 0.46 (B3PW91) eV. The structure with the $^2A_1$ state (Figure 2b) is less stable in energy than that with the $^2B_2$ state (Figure 2 a) by approximately 0.98 (BHLYP), 0.79 (B3LYP), 0.64 (BLYP), 0.78 (BPW91), and 0.91 (B3PW91) eV. That is, the structure shown in Figure 2b is a local minimal point on the potential energy surface.

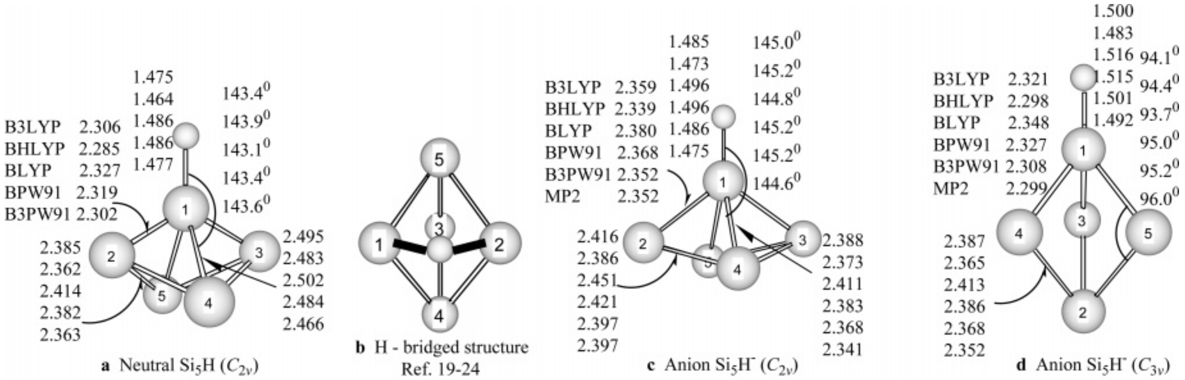
The calculated bond lengths for Si_5H are shown in Figure 2. No experimental or theoretical data are available for comparison. The BHLYP method, deemed to be the most reliable, predicts that the Si−Si bond distances are 2.285, 2.483, and 2.362 Å. The B3LYP method, thought to be the most reliable, predicts that the H−Si bond length is 1.475 Å.

For the structure of the ground state of the anion Si_5H^-, our DFT results show C_{2v} symmetry with a $^1A_1$ state (shown in Figure 2c) at the BHLYP and the B3PW91 levels of theory, whereas other methods show C_{3v} symmetry with a $^1A_1$ state (shown in Figure 2d). The BHLYP and B3PW91 functionals predict that C_{2v} symmetry is more stable in energy than is C_{3v} symmetry by 0.07 and 0.05 eV, respectively, whereas the B3LYP, BLYP, and BPW91 functionals predict that C_{3v} symmetry is more stable in energy than is C_{2v} symmetry by 0.02, 0.10, and 0.01 eV, respectively. In this case, we employed the MP2/6-311G(d,p) method. At the MP2/6-311G(d,p) level of theory, the structure of C_{2v} symmetry is more stable in energy than that of C_{3v} symmetry by 0.03 eV. All of these values indicate that the potential energy surface of Si_5H^- is very flat, that many isomeric arrangements are possible, and that accurate predictions of equilibrium geometries require advanced quantum mechanical investigations. The BHLYP and B3PW91 results for the C_{2v} symmetry of the ground state of Si_5H^- are perhaps the most reliable because they are consistent with the MP2/6-311G(d,p) result.

The calculated bond lengths for Si_5H^- are shown in Figure 2. For the structure of C_{2v} symmetry, the most reliable values for the Si−Si bond lengths are 2.339 Å (BHLYP) for the two equivalent Si_1−Si_2 and Si_1−Si_3 bonds, 2.373 Å (BHLYP) for the two equivalent Si_1−Si_4 and Si_1−Si_5 bonds, and 2.386 Å (BHLYP) for the four equivalent Si−Si bonds, and the most reliable value for the Si−H bond length is 1.485 Å (B3LYP). For the structure of C_{3v} symmetry with a $^1A_1$ state, the most reliable values for the bond lengths are 2.298 Å (BHLYP) for the three equivalent Si−Si bonds of the adjacent hydrogen atom, 2.356 Å (BHLYP) for the three equivalent Si−Si bonds of the nonadjacent hydrogen atom, and 1.500 Å (B3LYP) for the H−Si bonds, all of which are similar to the MP2/6-311G(d,p) results: 2.299, 2.352, and 1.492 Å, respectively.

