Thermochemistry of Silicon−Hydrogen Compounds Generalized from Quantum Chemical Calculations

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Particulate contamination formed by homogeneous clustering reactions of silicon hydrides within silicon chemical vapor deposition processes is an important source of yield loss during semiconductor processing. On the other hand, intentional synthesis of silicon nanoparticles may be of great interest because of the unique optical and electronic properties of nanostructured silicon. Kinetic modeling can play an important role in developing a fundamental understanding of the particle clustering chemistry, and knowledge of the thermochemistry and reactivity of these silicon hydrides is necessary if a mechanistic kinetic model is to be constructed. Experimental measurements of thermochemical properties are usually expensive and difficult, and it is desirable to use computational quantum chemistry as an alternative. In this work, several theoretical methods were used to calculate thermochemical properties of silicon hydrides. Among the methods used, Gaussian-3 theory (G3) using the geometries from B3LYP density functional theory (B3LYP/6-31G(d)), referred to as G3//B3LYP, showed the most promising results with an average absolute deviation of 1.23 kcal/mol from experimental data for standard enthalpies of formation of small ($<Si_4$) silicon hydrides. A series of calculations using G3//B3LYP was carried out on small to medium ($<Si_8$) silicon hydrides to obtain thermochemical properties, and a bond additivity correction was incorporated to obtain more accurate thermochemical properties. A group additivity scheme was fit to these corrected values, allowing accurate estimation of the thermochemical properties of arbitrary silicon−hydrogen clusters. This generalization of the results is essential, since the many thousands of possible isomers of these molecules cannot be treated quantum chemically at even the least expensive levels of theory.

Introduction

Particulate contamination is a leading source of yield loss during semiconductor processing, and particles formed by homogeneous clustering reactions within process equipment are an important and growing source of this contamination. Chemical vapor deposition (CVD) processes using silane (SiH_4) as the precursor are widely used, and particle nucleation in these processes can limit film growth rates and reactor productivity. On the other hand, intentional synthesis of silicon nanoparticles with controlled size and morphology may be of great interest due to the unique optical and electronic properties of nanostructured silicon. Detailed kinetic modeling can play a critical role in developing a fundamental understanding of this particle clustering chemistry and therefore in controlling particle nucleation. Knowledge of the thermochemistry and reactivity of silicon−hydrogen molecules is essential to the development of detailed chemical kinetic models of the particle nucleation process. However, experimental measurements of these thermochemical properties are usually expensive and difficult. In addition, the sheer number of relevant chemical species makes construction of a database by experiment infeasible. Therefore, it is highly desirable to use computational chemistry as an alternative.

Calculation of molecular thermochemical data using ab initio quantum chemistry calculations has been performed extensively, and it has been shown that accurate prediction requires going well beyond Hartree−Fock level of theory to include higher-order treatments of electron correlation.[1] Several very high-level methods with extrapolation, including coupled cluster theory with single, double, and noniterative triple excitations [CCSD(T)] and quadratic configuration interaction methods with single, double, and noniterative triple excitations [QCISD(T)], have been studied using very large basis sets to accurately predict thermochemical properties of molecules.[2,3] However, these methods are computationally expensive and therefore limited to small molecules. As an alternative, composite methods comprised of moderate-level calculations with medium-sized basis sets can be implemented and parametrized to approach the accuracy of more expensive calculations. The Gaussian-*n* (G*n*) series[4−14] and complete basis set (CBS) family[15−18] are two of the most popular methods in this category. These methods apply molecule-independent empirical parameters, which are fit according to a test set of relatively small molecules. The thermochemical properties calculated from these methods agree very well with experimental data. For example, the average absolute deviations between experimental and calculated enthalpies of formation of 148 molecules in the G2/97 test set were 0.94 and 1.19 kcal/mol for G3 theory and the CBS-QB3 method, respectively. In addition, the performance of these calculations can be further enhanced by using bond additivity corrections[19] or constructing isodesmic,[20] homodesmotic,[21] and bond separation reactions[22] when dealing with larger compounds.[23] Therefore, the thermochemical properties estimated

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from these calculations are an excellent surrogate when experimental measurements are not available.

While composite methods reduce the computational burden, they are still prohibitive for large molecules. A companion approach for estimating thermochemical properties is to use a group additivity scheme. Benson's group additivity approach[24] has been widely used to predict the thermochemistry of organic molecules. In this approach, a molecule is divided into groups defined by a non-hydrogen atom and the atoms to which it is bonded, and the estimated thermochemical value of the molecule is calculated as the sum of the contributions of these groups. Since only the smallest silicon hydrides have experimental thermochemical data available, group additivity is an attractive approach to estimate the properties of large species that are also inaccessible to quantum chemical calculations. However, only a limited set of group additivity values (GAVs) for silicon hydrides is available. Swihart and Girshick[25] have tabulated the GAVs for silicon hydrides on the basis of the extensive ab initio calculations of Katzer et al.[26] These groups encompass silanes (saturated), silenes (one double silicon−silicon bond), silylenes (one silicon center with a pair of nonbonded electrons), and some cyclic molecules. These GAVs, however, are not exhaustive and most notably can only be applied to molecules with a single functionality, that is, a double bond or a silylene center. The GAVs required for molecules with multiple functionalities are not available, and augmentation of this set of GAVs is needed to enable the study of the reaction kinetics of systems consisting of more complicated molecules.

In this work, several different theoretical methods were used to calculate thermochemical properties of silicon−hydrogen molecules, and the predicted values from these methods were compared to available experimental data. Among the methods used, Gaussian-3 theory using the geometries from B3LYP/6-31G(d) density functional theory, referred to as G3//B3LYP,[13] showed the most accurate results with an average absolute deviation of 1.23 kcal/mol from experimental data for standard enthalpies of formation of small ($<Si_4$) silicon hydrides. A series of calculations using G3//B3LYP was carried out on 135 small to medium ($<Si_8$) silicon−hydrogen molecules to obtain thermochemical properties such as standard enthalpy of formation, standard entropy, and heat capacities for a range of temperatures. Empirical bond additivity corrections were incorporated, and a group additivity scheme was then fit to the corrected values, allowing accurate estimation of the thermochemical properties of arbitrary silicon−hydrogen clusters. This generalization of the results is essential, since the many thousands of possible isomers of these molecules cannot be treated quantum chemically at even the least expensive levels of theory.

Computational Methods

The ab initio molecular orbital calculations were carried out using Gaussian 98.[27] Four different methods, G2, G3//B3LYP, CBS-Q, and CBS-QB3, were evaluated for their accuracy in predicting thermochemical properties of small silicon−hydrogen molecules with experimental data available. This molecule set is summarized in Table 1. Gaussian-2 (G2) theory is a composite method in which a sequence of ab initio molecular orbital calculations is performed to approximate the results of QCISD(T)/6-311+G(3df,2p) calculations for a given species.[6] Geometries of the molecules are optimized using Møller−Plesset perturbation theory to the second order with the 6-31G(d) basis set [MP2/6-31G(d)], and a series of single point calculations is carried out to correct the MP2 energy. Zero-point energies (ZPE) are evaluated at the Hartree−Fock level with the 6-31G(d) basis set [HF/6-31G(d)] using the vibrational frequencies scaled by 0.8929, and a two-parameter empirical high-level correction (HLC) is introduced to overcome remaining deficiencies. Gaussian-3 theory using the geometries from B3LYP density functional theory with the 6-31G(d) basis set (G3//B3LYP) is a composite method similar to G2.[13] In this method, both geometries and zero-point energies are evaluated at the B3LYP/6-31G(d) level. The vibrational frequencies are scaled by 0.96, and a four-parameter HLC is included. The complete basis set (CBS) series is comprised of extrapolation procedures to determine the projected second-order (MP2) energy in the limit of a complete basis set. The CBS-Q method evaluates zero-point energies at the HF/6-31G(d′) level with the frequencies scaled by 0.918 44, and molecular geometries are optimized at the MP2/6-31G(d′) level.[16] CBS-QB3 is a modification of the CBS-Q method that uses B3LYP/6-311G(2d,d,p) geometries and zero-point energies, which are based on vibrational frequencies scaled by 0.99.[18] Both CBS methods perform a sequence of calculations with a variety of basis sets to evaluate the contributions of higher-order correlation, and several empirical corrections similar to the high-level corrections in Gaussian-*n* methods are also included in the resulting energies. Spin−orbit corrections, which are included inherently in the G3//B3LYP and CBS-QB3 methods, are added for the G2 and CBS-Q methods when dealing with atomic species. In this work, we chose two density functional theory (DFT)-based methods, G3//B3LYP and CBS-QB3, because they are widely known to give better frequency estimations than Hartree−Fock calculations and are also computationally inexpensive relative to MP2. In addition, DFT calculations can help avoid the problems of spin contamination or restricted (RHF) to unrestricted Hartree−Fock (UHF) instability that plague Hartree−Fock calculations on restricted open-shell species such as silylene molecules.

TABLE 1: Comparison of Experimental Heats of Formation of Small Silicon Hydride Species to the Results from Various Quantum Chemical Methods

species	exptl[a] $\Delta H^\circ_{f,298}$ (kcal/mol)	deviation from experiments (theory − experiment) (kcal/mol)			
		G2	G3//B3LYP	CBS-Q	CBS-QB3
H_2	0.00	−1.08	−0.42	−1.14	−1.14
SiH_4	8.20 ± 0.74	−1.55	−0.77	−2.08	−2.83
$:SiH_2$ (singlet)	65.20 ± 0.50	−2.20	−1.91	−1.69	−2.51
$:SiH_2$ (triplet)	86.66 ± 0.72	−0.29	−1.67	−1.34	−1.97
H_3SiSiH_3	19.05 ± 0.31	−1.56	−0.99	−2.07	−3.46
$:SiHSiH_3$	75.05 ± 1.91	−1.98	−1.99	−1.59	−3.16
$H_2Si{=}SiH_2$	65.73 ± 0.96	0.23	0.04	−0.05	−1.56
$H_3SiSiH_2SiH_3$	28.90 ± 1.00	−2.27	−2.09	−2.95	−4.97
AAD[b]		1.39	1.23	1.61	2.70

[a] The experimental data are taken from Katzer et al.[26] [b] Absolute average deviation (AAD).

The heat of formation of a given molecule Si_xH_y can be calculated from its atomization energy using the following equation:

$$\Delta H^\circ_{f,298}(Si_xH_y) = [x\Delta H^\circ_{f,298}(Si) + y\Delta H^\circ_{f,298}(H)] - \Delta H^\circ_{a,298}(Si_xH_y) \quad (1)$$

where the heats of formation of atomic silicon and hydrogen are the experimental values obtained from the JANAF tables[28] ($\Delta H^\circ_{f,298}(Si) = 107.55$ kcal/mol, $\Delta H^\circ_{f,298}(H) = 52.10$ kcal/mol) and $\Delta H^\circ_{a,298}(Si_xH_y)$ is the atomization energy defined as the

TABLE 2: Electronic Energy (E_{el}), Enthalpy at 298 K (H^{298}), Standard Heats of Formation Using Atomization Energies [$\Delta H^{\circ}_{f,298}$(AE)] and Standard Heats of Formation Using Bond Additivity Corrections [$\Delta H^{\circ}_{f,298}$(BAC)] of 135 Silicon Hydrides from G3//B3LYP Calculations Compared with the Values Taken from Katzer et al.[26]

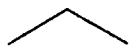
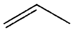
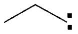
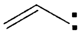
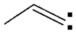
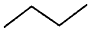
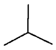
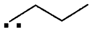
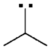
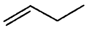
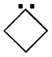
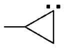
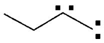
Species		E_{el} (Hartree)	H^{298} (Hartree)	$\Delta H^{0}_{f,298}$ (AE) (kcal/mol)	$\Delta H^{0}_{f,298}$ (BAC) (kcal/mol)	$\Delta H^{0}_{f,298}$ (Katzer) (kcal/mol)
Structure	#					
H_2	**(1)**	-1.167475	-1.164170	-0.4	0.0	0.0
			Si_1 -Si_2			
SiH_4	**(2)**	-291.771258	-291.707211	7.4	8.1	8.2
$:SiH_2$	**(3)**	-290.458501	-290.454686	63.3	65.2	65.2
$H_2Si{=}Si:$	**(4)**	-579.784725	-579.779785	105.3	105.0	108.8
H_3SiSiH_3	**(5)**	-582.251907	-582.245826	18.1	19.3	19.1
$H_3SiSi:H$	**(6)**	-581.000538	-580.994669	73.1	75.1	76.2
$H_2Si{=}SiH_2$	**(7)**	-581.011805	-581.006288	65.8	65.7	67.2
$HSi:Si:H$	**(8)**	-579.779893	-579.774655	108.5	111.0	111.0
			Si_3			
	**(9)**	-872.796072	-872.787429	26.8	28.8	28.8
	**(10)**	-871.560745	-871.552760	71.5	72.1	74.6
	**(11)**	-871.546867	-871.538688	80.3	82.4	86.2
	**(12)**	-871.546688	-871.538482	80.4	83.1	86.1
	**(13)**	-871.574714	-871.567282	62.4	64.3	67.3
	**(14)**	-870.326131	-870.318807	115.7	117.0	-
	**(15)**	-870.332297	-870.324737	112.0	114.5	-
	**(16)**	-870.335466	-870.328255	109.7	110.1	-
	**(17)**	-870.347140	-870.340463	102.1	104.2	115.5
	**(18)**	-870.345874	-870.339181	102.9	103.5	112.0
	**(19)**	-869.112992	-869.106020	146.6	149.6	-
	**(20)**	-869.152278	-869.146519	121.2	123.0	-
			Si_4			
	**(21)**	-1163.340732	-1163.329489	35.3	37.9	38.3
	**(22)**	-1163.343582	-1163.332093	33.6	36.2	37.5
	**(23)**	-1162.153423	-1162.144152	49.0	51.6	55.3
	**(24)**	-1162.124672	-1162.114619	67.5	70.2	74.1
	**(25)**	-1162.093434	-1162.082648	87.6	90.3	96.4
	**(26)**	-1162.091508	-1162.080706	88.8	92.1	95.5
	**(27)**	-1162.096321	-1162.085363	85.9	89.2	92.2
	**(28)**	-1162.106043	-1162.095477	79.5	80.8	84.5
	**(29)**	-1160.909930	-1160.901079	98.9	101.7	108.8
	**(30)**	-1160.896579	-1160.887302	107.5	110.3	121.2
	**(31)**	-1160.929882	-1160.921292	86.2	87.5	95.6
	**(32)**	-1160.879165	-1160.869123	119.0	122.2	-

