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LETTERS

A Definitive Heat of Vaporization of Silicon through Benchmark *ab Initio* Calculations on SiF_4

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To resolve a significant uncertainty in the heat of vaporization of silicon—a fundamental parameter in gas-phase thermochemistry—$\Delta H^\circ_{f,0}$ [Si(g)] has been determined from a thermochemical cycle involving the precisely known experimental heats of formation of SiF_4(g) and F(g) and a benchmark calculation of the total atomization energy (TAE_0) of SiF_4 using coupled-cluster methods. Basis sets up to [8s7p6d4f2g1h] on Si and [7s6p5d4f3g2h] on F have been employed, and extrapolations for residual basis set incompleteness applied. The contributions of inner-shell correlation (−0.08 kcal/mol), scalar relativistic effects (−1.88 kcal/mol), atomic spin−orbit splitting (−1.97 kcal/mol), and anharmonicity in the zero-point energy (+0.04 kcal/mol) have all been explicitly accounted for. Our benchmark $TAE_0 = 565.89 \pm 0.22$ kcal/mol leads to $\Delta H^\circ_{f,0}$ [Si(g)] $= 107.15 \pm 0.38$ kcal/mol ($\Delta H^\circ_{f,298}$ [Si(g)] $= 108.19 \pm 0.38$ kcal/mol): between the JANAF/CODATA value of 106.5 ± 1.9 kcal/mol and the revised value proposed by Grev and Schaefer [*J. Chem. Phys.* **1992**, *97*, 8389], 108.1 ± 0.5 kcal/mol. The revision will be relevant for future computational studies on heats of formation of silicon compounds. Among standard computational thermochemistry methods, G2 and G3 theory exhibit large errors, while CBS-Q performs relatively well, and the very recent W1 theory reproduces the present calibration result to 0.1 kcal/mol.

Introduction

For three of the first- and second-row elements, namely, Be, B, and Si, the tabulated heats of formation of the atoms in the gas phase carry experimental uncertainties in excess of 1 kcal/mol. Aside from being propagated into uncertainties for experimental gas-phase thermochemical data for compounds involving these elements, they adversely affect the accuracy of any *directly computed* heat of formation—be it ab initio or semiempirical—of any Be, B, or Si-containing compounds through the identity

$$\Delta H^\circ_{f,T}(X_kY_lZ_m...) - k\Delta H^\circ_{f,T}(X) - l\Delta H^\circ_{f,T}(Y) - m\Delta H^\circ_{f,T}(Z) - ... = E_T(X_kY_lZ_m...) + RT(1 - k - l - m - ...) - kE_T(X) - lE_T(Y) - mE_T(Z) - ... \quad (1)$$

Particularly given the importance of boron and silicon compounds, this is a rather unsatisfactory state of affairs.

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Recently we succeeded[1] in reducing the uncertainty for boron by almost an order of magnitude (from 3 to 0.4 kcal/mol) by means of a benchmark calculation of the total atomization energy (TAE_0) of BF_3(g). By combining the latter with the experimentally precisely known[2] heat of formation of BF_3, we were able to indirectly obtain the vaporization enthalpy of boron to high accuracy. It was thus shown that a 1977 experiment by Storms and Mueller,[3] which was considered an outlier by the leading compilation of thermochemical tables,[4] was in fact the correct value.

The heat of formation of Si(g) is given in the JANAF[4] as well as the CODATA[2] tables as 106.5 ± 1.9 kcal/mol. Desai[5] reviewed the available data and recommended the JANAF/CODATA value, but with a reduced uncertainty of ± 1.0 kcal/mol. Recently, Grev and Schaefer (GS)[6] found that their ab initio calculated TAE[SiH_4], despite basis set incompleteness, was actually *larger* than the value derived from the experimental heats of formation of Si(g), H(g), and SiH_4(g). They suggested that the heat of vaporization of silicon be revised upward to $\Delta H^\circ_{f,0}$ [Si(g)] = 108.07 ± 0.50 kcal/mol, a suggestion supported by Ochterski et al.[7]

