Accurate Heats of Formation for SiF_n and SiF_n^+, for $n = 1-4$

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Accurate heats of formation are computed for SiF_n and SiF_n^+, for $n = 1-4$. The vibrational frequencies are determined at the B3LYP level of theory. The energetics are determined at the CCSD(T) level of theory. Basis set limit values are obtained by extrapolation. In those cases where the CCSD(T) calculations become prohibitively large, the basis set extrapolation is performed at the MP2 level. The temperature dependence of the heat of formation, heat capacity, and entropy are computed for the temperature range 300−4000 K and fit to a polynomial. The CCSD(T) bond energies are compared with those obtained at the B3LYP, MP2, G2, and G2MP2 levels of theory.

1. Introduction

Accurate heats of formation of SiF_n and SiF_n^+, $n = 1-4$, are critical in modeling processes that are important to the semiconductor industry, such as deposition and etching. It is therefore not surprising that these species have been the subject of several previously studies, both theoretical[1−4] and experimental.[5−7] While the heat of formation of SiF_4 at 298 K has been determined accurately (-386.2 ± 0.1 kcal/mol[8]), the values for the other species are less well-known. Because of this uncertainty in the experimental values, calculations have been performed to obtain accurate heats of formation. Unfortunately, the SiF_n species are difficult to treat accurately,[9] and many of the more approximate methods have much larger errors for SiF_n than they do for most other systems. To circumvent these limitations, the computational studies[1−4] have used isodesmic reactions and/or experimental data to correct the computed results. While these approaches can be very reliable, if one of the experimental quantities is in error or the errors in the computed results are not uniform, the corrected results may be less reliable than desired.

In this paper we report on calculations for the SiF_n and SiF_n^+ species using higher levels of theory than used previously. The SiF_n and SiF_n^+ heats of formation are determined using the computed bond energies, without any experimental input other than the heats of formation of F[7] and SiF_4 and ionization potential of Si.[10] The results of the high-level calculations are compared with a variety of lower levels of theory.

2. Methods

The more approximate methods used in this work are the G2,[11] G2MP2,[12] G2MP2(B3LYP),[13] G2MP2(B3LYP/CC),[13] B3LYP,[14,15] and MP2[16] approaches. These calculations use the basis sets developed by Pople and co-workers,[17] the largest set used in this work being 6-311+G(3df,2p). The most accurate calculations are the restricted coupled cluster singles and doubles approach[18,19] including the effect of connected triples determined using perturbation theory,[20,21] RCCSD(T). In these RCCSD(T) calculations only the valence electrons (the Si 3s and 3p and F 2s and 2p) are correlated using the augmented-correlation-consistent polarized valence (aug-cc-pV) sets developed by Dunning and co-workers.[22−25] We use the triple-zeta (TZ), quadruple-zeta (QZ), and quintuple-zeta (5Z) sets. Previous work[26] has shown that the effect of core−valence correlation is about 0.6 and 0.7 kcal/mol for SiF and SiF^+, respectively. Since this is relatively small and it is very difficult to compute the CV effect for the larger systems, it is ignored, but its neglect probably leads to a slight underestimation of the bond energies in this work. To improve the accuracy of the results, several extrapolation techniques are used: the two-point (r^{-4}), three-point ($r^{-4} + r^{-6}$), and variable α ($r^{-\alpha}$) schemes described by Martin[27] and the logarithmic convergence approach described by Feller.[28] Unfortunately it is not possible to perform the RCCSD(T) calculations in the aug-cc-pVQZ and aug-cc-pV5Z basis sets for the largest systems; therefore MP2 calculations are performed using the correlation-consistent sets to help in the extrapolation of the RCCSD(T) results to the basis set limit. The RCCSD(T) are performed using Molpro 96,[29] while all other calculations are performed using Gaussian94.[30]

