

Ion cyclotron resonance studies of endothermic reactions of UF_6^- generated by surface ionization

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Ion cyclotron resonance spectroscopy is used to investigate endothermic reactions of UF_6^- . At temperatures below those required for electron emission, UF_6^- is formed by negative surface ionization on a directly heated rhenium filament. The reactant ion is accelerated to a known energy and traverses the source region of the ICR cell in the direction of the magnetic field. Slow products from reactive and nonreactive encounters are confined in the trapping well and detected in the usual manner. The formation of UF_7^- , UF_6^- , UF_5^- , and UF_3^- from the reaction of UF_6^- with UF_6 is studied over the energy range 0–40 eV in the center of mass. The cross section for UF_7^- formation exhibits a threshold at a relative kinetic energy of 2.7 eV. Reaction of UF_6^- with BF_3 leads to formation of BF_4^- with a threshold of 1.6 eV in the center of mass. From these thresholds, $E.A.(\text{UF}_6) = 4.9 \pm 0.5$ eV is deduced and the bond dissociation energies $D(\text{UF}_5-\text{F}^-) = 108 \pm 6$ kcal/mole and $D(\text{UF}_6-\text{F}^-) = 46 \pm 10$ kcal/mole are calculated. The endothermic reaction of UF_6^- with SF_6 to produce SF_6^- is also investigated, the cross section for the process exhibiting a gradual onset at ~ 7.5 eV, considerably above the thermodynamic threshold. The experimental techniques for using ion cyclotron resonance spectroscopy to study endothermic reactions of positive and negative ions formed by surface ionization are considered in detail.

I. INTRODUCTION

Ion cyclotron resonance spectroscopy (ICR) has previously been employed to investigate the formation and reactions of positive and negative ions derived from uranium hexafluoride,¹ considerably extending the earlier negative ion studies of Stockdale, Compton, and Schweinler.² With thermal electrons the attachment reaction



leads to the formation of UF_6^- with an unusually slow rate constant ($k \cong 5 \times 10^{-10}$ cm³ molecule⁻¹ · sec⁻¹) at low pressures ($< 10^{-5}$ torr).¹ At higher electron energies the dissociative attachment Process (2) is observed, with a threshold of 0.9 ± 0.1 eV.² The species UF_5^- reacts rapidly with UF_6 by electron transfer



electron transfer from other negative ions, including Cl^- and SF_6^-



appears to be a general process leading to the formation of UF_6^- .¹

The electron transfer Reaction (4) indicates a high electron affinity for UF_6 (≥ 3.61 eV) and lattice energy calculations for the crystalline solid NO^+UF_6^- suggest a value of 6.1 eV.³ The surface ionization estimate of 2.9 eV by Page and Goode appears to be somewhat low.⁴ The internal energy of UF_6^- formed in the direct electron attachment Reaction (1) can be appreciable, and it was suggested that UF_6^- containing excess internal excitation reacts to form the species UF_7^- observed in UF_6 alone,¹



The majority of the UF_6^- formed by electron attachment

is unreactive with UF_6 . The reaction of SF_5^- with UF_6 indicates that the species UF_7^- is reasonably stable,



with $D(\text{UF}_6-\text{F}^-) \geq 54 \pm 10$ kcal/mole.¹

The present study was initiated to investigate endothermic reactions of UF_6^- with translational energy in the range 0–40 eV in order to better characterize the thermochemical properties and processes which lead to formation of the various species UF_n^- in UF_6 alone. In earlier studies the failure to observe reactions of UF_6^- with other molecules at thermal ion energies was attributed to the thermochemical stability of the reactant ion.¹ In the present study endothermic reactions of UF_6^- with BF_3 and SF_6 are also examined. In accomplishing these objectives new ICR techniques have been developed which promise to have wide application for the investigation of endothermic reactions of positive and negative ions which can be generated by surface ionization.