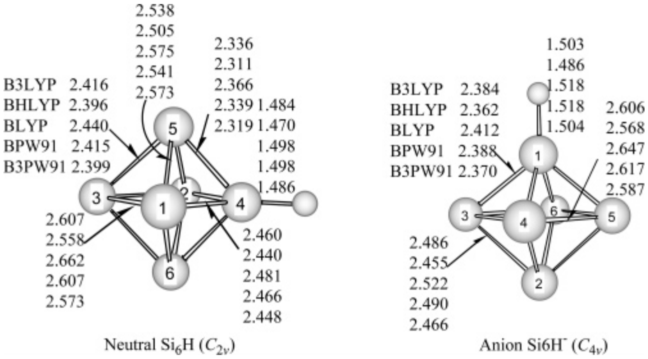
The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for $^2B_2 \leftarrow {}^1A_1(C_{2v})$ ranges from 2.59 to 2.95 eV with the five different functionals. The EA_{vert} values range from 2.24 to 2.60 eV. The range of VDE is from 2.90 to 3.24 eV. Among these, the values predicted by the B3LYP functional are very close to the values predicted by the BPW91 functional. For $^2B_2 \leftarrow {}^1A_1(C_{3v})$, the predicted EA_{ad} ranges from 2.69 to 2.90 eV. The range of VDE is from 3.11 to 3.85 eV. No experimental data are available for comparison.

Si_6H and Si_6H^-. There are a few previous theoretical studies on the structure of the ground state of the Si_6H cluster. At the NTBMD level of theory, the ground-state geometry of Si_6H is predicted to consist of nonclassical H-bridged Si−Si−Si triangular surfaces.[21] At the CPMD level of theory, the ground-state geometry of Si_6H is predicted to have C_s symmetry.[19,20] At the GAs level of theory, the geometry of the ground state of Si_6H is calculated to consist of H-bridged Si−Si−Si triangular surfaces.[22,23] At the MP2/6-311G(d,p) level of theory, the ground-state geometry of Si_6H is predicted to have C_{2v} symmetry.[5]



a Neutral Si_5H (C_{2v}) **b** H - bridged structure Ref. 19-24 **c** Anion Si_5H^- (C_{2v}) **d** Anion Si_5H^- (C_{3v})

Figure 2. (a−d) The optimized geometries for neutral Si_5H and its anion. The Si_5H^- geometries are obtained by DFT methods with a DZP++ basis set and at the MP2/6-311G(d,p) level of theory. Only silicon atoms are numbered. Black solid lines indicate bridged bonding between a hydrogen and a silicon atom. Bond lengths and bond angles are in angstroms and degrees, respectively.



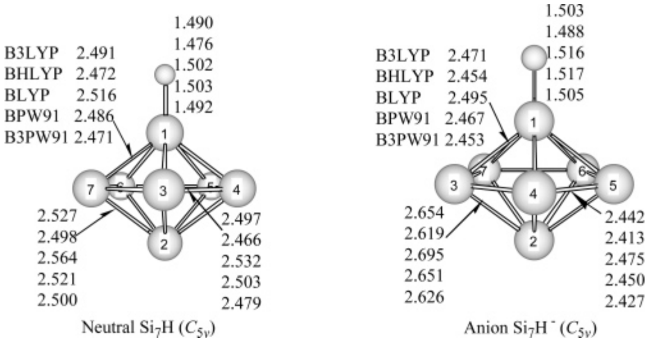
Neutral Si_6H (C_{2v}) Anion Si6H$^-$ (C_{4v})

Figure 3. The optimized geometries for neutral Si_6H and its anion Si_6H^-. Only silicon atoms are numbered. Bond lengths are in angstroms.

Our DFT results show C_{2v} symmetry with the $^2B_1$ state (shown in Figure 3) for the ground state of neutral Si_6H. This result is the same as the previous result obtained by Chambreau et al.[5] The most reliable prediction of bond lengths are 2.311 Å (BHLYP) for the two equivalent Si_4-Si_5 and Si_4-Si_6 bonds of the adjacent hydrogen atom, 2.440 Å (BHLYP) for the other two equivalent Si−Si bonds of the adjacent hydrogen atom, 2.396 Å (BHLYP) for the two equivalent Si_3-Si_5 and Si_3-Si_6 bonds of the nonadjacent hydrogen atom, 2.558 Å (BHLYP) for the other two equivalent Si−Si bonds of the nonadjacent hydrogen atom, 2.505 Å (BHLYP) for the four equivalent Si−Si bonds, and 1.484 Å (B3LYP) for the H−Si bonds. These values are similar to the MP2/6-311G(d,p) values of 2.313, 2.451, 2.512, 2.568, 2.512, and 1.482 Å, respectively.[5] No experimental data are available for comparison.

