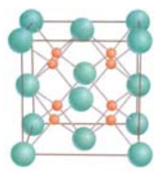
# Raman Spectroscopy of $UH_3$ from the Hydrogen Corrosion of Uranium

N. Smyrl, A. C. Stowe, G. L. Powell
Y-12 National Security Complex, Oak Ridge, TN

## Introduction

- Hydrogen reacts with a uranium surface to form a fine, pyrophoric metal powder ($UH_3$).
- Few spectroscopic studies have been conducted to study this reaction.
- Advances in Raman spectroscopy permit the application of the Raman method to formally difficult areas of chemistry such as the hydrogen corrosion of uranium.
  - availability of multiple laser excitation wavelengths
  - fiber optics delivery and collection systems
  - upgraded instrumentation and detection techniques
  - development of special enclosed *in situ* reactor cells
- $UH_3$ vibrations are expected to occur at low frequencies due to extended U-H-U structure.



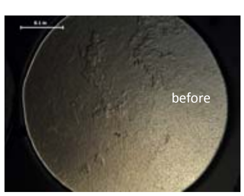
Uranium hydride structure.

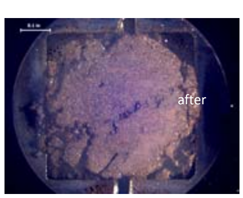
## *In situ* Spectroscopic Cell

- Aluminum design prevents hydrogen outgassing providing a cleaner reactor chamber.
- Multiple gas inlets for introduction of reactive and cover gases in close proximity to the sample.
- Glass, quartz, and sapphire conflat windows can be interchanged depending on light transmission and gas pressure characteristics of the specific experiment.
- Sample sits on variable height thermowell with cartridge heater assembly.
- Aluminum conductivity transfers heat rapidly from the sample zone throughout the reactor body limiting maximum heating to 300 °C.
- Similar vessel with stainless steel construction achieves 550 °C, but suffers from hydrogen outgassing.

## Sample Preparation

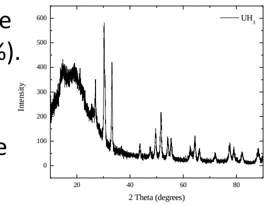
- Uranium metal disk (*before*) was placed in a stainless steel vacuum reactor chamber with a quartz window.
- Sample exposed to 7.6 mmol $H_2$ gas pressure at 25 °C for one week.
  - Sample surface darkened.
- The sample was heated to 500 °C under high vacuum to remove $H_2$.
  - Not all $H_2$ pressure was recovered.
  - Surface oxide layer was conditioned.
- Sample exposed again to 400 torr $H_2$ at 25 °C
- 5.4 mmol $H_2$ reacted within 12 hrs resulting in significant powdering of the disk and $UH_3$ powder growth (*after*).
- $UH_3$ and $UO_3$ powders were also investigated separately under quartz.
- FT-Raman (λ = 1064 nm) and UV Raman (λ = 325 nm) spectra were collected.



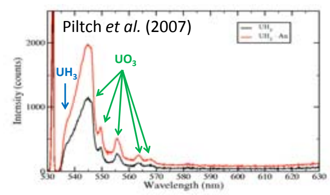



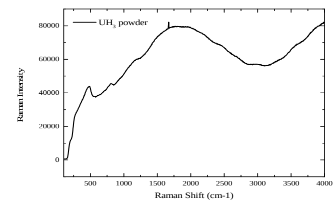

## Uranium Hydride Powder

- X-ray diffraction indicates uranium hydride powder to be free of uranium oxides (<1%).
- A Kapton film was used to protect $UH_3$ powder from exposure to air during the analysis and gives the broad feature in the XRD spectrum centered at 20 degrees.

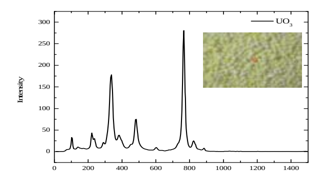



- Two features appear at low frequency which are potentially $UH_3$ vibrations.
- These features are similar to the SERS experiments published by Piltsch *et al.*



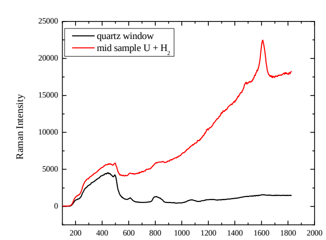




- Piltsch indicated that the spectrum they collected was primarily comprised of scattering from uranium oxide contaminants.
- The spectrum of $UO_3$ was therefore collected as a reference oxide to ensure that no features in the hydride spectrum was from residual oxides at quantities smaller than 1%.




## Hydriding of Uranium

- After the initial hydride, no Raman features were observed, despite visually observing a darkening of the uranium surface typical of hydriding.
- Raman spectra collected of powder on the uranium surface after the second hydriding gave a similar spectrum to the free $UH_3$ powder.
- A new feature was observed at 1607 $cm^{-1}$ which does not appear in the free $UH_3$ powder.
- The 1607 $cm^{-1}$ feature is in a region of the spectrum where carbon appears; however, the frequency **does not** correspond to the carbon band observed in the carbon enhanced uranium hydriding work of Shamir (*Shamir (2010)*).
- Excitation with visible wavelengths may provide better Raman spectra in the low Raman shift frequency region due to improved optics and scattering intensity.




## Acknowledgements

- This work was funded by the Y-12 Plant Directed research and Development program.

National Security Complex