Enhancing MQMAS of Low-γ Quadrupolar Nuclei using High B_0 and B_1 Fields

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Introduction

Many quadrupolar nuclei, ^{25}Mg, ^{39}K, ^{43}Ca, ^{45,47}Ti, ^{67}Zn, ^{73}Ge, ^{95,97}Mo and ^{99,101}Ru, commonly found in glasses, minerals, catalysts, ceramics and semiconductors have very low gyro-magnetic ratio γ. Solid state NMR of low–γ nuclei is challenging due to the intrinsic low-sensitivity. This report presents the development for enhancing sensitivity of low–γ quadrupolar nuclei and especially for the MQMAS experiment. These methods includes a high B_0 magnetic field, an efficient probe using a balanced circuit for generating high B_1 magnetic field, and an optimal MQMAS sequence.

Experimental

All measurements were performed using a 19.6T (830MHz) narrow bore instrument at the NHMFL with an NHMFL-built 4mm magic-angle spinning probe.

Results and Discussion

2D MQMAS experiment is a widely used and powerful experiment for quadrupolar nuclei. The efficiency of MQMAS is highly dependent on the *rf* magnetic field strength B_1. Figure 1 shows a balanced circuit that can quadruple the power handling for generating high B_1 field. Conventional resonant loop consists of one tuning capacitor *C* and sample coil *L*. One end of the coil is ground and the other end has the peak voltage *V*. The balanced circuit has two tuning capacitors that split the voltage to *V*/2 and –*V*/2 with the middle point of the coil at virtual ground. This simple modification effectively reduces the peak voltage by factor of 2 and enables the doubling of *rf* field provided the availability of a strong-enough rf amplifier. For selecting a MQMAS pulse sequence, the shifted-echo type experiment has higher efficiencies than the *z*-filtered one, therefore is preferred for low–γ quadrupolar nuclei. Figure shows the *s*oft-*p*ulse-*a*dded-*m*ixing (SPAM) shifted-echo pulse sequence that can enhance the MQMAS by approximately 50% by simply adding a central-transition selective 90° pulse before the shifted-echo. The sensitivity gains by high B_1 field and SPAM are demonstrated with ^{25}Mg MQMAS of a Layered Double Hydroxide sample.

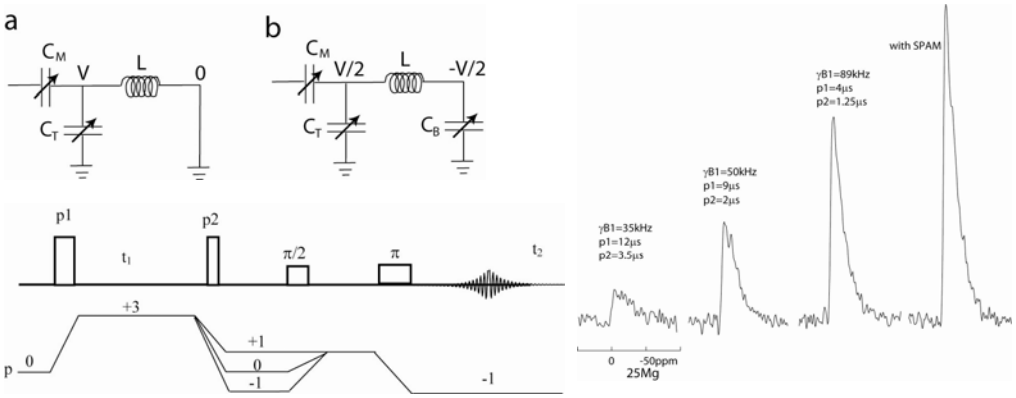

Figure (1 top left) conventional and balanced resonant circuit, (bottom left) SPAM-MQMAS pulse sequence and (right) ^{25}Mg MQMAS sensitivity enhancement using an Al/Mg Layered-Double-Hydroxide sample.

Conclusions

High B_0 and B_1 magnetic fields and efficient pulse sequences can provide the critically needed sensitivity for low–γ quadrupolar nuclei.