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Insights into the Nature of SiH_4−BH_3 Complex: Theoretical Investigation of New Mechanistic Pathways Involving $SiH_3^{\bullet}$ and $BH_4^{\bullet}$ Radicals

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We have investigated a new type of interaction between silane (SiH_4) and borane (BH_3) using high level ab initio calculations. The SiH_4−BH_3 complex is found to be extremely stable with the formation of a bridged hydrogen bond between SiH_4 and BH_3. Hence, it might have a hitherto unknown role in the mechanism of chemical vapor deposition (CVD), which is employed in the fabrication of boron doped silicon semiconductor materials. In an attempt to unravel this role and the underlying reasons responsible for the stability of this complex, we have carried out a detailed analysis based on the structure and molecular orbitals. The results indicate that the binding strength and electronic character of the bridged hydrogen bond in the SiH_4−BH_3 complex is between those observed in double hydrogen bridged B_2H_6 and mono-hydrogen bridged anion $B_2H_7^-$. In contrast to B_2H_6 and $B_2H_7^-$, it should be noted that the complex is stabilized by direct strong electrostatic interaction between the positively charged Si atom and the negatively charged B atom as well as by monobridged hydrogen bonding. Furthermore, we also note that the SiH_4−BH_3 complex would dissociate to form $SiH_3^{\bullet}$ and $BH_4^{\bullet}$ radicals. The existence of this complex is also inferred from good agreement between the calculated IR spectra and experimentally observed spectra of thin solid films of boron doped silicon semiconductor materials.

I. Introduction

A lot of interest has been evinced in the use of thin film technology in the fabrication of microelectronic devices. The chemical vapor deposition (CVD) technique[1] in particular has been widely employed in producing amorphous,[2−6] polycrystalline,[7−12] and single crystalline[13−17] silicon films. In this technique, p- or n-type dopant molecules interact with the source gas silane (SiH_4) through thermal initiation. The quality of the doped film growth depends on the nature of fragmented species (of hydrogen-containing ions, radicals, and small molecules) adsorbed and deposited on the silicon thin films. Therefore, several interdependent factors influence the progress of the reaction and the quality of the thin film produced. These include decomposition temperature, concentration of source gas, substrate temperature, etc.[6,7] At lower temperatures, the decomposition of B_2H_6 into BH_3 is more probable than the dissociation of either SiH_4 or H_2 because of the lower dissociation energy of B_2H_6.[18−21] Thus, the interaction of BH_3 with SiH_4 might have a significant role in the initial steps of the CVD mechanism. Though many efforts have been made to understand and control the chemical reactions involved in the CVD mechanism to produce better quality thin films, little is known about the initial steps of the mechanism of CVD.[22−29] Therefore, it would be interesting to investigate theoretically the initial steps of the CVD mechanism.

Several examples of the interaction of silane with borane are known in conventional organic synthesis. Thus, in a recent study it was shown that substituted borane can function as a catalyst in silation of carbonyl compounds, with the interaction of borane with silane preceding the interaction of the activated silane with the carbonyl compounds.[30,31] There also have been reports of silane enhancing the activity of boron-containing reagents in boration reactions.[32,33] It therefore seems likely that a hitherto unknown interaction between silane and borane may be responsible for the observed catalytic activity.

It is interesting to note that unlike typical hydrocarbons, wherein double or triple bonds exist, unsaturated silicon hydrides exhibit a tendency to form bridged hydrogen bonds. On a similar note, unsaturated silyboranes $SiBH_{1-5}$ also seem to exhibit the existence of bridged hydrogen bonds.[34−38] However, little is known about the existence of similar bridged hydrogen bonds in the interaction of saturated silicon hydrides with borane.

In an effort to address most of the aforementioned issues, we have carried out high level ab initio and density functional theory (DFT) calculations on the interaction of SiH_4 with BH_3. Along with a description of the novel features of the SiH_4−BH_3 complex, we have also expended some effort in detailing the mechanism of its formation and its relevance in the CVD mechanism.

