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Improved quantitation in 3QMAS of spin $\frac{5}{2}$ nuclei by RF power modulation of FAM-II

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Abstract

High-resolution NMR of quadrupolar $I = \frac{5}{2}$ nuclei using triple-quantum magic angle spinning (3QMAS) techniques can provide more accurate quantitative information on sites with small quadrupolar coupling constants by changing the pulse strength in addition to the pulse length in the FAM-II multiple-quantum conversion sequence. These effects are illustrated using ^{27}Al NMR of yttrium aluminium garnet and andalusite.

Keywords: Quadrupolar nuclei; FAM-II; MQMAS; Solid-state NMR; ^{27}Al NMR

1. Introduction

Quadrupolar nuclei comprise the vast majority of NMR-active nuclei in the periodic table. The major obstacle to solid-state NMR of quadrupolar nuclei is that quadrupolar interactions are often several orders of magnitude larger than other nuclear spin interactions such as dipolar coupling or chemical shifts, hence very broad NMR peaks are usually observed, even under magic angle spinning. In 1995, Frydman and Harwood [1] developed a new two-dimensional technique known as multiple-quantum magic-angle spinning (MQMAS) NMR, which, when combined with standard magic-angle spinning, removes the broadening by second-order quadrupolar coupling in one dimension, while the MAS-narrowed second-order quarupolar spectra are observed in the other dimension. After this report, many others have focused on the improvement of the MQMAS performance. Simultaneously selecting echo and anti-echo coherence pathways [2–5], applying a Z-filter [6], use of a split-t_1 sequence [7] and whole echo acquisition [4,8] were used to obtain the pure-absorption peaks in MQMAS. A two-pulse sequence [2,5] took the place of the original three-pulse sequence to provide high efficiency in multiple quantum (MQ) excitation and less sensitivity to the magnitude of quadrupolar interactions. High rf fields [9] were shown to provide higher efficiency in MQMAS, although recent work has noted interesting rotary resonance effects at lower rf field amplitudes [10,11].

The main drawback of MQMAS is its low sensitivity, which is due to the low efficiency in MQ excitation and MQ-to-single quantum (1Q) conversion. The efficiency of MQ excitation has been optimized by a variety of approaches, including composite pulse excitation [12], shaped-pulse excitation [13], rotation-induced adiabatic coherence transfer (RIACT) excitation [14], and RIACT excitation with rotor assisted population transfer (RAPT) [15–17] manipulation of the population of the external satellites by multiple frequency sweeps (MFS) prior to hard pulse excitation to enhance the excitation efficiency [18] and CW-fast-amplitude-modulation (FAM) hybrid excitation pulses [19]. However, the low efficiency in conversion of MQ coherences to observable single-quantum magnetization is the main culprit in low sensitivity of the MQMAS family of experiments. Attempts to improve the MQ-to-1Q conversion

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efficiency have included RIACT [14], FAM [20–22], double frequency sweep (DFS) [23] and Sin x/x-shaped-pulses [24]; each can more efficiently convert MQ to 1Q coherences than a single pulse. Most of these strategies have been applied to $I = \frac{3}{2}$ nuclei, with only two reports [21,22] to $I = \frac{5}{2}$ nuclei such as ^{17}O and ^{27}Al. It has been demonstrated by Vega [25] that pure adiabatic population transfer between the $|3/2\rangle$ and $|1/2\rangle$ (and $-|3/2\rangle$ and $-|1/2\rangle$) states of $I = \frac{5}{2}$ nuclei does not occur during CW irradiation in rotating samples. Hence the direct coherence transfer FAM-II [21] yields a significant sensitivity enhancement in 3QMAS of $I = \frac{5}{2}$ nuclei, as has also been shown by Vosegaard and coworkers [22]. Recently, FAM-II pulse was assessed to be particularly useful for nuclei ($I = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$) in distorted local environments through a comprehensive experimental and numerical study [26].

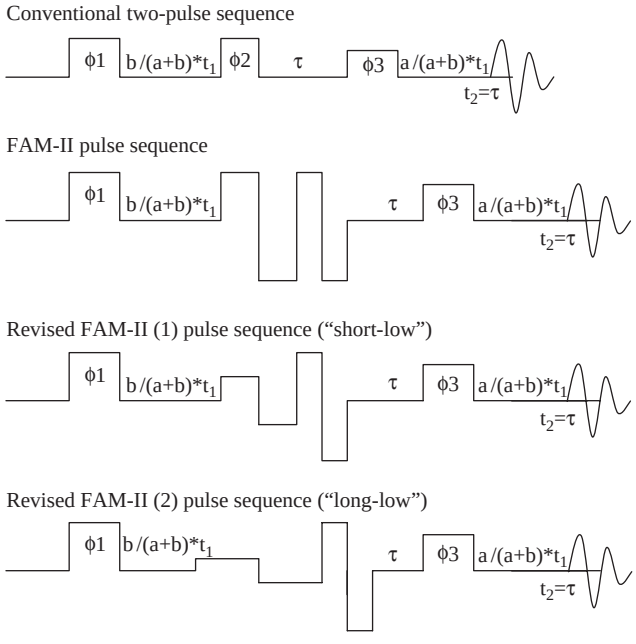
In this work, we present an iteration of FAM-II that modulates both the duration and amplitude of the 3Q-to-1Q conversion pulses. We have found that this method improves the quantitative nature of the resulting ^{27}Al 3QMAS spectra; however, it does not show any improvement in terms of the range of quadrupolar interactions that can be harnessed in MQMAS. These changes have been rationalized in terms of the influence of the ν_Q/ν_{rf} ratio illustrated with calculations using the SIMPSON package [27].

