Supporting Information

Manuscript title: Experimental Investigation of Uranium Volatility During Vapor Condensation

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Literature Review on Optical Diagnostics of Uranium Oxide Species

Various optical diagnostic techniques are available for detecting uranium and its oxides. Optical emission spectroscopy (OES) is an *in situ* measurement technique that is widely used for detection of uranium and uranium monoxide at elevated temperatures. Pulsed-lasers are commonly used to ablate solid uranium oxide targets to create a plasma plume that is monitored using OES to study the chemical evolution of the plume as a function of time. Previous studies used this method to investigate early gas-phase oxidation of uranium and to detect uranium isotopes. Hundreds of electronic transitions of atomic uranium have been reported in the UV-VIS wavelengths, resulting in a congested emission spectrum that is difficult to resolve and deconvolute. The presence of unidentified higher uranium oxides (e.g. UₓOᵧ) was given as a contributing factor to the continuous background emission of laser-produced uranium plasmas in recent studies.

Infrared spectroscopy is another technique that can be used to more definitively identify the polyatomic forms of uranium oxides. Fourier Transform Infrared (FTIR) spectrometers were used in the past to detect UO₂ and UO₃ molecules that were produced by laser ablation or continuously heated Knudsen cells. However, the spectral features reported in these studies were recorded at cryogenic conditions (e.g. uranium oxides produced at elevated temperatures were trapped in solid argon or neon matrices at 4 K or 10 K). In this way, the fine structures from rotational transitions were suppressed and the isolated infrared absorption peaks were used to provide the vibrational frequencies of UO₂ and UO₃ molecules. Other *in situ* spectroscopic techniques used to detect higher oxides of uranium in the gas phase include time-of-flight mass spectrometry with resonantly enhanced multiphoton ionization (REMPI) and laser-induced fluorescence (LIF). Both methods have been used to measure the electronic spectra of UO₂.
The infrared spectra of condensed phases of uranium oxides (e.g. UO$_2$, UO$_3$, U$_3$O$_8$, U$_4$O$_9$) were measured in the past by an FTIR spectrometer$^{21}$. The spectral features were reported to be very broad with FWHMs of several tens of wavenumbers and located between 300 cm$^{-1}$ and 1000 cm$^{-1}$. UO$_2$ has a strong absorption frequency near 450 cm$^{-1}$, whereas U$_3$O$_8$ and UO$_3$ have broad peaks around 740 cm$^{-1}$ and 900 cm$^{-1}$, respectively. The spectral signatures of UO$_3$ are particularly interesting, because UO$_3$ may exist in various forms of polymorphs (i.e., α-, β-, γ-, δ-, and ε-UO$_3$) and the spectral features vary depending on the synthesis method, making its fingerprints useful for nuclear forensics analysis.$^{22-26}$

In this study, an FTIR spectrometer is first used to identify the spectral positions of the uranium oxide nanoparticles synthesized by our plasma flow reactor. We then use a pulsed IR laser for in situ detection of the uranium oxide nanoparticles at high temperatures (T ~ 1100 K). The laser is tuned over the spectral positions that are determined from the initial FTIR measurements at room temperature. The details of the in situ measurements are given in the Experimental Section of our paper.

**Optical Emission Spectra of U(g) and UO(g)**

The grating spectrometer described in the Experimental Section of our paper was used to record the optical emission spectra of uranium atoms and uranium monoxide molecules at various locations (i.e., temperatures) along the plasma flow reactor. Measured spectra are shown as a function of temperature in Figures S1. Uranium atoms have a strong optical emission line at 591.5 nm, whereas the UO emission is centered at 593.6 nm$^7$. The presence of uranium monoxide close to the argon plasma indicates fast oxidation of uranium atoms at high temperatures. As the temperature decreases from 4025 K to 1960 K, the emission intensities decrease as well. The optical emission intensities of U and UO approach zero (SNR <5) below 1960 K (x = 12cm), which
suggests performing the IR spectral measurements further downstream of this position will enhance the likelihood that reactions forming UO$_3$ will have run to completion. In these experiments the IR spectral data were collected at a temperature of 1100 K (x = 21 cm from the RF coil).

Figure S1. Emission spectra of atomic uranium and molecular uranium monoxide taken at different locations (i.e. temperatures) along the plasma flow reactor. (a) x = 3 and x = 4 cm from RF coil, (b) x = 5, 6, 7, 10, 12 cm from RF coil. The experiment was performed at high oxygen concentration.

References


