Contract No:

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LDRD-2020-0006
LDRD External Report Summary

Fundamental Uranium-235 Nuclear Resonance Spectroscopy

Summary Statement

Enriched uranium (U-235) is ubiquitous in the nuclear industry yet many of its fundamental properties have never been studied using magnetic resonance. To remedy this we built a high frequency nuclear quadrupole resonance spectrometer that is capable of measuring the very high quadruple resonance signals of U-235.

Introduction

Conventional nuclear magnetic resonance techniques are ill-suited for characterizing ^{235}U due to the small gyromagnetic ratio and extremely large quadrupole moment of this spin $^{7}/_{2}$ isotope. Thus, we have designed and built a high-frequency nuclear quadrupole resonance spectrometer for measuring the quadrupole resonance of this important isotope. Our detection system uses a solenoid coil and capacitor design to produce and measure resonance frequencies as low as 500 kHz and as high as 3 GHz. To date, we have performed successful NQR measurements of several non-uranium materials that have quadrupole resonance signals as high as several hundred gigahertz. We continue to search for the quadrupole resonance signal of U-235, and we are hopeful the signal will be uncovered in the near future. A successful nuclear quadrupole resonance measurement of ^{235}U would be a significant accomplishment and could yield valuable physical parameters such as chemical shifts, local electric field gradients, and through-bond and through-space internuclear couplings, all of which are directly related to local structure. These terms can be used to understand structural details of poorly characterized uranium materials and can improve computational models of uranium for which accurate reference data is lacking.

Approach

Because the quadrupole moment of nuclei is orientation-dependent, we first developed robust synthetic techniques for producing high quality single crystals of different uranium compounds with varying levels of U-235. We also produced crystals of uranyl nitrate that contained up to 50% N-15 to support NMR analysis. We then designed and built a high frequency NQR spectrometer with a robust solenoid coil detection system. The NQR spectrometer was installed within SRNL's Category II Nuclear Facility in FY22. After functional and benchmark testing of our NQR spectrometer using chemical standards, enriched uranium-containing samples were analyzed and are still undergoing analysis as of the end of FY22. Some follow-on funding has been acquired to support additional development of this research program.

Accomplishments

- Designed and built a novel high frequency NQR spectrometer capable of measuring resonance signals up to several gigahertz
- Performed functional and benchmark tests of the high frequency NQR spectrometer up to several hundred gigahertz using validated chemicals
- Published two peer-reviewed manuscripts on uranium tetrafluoride
- Performed extensive N-15 NMR measurements of depleted uranyl nitrate hexahydrate crystals
- Performed preliminary N-15 NMR measurements of enriched uranyl nitrate hexahydrate crystals
- Found that N-15 NMR measurements should aid in understanding how U-235 affects the NMR spectra of neighboring nuclei; prepared a draft manuscript on this subject.
- Delivered a presentation at the 22nd International Society of Magnetic Resonance Conference
- Installed and operated our high-frequency NQR spectrometer in SRNL's Category II Nuclear Facility in FY22.

- Designed a solenoid and capacitor high frequency generation and detection system that delivers significant operational flexibility for a variety of zero-field spectroscopic experiments.
- Equipped multiple radiological laboratory spaces for chemical synthesis
- Developed robust methods for the synthesis of multiple uranium-bearing single-crystals
- Procured depleted and highly enriched uranium certified reference materials

Peer-reviewed Publications

Foley, B. J.; Christian, J. H.; Klug, C. A.; Villa-Aleman, E.; Wellons, M. S.; DeVore, M.; Groden, N.; Darvin, J., Probing the hydrolytic degradation of UF4 in humid air. *Dalton Transactions* **2022,** *51* (15), 6061-6067.

Christian, J. H.; Klug, C. A.; DeVore, M.; Villa-Aleman, E.; Foley, B. J.; Groden, N.; Baldwin, A. T.; Wellons, M. S., Characterizing the solid hydrolysis product, UF4(H2O)2.5, generated from neat water reactions with UF4 at room temperature. *Dalton Transactions* **2021,** *50* (7), 2462-2471.

SRNL is the lead research organziation for both manuscripts.

Intellectual Property

N/A

Total Number of Post-Doctoral Researchers

Garret Gothelf, Separation Sciences and Engineering Group
Jason Darvin, Trace Nuclear Measurement Technology Group
Bryan Foley, Separation Sciences and Engineering Group (transitioned to Senior Scientist in 2022)
Nicholas Groden, Cybersecurity and Threat Assessment Group (transitioned to Senior Scientist in 2021)

Total Number of Student Researchers

N/A

Figures

Figure 1. SRNL's new NQR spectrometer installed in a radiological laboratory to facilitate measurements with enriched uranium and other radioactive materials.

