

Enhancing MQMAS of low- γ nuclei by using a high B_1 field balanced probe circuit

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ABSTRACT

A balanced probe circuit is used to generate high B_1 magnetic field for sensitivity enhancement of multiple-quantum magic-angle spinning (MQMAS) experiment applied to low- γ quadrupolar nuclei. Electrical balancing of the sample coil can cut the peak voltage by a half, therefore improving the power handling when generating a two-fold higher B_1 field. Experimental results, illustrated here with ^{25}Mg data for two layered double hydroxides, show that the MQMAS efficiency increases more than linearly with the B_1 field strength. The multiplicative enhancements from high B_0 and B_1 fields and an optimized MQMAS pulse sequence provide the critically needed sensitivity for acquiring MQMAS spectra of low- γ quadrupolar nuclei such as ^{25}Mg at natural abundance.

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1. Introduction

Multiple-quantum magic-angle spinning (MQMAS) has become a widely used experiment for solid state NMR spectra of half-integer quadrupolar nuclei [1]. The two-dimensional experiment obtains high-resolution isotropic spectra along one dimension and separates the second-order quadrupolar line shape along the other dimension. The efficiency of the MQMAS experiment is often the limiting factor for applications with low- γ quadrupolar nuclei. The multiple-quantum excitation and conversion are far from ideal and highly dependent on the radio-frequency (rf) field strength [2]. The efficiency and sensitivity problems add to the difficulties for low- γ nuclei with the intrinsic low signal and low γB_1 associated with the gyromagnetic ratio γ . We describe here the use of a balanced probe circuit for generating a high B_1 field to alleviate this problem. A simple modification of the conventional LC resonant circuit quadruples the power handling capability. It will be shown that through the enhancement from high rf field and the use of high field magnets in addition to the implementation of optimal MQMAS pulse sequences, the overall sensitivity of the MQMAS experiment can increase dramatically, facilitating its application to low- γ quadrupolar nuclei. The utility of ^{25}Mg MQMAS has been recently demonstrated for Mg/Al layered double hydroxides, where a single local environment was confirmed which provided unambiguous evidence for cation ordering of the 33% Al-doped sample [3]. The MQMAS spectrum was first acquired using a

100% ^{25}Mg enriched sample. The enhanced sensitivity described here allows now the acquisition of ^{25}Mg MQMAS spectra of Mg/Al layered double hydroxides at $\sim 10\%$ natural abundance.

2. Balanced LC resonant circuit

The strength of the rf magnetic field B_1 is an important parameter for many NMR experiments. High B_1 field can be achieved by using a higher power amplifier and strengthening the probe's power handling capability in addition to improving the probe circuit efficiency. For low- γ nuclei detection, it is common for a MAS probe to use unbalanced matching networks depicted in Fig. 1a. It consists of a resonant loop with the coil L and tuning capacitor C_2 and an in-line capacitor C_1 for impedance matching with the transmitter. One end of the coil is at ground potential, while the trimmer capacitors at the other end are exposed to the highest voltage in the circuit V , which scales with $(\gamma B_1)B_0$ [4]. When the voltage gradients reach ionization threshold for air molecules, corona discharge will occur towards the nearby grounded areas [5]. For our 19.6 T ultra-narrow bore (31 mm) magnet, the strong magnetic field B_0 and the limited space inside probehead (ID = 27 mm) increase electric fields and the risk of arcing in the probehead. The close proximity of the probe's grounded shield to the high-voltage components can also reduce the probe's power efficiency $(\gamma B_1)^2/P$ as it induces eddy currents in the shield cover.

Electrical balancing of the sample rf coil has been used to reduce unwanted eddy currents caused by shields in MRI coils [6], to mitigate B_1 field distortions from wavelength effects in high-frequency spectroscopy applications [5,7–9] and to extend the power

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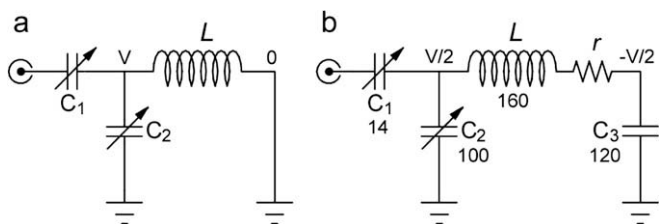


Fig. 1. (a) conventional and (b) voltage-balanced LC resonant circuit approaches for low- γ nuclei. The balanced circuit reduces the peak rf voltage from V to $V/2$. The shown values (pF and nH) are for a 4 mm MAS probe tuned to ^{25}Mg (50.8 MHz at 19.6 T) with $Q \approx 80$.

