A Combined Experimental and Theoretical Study of Sulfur Oxyfluoride Anion and Neutral Thermochemistry and Reactivity[†]

Susan T. Arnold,* Thomas M. Miller, and A. A. Viggiano

Air Force Research Laboratory, Space Vehicles Directorate, 29 Randolph Road,
Hanscom Air Force Base, Massachusetts 01731

Received: February 27, 2002; In Final Form: April 18, 2002

The structure, thermochemistry, and reactivity of numerous sulfur oxyfluorides have been examined in a combined theoretical and experimental study. Calculations were carried out for $SOF_{n=0-5}$, $SO_2F_{n=0-3}$, $SO_3F_{n=0-1}$, and their corresponding anions using the Gaussian-2 procedure. Structural parameters, standard entropies, and integrated heat capacities were calculated at the MP2(full)/6-31G(d) level of theory. Electron affinities, vertical detachment energies, fluoride affinities, neutral bond dissociation energies, and neutral and anion heats of formation were derived from the G2 total energies (0 K) and enthalpies (298 K). This comprehensive dataset of thermochemical properties for both neutrals and anions is compared to available experimental results and to previous theoretical treatments of individual S/O/F compounds. A number of significant discrepancies are noted. Using a selected ion flow tube, a series of laboratory measurements were made to test the theoretical results and to examine $SO_mF_n^-$ reaction kinetics, including oxidation reactions. Rate constants and product ion distributions at 298 K are reported for over 60 reactions, and reactivity trends are discussed.

1. Introduction

Sulfur hexafluoride, SF_6, is an efficient electron scavenger and is commonly used to minimize dielectric breakdown in transformers and other electrical devices. The compound is also used as a source of fluoride in plasma etching processes.[1] Because ionization of SF_6 in discharges necessarily involves interactions of the primary ions that are formed from electron impact processes with any impurities that may be present, such as trace oxygen or water vapor, a complex array of ion and neutral processes can occur in such discharges. Examples of major long-lived neutral byproducts that result from the decomposition of SF_6 in the presence of O_2 and H_2O include SOF_2, SOF_4, SO_2F_2, SO_2, and HF, while examples of anions observed in SF_6/H_2O negative corona include SOF_4^-, SOF_5^-, SO_2F^-, and $SO_2F_2^-$.[2−6] Thus, modeling the plasma chemistry of SF_6 discharges requires fundamental knowledge not only of the sulfur fluoride breakdown products but also knowledge of the oxidation species and processes. Although a few sulfur oxyfluoride species have been the subject of detailed experimental or theoretical studies, only a limited amount of thermochemical and reactivity data are available for most S/O/F compounds.

The structure, thermochemistry, and reactivity of numerous sulfur oxyfluoride neutral and anionic species are examined here in a combined theoretical and experimental study. Calculations have been carried out using the Gaussian-2 (G2) procedure of the G98W program system. Structural parameters, standard entropies, integrated heat capacities, electron affinities, vertical detachment energies, fluoride affinities, neutral bond dissociation energies, and enthalpies of formation are reported here for $SOF_{n=0-5}$, $SO_2F_{n=0-3}$, $SO_3F_{n=0-1}$ and their corresponding anions. The present results are compared to the limited experimental data that are available for S/O/F compounds and to previous theoretical treatments. A series of laboratory measurements were made to test the theoretical results and to examine $SO_yF_x^-$ reaction kinetics. Rate constants and product ion distributions at 298 K are reported for over 60 reactions, and reactivity trends are discussed.

2. Computational Details

Calculations were carried out using the G2 procedure of the G98W program system.[7] This method givens an approximation to a frozen-core, quadratic configuration interaction calculation [QCISD(T)/6-311+G(3df,2p)] for geometries optimized at the MP2(full)/6-31G(d) level of theory. The base energy is calculated at the MP4/6-311G(d,p) level, which denotes fourth-order Møller−Plesset perturbation theory carried out with a valence triple-split basis set augmented with *d*-polarization functions on non-hydrogen atoms, and additional p-polarization on hydrogen atoms, and diffuse functions on non-hydrogen atoms. An isogyric correction is applied that is based on the number of α and β electrons. Finally, in the G2 method, zero-point energy (ZPE) and thermal energy corrections are applied based on harmonic frequencies calculated at the Hartree−Fock level [HF/6-31G(d)//HF/6-31G(d)] and scaled by an empirical factor of 0.8929. The frequency calculations also provide a check against saddle point geometries that are not true minima and yield negative force constants. The stability of the wave functions for the molecules studied in this work was confirmed at the HF level. That is, the molecular orbitals were varied to be certain that the solution to the SCF equations (the wave function) was of lowest energy. Molecular symmetries were enforced in the calculations, primarily so the rotational symmetry number would be correct in the entropy and free energy computations.

Electron affinities (EAs) were determined as the difference in energy between the neutral molecule and the molecular anion with both species in their ground electronic, vibrational, and rotational states. Vertical detachment energies (VDE) were

---

[†] Part of the special issue "Jack Beauchamp Festschrift".

* To whom correspondence should be addressed.

10.1021/jp020557w CCC: $22.00

calculated for several anionic species as the minimum energy required to eject the electron from the ground-state anion without allowing a change to occur in the equilibrium geometry. Fluoride affinities (FA) were determined as the difference in enthalpy between the molecular anion, XF^-, and the sum for F^- and X. Homolytic bond dissociation energies (D°_{298}) were determined as the difference in enthalpy between the molecular species and the sum of the fragment species. Enthalpies of formation at 0 K for neutral molecules were calculated from G2 atomization energies and the following experimental enthalpies of formation for the atoms:[8] $\Delta_f H^\circ_0(S) = 65.66$ kcal mol^{-1}, $\Delta_f H^\circ_0(O) = 58.99$ kcal mol^{-1}, and $\Delta_f H^\circ_0(F) = 18.47$ kcal mol^{-1}. As described in the Results section, an empirical correction was then applied based on the well-known enthalpies of formation for SO, SO_2, SO_3, and SF_6. Thermal corrections to 298.15 K were made using the calculated molecular integrated heat capacities and the following recommended atomic values:[8] 1.05, 1.04, and 1.05 kcal mol^{-1} for S,O, and F, respectively. Enthalpies of formation for the ions at 0 K were derived from the neutral molecules 0 K heat of formation and the calculated EA. For ion chemistry at 298 K, the ion convention was adopted.[9] The symbol $\Delta_f H_{298}$ is used to denote 298.15 K heats of formation for the ions, while $\Delta_f H^\circ_{298}$ is used to denote the standard enthalpy of formation at 298.15 K for the neutral species. The conventions are related as follows: $\Delta_f H^\circ_{298}(X^+) = \Delta_f H_{298}(X^+) + 1.48$ kcal mol^{-1}. For comparison purposes, standard enthalpies of formation for SOF_4 and SOF_5 were also determined using the isodesmic reaction method, combining experimental 298 K heats of formation with calculated G2 reaction enthalpies for the following reactions

$$SOF_5 + FO \rightarrow SF_6 + O_2 \qquad (1)$$

$$2SOF_4 + CF_4 \rightarrow 2SF_6 + CO_2 \qquad (2)$$

The expected uncertainty in G2 calculations of the EA, FA, and D° is $\pm$ 2 kcal mol^{-1} (0.1 eV).[10] The uncertainty in the reported enthalpies of formation is slightly higher; for the neutral species, the uncertainty is $\pm$ 3 kcal mol^{-1}, while the uncertainty in the anion enthalpies of formation, which includes the uncertainty in the associated EA calculation, is $\pm$ 4 kcal mol^{-1}.

3. Experimental Section

The reactivity of sulfur oxyfluoride anions and neutrals was studied using the Air Force Research Laboratory's Selected Ion Flow Tube. This instrument has been described previously in detail,[11] and only a brief description of the method and details pertinent to the present study are given here. Reactant ions were produced in a moderate pressure ion source (0.1−1 Torr) by electron impact on a precursor compound. More details on ion production are given below. The reactant ion of interest was mass selected in a quadrupole mass filter and injected into the flow tube through a Venturi inlet into a fast flow (~100 m s^{-1}) of He buffer gas (He, 99.997%). The flow tube was maintained at 0.4−0.5 Torr. With the exception of ozone, neutral reactant gases were obtained commercially and used without further purification. A 5% O_3 in O_2 mixture was generated using a commercial ozonator, with the O_3 concentration being determined via optical absorption at 248 nm. Details of the ozone production and measurement have been described previously.[12] The reactant was introduced downstream through an inlet entering the flow tube perpendicular to the flow and terminating at the radial center of the tube. The reaction time was determined from previous time-of-flight measurements. A small fraction of the gas in the tube flowed through a sampling orifice, and the reactant and product ions in this flow were mass analyzed in a second quadrupole mass filter and detected by a particle multiplier. Rate constants were extracted from least-squares fits of the plots of the logarithm of the reactant ion signal versus the concentration of the reactant neutral. The accuracy of the measured overall rate constants is ± 25%, while the relative accuracy is ±15%.[11]

Product branching fractions were determined by recording the product ion count rates as a function of the reactant neutral flow rate. To account for the effects of secondary reactions between the product ions and the reactant neutral, the reported branching fractions were determined by extrapolating the measured values to a neutral reactant flow rate of zero. Uncertainties in the product distributions are 5%age points.

