

Properties and reactions of uranium hexafluoride by ion cyclotron resonance spectroscopy

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Ion cyclotron resonance spectroscopy has been employed to investigate the formation and reactions of both positive and negative ions derived from uranium hexafluoride. Positive ion reactions are dominated by processes whereby the various UF_n^+ fragments ($n = 1-3,5$) react to form UF_4^+ , and by clustering of UF_n^+ ($n = 3-5$) with UF_6 . Trapped negative ion studies indicate that UF_6^- can be generated both by electron attachment, which is unusually slow, and by electron transfer from other species, including UF_5^- , SF_6^- , and Cl^- . In addition, UF_7^- is observed, both in UF_6 alone, and in higher abundance when fluoride donors such as SF_5^- are present. Certain limits on the thermochemical properties of ions derived from UF_6 have been determined, and a high electron affinity is indicated for UF_6 . The species UF_6^- is especially stable and much less reactive than SF_6^- in mixtures with acidic neutrals. The propensity of negative ions derived from UF_6 to form clusters is substantially less than observed for positive ions.

I. INTRODUCTION

Despite the technological importance of such information, very little is known about the behavior of volatile uranium compounds in ionized gases. It is of interest from a historical point of view that one of the earliest ion cyclotron resonance experiments was conducted with uranium plasmas during the Manhattan Project in an attempt to develop a high throughput electromagnetic isotope separation process.¹ This effort was aborted when it was decided that random electric fields in the plasma interfered with the resonance acceleration of charged particles at high ion densities. Information on the behavior of uranium compounds in ionized gases is also required to better understand phenomena associated with gas core reactors, where research has progressed to the point of achieving a critical state for a gaseous UF_6 core configuration.^{2,3} Gas core reactors are considered to have unique applications in nuclear rocket propulsion systems and in the generation of electric power using magnetohydrodynamic methods to directly extract current from the high temperature ionized gas. Experiments in conjunction with the development of gas core reactors have demonstrated that free electrons are replaced by negative ions when UF_6 is added to an argon ion plasma.⁴ While the negative ion species were not investigated, the results have important consequences since the electromagnetic properties of a plasma are greatly modified when free electrons are replaced by negative ions.

More specific results relating to the behavior of UF_6 in ionized gases have been reported by Stockdale, Compton, and Schweinler.⁵ Unlike SF_6 and other hexafluoride molecules, UF_6 is not reported to attach low energy electrons to form UF_6^- , in the reaction⁵



The fragment ion UF_5^- is formed in the dissociative electron capture process 2,



which has a threshold at 0.9 eV with the cross section rising to a maximum at 2.1 eV electron energy.⁵ The

ion UF_6^- is observed in UF_6 alone and in a mixture of SF_6 with UF_6 , it being reported that this species results from the electron transfer processes



and



respectively. In addition to mass spectrometric investigations of positive ion formation in UF_6 ,^{6,7} other recent studies of processes involving ions containing uranium include determination of uranium ion reactions and mobilities in several gases⁸ and elucidation of chemi-ionization processes resulting from the reaction of uranium atoms with O and O_2 .⁹

In this paper we report an investigation of the formation and reactions of positive and negative ions in UF_6 alone and in mixtures with other gases. This work represents a continuation of our efforts in applying ion cyclotron resonance techniques to determine the properties and reactions of inorganic molecules in general¹⁰⁻¹⁶ and hexafluorides in particular.¹⁴⁻¹⁶

II. EXPERIMENTAL

UF_6 was obtained from Varlacoid Chemical Company and distilled under vacuum into a stainless steel sampling cylinder. This was attached directly to the all stainless steel inlet system of the ion cyclotron resonance spectrometer. The pressure in the inlet system was maintained at 18 torr by immersing the UF_6 cylinder in an ice bath at 0 °C.¹⁷ When UF_6 was first admitted to the spectrometer, impurities dominated the observed positive ion mass spectrum. Presumably these resulted from interaction of UF_6 with trace quantities of residual organics in the inlet system. After several hours of using UF_6 in the instrument, the impurities disappeared and only ions derived from UF_6 were observed. Difficulties due to decomposition of UF_6 on heated surfaces were encountered and a green deposit, presumably UF_4 , was formed on filament mounts. Filaments made from Rhenium wire and ribbon operated satisfactorily in the presence of UF_6 at pressures up to 10^{-3} torr. The ICR spectrometer used in these studies utilizes a 15 in. magnet system and was built