The calculations by GS neglected relativistic contributions, which were very recently considered by Collins and Grev (CG).[8] Using relativistic (Douglas−Kroll[9]) coupled-cluster methods, these authors found that the TAE of SiH_4 contains a relativistic contribution of − 0.67 kcal/mol. Combined with the earlier calculations of GS, this yields $\Delta H^\circ_{f,0}$ [Si(g)] = 107.4 ± 0.5 kcal/mol, within Desai's reduced error bar. However, as discussed there,[8] the experimental data for silane, SiH_4, involve an ambiguity. The JANAF heat of formation of silane, 10.5 ± 0.5 kcal/mol is in fact the Gunn and Green[10] measurement of 9.5 kcal/mol increased with a correction[11] of +1 kcal/mol for the phase transition Si(amorphous) → Si(cr), which was considered an artifact of the method of preparation by Gunn and Green. If one were to accept their argument, the GS and CG calculations on SiH_4 would actually support the original JANAF/CODATA $\Delta H^\circ_{f,0}$ [Si(g)].

No such ambiguities exist for tetrafluorosilane, SiF_4, for which a very accurate experimental heat of formation has been determined[12] by direct combination of the pure elements in their respective standard states in a fluorine bomb calorimeter. Johnson's[12] heat of formation at 298.15 K, − 386.18 ± 0.11 kcal/mol, is slightly higher in absolute value and slightly more precise than the CODATA value of −386.0 ± 0.2 kcal/mol, itself based on an earlier experiment from the same laboratory.[13]

Clearly, if a benchmark quality (preferably ± 0.3 kcal/mol or better) TAE[SiF_4(g)] could be calculated, then an unambiguous redetermination of $\Delta H^\circ_{f,0}$ [Si(g)] would be possible. Our previous study on BF_3 being at the limit of the then available computational hardware, a similar study on SiF_4—which contains an additional heavy atom and eight additional valence electrons, leading to an expected increase in CPU time and memory requirements by a factor of about 3.7 (see below)—could only be completed most recently, and is reported in the present contribution.

Methods

Most electronic structure calculations reported here were carried out using MOLPRO 97.3[14] running on SGI Octane and SGI Origin 2000 minisupercomputers at the Weizmann Institute of Science. The very largest calculation, a full-valence coupled-cluster calculation involving 620 basis functions, was carried out on the National Partnership for Advanced Computational Infrastructure CRAY T90 at the San Diego Supercomputer Center.

As in our previous study on BF_3, all electron correlation calculations involved in determining the valence and inner-shell correlation contributions to TAE were carried out using the CCSD[15] and CCSD(T)[16,17] coupled-cluster methods. (For the energies of the constituent atoms, the definition of ref 17 for the open-shell CCSD(T) energy was employed.) Both the very low $\mathcal{T}_1$ diagnostic[18] of 0.012, and inspection of the largest coupled-cluster amplitudes, suggest a system essentially totally dominated by dynamical correlation. From experience it is known[19] that CCSD(T) yields results very close to the exact (full configuration interaction) basis set correlation energy under such circumstances.

Basis set limits for the SCF and valence correlation contributions to TAE were extrapolated (see below for details) from calculated results using the (A)VTZ + 2d1f, (A)VQZ + 2d1f, and (A)V5Z + 2d1f basis sets. For silicon, those basis sets consist of the standard Dunning correlation consistent[20,21] cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets augmented with two high-exponent d and one high-exponent f functions with exponents obtained by progressively multiplying the highest exponent already present by a factor of 2.5. The addition of such "inner shell polarization functions"[22] has been shown[22−25] to be essential for smooth basis set convergence in second-row compounds, particularly those containing highly polar bonds such as SiF_4.[26] (It should be recalled that inner shell polarization is a pure SCF effect and bears little relationship to inner shell correlation. In the present case of SiF_4, the contribution of the inner polarization functions to the SCF/(A)VTZ + 2d1f TAE was found to be no less than 9.81 kcal/mol.) For fluorine, the basis sets given correspond to Dunning (diffuse function)-augmented correlation consistent[27] aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets—it was shown repeatedly (e.g., ref 28) that the use of augmented basis sets on highly electronegative elements such as F in polar compounds is absolutely indispensable for accurate binding energies. The final basis sets for SiF_4 involve 235, 396, and 620 basis functions, respectively, for (A)VTZ + 2d1f, (A)VQZ + 2d1f, and (A)V5Z + 2d1f.

