Controlled Reaction Dynamics of Binary Hexafluorides for New Chemical Signatures

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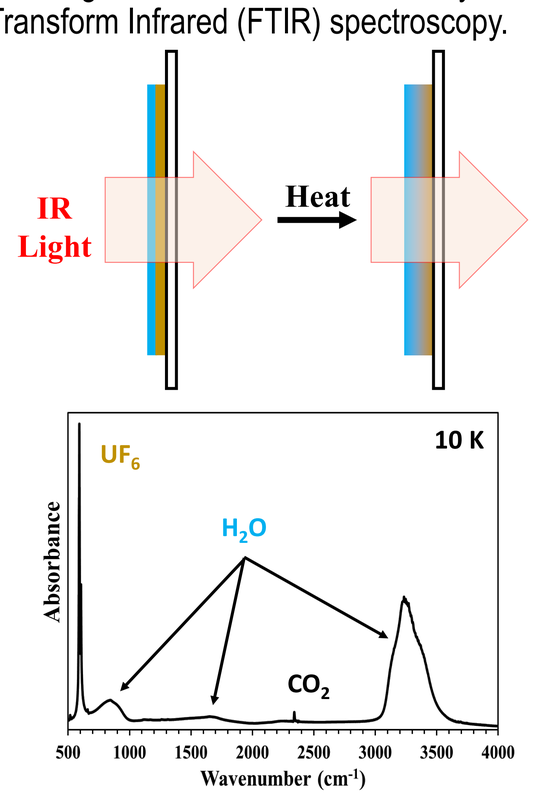
Introduction

Uranium hexafluoride (UF_6) is the primary chemical form of uranium utilized in modern enrichment technologies. It is highly reactive, rapidly hydrolyzing upon exposure to atmospheric water vapor to generate uranyl fluoride (UO_2F_2) and hydrofluoric acid (HF). Although these stable end products are well-known, the underlying transient reaction pathways remain poorly characterized. This study investigates the hydrolysis mechanism by capturing transient intermediates within a custom cryogenic setup designed to arrest the rapid reaction. To isolate specific mechanistic steps and probe steric effects, we react UF_6 with water as well as a series of structurally hindered alcohols with increasingly large R-groups. Additionally, UF_6 is reacted with nitrogen-containing small molecules, such as ammonia and pyridine, to further elucidate the fundamental chemistry of hexavalent uranium. Findings from this work support the development of spectroscopic signatures with the aim of bolstering standoff detection capabilities for nuclear forensic applications.

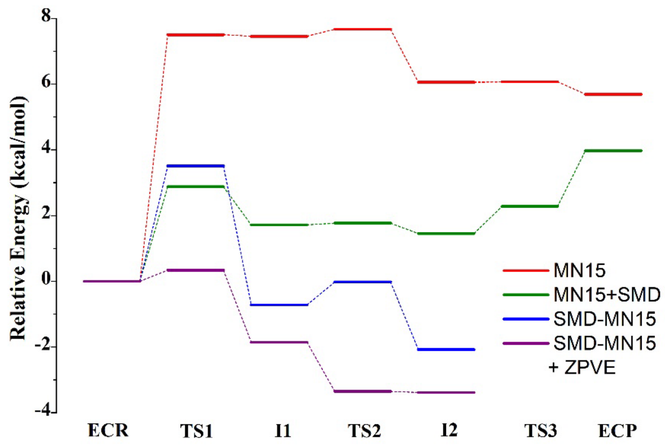
$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

Methods

Experiment: UF_6 and selected reactants were layered onto a diamond substrate held at under vacuum and cooled to 10 K by a closed-cycle liquid helium cryostat. The diamond was then slowly heated while the resulting reaction was monitored by Fourier Transform Infrared (FTIR) spectroscopy.



Theory (R-OH): MN15/DZ is based on the DFT/MN15 method along with the aug-cc-pVDZ basis for the main group elements (H, C, O, F) and cc-pVDZ-PP basis for U. Long-range solvent effects were considered through the polarizable continuum model (SMD) using optimized parameters for methanol. Calculations were performed using HPC resources at Auburn University.



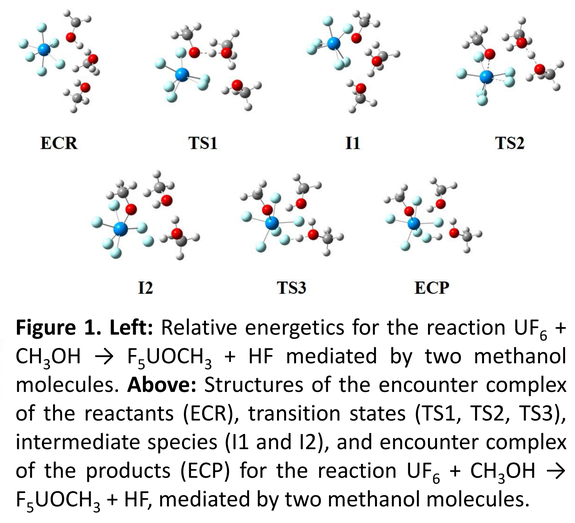


Figure 1. Left: Relative energetics for the reaction UF_6 + $CH_3OH \rightarrow F_5UOCH_3$ + HF mediated by two methanol molecules. **Above:** Structures of the encounter complex of the reactants (ECR), transition states (TS1, TS2, TS3), intermediate species (I1 and I2), and encounter complex of the products (ECP) for the reaction UF_6 + $CH_3OH \rightarrow F_5UOCH_3$ + HF, mediated by two methanol molecules.