A variety of chemical reactions were used to produce reactant ions in the high-pressure electron impact ion source. The O^- and O_2^- reactants were formed from O_2; SO_2^- from SO_2; and SF_6^-, SF_5^-, and F^- from SF_6 source gases, respectively. The SOF_5^- reactant ion was produced from the effluents of a microwave discharge of O_2 and 1% SF_6, presumably via the rapid reaction between SF_6^- and SOF_4.[13] The SOF_4^- reactant ion was produced from a mixture of H_2O and 1% SF_6 in He by the cluster-mediated reaction of SF_6^- and H_2O.[14] Because the $SF_6^-(H_2O)$ cluster bond is relatively weak,[15] production of SOF_4^- required the source to be cooled to 262 K. Without cooling, SOF_4^- was observed for only several minutes after the filament was initially started. Injecting SOF_4^- into the flow tube at high energy resulted in SOF_3^- being formed by collisional breakup: this produced an approximately 90% pure signal of SOF_3^-. The SO_2F^- and $SO_2F_2^-$ reactant ions were made from SO_2 and 1% SF_6 in He via the well-known reaction of SF_6^- with SO_2.[16−19] To produce $SO_2F_2^-$, only a trace of SO_2 was present in the ion source, limiting the known secondary chemistry. The SO_3F^- reactant ion was made from SOF_2 that contained an SO_2 impurity; however, the chemistry leading to the formation of this ion is unclear. Repeated attempts to produce $SO_2F_3^-$, SOF_2^-, and SOF^- in the electron impact ion source were unsuccessful; however, the SOF_2^- ion was observed in the flow tube as a product of the reaction between O_2^- and SOF_2, and the $SO_2F_3^-$ ion was observed as a product of the reaction between SOF_4^- and O_3.

4. Results

The equilibrium structures for SOF, SOF_2, SOF_3, SOF_4, SOF_5, SO_2F, SO_2F_2, SO_2F_3, SO_3F, and their corresponding anions, calculated at the MP2(full)/6-31G(d) level of theory, are shown in Figures 1 and 2. At this level of theory, the S−F bonds in neutral sulfur oxyfluoride molecules are generally 1.60 Å, lengthening 6−12% upon electron attachment. Particularly long S−F bonds are observed in SO_2F^-, $SO_2F_2^-$, and SOF_3^-. Except as noted below, the neutral molecule S−O bond lengths are 1.44 Å, characteristic of S═O double bonds, with the bonds lengthening slightly to 1.47 Å upon electron attachment. As we have previously reported, the SO_3F, SO_2F_3, and SOF_5 neutral molecules each contain one significantly longer S−O bond, ~1.61 Å, which shortens to the typical 1.47 Å S−O bond length upon electron attachment as the additional electron is accommodated predominately in an S−O bonding orbital.[20] In several cases, attachment of the electron results in a large structural change, e.g., SOF_2/SOF_2^- and $SO_2F_2/SO_2F_2^-$.

The structures of several sulfur oxyfluoride species have been reported previously, and those shown in Figures 1 and 2 are in good agreement with the earlier studies. The structures of SOF_2,[21] SO_2F_2,[22] and SOF_4,[23] have been determined by either

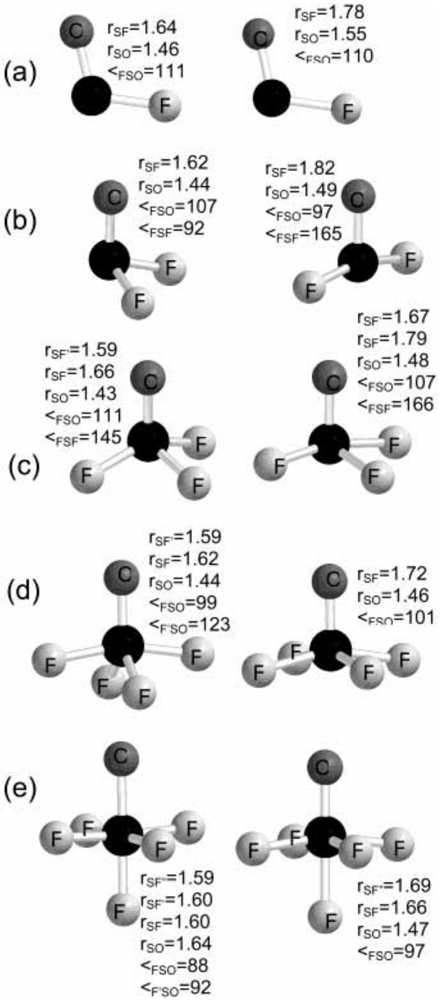

Figure 1. Equilibrium structures of (a) SOF, SOF^-, (b) SOF_2, SOF_2^-, (c) SOF_3, SOF_3^-, (d) SOF_4, SOF_4^-, and (e) SOF_5, SOF_5^- calculated at the MP2(full)/6-31G(d) level of theory.

microwave or electron diffraction spectroscopy, and the calculated bond lengths are within 2% of the experimental values. A difference of 4% is noted, however, between the calculated OSF bond angles within SOF_4 and those determined experimentally. Good agreement is also observed between the present results and previously reported calculated structures for SOF, SOF_3^-, SOF_4^-, SO_2F, and SO_2F^-.[24−29] Comparing various theoretical treatments of sulfur oxyfluoride species to available experimental data demonstrates that the S−F bond length is more sensitive than either the S−O bond or the bond angles to the theoretical method and the size of the chosen basis set.

G2 total energies (0 K), enthalpies (298 K), and free energies (298 K) for the species shown in Figures 1 and 2 are given in Table 1. Also shown in Table 1 are the G2 results for several associated molecules that were used to derive thermochemical properties. The EA, FA, D°_{298}[S−F], and D°_{298}[S−O] were calculated as described above and are presented in Table 2 together with previously reported experimental or calculated values. Unpublished G2 enthalpies (298 K) for $SF_{n=1-5}$ were used to calculate D°_{298}[S−O] for the series of SOF_x compounds.[30] With the exception of SO_2F_3, all neutral species shown in Figures 1 and 2 are stable relative to dissociation. Although a minimum energy structure was obtained for SO_2F_3, the compound is metastable with respect to dissociation into SO_2F_2 and F.

Calculated integrated heat capacities and standard entropies are reported in Table 3, together with anion and neutral

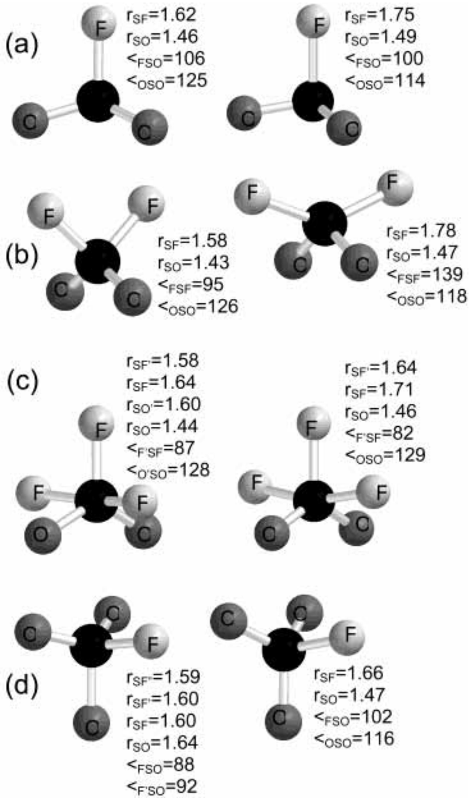

Figure 2. Equilibrium structures of (a) SO_2F, SO_2F^-, (b) SO_2F_2, $SO_2F_2^-$, (c) SO_2F_3, $SO_2F_3^-$, and (d) SO_3F, SO_3F^- calculated at the MP2-(full)/6-31G(d) level of theory.