The geometry of SiF_4 was optimized by repeated parabolic interpolation at the CCSD(T)/cc-pVQZ + 1 level, where the suffix "+1" stands for the addition of a tight d function with an exponent[24] of 2.082 on Si. In previous work on H_2SiO,[25] one of us found that this recovers essentially all of the inner polarization effect on the molecular geometry. The bond length thus obtained, r_e [SiF_4] = 1.56043 Å, was used throughout this work. (For comparison, the experimental r_0 = 1.5598(2) Å;[29] to our knowledge, no experimentally derived r_e is available.)

The inner-shell correlation contribution was determined by comparing the computed binding energies correlating all electrons except Si(1s), and correlating only valence electrons, using the MT small basis set.[30] The latter is a variant of the Martin−Taylor core correlation basis set[31,32] in which the very tightest p, d, and f functions were deleted at no significant loss in accuracy on the contributions to TAE.

The scalar relativistic contributions were obtained as expectation values of the first-order Darwin and mass−velocity operators[33,34] at the ACPF (averaged coupled-pair functional[35]) level using the MT small basis set. All electrons were correlated in this calculation, and it should be noted that the MT small basis set is completely uncontracted and therefore flexible enough in the s and p functions for this purpose. For the sake of illustration, this approach yields − 0.67 kcal/mol for SiH_4, identical to two decimal places with the more rigorous relativistic coupled-cluster value.[8]

TABLE 1: Computed Thermochemical Properties for SiF_4 and Si in the Gas Phase[a]

components of TAE	SCF	CCSD-SCF	CCSD(T)-CCSD
(A) VDZ + 2d	429.45	100.39	6.03
(A) VTZ + 2d1f	446.41	108.32	9.11
(A) VQZ + 2d1f	448.25	114.85	9.61
(A) V5Z + 2d1f	448.41	117.01	
extrap. {D,T,Q}	448.47	119.62	9.98
extrap. {T,Q,5}	448.43	119.28	

best estimates		best estimates	
valence correlation	129.26	best TAE_e	573.92
inner-shell correlation	0.08	ZPVE	8.03
Darwin & mass−velocity	−1.88	best TAE_0	565.89
atomic fine structure	−1.97		

derivation of revised $\Delta H^\circ_{f,0}$[Si(g)]	$\Delta H^\circ_{f,298}$	$H_{298} - H_0$	$\Delta H^\circ_{f,0}$
Si(cr)[2]	0	0.769 ± 0.002	0
Si(g)[2]	107.6 ± 1.9	1.8045 ± 0.0002	106.5 ± 1.9
SiF_4(g)[2]	−386.0 ± 0.2	3.67 ± 0.01	−384.7 ± 0.2
SiF_4(g)[12]	−386.18 ± 0.11		−384.86 ± 0.13[b]
F(g)[2]	18.97 ± 0.07	1.5578 ± 0.0002	18.47 ± 0.07
F_2(g)[2]	0	2.1092 ± 0.0002	0
Si(g) this work	108.19 ± 0.38		107.15 ± 0.38[b]

[a] All values are in kcal/mol. [b] CODATA values[2] for $H_{298} - H_0$ have been employed.

