

Battery electrolytes – Multi-nuclear Fast Field Cycling relaxometry reveals important molecular dynamics information

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INTRODUCTION

Nowadays, the storage of electrical energy is an important issue due to the growing need of energy required to power portable electronic devices and electric vehicles. The **Fast Field Cycling (FFC) technique** [1,2] can be applied to ionic liquids and solids for obtaining useful information which could be exploited in the construction of batteries. In this work we studied the diffusion coefficients for two different electrolytes considering several different nuclei, such as ¹H, ⁷Li, ³¹P and ¹⁹F. We would like to highlight that FFC can provide other important information on electrolytes, such as:

- **Self-diffusion coefficient (as in the pulsed field gradient, PFG, methods)**
- **Relative diffusion coefficient (e.g. cation-anion)** - provides valuable information on correlation of ion dynamics
- **Diffusion coefficients of difficult nuclei (e.g. ²³Na)**:- ²³Na, can be problematic in viscous electrolytes and especially in solid electrolytes. **FFC yields reliable diffusion measurements** where both methods (FFC & PFG) can be applied, and **thus can be an invaluable tool when the PFG technique becomes intractable**
- **Information about the presence of clusters and their size**
- **Information on transport properties of different nuclei (correlation times, etc.)**

MATERIALS AND METHODS

Measurements were performed on STELAR's FFC SPINMASTER 2000 (www.stelar.it). An initial polarization field $B_{pol}=25$ MHz was applied only for the resonance frequencies below 10 MHz, while the detection field B_{det} was always kept at 15 MHz. ¹H, ¹⁹F, ⁷Li and ³¹P spin-lattice relaxation experiments were performed in a broad frequency range: 5 kHz - 30 MHz.

SAMPLES

1. **LIQUID:** bis(trifluoromethane)sulfonimide lithium salt ($C_2F_6LiNO_4S_2$, LiTFSI) aqueous solution (21 molal)
2. **SOLID:** lithium phosphorus sulfide (Li_3PS_4)