The zero-point energy is computed by scaling half the sum of harmonic frequencies; the scale factor for the Hartree−Fock (HF) level is 0.893,[11] for B3LYP the scale values[13] are 0.98 for the 6-31G* basis set and 0.989 for the 6-311+G(3df,2p) set, and for the MP2 the scale factor is 0.967 for the 6-31G* basis set.[31] The MP2 result in the 6-311+G(3df,2p) set is not scaled. As we show below, the values do not vary significantly with level of theory. Therefore, we use the scaled B3LYP/6-31G* values in the calculation of the bond energies. The one exception is the C_s structure of SiF_4^+, where the scaled HF/6-31G* value is used since this structure is not a minimum on the B3LYP potential. The heat capacity, entropy, and temperature dependence of the heat of formation are computed for 300−4000 K using a rigid rotor/harmonic oscillator approximation. The scaled B3LYP/6-31G* frequencies are in these calculations. These results are fit in two temperature ranged, 300−1000 and 1000−4000 K using the Chemkin[32] fitting program and following their constrained three-step procedure. The effect of spin−orbit coupling on the dissociation energy is computed using experiment. For the atoms, we use the difference between the lowest m_j component and the m_j weighted average energy.[10] For SiF, we assume that the spin−orbit effect is half the separation between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels.[33]

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TABLE 1: Geometries and Zero-Point Energies of SiF_n

	r(Si−F)	∠(FSiF)	ZPT	scaled[a]
	SiF			
HF/6-31G*	1.605		1.31	1.17
B3LYP/6-31G*	1.626		1.24	1.22
B3LYP/G(3df,2p)[b]	1.626		1.16	1.15
MP2/6-31G*	1.628		1.27	1.23
MP2/G(3df,2p)	1.625		1.18	1.18
RCCSD(T)/ATZ[c]	1.625			
RCCSD(T)/AQZ	1.613			
RCCSD(T)/A5Z	1.608			
expt[d]	1.601			
	SiF_2			
HF/6-31G*	1.592	99.59	3.23	2.88
B3LYP/6-31G*	1.616	101.11	2.99	2.93
B3LYP/G(3df,2p)	1.614	101.07	2.83	2.79
MP2/6-31G*	1.617	100.91	3.06	2.96
MP2/G(3df,2p)	1.612	101.06	2.88	2.88
RCCSD(T)/ATZ	1.612	100.18		
RCCSD(T)/AQZ	1.602	100.53		
expt	1.591	100.98		
	SiF_3 (C_{3v})			
HF/6-31G*	1.575	107.72	5.77	5.15
B3LYP/6-31G*	1.600	108.04	5.32	5.22
B3LYP/G(3df,2p)	1.591	108.10	5.17	5.11
MP2/6-31G*	1.601	108.18	5.46	5.28
MP2/G(3df,2p)	1.588	108.27		
RCCSD(T)/ATZ	1.590	107.96		
	SiF_4 (T_d)			
HF/6-31G*	1.557		8.49	7.58
B3LYP/6-31G*	1.579		7.98	7.82
B3LYP/G(3df,2p)	1.569		7.78	7.70
MP2/6-31G*	1.583		8.06	7.80
MP2/G(3df,2p)	1.569			
RCCSD(T)/ATZ	1.571			
expt	1.552			

[a] Scale factors are given in the text. [b] Signifies the 6-311+G(3df,2p) basis set. [c] ATZ signifies the aug-cc-pVTZ basis set. [d] Experimental values taken from JANAF.[7]

