Accurate Heats of Formation for SF_n, SF_n^+, and SF_n^- for $n = 1-6$

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Received: February 11, 1998; In Final Form: April 1, 1998

Accurate heats of formation are computed for SF_n, SF_n^+, and SF_n^-, for $n = 1-6$. The geometries and vibrational frequencies are determined at the B3LYP level of theory. The energetics are determined at the CCSD(T) level of theory. Extrapolation to the basis set limit is discussed. 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.

I. Introduction

The SF_n species, and their ions, are of interest in the processing of semiconductors. While the SF_6 heat of formation[1−3] is well established, there appears to be significant uncertainty for many of the other species. For example, the recent study by Fisher, Kickel, and Armentrout[4] (FKA) reported −0.4 ± 4.1 kcal/mol for the heat of formation of SF_5^+, while Latimer and Smith[5] reported an upper bound of 25.0 ± 2.0 kcal/mol; these values are to be compared with the value of 42.2 ± 5.0 kcal/mol recommended by JANAF.[1] Recently, Irikura[6] studied the neutral and cationic SF_n species using the G2[7] and G2(MP2)[8] approaches. While these approaches have been found to be accurate (±2 kcal/mol) for many species, the errors tend to be larger for molecules composed of a second row atom and fluorine atoms. Irikura estimated that the G2 atomization energy for SF_6 would be in error by 4.5 kcal/mol, while the less rigorous G2(MP2) approach had an error of only 0.7 kcal/mol. In addition, he found the SF_n^+ atomization energies to be unreliable, so he computed the SF_n^+ heats of formation using his computed neutral heats of formation and ionization potentials (IPs). His SF_5^+ heat of formation, 22.7 ± 3.8 kcal/mol, falls between the values of JANAF and FKA, being close to the upper bound of Latimer and Smith.

Recently, Miller et al.[9] reviewed the SF_n electron affinities (EA) and they recommended values for the EAs; the uncertainty in some of the values is large; for example, their recommendations for SF_2 and SF_5 were 0.7−1.6 and 2.65−4.35 eV, respectively. Using density functional theory (DFT), King, Galbraith, and Schaefer[10] (KGS) computed the EAs of the SF_n species. They concluded that the DFT approach was useful in establishing trends, but that the EA values were not highly accurate.

Given the uncertainty in the heats of formation and electron affinities, it is useful to study these species using higher levels of theory. It has been found that the coupled cluster singles and doubles[11] results, including a perturbational estimate of the triple excitations[12] (CCSD(T)) and extrapolation to the complete basis set (CBS) limit, are very accurate. Unfortunately, it is not straightforward to apply this level to systems as large as SF_6. We have recently found[13] that it is possible to correct the CCSD(T) results, using the second-order Møller−Plesset[14] (MP2) CBS results, to yield accurate bond energies. That is the approach we apply to SF_n, SF_n^+, and SF_n^-. Our only experimental inputs are the well-established heats of formation[1] of S, S^+, F, F^-, and SF_6, and the experimental[15,16] spin−orbit splitting in S, S^+, F, and SF.

II. Methods

Geometries are optimized using density functional theory (DFT); more specifically, the hybrid[17] B3LYP[18] approach is used in conjunction with the 6-31+G* basis set.[19] The diffuse functions are added to improve the description of the negative ions. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies. For SF_2^- the 6-31+G* basis set resulted in a nonphysical, slightly bent, structure, so it was also studied using the 6-311+G(2df) basis set.

The energetics are computed using the restricted coupled cluster singles and doubles approach,[11,20] including the effect of connected triples determined using perturbation theory,[12,21] RCCSD(T). In these RCCSD(T) calculations only the valence electrons (the S 3s and 3p and F 2s and 2p) are correlated. The basis sets are derived from the augmented-correlation-consistent polarized valence (aug-cc-pV) sets developed by Dunning and co-workers.[22−25] We use the triple-ζ (TZ), quadruple-ζ (QZ), and quintuple ζ (5Z) sets. However, as discussed below, it is necessary to add tight functions to S to obtain a good description of the SF_n species.

