

Homonuclear Correlation Experiments of Half-Integer Quadrupolar Nuclei Using Multiple-Quantum Techniques Spinning at a P_4 Magic Angle

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In solid-state nuclear magnetic resonance (NMR) of half-integer quadrupolar nuclei, the central transition ($-1/2 \leftrightarrow 1/2$) is usually observed as it is unaffected by the first-order quadrupolar interaction. However, the second-order quadrupolar interaction broadens the central transition significantly.¹ Magic angle spinning (MAS) averages second rank anisotropic interactions such as the dipolar interaction and the chemical shift anisotropy (CSA) but is unable to suppress the second-order quadrupolar interaction. An important focus of solid-state NMR has been to obtain high resolution of half-integer quadrupolar nuclei, devoid of anisotropic broadening. Methods such as dynamic angle spinning (DAS),² double rotation (DOR),³ multiple quantum magic angle spinning (MQMAS),⁴ and satellite-transition magic angle spinning (STMAS)⁵ are efforts in this direction. MQMAS is the most popular among them because of its technical simplicity.

In MQMAS, due to sample spinning at the magic angle, the dipolar interaction is averaged. The dipolar interaction is the key interaction that can be rigorously related to the geometry of the spin system and is therefore very valuable for structural information. In solids, great strides have been made to reintroduce the homonuclear dipolar interaction for spin- $1/2$ systems under MAS using various radio frequency (rf) pulse sequences.⁶ For quadrupolar nuclei, such schemes are not successful because of the specific behavior of these nuclei under rf-irradiation. Considering the fact that quadrupolar nuclei are generally encountered in materials science and many biological systems, we find it is evident that there is a need for robust homonuclear correlation experiments to establish spatial proximity between various quadrupolar sites, which is the topic of this communication.

There have been several approaches to reintroduce homonuclear dipolar couplings between half-integer quadrupolar nuclei in MAS exchange spectroscopy. Hartmann et al. proposed to reintroduce the dipolar coupling in an exchange experiment with the spinning angle switched from the magic angle during the mixing time.⁷ This experiment is difficult to implement as it requires angle switching during the mixing time. Radio frequency driven recoupling was introduced in the context of quadrupolar nuclei by Baldus et al.,⁸ which has the drawback that low rf-fields have to be employed limiting the technique to nuclei with small chemical shift dispersion. Nijman et al. proposed an MAS exchange experiment in which the dipolar coupling is reintroduced by sweeping the spinning frequency through the rotational resonance condition for all orientations in the powder sample.⁹ Spinning speed sweeps are difficult to realize in practice, although significant progress has been reported in this respect.¹⁰ Finally, Frydman and co-workers have shown that under specific circumstances recoupling of dipolar interaction is present under MAS alone due to cross-terms of the noncommuting quadrupolar and dipolar interactions.¹¹

To improve resolution, it is attractive to perform homonuclear correlation experiments in combination with MQMAS. Recently, for this purpose, two 3D experiments were proposed building on

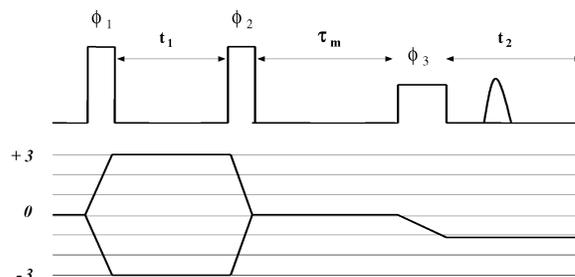


Figure 1. Pulse sequence for the MQP₄MAS/MQMAS exchange experiment for half integer quadrupolar nuclei. A 24 step phase cycle is used to select the coherence pathway $\{0 \pm 3 0 -1\}$.