TABLE 2: Geometries and Zero-Point Energies of SiF_n^+

	r(Si−F)	∠(FSiF)	ZPT	scaled[a]
	SiF^+			
HF/6-31G*	1.533		1.58	1.41
B3LYP/6-31G*	1.559		1.47	1.44
B3LYP/G(3df,2p)	1.547		1.43	1.41
MP2/6-31G*	1.559		1.50	1.45
MP2/G(3df,2p)	1.546			
RCCSD(T)/ATZ	1.548			
RCCSD(T)/AQZ	1.538			
RCCSD(T)/A5Z	1.533			
	SiF_2^+			
HF/6-31G*	1.528	118.14	3.66	3.27
B3LYP/6-31G*	1.558	119.77	3.31	3.24
B3LYP/G(3df,2p)	1.543	120.03	3.26	3.22
MP2/6-31G*	1.556	119.97	3.45	3.34
MP2/G(3df,2p)	1.539	120.09		
RCCSD(T)/ATZ	1.544	119.94		
RCCSD(T)/AQZ	1.534	119.60		
	SiF_3^+ (D_{3h})			
HF/6-31G*	1.512		6.48	5.79
B3LYP/6-31G*	1.539		6.00	5.88
B3LYP/G(3df,2p)	1.524		5.94	5.87
MP2/6-31G*	1.542		6.11	5.90
MP2/G(3df,2p)	1.523			
RCCSD(T)/ATZ	1.528			
RCCSD(T)/AQZ	1.520			

[a] Scale factors are given in the text.

3. Results and Discussion

3.1. Geometries and Zero-Point Energies. The geometries of all systems were optimized at the HF, MP2, and B3LYP levels using the 6-31G* basis set and the MP2 and B3LYP levels using the 6-311+G(3df,2p) set. In addition, because of the high symmetry it was possible to optimize all systems, except for SiF_4^+, at the RCCSD(T) level using the correlation-consistent basis sets. The zero-point energies were also computed at several levels. These results are summarized in Tables 1, 2, and 3. An inspection of the tables shows good agreement between all methods for all cases, except SiF_4^+. For SiF, SiF_2, and SiF_4 the computed results are in good agreement with the available experimental results.[7] Thus it is highly unlikely that any problems associated with computing the heats of formation for all of these systems, with the possible exception of SiF_4^+, arises from any problems associated with the determination of the optimal geometry or the calculation of the zero-point energies.

SiF_4^+ is the one problem case encountered in this work. Ignacio and Schlegel[4] reported a HF geometry for SiF_4^+; starting from the T_d structure for SiF_4, one bond is greatly lengthened. There is also a small distortion of the remaining SiF_3 subunit, so that the final geometry has only C_s symmetry. Their HF 6-31G* geometry is, of course, the same as that reported in Table 3. For $SiCl_4^+$, Bauschlicher and Partridge[34] found a similar C_s structure at the HF level, but when correlation was included at the B3LYP level, the C_s structure was not longer a minimum on the potential surface. The $SiCl_4^+$ equilibrium geometry at the B3LYP level of theory had C_{2v} symmetry, where relative to $SiCl_4$, one pair of Si−Cl bonds lengthened slightly and their ClSiCl angle was significantly smaller than the tetrahedral angle of the neutral. The other pair of Si−Cl bonds contracted and their angle opened relative to the neutral. We find a similar C_{2v} structure of SiF_4^+ at the B3LYP level, and as for $SiCl_4^+$, the C_s structure is not a minimum on the B3LYP potential surface. This is true for both basis sets used in the B3LYP calculations. We are able to optimize the C_{2v} structure at the HF level, where it is 28 kcal/mol above the C_s structure and 14 kcal/mol above SiF_3^+ + F using the aug-cc-pVQZ basis set. It is also possible to optimize both structures at the MP2 level, and now the two structures differ by only 1 kcal/mol.

An inspection of Table 3 shows that the geometries of the two structures are not strongly dependent on the level theory, excluding the B3LYP approach, where the C_s structure is not a minimum. The MP2 vibrational frequencies of the C_{2v} structure are unreasonable; one Si−F stretch has a frequency of 4260 cm^{-1}. While the frequency of this stretch is more reasonable at the HF level, the IR intensity is very large, which is also true of the MP2 approach. This strongly suggests that the HF and MP2 are near a symmetry-breaking point,[35] which would presumably lead to the lower C_s structure.