For the anionic Si_6H^- molecule, the C_{4v}-symmetry structure of the $^1A_1$ ground state is shown in Figure 3. Comparison with the neutral Si_6H shows that there is a substantial change in the geometry between the neutral cluster and the anion. The most reliable prediction of the bond lengths for Si_6H^- are 2.362 Å (BHLYP) for the four equivalent axial−equatorial Si−Si bonds of the adjacent hydrogen atom, 2.455 Å (BHLYP) for the four equivalent axial−equatorial Si−Si bonds of the nonadjacent hydrogen atom, 2.568 Å (BHLYP) for the four equivalent equatorial Si−Si bonds, and 1.503 Å (B3LYP) for the H−Si bonds. 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_6H is predicted to be 2.86 (B3LYP), 2.81 (BHLYP), 2.63 (BLYP), 2.83 (BPW91), and 2.94 (B3PW91) eV. The EA_{ad} value predicted by B3PW91 is the largest and the value predicted by BLYP is the smallest among all of these methods. The EA_{vert} values range from 2.17 to 2.48 eV. The range of VDE is from 3.20 to 3.49 eV. No experimental values are available.



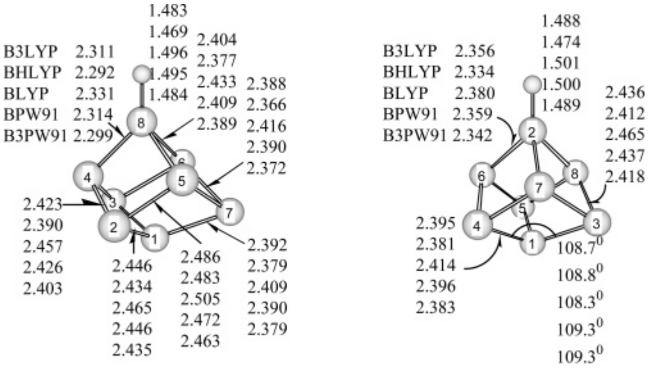
Neutral Si_7H (C_{5v}) Anion Si_7H^- (C_{5v})

Figure 4. The optimized geometries for neutral Si_7H and its anion Si_7H^-. Only silicon atoms are numbered. Bond lengths are in angstroms.

Si_7H and Si_7H^-. The C_{5v}-symmetry structure of the $^2A_1$ ground state for neutral Si_7H and the C_{5v}-symmetry structure of the $^1A_1$ ground state for the anion Si_7H^- are displayed in Figure 4. Our results for the geometry of the ground state of Si_7H are the same as the previous results obtained by Balamurugan et al.[19] However, this result differs from the previous studies in which the NTBMD and GAs methods were used.[21,22] For neutral Si_7H, the most reliable bond lengths of Si−Si bonds calculated by BHLYP are 2.472 Å for the five equivalent axial−equatorial Si−Si bonds of the adjacent hydrogen atom, 2.498 Å for the five equivalent axial−equatorial Si−Si bonds of the nonadjacent hydrogen atom, and 2.466 Å for the five equivalent equatorial Si−Si bonds. The most reliable bond length of H−Si calculated by B3LYP is 1.490 Å. No other theoretical or experimental bond lengths are available for comparison.

For the Si_7H^- anion, no experimental data are available. The five equivalent axial−equatorial Si−Si bonds of the adjacent hydrogen atom have been elongated from the neutral Si_7H structure by ∼0.020 Å. The five equivalent axial−equatorial Si−Si bonds of the nonadjacent hydrogen atom have been elongated from its neutral structure by ∼0.127 Å. The five equivalent equatorial Si−Si bonds have been shortened from the neutral Si_7H structure by ∼0.054 Å. And the H−Si bond length has been elongated from its neutral structure by ∼0.013 Å. The most reliable predictions of bond lengths are 2.45, 2.619, and 2.413 Å for the Si−Si bonds (BHLYP), and 1.503 Å for the H−Si bonds (B3LYP).

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The EA_{ad} for Si_7H is predicted to be 3.19 (B3LYP), 3.08 (BHLYP), 2.99 (BLYP), 3.12 (BPW91), and 3.21 (B3PW91) eV. Again, the EA_{ad} values calculated by B3PW91 are the



Neutral Si_8H (C_s) Anion Si_8H^- (C_{3v})

Figure 5. The optimized geometries for neutral Si_8H and its anion Si_8H^-. Only silicon atoms are numbered. Bond lengths and bond angles are in angstroms and degrees, respectively.

largest and the values calculated by BLYP are the least among all of these methods. The EA_{vert} values range from 2.53 to 2.72 eV. The range of VDE is from 3.53 to 3.68 eV. No experimental values are available.