To improve the accuracy of the results, several extrapolation techniques are used. We use the two-point n^{-3} scheme described by Helgaker et al.[26] We also use the two-point n^{-4}, three-point ($n^{-4} + n^{-6}$), and variable α ($n^{-\alpha}$) 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 Gaussian 94.[30] The zero-point energies are computed as half the sum of the harmonic

S1089-5639(98)01084-6 CCC: $15.00

TABLE 1: Extrapolation of Atomization Energies, in kcal/mol

	method[a]						
basis[b]	n^{-3}(TZ,QZ)	n^{-3}(QZ,5Z)	n^{-4}(TZ,QZ)	n^{-4}(QZ,5Z)	$n^{-4} + n^{-6}$(TZ,QZ,5Z)	α[c](TZ,QZ,5Z)	log(TZ,QZ,5Z)
				MP2			
SF							
cc	89.69	90.33	89.24	90.01	90.28	91.13 (2.383)	90.08
cc + d	90.05	90.02	89.65	89.81	89.86	89.93 (3.590)	89.55
cc + dfg	90.13	90.06	89.72	89.84	89.88	89.94 (3.674)	89.58
SF_2							
cc	188.62	190.07	187.73	189.41	190.01	192.03 (2.251)	189.69
cc + d	189.39	189.39	188.62	188.96	189.08	189.25(3.525)	188.49
cc + dfg	189.53	189.46	188.74	189.03	189.13	189.27(3.605)	188.54
SF_3							
cc + dfg	252.81	252.51	251.87	252.02	252.07	252.14(3.820)	251.38
SF_4							
cc + dfg	360.12	360.10	358.81	359.37	359.57	359.85(3.536)	358.57
SF_5							
cc + dfg	406.00		404.51				
SF_6							
cc	522.56	527.89	519.91	525.80	527.88	536.41 (2.004)	527.62
cc + d	524.62	525.01	522.79	523.96	524.37	525.02 (3.331)	522.98
cc + dfg	524.86	525.08	523.01	524.04	524.40	524.94 (3.414)	522.99
SF^+							
cc	91.27	92.48	90.69	92.02	92.48	94.46 (1.963)	92.46
cc + d	91.82	91.97	91.33	91.68	91.81	92.01 (3.254)	91.44
cc + dfg	91.92	92.01	91.42	91.72	91.83	92.00 (3.358)	91.45
SF_2^+							
cc	190.81	193.39	189.65	192.45	193.44	197.98 (1.861)	193.55
cc + d	191.92	192.29	190.98	191.73	191.99	192.46 (3.176)	191.29
cc + dfg	192.10	192.38	191.15	191.82	192.05	192.44 (3.273)	191.33
SF_3^+							
cc + dfg	300.80		299.43				
SF_4^+							
cc + dfg	318.50		316.95				
SF_5^+							
cc + dfg	425.55	426.79	423.62	425.58	426.26	427.67 (2.978)	424.89
SF_6^+							
cc + dfg	427.37		425.46				
SF^-							
cc	57.17	57.59	56.79	57.33	57.52	58.02 (2.623)	57.29
cc + d	57.44	57.40	57.08	57.20	57.25	57.31 (3.621)	56.98
cc + dfg	57.52	57.45	57.16	57.26	57.29	57.33 (3.699)	57.02
SF_2^-							
cc + dfg	134.45		133.98				
SF_3^-							
cc + dfg	236.59		235.77				
SF_4^-							
cc + dfg	304.36		303.41				
SF_5^-							
cc + dfg	413.37		412.09				
SF_6^-							
cc + dfg	455.47		454.05				
				CCSD(T)[d]			
SF							
cc	84.34	84.74	83.88	84.44	84.63	85.08 (2.808)	84.32
cc + dfg	84.76	84.46	84.34	84.27	84.24	84.22 (4.195)	83.95
SF^+							
cc	87.86	88.69	87.24	88.25	88.61	89.66 (2.461)	88.29
cc + d	88.39	88.21	87.85	87.94	87.97	88.00 (3.828)	87.57
cc + dfg	88.50	88.24	87.95	87.97	87.98	87.98 (3.961)	87.58
SF^-							
cc	59.23	59.26	58.83	59.04	59.11	59.22 (3.449)	58.80
cc + dfg	59.55	59.10	59.16	58.94	58.86	58.82 (4.697)	58.64
SF_2							
cc + dfg	176.72		175.93				

