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# Online monitoring the hydrolysis of uranium hexafluoride for intermediates by cryogenic layering and FTIR

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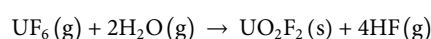
Uranium hexafluoride (UF<sub>6</sub>) is a commonly utilized material feedstock in uranium enrichment processes due to its high vapor pressure and ease of sublimation. When exposed to air, UF<sub>6</sub> undergoes spontaneous hydrolysis to form uranyl fluoride (UO<sub>2</sub>F<sub>2</sub>) particulates which are utilized for the detection of undeclared nuclear activities by nuclear safeguards organizations. The kinetics of the hydrolysis reaction and how they relate to particle morphology of the product are still debated in the literature. Here, we report the direct, *in situ* observation of UF<sub>6</sub> reaction intermediates by cooling the reaction to cryogenic temperatures to significantly reduce the rate of hydrolysis. The reaction is then observable by Fourier transform infrared (FTIR) spectroscopy. The conversion of UF<sub>6</sub> to UOF<sub>4</sub> is observed as well as several other bands associated with possible long lived intermediate complexes. Chemometrics are used to further elucidate the reaction pathway from UF<sub>6</sub> to UO<sub>2</sub>F<sub>2</sub>.

## KEYWORDS

uranium hexafluoride, reaction kinetics, hydrolysis, cryogenic, FTIR, spectroscopy

## 1 Introduction

In the 1980s, the Oak Ridge Gaseous Diffusion Plant conducted several characterization experiments on the spontaneous reaction of uranium hexafluoride (UF<sub>6</sub>) hydrolysis in a controlled environment (Bostick et al., 1983; Pickrell, 1984; Bostick et al., 1985; Pickrell, 1985). These studies show a correlation between physical features observed in the aerosol, the relative humidity, and the temperature of the UF<sub>6</sub> at the time of release. This phenomenon, observed over 40 years ago, has yet to be fully understood and plays a key role in nuclear forensics and safeguards. There is consensus across the scientific literature that the simplified reaction:



can be used to describe the hydrolysis of UF<sub>6</sub> with products of hydrofluoric acid and uranyl fluoride (UO<sub>2</sub>F<sub>2</sub>). Armstrong, Bostick, and Fletcher isolated the product of hydrolysis, UO<sub>2</sub>F<sub>2</sub>, and assigned the observed features in the IR spectrum (Armstrong et al., 1991). Sherrow and Hunt published a seminal spectroscopic study where they observed the formation of UOF<sub>4</sub> by co-condensing water and UF<sub>6</sub> in an argon matrix then initiating the hydrolysis reaction by photolysis (Sherrow and Hunt, 1992). Over the next several decades, multiple computational studies were published suggesting a UF<sub>5</sub>OH intermediate is more

favorable than  $\text{UOF}_4$  (Garrison and Becnel, 2008; Hu et al., 2008; 2009; Lind et al., 2010; Hu et al., 2014; Lutz et al., 2022). Experimentalists have continued to attempt to elucidate the kinetics and identify intermediate compounds formed during the hydrolysis reaction, but the mechanism behind  $\text{UF}_6$  hydrolysis remains heavily debated in the literature (Paine et al., 1975; Klimov et al., 1992; Kips et al., 2007; Wagner et al., 2015; Richards et al., 2020; Pastoor et al., 2021). To date, there has been no experimental evidence for the formation of  $\text{UF}_5\text{OH}$  and no *in situ* observations of any intermediate formation during the  $\text{UF}_6$  hydrolysis reaction.

Here, we demonstrate the ability to monitor the generation of reaction intermediates by cryogenic layering. We explore the hydrolysis of  $\text{UF}_6$  through temperature dependent infrared spectroscopy based on methods recently developed to better understand the hydrolysis of molybdenum hexafluoride ( $\text{MoF}_6$ ) (McNamara et al., 2023). By layering the reactant at cryogenic temperatures, the hydrolysis reaction is effectively halted until the sample layers are warmed sufficiently to overcome the activation barrier of each step in the hydrolysis reaction. Continuous monitoring of the sample layers by FTIR allows for the direct, *in situ*, observation of intermediates forming and being consumed as the reaction progresses. The data presented here is the initial findings from applying this technique to  $\text{UF}_6$ .