TABLE 2 (Continued)

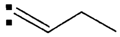
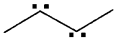
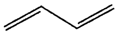
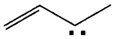
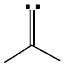
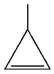
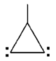
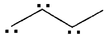
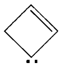
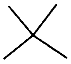
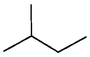
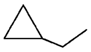
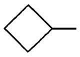
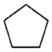
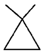
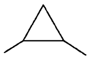
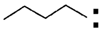
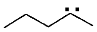
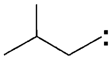
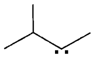
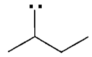
Species		E_{el} (Hartree)	H^{298} (Hartree)	$\Delta H^{o}_{f,298}$ (AE) (kcal/mol)	$\Delta H^{o}_{f,298}$ (BAC) (kcal/mol)	$\Delta H^{o}_{f,298}$ (Katzer) (kcal/mol)
Structure	#					
	**(33)**	-1160.880713	-1160.870909	117.8	118.8	-
	**(34)**	-1160.885663	-1160.875534	114.9	117.6	-
	**(35)**	-1160.871847	-1160.861858	123.5	123.5	-
	**(36)**	-1160.873728	-1160.863648	122.4	123.8	-
	**(37)**	-1160.889511	-1160.879675	112.3	113.3	-
	**(38)**	-1160.899152	-1160.889748	106.0	107.3	116.9
	**(39)**	-1160.892124	-1160.882550	110.5	111.9	121.1
	**(40)**	-1159.697281	-1159.688495	129.7	132.4	-
	**(41)**	-1159.670232	-1159.661344	146.7	149.9	-
	**(42)**	-1159.719182	-1159.711361	115.4	116.8	-
Si$_5$						
	**(43)**	-1453.894433	-1453.879934	38.5	41.7	45.0
	**(44)**	-1453.888771	-1453.874726	41.7	45.0	46.9
	**(45)**	-1453.885744	-1453.871814	43.6	46.8	47.7
	**(46)**	-1452.669882	-1452.657167	75.7	79.0	83.5
	**(47)**	-1452.701784	-1452.689680	55.3	58.6	63.2
	**(48)**	-1452.715110	-1452.703418	46.3	49.7	52.9
	**(49)**	-1452.677903	-1452.665079	70.7	74.0	79.9
	**(50)**	-1452.675118	-1452.662362	72.4	75.7	80.7
	**(51)**	-1452.636454	-1452.623049	97.1	101.0	105.5
	**(52)**	-1452.638695	-1452.625312	95.7	99.0	106.2
	**(53)**	-1452.640536	-1452.627225	94.5	97.8	106.5
	**(54)**	-1452.639943	-1452.626392	95.0	98.9	104.8
	**(55)**	-1452.643068	-1452.629418	93.1	96.5	103.2
	**(56)**	-1452.641757	-1452.628186	93.9	97.8	103.5

TABLE 2 (Continued)

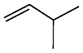
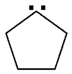
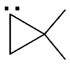
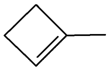
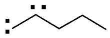
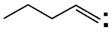
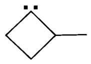
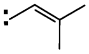
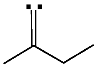
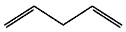
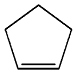
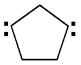
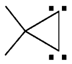
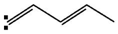
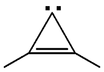
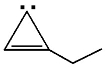
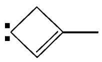
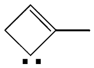
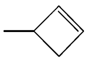
Species		E_{el} (Hartree)	H^{298} (Hartree)	$\Delta H^0_{f,298}$ (AE) (kcal/mol)	$\Delta H^0_{f,298}$ (BAC) (kcal/mol)	$\Delta H^0_{f,298}$ (Katzer) (kcal/mol)
Structure	#					
	**(57)**	-1452.650906	-1452.637686	87.9	89.8	93.8
	**(58)**	-1452.653849	-1452.640445	86.2	88.1	92.2
	**(59)**	-1451.471304	-1451.460092	96.4	99.9	107.5
	**(60)**	-1451.444485	-1451.432035	114.3	117.8	126.5
	**(61)**	-1451.481583	-1451.470200	90.4	92.4	101.6
	**(62)**	-1451.424319	-1451.411635	127.1	131.0	-
	**(63)**	-1451.425704	-1451.413233	126.1	127.8	-
	**(64)**	-1451.432532	-1451.419980	121.9	125.2	-
	**(65)**	-1451.460524	-1451.448904	103.7	107.2	116.2
	**(66)**	-1451.442649	-1451.430708	115.2	118.6	131.1
	**(67)**	-1451.421040	-1451.408464	129.1	131.2	-
	**(68)**	-1451.425147	-1451.412406	126.7	129.3	-
	**(69)**	-1451.435271	-1451.422832	120.1	121.8	-
	**(70)**	-1451.415760	-1451.403168	132.4	133.1	-
	**(71)**	-1451.488928	-1451.477888	85.6	87.5	94.5
	**(72)**	-1450.217505	-1450.205914	153.6	156.6	-
	**(73)**	-1450.230086	-1450.219295	145.2	148.8	-
	**(74)**	-1450.251303	-1450.239899	132.3	135.6	-
	**(75)**	-1450.197747	-1450.185918	166.2	167.5	-
	**(76)**	-1450.259024	-1450.247588	127.5	129.6	-
	**(77)**	-1450.251475	-1450.240362	132.0	134.1	-
	**(78)**	-1450.270471	-1450.259788	119.8	121.9	-
	**(79)**	-1450.271631	-1450.260927	119.1	121.2	-
	**(80)**	-1450.269252	-1450.258614	120.6	122.7	-

TABLE 2 (Continued)

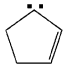
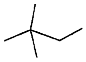
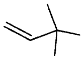
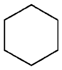
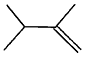
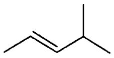
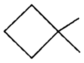
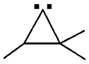
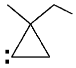
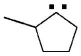
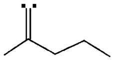
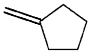
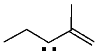
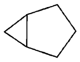
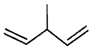
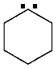
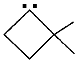
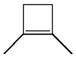
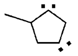
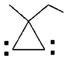
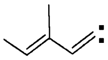
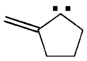
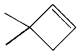
Species		E_{el} (Hartree)	H^{298} (Hartree)	$\Delta H^0_{f,298}$ (AE) (kcal/mol)	$\Delta H^0_{f,298}$ (BAC) (kcal/mol)	$\Delta H^0_{f,298}$ (Katzer) (kcal/mol)
Structure	#					
	**(81)**	-1450.198353	-1450.186423	165.9	166.6	-
	**(82)**	-1450.261239	-1450.250899	125.4	127.5	-
			Si_6			
	**(83)**	-1744.440455	-1744.423336	46.1	50.0	-
	**(84)**	-1743.205715	-1743.189295	90.4	93.0	-
	**(85)**	-1743.266882	-1743.252867	50.5	54.4	-
	**(86)**	-1743.206613	-1743.190458	89.6	92.2	-
	**(87)**	-1743.203847	-1743.187631	91.4	94.0	-
	**(88)**	-1743.253946	-1743.238896	59.2	63.2	-
	**(89)**	-1741.996465	-1741.981323	118.3	122.4	-
	**(90)**	-1741.990262	-1741.975198	122.1	126.2	-
	**(91)**	-1742.019683	-1742.005587	103.0	107.1	-
	**(92)**	-1741.980438	-1741.965326	128.3	130.6	-
	**(93)**	-1742.034029	-1742.020347	93.8	96.4	-
	**(94)**	-1741.973798	-1741.958542	132.6	135.3	-
	**(95)**	-1742.054050	-1742.040980	80.8	84.8	-
	**(96)**	-1741.965154	-1741.949717	138.1	139.4	-
	**(97)**	-1742.022780	-1742.009200	100.8	104.9	-
	**(98)**	-1742.012588	-1741.997960	107.8	111.9	-
	**(99)**	-1742.033295	-1742.019037	94.6	97.2	-
	**(100)**	-1740.780631	-1740.766993	150.2	154.4	-
	**(101)**	-1740.798257	-1740.784283	139.3	143.3	-
	**(102)**	-1740.749747	-1740.735070	170.2	171.2	-
	**(103)**	-1740.804893	-1740.791731	134.6	137.4	-
	**(104)**	-1740.820791	-1740.807149	125.0	127.7	-

TABLE 2 (Continued)

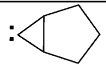
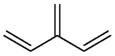
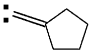
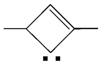
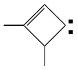
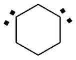
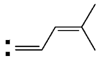
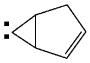
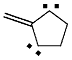
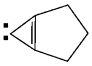
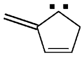
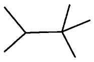
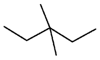
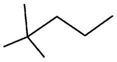
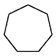
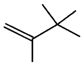
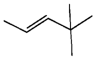
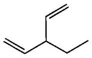
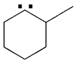
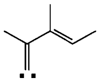
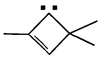
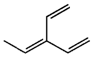
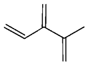
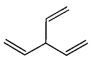
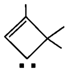
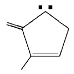
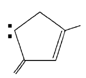
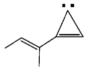
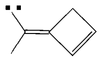
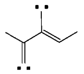
Species		E_{el} (Hartree)	H^{298} (Hartree)	$\Delta H^0_{f,298}$ (AE) (kcal/mol)	$\Delta H^0_{f,298}$ (BAC) (kcal/mol)	$\Delta H^0_{f,298}$ (Katzer) (kcal/mol)
Structure	#					
	**(105)**	-1740.825773	-1740.813178	121.2	125.3	-
	**(106)**	-1740.736290	-1740.721486	178.7	178.7	-
	**(107)**	-1740.811417	-1740.798532	130.4	132.7	-
	**(108)**	-1740.822099	-1740.808582	124.1	126.8	-
	**(109)**	-1740.821244	-1740.807705	124.6	127.4	-
	**(110)**	-1740.779037	-1740.765894	150.8	155.1	-
	**(111)**	-1740.750213	-1740.735643	169.8	170.8	-
	**(112)**	-1739.596493	-1739.584377	162.1	165.0	-
	**(113)**	-1739.572785	-1739.560103	177.4	180.3	-
	**(114)**	-1739.631919	-1739.619915	139.8	142.7	-
	**(115)**	-1739.577589	-1739.564801	174.4	175.9	-
Si_7						
	**(116)**	-2034.989773	-2034.969834	51.8	56.4	-
	**(117)**	-2034.986538	-2034.966834	53.7	58.2	-
	**(118)**	-2034.985654	-2034.965909	54.2	58.8	-
	**(119)**	-2033.809901	-2033.793220	60.0	64.6	-
	**(120)**	-2033.758967	-2033.739909	93.5	96.7	-
	**(121)**	-2033.755887	-2033.736682	95.5	98.7	-
	**(122)**	-2032.517403	-2032.498980	142.0	144.0	-
	**(123)**	-2032.510933	-2032.492864	145.9	147.8	-
	**(124)**	-2032.572420	-2032.555988	106.3	111.0	-
	**(125)**	-2031.305963	-2031.288260	171.7	173.3	-

TABLE 2 (Continued)

Species		E_{el} (Hartree)	H^{298} (Hartree)	$\Delta H^0_{f,298}$ (AE) (kcal/mol)	$\Delta H^0_{f,298}$ (BAC) (kcal/mol)	$\Delta H^0_{f,298}$ (Katzer) (kcal/mol)
Structure	#					
	**(126)**	-2031.373683	-2031.357146	128.4	131.9	-
	**(127)**	-2031.286531	-2031.269042	183.7	184.3	-
	**(128)**	-2031.289383	-2031.271829	182.0	182.6	-
	**(129)**	-2031.275998	-2031.258547	190.3	190.9	-
	**(130)**	-2031.373240	-2031.356621	128.8	132.2	-
	**(131)**	-2030.131671	-2030.115938	177.2	179.3	-
	**(132)**	-2030.130962	-2030.115232	177.6	179.7	-
	**(133)**	-2030.121837	-2030.105749	183.6	185.7	-
	**(134)**	-2030.123046	-2030.107574	182.4	185.1	-
	**(135)**	-2030.070427	-2030.053780	216.2	218.5	-

enthalpy change upon decomposition of a molecule into its component atoms, which can be evaluated as

$$\Delta H^\circ_{a,298}(Si_xH_y) = [xH^{298}(Si) + yH^{298}(H)] - H^{298}(Si_xH_y) \quad (2)$$

where $H^{298}(Si)$ and $H^{298}(H)$ are the enthalpies of atomic silicon and hydrogen at 298 K, respectively, and $H^{298}(Si_xH_y)$ is the enthalpy of Si_xH_y at the same temperature. These enthalpies can be calculated as the sum of the electronic energies (E_{el}), zero-point energies (ZPE), and thermal corrections (E^{298}_{vib}, E^{298}_{tran}, and E^{298}_{rot}) from 0 to 298 K as follows:

$$H^{298} = E_{el} + ZPE + E^{298}_{vib} + E^{298}_{tran} + E^{298}_{rot} + \Delta PV \quad (3)$$

All of the quantities on the right-hand side of eq 3 are obtained from the quantum chemical calculations, and the heat of formation of Si_xH_y is then calculated.