II. EXPERIMENTAL

The formation of negative ions on heated surfaces is a widely recognized phenomenon.^{4,5} Although previous studies have suggested the possible formation of negative ions on the directly heated filament of an ICR spectrometer,⁶ the conditions under which this occurs and the various manifestations of the process have not been well characterized. A cross sectional view of the ICR cell used in this study is shown in Fig. 1(a).⁷ The spacing of the trapping and drift electrodes are 2.54 and 1.0 cm, respectively. Charged particles generated by thermionic emission from a rhenium ribbon filament (dimensions 0.001×0.032 in.) enter through a 2 mm circular aperture in the trapping electrode, traverse the cell in the direction of the magnetic field and are collected on an electrode used to monitor the emission current. The entrance and exit apertures are covered with a 85% open mesh screen to prevent field penetra-

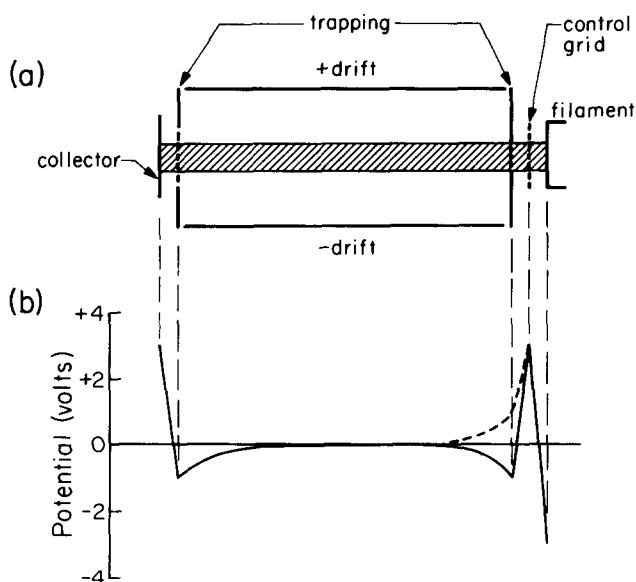


FIG. 1. (a) Cross sectional view of ICR cell. The shaded region indicates thermionically emitted particles which traverse the cell in the direction of the primary magnetic field. (b) Space potential along the ion beam. In the configuration shown negative ions have a kinetic energy of 3 eV in the cell, which confines scattered and product ions with a kinetic energy less than 1 eV (determined by the trapping voltage). The dashed portion of the curve indicates the change in space potential effected by modulating the voltage applied to the trapping plate adjacent to the filament.

tion into the cell. A control grid is mounted between the filament and the trapping electrode. In trapped ion experiments⁸ this grid is used in gating the electron beam. In the present studies the grid is biased to assist in the extraction of electrons and negative ions from the ribbon filament. This considerably increases the usable currents at low energies.

The total negative collector current at 70 eV, recorded in the presence of 10^{-6} torr UF_6 , is shown as a function of filament current in Fig. 2. The onset of thermionic emission of electrons in the absence of UF_6 occurs at ≈ 2 A. In the presence of UF_6 the onset for emission is 0.8 A (Fig. 2). The shape of the curve suggests that negative surface ionization is occurring at low filament currents, with the increase in current above 2 A being due to electron emission.

To verify that the UF_6 does not alter the electron emission characteristics of the filament, the yield of UF_5^+ formed by electron impact ionization was measured as a function of filament current (Fig. 2). The yield of UF_5^+ is directly proportional to the electron emission current. Above 2 A the collector current and UF_5^+ signal follow each other closely. Below 2 A the UF_5^+ signal vanishes, leading to the conclusion that thermionic emission at low filament currents is due entirely to negative ions. There is no visual access to the filament in the ICR apparatus used in these experiments. A rhenium ribbon filament of similar dimensions was mounted on a test stand and exposed to UF_6 at a pressure of 5×10^{-6} torr as measured by an ionization gauge. Negative ion emission was observed with a yield curve iden-

tical to that shown in Fig. 2. The onset for negative ion emission occurs at a filament temperature of 800°C , determined by viewing the assembly through a quartz window with an optical pyrometer. At this temperature radiation from the filament is just barely visible.

The kinetic energy of ions formed by surface ionization in the ICR cell is determined by the bias applied to the filament. The variation of potential along the negative ion beam is shown in Fig. 1(b), with conditions appropriate for having negative ions at 3 eV in the ICR cell. The trapping well confines product ions with translational energy less than 1 eV in the direction of the ion beam. These ions drift from the source to the resonance region where they are observed using a marginal oscillator detector.⁷ Lock-in detection and amplification of the signal is accomplished by modulating the voltage applied to the trapping plate adjacent to the filament.⁹ A square wave voltage is applied symmetrically with respect to ground. The potential illustrated in Fig. 1(b) is appropriate for the trapping portion of the cycle. During the other half cycle the modification of the potential indicated by the dashed line does not allow for ion confinement.

