Monitoring the Reaction Dynamics of UF_6 by Cryogenic Layering and FTIR Spectroscopy

Louis E. McNamara, Abigail M. Waldron, John T. Kelly, Samuel Uba, Eliel Villa-Aleman,
Kimberly A. S. Fessler
Savannah River National Laboratory, Aiken, SC, USA 29808-0001

ABSTRACT

Uranium hexafluoride (UF_6) is a commonly used material feedstock for uranium enrichment processes. When introduced to water in the atmosphere, it reacts rapidly to form uranyl fluoride (UO_2F_2). Here, we investigate the UF_6 hydrolysis reaction by cryogenically trapping reaction intermediates and characterizing the trapped species by FTIR. The reactant species are sequentially layered onto a diamond substrate held at 10K by a closed cycle liquid helium cryostat. At this temperature, the hydrolysis reaction is not spontaneous and can be catalyzed by the introduction of heat. Upon heating, the reaction moves through several intermediate compounds before proceeding to the final UO_2F_2 product. Several previously unobserved bands appear while the reaction progresses which may help to elucidate the mechanism behind UF_6 hydrolysis.

Keywords: Uranium hexafluoride, kinetics, cryogenic, FTIR

1. INTRODUCTION

Uranium enrichment is the process of increasing the relative isotopic composition of ^{235}U from naturally occurring to the level needed for nuclear fuel. Popular enrichment techniques such as gas diffusion, gas centrifuge, and laser enrichment all utilize uranium hexafluoride (UF_6) as the material feedstock for the enrichment process. UF_6 is an ideal candidate for uranium enrichment due to its advantageous material properties. It is a solid at room temperature but possess a large vapor pressure which allows it to be easily sublimated through heating. Since there is only one naturally abundant fluorine isotope, all of the mass separating is achieved by the different isotopes of uranium. Working with UF_6 has one major limitation, it is highly reactive. This means it must be kept under vacuum or inert atmosphere. At elevated temperatures, even stainless steel is known to quickly corrode upon exposure to UF_6. UF_6 release to the atmosphere results in the rapid and spontaneous hydrolysis reaction $UF_6 + 2H_2O \text{ -> } UO_2F_2 + 4HF$. The uranyl fluoride hydrate produced by the reaction plays a critical role in nuclear nonproliferation and safeguards efforts. Despite a vast amount of knowledge being developed over the last 70 years from the industrial uses of UF_6, there is still much debate over the reaction dynamics governing its hydrolysis.

Investigations into the hydrolysis of UF_6 began as early as 1943 by H. E. Eduljee at the Imperial Chemical Industries, Ltd.[1] who was able to obtain different UO_2F_2 hydrate complexes by varying the relative concentrations of water and UF_6. Eduljee's work was quickly followed by several X-ray diffraction studies which corroborated Eduljee's finding and observed multiple forms of UO_2F_2 hydrate as the product of UF_6 hydrolysis.[2-4] In 1956, the intermediate compound UOF_4 was proposed by Brooks et al. as the product of the first half reaction in the hydrolysis:[5]

$$UF_6 + H_2O \rightarrow UOF_4 + 2HF$$

$$UOF_4 + H_2O \rightarrow UO_2F_2 + 2HF$$

Brooks et al. attempted to isolate UOF_4 by reacting small quantities of water with large amounts of UF_6 over varying time frames but were unable to observe compounds other than hydrates of UO_2F_2. Attempts to isolate UOF_4 by reacting sub stoichiometric quantities of water and UF_6 were continued by Otey and LeDoux in 1967. Ratios as low as 9 grams of water to almost one ton of UF_6 were attempted without success.[6] UOF_4 had been synthesized by a SeF_4-UO_3 reaction,[7] but Otey and LeDoux concluded UOF_4 could not be synthesized by controlling the stoichiometry between water and UF_6. However, under the reaction conditions of their experiment, Otey and LeDoux were able to isolate $U_2O_3F_6$ and $U_3O_5F_8$ as intermediate compounds formed during the hydrolysis. $U_2O_3F_6$ would later be prepared and further characterized by Wilson in 1974 and another compound, $U_2O_2F_7$, would be prepared and characterized by Asada et al. in