RESULTS for SAMPLE 1 : $C_2F_6LiNO_4S_2$ - Liquid

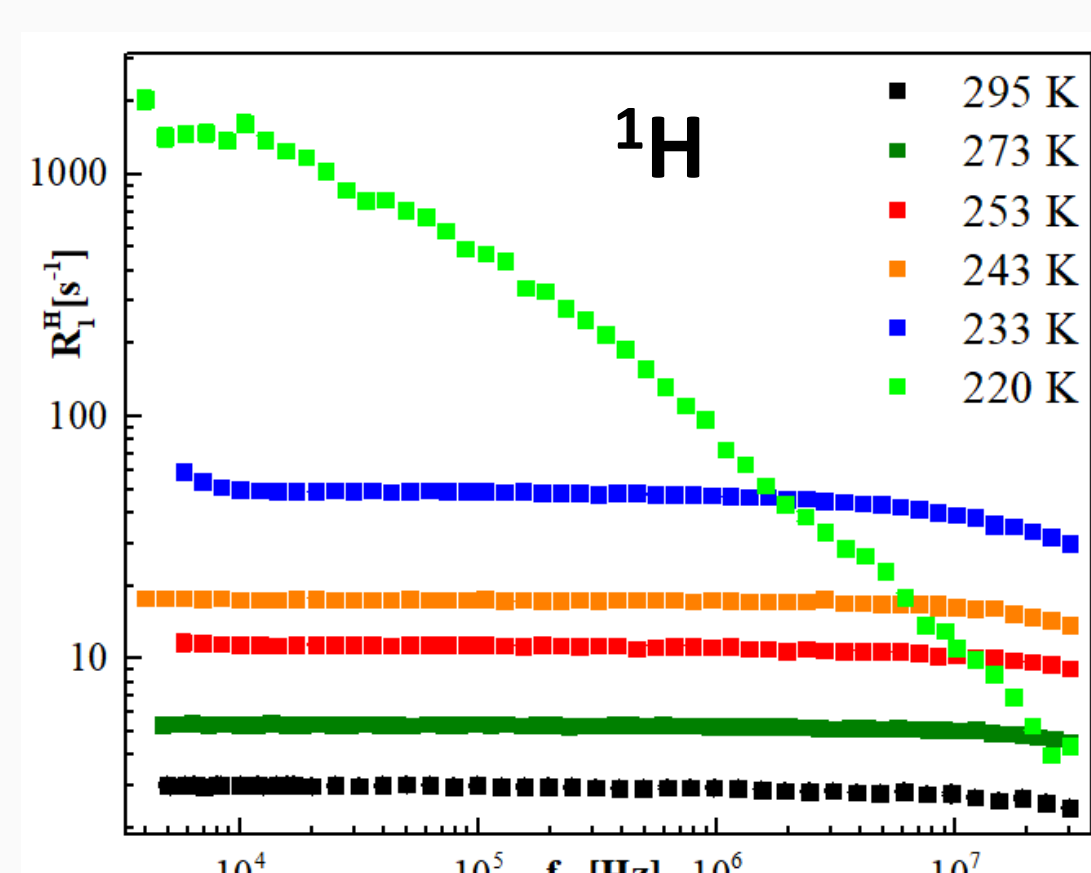


Fig. 1: NMRD profiles of $C_2F_6LiNO_4S_2$ aqueous solution acquired at different temperatures for the ¹H nucleus.

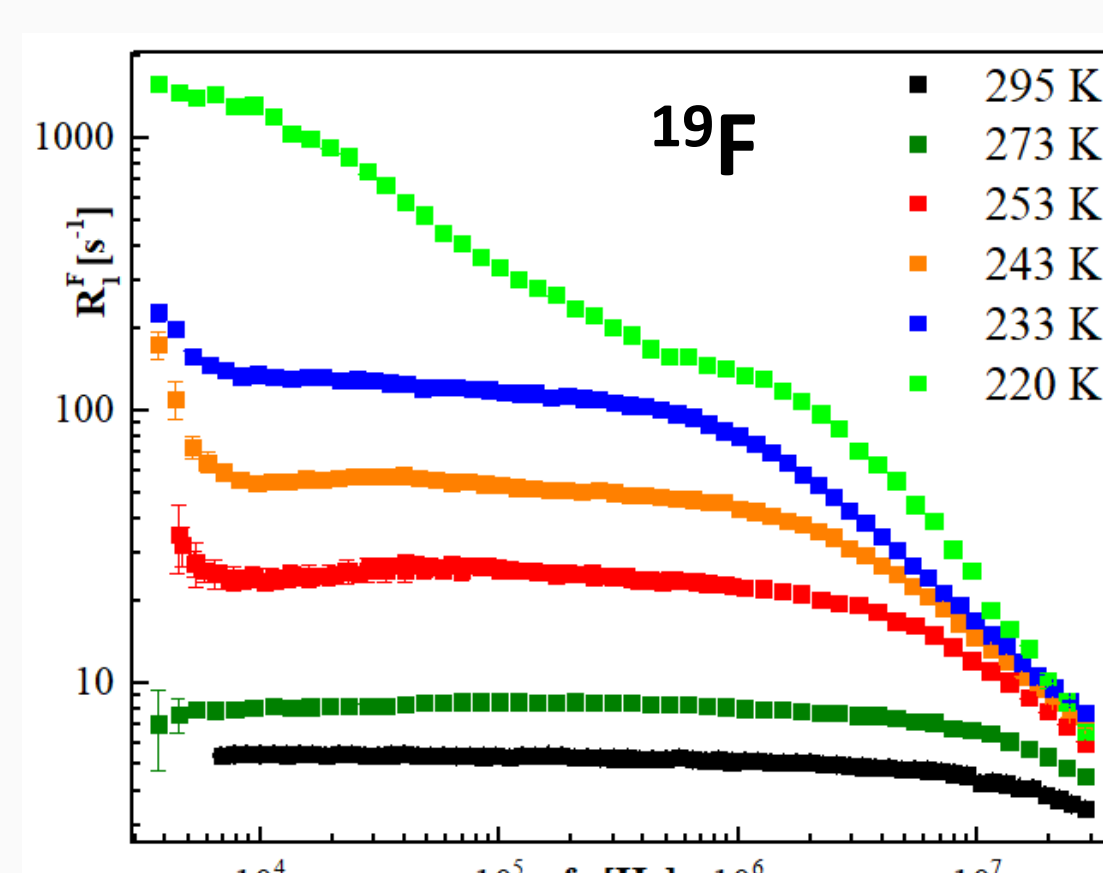


Fig. 2: NMRD profiles for $C_2F_6LiNO_4S_2$ aqueous solution acquired at different temperatures for the ¹⁹F nucleus.

