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Combining Theory with Experiment: Assessment of the Thermochemistry of SF_n, SF_n^+, and SF_n^-, $n = 1-6$

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Abstract: The Gaussian-2 [(G2) or G2(MP2)] *ab initio* quantum chemical calculations allow the examination of the consistency of experimental thermochemical data for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) in the literature. Based on comparisons between G2 and G2(MP2) theoretical predictions and experimental measurements, we recommend the following self-consistent set of experimental heats of formation at 0 K ($\Delta_f H^\circ_0$) for SF_n, SF_n^+, and SF_n^- ($n = 1-6$): $\Delta_f H^\circ_0(SF) = 2.9 \pm 1.4$ kcal/mol, $\Delta_f H^\circ_0(SF^+) = 240.9 \pm 1.2$ kcal/mol, $\Delta_f H^\circ_0(SF^-) = -43 \pm 13$ kcal/mol, $\Delta_f H^\circ_0(SF_2) = -69.4 \pm 2.6$ kcal/mol, $\Delta_f H^\circ_0(SF_2^+) = 163.2 \pm 2.6$ kcal/mol, $\Delta_f H^\circ_0(SF_3) = -103 \pm 5$ kcal/mol, $\Delta_f H^\circ_0(SF_3^+) = 85.6 \pm 5.0$ kcal/mol, $\Delta_f H^\circ_0(SF_3^-) = -174.5 \pm 6.8$ kcal/mol, $\Delta_f H^\circ_0(SF_4) = -181 \pm 5$ kcal/mol, $\Delta_f H^\circ_0(SF_4^+) = 93 \pm 5$ kcal/mol, $\Delta_f H^\circ_0(SF_4^-) = -215.6 \pm 6.8$ kcal/mol, $\Delta_f H^\circ_0(SF_5) = -205.9 \pm 3.4$ kcal/mol, $\Delta_f H^\circ_0(SF_5^+) = 15.5 \pm 3.6$ kcal/mol, $\Delta_f H^\circ_0(SF_5^-) = -291 \pm 5.7$ kcal/mol, $\Delta_f H^\circ_0(SF_6) = -288.4 \pm 0.2$ kcal/mol, and $\Delta_f H^\circ_0(SF_6^-) = -314.5 \pm 2.4$ kcal/mol. For $\Delta_f H^\circ_0(SF_2^-)$, which is not known experimentally, we recommend a G2 value of −102.4 kcal/mol. At the MP2/6-31+G(d) level, SF_6^+ is found to be unstable with respect to dissociation forming lower sulfur fluoride cations. We have rationalized the theoretical structures for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) using the valence-shell-electron-pair-repulsion theory. The alternating patterns of high and low values observed for the $SF_{n-1}-F$ ($n = 2-6$), SF_{n-1}^+-F ($n = 3-5$), and $SF_{n-1}-F$ ($n = 2-6$) bond dissociation energies at 0 K and for the ionization energies and electron affinities of SF_n ($n = 1-6$) are attributed to special stabilities for closed-shell molecular species, (SF_3^+, SF_2, and SF^-), (SF_5^+, SF_4, and SF_3^-), and (SF_6 and SF_5^-), with fully-filled 8, 10, and 12 valence electron shells around the central S atoms, respectively.

I. Introduction

Reliable thermochemical data are among the most fundamental and useful information for chemical species and are used to predict their chemical reactivities. Fluorinated molecules such as SF_6 have found widespread use as gaseous dielectrics in the electric power industry and as plasma etching gases in the semiconductor industry. For sulfur hexafluoride, SF_n, SF_n^+, and SF_n^- ($n = 1-5$) are expected to be formed as byproducts.[1−12] Sulfur hexafluoride has also been suggested as a tracer in hazardous waste incineration systems.[13] The toxic nature of breakdown byproducts of SF_6 in these applications is of environmental concern.[14,15] Accurate thermochemical data for F- and S-containing neutral and ionic species are critical for understanding the complex kinetics involved in these applications.

In addition to practical industrial applications, sulfur fluorides are excellent examples of hypervalent[16] compounds. The studies[17−19] of the neutral and ionic sulfur fluoride species have also been motivated to understand their structures as a model system for achieving deeper insight into the bonding of hypervalent species.

Despite the existence of a large body of thermochemical data for the SF_n and SF_n^+ ($n = 1-6$) systems, general agreement among previous measurements for many sulfur fluorides is lacking.[20] Several recent reports address the inconsistency of the literature thermochemistry for the SF_n and SF_n^+ systems.[20−24] The ion collision-induced dissociation (CID) and endothermic charge transfer study of SF_n^+ ($n = 1-5$) by Fisher, Kickel, and Armentrout[20] represents the most comprehensive measurements of the ionization energies (IEs) for SF_n ($n = 1-6$) and the

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sequential bond dissociation energies at 0 K ($D°_0$) for SF_{n-1}^+-F. They also provide a detailed summary of the literature thermochemical data for SF_n and SF_n^+ ($n = 1-6$) published before 1992.

Traditionally, the sequential bond dissociation energies for SF_{n-1}^+-F ($n = 1-6$) are measured by electron impact[25–27] or photoionization[28–34] mass spectrometry (PIMS). In these experiments, the IE for SF_6 and the appearance energies (AEs) for SF_n^+ ($n = 1-5$) formed in the dissociative ionization of SF_6 are measured. The parent SF_6^+ ion has not been observed experimentally.[20,25,30,32] This, together with the observation that the ionization onset for SF_6 observed by photoelectron (PE) spectroscopy[35–38] is nearly identical to the AE for SF_5^+ from SF_6 measured by PIMS experiments,[28–30,32] indicates that SF_6^+ is unstable with respect to $SF_5^+ + F$. We note that SF_6^+ may exist in the form of an ion complex, $SF_5^+\cdots F$. The heats of formation at 0 K ($\Delta H°_{f0}$) determined for SF_3^+ and SF_4^+ in the CID experiment[20] are found to be incompatible with those derived from previous PIMS experiments.

Regardless of the minor difficulties due to the rotational and vibrational hot band effects and the poor Franck–Condon factor for ionization excitations, the most serious problem encountered in AE measurements is the kinetic shift effect, which may prevent observation of the true AE for a given product species.[39] Depending on the dissociation dynamics of the parent ion produced in photoionization, the photofragments may be formed in an excited state. If the excited state cannot be identified, the $D°_0$ deduced from the experimental AE is erroneous. Since the kinetic shift effect is statistical in nature, it does not depend on the mode of energization of the precursor ions. Thus, the kinetic shift effect may affect the AEs measured in the ion CID[20] as well as in the PIMS experiments.[28–34] Considering that each experimental technique has its own advantages and limitations, reliable thermochemical data for a complex system such as the sulfur fluorides require the application of as many experimental methods as possible.

When thermochemical data obtained by different experimental methods do not agree, theoretical predictions calculated using a reliable *ab initio* quantum chemical procedure help to reveal possible experimental problems. It has been shown that the Gaussian-2 (G2) *ab initio* procedure[40] yields accurate predictions for $D°_0$'s, adiabatic IEs, adiabatic electron affinities (EAs), and proton affinities of molecules and radicals consisting of the first- and second-row elements. Most recently, Curtiss *et al.* have introduced two variations of the G2 theory at reduced Møller–Plesset (MP) perturbation orders.[41] The basis-set extension energy corrections obtained at the second and third orders are referred to as the G2(MP2) and G2(MP3) theories, respectively. These theories give slightly poorer results than the G2 theory but require significantly less computational time and disk storage. In recent experimental and theoretical studies, we have performed G2, G2(MP3), and G2(MP2) *ab initio* calculations of the energetics for sulfur-containing polyatomic neutral species CH_3S (ref 42), CH_3SS (ref 43), C_2H_5S (ref 44), and CH_3SSCH_3 (ref 45) and their ions for comparison with experimental measurements. These comparisons indicate that G2 predictions for the adiabatic IEs and $\Delta_f H°_0$'s and heats of formation at 298 K ($\Delta_f H°_{298}$) are accurate to ±0.15 eV.

In this report, we present a theoretical investigation of the thermochemistry of the SF_n, SF_n^+, and SF_n^- ($n = 1-6$) systems. We have performed extensive *ab initio* calculations on SF_n, SF_n^+, and SF_n^- ($n = 1-6$) using the G2 and G2(MP2) procedures. A preliminary report on the G2(MP2) calculations of the energetics for SF_n ($n = 4-6$) and SF_n^+ ($n = 4,5$) and their comparison with the literature thermochemical data for these species has been published.[23] The G2 and G2(MP2) calculations make possible a thorough assessment of the literature thermochemical data[46] for the SF_n, SF_n^+, and SF_n^- ($n = 1-6$) systems. The detailed comparison presented here allows the selection of a self-consistent, possibly more reliable, set of experimental values for the IEs and EAs of SF_n and $\Delta_f H°_0$'s of SF_n, SF_n^+, and SF_n^- ($n = 1-6$). The G2 and G2(MP2) $\Delta_f H°_0$ values for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) are found to be in good agreement with available experimental results.