A simple experiment permits observation of the ions being formed on the filament. By adjusting the ion energy so that it is less than the depth of the trapping well, negative ions will be reflected as they approach the trapping electrode. With trapping voltage modulation, however, ions traverse the cell and are reflected by the trapping plate adjacent to the collector. When the trapping plates come to the same potential, ions

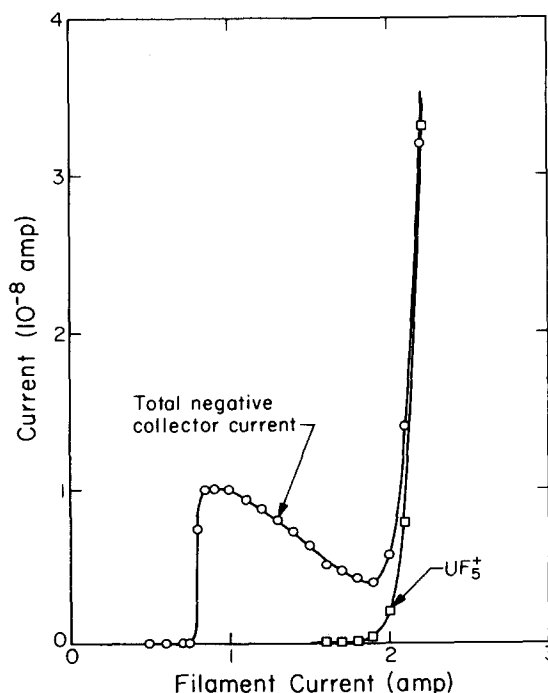


FIG. 2. Total negative ion current reaching the collector as a function of the filament current. The accelerating voltage is 70 eV. Also included is the signal intensity of UF_5^+ resulting from electron impact ionization of UF_6 . The two curves are normalized together at 2.3 A, where UF_6^- formation is negligible in comparison to electron emission.

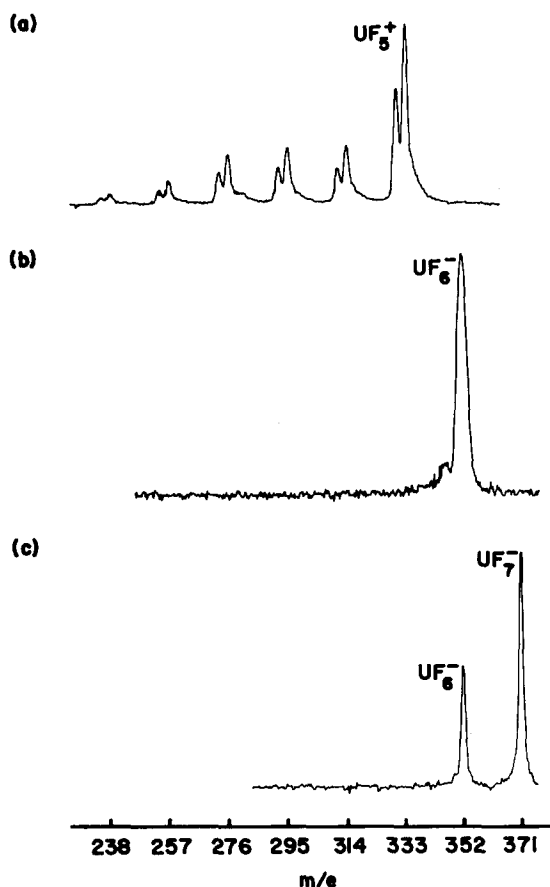


FIG. 3. ICR single resonance spectra of (a) positive ions formed at 70 eV in an enriched sample containing 40.7% $^{235}\text{UF}_6$, (b) negative ions being formed on the filament, and (c) product ions observed from reaction of UF_6^+ with UF_6^- at a relative kinetic energy of 5.0 eV. The major species are identified in each instance and the m/e values correspond to the series $^{238}\text{UF}_n$, $n=0-7$.

present in the cell at that instant of time will be confined in the well and can be detected. The signal appears as a transient absorption at the beginning of the trapping cycle. Signal intensities are sufficient to use the phase-sensitive detector. A boxcar integrator gives a better signal to noise ratio, however. The 70 eV positive ion mass spectrum of UF_6 and the negative ion spectrum at 1 amp filament current are compared in Figs. 3(a) and 3(b). The only negative ion observed over the full range of filament currents is UF_6^- .