Si_8H and Si_8H^-. The C_s-symmetry structure of the $^2A''$ ground state for neutral Si_8H is displayed in Figure 5. Our results for the geometry of the ground state of Si_8H not only differ from the results obtained by Balamurugan et al.[19] using the CPMD method, but they also differ from the previous studies[21,22] in which the NTBMD and GAs methods were used. At the DFT levels of theory, their structures (not shown in this paper) are not the most stable. For example, the CPMD structure (see ref 19) is less stable in energy than is the DFT structure by approximately 0.22 (B3LYP), 0.31 (BHLYP), 0.19 (BLYP), 0.01 (BPW91), and 0.07 (B3PW91) eV. For neutral Si_8H, the most reliable bond lengths of Si−Si bonds predicted by the BHLYP method are 2.434 Å for the two equivalent Si_1-Si_2 and Si_1-Si_3 bonds, 2.390 Å for the two equivalent Si_4-Si_2 and Si_4-Si_3 bonds, 2.366 Å for the two equivalent equatorial Si_7-Si_5 and Si_7-Si_6 bonds, 2.377 Å for the two equivalent equatorial Si_8-Si_5 and Si_8-Si_6 bonds, 2.483 Å for the two equivalent equatorial Si_2-Si_5 and Si_3-Si_6 bonds, 2.379 Å for the Si_1-Si_7 bonds, and 2.292 Å for the Si_4-Si_8 bonds. The most reliable bond length of H−Si calculated by B3LYP is 1.483 Å. No other theorectical or experimental bond lengths are available for comparison.

For the anion Si_8H^-, the structure of the ground state possesses C_{3v} symmetry with a $^1A_1$ electronic state (shown in Figure 5). Comparison with the neutral Si_8H shows that there is a substantial change in the geometry between the neutral cluster and the anion. The most reliable prediction of bond lengths are 2.334 Å (BHLYP) for the three equivalent Si−Si bonds of the adjacent hydrogen atom, 2.383 Å (BHLYP) for the three equivalent Si−Si bonds of the nonadjacent hydrogen atom, 2.412 Å (BHLYP) for the other six equivalent Si−Si bonds, and 1.488 Å (B3LYP) for the H−Si bonds. No experimental values are available.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The calculated EA_{ad} for Si_8H ranges from 2.89 to 3.26 eV with the five different functionals. The EA_{vert} values range from 2.63 to 2.98 eV. The range of VDE is from 3.27 to 4.13 eV. As can been seen from Table 1, the B3LYP EA_{ad} value of 3.14 eV, EA_{vert} value of 2.87 eV, and VDE value of 3.56 eV are very close to the BPW91 values of 3.13, 2.87, and 3.51 eV, respectively. No experimental values are available.

Neutral Si_9H (C_1) Anion Si_9H^- (C_s)

Figure 6. The optimized geometries for neutral Si_9H and its anion Si_9H^-.

TABLE 2: Bond Lengths (in Angstroms) for Neutral Si_9H Calculated with DZP++ Basis Sets

bonds	B3LYP	BHLYP	BLYP	BPW91	B3PW91
Si_1-Si_2	2.369	2.358	2.389	2.363	2.347
Si_1-Si_4	2.374	2.353	2.397	2.380	2.360
Si_1-Si_6	2.665	2.615	2.722	2.649	2.617
Si_1-Si_8	2.394	2.376	2.418	2.397	2.378
Si_2-Si_3	2.387	2.370	2.413	2.376	2.357
Si_2-Si_6	2.386	2.373	2.405	2.394	2.375
Si_3-Si_5	2.407	2.383	2.441	2.406	2.379
Si_3-Si_6	2.667	2.622	2.723	2.645	2.612
Si_3-Si_7	2.486	2.460	2.512	2.488	2.468
Si_4-Si_5	2.342	2.316	2.365	2.350	2.330
Si_4-Si_9	2.450	2.428	2.483	2.451	2.423
Si_4-H	1.489	1.476	1.501	1.502	1.489
Si_5-Si_7	2.724	2.857	2.709	2.637	2.649
Si_5-Si_9	2.626	2.626	2.649	2.595	2.586
Si_6-Si_7	2.555	2.506	2.591	2.564	2.537
Si_6-Si_8	2.358	2.348	2.378	2.362	2.341
Si_6-Si_9	2.796	2.761	2.848	2.762	2.733
Si_7-Si_9	2.386	2.364	2.409	2.389	2.368
Si_8-Si_9	2.466	2.454	2.492	2.445	2.429

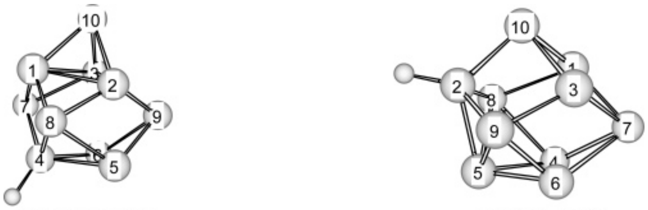
Si_9H and Si_9H^-. The geometry of the ground state of Si_9H is displayed in Figure 6. As can be seen from Figure 6, the silicon atoms 1, 4, 5, 7, and 6 and the hydrogen atom do not lie in a plane. Hence, the symmetry of Si_9H is C_1. This DFT result is different from the CPMD result[19] and the NTBMD result.[21] The calculated bond lengths for Si_9H are shown in Table 2.