The theoretical structures for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) optimized at the MP2/6-31G(d) level are presented. We rationalize these structures based on the valence-shell-electron-pair-repulsion (VSEPR) theory.[47] The experimental trends observed for the $D°_0$'s, IEs, and EAs of these molecular species are also rationalized.

II. Theoretical Methods

The *ab initio* G2 theoretical procedure has been described in detail by Curtiss et al.[40] Briefly, at the G2 level of theory, molecular structures are optimized using MP2 perturbation calculations with the 6-31G(d) basis set and all the electrons are included [MP2(full)/6-31G(d)]. Equilibrium structures are found for all sulfur fluoride species except SF_6^+, where attempts to locate an equilibrium structure at the MP2/6-31G(d) and MP2/

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6-31+G(d) levels have been unsuccessful. All single-point calculations involved are based on the MP2/6-31G(d) optimized structures. The G2 method, an approximation of a QCISD(T)/6-311+G(3df,2p) calculation, requires single-point calculations at the MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-311G-(2df,p), QCISD(T)/6-311G(d,p), and MP2/6-311+G(3df,2p) levels. A small semiempirical correction is applied to account for high level correlation effects. The MP2/6-31G(d) harmonic vibrational frequencies, scaled by 0.93, are used to correct zero-point vibrational energies (ZPVE).[42] The total energy at 0 K (E_0) is equal to E_e + ZPVE, where E_e is the total electronic energy. All calculations are carried out on IBM RS6000-320h and RS6000/340 work stations or CRAY-YMP and CRAY-2 using the Gaussian 90 and Gaussian 92 package programs.[48]

Recently, Curtiss et al. have introduced two variations of G2 theory [G2(MP2) and G2(MP3)] at reduced Møller−Plesset (MP) perturbation orders.[41] The G2(MP2) and G2(MP3) theories, which provide substantial savings in computational time and disk storage, have been tested on the same set of 125 systems used for validation of the G2 theory.[40,41] The average absolute deviations of G2(MP2) and G2(MP3) theories from experiment are only ≤0.4 kcal/mol greater than that observed for G2 theory.

Due to the relatively large size of the molecule, we have performed calculations for SF_n, SF_n^+, and SF_n^- ($n = 3-6$) only at the G2(MP2) levels of theory. In order to verify the accuracy of G2(MP2) and G2(MP3) predictions as compared to G2 predictions, we have compared the results obtained by G2(MP2) and G2(MP3) on SF_n, SF_n^+, and SF_n^- (n = 1,2) with those calculated using the G2 procedure, since the energetics for the SF_n, SF_n^+, and SF_n^- (n = 1,2) species are relatively well-known. This comparison of G2 predictions and experimental molecular energies for these smaller sulfur fluorides also serves to verify the accuracy of the G2 procedure.

Among the closed-shell species, only SF^+ is found to be RHF unstable,[49] i.e., the UHF wave function yields lower energy than the RHF wave function. Hence, in the optimization and subsequent single-point energy calculations, the UHF wave function is employed for SF^+. Restricted HF wave functions are used for other closed-shell species, SF^-, SF_2, SF_3^+, SF_3^-, SF_4, SF_5^+, SF_5^-, and SF_6.

Because of the very large size of SF_6^-, the UQCISD(T)/6-311G(d,p) single-point energy calculation is computationally very demanding. Hence, we obtain the G2(MP2) energy by approximating the UQCISD(T)/6-311G(d,p) energy using the following approximated additivity rule:

$$\begin{aligned} &E[\text{QCISD(T)/6-311G(d,p)}] \\ &\quad = E[\text{MP4/6-311G(d,p)} + \{E[\text{QCISD(T)/6-311G(d,p)}] - \\ &\qquad\qquad E[\text{MP4/6-311G(d,p)}]\} \\ &\quad \approx E[\text{MP4/6-311G(d,p)} + \{E[\text{QCISD(T)/6-31G(d,p)}] - \\ &\qquad\qquad E[\text{MP4/6-31G(d,p)}]\} \quad (1) \end{aligned}$$

The same approximation is repeated for other sulfur fluoride species in verification calculations. Comparisons between IE, EA, and $\Delta_f H^\circ_0$ predictions calculated using this approximated G2(MP2) [AG2] and G2(MP2) schemes are made.

IV. Results and Discussion

A. Theoretical Structures for SF_n, SF_n^+, and SF_n^- (n = 1−6). Figure 1 shows the equilibrium structures for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) optimized at the MP2/6-31G(d) level. Bond distances (r) are in Å and bond angles (∠) are in degrees. Many of these molecules are hypervalent species, and their structures can be rationalized by the VSEPR model.[47] Traditionally, the bonding and structures for some of these hypervalent sulfur fluorides are described by VSEPR along with the valence bond sp^3d and sp^3d^2 hypbridization schemes. However, recent reliable *ab initio* investigations[50] of main group hypervalent species indicate that the d-orbital participation in the bonding of SF_4 and SF_6 is insignificant. Thus, the equilibrium structures for SF_n, SF_n^+, and SF_n^- (n = 1−6) are rationalized below using the VSEPR model without invoking the sp^3d and sp^3d^2 hypbridization schemes.

We note that r(S-F) increases from SF^+ to SF to SF^-. This trend is expected since the nonbonding electron density on sulfur increases from SF^+ to SF to SF^-, and hence the repulsion between the nonbonding electrons on S and F and r(S-F) increases accordingly.

The r(S−F) increases and ∠F−S−F decreases from SF_2^+ to SF_2. As both S atoms in SF_2^+ and SF_2 are sp^3 hybridized, the higher nonbonding electron density localized in the S sp^3 orbital in SF_2 leads to longer r(S-F) and smaller ∠F−S−F. In the case of SF_2^-, r(S−F) is longer and ∠F−S−F is greater than those for SF_2^+ and SF_2. The anion SF_2^- is a hypervalent species with 4$^1/_2$ electron pairs around the S atom. The VSEPR model predicts that the two F atoms occupy the axial positions and that the two and a half lone pairs occupy the equatorial positions of a trigonal bipyramidal structure. Since the three equatorial lone pair lobes are only partially filled, the 3-fold axis cannot be maintained and the anion is distorted from linearity. The increasing nonbonding electron density at the S atom in SF_2^- is also responsible for the longer r(S−F) (1.67−1.80 Å) for SF_2^- than those for SF_2^+ (1.535 Å) and SF_2 (1.60−1.67 Å).

The bonding of F atoms to S in SF_3^+ obeys the octet rule, and the sp^3 hybridization on the S atom leads to a trigonal pyramidal molecule with C_{3v} symmetry. Both SF_3 and SF_3^- are hypervalent species with 4$^1/_2$ and 5 electron pairs, respectively, around the S atoms. In SF_3^-, the two lone pairs on the S atom occupy the equatorial positions of a trigonal bipyramidal arrangement, resulting in a T-shaped (C_{2v}) structure. When one electron is taken from a sulfur lone pair, the nonbonding electron densities associated with the two equatorial lobes are no longer equivalent. The two axial F atoms are expected to be distorted out of the molecular plane, yielding a structure with C_s symmetry for SF_3.

Similarly, the C_{2v} symmetry structures of SF_4^+ and SF_4 are easily understood via the VSEPR theory. In these cases, the half-filled and the lone pair reside in an equatorial position of a trigonal bipyramidal arrangement around the S atoms in SF_4^+ and SF_4, respectively. Two structures with C_{4v} and C_{2v} symmetries are located for SF_4^-. There are 5$^1/_2$ electron pairs (4 bonded pairs and 1$^1/_2$ lone pairs) around the S atoms in SF_4^-. To arrange the electron pairs in an octahedral arrangement in SF_4^-, the 1$^1/_2$ lone pair lobes can be in a *trans* or a *cis* configuration, which corresponds to the $SF_4^-(C_{4v})$ or $SF_4^-(C_{2v})$ isomer, respectively. If the two nonequivalent lobes are in *cis* configuration, the axial F atoms are expected to distort from the plane containing these F atoms, as in the case of SF_3. The three nonbonding electrons on S in the $SF_4^-(C_{2v})$ isomer are subject to greater interelectron repulsion than those in the $SF_4^-(C_{4v})$ isomer, where the two lobes of the nonbonding electrons point in opposite directions. This picture is consistent with the G2(MP2) prediction that the $SF_4^-(C_{4v})$ isomer is more stable than the C_{2v} isomer by 11.3 kcal/mol.