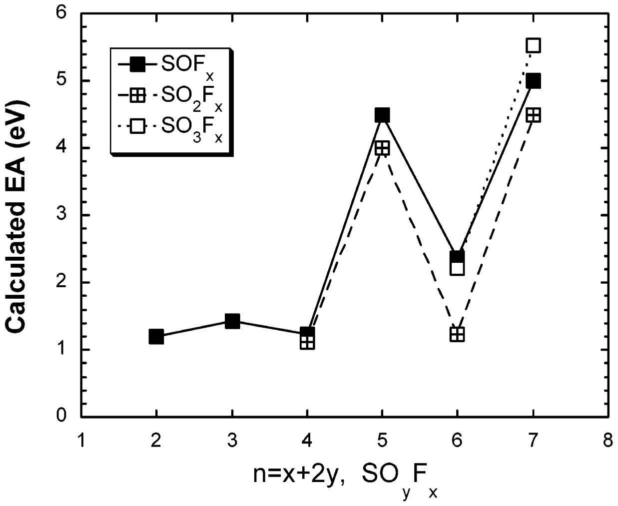

Figure 3. EAs for the series of sulfur oxide and sulfur oxyfluoride species plotted as a function of the effective sulfur coordination number *n*, where *n* represents twice the number of SO bonds plus the number of SF bonds in the molecule.

enthalpies of formation at 0 and 298 K. While G2 atomization energies are generally reported to be accurate to within ∼2.4 kcal mol^{-1}, the G2 atomization energy for SO_2 is known to be in error by 5 kcal mol^{-1}, making it the worst outlier among the original G2 set of molecules.[31] Because the enthalpies of formation calculated in this study are derived from atomization energies, an empirical correction to the G2 results seems warranted. However, because there are few solid experimental values for S/O/F enthalpies of formation, the final results shown in Table 3, denoted as G2*, were obtained by applying two correction factors to the raw G2 results, one based on the number of O atoms in the molecule and one based on the number of F

TABLE 1: G2 Total Energies (0 K), Enthalpies (298 K), and Free Energies (298 K) in Hartree

species	energy	enthalpy	free energy
F	−99.63281	−99.63045	−99.64763
O	−74.98203	−74.97967	−74.99698
SO	−472.82948	−472.82616	−472.85132
SOF	−572.59773	−572.59353	−572.62368
SOF_2	−672.37494	−672.37013	−672.40180
SOF_3	−772.03850	−772.03260	−772.06762
SOF_4	−871.81065	−871.80453	−871.83917
SOF_5	−971.48339	−971.47666	−971.51319
SO_2	−548.01574	−548.01173	−548.03985
SO_2F	−647.71095	−647.70624	−647.73828
SO_2F_2	−747.50980	−747.50456	−747.53691
SO_2F_3	−847.13155	−847.12537	−847.16127
SO_3	−623.12532	−623.12086	−623.14996
SO_3F	−722.81867	−722.81329	−722.84714
F^-	−99.76060	−99.75824	−99.77476
SO^-	−472.87359	−472.87015	−472.89527
SOF^-	−572.65041	−572.64604	−572.67597
SOF_2^-	−672.42029	−672.41469	−672.44799
SOF_3^-	−772.20356	−772.19751	−772.23216
SOF_4^-	−871.89733	−871.89032	−871.92655
SOF_5^-	−971.67235	−971.66554	−971.70091
SO_2^-	−548.05817	−548.05408	−548.08316
SO_2F^-	−647.85796	−647.85317	−647.88473
$SO_2F_2^-$	−747.55486	−747.54884	−747.58345
$SO_2F_3^-$	−847.33376	−847.32760	−847.36215
SO_3-	−623.20651	−623.20198	−623.23256
SO_3F^-	−723.02197	−723.01684	−723.04855

atoms. Comparing the raw G2 derived enthalpies of formation for SO, SO_2, and SO_3 at 0 K to the well-known experimental values demonstrates a discrepancy that is linear with respect to the number of O atoms n in the molecule [$-2.05(n) -0.637$, in units of kcal mol^{-1}, $r = 0.99$]. This "O atom" correction factor was applied to the raw G2 values for S/O/F neutrals at 0 K. An additional (and smaller) "F atom" correction factor was also applied to account for the fact that the G2 method does not accurately calculate enthalpies of formation for sulfur fluoride compounds. Irikura[32] previously demonstrated that the G2(MP2) method yielded results for $SF_{n=1-6}$ that were within 1 kcal mol^{-1} of the literature values, while the G2 results were in error by as much as 4 kcal mol^{-1}. Because the difference between the G2 and the G2(MP2) results, and thus the experimental results, was found to be linear with respect to the number of F atoms in the molecule n, Irikura applied a correction factor [$0.935(n) - 0.375$, in units of kcal mol^{-1}, $r = 0.99$] that essentially prorated the differences between the G2 and G2(MP2) results by the number of F atoms. This "F-atom" correction factor was also applied to the present S/O/F results. Standard temperature corrections were then made to obtain $\Delta_fH°$ at 298 K from the G2* results at 0 K.

Rate constants and product branching ratios for a large number of sulfur oxyfluoride anion and neutral reactions were measured in the laboratory at 298 K, and the results are presented in Table 4. Collisional rate constants were estimated by the method of Su and Chesnavich[33] using experimental values for the neutral reactant's dipole moment and polarizability where available. In the case of SOF_2, SO_2F_2, and PF_3, the polarizabilities were estimated to be 4.6, 5., and 4.5 Å^3, respectively, using the standard additivity methods of Miller.[34] Because many of the reactions reported in Table 4 were studied in part to support the present EA and FA calculations, by bracketing or by setting limits on EAs and FAs, the thermochemical implications of most reactions are indicated in the table. Data for several reactions reported in Table 4 were derived or inferred from secondary ion chemistry that occurred in the flow tube.

5. Discussion

A. Electron Affinities. The EAs of SO and SO_2, calculated at the G2 level, compare well with the experimental values determined by laser spectroscopy:[35,36] the calculated EAs for SO and SO_2 are only 75 and 43 meV larger than the experimental values, respectively. Such errors are within the reported accuracy of the G2 method. The EA of SO_3 has not been determined as precisely via experiment. A collisional ionization study by Rothe et al.[37] established a lower limit of EA(SO_3) ≥ 1.7 eV. Gleason[38] bracketed the EA of SO_3 between 1.86 and 2.32 eV using ion−molecule charge-transfer reactions and recommended a value of 1.9 ± 0.1 eV based upon additional bracketing via clustering reactions. A high-temperature equilibrium study by Rudnyi et al.[39] yielded a value for EA(SO_3) of 2.1 ± 0.2 eV. A recent photoelectron detachment study of SO_3^- did not yield a more precise value due to the fact that the origin was not directly observed in the spectrum.[40] A previous G2 calculation of the EA of SO_3 has been reported by McKee.[41] The previous G2 value of 2.15 eV differs from the present result by 60 meV, with the difference being attributed to McKee's use of the frozen core approximation in the post-HF calculations. Both G2 results are consistent with these experimental determinations, particularly the value derived from the high-temperature equilibrium study.

As we have reported previously, several sulfur oxyfluoride species were found to have exceptionally high EAs.[20] The EAs of SO_3F, SO_2F_3, and SOF_5 were calculated to be 5.53, 5.50, and 5.14 eV, respectively. Only one previous EA estimate exists for any of these three species. Viggiano et al.[42] experimentally bracketed the gas-phase acidity of FSO_3H and used this result to estimate EA(SO_3F) = 4.8 eV. However, our recent reexamination of the bond dissociation energy in FSO_3H suggests the experimental EA estimate should be revised upward to 5.2 eV.[20] The calculated EA(SO_3F) is in agreement with the revised experimental estimate.

In the present study, SOF_3 and SO_2F were also found to have relatively high EAs, ranging from 4 to 4.5 eV. The present results for EA(SO_2F) would seem to be of particular importance since SO_2F^- is a prevalent species in SF_6 plasma environments, yet the experimental value of 2.8 eV for EA(SO_2F) that is listed in the NIST Chemistry WebBook[43] is not considered reliable. In addition to the one value noted in the NIST WebBook, Sauers et al.[3] estimated the EA(SO_2F) to be ≥4.1 eV, based on relative cross section measurements for anion formation from SO_2F_2. Measurements with SOF_4 yielded a similar estimate for EA(SOF_3) ≥4.1 eV. The present results of 4.00 ± 0.1 eV and 4.50 ± 0.1 eV for the EA(SO_2F) and the EA(SOF_3), respectively, are generally consistent with the experimental estimates reported by Sauers et al. The charge exchange reactions conducted as part of this overall study indicate only that SO_2F and SOF_3 have EAs greater than 2.27 eV.