In this work, the standard entropy and the heat capacities of the molecules were estimated from the vibrational frequencies obtained from quantum chemical calculations, scaled by appropriate scaling factors suggested by Scott and Radom.[29] The rigid-rotor, harmonic-oscillator approximation was used for all molecules. Symmetry corrections were included in standard entropy values, but they were removed before fitting the group additivity values as suggested by Benson.[24]

Results and Discussion

I. Thermochemical Properties Calculated from Quantum Chemistry. Heats of formation of eight small ($<Si_4$) silicon hydrides with experimental data available were estimated from the four different methods mentioned above, and the deviations between the predicted and experimental values are listed in Table 1. Among the methods used, G3//B3LYP was the most accurate with an average absolute deviation of 1.23 kcal/mol from experimental measurements. In addition, G3//B3LYP had the smallest maximum absolute deviation of 2.09 kcal/mol. Note that the average uncertainty in the experimental measurements is 0.77 kcal/mol, and thus it may contribute significantly to the deviations observed between the experimental and calculated results. The performance of G3//B3LYP is consistent with results in the literature, where G3//B3LYP has the smallest average absolute deviation of 0.93 kcal/mol, compared to 1.56 kcal/mol for G2, 1.54 kcal/mol for CBS-Q, and 1.26 kcal/mol for CBS-QB3, when heats of formation of 148 molecules in the G2/97 test set were evaluated.[1] We also investigated the efficiencies of these methods using four saturated silicon−hydrogen molecules of different size, and the run time for each method was normalized to the CBS-Q run time for a given molecule. As shown in Figure 1, CBS-Q is the least expensive method and CBS-QB3 is the most expensive method for Si_1−Si_3 and comparable to the most expensive method, G2, for Si_4. G3//B3LYP takes about twice as long as G2 to run for silane (SiH_4) and about 1.5 times longer than G2 for disilane (Si_2H_6). However, G2 becomes more expensive than G3//B3LYP for the larger molecules, where G3//B3LYP only takes 0.99 of the G2 run time for trisilane (Si_3H_8) and 0.75 of the G2 run time for tetrasilane (Si_4H_{10}). The normalized G2 run time goes up with increasing molecule size, while the normalized run time for the other methods remains essentially the same. This is because the longest single-point calculation in G2 theory is at

TABLE 3: Thermochemical Properties Including Standard Entropies (S^{298}) and Heat Capacities (C_p) at Various Temperatures of 135 Silicon Hydrides Calculated from G3//B3LYP Calculations

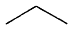
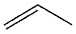
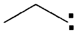
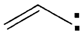
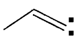
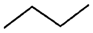
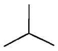
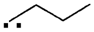
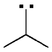
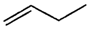
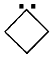
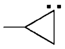
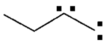
Species		S^{298}	C_p (cal/(mol K))						
Structure	#	(cal/(mol K))	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
H_2	**(1)**	32.5	7.0	7.0	7.0	7.0	7.0	7.1	7.5
				Si_1 -Si_2					
SiH_4	**(2)**	53.8	10.2	12.3	14.1	15.7	18.3	20.2	22.9
$:SiH_2$	**(3)**	51.0	8.3	8.8	9.3	9.9	10.9	11.7	12.8
$H_2Si{=}Si:$	**(4)**	63.1	13.0	14.0	14.8	15.5	16.6	17.4	18.6
H_3SiSiH_3	**(5)**	68.8	19.0	22.9	25.9	28.5	32.5	35.4	39.4
$H_3SiSi:H$	**(6)**	69.0	16.6	18.9	20.8	22.3	24.8	26.6	29.1
$H_2Si{=}SiH_2$	**(7)**	65.4	16.8	19.2	20.9	22.4	24.8	26.5	29.0
$HSi:Si:H$	**(8)**	64.1	13.7	14.6	15.2	15.8	16.8	17.6	18.7
				Si_3					
	**(9)**	84.3	28.1	33.5	37.8	41.2	46.6	50.5	55.8
	**(10)**	80.8	25.3	29.4	32.4	34.9	38.7	41.5	45.4
	**(11)**	82.4	25.2	29.1	32.2	34.7	38.7	41.5	45.5
	**(12)**	83.2	25.4	29.4	32.5	35.0	38.9	41.7	45.5
	**(13)**	76.3	25.3	29.6	32.6	35.1	38.9	41.6	45.5
	**(14)**	78.2	22.3	25.0	26.9	28.5	30.9	32.7	35.1
	**(15)**	82.2	21.6	24.3	26.3	27.9	30.5	32.3	34.9
	**(16)**	78.8	21.2	24.0	26.1	27.8	30.4	32.3	34.9
	**(17)**	73.9	21.4	24.3	26.4	28.0	30.6	32.4	35.0
	**(18)**	73.9	21.4	24.4	26.5	28.1	30.7	32.5	35.0
	**(19)**	78.5	18.8	20.1	21.0	21.7	22.9	23.7	24.7
	**(20)**	70.3	17.4	19.2	20.3	21.1	22.4	23.3	24.5
				Si_4					
	**(21)**	99.5	37.1	44.1	49.5	53.9	60.7	65.6	72.3
	**(22)**	100.4	37.3	44.2	49.5	53.9	60.7	65.5	72.3
	**(23)**	86.0	33.1	39.3	43.8	47.4	52.8	56.6	61.9
	**(24)**	91.2	34.1	39.9	44.2	47.6	52.9	56.6	61.9
	**(25)**	98.3	34.1	39.6	43.9	47.4	52.7	56.6	61.9
	**(26)**	99.4	34.5	40.1	44.3	47.7	53.0	56.8	62.0
	**(27)**	98.9	34.4	39.9	44.1	47.6	52.9	56.7	61.9
	**(28)**	96.0	34.4	40.0	44.2	47.6	52.9	56.6	61.9
	**(29)**	84.8	30.0	34.7	38.1	40.7	44.7	47.6	51.5
	**(30)**	88.0	30.2	34.7	38.0	40.6	44.6	47.4	51.4
	**(31)**	84.3	29.5	34.5	37.9	40.6	44.6	47.5	51.4
	**(32)**	96.7	30.6	34.9	38.1	40.6	44.6	47.4	51.4

TABLE 3 (Continued)

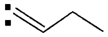
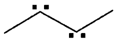
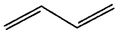
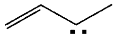
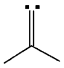
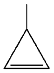
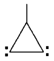
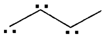
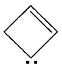
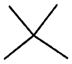
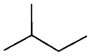
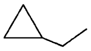
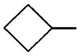
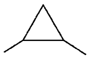
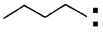
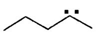
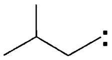
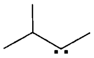
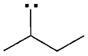
Species		S^{298} (cal/(mol K))	C_p (cal/(mol K))						
Structure	#		300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	**(33)**	93.9	30.3	34.7	37.9	40.5	44.5	47.4	51.4
	**(34)**	102.3	29.6	34.0	37.3	40.0	44.2	47.1	51.2
	**(35)**	92.6	31.9	36.0	39.0	41.3	45.0	47.7	51.5
	**(36)**	95.6	31.0	35.2	38.3	40.8	44.8	47.5	51.4
	**(37)**	95.3	29.5	33.9	37.3	40.0	44.2	47.2	51.3
	**(38)**	91.1	29.8	34.4	37.8	40.4	44.5	47.4	51.4
	**(39)**	90.0	30.7	35.1	38.3	40.9	44.8	47.6	51.5
	**(40)**	90.1	26.1	29.3	31.6	33.5	36.2	38.2	40.9
	**(41)**	88.9	26.7	29.8	32.0	33.8	36.5	38.4	41.0
	**(42)**	80.4	26.0	29.5	31.9	33.7	36.4	38.3	40.9
					Si_5				
	**(43)**	116.7	46.6	54.8	61.3	66.5	74.7	80.7	88.7
	**(44)**	114.6	46.3	54.8	61.3	66.6	74.8	80.6	88.7
	**(45)**	115.7	46.2	54.8	61.4	66.7	74.9	80.7	88.7
	**(46)**	106.7	43.1	50.6	56.0	60.4	67.0	71.7	78.3
	**(47)**	101.4	42.2	49.9	55.5	60.0	66.9	71.7	78.3
	**(48)**	96.8	40.7	48.7	54.4	59.0	65.8	70.7	77.3
	**(49)**	105.8	42.9	50.3	55.7	60.1	66.8	71.6	78.3
	**(50)**	106.0	42.9	50.3	55.8	60.1	66.9	71.6	78.3
	**(51)**	113.5	43.5	50.7	56.1	60.5	67.2	71.9	78.5
	**(52)**	113.5	43.1	50.3	55.7	60.1	66.9	71.7	78.3
	**(53)**	112.6	43.0	50.2	55.6	60.0	66.8	71.6	78.3
	**(54)**	113.0	43.6	50.7	56.1	60.4	67.1	71.9	78.4
	**(55)**	114.5	43.2	50.3	55.6	60.0	66.8	71.6	78.3
	**(56)**	113.9	43.5	50.6	55.9	60.3	67.0	71.8	78.4

TABLE 3 (Continued)

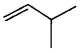
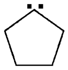
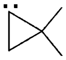
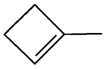
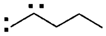
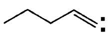
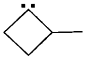
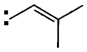
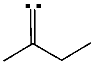
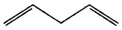
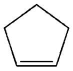
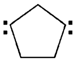
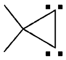
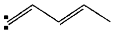
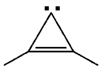
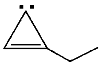
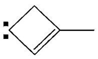
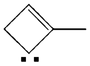
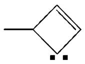
Species		S^{298}	C_p (cal/(mol K))						
Structure	#	(cal/(mol K))	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	**(57)**	111.0	43.5	50.7	56.0	60.3	67.0	71.7	78.3
	**(58)**	111.0	43.6	50.7	56.0	60.3	67.0	71.7	78.3
	**(59)**	96.1	37.8	44.2	48.8	52.4	57.9	61.7	66.9
	**(60)**	107.9	39.4	45.2	49.6	53.1	58.6	62.4	67.8
	**(61)**	100.0	38.2	44.7	49.3	53.0	58.5	62.4	67.8
	**(62)**	111.4	39.7	45.6	49.9	53.4	58.8	62.6	67.9
	**(63)**	109.5	39.3	45.3	49.7	53.2	58.7	62.5	67.8
	**(64)**	114.3	38.5	44.6	49.1	52.7	58.3	62.2	67.7
	**(65)**	100.0	38.9	45.2	49.7	53.3	58.7	62.6	67.9
	**(66)**	102.9	39.3	45.3	49.8	53.3	58.7	62.5	67.8
	**(67)**	109.1	40.0	45.8	50.1	53.5	58.8	62.6	67.9
	**(68)**	109.3	39.8	45.6	49.9	53.4	58.8	62.6	67.9
	**(69)**	110.0	38.6	44.6	49.1	52.7	58.3	62.3	67.7
	**(70)**	107.6	40.8	46.6	50.7	54.0	59.1	62.8	67.9
	**(71)**	98.0	38.4	45.0	49.6	53.2	58.7	62.5	67.8
	**(72)**	103.9	35.8	40.4	43.8	46.5	50.6	53.5	57.4
	**(73)**	95.7	35.7	40.6	44.0	46.7	50.8	53.6	57.5
	**(74)**	103.3	34.7	39.4	43.0	45.8	50.0	53.0	57.2
	**(75)**	106.0	36.1	40.7	44.0	46.6	50.6	53.4	57.4
	**(76)**	105.7	34.5	39.3	42.9	45.7	50.0	53.0	57.2
	**(77)**	102.5	35.0	39.9	43.4	46.1	50.3	53.2	57.3
	**(78)**	96.7	34.8	39.8	43.4	46.1	50.3	53.2	57.3
	**(79)**	96.8	34.8	39.8	43.3	46.1	50.3	53.2	57.3
	**(80)**	95.3	35.1	40.1	43.6	46.4	50.5	53.4	57.4
	**(81)**	104.5	37.3	41.7	44.7	47.1	50.9	53.6	57.4

