ION-MOLECULE CHEMISTRY RELATED TO PLASMA DEPOSITION AND ETCHING OF SILICON

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**Title:** Ion-Molecule Chemistry Related to Plasma Deposition and Etching of Silicon

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**Abstract:**
During the 5 years of this contract, we used guided ion beam tandem mass spectrometric methods to study a variety of gas-phase ion-molecule reactions relevant to plasma deposition and etching of silicon. Absolute cross sections over a wide range of kinetic energies for reactions involving both atomic and polyatomic ions were measured. The results yielded energy dependent cross sections, temperature dependent rate constants, and thermochemical data, information vital to further understanding of the chemical mechanisms involved in plasma processing.

**Subject Terms:**
- Ion-molecule reaction rates
- Plasma etching
- Plasma deposition
- Ion-molecule cross sections
1. Project Description

The results of the work performed in our laboratory during the course of this contract have been disseminated in 20 published papers,\textsuperscript{1-20} and 2 papers submitted for publication.\textsuperscript{21,22} In addition, 6 invited seminars and 4 contributed papers concerning Air Force supported work have been presented by the PI or members of my group. The work falls into several categories and is summarized below.

A. Introduction and Background

An important tool in the fabrication of microelectronic devices is the use of plasmas to etch and deposit silicon, silicon oxide, silicon carbide, silicon nitride, and other semiconductor material layers. During etching, highly reactive radicals and ions present in the plasma bombard the surface and volatilize the silicon, silicon dioxide, silicon nitride, or other components of the surface. Deposition of silicon dielectric films involves polymerization of silicon-containing radicals and ions. The role of gas-phase ion-molecule reactions in these processes is as yet unclear. Although radical-molecule reactions dominate the chemistry at the surface, gas-phase ion-molecule reactions are a substantial source of neutral radicals that can rival their production via electron-impact dissociation.\textsuperscript{23,24} Therefore, the role of ion-molecule reactions in plasma processing deserves further investigation, and must be included in accurate modeling of the plasma environment.\textsuperscript{25}

In the past, such modeling was often forced to assume that the ion-molecule reactions are independent of collision energy, an assumption that we have subsequently shown is often invalid.\textsuperscript{3,6,10,12} Accurate modeling of these systems requires cross sections or rate constants as a function of energy up to at least 40 eV, information provided in our work.

During the course of the contract, we studied a number of ion-molecule reactions related to plasma deposition and etching of silicon. Our studies examine these reactions over a broad range of kinetic energies by using guided ion-beam mass spectrometry. The
basic information provided is absolute reaction cross sections as a function of kinetic energy. In most studies, this information is interpreted to determine mechanisms of the reactions and relevant thermochemistry of the reactive ionic and neutral species of potential importance in plasma environments. Such thermodynamic information is a critical tool in understanding deposition and etching processes and in evaluating the optimum conditions for plasma reactors.26

B. Experimental Methods

General. The experimental technique used throughout these studies was guided ion beam tandem mass spectrometry.27 In this instrument, ions are produced by one of several techniques described below. The ions are then focused into a beam, mass analyzed, and decelerated to a desired kinetic energy. The ion beam is injected into an rf octopole beam guide,28 which acts as an ion trap. This ensures efficient collection of product ions and allows low energy (thermal) ion beams to be studied. The octopole passes through a reaction cell containing a neutral reactant gas maintained at sufficiently low pressure to ensure single-collision conditions. The product and unreacted ions drift out of the gas chamber to the end of the octopole where they are focused into a quadrupole mass filter for mass separation and detected by using a secondary electron scintillation detector and standard ion pulse counting techniques. Data collection is under computer control, which allows extensive signal averaging. The instrument incorporates extensive differential pumping that allows precise control over the conditions in the critically important reaction region.