The point group for SF_5^+ is D_{3h}, while those for SF_5 and

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SF_5^- are C_{4v}. Since SF_5^+ is isoelectronic with PF_5, the five bonded electron pairs in SF_5^+ are expected to distribute around the S atom in a normal trigonal bipyramidal structure. The neutral SF_5 and anionic SF_5^- have a half-filled and a filled lone pair, respectively, whose roles in the molecular geometry are similar to the lone pair in ClF_5. Thus, SF_5 and SF_5^-, similar to ClF_5, are predicted by the VSEPR theory to possess a square pyramidal (C_{4v}) structure.

Sulfur hexafluoride has six bonded electron pairs around the S atom and is predicted to have O_h symmetry by the VSEPR model. As indicated above, an equilibrium structure for SF_6^+ is not found because the cation tends to dissociate to $SF_4^+ + F_2$ at the MP2/6-31G(d) and MP2/6-31G+(d) levels. We note that the highest occupied molecular orbital for SF_6 has T_{1g} symmetry. Upon ionization, the resulting electronic configuration $[...(t_{1g})^5]$ corresponds to a triply degenerate state. The fact that this state is subject to Jahn-Teller distortion may be the source of the instability of SF_6^+. Although SF_6^+ may not be chemically bound, it may exist in the form $SF_4^{+\bullet}\cdot\cdot F_2$, stabilized by long range forces such as the charge-induced-dipole interaction. The formation of SF_6^- can be considered by adding an electron to the lowest unoccupied molecular orbital (LUMO). Since this LUMO has A_{1g} symmetry, the O_h structure is preserved for SF_6^-. However, the antibonding character of the a_{1g} orbital causes $r(S-F)$ to lengthen by 0.118 Å in SF_6^- compared to that in SF_6.

B. Comparison of G2, G2(MP3), and G2(MP2) Predictions. In order to verify the accuracy of the G2(MP2) procedure which is applied to predict the energetics of higher sulfur fluorides SF_n, SF_n^+, and SF_n^- (n = 3−6), we have compared the predictions for the IEs, EAs, $\Delta_f H°_0$'s, and $\Delta_f H°_{298}$'s of SF_n, SF_n^+, and SF_n^- (n = 1,2) obtained using the G2 and G2(MP2) procedures. These predictions, together with those calculated using the G2(MP3) procedure, are listed in Table 1. The available experimental results for SF_n, SF_n^+, and SF_n^- (n = 1,2) are also included in the table.[20,25,46,51−53] Detailed comparisons between the experimental and theoretical results are made in a later section. Here, we just point out that the G2, G2(MP3), and G2(MP2) predictions for the $\Delta_f H°_0$'s, $\Delta_f H°_{298}$'s, IEs, and EAs of SF_n, SF_n^+, and SF_n^- (n = 1,2) fall within the range of the experimental measurements reported in the literature. We note that MP2/6-31G(d) vibrational frequencies for SF_n, SF_n^+, and SF_n^- species are used for the conversion of experimental $\Delta_f H°_{298}$ values to corresponding $\Delta_f H°_0$ values shown in Tables 1 and 2.

The deviation between the G2 and G2(MP2) values, Δ[G2-G2(MP2)], for E_0's, $\Delta_f H°_0$'s, IEs, and EAs of SF_n, SF_n^+, and SF_n^- (n = 1,2) are also shown in Table 1. The theoretical E_0's are found in the order $E_0(G2) < E_0[G2(MP3)] < E_0[G2(MP2)]$, a trend consistent with the expectation that E_0 is lower as the degree of correlation increases. The E_0(G2) values are lower than the corresponding E_0[G2(MP2)] values by 0.007−0.016 hartree. The differences between the G2 and G2(MP2) predictions for the IEs and EAs of SF and SF_2 are ≤0.09 eV. The absolute values for Δ[G2-G2(MP2)] of $\Delta_f H°_0$ [or $\Delta_f H°_{298}$] are ≤1.5 kcal/mol for SF, SF^-, SF_2, and SF_2^-. The higher Δ[G2−G2(MP2)] values of 2.6 and 3.2 kcal/mol are observed for $\Delta_f H°_0(SF^+)$ and $\Delta_f H°_0(SF_2^+)$ [or $\Delta_f H°_{298}(SF^+)$ and $\Delta_f H°_{298}(SF_2^+)$], respectively. Based on these and previous comparisons of experimental and G2(MP2) results,[43,45] we conclude that the G2(MP2) procedure is capable of providing reliable energetic predictions for the sulfur fluorides and their ions of interest.

C. Comparison of Experimental and Theoretical Results for SF_n, SF_n^+, and SF_n^- (n = 1−6). The main motivation for performing G2 and G2(MP2) calculations for SF_n, SF_n^+, and SF_n^- (n = 1−6) is to help choose reliable experimental data from widely scattered experimental measurements. The comparisons of theoretical and experimental[18−25,30,32,34,46,53−58] results for SF_n, SF_n^+, and SF_n^- (n = 3−6) are made in Tables 1 and 2. Where G2 and G2(MP2) predictions are available, the G2 value is preferred for comparison with experimental values. After considering the experimental uncertainties and estimated errors for G2 and G2(MP2) calculations, we have highlighted in bold font the experimental values which are in reasonable accord with the corresponding G2 and G2(MP2) predictions. The underlined experimental IE, EA, and $\Delta_f H°_0$ values are recommended values for SF_n, SF_n^+, and SF_n^- (n = 1−6) based on these comparisons.

The experimental values for $\Delta_f H°_0$(SF) range from 2.9 to ≥8.0 kcal/mol. The lowest value 2.9 ± 1.4 kcal/mol, is closest to the G2 prediction of 2.3 kcal/mol for $\Delta_f H°_0$(SF), and is recommended for $\Delta_f H°_0$(SF). Taking into account the experimental uncertainties, the value 6.6 ± 4.1 kcal/mol determined in the recent CID and charge transfer study[20] is also consistent with the G2 prediction. The experimental IE(SF) = 10.16 ± 0.17 eV,[20] EA(SF) = 2.285 ± 0.006 eV,[59] $\Delta_f H°_0(SF^+)$ = 240.9 ± 1.2 kcal/mol,[20] and $\Delta_f H°_0(SF^-)$ = −49.8 ± 1.4 kcal/mol[59] are consistent with the corresponding G2 predictions.

The experimental $\Delta_f H°_0(SF_2^-)$ and EA(SF_2) are unknown. However, the experimental IE(SF_2) = 10.08 ± 0.05 eV[52] agrees very well with the IE(G2) value of 10.15 eV. The experimental $\Delta_f H°_0(SF_2^+)$ = 163.2 ± 2.6 kcal/mol[20] is also in accord with the G2 [G2(MP2)] prediction of 166.2 [163.0] kcal/mol. Combining these experimental values, a value of −69.2 ± 2.8 kcal/mol[20] is calculated for $\Delta_f H°_0(SF_2)$, which is essentially identical with the value of −69.6 ± 2.4 kcal/mol given by ref 55 and compares well with the G2 [G2(MP2)] value of −67.9 [−69.3] kcal/mol. Here, we recommend $\Delta_f H°_0(SF_2)$ = −69.4 ± 2.6 kcal/mol, the average of the experimental values of refs 20 and 55. We note that after taking into account experimental uncertainties, the other experimental values $\Delta_f H°_0(SF_2)$= −70.4 ± 4.0 kcal/mol[46] and $\Delta_f H°_0(SF_2^+)$ = 167 ± 11 kcal/mol[53] listed in Table 1 are also consistent with the G2 and G2(MP2) predictions.