II. Calculation Methods

The geometries of various orientations of the SiH_4−BH_3 complex possessing different symmetries were initially optimized. Vibrational frequencies were then evaluated to confirm that the optimized structures were genuine minima on the potential energy surfaces. Both MP2 and density functional methods [Becke-3-parameter with Lee−Yang−Parr correlation functional (B3LYP)] were employed in calculations of the geometries and frequencies. Coupled cluster singles doubles with triples excitation [CCSD(T)] calculations were carried out on a

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TABLE 1: Selected Geometric Data and Interaction Energy of SiH_4-BH_3[a]

	r_{B-H4}	r_{Si-H4}	r_{B-Si}	r_{Si-H2}	r_{B-H2}	$r_{B-H5(6)}$	r_{Si-H7}	$r_{Si-H8(9)}$	$-\Delta E_e$[b]	$-\Delta E_0$[b]
MP2/6-31+G*	1.310	1.588	2.248	2.107	1.210	1.197	1.486	1.472	5.14	0.75
MP2/aug-cc-pVDZ	1.326	1.599	2.269	2.116	1.222	1.205	1.491	1.476	9.68(6.47)	5.38
MP2/aug-cc-pVTZ	1.274	1.627	2.146	1.889	1.214	1.186	1.481	1.467	15.37(9.98)	10.81(5.42)
MP2/aug-cc-pVQZ[c]	1.276	1.604	2.152	1.922	1.213	1.186	1.465	1.453	14.48(11.39)	9.91(6.82)
B3LYP/6-31+G*	1.325	1.602	2.268	2.108	1.215	1.199	1.491	1.476	5.13	1.07
B3LYP/aug-cc-pVDZ	1.345	1.598	2.318	2.206	1.218	1.204	1.499	1.483	7.46(6.54)	3.57
B3LYP/aug-cc-pVTZ	1.308	1.612	2.240	2.070	1.213	1.193	1.489	1.473	7.63(7.38)	3.61(3.36)
B3LYP/aug-cc-pVQZ	1.307	1.608	2.234	2.061	1.212	1.192	1.486	1.470	7.81(7.68)	3.71(3.58)
CCSD(T)/6-31+G*			2.285						5.06	
CCSD(T)/aug-cc-pVDZ			2.332						8.52(5.51)	

[a] Bond lengths (r) are in Å. See Figure 2 for the numbering scheme of atoms. [b] ΔE_e and ΔE_0 denote the interaction energies (in kcal/mol) without and with ZPE correction, respectively. The BSSE-corrected energies are in parentheses. [c] The ZPE in this calculation used the MP2/aug-cc-pVTZ value.

few selected structures to obtain more reliable structural and energetic information. All calculations were carried out using 6-31+G* basis sets and correlation consistent basis sets[39] [double-ζ (aug-cc-pVDZ) to quadruple-ζ (aug-cc-pVQZ)]. The relative stabilities of the various isomers were assessed both in terms of the zero point energy (ZPE) uncorrected (ΔE_e) and ZPE corrected (ΔE_0) energies. The enthalpies (ΔH_{298}) of all the monomers and the complex were also evaluated. Basis set superposition error (BSSE) corrections generally have to be carried out to obtain reliable structures and energetics of intermolecular complexes.[40,41] However, in the present system (SiH_4-BH_3), the bridged hydrogen bond is shared between SiH_4 and BH_3. Since the interaction between SiH_4 and BH_3 is not a nonbonding type, but a covalent bonding type, the supermolecular approach would not be appropriate. Nevertheless, we carried out the BSSEs to estimate the upper bound of the errors. Since investigations of the mechanism of CVD entail calculations on several open shell species, it is important that one should employ reliable theoretical methods to obtain their correct structural and energetic information. In this context, it was recently shown that both unrestricted MP2 and B3LYP methods provide reliable estimates of the energies and descriptions of the geometries.[42,43] Hence most of the calculations on the open shell species discussed in this study were carried out at these levels using the Gaussian suite.[44]

III. Results and Discussion

A. Geometries and Energies. Various possible structures of the SiH_4-BH_3 complex are displayed in Figure 1. At the MP2/6-31+G* level, structure I, which has a bridged hydrogen bond, is a genuine minimum (all positive vibrational frequencies). Except for structure II (C_s symmetry perpendicular to the paper plane), which is a transition state between structure I (C_s symmetry with respect to the paper plane) and the mirror image perpendicular to the paper plane (which is essentially the same structure with I), all the other isomers are much higher in energy. It is however interesting to note that isomers IV to VIII exhibit characteristics of dihydrogen bonding.[45]