Laboratory (lab) ion energies are converted to energies in the center-of-mass (CM) frame, the actual energy available for reaction. At each CM energy, E, the intensities of transmitted reactant and product ions are converted to absolute reaction cross sections for each product channel, \( \sigma(E) \).27 These cross sections have absolute uncertainties of \( \pm 20\% \) up
to ±50% for some charge transfer reactions. Relative cross section values are accurate to
about ±5%. By using methods described elsewhere, the thermodynamic thresholds of
endothermic processes can be determined. We have demonstrated that these methods can
provide accurate thermochemistry on a variety of transient species. Many of the studies
summarized below are examples.

**Ion Sources.** In our work, ions may be generated by using several types of ion
sources. This versatility permits the production of atomic and polyatomic ions with
controlled internal excitation. This is important for two reasons. First, ions produced in a
plasma environment have varying degrees of vibrational and/or electronic excitation. It has
been shown previously in our laboratory that such excitation can have a significant effect
on reactivity. This effect can be studied explicitly by examining the reactions of ions
generated under plasma-like conditions and those of ions with controlled internal excitation.
The resulting state-specific cross sections and reactivity will be most useful in
understanding and modeling the chemical and physical processes involved in the plasma
systems of interest here. Second, accurate derivation of thermochemistry from the kinetic
energy dependence of the reaction cross sections requires ions with well-characterized
internal energies. This is most easily achieved by creating ions in their vibrational and
electronic ground states.

**Electron Impact Source.** One method of ion production used in these studies is the
standard electron impact (EI) source with variable electron energy. This source produces
ions having a distribution of internal states, such that higher electron energies increase the
probability of producing electronically excited ions. Only for ions with no low-lying
excited states such as the rare gas ions can a ground electronic state beam be produced with
the EI source.

**Surface Ionization Source.** In the surface ionization (SI) source, a filament is
resistively heated and exposed to the parent gas resulting in decomposition and ionization.
The ions are assumed to equilibrate at the filament with electronic state populations well-characterized by a Maxwell-Boltzmann distribution. The validity of this assumption has been discussed in the literature and has recently been confirmed by van Koppen, et al.

C. Ion source development

Because of the importance of controlling the internal energy of the ions, one component of the contract work was to develop an ion source capable of producing polyatomic ions at a controlled temperature. The use of flow tube technology was used to accomplish this and our flow tube ion source is described in a paper supported by the Air Force. Our flow tube can be varied in length (25, 50, 75 or 100 cm) and is pumped by a 600 cfm roots blower. The flow tube is followed by a 13-cm-long region that is held to about 10⁻⁴ Torr by an unbaffled 6" diffusion pump. Ion lenses in this region have an open construction in order to maximize pumping speed. Ions exit through an aperture into the first chamber of the guided ion beam apparatus (held below 10⁻⁶ Torr by a baffled 6" diffusion pump).

For a flow tube that is 1 m in length, the ions undergo ~10⁵ collisions with the carrier gas (typically He or Ar) at a pressure of ~0.5 Torr. For the internal modes of polyatomic ions, Lineberger and coworkers have shown that these collisions serve to thermalize the ions, at worst to 1000 K, but more typically to 300 K. Some limitations on the degree of collisional cooling do exist. For vibrational excitation, Ferguson has shown that vibrational quenching of small diatomic ions is very inefficient in He. The use of argon as a bath gas or the addition of a more efficient quencher to the flow can alleviate such problems. For example, we have shown that we can effectively quench excited vibrational states of O₂⁺ and N₂⁺. Our data for the covalently bound species, SiF₄⁺ (n = 1 - 4) and SF₆⁺ (n = 1 - 5), are consistent with thermalized ions, and studies of more weakly bound species, such as N₄⁺, Fe(CO)₅⁺ (n = 1 - 5), Cr(CO)₆⁺ (n = 1 - 6), and H₂O⁺(H₂O)ₙ.
(n = 1 - 5) have shown that the internal energy of these ions is well described by a Maxwell-Boltzmann distribution of rotational and vibrational states corresponding to 298 K.