Exact calibration of the ion energy in the ICR cell is difficult. A correction for the electron energy scale can be generated by observing inelastic excitation spectra¹⁰ and is generally less than 0.4 eV. The excitation spectra measurements give only an estimate of the peak in the distribution and not the complete distribution. Using the trapping electrodes as a stopping grid assembly leads to vanishing negative ion currents at the collector within 0.2 eV of the nominal value. Reported laboratory ion energies are estimated to be correct to within 0.3 eV. While this leaves much to be desired, the specific construction features and dimensions of the ICR cell provide constraints which would make it difficult to install a stopping grid analyzer which would de-

termine the ion energy distribution in the center of the ICR cell under actual operating conditions.

General descriptions of ICR techniques and apparatus are given elsewhere.⁷⁻⁹ These experiments employed an instrument with a 15 in. magnet capable of a maximum field of 23.5 kG. The cell used is similar to that described by McMahon and Beauchamp,⁸ and is equipped for operation either in drift or trapped ion modes. The best resolution which could be achieved in the drift mode with an oscillator frequency of 95 kHz at m/e 352 was a peak width of 1.3 amu (FWHM). This was sufficient to resolve $^{235}\text{UF}_6^-$ from $^{238}\text{UF}_6^-$ [Fig. 3(a)] and is limited by coherence times of ions in the radio frequency field of the detector.⁷

UF_6 was obtained from Varlacoid Chemical Co. An enriched sample containing 40.7% $^{235}\text{UF}_6$ was made available by Dr. R. N. Compton of Oak Ridge National Laboratory. Other chemicals were readily available commercial samples and were used as supplied except for degassing at liquid nitrogen temperatures. All mixtures were prepared by admitting the components through separate leak valves. As noted previously,¹ difficulties are encountered in measuring the pressure of UF_6 . Consequently the reported values are only approximate.

III. RESULTS

A. Reactions in UF_6 alone

In the pressure range between 10^{-6} and 10^{-5} torr secondary products from reactions of thermionically generated UF_6^+ and UF_6^- are observed [Fig. 3(c)]. In the transverse geometry of the present experiment, only the slow products are detected. The yield of various UF_n^- ions in UF_6 alone are shown in Fig. 4, with UF_6^- energies between 0 and 40 eV in the center of mass.

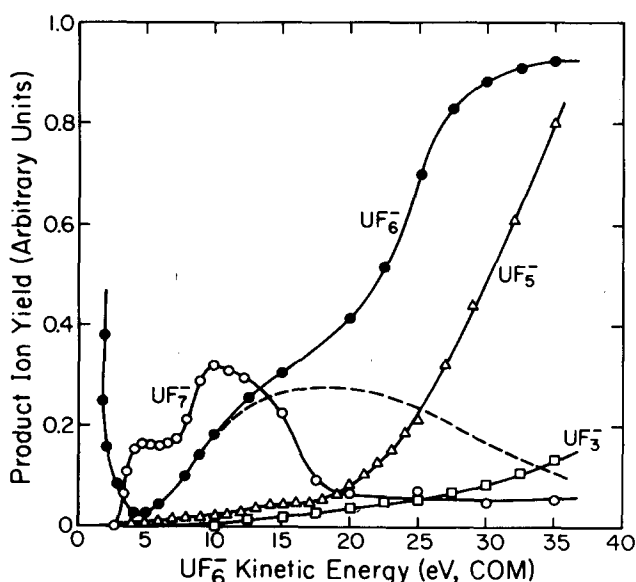


FIG. 4. Product ion yields as a function of ion energy in the center of mass (COM) from the reaction of UF_6^+ with UF_6^- at 3×10^{-6} torr. The yield for UF_6^- has been reduced by a scale factor of 3.0 to compare with the remaining products.

