

Communication

Double-resonance magic angle coil spinning

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ABSTRACT

We present an extension of magic angle coil spinning (MACS) solid-state NMR spectroscopy to double-resonance experiments, enabling implementation of powerful double-resonance solid-state NMR methodologies including cross polarization, proton decoupling, and two-dimensional correlation spectroscopy etc., while still enjoying the merits that are intrinsic to MACS, such as high concentration sensitivity, eliminated magnetic susceptibility-induced field distortion, and an easy-to-use approach with the conventional and widespread hardware.

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Studies of molecular structure and motion by means of NMR spectroscopy are powerful but the sensitivity is low. In many applications of NMR to materials of chemical/biological interest, the concentration sensitivity, i.e., the sensitivity per unit sample volume, is often more important than that of the mass sensitivity, and the need to gain the former in NMR analysis of sparse, volume-limited samples stimulated development of a tiny detection coil called as a microcoil, which was firstly applied to investigate liquid samples with a volume of as small as 5 nl [1], and then to stationary solid materials with less than a milligram [2,3]. By reducing the size of the coil one can significantly enhance the filling factor (the ratio of the sample volume to the coil volume) and thereby the attainable concentration sensitivity [4,5].

The standard and widespread approach for high-resolution NMR of polycrystalline and amorphous materials demands Magic Angle Spinning (MAS) [6,7], which has recently stimulated its combination with microcoil NMR in the context of concentration sensitivity. Among several reports on microcoil-MAS NMR spectroscopy [8–10], a remarkable idea put forth by Sakellariou et al. involves spinning of the microcoil together with the sample of interest, and wireless, inductive signal transmission between the spinning microcoil and the primary circuit of the MAS probe [11]. In this outstanding strategy, referred to as Magic Angle Coil Spinning (MACS), the coil can be wound directly around the capillary sample so as to gain the filling factor, while inhomogeneous magnetic field distortion due to bulk magnetic susceptibility of the wire of the microcoil is eliminated by spinning the microcoil at the magic angle. Furthermore, the importance of the MACS approach cannot be overstated from the practical point of view,

because it requires no other than a standard, popularly used MAS probe, while any other approaches for microcoil MAS [8–10] do require some hardware modification inside the MAS probe. Thus, the idea of MACS provides a versatile strategy toward high-resolution solid-state NMR measurements with enhanced concentration sensitivity for mass-limited samples.

Currently, the MACS experiments are demonstrated in ^1H MAS NMR, ^{29}Si NMR, and ^{23}Na multiple-quantum MAS NMR [11], while it is often required in solid-state NMR spectroscopy to simultaneously handle two nuclear spin species having different gyromagnetic ratios and thereby different resonance frequencies. For example, in many solid-state ^{13}C NMR studies of biomolecules and polymers, the ^{13}C magnetization is enhanced by means of Cross Polarization (CP) [12]. Also, the ^{13}C magnetization is usually observed after CP under both MAS and intense rf irradiation at the ^1H spin for the purpose of decoupling, i.e., of eliminating the dipolar interaction between the ^{13}C and the ^1H spins so as to enhance spectral resolution. In this work, we integrate MACS and double-resonance NMR spectroscopy into an easy-to-use, powerful, and sensitive analytical tool for intrinsically mass-limited polycrystalline and amorphous solid materials with a small volume of the order of 0.1mm^3 or less, opening a new arena of chemical analysis in which one can enjoy benefits from both MACS and double-resonance NMR spectroscopy. Here we demonstrate ^1H – ^{13}C double-resonance MACS experiments in a magnetic field of 7 T. All NMR spectra presented in this work were acquired using an OPENCORE NMR spectrometer [13], which is a home-built, FPGA-based NMR spectrometer [14].

