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TITLE: Determination of Intermediates and Products of the Uranyl Aerosol Formation in UF<sub>6</sub> Hydrolysis in the Gas Phase

## SUPPORTING INFORMATION

### (1) Production of neutral clusters of UF<sub>6</sub>, H<sub>2</sub>O, and HF in the molecular beam expansion

Examination regarding the formation of neutral clusters like (UF<sub>6</sub>)<sub>n</sub>, (H<sub>2</sub>O)<sub>n</sub>, and (HF)<sub>n</sub> in the sampling inlet to our MBMS, by cooling condensation in the expanding molecular beam, is presented here. The *n* as in (HF)<sub>n</sub> is an integer. The aerosol particles were produced at the reaction point where the two reactant jets impinged on each other and were then pulled into the Stage 1 of the mass spectrometer through a 100 μm diameter critical orifice. The total length from the reaction point to the Stage 1 of the MBMS was about 18.6 cm. Once the gas exited the orifice, the gas (containing cluster species) would be expanded quickly through the skimmer. The upstream pressure of this length was approximately 760 torr, while the downstream pressure in the Stage 1 was 0.1 torr as described in the manuscript. Under the working conditions, the production of the neutral clusters [(UF<sub>6</sub>)<sub>n</sub>, (H<sub>2</sub>O)<sub>n</sub>, and (HF)<sub>n</sub>] was unobservable, as reflected in our mass spectrometer (MS) signals. The following paragraphs describe the results that support the above remarks.

For UF<sub>6</sub>-only cases as shown in Figure 2 in the manuscript, the observable *m/z* values (from 50 to 1000) were 352 for (UF<sub>6</sub>)<sub>1</sub> and 704 for (UF<sub>6</sub>)<sub>2</sub>. The signal intensities were averaged over 901 spectra for these two masses, which were collected for a UF<sub>6</sub> concentration of 200 ppm. The averaged intensities were 86 for (UF<sub>6</sub>)<sub>1</sub> and 15 for (UF<sub>6</sub>)<sub>2</sub>, respectively. The standard deviation for these two intensities were 23 and 10 for these two masses, respectively. As compared to the signal intensities for our calibration curve, the intensities for the two cluster species were two orders of magnitude smaller. Therefore, it was reasonable not to include these neutral cluster species in the data interpretation.

For H<sub>2</sub>O-only case, the mass spectral intensities were calculated for the following neutral species, (H<sub>2</sub>O)<sub>n</sub> where *n* = 2-60, as predicted by Kulkarni et al. (2005) J. Phys. Chem. and Maheshwary et al. (2001) J. Phys. Chem. The observable *m/z* values by our instrument for the neutral clusters were with *n* = 3 – 55. It was unfortunate the water dimer was unobservable with this instrument. Using the 10%-Rh case as an example, a plot of the averaged signal intensities for the water clusters from *n* = 3 (*m/z* = 54) to 55 (*m/z*=990) is presented in Figure S1. The error bar is the averaged standard deviation of the 901 spectra for each *m/z*.

