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Theoretical Study of the Heats of Formation of Small Silicon-Containing Compounds

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Heats of formation for nine small silicon-containing molecules were obtained from large basis set ab initio calculations using coupled cluster theory with a perturbative treatment of triple excitations. After adjusting the atomization energies for the finite basis set truncation error, core/valence correlation, scalar relativistic, higher order correlation, and atomic spin−orbit effects, the theoretical and experimental 0 K values of ΔH_f values were in good agreement. Using 106.6 kcal/mol as the heat of formation of silicon, we obtain ΔH_f values of SiH = 87.7 ± 0.4 vs 89.5 ± 0.7 (expt); $SiH_2(^1A_1)$ = 64.1 ± 0.4 vs 65.5 ± 0.7 (expt); $SiH_2(^3B_1)$ = 85.4 ± 0.4 vs 86.5 ± 0.7 (expt); SiH_3 = 47.3 ± 0.5 vs 47.7 ± 1.2 (expt); SiH_4 = 8.7 ± 0.6 vs 9.5 ± 0.5 (expt); Si_2 = 138.8 ± 0.4 vs 139.2 (expt); Si_2H_6 = 19.7 ± 0.5 vs 20.9 ± 0.3 (expt); SiF = −14.8 ± 0.4 vs −5.2 ± 3 (expt); SiF_2 = −151.7 ± 0.5 vs −140.3 ± 3 (expt); and SiF_4 = −384.5 ± 0.9 vs −384.9 ± 0.2 (expt). Based on the present work, we suggest a number of revisions in the interpretation of the experimental data. Although a revision in $\Delta H_f°(Si)$ to 107.4 ± 0.6 kcal/mol at 0 K leads to improved agreement between theory and experiment for the Si_xH_y compounds, it worsens agreement for SiF_4. Given the remaining uncertainties in the theoretical approach, more definitive conclusions do not appear to be warranted.

I. Introduction

Gas-phase silicon compounds play an important role in the semiconductor processing industry because of their use in chemical vapor deposition processes and in etching processes. Despite their technological importance, the heats of formation of simple model silicon compounds in the gas phase are not as well-established as one would like. Indeed, there is still some controversy over the precise heat of formation of the free Si atom, as well as that of the simplest derivative SiH_4.

In a carefully performed, high-level study of the heats of formation of small hydrocarbons and their silicon analogues (CH_n and SiH_n, $n = 1-4$), Grev and Schaefer[1] reported silane atomization energies that were significantly larger than the available experimental values. Their estimated exact nonrelativistic atomization energy of SiH_4 was 1.5 kcal/mol above the value derived from the JANAF Tables,[2] after correcting for atomic spin−orbit effects. This was in contrast to the situation with most of the hydrocarbons, where agreement was excellent. In light of the large atomic natural orbital (ANO) basis sets and extensive correlation treatment, Grev and Schaefer concluded that either relativistic effects (not included in their 1992 work) were important or the experimental heats of formation of Si and SiH_4 were incompatible. Subsequent Hartree−Fock−Dirac relativistic calculations by Visser et al.[3] predicted a reduction in the SiH_4 atomization energy of 1.3 kcal/mol, including atomic spin−orbit effects. A larger basis set, Douglas−Kroll relativistic calculations by Collins and Grev,[4] produced a molecular, scalar relativistic correction of −0.7 kcal/mol, using coupled cluster theory with single and double excitations and a quasi-perturbative treatment of triples (CCSD(T)). Another 0.43 kcal/mol reduction arises from the need to properly treat of the silicon atom spin multiplets. In addition, Ricca and Bauschlicher[5] have recently reported bond dissociation energies for SiF_n and SiF_n^+ and the associated heats of formation based on the well-established heats of formation of SiF_4 and F.

The latest edition of the JANAF Tables[2] lists the heat of formation, $\Delta H_f°(0\ K)$, of the free silicon atom as 106.6 ± 1.9 kcal/mol and $\Delta H_f°(SiH_4)$ = 10.5 ± 0.5 kcal/mol. Desai[6] has recommended that tighter error bars (±1.0 kcal/mol) be adopted for Si. JANAF's value for SiH_4 was based on the work of Gunn and Green.[7] The original report listed a value of 9.5 kcal/mol for $\Delta H_f°(SiH_4)$. The JANAF team revised the value upward on the assumption that the final state of silicon in the original experiment was amorphous, not crystalline. The heat of formation of SiF_4, by contrast, has been determined quite accurately by measurement of the direct combination of the elements in a bomb calorimeter with an accuracy of ±0.2 kcal/mol. This experimental measurement does not suffer from the difficulties resulting from an uncertain final state of the elements.

