

Application note

Fast Field Cycling NMR Relaxometry on Hetero-nuclei

Overview

In this application note we present a series of Fast Field Cycling NMR experiments for the direct observation of hetero-nuclei with low receptivity and detectability. It is an important complement to the conventional ^1H -detected FFC approach, to be able to investigate content and /or to characterize compounds of important NMR-sensitive nuclei, such as ^2D , ^{13}C , ^{19}F . The experiments were performed on a Spinmaster FFC2000 1T instrument, equipped with a digital receiver with detection from 500 kHz to 90 MHz, which permits the direct acquisition of some important hetero-nuclei with low gyromagnetic ratios. The multi-nuclear approach extends the potential of Fast Field Cycling applications thus allowing exploration of the field dependence of NMR spin-lattice relaxation time T_1 of important hetero-nuclei and substances, especially at low Larmor frequencies (down to 10 ^1H kHz), where other conventional NMR experiments present severe signal-to-noise (S/N) ratio degradation.

Generally, FFC relaxometry is used to determine the longitudinal relaxation time (T_1) over a range of B_0 -fields spanning about six decades, from about 10^{-6} T up to ~ 1 T without varying the frequency of the spectrometer.

The main information expected from the relaxation dispersion curves, T_1 or $R_1=1/T_1$ versus the Larmor frequency ω ($\omega=\gamma B_0$, γ is the gyromagnetic ratio) concerns molecular motions characterized by temperature-activated frequencies and described by means of spectral density $J(\omega)$.

The data obtained may, therefore, be correlated directly to the physical/chemical properties of complex materials providing information on the dynamics and structural features of molecules.

Furthermore, the possibility of setting and controlling the sample temperature in the range between -140 °C and $+140$ °C, in combination with the NMRD profile (R_1 versus the Larmor frequency) makes FFCR a very important source of dynamic information on both the global and local scale, as this technique succeeds in exploring molecular motions with correlation times ranging from 1 ns to a few μs .

Herein we show the applicability of the SPINMASTER FFC2000-1T for the acquisition of the longitudinal relaxation decay of some important hetero-nuclei.

²H

D₂O profiles in fuel cell membranes have been measured directly on solid samples:

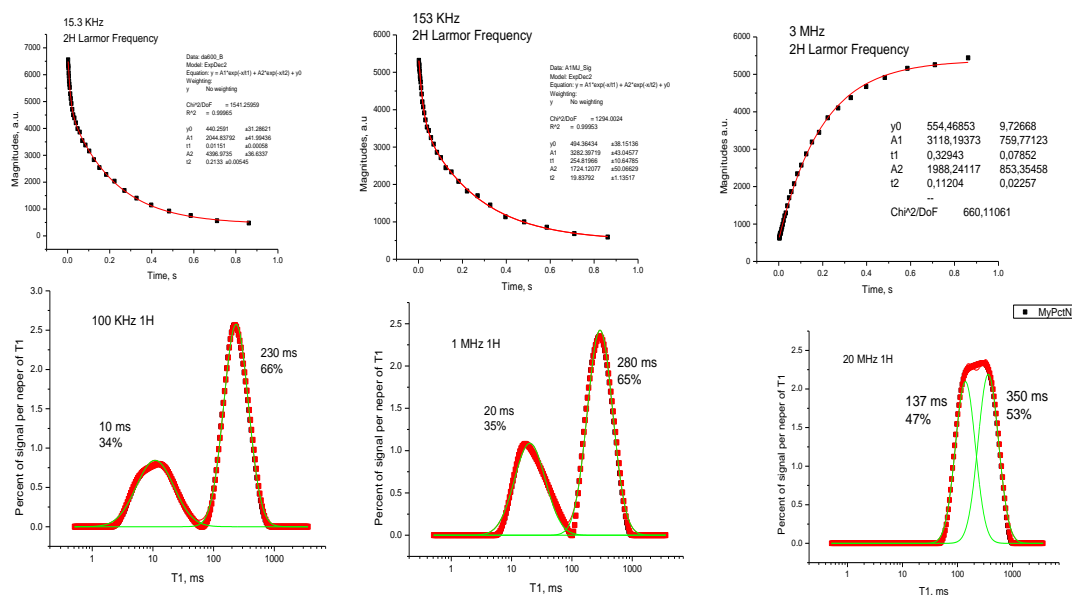


Figure 1

The Deuteron T₁ decay acquired on the above sample showed an evident multi-exponentiality particularly at low field. In Figure 1 the relaxation data at the three different fields (0.0023 T, 0.023 T and 0.5 T) were evaluated with discrete and continuous methods, using a two component traditional multi-exponential fitting as well as by means of a Laplace inversion algorithm (Open algorithm) in order to evaluate the distribution curve of T₁.

⁷Li

NMR spin relaxometry is known to be a powerful tool for the investigation of Li⁺ dynamics in (non-paramagnetic) crystalline and amorphous solids.