1987.[8, 9] The $U_3O_5F_8$ compound does not appear to have been further characterized in the literature. Around the same time as Otey and LeDoux, attempts to study the reaction in reverse by reacting UO_2F_2 with HF, ClF_3 and SF_4 were performed in order to better understand UO_2F_2 chemistry.[10-12] These reactions were successful in turning UO_2F_2 back into UF_6 and generating various new uranyl fluoride hydrates, but UOF_4 was not observed. Three papers published in the early 1970 successfully synthesized UOF_4 through the use of liquid HF and were able to obtain Raman, infrared, and x-ray crystallographic data on the synthesized compound.[13-15]

Work studying the hydrolysis of UF_6 continued through the early 1990s at the Oak Ridge Gaseous Diffusion Plant where several studies were performed by controlled release of UF_6 gas into different atmospheric conditions.[16-20] From these studies, the group at Oak Ridge was able to study the kinetics and thermodynamics of the reaction and the resulting UO_2F_2 formation. Progress on capturing the elusive UOF_4 intermediate culminated in 1992 in a seminal manuscript by Sherrow and Hunt.[21] Sherrow and Hunt performed gas deposition and matrix isolation experiments at 12K in order to isolated intermediate complexes during the hydrolysis of UF_6. The isolated compounds were reacted through a combination of annealing and photolysis by 254 nm light source. They observed little affect due to annealing up to 60K in the case of the matrix isolated experiments, but were able to catalyze the reaction by UV induced photolysis of UF_6. Photolysis resulted in the formation of a new doublet in the IR spectrum at 567 and 868 cm^{-1}, which they attributed to the formation of UOF_4. These results were corroborated by their solid deposition experiments where a doublet was also observed and could be produced through annealing up to 172K. Identification of the UOF_4 mode was also supported by isotopic substitution experiments.

Sherrow and Hunt assigned initial absorption bands to a 1:1 complex with the anti-hydrogen-bonded structure UF_6-OH_2. This proposed structure was anticipated due to the high affinity of U(VI) for oxygen ligands and the Lewis acidity of UF_6. Sherrow and Hunt concluded that the hydrolysis reaction could only be initiated through UF_6-n(OH_2) ($n \geq 1$) complexes. The UOF_4 bands then appeared only after catalyzing the reaction through UF_6-n(OH_2) complexes and no other bands for other possible intermediate complexes were reported. This growth pattern would be anticipated for the first step in the hydrolysis reaction. The UO_2F_2 absorption band grew in at the expense of the assigned UOF_4 bands, which suggests the product species is due to the further hydrolysis of UOF_4. Sherrow and Hund concluded the UF_6-OH_2 complex reacts spontaneously with excess water to form UOF_4, even at temperatures below 30K. However, this complex was required to be formed in the gas phase.

As computational chemistry developed, there were many theoretical studies performed on UF_6 due to its importance in the nuclear industry, as well as the abundance of experimental data which made it an excellent test case for new methods.[22] Calculations on the mechanism behind the hydrolysis of UF_6 did not begin until the early 2000s. In 2002 Privalov et al. published work comparing the thermodynamic properties of various uranium oxyfluoride compounds theoretical and experimental values.[23] Interestingly, the results of Privalov's work predicted that the hydrolysis of UF_6 should be endothermic, in direct contrast with experimental data. Over the next 2 decades several computational studies would be performed in order to try and rectify the discrepancies between theory and experiment.[24-29] These studies all suggest the UF_6 hydrolysis mechanism is more complicated than previously believed. In particular, the proposed mechanisms rely on the generation of an elusive UF_5OH intermediate, which has never been observed experimentally.

Since the hydrolysis reaction of UF_6 is of recurring fundamental concern, further examination of this reaction mechanism is of interest. Here we present new data collected on the hydrolysis of UF_6 by cryogenically layering reactants and trapping intermediate compounds then characterizing the compounds with FTIR spectroscopy.