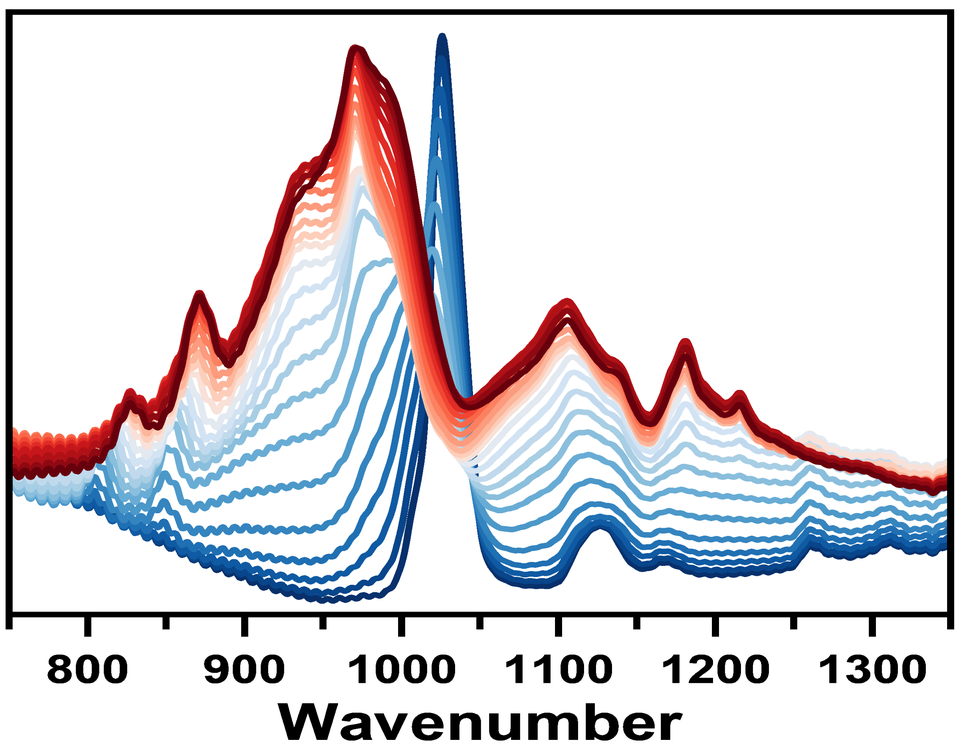


Figure 2. Spectra of UF_6 + MeOH reaction. Spectra are cold (blue, 80K) to warm (red 100K).

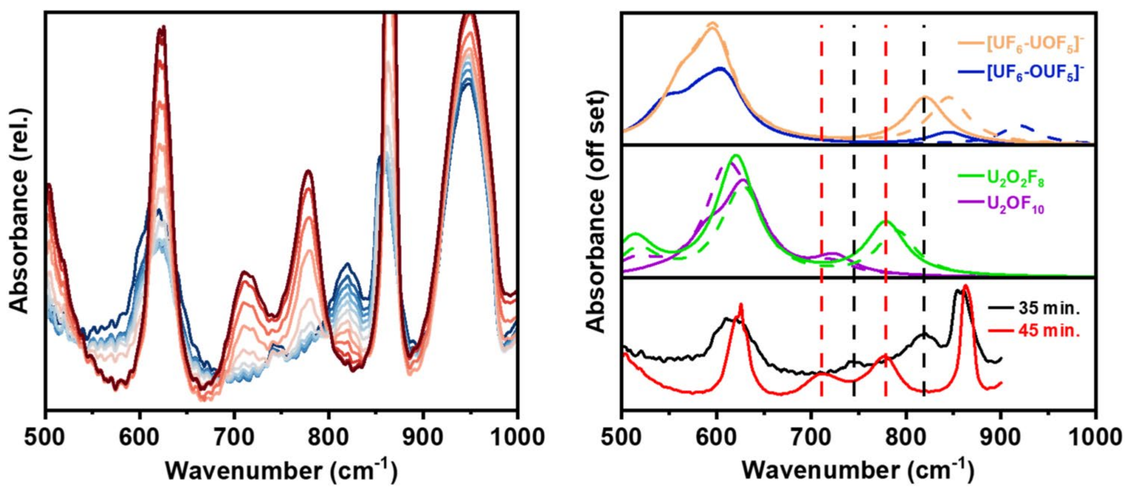


Figure 3. (Left) FTIR spectra of the hydrolysis reaction under water-saturated conditions (H_2O: UF_6 > 10: 1) highlighting distinct intermediate bands at 750/815 cm^{-1} and 715/775 cm^{-1}. **(Right)** Comparison between experimental spectra and DFT-simulated spectra identifying the 715 and 785 cm^{-1} features as bridged U_2OF_{10} and $U_2O_2F_8$ structures

