Matrix IR Spectra of the Products from F_2, ClF, and Cl_2 Reactions with Pulsed-Laser Evaporated Uranium Atoms

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Received June 16, 1993®

Pulsed Nd:YAG laser ablated uranium atoms were codeposited with F_2 and excess Ar onto a CsI window at 12 K. Infrared spectra revealed the presence of several uranium fluorides including the previously characterized UF_4, UF_5, and UF_6. Lower laser energy favored new absorptions at 400, 446, 496, and 561 cm^{-1}. These product absorptions increased stepwise during annealings which permitted diffusion and reaction of the fluorine. Similar studies with ClF produced the above absorptions plus a new band at 554 cm^{-1} which is tentatively assigned to ClF_2^-. The first bands appearing at 400 and 446 cm^{-1} are assigned to UF and UF_2, respectively. The 496- and 561-cm^{-1} bands are tentatively assigned to UF_3 and F_3^-, respectively. Finally, uranium atoms were reacted with Cl_2. In addition to several absorptions due to UCl_4, a new doublet at 312 and 308 cm^{-1} is assigned to UCl_2.

Introduction

Since uranium halides play critical roles in the realization of nuclear energy, these halides have been the subjects of numerous basic and applied studies. The three most common halides, UCl_4, UF_4, and UF_6, have received most of the attention due to their importance in chemical processes. UF_6 and UCl_4 are used in large-scale isotope separation schemes while UF_4 has been used as a molten-salt reactor fuel.[1] Isolated UCl_4,[2] UF_4,[3] and UF_6[4,5] have already been characterized using matrix isolation infrared spectroscopy. Other matrix IR studies have examined the products that are formed during the fluorination and chlorination with UF_4 and UCl_4. These products included UF_5,[6] UF_4Cl, UF_4Cl_2,[7] UCl_6, UCl_5, UCl_4F_2, and UCl_4F.[8] The matrix isolation technique is ideally suited for examining these reactions since the inert gas matrix can prevent the intermediates from undergoing further reaction.

In sharp contrast, uranium halides with less than four halogens have received very little attention due to their difficult preparations and their nonvolatile nature. Solid UF_3, which is exceptionally stable in air at room temperature, can be produced by reducing UF_4 with Al,[9] UH_3,[10] and H_2[11] at a minimum of 900 °C. At temperatures above 1000 °C, UF_4 and U will react to form UF_3.[1] In recent mass spectrometry studies, gaseous UF and UF_2 were prepared by reacting gaseous BaF_2 and UF_6 with solid UC in a graphite effusion cell at temperatures ranging from 2100 to 2400 K.[12,13] In a matrix isolation IR study on UCl_2,[14] uranium metal was reacted with $CaCl_2$, HCl, and Cl_2 at temperatures ranging from 1350 to 1500 °C. The inherent problems of studying refractory uranium halides can be greatly alleviated through use of Nd:YAG laser ablation with the matrix isolation technique.[15,16] Recent laser ablation matrix IR studies have characterized the products from the atomic uranium reactions with oxygen[17] and nitrogen[18] even though a temperature of 2200 K is needed for an uranium vapor pressure of 10^{-6} atm. Laser ablation also minimizes problems such as heating effects and contanimants that are normally encountered with more conventional high-temperature furnaces. The primary purpose of this matrix IR investigation was to characterize the small uranium halides that are formed by reacting uranium atoms with molecular fluorine, chlorine fluoride, and molecular chlorine.