In a series of recent papers, we have begun calibrating a composite theoretical approach that is intended to reliably predict a variety of thermodynamic quantities, including heats of formation, without recourse to empirical parameters. The approach is based, in part, on calculating absolute total bond dissociation energies. Our approach starts with existing, reliable thermodynamic values (from either experiment or theory). Missing pieces of information are then computed by using high-level ab initio electronic structure methods. Our approach to calculating heats of formation thus requires good values for $\Delta H_f°(A)$ where A is an atom. In the present work we examine nine small silicon-containing compounds, $SiH(^2\Pi)$, $SiH_2(^1A_1$ and $^3B_1)$, $SiH_3(^2A_2'')$, $SiH_4(^1A_1)$, $Si_2(^3\Sigma_g^-)$, $Si_2H_6(^1A_{1g})$, $SiF(^2\Pi)$, $SiF_2(^1A_1)$ and $SiF_4(^1A_1)$. We adopted the CCSD(T) method, as did Grev and Schaefer for the majority of their work, but depart from their approach in our choice of one-particle basis functions. Instead of ANOs, we used the diffuse function augmented correlation consistent[8−11] family of basis sets, aug-

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cc-pV*x*Z, $x = $ D, T, etc. We also differ from them in the use of unrestricted Hartree−Fock (UHF) wave functions for open shell systems. The use of the correlation-consistent basis sets should provide an independent estimate of the heats of formation in the complete basis set (CBS) limit. Small, but still significant, corrections for core/valence and scalar relativistic effects were applied. Wherever possible, we will compare our findings with results obtained from the recently introduced Gaussian-3 (G3) procedure.[12] G3 is the latest modification of the Gaussian-x series of model chemistries.[13,14]

II. Procedure

The first step in our procedure is to calculate optimal geometries and complete basis set atomization energies, $\sum D_e$. In the present study these were obtained from frozen-core coupled cluster calculations, denoted as CCSD(T)(FC). Polyatomic molecules were optimized with a gradient convergence criterion of 1.5×10^{-5} E_h/a_0, whereas for the diatomics r_{SiH} and r_{Si_2} were determined from a seven-point Dunham fit in the bond lengths. However, due to the expense of the larger basis set calculations, a looser convergence criterion of 4.5×10^{-4} E_h/a_0 was adopted for the quadruple and quintuple zeta basis sets. In some cases, such as Si_2H_6, even this proved prohibitively expensive. For Si_2H_6 we estimated the aug-cc-pV5Z bond lengths and bond angles by fitting the internal coordinates obtained from three smaller basis sets with an exponential function.

Unless otherwise noted, all atomic and molecular open shell CCSD(T) energies were based on UHF zero-order wave functions, i.e., UCCSD(T). All such calculations were performed with the Gaussian-94 program.[15] Our choice of UCCSD(T) was predicated on a desire to maintain consistency with a large body of previously obtained atomization energies and for direct comparison with the results obtained from G2 and G3. Orbital symmetry and equivalence restrictions were not imposed in our atomic calculations. Closed shell CCSD(T) calculations were performed with MOLPRO-97[16] and Gaussian-94. Two alternative open shell CCSD(T) techniques, both based on restricted open shell Hartree−Fock (ROHF) wave functions, have been proposed. The first is a completely restricted method, which we will denote as RCCSD(T).[17−19] The second approach relaxes the spin constraint in the coupled cluster calculation and will be referred to as R/UCCSD(T).[20,21] To make matters somewhat confusing, the latter method is requested in MOLPRO by the keyword “UCCSD(T)”. Although energy differences among the various open shell coupled cluster methods are not large, the cumulative effect for some of the molecules was significant in light of the accuracy being sought.

The effects of higher order correlation on the atomization energies were estimated by carrying out full CCSDT calculations with the ACES II program[22] using unrestricted Hartree−Fock (UHF) zero-order wave functions for the open shell systems. A recent study[23] on a small number of chemical systems has shown that CCSDT appears to do a good job of reproducing higher order correlation effects on binding energies, as judged by full configuration interaction (FCI) or estimated FCI calculations. Grev and Schaefer[1] explored the accuracy of the perturbative treatment of triple excitations, i.e., the “(T)” approximation, by performing complete CCSDT calculations on CH_4 and CH_2. Using a basis set of approximately triple zeta quality, they reported a 0.3 kcal/mol change in ΔE_{rxn} for the reaction $CH_4 \rightarrow CH_2 + 2H$, a rather substantial amount considering the small number of electrons in the system.

All calculations were performed on a 16 processor Silicon Graphics, Inc. PowerChallenge, a 32 processor SGI Origin 2000, or an SGI/Cray J90 at DOE’s National Energy Research Supercomputing Center. The largest CCSD(T) calculation reported in this study was the aug-cc-pV5Z run on Si_2H_6, which included 734 functions. All results were stored and analyzed using the Environmental Molecular Sciences Laboratory (EMSL) Computational Results Database.[24]

As described above, our calculations were performed with the augmented correlation consistent sequence of basis functions, using up through sextuple zeta level sets, in some cases. The systematic convergence properties of this sequence facilitate extrapolation of the total energies to the CBS limit. Although several simple expressions have been suggested, including an empirically motivated exponential

$$E(x) = E_{CBS} + b e^{-cx} \tag{1}$$

where x is a basis set index, $x = 2$ (DZ), 3(TZ), etc.,[25−29] and an inverse power of l_{max}

$$E(l_{max}) = E_{CBS} + 1/(l_{max} + {}^1/_2)^4 \tag{2}$$

where l_{max} is the maximum angular momentum present in the basis set,[30] we adopt as our best estimate a mixed exponential/Gaussian of the form:

$$E(x) = E_{CBS} + b e^{-(x-1)} + c e^{-(x-1)**2} \tag{3}$$

where x is defined as in eq 1.[31,32] For second- and third-row correlation consistent basis sets, x (eqs 1 and 3) $= l_{max}$ (eq 2). Feller and Peterson[33] have shown that all three of these expressions are effective in reproducing experimental values as measured by the mean absolute deviation, ϵ_{MAD}, of the calculated values of $D_0°$ with respect to experiment. In their recent study of 73 compounds, the mixed expression produced slightly smaller values of ϵ_{MAD}, although the differences were not statistically significant. We use the spread in the CBS results obtained from eqs 1−3 as a crude estimate of the uncertainty associated with the extrapolation.