The importance of electron correlation in the description of the SiH_4-BH_3 complex can be noted by the fact that Hartree–Fock calculations fail to yield structures resembling I. The calculated binding energies of structure I seem to indicate that the SiH_4-BH_3 complex is stronger than the conventional intermolecular hydrogen bond observed in the water dimer.[46] Given the importance of electron correlation in the description of structure I, we thought it would be useful to investigate this complex using both larger basis sets and higher levels of correlation. It can be seen from Table 1 that the B3LYP has small BSSEs, while MP2 and CCSD(T) have large BSSEs, as

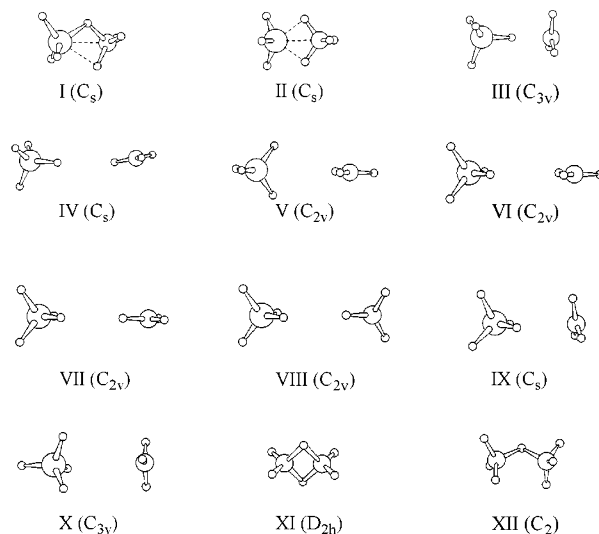

Figure 1. Geometric structures of SiH_4-BH_3 isomers (I to X), B_2H_6 (XI), and $B_2H_7^-$ (XII) optimized at the MP2/6-31+G* level. The MP2/aug-cc-pVTZ//MP2/6-31+G* complexation energies for SiH_4-BH_3 are I: 14.60, II: 14.28, III: 4.19, IV: 0.45, V: 0.56, VI: 0.35, VII: 0.45, VIII: 0.51, IX: 1.53, and X: 0.64 kcal/mol.

noted in many previous calculations.[40,47] Without BSSE correction, the B3LYP, MP2, and CCSD(T) binding energies ($-\Delta E_e$) for the aug-cc-pVDZ basis set are predicted to be 7.46, 9.68, and 8.52 kcal/mol, respectively. Thus, the CCSD(T) gives a mid value between the B3LYP and MP2 results. In the case of B3LYP, the binding energy is almost constant beyond the aug-cc-pVDZ basis set. In the case of MP2 calculations, which are sensitive to the basis set size, the binding energy of the SiH_4-BH_3 complex gets saturated beyond the aug-cc-pVTZ basis set, which gives similar results to the aug-cc-pVQZ basis set. For the aug-cc-pVQZ basis set, the B3LYP and MP2 binding energies ($-\Delta E_e$) are 7.81 and 14.48 kcal/mol, and the ZPE-corrected binding energies ($-\Delta E_0$) are 3.71 and 9.91 kcal/mol. With full BSSE correction, the $-\Delta E_0$ of B3LYP and MP2 using aug-cc-pVQZ are 3.58 and 6.82 kcal/mol. Both binding energies are much greater than the hydrogen bonding energy in the water dimer, and the MP2 results show stronger hydrogen bonding strength than those in water clusters.[48]

Furthermore, the BSSE-corrected and ZPE-corrected MP2 binding energies are likely to be underestimated due not only to insufficient basis set size (responsible for insufficient electron correlation energy) but also to overcorrected ZPE (due to the overestimated frequencies based on the BSSE-uncorrected potential energy surface). Since the CCSD(T) binding energy is near the mid value between the B3LYP and MP2 results for the same size of basis set in the present system, we expect that

