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Structure and thermochemistry of sulfur fluorides SF_n (n = 1–5) and their ions SF_n⁺ (n = 1–5)

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Ab initio calculations, including the GAUSSIAN-2 procedures, have been performed to determine the molecular structure and thermochemistry of the sulfur fluorides SF_n (n = 1–5) and sulfur fluoride cations SF_n⁺ (n = 1–5) in the gas phase. Based upon a comparison between calculated and experimental heats of formation of SF₆, standard enthalpies of formation are derived for the ten title species. Values for SF₃, SF₅, and SF₅⁺ differ from literature values by more than 50 kJ/mol. Bond energies are also derived (uncertainties are 2σ): $D_0^\circ(\text{SF}_5\text{-F})=444\pm 6$, $D_0^\circ(\text{SF}_4\text{-F})=159\pm 7$, $D_0^\circ(\text{SF}_3\text{-F})=398\pm 7$, $D_0^\circ(\text{SF}_2\text{-F})=227\pm 6$, $D_0^\circ(\text{SF-F})=374\pm 6$, and $D_0^\circ(\text{S-F})=345\pm 6$ kJ/mol for the neutral species, and $D_0^\circ(\text{SF}_4^+\text{-F})=371\pm 6$, $D_0^\circ(\text{SF}_3^+\text{-F})=56\pm 6$, $D_0^\circ(\text{SF}_2^+\text{-F})=400\pm 6$, $D_0^\circ(\text{SF}^+\text{-F})=372\pm 6$, and $D_0^\circ(\text{S}^+\text{-F})=367\pm 8$ kJ/mol for the ions. Adiabatic ionization energies are calculated to be 10.13 ± 0.20 , 10.15 ± 0.19 , 8.36 ± 0.18 , 11.90 ± 0.16 , and 9.71 ± 0.16 eV for SF through SF₅, respectively. Calculated geometries, vibrational frequencies, entropies, integrated heat capacities, and vertical ionization energies are also reported. Energy levels for low-frequency vibrations are determined variationally.

I. INTRODUCTION

The decomposition of sulfur hexafluoride is important in the plasma processing of semiconductors¹ and in high voltage power systems, where it is employed as an insulator.² Although significant progress has been made in modeling these processes at the elementary reaction level, the lack of kinetics and thermodynamic data has been a serious impediment to success.³ In a recent review, discrepant values or large uncertainties were identified for neutral SF_n (n = 2–5).⁴ A later reanalysis of experimental data indicated that the accepted value of $\Delta_f H_0^\circ(\text{SF}_5)$ is too low by 30 kJ/mol.⁵ Very recent *ab initio* calculations also suggest that $\Delta_f H_0^\circ(\text{SF}_5)$ is too low, by about 40 kJ/mol.⁶ Among the ions, results of recent experiments⁷ include a value of $\Delta_f H^\circ(\text{SF}_5^+)$ that differs from the value in the JANAF tables⁸ by 178 kJ/mol! Such large disagreements suggest that a careful calculational study will be of value.

The present work is based upon the GAUSSIAN-2 (or G2) procedure.⁹ Thermochemistry based upon G2 atomization energies is typically accurate to about 10 kJ/mol, but has not been well-tested for molecules containing at least one third-period atom (Na–Ar) in addition to other nonhydrogen atoms. Errors for such molecules can be significantly larger. For example, the errors obtained for $\Delta_f H_0^\circ(\text{PF}_5)$ and $\Delta_f H_0^\circ(\text{PF}_3)$ are +27 and +22 kJ/mol,¹⁰ respectively, and the error obtained for $\Delta_f H_0^\circ(\text{SO}_2)$ is +21 kJ/mol.⁹ Thus, G2 calculations of the thermochemistry of the sulfur fluorides serve two purposes; (1) to determine thermochemical values, and (2) to test the accuracy of the G2 procedure. The direct results of the calculations, comparisons with benchmark experimental values, and empirical adjustments to the calculated thermochemistry are presented in Sec. III below. Comparisons of the present results with previous work are

detailed in Sec. IV. Points (1) and (2) above are summarized in Sec. V.

II. COMPUTATIONAL PROCEDURES

A. Base calculations

The G2 series of approximations is defined for all molecules composed entirely of elements lighter than potassium.⁹ The principle behind the procedure is to assume additivity of two effects; augmentation of the one-electron basis set and treatment of dynamic electron correlation. The validity of this additivity assumption has been verified for many molecules.¹¹ Energy increments are determined for the molecule of interest and are then applied to a base energy calculated at the frozen-core MP4/6-311G** level (fourth-order perturbation theory and a valence triple-split basis augmented with a set of *d*-polarization functions on nonhydrogen atoms and a set of *p*-polarization functions on hydrogen atoms). The intention is to approximate the energy that would result from a calculation at the frozen-core QCISD(T)/6-311+G(3*df*,2*p*) level (quadratic configuration interaction including single and double excitations and a perturbative correction for triple excitations¹² and a 6-311G basis augmented with a diffuse *sp*-shell on nonhydrogen atoms, three sets of *d*- and one set of *f*-polarization functions on nonhydrogen atoms, and two sets of *p*-polarization functions on hydrogen atoms). A final “higher level correction,” based upon the number of valence electrons and the spin multiplicity, is added to account for additional correlation energy in an empirical way. At this time, G2 calculations are not generally feasible for molecules containing more than six nonhydrogen (“heavy”) atoms.

A similar but less expensive alternative procedure known as G2(MP2) has also been introduced.¹³ Corrections for basis set augmentation are calculated at the MP2 level instead of MP4, and the empirical correction is the same as

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TABLE I. Molecular geometries and ground state symmetries for SF_n ($n=1-6$) and SF_n⁺ ($n=1-5$) calculated at the MP2=full/6-31G* level. Where there are chemically distinct types of fluorine atom in a molecule, the subscript 1 refers to the less numerous or axial type. Distances are in Å, angles in deg. Experimental values (averaged over the vibrational ground state) are given in parentheses.

Molecule	Point group	Ground state	r_1	r_2	θ_{11}	θ_{12}	θ_{22}	Expt Ref.
SF	$C_{\infty v}$	$^2\Pi$	1.627 (1.596) ^a					62
SF ₂	C_{2v}	1A_1	1.620 (1.587) ^a		99.2 (98.0) ^a			63
SF ₃	C_s	$^2A'$	1.601	1.672		87.8	157.5	
SF ₄	C_{2v}	1A_1	1.663 (1.646)	1.585 (1.545)	171.1 (173.1)	87.2	102.0 (101.6)	64
SF ₅	C_{4v}	2A_1	1.577	1.623		91.4	90.0	
SF ₆	O_h	$^1A_{1g}$	1.593 (1.557)					65
SF ⁺	$C_{\infty v}$	$^3\Sigma^-$	1.540					
SF ₂ ⁺	C_{2v}	2B_1	1.540		101.9			
SF ₃ ⁺	C_{3v}	1A_1	1.536 (1.51)		99.5 (97)			36, 66
SF ₄ ⁺	C_{2v}	2A_1	1.575	1.526	160.3	96.0	104.1	
SF ₅ ⁺	D_{3h}	$^1A'_1$	1.558	1.533	180	90	120	

^aEquilibrium value.

in the original G2 procedure. G2(MP2) atomization energies appear to be as accurate as G2 atomization energies (~10 kJ/mol). Interestingly, the atomization energy for SO₂ is in error by only -5 kJ/mol at the G2(MP2) level, while at the G2 level it is the worst outlier (error of -21 kJ/mol) among the original G2 set of molecules.⁹

All calculations in this study were done using the Gaussian series of programs.¹⁴⁻¹⁷ The basis sets were used as defined within these programs. As prescribed in the G2 and G2(MP2) procedures, vibrational frequencies are calculated at the HF/6-31G* level and then scaled by 0.893. In the present work, experimental vibrational fundamental frequencies are used when available. Only gas-phase or matrix-isolation values are used here. In particular, the frequencies for SF₃⁺ in solid or molten salts are not used. Thermal corrections are calculated based upon a vibrational model that is harmonic for frequencies greater than 300 cm⁻¹ and includes explicit energy levels for lower-frequency motions. Low-frequency vibrations are treated explicitly here because they make large contributions to the entropy. Zero-point vibrational energies are taken as one-half the sum of the frequencies except for those modes treated explicitly.