TABLE 1 (Continued)

	method[a]						
basis[b]	n^{-3}(TZ,QZ)	n^{-3}(QZ,5Z)	n^{-4}(TZ,QZ)	n^{-4}(QZ,5Z)	$n^{-4} + n^{-6}$(TZ,QZ,5Z)	α^c(TZ,QZ,5Z)	log(TZ,QZ,5Z)
				CCSD(T)[d]			
SF_2^+							
cc + dfg	182.15		181.13				
SF_2^-							
cc + dfg	129.14	128.44	128.64	128.24	128.10	128.05 (5.018)	127.85

[a] The methods are defined in the text. The basis sets used in the extrapolation are given in parentheses. [b] "cc" signifies standard aug-cc-pV sets. "cc + d" signifies that a tight d function has been added to S basis sets. "cc + dfg" signifies that a tight d function is added to the S TZ set, a tight d and f function is added to the S QZ set, and a tight d, f, and g function is added to the S 5Z set. [c] The optimized α value is given in parentheses. [d] The aug-cc-pVTZ+d CCSD(T) atomization energies, for $n = 1-6$, are (SF_n) 80.00, 167.70, 221.25, 316.20, 353.37, 460.49; (SF_n^+) 82.31, 170.57, 266.30, 277.79, 369.33, 371.48; and (SF_n^-) 55.13, 123.51, 214.24, 272.17, 369.21, and 403.76.

frequencies. 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. We include the effect of electronic excitation for the atoms using the data from Moore[15] and the two sublevels of the SF $^2\Pi$ state. The B3LYP/6-31+G* frequencies are used in these calculations, except for SF_2^- where the larger basis set results are used. These results are fit in two temperature ranges, 300−1000 and 1000−4000 K, using the Chemkin[31] 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.[15] The spin−orbit effect for SF is taken as half the splitting between the $^2\Pi$ sublevels given in Huber and Herzberg.[16]

III. Results and Discussion

A. Geometry and Vibrational Frequencies. The optimized B3LYP/6-31+G* geometries are very similar to the MP2 values reported by Irikura for SF_n and SF_n^+ and the DFT values reported by KGS for SF_n and SF_n^-. To be more specific, our B3LYP values tend to have slightly longer S−F bond lengths than those obtained in previous work; for example, our value for SF_6 is 1.608 Å, compared with 1.593 Å obtained by Irikura and 1.597 Å obtained by KGS, also using the B3LYP approach, but using a DZP++ basis set. The bond angles are very similar to those reported in the previous work. As noted by Irikura, his MP2 values tend to be 0.02−0.04 Å longer than experiment; thus our values tend to be 0.03−0.05 Å too long.

One geometry worthy of note is that for SF_2^-, where the B3LYP (and BP86[32,33]) approach yields a slightly bent ($\angle$(FSF) = 174.8°) system. Improving the basis set to 6-311+G(2df) yields a linear molecule. KGS found a linear molecule with their DZP++ basis set, but a bent molecule with their DZP set. That is, the molecule tends to be linear in larger basis sets at the DFT level. We should also note that SF_2^- is linear at the MP2 level using both the 6-31+G* and 6-311+G(2df) basis sets. Therefore we conclude that SF_2^- is really linear. SF_6^+, which was not considered in previous work, is found to be a slightly distorted SF_5^+ with a weakly bound F atom 3.35 Å away from the S atom.