TABLE 2: Geometric Comparison of SiH_4-BH_3, B_2H_6, $B_2H_7^-$, and Component Species[a]

	r_{B-H4}	r_{B-H2}	$r_{B-H5/6}$	$r_{B-Si/B}$	$\angle_{B-H4-Si/B}$	$\angle_{B-H2-Si/B}$	$\angle_{H4-B-H2}$	$\angle_{H5-B-H6}$	$\angle_{H4-B-H5}$
SiH_4-BH_3	1.274	1.214	1.186	2.146	94.65	84.58	110.23	121.61	101.19
B_2H_6	1.304	1.304	1.181	1.744	83.97	83.97	96.03	122.32	108.82
$B_2H_7^-$	1.297	1.206	1.200	2.303	125.27	61.97	113.03	113.58	105.48
BH_3	1.181	1.181	1.181				120.00	120.00	120.00
$BH_4^{\bullet}$	1.277	1.277	1.174				46.99	130.27	112.71
BH_4^-	1.228	1.228	1.228				109.47	109.47	109.47
$BH_3^{-\bullet}$	1.204	1.204	1.204				120.00	120.00	120.00

	r_{Si-H4}	r_{Si-H2}	r_{Si-H7}	$r_{Si-H8/9}$	$\angle_{H4-Si-H7}$	$\angle_{H8-Si-H9}$	$\angle_{H4-Si-H8}$	$\angle_{H7-Si-H8}$
SiH_4-BH_3	1.627	1.889	1.481	1.467	86.74	115.20	117.76	106.92
SiH_4	1.476		1.476	1.476	109.47	109.47	109.47	109.47
$SiH_3^{\bullet}$	1.531		1.531	1.531	95.11	95.11	95.11	95.11
SiH_3^+	1.456		1.456	1.456	120.00	120.00	120.00	120.00
$SiH_4^{+\bullet}$	1.825		1.868	1.464	24.45	120.77	100.77	88.91
SiH_3^-	1.531		1.531	1.531	95.10	95.10	95.10	95.10

[a] Bond lengths (r) are in Å. Bond angles ($\angle$) are in degrees. See Figure 2 for the numbering scheme of atoms. All geometric parameters were optimized at the MP2/aug-cc-pVTZ level of theory.

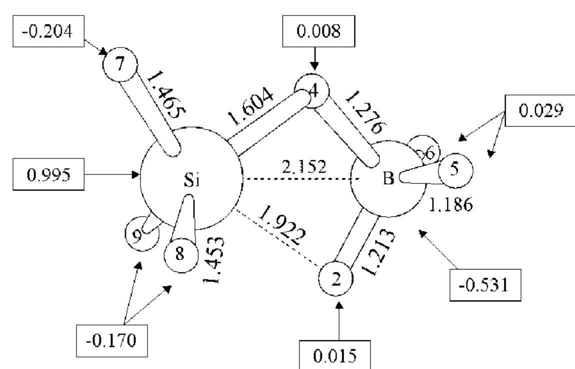

Figure 2. Structure (MP2/aug-cc-pVQZ) and NBO charge (MP2/aug-cc-pVTZ) of SiH_4-BH_3 complex. Bond distances are in Å. Charges (in boxes) are in au.

the BSSE-corrected and ZPE-corrected binding energies would be ~5 kcal/mol. For this bridged hydrogen bond system, the BSSE is very large even at the MP2/aug-cc-pVQZ level. Thus, the binding energy with full BSSE correction would be underestimated due to the incomplete recovery of the electron correlation. In this case, the 50%-BSSE correction[40,41] could be a better estimation of the binding energy, as has been noted in hydrogen bonding systems of water clusters and benzene–water systems. The 50% BSSE corrected MP2 binding energy is ~8 kcal/mol (in $-\Delta E_0$). If the CCSD(T) is assumed to give the mid value between the B3LYP and MP2 values, the value of $-\Delta E_0$ could be ~6 kcal/mol. Thus, the present novel type of interaction is very strong, which is intriguing. Though the CCSD(T) predicted binding energies are between the MP2 and B3LYP values at the aug-cc-pVDZ basis set, the CCSD(T) is similar to the MP2 in the dependency of the BSSE on the basis set size. The increase in the binding energy with the increase in the basis set size is expected for both CCSD(T) and MP2 results. Thus, our discussions and analyses will be primarily based on MP2/aug-cc-pVTZ results, which are available for all species studied here.