B. Low-frequency vibrations

To treat the low-frequency motions, normal modes corresponding to scaled HF/6-31G* frequencies less than 300 cm⁻¹ are first projected onto internal coordinates. Since all these modes are essentially bending motions, the small components involving bond lengths are deleted. A one-dimensional HF/6-31G* potential energy curve is then generated by displacing the molecule from its equilibrium position along the pure bending mode. The range is selected so that the high energy at each end (positive and negative displacements) is at least 2000 cm⁻¹. In the case of SF₃, which has a double well, energies along the central hump of

the potential are scaled slightly so that the central maximum has the value (617 cm⁻¹) obtained from a HF/6-31G* transition-state calculation. The potential curve is then fitted with an analytic function such as a polynomial or a rational function. If the fitting function decreases at displacements beyond those actually calculated, it is joined to a constant potential (greater than 2000 cm⁻¹) for such large displacements. The metric of the abscissa is scaled slightly in order to obtain the correct curvature at the bottom of the well. Vibrational energy levels and eigenvectors are calculated using the Fourier grid Hamiltonian method¹⁸ and the mass from the (harmonic) normal mode calculation. If a gas-phase, experimental fundamental frequency is available, all the calculated vibrational energy levels are scaled so that the 0-1 interval matches the experimental value. If not, and if the potential is close to harmonic (i.e., single-well), the energy levels are scaled so that the 0-1 interval matches the scaled (0.893) harmonic HF/6-31G* frequency.

C. Thermochemistry

For additional accuracy in the calculated entropy, experimental geometries are used when available in order to calculate thermal functions (but not to replace the MP2=full/6-31G* geometries in the *ab initio* calculations). Since the calculated bond lengths are too large by 0.028 Å on average (Table I), they are shortened accordingly when calculating thermal functions for molecules lacking experimental geometries. Since the present calculations ignore spin-orbit coupling, a range is indicated for S₂₉₈^o(SF) ($^2\Pi$ ground state) that corresponds to the limits of degeneracy $g=2$ ($|A|=\infty$) and $g=4$ ($A=0$).

Enthalpies of formation for the neutral SF_n are derived from the calculated atomization energies. As described in detail in the Results and Analysis, an empirical correction is

TABLE II. Vibrational frequencies for SF_n ($n=1-6$) and SF_n⁺ ($n=1-5$) calculated at the HF/6-31G* level. The scale factor is 0.893. Experimental values are fundamental frequencies unless noted as harmonic. The experimental values for SF₃⁺ are for salts of the ion.

Molecule	Mode symmetry	Scaled frequencies	Experimental frequencies	Expt Ref.
SF	σ	823	838 ^a	62
SF ₂	a_1	840, 339	839, 357	63, 67
	b_2	827	813	67
SF ₃	a'	860, 604, 368, 203	844	23
	a''	728, 457	682	
SF ₄	a_1	893, 584, 518, 210	892, 558, 475, 223	24, 68
	a_2	460	414	
	b_1	769, 522	867, 532	
SF ₅	b_2	889, 355	730, 353	
	a_1	895, 649, 541	885	23
	b_1	446		
	b_2	616, 235		
SF ₆	e	875, 505, 345	812, 552	69
	a_{1g}	755	774	70
	e_g	658	642	
	t_{1u}	982, 576	948, 616	
	t_{2g}	489	525	
SF ⁺	σ	330	347	
SF ₂ ⁺	a_1	975		
	b_2	956, 389		
SF ₃ ⁺	a_1	951, 502	940, 530	66, 71
	e	972, 366	920, 410 or 360	66, 71, 72
SF ₄ ⁺	a_1	950, 609, 477, 250		
	a_2	394		
	b_1	1010, 289		
	b_2	727, 478		
SF ₅ ⁺	a'_1	804, 714		
	a''_2	1036, 586		
	e'	1058, 541, 190		
	e''	526		

^aHarmonic frequency (ω_e).

applied based upon the well-determined value for $\Delta_f H_0^\circ(\text{SF}_6)$.

For the cations SF_n⁺, however, calculated atomization energies are found to be unreliable. Experimentally, the ionization energy of the sulfur atom IE(S)=10.36 eV,¹⁹ but the values from G2 and G2(MP2) theory are 10.20 and 10.08 eV, respectively.^{9,13} In contrast, G2 and G2(MP2) ionization energies are fairly accurate for the molecular species H₂S [G2 = 10.43 eV,⁹ G2(MP2)=10.40 eV,¹³ expt=10.453±0.008 eV (Ref. 20)] and SF₂ [G2=10.15 eV, G2(MP2)=10.07 eV, expt = 10.08±0.05 eV (Ref. 21)]. Since there are large errors in the calculated ionization energy for the sulfur atom, but not for the molecules, large errors in the calculated atomization energies for the SF_n⁺ ions are obtained.

Since ionic atomization energies are unreliable, the ion thermochemistry derived here is based upon ionization energies instead of atomization energies, using the relation $\Delta_f H_0^\circ(\text{SF}_n^+) = \Delta_f H_0^\circ(\text{SF}_n) + \text{IE}(\text{SF}_n)$. The ionization energies for a set of 38 atoms and small molecules have been found to be too low by 0.027 eV ($2\sigma=0.130$ eV) at the G2 level and too low by 0.052 eV ($2\sigma=0.171$ eV) at the G2(MP2) level, on average.^{9,13} The ionization energies in this work are therefore corrected by these amounts before being used to calculate the ion thermochemistry.

Experimental measurements of ionization energies can be problematic if the ionization process is very nonvertical. The difference between the vertical and adiabatic ionization energies is the relevant quantity. It is calculated here at the QCISD(T)/6-311G*//MP2=full/6-31G* level, with vibrational zero-point energy neglected.

The standard pressure is 100 kPa. The standard temperature of 298.15 K is denoted by a subscript 298; a subscript 0 refers to absolute zero temperature.

III. RESULTS AND ANALYSIS

Molecular geometries and vibrational frequencies were calculated at the HF/6-31G* level. In each case, the vibrational analysis confirms that the geometry obtained is a minimum on the molecular potential energy surface (NIMAG = 0). Geometries were subsequently refined at the MP2=full/6-31G* level (no frozen orbitals). The final geometries, the molecular point group, and the spin and spatial symmetries of the electronic ground states are collected in Table I. The scaled, harmonic vibrational frequencies are listed in Table II. Experimental frequencies are also included in Table II.

TABLE III. Vibrational isotope shifts $\nu(^{34}\text{SF}_4) - \nu(^{32}\text{SF}_4)$ from scaled (0.893) HF/6-31G* calculations and from argon matrix experiments (Ref. 23) and infrared intensities from HF/6-31G* calculations and from experiment (Ref. 24). Coordinate axes are oriented as in Ref. 68.

Mode	Shift (cm ⁻¹)		Intensity	
	Calc	Expt	Calc (km/mol)	Expt
ν_1	-11.3		138.1	<i>s</i>
ν_2	-0.2		2.2	<i>m</i>
ν_3	-4.3		39.4	<i>vw</i>
ν_4	0.0		0.8	<i>w</i>
ν_5	0.0		0	
ν_6	-13.5	-10.5	689.5	<i>s</i>
ν_7	-1.2		5.5	<i>ms</i>
ν_8	-11.3	-12.9	185.1	<i>vs</i>
ν_9	-2.2		15.7	<i>ms</i>

For SF₄, there is some confusion in the literature over the assignment of the vibrational spectrum, ν_6 and ν_8 in particular.²² To help resolve the discrepancy, vibrational frequencies were calculated for the ³⁴SF₄ isotopomer. The calculated and experimental²³ isotope shifts, as well as calculated and experimental²⁴ intensity information, are collected in Table III.