The geometry of the ground state of Si_9H^- is also shown in Figure 6. As can be seen from Figure 6, the silicon atoms 1, 4, 5, 6, and 7 and the hydrogen atom lie in the same plane, and this cluster has a mirror symmetry about this plane. So the symmetry of Si_9H^- is C_s. The electronic state is $^1A'$. Compared with Si_8H^-, this geometry can be considered to be "capped" by one silicon atom on the plane that is formed by silicon atoms 2, 7, 3, and 8 (or 2, 6, 4, and 7, or 2, 6, 5, and 8) in the geometry of Si_8H^- (see Figure 5). The calculated bond lengths for Si_9H^- are shown in Table 3.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for Si_9H ranges from 3.05 to 3.51 eV with the five different functionals. The EA_{vert} values range from 2.57 to 2.82 eV. The range of VDE is from 3.38 to 3.79 eV. As can been seen from Table 1, the B3LYP EA_{ad} value of 3.36 eV is close to the BPW91 EA_{ad} value of 3.34 eV. No experimental values are available.

$Si_{10}H$ and $Si_{10}H^-$. The C_s-symmetry structure of the $^2A'$ ground state for neutral $Si_{10}H$ and the C_s-symmetry structure of the $^1A'$ ground state for the anion $Si_{10}H^-$ are displayed in Figure 7. For neutral $Si_{10}H$, silicon atoms 4, 1, 10, and 9 and the hydrogen atom lie in the same plane, and this cluster has a mirror symmetry about this plane. This result is the same as that of the previous studies.[19,21] The bond lengths predicted by all five DFT functionals are listed in Table 4.

For the negatively charged ion $Si_{10}H^-$, silicon atoms 2, 5, 7, and 10 and the hydrogen atom (in Figure 7) lie in the same plane, and $Si_{10}H^-$ has a mirror symmetry about this plane. The calculated bond lengths are listed in Table 5. No experimental data are available for comparison.



Neutral $Si_{10}H$ (C_s) Anion $Si_{10}H^-$ (C_s)

Figure 7. The optimized geometries for neutral $Si_{10}H$ and its anion $Si_{10}H^-$.

TABLE 3: Bond Lengths (in Angstroms) for the Anion Si_9H^- Calculated with DZP++ Basis Sets

bonds	B3LYP	BHLYP	BLYP	BPW91	B3PW91
Si_1-Si_2	2.508	2.485	2.534	2.508	2.490
Si_1-Si_4	2.573	2.549	2.610	2.553	2.535
Si_1-Si_6	2.327	2.304	2.353	2.337	2.318
Si_1-Si_8	2.508	2.485	2.534	2.508	2.490
Si_2-Si_3	2.511	2.490	2.540	2.503	2.486
Si_2-Si_4	2.420	2.402	2.443	2.423	2.409
Si_2-Si_6	2.681	2.633	2.745	2.659	2.628
Si_3-Si_5	2.381	2.360	2.405	2.388	2.370
Si_3-Si_6	2.582	2.530	2.647	2.565	2.531
Si_3-Si_7	2.409	2.388	2.432	2.419	2.401
Si_3-Si_9	2.638	2.584	2.700	2.633	2.595
Si_4-Si_5	2.481	2.480	2.488	2.467	2.464
Si_4-Si_8	2.420	2.402	2.443	2.423	2.409
Si_4-H	1.501	1.487	1.514	1.513	1.502
Si_5-Si_9	2.381	2.360	2.405	2.388	2.370
Si_6-Si_7	2.389	2.370	2.416	2.384	2.369
Si_6-Si_8	2.681	2.633	2.745	2.659	2.628
Si_6-Si_9	2.582	2.530	2.647	2.565	2.531
Si_7-Si_9	2.409	2.388	2.432	2.419	2.401
Si_8-Si_9	2.511	2.490	2.540	2.503	2.486

TABLE 4: Bond Lengths (in Angstroms) for Neutral $Si_{10}H$ Calculated with DZP++ Basis Sets

bonds	B3LYP	BHLYP	BLYP	BPW91	B3PW91
Si_1-Si_2	2.699	2.638	2.769	2.676	2.637
Si_1-Si_4	2.748	2.738	2.795	2.680	2.667
Si_1-Si_7	2.447	2.422	2.474	2.455	2.436
Si_1-Si_{10}	2.373	2.354	2.395	2.377	2.363
Si_2-Si_5	2.532	2.518	2.557	2.525	2.513
Si_2-Si_8	2.403	2.376	2.427	2.415	2.395
Si_2-Si_9	2.500	2.476	2.532	2.485	2.466
Si_2-Si_{10}	2.389	2.366	2.417	2.389	2.371
Si_4-Si_5	2.459	2.437	2.486	2.456	2.440
Si_4-Si_7	2.445	2.429	2.466	2.441	2.428
Si_5-Si_6	2.663	2.627	2.690	2.676	2.655
Si_5-Si_8	2.694	2.699	2.737	2.622	2.614
Si_5-Si_9	2.481	2.457	2.510	2.482	2.465
Si_4-H	1.487	1.472	1.500	1.500	1.488

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 1. The predicted EA_{ad} for $Si_{10}H$ ranges from 3.32 to 3.56 eV with the five different functionals. The EA_{vert} values range from 2.66 to 2.88 eV. The range of VDE is from 3.72 to 4.10 eV. No experimental values are available.