Experimental Section

The vacuum and cryogenic apparatus and the pulsed Nd:YAG laser evaporation technique have been thoroughly described earlier.[15,16] A Quanta Ray DCR-11 Nd:YAG laser was operated at 1064 nm in the Q switch mode with a 10-ns pulse duration. The laser energy at the target was set at 20–50 mJ/pulse with a 3-Hz repetition rate; the laser fluence was on the order of 10 J/cm² at the target. Lower laser energies were used in the majority of the experiments in order to minimize the intensity of the plasma that is formed during the ablation process. This plasma can lead to unwanted photochemistry. In addition, the higher laser energies dramatically increased the amount of molecular and atomic fluorine migration during the matrix formation. A polished uranium sample was rotated at 1 rpm to avoid creating a cavity in the target. The halogen samples that included F_2 (Matheson), ClF (Ozark Mahoning), and Cl_2 (Matheson) were used without further purification in a passivated stainless steel manifold. The argon-diluted halogen samples were prepared manometrically in molar ratios from 100/1 to 1000/1 (Ar/halogen). These argon-diluted halogen samples and uranium atoms were codeposited onto a 12 K CsI window at 2–3 mmol/h for 6 h. The infrared spectra were recorded with a Nicolet 5DXB Fourier transform infrared spec-

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® Abstract published in *Advance ACS Abstracts,* December 15, 1993.

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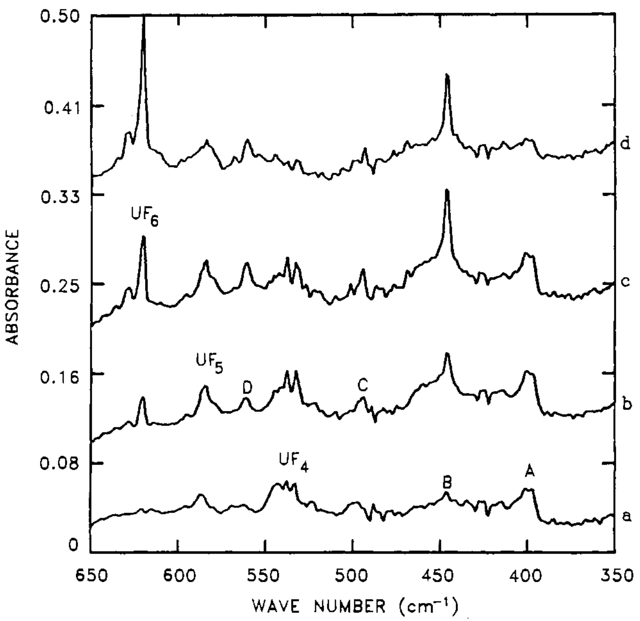

Figure 1. FTIR spectra at 2-cm^{-1} resolution in the 650–350-cm^{-1} region: (a) after a 6-h codeposition of uranium atoms from a 30-mJ ablation and an Ar/F_2 = 200/1 sample at 12 ± 1 K; (b) after annealing matrix a to 20 ± 2 K; (c) after warming matrix b to 25 ± 2 K; (d) after annealing matrix c to 35 ± 2 K.

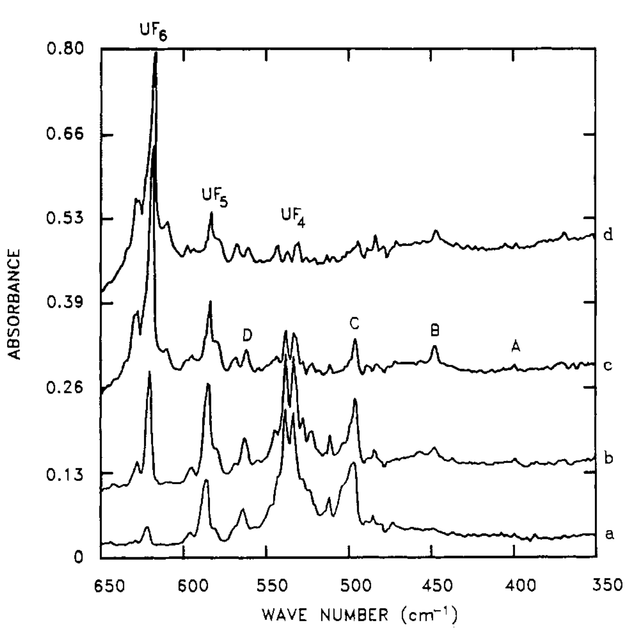

Figure 2. FTIR spectra at 2-cm^{-1} resolution in the 650–350-cm^{-1} region: (a) after a 6-h codeposition of uranium atoms from a 40-mJ ablation and an Ar/F_2 = 200/1 sample at 12 ± 1 K; (b) after warming matrix a to 20 ± 2 K; (c) after annealing matrix b to 32 ± 2 K; (d) after warming matrix c to 40 ± 2 K.

