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A practical comparison of MQMAS techniques

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Abstract

A systematic experimental evaluation of several approaches to multiple-quantum MAS NMR was performed for spin-5/2 nuclei using ^{27}Al NMR of the aluminosilicate andalusite and the porous aluminum phosphate $AlPO_4$-14 as model. Experiments were conducted in the fields of 9.4 and 17.6 T using magic-angle spinning frequencies up to 30 kHz and rf-field strengths of 250 and 120 kHz. Numerical SIMPSON optimizations of the NMR parameters were performed alongside the experimental evaluations. Both theory and experiment show that the optimization is most critical for the species in the sample that have the largest quadrupolar coupling constant. For 5QMAS experiments it could be confirmed that the highest available rf-field strength and rotation frequency are favorable for the efficiency of the experiments. For 3QMAS experiments of sites with moderate quadrupolar coupling constants optimum results were obtained at less stringent conditions. The comparison of a FAM II-modification and DFS gave the expected improvement by a factor of about two with respect to a rectangular pulse. No significant difference between these techniques concerning the signal-to-noise ratios was obtained. An actual improvement of the isotropic resolution by a factor of about two was obtained going from 3QMAS to 5QMAS. In addition the resolution of the spectra increases by a factor of about two going from 9.4 to 17.6 T.

Keywords: Multiple-quantum; MQMAS NMR; Quadrupolar nuclei; ^{27}Al

1. Introduction

Several methods were introduced for obtaining isotropic solid-state NMR spectra of quadrupolar nuclei with half-integer spin, amongst them *double rotation* (DOR) [1], *multiple-quantum magic-angle spinning* (MQMAS) [2], and *satellite-transition magic-angle spinning* (STMAS) [3]. MQMAS offers an approach that employs conventional MAS hardware and does not require such a high degree of accuracy in setting the magic angle compared to STMAS [4]. Therefore, MQMAS is now the most applied method for refocusing the anisotropic fourth-rank elements of the second-order quadrupolar Hamiltonian in spin space.

A drawback of the MQMAS experiment is its low efficiency in exciting and converting multiple-quantum to single quantum coherence. Numerous variations and improvements of the original MQMAS experiment [2] can be found in the literature. Review articles were provided by Brown and Wimperis [5], Amoureux and Pruski [6], and Goldbourt and Madhu [7,8]. Pruski et al. [9] performed a systematic experimental and numerical evaluation of several approaches to triple-quantum MAS NMR for spin-3/2 nuclei. The present study continues the experimental comparison of the most applied MQMAS techniques to spin-5/2 nuclei, especially ^{27}Al.

Setting up MQMAS NMR pulse sequences requires the adjustment of the various pulses for multiple-quantum excitation and conversion. An optimization of the pulse durations is commonly performed for one signal with a certain quadrupolar coupling constant C_{qcc}. But several signals with different C_{qcc} values are often present in a spectrum. Therefore, we used model substances consisting of aluminum species with C_{qcc} values covering a broad range of 15 MHz. The aluminosilicate andalusite [10] and the porous aluminum phosphate $AlPO_4$-14 [11] were chosen for this study as they are well characterized in literature, and their ^{27}Al NMR quadrupolar coupling

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constants range from 1.7 to 15.3 MHz covering a representative area for investigations of many $I = 5/2$ nuclei, especially ^{27}Al.

In regular MAS experiments of quadrupolar nuclei the resolution (in ppm) improves with the square of the external magnetic field, due to the decrease of the second-order quadrupolar line broadening. In MQMAS experiments the resolution of the isotropic dimension is most important for resolving various sites in a spectrum. We used two field values in this study, 9.4 and 17.6 T. 9.4 T can be considered a standard broadly available field for solid-state NMR whereas 17.6 T is among the highest field available for solid-state NMR.

A high MAS frequency is advantageous in MQMAS experiments. First, in rotation-synchronized measurements which is advantageous to avoid spinning sidebands for sites with large quadrupolar interaction, the spectral window increases with the rotation frequency. Second, the rotation frequency in principle has to be larger than the static spectral width of the central transition or at least larger than the linewidth of the central transition under the magic-angle spinning condition. For example, a linewidth of 20 kHz is found in the MAS spectrum of andalusite at 9.4 T. In order to demonstrate the influence of the sample rotation frequency, a comparison of pulsed z-filtered 3QMAS spectra spinning at 30 and 5 kHz was undertaken. For the rest of this study a spinning speed of 30 kHz was employed.