The contribution of atomic spin−orbit splitting derived from the experimental atomic fine structures[36] of Si(^3P) and F(^2S) is −1.968 kcal/mol. For comparison, we also carried out all-electron CASSCF/CI spin−orbit calculations[37] using the spdf part of a completely uncontracted aug-cc-pV5Z basis set, augmented with a single tight p, three tight d, and two tight f functions in even-tempered series with ratio 3.0. In this manner, we obtain a contribution of −1.940 kcal/mol. In short, to the accuracy relevant for this purpose it is immaterial whether the computed or the experimentally derived value is used.

The zero-point energy was obtained from the experimentally derived harmonic frequencies and anharmonicity constants of McDowell et al.[29] This leads to a value of 8.029 kcal/mol, whereas one would obtain 8.067 kcal/mol from one-half the sum of the harmonic frequencies, $\sum_i d_i \omega_i/2$ and 7.975 from one-half the sum of the fundamentals, $\sum_i d_i \nu_i/2$. The approximation $\sum_i d_i(\omega_i + \nu_i)/4$, at 8.021 kcal/mol, yields essentially the exact result.

Results and Discussion

All relevant data are given in Table 1. As expected, the SCF contribution of TAE converges quite rapidly. We have shown previously[38] that the SCF convergence behavior is best described by a geometric extrapolation $A + B/C^n$ of the type first proposed by Feller,[39] with extrapolation from the TAE contributions to be preferred over extrapolation from the constituent total energies. From the (A)VTZ + 2d1f, (A)VQZ + 2d1f, and (A)-V5Z + 2d1f results, i.e., Feller(TQ5), we obtain a basis set limit of 448.43 kcal/mol, 0.02 kcal/mol more than the SCF/(A)V5Z + 2d1f result itself. An extrapolation from the (A)VDZ + 2d, (A)VTZ + 2d1f, and (A)VQZ + 2d1f basis sets would have yielded 448.47 kcal/mol, an increment of 0.22 kcal/mol over the (A)VQZ + 2d1f result.

Given the large number of valence electrons, connected triple excitations account for a rather small part of the binding energy: 9.61 kcal/mol at the CCSD(T)/(A)VQZ + 2d1f level, compared to a CCSD valence correlation contribution of 114.85 kcal/mol and an SCF contribution of 448.25 kcal/mol. Since a CCSD(T)/(A)V5Z + 2d1f calculation is beyond the limits particularly of memory and available CPU time for this system, this suggests an approach in which only the CCSD valence correlation contribution be obtained from the largest basis set, while the (T) contribution is obtained from an extrapolation on smaller basis sets. Indeed, Martin and de Oliveira (MdO) recently found in a systematic study[30] on a wide variety of first- and second-row molecules that this essentially does not affect the quality of the results, except when the (T) contribution is a dominant component to the binding energy. Helgaker and co-workers[40] previously noted the more rapid basis set convergence behavior of connected triple excitations as compared with the CCSD correlation energy.

The CCSD/(A)V5Z + 2d1f calculation required over 3GB of memory, some 120 GB of disk space, and 43 h of real time (82 h of CPU time) running on 8 CPUs of the NPACI CRAY T90. (Close to 99% parallellism was achieved in the CCSD code simply by adapting it to use vendor-supplied parallel BLAS and LAPACK libraries.) To our knowledge, this is the largest coupled-cluster calculation ever carried out using a conventional algorithm.

We have considered two extrapolation formulas based on the asymptotic behavior of pair correlation energies,[41,42] namely the 3-point extrapolation $A + B/(l + 1/2)^\alpha$ due to Martin, and the 2-point extrapolation $A + B/l^3$ formula due to Helgaker and co-workers.[43] (In both formulas, l stands for the maximum angular momentum present in the basis set.) MdO found[30] that both formulas tend to predict the same basis set limit if extrapolated from sufficiently large basis sets, but that the limits predicted by the $A + B/l^3$ formula are much more stable with respect to reduction of the sizes of the basis sets used in the extrapolation. This is at least in part related to the fact that the three-point extrapolation involves, of necessity, one value with an even smaller l than the two-point extrapolation.

