

Ultra-Low Field NMR of UF₆ for ²³⁵U Detection and Characterization

Per E. Magnelind, Andrei N. Matlashov, Petr L. Volegov, and Michelle A. Espy

Abstract—We have demonstrated the first ultra-low field (ULF) nuclear magnetic resonance measurements of uranium hexafluoride (UF₆), which is used in the uranium enrichment process. A sensitive non-invasive detection system would have an important role in non-proliferation surveillance. A two-frequency technique was employed to remove the transients induced by rapidly switching off the 50 mT pre-polarization field. A mean transverse relaxation time T_2 of 24 ms was estimated for the un-enriched UF₆ sample measured at a mean temperature of 80 °C.

Index Terms—uranium hexafluoride, ULF-NMR, SQUID.

I. INTRODUCTION

SEVERAL ultra-low field (ULF) nuclear magnetic resonance applications have emerged over the last years [1]-[4]. The narrow NMR line widths and the smaller magnetic field induced artifacts are only two of the factors that make the ULF NMR systems attractive. Also, the lower frequencies of ULF NMR enable NMR measurements through metal sheets or pipes [5],[6].

Uranium hexafluoride (UF₆) is used in the enrichment process of uranium. It is a white solid at room temperature and atmospheric pressure and there exists a triple point at 64 °C. At temperatures above the triple point the UF₆ consists of a mixture of liquid and vapor.

Several methods have been proposed to determine the level of ²³⁵U enrichment, such as the destructive method: thermal ionization mass spectroscopy [7]; and the non-destructive methods: thermal neutron method [8], gamma-ray dose rate measurements [9], and NMR [10]. The non-destructive methods have the advantage that they can be fitted around existing pipes in the facilities. A non-destructive ULF-NMR enrichment verification system could serve an important role in non-proliferation surveillance.

NMR provides an indirect method to determine the presence of ²³⁵U in uranium hexafluoride liquid and vapor as the properties of the fluorine is studied. Direct ULF NMR of ²³⁵U is a great challenge due to the lower molecular abundance (1/6 of the fluorine) and lower NMR sensitivity (small magnetogyric ratio and short spin-lattice relaxation time [10]). However, high field NMR of ²³⁵U has been demonstrated [11].

The isotope ²³⁵U has a spin quantum number of $S=7/2$ and ¹⁹F has $S=1/2$, which in UF₆ generates a multiplet structure at frequencies

$$\nu = \nu_0 + JM_s, \quad (1)$$

where ν_0 is the Larmor frequency of ¹⁹F nuclei, M_s is the magnetic quantum number, and J is the ¹⁹F-²³⁵U scalar coupling constant [10].

In this article we report measurements on un-enriched UF₆ liquid as a first step of proof-of-concept for a non-destructive surveillance system.

II. EXPERIMENTAL METHODS

A. Two-frequency approach

The most common ULF NMR/MRI approach is polarizing the sample in a large pre-polarizing field B_p followed by switching off B_p in a short time to record the free induction decay (FID) of the sample magnetization at a low field B_m . With non-adiabatic B_p switching ($dB_p/dt \geq \gamma B_m^2$) the magnetization remains aligned along B_p and if B_m is not parallel to B_p , the magnetization of the sample will precess around B_m . Unfortunately, transient fields are generated by the rapid switching of the magnetic field as currents proportional to dB/dt are induced in conductive materials.

To correct for the transients we have used an approach where two slightly different measurement fields are used and the difference between the measured FIDs at the different fields is used in the processing. This approach assumes that the transient-induced signal does not depend on the measurement field. A more detailed description of this method can be found in [12].

