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Gas-Phase Reactions of Bare and Ligated Uranium Ions with Sulfur Hexafluoride

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Reactions of bare and ligated uranium ions with sulfur hexafluoride were studied in a quadrupole ion trap mass spectrometer. Bare U^+ was found to react rather efficiently with SF_6 ($k/k_{ADO} \sim 0.4$) to produce both UF_n^+ ($n = 1, 2, 3, 4$) and SF_n^+ ($n = 1, 2, 3$). Whereas the UF^+/SF_6 reaction rate was essentially the same as that for U^+/SF_6, both UF_2^+ and UF_3^+ were inert; this is attributed to a repulsive interaction between UF_n^+ and SF_6 when n exceeds 1. Reactions of UF^+ ($k/k_{ADO} \sim 0.2$) and UF_2^+ ($k/k_{ADO} \sim 0.05$) with H_2O resulted in both F → OH exchange and oxidation. In contrast, UF_3^+ reacted very efficiently with H_2O ($k/k_{ADO} \sim 1$), exhibiting only F → OH exchange. The primary ion products of the UO^+/SF_6 reaction ($k/k_{ADO} \sim 0.2$) were SF_3^+ and UOF_2^+; those of the UOH^+/SF_6 reaction ($k/k_{ADO} \sim 0.3$) were SF_3^+ and UOF^+. The reaction results are discussed in the context of a previously proposed reaction model, the distinctive chemistry of uranium, and thermodynamic considerations. The results illuminate the nature of uranium as well as general aspects of the interaction of bare and ligated transition-metal ions with SF_6. Results for collision-induced dissociation (CID) of selected uranium molecular ions support the concept of CID being a quasithermal process under these experimental conditions, with rearrangements prior to fragmentation possible for certain ions.

Introduction

Sulfur hexafluoride is a rather remarkable molecule in that it is chemically inert despite the high sulfur valence state and relatively weak S−F bonds.[1] This is in distinct contrast to SF_4, which is highly reactive and is an effective fluorinating agent. The inert nature of SF_6 is attributed to a steric effect, whereby the octahedrally coordinated sulfur center is effectively shielded by the fluorine atoms. Sulfur hexafluoride is a good electrical insulator, and its primary application is in high-voltage equipment.[2] It is also employed as a source of F atoms in plasma etching of silicon.[3]

As summarized by Jiao and Freiser,[4] several studies of gas-phase reactions of highly electrophilic ions with SF_6 have been performed, and the results have shown either (a) electron transfer from SF_6 followed by F-atom loss from the unstable SF_6^+ product or (b) F^- transfer to the reactant cation. Reactions of SF_6 with cations by dissociative charge transfer have been performed recently to obtain a better understanding and optimal conditions for plasma etching with SF_6.[3]

Jiao and Freiser[4] carried out the first systematic investigation of reactions of metal cations with SF_6, with a particular emphasis on Sc^+. Their primary goal was to understand better the nature of the bonding and reactivity of SF_6 by examining its interaction with transition-metal ions. On the basis of the observations that early-transition-metal ions display reactive character whereas late-transition-metal ions display inert behavior with SF_6, Jiao and Freiser proposed that at least one empty valence d orbital with the proper symmetry is required for reaction to occur. It was postulated that these vacant d orbitals at the metal center interact with molecular orbitals of SF_6 that have a significant contribution from the sulfur 3d orbitals.[4] The result is an $[M{\cdots}SF_6]^+$ type of intermediate that is sufficiently long lived

to allow F-atom transfer to the metal center to occur prior to dissociation.[4]

The ground-state electronic configuration of U^+ is [Rn]-$5f^57s^2$, and the [Rn]$5f^56d7s$ configuration is only 3 kJ mol^{-1} higher in energy[5] ([Rn] designates the closed radon core). As U^+ has several empty valence 6d orbitals, the reaction model of Jiao and Freiser[4] predicts that this actinide ion should be able to activate SF_6. Because the highest normal oxidation state of scandium is Sc(III), the highest fluoride produced by the reaction of Sc^+ with SF_6 is ScF_2^+.[4] In contrast, hexavalent uranium is commonly observed in species such as the uranyl ion, UO_2^{2+}, and uranium hexafluoride.[6] Because of the accessibility of high oxidation states, it might be anticipated that additional reaction channels would be observed with U^+ compared with Sc^+. Uranium is also of interest as an actinide element in which the quasivalence 5f electrons can play a role in bonding under certain circumstances.[7]

The primary goal of the studies reported here was to explore the distinctive chemistry of uranium via reactions of bare and ligated uranium cations with SF_6. Sulfur hexafluoride is an appropriate reagent to extend understanding of the gas-phase ion chemistry of uranium (and other actinide) ions because of its unique properties. Reactions of uranium ions with SF_6 also provide a source of fluorinated primary product ions that can be isolated for subsequent reactivity and CID studies. In addition to the primary reactions of bare U^+ with SF_6, reactions of isolated UF_n^+ ($n = 1, 2, 3$) with SF_6 and H_2O and of UO^+ and UOH^+ with SF_6 were also studied. Collision induced dissociation (CID) was performed on selected product ions. The results illuminate the interactions of metal ions, particularly ligated metal ions, with SF_6.

Experimental Section

The present studies were carried out in a quadrupole ion trap mass spectrometer (QIT-MS) coupled with a pulsed glow

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discharge ion source. The apparatus and experimental techniques have been described elsewhere.[8–10] Only a summary and certain details for these particular experiments are included here. Uranium ions were produced in the argon glow discharge source from a cathode of either pure uranium metal or uranium oxide embedded in indium[11] and extracted into the trap by a series of ion lenses.

The ion trap bath gas was 5×10^{-4} Torr of helium. During the experiments, both the introduced SF_6 (Matheson, 99.99%) and background H_2O were available for reaction with uranium ions. Prior to each experiment, the H_2O pressure in the absence of SF_6 was determined by measuring the reaction rate (s^{-1}) of Ar$^+$ ions from the discharge and dividing by the Ar$^+$/H$_2$O reaction rate constant, $k = 1.8 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[12] A typical value for the measured water pressure was 2.3×10^{-7} Torr. Sulfur hexafluoride was then added, and the total reaction rate of Ar$^+$ was redetermined. The reaction rate of Ar$^+$ with the added SF_6 could then be derived from the incremental increase in the total reaction rate, and the SF_6 pressure was obtained by dividing this value by the Ar$^+$/SF$_6$ reaction rate constant, $k = 9.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[12] A typical value for the sulfur hexafluoride pressure was 1.1×10^{-6} Torr, which was substantially greater than the water pressure.

The pseudo-first-order reaction rate for U$^+$ with the two neutral reagents was then determined by repeating the reactions using different reaction times and plotting $-\ln(U^+_t/U^+_{t=0})$ vs time, where U$_t^+$ is the U$^+$ ion signal at time t and U$^+_{t=0}$ is the initial U$^+$ ion signal. Pseudo-first-order kinetics are exhibited under these conditions because the concentrations of the neutral reactants were constant and much greater than that of the reactant uranium ions. The linearity of these plots ($R^2 > 0.98$) confirmed that the reactions were pseudo first order and thus that the products were from primary reactions of a uranium ion with a single SF_6 or H_2O molecule. The linearity of the rate plots provide evidence that excited-state ions are not abundant reactants as their population would diminish for long reaction (and ion cooling) times. The overall reaction rates determined from the slopes of these plots, along with the branching ratios for the SF_6 and H_2O product ions, provided the individual reaction rates for the two reactants. The product branching ratios were determined from relative peak heights and did not vary significantly with reaction time. The rate constants for U$^+$ with SF_6 and H_2O were then established by dividing the two rates by the corresponding number densities.