## 2 Methods

The experimental design has been previously reported for studies of  $\text{MoF}_6$  hydrolysis (McNamara et al., 2023). In brief, 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  $\text{UF}_6$  and water vapor were cryogenically condensed under vacuum by means of a 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 (Ap-plied 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  $2\text{ cm}^{-1}$  resolution, 8 averages, and a 500 to  $5,000\text{ cm}^{-1}$  spectral range while the cell warmed to room temperature.

## 3 Results

The final product of the reaction aligns well with previously reported IR spectra of uranyl fluorides. A strong absorption band at  $940\text{ cm}^{-1}$  is observed which is attributed to U-O stretching of  $\text{UO}_2\text{F}_2$ . Two distinct bands around  $1,700\text{ cm}^{-1}$  and a broad absorption band from  $2,500\text{--}3,500\text{ cm}^{-1}$  are observed, which are attributed to  $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O} \cdot y\text{HF}$  complexes. The resulting product is spectroscopically identical to the product observed by Armstrong et al., suggesting we have formed the same final product despite the reaction being performed in the condensed phase.

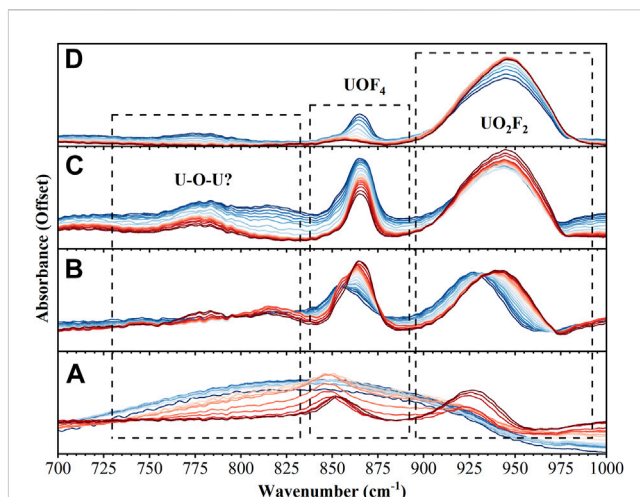


FIGURE 1

FTIR spectra from  $700\text{--}1,000\text{ cm}^{-1}$  over 4 different time intervals: (A) 0–30 min (B) 31–40 min (C) 41–60 min (D) 61–72 min. Spectra in dark blue are the earliest while dark red represents the last spectra in that time interval.

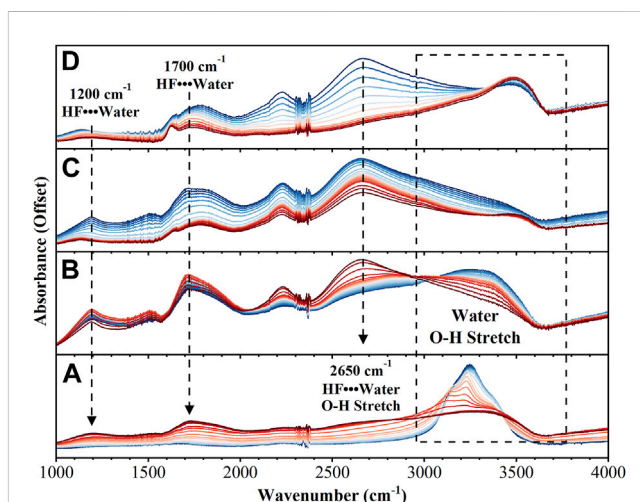
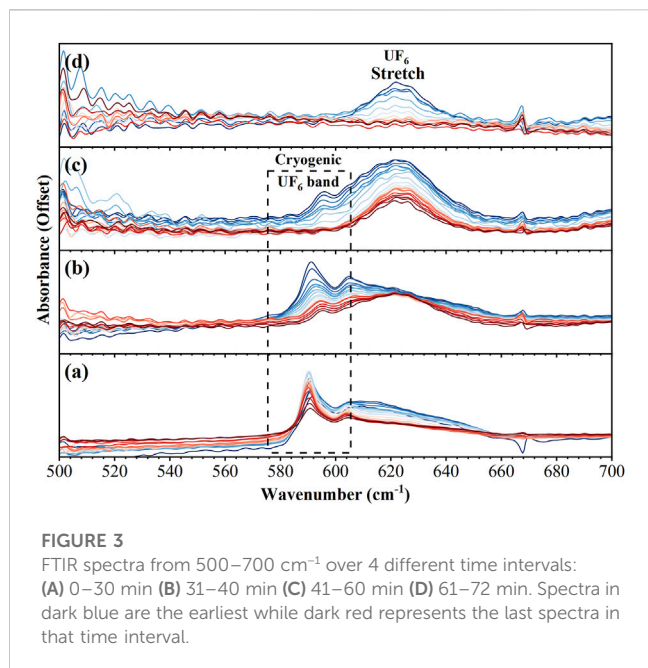


FIGURE 2

FTIR spectra from  $1,000\text{--}4,000\text{ cm}^{-1}$  over 4 different time intervals: (A) 0–30 min (B) 31–40 min (C) 41–60 min (D) 61–72 min. Spectra in dark blue are the earliest while dark red represents the last spectra in that time interval.