D. Silane chemistry

To complement earlier work on the reactions of Si+ with silane, we performed two studies of the reactions of silane with various ions. In the first, the dissociative charge transfer reactions of silane with the rare gas ions (He+, Ne+, Ar+, Kr+, and Xe+) was studied. State-specific data for the 2P3/2 ground spin-orbit states of Kr+ and Xe+ were included. The products observed in the He, Ar, and Kr systems are SiHn+ (n = 0 - 3). For the Ne system, formation of SiHn+ (n = 0 - 2) is seen, while in the Xe system only SiH3+ and SiH2+ are observed. Reactions of He+, Ne+, Kr+, and Xe+ show little dependence on kinetic energy, but for the case of Ar+, the reaction probability and the product distribution are highly sensitive to the kinetic energy of the system. The results for these reactions were explained in terms of vertical ionization from the 1t2 and 3a1 bands of SiH4. Thermal reaction rates were also provided and discussed.

The second study was published in a special issue of Z. Phys. D on "Collision Processes Relevant to Low Temperature Plasmas." Here, we examined the reactions of SiH4 with O+(1S), O2+(3Πg, v = 0), N+(3P), and N2+(3Σu+, v = 0). All four ions react with silane by dissociative charge-transfer to form SiHn+ (n = 0 - 3), and all but N2+ also form SiXHn+ products where (n = 0 - 3) and X = O, O2 or N. The overall reactivity of the O+, O2+, and N+ systems show little dependence on kinetic energy, but for the case of N2+, the reaction probability and product distribution relies heavily on the kinetic energy of the system. These results can be understood by comparison with the rare gas ion study and were again explained in terms of vertical ionization from the 1t2 and 3a1 bands of SiH4. Thermal reaction rates were also provided and discussed.
E. Silicon tetrafluoride chemistry

Building on an earlier study of the reaction of Si⁺ with SiF₄, we also studied the reactions of SiF₄ with He⁺, Ne⁺, Ar⁺, O⁺, and O₂⁺, and with N⁺(3P), N₂⁺(2Σ⁺), Ar⁺(2P₃/₂), and Kr⁺(2P₃/₂). In the first of these studies, dissociative charge transfer reactions are the sole processes observed. All SiF₄⁺ (n = 0 - 4) products are observed, except for SiF₄⁺ from reaction with Ne⁺ and He⁺, and Si⁺ from reaction with Ar⁺. At high energies, the dominant products are SiF₃⁺ in the Ar system, and SiF⁺ in both the Ne and He systems. There is some evidence in the Ne system for an excited state of SiF₃⁺ at 5.7 eV. In the Ar⁺ and Ne⁺ reactions, the observed energetics are consistent with literature thermochemistry, but with He⁺, reaction barriers are observed. The observed product distributions and energetics were explained by consideration of the potential energy surfaces and the difference in ionization energies of the rare gases.

In the second study, the major reactions are again dissociative charge transfer processes, although O⁺ also reacts to form OF + SiF₃⁺ efficiently and O₂⁺ reacts to form minor amounts of SiOF⁺⁺ (n = 1 - 3). Reactions of excited O₂⁺ ions with SiF₄ are more efficient than reactions of ground state ions. Our work on the reactions of N⁺(3P), N₂⁺(2Σ⁺), Ar⁺(2P₃/₂), and Kr⁺(2P₃/₂) with SiF₄ was designed primarily to determine the thermochemistry for SiF₄⁺ and SiF₃⁺ more accurately. From the O⁺ and N⁺ systems, the adiabatic ionization energy, IE, of SiF₄ is 15.29 ± 0.08 eV, consistent with less precise determinations in the literature. The heat of formation of SiF₃⁺ at 0 K is determined as -29.3 ± 0.6 kcal/mol, and that for NF as 63.4 ± 3.9 kcal/mol.