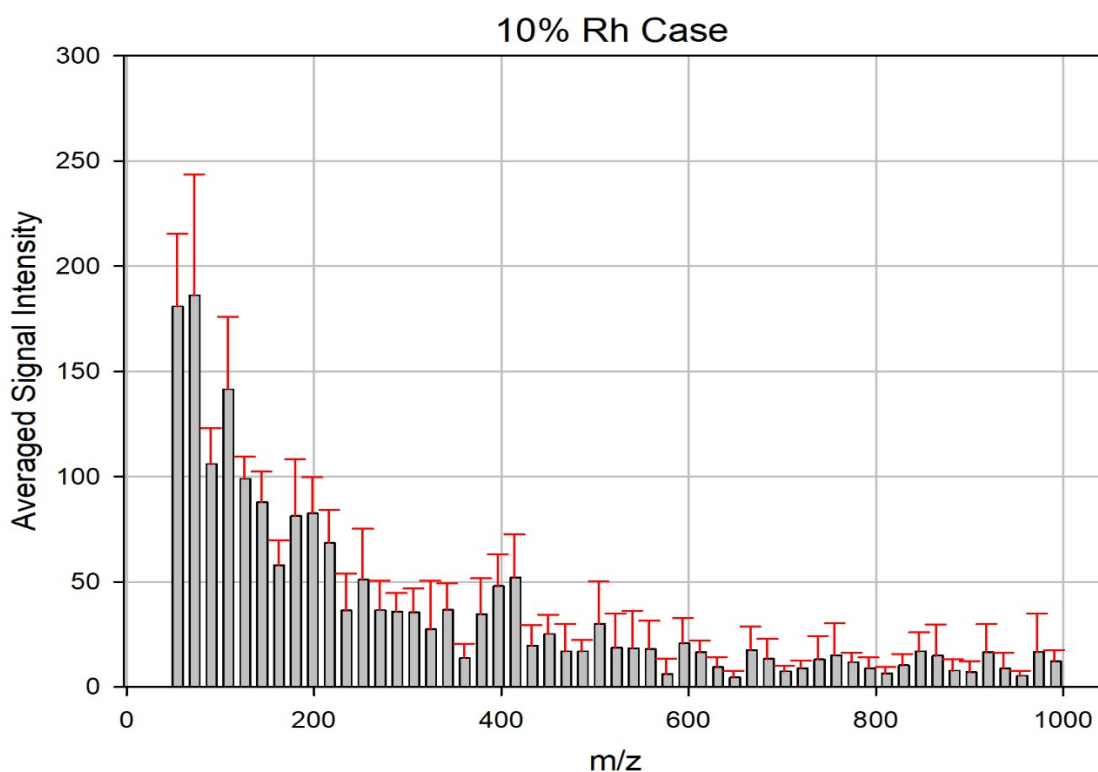


Figure S1. Averaged intensities for (H<sub>2</sub>O)<sub>n</sub> masses. Error bar plotted for each mas was based on the standard deviations of 901 samples.

A few observations can be found here: the signal intensities for all water clusters were relatively small (no higher than 250) compared to other signal intensities of interest to us (e.g., for those reported in Figure 2 in the manuscript). The water cluster<sub>2</sub> signals were 1-2 orders of magnitude weaker, even for the trimer and tetramer. In other words, the signal intensities for the

observable water clusters were in the noise. Again, the production of neutral water clusters was considered to be questionable.

About neutral  $(\text{HF})_n$  clusters where  $n \geq 2$ , to detect whether  $(\text{HF})_n$  clusters were produced in the inlet was not in our scope of study. HF gas was not released alone into the system as we did for  $\text{UF}_6$  and  $\text{H}_2\text{O}$ . However, reanalysis of mass spec signal for HF oligomers,  $n = 4$  to  $10$ , observable by our mass spec, the signals of these neutral clusters were also in the noise. We believe most of the HF produced by the reaction probably ended up in the cluster complexes. The hydrogen bonding of the molecules facilitate complexation of HF with other intermediate species. Any free  $(\text{HF})_n$  molecules from the reaction were likely below the sensitivity of our mass spec. Furthermore, the initial concentrations of our hydrolysis reactants were low compared. We expected the produced HF and oligomers are no comparison with the accidental release of HF at industrial scale. The chance of polymerization of HF (Cheng, 2018, J. Atmos. Chem.) was likely to be weak in our experiments and the signal for  $(\text{HF})_n$  clusters could be unobservable.

## (2) Formation of clusters by reactions occurred in the beam expansion

We contend that the signal of molecular clusters detected by our mass spec were all due to the hydrolysis reactions at the Tee where the two reactant jets met. Nevertheless, the possibility exists that the cluster signal could be produced from the continuous reaction between residual  $\text{UF}_6$  and  $\text{H}_2\text{O}$ , if any, during sample expansion at the nozzle of the MS. In other words, what is the relative intensity of this residual signal compared to that mainly produced by the hydrolysis reaction?

