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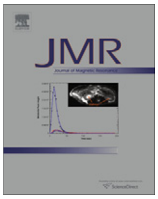

High homogeneity B_1 30.2 MHz Nuclear Magnetic Resonance Probe for off-resonance relaxation times measurements

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ABSTRACT

This paper reports on design and construction of a double coil high-homogeneity ensuring Nuclear Magnetic Resonance Probe for off-resonance relaxation time measurements. NMR off-resonance experiments pose unique technical problems. Long irradiation can overheat the sample, dephase the spins because of B_1 field inhomogeneity and degrade the signal received by requiring the receiver bandwidth to be broader than that needed for normal experiment. The probe proposed solves these problems by introducing a separate off-resonance irradiation coil which is larger than the receiver coil and is wound up on the dewar tube that separates it from the receiver coil thus also thermally protects the sample from overheating. Large size of the irradiation coil also improves the field homogeneity because as a ratio of the sample diameter to the magnet (coil) diameter increases, the field inhomogeneity also increases (Blümich et al., 2008) [1]. The small receiver coil offers maximization of the filling factor and a high signal to the noise ratio.

1. Introduction

Only a few authors have reported on the apparatus for off-resonance experiments in solids [3]. Jacquinot and Goldman have described a method allowing proton magnetization to be measured by fast passage after irradiation for a preset time with an rf off-resonance field. Other authors have described [4] the apparatus for off-resonance experiments in liquids which does not require strong B_1 fields.

One of the most important parts of the nuclear magnetic resonance spectrometer is the measuring probe. It is a vital element detecting microvolt signals from the measured sample as well as permitting transfer of high power rf pulses needed to generate rf magnetic field B_1 from a transmitter.

The NMR probe also determines the signal to noise ratio S/N, which is a highly important parameter for proper detection of the magnetization free induction decay signal. Another vital parameter, especially important for slow molecular motion detection in polymers, is the homogeneity of rf magnetic field B_1. The special construction of the probe described in this paper allowed us to considerably reduce the inhomogeneity.

During the off-resonance experiment in the rotating frame, the rf pulses of high power and long duration (with some times over 50 s) are applied to the measurement coils. The standard probe construction with a single measurement coil (for rf pulses and for the detection of FID signal) does not prevent from overheating the substance inside the coil (which could damage the sample or change its properties) [2]. Another important parameter is the range of the frequency band of the probe. In the off-resonance experiments, it is sometimes necessary to overtune the probe from resonance by more than 1 MHz, which is out of the frequency band of the classical measurement probe (a few kHz).

As a result, the power of the transmitter is not efficiently used. It generates a standing wave which may damage the power transmitter and also decrease the signal to noise ratio of the free induction decay signal – FID. In view of the above, the off-resonance measurements in the rotating frame are very difficult from both theoretical and experimental point of view. The NMR probe constructed in our laboratory is free from the above limitations. A few hitherto published papers have dealt with some other double coil solutions based on broadband frequency decoupling between the resonant circuits, which is useless in off-resonant experiments. The authors of [10] have proposed a transmission line tuning the circuit to a rapidly tuned single coil. The inductive coupling matching the circuit for NMR coils for in vivo experiments has been described in [11]. The use of two or more local coils without mutual inductance interactions for imaging experiments is reported in [12]. Other papers for example [6,7] show off-resonance experiments which work with classical probes. These probes have one single coil, which acts as both transmitting and receiving one. This solution has caused a lot of measuring problems, including

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low efficiency of the transmitter's power use together with slight detuning and low homogeneity of the rf magnetic field. These problems implied the need of application of complicated measuring sequences in order to eliminate the inhomogeneity of B_1 field, which led to increase in the measurement time (even 12 h for one measuring point) [6]. It was not certain if together with detuning from resonance, the induction of B_1 field at the site of the sample would change. Elimination of the above problems, apart from the change in induction of B_1 field and frequency, has been the subject of interest of the authors of [2]. They proposed a solution with two transmitters. The probe designed and constructed by us has been so far the best of those known from literature. It eliminates all the above mentioned construction drawbacks as will be presented below.

2. NMR probe

To perform a reliable off-resonance experiment in solids, the following conditions have to be fulfilled:

(a) The DC magnetic field should be constant during the off-resonance experiment.
(b) The level of the long off-resonance B_1 field should be adjustable from hundreds of milligauss up to at least 10 G for a frequency offset from 1 kHz up to 1 MHz.
(c) The level of the on-resonance B_1 field should be constant and independent of B_1 for the off-resonance condition.
(d) The bandwidth of the probe should be at least 1.5 MHz to cover a frequency offset of up to 500 kHz and simultaneously it ought to ensure good sensitivity for FID observation.
(e) Good isolation between the probe and the receiver is required during the operation of the off-resonance B_1 field. Similarly, good isolation is required between the transmitter and the receiver during the acquisition of FID [5].
(f) Good homogeneity of B_1 field especially during off-resonance experiment under the magic angle spinning [6,7].