Dissociation Energies. The first bond dissociation energies for Si_nH/Si_nH^- ($n = 4-10$) are given in Tables 6 and 7. As can be seen from Table 6, the theoretical results for the $Si_4H \rightarrow Si_4 + H$ dissociation energy predicted by all five of the DFT functionals are in good agreement with each other, ranging from 2.20 to 2.29 eV. The theoretical dissociation energies range from 2.30 to 2.83 ($Si_5H \rightarrow Si_5 + H$), 2.12 to 2.41 ($Si_6H \rightarrow Si_6 + H$), 1.75 to 2.03 ($Si_7H \rightarrow Si_7 + H$), 2.41 to 2.72 ($Si_8H \rightarrow Si_8 + H$), 1.86 to 2.11 ($Si_9H \rightarrow Si_9 + H$), and 1.92 to 2.27 ($Si_{10}H \rightarrow Si_{10} + H$) eV. Among these DFT methods, the BHLYP predicts the largest dissociation energies, and the BLYP or the BPW91 predicts the smallest dissociation energies.

TABLE 5: Bond Lengths (in Angstroms) for the Anion $Si_{10}H^-$ Calculated with DZP++ Basis Sets

bonds	B3LYP	BHLYP	BLYP	BPW91	B3PW91
Si_1-Si_3	2.672	2.634	2.711	2.655	2.632
Si_1-Si_4	2.636	2.617	2.667	2.604	2.591
Si_1-Si_7	2.415	2.380	2.450	2.425	2.400
Si_1-Si_8	2.480	2.464	2.504	2.476	2.461
Si_1-Si_{10}	2.375	2.349	2.405	2.372	2.353
Si_2-Si_5	2.474	2.455	2.498	2.471	2.456
Si_2-Si_8	2.435	2.418	2.456	2.435	2.421
Si_2-Si_{10}	2.377	2.362	2.399	2.373	2.360
Si_2-H	1.496	1.481	1.509	1.511	1.498
Si_4-Si_5	2.491	2.468	2.516	2.498	2.479
Si_4-Si_6	2.602	2.575	2.638	2.578	2.561
Si_4-Si_7	2.648	2.661	2.659	2.611	2.611
Si_4-Si_8	2.411	2.390	2.438	2.413	2.396
Si_5-Si_8	2.678	2.635	2.731	2.650	2.625

TABLE 6: Dissociation Energies (D_e) for the Neutral $Si_nH \rightarrow Si_n + H$ ($n = 4-10$) in eV[a]

dissociation	B3LYP	BHLYP	BLYP	BPW91	B3PW91
$Si_4H \rightarrow Si_4 + H$	2.26	2.28	2.20	2.23	2.29
$Si_5H \rightarrow Si_5 + H$	2.57	2.83	2.30	2.47	2.71
$Si_6H \rightarrow Si_6 + H$	2.27	2.41	2.12	2.14	2.28
$Si_7H \rightarrow Si_7 + H$	1.88	2.03	1.75	1.75	1.89
$Si_8H \rightarrow Si_8 + H$	2.61	2.72	2.47	2.41	2.56
$Si_9H \rightarrow Si_9 + H$	2.06	2.11	2.00	1.86	1.94
$Si_{10}H \rightarrow Si_{10} + H$	2.09	2.27	1.95	1.92	2.08

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

TABLE 7: Dissociation Energies (D_e) for the Anion $Si_nH^- \rightarrow Si_n^- + H$ ($n = 4-10$) in eV[a]

dissociation	B3LYP	BHLYP	BLYP	BPW91	B3PW91
$Si_4H^- \rightarrow Si_4^- + H$	2.69	2.67	2.64	2.56	2.62
$Si_5H^- \rightarrow Si_5^- + H$	2.95	3.01	2.84	2.80	2.90
$Si_6H^- \rightarrow Si_6^- + H$	3.00	3.06	2.89	2.86	2.96
$Si_7H^- \rightarrow Si_7^- + H$	2.96	3.03	2.84	2.80	2.93
$Si_8H^- \rightarrow Si_8^- + H$	2.87	2.92	2.77	2.69	2.79
$Si_9H^- \rightarrow Si_9^- + H$	3.11	3.18	2.98	2.92	3.04
$Si_{10}H^- \rightarrow Si_{10}^- + H$	3.17	3.25	3.07	2.89	3.01