As shown in Table 2, the experimental[46] IE(SF_3) (= 8.18 ± 0.07 eV) and EA(SF_3) (= 3.1 ± 0.2 eV) are in good accord with IE[G2(MP2)] (= 8.27 eV) and EA[G2(MP2)] (= 3.09 eV). However, the experimental $\Delta_f H°_0(SF_3)$ values of −111.6 ± 3.6[20] and −115.2 ± 5.8[18] kcal/mol from the literature are too low compared to the G2(MP2) prediction of −105.2 kcal/mol. The experimental $\Delta_f H°_0(SF_3^+)$ values of 93.8 ± 8.0[53] and 77.0 ± 3.2[20] kcal/mol also deviate significantly from the G2(MP2) values. The appearance energy (AE) for the process

$$SF_4 + h\nu \rightarrow SF_3^+ + F + e^- \qquad (2)$$

has been measured at 298 K to be 12.40 eV in a previous PIMS

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Table 1. Comparisons between G2, G2(MP3), and G2(MP2) E_0, $\Delta_fH^\circ_0$, IE, and EA Values and Experimental $\Delta_fH^\circ_0$, IE, and EA Values for SF_n, SF_n^+, and SF_n^- (*n* = 1 and 2)

	G2	G2(MP3)	G2(MP2)	Δ[G2-G2(MP2)][a]	expt[b]
SF					
E_0 (hartree)	−497.41824	−497.41336	−497.40726	−0.01098	
H_{298} (hartree)	−497.41486	−497.40998	−497.40387	−0.01099	
$\Delta_fH^\circ_0$ (kcal/mol)[c]	2.3	3.7	1.7	0.6	**2.9 ± 1.4** **6.6 ± 4.1**[d] 8.3 ± 2.6[d] ≥8.0[e]
$\Delta_fH^\circ_{298}$ (kcal/mol)[f]	2.5	3.9	1.9	0.6	**3.1 ± 1.4**
IE (eV)	10.40	10.33	10.31	0.09	**10.16 ± 0.17**[d] **10.09 ± 0.10**[g]
EA (eV)	2.33	2.33	2.29	0.04	**2.285 ± 0.006**[h]
SF^+					
E_0 (hartree)	−497.03622	−497.03391	−497.02850	−0.00772	
H_{298} (hartree)	−497.03288	−497.03056	−497.02516	−0.00772	
$\Delta_fH^\circ_0$ (kcal/mol)[c]	242.0	241.8	239.4	2.6	**240.9 ± 1.2**[d] 235.6±4.0
$\Delta_fH^\circ_{298}$ (kcal/mol)[f]	242.2	242.0	239.6	2.6	
SF^-					
E_0 (hartree)	−497.50372	−497.49692	−497.49130	−0.01242	
H_{298} (hartree)	−497.50028	−497.49347	−497.48786	−0.01242	
$\Delta_fH^\circ_0$ (kcal/mol)[c]	−51.4	−48.7	−51.0	−0.4	**−49.8 ± 1.4**[i]
$\Delta_fH^\circ_{298}$ (kcal/mol)[f]	−51.1	−48.5	−50.8	−0.3	
$SF_2(C_{2v})$					
E_0 (hartree)	−597.19238	−597.18512	−597.17896	−0.01342	
H_{298} (hartree)	−597.18804	−597.18077	−597.17461	−0.01343	
$\Delta_fH^\circ_0$ (kcal/mol)[c]	−67.9	−65.5	−69.3	1.4	**−69.4 ± 2.6**[j] **−70.4 ± 4.0**
$\Delta_fH^\circ_{298}$ (kcal/mol)[f]	−68.1	−65.7	−69.6	1.5	
IE (eV)	10.15	10.06	10.07	0.08	**10.08 ± 0.05**[k]
EA (eV)	1.51	1.35	1.43	0.08	
$SF_2^+(C_{2v})$					
E_0 (hartree)	−596.81927	−596.81525	−596.80878	−0.01049	
H_{298} (hartree)	−596.81505	−596.81102	−596.80455	−0.01050	
$\Delta_fH^\circ_0$ (kcal/mol)[c]	166.2	166.6	163.0	3.2	**163.2 ± 2.6**[d] **167 ± 11**[l] 162.0
$\Delta_fH^\circ_{298}$ (kcal/mol)[f]	165.9	166.3	162.7	3.2	**162.9 ± 2.6**[m] 161.6
$SF_2^-(C_{2v})$					
E_0 (hartree)	−597.24780	−597.23456	−597.23163	−0.01617	
H_{298} (hartree)	−597.24295	−597.22970	−597.22677	−0.01618	
$\Delta_fH^\circ_0$ (kcal/mol)[c]	−102.7	−96.5	−102.4	−0.3	
$\Delta_fH^\circ_{298}$ (kcal/mol)[f]	−102.6	−96.4	−102.3	−0.3	

[a] Difference between G2 and G2(MP2) values. [b] Experimental values. Unless specified, values are from ref 46. The underlined values are recommended values. The values in bold font are consistent with the G2 and G2(MP2) predictions. [c] Calculated using $\Delta_fH^\circ_0$ values of S (65.6 kcal/mol) and F (18.5 kcal/mol) from ref 46; E_0(G2) values S (−397.65495 hartree) and F (−99.63282 hartree) from ref 40; E_0[G2(MP3)] values of S (−397.65326 hartree) and F (−99.63194 hartree) and E_0[G2(MP2)] values of S (−397.64699 hartree) and F (−99.62894 hartree) from ref 41. [d] Reference 20. [e] Reference 51. [f] Calculated using the $\Delta_fH^\circ_{298}$ values of S (66.2 kcal/mol) and F (19.0 kcal/mol) from ref 46. H_{298}[G2, G2(MP3), or G2(MP2)] values for these atoms are obtained by adding E_{trans} + PV (= $^5/_2RT$ = 2.36 millihartree at 298 K) to their E_0[G2, G2(MP3), or G2(MP2)] values. [g] References 25 and 46. [h] Reference 59. [i] Calculated using EA(SF) = 2.285 ± 0.006 eV and $\Delta_fH^\circ_0$(SF) = 2.9 ± 1.4 kcal/mol (ref 46). [j] This is the average value of −69.6 ± 2.4 and −69.2 ± 2.8 kcal/mol given by ref 55 and 20, respectively. [k] Reference 52. [l] Reference 53. [m] Value converted from $\Delta_fH^\circ_0(SF_2^+)$ = 163.2 ± 2.6 kcal/mol using MP2/6-31G(d) vibrational frequencies of SF_2^+.

experiment.[34] We have reexamined the AE for process 2 and have obtained essentially the same value.[60] Since this is the lowest energy dissociation channel, the kinetic shift for process 2 should be insignificant. In principle, the $\Delta_fH^\circ_0(SF_3^+)$ can be determined using the AE of this process and the experimental value for $\Delta_fH^\circ_0(SF_4)$.

The literature accepted $\Delta_fH^\circ_0(SF_4)$ value of −181 ± 5 kcal/mol has a large uncertainty. The value $\Delta_fH^\circ_0(SF_4)$ = −182.3 ± 3.7 kcal/mol [$\Delta_fH^\circ_{298}(SF_4)$ = −183.5 ± 3.7 kcal/mol] is obtained by combining $\Delta_fH^\circ_0(SF_4^+)$ = 87.2 ± 3.4 kcal/mol and IE(SF_4) = 11.69 ± 0.06 eV determined in the recent CID and endothermic charge transfer study.[20] However, the latter IE value is lower than the value of 11.90 ± 0.03 eV determined in the PIMS and PE spectroscopy study[34] and the G2(MP2) prediction of 11.85 eV. Furthermore, the $\Delta_fH^\circ_0(SF_4^+)$ = 87.2 ± 3.4 kcal/mol is also lower than the G2(MP2) value of 91.1 kcal/mol. This comparison indicates that the agreement observed between the $\Delta_fH^\circ_0(SF_4)$ value (−182.3 ± 3.7 kcal/mol) determined in ref 20 and the G2(MP2) prediction (−182.2 kcal/mol) may be fortuitous. For this reason, we recommend the experimental value $\Delta_fH^\circ_0(SF_4)$ = −181 ± 5 kcal/mol or $\Delta_fH^\circ_{298}(SF_4)$ = −182.2 ± 5.0 kcal/mol.[46]

Using the AE of 12.40 eV obtained at 298 K for process 2,[34,60] together with $\Delta_fH^\circ_{298}(SF_4)$ = −182.2 ± 5.0 kcal/mol, we calculate $\Delta_fH^\circ_{298}(SF_3^+)$ = 84.7 ± 5 kcal/mol or $\Delta_fH^\circ_0(SF_3^+)$ = 85.6 ± 5.0 kcal/mol. By subtracting the IE(SF_3) = 8.18 ± 0.07 eV from the $\Delta_fH^\circ_0(SF_3^+)$ values, we obtain $\Delta_fH^\circ_0(SF_3)$ = −103 ± 5 kcal/mol. We note that these recommended

