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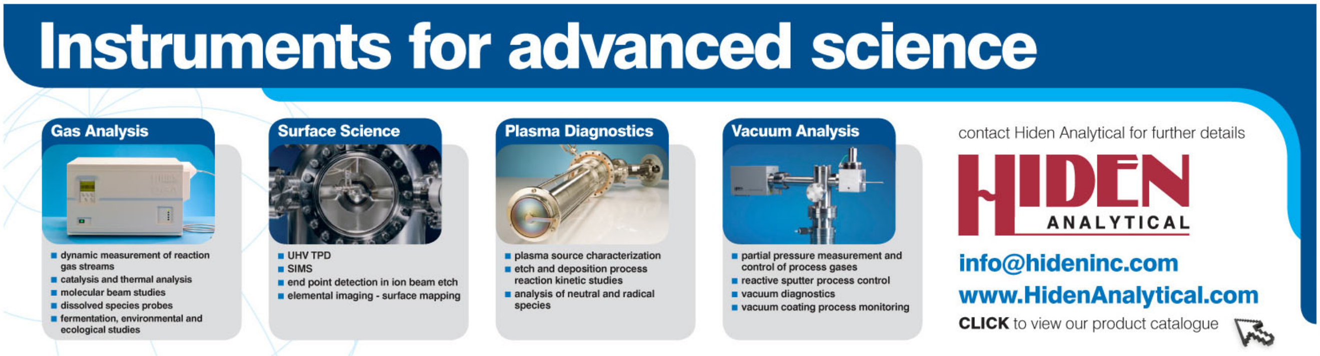

Negative ion–molecule reactions of SF$_4$[a)]

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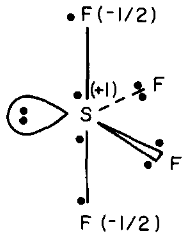
A study of some negative ion–molecule reactions involving SF$_4$ has been carried out by the flowing afterglow technique at ambient temperature. By examining a series of charge exchange reactions of SF$_4$ and SF$_4^-$, the electron affinity of SF$_4$ has been determined to be 2.35 ± 0.1 eV. Rate coefficients for the charge exchange reactions of HS$^-$, S$^-$, OH$^-$, and O$^-$ with SF$_4$ and of SF$_4^-$ with Cl$_2$ and NO$_2$ are reported. In addition, the fluoride transfer reactions of SF$_4^-$ and SF$_6^-$ with SF$_4$ to produce SF$_5^-$ have been examined. That both reactions proceed indicates that the fluoride affinity of SF$_4$ is greater than that of SF$_3$ or SF$_5$. A lower limit of 3.7 eV for the electron affinity of SF$_5$ may also be deduced from the fluoride transfer reactions. The two body addition of halide ions (X$^-$) to SF$_4$ to form the adduct SF$_4$X$^-$ proceeds at near the collision limit ($k = 9.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) for F$^-$, very slowly ($k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) for Cl$^-$, and not at all within experimental limits ($k < 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) for Br$^-$.

I. INTRODUCTION

The sulfur fluorides have received a great deal of attention, most recently due to studies in areas such as isotope separation[1] and multiphoton processes.[2,3] Sulfur tetrafluoride has been of interest for several reasons. Because it has a lone pair of electrons, it can act as a weak Lewis base,[4] but its unoccupied *d* orbitals and the tendency of sulfur to form hexavalent species give it properties of a weak Lewis acid as well.[5] It is highly reactive and has been widely employed as a unique, specific fluorinating agent.[6] Sulfur tetrafluoride has also been investigated as a scavenger for excited species such as ClF*.[7] In contrast to sulfur hexafluoride, SF$_4$ is coordinatively unsaturated, contains sulfur in the 4+ rather than the 6+ oxidation state, has two sets of nonequivalent S–F bonds,[8–10] and has a nonzero dipole moment ($\mu = 0.632$ D).[11] Since the reactions of SF$_6$ have been extensively studied,[12–14] an examination of the reactions of SF$_4$ may allow some insight into the effects that the above factors may have upon chemical reactively.