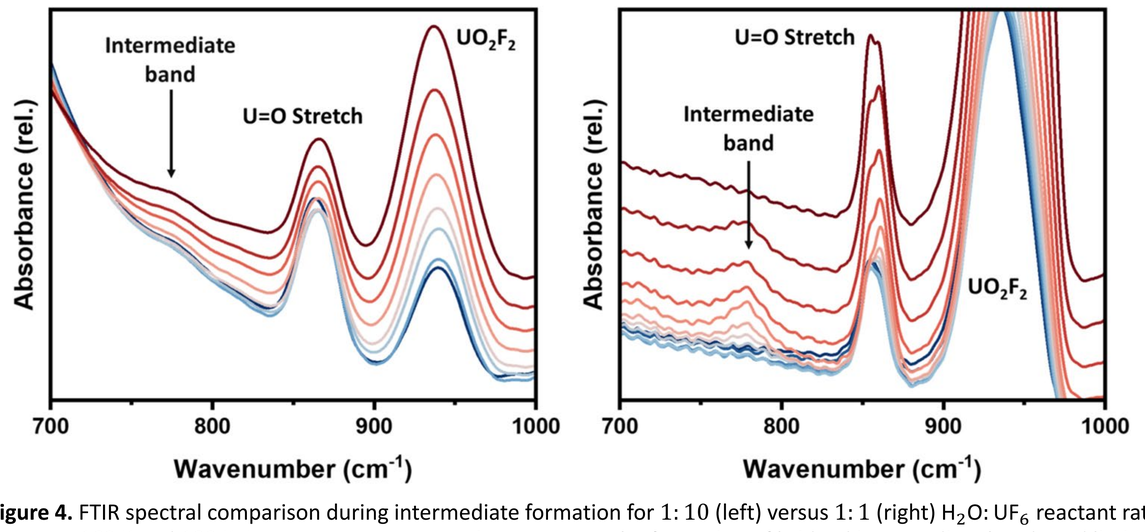


Figure 4. FTIR spectral comparison during intermediate formation for 1: 10 (left) versus 1: 1 (right) H_2O: UF_6 reactant ratios between 160 K and 180 K. Lower water concentrations suppress the formation of bridged intermediate bands and limit the spectral shifting of $[UOF_5]^-$ and UO_2F_2, demonstrating that reaction kinetics and pathways strongly depend on water availability

Results

Reactions with H_2O:

By coupling cryogenic trapping and temperature-dependent FTIR with DFT, this work provides direct evidence of competing reaction pathways in the hydrolysis of UF_6. The observed dynamics, intermediate lifetimes, and final uranyl fluoride characteristics are governed by complex interplay of the H_2O:UF_6 ratio as well as isotopic substitution. Notably, unexpected transient species such as a candidate bridged uranium-oxyfluoride network and ionic complexes, point toward alternative mechanisms where proton-shuttling dynamics and reversible steps may dictate product formation.

Reactions with R-OH:

Experimental results show that the reaction is spontaneous at ~60K. This is much lower than the hydrolysis reaction, which is effectively halted at 150K. This result was unexpected as the increased sterics from moving from water to MeOH was predicted to increase the reaction barrier. Theoretical calculation were able to come close to the 60K (~0.15 kcal/mol) reaction barrier. The formation of F_4UO from F_5UOCH_3 occurs via an SN2-type mechanism where the OH group of an incoming methanol acts as a nucleophile and attacks the carbon atom of F_5UOCH_3. The produced species are F_4UO and the $(CH_3)_2OH{+}F^-$ ion pair. When an additional methanol is included in the model, a proton hops from $(CH_3)_2OH+$ to the available methanol forming CH_3OCH_3 and the $CH_3OH_2{+}F^-$ ion pair.

$$UF_6 + H_2O \rightarrow UOF_5^- + H_3O^+$$

$$UF_6 + UOF_5^- \rightarrow UF_6\text{-}UOF_5^-$$

$$UF_6\text{-}UOF_5^- \rightarrow UF_6\text{-}OUF_5^-$$

$$UF_6\text{-}OUF_5^- \rightarrow U_2OF_{10} + F^-$$

$$U_2OF_{10} \rightarrow \underline{U_2O_2F_8} \rightarrow \underline{U_2O_4F_4} \rightarrow UO_2F_2$$

Scheme: A proposed reaction scheme to the formation of intermediates is shown above. It is still unclear how some of these intermediates eventually result in the formation of UO_2F_2, but previous computational work has suggested that the bridged $U_2O_4F_4$ compound very favorably decomposes into $2UO_2F_2$ so here it is speculated as the final intermediate stage.

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