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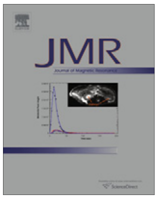

THz-waves channeling in a monolithic saddle-coil for Dynamic Nuclear Polarization enhanced NMR

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ABSTRACT

A saddle coil manufactured by electric discharge machining (EDM) from a solid piece of copper has recently been realized at EPFL for Dynamic Nuclear Polarization enhanced Nuclear Magnetic Resonance experiments (DNP-NMR) at 9.4 T. The corresponding electromagnetic behavior of radio-frequency (400 MHz) and THz (263 GHz) waves were studied by numerical simulation in various measurement configurations. Moreover, we present an experimental method by which the results of the THz-wave numerical modeling are validated. On the basis of the good agreement between numerical and experimental results, we conducted by numerical simulation a systematic analysis on the influence of the coil geometry and of the sample properties on the THz-wave field, which is crucial in view of the optimization of DNP-NMR in solids.

1. Introduction

Transferring the high polarization of electron spins to the less polarized nuclear spins is at the basis of DNP techniques, which is emerging as an extremely powerful approach to increase the sensitivity of NMR [1–9].

DNP can cover a broad range of applications, including NMR on solids, liquids or surfaces, solely requiring the presence of a paramagnetic species in the sample. DNP-NMR techniques have been investigated since the 50s both theoretically and experimentally. These studies were conducted mainly at low magnetic fields [10–12], with notable exceptions [13–15]. It is only in the last two decades that these techniques have drawn important interest, owing to the studies of the polarization mechanisms [16] and to new instrumental achievements. The development of cyclotron resonance masers (gyrotrons) as THz-wave sources with output power and spectral purity suited for DNP NMR, lead to the seminal work by Griffin and co-workers in the early 90s on DNP NMR of solids with magic angle spinning. These results demonstrated about two orders of magnitude signal enhancement, corresponding to a reduction in the acquisition time of about four orders of magnitude or, at a fixed acquisition time and signal-to-noise, to a reduction of two orders of magnitude in the size of sample [17,18] . Alternatively, DNP enhancement can be used to reduce the acquisition time of multi-dimensional spectra [19].

In parallel to the development of efficient THz-wave sources, consistent efforts have been dedicated to the development of innovative probe-heads, capable to establish the state-of-the-art in their radio-frequency (RF) and microwave (THz) performances, mainly in the current-to-magnetic field conversion factor for the radio-frequency part [20], and power-to-magnetic field conversion factor, for the microwave part [21]. Since an efficient DNP polarization is expected for an intense microwave irradiation of the sample, a typical problem related to this technique is given by the possible microwave heating. This issue is of crucial importance in the case of liquid-state NMR, where the DNP enhancement effect is determined by the Overhauser effect [10,11]. According to the common theoretical models [12], the liquid-state DNP enhancement, ϵ, is provided by

$$\epsilon = \left|\frac{\gamma_e}{\gamma_n}\right| \cdot \xi \cdot f \cdot s \qquad (1)$$

where $\gamma_e = -28.02$ GHz/T (resp. $\gamma_n = 42.6$ MHz/T) is the free electron gyromagnetic ratio (resp. nuclear), ξ is the coupling factor that describes the magnetization transfer (cross relaxation) from the electron to the nuclear spin, f is the leakage factor representing the paramagnetic enhancement to the nuclear relaxation rate over the

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total nuclear relaxation rate, and s the saturation factor that represents the saturation of the electron Zeeman transitions. Assuming that the leakage factor and the saturation factor are relatively close to unity, as typical in the most advances experimental conditions, the efficiency of the nuclear polarization is related to the coupling factor, which in turn is strongly dependent on the temperature of the sample [22,23]. At high T, the DNP enhancement can deteriorate [23]. Moreover, a significant increase in the sample temperature is in any case detrimental for biological samples, where it induces denaturation. The fact that biological samples are characterized by high dielectric losses motivates the importance of a very well controlled THz-field distribution in the sample region. Moreover, the constraints related to DNP add to those typical of pulsed NMR techniques. Among them, it is worthwhile to mention the homogeneity of the RF magnetic field, B_{RF}. The importance of this homogeneity can be understood considering the nutation angle, Θ, imposed by the RF on the nuclear magnetization, given by:

$$\Theta = 2\pi \cdot B_{RF} \cdot \gamma_n \cdot \tau \tag{2}$$

where γ is the gyromagnetic ratio of the considered nucleus, and τ is the pulse duration. An inhomogeneous magnetic field B_{RF} inside the sample volume implies that not every spin gets the same tip angle, which means that after few or long pulses, as those required in the most advanced spin sequences or in 2D studies, the magnetization is scrambled and consequently the signal-to-noise ratio decreases.