Since the present treatment of vibrations, rotations, and ion energies is somewhat different from the standard G2 and G2(MP2) procedures, the modified procedures are denoted here with a prime, G2' and G2(MP2)'. G2' and G2(MP2)' energies are collected in Table IV. Consequent atomization energies for neutral molecules and corrected ionization energies for ions are also listed in Table IV. For comparison, unmodified G2 and G2(MP2) energies are also included in Table IV. The G2 and G2(MP2) atomic energies are from the literature.^{9,13} For SF₆, the G2 calculation was not possible with the available computational resources. For the open-shell cases, spin contamination in the UHF references is negligible; $\langle S^2 \rangle$ does not exceed the correct value by more than 0.03 for any of the molecules in this study.

Standard enthalpies of formation at 0 K are listed in Table V. Values for neutral species are based upon atomization energies. Values for ions are derived from the neutral

TABLE V. Uncorrected enthalpies of formation at 0 K ($\Delta_f H_0^\circ$) standard entropies at 298.15 K (S_{298}°), and integrated heat capacities [$H^\circ(298.15) - H^\circ(0)$]. Entropies and heat capacities are calculated as described in the text. $\Delta_f H_0^\circ$ values are calculated from G2' and G2(MP2)' atomization energies for neutral species (Table IV). For ions, $\Delta_f H_0^\circ$ values are calculated from the neutral values and the corrected ionization energies (Table IV).

Molecule	Uncorr. $\Delta_f H_0^\circ$ (kJ/mol)		S_{298}° (J/mol K)	$\int C_p dT$ (kJ/mol)
	G2'	G2(MP2)'		
SF	9.7	7.4	224.8±2.9	8.9
SF ₂	-283.7	-289.7	257.6	11.22
SF ₃	-429.9	-440.0	294.4	13.89
SF ₄	-747.1	-762.2	295.9	15.26
SF ₅	-826.0	-843.3	308.3	16.68
SF ₆		-1210.7	291.4	16.90
SF ⁺	990.7	981.9	224.1	8.78
SF ₂ ⁺	698.5	687.1	260.9	10.98
SF ₃ ⁺	379.0	363.6	270.6	12.64
SF ₄ ⁺	402.6	384.7	301.7	15.27
SF ₅ ⁺	111.6	91.9	298.5	16.25

molecules' enthalpies and the corrected ionization energies. The values $\Delta_f H_0^\circ(\text{S}) = 274.73 \pm 0.25$ and $\Delta_f H_0^\circ(\text{F}) = 77.28 \pm 0.30$ kJ/mol are employed.⁸ For ion thermochemistry at temperatures above 0 K, the ion convention is adopted.²⁰ Where appropriate and convenient, use of the ion convention is emphasized by using the notation $\Delta_f H$ instead of $\Delta_f H^0$ for heats of formation above 0 K.²⁰ The conventions are related by Eq. (1),

$$\Delta_f H_{298}^\circ(\text{M}^+) = \Delta_f H_{298}(\text{M}^+) + 6.197 \text{ kJ/mol.} \quad (1)$$

Standard entropies S_{298}° and integrated heat capacities $H^\circ(298.15) - H^\circ(0) (\equiv \int C_p dT)$ are also included in Table V. Uncertainties (2 σ) for S_{298}° and $H^\circ(298.15) - H^\circ(0)$ are estimated by assuming a 25 cm⁻¹ (unscaled) uncertainty in the lowest, possibly degenerate, vibrational frequency only. Where an experimental value has been adopted for the lowest frequency, a 5 cm⁻¹ uncertainty is assumed.

Although energetics based upon atomization energies is expected to be less accurate than energetics based upon isogyric and isodesmic reactions,²⁵ no such clever reaction

TABLE IV. G2, G2(MP2), G2', and G2(MP2)' total energies, G2' and G2(MP2)' atomization energies for neutral molecules, and corrected (see text, Sec. II C) G2' and G2(MP2)' ionization energies for ions.

Molecule	Total energy (hartree)				E_{at} (kJ/mol) or IE (eV)	
	G2	G2(MP2)	G2'	G2(MP2)'	G2'	G2(MP2)'
SF	-497.418 197	-497.407 208	-497.418 163	-497.407 174	342.3	344.6
SF ₂	-597.192 148	-597.178 705	-597.192 141	-597.178 698	713.0	718.9
SF ₃	-696.910 037	-696.894 271	-696.910 103	-696.894 337	936.5	946.6
SF ₄	-796.692 778	-796.675 064	-796.693 146	-796.675 432	1330.9	1346.0
SF ₅	-896.385 383	-896.364 611	-896.385 476	-896.364 704	1487.2	1504.5
SF ₆		-996.163 350		-996.162 982		1949.0
SF ⁺	-497.045 476	-497.037 926	-497.045 476	-497.037 926	10.169	10.100
SF ₂ ⁺	-596.819 027	-596.808 593	-596.819 027	-596.808 593	10.180	10.123
SF ₃ ⁺	-696.602 998	-696.590 154	-696.602 998	-696.590 154	8.384	8.329
SF ₄ ⁺	-796.256 246	-796.240 500	-796.256 263	-796.240 517	11.915	11.887
SF ₅ ⁺	-896.029 351	-896.010 424	-896.029 346	-896.010 419	9.718	9.693

TABLE VI. Empirically derived corrections and the resulting corrected $\Delta_f H_0^\circ$ values from G2' and G2(MP2)' calculations. Uncertainties represent 1σ and refer only to the correction procedure.

Molecule	Correction (kJ/mol)		$\Delta_f H_0^\circ$ (kJ/mol)	
	G2'	G2(MP2)'	G2'	G2(MP2)'
SF	-3.2	0.5	6.5±0.1	7.9±0.1
SF ₂	-6.3	1.0	-290.0±0.2	-288.7±0.2
SF ₃	-9.5	1.5	-439.4±0.1	-438.5±0.1
SF ₄	-12.6	2.0	-759.7±1.1	-760.2±1.1
SF ₅	-15.8	2.5	-841.8±0.7	-840.8±0.7
SF _n ⁺	-3.2	0.5	987.6±0.2	982.4±0.2
SF ₂ ⁺	-6.3	1.0	692.2±0.4	688.1±0.4
SF ₃ ⁺	-9.5	1.5	369.5±0.7	365.1±0.7
SF ₄ ⁺	-12.6	2.0	390.0±0.4	386.7±0.4
SF ₅ ⁺	-15.8	2.5	95.8±0.5	94.4±0.5

schemes could be identified. Instead, empirical corrections are made based upon the heat of formation of SF₆, which is well-established experimentally. $\Delta_f H_0^\circ(\text{SF}_6) = -1207.7 \pm 0.3$ kJ/mol is obtained by applying the thermal adjustment of 14.0 kJ/mol (Ref. 8) to the most recent room-temperature value $\Delta_f H_{298}^\circ(\text{SF}_6) = -1221.7 \pm 0.3$ kJ/mol.²⁶ Comparison with the G2(MP2)' value in Table V indicates that the G2(MP2)' value is in error by -3.0 kJ/mol. Moreover, the difference between the G2' and G2(MP2)' heats of formation is linear in n for SF_n (difference = $3.91n - 1.57$, $R = 0.995$; $n = 1-5$). This suggests that the G2' value for $\Delta_f H_0^\circ(\text{SF}_6)$ will be -1188.8 kJ/mol, which is in error by +18.9 kJ/mol. Prorating these errors according to the number of fluorine atoms n results in the corrections listed in Table VI. The corresponding values of $\Delta_f H_0^\circ$ are also listed in Table VI. The uncertainties in Table VI are based upon (1) the prorated uncertainty in $\Delta_f H_{298}^\circ(\text{SF}_6)$, and (2) the deviation from linearity in n of the difference between the G2 and G2(MP2) enthalpies.