Our computed vibrational frequencies tend to be slightly smaller than those reported by Irikura; and thus our temperature corrections are slightly larger, while most differences are less than 0.1 kcal/mol, the difference becomes as large as 0.28 kcal/mol for SF_6. Excluding SF_6^-, our zero-point energies are slightly larger than the BLYP/DZP results given by KGS. The maximum difference is 0.54 kcal/mol and decreases with a decreasing number of fluorines. We should note that the zero-point energy of SF_2^- is 0.42 kcal/mol larger using the linear 6-311+G(2df) basis set result rather than the bent 6-31+G* result. For SF_2 the zero-point energy is only 0.04 kcal/mol larger for the larger basis set. Therefore we conclude that the change in the SF_2^- result is not due to the larger basis set, but rather to the change in geometry, and we take the larger value as we believe that the molecule is linear and not bent.

B. Basis Set and Extrapolation. Extrapolation to the basis set limit is required to achieve accurate bond energies. In Table 1 we summarize our extrapolation tests at the MP2 and CCSD(T) levels of theory. An inspection of the results obtained with the standard aug-cc-pV basis sets, denoted cc in the table, shows that the agreement between the different extrapolation techniques is not very good. A comparison of the MP2 and CCSD(T) results for SF suggests that the extrapolation of MP2 results is more difficult than for the CCSD(T) results, as indicated by α, which is 2.4 for the MP2 but 2.8 at the CCSD(T) level. While the better agreement at the CCSD(T) level is encouraging, it is not especially useful since only the MP2 approach can be used for the largest systems. The MP2 results for SF_6 show how serious the problem is; the three-point $n^{-4} + n^{-6}$ and variable α approaches differ by more than 8 kcal/mol, and α is near 2.0. For an accurate extrapolation, an α larger than 3 is desired. The agreement between the two-point approaches is equally poor.

In previous work[34] we noted that missing tight functions can lead to problems with the extrapolation approaches. Test calculations showed that missing tight functions on S were the origin of the problems observed for SF_n; tight functions on F were found to be unimportant and are therefore not included. Two different series of tests were performed. In both series, the tight functions are added in an even-tempered manner, where the β is the smaller of the ratio betwen the two tightest functions in the original basis set or 3.0. In the first a tight d function is added to the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z; this set is denoted cc + d in the table; the exponents are 2.46, 3.10, and 8.009, respectively. In the second test, a tight d (2.46) is added to the aug-cc-pVTZ set, a tight d (3.10) and f (2.254) are added to the aug-cc-pVQZ set, and a tight d (8.009), f (2.271), and g (2.477) are added to the aug-cc-pV5Z set. This aug-cc-pVTZ+d, aug-cc-pVQZ+df, and aug-cc-pV5Z+dfg sets are denoted cc + dfg.

An inspection of Table 1 shows that the agreement among the various extrapolation techniques is much better for the cc + d and cc + dfg basis sets. The cc + d and cc + dfg sets yield about the same result, strongly suggesting that a tight d is the primary cause of the problems encountered with the cc basis set. We used the cc + dfg for all systems, since the cost of the two sets is similar.

Since the aug-cc-pV5Z+dfg calculations are very expensive, even at the MP2 level, it is desirable to be able to perform a