The excitation of multiple-quantum coherence and its subsequent conversion to observable single-quantum coherence depend critically on the size of the quadrupolar coupling constant and the rf-field strength. For spectra with sites experiencing different quadrupolar interactions a judicious choice is necessary. Here we compare the performance using rf-field strengths of $\nu_{rf} = 250$ and 120 kHz at 9.4 T.

Optimization of pulse lengths in MQMAS experiments on the spectrometer can require an excessive amount of measurement time for observing spectra with weak signals. Numerical packages for the simulation of NMR spectra are becoming readily available. Therefore, we want to establish the reliability of numerical simulations for the MQMAS variations studied here, in order to optimize the conditions that can be implemented on the spectrometer. Here we use the SIMPSON [12] package, which is freely available and well-documented. A limitation to this procedure is obvious that there is some knowledge about the NMR parameters of the compound under study. In general it is possible, however, to get some insight into these parameters from a direct MAS experiment of the compound. For the compounds used in this study all parameters are well established.

The present investigation focuses primarily on the commonly used multiple-quantum techniques, which generate pure absorption-mode line shapes. This condition excludes the original two-pulse sequence [2]. The z-filter experiment with two hard rectangular pulses (RPs) and one soft $\pi/2$ pulse [13] gives a pure absorption spectrum by the symmetrical echo and anti-echo coherence transfer pathways. In this case a shearing procedure [13] of the two-dimensional spectra is necessary to get an isotropic dimension in the spectra. A disadvantage of the z-filter experiment is that it is not straightforward to implement sensitivity-enhancement schemes which need adiabatic transitions such as fast amplitude modulation (FAM/FAM-II) [14,15] or double frequency sweeps (DFS) [16]. Here, we base our MQMAS comparisons on the MQMAS-*split*-t_1-*whole echo* experiment [17,18]. It generates pure absorption spectra, and no shearing procedure necessary to generate perpendicular isotropic and anisotropic dimensions. The focus of the optimization in this experiment is on the MQ to 1Q coherence transfer by RPs, DFS or an adapted FAM-II type pulse. Further sensitivity enhancement techniques that can be used be alongside this experiments are QCPMG (MAS-rotor-synchronized quadrupolar Carr-Purcell-Meiboom-Gill) detection [19] and adaptations of the excitation pulse [20–22]. Alternative schemes such as soft-pulse added mixing (SPAM) [23,24], SW-FAM [25], and hyperbolic secant pulses [26] were not taken into consideration. Furthermore, we would like to point out that this paper does not aim to scan the entire parameter space for optimal signal-enhancement of the MQMAS experiments. Its main goal is to compare some of the most popular experiments and optimize them numerically and experimentally under commonly used conditions for spinning and rf-field strength without losing too much time on the spectrometer set-up. The results are then judged for sensitivity and resolution.

2. Experimental

The following MQMAS experiments were evaluated as *split*-t_1-*whole echo* experiments: RP-3QMAS and RP-5QMAS, DFS-3QMAS, DFS-5QMAS, FAM II-3QMAS, and FAM II-5QMAS. In addition, z-filter experiments were performed for RP-3QMAS and RP-5QMAS. The scaling procedures were performed based on the conventions proposed by Amoureux, Fernandez and Steuernagel [13,27]. Ordinary MAS and DOR experiments were incorporated for comparison of sensitivity and resolution. Each experiment was applied to the samples $AlPO_4$-14 and andalusite at fields of 9.4 and 17.6 T giving a total of 40 experiments. The rf-field strength ν_{rf} and the MAS frequency ν_{rot} were additionally varied in a few cases. Basic procedure for the quantitative evaluation of the several MQMAS techniques is the comparison of the signal-to-noise ratios (determined by the BRUKER software XWIN-NMR) of the one-dimensional spectra with the shortest evolution time $t_1 = 4\,\mu s$, see Table 1. This approach corresponds to a comparison of the signal intensities (area under the line) in the F1-direction.

For all experiments 3360 and 480 acquisitions were acquired for andalusite and $AlPO_4$-14, respectively. Except for the quintuple-quantum experiments where 3360 scans