From time zero, it takes roughly 10 min for the layered reactants to warm enough to initiate the reaction. No temperature data could be recorded for these experiments, but temperatures have been estimated based on temperature data from previous experiments: time zero  $\sim 10\text{ K}$ , after 30 min.  $\sim 180\text{ K}$ , after 60 min.  $\sim 240\text{ K}$ , after 72 min.  $\sim 250\text{ K}$ . Based on the 100 mTorr pressure of the chamber and the phase diagrams of pure water and  $\text{UF}_6$ , it seems likely the reaction progressed primarily in the solid state with excess  $\text{H}_2\text{O}$  and  $\text{UF}_6$  sublimating away near the 60 min. (240 K) point. Figure 1 summarizes the observed spectroscopic signals during the reaction in the  $700\text{--}1,000\text{ cm}^{-1}$  region. Initially, the intensity of the bands associated with  $\text{UF}_6$  from  $590\text{--}630\text{ cm}^{-1}$  and the ice libration band at

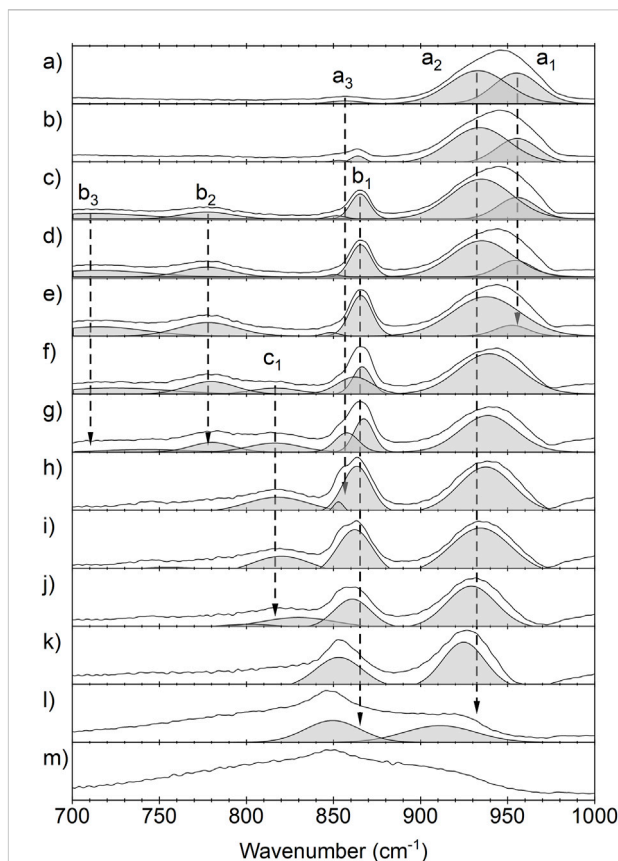


850  $\text{cm}^{-1}$  are observed to be decreasing while a much narrower peak at 850  $\text{cm}^{-1}$  begins to grow. The growth of the feature at 850  $\text{cm}^{-1}$  is quickly followed by the formation of a band at 930  $\text{cm}^{-1}$ . Next, three smaller bands at 715, 780, and 815  $\text{cm}^{-1}$  appear while the bands at 850  $\text{cm}^{-1}$  and 930  $\text{cm}^{-1}$  blue shift. Finally, all bands in this region disappear except for the strong band at 940  $\text{cm}^{-1}$  and small band at 865  $\text{cm}^{-1}$  which are associated with the product.