Core/valence correlation energy corrections to the binding energy, ΔE_{CV}, were obtained from calculations using the cc-pCVTZ and cc-pCVQZ basis sets for fluorine[34] and the cc-pwCVTZ and cc-pwCVQZ weighted correlation consistent sets for silicon.[35] Rather than incur the expense of reoptimizing the geometries with the core/valence basis sets, we chose to evaluate ΔE_{CV} at the optimal CCSD(T)/aug-cc-pVTZ geometries. The 1s pair of electrons on silicon was treated as a frozen core. By performing calculations with two levels of core/valence basis sets, we were able to gauge the degree of convergence in ΔE_{CV}. In the worst case, SiF_4, the change in ΔE_{CV} between the triple and quadruple zeta basis sets was 0.4 kcal/mol. Since each step up in basis set size typically cuts the change in ΔE_{CV} by a factor of 2 or more, we tentatively conclude that our core/valence corrections should be accurate to 0.2 kcal/mol, or better. Throughout the remainder of this work, discussions of the core/valence effect will be based on the quadruple zeta core/valence results.

Atomic spin−orbit (SO) and molecular/atomic scalar relativistic corrections were added to our nonrelativistic atomization energies in order to account for these sometimes significant effects. They are denoted ΔE_{SO} and ΔE_{SR}, respectively. The former account for the improper description of the atomic asymptotes, since atomic energies determined by our calculations correspond to an average over spin multiplets, rather than the lowest energy multiplet. The $^2\Pi$ state of SiH has an additional *molecular* spin−orbit correction due to the splitting of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states, which partially cancels the atomic SO correction. Spin−orbit corrections were taken from the atomic (−0.385 kcal/mol for F and −0.43 kcal/mol) and molecular values reported by Dunning and co-workers,[29,32] which are based on the experimental values of Herzberg[36] and Moore.[37]

Scalar relativistic corrections were obtained from frozen-core configuration interaction wave functions including single and double excitations (CISD) using the cc-pVTZ basis set. The CISD(FC) wave function was used to evaluate the dominant one-electron Darwin and mass-velocity terms in the Breit−Paul Hamiltonian. Tests were performed with a variety of contracted and completely uncontracted basis sets, some with additional tight functions to account for core/valence correlation, but ΔE_{SR} was found to be largely insensitive to the choice of basis set and the inclusion of all electrons in the correlation treatment.

Zero-point energies (ZPEs) were obtained from experimental frequencies or harmonic CCSD(T) frequencies. In the case of SiH and Si_2, where experimental anharmonic ZPEs were available,[38] the difference between ZPE_{harm} and ZPE_{anharm} was less than 0.1 kcal/mol. For SiF_2, the ZPE was taken as the average of the ZPEs based on the experimental fundamentals[39] and CCSD(T) harmonic frequencies, i.e., $\sum(\nu_i + \omega_i)/4$. Potential errors for larger molecules attributable to the use of $^1/_2\sum\omega$ for the zero-point energy are harder to estimate. An experimental ZPE of 8.02 kcal/mol has been reported by McDowell et al.[40] for SiF_4. In the study of Feller and Peterson,[33] 43 comparisons were made between harmonic frequency based ZPEs and ZPEs obtained using anharmonic corrections. Typical differences between the two sets were ≤0.2 kcal/mol, with the largest being 0.8 kcal/mol for C_2H_2. Harmonic frequencies were obtained for SiF_4 at the CCSD(T) level. With the aug-cc-pVDZ basis set, the use of $^1/_2\sum\omega$ yielded a ZPE(SiF_4) that was 0.5 kcal/mol smaller than the value of McDowell et al. However, increasing the basis set to the aug-cc-pVTZ level reduces this difference to 0.1 kcal/mol, supporting the notion that for many systems $^1/_2\sum\omega$ provides a reasonable approximation to the true ZPE, as long as the frequencies are obtained from sufficiently high level calculations.

III. Results

Optimized CCSD(T)(FC) geometries and total energies are listed in Table 1, along with the available experimental data.[38,40−46] Agreement between theory and experiment is generally good, with deviations in bond lengths for the di- and triatomics being on the order of 0.005 Å or less. Instances of both overestimating and underestimating r_{expt} are present. For the larger molecules, where the experimental values are less certain, the deviations increase to as much as 0.017 Å (Si_2H_6), with the theoretical calculations predicting longer bond distances than experiment. It should be noted that core/valence and scalar relativistic corrections will tend to contract bond lengths. For example, the Si−H distance in SiH_4 contracts by 0.001 Å due to scalar relativistic effects and 0.004 Å from core/valence effects, bringing the theoretical value to within 0.001 Å of experiment.

Theoretical and experimental atomization energies are presented in Table 2. The reported experimental uncertainties, where available, are also listed.[2,7,38,47−56] Variations among the CCSD(T)(FC)/CBS estimates of $\sum D_e$ are ≤ 0.4 kcal/mol with respect to the variations in the size of the underlying basis sets. The difference in the aDTQ and aTQ5 extrapolations is small, with 0.4 kcal/mol being the largest difference. In most cases, the extrapolation with the smaller basis sets leads to slightly larger values for $\sum D_e$.