TABLE 3 (Continued)

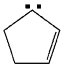
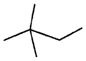
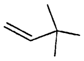
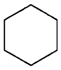
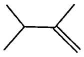
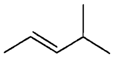
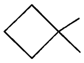
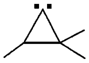
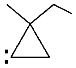
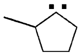
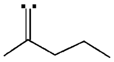
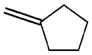
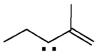
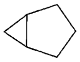
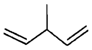
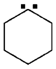
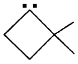
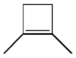
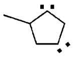
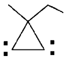
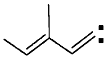
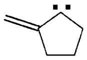
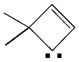
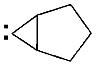
Species		S^{298}	C_p (cal/(mol K))						
Structure	#	(cal/(mol K))	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	**(82)**	93.9	34.9	40.1	43.7	46.5	50.6	53.4	57.4
			Si$_6$						
	**(83)**	131.3	55.7	65.5	73.1	79.3	88.9	95.7	105.1
	**(84)**	126.6	53.0	61.4	67.8	73.0	81.0	86.7	94.7
	**(85)**	109.6	50.4	60.1	67.0	72.6	80.9	86.7	94.8
	**(86)**	126.7	52.4	61.0	67.5	72.7	80.9	86.6	94.7
	**(87)**	127.6	52.3	61.0	67.5	72.8	80.9	86.7	94.7
	**(88)**	116.7	51.4	60.5	67.2	72.6	80.9	86.7	94.7
	**(89)**	122.1	48.1	55.6	61.1	65.6	72.5	77.4	84.2
	**(90)**	122.4	48.4	55.9	61.4	65.9	72.7	77.5	84.2
	**(91)**	113.0	47.9	55.8	61.5	66.0	72.9	77.7	84.4
	**(92)**	125.4	47.6	55.2	60.9	65.5	72.5	77.4	84.2
	**(93)**	110.8	47.6	55.7	61.5	66.0	72.8	77.6	84.3
	**(94)**	123.2	48.7	56.0	61.5	65.9	72.7	77.5	84.2
	**(95)**	104.3	47.3	55.7	61.5	66.1	72.9	77.7	84.3
	**(96)**	122.9	50.1	57.3	62.6	66.7	73.2	77.9	84.4
	**(97)**	109.0	47.3	55.5	61.3	65.9	72.8	77.7	84.3
	**(98)**	116.0	48.1	55.7	61.3	65.8	72.7	77.6	84.3
	**(99)**	115.9	47.0	54.9	60.8	65.4	72.4	77.3	84.1
	**(100)**	111.0	44.8	51.1	55.7	59.3	64.8	68.7	73.9
	**(101)**	117.1	43.8	50.1	54.8	58.5	64.2	68.1	73.6
	**(102)**	122.0	45.0	51.0	55.5	59.1	64.5	68.4	73.7
	**(103)**	109.4	44.3	50.9	55.5	59.2	64.7	68.5	73.8
	**(104)**	110.8	44.4	50.8	55.3	59.0	64.5	68.4	73.8
	**(105)**	104.7	43.5	50.5	55.3	59.1	64.6	68.5	73.8

TABLE 3 (Continued)

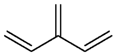
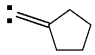
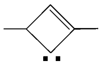
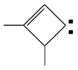
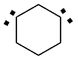
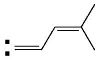
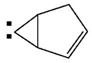
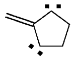
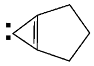
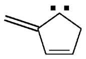
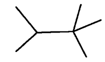
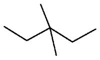
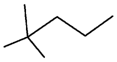
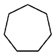
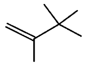
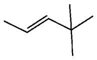
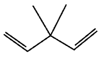
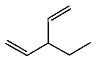
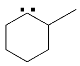
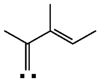
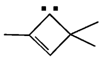
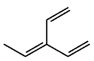
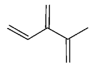
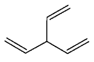
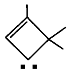
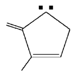
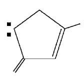
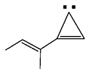
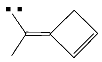
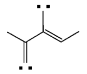
Species		S^{298}	C_p (cal/(mol K))						
Structure	#	(cal/(mol K))	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	**(106)**	120.7	47.2	53.0	57.0	60.2	65.2	68.8	73.9
	**(107)**	110.6	43.1	50.0	54.9	58.7	64.4	68.3	73.7
	**(108)**	111.7	43.8	50.3	55.0	58.7	64.3	68.3	73.7
	**(109)**	111.6	43.9	50.4	55.1	58.8	64.4	68.3	73.7
	**(110)**	109.0	44.2	50.8	55.5	59.2	64.7	68.6	73.9
	**(111)**	121.2	44.8	50.9	55.4	59.0	64.5	68.4	73.7
	**(112)**	102.8	40.6	46.1	49.7	52.5	56.6	59.5	63.4
	**(113)**	107.5	41.0	46.1	49.7	52.4	56.5	59.4	63.4
	**(114)**	104.8	39.2	44.8	48.7	51.7	56.1	59.1	63.2
	**(115)**	107.7	41.5	46.6	50.0	52.7	56.6	59.5	63.4
			Si$_7$						
	**(116)**	146.3	64.9	76.2	84.9	92.0	103.0	110.7	121.5
	**(117)**	145.0	64.7	76.2	84.9	92.0	103.0	110.8	121.6
	**(118)**	146.0	64.7	76.1	84.9	92.0	103.0	110.8	121.6
	**(119)**	124.5	59.4	70.6	78.8	85.3	95.0	101.8	111.2
	**(120)**	140.8	61.7	71.6	79.2	85.3	94.9	101.6	111.1
	**(121)**	142.7	61.6	71.6	79.2	85.4	94.9	101.7	111.1
	**(122)**	137.6	59.4	68.0	74.3	79.4	87.2	92.9	100.8
	**(123)**	137.3	59.1	68.0	74.4	79.5	87.3	93.0	100.8
	**(124)**	124.4	56.4	66.0	73.0	78.5	86.8	93.0	100.7
	**(125)**	138.6	53.4	61.1	66.8	71.3	78.3	83.2	90.1
	**(126)**	127.4	53.1	60.9	66.7	71.3	78.3	83.3	90.1
	**(127)**	134.5	55.8	63.2	68.5	72.7	79.2	83.8	90.3

TABLE 3 (Continued)

Species		S^{298}	C_p (cal/(mol K))						
Structure	#	(cal/(mol K))	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	**(128)**	134.8	55.9	63.2	68.4	72.6	79.1	83.8	90.3
	**(129)**	135.0	56.4	63.8	69.0	73.1	79.5	84.0	90.4
	**(130)**	128.0	53.3	61.1	66.8	71.4	78.4	83.3	90.1
	**(131)**	126.5	50.2	56.7	61.4	65.0	70.5	74.4	79.7
	**(132)**	126.3	50.1	56.7	61.4	65.0	70.5	74.4	79.7
	**(133)**	131.0	49.8	56.3	61.0	64.7	70.3	74.2	79.6
	**(134)**	124.1	49.9	56.7	61.5	65.1	70.7	74.5	79.8
	**(135)**	134.6	50.4	56.7	61.3	64.9	70.5	74.4	79.7

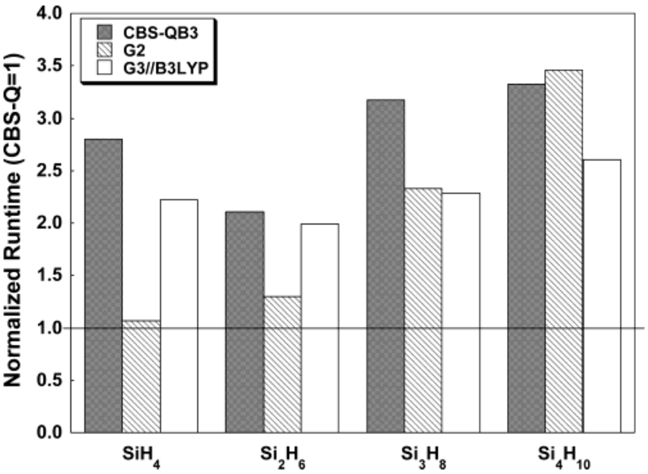


Figure 1. Comparison of the efficiencies of various quantum chemical methods applied to small silicon hydrides. Run time shown was normalized by the CBS-Q run time for each molecule size. Actual run time increases with increasing molecule size for all four methods.

TABLE 4: The Scaling Factors Used to Estimate Standard Entropies and Heat Capacities at Different Temperatures Based on B3LYP/6-31G(d) Frequencies

temperature (K)	298	300	400	500	600	800	1000	1500
scaling factor[a]	1.002	1.001	0.998	0.994	0.991	0.984	0.977	0.960

[a] Values were extrapolated from Scott and Radom,[29] where the scaling factors of 1.0015 at 298 K, 0.9957 at 450 K, and 0.9910 at 600 K are suggested.

the MP4 level [MP4/6-311G(2df,p)], which has higher scaling than the most computationally expensive steps in the other three methods, which are at the MP2 level of theory.

On the basis of its superior accuracy and its relative efficiency, we chose G3//B3LYP to evaluate the thermochemistry of silicon hydrides that have no experimental thermochemical data available. A total of 135 molecules up to a moderate size ($<Si_8$) were investigated. The ground state for all molecules is reported as the singlet state. This assumption was supported by the calculations performed by Katzer et al.[26] and our own selected B3LYP/6-31G(d) calculations of species containing multiple adjacent silylene atoms such as HSi:Si:H and HSi:Si:Si:H for which the singlet state was lower in energy than the triplet state. The electronic energies, the enthalpies at 298 K, and the heats of formation derived from the G3//B3LYP calculations for all of these molecules are listed in Table 2, along with the ab initio values with empirical corrections reported by Katzer et al.,[26] and the standard entropies and heat capacities at different temperatures from the G3//B3LYP calculations are summarized in Table 3. The standard entropy values are based on the B3LYP/6-31G(d) vibrational frequencies scaled by 1.0015 as suggested by Scott and Radom.[29] On the basis of the values suggested by Scott and Radom for estimating the entropies at different temperatures using B3LYP/6-31G(d) frequencies, we also extrapolated a temperature dependence of the scaling factor as shown in Table 4. This extrapolation was then used to calculate the heat capacities at different temperatures. To our knowledge, no scaling factors for the temperature range of interest for the heat capacities have been reported.