As for the neutral series, the difference between the G2' and G2(MP2)' heats of formation is linear in n for SF_n⁺ ($n = 1-5$), once again suggesting that systematic errors will be proportional to the number of S-F bonds. For the ions, however, no well-established, experimental heats of formation are available. The correction for SF_n⁺ is therefore taken to be the same as for the corresponding neutral SF_n. This choice leaves ionization energies unchanged.

Table VII contains the final $\Delta_f H_0^\circ$ and $\Delta_f H_{298}^\circ$ values obtained in this study. Final values for $\Delta_f H_0^\circ$ are obtained by averaging the G2'- and G2(MP2)'-based results from Table VI. Thermal corrections to 298.15 K are made using the integrated heat capacities from Table V and the atomic values 6.657 and 6.518 kJ/mol for S and F, respectively.⁸ The uncertainties given in Table VII are intended to represent 2σ (about 95% confidence interval) and include the discrepancies between G2'- and G2(MP2)'-derived values in addition to the sources of uncertainty included in Table VI. An additional contribution of 6 kJ/mol (2σ) is included as an estimate of the uncertainty in the various assumptions used in the correction procedure and also of nonsystematic errors that remain after the empirical corrections. For the ions, uncertainty in the ionization energies is also included (see Sec.

TABLE VII. Final heats of formation determined in this study. Uncertainties represent 2σ .

Molecule	$\Delta_f H^\circ$ or $\Delta_f H$ (kJ/mol)		
	0 K	298.15 K	Uncertainty
SF	7.2	7.2	± 6.2
SF ₂	-289.3	-291.4	± 6.2
SF ₃	-439.0	-442.8	± 6.1
SF ₄	-759.9	-766.8	± 6.4
SF ₅	-841.3	-851.2	± 6.2
SF _n ⁺	985.0	985.0	± 16.4
SF ₂ ⁺	690.2	687.9	± 16.1
SF ₃ ⁺	367.3	362.3	± 16.2
SF ₄ ⁺	388.3	381.5	± 16.0
SF ₅ ⁺	95.1	84.8	± 15.7

II C), and is the largest source of uncertainty.

A number of experimentally observable quantities can be calculated using the heats of formation in Table VII. Bond dissociation energies (BDEs) are calculated as the differences $\Delta_f H^\circ(\text{M-F}) - \Delta_f H^\circ(\text{M}) - \Delta_f H^\circ(\text{F})$, both at 0 K (D_0°) and at 298.15 K (D_{298}°), and are listed in Table VIII. The stated uncertainties in Table VIII are smaller than would be expected from the uncertainties listed in Table VII because of correlations among uncertainties. The alternation of bond strengths has been discussed elsewhere,^{7,27} and will not be discussed further here. Adiabatic ionization energies (IE_a s), also included in Table VIII, represent averages of the G2' and G2(MP2)' values from Table IV.

Table IX lists the differences between adiabatic and vertical ionization energies at the QCISD(T)/6-311G**//MP2=full/6-31G* level, with vibrational energy neglected. Differences are listed in both eV and cm⁻¹ for convenience.

IV. DISCUSSION

A. Structures

Comparison of the calculated geometries with available experimental structures (Table I) suggests that the calculations yield bond angles reliable to better than 2° but bond lengths too great by 0.02–0.04 Å. Density functional

TABLE VIII. Bond dissociation energies (at 0 K and at 298.15 K) and adiabatic ionization energies. Uncertainties represent 2σ .

Molecule	BDE(SF _{n-1} -F) (kJ/mol)			IE_a (eV)	
	D_0°	D_{298}°	Uncertainty	IE_a	Uncertainty
SF	344.8	349.1	±6.2	10.13	±0.20
SF ₂	373.8	378.0	±6.0	10.15	±0.19
SF ₃	226.9	230.8	±6.1	8.36	±0.18
SF ₄	398.3	403.4	±6.6	11.90	±0.16
SF ₅	158.6	163.8	±6.7	9.71	±0.16
SF _n ⁺	443.7	449.9	±6.3		
SF ₂ ⁺	366.6	370.5	±8.0		
SF ₃ ⁺	372.1	376.5	±6.2		
SF ₄ ⁺	400.1	405.0	±6.2		
SF ₅ ⁺	56.3	60.2	±6.4		
SF ₅ ⁺	370.5	376.0	±6.4		

TABLE IX. Differences between adiabatic and vertical ionization energies calculated at the QCISD(T)QCISD(T)=Fc/6-311G*/MP2=full/6-31G* level. Vibrational zero-point energies are neglected.

Molecule	IE _v - IE _a	
	eV	cm ⁻¹
SF	0.111	895
SF ₂	0.214	1 730
SF ₃	2.569	20 720
SF ₄	0.929	7 500
SF ₅	1.757	14 170

calculations^{28,29} show slightly better agreement with experimental bond lengths and are in general agreement with the present results except for SF₃.

Using an uncontracted TZ2P basis and nonlocal exchange corrections, density functional calculations predict a planar, C_{2v} geometry for SF₃.²⁹ This is in accord with the interpretation of esr measurements,³⁰ but in conflict with the butterfly-shaped C_s structure found in a HF/4-31G study (dihedral angle $\phi=156.2^\circ$).³¹ In the present work, $\phi=155.4^\circ$ was obtained at the UHF/6-31G* level, $\phi=157.1^\circ$ at the MP2=full/6-31G* level (Table I), $\phi=162.5^\circ$ at the MP4/6-31+G* level, and $\phi=161.3^\circ$ at the QCISD/6-31+G* level (which also yields $r_1=1.607$ Å, $r_2=1.699$ Å, $\theta_{11}=87.7^\circ$, and $\theta_{12}=160.8^\circ$). A nonplanar geometry is therefore recommended. Note that the molecular symmetry is important in calculating thermodynamic quantities because it determines the rotational symmetry number σ ($\sigma=1$ for C_s and $\sigma=2$ for C_{2v}).

Following a tentative experimental suggestion,³² it has been reported recently that there exist two stable isomers of SF₅ and two stable isomers of SF₅⁺, one each of molecular point group D_{3h} and C_{4v}.³³ This report has been challenged in a Comment,⁶ and the present work is in agreement with the Comment. The question of isomerism was reinvestigated in the present study because of its important thermochemical ramifications. For SF₅⁺, a HF/6-31G* geometry optimization was successfully constrained to C_{4v} symmetry. Vibrational analysis, however, reveals this structure to be a saddle point (NIMAG=1) on the HF/6-31G* potential energy surface with the offending frequency 162i cm⁻¹ (unscaled). At the MP2/6-31G* level (active core), the optimized C_{4v} structure is 0.22 eV above the D_{3h} minimum, in agreement with the prior report,³³ but there is again one imaginary frequency (139i cm⁻¹). Thus, the present study fails to confirm the existence of a C_{4v} isomer of SF₅⁺. Note that SF₅⁺ is isoelectronic with PF₅, and is expected to have a similar potential energy surface.

For neutral SF₅ at the HF/6-31G* level, the D_{3h}-constrained minimum has three imaginary frequencies (951i, 951i, and 219i cm⁻¹). At the MP2/6-31G* (active core) level, there are two imaginary frequencies, which are fairly close to zero (74i and 74i cm⁻¹). Ionic bonding is better described at the MP2/6-31+G* (frozen core) level, which again yields two imaginary frequencies (108i and 104i cm⁻¹). The (doubly-degenerate) direction of negative curvature corresponds to a distortion of the molecule in the

TABLE X. Changes in standard entropy, integrated heat capacity, and vibrational zero-point energy due to explicit treatment of low-frequency vibrations. Changes are relative to the harmonic model. Harmonic frequencies and anharmonicities, derived from a HF/6-31G* potential curve, are also listed where appropriate.