This thermochemistry was a necessary foundation to the follow-up study on the collision-induced dissociation (CID) and charge transfer reactions of SiF₄⁺ (n = 1 - 4). Energy dependences of the CID cross sections were analyzed to yield the following 0 K bond dissociation energies (BDEs): D(SiF₃⁺-F) = 0.85 ± 0.16 eV, D(SiF₂⁺-F) = 6.29 ± 0.10 eV, D(SiF⁺-F) = 3.18 ± 0.04 eV, and D(Si⁺-F) = 7.04 ± 0.06 eV. The ionization energies,
IE(SiF$_2$) = 10.84 ± 0.13 eV and IE(SiF$_3$) = 9.03 ± 0.05 eV, were also measured from analysis of endothermic charge transfer reactions. Combined with two other studies in our laboratories, these results allowed us to derive heats of formation for the silicon fluoride cations and neutrals, Table I, that provide a self-consistent set of thermochemical data for the silicon fluoride species. In some cases, the thermochemical values determined here are considerably different from available literature values but are in good agreement with theory.\textsuperscript{40,41,42,43}

Finally, in a study now ready for submission, we have examined the reactions of SiF$_n^+$ ($n = 1 - 3$) with SiF$_4$.\textsuperscript{21} Absolute cross sections are measured as a function of kinetic energy from thermal to 20 eV. Transfer of F and F between the neutral and ion reactant are the major reaction channels and are distinguished by silicon isotope labeling. For all systems investigated, transfer of F$^-$ is the dominant channel. Also observed is simple collision-induced dissociation of the reactant ions by sequential loss of fluorine atoms. The isothermal F$^-$-transfer reaction of SiF$_3^+$ with SiF$_4$ exhibits an activation barrier of 0.29 ± 0.03 eV. All the reactions may be rationalized by collision-induced dissociation or attack on a F atom of SiF$_4$ by the Si atom of the ionic reactant. The propensities for F vs F atom transfer are rationalized in terms of molecular orbital correlations.

F. Silicon tetrachloride chemistry

Our work on silicon tetrachloride involves three studies. In the first, the reaction of Si$^+$ with SiCl$_4$ was studied.\textsuperscript{2} Exothermic production of SiCl$^+$ + SiCl$_3$ is the dominant process occurring on nearly every collision. SiCl$_3^+$ + SiCl and SiCl$_2^+$ + SiCl$_2$ production are both found to be slightly endothermic, and the dissociative channels, SiCl$^+$ + Cl + SiCl$_2$ and SiCl$_2^+$ + Cl + SiCl, are also observed, but no Si$_2$Cl$_n^+$ species are observed. Isotopic labeling studies indicate that SiCl$^+$ and SiCl$_3^+$ are produced by direct, coupled mechanisms, while SiCl$_2^+$ is formed through an intimate collision involving a symmetric
intermediate. These mechanisms were interpreted in terms of the molecular orbital correlations. The cross section behavior and proposed mechanisms are consistent with those in our analogous study of the Si$^+$ + SiF$_4$ reaction. Reaction thresholds were analyzed to derive the following thermochemical values: $\Delta_h^o$($\text{SiCl}$) = 44 ± 6 kcal/mol, $\Delta_h^o$($\text{SiCl}^+$) = 217 ± 7 kcal/mol, IE($\text{SiCl}$) = 7.44 ± 0.40 eV, and $\Delta_h^o$($\text{SiCl}^+_2$) = 188 ± 3 kcal/mol and 190 ± 6 kcal/mol.

In the second study, reactions of SiCl$_4$ with O$_2^+$, Ar$^+$, Ne$^+$, and He$^+$ were examined. All reactions are fairly efficient with thermal energy rate constants that exceed 66% of the collision rate. The major products observed in the O$_2^+$ and Ar$^+$ reactions are SiCl$_4^+$ and SiCl$_3^+$, while for the Ne$^+$ and He$^+$ reactions, the major product is SiCl$^+$. Thermochemistry derived from these SiCl$_4$ systems includes the determination of $\Delta_h^o$($\text{SiCl}_3^+$) = 99.8 ± 1.6 kcal/mol and $\Delta_h^o$($\text{OSiCl}_3^+$) < 97 kcal/mol from the O$_2^+$ system, and $\Delta_h^o$($\text{SiCl}_2^+$) = 184.9 ± 2.6 kcal/mol and $\Delta_h^o$($\text{SiCl}^+$) = 203.9 ± 2.5 kcal/mol from the Ar$^+$ system. We also derived the ionization energies: IE($\text{SiCl}_3^+$) = 7.65 ± 0.15 eV, IE($\text{SiCl}_2^+$) = 9.81 ± 0.10 eV, and IE($\text{SiCl}$) = 6.79 ± 0.24 eV.