For the three smallest systems (SiH, SiH_2, and Si_2) we could afford calculations with the very large aug-cc-pV6Z basis set, which corresponds to a (22s,15p,6d,5f,4 g,3h,2i) → [9s,8p,6d,-5f,4g,3h,2i] contracted set on silicon and (11s,6p,5d,4f,3g,2h) → [7s,6p,5d,4f,3g,2h] on H. The differences between the raw aV6Z atomization energies and the CBS estimates were small, ranging from −0.1 kcal/mol in SiH and Si_2 to −0.2 kcal/mol in SiH_2 (see Table 2). On the other hand, the raw aV5Z and aV6Z values of $\sum D_e$ differed by amounts that are 2−3 times larger. In agreement with the conclusion reached elsewhere,[33] this suggests that the CBS extrapolations are effective and that the completeness of the one-particle basis has largely been eliminated as a potential source of error for this particular collection of molecules.

The core/valence corrections shown in Table 2 are all ≤0.5 kcal/mol in magnitude. For SiH_n, $n = 2−4$, ΔE_{CV} is negative, decreasing $\sum D_e$, whereas, ΔE_{CV} is positive for Si_2, SiF, SiF_2, and SiF_4, increasing $\sum D_e$. Scalar relativistic corrections (ΔE_{SR}) are of similar magnitude and sign to ΔE_{CV}, with the exceptions of Si_2, Si_2H_6, and SiF_4. $\Delta E_{SR}(Si_2H_6) = 1.1$ kcal/mol, and for SiF_4 the correction is even larger, reaching a maximum of −2.4 kcal/mol. This situation, where $\Delta E_{SR} > \Delta E_{CV}$, is in contrast to what was observed for first- and second-period elements. For example, in the case of ethylene, $\Delta E_{CV} = 2.4$ and $\Delta E_{SR} = -0.4$ kcal/mol.[33]

Error bars for the theoretical $\sum D_0$ column in Table 2 are based, in part, on the uncertainties associated with the CBS extrapolations. As described above, we have adopted the spread in the CBS estimates obtained from eqs 1−3 as a crude measure of this uncertainty. The contributions to the error arising from the use of harmonic frequencies, when necessary, and the core/valence, scalar relativistic, and higher order correlation corrections are each assumed to contribute ∼ 0.1 kcal/mol. The scalar relativistic error estimate is based on a number of comparisons of CISD results with more sophisticated calculations. For example, our calculations predict $\Delta E_{SR}(SiH_4) = -0.55$ vs −0.67 kcal/mol from the Douglas−Kroll relativistic calculations of Collins and Grev.[4] Our error analysis assumes no cancellation of error, although given the variations in sign of the different effects some cancellation is likely to occur.

As seen in Table 2, the effect of higher order excitations, ΔE_{HO}, as measured by the CCSDT/cc-pVTZ calculations, is ≤−0.3 kcal/mol for the Si_xH_y compounds, but grows to −0.5 and −0.9 kcal/mol for SiF_2 and SiF_4. The present higher order corrections should be viewed as preliminary, since estimated full CI results have not been reported for any SiF_x compounds. The column labeled "total $\sum D_0$" in Table 2 represents our best estimate, obtained by adding the zero-point energy together with the effects of the four smaller corrections. For SiF_4 we predict $\sum D_0 = 564.5 \pm 0.9$ kcal/mol, using UCCSD(T) to treat the atoms.

By combining the known heats of formation of hydrogen (61.63 ± 0.001), fluorine (18.47 ± 0.07), and silicon (106.6 ± 1.9 kcal/mol) with the $\sum D_0$ values in Table 2, we calculated the 0 K heats of formation listed in Table 3. The observed errors (theory − experiment) for the SiH_x molecules are −1.8 (SiH), −1.4 (SiH_2-$^1A_1$), −1.1 (SiH_2-$^3B_1$), −0.4 (SiH_3), and −0.6 kcal/mol (SiH_4), where the top experimental entry has been used in those cases where more than one is available. Errors for the other molecules are −0.2 (Si_2), −0.9 (Si_2H_6), −9.6 (SiF), −10.6 (SiF_2), and +0.9 kcal/mol (SiF_4). Compared with the typical errors found in the 73-molecule study of Feller and Peterson,[33] the SiH_x errors are larger by a factor of 2−3. For the SiH_x

TABLE 1: Total Energies and Geometries[a]

