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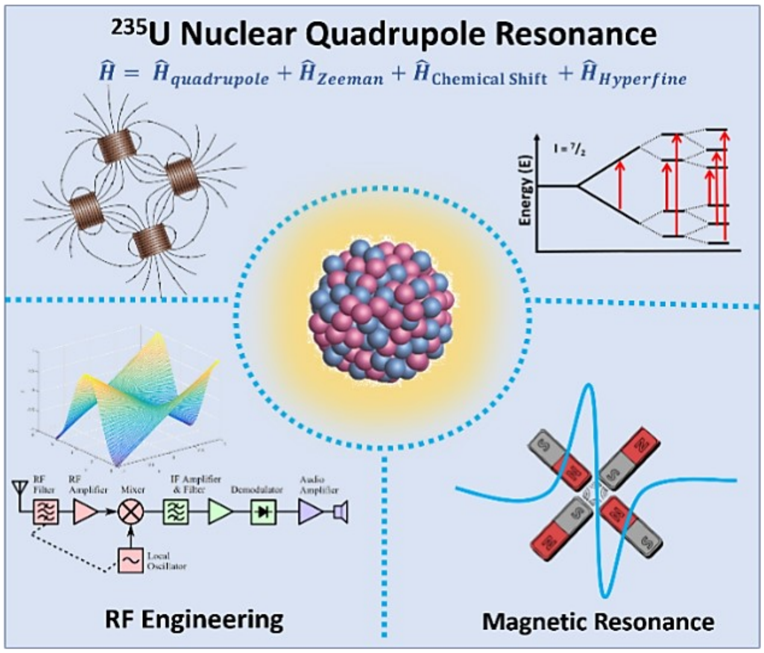
Fundamental ^{235}Uranium Nuclear Resonance Spectroscopy

Project highlight. Enriched uranium is ubiquitous in the nuclear industry, yet many of its quantum mechanical properties have never been observed using magnetic resonance. Using high frequency nuclear quadrupole spectroscopy, we seek to become the first research team to observe the quadruple resonance of the uranium-235 isotope.



Awards and Recognition

Parts of this project were presented at the 22nd International Society of Magnetic Resonance Conference via an invited presentation; the presentation was delivered in August 2021.

Some of the results from this project were published in the manuscript, Characterizing the solid hydrolysis product, $UF_4(H_2O)_{2.5}$, generated from neat water reactions with UF_4 at room temperature, Dalton Trans., 2021, **50**, 2462-2471.

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

Signature **Date**

Fundamental ^{235}Uranium Nuclear Resonance Spectroscopy

Project Team: Jonathan Christian (PI), A. Taylor Baldwin, Bryan Foley, Thomas Shehee, Michael Bronikowski, Matthew Wellons.

Subcontractor: Christopher Klug (Naval Research Labs), Joel Miller (Naval Research Labs)

Project Type: Discovery Science

Project Start Date: October 1, 2019
Project End Date: June 30, 2022

Uranium-235 is ubiquitous in the nuclear industry however, detailed characterization by magnetic resonance spectroscopy has remained largely elusive to-date. 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. 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.

FY2021 Objectives

- Assemble high-frequency nuclear quadrupole resonance spectrometer using instrument components purchased in FY20.
- Perform functional tests of high-frequency nuclear quadrupole resonance spectrometer using well-characterized standards
- Have SRNL staff gain competency in the assembly and operation of the high-frequency nuclear quadrupole resonance spectrometer.
- Execute solid-state ^{15}N NMR measurements on ^{15}N-enriched uranyl nitrate hexahydrate crystals
- Prepare ^{235}U-enriched uranyl nitrate hexahydrate crystals
- Perform preliminary nuclear quadrupole resonance measurements on ^{235}U-enriched samples.
- Prepare publications pertaining to the NMR of uranium in UF_4.

Introduction

Because of its non-zero spin, ^{235}U is potentially measurable via magnetic resonance spectroscopy (MRS). However, the gyromagnetic ratio of ^{235}U is estimated at 0.78 MHz/T, meaning the nuclear magnetic resonance (NMR) frequency, ν, of ^{235}U due to Zeeman splitting in a magnetic field of 11.7 Tesla is 9.13 MHz, compared to 500 MHz for ^{1}H. Therefore, conventional NMR spectrometers are inapt at measuring this rare isotope. Furthermore, since signal-to-noise generally scales as $\nu^{5/2}$, detection of ^{235}U NMR at very low frequencies is challenging. The significance of these obstacles is evidenced by the scarcity of magnetic resonance literature pertaining to ^{235}U. The only published ^{235}U NMR reference is a two-and-a-half-page letter from 1983 involving 93.5% enriched liquid uranium hexafluoride heated to 380 K. The linewidth at 11.747 T was said to be 20 KHz, but no other relaxation information was given. This work has been rarely cited and most of those papers are theoretical.