2. EXPERIMENT

The experimental design has been previously reported for studies of MoF_6 and UF_6 hydrolysis.[30, 31] A Jasco FT-IR 6300 (Jasco Inc, Easton, MD, USA) was employed for the acquisition of infrared spectra. To control the initiation of the hydrolytic reaction, the UF_6 and water vapor were cryogenically condensed under vacuum by means of a closed cycle liquid helium cryostat (Janis Research, VPF Series). The cryogenic layers were held under a vacuum of 100 mTorr (13 Pa) during the duration of the entire experiment. The cell was constructed with 2-inch diameter uncoated zinc selenide windows (Edmund Optics, ZC-W-50-2) with a thin polished polycrystalline diamond window for cryogenic layering (Applied Diamond, Inc., 18 mm diameter, 150 microns thin). The cell was brought under vacuum (Edwards Oil-Free Scroll Pump) to evacuate air and water vapor prior to and while achieving cryogenic conditions. A scan was taken periodically with a 2 cm^{-1} resolution, 8 averages, and a 500 to 4000 cm^{-1} spectral range while the cell warmed to room temperature. UF_6 was obtained from Oak Ridge National Laboratory with natural isotopic distribution of uranium. D_2O and $H_2{}^{18}O$ were purchased from Sigma Aldrich and used without further purification. H_2O was pulled from the atmosphere.

3. RESULTS AND DISCUSSION

Initial spectra of the sequentially layered UF_6 and H_2O reactants suggest that the reaction is successfully halted at cryogenic temperatures. IR absorbance spectra of the layered reactants show the characteristic absorbance of both UF_6 and H_2O, **Figure 1A**. Since the water for this experiment was drawn directly from the air, a small band for CO_2 is also present. Once the layered reactants begin to warm up to room temperature, the reaction proceeds. Bands associated with UF_6 begin to deplete and bands attributed to UO_2F_2, UOF_4, and unknown intermediates grow in over time, **Figure 1B**. In addition to observable changes in the 500-1000 cm^{-1} region which are associated with U-O and U-F bonding, a rich and dynamic hydrogen bonding network is observed from 1000-4000 cm^{-1}, which corresponds well with previous experimental spectra of cryogenic solution of HF.[32-34] The presence of the extended hydrogen bonding network and structure of the bands associated with the UO_2F_2 product demonstrate the level of hydration within the experiment. All off the observed bands are likely associated with hydrates of the corresponding compounds and the hydration will result in shifting of the observed bands.

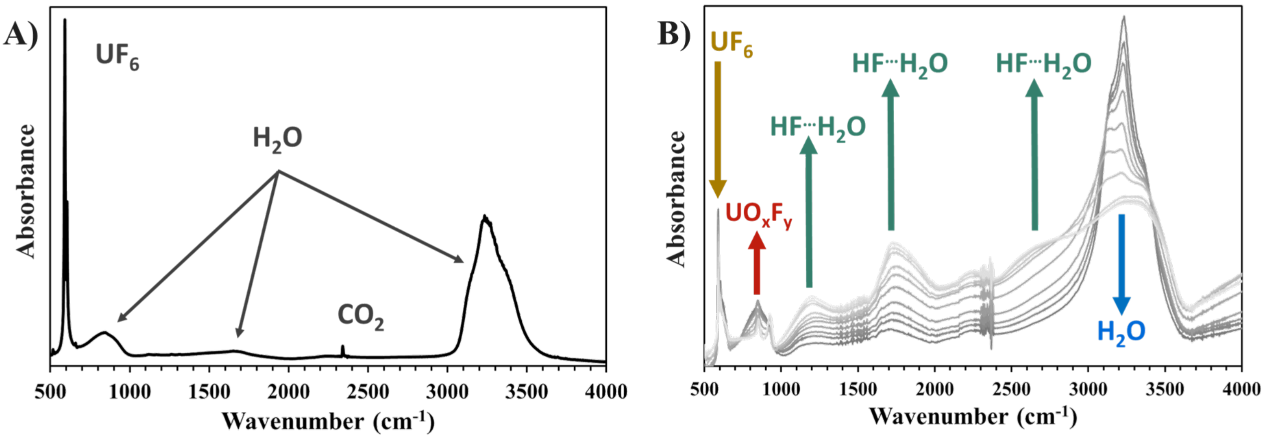

Figure 1. A) Initial FTIR spectra of layered UF_6 and H_2O reactants on diamond substrate. This initial spectrum shows characteristic bands for UF_6 and H_2O but does not contain and bands associated with product or intermediate compounds. B) As the system heats, the reaction begins, and bands associated with reactant compounds diminish while bands associated with product and intermediate compounds grow. In addition, a dynamic hydrogen bonded network appears showing the formation of HF. Color change from dark grey to light grey represents the reaction moving forward in time.