The remaining sulfur oxyfluoride neutrals included in this study (SOF, SOF_2, SOF_4, and SO_2F_2) have EAs ranging from 1.2 to 2.4 eV. The previously reported experimental estimate for EA(SO_2F_2) is an upper limit of 3.08 eV, based on the observation that SO_2F_2 does not undergo charge exchange with F_2^-.[43] The present results indicate EA(SO_2F_2) is 1.23 ± 0.10 eV, which is significantly less than the previously established upper limit. This lower value is supported by the charge exchange reactions of SO_2F_2 reported in Table 4: the reaction with O_2^- is rapid while the reaction with SO_2^- does not occur, suggesting 0.45 eV < EA(SO_2F_2) < 1.1 eV. (As discussed below, it is believed that the more exothermic charge exchange reactions between $SO_2F_2^-$ and O_3 and NO_2 have rate constants

TABLE 2: G2 Level Electron Affinities (EA) and Vertical Detachment Energies (VDE) in eV, Fluoride Affinities (FA), and Neutral Homolytic Bond Dissociation Energies (D°_{298}[S−F], and D°_{298}[S−O]) in kcal mol^{-1} (Present Results Compared to Previously Cited Values)

	EA		VDE	FA		D°_{298}[S−F]		D°_{298}[S−O]	
species	present work	expt	present work	present work	expt	present work	other theory or expt (*x*)	present work	other theory
SO	1.20	1.125[a]		38.7				121.7	
SOF	1.43			39.5		85.9	69.6[j] 88.4[l] 87.0[k] (*x*) ≤80.7[b]	124.9	126.9[k]
SOF_2	1.23		3.18	43.4	37.4[h]	91.7	(*x*) 87.5[m] 92.7[k]	127.1	129.3[k]
SOF_3	4.49	≥4.1[b]		62.4		20.1	52.3[j] 20.6[k]	92.2	94.6[k]
SOF_4	2.36			64.5	58.0[h]	88.8	95.6[j] 89.1[k] (*x*) ≤124.5[b]	86.5	87.2[k]
SOF_5	5.14		5.98			26.2	(*x*) 28.8[n] 26.3[k]	72.8	74.6[k]
SO_2	1.15	1.107[c]		52.2	43.8[h] 52.7[i]			129.2	
SO_2F	4.00	2.8[d] ≥4.1[b]	4.34	52.9		40.2	50.2[j] 40.2[k] 41.3[l]	83.5	84.6[k]
SO_2F_2	1.23	<3.08[d]		40.7	35.8[h]	105.3	100[o] 98.0[j] 105.9[k]	97.1	97.8[k]
SO_2F_3	5.50		6.29			−6.0	−16[k]	71.0	60.7[k]
SO_3	2.21	1.9[e] 2.1[f]		86.4	78.0[h]			81.2	
SO_3F	5.53	5.2[g]	5.53			38.9	36.8[k]	79.9	78.6[k]

[a] Polak et al.[35] [b] Sauers et al. [3] [c] Nimlos and Ellison.[36] [d] NIST Chemistry WebBook.[43] [e] Gleason.[38] [f] Rudnyi et al.[39] [g] Viggiano et al.,[42] Arnold et al.[20] [h] Larson and McMahon.[46] [i] Sunderlin.[47] [j] Herron.[57] [k] Irikura.[52] [l] Badenes et al.[29] [m] Kiang and Zare.[53] [n] Czarnowski and Schmacher.[54] [o] Benson.[56]

significantly below the collision rate constant due in part to spin considerations.) Additional charge exchange reactions shown in Table 4 crudely bracket EA(SOF_2) to be between 0.5 and 1.1 eV, which is consistent with the calculated result.

Calculated EAs for the series of sulfur oxide and sulfur oxyfluoride species are plotted in Figure 2 as a function of the effective sulfur coordination number, n, where n represents twice the number of S−O bonds plus the number of S−F bonds in the molecule. A general similarity is observed in the EAs among species with the same effective coordination number, and the odd−even oscillation mirrors that previously reported for EA(SF_n).[44] As was noted for EA(SF_n), neutral S/O/F species that form closed shell anions have large electron affinities, while closed shell neutrals have smaller EAs. Species with effective coordination numbers of 5 and 7 are found to have very high EAs.

Anion vertical detachment energies (VDE) were calculated for several species shown in Figures 1 and 2: anions whose corresponding neutrals have very high EAs (SO_3F, SO_2F_3, SOF_5), one anion whose neutral undergoes a large geometry change upon electron attachment (SOF_2), and one anion which has only minor structural differences compared to the neutral (SO_2F). As Christophorou[45] has noted previously, EA ≤ VDE with these values being equal only when the geometries of the anion and the corresponding neutral are nearly the same. The large difference between the EA and the VDE calculated for SOF_2/SOF_2^- is consistent with the anticipated large geometry change, while the similarity of the EA and the VDE for SO_2F/SO_2F^- is consistent with the minor structural changes that are anticipated upon electron attachment or detachment.

B. Fluoride Affinities. The experimental kinetic data for fluoride ion transfer reactions shown in Table 4 establish the relative FA ordering for most of the sulfur oxide and sulfur oxyfluoride species included in this study: FA(SOF) < FA(SOF_2) < FA(SO_2F) ≈ FA(SO_2) < FA (SOF_3) ≈ FA(SOF_4) < FA(SO_3). In addition, the data demonstrate that FA(SO_2F_2) < FA(SO_2) and FA(SO_2F_2) < FA(SF_4). This ordering is consistent with the calculated values shown in Table 2. Experimental FA values that have been reported for SOF_2, SOF_4, SO_2, SO_2F_2, and SO_3 are also shown in Table 2. Without exception, the calculated FAs presented here are 4−8 kcal mol^{-1} higher than the experimental values of Larson and McMahon.[46] Because such differences are outside the anticipated 2 kcal mol^{-1} accuracy of the G2 method, a complete basis set calculation for FA(SO_2) was carried out for comparison. The G2 method yields FA(SO_2) = 52.2 kcal mol^{-1}, while the complete basis set method (CBS-q) yields a value of 53.0 kcal mol^{-1}. A recent determination of FA(SO_2) by Sunderlin et al.[47] via collisional induced dissociation (CID) of SO_2F^- yielded a value of 52.7 kcal mol^{-1}. This new experimental result is more consistent with the current calculations than with the commonly used value of 43.8 kcal mol^{-1} reported by Larson and McMahon.

The fact that the present calculations and the recent CID determination yield FAs consistently higher than those of Larson and McMahon suggests the experimental FA ladder, which is constructed from several absolute and numerous relative measurements, may need to be reexamined and perhaps readjusted upward by several kcal mol^{-1}. The accuracy of the ladder's anchor values has been questioned previously,[48,49] and a reexamination of one anchor species, H_2O, indicated the FA is 4.1 kcal mol^{-1} larger than the original value on which the FA scale is currently anchored.[49] Recent fluoride affinity calculations by Bartmess[50] and by Christe et al.[51] also support readjusting the FA ladder upward.

C. Bond Dissociation Energies. The 298 K G2 homolytic bond dissociation energies, D°_{298}[S−F] and D°_{298}[S−O], re-

TABLE 3: Standard Entropies at 298.15 K (S°_{298}) in cal mol^{-1} K^{-1} and Integrated Heat Capacities $\int C_p\,dT \equiv (H^\circ_{298} - H^\circ_0)$ in kcal mol^{-1}, with Literature Values for These Properties Shown in Parentheses Where Available (Raw G2 and Corrected (G2*) Values for Enthalpies of Formation for Neutrals ($\Delta_f H^\circ$) and Ions ($\Delta_f H$) in kcal mol^{-1}, the Ion Convention Was Adopted for Anion Values above 0 K, and Present Results Are Compared to Previously Cited Values)

						previous $\Delta_f H^\circ_{298}$ values	
species	S°_{298}	$\int C_p\,dT$	raw G2 $\Delta_f H^\circ_{298}$	G2* $\Delta_f H^\circ_0$	G2* $\Delta_f H^\circ_{298}$	exptl[b]	theoret
SO	50.8 (53.0)[g]	2.08 (2.09)[g]	3.8	1.5	1.5	1.2	3.2[e]
SOF	63.5 (62)[h] (61)[i]	2.63	−63.2	−66.0	−66.5		−65.7[e] −69.9[f] −49.5[g] −63.3[i]
SOF$_2$	66.7 (66.7)[g] (67)[i]	3.02 (3.02)[g]	−136.0	−139.0	−140.2	−138.6	−139.4[e] −118.1[h] −127.6[i]
SOF$_3$	73.8 (72)[h] (72)[i]	3.70	−137.2	−140.8	−142.3		−141.1[e] −151.3[h] −185.2[i]
SOF$_4$	74.3 (74.7)[h] (75)[i]	3.84	−207.0	−210.7	−213.1 −212[a]		−211.5[e] −228.0[h] −235.7[i]
SOF$_5$	78.3 (70)[h]	4.23	−214.3	−218.2	−221.3 −220[a]		−218.9[e] −238.0[h]
SO$_2$	59.2 (59.3)[g]	2.51 (2.52)[g]	−65.9	−69.8	−70.4	−70.9	−69.6[e]
SO$_2$F	67.5 (65)[i]	2.95	−87.2	−91.4	−92.6		−90.9[e] −96.2[f] −102.3[h] −113.3[i]
SO$_2$F$_2$	68.1 (67.8)[g]	3.28 (3.23)[g]	−173.7	−178.0	−180.0	−181.3 −183.4[c]	−177.8[e]
SO$_2$F$_3$	75.6	3.87	−148.7	−153.6	−156.0		−142.4[e]
SO$_3$	64.8 (61.4)[g]	2.80 (2.80)[g]	−87.7	−92.9	−94.3	−94.6	−92.3[e]
SO$_3$F	71.3	3.38	−107.7	−113.4	−115.2		−110.2[e]
SO$^-$	52.9	2.16	−23.8	−26.	−26.1	−24.9 −26.5 −24.0	
SOF$^-$	63.0	2.74	−96.1	−99.0	−99.4		
SOF$_2^-$	71.5	3.51	−163.9	−167.5	−168.2		
SOF$_3^-$	73.0	3.79	−240.7	−244.4	−245.8	−216.1	
SOF$_4^-$	79.1	4.40	−260.9	−265.1	−267.0	≤−243.5	
SOF$_5^-$	77.3	4.28	−332.8	−336.8	−339.8		
SO$_2^-$	61.2	3.68	−92.5	−96.4	−97.0	−96.5	
SO$_2$F$^-$	66.5	3.00	−179.4	−183.7	−184.8	−183.1[d] −183.2 −174.2 −171.0 −122.2	
SO$_2$F$_2^-$	72.9	3.78	−201.4	−206.3	−207.8		
SO$_2$F$_3^-$	74.1	3.86	−275.6	−280.4	−282.9	−276.8 −306.9	
SO$_3^-$	66.6	2.84	−138.6	−143.9	−145.2	−138.4 −142.2 −133.8	
SO$_3$F$^-$	69.0	3.22	−235.5	−240.9	−242.9	−235.6 −232.0	