B. Instrumentation

The measurement set-up is shown in Fig. 1. The sample consisted of a 200 ml PTFE cylinder filled with 17 g of un-enriched UF₆. The cylinder was surrounded by resistive heaters, which were covered by PTFE insulation cylinders. The sample cylinder was placed horizontally below the tail of a liquid helium cryostat holding a low- T_c SQUID coupled to a second order axial superconducting gradiometer (25 mm diameter and 40 mm baseline). The gradiometer had a corresponding magnetic field noise of 3.5 fT/Hz^{1/2}. The sample was pre-polarized in a magnetic field, B_p of up to 50 mT. The pre-polarization field was generated by a pair of coils positioned orthogonal to the length of the cylinder and to

the tail of the cryostat. Multi-stranded Litz wire was used to minimize the thermal Johnson noise generated by the coils. The measurement fields, B_m , were of the order of 0.1 mT. The whole system was operated in a single-layer magnetically shielded room equipped with an HF monitor to detect any UF_6 leak as the moisture in the air reacts with UF_6 to create HF.

The sample was pre-polarized for a time $>T_1$ of UF_6 . During the pre-polarization the SQUID electronics was switched off. At the beginning of the epoch the B_p field was rapidly switched off. When the current through the B_p coils was sufficiently low the SQUID electronics was turned on to record the free induction decay.

The pre-polarization time as well as the acquisition time for each epoch were 150 ms. During the pre-polarization the B_m field was switched between its two values: 116 μ T and 120 μ T, which corresponds to a frequency shift of 180 Hz.

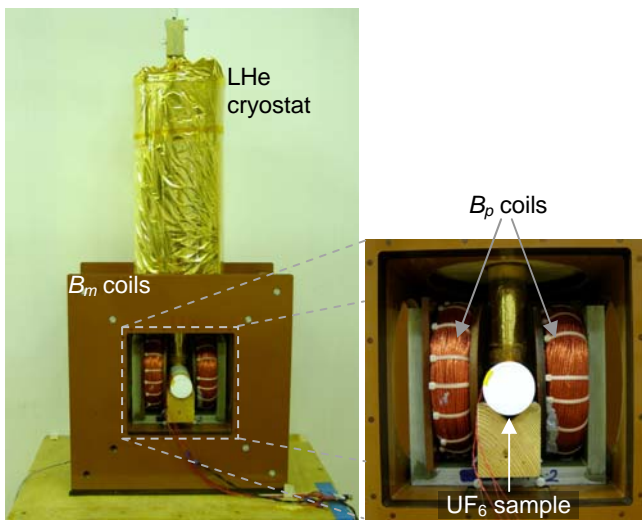


Fig. 1. Experimental set-up with the liquid helium cryostat wrapped in a gold mylar rf-shield, the B_m coils, the PTFE cylinder with heaters containing the UF_6 sample, and the B_p coils.

III. RESULTS

FIDs have been recorded from our heated UF_6 sample using the two-frequency approach. The results measured at a mean temperature of 80 $^{\circ}$ C are shown in Fig. 2. The fluorine peaks have been detected and match the frequencies of a reference liquid fluorine sample (perfluorodecalin; $C_{10}F_{18}$). The peaks at lower frequencies (1 kHz and lower) are artifacts from the coils. The fluorine peaks appear at 4642 Hz and 4822 Hz as shown in Fig. 3.

The FIDs have been analyzed using bootstrapping [13] to find the corresponding spin-spin relaxation time T_2 . The bootstrap analysis consisted of randomly sampling 11131 differentiated epochs to be averaged. The frequency and transverse relaxation time of the averaged random epochs were estimated using Lorentz fits with a fixed frequency difference to the peaks in the frequency domain. This procedure was repeated 10000 times to create a distribution of frequencies and T_2 estimations. The distribution of the T_2 values is shown in Fig. 4. A lognormal fit has been used to retrieve a mean of 24 ms and a variance of 13 ms.

