

Characterizing the Solid Hydrolysis Product, $\text{UF}_4(\text{H}_2\text{O})_{2.5}$, Generated from Neat Water Reactions with UF_4 at Room Temperature

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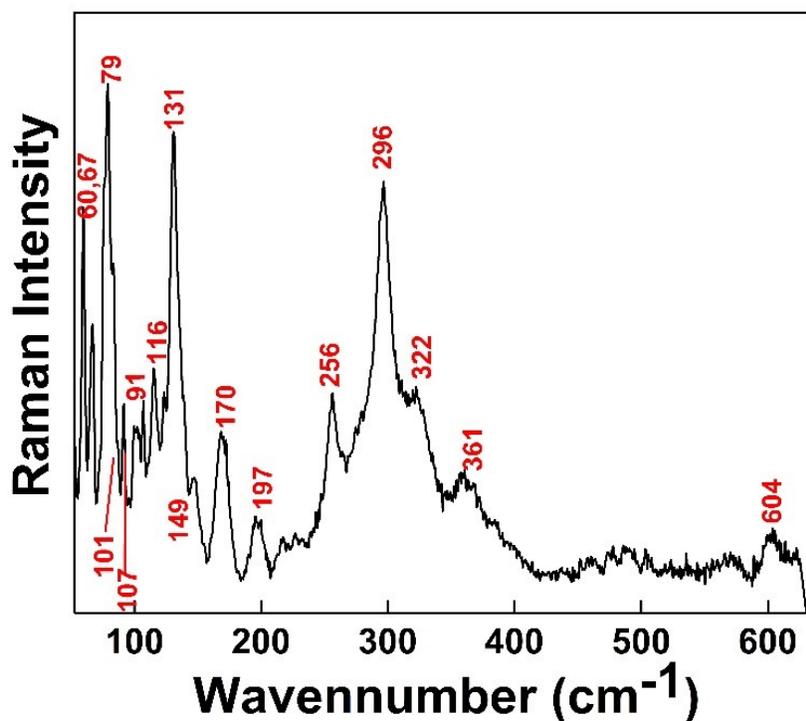
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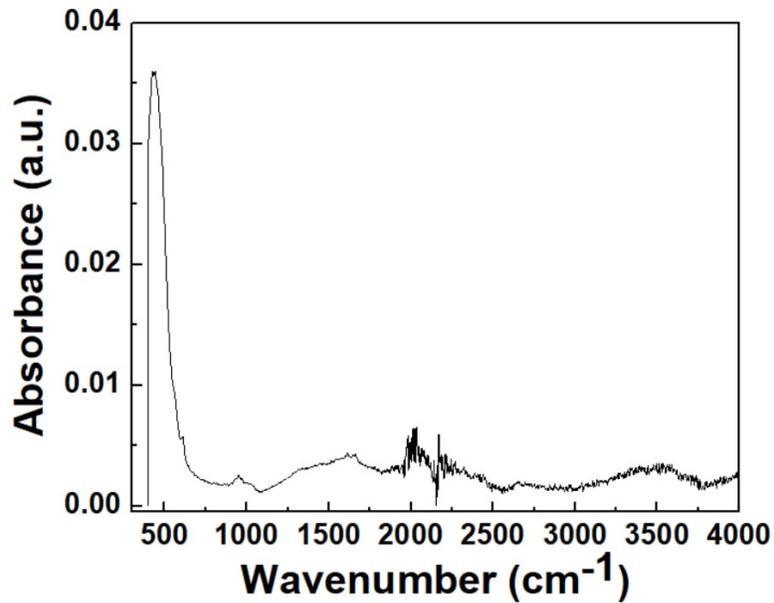
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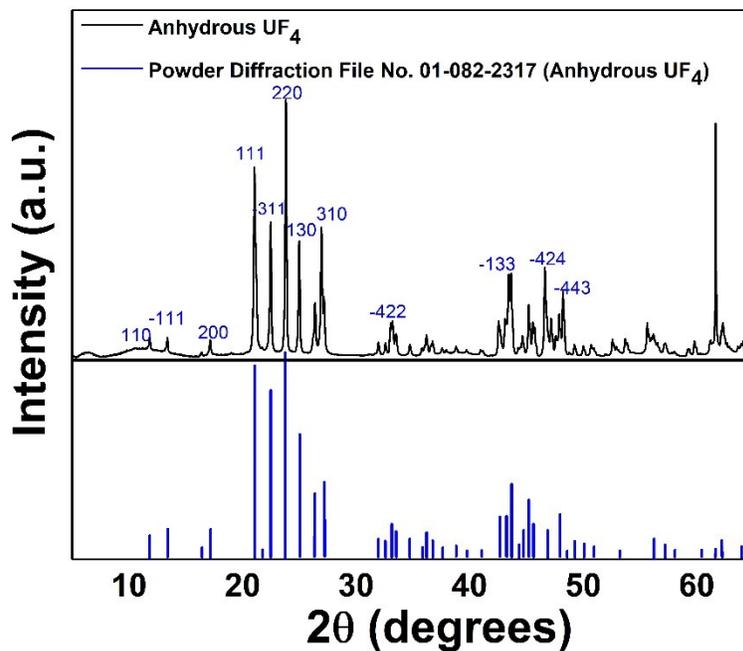
Supporting Information:



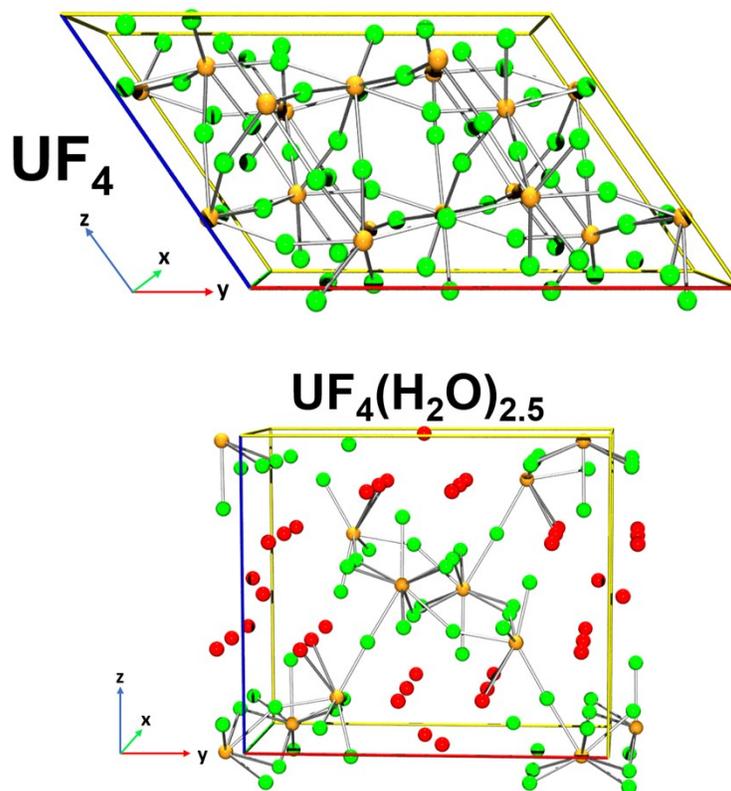
SI Figure 1. Raman spectrum of anhydrous UF_4 (black trace) with 16 distinct bands between 50 and 610 cm^{-1} and one broad band at 4300 cm^{-1} . Band locations are identified in red. The spectrum was acquired with a 785 nm excitation laser.



SI Figure 2. The infrared spectrum of anhydrous UF₄ is featureless and is consistent with UF₄ having no IR-active vibrational modes in the measured spectral range. The sharp feature near 500 cm⁻¹ is fluorescence and the sharp features between 2000 - 2200 cm⁻¹ are artifacts of the diamond ATR in the spectrometer.



SI Figure 3. (Top): Powder X-ray diffraction pattern of anhydrous UF₄ (black trace) with Miller indices for select peaks (blue text). (Bottom): ICDD diffraction lines of UF₄ (Powder Diffraction File No. 01-082-2317).



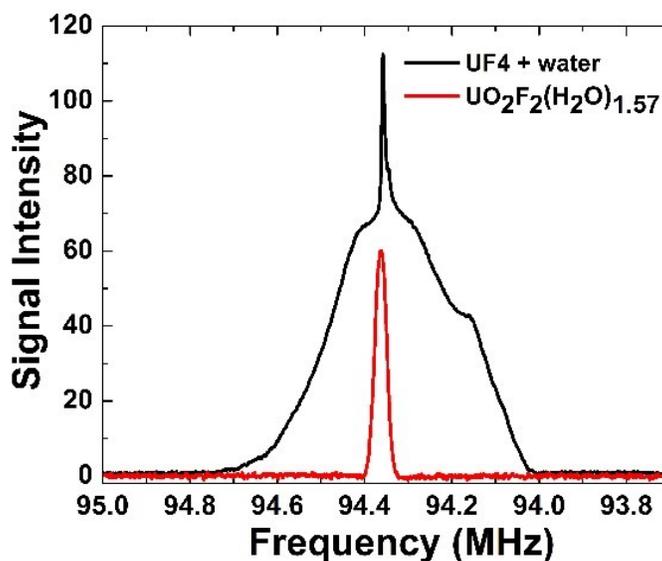
SI Figure 4. Ball and stick representations of the crystallographic structure within a single unit cell for anhydrous UF_4 (top) and $UF_4(H_2O)_{2.5}$ (bottom). Yellow = uranium, green = fluorine, red = oxygen. Water hydrogens are omitted for clarity