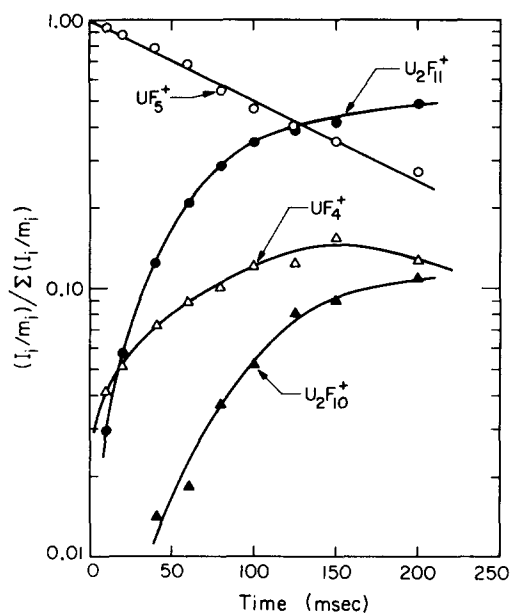


FIG. 1. Temporal variation of positive ion concentrations in UF_6 following a 10 msec electron beam pulse at 16 eV and 3.5×10^{-6} torr.

in Caltech shops. This instrument and ICR techniques have been described in detail elsewhere.^{11,18,19} The Schulz-Phelp gauge used for pressure measurements behaved erratically, presumably due to the problem noted above with decomposition of UF_6 . In addition, the MKS Instruments Model 90H-1 Capacitance Manometer used to calibrate the Schulz-Phelp gauge exhibited a higher than normal drift rate with UF_6 . With these difficulties accurate pressure measurements were not possible and pressures and rate constants quoted below are subject to considerable error. They are probably correct only to within a factor of two.

All other chemicals were readily available from commercial sources and were used as supplied except for removal of noncondensable impurities at liquid nitrogen temperatures.

III. RESULTS

A. Positive ion chemistry

The ICR mass spectrum of UF_6 recorded at 70 eV is presented in Table I and compared to published spectra recorded on a magnetic sector instrument.⁷ The spectra are nearly identical, with slightly less fragmentation being observed in the ICR spectrum. As the electron energy is lowered, the abundance of the UF_n^+ fragment ions decreases in accordance with appearance potentials which decrease regularly with increasing n up to 5.⁶ The abundance of UF_6^+ relative to UF_5^+ increases only slightly at the lowest electron energies for which a spectrum could be recorded.

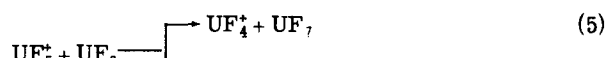
At 16 eV only the fragment ion UF_5^+ is present in abundance. The variation of ion concentrations with time at a pressure of 3.5×10^{-6} torr and 16 eV electron energy is shown in Fig. 1. The two reactions

TABLE I. Mass spectrum of UF_6 at 70 eV electron energy.

Species ^a	Relative abundance	
	ICR	Magnetic sector instrument ^b
U^+	0.020	0.026
UF^+	0.041	0.052
UF_2^+	0.091	0.103
UF_3^+	0.105	0.105
UF_4^+	0.143	0.147
UF_5^+	0.592	0.566
UF_6^+	0.007	0.002

^aOnly singly charged ions containing uranium were recorded.