Sulfur tetrafluoride is also of intrinsic interest because it violates the Lewis octet rule. There have been a number of theoretical and experimental studies of the structure[9,10] and bonding[15,16] in SF$_4$. Tetravalent sulfur exists only with O and F ligands; the fluorine ligand has been found to be most successful at stabilizing sulfur in its expanded octet forms.[17] Sulfur tetrafluoride is a trigonal bipyramid in which the lone pair of electrons occupies an equatorial position. The equatorial S–F bond length[11] is 1.55 Å which is the same as the S–F length in SF$_6$, 1.52 Å, where the six fluorine ligands are equivalent.[18] The axial bonds are slightly longer at 1.65 Å and also contain more ionic character.[11] The valence bond structure of SF$_4$ invokes a *dsp*^{3} hybridization in which a 3*p* electron on sulfur has been unpaired and promoted to a 3*d* orbital. Formation of the additional sulfur bonds "pays for" the energy of promoting the electron. However, because of the high energy of the sulfur 3*d* orbitals, it is generally agreed that they do not play as important a role in bonding as valence bond theory would indicate. Coulson[17] calculated that sulfur requires six F ligands (i.e., SF$_6$) in order to stabilize the 3*d* orbitals to significantly participate in bonding. Molecular orbital calcalculations as well as generalized valence bond (GVB) calculations[15,16,19] indicate that one need not invoke 3*d* orbitals at all in order to satisfactorily account for the bonding in SF$_4$. The equatorial bonds can be described as a system of three two-center, two-electron bonds. The axial S–F bonds may be described by Rundle's[20] three-center, four-electron bond. This is a molecular orbital concept in which the *d* orbitals provide some polarization of the electron distribution, but in which the bonding character is understood in terms of *s* and *p* orbitals alone. One representation of the bonding in SF$_4$ is shown below:



This picture indicates the ionic character of the three-center, four-electron axial bonds. Sulfur tetrafluoride has been likened to the dihalide complexes of the rare gases: the equatorial:SF$_2$ system appears as a pseudo-argon atom.[21] Thus, the interesting bonding nature of SF$_4$ and its resemblance to rare gas dihalides make it of great interest to study.

Harland and Thynne[22,23] have reported appearance potentials for negative ions from neutral SF$_6$ and SF$_5$Cl. From these they deduce values for the electron affinity of SF$_4$ of 1.7 eV (from SF$_6$) and 1.0 eV (from SF$_4$Cl). Because they must assume ground state products in their thermochemical calculation, these values are in fact lower limits for the electron affinity. If their value for A.P.(SF$_4^-$/SF$_6$) is combined with recent bond energy measurements,[24,25] the lower limit, E.A.(SF$_4$) $\geq$ 1.2 eV, may be established. Compton *et al.*[26] have studied the collisional ionization of SF$_4$ with alkali atoms and report E.A.(SF$_4$) = 0.78 eV. This, likewise, must be considered to be a lower limit. We present here the results of

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[a)] Work performed under the auspices of the U. S. Department of Energy.

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examining a series of charge exchange reactions involving SF_4 and SF_4^-. Use of the flowing afterglow technique allows an adiabatic electron affinity to be determined within ± 0.1 eV for SF_4. Photodetachment and appearance potential studies may be complicated by nonadiabatic transitions which then yield either upper limit or lower limit results, respectively, for the electron affinity

While the thermodynamic[24,27–29] and structural[10,11,16,19] properties of SF_4 have been examined in detail, the gas phase reactions of SF_4 and ion-molecule reactions in particular, have received little attention. We have measured rates of several negative ion-molecule reactions of SF_4. Included in this list are charge exchange reactions with both monatomic and polyatomic anions. Rate coefficients based upon the Langevin theory[30,31] are presented for these reactions, and are compared to the experimental values. The use of average dipole orientation theory (ADO) to calculate rates is discussed. In addition to charge exchange reactions, we have also examined the series $SF_4 + X^- \rightarrow SF_4X^-$ for X = F, Cl, and Br. The results are discussed in terms of the unique bonding character of SF_4. Sulfur tetrafluoride will adstract a fluoride ion (producing SF_5^-) from both SF_6^- and SF_4^-. These processes have been studied, and rate constants as well as comments concerning the relative fluoride affinities of SF_4, SF_5, and SF_6 are presented. We are able to place a lower limit upon E.A.(SF_5) on the basis of the relative fluoride affinities.

II. EXPERIMENTAL

All experiments were conducted using the room temperature flowing afterglow apparatus described previously.[25,32] Source gases for all reactant ions and neutrals were obtained from commercial suppliers and used without further purification. Sulfur tetrafluoride was withdrawn from the cylinder at approximately −40 C.

Commercially obtainable sulfur tetrafluoride contains about 6% SOF_2. The similarity in boiling points of the two (b.p. $SF_4 = -40$ C, b.p. $SOF_2 = -43.8$ C)[33] makes purification of SF_4 impracticable. Interference in the positive ion regime by SOF_2 made it impossible to study the positive ion-molecule chemistry of SF_4. The SOF_2 did not seem to interfere with the negative ion molecule studies of SF_4.