TABLE 2: Atomization and Bond Energies

	atomization energy[a]				bond energy[b]	
	no ZPE	+ZPE	+SO	298 K	0 K	298 K
SF	84.31	83.15	82.78	83.66	82.78	83.66
SF_2	175.96	173.25	171.92	173.90	89.14	90.24
SF_3	230.98	226.77	225.06	227.88	53.14	53.98
SF_4	329.83	322.99	320.89	324.96	95.83	97.08
SF_5	368.76	360.01	357.53	362.62	36.64	37.66
SF_6	479.62	467.19	464.32	470.95	106.80	108.33
SF^+	87.68	86.29	85.90	86.84	85.90	86.84
SF_2^+	180.74	177.52	176.75	178.70	90.84	91.86
SF_3^+	280.83	275.17	274.01	277.10	97.27	98.40
SF_4^+	293.99	286.93	285.39	289.34	11.38	12.24
SF_5^+	389.31	378.76	376.83	382.09	91.44	92.76
SF_6^+	391.33	380.57	378.26	383.51	1.43	1.41
SF^-	59.41	58.52	57.96	58.87	57.96	58.87
SF_2^-	128.62	126.89	125.94	127.40	67.98	68.53
SF_3^-	222.95	219.43	218.10	220.69	92.16	93.29
SF_4^-	282.13	277.48	275.76	278.99	57.66	58.31
SF_5^-	382.67	375.41	373.31	377.83	97.54	98.84
SF_6^-	418.62	410.95	408.46	413.20	35.16	35.37

[a] For SF_n^+, the atomization energy is to $S^+ + nF$ and for SF_n^- it is to $S + F^- + (n - 1)F$. [b] Energy for the loss of one F atom, except for SF^-, where the dissociation is to $S + F^-$.

TABLE 3: IP and EA Values, in eV

EA

	theory		experiment		
	present work	BHLYP[10]	recommended[9]	other	JANAF[1]
SF	2.32	2.25	2.285 ± 0.006	2.285 ± 0.006[37]	2.0 ± 0.5
SF_2	1.41	1.69	0.7−1.6		1.0 ± 0.5
SF_3	3.10	3.27	2.9 ± 0.2		2.72 ± 0.65
SF_4	1.44	1.99	1.5 ± 0.2	2.35 ± 0.1[40]	1.25 ± 0.56
SF_5	4.08	4.29	2.65−4.35	3.8 ± 0.15[38] 3.8 ± 0.14[39]	3.7 ± 0.2
SF_6	0.90	1.61	1.05 ± 0.1		1.2 ± 0.3

IP

	theory		experiment		
	present work	Irikura[6]	FKA[4]	Lias[41]	JANAF[1]
SF	10.22	10.12 ± 0.20	10.16 ± 0.17	10.09	10.09 ± 0.1
SF_2	10.15	10.15 ± 0.19		(10.08)	10.29 ± 0.3
SF_3	8.24	8.36 ± 0.18	8.18 ± 0.07		9.24 ± 0.7
SF_4	11.90	11.90 ± 0.16	11.69 ± 0.06	12.03 ± 0.05	12.15 ± 0.3
SF_5	9.52	9.71 ± 0.16	9.60 ± 0.05	10.5 ± 0.1	11.14 ± 0.37

two-point extrapolation using the TZ and QZ derived basis sets. For the small molecules, the n^{-4}(TZ,QZ) and n^{-4}(QZ,5Z) extrapolations are in reasonable agreement with each other and with the three-point schemes. This is also true for n^{-3}(TZ,QZ) and n^{-3}(QZ,5Z) extrapolations. However for the larger molecules, see for example the results for SF_5^+ and SF_6, the n^{-3}(TZ,QZ) approach seems to be much better than the n^{-4}(TZ,QZ) approach. Therefore, on the basis of the calibrations, we picked the n^{-3}(TZ,QZ) approach to compute our MP2 CBS atomization energies. We should note, however, that for the CCSD(T) approach, the n^{-4}(TZ,QZ) extrapolation appears to be in agreement with the three-point approaches as well as with the two-point (QZ,5Z) approaches. Unfortunately, we do not have CCSD(T) results for the larger systems to see if this conclusion applies to only the small molecules.

We estimate the CCSD(T) basis set limit values as

$$\mathrm{CCSD(T)(aug - cc - pVTZ + d)*MP2(CBS)/MP2(aug - cc - pVTZ + d)}$$

which we summarize in Table 2. A comparison of the extrapolated CBS CCSD(T) values in Table 1 and estimated CBS CCSD(T) results in Table 2 shows that estimated results are in good agreement with the extrapolated values. The largest error is for the negative ions, where estimated values for SF^- and SF_2^- are about 0.5 kcal/mol larger than the extrapolated values.