Vibration	$\Delta(S_{298}^\circ)$ (J/mol K)	$\Delta[H^\circ(298.15) - H^\circ(0)]$ (kJ/mol)	$\Delta(\text{ZPE})$ (kJ/mol)	ω (cm ⁻¹)	x (cm ⁻¹)
SF ₃ (ν_4)	-0.01	0.10	0.19	n.a.	n.a.
SF ₄ (ν_4)	0.07	0.01	0.01	224.5	0.84
SF ₅ (ν_6)	-0.02	0.00	0.00	234.5	-0.24
SF ₄ ⁺ (ν_4)	0.01	0.00	0.00	250.4	0.21
SF ₄ ⁺ (ν_7)	-0.20	-0.04	-0.05	278.6	-6.2
SF ₅ ⁺ (ν_7)	0.08	0.02	0.01	191.0	0.65

direction of a square pyramidal (C_{4v}) structure. Although the present results indicate that there is no local minimum of D_{3h} symmetry, the curvature of the potential energy surface does appear to be sensitive to the level of theory applied, and it is conceivable that a second, shallow minimum could be revealed at a higher level of theory.

B. Vibrations

With the exception of the two vibrations discussed in Sec. IV C, the scaled HF/6-31G* vibrational frequencies are in generally good agreement with experimental values listed in Table II (rms difference of 28 cm⁻¹, using the lower experimental value for ν_4 of SF₃⁺). As mentioned above, low-frequency vibrations make large contributions to the molecular entropy, and are treated explicitly here for motions with predicted frequencies less than 300 cm⁻¹. The modes selected for special treatment are therefore ν_4 of SF₃, ν_4 of SF₄, ν_6 of SF₅, ν_4 and ν_7 of SF₄⁺, and ν_7 of SF₅⁺. The effects of the explicit treatment of these vibrations upon the calculated entropy, integrated heat capacity, and zero-point vibrational energy (ZPE) are summarized in Table X. Note that the typical scaling of HF/6-31G* frequencies changes the thermal functions for a 300 cm⁻¹ harmonic oscillator by 0.81 J/mol K (S₂₉₈^o), 0.11 kJ/mol (integrated heat capacity), and -0.20 kJ/mol (ZPE), so changes of much smaller magnitude are not significant. The derived values for harmonic frequencies ω_i and anharmonicities x_i are also listed in Table X.

The greatest deviation from harmonicity is for the symmetric dihedral bend (ν_4) of SF₃. The potential energy curve and vibrational energy levels for this motion are illustrated in Fig. 1. The double well for the SF₃ motion results in much lower energy levels than are predicted from the harmonic model. Despite the C_s symmetry of the molecule, explicit consideration of the double-well potential requires that the rotational symmetry number be taken as $\sigma=2$ when calculating thermodynamic functions.³⁴ This compensates the effective doubling of the energy levels at low temperatures, resulting in essentially no net effect on S₂₉₈^o (Table X).

C. Vibrational assignments in SF₄

Comparison of experimental and scaled HF/6-31G* vibrational frequencies for SF₄ shows good agreement except for ν_6 (b_1) and ν_8 (b_2), which appear to be interchanged

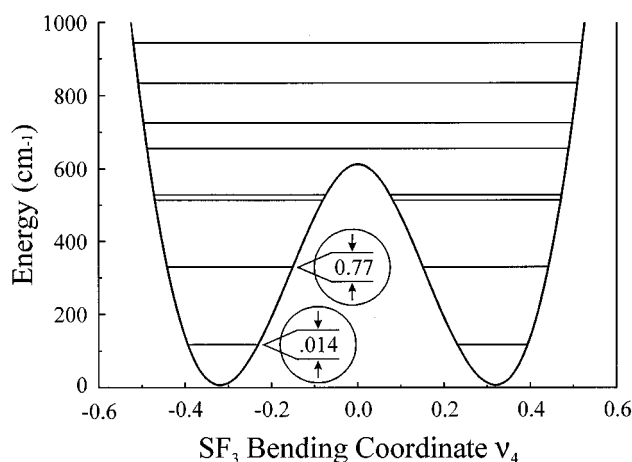


FIG. 1. Potential energy curve and vibrational eigenvalues for the ν_4 bend of SF₃, calculated at the HF/6-31G* level.

(Table II). Moreover, the calculated intensities are in the order $I(\nu_8) > I(\nu_6)$, which is the opposite of the experimental ordering as most recently accepted²³ (Table III). The calculated ³⁴S isotope shifts are also reversed from the experimental values (Table III). Thus, it appears that the accepted assignment of the vibrational spectrum of SF₄ should be revised to switch the assignments for ν_6 and ν_8 . The present calculations therefore favor the set of assignments due to Frey *et al.*³⁵

D. Standard entropies and integrated heat capacities

Values for S_{298}° and $\int C_p dT$ from the present work are compared with those from the JANAF tables⁸ in Table XI. Since more accurate (experimental, where available) vibrational and structural information were used to derive them, the S_{298}° values from the present work are favored over those in the JANAF tables⁸ except for SF and SF₂. (For SF₂, the same spectroscopic data are used in the present work and in the JANAF tables.)

Likewise, the present values are preferred for integrated heat capacities except for SF and SF₂. The present calculations underestimate the value for SF because the effect of the spin-orbit levels on the heat capacity is ignored. For both entropies and heat capacities, accurate vibrational frequencies are more important than accurate molecular structures.

Note that the JANAF value for $S_{298}^\circ(\text{SF}_4)$ is in error because an incorrect vibrational frequency was used (233 cm⁻¹ instead of 414 cm⁻¹), probably as a result of the confusion in vibrational assignments for SF₄ (see Sec. IV C above). Use of the correct vibrational frequency shifts the JANAF entropy value from 299.64 to 295.69 J/mol K.

E. Enthalpies of formation

Present values (from Table VII) for standard enthalpies of formation at 0 K, $\Delta_f H_0^\circ$, are compared with selected prior values from the experimental literature in Table XII. Where necessary, experimental values at 298 K have been corrected to 0 K using differences from Table VII. There is fairly good

TABLE XI. Comparison of present work with experiment; standard entropies (in J/mol K) and integrated heat capacities (in kJ/mol). Uncertainties in values from the present work are estimates for 2σ .

Molecule	S_{298}° (J/mol K)		$H^\circ(298.15) - H^\circ(0)$ (kJ/mol)	
	This work	JANAF ^a	This work	JANAF ^a
SF	224.8 ± 2.9	225.3 ± 0.8	8.9 ^b	9.48
SF ₂	257.6 ± 0.1	257.70 ± 0.08	11.22 ± 0.01	11.22
SF ₃	294.4 ± 0.9	286.2 ± 4.2	13.89 ± 0.09	13.60
SF ₄	295.9 ± 0.2	299.6 ± 0.4	15.26 ± 0.02	15.78
SF ₅	308.3 ± 0.8	304.8 ± 8.4	16.68 ± 0.09	16.32
SF ₆	291.4 ± 0.3	291.5 ± 0.4	16.90 ± 0.04	16.92
SF ⁺	224.1 ± 0.1	225.4 ± 9.2	8.78 ± 0.01	8.86
SF ₂ ⁺	260.9 ± 0.4	263.5 ± 0.4	10.98 ± 0.06	11.23
SF ₃ ⁺	270.6 ± 0.8	269.0 ± 2.1	12.64 ± 0.13	12.41
SF ₄ ⁺	301.7 ± 0.7	311.7 ± 8.0	15.27 ± 0.08	16.51
SF ₅ ⁺	298.5 ± 1.9	298.2 ± 8.4	16.25 ± 0.19	16.35

^aReference 8.

^bSpin-orbit splitting ignored.

agreement between the present work and experiment for SF, SF₂, and SF₄. For SF₃ and SF₅, the values determined here are substantially higher (about 50 and 60 kJ/mol, respectively) than the experimental values. The higher $\Delta_f H_0^\circ$ values correspond to stronger S–F bonds in SF₄ and SF₆. The bond energy $D(\text{SF}_5\text{--F})$ is discussed in detail below (Sec. IV G). Since the same experimental procedure²⁷ was used to derive $D(\text{SF}_5\text{--F})$ and $D(\text{SF}_3\text{--F})$, a similar discussion applies to $D(\text{SF}_3\text{--F})$ as to $D(\text{SF}_5\text{--F})$.