Table 2. E_0, $\Delta_f H°_0$, IE, and EA Values Obtained at the G2(MP2) Levels and Experimental $\Delta_f H°_0$ [$\Delta_f H°_0$(exp)], IE [IE(exp)], and EA [EA(exp)] Values for SF_n, SF_n^+, and SF_n^-, $n = 3-6$

species	E_0[G2(MP2)] (hartree)	$\Delta_f H°_0$[G2(MP2)]^a (kcal/mol)	$\Delta_f H°_0$(exp)^b (kcal/mol)	IE/EA[G2(MP2)] (eV)	IE(exp)^b (eV)	EA(exp)^b (eV)
			Neutrals			
$SF_3(C_s)$	−696.89453	−105.2 (−105.8)	**−103 ± 5**^{c} −111.6 ± 3.6^d −115.2±5.8^e	8.27/3.09	**8.18 ± 0.07**	**3.1 ± 0.2** **2.9** ± 0.1
$SF_4(C_{2v})$	−796.67566	−182.2 (−183.4)	**−181 ± 5** **−182.3 ± 3.7**^{d}	11.85/1.52^f, 1.02^f	**11.90 ± 0.03**	**1.5 ± 0.2** **12.03 ± 0.05** **11.69 ± 0.06**
$SF_5(C_{4v})$	−896.36530	−201.8 (−203.6)	**−205.9 ± 3.4**^{e,h} −215.7 ± 3.2^e −221.8 ± 4.3	9.63/4.07	**9.60 ± 0.05**^{i}	**3.70 ± 0.2** >**3.7 ± 0.3** 3.01 ± 0.29
$SF_6(O_h)$	−996.16457	−290.2 (−292.8)	**−288.4 ± 0.2**	.../1.04	≤15.27	**1.05 ± 0.10**^{j}
			Cations			
$SF_3^+(C_{3v})$	−696.59058	85.5 (84.7)	**85.6 ± 5.0**^{k} 93.8 ± 8.0^l 77.0 ± 3.2^d			
$SF_4^+(C_{2v})$	−796.24009	91.1 (89.9)	**93 ± 5**^{m} **87.2 ± 3.4**^{d} 96.7 ± 5.0			
$SF_5^+(D_{3h})$	−896.01141	20.3 (18.3)	**15.5 ± 3.6**^{n} ≤25.0 ± 2.0^o 5.6 ± 3.5^i −0.4 ± 4.1^d			
SF_6^+	*p*					
			Anions			
$SF_3^-(C_{2v})$	−697.00818	−176.5 (−177.0)	**−174.5 ± 6.8**^{q} **−187.1 ± 10.5**^{r}			
$SF_4^-(C_{2v})$	−796.71324	−205.8 (−206.6)				
$SF_4^-(C_{4v})$	−796.73136	−217.1 (−217.8)	**−215.6 ± 6.8**^{s}			
$SF_5^-(C_{4v})$	−896.51473	−295.6 (−297.0)	**−291.2 ± 5.7**^{s} −275.3 ± 7.5^t			
$SF_6^-(O_h)$	−996.20296^u	−314.3^u (−315.6)^u	**−314.5 ± 2.4**^{w}			

[a] Calculated using $\Delta_f H°_0$ values of S (65.6 kcal/mol) and F (18.5 kcal/mol) from ref 46, and E_0[G2(MP2)] values of S (−397.64699 hartree), and F (−99.62894 hartree) from ref 41. The values in parentheses are $\Delta_f H°_{298}$[G2(MP2)] values. [b] Experimental values. Unless specified, values are from ref 46. The underlined values are recommended values. The values in bold font are consistent with the G2(MP2) predictions. [c] Calculated using the $\Delta_f H°_0(SF_3^+)$ = 85.6 ± 5.0 kcal/mol (see footnote *k* of this table) and IE(SF_3) = 8.18 ± 0.07 eV. [d] Reference 20. [e] Reference 18. [f] The EA[G2(MP2)] values of 1.52 and 1.02 eV correspond to the processes, $SF_4^-(C_{4v}) \rightarrow SF_4(C_{2v}) + e^-$ and $SF_4^-(C_{2v}) \rightarrow SF_4(C_{2v}) + e^-$, respectively. [g] Reference 34. The uncertainty given here is an estimate based on the wavelength resolution used in the photoionization experiment. [h] Reference 22. [h] Value calculated using the experimental $D°_0(SF_5-F)$ = 101.0 ± 3.4 kcal/mol. See the text and ref 18. [i] Reference. [j] Reference 56. [k] $\Delta_f H°_0(SF_3^+)$ value converted from $\Delta_f H°_{298}(SF_3^+)$ = 84.7 ± 5.0 kcal/mol, which is calculated using the experimental AE of 12.40 eV obtained at 298 K for process 2 (ref 34) and $\Delta_f H°_{298}(SF_4)$ = −182.2 ± 5.0 kcal/mol (ref 46) for $\Delta_f H°_0(SF_4)$. [l] Reference 53. [m] Calculated using the experimental IE = 11.90 ± 0.03 eV for SF_4 (ref 34) and the $\Delta_f H°_0(SF_4)$ = −181 ± 5 kcal/mol (ref 46). [n] Value calculated using the experimental $D°_0(SF_5-F)$ = −101 ± 3.4 kcal/mol and IE(SF_5) = 9.60 ± 0.05 eV (ref 22). The value of 16.4 ± 3.6 kcal/mol given in ref 34 is incorrect. [o] Reference 24. [p] Equilibrium structure for SF_6^+ is not found. [q] Calculated using $\Delta_f H°_0(SF_3)$ = 103 ± 5 kcal/mol and EA(SF_3) = 3.1 ± 0.2 eV. [r] Reference 46. Converted from $\Delta_f H°_{298}$ values. [s] Calculated using $\Delta_f H°_0(SF_4)$ = −181 ± 5 kcal/mol and EA(SF_4) = 1.5 ± 0.2 eV. [t] Calculated using $\Delta_f H°_0(SF_5)$ = −205.9 ± 3.4 kcal/mol and EA(SF_5) = 3.7 ± 0.2 eV. [u] Calculated using $\Delta_f H°_0(SF_5)$ = −205.9 ± 3.4 kcal/mol and EA(SF_5) = 3.01 ± 0.29 eV. [v] Calculated using the approximated G2(MP2), i.e., AG2 scheme. [w] Converted from $\Delta_f H°_{298}(SF_6^-)$ = −315.9 ± 2.4 kcal/mol, which is calculated using $\Delta_f H°_{298}(SF_6)$ = −291.7 ± 0.2 kcal/mol (ref 46) and EA(SF_6) = 1.05 ± 0.10 eV (ref 56, 298 K value).

experimental $\Delta_f H°_0(SF_3^+)$ (85.6 ± 5.0 kcal/mol) and $\Delta_f H°_0(SF_3)$ (−103 ± 5 kcal/mol) values are consistent with the respective G2(MP2) predictions of 85.5 and −105.2 kcal/mol. Using $\Delta_f H°_0(SF_3)$ = −103 ± 5 kcal/mol and EA(SF_3) = 3.1 ± 0.2 eV,[46] we obtain $\Delta_f H°_0(SF_3^-)$ = −174.5 ± 6.8 kcal/mol, in agreement with the G2(MP2) value of −176.5 kcal/mol. On the basis of this analysis, there is clearly a need to reduce the uncertainty for $\Delta_f H°_{298}(SF_4)$.

The experimental IE(SF_4) = 11.90 ± 0.03 eV is in excellent agreement with the IE[G2(MP2)] value of 11.85 eV. Combining this experimental IE and $\Delta_f H°_0(SF_4)$ = −181 ± 5 kcal/mol yields $\Delta_f H°_0(SF_4^+)$ = 93 ± 5 kcal/mol, a value also in accord with the $\Delta_f H°_0$[G2(MP2)] value of 91.1 kcal/mol. Because SF_4^- is found to have two stable structures, two EAs are predicted by G2(MP2) calculations. The EA[G2(MP2)] values of 1.52 and 1.02 eV are measures of the transition energies for the detachment reactions, $SF_4^-(C_{4v}) \rightarrow SF_4(C_{2v}) + e^-$ and $SF_4^-(C_{2v}) \rightarrow SF_4(C_{2v}) + e^-$, respectively. Since the structures for $SF_4(C_{2v})$, $SF_4^-(C_{2v})$, and $SF_4^-(C_{4v})$ are quite different, the Franck–Condon factors for these detachment processes are not favorable. Because $SF_4^-(C_{4v})$ is the more stable isomer, the experimental EA(SF_4) = 1.5 ± 0.2 eV is associated with the process, $SF_4^-(C_{4v}) \rightarrow SF_4(C_{2v}) + e^-$. Combining this experimental EA(SF_4) and $\Delta_f H°_0(SF_4)$ = −181 ± 5 kcal/mol, we calculate $\Delta_f H°_0(SF_4^-)$ = −215.6 ± 6.8 kcal/mol, compared to the G2(MP2) prediction of −217.1 kcal/mol.