		CCSD(T)(FC)			expt	
molecule	basis	*E*	r_e (Å)	∠ (deg)	r_e (Å)	∠ (deg)
SiH($^2\Pi$)	aVDZ	−289.5146	1.543		1.520[b]	
	aVTZ	−289.5482	1.529			
	aVQZ	−289.5542	1.526			
	aV5Z	−289.5562	1.522			
	aV6Z	−289.5568	(1.521)			
SiH_2($^1A_1$)	aVDZ	−290.1438	1.536	92.1	1.521[c]	92.1[c]
	aVTZ	−290.1729	1.523	92.2		
	aVQZ	−290.1808	1.518	92.3		
	aV5Z	−290.1834	1.517	92.3		
	aV6Z	−290.1842	1.516	92.3		
SiH_2($^3B_1$)	aVDZ	−290.1134	1.496	118.7		
	aVTZ	−290.1408	1.485	118.5		
	aVQZ	−290.1485	1.482	118.4		
	aV5Z	−290.1509	1.480	118.4		
SiH_3($^2A_1$)	aVDZ	−290.7548	1.495	111.2	1.468[d]	110.5[d]
	aVTZ	−290.7888	1.484	111.3		
	aVQZ	−290.7982	1.482	111.3		
	aV5Z	−290.8017	(1.481)	(111.3)		
SiH_4($^1A_1$)	aVDZ	−291.3998	1.493		1.474[e]	
	aVTZ	−291.4401	1.483			
	aVQZ	−291.4516	1.480			
	aV5Z	−291.4553	1.480			
Si_2($^3\Sigma_g^-$)	aVDZ	−577.9370	2.296		2.246[b]	
	aVTZ	−577.9810	2.268			
	aVQZ	−577.9933	2.256			
	aV5Z	−577.9977	2.253			
	aV6Z	−577.9992	2.252			
Si_2H_6($^1A_{1g}$)	aVDZ	−581.6250	2.369 1.497	108.7	2.327[f]	107.8[f]
	aVTZ	−581.7005	2.351 1.487	108.7		
	aVQZ	−581.7222	2.346 1.484	10.8		
	aV5Z	−581.7294	(2.344) (1.483)	(108.8)		
SiF($^2\Pi$)	aVDZ	−388.6705	1.672		1.601[b]	
	aVTZ	−388.7788	1.625			
	aVQZ	−388.8140	1.613			
	aV5Z	−388.8261	1.610			
SiF_2($^1A_1$)	aVDZ	−488.4465	1.656	99.3	1.590[g]	100.8[g]
	aVTZ	−488.6478	1.612	100.2		
	aVQZ	−488.7140	1.602	100.5		
	aV5Z	−488.7370	1.599	100.5		
SiF_4($^1A_1$)	aVDZ	−687.9307	1.607		1.5598[h]	
	aVTZ	−688.3272	1.571		1.552[i]	
	aVQZ	−688.4558	1.564			
	aV5Z	−688.5008	1.562			

[a] Results for open shell systems were obtained from UCCSD(T) calculations. Energies are in hartrees. Values given in parentheses were estimated from an exponential extrapolation of the preceding three values. The angle given for SiH_3 is the HSiH angle. For Si_2H_6 the first bond length corresponds to r_{SiSi} and the second one, which appears below the first, corresponds to r_{SiH}. The angle listed for Si_2H_6 is the HSiH angle. [b] Huber and Herzberg, ref 38. [c] Dubois, ref 41. [d] Yamada and Hirota, ref 42. [e] Ohno et al., ref 43. [f] Shotten et al., ref 44. The SiH distance was assumed. [g] Shoji et al., ref 45. [h] McDowell et al., ref 40. [i] Beagley et al., ref 46.

molecules, G3 is within 1 kcal/mol of our best estimates, while the difference for SiF_4 increases slightly, to 2.8 kcal/mol for $\sum D_e$.

Excellent agreement was found between the present theoretical value for $\Delta H_f°(SiF_4) = -384.0$ kcal/mol and the very well determined experimental values given by Johnson[56] and the JANAF[2] and CODATA tables.[57] If the RCCSD(T) method is used to describe the Si and F atoms, the agreement with experiment becomes even better, −385.0 (theory) vs −384.9 (expt) kcal/mol. As expected, the same change to RCCSD(T) atoms increases the SiF_2 heat of formation by only half as much. The comparable changes for the Si_xH_y compounds is ≤0.3 kcal/mol. At present, it is not known if either of the two coupled cluster methods for treating open shell atoms can reliably be expected to lie closer to the FCI limit. We adopt a conservative approach and take the average of the UCCSD(T) and RCCSD(T) values as our final best estimate for the heat of formation, $\Delta H_f°(SiF_4) = -384.5 \pm 0.9$ kcal/mol.

On the basis of the use of the heat of formation of Si in our calculation of $\Delta H_f°(SiF_4)$ and the close agreement between theory and experiment, our work does not support the revision in $\Delta H_f°(Si)$ from 106.6 to 108.1 kcal/mol, the latter value appearing in Table 9 of the work by Grev and Schaefer.[1] Ochterski et al.[58] interpreted the 108.1 kcal/mol value, which is consistent with the computed nonrelativistic heat of formation of SiH_4, as being recommended by Grev and Schaefer in favor of the JANAF value. However, no such recommendation appears in the original text. We note that our calculations predict a heat of formation for SiH_4 that is too negative (i.e., too large a value for $\sum D_e$). If we assume that all of the difference between our best $\Delta H_f°(SH_4)$ and the experimental value of Gunn and Green[7] (9.5 ± 0.5 kcal/mol) arises from an error in $\Delta H_f°(Si)$, it would

TABLE 2: CCSD(T) Atomization Energies[a]