Fig. 1a describes a circuit diagram for a doubly-tuned MACS resonator, to be put inside a rotor and spun together with the rotor in the conventional doubly-tuned MAS probe. The doubly-tuned MACS resonator is composed of two capacitors C_1 and C_2 and

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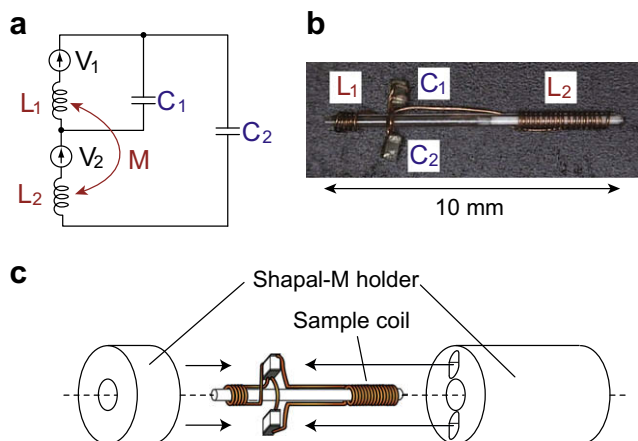


Fig. 1. (a) A circuit diagram for implementing double-resonance MACS experiments. The two inductors L_1 and L_2 were wound with $80\ \mu\text{m}$ polyurethane-coated copper wire into $0.5\ \text{mm}$ ϕ microcoils, and a doubly-tuned MACS resonator was fabricated with two $1 \times 0.5 \times 0.5\ \text{mm}$ chip capacitors, as shown in (b). (c) Illustrates how the coils and the capacitors are supported by a Shapal-M holder.

two inductors L_1 and L_2 , and their mutual inductance is denoted by M . V_1 and V_2 represent electromotive forces induced by the primary circuit (not described in the figure) in the probe through the inductive couplings. Using the first and second Kirchhoff's laws, we obtain an equation of resonance for a given set of L_1 , L_2 , M , C_1 , C_2 , and the resonance frequency ω :

$$0 = 1 - [L_1 C_1 + (L_1 + L_2 + 2M) C_2] \omega^2 + C_1 C_2 (L_1 L_2 - M^2) \omega^4. \quad (1)$$

By setting the individual resonance frequencies to the Larmor frequencies ω_1 and ω_5 of the nuclear spin species under interest, double-resonance NMR is realized.

We wound two coils (inner diameter: $0.5\ \text{mm}$) with $80\ \mu\text{m}$ polyurethane-coated copper wire, and assembled the doubly-tuned MACS resonator in an axially symmetric form using two chip capacitors, as shown in Fig. 1b. As discussed extensively by the Sakellariou group in their pioneering papers [11,15], the eddy current induced in the spinning coils and capacitors can have a considerable sample-heating effect. In order to minimize the amount of metal and thus creation of heat, we employed spot welding as a means of contacting the wire onto the electrodes of the chip capacitor, since it does not add any extra metal unlike soldering. Also, for effective heat dissipation, Shapal-M, machinable ceramic known to have an excellent thermal conductivity, was used [11] for the spacer holding the MACS resonator inside a spinning sample tube.

Fig. 1(c) illustrates the Shapal-M insert for a Varian 5 mm rotor. It is composed of two parts sandwiching the two chip capacitors, which were placed in a way that they balance each other. Using a Varian 5 mm triple-resonance CP-MAS probe, we verified stable spinning at up to 10 kHz both inside and outside a wide-bore 7 T superconducting magnet. We cautiously did not try to spin it at the certificated maximum spinning speed of 12 kHz.

We put the two coils apart from each other, so that their coupling M is negligible. We then obtain from Eq. (1)

$$L_1 = \frac{\beta C_1 \pm \sqrt{\beta^2 C_1^2 - 4\alpha C_1 (C_1 + C_2)}}{2C_1 (C_1 + C_2)}, \quad (2)$$

$$L_2 = \frac{\beta C_1 \mp \sqrt{\beta^2 C_1^2 - 4\alpha C_1 (C_1 + C_2)}}{2C_1 C_2}, \quad (3)$$