The thermochemical properties of cyclopentasilane (**48**) and cyclopentasilylene (**59**) were corrected slightly from the values calculated from G3//B3LYP theory. As suggested by Katzer et al.,[30,31] both molecules have one very low-frequency vibrational mode, which is best treated as a pseudorotation, as is done for cyclopentane (C_5H_{10}).[32,33] This treatment lowers the heat of formation and heat capacity by $RT/2$ and $R/2$, respectively, where R is the universal gas constant and T is the absolute temperature. It also lowers the standard entropy at 298 K by 4.419 cal/(mol K) for cyclopentasilane and 0.358 cal/(mol K) for cyclopentasilylene, as reported by Katzer.[34]

It is widely known that constructing isodesmic reactions can improve predictions of heats of formation using quantum chemical calculations. In this approach, a hypothetical reaction is chosen with the same number of chemical bonds of each type on both sides of the reaction. The reaction is comprised of reference molecules, that is, those species with experimental

TABLE 5: Comparison of Heats of Formation Calculated Using Atomization Energies (AE), Bond Additivity Corrections (BAC), and Homodesmotic Reactions (HR) from G3//B3LYP

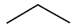
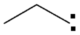
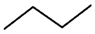
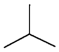
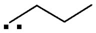
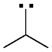
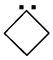
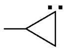
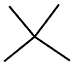
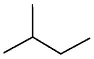
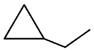
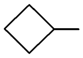
Species		Homodesmotic Reactions	$\Delta H^0_{f,298}$ (kcal/mol)		
Structure	#		HR	AE	BAC
	**(9)**	**(9)** + $SiH_4 \rightarrow 2\ H_3SiSiH_3$	28.02	26.81	28.75
	**(11)**	**(11)** + $:SiH_2 \rightarrow 2\ H_3SiSi{:}H$	82.36	80.29	82.36
	**(12)**	**(12)** + $SiH_4 \rightarrow H_3SiSiH_3 + H_3SiSi{:}H$	82.64	80.42	83.07
		(12) + $1/2\ SiH_4 \rightarrow 1/2\ H_3SiSiH_2SiH_3 + H_3SiSi{:}H$	83.07		
	**(13)**	**(13)** + $3\ SiH_4 \rightarrow 3\ H_3SiSiH_3$	63.03	62.35	64.33
		(13) + $2\ SiH_4 \rightarrow H_3SiSiH_2SiH_3 + H_3SiSiH_3$	63.90		
		(13) + $3/2\ SiH_4 \rightarrow 3/2\ H_3SiSiH_2SiH_3$	64.33		
		(13) + $3\ H_3SiSiH_3 \rightarrow 3\ H_3SiSiH_2SiH_3$	65.64		
	**(17)**	**(17)** + $2\ SiH_4 + :SiH_2 \rightarrow H_3SiSiH_3 + 2\ H_3SiSi{:}H$	103.61	102.08	104.19
		(17) + $3/2\ SiH_4 + :SiH_2 \rightarrow 1/2\ H_3SiSiH_2SiH_3 + 2\ H_3SiSi{:}H$	104.04		
	**(21)**	**(21)** + $2\ SiH_4 \rightarrow 3\ H_3SiSiH_3$	36.71	35.27	37.88
		(21) + $SiH_4 \rightarrow H_3SiSiH_2SiH_3 + H_3SiSiH_3$	37.58		
		(21) + $1/2\ SiH_4 \rightarrow 3/2\ H_3SiSiH_2SiH_3$	38.02		
	**(22)**	**(22)** + $2\ SiH_4 \rightarrow 3\ H_3SiSiH_3$	35.08	33.64	36.24
		(22) + $SiH_4 \rightarrow H_3SiSiH_3 + H_3SiSiH_2SiH_3$	35.95		
		(22) + $1/2\ SiH_4 \rightarrow 3/2\ H_3SiSiH_2SiH_3$	36.39		
	**(23)**	**(23)** + $4\ SiH_4 \rightarrow 4\ H_3SiSiH_3$	49.87	48.97	51.61
		(23) + $3\ SiH_4 \rightarrow H_3SiSiH_2SiH_3 + 2\ H_3SiSiH_3$	50.74		
		(23) + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_2SiH_3$	51.61		
		(23) + $4\ H_3SiSiH_3 \rightarrow 4\ H_3SiSiH_2SiH_3$	53.36		
	**(24)**	**(24)** + $4\ SiH_4 \rightarrow 4\ H_3SiSiH_3$	68.40	67.50	70.15
		(24) + $3\ SiH_4 \rightarrow H_3SiSiH_2SiH_3 + 2\ H_3SiSiH_3$	69.82		
		(24) + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_2SiH_3$	70.15		
	**(25)**	**(25)** + $SiH_4 + :SiH_2 \rightarrow H_3SiSiH_3 + 2\ H_3SiSi{:}H$	89.86	87.56	90.29
		(25) + $1/2\ SiH_4 + :SiH_2 \rightarrow 1/2\ H_3SiSiH_2SiH_3 + 2\ H_3SiSi{:}H$	90.29		
	**(26)**	**(26)** + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_3 + H_3SiSi{:}H$	91.22	88.78	92.09
		(26) + $SiH_4 \rightarrow H_3SiSiH_2SiH_3 + H_3SiSi{:}H$	92.09		
	**(27)**	**(27)** + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_3 + H_3SiSi{:}H$	88.30	85.86	89.17
		(27) + $SiH_4 \rightarrow H_3SiSiH_2SiH_3 + H_3SiSi{:}H$	89.17		
	**(29)**	**(29)** + $3\ SiH_4 + :SiH_2 \rightarrow 2\ H_3SiSi{:}H + 2\ H_3SiSiH_3$	100.65	98.90	101.67
		(29) + $2\ SiH_4 + :SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_2SiH_3$	101.52		
	**(30)**	**(30)** + $3\ SiH_4 + :SiH_2 \rightarrow 2\ H_3SiSi{:}H + 2\ H_3SiSiH_3$	109.30	107.54	110.31
		(30) + $2\ SiH_4 + :SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_2SiH_3$	110.17		
	**(43)**	**(43)** + $3\ SiH_4 \rightarrow 4\ H_3SiSiH_3$	40.14	38.47	41.74
		(43) + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	41.01		
		(43) + $SiH_4 \rightarrow 2\ H_3SiSiH_2SiH_3$	41.88		
	**(44)**	**(44)** + $3\ SiH_4 \rightarrow 4\ H_3SiSiH_3$	43.41	41.74	45.01
		(44) + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	44.28		
		(44) + $SiH_4 \rightarrow 2\ H_3SiSiH_2SiH_3$	45.15		
	**(45)**	**(45)** + $3\ SiH_4 \rightarrow 4\ H_3SiSiH_3$	45.24	43.57	46.83
		(45) + $2\ SiH_4 \rightarrow 2\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	46.11		
		(45) + $SiH_4 \rightarrow 2\ H_3SiSiH_2SiH_3$	46.98		
	**(46)**	**(46)** + $5\ SiH_4 \rightarrow 5\ H_3SiSiH_3$	76.79	75.66	78.96
		(46) + $4\ SiH_4 \rightarrow 3\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	77.66		
		(46) + $3\ SiH_4 \rightarrow H_3SiSiH_3 + 2\ H_3SiSiH_2SiH_3$	78.53		
		(46) + $5/2\ SiH_4 \rightarrow 5/2\ H_3SiSiH_2SiH_3$	78.96		
	**(47)**	**(47)** + $5\ SiH_4 \rightarrow 5\ H_3SiSiH_3$	56.38	55.26	58.56
		(47) + $4\ SiH_4 \rightarrow 3\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	57.26		
		(47) + $3\ SiH_4 \rightarrow H_3SiSiH_3 + 2\ H_3SiSiH_2SiH_3$	58.13		
		(47) + $5/2\ SiH_4 \rightarrow 5/2\ H_3SiSiH_2SiH_3$	58.56		

TABLE 5 (Continued)

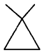
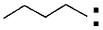
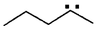
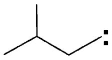
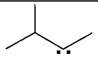
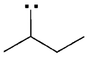
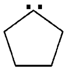
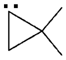
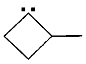
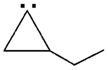
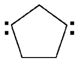
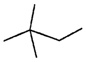
Species		Homodesmotic Reactions	$\Delta H^{0}_{f,298}$ (kcal/mol)		
Structure	#		HR	AE	BAC
	**(48)**	**(48)** $+ 5\ SiH_4 \rightarrow 5\ H_3SiSiH_3$	47.47	46.34	49.65
		(48) $+ 4\ SiH_4 \rightarrow 3\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	48.34		
		(48) $+ 3\ SiH_4 \rightarrow H_3SiSiH_3 + 2\ H_3SiSiH_2SiH_3$	49.21		
		(48) $+ 5/2\ SiH_4 \rightarrow 5/2\ H_3SiSiH_2SiH_3$	49.65		
		(48) $+ 5\ H_3SiSiH_3 \rightarrow 5\ H_3SiSiH_2SiH_3$	51.82		
	**(49)**	**(49)** $+ 5\ SiH_4 \rightarrow 5\ H_3SiSiH_3$	71.82	70.70	74.00
		(49) $+ 4\ SiH_4 \rightarrow 3\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	72.69		
		(49) $+ 3\ SiH_4 \rightarrow H_3SiSiH_3 + 2\ H_3SiSiH_2SiH_3$	73.56		
		(49) $+ 5/2\ SiH_4 \rightarrow 5/2\ H_3SiSiH_2SiH_3$	74.00		
	**(50)**	**(50)** $+ 5\ SiH_4 \rightarrow 5\ H_3SiSiH_3$	73.53	72.40	75.70
		(50) $+ 4\ SiH_4 \rightarrow 3\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	74.40		
		(50) $+ 3\ SiH_4 \rightarrow H_3SiSiH_3 + 2\ H_3SiSiH_2SiH_3$	75.27		
		(50) $+ 5/2\ SiH_4 \rightarrow 5/2\ H_3SiSiH_2SiH_3$	75.70		
	**(51)**	**(51)** $+ 3\ SiH_4 \rightarrow H_3SiSi{:}H + 3\ H_3SiSiH_3$	99.73	97.07	101.04
		(51) $+ 2\ SiH_4 \rightarrow H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	100.61		
		(51) $+ 3/2\ SiH_4 \rightarrow H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	101.04		
	**(52)**	**(52)** $+ 2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 2\ H_3SiSiH_3$	98.17	95.65	99.04
		(52) $+ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_2SiH_3$	99.04		
	**(53)**	**(53)** $+ 2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 2\ H_3SiSiH_3$	96.97	94.45	97.84
		(53) $+ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_2SiH_3$	97.84		
	**(54)**	**(54)** $+ 3\ SiH_4 \rightarrow H_3SiSi{:}H + 3\ H_3SiSiH_3$	97.64	94.97	98.94
		(54) $+ 2\ SiH_4 \rightarrow H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	98.51		
		(54) $+ 3/2\ SiH_4 \rightarrow H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	98.94		
	**(55)**	**(55)** $+ 2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 2\ H_3SiSiH_3$	95.59	93.07	96.46
		(55) $+ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_2SiH_3$	96.46		
	**(56)**	**(56)** $+ 3\ SiH_4 \rightarrow H_3SiSi{:}H + 3\ H_3SiSiH_3$	96.51	93.85	97.82
		(56) $+ 2\ SiH_4 \rightarrow H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	97.38		
		(56) $+ 3/2\ SiH_4 \rightarrow H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	97.82		
	**(59)**	**(59)** $+ 4\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3\ H_3SiSiH_3$	98.41	96.43	99.86
		(59) $+ 3\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	99.28		
		(59) $+ 5/2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	99.71		
	**(60)**	**(60)** $+ 4\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3\ H_3SiSiH_3$	116.31	114.33	117.76
		(60) $+ 3\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	117.18		
		(60) $+ 5/2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	117.62		
	**(65)**	**(65)** $+ 4\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3\ H_3SiSiH_3$	105.72	103.74	107.18
		(65) $+ 3\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	106.60		
		(65) $+ 5/2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	107.03		
	**(66)**	**(66)** $+ 4\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3\ H_3SiSiH_3$	117.14	115.16	118.59
		(66) $+ 3\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + H_3SiSiH_3 + H_3SiSiH_2SiH_3$	118.01		
		(66) $+ 5/2\ SiH_4 + {:}SiH_2 \rightarrow 2\ H_3SiSi{:}H + 3/2\ H_3SiSiH_2SiH_3$	118.45		
	**(73)**	**(73)** $+ 3\ SiH_4 + 2\ {:}SiH_2 \rightarrow 4\ H_3SiSi{:}H + H_3SiSiH_3$	148.06	145.22	148.78
		(73) $+ 5/2\ SiH_4 + 2\ {:}SiH_2 \rightarrow 4\ H_3SiSi{:}H + 1/2\ H_3SiSiH_2SiH_3$	148.49		
	**(83)**	**(83)** $+ 4\ SiH_4 \rightarrow 5\ H_3SiSiH_3$	47.99	46.10	50.02
		(83) $+ 3\ SiH_4 \rightarrow 3\ H_3SiSiH_3 + H_3SiSiH_2SiH_3$	48.86		
		(83) $+ 2\ SiH_4 \rightarrow H_3SiSiH_3 + 2\ H_3SiSiH_2SiH_3$	49.73		
		(83) $+ 3/2\ SiH_4 \rightarrow 5/2\ H_3SiSiH_2SiH_3$	50.17		

TABLE 5 (Continued)