Materials which are suitable for all-solid-state lithium-ion battery applications benefit from a high Li⁺ self-diffusion. Investigating the Li ion dynamics by Nuclear Magnetic Resonance methods helps to identify potential electrode and electrolyte materials

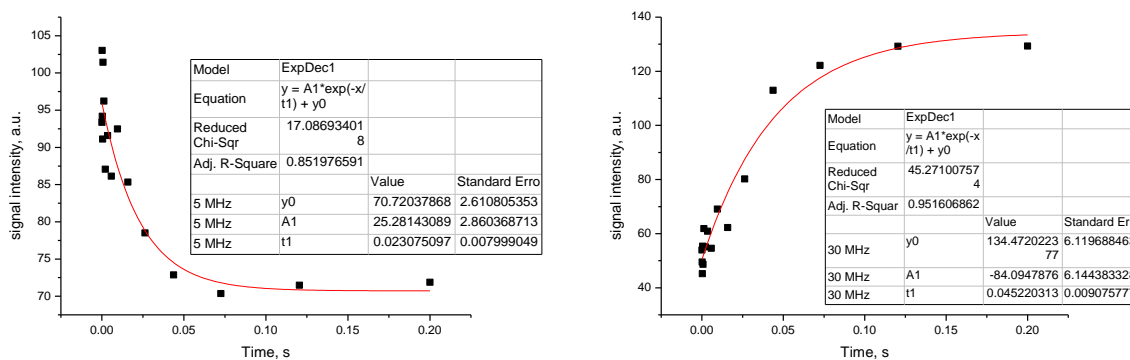


Figure 2. Longitudinal relaxation decay at two magnetic field strengths (0.12 T and 0.7 T) on ⁷Li.

The red lines are fitting curves

With FFC spin-lattice relaxation measurements and NMR profiles information on Li self-diffusion parameters such as jump rates and activation energies are accessible.

19F

¹⁹F Fast Field Cycling NMR relaxometry was applied to the investigation of the molecular dynamics of a liquid crystal.

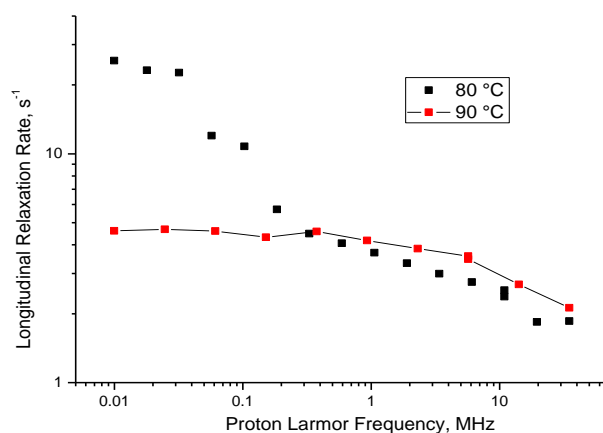


Figure 3

Figure 3 shows ¹⁹F NMRD profiles of the calamitic mesogen 4DBF2, fluorinated in two positions of the aromatic core. It exhibits a transition from the isotropic to nematic phase between 67 °C and 86 °C.

13C

Tests were carried out to obtain a NMR signal of ¹³C on enriched samples with the objective to understand and estimate the relative sensitivity of the SPINMASTER FFC2000-1T relaxometer:

- **Longitudinal Relaxation Decay on 1 ml of a Carboxylic Acid**

@ 2.35 mT (0.1 1H MHz) and -120 °C

| | | |
|-----------------|--------------------|-------------|
| FFC parameter : | Polarization Time | 60 s |
| | Polarization Field | 30 (1H MHz) |
| | Relaxation Field | 0.1 1H MHz |
| | Acquisition Field | 27 1H MHz |
| | System Frequency | 6.8 MHz |
| | Number Scans | 4 |
| | PW90 | 13.5 μs |

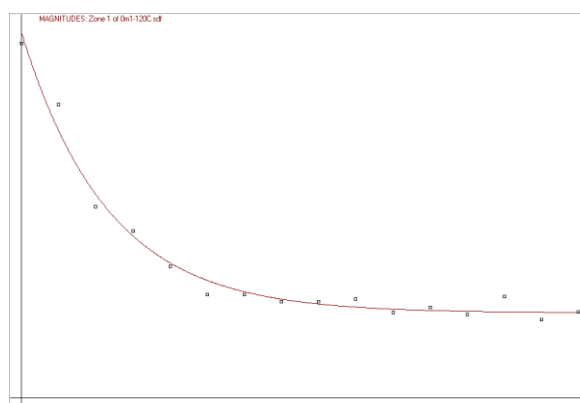
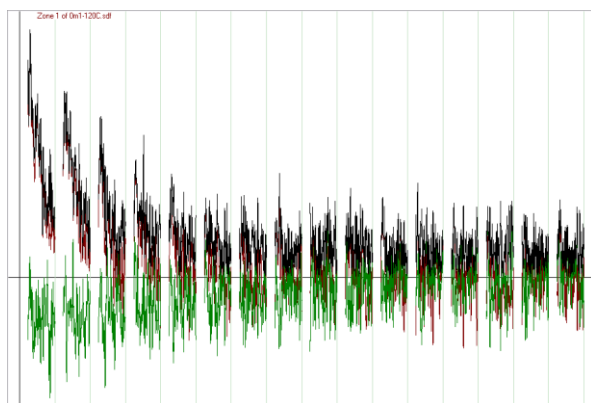