Intermediate spectra of the reaction are presented in **Figure 2**. From these spectra, the initial UF_6 bands are seen at 600 cm^{-1} as well as the previously observed UOF_4 doublet around 860 cm^{-1} and the UO_2F_2 hydrate product band at 950 cm^{-1}. The UOF_4 doublet is attributed to the axial and equatorial isomers of UOF_4. Here, the doublet is observed to transition to a singlet over time, suggesting one of the isomers becomes more dominant as the reaction progresses. In addition to the observed bands for the UOF_4 intermediate, four new bands are observed at 715 cm^{-1}, 750 cm^{-1}, 780 cm^{-1}, and 815 cm^{-1}. A pair of bands observed at 750 cm^{-1} and 815 cm^{-1} appear after the initial formation of UOF_4. This pair of bands may form earlier, but significant overlap with the ice libration band in the initial spectra make it difficult to observe the initial formation. These bands then deplete as the two bands at 715 cm^{-1} and 780 cm^{-1} grow. We have previously reported three of these bands[31] but their intensities relative to the UOF_4 and product bands has been significantly increased by altering the ratio of UF_6 to H_2O to ensure a large excess of H_2O in the experiment. The relative abundance of the intermediate compounds associated with these new intermediate bands appears to be a function of the UF_6:H_2O ratio. There is little experimental evidence for what compounds these new bands could represent and due to the complex nature of the extended hydrogen bonding network and the changes in temperature, it is difficult to assign these bands from the performed experiment alone. The depletion of the bands at 750 cm^{-1} and 815 cm^{-1} and formation of the pair of bands at 715 cm^{-1} and 780 cm^{-1} is highly correlated with significant blue shifting of UOF_4 and UO_2F_2 bands. It does not appear that these bands are associated with any other new bands which could help elucidate the nature of the intermediate