[a] Calculated from isodesmic reaction method as described in text. [b] All experimental numbers from *NIST WebBook*[43] except where noted. [c] Cartwright and Woolf.[64] [d] Sunderlin.[47] [e] Irikura.[52] [f] Badenes et al.[29] [g] JANAF.[59] [h] Herron.[57] [i] Dittmer and Niemann.[59]

ported in Table 2 for neutral sulfur oxyfluorides are in good agreement with the unpublished G2(MP2) results of Irikura,[52] with only the values for the metastable species SO$_2$F$_3$ differing by more than 3 kcal mol^{-1}. The present results for D°_{298}[S−F] of SOF and SO$_2$F are also in agreement with a recent theoretical study by Badenes et al.[29] Agreement among the recent calculations of D°_{298}[S−F] for SOF suggests the previous estimate included in the JANAF tables was significantly low. Experimental determinations have been reported for the D°_{298}[S−F] of SOF$_2$,[53] SOF$_5$,[54] and SO$_2$F$_2$.[55−57] The calculated values for SOF$_2$ and SOF$_5$ are within 2−4 kcal mol^{-1} of the experimental values, which is within the uncertainties of the combined methods, while there is a nearly 7 kcal mol^{-1} discrepancy noted with the experimental value for SO$_2$F$_2$. (Note, the experimental estimates of 98 and 100 kcal mol^{-1} for D°_{298}[S−F] of SO$_2$F$_2$ both result from a reanalysis of the original shock tube pyrolysis study of SO$_2$F$_2$ that initially yielded a value of ∼ 81 kcal mol^{-1}.[55]) Previous estimates[57] of D°_{298}[S−F] have been reported for several other species shown in Table 2 by extending the limited experimental data with methods similar to that of Benson. Although the initial estimates for some species are within 4 kcal mol^{-1} of the recently calculated values shown here, others differ by 10−30 kcal mol^{-1}. A particularly large difference of 32 kcal mol^{-1} is noted for the D°_{298}[S−F] of SOF$_3$. The present calculation suggests that SOF$_3$ has a small bond energy (weaker even than that of SOF$_5$). The derived bond

TABLE 4: Rate Constants k_2 and Product Distributions for Reactions of Sulfur Oxyfluoride Neutrals and Anions, as Measured at 298 K Using the Selected Ion Flow Tube[a]

reaction	k_2 (10^{-9} cm^3 s^{-1})	k_c (10^{-9} cm^3 s^{-1})	implications
$O_2^- + SOF_2 \rightarrow SOF_2^- + O_2$	1.5	2.0	EA(SOF_2) > 0.45 eV
$SOF_2^- + SOF_2 \rightarrow SOF_3^- + SOF$[b]	1.4	1.4	FA(SOF) < FA(SOF_2)
$Cl^- + SOF_2 \rightarrow$ n.r.	<0.01	1.9	EA(SOF_2) < 3.6 eV
$O^- + SOF_2 \rightarrow SO_2F^- + F$	2.6	3.0	
$SO_2F^- + SOF_2 \rightarrow$ n.r.	<0.01	1.4	FA(SOF_2) < FA(SO_2)
$SO_2^- + SOF_2 \rightarrow SO_2^- \cdot SOF_2$	0.0047	1.6	EA(SOF_2) < 1.1 eV
$SF_6^- + SOF_2 \rightarrow$ n.r.	<0.04	1.3	EA(SOF_2) < 1.1 eV
$SOF_3^- + SF_6 \rightarrow$ n.r.	<0.0005	0.77	EA(SOF_3) > 1.1 eV
$SOF_3^- + O_2 \rightarrow$ n.r.	<0.2	0.59	EA(SOF_3) > 0.45 eV
$SOF_3^- + CO_2 \rightarrow$ n.r.	<0.0008	0.74	FA(SOF_2) > FA(CO_2)
$SOF_3^- + PF_3 \rightarrow PF_4^- + SOF_2$	1.1	1.0	FA(SOF_2) < FA(PF_3)
$SOF_3^- + SO_2 \rightarrow SO_2F^- + SOF_2$	1.4	1.4	FA(SOF_2) < FA(SO_2)
$SOF_3^- + SiF_4 \rightarrow SiF_5^- + SOF_2$	0.82	0.85	FA(SOF_2) < FA(SiF_4)
$SOF_3^- + BF_3 \rightarrow BF_4^- + SOF_2$	0.69	0.66	FA(SOF_2) < FA(BF_3)
$SOF_3^- + O_3 \rightarrow$ n.r.	<0.01	0.88	EA(SOF_3) > 2.1 eV
$SOF_3^- + NO_2 \rightarrow$ n.r.	<0.002	0.79	EA(SOF_3) > 2.4 eV
$SOF_4^- + SF_6 \rightarrow$ n.r.	<0.002	0.73	EA(SOF_4) >1.1 eV
$SOF_4^- + O_2 \rightarrow$ n.r.	<0.0005	0.58	EA(SOF_4) > 0.45 eV
$SOF_4^- + H_2O \rightarrow$ n.r.	<0.02	2.2	FA(SOF_3) > FA(H_2O)
$SOF_4^- + N_2O \rightarrow$ n.r.	<0.0003	0.75	FA(SOF_3) > FA(N_2O)
$SOF_4^- + SOF_2 \rightarrow$ n.r.	<0.02	1.3	FA(SOF_3) > FA(SOF_2)
$SOF_4^- + PF_3 \rightarrow$ n.r.	<0.009	0.99	FA(SOF_3) > FA(PF_3)
$SOF_4^- + COF_2 \rightarrow$ n.r.	<0.001	0.90	FA(SOF_3) > FA(COF_2)
$SOF_4^- + SO_2 \rightarrow SO_2F_2^- + SOF_2$ (>85%) $SO_2F^- + SOF_3$ (<15%)	0.10	1.4	
$SOF_4^- + SiF_4 \rightarrow SiF_5^- + SOF_3$	0.49	0.82	FA(SOF_3) ~ FA(SiF_4)
$SOF_4^- + BF_3 \rightarrow BF_4^- + SOF_3$	0.65	0.64	FA(SOF_3) < FA(BF_3)
$SOF_4^- + O_3 \rightarrow SO_2F_3^- + FO_2$	0.050	0.85	
$SOF_4^- + NO_2 \rightarrow NO_2^- + SOF_4$	0.011	0.77	EA(SOF_4) ~ 2.3 eV
$SOF_5^- + O_2 \rightarrow$ n.r.	<0.0004	0.58	EA(SOF_5) > 0.45 eV
$SOF_5^- + SO_2 \rightarrow$ n.r.	<0.0007	1.4	FA(SOF_4) > FA(SO_2)
$SOF_5^- + SiF_4 \rightarrow SiF_5^- + SOF_4$	0.29	0.70	FA(SOF_4) ~ FA(SiF_4)
$SOF_5^- + WF_6 \rightarrow WF_7^- + SOF_4$	0.16	0.75	FA(SOF_4) < FA(WF_6)
$SOF_5^- + BF_3 \rightarrow BF_4^- + SOF_4$	0.51	0.63	FA(SOF_4) < FA(BF_3)
$SOF_5^- + O_3 \rightarrow$ n.r.	<0.01	0.84	EA(SOF_5) > 2.1 eV
$SOF_5^- + NO_2 \rightarrow$ n.r.	<0.001	0.76	EA(SOF_5) > 2.4 eV
$SO_2F^- + CO_2 \rightarrow$ n.r.	<0.001	0.74	FA(SO_2) > FA(CO_2)
$SO_2F^- + PF_3 \rightarrow$ n.r.	<0.02	1.2	FA(SO_2) > FA(PF_3)
$SO_2F^- + WF_6 \rightarrow WF_7^- + SO_2$	1.0	0.92	FA(SO_2) < FA(WF_6)
$SO_2F^- + O_2 \rightarrow$ n.r.	<0.003	0.61	EA(SO_2F) > 0.45 eV
$SO_2F^- + O_3 \rightarrow$ n.r.	<0.006	0.91	EA(SO_2F) > 2.1 eV
$SO_2F^- + NO_2 \rightarrow$ n.r.	<0.006	0.82	EA(SO_2F) > 2.4 eV
$SO_2F_2^- + O_2 \rightarrow$ n.r.	<0.004	0.60	EA(SO_2F_2) > 0.45 eV
$SO_2F_2^- + CO_2 \rightarrow$ n.r.	<0.001	0.72	FA(SO_2F) > FA(CO_2)
$SO_2F_2^- + SOF_2 \rightarrow$ n.r.	<0.04	1.4	FA(SO_2F)> FA(SOF_2)
$SO_2F_2^- + HCN \rightarrow SO_2FCN^- + HF$ (96%) $(SO_2F_2 \cdot HCN)^-$ (4%)	0.59	3.3	
$SO_2F_2^- + COF_2 \rightarrow$ n.r.	<0.01	0.90	FA(SO_2F) > FA(COF_2)
$SO_2F_2^- + SO_2 \rightarrow SO_2F^- + SO_2F$	0.39	1.5	FA(SO_2F) ~ FA(SO_2)
$SO_2F_2^- + SiF_4 \rightarrow SiF_5^- + SO_2F$	0.87	0.77	FA(SO_2F) < FA(SiF_4)
$SO_2F_2^- + O_3 \rightarrow O_3^- + SO_2F_2$ (70%) $SO_3F^- + FO_2$ (30%)	0.038	8.8	
$SO_2F_2^- + NO_2 \rightarrow NO_2^- + SO_2F_2$ (91%) $SO_3F^- + FNO$ (9%)	0.024	0.79	
$O_2^- + SO_2F_2 \rightarrow SO_2F_2^- + O_2$	1.1	1.6	EA(SO_2F_2) > 0.45 eV
$SF_6^- + SO_2F_2 \rightarrow$ n.r.	<0.01	0.99	FA(SO_2F_2) < FA(SF_5)
$SO_2^- + SO_2F_2 \rightarrow$ n.r.	<0.003	1.2	EA(SO_2F_2) < 1.1 eV
$O^- + SO_2F_2 \rightarrow SO_3F^- + F$	1.5	2.3	
$SF_5^- + SO_2F_2 \rightarrow$ n.r.	<0.002	1.0	FA(SO_2F_2) < FA(SF_4)
$F^- + SO_2F_2 \rightarrow$ n.r.	< 0.07	2.1	EA(SO_2F_2) < 3.4 eV
$SO_2F_2^- + SO_2F_2 \rightarrow$ n.r.	<0.01	1.1	FA(SO_2F_2) < FA(SO_2F)
$SO_3F^- + SO_2F_2 \rightarrow$ n.r.	<0.01	1.1	FA(SO_2F_2) < FA(SO_3)
$SO_3F^- + O_2 \rightarrow$ n.r.	< 0.1	0.60	EA(SO_3F) > 0.45 eV
$SO_3F^- + O_3 \rightarrow$ n.r.	<0.006	0.88	EA(SO_3F) > 2.1 eV
$SO_3F^- + WF_6 \rightarrow$ n.r.	<0.06	0.86	EA(SO_3F) > 3.4 eV FA(SO_3) > FA(WF_6)
$SO_3F^- + BF_3 \rightarrow SO_3F^- \cdot BF_3$	0.036	0.67	FA(SO_3) > FA(BF_3)