SI Table 1. Crystallographic features of UF_4 and $UF_4(H_2O)_{2.5}$

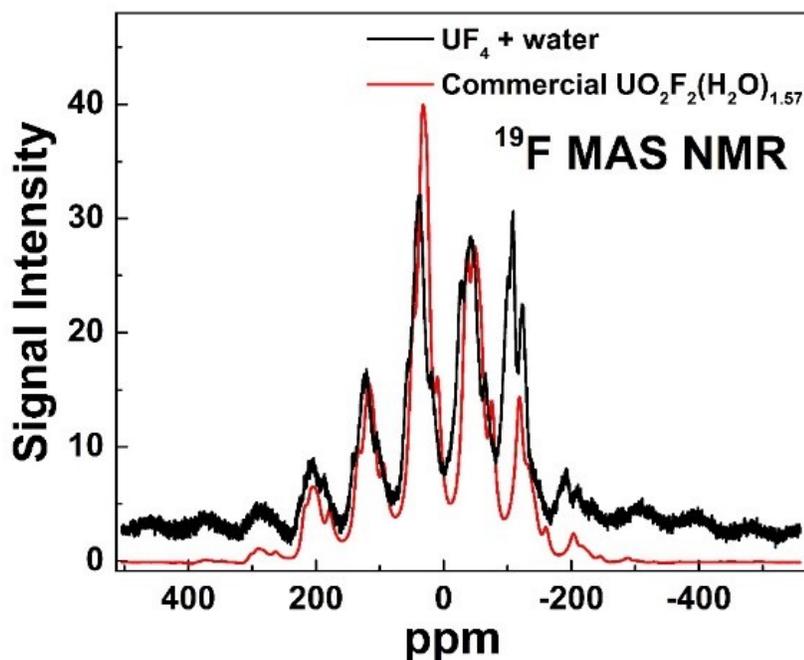
	UF_4	$UF_4(H_2O)_{2.5}$
Space Group	$C2/c$ (No. 15)	$Pnma$ (No. 62)
U-F polyhedral	UF_8	UF_9
U-O-F polyhedral	-	UO_4F_5
Density	6.7	4.754

¹⁹F Magic Angle Spinning Nuclear Magnetic Resonance:

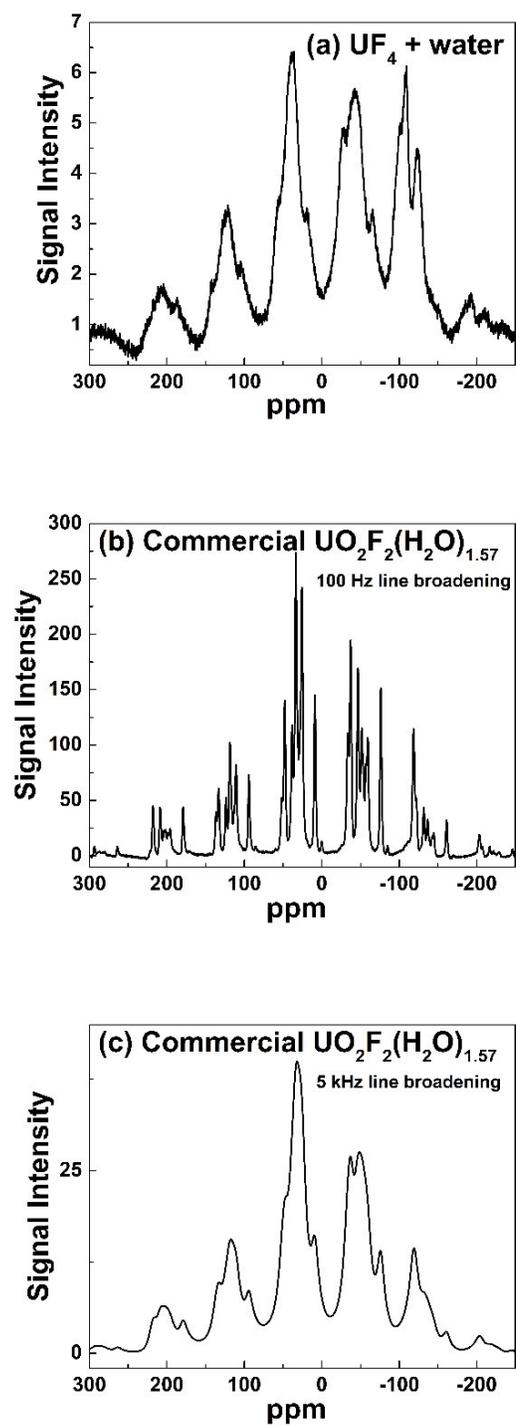
To probe the sharp peak observed in our ¹⁹F NMR measurements after UF₄ had soaked in water, a small aliquot of solid sample was removed from the water and was analyzed by MAS NMR. ¹⁹F Magic Angle Spinning (MAS) NMR spectra were obtained at 11.7 T (¹⁹F resonance frequency of 470.6 MHz) using a Varian NMR500 spectrometer and a 1.2 mm double-resonance UltraFast MAS NMR probe. The MAS NMR spectrum showed a series of spinning sidebands which are in close agreement with a broadened set of sidebands associated with uranyl fluoride – UO₂F₂(H₂O)_{1.57} (SI Figures 7 and 8).¹ The close agreement between these spectra indicates that uranyl fluoride forms - albeit to a small extent - when UF₄ is exposed to water. The broadening in all ¹⁹F MAS NMR spectra is likely due to the non-crystalline nature of the uranyl fluoride as has been observed previously.¹