Reactant negative ions were produced by interaction of an appropriate neutral with the helium afterglow plasma. The Br_2^-, NO_2^-, Cl_2^-, SF_6^-, and SF_4^- ions were produced by thermal electron attachment to the corresponding neutrals. Other ions were produced via dissociative electron attachment: F^- from CF_4 or CF_3Cl; Cl^- from CCl_4, CF_3Cl, or Cl_2; Br^- from Br_2; O^- from O_2; and HS^- and S^- from H_2S.

The buffer gas used for all measurements was helium, cleaned by being passed through a molecular sieve trap maintained at 77 K. The carrier gas flow was typically 180 atm cm^3 s^{-1}. All gas flows were measured with linear mass flowmeters which were calibrated for the gases involved. Rate coefficient measurements were made over a pressure range of 0.2–1.0 Torr as measured by an electronic capacitance manometer.

Rate constants were obtained from semilogarithmic plots of the reactant ion signal as a function of added neutral. The treatment of flowing afterglow data has been discussed previously.[25,34] Rate coefficients were measured with a precision typically no worse than ±10%. Accuracy is believed to be ±30% due to the propagation of other errors, primarily in flow measurement. The fact that up to 6% of the nominal SF_4 flow is actually SOF_2 would require that the rate constants for those reactions in which SF_4 is the neutral reactant be adjusted upwards as much as 6%. Since the SF_4 was not analyzed and the maximum correction of 6% is well within the 30% limits, we did not adjust the rate constants.

III. RESULTS AND DISCUSSION

A. Electron affinity of SF_4

The electron affinity of a substance is defined as the difference in energy between the respective ground states of the neutral and of the negative ion. Operationally, it is equal to $-\Delta H$ for the attachment process $AB + e \rightarrow AB^-$ in which AB and AB^- are both in their ground states. Thus, a positive electron affinity indicates that AB^- is thermodynamically more stable than AB. A common method for obtaining electron affinities is photodetachment. Analysis of threshold data for the process $AB^- \xrightarrow{h\nu} AB + e$ to obtain adiabatic electron affinities may be complicated if the vertical transition leaves the neutral in an excited vibrational state. When this occurs, the vertical detachment energy is an upper limit for the electron affinity. Electron affinities may also be obtained from appearance potentials for the negative ion as a result of electron or atom collision processes. In this case a lower limit for the electron affinity is determined due to the assumption that the negative ion is created with no excess internal energy. In the flowing afterglow the electron affinity of some species may be bracketed by observing that charge transfer reactions do or do not proceed with the negative ions of neutrals of known electron affinity. The state of the product ion, though assumed to to be ground, is not important because it is realized that each charge transfer reaction of the type $A^- + C \rightarrow A + C^-$ in which the electron affinity of A is well determined merely sets a lower limit on E.A.(C); i.e., E.A.(C) $\geq$ E.A.(A). If A^- does not charge transfer to C, it is probable that E.A.(C) < E.A.(A). However, in such cases the reverse reaction $C^- + A \rightarrow C + A^-$ should be examined if possible. If this charge exchange occurs, then E.A.(C) $\leq$ E.A.(A). Lifschitz *et al.*[35] have pointed out that charge transfer from polyatomic ions may not occur even if energetically favorable. Thus it is imperative for the purposes of bracketing an electron affinity to test cases of no charge exchange in the opposite direction. We were able to do this for most cases in which charge exchange was not observed and we found no anomalies, as did Lifschitz *et al.*[35] in which the charge exchange did not take place in either direction. The series of charge exchange reactions we studied and the inferences which may be drawn from each are presented in Table I. If the data involving HS^- and NO_2^- are considered definitive, then $(2.32 \pm 0.01)^{36} \leq$ E.A.(SF_4) $\leq (2.38 \pm 0.06)^{37}$ or conservatively, E.A.(SF_4) = 2.35 ± 0.1 eV. Product ions were monitored for all charge

TABLE I. Electron affinity of SF_4.

Reaction	E.A.(M) (eV)	E.A.(SF_4) (eV)
SF_4+M^-		
$SF_4+CN^- \nrightarrow$	3.82	<3.82
$SF_4+Cl^- \nrightarrow$	3.61	<3.61
$SF_4+Br^- \nrightarrow$	3.37	<3.37
$SF_4+Br_2^- \nrightarrow$	2.51	<2.51
$SF_4+Cl_2^- \nrightarrow$	2.46	<2.46
$SF_4+NO_2^- \nrightarrow$	2.38	<2.38
$SF_4+HS^- \rightarrow SF_4^- + HS$	2.32	≥2.32
$SF_4+S^- \rightarrow SF_4^- + S$	2.08	≥2.08
$SF_4+OH^- \rightarrow SF_4^- + OH$	1.83	≥1.83
$SF_4+O^- \rightarrow SF_4+O$	1.47	≥1.47
SF_4^-+M		
$SF_4^-+Br_2 \rightarrow Br_2^- + SF_4$	2.51	≤2.51
$SF_4^-+Cl_2 \rightarrow Cl_2^- + SF_4$	2.46	≤2.46
$SF_4^-+NO_2 \rightarrow NO_2^- + SF_4$	2.38	≤2.38
$SF_4^-+CCl_4 \nrightarrow$	2.12	>2.12