^bData from Ref. 7.



account for the disappearance of UF_5^+ . In analogy with the clustering reaction (6), the product of Reaction (5) undergoes the reaction



to form $\text{U}_2\text{F}_{10}^+$. The upper mass limit in our experiments of approximately 740 amu did not permit possible product ions containing three or more uranium atoms to be observed. The trapped ion data suggested that if the products of Reactions (6) and (7) cluster or react further with UF_6 , then they do so at a much slower rate than that observed for Reactions (6) and (7). The ion losses at long time were comparable to those normally observed for diffusive ion loss.¹⁹

The reaction sequence at higher electron energy is somewhat more complex. Figure 2 illustrates the

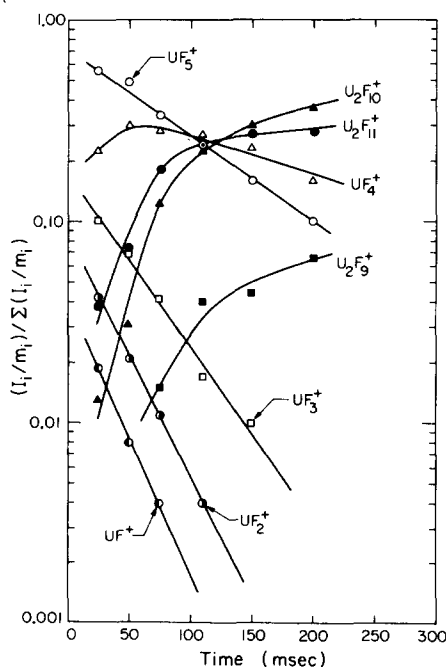
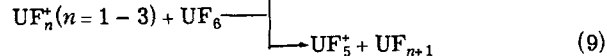
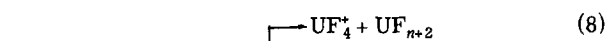


FIG. 2. Temporal variation of positive ion concentrations in UF_6 following a 10 msec electron beam pulse at 70 eV and 5.0×10^{-6} torr.

variation of ion abundance with time at 70 eV. The fragments UF_n^+ ($n = 1-3$) react as indicated in the equations



to form both UF_5^+ and UF_4^+ , with ion ejection experiments indicating that the latter ion is the major product in each case.²⁰ This is evident in the data of Fig. 2 where UF_4^+ and its clustering product comprise ~53% of the observed ion abundance at long times. In comparison, the abundance of UF_5^+ and $U_2F_{11}^+$ at long times is 40%. The only other species remaining at long times is $U_2F_9^+$, formed in the reaction



Reactions (6), (7), and (10) are formally clustering reactions, and normally are not observed in trapped ion ICR experiments unless the lifetime of the cluster is relatively long, approaching either the time between collisions, such that collisional stabilization is an important process, or the sampling time in ICR trapped ion experiments. Both of these conditions suggest cluster lifetimes in excess of several msec for the data shown in Figs. 1 and 2. The kinetics of these processes was not investigated over a wide range of pressures due to the difficulties encountered in making accurate absolute pressure measurements. Rate constants determined from the limiting slopes for disappearance of the reactant ions at 70 eV are summarized in Table II. The abundance of U^+ and UF_6^+ were not sufficient to permit their observation in the trapped ion experiments.

B. Negative ion chemistry

The only negative ions observed in UF_6 alone were UF_5^- , UF_6^- , and UF_7^- . The latter species was not reported in the earlier study of negative ion formation in UF_6 .⁵ The yield of UF_5^- as a function of electron energy was recorded at low pressures. In addition to the low energy peak reported by Stockdale, Compton, and Schweinler,⁵ a second process was observed with a broad peak in the region 7–11 eV. Below 10^{-5} torr the observed abundance of UF_6^- was very low in the drift mode of operation with a detection time of ~1

TABLE II. Rate constants for disappearance of positive ions observed in UF_6 at 70 eV electron energy.

Species	Total rate constant ^a $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$
UF^+	1.9
UF_2^+	1.7
UF_3^+	1.2
UF_4^+	0.3
UF_5^+	0.6

^aDetermined from the limiting slopes of data in Fig. 2. Absolute rates are correct only to within a factor of two due to uncertainties in pressure measurement (see experimental).