For the ions, there is good agreement for SF₂⁺ and acceptable agreement for SF⁺. For the heavier ions, agreement is poor; even among the experimental values there is serious disagreement. The experimental $\Delta_f H_0^\circ$ values in the JANAF tables⁸ are derived from neutral thermochemistry combined with ionization energies or appearance energies. Discrepancies between the present work and the JANAF values⁸ can therefore be traced to discrepancies in ionization energies, which are discussed below (Sec. IV F). For SF₃⁺ and SF₅⁺, there are also discrepancies in the underlying neutral thermochemistry. $\Delta_f H_0^\circ$ values from energy threshold measurements are derived from measured bond strengths in the ions.⁷ Discrepancies with the present work can therefore be traced to discrepancies in bond strengths $D(\text{SF}_{n-1}^+\text{--F})$ as discussed separately below (Sec. IV I).

A value for the heterolytic bond dissociation energy $D(\text{SF}_3^+\text{--F}^-) = 883 \pm 33$ kJ/mol has been determined from lattice energy calculations for SF₃BF₄.³⁶ When combined with $\Delta_f H_{298}^\circ(\text{SF}_4) = -767 \pm 6$ kJ/mol (Table VII) and $\Delta_f H_{298}^\circ(\text{F}^-) = -248.9 \pm 0.6$ kJ/mol,⁸ this leads to $\Delta_f H_{298}^\circ(\text{SF}_3^+) = 365 \pm 34$ kJ/mol, in agreement with the present value of 362 ± 16 kJ/mol (Table VII). A more recent value for $D(\text{BF}_3\text{--F}^-)$,³⁷ however, is 84 kJ/mol lower than that used in Ref. 36 and implies $\Delta_f H_{298}^\circ(\text{SF}_3^+) = 281 \pm 30$ kJ/mol. The present results are therefore more consistent with the older fluoride affinity value $\text{FA}(\text{BF}_3) = 385 \pm 25$ kJ/mol.³⁶

As can be seen from Table XII, $\Delta_f H_0^\circ(\text{SF}_5^+)$ has been particularly controversial. It is discussed separately below (Sec. IV H).

TABLE XII. Comparison of present work with selected prior experimental values; $\Delta_f H_0^\circ$ (in kJ/mol). Uncertainties in values from the present work are 2σ .

Molecule	Present work	Experiment
SF	7.2 ± 6.2	12.3 ± 6.3 ^{a,b}
SF ₂	-289.3 ± 6.2	-294.7 ± 16.7 ^{a,b}
SF ₃	-439.0 ± 6.1	-484.5 ± 25.0, ^a -499.0 ± 33.5 ^b
SF ₄	-759.9 ± 6.4	-756.9 ± 20.9, ^{a,b} -746 ± 12 ^c
SF ₅	-841.3 ± 6.2	-902.6 ± 13.4, ^a -898.3 ± 15.1, ^b -871 ± 10, ^c -903 ± 16 ^d
SF ⁺	985.0 ± 16.4	1007.9 ± 5.0, ^e 985.7 ± 16.7 ^b
SF ₂ ⁺	690.2 ± 16.1	682.8 ± 10.9, ^e 698.2 ± 46.0, ^b 710 ^f
SF ₃ ⁺	367.3 ± 16.2	322.2 ± 13.4, ^e 392.6 ± 33.5, ^b 370 ± 34, ^g 355 ^f
SF ₄ ⁺	388.3 ± 16.0	364.8 ± 14.2, ^e 415.4 ± 50.0, ^b 384 ^f
SF ₅ ⁺	95.1 ± 15.7	-1.7 ± 17.2, ^e 176.6 ± 20.9, ^b 42.3 ± 2.9, ^h ≤28.5, ⁱ ≤104.6 ± 8.4 ^j

^aReference 4.^bReference 8.^cReference 5.^dReference 38.^eReference 7.^fReference 73.^gReference 36; see also Sec. IV E.^hReference 53.ⁱReference 54.^jReferences 58 and 59.

F. Ionization energies

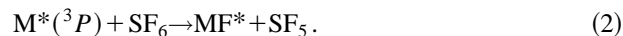
Adiabatic ionization energies obtained in the present work (from Table VIII) are compared with experimental values in Table XIII. There is good agreement in all cases, with the present values tending to be slightly higher than the experimental values. In particular, the calculations support the more recent, lower values for IE_a(SF₃) (Ref. 7) and for IE_a(SF₅).³⁸ Earlier values were probably too high because of the especially nonvertical nature of these two ionization processes (Table IX).

It is evident from Table XIII that some IE values adopted in the JANAF tables are too high. This has resulted in inaccurate ion thermochemistry (see Sec. IV E and Table XII).

G. Bond energy D(SF₅-F)

The heat of formation of SF₅ and the bond energy in SF₆ are very important for modeling chemical systems involving SF₆ and (toxic) S₂F₁₀, as has been discussed recently.³⁻⁵ The conventional value for $\Delta_f H_{298}^\circ(\text{SF}_5)$ is -912.5 ± 13.4 kJ/mol,⁴ and is based primarily upon the upper bound $D_0^\circ(\text{SF}_5-\text{F}) \leq 381.2 \pm 13.4$ kJ/mol determined from studies of the chemiluminescence resulting from reactions between

metastable metal atoms (Ca* and Sr*) and SF₆ [reaction (2)] and using $D_0^\circ(\text{Sr}-\text{F}) = 535.6 \pm 8.4$ kJ/mol and $D_0^\circ(\text{Ca}-\text{F}) = 531.8 \pm 8.4$ kJ/mol,^{27,39}



This value for $D_0^\circ(\text{SF}_5-\text{F})$ is supported by arguments based upon positive and negative ion chemistry.^{7,38} Shock-tube experiments yielded a bond energy of 318 kJ/mol,⁴⁰ but were later reinterpreted to obtain a value of about 385 kJ/mol,⁴¹ again supporting the chemiluminescence results.

Recently, however, this value for the bond strength has come under attack. In particular, the shock-tube data have been reinterpreted yet again, this time yielding the much higher value $D_{298}^\circ(\text{SF}_5-\text{F}) = 420 \pm 10$ kJ/mol.⁵ In addition, very recent G2(MP2) calculations indicate a value $D_0^\circ(\text{SF}_5-\text{F}) = 447$ kJ/mol, even higher.⁶ As shown in Table VIII, the result from the present work is essentially the same, $D_0^\circ = 443.7 \pm 6.3$ kJ/mol.

Each of the recent, high values for $D_0^\circ(\text{SF}_5-\text{F})$ has been accompanied by a criticism of the chemiluminescence results. Both of the newer papers^{5,6} have noted that different results were obtained using calcium atoms and strontium atoms.²⁷ No explanations have been offered for this apparent inconsistency. There is also the suggestion⁵ that some of the chemiluminescence arose from secondary chemistry such as reaction (3), involving ground



state metal atoms. $D(\text{SF}_4-\text{F})$ is very small (Table VII), so unwanted chemiluminescence from such a reaction will lead to a misleadingly low apparent bond strength. Since 20% or 30% of the effusive metal atom beam may be excited,^{42,43} significant concentrations of reaction products may develop. Thus, secondary reactions, perhaps even involving excited metal atoms, are a serious concern. If the bluest chemiluminescence were due to reaction (3), the upper limits on $D_0^\circ(\text{SF}_4-\text{F})$ would be 239.3 ± 14.2 kJ/mol from the Ca reac-

TABLE XIII. Comparison of present work with selected prior experimental values; adiabatic ionization energies (in eV). Uncertainties in values from the present work are 2σ .