Reactions of primary products with SF_6 and H_2O were studied by allowing the bare U$^+$ to react for a sufficiently long time to achieve a substantial population of the primary product of interest. This particular ion was then isolated by increasing the rf trapping amplitude to limit the low-mass cutoff of ions that are stable in the trap and applying filtered noise fields to eject unwanted ions.[13] Following this procedure, the reaction of the isolated ion of interest with SF_6 and H_2O was studied in a manner similar to that employed for bare U$^+$.

CID was performed for selected uranium molecular product ions. Product ions were isolated as described above and then subjected to an on-resonance excitation voltage applied in a dipolar fashion to the end caps of the ion trap.[14] By use of an automated software program, it was possible to apply increasingly larger excitation amplitudes to assess the effect of energetic collisions with the helium bath gas on the degree and nature of ion fragmentation. By use of the same software, the rf trapping amplitude could also be varied at a fixed resonance excitation amplitude and frequency to establish optimum on-resonance conditions.

TABLE 1: Primary Products for the Reaction U$^+$ + SF$_6$ [a]

| ion	neutral[b]	branching ratio	ΔH_r^c (kJ mol^{-1})
UF$^+$	SF$_5$	5%	-277 ± 29
UF$_2^+$	SF$_4$	47%	-605 ± 33
UF$_3^+$	SF$_3$	31%	-789 ± 18
UF$_4^+$	SF$_2$	<1%[d]	-885 ± 8
(UF$_5^+$)[e]	(SF)[e]	N. D.[e]	-739 ± 17
SF$^+$	UF$_5$	<1%[d]	-854 ± 14
SF$_2^+$	UF$_4$	7%	-806 ± 9
SF$_3^+$	UF$_3$	10%	-574 ± 11
(SF$_4^+$)[e]	(UF$_2$)[e]	N. D.[e]	-24 ± 16

[a] The measured reaction rate is $k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; this corresponds to $k/k_{ADO} = 0.37$. [b] The neutral products were not determined and are inferred. [c] The thermodynamic data are from ref 17 for the UF$_n^+$, from ref 18 for the neutral UF$_n$, and from ref 4 for the SF$_n^+$ and SF$_n$. [d] Product ion was observed just above the detection limit (e.g., see the UF$_4^+$ peak in Figure 1). [e] The product ion was not detected, but the thermochemical values are included for comparison.

Results and Discussion

An emphasis was placed on the primary reaction of bare U$^+$ with SF_6. Reactions of the primary UF$_n^+$ product ions with both SF_6 and H_2O were also studied, as were those of SF_6 with UO$^+$ and UOH$^+$ produced by the reaction of U$^+$ with H_2O. The uncertainties for the measured reaction rates are estimated as $\pm10\%$. The average dipole orientation model[15] was used to estimate the limiting reaction rate constants, k_{ADO}; the parameters used to derive the k_{ADO} values are from ref 16. As an indication of the measured rate constants relative to the theoretical limit, the k/k_{ADO} ratios are considered accurate to $\pm30\%$.

In all of the assessments of reaction thermochemistries, the enthalpies of formation for neutral and ionic sulfur hexafluoride species and the scandium species are from Jiao and Freiser,[4] those for the charged uranium species are from Hildenbrand et al.,[17] those for neutral uranium species are from Morss,[18] and those for all other species are from Lias et al.[19] To the extent that entropy may play a role under these conditions, it should be minor as almost all of the reactions correspond to the formation of two product particles from two reacting particles; accordingly, only the reaction enthalpies, not their free energies, are considered. The uncertainties associated with the derived enthalpies and molecular ion bond dissociation energies (BDEs) are dominated by the uncertainties in the thermodynamics for the neutral and charged uranium species.[17,18]

Reactions of Bare U$^+$ with SF$_6$. The products from the reaction of U$^+$ with a single SF_6 molecule are given in Table 1; the pseudo-first-order kinetics confirm that the reactions correspond to interactions between a uranium ion and one reactant molecule. These products are referred to as primary products because they result from a single ion–molecule interaction, as evidenced by pseudo-first-order kinetics and a constant branching ratio with increasing time. These kinetics are illustrated by the linearity of the rate plot shown in Figure 1. The data in this figure correspond to the depletion of U$^+$ as a function of time; the first data point appears at 22 ms as this is the shortest time required to scan the relatively massive ^{238}U$^+$ from a position of low-energy trapping ($q_z \approx 0.2$) to one of resonance ejection ($q_z \approx 0.9$). A uranium product ion mass spectrum for the U$^+$/SF$_6$ reaction is shown in Figure 2. This spectrum was acquired after a reaction period of 34 ms, a short enough time that the spectrum is dominated by the primary reaction products. The relative ion signal of the off-scale unreacted U$^+$ peak is 100 and the low mass products, SF$^+$, SF$_2^+$ and SF$_3^+$, appeared with intensities in accord with those reported in Table 1. The two unlabeled peaks in Figure 2 correspond to
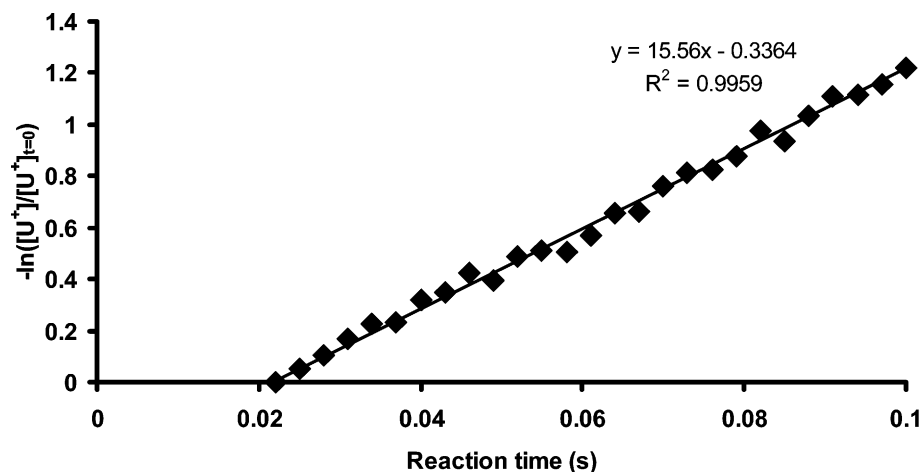
Figure 1. Plot of $-\ln(U^+/U^+_{t=0})$ as a function of time. The depletion of U^+ is due to reactions with SF_6 and H_2O, and the resulting rate is deconvoluted to derive the contribution from each reaction. The good linear fit to the data indicate pseudo-first-order reactions of U^+ with the neutrals. Data accumulation begins at 22 ms because, at a scan rate of 10 000 amu s^{-1}, it takes this long before $^{238}U^+$ is ejected from the trap.
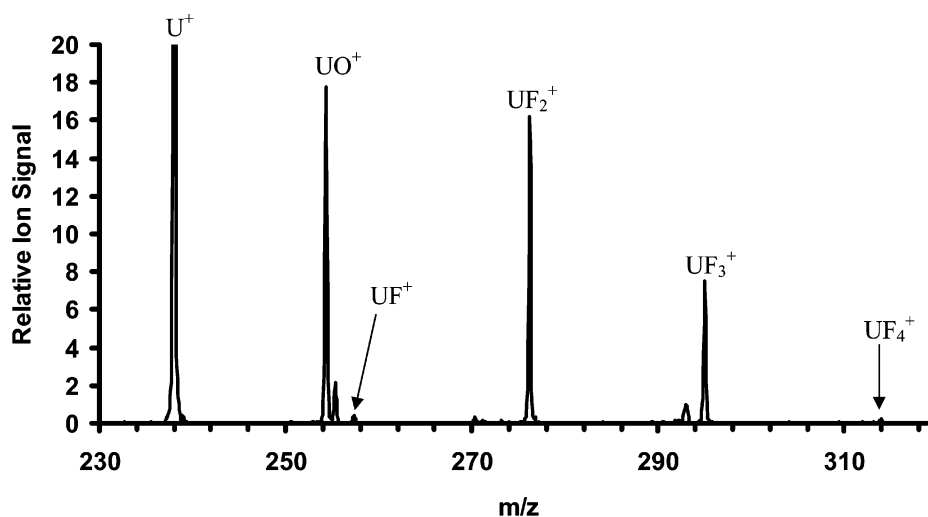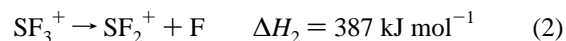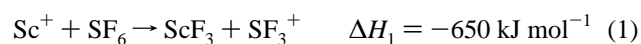

Figure 2. Mass spectrum for the reaction of U^+ with SF_6. The spectrum was acquired after a reaction period of 34 ms and the identified ions are primary products. The unreacted U^+ peak is off scale, at a relative ion signal of 100. The UO^+ results from reaction of U^+ with water. The low-mass portion of the spectrum where the SF_n^+ products appear is not shown.