trometer at 2-cm^{-1} resolution. The reported spectra are averages of 500 scans; the frequency accuracy is better than 1 cm^{-1}. In a few experiments, a 175-W medium-pressure mercury arc lamp (Philips H39KB) without the globe was used to photolyze the matrix at 30-min intervals. The argon matrices were annealed several times from 20 to 40 K to promote further halogen reactions with the uranium atoms and the uranium halides. Matrix FTIR spectra were taken before and after the sample deposition and after each photolysis/annealing.

Results

Matrix IR experiments were performed separately on F_2, ClF, and Cl_2 reactions with pulsed-laser evaporated uranium atoms.

U + F_2. A series of uranium atom and fluorine experiments was performed over a wide range of fluorine concentrations and laser energies. The commercial fluorine sample contained the usual trace impurities of HF, CF_4, SiF_4, and OCF_2. Figures 1 and 2 illustrate the pronounced effects that a relatively small increase in laser energy has on the product absorptions in the U–F stretching region using Ar/F_2 = 200/1 samples. The spectrum in Figure 1a was recorded after a 6-h deposition of uranium atoms from a 30 mJ/pulse ablation with an Ar/F_2 sample. Th strongest product band (labeled A) appeared at 400 cm^{-1} while a considerably weaker product absorption (labeled B) was detected at 446 cm^{-1}. Other product absorptions included the UF_5 band at 584 cm^{-1}, the UF_4 doublet at 537 and 532 cm^{-1}, and weak broad bands at 496 an 561 cm^{-1} (labeled C and D, respectively). Figure 1b shows the effects of annealing the matrix to 20 K. The annealing increased the intensity of each product band. The B band exhibited the largest increase while the A absorption had the smallest increase. In addition, the product bands at 496 and 561 cm^{-1} sharpened while the UF_6 absorption appeared at 620 cm^{-1}. The spectrum in Figure 1c was obtained after the matrix was annealed to 25 K. The UF_6, C, D, and B bands exhibited the largest increases in intensities. It is important to note the different growth patterns of the UF_5 and D bands in the present experiments since earlier matrix IR studies[4,6] assigned 584- and 561-cm^{-1} absorptions to UF_5. In the earlier works, the intensity ratio of the 584-cm^{-1} band to the 561-cm^{-1} absorption remained a constant 8:3.[4,6] The spectrum in Figure 1d displays the results of annealing the matrix to 35 K. The UF_6 product band grew at the expense of the other product absorptions. The B band, which was the strongest absorption after the 25 K annealing, remained a prominent feature. Additional higher frequency bands were observed at 706, 776, 872, 938, and 986 cm^{-1}; the 776-cm^{-1} absorption is due to UO_2.[17] Annealing produced a 695-cm^{-1} band and increased UO_2, 872-, and 938-cm^{-1} absorptions. In contrast, the 706- and 986-cm^{-1} bands decreased. The growth patterns of the higher frequency bands were different from the patterns of the new U + F_2 species in Figure 1.