3.2. Complete Basis Set Limit Bond Energies. The extrapolation of the CCSD(T) results for SiF and SiF^+ in the aug-cc-pV basis sets is summarized in Table 4. For SiF, the agreement of the various extrapolation procedures is very good. It is especially encouraging that the relatively inexpensive 2-pt(TZ,QZ) method is in good agreement with the 2-pt(QZ,5Z), 3-pt(TZ,QZ,5Z), and 3-pt variable α approaches. We therefore adopt the 2-pt(TZ,QZ) approach for the neutral systems. The agreement between the extrapolation approaches is less satisfactory for SiF^+. Therefore we adopt the 3-pt(TZ,QZ,5Z) for the ions, even though it is significantly more work.

The CCSD(T) and MP2 bond energies are summarized in Table 5 along with the complete basis set (CBS) extrapolated values. The values for SiF and SiF^+ are those given in Table 4 and therefore do not require any additional comments. For SiF_2 it is possible to perform CCSD(T) calculations using both

TABLE 3: SiF_4^+ Geometries and Zero-Point Energies

C_{2v}	r(Si−F(1,2))	r(Si−F(3,4))	∠(F1SiF2)	∠(F3SiF4)	ZPT
HF/6-31G*	1.640	1.517	72.60	119.72	9.77
B3LYP/6-31G*	1.665	1.542	75.51	119.48	7.06
B3LYP/G(3df,2p)	1.652	1.528	76.52	119.48	6.93
MP2/6-31G*	1.669	1.545	71.31	119.81	12.77
MP2/G(3df,2p)	1.650	1.527	72.20	120.00	

C_s	r(Si−F1) ∠(F1SiF3)	r(Si−F2) ∠(F2SiF4)	r(Si−F(3,4)) ∠(F3SiF4)	∠(F1SiF2) ZPT
HF/6-31G*	2.005	1.520	1.519	92.90
	97.07	119.33	118.45	7.27
MP2/6-31G*	2.014	1.548	1.547	92.22
	97.48	119.31	118.43	6.92
MP2/G(3df,2p)	2.001	1.531	1.530	92.19
	97.59	119.34	118.32	

TABLE 4: Test of D_e Extrapolation,[a] in kcal/mol

	Si−F	Si^+−F
aug-cc-pVTZ	136.50	154.13
aug-cc-pVQZ	140.35	158.36
aug-cc-pV5Z	141.64	159.97
Extrapolation		
2-pt(TZ,QZ)	142.57	160.80
2-pt(QZ,5Z)	142.69	161.28
3-pt(TZ,QZ,5Z)	142.73	161.45
3-pt variable α[b]	142.78	161.73
3-pt Feller	142.29	160.96

[a] Taken from ref 26. [b] α for neutral is 3.740 and for the ion is 3.184.

TABLE 5: Computed Bond Energies,[a] in kcal/mol, without Zero-Point Energies

molecule	method	ATZ[b]	AQZ	A5Z	CBS1[c]	CBS2
Si−F	CCSD(T)	136.50	140.35	141.64	142.57	142.73
	MP2	143.22	146.81		148.88	
SiF−F	CCSD(T)	151.56	155.33		157.50	
	MP2	159.58	163.19		165.27	
SiF_2−F	CCSD(T)	103.39			(108.33)	
	MP2	113.70	117.14		119.13	
SiF_3−F	CCSD(T)	162.80			(168.45)	
	MP2	168.83	172.55		174.69	
Si^+−F	CCSD(T)	154.13	158.36	159.97	160.80	161.45
	MP2	161.97	166.02	167.69	168.37	169.27
SiF^+−F	CCSD(T)	72.66	76.85		79.27	(79.30)
	MP2	83.54	87.27	88.72	89.43	90.06
SiF_2^+−F	CCSD(T)	141.92	145.82		148.08	(149.16)
	MP2	148.49	152.37	154.12	154.61	155.86
SiF_3^+−F(C_s)	CCSD(T)	18.95			(20.03)	
	MP2	15.15	15.70		16.01	
SiF_3^+−F(C_{2v})	CCSD(T)	17.22			(18.92)	
	MP2	13.38	14.22		14.71	