exchange reactions to ensure that charge exchange rather than chemical reaction was responsible for the decrease in reactant ion count rate.

Our result for the electron affinity of SF_4 is substantially higher than previous measurements of 1.2 eV[22] (corrected for newly available bond energies[24,25]) and 0.78 eV.[26] However, those values are, in fact, lower limits because they are derived from threshold appearance potentials. If strictly interpreted as lower limits, these results are not in disagreement with our result.

Hildenbrand[27] has pointed out that both the bond dissociation energies and the electron affinities of SF_n ($n = 1$–6) follow an alternating pattern. The primary bonds for $n = 2, 4, 6$ are stronger than those for $n = 1, 3, 5$. The electron affinities alternate in the opposite fashion: those for $n = 1, 3, 5$ are more positive than those for $n = 2, 4, 6$. Table II presents electron affinity values for SF_n. Our value of E.A.(SF_4) = 2.35 eV is seen to fit the alternating pattern. It has been suggested[26] that a reason for the higher electron affinities of SF_3 and SF_5 is due to the lower symmetry of these two species; two low-lying orbitals mix to give a lower MO for the added electron. Table II also presents the stepwise bond dissociation energies for the SF_6 molecule. Both the electron affinities and bond dissociation energies for SF_n, $n = 1$–6, are plotted in Fig. 1. That the two alternate in opposite fashion is immediately apparent. It may be more informative to examine the data in light of the fact that SF_n and SF_{n-1}^- are isoelectronic. Figure 1 also depicts the curve for E.A.(SF_{n-1}), and it follows very closely the curve for D(SF_{n-1}–F). Now it is clear that the alternation in both the bond strengths and the electron affinities can be discussed in terms of the same phenomenon: the formation of the three-center four-electron bond mentioned previously. Starting with SF_2, which is not a hypervalent species, one can look at the stepwise addition of F atoms. SF_2 has C_{2v} symmetry with two lone pairs of electrons. The first F atom can approach either of these lone pairs and form a two-center three-electron bond. The second then adds to form the three-center four-electron bond. The same process is repeated for SF_5 and SF_6. The alternation in bond strengths is the result of successive formations of a weak two-center three-electron bond, and then a stronger three-center four-electron bond. Such an explanation has been advanced by Kiang and Zare.[24] Hay[16] has done calculations which indicate that charge transfer to increase the ionic character of the S–F bonds is a major factor in producing the hypervalent SF_n species. He postulates that the $SF_2 + 2F$ surface crosses the ionic $SF_3 + F^-$ curve. Thus resonance stabilization increases the strength of the primary SF_4 bond:

$$F^-(SF_2)-F^+ \leftrightarrow F-(SF_2^+)F^- .$$

A similar argument applies to SF_6. The alternating bond

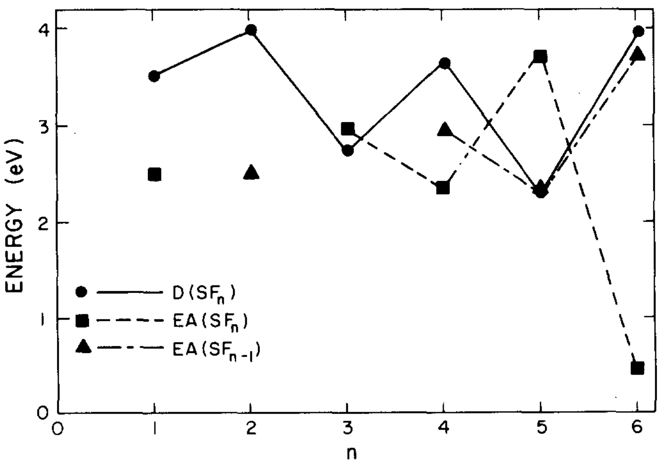


FIG. 1. Graph of E.A.(SF_n), E.A.(SF_{n-1}), and D(SF_{n-1}–F) vs the number of coordinated fluoride ligands. Data are given in Table II.