The spectrum in Figure 2a shows the effects of a slightly higher laser energy, 40 mJ, during the 6-h codeposition process with an Ar/F_2 = 200/1 sample. The most intense product absorptions were the UF_4 bands at 537 and 532 cm^{-1}. Other intense product bands included the UF_5 and C bands while the intensities of the UF_6 and D absorptions were relatively weak. It should be noted that A and B product absorptions did not appear following the codeposition process with the higher laser ablation energy. Figure 2a displays the effects of annealing the matrix to 20 K. The UF_6 absorption grew by a factor of 6. The intensity of the UF_5 band increased by 50%, and very weak A and B bands appeared. In contrast, the UF_4 and C absorptions were slightly reduced. After the matrix was annealed to 32 K, the spectrum in Figure 2c was taken. The UF_6 and B absorptions doubled in intensities while the UF_4 doublet was reduced by 67%. The intensities of the other products were reduced slightly. The spectrum in Figure 2d shows the effects of annealing the matrix to 40 K. The satellite bands around the primary UF_6 absorption grew while the other product bands were reduced significantly.

Another experiment was conducted with still lower laser energy (20 mJ/pulse). The A band was comparable in intensity to its counterpart in Figure 1a while the only other product bands B, C, and D were weaker by a factor of 4. No UF_4, UF_5, or UF_6 was observed. Stepwise annealings to 20, 25, 30, and 40 K had the same effects as described earlier. The four new product bands increased slightly on 20 K annealing, and the UF_4, UF_5 and UF_6 absorptions were weak. On annealing to 25 and 30 K, the growth of B and D bands was most pronounced, and the *D band was 3 times stronger* than the UF_4 and UF_5 bands. The UF_6 absorption was dominated after the 40 K thermal cycle.

Two final experiments employed higher fluorine concentration (1%). In the experiment with the higher laser energy (50 mJ/

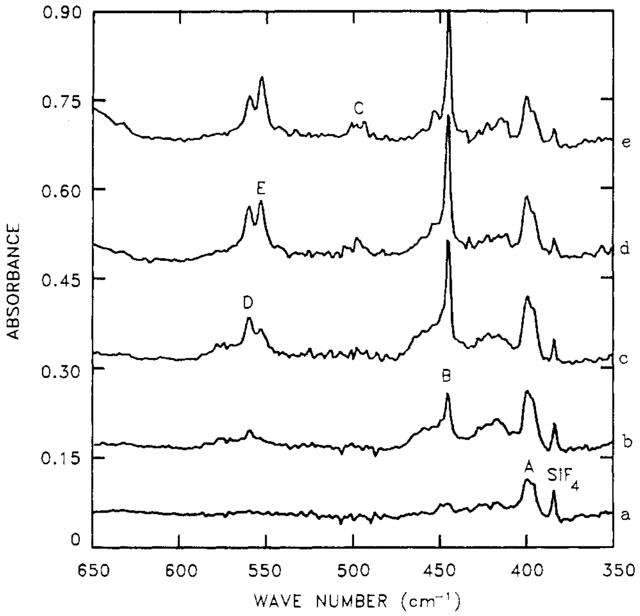

Figure 3. FTIR spectra at 2-cm^{-1} resolution in the 650–350-cm^{-1} region: (a) after a 6-h codeposition of uranium atoms from a 30-mJ ablation and an Ar/ClF = 1000/1 sample at 12 ± 1 K; (b) after annealing matrix a to 20 ± 2 K; (c) after warming matrix b to 25 ± 2 K; (d) after annealing matrix c to 30 ± 2 K; (e) after annealing matrix d to 35 ± 2 K.

Table 1. Product Absorptions (cm^{-1}) of Uranium Halides Observed in Uranium Atom Reactions with Fluorine, Chlorine Fluoride, and Chlorine in Solid Argon

U + F_2		U + ClF		U + Cl_2	
abs	product	abs	product	abs	product
620	UF_6	561	F_3^-	346	UCl_4
584	UF_5	554	(ClF_2^-)	337	UCl_4
561	F_3^-	496	UF_3	335	UCl_4
537	UF_4	446	UF_2	327	UCl_4
532	UF_4	400	UF	323	UCl_4
496	UF_3			312	UCl_2
446	UF_2			308	UCl_2
400	UF			283	(UCl)

pulse), the UF_5 (584 and 561 cm^{-1}) and the UF_4 (537 and 532 cm^{-1}) bands were dominant while the UF_6 and C absorptions were also present. Photolysis increased UF_5 and UF_4 at the expense of UF_6 and C absorptions. The 20 K annealing increased UF_6 and decreased the UF_4 and C bands. The final 30 K annealing decreased all bands with the exception of UF_6. The A and B bands were not detected in this experiment. With the lower laser energy (20 mJ/pulse), the A and B bands were observed, and the D band grew more strongly during the annealings than the UF_5 band at 584 cm^{-1}. In all of these experiments, a weak O_2F band at 1489 cm^{-1} increased on annealing.[19]

