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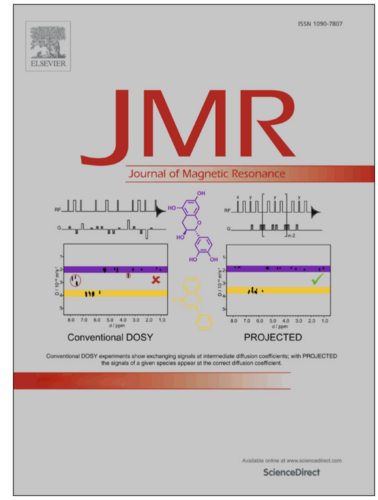

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^{1}H NMR at Larmor frequencies down to 3 Hz by means of Field-Cycling techniques

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Abstract

Field-Cycling (FC) NMR experiments were carried out at ^{1}H Larmor frequencies down to about 3 Hz. This could be achieved by fast switching a high polarizing magnetic field down to a low evolution field which is tilted with respect to the polarization field. Then, the low frequency Larmor precession of the nuclear spin magnetization about this evolution field is registered by means of FIDs in a high detection field. The crucial technical point of the experiment is the stabilization of the evolution field, which is achieved by compensating for temporal magnetic field fluctuations of all three spatial components. The paper reports on some other basic low field experiments such as the simultaneous measurement of the Larmor frequency and the spin-lattice relaxation time in such small fields as well as the irradiation of oscillating transversal magnetic field pulses at very low frequencies as a novel method for field calibration in low field FC NMR. The potential of low field FC is exemplified by the ^{1}H relaxation dispersion of water at frequencies below about 2 kHz stemming from the slow proton exchange process.

Keywords: FC NMR, low field, small Larmor frequencies, magnetic field calibration, relaxometry, proton exchange

1. Introduction

With the availability of suitable instrumentation Field-Cycling (FC) NMR relaxometry has recently gained some renaissance [1]. For getting a feeling of the progress in this field we like to refer to two previous review papers on FC NMR, the pioneering work of Noack [2] and a more application oriented review [3] as well as a short recent review also focusing on some commercial applications [4]. FC NMR allows measuring nuclear spin-lattice relaxation rates over a wide range of Larmor frequencies thereby tracking the spectral densities of the corresponding underlying ionic or molecular motional processes in condensed matter systems. For instance, in soft matter materials such as polymers or other supramolecular structures motional modes are expected to cover many orders of magnitude in frequency – from THz down to the Hz range. A number of broad-band dynamic susceptibility measurement techniques are available to study these processes – such as quasielastic neutron scattering, diverse light scattering methods, dielectric relaxation, mechanical relaxation and others. But there is still need for more techniques, especially aiming at more specificity or selectivity as well as – generally speaking – lower frequencies.

The slow reptation dynamics of long chain polymer melts is a typical field of broad interest for the study of which FC NMR relaxometry proves to be perfectly suited [5, 6, 7, 8, 9]. This also applies to other macromolecules like dendrimers, proteins or to the dynamics of liquids in the vicinity of such macromolecules [10, 11, 12, 13]. By isotope dilution experiments, separating intra- and intermolecular relaxation, rotational and translational motion can be investigated individually [8]. In the motional narrowing regime, where the intramolecular relaxation is dispersionless, the intermolecular relaxation can be investigated with the help of low frequencies without elaborate isotope dilution experiments [7].

Such low field experiments meet instrumental limitations (i) at high relaxation rates, typically for T_1^{-1} above $10^3\,s^{-1}$, due to finite field switching rates and (ii) at low evolution frequencies, mainly due to field instabilities. Actually, todays commercial instrumentation [14] hardly reaches down below 10 kHz. This lack has been our motivation for developing an improved FC relaxometer allowing for evolution frequencies as low as possible.

2. Experimental

Let us, for the sake of completeness, very shortly recall the basic idea of FC NMR. For more detailed information we refer to our recent review paper [1]. As indicated by Fig. 1, the essence of FC NMR consists in applying a suitably time dependent magnetic field.

The field cycle may start, for instance, by a strong polarization field B_{pol} being applied over a sufficiently long time interval t_{pol} in order to establish a nuclear magnetization M as high as possible. Then, the field is rapidly

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