[a] The CCSD(T) optimized geometries are used in all cases, except SiF_4^+, where the MP2 6-311+G(3df,2p) values are used. [b] ATZ signifies the aug-cc-pVTZ set. [c] The CBS1 values are obtained using the 2-pt (TZ,QZ) approach, while CBS2 values are obtained using the 3-pt(TZ,QZ,5Z). The values in parentheses are estimated using the CBS MP2 values, as described in the text.

the aug-cc-pVTZ and aug-cc-pVQZ sets; therefore it is straightforward to perform the extrapolation. For both SiF_3 and SiF_4 the disk space required for the CCSD(T) calculations using the aug-cc-pVQZ basis set is prohibitively large. The problem is more severe for the ions, where we need the aug-cc-pV5Z results. Therefore it is not possible to extrapolate all of the CCSD(T) values to the CBS limit. However, it is noticed that the ratio of the CCSD(T) D_e to the MP2 D_e is nearly independent of basis set for a given bond. Therefore we performed MP2 calculations for the aug-cc-pVTZ and aug-cc-pVQZ sets for the neutrals and for all three sets for the ions and extrapolated the MP2 results to the CBS limit. The CCSD(T) CBS value is then estimated using the ratio of the CCSD(T) and MP2 results in the largest basis set where both calculations were possible and the MP2 CBS limit value. These values are also given in Table 5.

TABLE 6: Computed Bond Energies (in kcal/mol), Corrected for Zero-Point Energy, Spin−Orbit Effects, and Temperature

molecule	D_e	+ZPT	+SO	D_{298}
Si−F	142.56	141.34	140.76	141.60
SiF−F	157.50	155.79	155.17	156.07
SiF_2−F	108.33	106.05	105.66	106.59
SiF_3−F	168.45	165.84	165.46	166.45
Si^+−F	161.45	160.01	159.08	159.95
SiF^+−F	79.30	77.49	77.11	77.99
SiF_2^+−F	149.16	146.52	146.13	147.12
SiF_3^+−F(C_s)	20.03	19.43	19.04	19.36
SiF_3^+−F(C_{2v})	18.92	17.88	17.50	18.16

For SiF_4^+, the MP2 calculations in the aug-cc-pV5Z basis set are very large. Since this species is weakly bound, it easily dissociated into SiF_3^+ + F, and therefore, it is not of great interest in etching processes. Thus we do not perform the aug-cc-pV5Z calulations and extrapolate using only the 2-pt(TZ,QZ) results. The energy difference between the C_s and C_{2v} forms of SiF_4^+ is small and similar for the MP2 and CCSD(T) approaches and is not significantly affected by the size of the basis sets. We note that from the norm of the singles amplitudes the CCSD(T) approach should be accurate for both structures. Therefore we conclude that the true structure of SiF_4^+ is probably C_s, but the energy difference is too small for a definitive determination of the equilibrium structure.

The CCSD(T) CBS D_e values were corrected for zero-point energy, spin−orbit effects, and temperature, using a combination of experiment and B3LYP frequencies as described in the Methods section. The results are summarized in Table 6. For the neutrals, the second and fourth bond energies are the largest because the molecule becomes a closed shell, with the Si valence satisfied. The third bond is weak since Si must promote from $3s^23p^2$, which can form two bonds, to $3s^13p^3$, which can form four bonds. The first bond is somewhat weaker than the second because the atomic exchange is lost in both cases, but for SiF_2 the loss is shared by two bonds. With one fewer Si valence electron, the ion trends are shifted by one relative to the neutral. The first Si−F bond in the ion is about as strong as the second in the neutral. The second ion bond is weak, like the third in the neutral, but the larger promotion energy[36] for Si^+ than Si makes the second bond in the ion even weaker than the third in the neutral. With only three valence electrons, it is not surprising that the fourth bond in the ion is weak.