handling ability of solid state NMR probes [4,5,7,9]. Fig. 1b depicts a balanced resonant circuit aimed at reducing rf voltage inside our dedicated MQMAS probe for low- γ quadrupolar nuclei. The balanced circuit has two tuning capacitors C_2 and C_3 , one on each side of the coil. The tuning capacitances are chosen in a way such that the voltages at the two ends are $V/2$ and $-V/2$, respectively, whereas the middle point of the coil is at virtual ground. This simple modification effectively halves the voltage and enables the doubling of the B_1 field provided that a high-enough rf amplifier is available. For low frequencies ω_0 of the low- γ nuclei where wavelength effects are negligible, the resonant and voltage balance conditions for the circuit elements are

$$\omega_0^2 L = \frac{C_1 + C_2 + C_3}{(C_1 + C_2)C_3} \quad (1)$$

$$C_1 + C_2 = C_3 \quad (2)$$

From these two equations, one obtains $C_3 = 2/(\omega_0^2 L)$. Values for C_1 and C_2 are determined from matching the circuit impedance at resonance to the 50Ω line:

$$\frac{(r + j\omega_0 L - j/\omega_0 C_3)(-j/\omega_0 C_2)}{r + j\omega_0 L - j/\omega_0 C_3 - j/\omega_0 C_2} - j/\omega_0 C_1 = 50 \Omega \quad (3)$$

Here $r = \omega_0 L/Q$ is the series resistance of a sample solenoid. In most practical cases, a high quality factor $Q \gg (C_1 + C_2)/C_1$ simplifies the input impedance to

$$Z = \frac{\omega_0 L}{Q} \left(\frac{C_1 + C_2}{C_1} \right)^2 = 50 \Omega. \quad (4)$$

This expression is in fact identical to the input impedance of an unbalanced circuit [10,11]. From here, capacitances C_1 and C_2 are found by using the balancing condition in (2):

$$C_1 = 2/\sqrt{\omega_0^3 L Q \cdot 50 \Omega} \quad (5)$$

$$C_2 = 2/\omega_0^2 L - 2/\sqrt{\omega_0^3 L Q \cdot 50 \Omega}. \quad (6)$$

3. MQMAS pulse sequence

For low- γ quadrupolar nuclei, the primary basis of choosing a specific MQMAS pulse sequence is the sensitivity. There are two types of commonly used MQMAS pulse sequences [12]. The first type acquires the 2D data in amplitude-modulated format by inserting a z-filter in the pulse sequence [13]. The z-filter ensures equal amplitude of the signals from the $q = \pm m$ multiple-quantum coherence transfer pathways that are complex conjugates of each other. The resulting pure amplitude-modulation yields MQMAS spectra with absorptive line shapes. The z-filter MQMAS sequence is often used for its simplicity and good line shapes with abundant high- γ nuclei where sensitivity is less of an issue. The z-filter can-

cel the signals from other coherence transfer pathways and therefore lowers the overall efficiencies. The second type of pulse sequence acquires the data from only one coherence transfer pathway that refocuses the quadrupolar broadening during the t_1 evolution of the 2D experiment [14]. The so-called echo pathway is determined by the relative signs of the second-order quadrupolar coefficients between the MQ and the central-transitions. For 3QMAS, the echo pathway is $p = -3(t_1) \rightarrow -1(t_2)$ for spin-3/2 and $p = +3(t_1) \rightarrow -1(t_2)$ for spin $> 3/2$. The signal of one coherence transfer pathway is phase-modulated and resulting line shape after 2D Fourier transformation is usually phase twisted. The phase twist can be reduced by shifting the t_2 time-origin using a spin-echo, namely a shifted-echo. The line shape becomes absorptive if a full shifted echo is acquired without any truncation at the beginning half of the echo. The choice between the two types of pulse sequence echo largely depends on the T_2 relaxation time and how rapid the time-domain signal decays due to the inhomogeneous broadening. The echo delay needs to be sufficiently long to avoid any truncation of a full echo. In the meantime, T_2 relaxation causes the signals to decay with increasing spin-echo delay. For low- γ nuclei, the homonuclear dipolar interaction is usually weak while the second-order quadrupolar broadening tends to be large due to lower Larmor frequencies. These features make the shifted-echo MQMAS pulse sequence more favorable over the z-filter sequence for low- γ quadrupolar nuclei.