[a] "n.r." indicates no reaction products were observed, and an upper limit is given for the reaction rate constant. Previously reported results for sulfur oxyfluoride anions reacting with ozone are included for completeness.[62] Collisional rate constants k_c were estimated using the method of Su and Chesnavich.[33] Thermochemical implications of the measurements are noted. [b] SOF_2^- produced in flow tube from reaction of O_2^- with SOF_2.

dissociation energies presented in Table 2 also indicate, perhaps surprisingly, that loss of O and loss of F are competitive dissociation pathways for both SOF_4 and SO_2F_2. It is our opinion that the bond energies calculated at a high level of theory should be considered more reliable than the early semiemperical estimates.

D. Standard Entropies and Enthalpies of Formation. Previously cited values for the integrated heat capacity and/or standard entropy are only available for a limited number of compounds included in the present study. Although no corrections have been applied to the MP2(full)/6-31G(d) results, there is generally good agreement between the present work and the results reported in the JANAF tables.[58] Perhaps the one exception is the standard entropy of SO_3, where the difference is 3.4 cal mol^{-1} K^{-1}. The previous estimate by Herron[57] for the standard entropy of SOF_5, which does not appear in the JANAF Tables, appears to be considerably low. The results of Dittmer et al.[59] shown in Table 3 are estimates based on experimental tungsten transport rates obtained in a gas-flow containing SO_2F_2.

The uncorrected G2 values shown in Table 3 for sulfur oxide and sulfur oxyfluoride $\Delta_f H^\circ_{298}$ are consistently less negative than well-established experimental numbers, differing in some cases by more than 10 kcal mol^{-1}. The uncorrected G2 values are also 4−5 kcal mol^{-1} less negative than the values derived by Irikura[52] from G2(MP2) atomization energies; an even larger difference is noted for SO_2F_3. When the correction procedure described in the Results section is applied to the G2 results, the modified values, denoted as G2*, are in closer agreement with both the experimental and the G2(MP2) results. In general, the G2* and G2(MP2) values agree within 2 kcal mol^{-1} with only the values for SO_2F_3 and SO_3F differing by more than that amount (13.6 and 5 kcal mol^{-1}, respectively). Differences of this magnitude were noted earlier for SO_2F_3 and likely result from the metastable nature of the molecule.

For several neutral species shown in Table 3, additional calculations of $\Delta_f H^\circ_{298}$ have been reported. (To our knowledge, there have been no previous calculations of sulfur oxyfluoride anion enthalpies of formation.) The earliest estimates of $\Delta_f H^\circ_{298}$ for SOF_2, SOF_3, SOF_4, SOF_5, and SO_2F that were reported by Dittmer et al.[60] and by Herron[57] differ from the recent G2* and G2(MP2) treatments by 9−44 kcal mol^{-1}. It is our opinion that the G2* and G2(MP2) results shown here are more accurate. Note, we have classified the commonly used "experimental" value of $\Delta_f H^\circ_{298}$ for SOF_4 as a theoretical estimate, since it is derived from a combination of SO_2F_2 measurements and an estimation method.[59] The G2* and G2(MP2) results for SOF_4 support the previous speculation by Christe et al.[61] that the commonly used value for $\Delta_f H^\circ_{298}(SOF_4)$ is likely in error. For SOF and SO_2F, Badenes et al.[29] have derived $\Delta_f H^\circ_{298}$ using isodesmic reactions and the CBS-q method. The G2* results are 3.5 kcal mol^{-1} less negative than those of Badenes et al. for both SOF and SO_2F. In the case of SOF, the combination of G2*, G2(MP2), and CBS-q studies all indicate that $\Delta_f H^\circ_{298}$ is approximately −68 kcal mol^{-1}, which differs significantly from the value of −49.5 reported in the JANAF Tables.[59]

Comparing the G2* derived $\Delta_f H^\circ_{298}$ values to experimental values reported previously in the literature, demonstrates that the agreement is within 2 kcal mol^{-1} for SO, SOF_2, SO_2, SO_2F_2, SO_3, SO^-, SO_2^-, and SO_2F^-. However, differences on the order of 3−11 kcal mol^{-1} are observed for $SO_2F_3^-$, SO_3^-, and SO_3F^-, and a very large discrepancy of 30 kcal mol^{-1} is observed for SOF_3^-. The large discrepancies between the calculated and experimental values are far outside the combined uncertainties of the two methods. However, it appears the experimental value for SOF_3^- that is reported in the NIST WebBook, which is derived from an experimental determination of D[$SOF_2\cdots F^-$] (via fluoride exchange equilibria measurements) and the known values of Δ_fH(F^-) and Δ_fH(SOF_2), needs to be revised. That determination utilized an early estimate for Δ_fH(SOF_2) rather than the more reliable experimental value. Using the experimental values for both D[$SOF_2\cdots F^-$] and $\Delta_f H$(SOF_2) yields an experimental value for $\Delta_f H_{298}$ for SOF_3^- of −235.5 kcal mol^{-1} with an uncertainty of 8 kcal mol^{-1} (based solely on the bond strength measurement). While this significantly reduces the discrepancy with the current calculation, there remains nearly a 10 kcal mol^{-1} difference. Given the broader unresolved issue discussed earlier regarding the relative affinities determined via the fluoride exchange equilibria measurements,[46] it is our opinion that the G2* and G2(MP2) value of $\Delta_f H_{298}$ for SOF_3^- are more accurate than even the revised experimental value. The G2* value for $SO_2F_3^-$ lies between the two experimental values, while the G2* values for SO_3^- and SO_3F^- are 7−9 kcal mol^{-1} more negative than all the experimental values. The G2* and G2(MP2) calculations provide the only available enthalpies of formation for a large number of species included in this study: SOF_3, SOF_5, SO_2F, SO_2F_3, SO_3F, SOF^-, SOF_2^-, SOF_4^-, SOF_5^-, and $SO_2F_2^-$.