TABLE 7: Computed Heats of Formation in kcal/mol at 298 K[a]

	PW[b]	HM[1]	IS[3,4]	MH[2]	FKA[5]	NBS[6]	JANAF[7]
Si	108.6	(107.36 ± 2)	(107.5 ± 2)		108.4 ± 0.7	108.9	107.6 ± 2
SiF	−14.0	−12.4 ± 3.0	−14.2 ± 2	−15.1	−11.2 ± 2.1	1.7	−4.8 ± 3
SiF_2	−151.1	−149.9 ± 4.0	−153.0 ± 2	−152.5	−152.4 ± 1.5	−148.	−140.5 ± 3
SiF_3	−238.7	−237.4 ± 1.9	−240.7 ± 2	−238.1	−238.4 ± 1.1		−259.4 ± 4
SiF_4	(−386.2 ± 0.1)	(−386.0 ± 1.0)	(−386.2 ± 0.1)		(−386.0 ± 0.2)	−386.0	−386.0 ± 0.2
Si^+	298.0		(297.1 ± 1.0)		297.8 ± 0.7	298.3	297.0 ± 2[c]
SiF^+	157.1		154.1 ± 4		153.3 ± 1.1		
SiF_2^+	98.0		98.3 ± 4		98.0 ± 1.2		
SiF_3^+	−30.1		−30.5 ± 4		−28.7 ± 0.6		
SiF_4^+	−30.5		−31.3 ± 4		−31.0 ± 1.4	−34.2	

[a] The thermal electron convention is used. The values in parentheses are used as reference points. [b] A conservative estimate of the uncertainty in the present work is ±2 kcal/mol. [c] Uncertainty has been increased to ±2 because this is the uncertainty in the neutral.

TABLE 8: Computed Bond Energies as a Function of Level of Theory[a]

	G2	G2MP2			B3LYP		MP2		CCSD(T)
			B3LYP	B3LYP/CC	6-31G*	(3df,2p)[b]	(3df,2p)	CBS	CBS
Si−F	138.7	139.2	139.0	138.8	135.0	139.1	141.8	147.7	141.3
SiF−F	153.6	154.4	154.2	154.1	148.1	148.9	158.1	163.6	155.8
SiF_2−F	101.7	102.0	102.0	101.9	99.8	100.9	112.4	116.9	106.1
SiF_3−F	164.2	164.4	164.1	164.1	158.2	156.5	167.5	172.1	165.8
Si^+−F	156.0	157.1	156.9	156.6	152.6	153.1	160.4	167.8	160.0
SiF^+−F	71.8	71.6	71.6	71.3	72.6	72.8	82.5	88.3	77.5
SiF_2^+−F	143.4	143.6	143.5	143.5	134.9	135.7	147.7	153.2	146.5

[a] The G2 and G2MP2 approaches use the scaled HF for the zero-point energy, while the scaled B3LYP/6-31G* values are used for the remaining approaches. [b] Signifies that the 6-311+G(3df,2p) basis set is used.

3.3. Heats of Formation. Combining our computed bond energies with some known data, it is possible to compute heats of formation for the species of interest. We follow previous workers and adopt the heat of formations (at 298 K) of SiF_4[8] (−386.2 ± 0.1 kcal/mol) and F[7] (18.97 ± 0.07 kcal/mol) as our standards. Our computed values, along with previous work, are given in Table 7. We first note that our heat of formation of Si agrees with the experimental values. Thus our atomization energy of SiF_4 agrees with the somewhat uncertain experimental value to within about 1 kcal/mol. This level of agreement is better than expected. We have neglected core−valence correlation, which is expected to add about 0.5 kcal/mol per bond, and the use of the 2-pt(TZ,QZ) extrapolation is expected to yield bond energies that could be about 0.5 kcal/mol too small. Thus we would have expected our atomization energy to be about 2 kcal/mol too small. We therefore appear to be benefiting from some cancellation of errors. While it is impossible to assign rigorous error bars, given the agreement for the atomization energy, we suspect that our values are accurate to ±1 kcal/mol and certainly to ±2 kcal/mol. Our values are in good agreement with previous calculations. In this regard we note that all of our values agree with those of Ho and Melius[1] and Ignacio and Schlegel[3] to within their error bars. This is also true for the recent experimental values of Fisher et al.[5] The biggest difference between our values and those of Fisher et al. is for SiF. Since it is almost impossible for our Si−F bond energy to be too large and our Si heat of formation is essentially the same as that found by Fisher et al., we believe that our value for the SiF heat of formation is more accurate. The present values, along with the other computed results and the recent experiments of Fisher et al., rule out the older values given in the NBS and JANAF compilations.