TABLE II. Alternating behavior of E.A.(SF_n) and D(SF_n).

n	E.A.(SF_n) (eV)[a]	D(SF_{n-1}–F) (eV)[f]
6	0.55[b]	3.95
5	3.7[c]	2.30
4	2.35[c]	3.65
3	2.95[d]	2.74
2	···	3.98
1	2.5[e]	3.52

[a] Electron affinity values determined at 300 K. Since the temperature dependence of molecular electron affinities is not well understood, no attempt has been made to extrapolate these values to 0 K.

[b] Reference 26.

[c] This work.

[d] Reference 23.

[e] Reference 48.

[f] Reference 24.

TABLE III. Charge exchange reactions SF_4.

Reaction[a]	k^b (cm^3 $molecule^{-1}$ s^{-1})	k^{calc} (cm^3 $molecule^{-1}$ s^{-1})
$SF_4 + O^- \rightarrow SF_4^- + O$	1.4×10^{-9}	1.54×10^{-9}
$SF_4 + OH^- \rightarrow SF_4^- + OH$	1.3×10^{-9}	1.50×10^{-9}
$SF_4 + S^- \rightarrow SF_4^- + HS$	1.1×10^{-9}	1.15×10^{-9}
$SF_4 + HS^- \rightarrow SF_4^- + HS$	9.5×10^{-10}	1.14×10^{-9}
$NO_2 + SF_4^- \rightarrow NO_2^- + SF_4$	5.7×10^{-11}	
$Cl_2 + SF_4^- \rightarrow Cl_2^- + SF_4$	3.2×10^{-11}	

[a] Plausible neutral products are indicated.

[b] Rate constants are reported to ± 30%.

behavior can then be explained by the fact that SF_3 and SF_5 contains a three-electron "half bond" while SF_4 and SF_6 have one covalent bond, one ionic bond, and some resonance stabilization.

Realizing that SF_n and SF_{n-1}^- are isoelectronic, one can explain the electron affinities using this same concept. The processes which define $D(SF_{n-1}-F)$ and $E.A.(SF_{n-1})$ are shown below:

$$SF_n \rightarrow SF_{n-1} + F ,$$

$$SF_{n-1}^- \rightarrow SF_{n-1} + e .$$

If one views the electron as a "ligand," it is clear that the bonding scheme presented above applies. Both SF_3^- and SF_5^- (isoelectronic with SF_4 and SF_6) contain the favored three-center four-electron bond, while SF_4^- contains the weaker two-center three-electron bond. Thus, one would expect $E.A.(SF_3) > E.A.(SF_4) < E.A.(SF_5)$, as is shown in Fig. 1.

B. Reactions of SF_4 and of SF_4^-

We have examined a variety of reactions of neutral SF_4 and of the SF_4^- ion, and have obtained values for the rate coefficients of these reactions. The processes studied fall into three broad categories and will be discussed as such. First are the reactions which are classified as simple charge exchange processes; no bonds are broken or formed. The second class of reaction involves fluoride transfer to neutral SF_4 to form SF_5^-. And lastly, are the halogen addition reactions of the general form: $SF_4 + X^- \rightarrow SF_4X^-$ $(X = F, Cl, Br)$.

1. Charge exchange reactions

The results of rate data measurements of charge exchange reactions of both SF_4 and SF_4^- are presented in Table III. For the reactions of the type

$$SF_4 + M^- \rightarrow SF_4^- + M$$

the rate constants follow the trend predicted by Langevin theory[30,31]; i.e., the ratio of the rate coefficients is equal to the ratio of the appropriate reduced masses. The Langevin rate coefficients are larger than the experimental values, but this may be expected since the Langevin expression is an upper limit. The Langevin expression

$$k = 2\pi q(\alpha/\mu)^{1/2}$$

requires a value for the molecular polarizability α. To our knowledge, this has not been determined for SF_4. Miller and Savchik[38] have presented a method for calculating average molecular polarizabilities by summing terms which depend upon the hybridization of each atom involved. If the atomic hybrid value of S in SF_6 is used as an approximation, the polarizability of SF_4 is calculated to be 6.02 $Å^3$. This fits the expected trend of increasing polarizability with decreasing oxidation number: i.e., $\alpha SF_6 = 4.48$ $Å^3$[39] and $\alpha SF_4 = 6.02$ $Å^3$.

Because SF_4 has a permanent dipole moment, $\mu = 0.632$ D,[11] one of the ADO type formulations[40,41] should be used to calculate the collision limit rate coefficient. However, these formulations involve the Langevin expression with an added term for the ion–dipole interaction, and thus predict a collision limit larger than that of the Langevin expression alone. Since the rate coefficients presented here are smaller than the Langevin limit, but do follow the expected reduced mass dependence, no additional information can be gained from the ADO theory.