Schematic diagram of the NMR measurement probe constructed is shown in Fig. 1. The most important feature of this circuit is the use of two coaxial coils. The first bigger coil or the outside coil L_1 is wound around the glass dewar tube (quartz glass), designed especially for this purpose. The parameters of the outside coil are: standard geometry, 2.2 cm in diameter and 2.2 cm in length. The outside coil is cooled by compressed air. Thanks to these solutions the coil Q factor remains stable even during long irradiation. It is well known that the most homogeneous magnetic field is exactly in the centre of the coil [8]. That is why the bigger outside coil allows generation of a highly homogeneous rf magnetic field in the sample placed in the smaller inside coil. The second smaller coil, the inside coil L_2, contains the sample and is placed inside the dewar tube. The parameters of the inside coil L_2 are: standard geometry, 0.7 cm in diameter and 1.6 cm in length.

The above-described configuration of the coils permits elimination of overheating of the samples measured even when long and strong rf pulses are applied (even over 50 s).

The sample diameters were designed to maximize the homogeneity of rf magnetic field, which was achieved for the sample of 1 cm in length and 0.6 cm in diameter. The most homogeneous magnetic field is directly in the centre of the inside coil. The off-resonance rf pulses are applied to the outside coil. The on-resonance rf pulses are applied to the inside coil. Free induction decay signal is detected by the inside coil.

Coaxial configuration of both coils ensures certain advantages, but only when the coils are alternatively detuned for a proper period of time. No detuning is equivalent to degradation of strong rf pulses or free induction decay signals. When the off-resonance rf pulse is applied to the outside coil – this coil must be in electric resonance. At the same time the inside coil must have high resistance with respect to the ground (this coil is detuned from the outside coil). It means that the inside coil does not absorb the energy from the outside coil. The current induced in the inside coil would generate a magnetic field of the direction opposite to that of B_1 from the outside coil. Thus, the effective rf magnetic field would be reduced.

After the application of the rf on-resonance pulse, the FID signal appears at G_7 output. The G_7 output is connected to the quarter wavelength wire with the crossed diodes on the preamplifier input. The inside coil must be in electric resonance and the outside coil must be simultaneously detuned, so it must have high impedance with respect to the ground. All these requirements are met by the probe proposed in this project.

It must be mentioned that both coils are supplied from the same source (transmitter), which is a great progress when compared to the solution from [2]. A difficult problem of rapid switches of high power and high frequency has also been solved in this project. The switching time between the coils is 100 µs, which is short enough for the proper experiment. The probe shown in Fig. 1A contains a number of quarter-wave length cables (1–7). To understand how the probe works the equivalent circuit is presented for three cases: *first*; when the off-resonance rf pulse is being activated, *second*; when the rf pulse on-resonance is applied, *third*; during free induction decay signal detection.

Fig. 1B shows the equivalent circuit of the probe when the off-resonance rf pulse is applied. In time t_1 the off-resonance rf pulse is applied only to coil L_1 (outside coil). At the same time coil L_2 (inside coil) is detuned (off, deactivated). This is a result of the fact that all diodes D_1–D_{10} (Fig. 1A) conduct in time t_1 by means of driving pulses. Coil L_1 is tuned to the electric resonance, which is the off-resonance frequency.

When the rf off-resonance pulse is switched off, all diodes D_1–D_{10} are blocked (do not conduct). However, when the rf on-resonance pulse 90° is applied, then only the crossed diodes D_{11}, D_{12} conduct. The equivalent circuit corresponding to the situation when the rf on-resonance pulse is applied is shown in Fig. 1C.

When the signal of free induction decay is observed, all of the diodes in the probe are blocked (deactivated). Not decreased FID signal goes from the inside coil to the receiver input. The equivalent circuit of the probe during signal detection is shown in Fig. 1D.

3. The calibration of NMR probe to measure relaxation times off-resonance

The off-resonance measurements, especially those in the rotating frame, require the knowledge of B_1 field induction (rf magnetic field) which in our case is generated by the outside coil. The knowledge enables us to assign effective magnetic field and the angle between the direction of the effective field and the constant magnetic field. To get the information on the B_1 field, a calibration procedure was applied, taking into account the influence of induction L and capacity C of the probe and the transmission lines. Each measurement had to be calibrated taking into account the frequency change.