UOH^+ at $m/z = 255$ and $UOHF_2^+$ at $m/z = 293$. The major UO^+ product and the minor UOH^+ product result from the reaction of U^+ with residual water, a reaction studied previously using this instrument and the same general methodology.[10] The $UOHF_2^+$ is the product of a secondary reaction of UF_3^+ with H_2O, as discussed below.

The reaction rate of U^+ with SF_6 is $k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to a collisional reaction efficiency $k/k_{ADO} = 0.37$. This substantial reaction efficiency is in accord with the model of Jiao and Freiser[4] in which it was proposed that the availability of empty valence d orbitals for the early-transition-metal ions enables an efficient bonding interaction of the metal ion with SF_6 and a long-lived $[M\cdots SF_6]^+$ complex. The measured reaction rate of U^+ with SF_6 is essentially the same as that of Sc^+.[4] The model for these reactions is that an F atom transfers from the sulfur center to the uranium center to produce a $[F_nU\cdots SF_{6-n}]^+$ complex prior to dissociation into the charged and neutral products. In general, the lower energy exit channel for a given intermediate complex is expected to be favored because reaction barriers should be smaller for the lower energy products as a result of a lowering of the potential energy surface.[4] For example, this is the case for the $[F_2U\cdots SF_4]^+$ intermediate, where UF_2^+ predominates over SF_4^+ (see Table 1). An anomaly would seem to be the

apparent dissociation of $[F_4U\cdots SF_2]^+$ into predominantly SF_2^+, with UF_4^+ barely above the detection limit. As discussed below, this evident inconsistency can be rationalized by considering the possibility of prompt autofragmentation of high-energy product ions, fragmentation of UF_4^+ in this particular case.
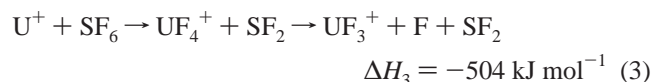
It is feasible that a significant contribution to some of the observed products is a result of prompt autofragmentation of primary products absent collision with a second SF_6 molecule. Such processes that occur on a time scale of less than $\sim$10 ms would appear as pseudo-first-order reactions in these experiments. All of the observed reaction products can be directly produced by the exothermic reactions indicated in Table 1. However, the ICR-MS studies of the reaction of Sc^+ with SF_6 suggest that autofragmentation of high-energy nascent products can also occur. In the ICR-MS studies of the reaction of Sc^+ with SF_6,[4] fragmentation of the primary SF_3^+ product to $SF_2^+ + F$ was found to proceed efficiently. The two relevant reactions and their associated enthalpies are given in eqs 1 and 2

$$Sc^+ + SF_6 \rightarrow ScF_3 + SF_3^+ \qquad \Delta H_1 = -650 \text{ kJ mol}^{-1} \quad (1)$$

$$SF_3^+ \rightarrow SF_2^+ + F \qquad \Delta H_2 = 387 \text{ kJ mol}^{-1} \quad (2)$$

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The net enthalpy for eqs 1 + 2 is −263 kJ mol^{-1}. It is apparent from these results that under the low-pressure conditions of the ICR experiments, intrinsically endothermic fragmentation of excited nascent products occurred before collisional cooling could occur. It is also noted that the creation of two particles from one in the fragmentation process might be enhanced by a favorable entropy change. In the ICR study,[4] the SF$_2^+$ appeared as a primary product. From Table 1, it is seen that the reaction of U$^+$ with SF$_6$ to produce UF$_3$ and SF$_3^+$ is exothermic by 574 kJ mol^{-1}. Because reaction 2 is endothermic by 387 kJ mol^{-1}, it is not known whether some of the observed SF$_2^+$ is derived from autofragmentation of the SF$_3^+$ primary product prior to collisional de-excitation or whether it is formed directly as a product along with UF$_4$. Similar thermodynamic considerations indicate that the small amount of SF$^+$ detected could have resulted from the formation of UF$_4$ and subsequent fragmentation of the SF$_2^+$ product ion ($\Delta H[\text{SF}_2^+ \rightarrow \text{SF}^+ + \text{F}] = 369$ kJ mol^{-1}). It is emphasized that the observed reactions are subject to both thermodynamic and kinetic constraints. Only where a reaction can be definitively identified as resulting from an exothermic process is it feasible to derive thermodynamic information; for the U$^+$/SF$_6$ reactions, all of the observed products are in accord with established thermochemistry; unknown kinetic factors determine the product distributions. In all cases, the product distributions are clearly subject to indeterminate kinetic control; further experimental studies are required to directly address the possible role of the postulated phenomenon of prompt autofragmentation on the observed distributions.
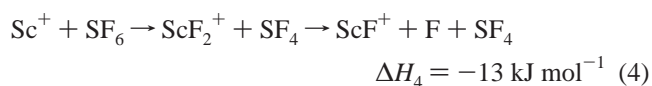
Because the formation of UF$_4^+$ + SF$_2$ is exothermic by 885 kJ mol^{-1} (Table 1) and the dissociation of UF$_4^+$ to UF$_3^+$ and F is endothermic by 381 kJ mol^{-1}, the reaction sequence 3 is exothermic by 504 kJ mol^{-1}

$$\text{U}^+ + \text{SF}_6 \rightarrow \text{UF}_4^+ + \text{SF}_2 \rightarrow \text{UF}_3^+ + \text{F} + \text{SF}_2$$
$$\Delta H_3 = -504 \text{ kJ mol}^{-1} \quad (3)$$

The corresponding autofragmentation processes for primary UF$_3^+$ to UF$_2^+$ and UF$_2^+$ to UF$^+$ are also exothermic, by 266 and 53 kJ mol^{-1}, respectively. Accordingly, it is thermodynamically possible that some of the observed UF$_n^+$ products result from autofragmentation of a UF$_{n+1}^+$ primary product, where $n = 1$, 2, and 3. The particularly favorable thermodynamics for the fragmentation of nascent UF$_4^+$ might account for its low abundance.

In contrast to the minuscule yield of UF$_4^+$, Jiao and Freiser[4] found that NbF$_4^+$ and TaF$_4^+$ were significant products of the reactions of the bare metal ions with SF$_6$. However, it is not clear that these tetrafluoride product ions resulted from primary reactions. This is because in the same context that NbF$_4^+$ and TaF$_4^+$ were reported as products, SF$_5^+$ was reported as a product for the reaction of Sc$^+$ with SF$_6$.[4] The more comprehensive study with Sc$^+$ [4] then revealed that SF$_5^+$ was produced only upon reaction of either primary ScF$^+$ or ScF$_2^+$ with a second SF$_6$ molecule.