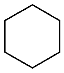
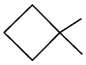
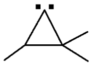
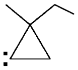
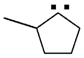
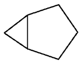
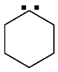
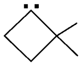
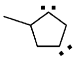
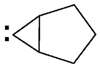
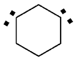
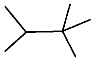
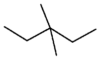
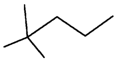
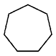
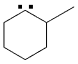
Species		Homodesmotic Reactions	$\Delta H^{0}_{f,298}$ (kcal/mol)		
Structure	#		HR	AE	BAC
	**(85)**	**(85)** + 6 $SiH_4 \rightarrow 6\,H_3SiSiH_3$	51.82	50.46	54.43
		(85) + 5 $SiH_4 \rightarrow 4\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	52.69		
		(85) + 4 $SiH_4 \rightarrow 2\,H_3SiSiH_3 + 2\,H_3SiSiH_2SiH_3$	53.56		
		(85) + 3 $SiH_4 \rightarrow 3\,H_3SiSiH_2SiH_3$	54.43		
		(85) + 6 $H_3SiSiH_3 \rightarrow 6\,H_3SiSiH_2SiH_3$	57.04		
	**(88)**	**(88)** + 6 $SiH_4 \rightarrow 6\,H_3SiSiH_3$	60.58	59.23	63.20
		(88) + 5 $SiH_4 \rightarrow 4\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	61.45		
		(88) + 4 $SiH_4 \rightarrow 2\,H_3SiSiH_3 + 2\,H_3SiSiH_2SiH_3$	62.33		
		(88) + 3 $SiH_4 \rightarrow 3\,H_3SiSiH_2SiH_3$	63.20		
	**(89)**	**(89)** + 5 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 4\,H_3SiSiH_3$	120.46	118.26	122.35
		(89) + 4 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	121.33		
		(89) + 3 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_2SiH_3$	122.21		
	**(90)**	**(90)** + 5 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 4\,H_3SiSiH_3$	124.31	122.10	126.19
		(90) + 4 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	125.18		
		(90) + 3 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_2SiH_3$	126.05		
	**(91)**	**(91)** + 5 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 4\,H_3SiSiH_3$	105.24	103.03	107.12
		(91) + 4 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	106.11		
		(91) + 3 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_2SiH_3$	106.98		
	**(95)**	**(95)** + 8 $SiH_4 \rightarrow 7\,H_3SiSiH_3$	81.63	80.82	84.83
		(95) + 7 $SiH_4 \rightarrow 5\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	82.51		
		(95) + 6 $SiH_4 \rightarrow 3\,H_3SiSiH_3 + 2\,H_3SiSiH_2SiH_3$	83.38		
		(95) + 5 $SiH_4 \rightarrow H_3SiSiH_3 + 3\,H_3SiSiH_2SiH_3$	84.25		
		(95) + 9/2 $SiH_4 \rightarrow 7/2\,H_3SiSiH_2SiH_3$	84.68		
	**(97)**	**(97)** + 5 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 4\,H_3SiSiH_3$	102.97	100.77	104.86
		(97) + 4 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_3 +$ SiH3SiH2SiH3	103.84		
		(97) + 3 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,SiH_3SiH_2SiH_3$	104.71		
	**(98)**	**(98)** + 5 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 4\,H_3SiSiH_3$	110.02	107.82	111.91
		(98) + 4 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	110.89		
		(98) + 3 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 2\,H_3SiSiH_2SiH_3$	111.77		
	**(100)**	**(100)** + 4 $SiH_4 + 2\,:SiH_2 \rightarrow 4\,H_3SiSi{:}H + 2\,H_3SiSiH_3$	153.21	150.15	154.37
		(100) + 3 $SiH_4 + 2\,:SiH_2 \rightarrow 4\,H_3SiSi{:}H + H_3SiSiH_2SiH_3$	154.08		
	**(105)**	**(105)** + 7 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 5\,H_3SiSiH_3$	122.83	121.17	125.30
		(105) + 6 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 3\,H_3SiSiH_3 + H_3SiSiH_2SiH_3$	123.70		
		(105) + 5 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + H_3SiSiH_3 + 2\,H_3SiSiH_2SiH_3$	124.58		
		(105) + 9/2 $SiH_4 + :SiH_2 \rightarrow 2\,H_3SiSi{:}H + 5/2\,H_3SiSiH_2SiH_3$	125.01		
	**(110)**	**(110)** + 4 $SiH_4 + 2\,:SiH_2 \rightarrow 4\,H_3SiSi{:}H + 2\,H_3SiSiH_3$	153.90	150.84	155.06
		(110) + 3 $SiH_4 + 2\,:SiH_2 \rightarrow 4\,H_3SiSi{:}H + H_3SiSiH_2SiH_3$	154.77		

TABLE 5 (Continued)

Species		Homodesmotic Reactions	$\Delta H^{0}_{f,298}$ (kcal/mol)		
Structure	#		HR	AE	BAC
	**(116)**	**(116)** + 5 SiH_4 → 6 H_3SiSiH_3	53.89	51.77	56.36
		(116) + 4 SiH_4 → 4 H_3SiSiH_3 + $H_3SiSiH_2SiH_3$	54.76		
		(116) + 3 SiH_4 → 2 H_3SiSiH_3 + 2 $H_3SiSiH_2SiH_3$	55.63		
		(116) + 2 SiH_4 → 3 $H_3SiSiH_2SiH_3$	56.51		
		(116) + 4 H_3SiSiH_3 → 5 $H_3SiSiH_2SiH_3$	58.25		
	**(117)**	**(117)** + 5 SiH_4 → 6 H_3SiSiH_3	55.77	53.66	58.24
		(117) + 4 SiH_4 → 4 H_3SiSiH_3 + $H_3SiSiH_2SiH_3$	56.65		
		(117) + 3 SiH_4 → 2 H_3SiSiH_3 + 2 $H_3SiSiH_2SiH_3$	57.52		
		(117) + 2 SiH_4 → 3 $H_3SiSiH_2SiH_3$	58.39		
		(117) + 4 H_3SiSiH_3 → 5 $H_3SiSiH_2SiH_3$	60.13		
	**(118)**	**(118)** + 5 SiH_4 → 6 H_3SiSiH_3	56.36	54.24	58.82
		(118) + 4 SiH_4 → 4 H_3SiSiH_3 + $H_3SiSiH_2SiH_3$	57.23		
		(118) + 3 SiH_4 → 2 H_3SiSiH_3 + 2 $H_3SiSiH_2SiH_3$	58.10		
		(118) + 2 SiH_4 → 3 $H_3SiSiH_2SiH_3$	58.97		
		(118) + 4 H_3SiSiH_3 → 5 $H_3SiSiH_2SiH_3$	60.71		
	**(119)**	**(119)** + 7 SiH_4 → 7 H_3SiSiH_3	61.58	60.00	64.63
		(119) + 6 SiH_4 → 5 H_3SiSiH_3 + $H_3SiSiH_2SiH_3$	62.45		
		(119) + 5 SiH_4 → 3 H_3SiSiH_3 + 2 $H_3SiSiH_2SiH_3$	63.32		
		(119) + 4 SiH_4 → H_3SiSiH_3 + 3 $H_3SiSiH_2SiH_3$	64.19		
		(119) + 7/2 SiH_4 → 7/2 $H_3SiSiH_2SiH_3$	64.63		
		(119) + 7 H_3SiSiH_3 → 7 $H_3SiSiH_2SiH_3$	67.67		
	**(124)**	**(124)** + 6 SiH_4 + :SiH_2 → 2 H_3SiSi:H + 5 H_3SiSiH_3	108.69	106.26	111.02
		(124) + 5 SiH_4 + :SiH_2 → 2 H_3SiSi:H + 3 H_3SiSiH_3 + $H_3SiSiH_2SiH_3$	109.56		
		(124) + 4 SiH_4 + :SiH_2 → 2 H_3SiSi:H + H_3SiSiH_3 + 2 $H_3SiSiH_2SiH_3$	110.43		
		(124) + 7/2 SiH_4 + :SiH_2 → 2 H_3SiSi:H + 5/2 $H_3SiSiH_2SiH_3$	110.87		

heats of formation available, and the target molecule, and the heat of reaction is evaluated using quantum chemical calculations. This heat of reaction and the experimental heats of formation for the reference molecules are then used to calculate the heat of formation of the target molecule. Raghavachari et al.[22] recently investigated the concept of bond separation reactions, which are isodesmic reactions consisting of the smallest possible reference molecules, and they showed that more accurate predictions were obtained using this approach for G2 theory than were calculated using atomization energies. Sumathi and Green[23] further suggested that using homodesmotic reactions, which conserve different types of bond environments between each pair of atoms, provides even better accuracy than bond separation reactions or atomization energies. We therefore constructed homodesmotic reactions for the molecules examined in this study at the G3//B3LYP level of theory using the compounds listed in Table 1 as the reference molecules, and the heats of formation calculated from this approach are tabulated in Table 5. Note that some of the 135 molecules are missing from this table since the reference molecule set is not sufficiently comprehensive to permit formulation of homodesmotic reactions. In particular, some of the bond types, such as :Si−Si: or =Si−Si bonds, are not present in the reference molecules. In addition, most molecules in Table 5 have more than one homodesmotic reaction that was constructed. The heat of formation values calculated from these reactions had an average deviation of 1.86 kcal/mol and a maximum deviation of 6.10 kcal/mol, in large part due to the experimental uncertainties in the reference molecules as reported in Table 1. Because it is necessary to have a uniform set of thermochemical values from which the group additivity values can be regressed, an alternative approach that is applicable to select representative values when using homodesmotic reactions was sought.

TABLE 6: The Bond Additivity Correction (BAC) Parameters of Various Bond Types for G3//B3LYP Calculations

bond type	H−H	Si−H, =Si−H	:Si−H	Si−Si	:Si−Si	Si=Si
BAC values (kcal/mol)	0.42	0.16	0.95	0.35	0.57	−0.66

Petersson et al.[19] proposed the concept of an isodesmic bond additivity correction (BAC) scheme based on the spirit of isodesmic reactions. In this approach, a set of reference molecules with experimental data available is compared to theoretical values, and the BAC parameters of different bond types are calculated by fitting to the experimental data. The heats of formation can be approximated as

$$\Delta H^{\circ}_{\mathrm{f},298}(\mathrm{BAC}) = \Delta H^{\circ}_{\mathrm{f},298}(\mathrm{calc}) + \sum_{i} N_i \mathrm{BAC}_i \tag{4}$$

where BAC_i is the BAC parameter of a certain bond type i, and the heats of formation estimated from BACs, $\Delta H^{\circ}_{\mathrm{f},298}$(BAC), can be defined as the heats of formation calculated on the basis of atomization energies, $\Delta H^{\circ}_{\mathrm{f},298}$(calc), corrected by the summation of the BAC_i parameters multiplied by the number of the bonds of that type (N_i). Although experimental uncertainties still affect this approach, representative values of the heats of formation obtained from homodesmotic reactions were chosen, and a single set of thermochemical values was

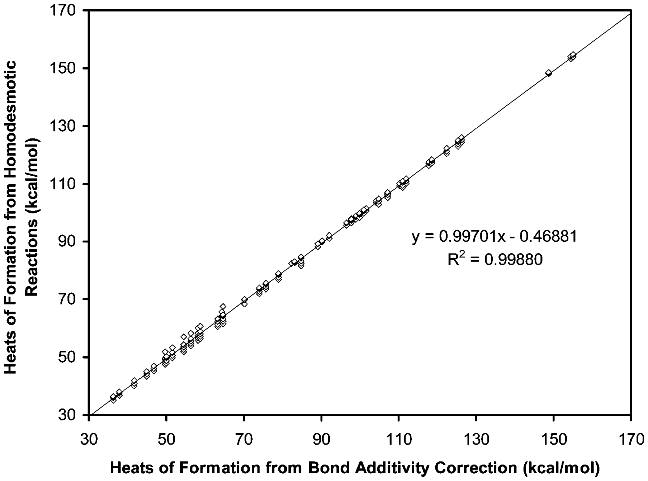


Figure 2. Comparison between the heats of formation obtained from atomization energies and those from homodesmotic reactions.

generalized. On the basis of this approach, we estimated six BAC parameters of various bond types from a comparison of the experimental data of seven molecules listed in Table 1 (all molecules listed except triplet SiH_2) with the values of G3//B3LYP calculations, and the results are tabulated in Table 6. We categorized the bonds into six different types according to the optimized geometries of these seven molecules from G3//B3LYP calculations, in which the silylene atoms (with two nonbonded electrons) behave differently than saturated silicon atoms or silicon atoms attached to double bonds. For example, the bond length of :Si−H bonds of 1.53 Å is longer than both Si−H and ═Si−H bond lengths of 1.49 Å, and the bond length of :Si−Si bonds of 2.40 Å is also different from both Si−Si and ═Si−Si bond lengths of 2.35 Å. We further used these BAC parameters to calculate the heats of formation of the molecules in Table 5 using eq 4. These heats of formation are compared to the values estimated from atomization energies and homodesmotic reactions in Table 5. As shown in the table, the heats of formation using BACs are in good agreement with the values from homodesmotic reactions, and the agreement between the BAC values and the values from all of the homodesmotic reactions can also be observed from the parity plot in Figure 2. To apply the BAC parameters to the molecules for which homodesmotic reactions could not be constructed, we approximated the values for the bonds missing from the reference molecules, that is, :Si−Si:, ═Si−Si, and :Si═Si bonds as :Si−Si, Si−Si, and Si═Si bonds, respectively. The resulting heats of formation using this approach are listed along with the heats of formation obtained from atomization energies in Table 2. The heats of formation obtained using the BAC parameters thus formed the comprehensive set of values for all 135 molecules. Subsequently, the values for all 135 molecules with the exception of the first four molecules in Table 2 that cannot be divided into groups were used to develop the group additivity scheme.