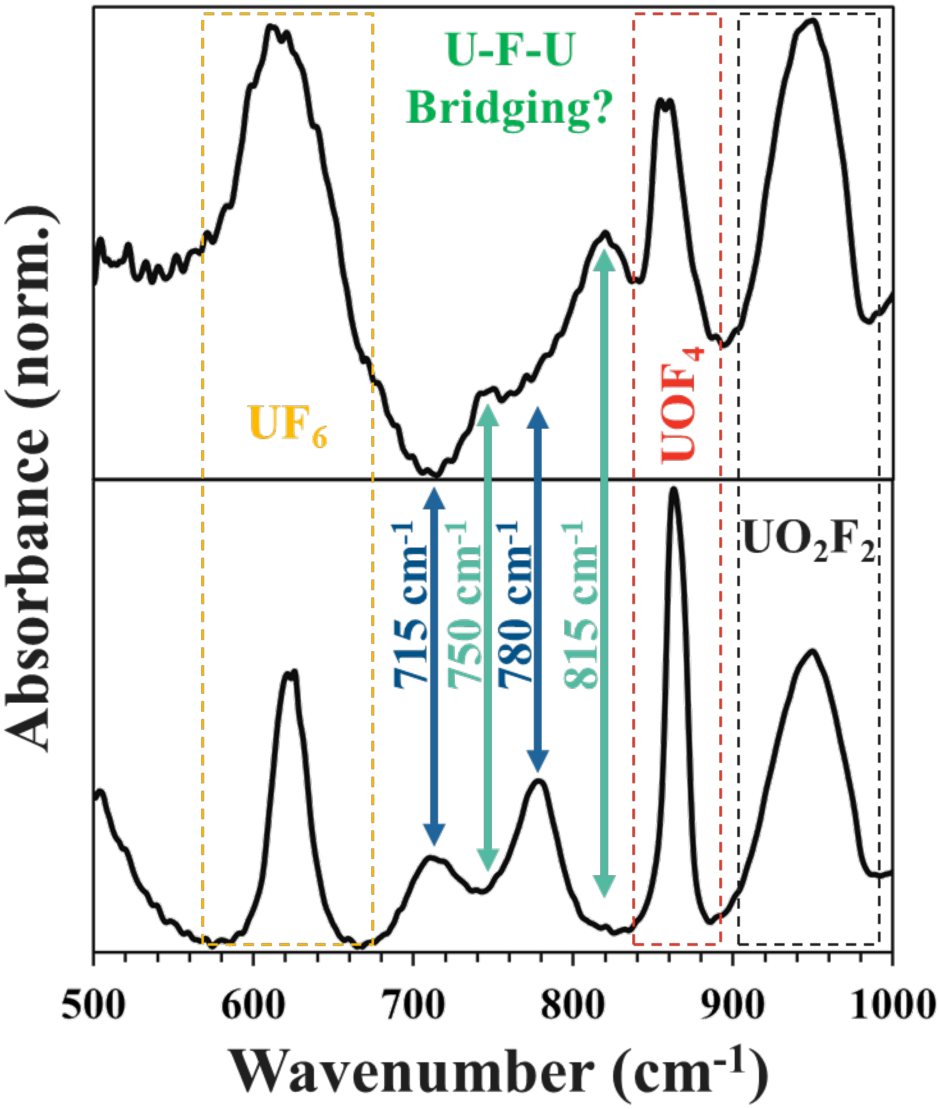

Figure 2. Top: FTIR spectrum of new intermediate bands seen at 750 cm^{-1} and 815 cm^{-1}. As the system continues to react these bands dimmish and the bottom spectrum is observed. Bottom: FTIR spectrum of intermediate bands seen at 715 cm^{-1} and 780 cm^{-1}. In addition to changes in the new intermediate bands, noticeable shifts in the UF_6, UOF_4, and UO_2F_2 bands are also observed as the reaction progresses.

complexes, but other associated bands could be eclipsed by the UOF_4 and UO_2F_2 signatures. The bands also do not appear to be previously reported $U_xO_yF_z$ complexes from the literature.[8, 9] Since literature for uranium oxyfluoride compounds which absorb in the 700-850 cm^{-1} region is very limited, our previous assignment of these bands as U-O-U bridged compounds came primarily from computational studies by Hu et al. in 2008 and 2009.[26, 27] Hue calculated several clusters of possible reaction intermediates with U-O and U-O-U bonding which absorb roughly in the region of interest. Computational predictions of the U-O bond stretching region for UF_5OH were predicted to be higher energy, ~860 cm^{-1}, than the observed bands. Although, a UOF_4●UF_5OH●HF cluster was predicted to absorb at 754 cm^{-1}. The theoretical frequency for the U-O-U stretching band in the bridged compound $(UF_5)_2O$ was calculated to be at 715 cm^{-1} and several clusters of $(UF_5)_2O$ with H_2O and HF were all predicted to absorb between 690 cm^{-1} and 720 cm^{-1}. There was no reported compound that recovered the observed pairs of band at 750/815 cm^{-1} and 715/780 cm^{-1}. Since these