The region between 1,000–4,000  $\text{cm}^{-1}$  also shows significant changes during the reaction, Figure 2. As the reaction proceeds a broad continuum of absorption bands from 1,000–3,500  $\text{cm}^{-1}$  is observed. This continuum is indicative of an aqueous proton network and depletes as the final product is formed. Before the reaction is initiated, the strong absorption due to OH stretching of amorphous solid water is observed at 3,250  $\text{cm}^{-1}$ . As the reaction proceeds five distinct bands are observed to shift, increase in intensity, and decrease in intensity over the duration of the experiment: 1,200  $\text{cm}^{-1}$ , 1,500  $\text{cm}^{-1}$ , 1,700  $\text{cm}^{-1}$ , 2,200  $\text{cm}^{-1}$ , and 2,650  $\text{cm}^{-1}$ . The bands at 1,200  $\text{cm}^{-1}$ , 1,700  $\text{cm}^{-1}$ , and 2,650  $\text{cm}^{-1}$ , have been observed in cryogenic mixtures of HF with water and their intensities are reported as directly proportional to HF concentration (Ayotte et al., 2005; Ayotte et al., 2008; Iftimie et al., 2008). By the end of the experiment, the only bands that remain are associated with the  $\text{UO}_2\text{F}_2$  product.

## 4 Discussion

Figure 3 shows the spectral range between 500 and 700  $\text{cm}^{-1}$ , which has been characterized here as the reactant region in which the  $\text{UF}_6$  antisymmetric stretching mode is centered at 624  $\text{cm}^{-1}$ ; however, a more dominant feature is observed at 590  $\text{cm}^{-1}$  during the initial cryogenic conditions. Modes in this region have previously been attributed to free  $\text{UF}_5$  and also to  $\text{UF}_6$  complexes with water (Sherrow and Hunt, 1992). Neither of these assignments seems likely here as the feature does not



resemble previously reported spectra of  $\text{UF}_5$  and is observed even before the addition of water (Kim et al., 2008; Krohn et al., 2008; Paine et al., 2008). Sherrow and Hunt also observed the formation of a broad absorption band centered at 550  $\text{cm}^{-1}$  when co-depositing  $\text{UF}_6$  and water, which they attributed to the initial formation of  $\text{UF}_6 \cdots x\text{H}_2\text{O}$  complexes and is not observed here (Sherrow and Hunt, 1992). We are attributing the feature at 590  $\text{cm}^{-1}$ , and the smaller feature at 610  $\text{cm}^{-1}$ , to cryogenic  $\text{UF}_6$  as we observed a similar red shifted band in cryogenic layers of  $\text{MoF}_6$  (McNamara et al., 2023). As the layers warm and the reaction proceeds, these two features give way to the expected  $\text{UF}_6$  absorption profile.

The spectral region between 700 and 1,000  $\text{cm}^{-1}$  is comprised of transient intermediate species and product ( $\text{UO}_2\text{F}_2$ ). The spectral region between 1,000 and 3,800  $\text{cm}^{-1}$  holds a rich dynamic signature of proton transfer processes that have been attributed to the fluoride-hydronium ion pair. The intermediate relationship of the negative fluoride ion and the positive hydronium ion has been described by Giguère and Turrell (1976) and Giguère and Turrell (1980). The canonical OH stretching region expresses a red-shifting progression to a continuous absorption from 3,800  $\text{cm}^{-1}$  to 2,000  $\text{cm}^{-1}$ . This is a well-characterized signature of proton

transfer but is more obvious in the dissolution of hydrofluoric acid (Cabarcos et al., 1999; Ayotte et al., 2000; Ayotte et al., 2005; Ayotte et al., 2008; Iftimie et al., 2008).

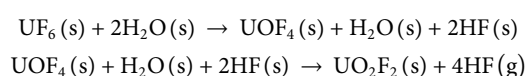
Figure 4 shows peak fits for the spectral features observed between 700 and 1,000  $\text{cm}^{-1}$  where m) is the initial spectrum of the reactants and a) is the spectrum of the final product. The features observed for the product display two major components centered at 955  $\text{cm}^{-1}$  and 933  $\text{cm}^{-1}$  (labelled as  $a_1$  and  $a_2$ ) and a minor feature at 857  $\text{cm}^{-1}$  ( $a_3$ ). The minor feature at 857  $\text{cm}^{-1}$  overlaps spectrally with the intermediate features in this region but can be observed in the final product. While the origin of the features can be attributed to the presence of  $\text{UO}_2\text{F}_2$  with the crystalline environment of residual water and hydrofluoric acid, the temporal onset to these features may provide a mechanistic understanding of to the  $a_1$ ,  $a_2$ , and  $a_3$  origins. Three features are observed most clearly at the end of hydrolysis; however,  $a_1$  and  $a_3$  have significant changes in intensity across the temperature dependent spectra. These features are likely the result of multiple uranyl ions being present in the aqueous environment.  $\text{UO}^{2+}$ ,  $(\text{UO}_2)_2\text{OH}_2^{2+}$ , and  $(\text{UO}_2)_3\text{OH}_5^+$  have previously been assigned to features of aqueous uranyl compounds in this region (Quilès and Burneau, 1998).