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

As can be seen from Table 7, the theoretical results for the $Si_4H^- \rightarrow Si_4^- + H$ dissociation energy calculated by all of the DFT functionals are in good agreement with each other, ranging from 2.56 to 2.69 eV. The theoretical dissociation energies range from 2.80 to 3.01 ($Si_5H^- \rightarrow Si_5^- + H$), 2.86 to 3.06 ($Si_6H^- \rightarrow Si_6^- + H$), 2.80 to 3.03 ($Si_7H^- \rightarrow Si_7^- + H$), 2.69 to 2.92 ($Si_8H^- \rightarrow Si_8^- + H$), 2.92 to 3.18 ($Si_9H^- \rightarrow Si_9^- + H$), and 2.89 to 3.25 ($Si_{10}H^- \rightarrow Si_{10}^- + H$) eV. At the same level of theory, the calculated dissociation energies of Si_5H^-, Si_6H^-, and Si_7H^- are consistent with each other. Of all of these levels of theory, the BHLYP predicts the largest dissociation energies.

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

Conclusions

The present work provides a systematic study of the silicon monohydride clusters Si_nH/Si_nH^- ($n = 4-10$) with five carefully selected DFT methods. The structures of the ground states of these clusters are reported to be traditional H−Si single-bond structures. For the prediction of bond lengths, the BHLYP method may provide the most reliable Si−Si bond lengths, and the B3LYP method may provide the most reliable Si−H bond distances. Compared with the limited experimental EA_{ad} values, the average absolute errors for all five DFT methods are 0.04

(B3LYP), 0.13 (BHLYP), 0.18 (BLYP), 0.08 (BPW91), and 0.08 (B3PW91) eV.[50] The B3LYP method is the most reliable. The EA_{ad}'s are predicted by the B3LYP method to be 2.59 (Si_4H), 2.84 (Si_5H), 2.86 (Si_6H), 3.19 (Si_7H), 3.14 (Si_8H), 3.36 (Si_9H), and 3.56 ($Si_{10}H$) eV. With the exception of Si_8H (which is slightly smaller than Si_7H), the electron affinity of a Si_nH cluster increases as the cluster size n increases.

In the case of unitary clusters, such as Si_n and As_n,[51] the BHLYP method yields the smallest dissociation energies. For binary clusters of neutral Si_nH and its anion Si_nH^-, the BHLYP method yields the largest dissociation energies. The first dissociation energies ($Si_nH \rightarrow Si_n + H$) predicted by all of these methods are 2.20−2.29 (Si_4H), 2.30−2.83 (Si_5H), 2.12−2.41 (Si_6H), 1.75−2.03 (Si_7H), 2.41−2.72 (Si_8H), 1.86−2.11 (Si_9H), and 1.92−2.27 ($Si_{10}H$) eV. For negatively charged ion clusters ($Si_nH^- \rightarrow Si_n^- + H$), the dissociation energies predicted are 2.56−2.69 (Si_4H^-), 2.80−3.01 (Si_5H^-), 2.86−3.06 (Si_6H^-), 2.80−3.03 (Si_7H^-), 2.69−2.92 (Si_8H^-), 2.92−3.18 (Si_9H^-), and 2.89−3.25 ($Si_{10}H^-$) eV.

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

Acknowledgment. This work was supported by a grant from the Inner Mongolia Natural Science Foundation of China.