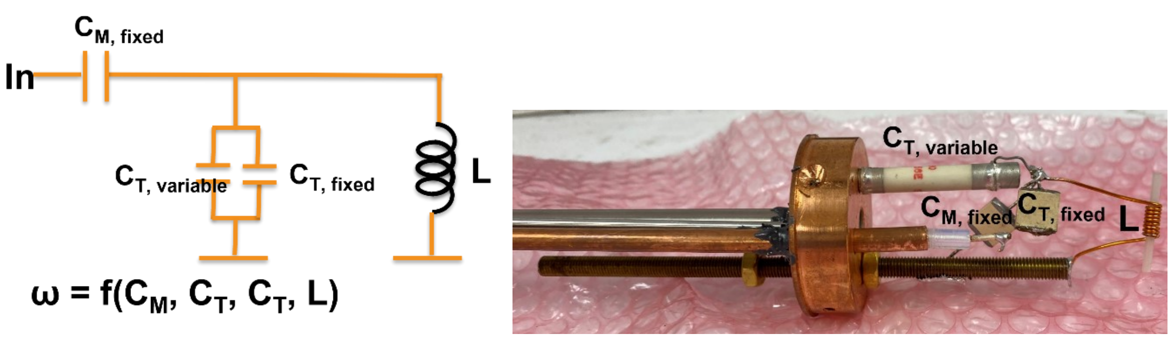

Figure 2. Left: Electrical diagram demonstrating the design of the high frequency NQR solenoid and capacitor system; Right: A photograph of the high frequency NQR solenoid and capacitor system with a sample placed inside a tube inside the solenoid coil (labeled L)

Figure 3. SRNL researchers evaluate newly-created uranium-containing single crystal compounds in a radiological laboratory.

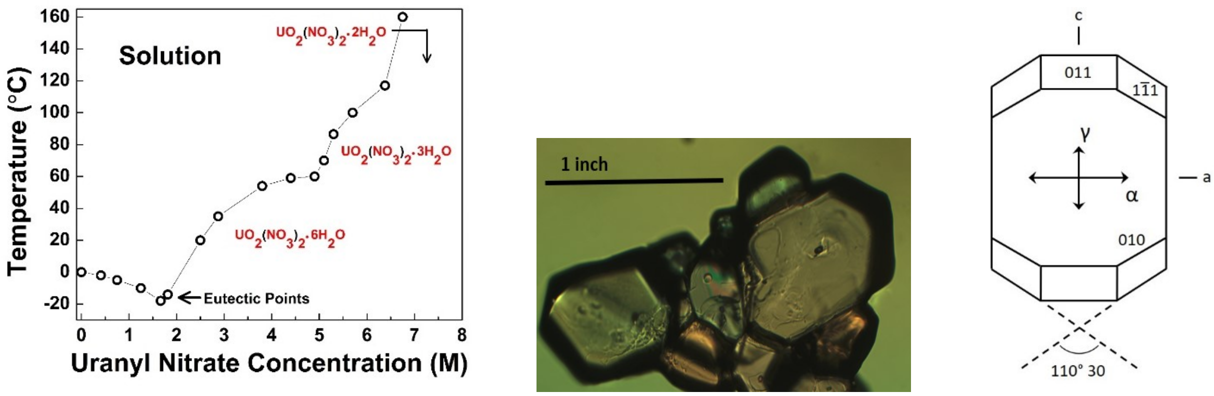

Figure 4. Left: The phase diagram of uranyl nitrate was used to develop a robust method for producing high quality single crystals of $UO_2(NO_3)_2 \cdot 6H_2O$; Middle: Micrograph of multiple single crystals of $UO_2(NO_3)_2 \cdot 6H_2O$; Right; Illustration of the crystallographic shape and axes for $UO_2(NO_3)_2 \cdot 6H_2O$ crystals.

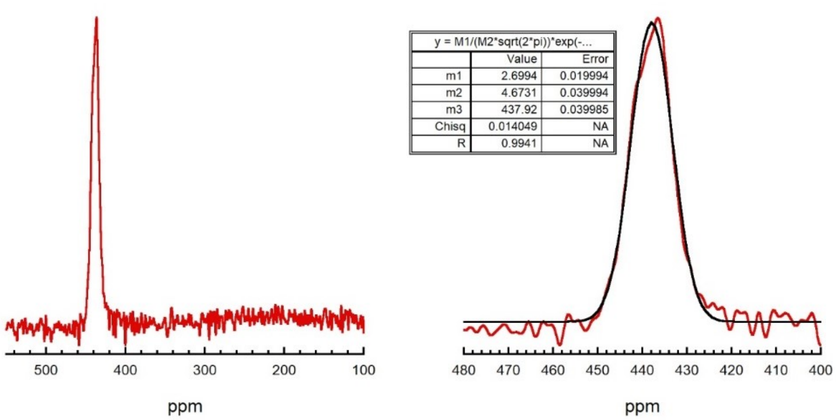

Figure 5: Left: N-15 NMR spectrum for a hexagonal crystal of uranyl nitrate hexahydrate; Right: The spectrum is fit to a simple Gaussian function with FWHM=11.0 ppm. These data were acquired using single pulse excitation and a wait time between scans varying from 1 to 64 sec. The total number of scans was 8960.