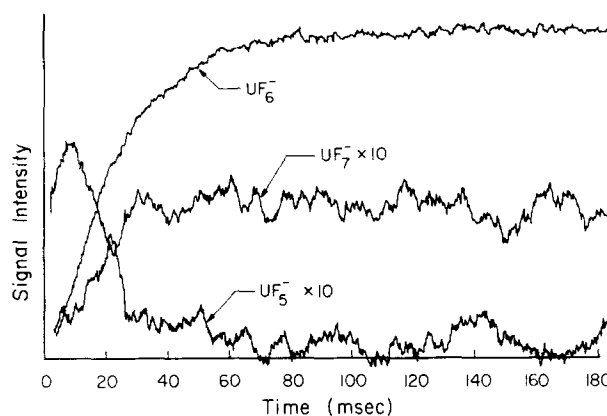


FIG. 3. Temporal variation of negative ion concentrations in UF_6 at 3.5×10^{-6} torr. The electron beam is gated on for 10 msec at 11 eV. The majority of UF_6^- is formed by attachment of electrons scattered and trapped in the source region of the ICR cell.

msec. In trapped ion experiments the abundance of UF_6^- is appreciable. Data recorded at 3.5×10^{-6} torr showing the temporal variation of negative ion abundances at 11 eV are displayed in Fig. 3. In these experiments the electron beam is gated on for 10 msec at the start of the trapped ion timing sequence.^{14,19} Direct formation of negative ions can occur during the beam pulse. In addition, electrons are scattered, trapped in the source region of the ICR cell, and subsequently lead to negative ion formation.¹⁴ The data shown in Fig. 3 are typical of that observed at all electron energies, the only difference being the abundance of UF_5^- observed at short times. It is apparent that UF_5^- is directly formed during the electron beam pulse. Double resonance experiments indicate that this ion reacts rapidly to form UF_6^- as previously reported [Reaction (3)].⁵ However, the amount of UF_5^- observed initially accounts for only ~10% of the UF_6^- formed at long times. Ejection of all possible precursors below m/e 352 did not reveal any other contributions to this species. The buildup of UF_6^- occurs at times much longer than the electron beam pulse and the intensity of this species at long times increases linearly with increasing electron beam current. These results are consistent with the formation of UF_6^- in Reaction (1) involving scattered trapped electrons. From the measured buildup of UF_6^- in Fig. 3, an attachment rate of $4.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$ is estimated. This is rather slow and the trapped electrons suffer ~ 10^3 collisions before attachment occurs. This may be sufficient to thermalize the electrons. Addition of a tenfold excess of CO_2 had no effect on the apparent attachment rate, indicating that the rate limiting step is not thermalization of the scattered electrons.¹⁴

Continuous ejection of UF_6^- leads to the disappearance of UF_7^- , identifying the reaction



Since not all of the UF_6^- reacts to form UF_7^- , the reaction likely involves an internally excited reactant. From the data in Fig. 3, 5% of the UF_6^- formed by electron attachment reacts to form UF_7^- . There is no pos-

sibility that the UF_6^- and UF_7^- observed in experiments such as shown in Fig. 3 are formed on the filament. Negative ions from the filament can enter the cell only when the electron beam is gated on, and would be observed immediately in the trapped ion timing sequence if they somehow were confined to the source region of the cell.

Negative ion processes in mixtures of two other species which attach low energy electrons were examined. The variation of ion abundance with time for the major species in a mixture of CCl_4 and UF_6 is shown in Fig. 4. The chemistry is dominated by the dissociative attachment process



followed by the rapid electron transfer reaction



Continuous ejection of both isotopes of Cl^- leads to a decrease of 86% in the abundance of UF_6^- observed at long times under the conditions used to record the data shown in Fig. 4.

In a mixture of SF_6 and UF_6 , SF_6^- is formed rapidly by electron attachment and reacts subsequently with UF_6 in the electron transfer process (4). In addition, the abundance of UF_7^- is substantially enhanced. Double resonance identifies SF_5^- as the precursor to UF_7^- , indicating the fluoride transfer reaction



Mixtures of HCl and HCN with UF_6 were also examined. Under the conditions of the experiment negative ions were not directly formed from the additives. No reactions of UF_6^- with either neutral were observed.