The predicted geometries of the SiH_4-BH_3 complex I with a bridged hydrogen bond (Table 1) indicate that with increasing basis set size, the B–Si distance tends to decrease along with the increase of the binding energy until the incomplete basis set error is insignificant (i.e., up to the aug-cc-pVTZ basis set). Figure 2 with the MP2/aug-cc-pVQZ structure of SiH_4-BH_3 gives the relevant atomic notations for our discussion. Given the electron-withdrawing nature of boron, there is significant electron transfer from Si to B. At the MP2/aug-cc-pVTZ level, the natural bond orbital[49] (NBO) charges of Si and B are 0.995 and −0.531 au, respectively, which will result in strong electrostatic interaction energy between Si and B atoms. This should be contrasted to the non-electrostatic interaction between two B atoms in diborane B_2H_6 (XI) and that between two B atoms in the monobridged diborane anion $B_2H_7^-$ (XII) (isoelectronic structure to $SiH_4-B_2H_6$), which is the product[50] of B_2H_6 attacked by a H^- donor. It can be seen from the geometries of B_2H_6 and $B_2H_7^-$ listed in Table 2, that the bridged hydrogen is much closer to boron in the SiH_4-BH_3 complex than in either B_2H_6 or $B_2H_7^-$. This seems to indicate the possibility of the SiH_4-BH_3 complex to dissociate into either $SiH_3^{\bullet}$ and $BH_4^{\bullet}$ radicals or SiH_3^+ and BH_4^- ions. To examine the energetic feasibility of such dissociation and its relevance in the CVD mechanism, we have evaluated the enthalpies of various possible dissociation schemes, which are discussed in more detail in the next section.

It is interesting to note in Figure 2 that H2 attached to B partially bridges B and Si atoms, thus, the bond length r_{B-H2} of 1.213 Å is slightly longer than $r_{B-H5(6)}$ of 1.186 Å, and the distance r_{Si-H2} 1.922 Å is not large. The result of geometric comparison shows that SiH_4-BH_3 is structurally between the doubly hydrogen-bridged B_2H_6 and the isoelectronic structure $B_2H_7^-$. This is strongly correlated with the fact that owing to the additional electrostatic interaction between Si and B atoms, the mono-hydrogen bridged Si···B interaction force in SiH_4-BH_3 is stronger than the mono-hydrogen bridged B···B interaction force in $B_2H_7^-$ but weaker than the doubly hydrogen bridged B···B interaction force in B_2H_6. This is more clearly understood from the comparison of the HOMOs of SiH_4-BH_3, B_2H_6, and $B_2H_7^-$ in Figure 3. While the HOMOs are not instructive, the HOMO-2s (MO 11) clearly illustrate the significant differences between the three species. Unlike either B_2H_6 or $B_2H_7^-$ with delocalization of the electron density on both the borons and the bridging hydrogen, the electron density around the bridging hydrogen of the SiH_4-BH_3 complex is shifted more toward the boron than silicon. This observation is in line with our earlier comments on the reasons responsible for the shortening of the B–H4 bond and the lengthening of the Si–H4 bond in the SiH_4-BH_3 complex. Though SiH_4 behaves more as an electron acceptor[51−55] than as an electron donor,[56,57] it can be seen that in the SiH_4-BH_3 complex it behaves as an electron donor.

B. SiH_4-BH_3 Complex in CVD Boron Doped Silicon Deposition. As was discussed earlier, the identification of the SiH_4-BH_3 complex in the CVD mechanism of boron doped