Finally, the matrices were photolyzed at various points during the experiments with a mercury arc lamp. However, the photolyses produced only slight changes in the product absorptions which indicates fluorination of uranium and uranium fluorides occurs spontaneously even at these cryogenic temperatures. It should be noted that the fluorine molecules were photolyzed during the codeposition process by the radiation emitted during laser ablation process. This photolysis probably leads to a substantial fluorine atom population in the matrix samples.

U + ClF. A set of experiments was conducted with uranium atoms and ClF in solid argon. The ClF sample contained $FClO_2$, CF_4, and SiF_4 impurities.[20] The spectrum in Figure 3a shows the product bands in the U–F stretching region after the 6-h codeposition of uranium atoms with an Ar/ClF = 1000/1 sample. The product absorptions at 400 and 446 cm^{-1} (labeled A and B, respectively) were produced earlier in the U atoms + F_2 experiments. The sharp band at 385 cm^{-1} is due to the SiF_4 impurity.[20] No product absorptions were detected in the U–Cl stretching region. While photolysis of the matrix failed to affect these product absorptions, sample annealing to 20 K caused significant changes that are displayed in Figure 3b. The intensities of the A and B absorptions increased by 50 and 500%, respectively, and a new product band (labeled D) appeared at 561 cm^{-1}. It should be noted that the UF_5 band at 585 cm^{-1} was not detected so this 561-cm^{-1} band cannot be due to UF_5. Parts c and d of Figure 3 display effects of annealing the matrix to 25 and 30 K, respectively. Both annealings increased the intensities of the B and C bands. The intensity of the A band increased slightly during the 25 K annealing and decreased during the 30 K annealing. A new product (labeled E) appeared at 554 cm^{-1} along with the ClF_2 radical[21] at 574 cm^{-1} and the C band at 496 cm^{-1}. The growth pattern at 35 K, which is shown in Figure 3e, was similar to the 30 K annealing pattern. These new products and their growth patterns were reproduced in similar dilute uranium atom and ClF experiments which minimized secondary reactions during the codeposition process. In contrast, the strongest absorptions in the experiments with high ClF concentrations were the UF_6 and UCl_4 bands due to the significant increase in secondary reactions.

U + Cl_2. A complementary study on uranium atom reactions with chlorine was performed. At high Cl_2 concentrations (Ar/Cl_2 = 200/1), the primary product was UCl_4, and the UCl_4 absorptions at 346, 337, 335, 327, and 323 cm^{-1} are in agreement with the results from earlier matrix IR studies.[2,8] New product bands included a weak doublet at 312 and 308 cm^{-1} and a very weak absorption at 283 cm^{-1}. At low Cl_2 concentrations (Ar/Cl_2 = 800/1), the new doublet was the dominant feature after the codeposition. Matrix annealing initially increased the weak 283-cm^{-1} band while the subsequent annealing increased the intensities of the UCl_4 absorptions at the expense of the doublet. The new product absorption at 283 cm^{-1} remained weak regardless of the experimental conditions. It should be noted that the UCl_5 and UCl_6 absorptions[8] were not detected in this study.

Discussion

The product bands, which are listed in Table 1, were only observed in high yields after the appropriate reagents were codeposited and annealed. The new absorptions will be identified and assigned based on their frequencies, their growth patterns, and the reaction conditions.