Clustering reactions of negative ions analogous to those involving positive ions were not observed in trapped negative ion experiments. To examine the possibility of negative ion clustering reactions the variation of ion abundance with pressure was recorded. Typical data are shown in Fig. 5 for an electron ener-

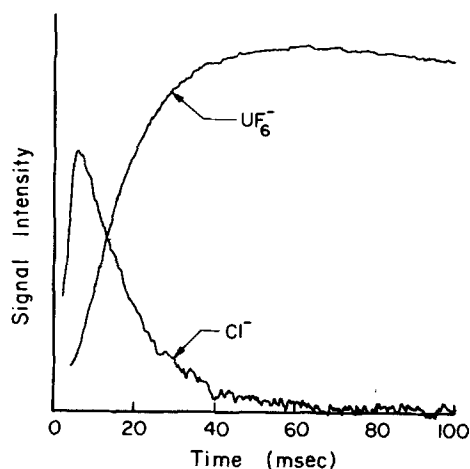


FIG. 4. Temporal variation of negative ion concentrations in a 1:1 mixture of CCl_4 and UF_6 at a total pressure of 7.0×10^{-6} torr. The electron beam is gated on for 10 msec at 11 eV. Detector gain is adjusted such that the signal intensities permit a direct comparison of ion abundances.

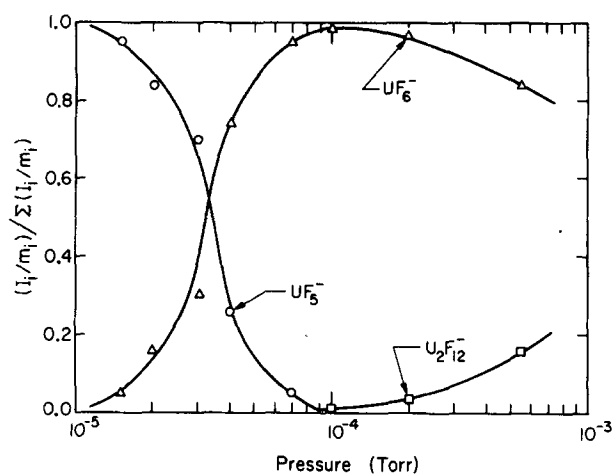


FIG. 5. Variation of negative ion abundance with pressure in UF_6 at 2 eV electron energy.

gy of 2 eV. As the pressure was increased it was observed that the total negative ion signal increased more rapidly than did the pressure, which again is in accord with the formation of UF_6^- in both processes (1) and (3). At pressures above 10^{-4} torr, the clustering process



is observed. The data in Fig. 5, which correspond to a reaction time of ~ 2 msec, suggest that the abundances of UF_6^- and $U_2F_{12}^-$ would be equal at $\sim 2 \times 10^{-3}$ torr.

Rate constants for processes involving negative ions derived from UF_6 are summarized in Table III. Included for comparison are the data of Stockdale, Compton, and Schweinler.⁵ The disagreement between the two studies is considerable, even considering the difficulties with absolute pressure measurement.

IV. DISCUSSION

It is somewhat surprising that the positive ion chemistry of UF_6 reveals many processes which lead to the formation of UF_4^+ , a radical cation. In general the ion chemistry of a species XF_n is dominated by reactions which yield XF_{n-1}^+ (an even electron species), usually generated by F^- transfer from XF_n to various frag-

TABLE III. Rate constants for processes involving negative ions.

Process	Rate constant $10^{10} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$	
	This work	Literature ^a
$UF_6 + e \rightarrow UF_6^-$	4.6	
$UF_5^- + UF_6 \rightarrow UF_6^- + UF_5$	4.0	14.0
$SF_6^- + UF_6 \rightarrow UF_6^- + SF_6$	2.4	15.0
$SF_5^- + UF_6 \rightarrow UF_7^- + SF_4$	2.0	
$Cl^- + UF_6 \rightarrow UF_6^- + Cl$	6.5	

^aData from Ref. 5.