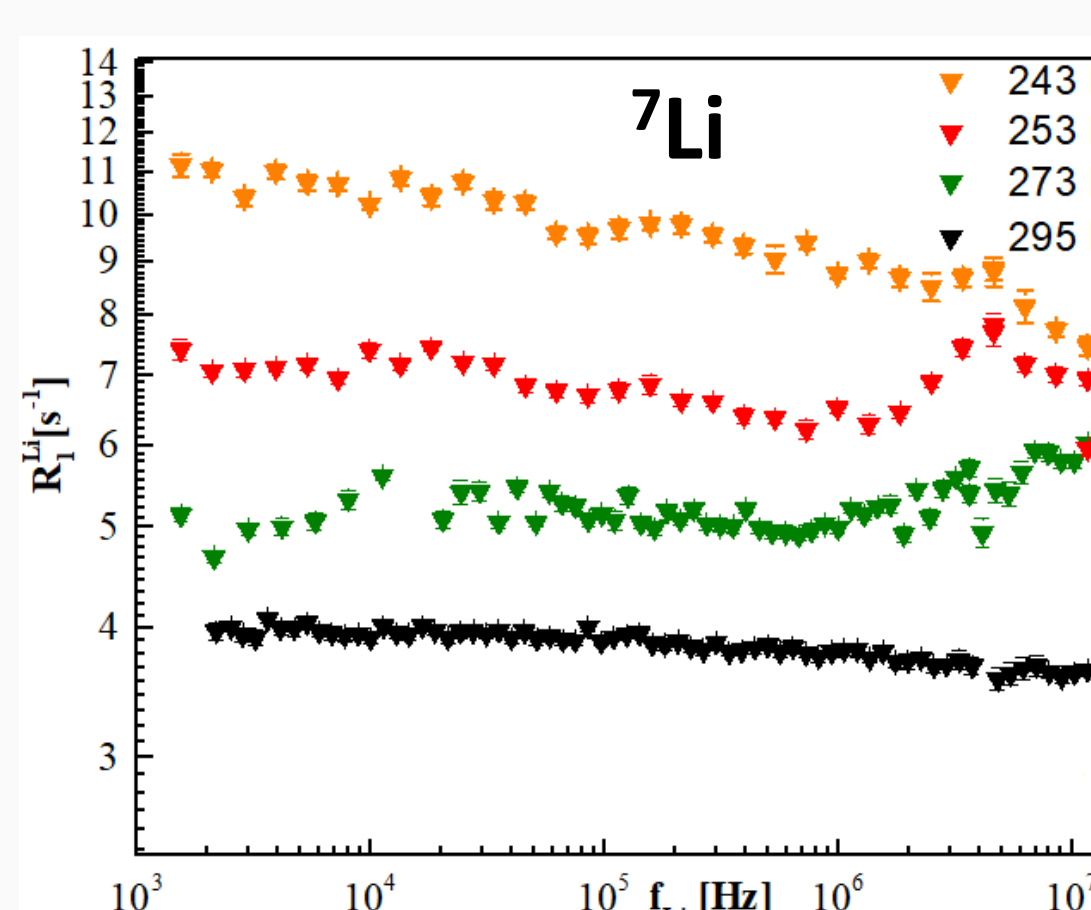