In the present study, the atomization method was used to derive enthalpies of formation primarily because of the ease in being able to derive a uniform data set. However, values obtained from isodesmic reactions are expected to be more accurate.[61] For comparison purposes, standard enthalpies of formation were derived for two compounds, SOF_4 and SOF_5, using the isodesmic reactions 1 and 2. This method yielded values that are 1−2 kcal mol^{-1} less negative than those obtained from the empirically corrected G2 atomization method. Both results are indicated in Table 3. Unfortunately, no solid experimental numbers exist that can be used to compare the two methods. (As noted earlier, the commonly used value for $\Delta_f H^\circ_{298}(SOF_4)$ is believed to be in error.)

E. Reactivity. In general, sulfur oxyfluoride anions are found to react at the collisional rate with small inorganic molecules via fluoride transfer or charge transfer when such channels are energetically allowed. Not all such reactions proceed at the collision rate, however. For example, the fluoride transfer reactions of SOF_4^- and SOF_5^- with SiF_4 proceed at 60% and 40% of their respective collisional rates, and the reaction of $SO_2F_2^-$ with SO_2 proceeds at ∼25% of the collisional rate. Analogous to other ion−molecule bracketing studies,[44] these measured rate constants are interpreted to be evidence for the FA of both SOF_3 and SOF_4 being comparable to that of SiF_4 and the FA of SO_2F being comparable to that of SO_2, all of which is consistent with the calculations. Several exothermic charge transfer reactions were also found to proceed at rates significantly below the collisional value. The reaction of SOF_4^- with NO_2 proceeds at only 1% of the collision rate, and the reactions of $SO_2F_2^-$ with NO_2 and O_3 proceed at 3% and 30% of their respective collisional values. Both charge-transfer reactions involving NO_2 are spin-forbidden (i.e., the sum of the spin multiplicities is not the same for the products and the reactants), which probably accounts for the very small rate constants. Note that a minor reactive channel, which is also spin-forbidden, is observed in the reaction of $SO_2F_2^-$ with NO_2. The reaction of SOF_4^- with O_3 is not spin-forbidden. As discussed in our previous report on the reactivity of sulfur oxide, sulfur fluoride, and sulfur oxyfluoride anions with O_3,[62] only those ions with a sulfur coordination of 4 or 6, that is species where the number of S−F bonds plus twice the number of S−O bonds equals 4 or 6 (e.g., SF_6^-, SOF_4^-, $SO_2F_2^-$, SO_3^-, and SO_2^-), were reactive with O_3, largely due to spin considerations. However, there appears to be a kinetic bottleneck even for the spin-allowed exothermic reactions, as they proceed at rates significantly below the collision value.

The fact that many of these species undergo fast fluoride ion transfer reactions explains why we were unable to form SOF_2^- in the ion source from SOF_2. Because FA(SOF) < FA(SOF_2), any SOF_2^- formed in the ion source from SOF_2 would rapidly transfer F^- to another parent molecule

$$SOF_2^- + SOF_2 \rightarrow SOF_3^- + SOF \quad (3)$$

Several reactions in Table 4 were found to proceed via mechanisms other than charge transfer or fluoride transfer. For example, the reaction of SOF_4^- with SO_2 proceeds via F_2^- transfer,

$$SOF_4^- + SO_2 \rightarrow SO_2F_2^- + SOF_2 \quad (4)$$

while the reactions of O^- with SOF_2 and SO_2F_2 involve exchange between O^- and F,

$$O^- + SOF_2 \rightarrow SO_2F^- + F \quad (5)$$

$$O^- + SO_2F_2 \rightarrow SO_3F^- + F \quad (6)$$

This O^- reactivity pattern suggests one possible mechanism to form $SO_2F_3^-$, another ion we were unable to generate in the ion source, may be from the reaction of O^- with SOF_4,

$$O^- + SOF_4 \rightarrow SO_2F_3^- + F \quad (7)$$

However, the relatively low FA of SO_2F_2 virtually ensures that $SO_2F_3^-$ generated via reaction 7 would undergo rapid secondary chemistry, transferring F^- to SOF_4 to form SOF_5^-.

Several slow clustering reactions were also observed:

$$SO_2^- + SOF_2 \rightarrow SO_2^-(SOF_2) \quad (8)$$

$$SO_3F^- + BF_3 \rightarrow SO_3F^-(BF_3) \quad (9)$$

For these reactions in which only the association channel is observed, charge transfer and F^- transfer are endothermic. Rate constants reported in the table are the effective binary rate constants. Ternary rate constants can be calculated using the He concentrations; for reaction 8, $k_3 = 4.1 \times 10^{-28}$ cm^6 s^{-1}, and for reaction 9, $k_3 = 2.8 \times 10^{-27}$ cm^6 s^{-1}. No attempt was made to determine the pressure dependence of the rate constants. A minor clustering channel was observed for the reaction of $SO_2F_2^-$ with HCN:

$$SO_2F_2^- + HCN \rightarrow SO_2FCN^- + HF\ (96\%)$$

$$\rightarrow (SO_2F_2{\cdot}HCN)^-\ (4\%) \quad (10)$$

The primary product ion, SO_2FCN^-, may form via dissociation of the cluster in the flow tube on the time scale of the experiment.

Karellas et al.[63] have reported that SO_3F^- is the primary anion formed in CH_4-O_2 flames doped with sulfur/fluorine additives, and the ion is reported to persist throughout the burnt gas region of the flame. The authors propose that oxidation of SO_2F^- by molecular oxygen is a significant mechanism for the formation of SO_3F^- in the flame environment. For this reason, the kinetics of SO_2F^- oxidation reactions were specifically examined in the present study. As shown in Table 4, we find SO_2F^- is not oxidized by either O_2, O_3, or NO_2. However, many other SO_3F^- formation mechanisms are likely to exist in an S/F doped flame environment. In fact, the high EA(SO_3F), combined with the high FA(SO_3), suggests many S/O/F plasma species will react to ultimately form SO_3F^-. For similar reasons, SOF_5^- is expected to be a very stable and unreactive negative ion that is formed in S/O/F plasma environments. In contrast, although SOF_3 and SO_2F_3 have relatively high EAs, the low FA of SOF_2 and SO_2F_2 will limit the formation of SOF_3^- and $SO_2F_3^-$ in environments containing SO_2, SF_4, or SOF_4.

6. Conclusion

Structural and thermochemical parameters were calculated for a series of sulfur oxyfluoride neutrals ($SOF_{n=0-5}$, $SO_2F_{n=0-3}$, and $SO_3F_{n=0-1}$) and their corresponding anions using the G2 procedure of the Gaussian 98W program suite. The calculated EAs presented here are considered accurate to within 0.1 eV. Several very high EA species were identified, including SO_3F, SO_2F_3, and SOF_5, which all have EAs exceeding 5 eV. Anion VDEs were calculated for several species, and the differences between the VDE and the EA are consistent with anticipated structural changes that occur upon electron attachment to these molecules. The G2 derived FAs are 4−8 kcal mol^{-1} higher than the experimental values of Larson and McMahon;[46] however, the present results are in good agreement with recent reexaminations of FAs, suggesting the original FA ladder may need to be readjusted upward by several kcal mol^{-1}. The calculated $D°$[S−F] and $D°$[S−O] presented here are in good agreement with available experimental values and should be considered more reliable than early estimates of $D°$[S−F], which were made for those compounds that have not been studied experimentally. The standard entropies and integrated heat capacities presented in this study are in good agreement with the limited experimental data that are available. However, the standard entropy of SO_3 was found to differ from the value reported in the JANAF Tables by 3.4 kcal mol^{-1}. Standard enthalpies of formation derived from G2 atomization energies were not found to be as accurate as is generally the case with this method. Empirical correction factors were applied, based on the number of O and F atoms in the molecule. The corrected (G2*) results are in good agreement with the G2(MP2) results of Irikura. The combination of recent high level treatments for S/O/F enthalpies of formation should be considerably more accurate than earlier estimates cited in the literature. For example, the commonly used values for $\Delta_fH°$ (SOF_4) and Δ_fH (SOF_3^-) are thought to be in error by over 20 kcal mol^{-1}.