TABLE IV. Thermochemical data.

Species	ΔH_f^{298} (kcal/mole)	Reference
UF ₆	-511	a
UF ₅	-455	a, b
UF ₄	-377	a
UF ₆ ⁻	≤ -594	c
UF ₅ ⁻	-509	d
UF ₇ ⁻	≤ -626	e
UF ₆ ⁺	-191	f
UF ₅ ⁺	-209	f
UF ₄ ⁺	≤ -84	g

^aM. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds* (Iver and Boyd, London, 1963).

^bA. S. Wolf, W. E. Hobbs, and K. E. Rapp, *Inorg. Chem.* 4, 755 (1965).

^cCalculated assuming E. A. (UF₆) ≥ E. A. (Cl) = 3.61 eV.

^dCalculated from threshold for UF₅⁻ formation from UF₆ (0.9 eV) reported in Ref. 5.

^eCalculated assuming $D(\text{UF}_6-\text{F}^-) \geq D(\text{SF}_4-\text{F}^-)$.

^fCalculated using data from Ref. 22 (see text).

^gCalculated from data in Ref. 6; this heat of formation is likely to be in error on the high side due to the method of measurement used.

ment ions.^{13,20} These results suggest that UF₄⁺ has some special stability. The abundance of UF₄⁺ in the mass spectra of UF₆ and UF₄ does not lead to a similar conclusion, however. In the case of UF₄, the relative intensities at 50 eV of UF₄⁺, UF₃⁺, UF₂⁺, UF⁺ and U⁺ are 0.054, 1.00, 0.157, 0.132, and 0.049, respectively.²¹ This suggests that the loss of F from UF₄⁺ occurs with very low activation energy. There are few thermochemical data of use in assessing the stability of various UF_n⁺ species. Recent photoionization experiments²² give I. P. (UF₆) = 13.86 eV and A. P. (UF₅⁺) = 13.89 eV, which, not surprisingly, are below the early electron impact results of White and Cameron,⁶ who report A. P. (UF₅⁺) = 15.5 eV. The only available appearance potential of UF₄⁺ from UF₆ is 20.1 eV,⁶ which yields $\Delta H_f(\text{UF}_4^+) = -84$ kcal/mole (Table IV) and I. P. (UF₄) = 12.7 eV. This is probably too high, since other U(IV) compounds are observed to have rather low ionization energies. For comparison, I. P. (UO₂) = 5.5 eV.^{9,21} If UF₄⁺ does not react with UF₆ to form UF₅⁺ because the process is endothermic, then $\Delta H_f(\text{UF}_4^+) \leq 153$ kcal/mole, and I. P. (UF₄) ≤ 9.7 eV. The formation of UF₄⁺ from UF₅⁺ in Reaction (5) could involve the breakup of an excited UF₅⁺ ion. The production of UF₄⁺ from UF₅⁺ did not depend markedly on electron energy from threshold to 70 eV, however. This implies that the neutral product in Reaction (5) should be formulated as UF₇ and suggests that this species is fairly stable even though it appears not to have been observed previously.

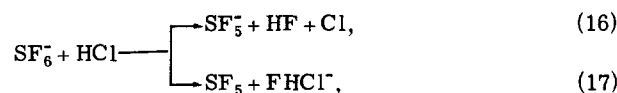
The observation of UF₆⁻ formation by electron attachment is in contrast to the results of Stockdale, Comp-ton, and Schweinler.⁵ The resonance curve for UF₆⁻