Although the predicted NMR frequency of ^{235}U is extremely low and there appears to be numerous barriers in measuring and analyzing an NMR signal from this isotope, the nuclear quadrupole resonance (NQR) of ^{235}U is predicted to be near 1 GHz.[1] This is over two orders of magnitude larger than the NMR frequency, meaning that the quadrupole term is the dominant energy term in the ^{235}U spin Hamiltonian. Therefore, direct measurement of this term would be a significant scientific achievement and should give further insight into the magnetic properties of this important isotope.

Approach

The ambitious goal of being the first research team to measure NQR signals from ^{235}U has necessitated a detailed experimental approach. A high-level summary of our approach is as follows.

SRNL will develop robust synthesis methods for producing high quality single crystals of different uranium compounds, and together with NRL, will develop a homebuilt high-frequency NQR spectrometer for analyzing said crystals.

Following functional and benchmark testing of the homebuilt NQR spectrometer using chemical standards, depleted and enriched uranium-containing samples will be analyzed. Ultimately, the NQR spectrometer will be installed within SRNL's Category II Nuclear Facility where it will be utilized for additional NQR studies on enriched uranium and other radioactive isotopes that are amenable towards analysis by NQR spectroscopy.

Results/Discussion

The NQR spectrometer designed for this project is comprised of a 50 W high power GaN amplifier, multiples heat sinks, a 100 W high power LDMOS amplifier, multiple power supplies, and a compact, modular, NMR / NQR Tecmag Redstone console configurable with multiple transmitters, receivers, and gradient channels. With its numerous options, the Redstone can be configured for any magnetic resonance application in the frequency range from ~ 2 kHz to 3.5 GHz and does not require manual heterodyning of excitation signals. In FY21, this instrument was assembled at NRL, as shown in Figure 1.

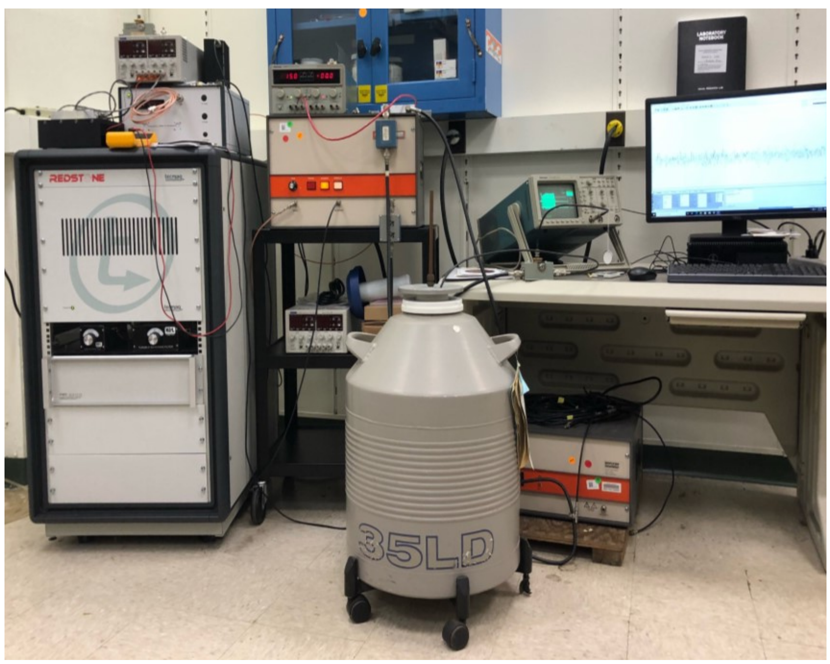


Figure 1. SRNL's new NQR spectrometer.

Functional and benchmark tests of the NQR spectrometer have proven successful up to 30 GHz. An example free-induction decay and Fourier transform NQR spectrum measured on the homebuilt NQR for ^{35}Cl in $KClO_3$ is shown in Figure 2.