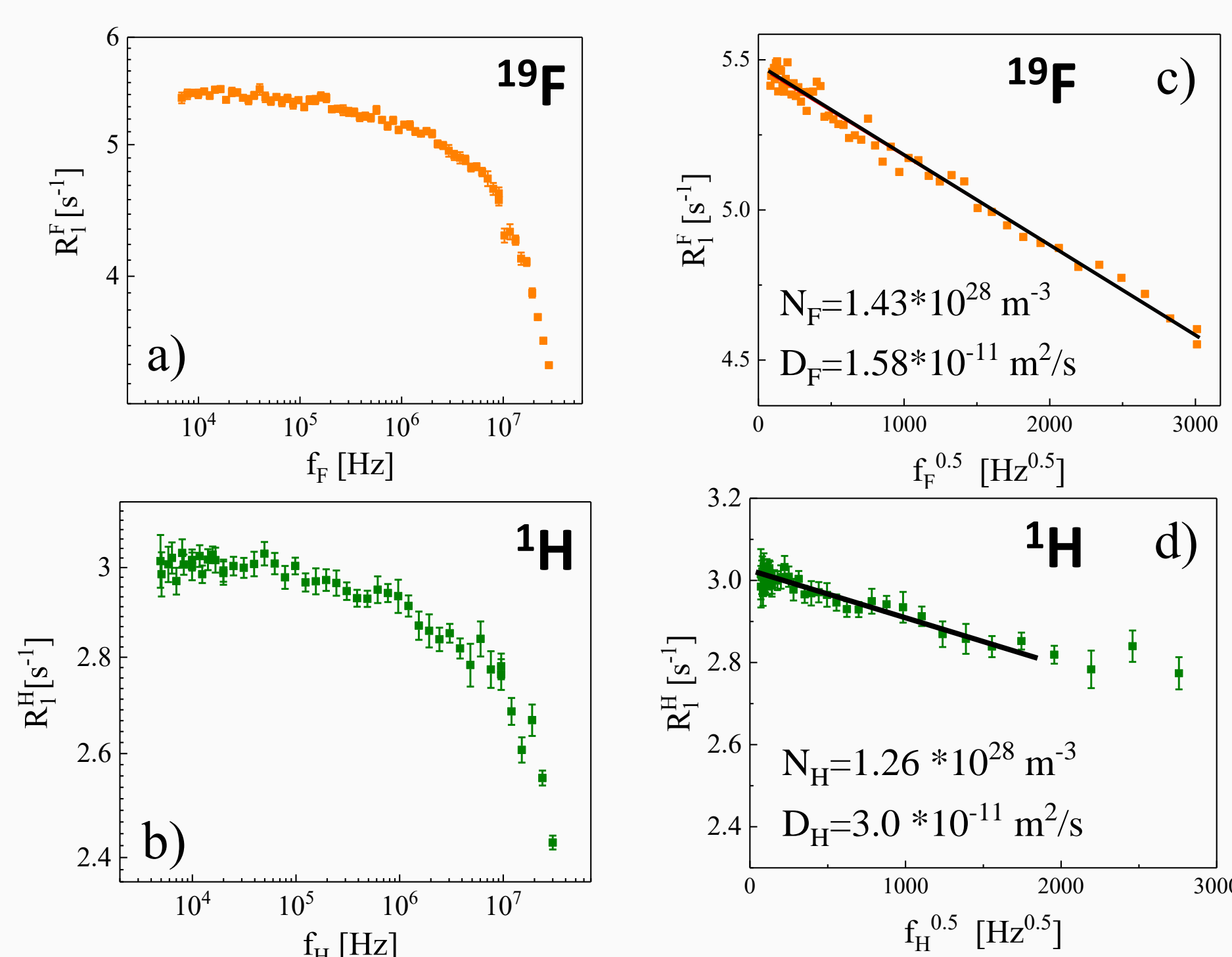