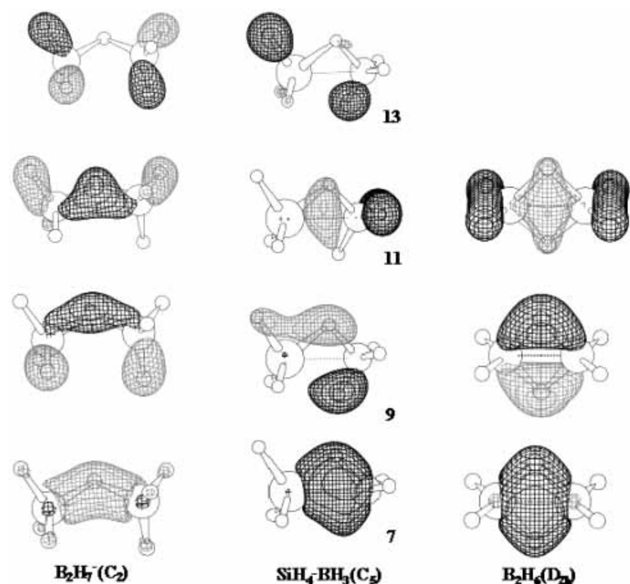

Figure 3. Molecular orbitals of SiH_4-BH_3 compared with those of the isoelectronic $B_2H_7^-$ and the doubly hydrogen-bridged B_2H_6 (MP2/aug-cc-pVTZ level). The numbers indicate MO numbers; MO 13 is the HOMO for both $B_2H_7^-$ and SiH_4-BH_3. The MOs indicate that the hydrogen bridge strength in SiH_4-BH_3 is between the mono-hydrogen bridge strength in $B_2H_7^-$ and the two-hydrogen bridge strength in B_2H_6.

TABLE 3: ΔH_{298} of the Chemical Reactions in Boron Doped Silicon Deposition

reactants	products	ΔH_{298} [a] (A)	(B)
stage 1 [b]			
H_2	$2H^•$	87.07	95.25
SiH_4	$SiH_3^• + H^•$	79.47	89.32
B_2H_6	$2BH_3$	35.46	42.45
stage 2 [b]			
$SiH_4 + BH_3$	SiH_4-BH_3	−1.93	−12.17
stage 3 [b]			
SiH_4-BH_3	$SiH_3^• + BH_4^•$	77.02	86.39
SiH_4-BH_3	$SiH_3^+ + BH_4^-$	189.09	199.00
SiH_4-BH_3	$SiH_4^{+•} + BH_3^{-•}$	266.69	265.37
stage 4 [b]			
$BH_4^• + BH_3$	$B_2H_6 + H^•$	−31.08	−27.36
$BH_4^•$	$BH_2^• + H_2$	11.89	19.53

[a] ΔH_{298} (kcal/mol) is the standard enthalpy change calculated at the MP2/6-31+G* (A) and MP2/aug-cc-pVTZ (B) levels. [b] The possible chemical reactions in the CVD gas phase are given at each stage.

silicon film would have significant ramifications in the field. The enthalpies of various possible dissociative mechanisms relevant in the CVD mechanism are listed in Table 3. It can be readily seen that among all the three possible dissociations, the dissociation of B_2H_6 into BH_3 is more favored in the first stage wherein there is an initiation of the reaction at low temperatures.[6,18−20,58] In the second stage, the highly reactive BH_3 would exothermically combine with SiH_4 to form the SiH_4-BH_3 complex. The polarized SiH_4-BH_3 complex can be easily adsorbed on the solid substrate surface and then primed for further deposition or activation depending on the prevailing reaction conditions, which is similar to the dissociation of NH_2 on the Si surface.[59] At high temperatures, there is a greater likelihood of the SiH_4-BH_3 complex dissociating into $SiH_3^•$ and $BH_4^•$ radicals (Stage 3). It is interesting to note that the $SiH_3^•$ radical has been detected by infrared vibrational absorption (Si:H film deposited at a hydrogen flow)[60] and mass spectrometry,[61] and has been known to influence significantly the quality

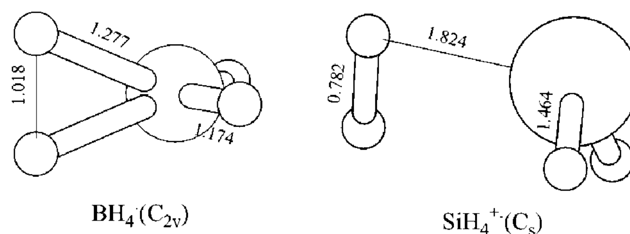

Figure 4. Structures of isoelectronic $BH_4^•$ and $SiH_4^{+•}$ (MP2/aug-cc-pVTZ level).

of amorphous silicon film growth.[2] On a similar note, the $BH_4^•$ radical has also been investigated by electron paramagnetic resonance spectroscopy.[62] The presence of these reactive radicals $SiH_3^•$ and $BH_4^•$ opens up the possibility of several mechanistic pathways. Two such pathways involving $BH_4^•$ (stage 4) are shown in Table 3.