	CBS/mixed $\sum D_e$											
molecule	(aDTQ)	(aTQ5)	(aQ56)	atoms[b]	ZPE[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{HO}[f]	atomic ΔE_{SO}[g]	total $\sum D_0$[h]	expt $\sum D_0$ (0 K)[i]	ref
SiH ($^2\Pi$)	73.5	73.5	73.7	UCCSD(T)	2.9	0.0	−0.1	0.0	−0.2	70.5 ± 0.4	68.7 ± 0.7	BGCR
			73.6[j]								68.6 ± 2.0	JANAF
											68.6 ± 1.2	EA
											68.6 ± 1.7	BA
											67.2 ± 1.7	BEA
SiH_2($^1A_1$)	153.9	153.7	153.7	UCCSD(T)	7.3	0.0	−0.2	0.0	−0.4	145.8 ± 0.4	144.4 ± 0.7	BGCR
			153.5[j]								140.5 ± 3.0	SB
											140.5 ± 2.0	BA
											146.3 ± 2.8	FBT
											144.5 ± 1.6	VTSR
											144.2 ± 1.7	FWW
SiH_2($^3B_1$)	133.6	133.3		UCCSD(T)	7.5	−0.5	−0.4	0.0	−0.4	124.5 ± 0.4	123.4 ± 0.7	BGCR
											123.3 ± 0.7	EA
SiH_3($^2A_1$)	228.0	228.4		UCCSD(T)	13.2	−0.2	−0.4	0.0	−0.4	214.2 ± 0.5	213.8 ± 1.2	DW
SiH_4($^1A_1$)	325.1	324.8		UCCSD(T)	19.4	−0.2	−0.6	0.0	−0.4	304.2 ± 0.6	303.6 ± 0.5	GG
	325.3	325.1		RCCSD(T)						304.5 ± 0.6	302.6 ± 0.5	JANAF
											302	LBLHLM
Si_2($^3\Sigma_g^-$)	75.5	75.6	75.6	UCCSD(T)	0.7	0.5	−0.1	−0.2	−0.9	74.2 ± 0.4	74.0	HH
			75.5[j]								73 ± 3	JANAF
Si_2H_6 ($^1A_{1g}$)	536.1	535.8		UCCSD(T)	30.5	0.0	−1.1	−0.3	−0.9	503.0 ± 0.5	502.1 ± 0.3	GG
											500.1	BLHLM
SiF($^2\Pi$)	142.4	142.1		UCCSD(T)	1.2	0.4	−0.3	−0.2	−0.8	139.9 ± 0.4	130.3 ± 3	JANAF
											128.5	HH
SiF_2($^1A_1$)	299.6	299.4		UCCSD(T)	2.9	0.6	−0.8	−0.5	−1.2	294.4 ± 0.5	283.8 ± 3	JANAF
	300.2	299.9		RCCSD(T)						294.9 ± 0.5		
SiF_4($^1A_1$)	577.5	577.2		UCCSD(T)	8.0	0.5	−2.4	−0.9	−2.0	564.5 ± 0.9	565.4 ± 0.1	Johnson
	578.4	578.2		RCCSD(T)						565.5 ± 0.9	565.1 ± 0.2	JANAF
											565.2 ± 0.2	CODATA

[a] Results are given in kcal/mol. The total theoretical value is defined as E[CCSD(T)(FC)/CBS] − $^1/_2\sum\nu_i$ + CV + scalar relativistic + higher order correlation + atomic/molecular SO. The highest level basis set extrapolations were used. Experimental values are denoted as follows: BGCR = Berkowitz et al., ref 47; JANAF = Chase, ref 2; EA = Elkind and Armentrout, ref 48; BA = Boo and Armentrout, ref 49; BEA = Boo et al., ref 50; SB = Shin and Beauchamp, ref 62; FBT = Francisco et al., ref 51; VTSR = Van Zoeren et al., ref 52; FWW = Frey et al., ref 53; DW = Doncaster and Walsch, ref 54; GG = Gunn and Green, ref 7; LBLHLM = Lias et al., ref 55; HH = Huber and Herzberg, ref 38; Johnson = G. K. Johnson, ref 56; CODATA = Cox et al., ref 57. [b] Method used for treating the atomic asymptotes. [c] Zero-point energies were taken from the anharmonic experimental values for SiH, Si_2, SiF, and SiF_4. For all other molecules it was computed as $^1/_2\sum\omega$, using CCSD(T) harmonic frequencies obtained from the aug-cc-pVTZ basis set (SiH_2) and the aug-cc-pVDZ basis set for all others. [d] Core/valence corrections were obtained with the cc-pCVQZ or cc-pwCVQZ (for second-row elements) basis sets at the optimized CCSD(T)/aug-cc-pVTZ geometries. A positive sign indicates that CV effects increase the stability of the molecule relative to the atomic asymptotes. [e] The scalar relativistic correction is based on CISD(FC)/cc-pVTZ calculations of the one-electron Darwin and mass-velocity terms evaluated at the CCSD(T)(FC)/aug-cc-pVTZ geometry. [f] Higher order correlation correction based on CCSDT/cc-pVTZ calculations. [g] Correction due to the improper treatment of the atomic asymptotes as an average of spin multiplets. For diatomics with a nonzero molecular spin−orbit contribution, e.g., SiH($^2\Pi$), this is the sum of the atomic and molecular contributions. [h] Using the best available CBS estimate for the CCSD(T)(FC) atomization energy. Error bars for $\sum D_0$ are based, in part, on the uncertainties associated with the CBS extrapolations. [i] Experimental values are based on the JANAF heat of formation of silicon (106.6 ± 1.9 kcal/mol). [j] The raw aug-cc-pV6Z value (listed here to provide some indication of the degree of convergence of the CBS extrapolation).

argue in favor of increasing $\Delta H_f°$(Si) by +0.8, to 107.4 ± 0.6 kcal/mol, where we have adopted the error estimate from the theoretical value. This error estimate is closer to the ±1.0 kcal/mol recommended by Desai.[6] Using this larger value for $\Delta H_f°$(Si) results in improved agreement with experiment for most of the Si_xH_y molecules listed in Table 3 (see values in parentheses). However, the evidence is far from unanimous, since an increase of 0.8 kcal/mol in $\Delta H_f°$(Si) would worsen agreement between theory and experiment for SiF_4. Despite carrying out very high level calculations, the residual uncertainties in the theoretical values make it very difficult to state unambiguously that the heat of formation of silicon should be revised.