Fig. 3: NMRD profiles for $C_2F_6LiNO_4S_2$ aqueous solution acquired at different temperatures on the ⁷Li nucleus.

□ Referring to Fig.2 (¹⁹F data), the strong dispersion at low fields is a fingerprint of slow dynamics indicating clustering of the anions. The relaxation dispersion profiles at the lowest temperature (220K) reflect the ionic dynamics in the solid phase – one can clearly see that the profiles include components associated with dynamical processes on different time scales.

□ Referring to Fig.3 (⁷Li data), the unusual shapes of the relaxation data require further analysis, but they give access to the translational dynamics (via ¹H-⁷Li and ¹⁹F-⁷Li dipole-dipole interactions) and rotational motion of the Li ions in a single experiment.

Fig. 4: NMRD profiles acquired at 295K for ¹⁹F and ¹H (a and b) and corresponding low-frequency linear dependence of square root of frequency (c and d). The values of spin density for Fluorine (N_F) and Hydrogen (N_H) nuclei are reported in pictures c and d together with the values of the diffusion coefficients D_F and D_H



DIFFUSION COEFFICIENT: THEORETICAL ASPECTS

The nuclear relaxation rate (R_1) is made up of 2 components: intra- and inter- molecular contributions [2,3,4,5]. The intra-molecular relaxation is related to molecular rotation. Regarding the inter-molecular relaxation, the interactions are mediated by the relative translational diffusion of the molecules. Although the intra-molecular contribution is the most relevant for relaxation, at low frequencies the inter-molecular contribution becomes dominant and thus the R_1 measured at low frequencies is mainly due to molecular diffusive dynamics.

By plotting the measured R_1 versus square root of the resonance frequency at low frequencies, the frequency dependence is linear and the diffusion coefficient D can be calculated by linear fitting [2,3,4]:

$$R_1 = A + B\sqrt{\omega} \quad \text{Eq. 1}$$

Then from the slope B of the fitting line one can straightforwardly determine the diffusion coefficient D , using: $B=C*D^{-3/2}$, where the proportionality constant C depends only on the number of spins N and on the nucleus being investigated [3].

RESULTS for SAMPLE 2 : Li_3PS_4 - Solid

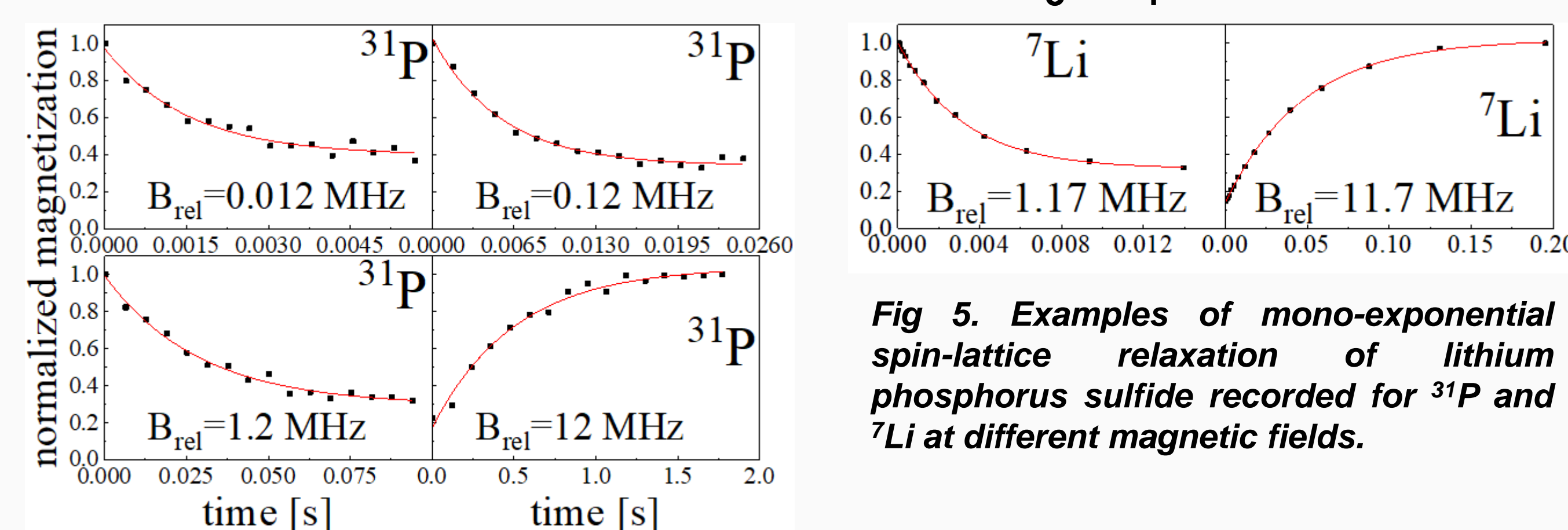


Fig 5. Examples of mono-exponential spin-lattice relaxation of lithium phosphorus sulfide recorded for ³¹P and ⁷Li at different magnetic fields.