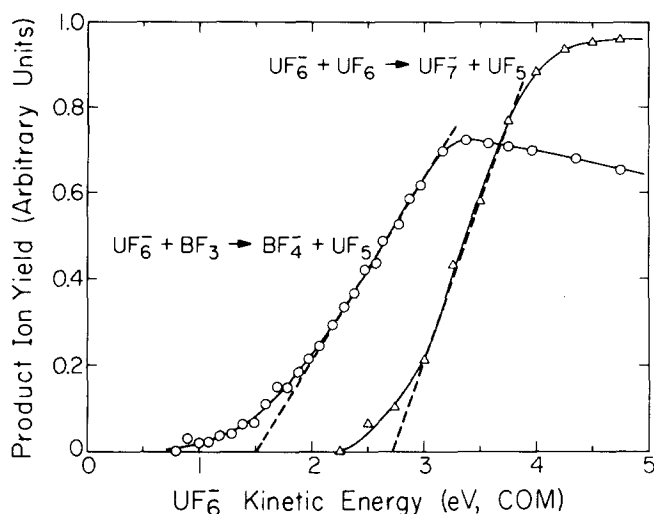


FIG. 5. Threshold region for reaction of UF_6^- with BF_3 and UF_6^- to give BF_4^- and UF_7^- , respectively.

Product ion signal intensities are divided by UF_6^- current measured on the collector to determine relative product ion yields. A filament current of 1.0 A (corresponding to a temperature of 900 °C) and a trapping voltage of 1.0 volt were employed. All curves are directly comparable except for UF_6^- which has been reduced by a scale factor of 3.0.

The cross section for the formation of UF_7^- from UF_6^- in the reaction



increases rapidly with kinetic energy above 2.3 eV. The threshold region, considered in greater detail below, is shown in Fig. 5, recorded with a trapping well depth of 0.4 eV. The structure at 7.5 eV (Fig. 4) suggests a second process leading to the formation of UF_7^- . Above 10 eV the decrease in the yield of UF_7^- may be due to momentum transfer to the product ion, causing it to escape the trapping well. Alternatively, excess internal energy in the product ion may subsequently lead to unimolecular decomposition. An attempt was made to determine the maximum cross section for formation of UF_7^- at 10 eV relative kinetic energy. Assuming a small attenuation of the reactant beam, the product ion current $I(\text{UF}_7^-)$ is given by

$$I(\text{UF}_7^-) = I(\text{UF}_6^-) n Q_r l \quad (9)$$

where $I(\text{UF}_6^-)$ is the UF_6^- beam current, n is the UF_6^- number density, Q_r is the reaction cross section, and l is the path length. By increasing the filament current such that electron emission dominates, the current of UF_5^+ can be recorded at 70 eV and is given by

$$I(\text{UF}_5^+) = I_e n Q_i l \quad (10)$$

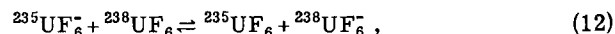
where Q_i is the 70 eV cross section for formation of UF_5^+ from UF_6^+ (UF_5^+ is 59% of the total ionization at 70 eV). By taking ratios, Q_r is given by

$$Q_r = \frac{I(\text{UF}_7^-) I_e Q_i}{I(\text{UF}_6^-) I(\text{UF}_5^+)} \quad (11)$$

ICR detection of UF_5^+ and UF_7^- yields the ratio $I(\text{UF}_7^-)/$

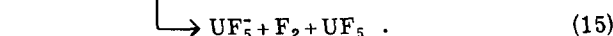
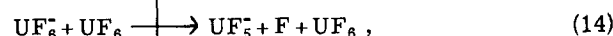
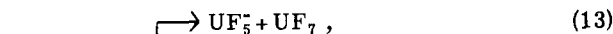
$I(\text{UF}_5^+)$ and the currents I_e and $I(\text{UF}_6^-)$ are directly measured at the collector. Repeated determinations gave $Q_r \approx Q_i$. Although the total ionization cross section of UF_6^- is not known, it is estimated to be $\sim 20 \text{ \AA}^2$.¹¹ Hence $Q_r \approx 12 \text{ \AA}^2$, which is probably correct within a factor of 2. Working backward using Eq. (9), this value for Q_r yielded a pressure of $\sim 6 \times 10^{-6}$ torr, which is within the estimated range employed.