In the third study, for which a manuscript is now being prepared for submission, we examined the reactions of SiCl$_n^+$ ($n = 1 - 3$) with SiCl$_4$.$^{22}$ Transfer of Cl$^-$ and Cl$^-$ between the neutral and ion reactant are the major reaction channels and are distinguished by silicon isotope labeling. For all systems investigated, transfer of Cl$^-$ is the dominant channel. Also observed is simple collision-induced dissociation of the reactant ions by sequential loss of chlorine atoms.

G. Fluorocarbon chemistry

In several studies, we have examined reactions yielding ionized fluorocarbons. In one, dissociative charge transfer reactions of CF$_4$ with Ar$^+$, Ne$^+$, and He$^+$ were studied from thermal to 50 eV.$^3$ Only CF$_n^+$ ($n = 1 - 3$) products are observed in the reactions of Ar$^+$ and
Ne'. In addition to the CF₃⁺ products, both C⁺ and F⁺ are seen at high kinetic energies for the He⁺ reactant. Reaction rates for these reactions were provided and compared with previous measurements. The energy dependences of the cross sections can be understood by considering the energies needed to access various states of the CF₄⁺ ion.

This study led us to conclude that the thermochemistry of the CF₃⁺ ion was not well established. In a second study, we performed a series of experiments designed to accurately determine the appearance energy of CF₃⁺ from CF₄." In contrast to a literature report," there is no fluoride transfer equilibrium between CF₃⁺ and SF₅⁺. Thresholds for formation of CF₃⁺ from reaction of ground state Kr⁺(2P₃/₂) with CF₄ and from collision-induced dissociation of CF₃⁺ by Xe are used to establish AE(CF₃'/CF₄). Both results are in good agreement although the former experiment yields the most precise value, 14.24 ± 0.07 eV.

In a third study, the reactions of O⁺ and O₂⁺ with CF₄ and C₂F₆ were examined." The predominant ions formed correspond to dissociative charge transfer reactions, with small amounts of FCO⁺ and F₂CO⁺ being formed. The thresholds and shapes of the dissociative charge transfer cross sections are explained in terms of vertical ionization to various electronic states of CF₄⁺ and C₂F₆⁺. In the O⁺ reactions, fluoride transfer to form CF₃⁺ + OF in the CF₄ system and C₂F₅⁺ + OF in the C₂F₆ system is also observed at thermal energies. The formation of carbon oxyfluoride ions in these systems is postulated to occur by insertion of the oxygen ions into C-F bonds of the fluorocarbon molecules. From the O₂⁺ + CF₄ and O⁺ + C₂F₆ systems, ΔH°(F₂CO⁺) = 6.30 ± 0.08 eV is determined.

H. Reactions of atomic silicon ions with hydrocarbons

Several studies were designed to investigate the reactions of atomic ground state silicon ions with gasses potentially present in plasma systems. The first of these involved reactions with methane." In this system, only endothermic processes are observed with
SiH⁺ and SiH₃C⁺ as the major ionic products. There is evidence that the latter species has two forms, Si⁺-CH₃ formed at low energies, and a higher energy form that could be a triplet state of SiCH₃⁺ or HSiCH₂⁺. Minor ionic products include SiCH₂⁺, CH₃⁺, and SiCH⁺. All observed products are consistent with a reaction that occurs via an HSiCH₃⁺ intermediate.

From the measured thresholds of the reactions and other information, the 298 K heats of formation (in kcal/mol) for the following silicon species are derived: ΔfH°(SiH) = 91.4 ± 1.8; ΔfH°(SiCH⁺) = 339 ± 7; ΔfH°(SiCH₂⁺) = 285 ± 3; and ΔfH°(SiCH₃⁺) = 235 ± 5.