As an illustration, let us consider the BF diatomic which was used to refine the BF_3 result.[1] From the three-point $A + B/(l + 1/2)^\alpha$ extrapolation applied to AVn Z (n = 3,4,5) valence correlation contributions to D_e, we obtain 38.35 kcal/mol, compared to 38.76 kcal/mol for AVn Z (n = 4,5,6). In contrast, a $A + B/l^3$ extrapolation applied to AVn Z (n = Q,5) yields 38.78 kcal/mol, just like AVn Z (n = 5,6) does; application to AVn Z (n = T,Q) results yields an overestimate of 39.08 kcal/mol.

In the present case, the $A + B/l^3$ formula predicts a CCSD limit contribution to TAE[SiF_4] of 119.28 kcal/mol from the (A)VQZ + 2d1f and (A)V5Z + 2d1f results, with the extrapolation accounting for 2.27 kcal/mol of the final result. For comparison, extrapolation from two smaller basis sets, (A)-VTZ + 2d1f and (A)VQZ + 2d1f, yields 119.62 kcal/mol, while the $A + B/(l + 1/2)^\alpha$ formula applied to all three values yields a much smaller value of 118.87 kcal/mol.

The (T) contribution is computed as 9.11 and 9.61 kcal/mol, respectively, in the (A)VTZ + 2d1f and (A)VQZ + 2d1f basis sets: assuming $A + B/l^3$ behavior, this extrapolates to a limit of 9.98 kcal/mol. We thus finally find a basis set limit valence correlation contribution of 129.26 kcal/mol.

As expected, the Si(2s,2p) and F(1s) inner-shell correlation energy is quite substantial in absolute terms, accounting for some 28% of the overall correlation energy excluding the very deep Si(1s) core. As we have seen in the past for second-row molecules, however, the differential contribution to TAE nearly cancels, in this case being only +0.08 kcal/mol. This contribution is definitely dwarfed by that of scalar relativistic effects, which as we noted we compute to be −1.88 kcal/mol.

Combining all of the above with the atomic spin−orbit correction noted in the Methods section, we finally obtain a "bottom-of-the-well" TAE_e of 573.92 kcal/mol; combined with the experimentally derived ZPE, we obtain $TAE_0 = 565.89$ kcal/mol.

Combining this with the CODATA heats of formation of F(g) and SiF_4(g), we finally obtain $\Delta H^\circ_{f,0}$ [Si(g)] = 107.34 kcal/mol. Using the more recent $\Delta H^\circ_{f,0}$ [SiF_4(g)] instead, this value is reduced to 107.15 kcal/mol.

To make an assessment of the probable error in these values, we should consider both the uncertainty in the calculated TAE_0 and the propagated experimental uncertainties in $\Delta H^\circ_{f,0}$ [SiF_4(g)] and $\Delta H^\circ_{f,0}$ [F(g)]. Using exactly the same method as we have employed, MdO obtained a mean absolute error of 0.22 kcal/mol for a wide variety of first- and second-row molecules, which dropped as low as 0.16 kcal/mol when some molecules with significant nondynamical correlation effects were eliminated. Erring on the side of caution, we assign 0.22 kcal/mol as a standard deviation rather than an upper limit to the error. Given uncertainties of 0.07 and 0.20 kcal/mol in the CODATA heats of formation for F(g) and SiF_4(g), respectively, we obtain 107.34 ± 0.41 kcal/mol for $\Delta H^\circ_{f,0}$ [Si(g)]. Employing the more recent Johnson[12] ΔH°_f [SiF_4(g)] instead, which has a smaller uncertainty, we propose $\Delta H^\circ_{f,0}$ [Si(g)] = 107.15 ± 0.38 kcal/mol as our final estimate. (At 298.15 K, using the CODATA $H_{298} - H_0$ functions, this corresponds to 108.19 ± 0.38 kcal/mol.)