2. Materials and methods

Experiments were performed on two samples: yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$) obtained from CERAC Inc., and andalusite (Al_2SiO_5) kindly provided by the Dana Mineral Collection of the Department of Earth Sciences, University of Western Ontario (London, Ontario, Canada). Both samples were ground to a fine powder and used without further purification. The ^{27}Al MAS NMR spectrum of YAG shows two sites in accord with previous work [28]: a tetrahedrally coordinated site (site 1) with $\chi = 6.0$ MHz ($\eta_Q = 0$, $\delta_{iso} = 74$ ppm) and an octahedrally coordinated site (site 2) with a nuclear quadrupolar coupling constant, $\chi = 0.6$ MHz ($\eta_Q = 0$, $\delta_{iso} = 0.8$ ppm), in the ratio of three tetrahedral sites for two octahedral. The ^{27}Al MAS NMR spectra of andalusite has two sites in the ratio of 1:1—a pentacoordinated Al site (site 1) with $\chi = 5.8$ MHz ($\eta_Q = 0.69$, $\delta_{iso} = 35.5$ ppm), and an octahedrally coordinated Al site (site 2) with $\chi = 15.3$ MHz ($\eta_Q = 0.08$, $\delta_{iso} = 13.0$ ppm), again in accord with previous work [29]. Together, these samples encompass a broad range of ^{27}Al chemical shifts and quadrupolar coupling constant values, spanning most of the breadth reported for various Al sites in a variety of materials, and make them ideal test samples for evaluating the efficiency of MQMAS for ^{27}Al.

All ^{27}Al NMR spectra were referenced relative to aqueous 1.0 M $Al(H_2O)_6^{3+}$ as an external frequency standard. All experiments were performed on a Bruker AVANCE DRX600 spectrometer (14.1 T magnet) with a 2.5 mm Bruker double-resonance MAS probe. The spinning speeds were 20 kHz. The ^{27}Al NMR spectra were acquired at a Larmor frequency of 156.375 MHz. In this work, four MQMAS pulse sequences were used with a phase cycling scheme [4] modified to 48-step that selects the (0) → (3) → (1) → (-1) (Fig. 1): conventional two-pulse MQMAS pulse sequence [2], FAM-II MQMAS pulse sequence [21], short-low revised FAM-II MQMAS pulse sequence and long-low revised FAM-II MQMAS pulse sequence. The split-t_1 whole-echo technique [8] was used in all pulse sequences to obtain pure absorption lineshapes.

In MQMAS experiments of YAG, the excitation pulse length 2.5 μs with rf power of 159.2 kHz was used in four pulse sequences. For the conventional two pulse sequence, the length of the second conversion pulse is 0.7 μs with rf power of 159.2 kHz. For FAM-II pulse sequence, the durations of the 4 segments were 0.9, 0.9, 0.5, 0.5 μs with rf power of 155.3 kHz. For short-low revised FAM-II pulse sequence, the durations of the 4



ϕ1: 0°, 30°, 60°, 90°, 120°, 150°, 180°, 210°, 240°, 270°, 300°, 330°

ϕ2: 0°

ϕ3: 0°, 0°, 0°, 0°, 0°, 0°, 0°, 0°, 0°, 0°, 0°, 0°
90°, 90°, 90°, 90°, 90°, 90°, 90°, 90°, 90°, 90°, 90°, 90°
180°, 180°, 180°, 180°, 180°, 180°, 180°, 180°, 180°, 180°, 180°, 180°
270°, 270°, 270°, 270°, 270°, 270°, 270°, 270°, 270°, 270°, 270°, 270°

ϕr: 0°, 270°, 180°, 90°, 0°, 270°, 180°, 90°, 0°, 270°, 180°, 90°
180.,90°, 0°, 270°, 180°,90°, 0°, 270°, 180°, 90°, 0°, 270°

Fig. 1. Pulse sequences and phase cycling used in these experiments.