A comparable study on the reactions of Si⁺(2P) with ethane (dₐ, 1,1,1-d₃, and d₆) was later conducted. At thermal energies, Si⁺-CH₃ accounts for 90% of all products. Exothermic dehydrogenation to form SiC₂H₄⁺ and demethanation to form SiCH₂⁺ are observed, but these processes are inefficient. When CH₃CD₃ is employed as the reactant neutral, all products are observed to incorporate hydrogen and deuterium atoms in near-statistical distributions at low energies. This suggests that the primary HSi⁺-CH₂CD₃, CH₃CD₂-SiD⁺, and CH₃-Si⁺-CD₂ intermediates are rapidly interconverted via a cyclic HDSi(CH₂CD₂)⁺ intermediate.

In reactions of Si⁺(2P) with methylsilane, SiH₃CH₃, the major products at thermal energies are SiCH₃⁺ and Si₂HCH₃⁺, and above 1 eV, Si₂H₂CH⁺. Labeling experiments involving ³⁰Si⁺ provide additional mechanistic information that SiCH₃⁺ is formed via three different mechanisms. The general mechanistic details of this system can be understood by extending potential energy surfaces calculated elsewhere. From the measured thresholds of the reactions and other information, we derived 298 K heats of formation (in kcal/mol) for the following disilicon ions: ΔfH°(Si₂H₂CH⁺) = 245 ± 7, ΔfH°(Si₂HCH₃⁺) < 290 ± 2, ΔfH°(Si₂CH⁺) = 258 ± 2, and ΔfH°(Si₂CH₂⁺) = 299 ± 2; the neutral silicon species: ΔfH°(SiCH₂) = 79 ± 7, ΔfH°(SiH₂CH₃) = 38.1 ± 2.3, and ΔfH°[SiH₂(CH₃)₂] = -17 ± 4; and ΔfH°(SiHCH₃⁺) = 248 ± 3, and ΔfH°(SiH₂CH⁺) = 210 ± 3.
I. Miscellaneous thermochemistry

Several studies were aimed at determining the thermochemistry of additional species of potential importance in plasma systems. One of these involved measurements of the heat of formation of the hydroperoxyl radical, $\text{HO}_2$, and the ionization energy of methane, $\text{IE}(\text{CH}_4)$, both by studying the reaction of $\text{O}_2^+(\tilde{\text{I}}\Pi_g, \nu = 0)$ with $\text{CH}_4$. The thermodynamic values derived are $\text{IE}(\text{CH}_4) = 12.54 \pm 0.07 \text{ eV}$, $\Delta H^0_{298}(\text{HO}_2) = 3.8 \pm 1.2 \text{ kcal/mol}$, $D^0_{298}(\text{H}-\text{OO}) = 48.3 \pm 1.2 \text{ kcal/mol}$, and $D^0_{298}(\text{H}-\text{OOH}) = 88.4 \pm 1.2 \text{ kcal/mol}$. In a more complete study of this reaction system, we observed three previously reported reaction products, $\text{CH}_2\text{OOH}^+$, $\text{CH}_3^+$, and $\text{CH}_4^+$, as well as $\text{CH}_2\text{O}_2^+$, $\text{H}_2\text{O}^+$, and $\text{CO}_2^+$ at higher energies. Reactions of excited $\text{O}_2^+$ ions were also examined and are shown to be more efficient than those for ground state ions. The thermochemistry and potential energy surfaces for this reaction are discussed as well as the effects of vibrational, electronic, and translational energy on the reaction system. A heat of formation for $\text{CH}_2\text{O}_2^+$ of $201.5 \pm 1.6 \text{ kcal/mol}$ was measured and tentatively assigned to the methyne hydroperoxy ion structure, $\text{HC-O-OH}^+$. Finally, a comprehensive study of the thermochemistry of sulfur fluoride cations and neutrals was performed. By analyzing the energy dependences of the cross sections for CID of $\text{SF}_n^+$ ($n = 1 - 5$) with $\text{Xe}$, we obtained the following $0$ K bond dissociation energies (BDEs): $D^\circ(\text{SF}_4^+-\text{F}) = 4.60 \pm 0.10 \text{ eV}$, $D^\circ(\text{SF}_3^+-\text{F}) = 0.36 \pm 0.05 \text{ eV}$, $D^\circ(\text{SF}_2^+-\text{F}) = 4.54 \pm 0.08 \text{ eV}$, $D^\circ(\text{SF}^+-\text{F}) = 4.17 \pm 0.10 \text{ eV}$, and $D^\circ(\text{S}^+-\text{F}) = 3.56 \pm 0.05 \text{ eV}$. The ionization energies, $\text{IE}(\text{SF}) = 10.16 \pm 0.17 \text{ eV}$, $\text{IE}(\text{SF}_3) = 8.18 \pm 0.07 \text{ eV}$, $\text{IE}(\text{SF}_4) = 11.69 \pm 0.06 \text{ eV}$, and $\text{IE}(\text{SF}_5) = 9.60 \pm 0.05 \text{ eV}$, were measured from analysis of endothermic charge-transfer reactions. From these BDEs and IEs, we derive heats of formation for the sulfur fluoride ions and neutrals that provide a self-consistent set of thermochemical data for the sulfur fluoride species, Table I.