Molecule	Present work	Experiment
SF	10.13 ± 0.20	10.09 ± 0.10, ^{a,b} 10.16 ± 0.17 ^c
SF ₂	10.15 ± 0.19	10.08 ± 0.05, ^d 10.29 ± 0.3 ^b
SF ₃	8.36 ± 0.18	8.18 ± 0.07, ^c 9.24 ± 0.69 ^b
SF ₄	11.90 ± 0.16	11.90, ^e 12.03 ± 0.05, ^f 12.08 ± 0.10, ^a 11.69 ± 0.06, ^c 12.28 ± 0.03, ^g 12.15 ± 0.3 ^b
SF ₅	9.71 ± 0.16	9.60 ± 0.05, ^h 11.14 ± 0.37 ^b

^aReference 74.^bReference 8.^cReference 7.^dReference 21.^eReference 73.^fReference 75.^gReference 76.^hReference 38.

tion and 202.9 ± 13.4 kJ/mol from the Sr reaction. These limits are consistent with both the old value $D_0^\circ(\text{SF}_4\text{-F}) = 222.2 \pm 25.1$ kJ/mol (Ref. 27) and the present value of 155.5 ± 6.7 kJ/mol (Table VIII).

Another possible problem with the chemiluminescence experiment is the presence of higher excited states in the metal atom beam. The 1D state is long-lived [1.1 ± 0.2 ms for Ca (Ref. 44)] and has been found in similar calcium atom sources, comprising up to 2% or 3% of the beam.⁴²⁻⁴⁴ Since the metastable 1D state is at higher energy than the metastable 3P state (by 78.2 kJ/mol for Ca and 62.8 kJ/mol for Sr),¹⁹ it can lead to an erroneously low apparent S-F bond strength. In particular, if the bluest chemiluminescence were actually due to reactions of 1D metal atoms, then the upper limits on the bond energy $D_0^\circ(\text{SF}_5\text{-F})$ would be 500.8 ± 14.2 kJ/mol for the Ca reaction and 444.0 ± 13.4 kJ/mol for the Sr reaction. The limit from the strontium reaction, which conventionally has been adopted as the bond energy,⁴ would then agree nicely with the present value (Table VIII).

A value of $D_{298}^\circ(\text{SF}_5\text{-F}) = 397 \pm 16$ kJ/mol (or $D_0^\circ = 391 \pm 16$ kJ/mol) has been derived³⁸ from the fluoride affinity $\text{FA}(\text{SF}_5) \equiv D(\text{SF}_5\text{-F}^-) = 169.9 \pm 13.4$ kJ/mol,⁴⁵ the electron affinity $\text{EA}(\text{SF}_6) = 1.05 \pm 0.1$ eV,⁴⁶ and $\text{EA}(\text{F}) = 3.399 \pm 0.003$ eV (Ref. 20) [Eq. (4)],

$$D(\text{SF}_5\text{-F}) = -\text{EA}(\text{SF}_6) + \text{FA}(\text{SF}_5) + \text{EA}(\text{F}). \quad (4)$$

The value for $\text{EA}(\text{SF}_6)$ is from equilibrium measurements.⁴⁶ The value for $\text{FA}(\text{SF}_5)$ relies partly upon failure to observe fluoride transfer from SF_6^- to SO_2 or SO_2F_2 .⁴⁵ Since many reactions of SF_6^- are abnormally slow,⁴⁵⁻⁴⁷ the lower bound on $\text{FA}(\text{SF}_5)$ is questionable, and a strict interpretation of the experimental results⁴⁵ allows only the upper limit $\text{FA}(\text{SF}_5) < 183$ kJ/mol. This leads to $D_{298}^\circ(\text{SF}_5\text{-F}) < 410 \pm 10$ kJ/mol, in conflict with the calculated bond strength $D_{298}^\circ(\text{SF}_5\text{-F}) = 450 \pm 6$ kJ/mol (Table VIII). Accepting the calculated bond strength and the value for $\text{EA}(\text{SF}_6)$ implies that $\text{FA}(\text{SF}_5) = 223.2 \pm 11.5$ kJ/mol. Conversely, accepting the calculated bond strength and the upper limit for $\text{FA}(\text{SF}_5)$ implies that $\text{EA}(\text{SF}_6) < 0.63 \pm 0.06$ eV. Further work will be needed to resolve this conflict. The *ab initio* literature is not helpful on this point; the most recent calculation is a MCSCF study that yielded $\text{EA}(\text{SF}_6) = -0.63$ eV,⁴⁸ clearly too low. A density-functional LSDA/NL calculation yielded $\text{EA}(\text{SF}_6) = 3.44$ eV,⁴⁹ but such calculations appear to be very unreliable for electron affinities.⁵⁰

Indirect support for the present value of $\Delta_f H_0^\circ(\text{SF}_5)$ comes from the consensus on $\text{IE}_a(\text{SF}_5)$ (present work and Refs. 38 and 7) and experimental support for the present value of $\Delta_f H_0^\circ(\text{SF}_5^+)$ (see Sec. IV H below).

H. $\Delta_f H_0^\circ(\text{SF}_5^+)$ and the appearance energy $\text{AE}(\text{SF}_5^+/\text{SF}_6)$

There have been many experimental limits and values reported for $\Delta_f H_0^\circ(\text{SF}_5^+)$, some of which are listed in Table XII. The very high value in the JANAF tables⁸ is based upon numerous and conflicting measurements of the appearance energy of SF_5^+ from SF_6 . As noted by Fisher *et al.*,⁷ appearance energy measurements are especially unreliable for $\text{SF}_5^+/\text{SF}_6$ because of the big change in geometry of the SF_5 fragment. Specifically, the relaxation energy at the

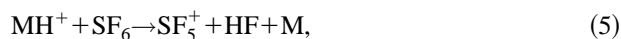
TABLE XIV. Thermochemistry of dissociative proton transfer reactions [Eq. (5)].

M	ΔH_{298}° (kJ/mol)	ΔS_{298}° (J/mol K)	ΔG_{298}° (kJ/mol)	ΔG_{350}° (kJ/mol)
CH ₄	49.1 ± 17.6	143.1 ± 2.0	6.5 ± 17.7	-1.0 ± 17.7
Cl	17.7 ± 15.8	153.1 ± 2.2	-27.9 ± 15.8	-35.9 ± 15.8
Br	56.9 ± 15.8	150.9 ± 2.2	11.9 ± 15.8	4.0 ± 15.8

QCISD(T)/6-311G**//MP2=full/6-31G* level is 187 kJ/mol (vibrational zero-point energy neglected). Hence, the measured thresholds and resulting $\Delta_f H_0^\circ$ values are too high. Direct ionization of SF_5 would also be prone to error, since the adiabatic ionization energy is so much lower (1.76 eV) than the vertical ionization energy (Table IX). Note that the thermochemical values in Table VII imply $\text{AE}(\text{SF}_5^+/\text{SF}_6) = 14.30 \pm 0.16$ eV, much lower than the value of 15.1 eV adopted in the JANAF tables but consistent with a recent limit $\text{AE}(\text{SF}_5^+/\text{SF}_6) > 14.1 \pm 0.3$ eV.⁵¹

In the ion beam experiment, $\Delta_f H_0^\circ(\text{SF}_5^+)$ is derived from the sum of the five successive bond strengths.⁷ Since each bond energy measurement is subject to uncertainty, the $\Delta_f H_0^\circ$ value for SF_5^+ is the least reliable in the study. Individual bond energies from the ion beam experiment and from the present calculations are compared below (Sec. IV I).