References and Notes

(1) Sari, L.; McCarthy, M. C.; Schaefer, H. F.; Thaodeus, P. *J. Am. Chem. Soc.* **2003**, *125*, 11409.
(2) Xu, W. G.; Yang, J. C.; Xiao, W. S. *J. Phys. Chem. A* **2004**, *108*, 11345.
(3) Wong, H. W.; Nieto, J. C. A.; Swihart, M. T. Broadbelt, L. J. *J. Phys. Chem. A* **2004**, *108*, 874.
(4) Su, M.-D. *J. Phys. Chem.* **2004**, *108*, 823.
(5) Chambreau, S. D.; Wang, L.; Zhang, J. *J. Phys. Chem. A* **2002**, *106*, 5081.
(6) Naruse, Y.; Ma, J.; Inagaki, S. *J. Phys. Chem. A* **2003**, *107*, 2860.
(7) Wang, W. N.; Tang, H. R.; Fan, K. N.; Iwata, S. *J. Chem. Phys.* **2001**, *114*, 1278.
(8) Xu, C.; Taylor, T. R.; Burton, G. R.; Neumark, D. M. *J. Chem. Phys.* **1998**, *108*, 7645.
(9) Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* **1975**, *62*, 541.
(10) Howling, A. A.; Sansonnes, L.; Dorier, J.-L.; Hollenstein, C. *J. Appl. Phys.* **1994**, *75*, 1340.
(11) Kessels, W. M. M.; Van de Sanden, M. C. M.; Schram, D. C. *Appl. Phys. Lett.* **1998**, *72*, 2397.
(12) Ma, B. Y.; Allinger, N. L.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 5731.
(13) Pak, C.; Rienstra-Kiracofe, J. C.; Schaefer, H. F. *J. Phys. Chem. A* **2000**, *104*, 11232.
(14) Sari, L.; Gonzale, J. M.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **2001**, *114*, 4472.
(15) Tonokura, K.; Murasaki, T.; Koshi, M. *J. Phys. Chem.* **2002**, *106*, 555.
(16) Swihart, M. T. *J. Phys. Chem. A* **2000**, *104*, 6083.
(17) Swihart, M. T.; Girshick, S. L. *J. Phys. Chem. B* **1999**, *103*, 64.
(18) Talukdar, S. S.; Swihart, M. T. *J. Aerosol Sci.* **2004**, *35*, 889.
(19) Balammurugan, D.; Prasad, R. *Phys. Rev. B* **2001**, *64*, 205406.
(20) Prasad, R. *Bull. Mater. Sci.* **2003**, *26*, 117.
(21) Gupte, G. R.; Prasad, D. *Int. J. Mod. Phys. B* **1998**, *12*, 1737.
(22) Chakraborti, N.; De, P. S.; Prasad, R. *Mater. Lett.* **2002**, *55*, 20.
(23) Chakraborti, N.; Prasad, R. *Bull. Mater. Sci.* **2003**, *26*, 127.
(24) Balammurugan, D.; Prasad, R. *Bull. Mater. Sci.* **2003**, *26*, 123.
(25) Fedders, P. A. *Phys. Rev. B* **2000**, *61*, 15797.
(26) Tuttle, B.; Van de Walle, C. G.; Adams, J. B. *Phys. Rev. B* **1999**, *59*, 5493.
(27) Sinha, A. K.; Agarwal, S. C. *J. Vac. Sci. Technol., B* **2000**, *18*, 1805.
(28) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
(29) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
(30) Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974.
(31) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1993**, *215*, 601.
(32) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1996**, *259*, 165.
(33) Nimlos, M. R.; Harding, B. L.; Ellison, G. B. *J. Chem. Phys.* **1987**, *87*, 5116.
(34) Arnold, C. C.; Neumark. D. M. *J. Chem. Phys.* **1994**, *100*, 1797.
(35) Raghavachari, K. *J. Chem. Phys.* **1986**, *84*, 5672; Raghavachari, K.; Rohlfing, C. M. *J. Chem. Phys.* **1988**, *89*, 2219.
(36) Ordejón, P.; Lebedenko, D.; Menon, M. *Phys. Rev. B* **1994**, *50*, 5645.
(37) Sieck, A.; Porezag, D.; Frauenheim, T.; Pederson, M. R.; Jackson, K. *Phys. Rev. A* **1997**, *56*, 4890.
(38) Li, Q. S.; Xu, W. G.; Xie, Y.; Schaefer, H. F. *J. Chem. Phys.* **1999**, *111*, 7945.
(39) Li, Q. S.; Xu, W. G.; Xie, Y.; Schaefer, H. F. *J. Phys. Chem. A* **1999**, *103*, 7496.
(40) Xu, W. G.; Li, G. L.; Yu, G.; Zhao, Y.; Li, Q. S.; Xie, Y.; Schaefer, H. F. *J. Phys. Chem. A* **2003**, *107*, 258.
(41) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231.
(42) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(43) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(44) The BH and HLYP method implemented in the Gaussian programs has the formula 0.5 × Ex(LSDA) + 0.5 × Ex(HF) + 0.5 × Delta − Ex(B88) + Ec(LYP), which is not the exact formulation proposed by Becke in his paper. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
(45) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(46) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(48) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293; Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823; Huzinaga, S. *Approximate Atomic Wave Functions II*; Department of Chemistry, University of Alberta: Edmonton, Alberta, Canada, 1971; Vol. 2; Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Publishing: New York, 1977; pp 1−27.
(49) Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 1784.
(50) The experimental EAs of SiH−Si_4H are 1.277 ± 0.009 (ref 9), 2.31 ± 0.01 (ref 8), 2.53 ± 0.01 (ref 8), and 2.68 ± 0.01 eV (ref 8), repectively. The theoretical EAs predicted by B3LYP, BHLYP, BLYP, BPW91, and B3PW91 are 1.30 (ref 13), 1.12 (ref 13), 1.17 (ref 13), 1.40, and 1.41 eV for SiH; 2.31 (ref 13), 2.21 (ref 13), 2.13 (ref 13), 2.26, and 2.34 eV for Si_2H; and 2.56, 2.45, 2.37, 2.56, and 2.64 eV for Si_3H (ref 2), respectively (see text for Si_4H). Comparison with the experimental data shows that the average absolute errors for all five DFT methods are 0.04 (B3LYP), 0.13 (BHLYP), 0.18 (BLYP), 0.08 (BPW91), and 0.08 (B3PW91) eV.
(51) Zhao, Y.; Xu, W. G.; Li, Q. S.; Xie, Y. M.; Schaefer, H. F. *J. Comput. Chem.* **2004**, *25*, 907.