By comparison, the two charge exchange reactions in which SF_4^- is the reactant ion are very slow. As seen in Table III, the reaction

$$SF_4^- + Cl_2 \rightarrow SF_4 + Cl_2^-$$

is nearly two orders of magnitude slower than the Langevin limit. This supports the observations of Lifschitz *et al.*[35] and Fehsenfeld[12] that exoergic charge transfer from polyatomic ions may be slow, presumably due to charge delocalization on the ion.

2. Fluoride transfer reaction

Neutral SF_4 abstracts a fluoride ion from both SF_4^- and SF_6^- to produce SF_5^-. The reactions and their rate coefficients are presented in Table IV. The fluoride affinity of A may be defined as $D(A-F^-)$. Murphy and Beauchamp[42] have made a comprehensive study of fluoride affinities as a measure of Lewis acidity. If the reaction between SF_4 and SF_6^- is written as

$$\begin{array}{ll} SF_6^- \rightarrow SF_5 + F^- & D(SF_5-F^-) \\ \underline{SF_4 + F^- \rightarrow SF_5^-} & \underline{-D(SF_4-F^-)} \\ SF_4 + SF_6^- \rightarrow SF_5^- + SF_5 , & \end{array}$$

it is seen that ΔH of the reaction is the difference in fluoride affinities of SF_4 and SF_5. Similarly, ΔH for the reaction of SF_4^- with SF_4 is the difference in fluoride affinities of SF_3 and SF_4. That both reactions proceed

TABLE IV. Fluoride transfer reactions of SF_4.

Reaction	k^a (cm^3 $molecule^{-1}$ s^{-1})
$SF_4 + SF_4^- \rightarrow SF_5^- + SF_3$	5.4×10^{-10}
$SF_4 + SF_6^- \rightarrow SF_5^- + SF_5$	3.7×10^{-10}

[a] Rate constants are reported to ± 30%.

indicates that the fluoride affinity of SF_4 is greater than that of SF_3 or SF_5, or $D(SF_3{-}F^-) \leq D(SF_4{-}F^-) \geq D(SF_5{-}F^-)$. The energies of reaction leading to a value of the fluoride affinity of a particular SF_n compound are defined by a series of elementary reaction steps

$$\begin{array}{ll} SF_n{-}F^- \rightarrow SF_n{-}F + e^- & +\mathrm{E.A.}(SF_n-F) \\ SF_n{-}F \rightarrow SF_n + F & D(SF_n{-}F) \\ F + e^- \rightarrow F^- & -\mathrm{E.A.}(F) \\ \hline SF_n{-}F^- \rightarrow SF_n + F^- & D(SF_n{-}F^-) \end{array}$$

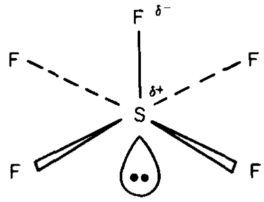
The stepwise bond dissociation energies of SF_6 are known,[24] as are $\mathrm{E.A.}(SF_6) = 0.55$ eV,[26] $\mathrm{E.A.}(SF_4) = 2.35$ eV, and $\mathrm{E.A.}(F) = 3.40$ eV.[43] From these data the fluoride affinity of SF_3 is calculated to be 2.60 ± 0.16 eV and that of SF_5 to be 1.10 ± 0.21 eV. Thus the lower limit for the fluoride affinity of SF_4 is established to be $D(SF_4{-}F^-) \geq 2.60 \pm 0.16$ eV. This limit and the above cycle may be used to place a lower limit on the electron affinity of SF_5; $\mathrm{E.A.}(SF_5) \geq 3.70 \pm 0.31$ eV. This limit agrees well with previous measurements of $\mathrm{E.A.}(SF_5) \geq 3.40 \pm 0.20$ eV,[44] $\mathrm{E.A.}(SF_5) \geq 3.20 \pm 0.2$ eV,[26] and $\mathrm{E.A.}(SF_5) = 3.70 \pm 0.04$ eV.[45]

From the relationship $D(SF_3{-}F^-) \leq D(SF_4{-}F^-) \geq D(SF_5{-}F^-)$, it is obvious that the fluoride affinities of the SF_n series alternate as do the electron affinities and bond strengths. It is evident that SF_5^- is thermodynamically favored over SF_4^- or SF_6^- which is, of course, identical to the result obtained by examining the electron affinities. Thus the preference of formation of the Rundle three-center four-electron bond may be invoked to qualitatively explain the fluoride transfer process.