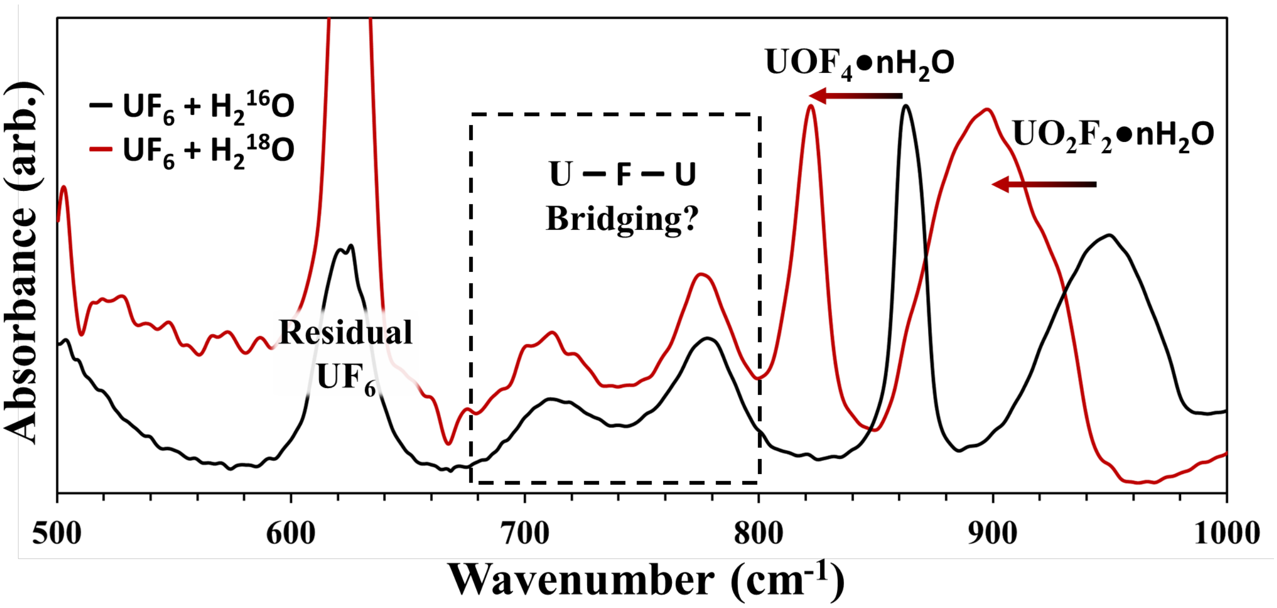

Figure 3. Comparison of 500-1000 cm^{-1} region of intermediate spectra for the hydrolysis reaction with $H_2{}^{16}O$ and $H_2{}^{18}O$. The bands associated with U-O bond stretching shift approximately 50 cm^{-1} but the newly observed intermediate bands do not shift.

calculated frequencies fall within the same region as the observed intermediate bands, the newly observed bands were initially attributed to similar compounds.

In order to better understand the nature of these intermediate complexes, isotopic substitution studies were performed using D_2O and $H_2{}^{18}O$. The results of isotopic substitution for the UOF_4 and product bands are as expected, D_2O has no effect on band position and $H_2{}^{18}O$ shifts the associated bands to lower energy by about 50 cm^{-1}, **Figure 3**.[35] Some amount of the spectral shift between the two isotopologues will also be due to differences in the hydrated species formed. In contrast, the newly observed intermediate bands behave unexpectedly. The pair of bands at 715 cm^{-1} and 780 cm^{-1} does not shift upon isotopic substitution of ^{16}O to ^{18}O, which suggests the bands are not part of a U-O-U bridged complex as previously speculated. Instead, these bands must be related to some form of U-F bonding, possibly U-F-U bridging, but there are no related compounds reported in the literature which absorb in this region. The band at 815 cm^{-1} is not observed upon isotopic substitution of ^{16}O with ^{18}O. This could be because the band at 815 cm^{-1} does not shift and is now eclipsed by the shifted UOF_4 band. The reverse is observed when D_2O is used for the hydrolysis reaction. The pair of bands at 715 cm^{-1} and 780 cm^{-1} is not observed and the band at 815 cm^{-1} is unshifted, though shifting is not expected in this region due to deuteration.

4. CONCLUSION

Intermediates species generated during the UF_6 hydrolysis reaction have been successfully trapped by cryogenically layering the reactants and slowly adding heat until the reaction progresses. The observed FTIR spectra of the generated products are in good agreement with previously reported UO_2F_2 spectra. The formation of UOF_4 was also observed and the associated bands are in good agreement with those reported by Sherrow and Hunt. In addition to UOF_4, two additional pairs of bands were observed which are attributed to at least two new intermediate complexes which have not been previously reported. Oxygen isotopic substitution studies reveal that these band are not U-O stretching and instead are likely due to U-F-U bridging.

ACKNOWLEDGEMENTS

This work was produced by Battelle Savannah River Alliance, LLC under Contract No. 89303321CEM000080 with the US Department of Energy. Publisher acknowledges the US Government license to provide public access under the DOE

Public Access Plan (http://energy.gov/downloads/doe-public-access-plan). Assistance from Dr. Jason Richards at ORNL for UF_6 expertise and samples is greatly appreciated. Financial support for this work was provided by the National Nuclear Security Administration under Defense Nuclear Nonproliferation R&D.