The electronic measurement of the rf magnetic field causes a lot of problems. Thus, to calibrate the probe, the nuclear magnetic resonance was used. It is sensitive enough as well as easy to make and does not cause experimental problems.

To determine the B_1 field intensity inside the probe, the following formula was used (1):

$$\gamma B_1 t_i = \pi \qquad (1)$$

where γ is a gyromagnetic ratio and t_i is the duration of the rf pulse. Thus, setting the duration of a simple rf pulse that flips the magne-

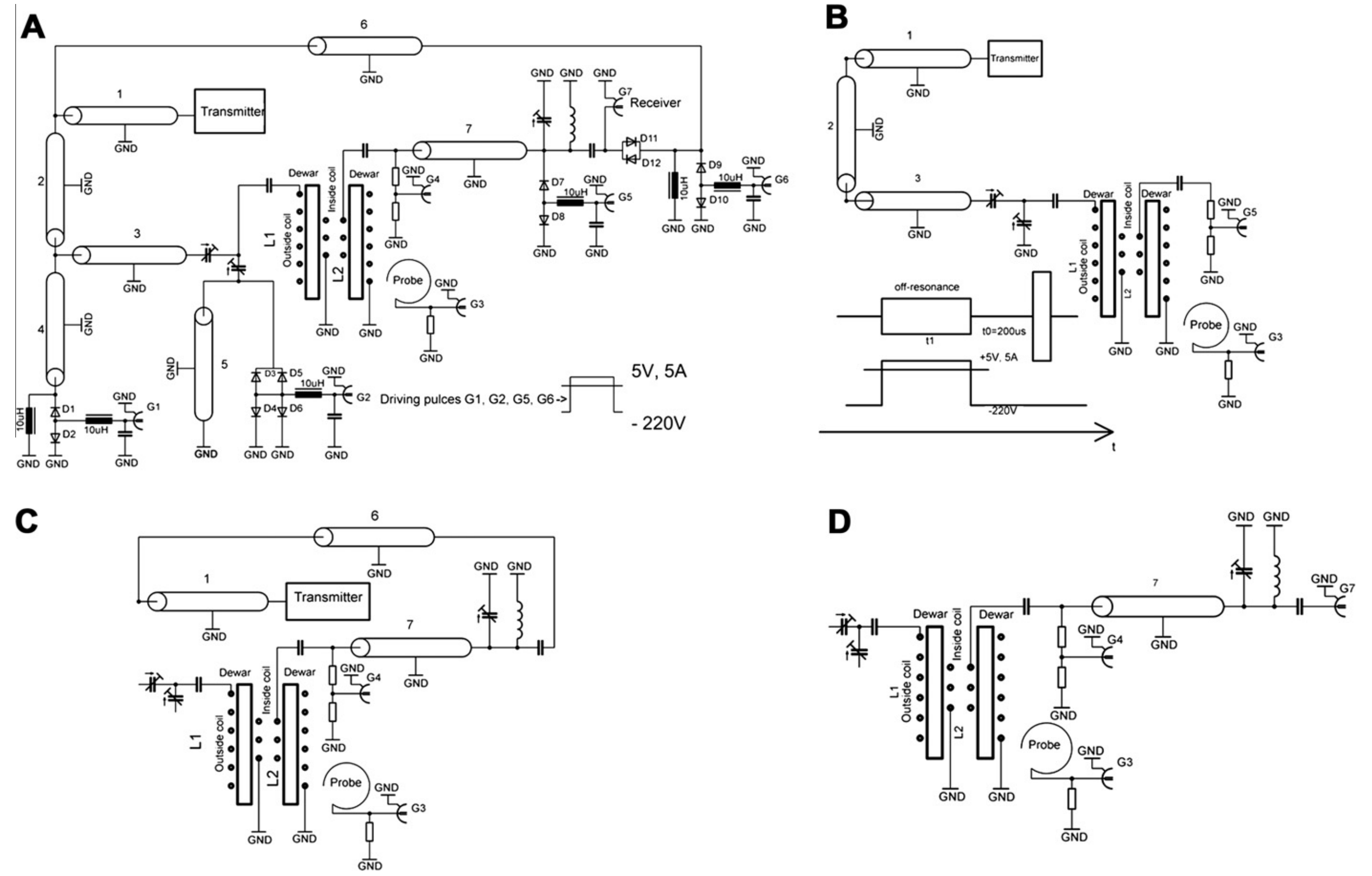

Fig. 1. Schematic diagram of the constructed high homogeneity NMR measurement probe for off-resonance experiments. (A) Complete scheme, (B) equivalent circuit of the probe for off-resonance rf pulse, (C) equivalent circuit of the probe for on-resonance rf pulse, (D) equivalent circuit of the probe during signal detection.

tization by 180°, we choose the value of the temporary magnetic field induction B_1 affecting the sample. Next, knowing the values of temporary B_1, parameter t_i and π (the flipping angle of magnetization) we can transform the rf magnetic field generated by the coil to rapidly changing voltage, which can be easily measured by the high frequency voltage probe shown in Fig. 1A–D (output G_3).