where

$$\alpha = (\omega_1 \omega_5)^{-2}, \quad (4)$$

$$\beta = \omega_1^{-2} + \omega_5^{-2}. \quad (5)$$

In this work we deal with ^1H - ^{13}C double-resonance NMR experiments in a magnetic field of 7 T, and in Fig. 2a and b, such L_1 and L_2 ($L_1 < L_2$) are plotted for various capacitances C_1 and C_2 that the circuit resonates at 300 and 75 MHz, which correspond to the ^1H and ^{13}C Larmor frequencies, respectively. As seen in Fig. 2a and b, it is possible to attain double-resonance by adjusting L_1 and L_2 for a wide range of the capacitances C_1 and C_2 , so that capacitance tolerance can be compensated. We used L_2 as the sample coil, into which we inserted a capillary sample tube (outer diameter: $0.5\ \text{mm}$, inner diameter: $0.3\ \text{mm}$) suitable for samples with a volume of $\sim 0.1\ \text{mm}^3$.

In the present work we have chosen the values of C_1 , C_2 , L_1 , and L_2 as follows. Firstly we tentatively set the length of the sample coil L_2 to ca. $2.5\ \text{mm}$, which, with its inner diameter determined by the capillary outer diameter of $0.5\ \text{mm}$ and a number of turns of ca. 18, gives its inductance to be $\sim 40\ \text{nH}$. Then, according to the region close to the $40\ \text{nH}$ contour line in Fig. 2b, we have chosen the capacitances out of the standard capacitances values to be $C_1 = 33\ \text{pF}$ and $C_2 = 82\ \text{pF}$, from which $L_1 = 11\ \text{nH}$ and $L_2 = 43\ \text{nH}$ were obtained from Eqs. (2) and (3).

After fabricating the resonator, we slightly shrank and stretched the coils several times until it resonated at the desired frequencies of 300 and 75 MHz. The resonance frequencies were checked by putting the MACS insert into the primary coil of the CP-MAS probe that was in advance tuned and matched using a network analyzer. When the resonance frequencies of the insert was close to that of the primary circuit, considerable deviation of the reflection coefficient was observed, while deviation as increasing the difference in the resonance frequencies. After verifying the resonance frequencies of the MACS insert, the final impedance matching was attained by adjusting the trimmer capacitors of the primary probe so that the reflection coefficients at the relevant frequencies were minimized.

Frequency mismatch of the MACS insert can apparently be compensated by adjusting the trimmer capacitors of the primary probe so as to give the minimum reflection coefficient. However, it should be small for efficient inductive rf transmission at the Larmor frequency. In order to study the mismatch tolerance, we examined the efficiencies of nutation for various resonance frequencies of the MACS insert over a range of 10 MHz around the ^{13}C resonance frequency of $\sim 75\ \text{MHz}$. We then found that mismatch by less than $\sim \pm 1\ \text{MHz}$ did not significantly disturb the performance. On the other hand, the rf efficiency degraded considerably for larger mismatch. Thus, we made a rough estimation of the Q factor of the present MACS resonator at the ^{13}C channel to be ~ 40 . It would be worth mentioning here that the width of this mismatch tolerance does not coincide with the frequency bandwidth of $-3\ \text{dB}$ return loss measured for the overall circuit, and we have not yet found a straightforward way of accurately measuring the Q factor of the doubly-tuned MACS resonator alone that gives us the mismatch tolerance bandwidth.

In order to evaluate sensitivity enhancement introduced by employing the doubly-tuned MACS resonator, we examined the frequencies of nutation for both the ^1H and ^{13}C channels of the Varian 5 mm CP-MAS probe with and without the tuned double-resonance MACS insert shown in Fig. 1. According to the principle of reciprocity[4], the electromotive force induced in the sample coil by a magnetic dipole at a point is proportional to the magnetic field created by a unit current in the coil at the same point. It follows that dependence of the nutation frequency on the power of rf irradiation gives a direct measure of the signal intensity for a given nuclear magnetization. In Fig. 3a, the ^1H and ^{13}C nutation frequencies are plotted for various radiofrequency powers, showing the enhancement factors of 5.4 ($= 46.2/8.60$) and 7.0 ($= 26.6/3.80$) for the ^1H and ^{13}C channels. Fig. 3b and c show ^{13}C CP-MAS spectra of an identical polycrystalline sample of uniformly ^{13}C - ^{15}N -labeled

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