For Si_2, the accuracy of our calculations can help to reduce the error in D_0. Spectroscopic measurements yield $D_0 = 70 \pm 4$ kcal/mol, with an upper limit of $D_0 \leq 74.0$ kcal/mol. Knudsen cell/third law measurements of Si and Si_2 yield D_0 values of 73.3, 74.3, and 70.4 kcal/mol (average = 72.7 kcal/mol). The CCSD(T)/CBS value of $D_0(Si_2) = 74.4 \pm 0.4$ kcal/mol is at the high end of these values but in good agreement with the 74.0 kcal/mol recommended by Huber and Herzberg,[38] which is based on several experimental measurements. Given the close agreement between the theoretical and experimental values of D_0 and the improved error limits that we are suggesting for $\Delta H_f°$(Si), our heat of formation for Si_2 should be quite accurate.

After correcting for core/valence and relativistic effects, the CCSD(T)/CBS value of D_0(SiH) = 70.5 ± 0.4 kcal/mol compares well with the upper limit of 70.6 kcal/mol derived from predissociation of the $B^2\Sigma^+$ state,[59] the corrected Birge−Sponer extrapolation of 70 kcal/mol,[2] and Huber and Herzberg's upper limit of 71.3 kcal/mol. The estimated value of Rao and Lakshman[60] of 68.7 kcal/mol appears to be too low. Conversely, the value of Carlson et al.[61] of 77.05 ± 0.6 kcal/mol appears too high, as noted by other workers. On the basis of use of the experimental value for $\Delta H_f°$(Si), we suggest that our value for $\Delta H_f°$(SiH) may be the most accurate estimate available. If this is true, the value for D_0(SiH) = 68.7 ± 0.7 kcal/mol obtained from photoionization experiments[47] is too low.

The theoretical heat of formation of SiH_2 ($^1A_1$) listed in Table 3 is smaller than the experimental values,[47] although it is within the revised value of 66 ± 3 kcal/mol based on the proton affinity of SiH_2.[62] The calculated values suggest that the lower value[47]

TABLE 3: Theoretical and Experimental 0 K Heats of Formation (kcal/mol)

molecule	this work[a]	G&S[b]	C&G[c]	G3[d]	expt[e]	ref
$SiH(^2\Pi)$	87.7 ± 0.4	87.74			89.5 ± 0.7	BGCR
	(88.5 ± 0.4)[f]				89.6 ± 2.0	JANAF
					89.6 ± 1.2	EA
					89.6 ± 1.7	BA
					91.0 ± 1.7	BEA
$SiH_2(^1A_1)$	64.1 ± 0.4	64.13		63.5	65.5 ± 0.7	BGCR
	(64.9 ± 0.4)[f]				69.4 ± 3.0	SB
					69.4 ± 2.0	BA
					63.6 ± 2.8	FBT
					65.4 ± 1.6	VTSR
					65.7 ± 1.7	FWW
$SiH_2(^3B_1)$	85.4 ± 0.4	85.27		85.3	86.5 ± 0.7	BGCR
	(86.2 ± 0.4)[f]				86.6 ± 0.7	EA
$SiH_3(^2A_1)$	47.3 ± 0.5	47.6		48.2	47.7 ± 1.2	DW
	(48.1 ± 0.5)[f]					
$SiH_4(^1A_1)$	8.7 ± 0.6	9.03	9.87	9.6	9.5 ± 0.5	GG
	(9.5 ± 0.6)[f]				10.5 ± 0.5	JANAF
					11	LBLHLM
$Si_2(^3\Sigma_g^-)$	138.8 ± 0.4				139.2	HH
	(139.6 ± 0.4)[f]				140.3 ± 3	JANAF
$Si_2H_6(^1A_{1g})$	19.7 ± 0.5			21.5	20.9 ± 0.3	GG
	(20.5 ± 0.5)[f]				22.9	LBLHLM
$SiF(^2\Pi)$	−14.8 ± 0.4				−5.2 ± 3	JANAF
	(−9.7 ± 0.4)[f]				−3.4	HH
$SiF_2(^1A_1)$	−151.7 ± 0.5				−140.3 ± 3	JANAF
	(−150.9 ± 0.5)[f]					
$SiF_4(^1A_1)$	−384.5 ± 0.9			−383.7	−384.9 ± 0.1	Johnson
	(−383.7 ± 0.9)[f]				−384.6 ± 0.2	JANAF
					−384.7 ± 0.2	CODATA