REFERENCES

1. Eduljee, H. E., *The Reaction Between Water and Uranium Hexafluoride and the Action of Heat on the Reaction Product Tube Alloys*. Imperial Chemical Industries, Ltd Billingham: 1943.
2. Peiser, H. S. A., T. C. *X-ray powder patterns of some metal compounds*; I.C.I. Northwich: 1945.
3. Zachariasen, W., Crystal chemical studies of the 5f-series of elements. III. A study of the disorder in the crystal structure of anhydrous uranyl fluoride. *Acta Crystallographica* **1948,** *1* (6), 277-281.
4. Belcher, R.; Tatlow, J. C., The determination of fluorine in organic compounds. *Analyst* **1951,** *76* (907), 593-595.
5. Brooks, L. H.; Garner, E. V.; Whitehead, E.; United Kingdom Atomic Energy Authority Industrial, G., *Chemical and x-ray crystallographic studies on uranyl fluoride*. United Kingdom Atomic Energy Authority, Industrial Group Headquarters Risley, Warrington, Lancashire, England: Risley, Warrington, Lancashire, England, 1958.
6. Otey, M. G.; LeDoux, R. A., U3O5F8—A new compound in the U□O□F system. *Journal of Inorganic and Nuclear Chemistry* **1967,** *29* (9), 2249-2256.
7. Bergmann, E. D.; Cohen, S.; King, H. G. C.; White, T.; Land, E. J.; Porter, G.; Halmann, M.; Kugel, L.; Pinchas, S.; Bu'Lock, J. D.; Gregory, H.; Hay, M.; Grove, J. F.; Flowers, M. C.; Frey, H. M.; Cromartie, R. I. T.; Scott, P. M.; Bartlett, N.; Robinson, P. L.; Arthur, H. R.; Tam, S. W.; Ng, Y. L., Notes. *Journal of the Chemical Society (Resumed)* **1961,** (0), 3537-3552.
8. Wilson, P. W., U2O3F6—Its preparation and properties. *Journal of Inorganic and Nuclear Chemistry* **1974,** *36* (8), 1783-1785.
9. Asada, K.; Ema, K.; Iwai, T., Preparation and Characterization of U2O2F7. *Bulletin of the Chemical Society of Japan* **1987,** *60* (9), 3189-3193.
10. Midgley, A.; Phillips, T. R.; Hamlin, A. G., Hydrolysis of U□O groups in uranyl fluoride and the possible existence of other fluorooxides of uranium. *Journal of Inorganic and Nuclear Chemistry* **1966,** *28* (12), 3047-3051.
11. Shrewsberry, R. C.; Williamson, E. L., Chemistry of the chlorine trifluoride-uranyl fluoride reaction. *Journal of Inorganic and Nuclear Chemistry* **1966,** *28* (11), 2535-2539.
12. Neveu, G. *Study of* UO_2F_2-H_2O-*HF Compounds; ETUDE DES COMPOSES* UO_2F_2-H_2O-*HF*; France, 1961; pp 1-19.
13. Wilson, P. W., Preparation of uranium oxide tetrafluoride. *Journal of the Chemical Society, Chemical Communications* **1972,** (22), 1241-1241.
14. Jacob, E.; Polligkeit, W., Beiträge zur Chemie der Uranfluoride und -oxidfluoride, I/ Chemistry of Uranium Fluorides and Oxide Fluorides, I. *Darstellung und Schwingungsspektren des Uranoxidtetrafluorids/Preparation and Vibrational Spectra of Uranium Oxide Tetrafluoride* **1973,** *28* (3-4), 120-124.
15. Paine, R. T.; Ryan, R. R.; Asprey, L. B., Synthesis, characterization, and structure of uranium oxide tetrafluoride. *Inorganic Chemistry* **1975,** *14* (5), 1113-1117.
16. Anderson, S. P. *Study of the hydrolysis of uranium hexafluoride by Fourier transform infrared spectroscopy*; United States, 1982; p Medium: ED; Size: Pages: 186.
17. Pickrell, P. W. *Characterization of the solid, airborne materials created by the interaction of UF/sub 6/ with atmospheric moisture in a contained volume*; United States, 1984; p Medium: ED; Size: Pages: 51.
18. Bostick, W. D.; McCulla, W. H.; Pickrell, P. W., Sampling, characterization, and remote sensing of aerosols formed in the atmospheric hydrolysis of uranium hexafluoride. *Journal of Environmental Science and Health . Part A: Environmental Science and Engineering* **1985,** *20* (3), 369-393.
19. Reiner, R. H. *Moist air reaction with excess* UF_6; United States, 1989; p Medium: ED; Size: 27 p.
20. Armstrong, D. P.; Bostick, W. D.; Fletcher, W. H., An FT-IR Study of the Atmospheric Hydrolysis of Uranium Hexafluoride. *Applied Spectroscopy* **1991,** *45* (6), 1008-1016.
21. Sherrow, S. A.; Hunt, R. D., FTIR spectra of the hydrolysis of uranium hexafluoride. *The Journal of Physical Chemistry* **1992,** *96* (3), 1095-1099.
22. Pepper, M.; Bursten, B. E., The electronic structure of actinide-containing molecules: a challenge to applied quantum chemistry. *Chemical Reviews* **1991,** *91* (5), 719-741.