The yield of UF_6^- passes through a minimum at 4.0 eV and rises sharply at higher and lower energies. The low energy portion of the curve is attributed to trapping of elastically scattered UF_6^- . The higher energy portion of the curve is probably due to electron transfer as well as decomposition of internally excited UF_7^- . The yield of UF_6^- at relative kinetic energies above 10 eV depended markedly on trapping voltage. With a well depth of 0.4 V, the product ion yield indicated by the dashed line was observed. This suggests that UF_6^- formation is accompanied by momentum transfer, and probably occurs only in energetic encounters at small impact parameters. With isotopically enriched UF_6^- , the electron transfer reaction



could not be observed in either the drift or trapped ion mode using ion cyclotron double resonance and ion ejection techniques.¹² Analogous results have been reported for SF_6^- , namely symmetric electron transfer is not observed at low ion energies.^{13,14}

The product ion UF_5^- becomes abundant at relative kinetic energies above 20 eV. The formation of slow UF_5^- at lower energy occurs with low probability, exhibiting an onset at ~ 5 eV. Possible processes for UF_5^- formation include



It has previously been shown that UF_7^- is a stable species.¹ Thus, Reaction (13) is the lowest energy process leading to formation of UF_5^- . This process would appear to be competitive with Reaction (7); the predominance of UF_7^- suggests that $E.A.(\text{UF}_7^-) \geq E.A.(\text{UF}_5^-)$, which is shown to be the case below. The minimum energy required for Process (14) is $E.A.(\text{UF}_6^-) + E_1 = 4.9 + 0.9 = 5.8$ eV, where E_1 is the threshold energy for Process (2) and the value for $E.A.(\text{UF}_6^-)$ is derived below. This is close to the observed threshold of ~ 5 eV. Reaction (15) would be energetically less favorable than Process (14) since $D(\text{F}-\text{F})$ is much less than $D(\text{UF}_5-\text{F})$; Process (15) might result, however, from the decomposition of UF_7^- .

Interestingly, UF_4^- is not observed. The species UF_3^- is observed with a gradual onset at a relative kinetic energy of 10 eV. Most likely UF_3^- results from the decomposition of UF_5^- formed with excess internal energy.

B. Mixture of UF_6^- with BF_3

In a 40:1 mixture of BF_3 and UF_6^- at a total pressure of $\sim 4 \times 10^{-5}$ torr, the reaction

TABLE I. Summary of thermodynamic data for uranium compounds.^a

Species	ΔH_f^{298} (kcal/mole)
UF ₇	≤ -493 ^b
UF ₆	-511
UF ₅	-455
UF ₄	-377
U	115
UF ₇ ⁻	-618 ^c
UF ₆ ⁻	-624 ^c
UF ₅ ⁻	-509

^aExcept as noted, data is from the summary given in Ref. 1.

^bCalculated assuming UF₇ is stable with respect to dissociation to give UF₆ + F (see text).

^cThis work.



results in the formation of BF₄⁻. The variation of reaction cross section with relative kinetic energy is shown in Fig. 5. The thermal motion of the target molecules leads to a significant doppler broadening in the interaction energy in experiments where a nominally monoenergetic beam interacts with gas molecules in a reaction chamber. This phenomenon has been treated in detail by Chantry.¹⁵ At the relative energy E_0 the distribution of kinetic energies in the center of mass has a full width at half maximum, given by

$$W_{1/2} = (11.1 \gamma kTE_0)^{1/2}, \quad (17)$$

where $\gamma = m/(m+M)$, m and M being the projectile and target molecule masses.¹⁵ Extrapolation of the rising linear portion of the cross section for Reaction (16) as indicated in Fig. 5 gives an onset of 1.5 eV in the center of mass. At $E_0 = 1.5$ eV, $W_{1/2} = 0.61$ eV. By considering model cross sections, Chantry has shown that extrapolation of the linear portion of a cross section which increases in proportion to the excess energy above threshold will lead to a threshold which is too low by $3\gamma kT$.¹⁵ For Reaction (16) this amounts to 0.066 eV, giving an estimated threshold of 1.6 ± 0.2 eV. This is higher than the apparent onset by an amount approximately equal to $W_{1/2}$, again in agreement with Chantry's analysis. Similarly, a threshold energy of 2.7 ± 0.2 eV is estimated for Reaction (8). At this energy $W_{1/2} = 0.62$ eV.