3. *Halide addition to SF_4*

The two-body addition reactions $SF_4 + X^- \rightarrow SF_4X^-$ for $X = F^-$, Cl^-, and Br^- were examined and the results are presented in Table V. Also listed are the Langevin limit rate coefficients. It is clear that while F^- adds to SF_4 with a rate of the expected order of magnitude, Cl^- and Br^- do not. The SF_4Cl^- adduct is formed ~300 times slower than predicted by the Langevin limit, while no SF_4Br^- is observed. Thus it is not simply a mass effect which causes the addition reaction to be much slower for Cl^- and, within our limits, nonexistent for Br^-.

It is known that for hypervalent species in general, the higher halogens are not as effective in stabilizing an expanded octet. This is true for the rare gas halides, the higher valence interhalogen compounds, and sulfur compounds. For example, the compounds SCl_6, SBr_4, and SBr_6 are not known. The importance of charge transfer and the resultant ionic character of the three-center four-electron bond has been mentioned. Below is a representation of the SF_5^- ion as a distorted tetragonal pyramid (the S atom lying slightly out of the equatorial plane and the lone pair of electrons occupying an axial position)[46,47]



Because of the role charge separation plays in stabilizing the three-center four-electron bond, more highly electronegative ligands should be better able to support an expanded octet species. The Pauling electronegativities for F, Cl, and Br are 4.0, 3.0, and 2.8, respectively. Thus Cl and Br will not be as effective in inducing the δ^+ charge on S and the δ^- on X which is helpful in stabilizing the SF_4X^- species.

Since these addition reactions require product stabilization, the possibility of a three-body component to the reaction was investigated over the pressure range 0.29–0.60 Torr. No pressure dependence was observed, as illustrated in Fig. 2 for the fluoride addition reaction. The lack of a three-body component qualitatively indicates that the lifetime of SF_5^{-*} must be in the microsecond range, not inconsistent with the autodetachment lifetimes of SF_4^{-*} and SF_6^{-*} which are many microseconds.[23]

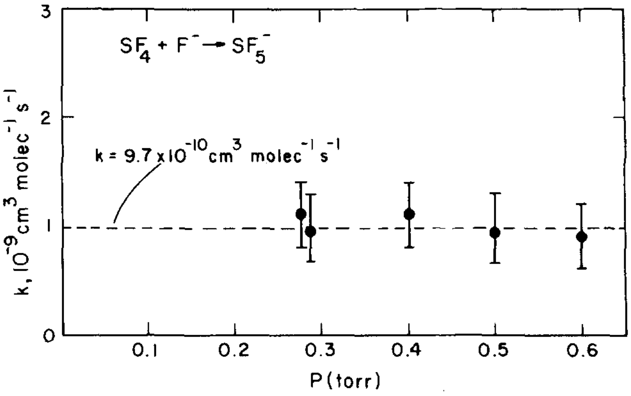


FIG. 2. Rate constant data for F^- addition to SF_4 plotted as a function of pressure. The rate constant k shows no pressure dependence over the range examined.

TABLE V. $SF_4 + X^-$ reactions

Reaction	k^a (cm^3 molecule^{-1} s^{-1})	k^{calc} (cm^3 molecule^{-1} s^{-1})
$SF_4 + F^- \rightarrow SF_5^-$	9.7×10^{-10}	1.4×10^{-9}
$SF_4 + Cl^- \rightarrow SF_4Cl^-$	2.6×10^{-11}	1.1×10^{-9}
$SF_4 + Br^- \rightarrow SF_4Br^-$	$< 2 \times 10^{-12}$	8.5×10^{-10}

[a] Rate constants are reported to ±30%.

IV. CONCLUSIONS

The negative ion chemistry of sulfur tetrafluoride has been thoroughly examined, and several thermodynamic quantities as well as reaction rate coefficients have been derived. It was determined that $\mathrm{E.A.}(SF_4) = 2.35 \pm 0.1$ eV, $\mathrm{E.A.}(SF_5) \geq 3.70 \pm 0.31$ eV, $D^0_{298}(SF_5{-}F^-) = 1.10 \pm 0.21$ eV, $D^0_{298}(SF_3{-}F^-) = 2.60 \pm 0.16$ eV, and that $D^0_{298}(SF_4{-}F^-) \geq 2.60 \pm 0.16$ eV. These data combined with