J. References


9. "Translational and Internal Energy Effects in Reactions of O* and O_2* with SiF_4"

10. "Reactions of O_2*, Ar*, Ne*, and He* with SiCl_x*: Thermochemistry of SiCl_x* (x = 1-3)"

11. "Reactions of N_4* with Rare Gases from Thermal to 10 eV c.m.: Collision-Induced Dissociation, Charge Transfer, and Ligand Exchange"

12. "Kinetic Energy Dependence of the Reactions of O* and O_2* with CF_4 and C_2F_6"

13. "C-H and C-C Bond Activations by Silicon. Thermochemistry and Mechanism of the Reaction of Si*(2P) with Ethane"

14. "Hydrogen Atom Transfer Reactions of N_2* with H_2, HD, and D_2 From Thermal to 10 eV c.m."


16. "Guided Ion Beam Studies of the Reaction of Si*(2P) with Methylsilane. Reaction Mechanisms and Thermochemistry of Organosilicon Species"

17. "Collision-Induced Dissociation and Charge Transfer Reactions of SF_x* (x = 1 - 5): Thermochemistry of Sulfur Fluoride Ions and Neutrals"
    Fisher, E. R.; Kickel, B. L.;

19. "Dissociative Charge Transfer Reactions of N\(^+\)(3\(^3\)P), N\(_2\)^+ (2\(^3\)Σ\(^+\)_g), Ar\(^+\)(2\(^3\)P\(_{3/2,1/2}\)), and Kr\(^+\)(2\(^3\)P\(_{3/2}\)) with SiF\(_4\). Thermochemistry of SiF\(_4\)^+ and SiF\(_3\)^+" Kickel, B. L.; Fisher, E. R.; Armentrout, P. B. J. Phys. Chem. 1993, 97, 10198.

20. "Collision-Induced Dissociation and Charge Transfer Reactions of SiF\(_x\)^+ (x = 1 - 4). Thermochemistry of SiF\(_x\) and SiF\(_x\)^+" Fisher, E. R.; Kickel, B. L.; Armentrout, P. B. J. Phys. Chem. 1993, 97, 10204.

21. "Energetics and Mechanisms in the Reactions of SiF\(_x\)^+ (x = 1 - 3) with SiF\(_4\)" Liu, A.; Kickel, B. L.; Armentrout, P. B. submitted for publication.

22. "Energetics and Mechanisms in the Reactions of SiCl\(_x\)^+ (x = 1 - 3) with SiCl\(_4\)" Liu, A.; Kickel, B. L.; Armentrout, P. B. submitted for publication.


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<td>-111.6 ± 3.6</td>
<td>SF₃⁺</td>
<td>77.0 ± 3.2</td>
</tr>
<tr>
<td>SF₄</td>
<td>-182.3 ± 3.7</td>
<td>SF₄⁺</td>
<td>87.2 ± 3.4</td>
</tr>
<tr>
<td>SF₅</td>
<td>-221.8 ± 4.3</td>
<td>SF₅⁺</td>
<td>-0.4 ± 4.1</td>
</tr>
</tbody>
</table>