II. Group Additivity Scheme Generalized from Thermochemical Properties. To develop the group additivity scheme for silicon−hydrogen molecules, we first defined four different kinds of silicon atoms. We use Si*A* to denote silicon atoms attached to a double bond, Si*B* for silicon atoms with two nonbonded electrons, Si*AB* for silicon atoms attached to a double bond *and* with two nonbonded electrons, and simply Si for silicon atoms without any functionality. The maximum possible number of combinations of these four atom types resulted in 62 different groups. Ring corrections also need to be applied to cyclic molecules, and among the 131 molecules that we examined, 19 ring corrections were defined. Therefore, there are a total of 81 groups, including 62 linear groups and 19 ring corrections, as tabulated in Table 7. For the linear groups, the first element in the notation represents the central atom, and the following elements denote the neighboring atoms. For the groups with Si*AB* as the central atom, a Si*A* atom is always attached to a Si*AB*. Therefore, the notation starting with Si*AB* represents the composite structure of :Si═Si with the two remaining neighbors of the Si*A* atom to be specified. In the process of defining the groups in the molecules that we examined, it became apparent that not all of the 62 groups were present in the 131 species used to develop the group additivity scheme, and some of the groups were missing. Molecules containing these missing groups were provided as input to the quantum chemical calculations, but no compounds containing these groups with stable geometries were identified after numerous attempts. Structures initially specified with these groups formed cyclic or bridging structures upon geometry optimization, thus altering the constituent groups of the molecule. In addition, two Si*A*-containing groups, Si/Si/Si*A*3 and Si/Si*A*4, could not be obtained because the smallest molecules containing these groups, Si_8H_{12} and Si_9H_{12}, were too large to be handled with present computational resources. There were a total of 18 missing groups, and they are labeled "NA" in Table 7. Since there were 131 molecules containing 63 groups (62 linear groups + 19 ring corrections − 18 missing groups), obtaining the GAVs is conceptually equivalent to solving 131

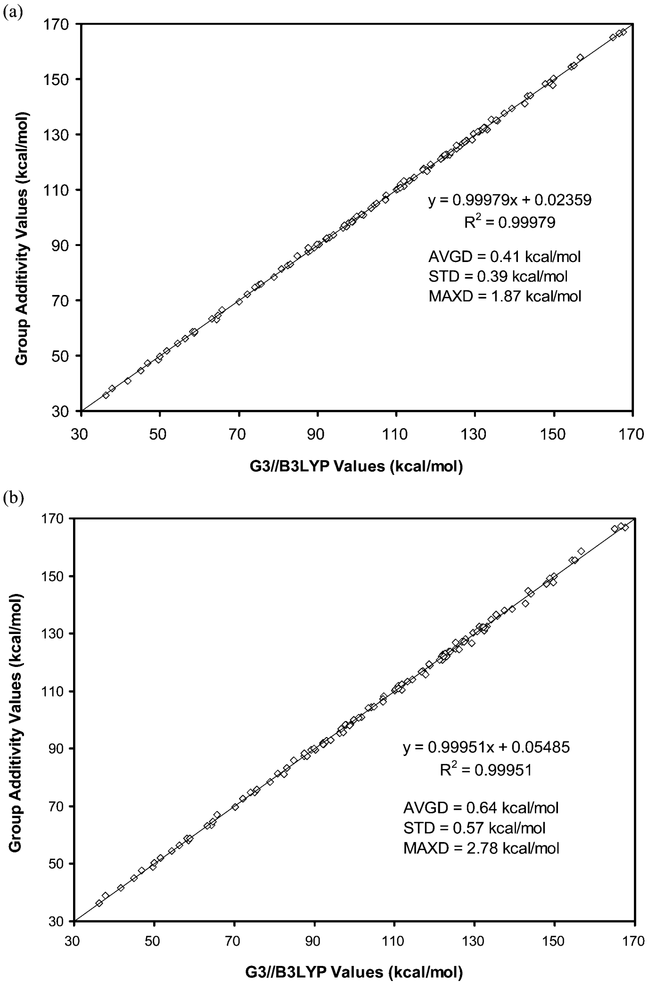


Figure 3. Parity plot of heats of formation predicted from group additivity versus quantum chemical values from G3//B3LYP: (a) specified exactly; (b) over-specified.

TABLE 7: The List of the Groups and Their Contribution to the Heats of Formation of Silicon−Hydrogen Molecules

Linear Groups

groups[b]	status[a]	group contribution[c] (kcal/mol)	groups[b]	status[a]	group contribution[c] (kcal/mol)
Si/Si/H3	EVK	10.75	Si/Si*A*2/Si*B*2	NA	*−1.46*
Si/Si*A*/H3	LDO	10.75	Si/Si*A*/Si*B*3	NA	*−1.46*
Si/Si*B*/H3	LDO	10.75	Si/Si*B*4	NA	*−1.46*
Si/Si2/H2	EVK	8.71	Si*A*/Si*A*/H2	EVK	33.54
Si/Si*A*2/H2	LDO	8.71	Si*A*/Si*A*/Si/H	LDO	28.32
Si/Si*B*2/H2	LDO	8.71	Si*A*/Si*A*/Si*A*/H	EVK	28.32
Si/Si/Si*A*/H2	LDO	8.71	Si*A*/Si*A*/Si*B*/H	LDO	28.32
Si/Si/Si*B*/H2	LDO	8.71	Si*A*/Si*AB*/Si/H	LDO	99.55
Si/Si*A*/Si*B*/H2	LDO	8.71	Si*A*/Si*AB*/Si*A*/H	EVK	99.55
Si/Si3/H	EVK	4.15	Si*A*/Si*AB*/Si*B*/H	NA	*99.55*
Si/Si*A*3/H	LDO	4.15	Si*A*/Si*A*/Si2	LDO	21.70
Si/Si*B*3/H	NA	*4.15*	Si*A*/Si*A*/Si/Si*A*	LDO	21.70
Si/Si/Si*A*2/H	LDO	4.15	Si*A*/Si*A*/Si/Si*B*	LDO	21.70
Si/Si/Si*B*2/H	LDO	4.15	Si*A*/Si*A*/Si*A*2	EVK	21.70
Si/Si/Si*A*/Si*B*/H	LDO	4.15	Si*A*/Si*A*/Si*A*/Si*B*	LDO	21.70
Si/Si2/Si*A*/H	LDO	4.15	Si*A*/Si*A*/Si*B*2	LDO	21.70
Si/Si2/Si*B*/H	LDO	4.15	Si*A*/Si*AB*/Si2	LDO	91.74
Si/Si*A*2/Si*B*/H	NA	*4.15*	Si*A*/Si*AB*/Si/Si*A*	LDO	91.74
Si/Si*A*/Si*B*2/H	NA	*4.15*	Si*A*/Si*AB*/Si/Si*B*	NA	*91.74*
Si/Si4	EVK	−1.46	Si*A*/Si*AB*/Si*A*2	NA	*91.74*
Si/Si3/Si*A*	LDO	−1.46	Si*A*/Si*AB*/Si*A*/Si*B*	NA	*91.74*
Si/Si3/Si*B*	LDO	−1.46	Si*A*/Si*AB*/Si*B*2	NA	*91.74*
Si/Si2/Si*A*2	LDO	−1.46	Si*B*/Si/H	LDO	63.95
Si/Si2/Si*A*/Si*B*	LDO	−1.46	Si*B*/Si*A*/H	LDO	55.15
Si/Si2/Si*B*2	LDO	−1.46	Si*B*/Si*B*/H	EVK	55.91
Si/Si/Si*A*3	NA	*−1.46*	Si*B*/Si2	LDO	59.50
Si/Si/Si*A*2/Si*B*	NA	*−1.46*	Si*B*/Si/Si*A*	LDO	51.04
Si/Si/Si*A*/Si*B*2	NA	*−1.46*	Si*B*/Si/Si*B*	LDO	47.29
Si/Si/Si*B*3	NA	*−1.46*	Si*B*/Si*A*2	LDO	43.71
Si/Si*A*4	NA	*−1.46*	Si*B*/Si*A*/Si*B*	NA	*39.81*[d]
Si/Si*A*3/Si*B*	NA	*−1.46*	Si*B*/Si*B*2	EVK	35.90

Ring Corrections

groups[b]	status[a]	group contribution[c] (kcal/mol)	groups[b]	status[a]	group contribution[c] (kcal/mol)
C3	EVK	37.35	C5B	EVK	5.71
C3B	EVK	27.52	C5A	EVK	5.63
C3A	EVK	38.79	C5BB(1,3)	LDO	4.08
C3BB	LDO	21.59	C5AB(1,2)	EVK	2.41
C3AB	EVK	21.59	C5AB(1,3)	EVK	3.93
C4	EVK	17.13	C6	EVK	2.18
C4B	EVK	15.46	C6B	EVK	1.61
C4A	EVK	13.28	C6BB(1,3)	LDO	1.61
C4AB	EVK	0.43	C7	EVK	3.67
C5	EVK	5.36			

[a] NA (not available) denotes that groups are not present in the molecules used in the G3//B3LYP calculations. EVK (exact value known) denotes that group values can be calculated exactly from the quantum chemical calculations. LDO (linearly dependent on others) denotes that group values are linearly dependent on other groups. [b] The numbers in the parentheses for the ring corrections stand for the position of the functional groups. For example, C5BB(1,3) represents the ring correction of the five-membered ring with two silylene atoms in the first and third positions. [c] Italicized numbers are the projected values for the missing groups. [d] The projected Si*B*/Si*A*/Si*B* value was obtained by taking the average of the values of Si*B*/Si*A*2 and Si*B*/Si*B*2 groups.

linear algebraic equations containing 63 unknown variables. Although there are more molecules (131 equations) than groups (63 variables), a significant number of the equations are linearly dependent on others, and the number of linearly independent equations is much smaller than 131. This can be verified by analyzing a matrix of 131 rows (compounds) and 63 columns (their constituent groups), where the *ij* entries in the matrix are the number of groups of type *j* that molecule *i* contains. The rank of this matrix was 58. This indicates that the number of linearly independent equations is less than the number of variables by five, and five degrees of freedom must be specified to obtain a set of unique solutions. This issue of linear dependence is not unique to silicon hydride molecules but would also be observed in other systems, including carbon−hydrogen molecules. Further analysis revealed that a subset of the 63 groups had values that were exactly specified. By eliminating linearly dependent equations, we found that the GAVs for 10 out of the 44 linear groups (62 linear groups − 18 missing groups) and 16 out of the 19 ring corrections could be exactly calculated. However, the remaining 37 groups, including 34 linear groups and 3 ring corrections, are linearly dependent on other groups, and only 32 linearly independent equations were found. It was not possible to specify additional linearly independent equations by adding molecules to the calculation set, as all molecules conceived simply added more linearly dependent equations.

Although five degrees of freedom must be specified, these degrees of freedom cannot be specified randomly. By carefully examining the equations and variables, we first set the values of two undetermined ring corrections, C3BB and C6BB(1,3),

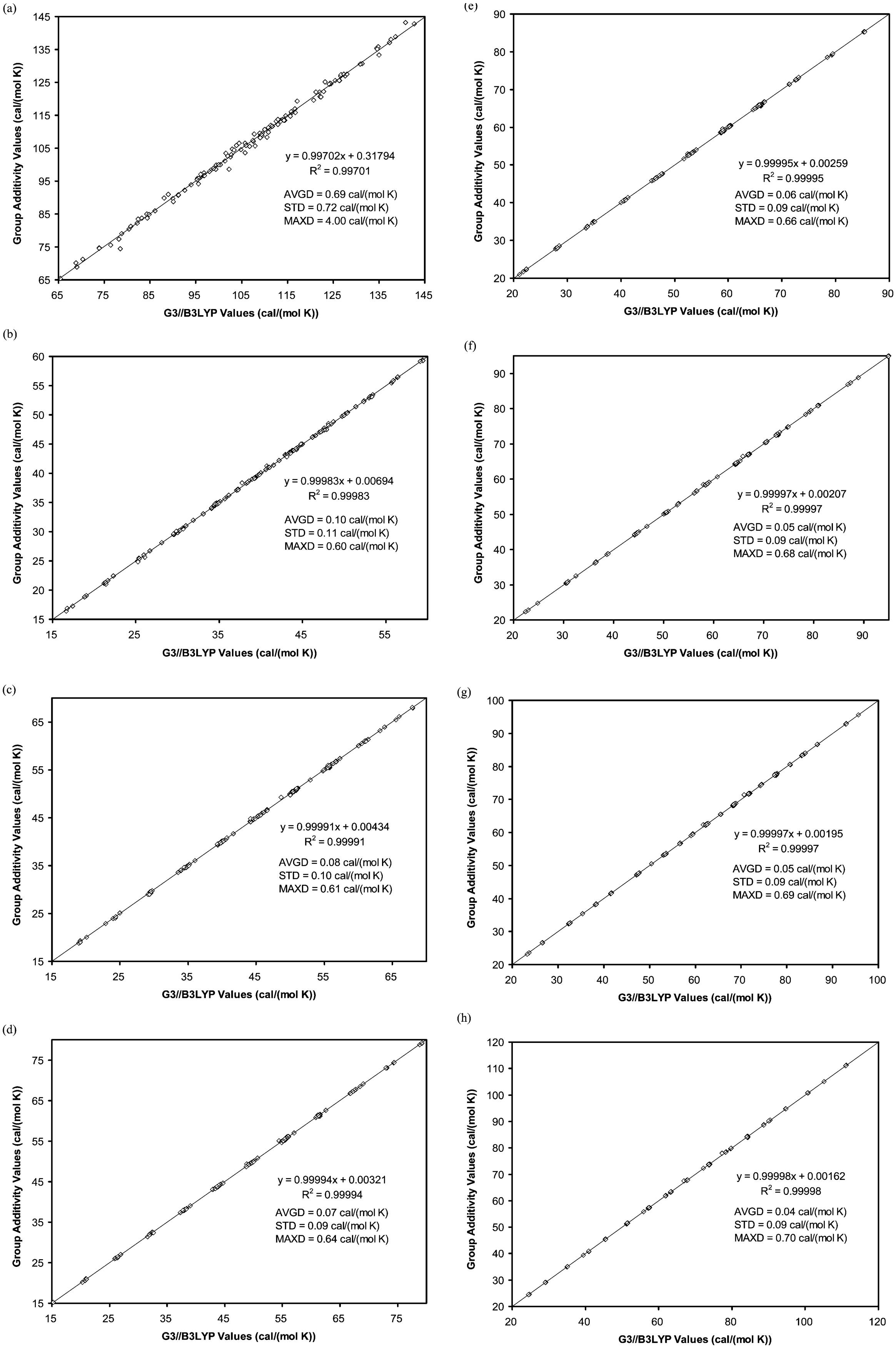


Figure 4. Parity plots of standard entropy and heat capacities at different temperatures predicted from group additivity versus quantum chemical values from G3//B3LYP: (a) standard entropy (S^{298}); constant pressure heat capacity (C_p) at (b) 300, (c) 400, (d) 500, (e) 600, (f) 800, (g) 1000, and (h) 1500 K.