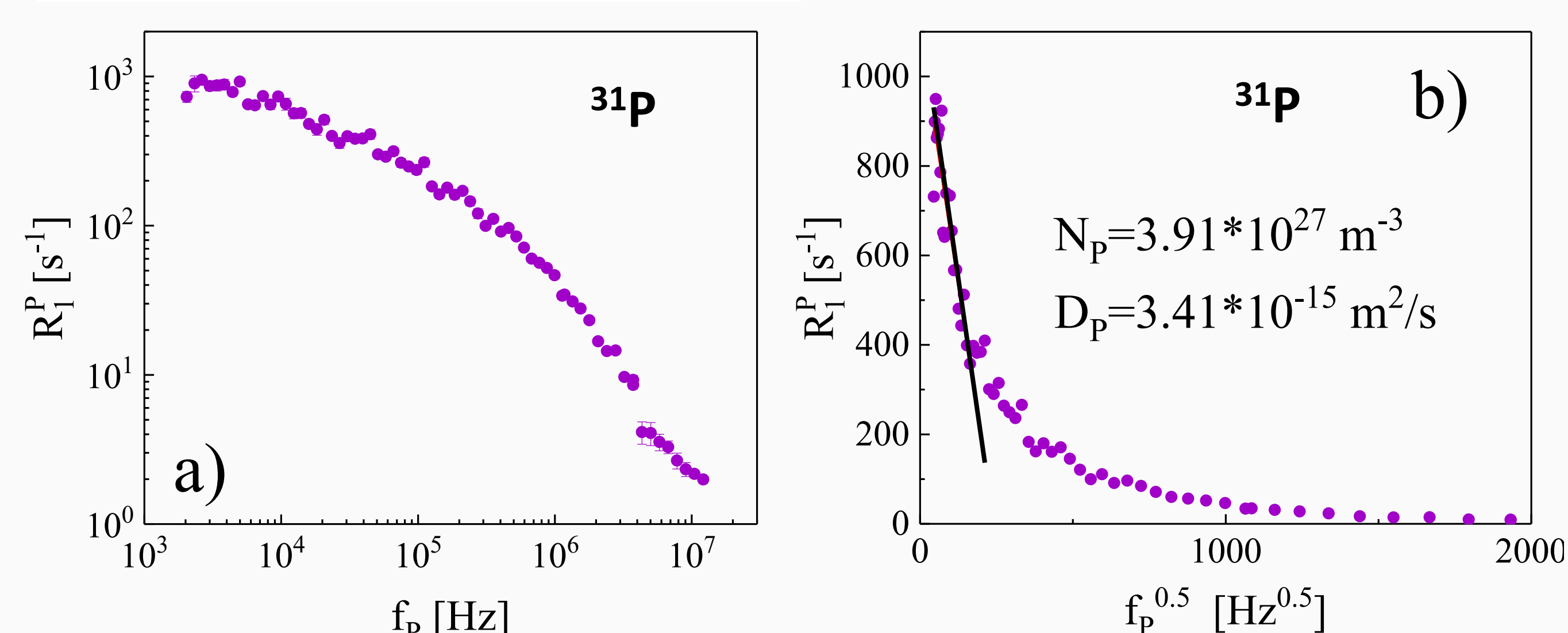


Fig 6. NMRD profile measured for ³¹P (a) and corresponding low-frequency linear dependence of square root of frequency (b). The values of the spin density (N_P) and diffusion coefficient (D_P) for ³¹P are reported in figure b.