23. Privalov, T.; Schimmelpfennig, B.; Wahlgren, U.; Grenthe, I., Structure and Thermodynamics of Uranium(VI) Complexes in the Gas Phase: A Comparison of Experimental and ab Initio Data. *The Journal of Physical Chemistry A* **2002,** *106* (46), 11277-11282.
24. Garrison, S. L.; Becnel, J. M., Transition State for the Gas-Phase Reaction of Uranium Hexafluoride with Water. *The Journal of Physical Chemistry A* **2008,** *112* (24), 5453-5457.
25. Hu, S.-W.; Lin, H.; Wang, X.-Y.; Chu, T.-W., Effect of H2O on the hydrolysis of UF6 in the gas phase. *Journal of Molecular Structure* **2014,** *1062*, 29-34.
26. Hu, S.-W.; Wang, X.-Y.; Chu, T.-W.; Liu, X.-Q., Theoretical Mechanism Study of UF6 Hydrolysis in the Gas Phase. *The Journal of Physical Chemistry A* **2008,** *112* (37), 8877-8883.
27. Hu, S.-W.; Wang, X.-Y.; Chu, T.-W.; Liu, X.-Q., Theoretical Mechanism Study of UF6 Hydrolysis in the Gas Phase (II). *The Journal of Physical Chemistry A* **2009,** *113* (32), 9243-9248.
28. Lind, M. C.; Garrison, S. L.; Becnel, J. M., Trimolecular Reactions of Uranium Hexafluoride with Water. *The Journal of Physical Chemistry A* **2010,** *114* (13), 4641-4646.
29. Lutz, J. J.; Byrd, J. N.; Lotrich, V. F.; Jensen, D. S.; Zádor, J.; Hubbard, J. A., A theoretical investigation of the hydrolysis of uranium hexafluoride: the initiation mechanism and vibrational spectroscopy. *Physical Chemistry Chemical Physics* **2022,** *24* (16), 9634-9647.
30. McNamara, L.; Waldron, A.; Thomas, M.; Jones, W.; O'Rourke, P.; Darrell, S.; Strange Fessler, K. A., Investigating the hydrolysis of cryogenically layered molybdenum hexafluoride through a disordered hydrogen-bonded network. *Physical Chemistry Chemical Physics* **2023,** *25* (4), 2990-2998.
31. McNamara, L. E.; Kelly, J. T.; Waldron, A. M.; Villa-Aleman, E.; Strange Fessler, K. A., Online monitoring the hydrolysis of uranium hexafluoride for intermediates by cryogenic layering and FTIR. *Frontiers in Nuclear Engineering* **2023,** *2*.
32. Ayotte, P.; Hébert, M.; Marchand, P., Why is hydrofluoric acid a weak acid? *The Journal of Chemical Physics* **2005,** *123* (18).
33. Ayotte, P.; Kelley, J. A.; Nielsen, S. B.; Johnson, M. A., Vibrational spectroscopy of the F−·H2O complex via argon predissociation: photoinduced, intracluster proton transfer? *Chemical Physics Letters* **2000,** *316* (5), 455-459.
34. Ayotte, P.; Plessis, S.; Marchand, P., Trapping proton transfer intermediates in the disordered hydrogen-bonded network of cryogenic hydrofluoric acid solutions. *Physical Chemistry Chemical Physics* **2008,** *10* (32), 4785-4792.
35. Rabinowitch, E., *Spectroscopy of Uranyl Salts in the Solid State*. U.S. Atomic Energy Commission: 1953.