C. Computed Energetics. Our estimated atomization energies are summarized in Table 2. The values given in the second column include the B3LYP zero-point energies (ZPE). Spin−orbit effects are added to the results in the third column. The fourth column includes a correction for thermal effects. The last two columns contain the bond enthalpies computed as differences in the atomization energies.

As noted in the Introduction, the heat of formation of SF_6 is well-known, as are the heats of formation of S and F. Our computed atomization energies for SF_6 at 0 and 298 K are 464.32 and 470.95 kcal/mol, respectively. These are to be compared with the analogous values from the NBS[2] tables of 462.09 and 468.87 kcal/mol and the JANAF[1] atomization energies of 464.85 and 471.75 kcal/mol. That is, our computed atomization energies fall between the NBS[2] and JANAF[1] values. Our values must benefit from some cancelation of errors; for example, we have neglected the effect of core-valence correlation. However, we expect our values to be very consistent, so that our other computed values are expected to be approximately as accurate as those found for SF_6.

A second calibration comes from the atomic EAs and IPs. The extrapolated ($n^{-4} + n^{-6}$) CCSD(T) values, corrected for spin−orbit effects,[15,35] for the EA(F), EA(S), and IP(S) are 3.404, 2.075, and 10.343 eV, respectively. The experimental values[15,36] are 3.401, 2.077, and 10.356 V. The values estimated using the MP2 CBS and aug-cc-pVTZ+d results and CCSD(T) aug-cc-pVTZ+d results are 3.398, 2.087, and 10.376 eV.

In Table 3 we summarize the computed EA and IP values along with experiment[1,4,37−42] and previous theory.[6,10] The IP and EA values are computed using our best estimates for the atomization energies from Table 2 and the experimental IP of S and EA of F. We first note that EA(SF) has been accurately measured, and our value is slightly too large. Part of the error arises from the MP2 extrapolation that yields an SF^- binding energy that is slightly too large; however, the agreement with experiment is still quite good. The agreement between our values and the DFT(BHLYP) values of KGS is only qualitative, with the differences for SF_4 and SF_6 being quite sizable. There is general agreement between our values and those recommended by Miller et al.[9] and the values given by JANAF,[1] however, the large error bars should be noted.

Our EA(SF_5) value is in good agreement with the measurements of Chen et al.[38] and Fenzlaff, Gerhard, and Illenberger.[39] However, to compute the EA, both groups used an SF_5−F bond energy that is significantly smaller than our computed value. Using our computed SF_5−F bond energy would change these experimental EA(SF_5) values from about 0.3 eV smaller than our computed EA to about 0.3 eV larger than our value. The work of Smith and co-workers[43,44] showed that $SF_6 + e \rightarrow SF_5^- + F$ is endothermic by 0.12 ± 0.02 eV, which, if combined with our SF_5−F bond energy, yields an EA(SF_5) of about 4.5 eV. Finally, we note that in their review, Miller et al. pointed out that the different determinations for EA(SF_5) could be reconciled only if the SF_4−F bond energy was in the range 1.1−1.5 eV, which was smaller than believed at the time. Our value of 1.6 eV for the SF_4−F bond energy supports the view that the smaller experimental values for EA(SF_5) are a result of using an SF_5 bond energy that is too large. For SF_4 our value is in