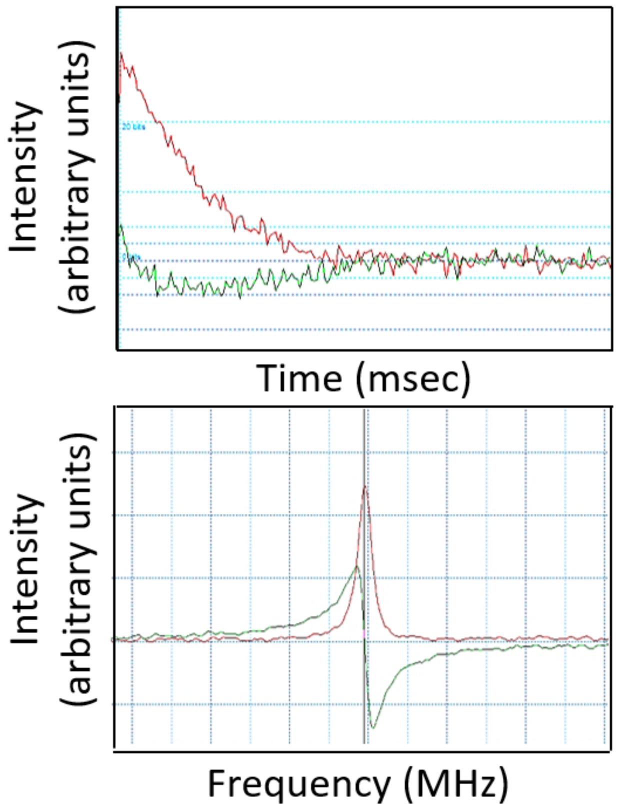


Figure 2. Top: Free induction decay of the ^{35}Cl NQR signal at 28.1 MHz measured with SRNL's new NQR spectrometer. Bottom: Fourier transformed spectrum.

Extensive ^{15}N NMR measurements on ^{15}N-enriched uranyl nitrate hexahydrate (UNH) crystals have proven fruitful. As shown in Figure 3, a crystal of this compound exhibits a single spectral peak with a narrow linewidth (full width at half maximum, FWHM ≈ 550 Hz at 11.7 T). The longitudinal relaxation time, T_1 for this compound was found to be 128 sec and the transverse relaxation time, T_2 was relatively slow such that spin echo experiments used a delay between pulses, τ , of 40 µsec. The ^{15}N NMR spectrum of UNH was also found to be highly anisotropic. That is, the spectrum varies greatly depending on the crystal orientation within an external magnetic field.

The narrow linewidth, relatively long relaxation times, and highly anisotropic nature of ^{15}N in UNH are promising attributes for several reasons. First, spectral anisotropy is related to molecular anisotropy. Thus, the molecular structure of UNH is clearly anisotropic (as expected), which is an important prerequisite for compounds to exhibit a quadrupole moment, and thus be measured using NQR spectroscopy. Second, the narrow linewidth and relatively long relaxation times may allow NQR perturbations to be observed in ^{15}N NMR measurements of enriched uranium crystals (> 20% ^{235}U). If such perturbations are observed, quantum mechanical calculations can be used to estimate the nuclear quadrupole moment of ^{235}U, thus allowing NMR to provide indirect detection of ^{235}U and providing our research team with an estimate of the currently unknown quadrupole resonance frequency of ^{235}U. An estimate of the quadrupole resonance frequency will greatly facilitate future NQR measurements.

Additional NMR analyses of ^{19}F in UF_4 with ancillary vibrational spectroscopy measurements have proved fruitful in analyzing chemical and structural changes that occur for this important nuclear compound, as described in detail in our recent publication (*Dalton Trans.,* 50, 2462-2471).