It is known that the rapidly changing voltage is proportional to the magnetic field induction B_1. This relation is described by the following equation:

$$B_1 = a \cdot U_1'' \left[\frac{\mathrm{mV}_{op}}{50\,\Omega}\right] \tag{2}$$

where a is the factor of proportionality and U_1'' is the amplitude measured upon the load of 50 Ω.

The amplitude detection can be performed by a digital oscilloscope, which guarantees high precision. To find the proportional factor a, the linear equation was fitted to the measuring points. It is worth pointing out that due to specific construction of the probe the a factor is independent of frequency, which will be shown further.

In the calibration procedure we applied the 180° transmitting pulse to the outside coil; however, the free induction decay signal was received by the inside coil. Glycerol was used as a sample (1 cm long, 6 mm diameter).

Next, the inside coil was used both as a transmitting and as a receiving system. The measurements and the analysis were similar to those in the previous test.

Both calibrations were conducted for the resonance frequency equal to 30.2 MHz. The results of the calibrations showed a linear dependence of the magnetic induction intensity on the voltage applied.

Because the experiments required detuning from the resonance frequency of 30.2–29.2 MHz, it was necessary to test the dependence of magnetic induction intensity B_1 on frequency from the range 30.2 to 29.2 MHz. When the off-resonance rf pulse is applied, one of the ends of the quarter-wave cable is grounded, while its impedance decreases when being detuned, which can lower the value of B_1 field in the sample. To find it out the measurements of the voltage amplitude as a function of frequency were conducted for the two situations:

(1) When the inside coil was connected to the quarter-wave cable which was grounded – U_1'' [mV/50 Ω] (the measurement with the cable).
(2) When the inside coil was detached from the quarter-wave cable – U_1'' [mV/50 Ω] (the measurement without the cable).

The results show that the ratio $\frac{U_1''\ \text{with the cable}}{U_1''\ \text{without the cable}}$ is in fact independent of frequency from the range 30.2 to 29.2 MHz. This means that the calibration factor a is frequency independent.

4. The measurements of B_1 magnetic field inhomogeneity generated by the constructed measuring probe

The crucial parameter influencing the quality of measurements is the magnetic field homogeneity. To measure it for the field generated by the probe, a well known literature procedure was used [9], which measured magnetization amplitude in the two situations: (1) after a 90° pulse and (2) after a 270° pulse.

On the basis of these measurements the Δ_w parameter related to B_1 magnetic field inhomogeneity in percent was obtained.

$$\Delta_w = \frac{M_0 - |M|}{M_0} \cdot 100\% \tag{3}$$

where M_0 is the amplitude of magnetization after rf pulse flipping magnetization at 90° and M is the amplitude of magnetization after rf pulse flipping magnetization at 270°.

For the calculations the absolute value of magnetization after a 270° pulse is used.

By the above-described method the magnetic field inhomogeneity was measured both for the field generated by the outside coil and for that generated by the inside coil. To improve the accuracy, all magnetization measurements were ten times repeated. Glycerol was used as a sample. The magnetic field generated by both measured coils was $B_1 = 10$ G. After placing the sample in the inside coil, a free precession signal was recorded in two ways:

(1) By applying rf pulses to the outside (bigger) coil while recording the free precession signals by the inside (smaller) coil. In that case the results were: $M_0 = 92.5$ a.u.; $|M| = 90$ a.u. – which gave $\Delta_w = 2.7\%$.
(2) By applying rf pulses to the inside coil and recording the signal by the same coil. The results were: $M_0 = 95.5$ a.u.; $|M| = 79.9$ a.u. – which gave $\Delta_w = 16.3\%$.

5. Conclusions

As follows from the testing measurements performed with the use of the newly designed and constructed NMR probe, the solution proposed ensures the magnetic field homogeneity six times better than that in the standard single coil construction.

Achievement of high homogeneity B_1 with a desired signal to noise ratio S/N and the frequency band of the probe larger than 1 MHz is a considerable success, which allows us to shorten the time of the off-resonance experiments in the rotating frame, especially spin–spin relaxation times measurements under the magic angle. Up to now such measurements have required application of the spin-echo method in order to eliminate the influence of the inhomogeneity of the B_1 field, which significantly prolonged the duration of the experiment. It is worth noting that in our solution we used only one high power transmitter.

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