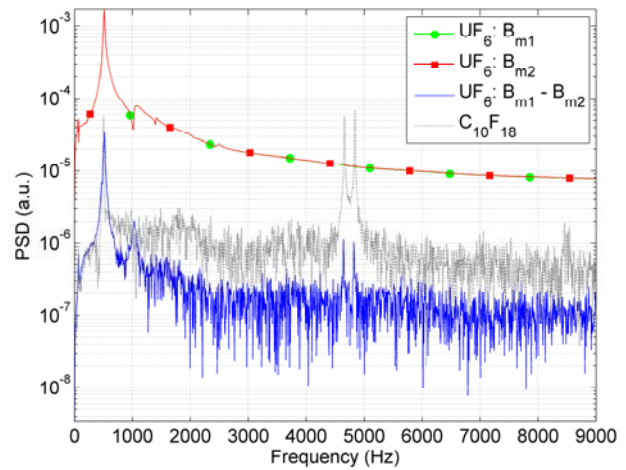


Fig. 2. Power spectral density of the FIDs from UF_6 and the reference liquid fluorine sample perfluorodecalin ($C_{10}F_{18}$). The PSDs from UF_6 are averages from 11131 odd and 11131 even epochs whereas the PSD from perfluorodecalin is an average from 464 odd and 464 even epochs. The effect of the two-frequency approach is shown as the PSDs from the odd and even epochs have a 100-fold higher noise level than the PSD of the differentiated FIDs.

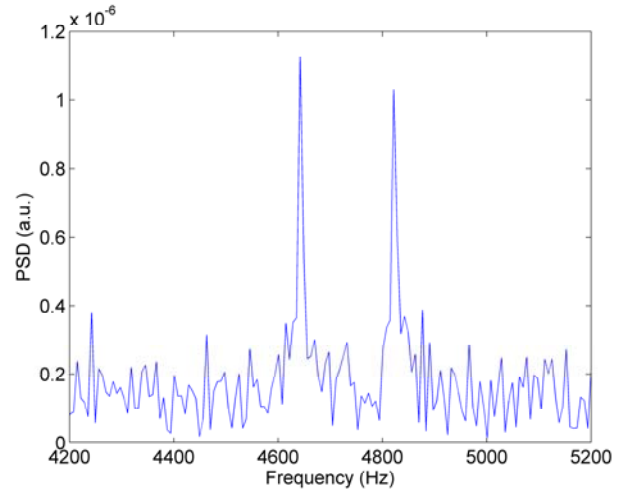


Fig. 3. Close-up of the PSD showing the fluorine peaks of the UF_6 sample at frequencies 4642 Hz and 4822 Hz.

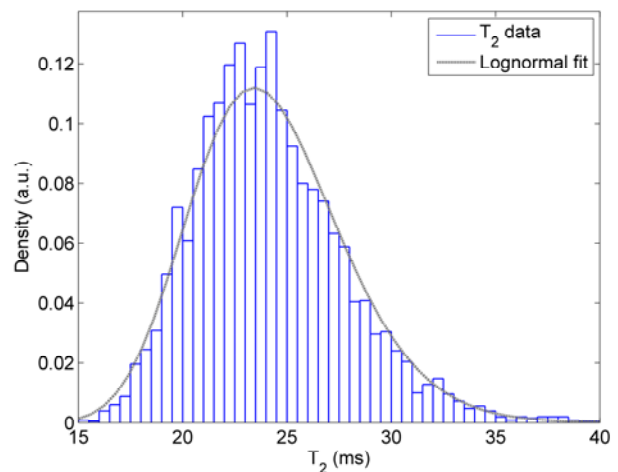


Fig. 4. T_2 distribution from bootstrapping analysis for UF_6 measured at a mean temperature of 80 $^{\circ}$ C. A lognormal fit shows a mean of 24 ms.

IV. DISCUSSION

The two-frequency approach was very effective in removing the transients and reducing the noise about 100 times. Without the two-frequency approach the fluorine peaks of the UF_6 would not have been visible.