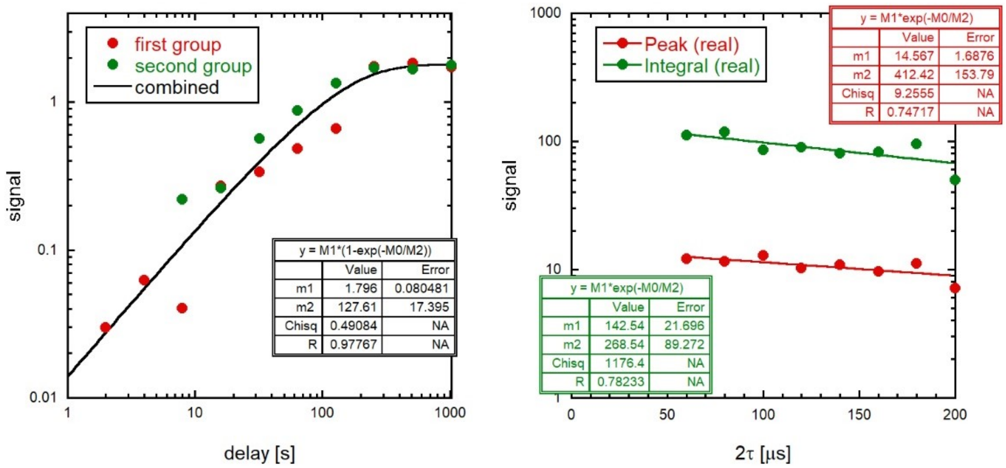

Figure 6: Plots of N-15 NMR signal sizes from relaxation measurements of a hexagonal crystal of uranyl nitrate hexahydrate. Left: Peak heights as a function of the delay between scans in a T_1 measurement along with a simple single-exponential fit to the data—single pulse excitation was used with a total number of scans per point of 64; Right: Peak heights and integrals as a function of twice the delay between pulses, τ, in a spin-echo experiment along with simple single-exponential fits to the data—spin echo excitation was used with a wait time between scans of 16 sec and a total number of scans per point of 512.

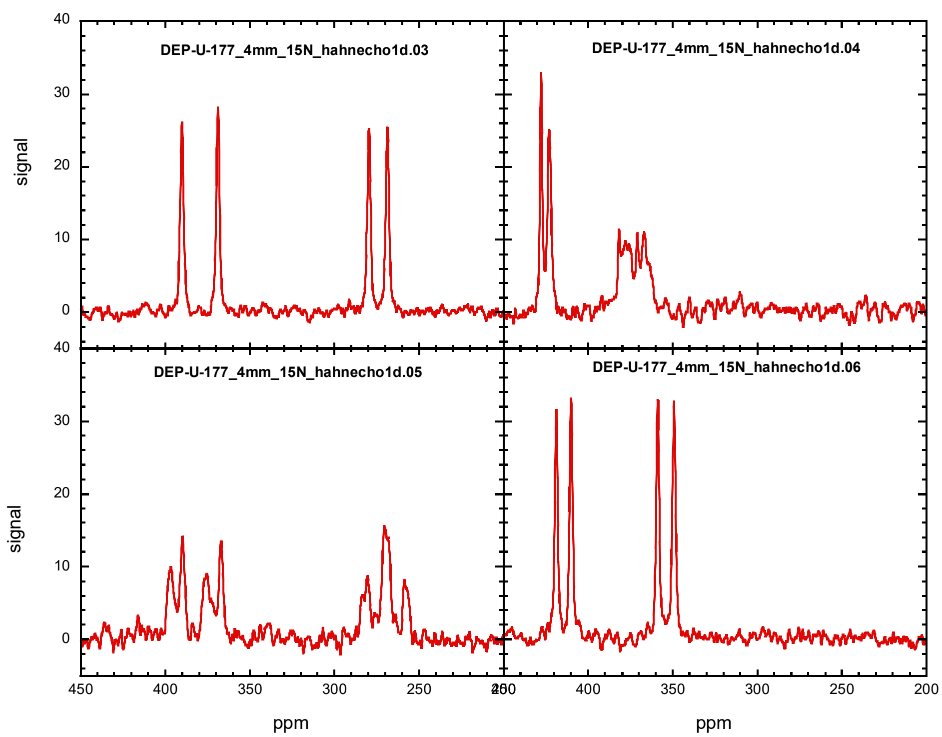

Figure 7: N-15 NMR spectra for a hexagonal crystal of uranyl nitrate hexahydrate obtained with four orientations in the MAS NMR probe—the sample was rotated roughly 90°

REVIEWS AND APPROVALS

1. Principal Investigator:

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Jonathan Christian Date

2. Technical Review:

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Bryan Foley Date

3. PI's Manager Signature:

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Marissa Reigel Date

4. PI's Division Director Signature:

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Frank Pennebaker Date

5. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Ryan Peterson Date