Because autofragmentation of UF$_n^+$ is considered as a possibility, comparison is made with the scandium results of Jiao and Freiser.[4] It was shown there that ScF$_2^+$ was a primary product of the reaction of Sc$^+$ with SF$_6$, and no autofragmentation of ScF$_2^+$ was reported.[4] The sequence that would result in ScF$^+$ from autofragmentation of primary ScF$_2^+$ is shown in eq 4

$$\text{Sc}^+ + \text{SF}_6 \rightarrow \text{ScF}_2^+ + \text{SF}_4 \rightarrow \text{ScF}^+ + \text{F} + \text{SF}_4$$
$$\Delta H_4 = -13 \text{ kJ mol}^{-1} \quad (4)$$

On the basis of this very small exothermicity of the process given by eq 4, this would not be expected to be a significant pathway, consistent with the substantial yield of ScF$_2^+$ as a primary product.[4]

Reactions of lanthanide ions with pentamethylcyclopentadiene (HCp*, C$_{10}$H$_{16}$) were studied using a QIT-MS under very similar conditions to those employed in the present study.[9] Direct comparison was made with low-pressure ICR-MS studies of the same reactions.[20] It was concluded that when relatively high bath gas pressures were employed in the QIT, the nascent product ions were collisionally cooled to such an extent that autofragmentation did not occur. The HCp* products have many more degrees of freedom compared with the small fluoride ions produced in the reactions studied here. It would thus be expected that the HCp* products would be less prone to promptly fragment because there are many more vibrational modes over which the reaction energy can be distributed. In the HCp* studies, sufficiently low pressures could be employed in the QIT such that autofragmentation became significant. It is not known whether the pressure regime of the present SF$_6$ experiments was sufficiently high to suppress fragmentation.

Fragmentation processes that occur on a time scale of ∼10 ms or less would not be manifested in the QIT experimental results. Babcock and Streit[21] examined the reaction of He$^+$ with SF$_6$ and found that SF$_4^+$ and SF$_3^+$ fragmentation products appeared at a rate at least as fast as that of the SF$_5^+$ primary product, $k = 2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. This rate is approximately 1 order of magnitude greater than the rate of reaction of U$^+$ with SF$_6$; such rapid autofragmentation that occurs on a time scale much shorter than the formation of the initial products would not be discernible, and the fragmentation species would appear as a pseudo-first-order reaction product in the U$^+$/SF$_6$ experiments. To ascertain the effects of collisional de-excitation of high-energy UF$_n^+$ products, it would be of interest to carry out reactions of U$^+$ with SF$_6$ at substantially higher pressures (e.g., >0.1 Torr) than can be employed in the QIT. Under such relatively high-pressure conditions, it may be possible to produce UF$_4^+$ in abundance and perhaps even some UF$_5^+$.

Several important conclusions can be made regardless of the possibility of prompt autofragmentation. On the basis of the appearance of a small amount of UF$_4^+$ and a more substantial amount of SF$_2^+$, it is apparent that a U$^+$ ion is able to abstract four F atoms from SF$_6$ during the lifetime of a [U···SF$_6$]$^+$ encounter complex. This observation is particularly intriguing in view of the secondary reactions that are described below. Before dissociating into the ion and neutral fragments, the complex that results in UF$_4^+$ can be represented as [F$_4$U···SF$_2$]$^+$, in which four F atoms are bonded to the uranium metal center. Although the more exothermic dissociation channel for this complex should be to UF$_4^+$ and SF$_2$, the UF$_4^+$ peak was barely above the detection limit whereas the SF$_2^+$ peak was present at 7% abundance. One explanation for this result is that UF$_4^+$ was produced in greater yield but promptly fragmented to the abundant UF$_3^+$ product, as discussed above.

The appearance of a very small amount of SF$^+$ under single-collision conditions for the U$^+$/SF$_6$ reaction might be taken to indicate transfer of five F atoms. However, the dissociation of SF$_2^+$ to SF$^+$ requires 369 kJ mol^{-1}, and the formation of SF$_2^+$ and UF$_4$ is exothermic by 806 kJ mol^{-1}. Accordingly, the observed SF$^+$ may have resulted from prompt autofragmentation

TABLE 2: Products for the Reaction $UF^+ + SF_6^a$

ion	neutral[b]	branching ratio	ΔH_r^c (kJ mol^{-1})
UF_2^+	SF_5	5%	-161 ± 44
UF_3^+	SF_4	43%	-460 ± 34
UF_4^+	SF_3	2%	-502 ± 30
$(UF_5^+)^d$	$(SF_2)^d$	N. D.^{d}	-460 ± 33
$(SF^+)^d$	$(UF_6)^d$	N. D.^{d}	-475 ± 29
SF_2^+	UF_5	3%	-555 ± 32
SF_3^+	UF_4	45%	-525 ± 30
$(SF_4^+)^d$	$(UF_3)^d$	N. D.^{d}	37 ± 31

^{a} The measured reaction rate is $k = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; this corresponds to $k/k_{ADO} = 0.45$. ^{b} The neutral products were not determined and are inferred. ^{c} The thermodynamic data are from ref 17 for the UF_n^+, from ref 18 for the neutral UF_n, and from ref 4 for the SF_n^+ and SF_n. ^{d} The product ion was not detected, but the thermochemical values are included for comparison.

of some of the primary SF_2^+. It is the appearance of UF_4^+ that provides definitive evidence for the transfer of four F atoms. In this regard, it should be noted that the absence of UF_5^+ does not exclude the possibility of transfer of five F atoms.

Abstraction of F atoms from fluorocarbons by monopositive cations of electropositive metals (such as U and Sc) evidently occurs by a so-called "harpoon" mechanism.[22] According to this description, the M^+ does not activate a C—F bond but rather abstracts an F atom through an $[M\cdots F\cdots C-]^+$ type of intermediate. The postulated $[FM\cdots SF_{n-1}]^+$ intermediate[4] is long lived because of the bonding between the metal center and sulfur. In contrast, the bonding between the fluorine and the carbon atom in the $[M-F\cdots C-]^+$ intermediate in the final stage of the "harpoon" process should be weak because a strong metal—fluorine bond has been formed. As a result, prompt dissociation to the MF^+ ion and the $C^\bullet$ radical ion would be expected. In accord with this, the primary products of the reaction of lanthanide ions, Ln^+, are the monofluorides, LnF^+;[22] for the "harpoon" mechanism, it would appear that after transfer of a single F atom to a Ln^+, the ionic and neutral products promptly separate prior to further F atom transfer. In accord with the model proposed by Jiao and Freiser,[4] a long-lived $[U\cdots SF_6]^+$ intermediate apparently enables the transfer of up to at least four F atoms from sulfur to uranium. Evidently, two very different types of mechanisms occur in the reactions of metal cations with fluorocarbons and SF_6.

Reactions of UF^+, UF_2^+, and UF_3^+ with SF_6. The UF^+ ion was found to be as reactive with SF_6 as is bare U^+, exhibiting a reaction rate $k = 2.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to an efficiency $k/k_{ADO} = 0.45$. The product distributions and reaction enthalpies for reactions of UF^+ with SF_6 are given in Table 2. The high reaction efficiency of UF^+ implies that a long-lived $[FU\cdots SF_6]^+$ complex is formed, presumably involving an interaction of the uranium metal center with the SF_6 molecule in a manner similar to that between bare U^+ and SF_6.[4]
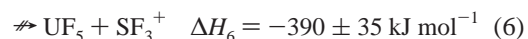
All of the reactions with UF^+ shown in Table 2 are exothermic, and the reactivity pattern is qualitatively similar to that of U^+. In both cases, the two dominant processes correspond to the transfer of two or three F atoms from SF_6 to the uranium metal center. The transfer of two F atoms produces UF_2^+ from the reaction with U^+ and produces UF_3^+ from the reaction with UF^+; both of these uranium fluoride ions are the thermodynamically favored products (SF_4^+ is not). As expected from thermodynamic considerations (Table 1), the transfer of three F atoms to U^+, in a presumed $[F_3U\cdots SF_3]^+$ intermediate, results in mostly UF_3^+ and a smaller amount of SF_3^+. In the case of UF^+, the transfer of three F atoms to give a $[F_4U\cdots SF_3]^+$

intermediate evidently produces primarily SF_3^+ and only a small amount of UF_4^+. Although the formation of SF_3^+ is slightly more thermodynamically favored over UF_4^+ according to the values given in Table 2 (note the large uncertainties), both are substantially exothermic and the very low yield of UF_4^+ is notable. One possible explanation for the dearth of UF_4^+ is its autodissociation to $UF_3^+ + F$, which requires 381 kJ mol^{-1}. A related explanation is that the kinetics for the observed dominant channel are more favorable. The ionization energy of SF_3 of 9.30 eV is slightly lower than that of UF_4 (IE = 9.51 eV). Therefore, the SF_3^+ fragmentation channel should be favored according to Stevenson's rule, whereby an excited-state molecular ion is predicted to dissociate into an R_1^+ ion and an R_2 neutral, with $IE[R_1] < IE[R_2]$.[23] However, it is surprising that such a small difference in ionization energies should so substantially favor the only slightly lower energy channel. It should be noted that this interpretation in the context of Stevenson's rule is essentially equivalent to the thermodynamic considerations given above, whereby the slightly more exothermic exit channel is favored. In a case such as this, where the exothermicities of the two exit channels are nearly the same, it might be expected that other aspects of the reaction energy surface would determine the dominant product ion.