The spectral features of  $\text{UOF}_4$ , assigned at 868  $\text{cm}^{-1}$  and 857  $\text{cm}^{-1}$  by Sherrow and Hunt, are observed as intermediate complexes (Sherrow and Hunt, 1992). The feature labeled  $b_1$  in Figure 3C is centered at 865  $\text{cm}^{-1}$  and expressed a strong spectral signature throughout hydrolysis. The feature is first observed immediately upon hydration of  $\text{UF}_6$  but redshifts  $\sim 10 \text{ cm}^{-1}$  and becomes more dominant in the infrared spectrum as water reacts and is later evaporated from the matrix. The two bands around 860  $\text{cm}^{-1}$  were previously observed and attributed to the axial and equatorial isomers of the  $\text{UOF}_4$ . Interestingly, the doublet was previously observed at a 50/50 ratio while we are observing a clear shift from one isomer to another. This shift between the isomers is attributed to the kinetically more favorable formation of one isomer followed by the conversion to the more thermodynamically favorable isomer. Since the experiment takes place in the condensed phase, intermediate and product compounds are likely complexed with HF and water. The frequencies of these compounds will be affected by both the temperature of the film and the relative abundance of HF and water in the observed aqueous proton network. The resolution of the current experiment does not allow the different possible complexes to be easily distinguished from one another.

During the intermediate reaction stage, a band at 815  $\text{cm}^{-1}$  is observed to grow and then deplete while two other bands at 715  $\text{cm}^{-1}$  and 780  $\text{cm}^{-1}$  grow. These two new bands, the  $\text{UOF}_4$  stretching mode at 865  $\text{cm}^{-1}$ , and the remaining  $\text{UF}_6$  then all deplete simultaneously as the final product continues to form. The new band observed at 815  $\text{cm}^{-1}$  seems to be correlated with the conversion between the two  $\text{UOF}_4$  isomers as it is depleted by the time the 865  $\text{cm}^{-1}$  component of the  $\text{UOF}_4$  band has reached its maximum intensity. The bands at 715  $\text{cm}^{-1}$  and 780  $\text{cm}^{-1}$  do not appear to depend on the formation of any other new bands in the spectrum but do deplete alongside the remaining  $\text{UF}_6$  and  $\text{UOF}_4$  bands. These two bands may be attributed to a previously unobserved intermediate complex. The region from 700 to

800  $\text{cm}^{-1}$  is indicative of U-O-U bridging compounds. This region lines up well with several computationally predicted intermediates with U-O-U bonds (Hu et al., 2008; 2009; Lind et al., 2010; Lutz et al., 2022); however, these bridged compounds are typically predicted to have formed through  $\text{UF}_5\text{OH}$  intermediates which there is not strong evidence of in this experiment. Other possibilities are  $\text{U}_2\text{O}_3\text{F}_6$  and  $\text{U}_3\text{O}_5\text{F}_8$ , which have been shown to form as intermediates with sub-stoichiometric mixtures of water and  $\text{UF}_6$ , though their IR spectra are not well documented (Otey and LeDoux, 1967). PCA was performed on the data set and the results support the previous discussion, see Supplementary Material for more detail.

The observations from this experiment support previous claims that  $\text{UF}_6$  hydrolysis is composed of two half reactions with a  $\text{UOF}_4$  intermediate:



In excess water, the final product is a hydrate of the form:  $\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$ . The formation of the three previously unobserved bands at 715  $\text{cm}^{-1}$ , 780  $\text{cm}^{-1}$ , and 815  $\text{cm}^{-1}$  suggest the formation of bridged O-U-O intermediates which can directly convert to  $\text{UO}_2\text{F}_2$ . These preliminary results show promise for this technique to further elucidate the chemistry governing  $\text{UF}_6$  hydrolysis by varying reactant isotopologues and employing other spectroscopic techniques.

## Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

## Author contributions

LM: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Visualization, Writing—original draft, Writing—review and editing. JK: Data curation, Formal Analysis, Writing—original draft, Writing—review and editing. AW: Conceptualization, Investigation, Methodology, Writing—review and editing. EV-A: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing—review and editing. KS: Funding acquisition, Resources, Supervision, Writing—review and editing.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fnuen.2023.1300544/full#supplementary-material>

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