To study this effect, elaborate experiments would be required that involves the new fabrication of the orifice of different diameter, changing the displacement between the orifice tip and the downstream skimmer, optimization to fine tune the mass spectrometer detection for each hardware change, etc. Because the reaction studied involves hazardous and radioactive materials, the trial-and-error efforts in the experiments will be non-trivial and expensive. We did not study this effect or signal interference experimentally, also because based on our experience with the  $\text{UF}_6$  chemistry and  $\text{UF}_6$  hydrolysis [1-3], the hydrolysis reaction between  $\text{UF}_6$  and  $\text{H}_2\text{O}$  was so fast that the residual reactant concentrations typically drop to sub ppbv in ms or shorter time in our experimental conditions. Therefore, at the exit of the critical orifice before the beam expansion, we believed the residual  $\text{UF}_6$  and  $\text{H}_2\text{O}$  would be very low and further reaction was halted at that point, resulting in minimal, if not zero, production of clusters during the expansion. Once the beam expanded, the reaction practically stops. If this was true, then the signal of clusters we detected by the mass spec would be totally from the reaction. In other words, the majority, or all, of the signals would have resulted from the hydrolysis reaction before the beam expansion, no production of clusters in the beam expansion that contributed any artifact signal.

Remember that the beam expansion did NOT produce detectable neutral cluster species as shown previously in Section 1. What is being addressed here in Section 2 is the possibility that the clusters could have been produced in the expansion inside the Stage 1. Since it would be tedious and expensive for such data collection to design and execute experiments inside the MS instrument as described previously, we have relied on computer simulation to provide an indirect evidence against this hypothesis.

Chemkin (ANSYS Inc.) version 2023R2 was used to calculate species concentrations and aerosol particle size inside the tube upstream of the orifice. Detailed descriptions of the physics and chemistry modeled in Chemkin can be found in other works by Hubbard et al. [1, 2]. Assuming choked flow at the  $100 \mu\text{m}$  orifice, the flowrate was calculated as 0.162 liters per minute. A plug flow reactor was setup with length of 7.62 cm and diameter of 0.635 cm. The inlet temperature was set to 293.15 K and the tube wall was modeled as adiabatic. The pressure was assumed to be constant upstream of the orifice: 101325 Pa. The sectional coagulation model was used with 48 bins, a section spacing factor of 2, and a minimum size of 1 monomer. A section spacing factor of 2 results in particle size bins of one, two, four, eight monomers, etc. The transition coagulation kernel was selected, and the inlet volumetric flow rate was set to 0.0027 liters per second. The inlet mole fractions were set to  $200 \times 10^{-6}$  for  $\text{UF}_6$  and either  $2.3 \times 10^{-3}$  (10% RH) or  $3 \times 10^{-4}$  (1.3% RH) for  $\text{H}_2\text{O}$ . The reaction mechanism published by Richards et al. was used to simulate the conversion of  $\text{UF}_6$  and  $\text{H}_2\text{O}$  into  $\text{UO}_2\text{F}_2$  [3].

Figure S2 shows the mole fraction of each reactant along the length of the 0.635-cm diameter tubing upstream of the  $100 \mu\text{m}$  orifice. Remember the mole fraction is numerically equal to PPM. At 1.3% RH, the reacted fraction of  $\text{UF}_6$  is approximately 11% by the time it reaches the orifice. The remaining amount of 0.19 ppb of  $\text{UF}_6$  and 0.21 ppb of  $\text{H}_2\text{O}$  could theoretical react further after the orifice before the beam expansion, although the concentrations were really low (in sub ppb level) at that point. However, after the large pressure drop across the orifice, then through a skimmer in Stage 1, the minute gas quickly expand, cool, and reaction would slow even further

to a halt. At 10% RH, the molar fraction of  $\text{UF}_6$  is approximately 100 times lower than at 1.3% RH. All the  $\text{UF}_6$  would have been converted by approximately 3 cm after the reacting point, practically terminated the cluster production process at that point prior to reaching the critical orifice. In other words, there was no more  $\text{UF}_6$  to be consumed in order to produce any more clusters beyond this distance. Zero production of clusters is expected in the beam expansion for the 10% Rh case.