UF and UF_2. The U + F_2 experiments with low laser power favored two new absorptions at 400 and 446 cm^{-1} (labeled A and B, respectively). Each of these new absorptions in the U–F stretching region exhibited a different growth pattern, and they are not due to the previously characterized UF_4, UF_5, or UF_6 molecules. The lower laser energy minimized fluorine reactions so these new uranium compounds probably contain one or two fluorine atoms. However, the analysis of the spectra is complicated by the presence of significant quantities of fluorine atoms. The radiation from the ablation process can photolyze fluorine molecules, and the yield of the fluorine atoms and the remaining molecular fluorine cannot be monitored by IR spectroscopy. Fortunately, these product absorptions were reproduced in the dilute ClF and U experiments. The radiation from the ablation process also photolyzes ClF and generates atomic fluorine and chlorine. Since fluorine atoms can migrate through a matrix easier than chlorine atoms or ClF, the primary reactions during the initial annealings should involve single fluorine atom additions. This is substantiated by the growth of ClF_2[21] and O_2F[19] radical

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absorptions during annealings. Therefore, controlled matrix annealings should produce UF and UF_2 in a stepwise manner. This sequential formation of uranium fluorides is clearly demonstrated in Figures 1–3. The A band is the dominant feature after the codeposition which suggests the A absorption is due to first reaction product. During the subsequent matrix annealings, the B band appeared first and remained stronger than the C absorption which indicates the B product is a precursor to the C product. Therefore, the 400- and 446-cm^{-1} absorptions are assigned to UF and UF_2, respectively. It is important to note that continued annealings favored C, UF_4, UF_5, and UF_6 absorptions at the expense of the lower fluorides.

The chemical evidence suggests that the first product formed by reaction 1 is UF; this reaction is exothermic by approximately 120 kcal/mol.[12] Diffusion and reaction of F atoms then produce

$$U + F_2 \rightarrow UF + F \qquad (1)$$

UF_2 by reaction 2,which is exothermic by 136 kcal/mol.[12] The

$$F + UF \rightarrow FUF \qquad (2)$$

direct insertion reaction (eq 1 plus eq 2) is exothermic by approximately 256 kcal/mol, which is more than enough to dissociate UF_2 (reverse of eq 2) and preclude its formation by insertion. Accordingly, the sharp B band at 446 cm^{-1}, which grows markedly on annealing, is best assigned to UF_2. The above assignment places the ν_3 fundamental of UF_2 at 446 cm^{-1} above the fundamental of UF at 400 cm^{-1}. The reverse trend was observed for the uranium oxides, UO_2 (776 cm^{-1}) and UO (820 cm^{-1}),[17] and the barium fluorides, BaF_2 (390 cm^{-1}) and BaF (465 cm^{-1}).[22] Barium difluoride is a bent molecule,[22] and theoretical considerations suggest that UF_2 is also bent.[23]

UF_3. The C (496 cm^{-1}) and D (561^{-1}) bands grow on annealing following the A and B bands and preceding UF_4, UF_5, and UF_6. Therefore, it is reasonable to expect the formation of UF_3 through reaction 3 in these experiments. In the lower laser energy

$$UF_2 + F \rightarrow UF_3 \qquad (3)$$

experiments with F_2 and ClF, the D band is not due to UF_5 since the strongest UF_5 band at 584 cm^{-1} is weaker or absent. It is reasonable to assign the 496-cm^{-1} band to the antisymmetric axial U–F stretching mode of UF_3. UF_3 is presumably a T-shaped molecule like SF_3[24] since the 496-cm^{-1} absorption is below the UF_4 bands at 537 and 532 cm^{-1}. Although the 561-cm^{-1} band behaves on annealing as a species with three F atoms, it is highly unlikely that the frequency of the antisymmetric axial U–F stretching mode of UF_3 would be higher than its UF_4 counterpart.