Our final estimate is in fact within the reduced error limits of Desai,[5] $\Delta H^\circ_{f,0}$ [Si(g)] = 106.5 ± 1.0 kcal/mol. It agrees to within combined uncertainties with the GS value after applying CG's relativistic correction, 107.4 ± 0.5 kcal/mol, which suggests that the "spurious" Si(cr) → Si(amorph) transition enthalpy discussed in the Introduction may indeed have been a fair estimate. In previous calculations[44,45] on SiF_4 and $SiCl_4$, respectively, Bauschlicher and co-workers derived values of 107.5 ± 2 and 107.8 ± 2 kcal/mol, respectively, in which the error bars are very conservative. In the context of a review article[38] on high-accuracy theoretical thermochemistry, Martin recently repeated the GS calculation on SiH_4 using techniques similar to those employed here, and obtained a TAE_0 [SiH_4(g)] consistent with $\Delta H^\circ_{f,0}$ [Si(g)] = 107.55 ± 0.5 kcal/mol if the Si(cr) → Si(amorph) phase transition enthalpy was indeed included. We conclude that all data support a slight increase in $\Delta H^\circ_{f,0}$ [Si(g)] to the 107.15 ± 0.38 kcal/mol value proposed in the present work.

As a final note, we consider the performance of some "standard" theoretical thermochemistry methods for this molecule, compared to our benchmark $TAE_e = 573.92 \pm 0.22$ kcal/mol. As noted previously,[46] G2 theory[47] fails dismally, underestimating TAE_0 by 8.2 kcal/mol even as both spin−orbit splitting and scalar relativistics were neglected, which would together have increased the gap by a further 3.85 kcal/mol. G3 theory[48] represents a substantial improvement, being 2.2 kcal/mol below our value including spin−orbit corrections: applying the scalar relativistic correction to their value (or, equivalently, deleting it from our own calculation) would however increase that gap to a still substantial 4.1 kcal/mol. Interestingly, both CBS-Q[49] and CBS-QB3[49] predict much higher values, 576.0 and 577.0 kcal/mol, respectively. Neither value includes spin−orbit or relativistic corrections: upon applying them, we find that they underestimate our best result by only −1.8 and − 0.8 kcal/mol, respectively. Finally, the W1 theory very recently proposed by Martin and de Oliveira[30] yields a value of 573.85 kcal/mol, only 0.07 kcal/mol below the present calibration result. (W1 theory includes both scalar relativistic and spin−orbit corrections as standard parts of the method.)

Conclusions

From an exhaustive ab initio calibration study on the SiF_4 molecule, we obtain a total atomization energy at 0 K of 565.89 ± 0.22 kcal/mol. This value includes rather substantial scalar relativistic (−1.88 kcal/mol) and atomic spin−orbit (−1.97 kcal/mol) effects, as well as more minor effects of inner-shell correlation (−0.08 kcal/mol) and anharmonicity in the zero-point energy (+0.04 kcal/mol). In combination with experimentally very precisely known heats of formation of F(g) and SiF_4(g), we obtain $\Delta H^\circ_{f,0}$ [Si(g)] = 107.15 ± 0.38 kcal/mol ($\Delta H^\circ_{f,298}$ [Si(g)] = 108.19 ± 0.38 kcal/mol). This confirms the suggestion of Grev and Schaefer[6] that the rather uncertain JANAF/CODATA value of 106.5 ± 1.9 kcal/mol should be revised upward, albeit to about 1 kcal/mol lower than their suggested 108.1 ± 0.5 kcal/mol. The revision will be relevant for future computational studies on heats of formation of silicon compounds. Among standard computational thermochemistry methods, G2 and G3 theory exhibit large errors, while CBS-Q performs relatively well and the very recent W1 theory reproduces the present calibration result to 0.1 kcal/mol.

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