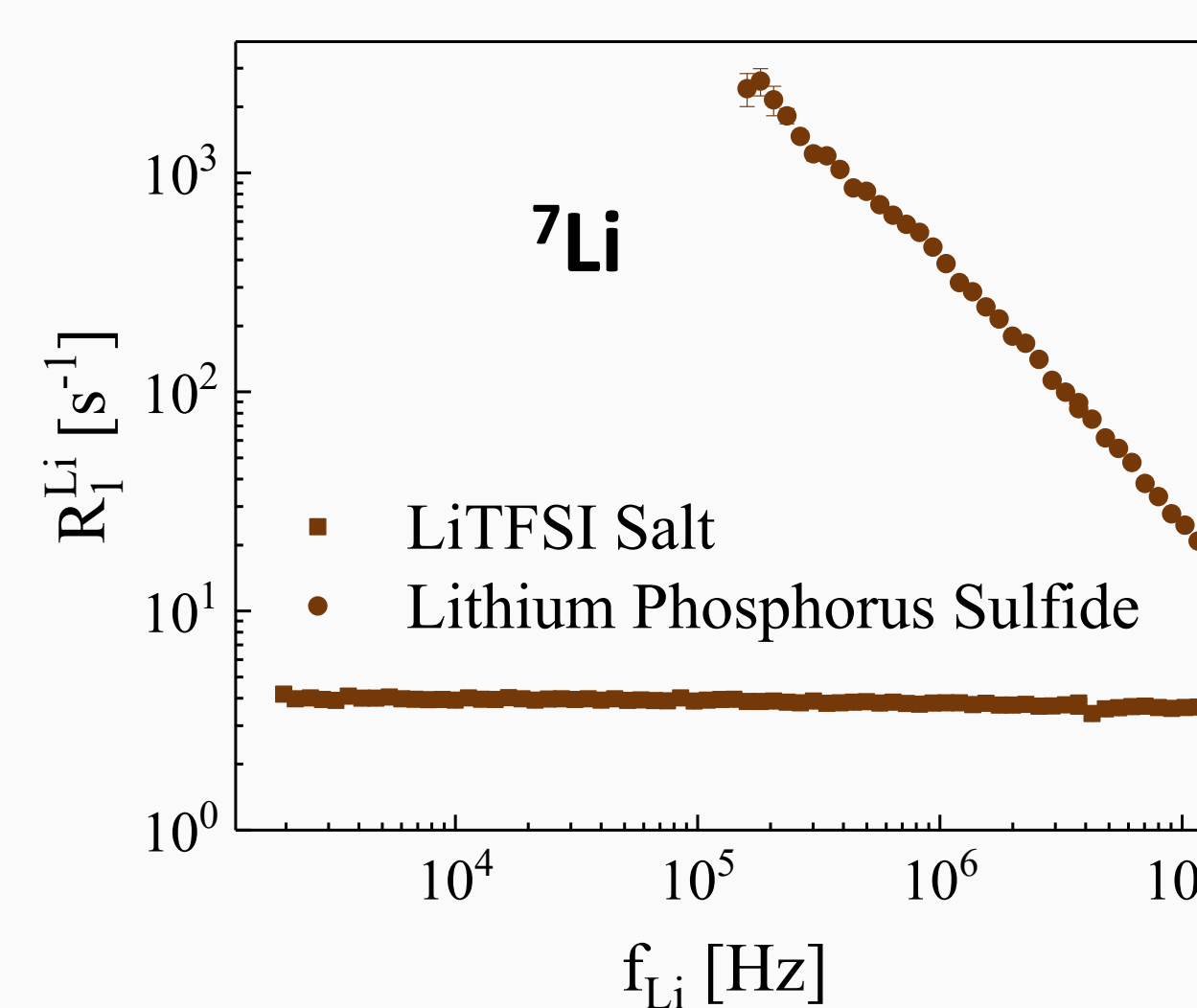


Fig 7. NMRD profile recorded for ⁷Li (diffusion coefficients have not been calculated due to complex quadrupolar relaxation contributions).

CONCLUSIONS

In this work we have shown that using the FFC technique it is possible to evaluate the diffusion coefficients for both solid and liquid electrolyte samples starting from their NMRD profiles and applying a simple formula (see Eq. 1). For ⁷Li, the diffusion coefficient has not been reported here, however, it will be possible to calculate from the experimental data as the ⁷Li data shows a strong coupling to the protons and fluorine in the sample.

- Diffusion coefficients for ¹⁹F, ¹H and ³¹P have been calculated from the inter-molecular relaxation contribution which turns out to be dominant at low frequencies.
- The ⁷Li results reported here are one of very few examples of applying NMR relaxometry to Li ions. They confirm that in this way one can directly access the dynamics of Li ions.
- The possibility to perform multi-nuclear analysis extends the potential of the FFC NMR technique that provides a powerful tool for characterization of electrolytes and for unlocking particular molecular dynamics information.
- The great advantage of NMR relaxometry is the possibility to probe translational and rotational dynamics of cations and anions as in most cases both of them contain NMR active nuclei.

References

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