was not broadened in comparison to other ionic species observed in this study. Broadening would result from observation of a species with a lifetime less than the transit time of ions through the resonance region (~2 msec).²³ The behavior of UF₆⁻ is in fact very similar to that observed in our recent experiments with SF₆⁻, where an infinite lifetime against autodetachment is indicated.¹⁴ In comparing the present results to the earlier time of flight mass spectrometric studies, the difference in electron energy distributions in the two experiments may be highly significant. In the ICR experiments the trapped electrons suffer ~10³ collisions with UF₆ before attachment occurs. This affords the opportunity to thermalize the electrons and the absence of a rate enhancement with the addition of CO₂ is consistent with this hypothesis.¹⁴ Klots has shown that autoionization lifetimes should decrease drastically as the internal energy of the negative ion increases above its electron affinity threshold.²⁴ Primary negative ion lifetimes are consequently very sensitive to the electron energy distribution and are appreciable only for truly zero energy electrons. Since the autodetachment lifetime measured for SF₆⁻ using time of flight techniques²⁵ is orders of magnitude smaller than that observed for the attachment of scattered electrons in ICR experiments,^{14,23,26} it would seem that the latter experiments are characterized by lower electron kinetic energies.

Observed electron transfer reactions indicate that UF₆ has a very high electron affinity. From the data in Table IV the electron affinity of UF₅ is estimated to be 2.3 eV. Reactions (3), (4), and (13) indicate that E. A. (UF₆) is greater than 2.3, 0.6, and 3.61 eV, respectively. Recent studies of collisional ionization of alkali atoms²⁷⁻²⁹ have led to very high reported electron affinities for other hexafluorides, the highest being WF₆, for which E. A. = 4.5 eV.²⁹

Interestingly, both UF₄⁺ and UF₆⁻ are U(V) radical ion species. The chemistry of U(V) species have recently been reviewed by Selbin and Ortego.³⁰ Compounds of UF₆⁻ can be formed by the reaction of UF₅ and MF (M = NH₄⁺, Li⁺, Na⁺, etc.).³¹ Absorption spectra of these blue salts reveal low lying excited electronic states, the A_{2u} - T_{2u} and A_{2u} - T_{1u} excitations being observed in the regions between 4000-7000 cm⁻¹ and 12 000-15 000 cm⁻¹, respectively.^{31,32} Recent SCF-Xα scattered wave calculations reproduce the observed excitation energies and provide a qualitative description of the bonding in the UF₆⁻ complex.³³ The high electron affinity of UF₆ along with the existence of excited electronic states below detachment thresholds may be related to the low attachment rate, and distinguish UF₆ from SF₆.

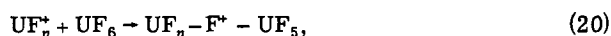
The high electron affinity of UF₆ is also responsible for the low reactivity of UF₆⁻ in comparison with SF₆⁻, which reacts readily with HCl and HCN in accordance with the equations^{15,16}





The bond energies $D(\text{UF}_4-\text{F}^-) \cong 71$ kcal/mole, $D(\text{UF}_5-\text{F}^-) \geq 78$ kcal/mole and $D(\text{UF}_6-\text{F}^-) \geq 104$ kcal/mole (Table IV) are all high in comparison to the corresponding bond energies for SF_6 .¹⁶ The observation of UF_7^+ has a counterpart in the ion chemistry of SF_6 , although the conditions which lead to the formation of SF_7^+ have not been well characterized.³⁴ The fluoride transfer Reaction (14) indicates $D(\text{UF}_6-\text{F}^-) \geq 54$ kcal/mole.

Positive ions exhibit a tendency to cluster more readily than do negative ions derived from UF_6 . This suggests a special stability is afforded the electron deficient positive ion species, possibly due to "onium" ion formation,



whereas the polarity of the U-F bonds mitigates against the formation of stable complexes with negative ions.

Finally, it is of interest to compare the results of the present study with the early attempts to separate isotopes using ion cyclotron resonance methods.¹ The most abundant positive ion observed in ionized UF_6 vapor was UF_4^+ , and positive ions at high mass were detected but not characterized. These results are entirely consistent with the present study which indicates that all of the UF_n^+ species react to form UF_4^+ , and that clustering of positive ions with UF_6 occurs readily. The situation with negative ions is less clear in that the only abundant negative ion detected in the early experiments appeared to have a mass to charge ratio approximately half that of UF_6^- . While the species UF_6^{2-} would be of considerable interest, it was not observed in the present experiments. If UF_6^{2-} does exist as a stable species, its formation may require high charged particle densities.

ACKNOWLEDGMENT

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†Contribution Number 5048.

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