F_3. The most likely assignment for the 561-cm^{-1} band is isolated F_3^- in solid argon. Electron capture processes are known to play a minor role in pulsed-laser experiments since BO_2^- and O_4^- have been observed.[15,17] Fluoride anion is clearly a stable electron trap. Reaction 4 is calculated to be exothermic by 26 kcal/mol,[25]

$$F_2 + F^- \rightarrow F_3^- \qquad (4)$$

and the analogous $Cs^+F^- + F_2 \rightarrow Cs^+F_3^-$ reaction has been characterized.[26] The present value of 561 cm^{-1} is in excellent agreement with the 550-cm^{-1} band of the $M^+F_3^-$ ion pairs in solid argon.[26,27] Similar bands at 566 and 554 cm^{-1} have been assigned to the $Cs^+ClF_2^-$ species,[27] and the present 554-cm^{-1} band in the ClF experiments is probably due to isolated $(FClF)^-$.

UCl_2 and UCl. Since Cl_2 is less photosensitive than F_2, the ablation process produced only small amounts of chlorine atoms. Therefore, nearly all of the uranium reactions will involve molecular chlorine. These uranium experiments generated two dominant products, UCl_4 and a new product with a 312- and 308-cm^{-1} doublet. The new doublet was more intense than the UCl_4 absorptions after the deposition of very dilute Cl_2 samples. During the matrix annealings the UCl_4 bands grew at the expense of the doublet, which indicates the doublet is a precursor to UCl_4. In addition, an earlier matrix IR study[14] assigned bands at 297 and 295 cm^{-1} to UCl_2 in solid nitrogen. The 312- and 308-cm^{-1} doublet is assigned to UCl_2, based on the growth pattern and frequency position. Since nitrogen matrices generally red shift vibrational modes of ionic molecules more than argon matrices, these assignments are in agreement.

The U + Cl_2 study also produced weak product absorption at 283 cm^{-1}, and it increased on annealing in the most dilute experiments. The UO absorption exhibited the same growth pattern in the U + O_2 study.[17] The 283-cm^{-1} band is red-shifted from the UCl_2 doublet by 29 and 25 cm^{-1}. A comparable red-shift of 46 cm^{-1} was observed from UF_2 to UF. These factors suggest that the 283-cm^{-1} absorption is due to the UCl diatomic molecule, but this identification is tentative.

Conclusions

Uranium atom reactions with F_2, ClF, and Cl_2 were examined using laser ablation matrix infrared spectroscopy. In the U + F_2 study the radiation emitted by the laser ablation process generated a significant amount of fluorine atoms. Matrix annealings and higher fluorine concentrations produced infrared absorptions of previously characterized UF_4, UF_5, and UF_6. The UF, UF_2, and UF_3 transient species and their absorptions at 400, 446, and 496 cm^{-1}, respectively, were favored when the Nd:YAG laser power was kept to a minimum. The U and ClF study verified the UF, UF_2, and UF_3 assignments since ClF is an excellent source of fluorine atoms in a matrix. A weak 561-cm^{-1} band in these experiments is identified as the isolated F_3^- anion. These transient lower uranium fluorides were reproduced in a stepwise manner by matrix annealings, which ultimately favored the stable higher uranium fluorides. At high ClF concentrations, UF_6 and UCl_4 were the dominant products instead of a mixture of uranium chloride fluorides. Additional IR spectra of atomic uranium reactions with Cl_2 were obtained, and a doublet at 308 and 312 cm^{-1} is assigned to UCl_2. Either UCl_4 or UCl_2 was the principal product depending on the chlorine concentration. Since Cl_2 is less photosensitive than F_2, the ablation process produced only small amounts of chlorine atoms. However, a weak absorption at 283 cm^{-1} is tentatively assigned to UCl. Finally, each atomic uranium and halogen reaction in this study required little or no activation energy as the products were formed on annealings from 20 to 40 K.

Acknowledgment. The research was sponsored by the National Science Foundation, under Grant CHE 91-22556 and by the Division of Chemical Sciences, U.S. Department of Energy, under Contract DE-AC05-84-OR21400 with the Martin Marietta Energy Systems, Inc.

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