TABLE 4: Heats of Formation, in kcal/mol

	298 K	0 K			
	present work[a]	present work[a]	Irikura	FKA	JANAF[1]
S	65.41	65.14			65.66 ± 0.06
SF	0.72	0.83	1.7 ± 1.5	6.6 ± 4.1	2.9 ± 1.5
SF_2	−70.55	−69.84	−69.1 ± 1.5	−69.2 ± 2.8	−70.4 ± 4.0
SF_3	−105.55	−104.51	−104.9 ± 1.5	−111.6 ± 3.6	−119.3 ± 8.0
SF_4	−183.65	−181.87	−181.6 ± 1.5	−182.3 ± 3.7	−180.9 ± 5.0
SF_5	−202.34	−200.04	−201.1 ± 1.5	−221.8 ± 4.3	−214.7 ± 3.6
SF_6	[−291.70]	[−288.36]			−288.36 ± 0.2
S^+	[306.48]	[304.57]			304.57 ± 0.1
SF^+	238.61	237.13	235.4 ± 3.9	240.9 ± 1.2	235.6 ± 4.0
SF_2^+	165.72	164.76	165.0 ± 3.8	163.2 ± 2.6	166.9 ± 11.0
SF_3^+	86.30	85.97	87.8 ± 3.9	77.0 ± 3.2	93.8 ± 8.0
SF_4^+	93.04	93.06	92.8 ± 3.8	87.2 ± 3.4	99.3 ± 12.0
SF_5^+	19.25	20.09	22.7 ± 3.8	−0.4 ± 4.1	42.2 ± 5.0
F^-	[−60.97]	[−59.91]			−59.91 ± 0.14
SF^-	−53.63	−52.21			−43.2 ± 13.0
SF_2^-	−103.19	−101.72			−93.5 ± 15.5
SF_3^-	−177.50	−175.41			−183.1 ± 7.0
SF_4^-	−216.83	−214.60			−209.8 ± 8.0
SF_5^-	−296.70	−293.67			−300.0 ± 8.0
SF_6^-	−313.09	−310.36			−316.0 ± 7.0

[a] The values in square brackets are taken from JANAF[1] as are the F heats of formation (18.47 and 18.97 kcal/mol at 0 and 298 K, respectively). Note the recent revised value[3] for SF_6 would subtract −0.29 kcal/mol from all of our neutral results.

good agreement with the value deduced from charge-transfer reactions,[42] which should be accurate. Since our calculations cannot have an error of 1 eV, we agree with Viggiano et al.[42] that the older value of Babcock and Streit[40] must be too large.

The agreement between our computed IP values and those of Irikura is very good. Excluding SF_4, the agreement between our computed IPs and those deduced by FKA is very good, and even the agreement for SF_4 is not too bad. Our calculations show that the SF_3 and SF_5 values recommended by JANAF are clearly too large and those of FKA are much superior.

Our heats of formation are given in Table 4 along with selected previous results. The first observation must be the excellent agreement between our values and those of Irikura. Excluding SF_3, SF_5, and SF_5^+, our values are in reasonable agreement with the values of FKA. There is also reasonable agreement with the JANAF results, although it must be noted that many of the JANAF values have sizable error bars. The recent determination of an upper bound for the SF_5^+ heat of formation at 0 K by Latimer and Smith[5] (25.0 ± 2.0 kcal/mol) is consistent with our computed value.

Given the excellent agreement with experiment for the atomization energy of SF_6, the atomic EA and IP, and the highly accurate EA for SF and the agreement between our results and those of Irikura, we conclude that our values are probably the most accurate and consistent heats of formation available for the SF_n neutrals and ions. We have therefore used our heats of formation at 298 K and the B3LYP frequencies and geometries to evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits are given as Supporting Information and can be found on the web.[45]

IV. Conclusions

The bond energies of SF_n, SF_n^+, and SiF_n^-, for $n = 1-6$, are computed using the CCSD(T) results, which have been extrapolated to the complete basis set limit. The temperature dependence of the heat of formation, the heat capacity, and entropy are computed and fit to the standard 14 coefficients,[31] which are available as Supporting Information and are also available on the web.[45]

Supporting Information Available: Temperature dependence data of the heat of formation, the heat capacity, and entropy (2 pages). Ordering information is given on any current masthead page.

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