In the $BH_4^•$ radical, a further dissociation toward radical $BH_2^•$ and molecular H_2 can be predicted. The structure of the $BH_4^•$ radical (Table 2 and Figure 4) shows that the H2−H4 distance is 1.018 Å, and the bond angle ∠H4−B−H2 is 47.0°. We also find that the isoelectronic species $SiH_4^{+•}$ (Table 2 and Figure 4) would also dissociate into $SiH_2^{+•}$ and H_2; the H4−H7 distance is 0.902 Å, and the bond angle ∠H4−Si−H7 is only 24.5°. The structures of the two isoelectronic structures $BH_4^•$ and $SiH_4^{+•}$ are shown in Figure 4.

C. Vibrational Spectra, Dipole Moments, and Rotational Constants. B_2H_6 is known to have several characteristic infrared spectral frequencies resulting from the stretching motion between bridged hydrogen and boron[63,64] (Table 4). Based on comparison with experimental values of B_2H_6, a scale factor of 0.917 is recommended for our calculated frequencies. Characteristic IR spectra were observed in some unsaturated silicon−boron systems from the boron-doped Si:H films deposited at a hydrogen flow, and used as experimental identification of the bridged hydrogen bonding structure.[65] Similar infrared absorption spectra for boron doped silicon films have been reported.[6,66,67] A sample of amorphous silicon film doped with boron shows absorption at two regions (1850∼2250 cm^{-1}).[6] In these regions, both frequencies and intensities of the observed peaks are in good agreement with the corresponding calculated values of the complex SiH_4-BH_3. This spectral feature appears at a higher frequency than the B−H−B stretch of B_2H_6. In addition, a shoulder at 2070∼2090 cm^{-1} corresponds to the Si−H7 stretch mode. The absorption spectra at 2400∼2600 cm^{-1} region agree well with the calculated boron 4-fold B−H stretch mode. Based on the positions and intensities of the calculated frequencies (Table 4), the experimental absorptions in the thin film seem to originate from the SiH_4-BH_3 complex. This observation seems to point to the fact that there is a direct deposition of the SiH_4-BH_3 complex on the silicon film. An organic intramolecular bridged Si−H−B bond structure reported recently,[32] indicates the existence of characteristic absorption peaks at the 1905 and 2055 cm^{-1}. To facilitate future experimental and theoretical studies, we have listed the vibrational frequencies and IR intensities of SiH_4-BH_3, B_2H_6, $B_2H_7^-$, SiH_4, BH_3, $SiH_3^•$, $BH_4^•$, SiH_3^+, and BH_4^- (Table 5) and their dipole moments and rotational constants (Table 6).

IV. Concluding Remarks

Based on our calculations, we infer that SiH_4 and BH_3 combine to form a stable SiH_4-BH_3 complex, with the SiH_4 behaving as an electron donor and BH_3 as an electron acceptor. Consequently, the complex is polarized with net negative charge

TABLE 4: Comparison of Calculated IR Spectra (MP2/aug-cc-pVTZ) with Experimental Data[a]

B_2H_6	B−H−B	B−H	B−H	B−H	−SiH_3	Si−H	BH_4^-	B−H
calc.	1788(480)	1954(0)	2053(7)	2209 (0)		2303(120)		2321(583)
scaled	1640	1792	1883	2026		2110		2200
expt.[b]	1610	1800	1850	2080		2100		2128
SiH_4−BH_3	**Si−H4**	**B−H4**	**Si−H7**	**Si−H8(9)**	**Si−H8(9)**	**B−H2**	**B−H5(6)**	**B−H5(6)**
calc.	1674(54)	2169(200)	2275(81)	2323(55)	2340(84)	2475(40)	2626(70)	2721(76)
scaled	1536(54)	1990(200)	2087(81)	2131(55)	2147(84)	2270(40)	2409(70)	2496(76)
expt.(a)[c]		1978(210)	2096 (65)				2425(100)	2472(160)
expt.(b)[c]		1990(180)	2070(80)				2456(60)	2485(70)

[a] Frequencies are in cm^{-1}, and the intensities are in parentheses in km/mol. Scaled frequencies are given with the scale factor of 0.917. [b] Experimental frequencies [ref 61]. [c] IR spectral data of amorphous silicon film [ref 6] (a) and (b) correspond to the film temperature 280 and 360 °C, respectively.