The previous experimental determinations of $\Delta_f H°_0(SF_5)$ and $\Delta_f H°_0(SF_5^+)$ are the most controversial. This issue is the subject of several recent reports.[19–24] This difficulty is partly due to the failure of the traditional PIMS method to find the AE of SF_5^+ from SF_6. The previously accepted $\Delta_f H°_0(SF_5)$ = −215.7 ± 3.2 kcal/mol is based on the upper limit of 91.1 ± 3.2 kcal/mol for $D°_0(SF_5-F)$ obtained in a study of the chemiluminescent reaction Sr(^3P) + SF_6.[18] In the same experiment, an upper limit of 101.0 ± 3.4 kcal/mol was obtained for $D°_0(SF_5-F)$ by the Ca(^3P) + SF_6 reaction. No logical arguments are given in ref 18 for the rejection of the Ca(^3P) + SF_6 results. Cheung et al.[23] point out that the latter limit is closer to the G2(MP2) prediction of 106.9 kcal/mol for $D°_0(SF_5-F)$. The $Ca(^3P) + SF_6$ result translates into a value of -205.9 ± 3.4 kcal/mol for $\Delta_f H°_0(SF_5)$, which is in reasonable accord with the G2(MP2) prediction of -201.8 kcal/mol after taking into account the experimental uncertainties and the estimated accuracy of the G2(MP2) procedure. One possible difficulty in the chemiluminescence experiment[18] is the existence of higher long-lived excited states such as the $Ca(^1D)$ [$Sr(^1D)$] state in the Ca (Sr) atomic beams. The presence of such higher excited states is expected to result in a lower value for the upper bound of $D°_0(SF_5-F)$. The possible difficulties arising from higher long-lived excited Sr and Ca atoms have been discussed in detail recently.[21]

The experimental $IE(SF_5) = 9.60 \pm 0.05$ eV[22] is in good agreement with IE[G2(MP2)] = 9.63 eV. The value $\Delta_f H°_0(SF_5^+) = 16.4 \pm 3.6$ kcal/mol derived by combining the experimental $IE(SF_5)$ and $\Delta_f H°_0(SF_5) = -205.9 \pm 3.4$ kcal/mol is again considered to be in accord with the $\Delta_f H°_0$[G2(MP2)] value of 20.3 kcal/mol. We note that in the most recent proton affinity study of SF_6, Latimer and Smith[24] report an upper limit of 25.0 ± 2.0 and 20.9 ± 2.0 kcal/mol for the heats of formation of SF_5^+ at 0 and 298 K, respectively. The experimental $EA(SF_5)$ values are in the range from $>3.7 \pm 0.3$ to 3.01 ± 0.29 eV. The G2(MP2) calculation yields an EA value of 4.07 eV for SF_5, suggesting the actual $EA(SF_5)$ is likely >3.7 eV. Without newer experimental measurements, we recommend $EA(SF_5) = 3.7 \pm 0.2$ eV.[53] Combining this latter value and $\Delta_f H°_0(SF_5) = -205.9 \pm 3.4$ kcal/mol, we calculate an $\Delta_f H°_0(SF_5^-)$ value of -291.2 ± 5.7 kcal/mol, which is in agreement with the G2(MP2) prediction of -295.6 kcal/mol after taking into account the experimental uncertainties.

The experimental value $\Delta_f H°_0(SF_6) = -288.4 \pm 0.2$ kcal/mol is well established. As pointed out above, the adiabatic IE for SF_6, and thus $\Delta_f H°_0(SF_6^+)$, are unknown both experimentally and theoretically. The results of the PIMS[30,32,57] and electron impact[27,58] experiments are consistent with the conclusion that SF_6^+ is unstable with respect to $SF_5^+ + F$. As noted above, the theoretical structure optimization of SF_6^+ indicates that SF_6^+ is unstable with respect to $SF_4^+ + F_2$. Since the $SF_5^+ \cdots F$ and $SF_4^+ \cdots F_2$ complexes are bound by ion-induced-dipole forces, these ion complexes can in principle be observed if mechanisms exist for relaxing their excess internal energies. Using the recommended $\Delta_f H°_0(SF_6) = -288.4 \pm 0.2$ kcal/mol[46] and $\Delta_f H°_0(SF_5^+) = 16.4 \pm 3.6$ kcal/mol,[23] along with $\Delta_f H°_0(F) = 18.5$ kcal/mol,[46] the true AE for SF_5^+ from the dissociative ionization of SF_6 is calculated to be 14.0 eV, which is ≈1.27 eV lower than the experimental AE for SF_5^+ from SF_6. Using the experimental $EA(SF_6) = 1.05 \pm 0.10$ eV[56] and $\Delta_f H°_{298}(SF_6) = -291.7 \pm 0.2$ kcal/mol, we calculate a value of -315.9 ± 2.4 kcal/mol for $\Delta_f H°_{298}(SF_6^-)$. We convert the latter value to $\Delta_f H°_0(SF_6^-) = -314.5 \pm 2.4$ kcal/mol using the theoretical MP2/6-31G(d) frequencies for SF_6^-.

In order to make possible the UQCISD(T)/6-311G(d,p) single-point energy calculation for SF_6^-, we invoke the additivity approximation shown in eq 1. To test the reliability of applying this approximation to G2(MP2) calculations, i.e., the AG2 procedure, we have compared the E_0, IE, EA, $\Delta_f H°_0(SF_6^-)$ values for S, F, SF_n, SF_n^+, and SF_n^- ($n = 1-6$) using the AG2 and G2(MP2) schemes and find excellent agreement between the two schemes. The AG2 results for E_0's, $\Delta_f H°_0$'s, IEs, and EAs of S, F, SF_n, SF_n^+, and SF_n^- ($n = 1-6$) calculated using the AG2 scheme are summarized in Table 3. The deviation E_0[G2(MP2)] − E_0(AG2) increases roughly as the size of the molecular species and has a maximum of 0.00093 hartree for $SF_4^-(C_{4v})$ and SF_5^-. Comparing the G2(MP2) predictions for $\Delta_f H°_0$'s in Tables 1 and 2 with the corresponding AG2 values in Table 3, we find that the agreement between the two schemes is surprisingly good, with the maximum deviation <1 kcal/mol. The deviations between G2(MP2) and AG2 predictions for $\Delta_f H°_0$'s also increase with molecular size. The G2(MP2) and AG2 predictions for IEs and EAs for SF_n ($n = 1-5$) are also in excellent accord, with differences <0.1 eV. The AG2 predictions $\Delta_f H°_0(SF_6^-) = -314.3$ kcal/mol and $EA(SF_6) = 1.04$ eV agree with the experimental results of 314.5 ± 2.4 kcal/mol and 1.05 ± 0.10 eV, respectively.

Table 3. Comparison between G2(MP2) and Approximated G2(MP2) [AG2] Theoretical Energetics for S, F, SF_n, SF_n^+, and SF_n^- ($n = 1-6$)[a]

species	E_0[AG2] (hartree)	E_0[G2(MP2)]− E_0[AG2] (hartree)	$\Delta_f H°_0(AG2)$[b] (kcal/mol)	IE/-EA(AG2) (eV)
S	−397.64694	−0.00005		
F	−99.62881	−0.00013		
SF	−497.40721	−0.00005	1.7 (1.8)	10.30/2.29
SF^+	−497.02857	+0.00007	239.3 (239.4)	
SF^-	−497.49131	+0.00001	−51.1 (−50.9)	
$SF_2(C_{2v})$	−597.17924	+0.00028	−69.7 (−69.9)	10.07/1.42
$SF_2^+(C_{2v})$	−596.80901	+0.00023	162.6 (162.3)	
$SF_2^-(C_{2v})$	−597.23158	−0.00005	−102.6 (−102.4)	
$SF_3(C_s)$	−696.89496	+0.00043	−105.8 (−106.3)	8.27/3.10
$SF_3^+(C_{3v})$	−696.59120	+0.00062	84.9 (84.0)	
$SF_3^-(C_{2v})$	−697.00872	+0.00054	−177.1 (−177.6)	
$SF_4(C_{2v})$	−796.67630	+0.00064	−183.0 (−184.2)	11.86/1.52[c]
$SF_4^+(C_{2v})$	−796.24051	+0.00042	90.5 (89.2)	
$SF_4^-(C_{4v})$	−796.73229	+0.00093	−206.7 (−207.5)	
$SF_5(C_{4v})$	−896.36586	+0.00056	−202.6 (−204.4)	9.62/4.08
$SF_5^+(D_{3h})$	−896.01217	+0.00076	19.4 (17.4)	
$SF_5^-(C_{4v})$	−896.51566	+0.00093	−296.6 (−298.0)	
$SF_6(O_h)$	−996.16512	+0.00055	−291.1 (−293.6)	.../1.04
SF_6^+[d]				
$SF_6^-(O_h)$	−996.20296		−314.3 (−315.6)	

[a] The QCISD(T)/6-311G(d,p) energies for G2(MP2) calculations are calculated using the approximation: [QCISD(T)/6-311G(d,p)] ≈ [QCISD(T)/6-31G(d,p)] + [MP4/6-311G(d,p)] − [MP4/6-31G(d,p)]. [b] Values in parentheses are $\Delta_f H°_{298}$ values. [c] EA for $SF_4(C_{2v}) + e^- \rightarrow SF_4^-(C_{4v})$. [d] Attempts to determine the SF_6^+ structure were unsuccessful.