Overall, we argue that all the cluster signals detected by the MBMS resulted from the hydrolysis reaction at the impinging point further upstream from the mass spectrometer.

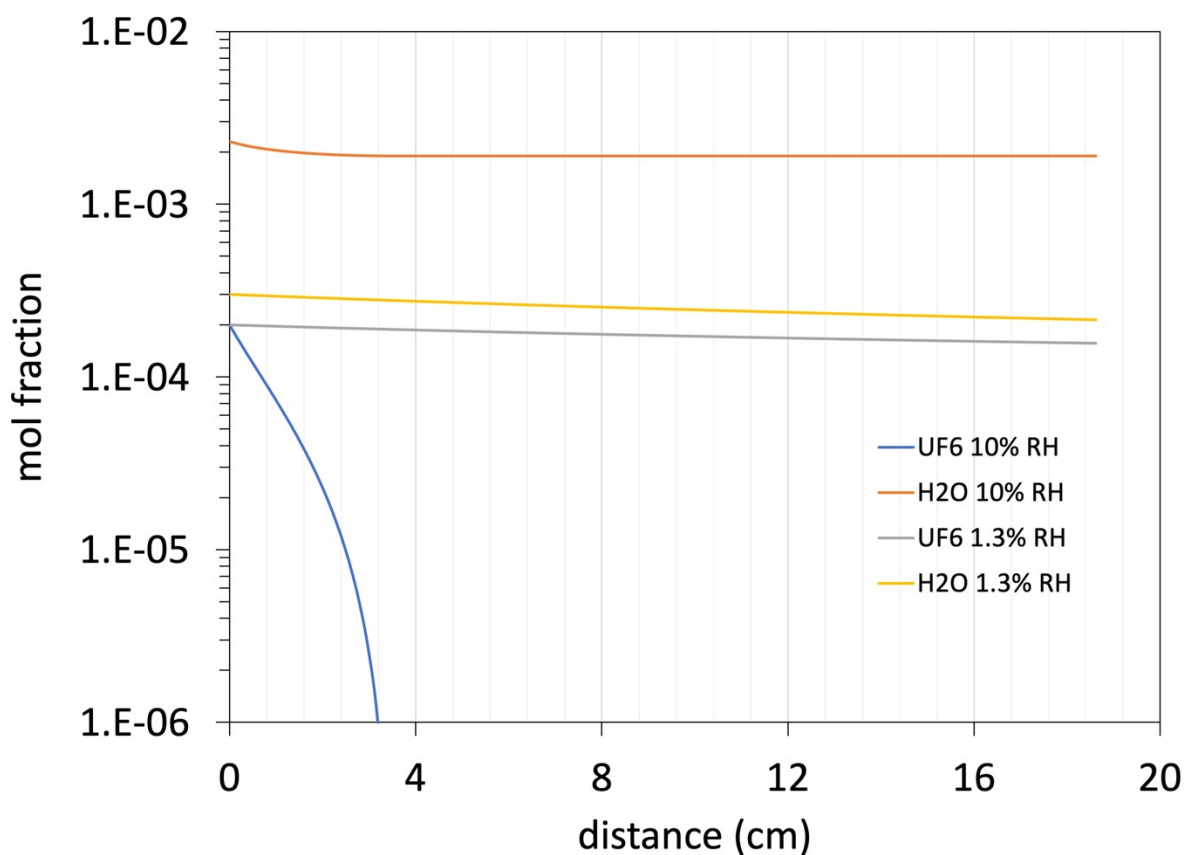


Figure S2. Reactant mol fraction upstream of the 100- $\mu\text{m}$  orifice

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3. Richards, J.M., L.R. Martin, G.A. Fugate, and M.-D Cheng, *Kinetic investigation of the hydrolysis of uranium hexafluoride gas*. RSC Advances, 2020. **10**(57): p. 34729-34731. <https://doi.org/10.1039/d0ra05520d>