Various multiple-quantum conversion schemes have been developed for enhancing MQMAS efficiency such as RIACT [15], DFS [16], FAM [17,18], SPAM [19], etc. Fig. 2 shows the SPAM (soft-pulse-added mixing) MQMAS pulse sequence that we have used for MQMAS efficiency enhancement. The SPAM scheme is simple – involving the addition of a central-transition selective $\pi/2$ pulse following the mixing pulse. The phase of this $\pi/2$ pulse is chosen such that the signals from three coherence transfer pathways depicted in Fig. 2 add constructively (the delay before the $\pi/2$ pulse is short enough such that the evolution of the $p = \pm 1$ signal can be neglected). It has been shown in Ref. [19] that for $\Delta p = +2$ or -2 coherence transfer pathway (the one in Fig. 2) the SPAM pulse needs to be 180° phase relative to the mixing pulse. For $\Delta p = +4$ or -4 pathways, no phase switch is required. Two pulses with fixed relative phase can be considered as one composite pulse. In this sense, SPAM is just one of many schemes with frequency and phase modulation as means for enhancing the multiple-quantum mixing efficiency. We choose SPAM here because of the simplicity and the clear physical picture for the enhancement. For low- γ nuclei, parameter optimization for the pulse sequence can become time consuming even for set-up samples due to the inherent low sensitivity. The SPAM method requires no additional parameter optimization. Another consideration is the narrow bandwidth of the low-frequency high- Q resonance circuit. Fast

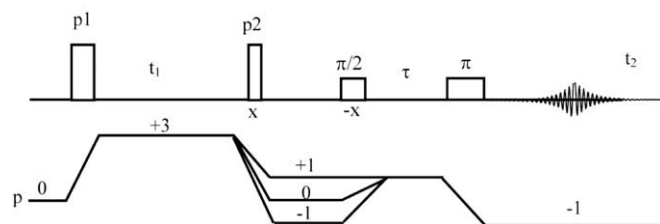


Fig. 2. SPAM shifted-echo MQMAS pulse sequence for spin $> 3/2$. The $\pi/2$ pulse with an 180° phase switch relative the p_2 mixing pulse adds the signals from the three coherence transfer pathways and result in sensitivity enhancement. The spin-echo delay τ needs to be long enough for a complete shift-echo. The p_1 excitation and the π pulses and the receiver phase are cycled to select the $p = -3(t_1)$ to $-1(t_2)$ pathway.

phase modulation of more sophisticated mixing schemes may exceed the probe bandwidth.

One important condition for the MQMAS experiment is the rotor synchronization of the evolution time t_1 [20]. The synchronization avoids any spinning sidebands both from anisotropic spin interactions and from the modulation between the multiple-quantum excitation and conversion [21]. The rotor synchronization can be viewed as a superposition or the summation of all spinning sidebands. It not only simplifies the spectra but also increases the MQMAS signal intensities. The rotor synchronization restricts the F1 spectral window to the spinning frequency. Peaks outside the spectral window are aliased in the F1 dimension. Care should be taken in the data processing, frequency-axis labeling and spectral interpretation in cases of aliasing.

4. Results and discussion

Fig. 3 shows the first t_1 increment $t_1 = \tau_r$ of the ^{25}Mg MQMAS experiment for a 100% ^{25}Mg -enriched ($\text{Mg}_{1-x}\text{Al}_x\text{Al}^{3+}_x(\text{OH})_2 \cdot \text{H}_2\text{O}$, $x = 0.19$) sample using various rf field strengths, with and without the SPAM pulse. The multiple-quantum excitation and conversion pulses were optimized individually for maximum intensities. Optimal pulse lengths of 131° – 161° and 36° – 44° , were found, for the excitation and conversion pulses, respectively, where 90° corresponds to a $\pi/2$ pulse under solution NMR conditions.

The comparison shows that the MQMAS efficiency increases more than linearly with the rf field. Before probe modification, the maximum achievable γB_1 was limited by arcing to about 50 kHz. Arcing in the probehead occurred when input power exceeded 350 W. With the electrically balanced rf matching network, the γB_1 field reaches 89 kHz and is now limited by the maximum power available from the 1 kW amplifier. We also noticed that it required ~ 0.5 db less power to achieve the same rf field. The slight increase in rf efficiency $(\gamma B_1)^2/P$ could be attributed to the decreased coupling between the sample coil and the probe shield as electric fields became smaller inside the probehead [6]. The last