We compute the heat of formation of Si^+ using our value for Si and the Si ionization potential given by Moore.[10] The remaining ion values are computed using our bond energies and the heat of formation of F. As for the neutrals, we believe that our values are accurate to ±2 kcal/mol. Our values are in very good agreement with those of Ignacio and Schlegel[4] and of Fisher et al.[5] The biggest disagreement occurs for SiF^+. Previous benchmark[26] calculations suggest that our heat of formation could be 1 kcal/mol too high; hence we suspect that the true value for SiF^+ falls between our result and that of Fisher et al. Regardless of the small differences, the obvious conclusion is that the present results, the previous results of Ignacio and Schlegel,[3,4] and the experimental results of Fisher et al.[5] are in very good agreement.

Using our heats of formation at 298 K and the scaled frequencies, we evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits can be found on the web.[37]

3.4. Comparison with Lower Levels of Theory. The work of Ignacio and Schlegel[3,4] shows that by using isodesmic reactions and some experimental data it is possible to obtain heats of formation as reliable as those computed using the highest levels of theory. However, it is not always possible to find accurate experimental data to calibrate the computed results. It is therefore of interest to compare our best results, the CCSD(T) CBS values, with those obtained using lower levels of theory; this is done in Table 8. We first note that the G2 and G2MP2 approaches are in excellent agreement. Thus the simplified estimate of basis set effects in the G2MP2 approach works well. The G2MP2 and G2MP2(B3LYP) approaches agree, showing that using the B3LYP approach for a geometry and zero-point energies has very little effect, as expected. Substituting the CCSD(T) approach for the QCI(T) approach,[38] the G2MP2(B3LYP) versus G2MP2(B3LYP/CC), makes no significant difference, implying that level of correlation treatment is not the origin of the difficulty in computing Si−F bond energies accurately.

The B3LYP results, in either basis set, are inferior to the G2 approaches; for example the B3LYP values for SiF−F, SiF_3−F, Si^+−F, and SiF_2^+−F are significantly smaller than the G2 results, which in some cases are already several kcal/mol smaller than the CCSD(T) CBS values. Clearly the B3LYP approach is not very accurate for SiF_n and SiF_n^+. A similar observation[34] was made for $SiCl_n$ and $SiCl_n^+$.

The MP2 CBS values are larger than the CCSD(T) CBS results, and therefore the MP2 method by itself is not sufficiently accurate to computer the bond energies. However comparison of the MP2 CBS results with those obtained with the 6-311+G(3df,2p) basis set suggests that the underestimation of the G2-based methods arises from basis set incompleteness of the 6-311+G(3df,2p) set. That is, the error in the MP2 6-311+G(3df,2p) set is larger than normal, so that the higher level correction does not fully account for the remaining basis set incompleteness.

4. Conclusions

The bond energies of SiF_n and SiF_n^+, for $n = 1-4$, are computed using the CCSD(T) approach. High accuracy is obtained by extrapolation of the CCSD(T) or MP2 results to the complete basis set limit. The only experimental data used in the calculation of these bond energies are the accurately known spin−orbit splitting in the atoms and SiF. Using these bond energies, the accurately known heats of formation of SiF_4 and F, and the ionization potential of Si, the heats of formation of the remaining systems are determined. The current values are in very good agreement with the previous values computed by Ignacio and Schlegel and the recent experimental values of Fisher et al. The temperature dependence of the heat of formation, the heat capacity, and entropy are computed and fit to the standard 14 coefficients,[32] which are available on the web.[37]

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