The number of F atoms transferred in the U^+/SF_6 and UF^+/SF_6 reactions can be compared. As with bare U^+, it would appear that the maximum number of F atoms transferred from SF_6 to UF^+ is four, producing a small amount of SF_2^+. However, the reaction that produces the dominant SF_3^+ product is exothermic by 525 kJ mol^{-1}, and the dissociation of SF_3^+ to SF_2^+ and F requires only 387 kJ mol^{-1}. Accordingly, the observed SF_2^+ may be a result of autofragmentation of the primary SF_3^+ product. If the transfer of four F atoms does indeed occur, the SF_2^+ exit channel is thermodynamically more favorable than the UF_5^+ channel so that the absence of UF_5^+ does not indicate the absence of a $[F_5U\cdots SF_2]^+$ intermediate. Although the transfer of five F atoms to give $SF^+ + UF_6$ is substantially exothermic, this product ion was not detected, suggesting that the transfer of five F atoms does not proceed efficiently. The formation of UF_6 would require transfer of another F atom in an $[F_5U\cdots SF_2]^+$ intermediate prior to dissociation. As uranium can form only six covalent bonds, such a process would seem unlikely.

The UF_2^+ and UF_3^+ primary products were also isolated and reacted with SF_6. In both cases, no reaction was observed to within the detection limit of $k/k_{ADO} < 0.01$.

Whereas both U^+ and UF^+ reacted with SF_6 with efficiencies $k/k_{ADO} \approx 0.4$, UF_2^+ was comparatively inert. In analogy with UF^+, the two most thermodynamically favorable reaction channels for UF_2^+ are the transfer of two or three F atoms from SF_6; these reactions are given by eqs 5 and 6, where "X" denotes that these reactions do not occur

$$UF_2^+ + SF_6 \nrightarrow UF_4^+ + SF_4 \quad \Delta H_5 = -289 \pm 34 \text{ kJ mol}^{-1} \quad (5)$$

$$\nrightarrow UF_5 + SF_3^+ \quad \Delta H_6 = -390 \pm 35 \text{ kJ mol}^{-1} \quad (6)$$

By comparison of the enthalpies for eqs 5 and 6 with those for the analogous formation of UF_3^+ and of SF_3^+ from the reaction with UF^+ (Table 2), it is seen that the corresponding reactions for transfer of the same number of F atoms to UF_2^+ are less exothermic by $\sim$171 and $\sim$135 kJ mol^{-1}, respectively. As the degree of fluorination of the U^+ ion increases, the thermodynamic driving force for transfer of additional F atoms from SF_6 to the uranium metal center diminishes. This is illustrated by comparison of the enthalpies in Tables 1 and 2 for the transfer

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of a given number of F atoms and essentially reflects the decrease in sequential U−F bond energies with increasing uranium oxidation state, e.g., BDE[U^+−F] = 668 kJ mol^{-1} vs BDE[FU^+−F] = 552 kJ mol^{-1}.

Reactions 5 and 6 are sufficiently exothermic that their nonappearance indicates kinetic barriers. It would appear that a long-lived [$F_2U\cdots SF_6$]$^+$ complex, in which F-atom transfer can occur, is not formed. Whereas the metal center in F−U^+ can evidently efficiently complex with SF_6, that in F−U^+−F cannot. The addition of the second fluorine atom to the uranium metal center would seem to prevent its facile complexation to SF_6. It was reported[4] that ScF_2^+ rather efficiently reacted with SF_6 to produce ScF_3 and SF_5^+. However, this reaction of ScF_2^+ with SF_6 is endothermic by 113 kJ mol^{-1}. As there is not a significant entropic thermodynamic driving force for this reaction (two reactant and two product particles), it can be assumed that this reaction occurred only because the primary ScF_2^+ reactant ion was in an excited state. Accordingly, direct comparison of the ScF_2^+ secondary reaction with that of the reactions of isolated and collisionally cooled UF_2^+ is not valid. Two possible effects could account for the inert character of UF_2^+. The first is that the uranium center cannot approach the sulfur center due to the repulsive interaction between the F atoms on a $F^{\delta-}$−$U^{2\delta+}$−$F^{\delta-}$ ion ({$2\delta+$} − {$2\delta-$} = +1) and the F atoms on SF_6. Whereas the uranium center in [F−U]$^+$ should be able to approach the SF_6 molecule with little interaction between its sole F atom and the F atoms of SF_6, such an approach between the two reactants would not be the case for an [F−U−F]$^+$ ion that can be assumed to be approximately linear due to the repulsive interaction between the electronegative fluoride ligands. A plausible, but perhaps less likely, explanation for the inert character of UF_2^+ is that the second U−F bond upon proceeding from UF^+ to UF_2^+ employs the particular valence 6d orbital that is of suitable symmetry for interaction with the SF_6 molecule.

As expected, F-atom-transfer reactions become even less thermodynamically favorable for UF_3^+ reacting with SF_6. The most exothermic reaction is the transfer of three F atoms and an electron to produce SF_3^+ and UF_6, for which $\Delta H_{rxn} = -156$ kJ mol^{-1}. Although significantly exothermic, the thermochemistry for this reaction is less favorable than for other observed reactions. Perhaps more importantly, as UF_2^+ does not form a long-lived intermediate complex with SF_6, it would be expected that the more protected metal center in UF_3^+ would very inefficiently associate with SF_6 to form a long-lived [$F_3U\cdots SF_6$]$^+$ intermediate. As with UF_2^+, the repulsive interaction between the F atoms on UF_3^+ and those on SF_6 would seem the most likely explanation for nonreactivity of the trifluoride ion.

The enthalpy for the reaction of UF_3^+ with SF_6 to produce UF_4^+ and SF_5 is 10 ± 19 kJ mol^{-1}; this nearly thermoneutral reaction would probably not be observed at moderate temperatures even in the absence of a kinetic barrier. In contrast, the formation of UF_4^+ from the reaction of U^+ with SF_6 is exothermic by 885 kJ mol^{-1}. The bond energies (in kJ mol^{-1}) for the uranium fluoride ions are as follows: BDE[U^+−F] = 668 ± 29; BDE[FU^+−F] = 552 ± 44; BDE[F_2U^+−F] = 523 ± 38; BDE[F_3U^+−F] = 381 ± 19; BDE[F_4U^+−F] = 243 ± 17; and BDE[F_5U^+−F] = 26 ± 11. The substantial net exothemicity of the formation of UF_4^+ from the reaction of U^+ with SF_6 is a result of the formation of the initial strong U−F bonds. In contrast to UF_n^+, the BDE[F_nS−F] vary relatively little and irregularly for n = 1−6, from a minimum of 224 kJ mol^{-1} for n = 4 to a maximum of 391 kJ mol^{-1} for n = 5. By

beginning with a partially fluorinated uranium metal ion, the driving force for transfer of one or more F atoms from SF_6 diminishes. The key to efficient fluorination is to begin with bare U^+ or UF^+, as both the kinetics and thermodynamics become unfavorable when starting with UF_2^+ or UF_3^+. It can be presumed that both UF_4^+ and UF_5^+ would be inert toward SF_6.
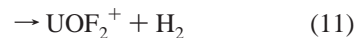
Reactions of UF^+, UF_2^+, and UF_3^+ with H_2O. As the results for the reaction of U^+ with H_2O concur with those recently carried out in this laboratory under similar conditions,[10] they are not discussed in detail here. The U^+/H_2O reaction rate, $k = 9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, corresponds to $k/k_{ADO} = 0.5$, and the product branching ratio was 90% UO^+ and 10% UOH^+.