The relaxation time has also been measured at high fields by, e.g., [10]. They report a relaxation time of 16 ms for an un-enriched UF_6 sample at 90 °C. The discrepancy between our value and that of Ursu *et al.* [10] could partly be attributed to the temperature difference between the measurements.

The signal-to-noise ratio of the measured sample was small, which was partly due to the long distance (~50 mm) between the UF_6 liquid at the bottom of the cylinder and the gradiometer's pick-up coils. A cryostat with the possibility to have the tail facing upwards would have been preferable to increase the signal strength. Another solution would be to use more UF_6 material in the cylinder. A larger signal-to-noise ratio would reduce the measurement time below the two hours or more presently used.

The gaseous phase of UF_6 has a short relaxation time of around 1 ms [10], which implies that in principle only the liquid phase can be measured in our system due to limitations in the B_p switching time and the problem with the field switching induced transients.

During the 160-minute measurement there was a temperature drift of 18 °C due to heat added from the current through the B_p coils. By reducing the heater current by the correct amount a stable temperature could be achieved. The temperature drift could have affected the width of the peaks and hence the T_2 estimation. Moreover, during the temperature increase the amount of liquid UF_6 changes from ~70 % down to ~50 % which would result in a smaller signal amplitude.

Our proposed enrichment detection method is based on comparing the fitted amplitudes of the multiplet $^{235}\text{UF}_6$ structures in relation to the amplitude of the singlet $^{238}\text{UF}_6$ structure. Theoretical line shapes [14],[15] for our two frequency method are shown in Fig. 5 where an enrichment factor of 70 % has been used together with a transverse relaxation time of 24 ms (for both $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$) and a scalar coupling constant of 213 Hz [14]. For each measurement field there exists an $^{235}\text{UF}_6$ octuplet and an $^{238}\text{UF}_6$ singlet. In the case of the octuplet structure being too small to detect, Ursu *et al.* [10] reports on decreasing T_2 times with increasing enrichment which might be applicable at low fields as well.

V. CONCLUSION

We have successfully demonstrated the first ULF NMR of fluorine in an un-enriched UF_6 sample. At a mean sample temperature of 80 °C we measured fluorine NMR FIDs with a relaxation time T_2 of 24 ms. The initial transients of the FIDs were removed in post-processing using a two-frequency method.

With improved performance and verification of the proposed ^{235}U characterization the system could be employed in surveillance for non-proliferation purposes.

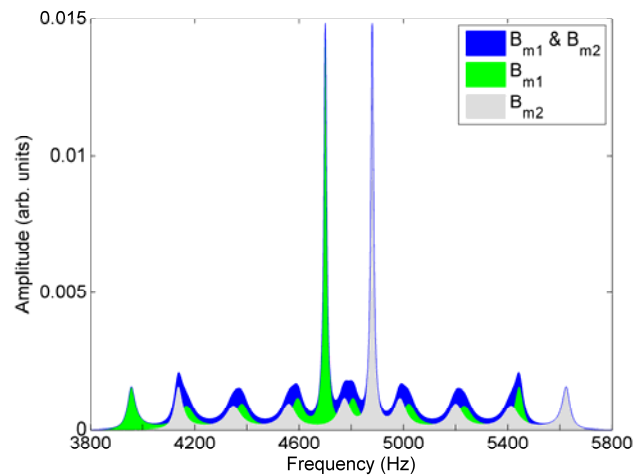


Fig. 5. Theoretical line shapes for our two frequency method for an enrichment factor of 70 %, Larmor frequencies of 4700 Hz and 4880 Hz, and $T_2=24$ ms. For each B_m there are $^{235}\text{UF}_6$ octuplet peaks and an $^{238}\text{UF}_6$ singlet peak. By fitting the measured peaks in the frequency domain to the singlet and the octuplet would give a measure of the enrichment factor as the singlet peak amplitude would decrease with enrichment whereas the octuplet peak amplitudes would increase.

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