TABLE 5: MP2/aug-cc-pVTZ Vibrational Frequency and IR Intensity[a]

freq (int.)	assign	freq (int.)	assign
SiH_4−BH_3		SiH_4	
895 (116)	bi/SiH8,9	961 (151)	d
1003 (314)	bo/SiH7,8,9	1064 (0)	b/HSiH
1058 (49)	d/SiH7,8,9	2303 (120)	sa/SiH
1172 (28)	bi/BH5,6	2312 (0)	ss/SiH
1254 (0)	d/BH2,5,6	$SiH_3^{\bullet}$	
1287 (18)	bo/BH2,5,6	784 (76)	bo/SiH
1674 (54)	s/SiH4	958 (68)	bi/SiH
2170 (200)	s/BH4	2266 (10)	ss/SiH
2275 (81)	s/SiH7	2301 (118)	sa/SiH
2323 (55)	ss/SiH8,9	SiH_3^+	
2340 (84)	sa/SiH8,9	884 (87)	bo/SiH
2475 (40)	s/BH2	936 (71)	b/SiH
2626 (70)	ss/BH5,6	2355 (0)	ss/SiH
2721 (76)	sa/BH5,6	2433 (0)	sa/SiH
B_2H_6		BH_3	
1009 (27)	bo/BH	1180 (90)	bo/HBH
1223(73)	bi/BH	1247 (16)	bi/HBH
1788 (480)	si/BH_B	2631 (0.0)	ss/BH
1954 (0)	so/BH_B	2765 (130)	sa/BH
2054 (7)	sa/BH_B		
2209 (0)	si/BH_B	$BH_4^{\bullet}$	
2656 (142)	sa/BH	1470 (53)	d + s/HH
2772 (166)	sa/BH	2236 (93)	ss/BH
$B_2H_7^-$		2715 (32)	ss/BH
1094 (417)	b/BH	2839 (75)	sa/BH
1210 (14)	b/BH		
1547 (4)	d/BH	BH_4^-	
2332 (1062)	ss/BH	1104 (52)	d
2436 (39)	s/BH_B+s/BH	1244 (0)	b/HBH
2436 (151)	s/BH	2314 (0.0)	ss/BH
2496 (102)	s/BH	2321 (583)	sa/BH
2555 (298)	s/BH		
2556 (290)	s/BH		

[a] Frequencies in cm^{-1}; intensities (int.) in km/mol. To compare with the experimental data, the scale factor of 0.917 is recommended. Notations: b = bending, bi = in-plane bending, bo = out-of-plane bendining, s = stretch, ss = sym stretch, sa = asym stretch, si = in-plane stretch, so = out-of-plane stretch, and d = deformation.

TABLE 6: MP2/aug-cc-pVTZ Dipole Moment (in debye) and rotational constants (A, B, C, in GHz)

	dipole	A	B	C
SiH_4−BH_3	1.586	50.60	9.17	9.09
B_2H_6	0	81.44	18.71	17.17
$B_2H_7^-$	-	61.15	10.88	10.87
SiH_4	0	86.37	86.37	86.37
$SiH_3^{\bullet}$	0.024	142.90	142.90	85.03
SiH_3^+	0	157.73	157.73	78.86
BH_3	0	239.50	239.50	119.75
$BH_4^{\bullet}$	1.362	179.88	138.26	93.25
BH_4^-	0	124.64	124.64	124.64

concentration on the BH_3 end. Owing to the strong electrostatic interaction between the Si and B atoms, the monobridged hydrogen bond in SiH_4−BH_3 is found to have an intermediate electronic character between the doubly hydrogen bridged B_2H_6 and the pure monohydrogen bridged $B_2H_7^-$. This new type of interaction present in the SiH_4−BH_3 complex has been investigated for the first time in the present study. In CVD deposition, the SiH_4−BH_3 complex can dissociate to form $SiH_3^{\bullet}$ and $BH_4^{\bullet}$ radicals. The calculated IR absorption of the complex at 1990 and 2087 cm^{-1} agree well with the experimentally observed peaks of a sample of boron doped silicon film.

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