Figure 4. Longitudinal Relaxation Decay on a Carboxylic Acid

• ^{13}C Hyperpolarized compounds

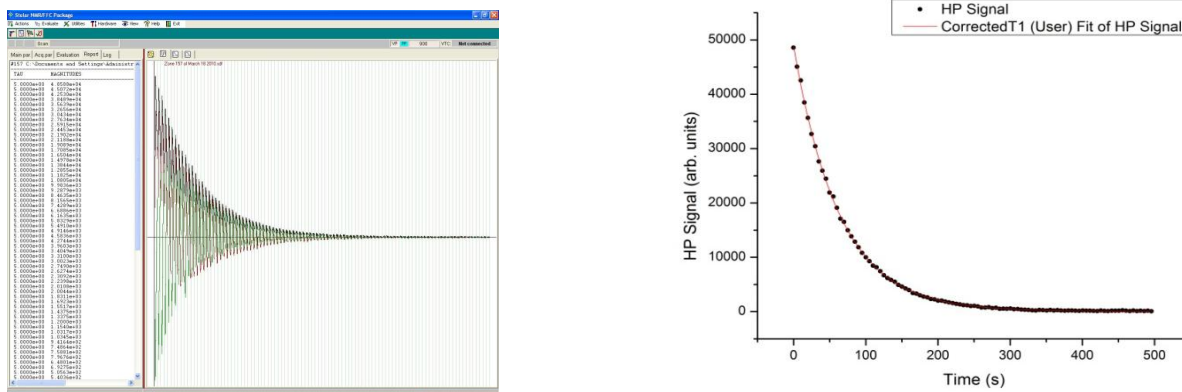
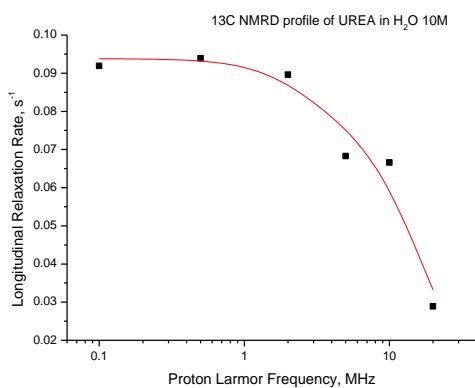


Figure 5. Longitudinal decay of polarization of a Hyperpolarized ^{13}C compound by DNP.

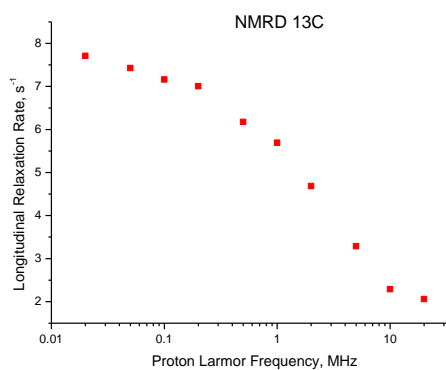
a) Transient state of the magnetization Fids. b) Envelope of a)

The Hyperpolarized samples in DNP experiments are usually moving in different magnet field. The knowledge of T_1 decay at lower field strengths as well as the capability of mapping the dependence is particularly important.

• ^{13}C NMRD profile of Urea in H_2O



^{13}C NMRD profile of Urea in H_2O



^{13}C NMRD profile of Urea in H_2O with the addition of Tempol

Figure 6

Conclusion

Spinmaster FFC2000 1T can be used to directly measure the longitudinal relaxation decay of hetero-nuclei at low magnetic field strengths.

Fast Field Cycling Relaxometry in combination with variable temperature measurements can be considered a valuable method for investigation of dipolar interaction at low frequencies, where the relaxation data reflect molecular reorientation and translational molecular motion.

Furthermore the multinuclear approach permits the

exploration of the presence of nuclei in a limited number of positions, thus providing important structural information.

FFC NMR relaxometry technology is now at a level of sophistication and maturity where industrial applications are possible. It is extremely versatile and can serve as an instrument for basic R&D, applied R&D and process monitoring. Applications for FFC NMR relaxometry appear in practically every physical and engineering science discipline