Table 4 compares the experimental and theoretical sequential $D°_0$'s for $SF_{n-1}-F$ ($n = 1-6$), SF_{n-1}^+-F (1−5), and SF_{n-1}^--F ($n = 1-6$). These experimental sequential $D°_0$'s are computed using the recommended (underlined) $\Delta_f H°_0$ values for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) shown in Tables 1 and 2. Since $\Delta_f H°_0(SF_6^+)$ is not available experimentally or theoretically, the $D°_0(SF_5^+-F)$ is not known. Because the experimental value for $\Delta_f H°_0(SF_2^-)$ is also unavailable, we cannot calculate the $D°_0(SF^--F)$ and $D°_0(SF_2^--F)$ values. We note that the EA of the F atom (3.4 eV)[46] is high, so the actual dissociation for the anions may involve the formation of F^-. Ion-pair processes producing F^- have been observed in PIMS studies of SF_6 (ref 30) and SF_4 (ref 34).

The 298 K values for $IE(SF_4)$ and AE of process 2 are 11.90 and 12.40 eV, respectively.[34] Our calculations show that the $IE(SF_4)$ for 0 K is essentially identical to the 298 K value, whereas the AE for process at 0 K is 0.9 kcal/mol lower than the 298 K value. No uncertainties were given for these experimental IE and AE in ref 34. We have assumed uncertainties of ±0.03 eV for these photoionization measurements. The experimental $D°_0(SF_3^+-F)$ value of 10.5 ± 1.0 kcal/mol is calculated based on the 0 K values for $IE(SF_4)$ and AE for process 2. Using $D°_0(SF^+-F) = 10.5 \pm 1.0$ kcal/mol, $IE(SF_4) = 11.90 \pm 0.03$ eV, and $IE(SF_3) = 8.18 \pm 0.07$ eV, we obtained the experimental $D°_0(SF_3-F) = 96.3 \pm 2.2$ kcal/mol. The experimental $D°_0(SF_3^--F) = 59.4 \pm 6.9$ kcal/mol is calculated using $D°_0(SF_3-F) = 96.3 \pm 2.2$ kcal/mol, $EA(SF_4) = 1.5 \pm 0.2$ eV, and $EA(SF_3) = 3.1 \pm 0.2$ eV.

Table 4. Comparisons between Experimental and G2 or G2(MP2) Bond Dissociation Energies at 0 K for $SF_{n-1}-F$, $SF_{n-1}^{+}-F$, and $SF_{n-1}^{-}-F$ ($n = 1-6$)^{a,b}

	neutral (kcal/mol)		cations (kcal/mol)		anions (kcal/mol)	
bond	experiment	theory	experiment	theory	experiment	theory
S−F	81.2 ± 1.4	81.8	81.6 ± 1.2	77.2	85.2 ± 1.4	89.3
			82.1 ± 1.2^{c}			
SF−F	90.8 ± 3.0	88.7	96.2 ± 2.9^{c}	94.3		69.8
SF_2−F	52.1 ± 5.6	54.4	96.1 ± 5.6	96.0		92.6
		55.8^{d}	104.7 ± 1.8^{c}	99.2^{d}		92.3^{d}
SF_3−F	96.3 ± 2.2^{e}	95.5	10.5 ± 1.0^{f}	12.9	59.4 ± 6.9^{g}	59.1
			8.3 ± 1.2^{c}			
SF_4−F	43.4 ± 6.0	38.1	96.0 ± 6.2	89.3	94.1 ± 8.9	97.0
			106.1 ± 2.3^{c}			
SF_5−F	101.0 ± 3.4^{h}	106.9			41.8 ± 6.5	36.2
sum	464.8 ± 9.7	466.8				443.7

[a] Unless specified, the experimental $D°_0$ values are calculated using experimental $\Delta_f H°_0$ values of S (65.6 kcal/mol), F(18.5 kcal/mol), S^+ (304.0 kcal/mol), and S^- (17.7 kcal/mol) from ref 46; and the recommended experimental $\Delta_f H°_0$ values (underlined and bolded) for SF_n and SF_n^+ ($n = 1-6$) given in Tables 1 and 2. [b] Unless specified, the theoretical $D°_0(SF_{n-1}-F)$, $D°_0(SF_{n-1}^{+}-F)$, and $D°_0(SF_{n-1}^{-}-F)$ ($n = 1, 2$) are G2 predictions, and $D°_0(SF_{n-1}-F)$, $D°_0(SF_{n-1}^{+}-F)$, and $D°_0(SF_{n-1}^{-}-F)$ ($n = 3-6$) are G2(MP2) predictions. These values are calculated using E_0(G2) or E_0[G2(MP2)] values or theoretical $\Delta_f H°_0$(G2) or $\Delta_f H°_0$[G2(MP2)] values for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) given in Table 1 and 2. The value E_0(G2) = −397.28016 and −397.72856 hartree for S^+ and S^- from ref 40 is used in the calculation of $D°_0(S^+-F)$ and $D°_0(S^--F)$. [c] Reference 20. [d] Values calculated using $\Delta_f H°_0$(G2) values for SF_2, SF_2^+, and SF_2^-, and $\Delta_f H°_0$[G2(MP2)] values for SF_3, SF_3^+, and SF_3^-. [e] Calculated using $D°_0(SF_3^+-F)$ = 10.5 ± 1.0 kcal/mol, IE(SF_4) = 11.90 ± 0.03 eV (ref 34) and AE (12.36 ± 0.03 eV) for process 2 at 0 K. See text. [f] Calculates using IE(SF_4) = 11.90 ± 0.03 eV and AE (12.36 ± 0.03 eV) for process 2 reported by ref 34. See text. [g] Calculated using $D°_0(SF_3-F)$ = 96.3 ± 2.2 kcal/mol, EA(SF_4) = 1.5 ± 0.2 eV, and EA(SF_3) = 3.1 ± 0.2 eV. [h] Reference 18. See the text.

The experimental $D°_0$'s for $SF_{n-1}-F$, $SF_{n-1}^{+}-F$, and $SF_n^{-}-F$ (n = 1−6) shown in Table 4 are in excellent agreement with those obtained from theoretical G2 and G2(MP2) calculations after taking into account the experimental uncertainties, except that for S^+-F. The lower theoretical $D°_0(S^+-F)$ of 77.2 kcal/mol compared to the experimental value of 81.6 ± 1.2 kcal/mol is partly attributed to the fact that the IE of S calculated by the G2 procedure is lower than the experimental IE(S) by 3.7 kcal/mol. Thus, we conclude that the difference observed between the experimental and theoretical $D°_0(S^+-F)$ is due to the inaccuracy of the G2 prediction. The sum of 464.8 ± 9.7 kcal/mol for the sequential experimental $D°_0(SF_{n-1}-F)$ ($n = 1-6$) values agrees with the value of 465 kcal/mol for the enthalpy of reaction at 0 K for the process $SF_6 \rightarrow S + 6F$. The differences between the experimental and theoretical $D°_0$ values for SF_4^+-F, SF_4-F, and SF_5-F are 5.7, 5.8, 5.3, and 5.9 kcal/mol, respectively. These relatively large differences call for more accurate experimental determinations for the $\Delta_f H°_0$ values for SF_4^+, SF_4, SF_5^+, and SF_5.

Considering the straightforward approach of applying the ion CID technique to determine the sequential $D°_0$'s for a system such as SF_6, it is interesting to compare the $D°_0(SF_{n-1}^{+}-F)$ ($n = 1-5$) determined in the CID experiment[20] with those calculated by theoretical procedures and also with those calculated using the recommended $\Delta_f H°_0(SF_n^+)$ data. As shown in Table 4, the sequential $D°_0(SF_{n-1}^{+}-F)$ ($n = 1-5$) determined by the ion CID are in general accord with those based on the recommended $\Delta_f H°_0(SF_n^+)$ data and G2 [or G2(MP2)] predictions. However, $D°_0(SF_2^+-F)$ = 104.7 ± 1.8 kcal/mol and $D°_0(SF_4^+-F)$ = 106.1 ± 2.3 kcal/mol determined in the CID study are likely too high.

The sequential $D°_0$'s for the neutral, cationic, and anionic sulfur fluorides all exhibit alternation patterns (Table 4). The trend of alternating high and low values observed for the neutral S−F bond dissociation energies has been discussed and rationalized previously without invoking the participation of the d-orbitals of the S atom in the bonding.[18,20] The pattern observed for the S−F bond dissociation energies of the sulfur fluoride cations is also discussed in ref 20. Interestingly, similar patterns are observed for the IEs and EAs of SF_n ($n = 1-6$) shown in Tables 1 and 2.