[a] Based on the $\sum D_0$ data from Table 2. The values for SiH_4, SiF_2, and SiF_4 represent an average of the values obtained with UCCSD(T) and RCCSD(T) atoms. [b] Best spin−orbit corrected, extrapolated values based on dissociation to atoms from Grev and Schaefer, ref 1. These values do not include a correction for scalar relativistic corrections, but do include estimates of the remaining 1-particle and *n*-particle incompleteness. [c] Best estimate from Collins and Grev, ref 4, including a −0.67 kcal/mol scalar relativistic correction from CCSD(T) Douglas−Kroll calculations. This estimate also includes the following corrections: +1.61 kcal/mol for expansion of the hydrogen polarization basis set from [2p,1d] to [3p,2d,1f]; +1.06 kcal/mol for remaining incompleteness in the 1-particle and *n*-particle basis sets; −0.43 kcal/mol for atomic spin−orbit effects; −0.31 kcal/mol for core/valence effects and −19.69 kcal/mol for ZPE effects. [d] Gaussian-3 values from ref 12. [e] Experimental references are given in footnote *a* of Table 2. [f] Based on a heat of formation for silicon of 107.4 kcal/mol.

for $\Delta H_f°(SiH_2) = 65.5 \pm 0.7$ kcal/mol is preferred over the higher value of 68.6 ± 0.8 kcal/mol. However, even the lower experimental value is still too high, consistent with the differences found for SiH. Our calculated value for the singlet−triplet splitting in SiH_2 of 21.3 kcal/mol at 0 K agrees well with the experimental measurement[47] of 21.0 ± 0.7 kcal/mol derived from the photoionization experiments. The calculated and experimental heats of formation for SiH_3 are also in excellent agreement.[54]

Our calculations suggest that the JANAF revision of Gunn and Green's[7] original $\Delta H_f°(SiH_4)$ estimate is not correct. Instead, we prefer the 9.5 ± 0.6 kcal/mol value, which places the calculated and experimental values within each other's error limits.

The heat of formation of Si_2H_6 has been measured to be 17.1 ± 0.3 kcal/mol at 298 K,[7] although recent work has suggested that this number be revised upward by 2 kcal/mol due to the final state of Si, as noted above. Conversion of $\Delta H_f°(Si_2H_6)$ from 298 to 0 K yields 20.9 ± 0.3 kcal/mol. This value is just outside the CCSD(T)/CBS value of 19.7 ± 0.5 kcal/mol. The extent to which theory and experiment agrees suggests that the original experimental values are indeed correct and need not be corrected by 1 kcal/mol per mol of Si, as was done in the JANAF value for $\Delta H_f°(SiH_4)$.

The nearly exact agreement between the current values of $\Delta H_f(SiH_x)$ and the values previous published by Grev and Schaefer[1] is somewhat misleading. For example, while our best CBS $\Delta H_f(SiH_4)$ value in Table 3 is only 0.1 kcal/mol smaller than their 9.0 kcal/mol, the underlying contributions to ΔH_f differ by somewhat more than that. The use of R/UCCSD(T)[17−19] atomic energies, as opposed to the UCCSD(T) energies used in the present study can sometimes lead to significant differences, but for silicon it amounts to only 0.04 kcal/mol at the basis set limit. The current zero point energy for SiH_4 (19.4 kcal/mol) was based on $\frac{1}{2}\sum\omega_e$, where ω_e are the CCSD(T)/aVDZ harmonic frequencies. If the experimental fundamentals are substituted for the CCSD(T) frequencies, ZPE drops to 19.2 kcal/mol. Grev and Schaefer used a value of ZPE = 19.7 kcal/mol, obtained by averaging the theoretical configuration interaction frequencies and the experimental fundamentals. Their $\Delta H_f(SiH_4)$ does not contain any scalar relativistic correction, whereas our value has been increased by 0.6 kcal/mol due to ΔE_{SR}. The value reported by Collins and Grev,[4] which does include a scalar relativistic correction, shows a greater deviation from our result. Finally, the basic electronic contributions to ΔH_f, the atomization energies, also differ by something on the order of 0.5 kcal/mol.

The difference between theory and experiment for SiF and SiF_2 shown in Tables 2 and 3 greatly exceeds what has been observed for all other first- and second-row compounds. In light of the level of agreement found for other silicon-containing molecules, we prefer the present theoretical values over their experimental counterparts.

IV. Conclusions

High-level electronic structure calculations have been used to determine the 0 K heats of formation of nine small silicon-containing compounds. At first glance the level of agreement with experiment is not as good as has recently been observed for a large number of other small molecules composed of first-through-third period elements. However, in light of assumptions made in the analysis of several relevant experimental data sets, which may not have been warranted, and larger error bars than were quoted in some summary tables, it is apparent that the level of agreement is indeed consistent with results for other molecules. With the exception of SiF and SiF_2, the differences between experiment and the calculated values fall into the 1−2 kcal/mol range when the original 106.6 kcal/mol 0 K heat of formation of silicon is used. The agreement for Si_xH_y molecules improves if a revised value of 107.4 ± 0.6 kcal/mol for ΔH_f(Si) is used, but it worsens for SiF_4. For SiF and SiF_2, we suggest that the calculated values are likely to be of higher accuracy than the experiments, based on realistic experimental error bars, and are to be preferred.

Differences between the present heats of formation and previous values from Grev and Schaefer[1] are very small, due in part to some cancellation of underlying differences in the contributions to ΔH_f that are considerably larger. G3 is generally within 1−2 kcal/mol of our best results, with the largest differences found for SiF_4 and Si_2H_6.

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