Three products were observed for the reaction of UF^+ with H_2O, as shown by reactions 7, 8, and 9

$$UF^+ + H_2O \rightarrow UOH^+ + HF \tag{7}$$

$$\rightarrow UOF^+ + H_2 \tag{8}$$

$$\rightarrow UOHF^+ + H \tag{9}$$
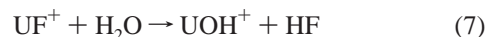
The rate of reaction of UF^+ with H_2O is 2.9×10^{-10} cm^3 molecule^{-1} s^{-1} ($k/k_{ADO} = 0.17$), and the branching ratio is 13% for 7 ($k_7/k_{7/ADO} = 0.02$), 57% for 8 ($k_8/k_{8/ADO} = 0.10$), and 31% for 9 ($k_9/k_{9/ADO} = 0.05$). Reaction 7 is particularly intriguing as it corresponds to exchanging a hydroxyl group for an F atom (F → OH) exchange.[24] The similarity of these two ligands has been demonstrated in many types of chemistry.[25] For this exchange reaction to be exothermic, then $\Delta H_f[UOH^+]$ < 570 ± 29 kJ mol^{-1} and BDE[U^+−OH] > 598 ± 29 kJ mol^{-1}; for comparison, BDE[U^+−F] = 668 ± 29 kJ mol^{-1}. Armentrout and Beauchamp[26] determined that $\Delta H_f[UOH^+]$ is in the range of 372−661 kJ mol^{-1}; the present results reduce the upper limit to 599 kJ mol^{-1}. Reactions 8 and 9 are directly analogous to the reported reactions of U^+ with H_2O to produce UO^+ and UOH^+.[10] A notable difference between U^+ and UF^+ is the much lower oxidation reaction efficiency for the latter; also, the hydroxide product is more prevalent for UF^+ compared with U^+. Both of these differences can be attributed to the higher oxidation state of uranium in the UF^+ reactant compared with the U^+ reactant.

The UF_2^+ ion reacted with H_2O at a rate $k = 9.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{ADO} = 0.05$. The relative contributions of the three reactions 10, 11, and 12 were 45% ($k_{10}/k_{10/ADO} = 0.02$), 27% ($k_{11}/k_{11/ADO} = 0.01$), and 28% ($k_{12}/k_{12/ADO} = 0.01$)

$$UF_2^+ + H_2O \rightarrow UOHF^+ + HF \tag{10}$$

$$\rightarrow UOF_2^+ + H_2 \tag{11}$$

$$\rightarrow UOHF_2^+ + H \tag{12}$$

The results are entirely analogous to those for UF^+. Reaction 10 corresponds to the exchange of the fluoride and hydroxyl group, as occurs with UF^+. The F → OH exchange efficiencies (k/k_{ADO}) are essentially the same for UF^+ and UF_2^+. A secondary reaction of $UOHF^+$ with H_2O at long reaction times produces $U(OH)_2^+$ in which complete substitution of hydroxyl groups for fluorine atoms has occurred. The exothermic occurrence of 10 indicates that $\Delta H_f[UOHF^+]$ < 97 ± 29 kJ mol^{-1} and BDE[FU^+−OH] > 482 ± 29 kJ mol^{-1}; this compares with BDE[FU^+−F] = 552 ± 44 kJ mol^{-1}. As with both bare U^+ and UF^+, UF_2^+ reacts with water to produce an oxide and a

hydroxide according to eqs 11 and 12. The very low efficiencies of these two processes and the equality between the two branching ratios (vs 90% UO^+ and 10% UOH^+ from the reaction of U^+ with H_2O) can be taken to reflect the greater difficulty in further oxidizing UF_2^+, as compared with U^+ and UF^+.

Only one reaction was observed between UF_3^+ and H_2O, producing $UOHF_2^+$ and HF. This reaction occurred at a rate $k = 1.9 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{ADO} = 1.15$. This exchange reaction indicates that ΔH_f-$[UOHF_2^+] < -347 \pm 18$ kJ mol^{-1} and BDE$[F_2U^+-OH] > 453 \pm 38$ kJ mol^{-1}. This latter value compares with BDE-$[F_2U^+-F] = 523 \pm 38$ kJ mol^{-1}. At longer reaction times, a secondary product, $U(OH)_2F^+$, indicates exchange of a second F atom for a hydroxyl group. The reaction between H_2O and UF_3^+ proceeds at essentially the collision limit, in contrast to the much less efficient reactions of UF^+ and UF_2^+ with H_2O. Because the thermodynamic driving force for F → OH exchange would not be expected to be appreciably greater in the case of UF_3^+, the faster reaction rate is attributed to a kinetic effect. As the number of F atoms around the uranium metal center increases, the efficiency for exchange might generally be expected to increase, if only as a result of statistical considerations. However, the low exchange efficiency is essentially the same for UF^+ and UF_2^+ ($k/k_{ADO} = 0.02$) and then increases to $k/k_{ADO} \approx 1$ for UF_3^+. It would appear that the association of an H and F atom and subsequent elimination of HF in the $[F_3U\cdots OH_2]^+$ complex is greatly enhanced by the addition of the third F atom to the system. The greater propensity for exchange in the case of UF_3^+ may be due to the closer approach between an H and F atom in the $[F_3U\cdots OH_2]^+$ intermediate, which would enhance the HF elimination process. Another consideration may be that the greater positive charge in the higher fluoride favors this particular reaction pathway. It is notable that UF^+ is highly reactive with SF_6 while UF_3^+ is inert. In contrast, UF_3^+ is ~5 times more reactive with H_2O than is UF^+. It would appear that the oxygen atom can complex to the uranium metal center in UF_3^+, whereas steric hindrance precludes association of the metal center in UF_3^+ to the sulfur center in SF_6.

The nonobservation of oxidation of UF_3^+ by H_2O to UOF_3^+ or $U(OH)F_3^+$, can be attributed to two factors. First, the F → OH exchange reaction occurs so rapidly that oxidation cannot effectively compete. Second, as the valence state of uranium in UF_3^+ is greater than in the lower fluorides, oxidation would be expected to be intrinsically less efficient. This latter effect was seen in the decreasing oxidation reaction rates by H_2O upon proceeding from U^+ to UF^+ to UF_2^+.

Reactions of UO^+ and UOH^+ with SF_6. Like UF^+, both UO^+ and $U(OH)^+$ have only one ligand bonded to the metal center, where a hydroxide structure is assumed for the latter ion. As UF^+ exhibited substantial reactivity with SF_6, it might also be expected that UO^+ and UOH^+ would be reactive, as was found to be the case. It is also noted that UO_2^+ and UOF^+ were inert toward SF_6 within the detection limit of $k/k_{ADO} < 0.01$; this is analogous to the inert character of UF_2^+ where the addition of a second ligand evidently precludes formation of a long-lived intermediate complex ion with SF_6. The reactive nature of UOH^+ and inert character of UOF^+ are consistent with the presumed structures as a hydroxide, $\{U-OH\}^+$, and an oxide fluoride, $\{O-U-F\}^+$. The similarly inert behaviors of UF_2^+, UO_2^+, and UOF^+ support the hypothesis that it is a repulsive interaction between the electronegative ligands bonded to uranium that prevents association and reaction with SF_6.