The general trends observed for $D°_0(SF_{n-1}-F)$ ($n = 2-6$), $D°_0(SF_{n-1}^{+}-F)$ ($n = 3-5$), $D°_0(SF_{n-1}^{-}-F)$ ($n = 2-6$), EA(SF_n) (1−6), and IE(SF_n) ($n = 2-5$) are understood by recognizing that molecular species with fully-filled 8, 10, and 12 valence electron shells around the S atoms are more stable than other species. Thus, for the systems of interest here, we have fully-filled 8 electron shells for SF_3^+, SF_2, and SF^-; fully-filled 10 electron shells for SF_5^+, SF_4, and SF_3^-; and fully-filled 12 electron shells for SF_6 and SF_5^-. Figure 2 is constructed to illustrate and to explain the variations of the observed $D°_0$'s, IEs, and EAs. The cations SF_n^+ ($n = 2-5$), the neutrals SF_n ($n = 1-6$), and the anions SF_n^- ($n = 1-6$) are shown in Figure 2 in three rows. The values on top of the horizontal arrows are the experimental $D°_0$'s in kcal/mol for dissociation from $SF_{n-1}-F$ to SF_{n-1}, $SF_{n-1}^{+}-F$ to SF_{n-1}^{+}, or $SF_{n-1}^{-}-F$ to SF_{n-1}^{-}, except those for $D°_0(SF_2^--F)$ and $D°_0(SF^--F)$ are theoretical values. The higher $D°_0$ values correspond to the S−F bond energies for SF_2 (90.8 ± 3.0 kcal/mol), SF_4 (96.3 ± 2.2 kcal/mol), SF_6 (101.0 ± 3.4 kcal/mol), SF_3^+ (96.1 ± 5.6 kcal/mol), SF_5^+ (96.0 ± 6.2 kcal/mol), SF_3^- (92.3 kcal/mol, theoretical value), and SF_5^- (94.1 ± 8.9 kcal/mol). In each of these cases, the dissociation involves the transformation from a higher and more stable neutral (or cationic, or anionic) sulfur fluoride to a lower and less stable neutral (or cationic, or anionic) sulfur fluoride plus an F atom. The lower S−F dissociation energies correspond to transformation from a high and less stable sulfur fluoride to a low and more stable sulfur fluoride plus an F atom. These latter cases are observed for SF_3 [$D°_0(SF_2-F)$ = 52.1 ± 5.6 kcal/mol], SF_5 [$D°_0(SF_4-F)$ = 43.4 ± 6.0 kcal/mol], SF_4^+ [$D°_0(SF_3^+-F)$ = 10.5 ± 1.0 kcal/mol], SF_2^- [$D°_0(SF^--F)$ = 69.8 kcal/mol, theoretical value], SF_4^- [$D°_0(SF_3^--F)$ = 59.4 ± 6.9 kcal/mol], and SF_6^- [$D°_0(SF_5^--F)$ = 41.8 ± 6.5 kcal/mol].

Ionization energy is a measure of the transition energy from the neutral to its cation, whereas electron affinity measures the transition from an anion to its corresponding neutral. The values in eV shown by the side of the vertical arrows in Figure 3 are either IEs or EAs. For the ionization transitions $SF_2 \rightarrow SF_2^+ + e^-$ and $SF_4 \rightarrow SF_4^+ + e^-$, the transitions correspond to

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(59) Polack, M. L.; Gilles, M. K.; Lineberger, W. C. *J. Chem. Phys.* **1992**, *96*, 7191.

(60) Chen, Y.-J.; Liao, C.-L.; Ng, C. Y. Unpublished results.

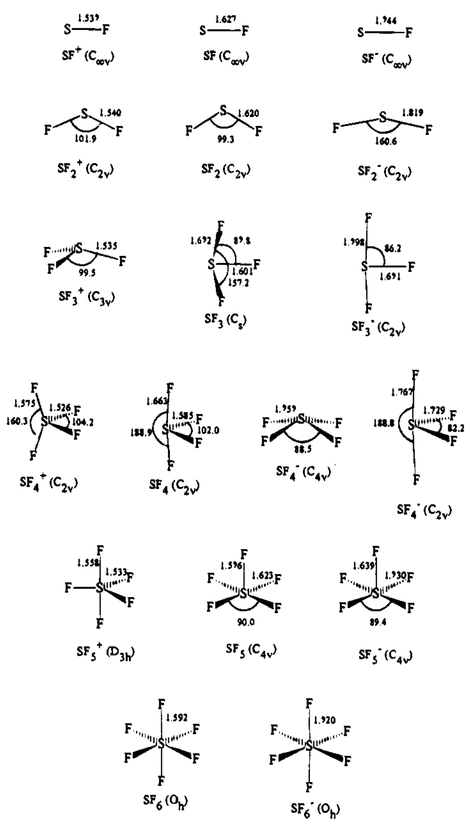

Figure 1. Theoretical equilibrium structures for SF_n ($n = 1-6$), SF_n^+ ($n = 1-5$), and SF_n^- ($n = 1-6$) optimized at the MP2/6-31G(d) levels. Bond distances are in Å and bond angles are in deg.

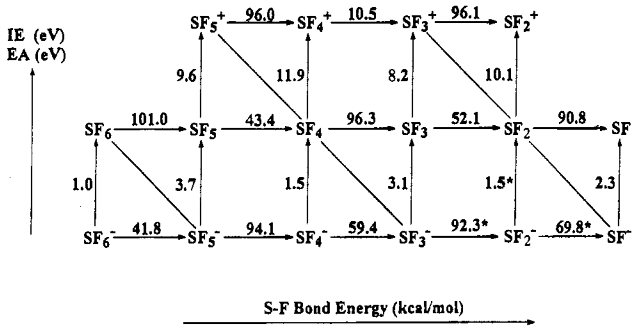

Figure 2. Schematic diagram illustrating the alternating patterns for $D°_0$'s for $SF_{n-1}-F$ ($n = 2-6$), SF_{n-1}^+-F ($n = 3-5$), and SF_{n-1}^--F ($n = 2-6$), IEs of SF_n, and EAs for SF_n ($n = 1-6$). The values marked by asterisks are theoretical values.

ionization from a stable neutral to a less stable cation, and thus the IEs of SF_2 (10.08 ± 0.05 eV) and SF_4 (11.90 ± 0.03 eV) are expected to have high values. The lower IEs for SF_3 (8.18 ± 0.07 eV) and SF_5 (9.60 ± 0.05 eV) are due to ionization transitions from a less stable neutral to a more stable cation. Similarly, the electron detachment transitions, $SF^- \rightarrow SF + e^-$, $SF_3^- \rightarrow SF_3 + e^-$, and $SF_5^- \rightarrow SF_5 + e^-$, involve transitions from a more stable to a less stable species. Therefore, we expect the EAs for SF (2.285 ± 0.006 eV), SF_3 (3.1 ± 0.2 eV) and SF_5 (3.7 ± 0.2 eV) to be higher than those for SF_2 (1.5 eV, theoretical value), SF_4 (1.5 ± 0.2 eV), and SF_6 (1.05 ± 0.10 eV), which correspond to detachment transitions from a less stable anion to a more stable neutral.

The picture presented above to explain the alternating patterns observed for $D°_0$'s, IEs, and EAs for the SF_n and SF_n^+ ($n = 1-6$) systems should also be applicable to similar systems involving other hypervalent species.

IV. Conclusions

The comparison of the experimental thermochemical data and G2 [or G2(MP2)] predictions for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) allows us to recommend a self-consistent set of experimental $\Delta_f H°_0$, IE, EA, $D°_0$ values for these systems. This work shows that for reliable determinations of the thermochemical data for a complex system such as SF_n, SF_n^+, and SF_n^- ($n = 1-6$), it is necessary to combine experimental measurements made using different techniques and theoretical predictions calculated using a sufficiently accurate theoretical procedure.

The comparison of experimental and theoretical results in this study further confirms that G2 and G2(MP2) procedures are reliable theoretical methods for providing energetic predictions accurate to 4-5 kcal/mol for complex sulfur-containing molecular species. On the experimental side, more accurate energetic measurements for SF_n ($n = 3-5$), SF_n^+ ($n = 3-5$), and SF_n^- ($n = 1-5$) are still needed to reduce the relatively large uncertainties for the $\Delta_f H°_0$'s of these sulfur fluorides.

The theoretical equilibrium structures obtained for SF_n, SF_n^+, and SF_n^- ($n = 1-6$) have been rationalized using the VSEPR theory. Furthermore, we have provided an explanation to account for the observed alternating patterns in IE, EA, and $D°_0$ values for SF_n, SF_n^+, and SF_n^- ($n = 1-6$). Alternating patterns in IE, EA, and $D°_0$ values are expected for other similar hypervalent species.

Note Added in Proof. A theoretical paper has recently appeared (Irikura, K. K. *J. Chem. Phys.* **1995**, *102*, 5357) which examines the structures and energetics of the SF_n neutrals and cations using the G2 or G2(MP2) procedure. These results are in agreement with the present calculations except that for IE(SF). We note that the IE(SF) = 10.31 eV obtained here is slightly higher than the value of 10.13 eV reported by Irikura.

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