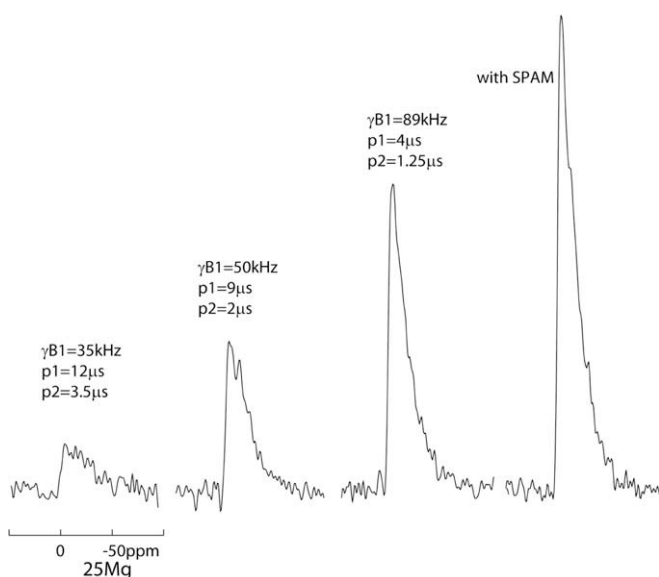


Fig. 3. First t_1 -increment of 2D shifted-echo MQMAS experiment for a 100% ^{25}Mg -enriched layered hydroxide sample as a function of γB_1 . The spectra were acquired at 19.6 T (833 MHz proton resonance frequency) using a home-built single-tuned 4 mm MAS probe. The spinning rate was 10 kHz. Each spectrum was acquired with 240 scans and 0.3 s recycle delay.

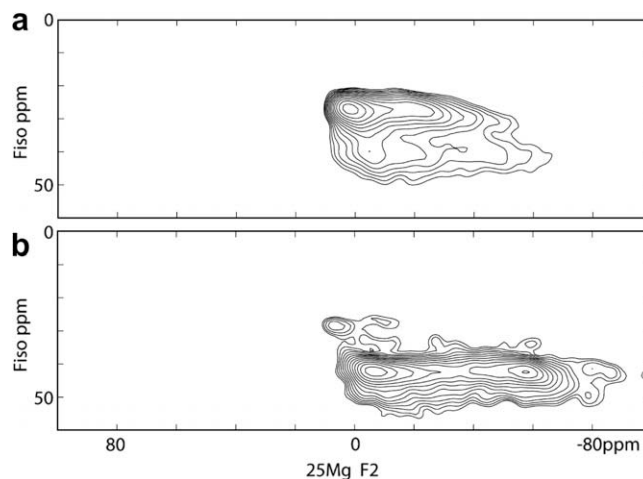


Fig. 4. ^{25}Mg MQMAS spectra of Mg/Al layered double hydroxides acquired at 19.6 T of a 100% ^{25}Mg -enriched 19% Al-doped sample (top) and a natural abundant 25% Al-doped sample (bottom). 240 and 24 k scans were collected, respectively, with a 0.3 s recycle delay for each of the 20 t_1 increments.

spectrum in Fig. 3 shows another $\sim 50\%$ increase after the addition of the SPAM pulse.

For quadrupolar nuclei, high B_0 magnetic fields increase signal intensity from the line narrowing of the second-order quadrupolar broadening in addition to the gains from the thermal Boltzmann polarization and resonance frequency [22]. The reduction of second-order broadening also lowers the spinning frequency requirement making the use of large sample volume possible for more sensitivity gain. We used a 9-turn solenoid coil and a standard 4 mm Bruker MAS rotor. The benefits of an efficient single-tuned circuit include not only the increase in signal intensity but also higher B_1 fields for the MQMAS experiment. A combination of all enhancements from high B_0 , high B_1 field, SPAM-MQMAS pulse sequence, efficient probe, and large sample volume results in sufficient sensitivity gain that it now becomes possible to acquire natural abundant ^{25}Mg MQMAS spectra of a layered double hydroxide sample (19% Al-doped) with good signal-to-noise (Fig. 4). For comparison, a spectrum of an enriched sample (25% Al-doped), obtained in less than half of an hour, is also shown. In both cases, at least two local environments are resolved by MQMAS in contrast to the 33% Al-doped sample [3] which shows a single site. Further details and analysis of the MQMAS spectra of layered double hydroxides will be presented in a future publication [23].

5. Conclusions

It has been shown that the balanced probe circuit can generate high B_1 field and increase the efficiency of MQMAS experiment of low- γ quadrupolar nuclei. Through the use of high field magnets and optimized MQMAS pulse sequences, the sensitivity enhancement obtained can extend the applications of MQMAS experiment to many low- γ quadrupolar nuclei, even those with low natural abundance.

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