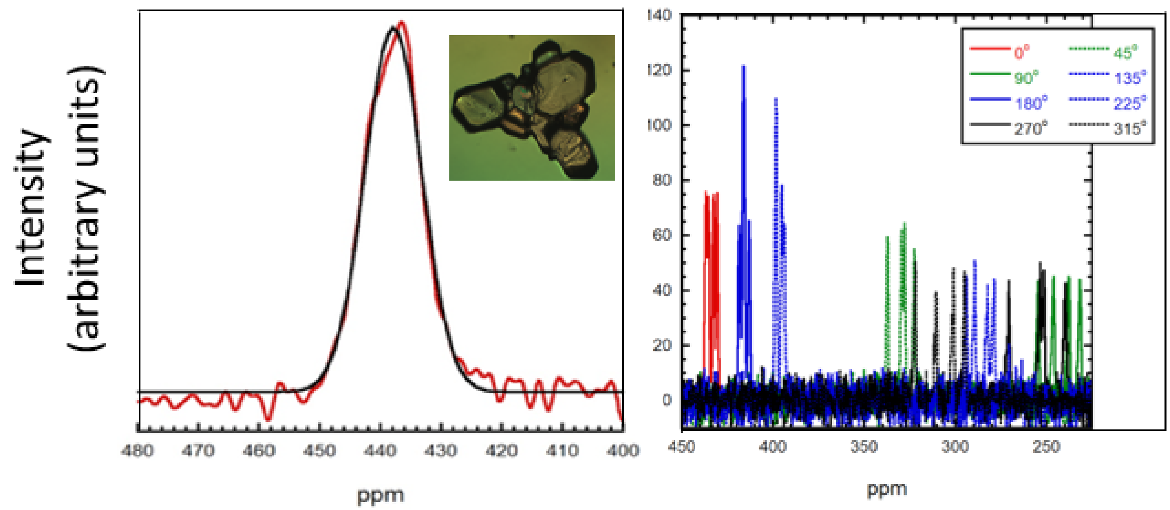


Figure 3. Left: ^{15}N NMR spectrum for a hexagonal crystal of uranyl nitrate hexahydrate (red trace) fit to a Gaussian function (black trace) with FWHM = 11.0 ppm (~ 550 Hz at 11.7 T). Right. ^{15}N NMR spectra measured at multiple crystal orientations using magic angle spinning. Spectra were acquired using a spin echo pulse sequence with a delay of 40 µsec between pulses and a wait time between scans of 128 s.

FY2021 Accomplishments

- A novel high-frequency NQR spectrometer was designed and built
- Functional and benchmark tests of the high-frequency NQR spectrometer have been performed up to 30 GHz.
- A manuscript describing chemical and structural details of UF_4 as measured by ^{19}F NMR was published in Dalton Transactions (Dalton Trans., 2021, **50**, 2462-2471).
- A manuscript describing chemical and structural details of naturally-occurring UF_4 hydrolysis products as measured by ^{19}F NMR has been drafted and will be submitted for publication in early FY22.
- Extensive ^{15}N NMR measurements of uranyl nitrate hexahydrate crystals have yielded interesting results that should support the goal of understanding how uranium enrichment affects NMR spectra.
- A manuscript describing ^{15}N NMR measurements of uranyl nitrate hexahydrate has been drafted and will be completed following enriched uranium measurements.
- Published data were presented at 22nd International Society of Magnetic Resonance Conference
- Enriched uranium samples have been synthesized and will be shipped to NRL in late FY21/early FY22.
- Significant logistical arrangements have been made to allow SRNL to accommodate shipment and installation of the high-frequency NQR spectrometer in FY22.
    - Logistical considerations included, radiological concerns, electrical requirements, asphyxiation concerns for liquid cryogenic use, space requirements, etc.

Future Directions

- Shipment of ^{235}U enriched samples
- Continued functional and benchmark testing of NQR spectrometer using validated chemicals
- Continued magnetic resonance measurements of crystals of varying ^{235}U content to extract the nuclear quadrupole energy from peak shapes.
- Perform NQR measurements on uranium compounds and optimize detection parameters.
- Publish results and use acquired spectral data to improve understanding of uranium's magnetic properties.
- Install NQR instrumentation at SRNL for a new lab capability.

Figure 4. LDRD researchers study enriched uranium materials inside a radiological glovebox within SRNL's Category II nuclear facility.

FY 2020 Peer-reviewed/Non-peer reviewed Publications

Characterizing the solid hydrolysis product, $UF_4(H_2O)_{2.5}$, generated from neat water reactions with UF_4 at room temperature. Dalton Trans., 2021, **50**, 2462-2471.

- SRNL was the lead lab on this publication.

Presentations

Characterizing the solid hydrolysis product, $UF_4(H_2O)_{2.5}$, generated from neat water reactions with UF_4 at room temperature. Presented at the 22nd International Society of Magnetic Resonance Conference.

References

1. Cho, H., Dependence of nuclear quadrupole resonance transitions on the electric field gradient asymmetry parameter for nuclides with half-integer spins. *Atomic Data and Nuclear Data Tables* **2016,** *111-112*, 29-40.

Acronyms

FWHM – Full Width at Half Maximum
FY – Fiscal Year
NMR – Nuclear Magnetic Resonance
NRL – Naval Research Laboratory
NQR – Nuclear Quadrupole Resonance
SRNL – Savanah River National Laboratory
UNH – Uranyl Nitrate Hexahydrate

Intellectual Property

N/A

Total Number of Post-Doctoral Researchers

Two post-doctoral researchers performed research on-site at SRNL:

- Bryan Foley (Ph.D. Inorganic Chemistry, Texas A&M, 2019)
- Nicholas Groden (Ph.D. Micro/Nanosytems Engineer, Louisiana Tech, 2018)

Total Number of Student Researchers

Student interns were going to be utilized for this project but were unavailable due to COVID-19 protocols.

External Collaborators (Universities, etc.)

- Christopher Klug – Naval Research Laboratory
- Joel Miller – Naval Research Laboratory