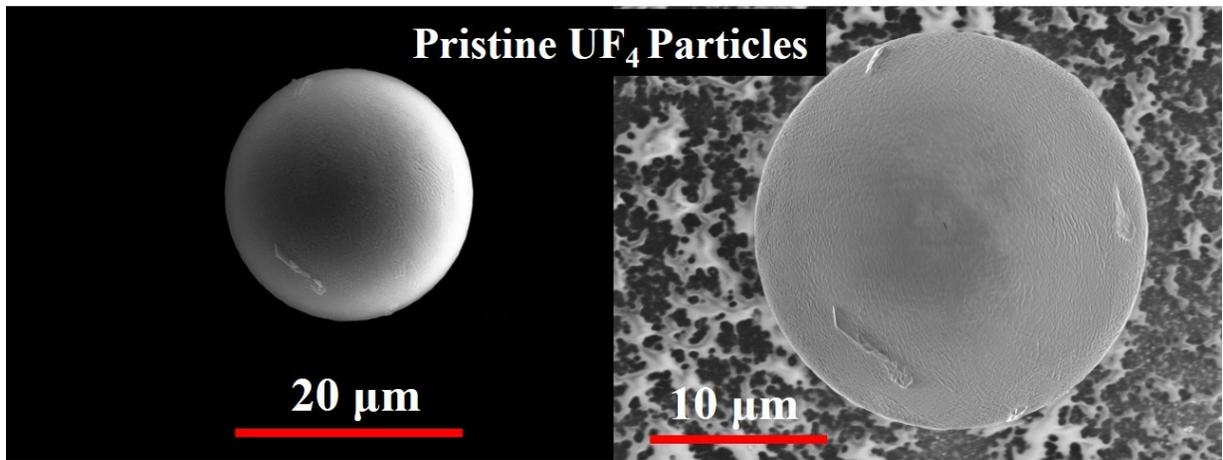
SI Figure 5 ¹⁹F NMR spectra acquired at a probe height where the field homogeneity was optimal and at a frequency where fluorine bound to diamagnetic species is likely to be observed (~ 94.3 MHz). The black spectrum is a central sub-spectrum corresponding to one of the 11 subspectra obtained in a point-by-point method for a wet sample of UF₄ acquired with a solid echo with pulse lengths of 0.6 μs, delay between pulses of 25 μs, wait time between scans of 4 ms and longer, and total number of scans equal to 20480. The spectrum in red was obtained for a commercial uranyl fluoride sample (UO₂F₂(H₂O)_{1.57}) using a solid echo with pulse lengths of 3.0 μs, delay between pulses of 11 μs, wait time between scans of 1 s and longer, and total number of scans equal to 1536.