Thermochemical data utilized in this study for compounds containing uranium are summarized in Table I. The bond dissociation energy $D(\text{BF}_3-\text{F}^-) = 71 \pm 5$ kcal/mole (3.1 eV) is known from other studies,¹⁶ and with the measured threshold for Reaction (16) gives $D(\text{UF}_5-\text{F}^-) = 108 \pm 6$ kcal/mole (4.7 eV). Using the values $\Delta H_f(\text{UF}_6) = -511$ kcal/mole, $\Delta H_f(\text{UF}_5) = -455$ kcal/mole, and $\Delta H_f(\text{F}^-) = -61$ kcal/mole, this bond energy gives $\Delta H_f(\text{UF}_6^-) = -624$ kcal/mole and E.A. (UF₆) = 4.9 ± 0.5 eV. This is low in comparison to the lattice energy estimate of 6.1 eV.³ Assuming that the latter is correct, the measured threshold for Reaction (11) gives $\Delta H_f(\text{UF}_5^-) = -481$ kcal/mole, which corresponds to $D(\text{UF}_5-\text{F}^-)$

= 49 kcal/mole. This is low in comparison to the average bond energy in UF₆ of 123 kcal/mole.

The threshold of 2.7 eV for Reaction (8) can be combined with $D(\text{UF}_5-\text{F}^-) = 108$ kcal/mole to give $D(\text{UF}_6-\text{F}^-) = 46 \pm 10$ kcal/mole (2.0 eV) and $\Delta H_f(\text{UF}_7^-) = -618$ kcal/mole. The derived value for $D(\text{UF}_6-\text{F}^-)$ of 46 ± 10 kcal/mole is somewhat below the lower limit of 54 ± 10 kcal/mole provided by observation of Reaction (7). The uncertainties in both measurements are considerable, however.

If UF₇ is stable with respect to dissociation to give UF₆ and F,¹ then the derived heat of formation for UF₇⁻ gives E.A. (UF₇) ≤ 5.5 eV. This is consistent with the derived value E.A. (UF₆) = 4.9 ± 0.5 eV and the fact that UF₇⁻ does not undergo electron transfer to UF₆.

The dissociation of UF₇⁻ to UF₆⁻ and F is endothermic by only 0.4 eV. If Reaction (8) proceeds by an idealized stripping mechanism¹⁷ at higher energies, then the internal excitation of UF₇⁻ will exceed 0.4 eV at a relative kinetic energy of 15.1 eV. At this energy the cross section for formation of UF₇⁻ drops off considerably with a rise in the cross section for UF₆⁻ (Fig. 4).

C. Mixture of UF₆ with SF₆

The electron transfer Reaction (5) is exothermic by E.A. (UF₆) - E.A. (SF₆) = $4.9 - 0.6 = 4.3$ eV. In a 40:1 mixture of SF₆ and UF₆ at a total pressure of $\sim 4 \times 10^{-5}$ torr, the reverse reaction



is observed at relative kinetic energies above 7.5 eV. Variation of the reaction cross section with kinetic energy in the center of mass is displayed in Fig. 6. The gradual onset above 7.5 eV is considerably higher than the calculated threshold of 4.3 eV and yields only an upper limit of ~ 8.1 eV for E.A. (UF₆).

IV. SUMMARY AND CONCLUSION

The present work supports a high value for the electron affinity of UF₆, the threshold for Reaction (11) giving E.A. (UF₆) = 4.9 ± 0.5 eV. This is compared with available data for other hexafluorides in Table II. The present results are not without the ambiguities which

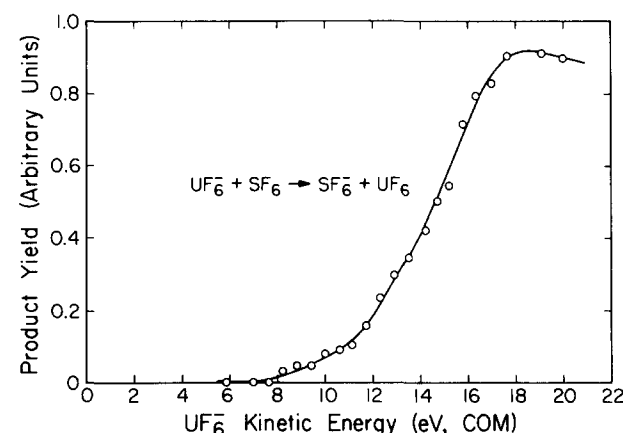


FIG. 6. Threshold region for endothermic electron transfer from UF₆⁻ to SF₆.