The reactivity of sulfur oxyfluoride anions was studied in the laboratory, and rate constants and product ion distributions were obtained for over 60 reactions with SOF_2^-, SOF_3^-, SOF_4^-, SOF_5^-, SO_2F^-, $SO_2F_2^-$, and SO_3F^-. These anions generally react at the collisional rate with small inorganic molecules via fluoride transfer or charge transfer when such channels are energetically allowed, although several exothermic reactions proceed slowly. In some cases, the slow rate is likely due to spin considerations; however, a kinetic bottleneck appears to occur in almost all O_3 oxidation reactions, even those that are spin-allowed. Many of the F^- and e^- transfer reactions studied provide experimental estimates or limits for FAs and EAs, corroborating the theoretical results. Additional reaction mechanisms were observed: F_2^- transfer, O^- and F exchange, and clustering. Several ions previously thought to undergo oxidation with O_2 were found not to react with O_2, O_3, or NO_2.

Acknowledgment. We thank Paul Mundis and John Williamson for technical support, Lee Sunderlin and Karl Irikura for sharing results prior to publication, and Paul Wenthold and Karl Christe for additional helpful discussions. This research has been supported by the Air Force Office of Scientific Research under Project no. 2303EP4. T.M.M. was supported through Visidyne (Burlington, MA) Contract no. F19628-99-C-0069.

References and Notes

(1) Miller, T. M.; Miller, A. E. S.; Paulson, J. F.; Liu, X. *J. Chem. Phys.* **1994**, *100*, 8841.

(2) Sauers, I.; Harman, G. *J. Phys. D: Appl. Phys.* **1992**, *25*, 761.

(3) Sauers, I.; Christophorou, L. G.; Spyrou, S. M. In *Proceedings of the 4th International Symposium on Gaseous Dielectrics*; Christophorou, L. G., Ed.; Pergamon: New York, 1984; pp 292. Sauers, I.; Christophorou, L. G.; Spyrou, S. M. *Plasma Chem. Plasma Proc*. **1993**, *13*, 17.

(4) Sauers, I. *Plasma Chem. Plasma Proc.* **1988**, *8*, 247.

(5) Sauers, I.; Ellis, H. W.; Christophorou, L. G. *IEEE Trans. Electr. Insul.* **1986**, *E1*, 111.

(6) Van Brunt, R. J.; Herron, J. T. *IEEE Trans. Electr. Insul.* **1990**, *25*, 7594.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Ochterski, J. W. *Thermochemistry in Gaussian*; Gaussian, Inc.: Pittsburgh, PA, 2000.

(9) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17, Suppl. 1*, 1.

(10) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *42*, 41.

(11) Viggiano, A. A.; Morris, R. A.; Dale, F.; Paulson, J. F.; Giles, K.; Smith, D.; Su, T. *J. Chem. Phys.* **1990**, *93*, 1149.

(12) Williams, S.; Campos, M. F.; Midey, A. J.; Arnold, S. T.; Morris, R. A.; Viggiano, A. A. *J. Phys. Chem. A* **2001**, *106*, 997, and references therein.

(13) Van Brunt, R. J.; Sieck, L. W.; Sauers, I.; Siddagangappa, M. C. *Plasma Chem. Plasma Proc.* **1988**, *8*, 225.

(14) Arnold, S. T.; Viggiano, A. A. *J. Phys. Chem. A* **2001**, *105*, 3527.

(15) Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6684.

(16) Ferguson, E. E. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 53.

(17) Streit, G. E. *J. Chem. Phys.* **1982**, *77*, 826.

(18) Huey, L. G.; Hanson, D. R.; Howard, C. J. *J. Phys. Chem.* **1995**, *99*, 5001.

(19) Arnold, S. T.; Seeley, J. V.; Williamson, J. S.; Mundis, P. L.; Viggiano, A. A. *J. Phys. Chem. A* **2000**, *104*, 5511.

(20) Arnold, S. T.; Miller, T. M.; Viggiano, A. A. *Intl. J. Mass Spectrom.* **2002**. In press.

(21) Hargitta, I.; Mijlhoff, F. C. *J. Mol. Struct.* **1973**, *16*, 69.

(22) Lide, D. R.; Mann, D. E.; Fristrom, R. M. *J. Chem. Phys.* **1957**, *26*, 734.

(23) Gunderson, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(24) Lork, E.; Mews, R.; Viets, D.; Watson, P. G.; Borrmann, T.; Vij, A.; Boatz, J. A.; Christe, K. O. *Inorg. Chem.* **2001**, *40*, 1303.

(25) Kornath, A.; Kadzimirsz, D.; Ludwig, R. *Inorg. Chem.* **1999**, *38*, 3066.

(26) Li, Z. *J. Phys. Chem.* **1997**, *101*, 9545.

(27) Maulitz, A. H.; Boese, R.; Kuhn, N. *J. Mol. Struct.* **1995**, *333*, 227.

(28) Christe, K. O.; Dixon, D. A.; Goldberg, I. B.; Schack, C. J.; Walther, B. W.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1993**, *115*, 1129.

(29) Badenes, M. P.; Tucceri, M. E.; Cobos, C. J. *Z. Phys. Chem.* **2000**, *214*, 1193.

(30) Miller, T. M.; Arnold, S. T.; Viggiano, A. A. *Intl. J. Mass Spectrom.* **2002**. In press.

(31) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(32) Irikura, K. K. *J. Chem. Phys.* **1995**, *102*, 5357.

(33) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183; Su, T. *J. Chem. Phys.* **1988**, *89*, 5355.

(34) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.

(35) Polak, M. L.; Fiala, B. L.; Lineberger, W. C.; Ervin, K. M. *J. Chem. Phys.* **1991**, *94*, 6926.

(36) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574.

(37) Rothe, E. W.; Tang, S. Y.; Reck, G. P. *J. Chem. Phys.* **1975**, *62*, 3829.

(38) Gleason, J. F. Ph.D. Thesis, University of Colorado, 1987.

(39) Rudnyi, E. B.; Sidorov, L. N.; Vovk, O. M. *High Temp.−USSR* **1985**, *23*, 238.

(40) Dobrin, S.; Boo, B. H.; Alconcel, L. S.; Continetti, R. E. *J. Phys. Chem. A* **2000**, *104*, 10695.

(41) McKee, M. L. *J. Phys. Chem.* **1996**, *100*, 3473.

(42) Viggiano, A. A.; Henchman, M. J.; Dale, F.; Deakyne, C. A.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 4299.

(43) Mallard, W. G., Linstrom, P. J., Eds. *NIST Chemistry WebBook, NIST Standard Reference Database No. 69*; National Instututes of Standards and Technology: Gaithersburg, MD, 2001 (http://webbook.nist.gov/chemistry).

(44) Miller, A. E. S.; Miller, T. M.; Viggiano, A. A.; Morris, R. A.; Van Doren, J. M.; Arnold, S. T.; Paulson, J. F. *J. Chem. Phys.* **1995**, *102*, 8865.

(45) Christophorou, L. G. In *Electron−Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic: New York, 1984; p 477.

(46) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944.

(47) Lobring, K. C.; Check, C. E.; Sunderlin, L. S. *Intl. J. Mass Spectrom.* **2002**. In press.

(48) Wenthold, P. G.; Squires, R. A. *J. Phys. Chem.* **1995**, *99*, 2002.

(49) Weis, P. W.; Kemper, P. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1999**, *121*, 3531.

(50) Bartmess, J. E. 2001. Personal communication.

(51) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J. Fluorine Chem.* **2000**, *101*, 151.

(52) Irikura, K. K. *personal communication* **2001**.

(53) Kiang, T.; Zare, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 4024.

(54) Czarnowski, J.; Schumacher, H. J. *Int. J. Chem. Kinet.* **1978**, *10*, 111.

(55) Wray, K. L.; Feldman, E. V. *J. Chem. Phys.* **1971**, *54*, 3445.

(56) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(57) Herron, J. T. *J. Phys. Chem.* **1987**, *16*, 1.

(58) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14, Suppl. 1*, 1.

(59) Dittmer, G.; Niemann, U. *Philips J. Res.* **1982**, *37*, 1.

(60) Christe, K. O.; Dixon, D. A.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.* **1997**, *119*, 3918.

(61) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(62) Viggiano, A. A.; Arnold, S. T.; Williams, S.; Miller, T. M. *Plasma Chem. Plasma Proc.* **2002**. In press.

(63) Karellas, N. S.; Goodings, J. J. *Int. J. Mass Spectrom. Ion Processes* **1989**, *87*, 187.

(64) Cartwright, M.; Woolf, A. A. *J. Fluorine Chem.* **1977**, *9*, 495.