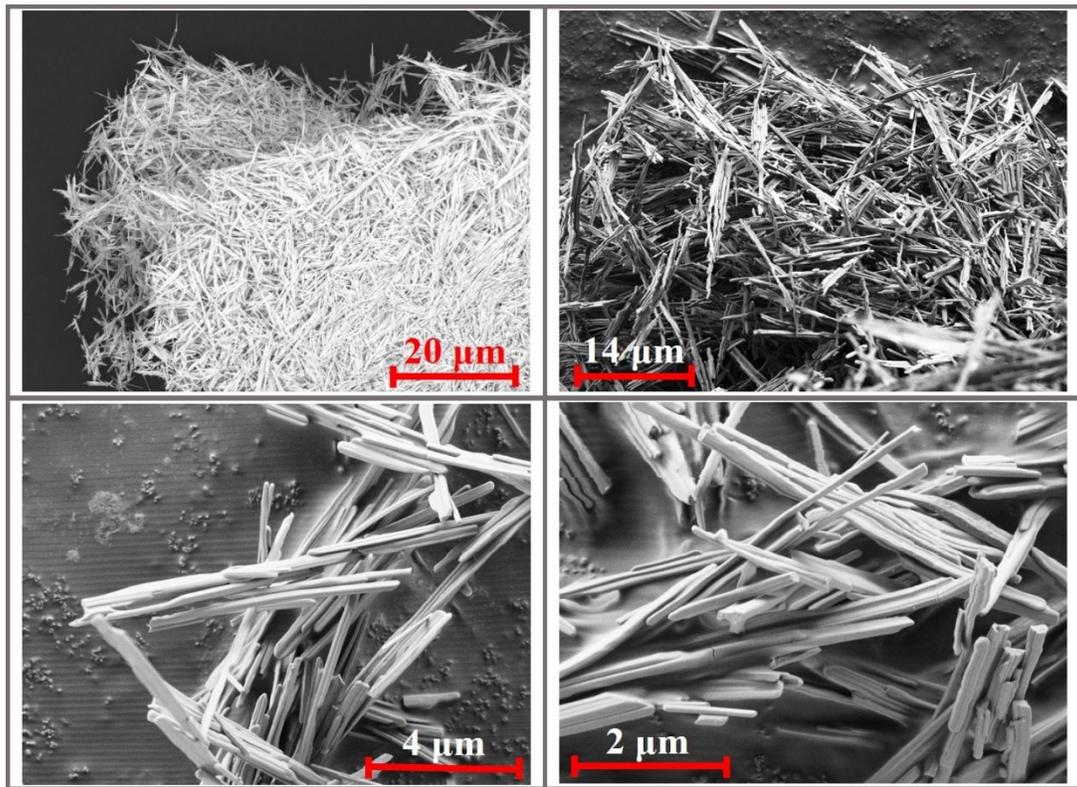
SI Figure 6. ^{19}F MAS NMR spectra obtained from Hahn echo experiments with a spinning frequency of 40 kHz for a) small aliquot (3.9 mg) of UF_4 sample that been exposed to water and left to stand for over a year. The pulse lengths in the echo were $0.8\ \mu\text{s}$ and $1.6\ \mu\text{s}$ for $\pi/2$ and π pulses respectively. The delay between pulses was equal to one rotor period, $25\ \mu\text{s}$. The delay between scans was 8 s. The total number of scans was 2816 corresponding to a total experiment time of 6.3 hours; b) commercial $\text{UO}_2\text{F}_2(\text{H}_2\text{O})_{1.57}$ (3.7 mg). The pulse lengths in the echo were $1.7\ \mu\text{s}$ and $3.4\ \mu\text{s}$ for $\pi/2$ and π pulses respectively. The delay between pulses was equal to four rotor periods, $100\ \mu\text{s}$. The delay between scans was 10 s. The total number of scans was 256 corresponding to a total experiment time of 42.7 minutes. To make the comparison clearer, the data was processed using a line broadening of 5 kHz.



SI Figure 7. ^{19}F MAS NMR spectra obtained for a) UF_4 in water, b) commercial $\text{UO}_2\text{F}_2(\text{H}_2\text{O})_{1.57}$ processed with 100 Hz line broadening, and c) commercial $\text{UO}_2\text{F}_2(\text{H}_2\text{O})_{1.57}$ processed with 5 kHz line broadening. The data indicate that a small amount of $\text{UO}_2\text{F}_2(\text{H}_2\text{O})_{1.57}$ forms during the UF_4 -water reaction.



SI Figure 8. SEM images of commercial anhydrous UF₄ before water exposure show that the dry pristine particles have spheroid morphology and a smooth surface.



SI Figure 9. Scanning electron micrographs of UF₄ hydrate (UF₄(H₂O)_{2.5}). This material was obtained after stirring anhydrous UF₄ in deionized water for 1 day. The top images show the bulk material; the bottom images show details of the needle-like crystals.

REFERENCES:

1. M. A. DeVore, C. A. Klug, M. R. Kriz, L. E. Roy and M. S. Wellons, *The Journal of Physical Chemistry A*, 2018, **122**, 6873-6878.