The other experimental values for $\Delta_f H_0^\circ(\text{SF}_5^+)$ listed in Table XII are from thermal ion chemistry experiments. Reactions between proton donors and SF_6 were observed to proceed rapidly at ambient temperature [Eq. (5), M=Br,⁵² Cl,⁵³ and CH₄ (Ref. 54)]. Since



these dissociative proton transfer reactions are spontaneous, they were presumed to be exothermic, as is typically assumed in the ion chemistry literature. However, these reactions are atypical. Since there are two reactants but *three* products, there is a large, positive entropy change for the reaction. Hence a negative enthalpy change is not assured. The enthalpy, entropy, and Gibbs' free energy changes for these three reactions are collected in Table XIV. $S_{298}^\circ(\text{SF}_5^+)$ and $S_{298}^\circ(\text{SF}_6)$ are from Table V and $\Delta_f H_{298}^\circ(\text{SF}_5^+)$ from Table VII. Other quantities are $\Delta_f H_{298}^\circ(\text{SF}_6) = -1221.7 \pm 0.3$ kJ/mol,²⁶ $\Delta_f H_{298}^\circ(\text{CH}_5^+) = 910$ kJ/mol (Ref. 55) (est. ± 8), $S_{298}^\circ(\text{CH}_5^+) = 224$ J/mol K (Ref. 56) (est. ± 0.5), $\Delta_f H_{298}^\circ(\text{HCl}^+) = 1137.6$ kJ/mol (Ref. 20) (est. ± 1), and $\Delta_f H_{298}^\circ(\text{HBr}^+) = 1089$ kJ/mol (Ref. 20) (est. ± 1). Entropies for HCl^+ (193 J/mol K) and HBr^+ (205 J/mol K) are calculated (est. ± 1 J/mol K) using a harmonic model (spin-orbit splitting ignored) and spectroscopic data from experiment.⁵⁷ The remaining data are from the JANAF tables;⁸ $\Delta_f H_{298}^\circ(\text{HF}) = -272.5 \pm 0.8$ kJ/mol, $S_{298}^\circ(\text{HF}) = 173.78 \pm 0.03$ J/mol K, $\Delta_f H_{298}^\circ(\text{CH}_4) = -74.87 \pm 0.34$ kJ/mol, $S_{298}^\circ(\text{CH}_4) = 186.25 \pm 0.04$ J/mol K, $\Delta_f H_{298}^\circ(\text{Cl}) = 121.302 \pm 0.008$ kJ/mol, $S_{298}^\circ(\text{Cl}) = 165.189 \pm 0.004$ J/mol K, $\Delta_f H_{298}^\circ(\text{Br}) = 111.86 \pm 0.06$ kJ/mol, and $S_{298}^\circ(\text{Br}) = 175.017 \pm 0.003$ J/mol K.

The ΔG_{298}° values in Table XIV show that the thermochemical values from the present work are compatible with the spontaneity of reaction (5). The value for M=Br of

TABLE XV. Comparison of present work with experiment; ionic sulfur fluoride bond energies $D_0^\circ(\text{SF}_n^+-\text{F})$ (kJ/mol). Uncertainties in values from the present work are 2σ .

Molecule	Present work	Experiment ^a
SF ⁺	367±8	344± 5
SF ₂ ⁺	372±6	402±10
SF ₃ ⁺	400±6	438± 8
SF ₄ ⁺	56±6	35± 5
SF ₅ ⁺	371±6	444±10

^aReference 7.

$\Delta_f H_0^\circ = 12 \pm 16$ kJ/mol suggests that the present value for $\Delta_f H_0^\circ(\text{SF}_5^+)$ may be a bit high. However, temperature has a strong effect on these entropy-driven reactions, as shown in the last column of Table XIV. Since minor errors in temperature can also explain much of the small discrepancy with the calculated thermochemistry, no revisions of the thermochemistry seem warranted.

In a very recent, clever experiment, complications due to entropy are avoided by conducting ion chemistry at 5 K.^{58,59} Proton transfer reactions of SF₆ were studied with a series of protonated bases. Assuming, as usual, that there is no barrier to proton transfer, the proton affinity was determined to be 577.0±8.4 kJ/mol.⁵⁸ When the proton transfer exothermicity reaches 88.7 kJ/mol, SF₅⁺ is produced in addition to SF₆H⁺.⁵⁸ This implies $\Delta_f H_0^\circ(\text{SF}_5^+) \leq 104.6 \pm 8.4$ kJ/mol,⁵⁹ with equality in the case of zero activation energy for the loss of HF from SF₆H⁺. This most recent value for $\Delta_f H_0^\circ(\text{SF}_5^+)$ is thus in good agreement with the present value of 95±16 kJ/mol.

I. Ionic bond dissociation energies $D(\text{SF}_n^+-\text{F})$

Bond strengths in the ions SF_n⁺ from the present calculations and from ion beam experiments⁷ are compared in Table XV. Agreement is fairly poor. The discrepancy for $D_0^\circ(\text{SF}_4^+-\text{F})$ is the largest at 73 kJ/mol. In the experiment, reaction cross sections are measured as a function of kinetic energy. Bond strengths are derived by fitting an empirical function to the data. The thermal (300 K) vibrational energy affects the resulting bond strength. Using frequency values from Table II instead of the estimates adopted in Ref. 7 changes the derived bond energies insignificantly, by +0.08, +0.26, -0.23, +1.20, and +0.15 kJ/mol for SF⁺ to SF₅⁺, respectively.

There is the possibility of kinetic shifts in the threshold experiment. To estimate whether this might be a problem, the energies of the ions SF_n⁺ ($n=1-4$) were calculated at the geometries of SF_{n+1}⁺ (with an appropriate fluorine atom deleted). At the QCISD(T)/6-311G**//MP2=full/6-31G* level, the relaxation energies of the SF_n⁺ fragments are then 0.0, 0.7, 7.8, and 45.1 kJ/mol for SF⁺ to SF₄⁺, respectively. If kinetic shifts are a problem, the effect will be most severe for the SF₅⁺→SF₄⁺+F fragmentation. Some of the discrepancy for SF₅⁺ in Table XV could be explained thus. However, this consideration does not explain the difference quantitatively, and can not explain the discrepancies for the other ions in Table XV. There is no satisfying explanation for the disagreement at this time.

J. Implications for S₂F₁₀ thermochemistry

As recently discussed,⁴ there are two experimental estimates for $\Delta_f H_{298}^\circ(\text{S}_2\text{F}_{10})$. A value of -2067±4 kJ/mol has been derived from a putative equilibrium between S₂F₁₀ and SF₆+SF₄.⁶⁰ Available rate data have been reanalyzed to yield a value of -2013±25 kJ/mol,⁶¹ markedly higher. Since both values depend upon the thermochemistry of the mono-sulfur fluorides, they are affected by the present revisions in that thermochemistry. In particular, the present values for $\Delta_f H_{298}^\circ$ differ from those used in Refs. 60 and 61 by +7, +61, and -13 kJ/mol for SF₄, SF₅, and SF₆, respectively. Updated analyses would therefore yield $\Delta_f H_{298}^\circ(\text{S}_2\text{F}_{10}) \approx -2073$ kJ/mol (equilibrium method) and $\Delta_f H_{298}^\circ(\text{S}_2\text{F}_{10}) \approx -1891$ kJ/mol (kinetics method). These wildly different values imply S-S bond strengths $D_{298}^\circ(\text{F}_5\text{S}-\text{SF}_5)$ of 371 and 181 kJ/mol, respectively. More work is sorely needed.

V. CONCLUSIONS

A. Thermochemistry

The thermochemistry of the sulfur fluorides SF_n ($n=1-5$) and their positive ions SF_n⁺ ($n=1-5$) has been revised based upon empirically-corrected *ab initio* calculations. The present values (Table VII) are recommended for enthalpies of formation of all these molecules. Values for SF₃, SF₅, and their cations are markedly different from previous accepted values. For standard entropies S_{298}° and integrated heat capacities $H^\circ(298.15) - H^\circ(0)$ (Table XI), the present values are recommended for all species except SF and SF₂, for which the JANAF (Ref. 8) values are recommended. Adiabatic ionization energies from this study are in agreement with prior values.

B. Theoretical models

For the sulfur fluorides, thermochemistry from G2 calculations is less accurate than thermochemistry from less expensive G2(MP2) calculations. G2(MP2) calculations are exceptionally accurate for these compounds. Entropy calculations do not require explicit consideration of low-frequency motions for any of the molecules in this study.

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