The reaction of UO^+ with SF_6 proceeded at a rate $k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{ADO} = 0.19$. As expected, a $[OU\cdots SF_6]^+$ intermediate is sufficiently long lived that extensive atom transfer between the uranium and sulfur centers occurs prior to dissociation. The seven ion/neutral products and their branching ratios are as follows: 56% $\{SF_3^+ + UOF_3\}$; 25% $\{UOF_2^+ + SF_4\}$; 8% $\{UOF^+ + SF_5\}$; 7% $\{UF_2^+ + SOF_4\}$; 3% $\{UF_3^+ + SOF_3\}$; <1% $\{SF_2^+ + UOF_4\}$; and <1% $\{SOF^+ + UF_5\}$. Enthalpies cannot be derived for the observed reactions as in each case the thermochemistry is unknown for one of the two products. The prevalent reactions involve the transfer of F atoms (and an electron in some cases) from SF_6 to UO^+. In close analogy with the behavior of both U^+ and UF^+, the two dominant processes involved the transfer of either two or three F atoms: $\{UOF_2^+ + SF_4\}$ and $\{SF_3^+ + UOF_3\}$. The minor reaction channels, $\{UF_2^+ + SOF_4\}$, $\{UF_3^+ + SOF_3\}$, and $\{SOF^+ + UF_5\}$, are notable in that the strong uranium−oxygen bond is cleaved and the O atom is evidently transferred to the nonmetal sulfur center. With UO^+, it would appear that up to five F atoms transferred from SF_6 to the uranium metal center, with a concomitant transfer of the O atom to the sulfur to produce $\{SOF^+ + UF_5\}$. Although no SOF_2^+ was detected, it is feasible that the small amount of SOF^+ instead derived from efficient autodissociation of an excited-state SOF_2^+ primary product.

The reaction of UOH^+ with SF_6 proceeded at a rate $k = 2.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which corresponds to $k/k_{ADO} = 0.33$. The two main product channels were 59% $\{UOF^+ + (HSF_5)\}$ and 41% $\{SF_3^+ + UOHF_3\}$; the neutral "HSF_5" product could reasonably be either $\{HF + SF_4\}$ or the SHF_5 molecule. Very small (<1%) yields of UOF_2^+ and SF_2^+ product ions were also detected. The $\{SF_3^+ + UOHF_3\}$ reaction channel is analogous to the formation of $\{SF_3^+ + UF_4\}$ from the reaction of UF^+ with SF_6; again, the similarity of the hydroxide and fluoride ligands is manifested. The dominant $\{UOF^+ + (HSF_5)\}$ reaction channel is unique and can be rationalized on thermodynamic grounds. If the neutral products are SF_4 and HF, then the net bonding in the $\{F-U-O\}^+$ product would have to be at least 185 kJ mol^{-1} stronger than in the $\{U-O-H\}^+$ reactant for this process to be exothermic (the formation of two neutral molecules should be entropically favorable for this reaction, although this factor is not quantitatively included in the present discussion). This is almost certainly the case, according to the following reasoning. It can be assumed that the U−OH and U−F bonds are of comparable strength and essentially cancel one another in the reactant vs product net bonding. It can be confidently assumed that the formed U=O double bond is >200 kJ mol^{-1} stronger than the broken UO−H bond; for comparison, BDE$[U^+-O] = 796$ kJ mol^{-1} vs BDE$[O-H] = 428$ kJ mol^{-1} (i.e., ΔBDE = 368 kJ mol^{-1} > 200 kJ mol^{-1}). If the SHF_5 neutral product is a more exothermic exit channel than is $\{HF + SF_4\}$, then the thermodynamics would be even more favorable.

CID. In contrast to dissociation induced by a single high-energy ion−molecule collision, CID in the QIT corresponds to relatively gradual "heating" of a molecular ion during the course of many sequential collisions, and can accordingly be modeled as a quasithermal process.[27] It has been demonstrated that excitation of a molecular ion in a QIT using small excitation amplitudes ("threshold resonance excitation") generally results in fragmentation by the lowest energy dissociation channel absent substantial kinetic barriers.[28] By increasing the excitation voltage applied to the parent ion, higher-energy fragmentation channels can be accessed.[29]

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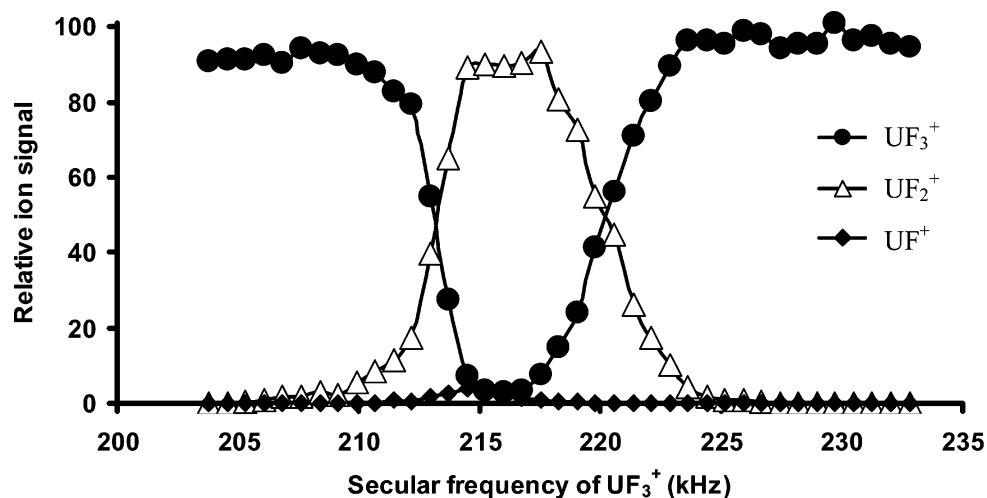
Figure 3. CID of the isolated UF_3^+ product. The UF_3^+ ion comes into resonant excitation at a secular frequency of 216 kHz. This CID plot corresponds to a relatively large excitation amplitude so that almost complete dissociation occurs on resonance, where the higher-energy UF^+ dissociation channel is observed. Off-resonance excitation represents lower-energy excitation conditions, whereby the only CID channel is the lower-energy single F loss to give UF_2^+ (e.g., at 222 kHz).

In Figure 3 are shown the results for QIT CID of UF_3^+. At low excitation voltages, or slightly off-resonance excitation (e.g., 212 kHz), loss of a single F atom to give UF_2^+ is the dominant process, with a negligible contribution from loss of two F atoms to give UF^+. As the excitation voltage becomes on resonant with the UF_3^+ parent ion at ~216 kHz, the latter high-energy channel becomes increasingly significant though still minor. Similarly, CID of UF_2^+ using on-resonance low excitation voltages results in almost exclusively UF^+, while increasing the voltage enhances the amount of the high-energy U^+ product. In the case of the loss of two fluorine atoms, the formation of F_2 as the neutral product would be the lowest-energy pathway. Because the F–F bond energy is only 158 kJ mol^{-1} whereas BDE[FU^+–F] ≈ 552 kJ mol^{-1} and BDE[U^+–F] ≈ 668 kJ mol^{-1}, the loss of a single F atom should be the lowest-energy channel for both UF_3^+ and UF_2^+, as was observed.

The enhancement of higher energy CID processes with increasing excitation voltage can be used to qualitatively assess relative bond strengths of different ligands bonded to a metal center. In UOF_2^+, for example, the U=O double bond is expected to be significantly stronger than the U–F single bonds. Accordingly, it was observed that low-energy QIT CID of UOF_2^+ results primarily in UOF^+. (Because BDE[O–F] is only 219 kJ mol^{-1}, OF elimination is not a low-energy fragmentation pathway.) An increase in the excitation energy results in a significant contribution of O loss to give the high-energy UF_2^+ product.