TABLE 8: Summary of Group Additivity Values of Silicon−Hydrogen Molecules Generalized from G3//B3LYP Calculations

groups[a]	$\Delta H^\circ_{f,298}$ (kcal/mol)	S^{298} (cal/(mol K))	C_p (cal/(mol K))						
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
Linear Groups									
Si/Si*X*/H3	10.75	35.04	9.53	11.45	12.97	14.24	16.24	17.68	19.68
Si/Si*X*2/H2	8.71	14.86	9.03	10.64	11.80	12.72	14.11	15.09	16.44
Si/Si*X*3/H	4.15	−5.09	8.64	9.82	10.60	11.17	11.98	12.51	13.23
Si/Si*X*4	−1.46	−24.33	8.33	8.96	9.30	9.50	9.71	9.81	9.92
Si*A*/Si*A*/H2	33.54	32.69	8.44	9.62	10.51	11.24	12.41	13.29	14.53
Si*A*/Si*A*/Si*X*/H	28.32	13.45	7.52	8.41	9.00	9.44	10.10	10.57	11.22
Si*A*/Si*AB*/Si*X*/H	99.55	43.93	11.64	12.52	13.09	13.52	14.17	14.62	15.25
Si*A*/Si*A*/Si*X*2	21.70	−5.39	6.73	7.20	7.45	7.60	7.76	7.82	7.91
Si*A*/Si*AB*/Si*X*2	91.74	25.78	10.57	11.12	11.42	11.59	11.77	11.85	11.94
Si*B*/Si/H	63.95	33.84	6.86	7.33	7.69	8.01	8.53	8.90	9.42
Si*B*/Si*A*/H	55.15	31.22	6.43	7.04	7.48	7.84	8.41	8.81	9.35
Si*B*/Si*B*/H	55.91	32.85	6.84	7.29	7.63	7.92	8.41	8.79	9.34
Si*B*/Si2	59.50	13.41	5.95	6.07	6.10	6.11	6.11	6.07	6.05
Si*B*/Si/Si*A*	51.04	12.96	5.55	5.78	5.89	5.95	6.01	6.02	6.04
Si*B*/Si/Si*B*	47.29	14.28	5.25	5.53	5.68	5.76	5.85	5.88	5.94
Si*B*/Si*A*2	43.71	14.18	5.23	5.53	5.69	5.78	5.87	5.92	5.96
Si*B*/Si*A*/Si*B*	39.81	11.49	5.17	5.52	5.71	5.82	5.94	5.98	6.00
Si*B*/Si*B*2	35.90	8.81	5.10	5.50	5.73	5.87	6.00	6.04	6.04
Ring Corrections									
C3	37.35	31.01	−2.22	−2.65	−3.00	−3.25	−3.55	−3.71	−3.86
C3B	27.52	31.64	−2.98	−3.30	−3.52	−3.67	−3.84	−3.89	−3.97
C3A	38.79	32.81	−2.74	−3.11	−3.35	−3.49	−3.66	−3.74	−3.86
C3BB, C3AB	21.59	30.18	−3.01	−3.34	−3.53	−3.66	−3.79	−3.86	−3.95
C4	17.13	26.57	−3.08	−3.26	−3.41	−3.53	−3.69	−3.76	−3.86
C4B	15.46	26.92	−3.19	−3.38	−3.54	−3.66	−3.79	−3.84	−3.93
C4A	13.28	27.14	−3.58	−3.63	−3.69	−3.74	−3.81	−3.84	−3.90
C4AB	0.43	25.68	−3.61	−3.71	−3.79	−3.86	−3.94	−3.96	−4.02
C5	5.36	23.12	−3.87	−3.89	−3.94	−3.99	−4.05	−4.08	−4.14
C5B	5.71	24.26	−3.72	−3.83	−3.93	−4.01	−4.11	−4.14	−4.24
C5A	5.63	26.45	−3.66	−3.72	−3.78	−3.82	−3.87	−3.88	−3.94
C5BB(1,3)	4.08	24.44	−3.33	−3.51	−3.64	−3.72	−3.83	−3.84	−3.96
C5AB(1,2)	2.41	24.37	−3.72	−3.73	−3.78	−3.82	−3.88	−3.89	−3.96
C5AB(1,3)	3.93	27.32	−3.35	−3.55	−3.68	−3.78	−3.89	−3.92	−4.01
C6	2.18	20.39	−3.78	−3.76	−3.77	−3.78	−3.79	−3.79	−3.84
C6B, C6BB(1,3)	1.61	21.86	−3.82	−3.82	−3.85	−3.88	−3.91	−3.80	−3.94
C7	3.67	20.49	−3.83	−3.80	−3.79	−3.78	−3.78	−3.77	−3.82

[a] Si*X* represents three possible types of silicon atoms, including Si, Si*A*, or Si*B*.

to be equal to two other structurally similar ring corrections, C3AB and C6B, respectively, for which the values are already exactly specified. The value of the ring correction C5BB(1,3) can thus be determined, since it is dependent on these values. We then assumed the values of Si/Si/H3, Si/Si*A*/H3, and Si/Si*B*/H3 to be equal to one another. This assumption essentially ignores the effect of the functionality of the neighboring silicon atom on the central silicon atom with no functionality when it has only one neighboring silicon atom. Thus, specification of these two additional degrees of freedom allowed any group containing only Si*A* or only Si*B* to be solved. Finally, we specified the last degree of freedom by setting the value of the undetermined group Si*A*/Si*A*/Si*B*/H to be equal to the value of the determined group Si*A*/Si*A*/Si*A*/H. The remaining GAVs were calculated after all five degrees of freedom were fixed, and the group additivity scheme for silicon hydrides was thus constructed, with the exception of the missing groups. The GAVs obtained from this approach can be found in the Supporting Material, and excellent agreement was found between the heats of formation calculated using the resulting GAVs using this procedure and the values estimated from G3//B3LYP calculations, as shown in the parity plot in Figure 3a. The average absolute deviation was 0.41 kcal/mol, and the corresponding maximum deviation was 1.87 kcal/mol.

To project the values of the 18 missing groups, we proposed an alternative way to solve the problem described above. According to the GAVs that were obtained when the five degrees of freedom were specified, we found that the GAVs for the Si- and Si*A*-centered groups depend strongly on the number of silicon atoms attached to the central atom, but they are only weakly dependent on the functionalities of the neighboring atoms. For example, the value of Si*A*/Si*A*/Si/H is very close to the value of Si*A*/Si*A*/Si*A*/H, and the value of Si/Si4 is comparable to the GAVs of Si/Si3/Si*A* and Si/Si3/Si*B*. We therefore proposed to solve for the GAVs by setting the GAVs to be equal for those groups having the same central atoms and the same number of neighboring silicon atoms, with the exception of Si*B*-centered groups. Thus, we over-specified the problem because the number of specifications that we imposed was larger than the number of degrees of freedom. However, the GAVs estimated from this approach were not substantially different from the GAVs obtained by specifying the problem exactly. The parity plot shown in Figure 3b reveals the excellent agreement between the values predicted from the over-specified GAVs and the G3//B3LYP-derived heats of formation. The average absolute deviation was 0.64 kcal/mol, and the corresponding maximum deviation was 2.78 kcal/mol; both of these are only slightly larger than the values when the problem was specified exactly. The sum of squares increased slightly from 41.58 kcal^2/mol^2 for the exactly specified case to 96.77 kcal^2/mol^2 for the over-specified approach.

Using these assumptions, we projected the GAVs of the Si- and Si*A*-centered groups that were missing, and the results are listed in italics in Table 7. The value of the only Si*B*-centered

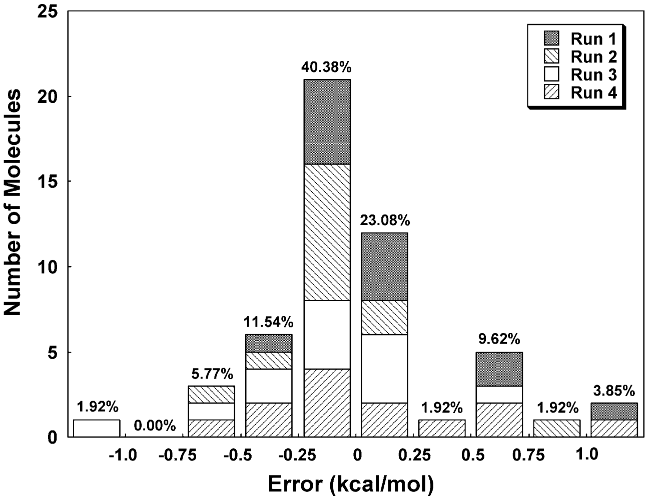


Figure 5. Histogram of sensitivity analysis of group values using Mavrovouniotis's[35] approach.

group that was missing, Si*B*/Si*A*/Si*B*, was projected by taking the average of the values of the Si*B*/Si*A*2 and Si*B*/Si*B*2 groups. The resulting GAV of 39.81 kcal/mol for Si*B*/Si*A*/Si*B* appeared to be reasonable, since its deviation from the value of the Si*B*/Si/Si*B* group of 7.48 kcal/mol is comparable to the difference between the values of the Si*B*/Si/Si*A* and Si*B*/Si*A*2 groups of 7.33 kcal/mol (both substituting one Si into Si*A*), and its deviation from the value of the Si*B*/Si/Si*A* group of 11.23 kcal/mol is comparable to the difference between the values of the Si*B*/Si/Si*B* and Si*B*/Si*B*2 groups of 11.39 kcal/mol (both substituting one Si into Si*B*). The same approaches were used to generalize the GAVs for standard entropy and heat capacities at different temperatures, and the parity plots in Figure 4 demonstrate the very good agreement between the values generalized using the group additivity scheme and the ab initio quantum chemical calculations. The summary of the GAVs of various thermochemical properties generalized from G3//B3LYP calculations using this approach is provided in Table 8. Overall, the group contribution values for 35 groups were generalized from 131 silicon−hydrogen molecules.

To verify the predictive capability of the GAVs, the method of sensitivity analysis proposed by Mavrovouniotis[35] was used. In this approach, 10% of the molecules (13 molecules in this work) were randomly taken out, and the GAVs were refitted without them. The new GAVs were then used to predict the thermochemical properties of the omitted molecules, and the differences between these properties and the values predicted from the old GAVs were calculated. The results of this analysis are shown in Figure 5, where four different sensitivity analysis runs were performed. As shown in the graph, 76.9% of the molecules had absolute errors within 0.5 kcal/mol, and the maximum deviation for all runs was 1.86 kcal/mol. This demonstrated that the GAVs that we generalized from the G3//B3LYP calculations are reliable, and the group additivity scheme performs well for species that were not used during regression.

Conclusions

Thermochemistry of silicon−hydrogen molecules predicted from quantum chemical calculations was investigated in this work. Among the methods that we studied, G3//B3LYP was the most accurate with an average absolute deviation of 1.23 kcal/mol from the available experimental values when the heats of formation of small ($<Si_4$) silicon hydrides were estimated. A total of 135 silicon−hydrogen ($<Si_8$) compounds were then investigated using the G3//B3LYP method, and their thermochemical properties were calculated with bond additivity corrections incorporated. A group additivity scheme based on the values calculated from G3//B3LYP was developed, where the GAVs of the Si- and Si*A*-centered groups with the same central atoms and the same number of neighboring silicon atoms were set equal. This generalization resulted in GAVs that extrapolated well. Thermochemical properties calculated from these GAVs agreed well with the theoretical predictions from G3//B3LYP. Implementation of a group additivity approach is essential since the many thousands of possible isomers of silicon−hydrogen molecules cannot be treated quantum chemically at even the least expensive levels of theory.

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Supporting Information Available: Group additivity values (GAVs) for silicon hydrides obtained from the group additivity scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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