When designing a general purpose DNP NMR probe, the above technical constraints can be summarized in: high radio-frequency current-to-magnetic field conversion factor, high THz-wave power-to-magnetic field conversion factor, and high spatial homogeneity of radio-frequency magnetic fields inside the sample volume. Moreover, a high homogeneity is also desirable for the THz magnetic field, B_{THz}, since this ensures a homogeneous DNP enhancement. Finally, the THz-wave propagation circuit should have moderate propagation losses, in order to exploit the power delivered by the source. Keeping this in mind, in this work we investigated the performance of a in-house designed monolithic saddle coil designed for a 400 MHz NMR spectrometer. The magnetic field of the NMR spectrometer being 9.4 T imposes the THz frequency as 263 GHz. The geometry of the coil [24], shown in Fig. 1a and b, seems suitable for the injection of the THZ-beam coaxially into the sample, an option that was recently used [25]. In particular, here we study the details of the propagation of a THz wave through the saddle coil for DNP-NMR purposes in solid samples. The simulations are compared with experimental data taken with a coil manufactured by electric discharge machining. The simulations also provide the radio-frequency magnetic field produced by a current injected into the saddle coil. All the simulations presented in this work have been run with *Multiphysics* 3.5*a* (Comsol, SE), which is a finite-element analysis software environment for the modeling and simulation of coupled physical and chemical problems. Since the simulated volume is strongly over-moded, *i.e.* is significantly larger than the wavelength in free space (∼1.14 mm at 263 GHz), this implies a very large number of meshing points for an accurate modeling. For this reason simulations have been run on a work station equipped with 144 GByte of RAM. This paper is organized as follows: Section 2 describes the numerical work done to evaluate the homogeneity and the time RMS intensity of the magnetic field at 400 MHz used for NMR. Section 3 introduces the experimental framework we developed to validate the numerical simulations at 263 GHz. The results are shown and commented in Section 4. We conclude and suggest some perspective in the last section.

2. Radio-frequency results

The saddle coil design proposed in this work, shown in Fig. 1a, is inspired by previous self standing coils [26,27], while being adapted to be compatible with standard liquid NMR test tubes and to our 9.4 T spectrometer. A high, continuous, and controlled electric conductivity through the structure, as well as a good mechanical stability, can be obtained by manufacturing the coil from a single solid piece of conductor, for instance by wire Electrical Discharge Machining (EDM). The obtained monolithic coil is not prone to the imperfections due to the soldering in the sample region. As can be seen in Fig. 1, the proposed Saddle coil has two connectors that point out perpendicularly to the axis of its cylindrical geometry. These connectors can be soldered to a standard NMR tuning and matching circuit in order to adjust its impedance at 400 MHz to the one of the NMR spectrometer. The impedance of the proposed saddle coil prototype alone was measured to be 58 nH at 400 MHz by using a network analyzer.

Saddle coils are widely used for NMR measurements and extensive research has been performed in order to optimize the radio-frequency magnetic field homogeneity over the sample region [27].

In particular, a possible, idealized monolithic saddle-coil geometry consists of a tube from which two diametrically opposite windows covering around 120° are removed. The proposed saddle coil

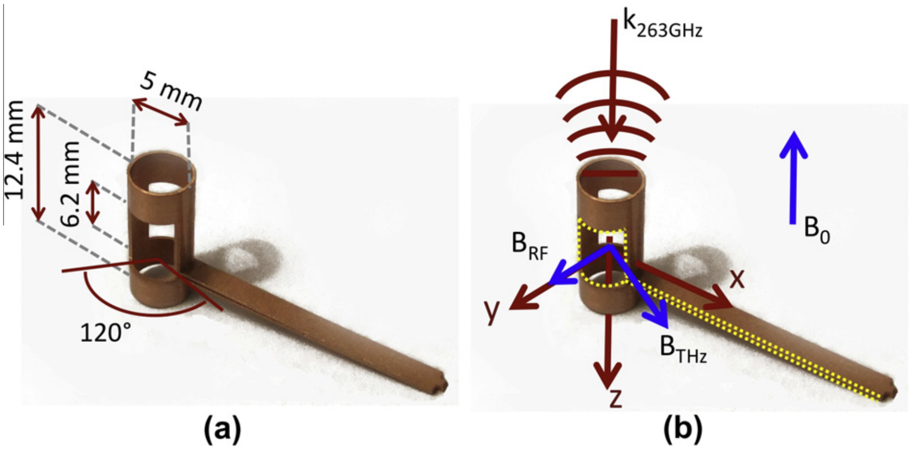

Fig. 1. (a) Picture of the saddle coil with superimposed geometry characteristics. (b) Relative directions of B_{RF}, and B_0 with respect of the saddle coil geometry. B_{THz}, useful for DNP purpose, is in the *XY*-plane. The Cartesian frame of reference is chosen with *Z*-axis along B_0 = 9.4 T, the origin at mid height of the coil windows, and *X*-axis is taken along the coil connection.