TABLE II. Electron affinities of selected hexafluoride molecules.

Species	Electron affinity (eV)	Reference
SF_6^-	0.6 ± 0.1	a, b
SeF_6^-	3.0 ± 0.2	c
TeF_6^-	3.2 ± 0.2	c
WF_6^-	4.5 ± 0.2	c
UF_6^-	4.9 ± 0.5	This work
PtF_6^-	6.8 ± 1.0	3

^aC. Lifshitz, T. O. Tiernan, and B. M.

Hughes, *J. Chem. Phys.* **59**, 3182 (1973).

^bR. N. Compton and C. D. Cooper, *J. Chem. Phys.* **59**, 4140 (1973).

^cC. D. Cooper and R. N. Compton, *Bull. Am. Phys. Soc.* **19**, 1106 (1974).

accompany the measurement of thermodynamic properties from reaction thresholds. Formation of UF_6^- by surface ionization undoubtedly leaves the reactant with considerable internal energy. Even at room temperature the average internal energy of UF_6^- is high (~ 0.2 eV). The present experiments do not allow the effects of internal excitation on the thresholds for Reactions (8), (16) and (18) to be determined. The method of extrapolation to zero current assuming a linear threshold dependence for the cross section leaves much to be desired, particularly since discrimination against fast products above threshold may distort the true dependence of the cross section on ion energy. If the threshold for Reaction (18) had been used to determine E.A. (UF_6^-), it would be difficult to explain the observed threshold for Reaction (16), which would be *too low* by nearly 3 eV. The higher threshold for Reaction (18) could result, however, from a vertical rather than an adiabatic process, leaving both UF_6^- and SF_6^- vibrationally excited. Because of these uncertainties it would be of interest to redetermine the threshold for Reaction (16) in a crossed beam experiment utilizing UF_6^- which has been collisionally relaxed in a high pressure ion source. Photodetachment experiments underway in our laboratory may also provide useful information relating to E.A. (UF_6^-).

The endothermicity of Reaction (8) is determined to be 2.7 ± 0.2 eV. This confirms the conjecture in the earlier trapped ion study of UF_6^- that Reaction (6) involves UF_6^- with excess internal excitation.¹ The formation of UF_6^- by attachment of thermal electrons could yield an ion with up to 4.9 eV internal excitation. In the experiments designed to directly observe ions from the filament, UF_6^- formed by surface ionization did not react to form UF_7^- at near thermal ion energies.

The experimental methodology developed in the course of this work has extensive applications for studying endothermic reactions of both positive and negative ions formed by surface ionization. Investigations of endothermic reactions of alkali ions would be of particular interest.^{18,19} It is important to note that the experimental arrangement discriminates against product ions which have appreciable kinetic energy in the direction of the reactant ion beam. For this reason

the processes observed tend to be those which occur at relatively large impact parameters with little momentum transfer. Processes amenable to study include electron transfer and stripping reactions in which atomic ion transfer to or from the neutral reactant leaves a slow product ion. Processes which take place at small impact parameter or involve complex formation are not good candidates for study except at kinetic energies comparable to the trapping well depth. It would be of interest to extend the results of the present study with an investigation of the energetic reactions of UF_6^- with UF_6^- using an in-line configuration to detect the fast products.

The ease with which UF_6^- can be formed by negative surface ionization is due in part to the high electron affinity of UF_6^- . This deserves further study, particularly with metal surfaces of low work function. It may be possible to develop simple but intense sources of UF_6^- for electromagnetic isotope separators and heavy ion accelerators. In addition the phenomenon provides the basis for the development of a very simple detector for the presence of UF_6^- in vacuum systems at low pressures.

ACKNOWLEDGMENTS

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⁶R. C. Dunbar, *J. Am. Chem. Soc.* **90**, 5676 (1968).

⁷For a general discussion of ICR, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.* **22**, 527 (1971).

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