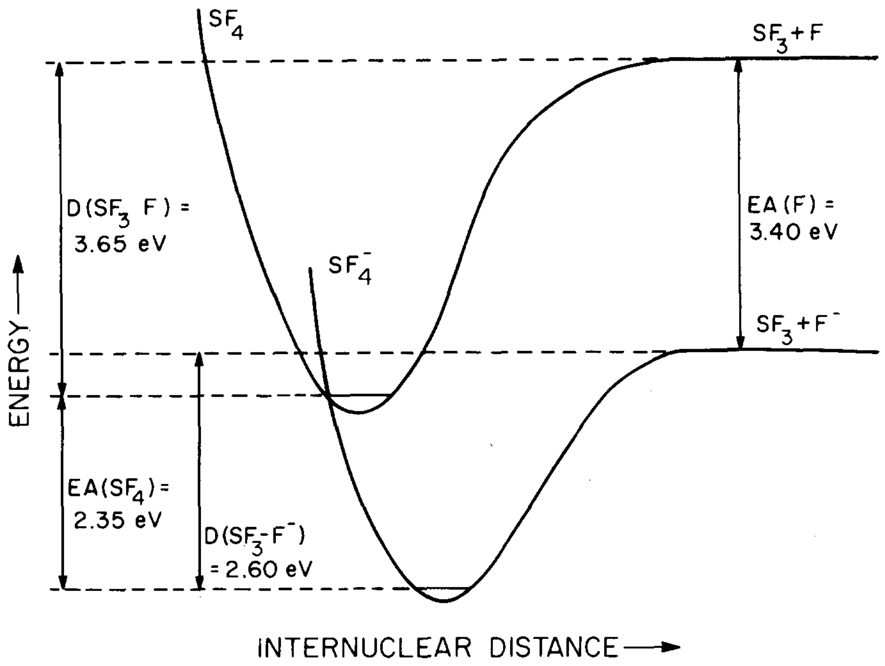


FIG. 3. Qualitative potential energy diagrams for SF_4 and SF_4^-. E.A.(SF_4) and D(SF_3F^-) are from this work; D(SF_3–F) is from Ref. 24 and E.A.(F) from Ref. 43.

other available thermodynamic data allow a qualitative representation of potential energy curves for SF_4 and SF_4^- to be made as shown in Fig. 3.

The thermodynamic values derived herein rest on the assumption that the neutral molecules and ions involved in the reactions possess a Boltzmann distribution of internal states at the temperature of the experiment. Numerous collisions with the helium buffer gas will rapidly quench excited vibrational and rotational states.[49] If the common assumption is made that vibration is more effective than rotation in promoting electron transfer or bond scission, the mean internal energy available at 300 K is on the order of a few hundredths of an electron volt (0.07 eV for a large polyatomic such as SF_6). While recognizing that this internal energy could overcome an endothermic reaction barrier, it is generally acknowledged that the observation of a reaction in the flowing afterglow defines the exothermic direction.[49,50]

Internal energy also plays a role in relating the determination of an electron affinity at zero point energy. However, the temperature dependence of ΔH for the reaction $e^- + AB \rightarrow AB^-$ is going to depend upon the detailed shape of the potential energy curves for AB and AB^-. Such an analysis is beyond the scope of this paper, so we make no attempt to extrapolate our derived electron affinities to 0 K.

Most of the rate coefficients measured are close to the Langevin collision limit and do show the expected mass dependent trend with a few notable exceptions. These exceptions occur in charge transfer reactions when SF_4^- is the reactant ion and in the two-body addition reactions of Cl^- and Br^- to SF_4. The former seems to be qualitatively explained by charge delocalization in a large polyatomic ion, a phenomenon which has been noted before.

The latter exception and, more importantly, the striking alternation in bond energies, electron affinities, and fluoride affinities in the SF_n and SF_n^- series may be explained qualitatively very well by a description of the bonding in the SF_n and SF_n^- series. That the bond strengths in SF_n and the electron affinities and fluoride affinities of SF_{n-1}^- alternate in parallel fashion is explained by the realization that SF_n and SF_{n-1}^- are isoelectronic. Then it is clear that the same phenomena is responsible for the trends seen in both the neutral and negative ion series. Starting with SF_2 and proceeding through the stepwise addition of F, an alternating series of two-center three-electron and three-center four-electron bonds are formed. The three-center four-electron bonds are favored due to some ionic character and resonance stabilization. Thus the bond dissociation energies for SF_n for n = even are higher than for n = odd. If adding an electron is similar to adding F, then one expects the n = odd electron affinities to be higher, and such is the case. Likewise the n = even fluoride affinities should be higher than those of n = odd because the result is an n n = odd negative ion. This has been shown to be true for n = 3, 4, and 5.

Lastly, the slow rate of addition of Cl^- and Br^- to SF_4 in contrast to the relatively fast rate of F^- addition may be explained by the lower electronegatives of Cl and Br, and the resultant failure to induce as much ionic character in the three-center four-electron bond.

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