A more complex fragmentation process was observed for $UOHF_2^+$. The structure of this ion is presumed to be a fluoride hydroxide, $U(OH)F_2^+$, rather than a fluoride hydride, UOF_2H^+, based on analogy with OH bonding to other electropositive metal ions such as Ti^+. Clemmer et al.[24] presented a convincing argument for a Ti^+–OH structure rather than a H–Ti^+=O structure, and this conclusion has been substantiated by theory.[30] High-energy single-collision CID of $U(OH)F_2^+$ might be expected to result in loss of a single ligand. Under QIT CID conditions, it was found that the dominant low-energy channel produced UOF^+, which corresponds to elimination of HF according to eq 13

$$U(OH)F_2^+ \rightarrow UOF^+ + HF \qquad (13)$$
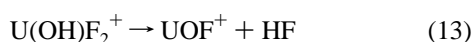
This illustrates the thermal nature of QIT CID whereby a low-

energy decomposition channel that presumably involves the cleavage of two bonds and formation of a neutral molecule is dominant. For purposes of estimating the thermochemistry for reaction 13, it is considered that the rupture of a F(OH)U^+–F and a F_2U^+–OH bond each requires ~520 kJ/mol, the same as the F_2U^+–F bond energy; for comparison, BDE[Ti^+–OH] = 473 kJ mol^{-1}.[31] The net enthalpy for reaction 13 is then estimated as: $\Delta H_{13} \approx$ {BDE[F(OH)U^+–F] ≈ 520 kJ mol^{-1}} + {BDE[F_2U^+–OH] ≈ 520 kJ mol^{-1}} + {BDE[O–H] = 428 kJ mol^{-1}]} − {BDE[U^+=O] ≈ 800 kJ mol^{-1}]} − {BDE[H–F] = 570 kJ mol^{-1}} ≈ 100 kJ/mol. It is evident that the decomposition according to reaction 13 is expected to be lower in energy than would be the loss of any individual ligand. The loss of HF is in accord with the presumed hydroxide, rather than oxide hydride, structure as BDE[U^+–H] is only 284 kJ mol^{-1},[32] and H loss might be expected to be a low-energy fragmentation channel for a hydride.

The UOH^+ product ion was also subjected to CID. The low-energy fragmentation channel corresponded to H elimination to give UO^+. At higher excitation energies, loss of OH was an increasingly significant minor secondary fragmentation channel. The structure of UOH^+ might initially be assumed to correspond to a hydroxide, U^+–OH; the alternative structure is the oxide hydride, O=U^+–H. The observed H elimination would certainly be the lowest-energy fragmentation channel for the oxide hydride because BDE[U^+–H] = 284 kJ mol^{-1}.[32] The enthalpy of fragmentation of U^+–OH to {[U^+=O] + H} can be estimated as {BDE[U^+–(OH)] ≈ BDE[U^+–F] ≈ 670 kJ mol^{-1}} + {BDE[O–H] = 428 kJ mol^{-1}} − {BDE[U^+=O] ≈ 800 kJ mol^{-1}} ≈ 300 kJ mol^{-1}. This thermodynamic assessment suggests that H loss from the two feasible structures should both require ~300 kJ mol^{-1} and that this would be the lowest-energy dissociation channel for both the hydride oxide and hydroxide atomic connectivities. For this species, the CID results do not illuminate the structure. However, as noted above, the UOH^+ hydroxide structure is assumed based on analogy with other systems.[24]

Summary

The bare U^+ ion reacted with SF_6 with a reaction rate efficiency $k/k_{ADO} = 0.37$. This substantial reactivity is in accord with the model for SF_6 activation by transition-metal ions put forth by Jiao and Freiser[4] and the availability of several vacant

valence 6d orbitals for U^+. The two dominant products, UF_2^+ and UF_3^+, correspond to the transfer of two and three F atoms from the sulfur center to uranium in the proposed $[U\cdots SF_6]^+$ reaction intermediate. The third most abundant product ion was SF_3^+ and all of the observed products can be formed by exothermic processes. The small yield of UF_4^+ provided evidence for the transfer of up to four F atoms. The possibility of autofragmentation of primary products on the millisecond time scale of the experiments implies that the measured branching ratios may not accurately reflect the initial product distributions. The present experiments provide no direct evidence for such prompt autofragmentation, but the results are presented with this caveat.

It was found that UF^+ is as reactive with SF_6 as is bare U^+ and exhibits a similar reactivity pattern, i.e., transfer of two or three F atoms to U^+. The main difference was that SF_3^+, rather than UF_4^+, was the primary product from the three F atom transfer; this apparent discrepancy can be rationalized based on the thermodynamics of the system. Both UF_2^+ and UF_3^+ are inert toward SF_6 to within the detection limit. This is attributed to repulsion between the electronegative ligands and SF_6. Whereas UF^+ can form a stable intermediate complex, $[FU\cdots SF_6]^+$, the addition of a second F atom to the uranium metal center evidently prevents effective association with SF_6. In accord with this interpretation, neither UO_2^+ nor UOF^+ reacted with SF_6.

Both UF^+ and UF_2^+ reacted with H_2O with moderate efficiencies. The two channels were $F \rightarrow OH$ exchange and oxidation by addition of either OH or O to the uranium fluoride cation. In contrast, UF_3 reacted with H_2O near the collisional limit and the sole channel was $F \rightarrow OH$ exchange to produce the hydroxide fluoride, $UOHF_2^+$ (+ neutral HF). The efficient exchange for UF_3^+ indicates that H_2O, unlike SF_6, can complex to this ion. Also, the presence of three, rather than one or two, F atoms evidently greatly enhances the probability for association of an H and F atom in the reaction intermediate, $[F_3U\cdots OH_2]^+$, and subsequent HF elimination.

In an analogous manner to UF^+, UO^+ reacted with SF_6 ($k/k_{ADO} = 0.19$) primarily by transfer of two or three F atoms, UOF_2^+ from UO^+ corresponds to UF_3^+ from UF^+; SF_3^+ was a major product for both the UO^+ and UF^+ reactions. Minor channels with UO^+ correspond to the cleavage of the strong uranium–oxygen bond and transfer of the O atom to the sulfur center. In accord with the similarities of the F and OH ligands, UOH^+ reacted with SF_6 with a roughly comparable efficiency ($k/k_{ADO} = 0.33$) to that of UF^+ ($k/k_{ADO} = 0.45$). One of the two main products for UOH^+/SF_6 was SF_3^+, in an analogy with the same product from the UF^+/SF_6 reaction. Because UF_3^+ was the other main product for UF^+, it might be expected that UOH^+ would correspondingly produce abundant $UOHF_2^+$. This latter product was not detected, and instead the dominant product was UOF^+. This distinctive reaction was rationalized on the availability of additional reaction pathways when OH is substituted for F.

CID in the QIT was manifested as a quasithermal process whereby the lowest energy dissociation channel predominates near threshold fragmentation energies. Thus, UF_2^+ and UF_3^+ lose a single F atom at low energies, with the loss of two F atoms increasing in significance at higher excitation energies. A particularly interesting example was CID of the hydroxide fluoride ion, $U(OH)F_2^+$, whereby low-energy CID occurs via rearrangement and HF elimination rather than cleavage of a single uranium–ligand bond.

In summary, the reaction of bare U^+ with SF_6 suggests that uranium is behaving as a typical d-block transition element that has readily accessible high valence states. The reactions of ligated uranium ions with SF_6 have served to illuminate such effects as the drastic inhibition of reactivity upon proceeding from one to two ligands attached to the metal center, this can be presumed to be a general phenomenon. The reaction of UF_3^+ with H_2O was particularly interesting as a demonstration of facile $F \rightarrow OH$ exchange. Finally, QIT CID of selected uranium molecular ions illustrated this as a quasithermal process that can result in either simple bond cleavage or more complex fragmentation processes.

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