some of the concepts described above.^{12,13} Alternatively, Duer et al.¹⁴ proposed a MQMAS experiment with excitation of a six-quantum coherence. This coherence is unique for a pair of coupled spin- $3/2$ nuclei. This is a very simple experiment to implement, but the excitation efficiency of the six-quantum coherence is very small, and the analysis of the 6QMAS spectra is not straightforward. Wimperis and co-workers^{15,16} suggested extending the regular MQMAS experiment with an exchange period allowing neighboring spins to communicate. In this case, one relies on the presence of strongly coupled abundant spins mediating spin diffusion of neighboring quadrupolar spins. Here, we propose an alternative approach by performing the two-dimensional multiple-quantum experiment spinning at one of the angles at which the fourth order Legendre polynomial vanishes (P_4 magic angle). In such an experiment, dipolar interactions are retained, whereas the second-order quadrupolar broadening is refocused by the MQ-1Q correlation scheme. By adding an exchange period to this pulse scheme, efficient homonuclear correlation experiments can be performed in a regular MAS probe head with minor modifications. As compared to a regular MQMAS experiment, the only drawback is that the CSA, albeit scaled, is also present which can compromise resolution. However, for many important nuclei such as ²³Na and ²⁷Al, CSA is very small. Moreover, CSA can be used as an extra structural parameter. In the context of measuring the CSA of half-integer quadrupolar nuclei, Wang et al. have described an experiment, called MQVAS, similar to the one that we are proposing.¹⁷ The pulse sequence for the MQP₄MAS exchange experiment is identical to the MQMAS experiment with z-filter¹⁸ using the zero-quantum evolution time as the mixing time as introduced by Dowell et al.^{15,16} earlier (Figure 1).

The MQP₄MAS exchange experiment is demonstrated for ²³Na in the model compound Na₂SO₃. The experiments were carried out on a Chemagnetics CMX-400 infinity spectrometer at a ²³Na Larmor frequency of 105.8 MHz. The rf powers used for the excitation, conversion, and z-filter pulses were 192, 192, and 5 kHz, respectively, for the MQP₄MAS and 175, 175, and 6 kHz for the MQMAS experiments. Na₂SO₃ is known to have three crystallographically different sites, which were measured to be resonating

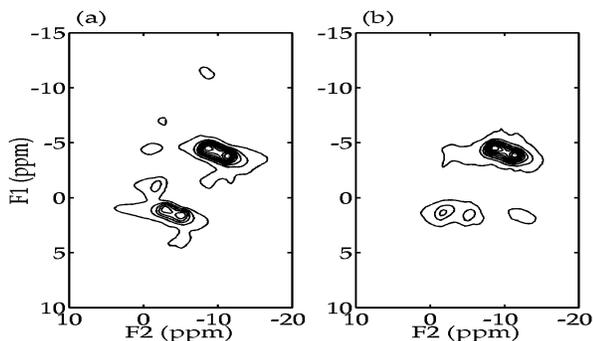


Figure 2. (a) The MQMAS exchange experiment of Na_2SO_3 with a mixing time of $10 \mu\text{s}$. This spectrum shows the three chemically inequivalent sites well resolved (b). Using a mixing time of 1 s shows weak cross-peaks between the two sites with a quadrupolar frequency of over 1 MHz. The third site with low quadrupolar frequency is absent. For both spectra, 10 contours with linear increments ranging from 2 to 100% are plotted.

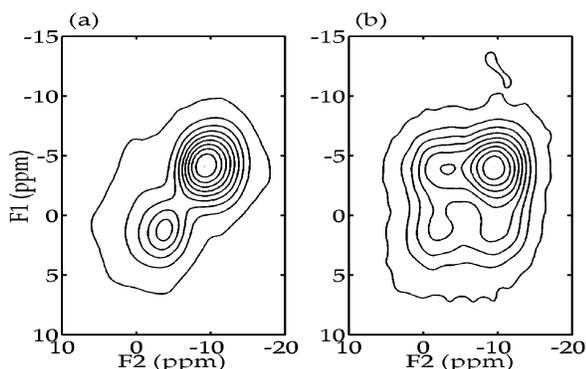


Figure 3. (a) The MQMAS exchange experiment of Na_2SO_3 with a mixing time of $10 \mu\text{s}$ showing the two sites well resolved, but broadened due to the CSA. (b) The MQMAS exchange spectrum with a mixing time of 1 s showing very strong cross-peaks between the two sites indicating their close spatial proximity. The contour levels are the same as in Figure 2.

at -7.3 , -1.1 , and -1.7 ppm (using solid NaCl as reference) with quadrupolar coupling constants (QCC) of 1.2, 1.1, and 0.35 MHz, respectively. They are clearly resolved in the MQMAS spectrum (Figure 2a). Because of its low QCC, the multiple-quantum excitation of site 3 is less efficient than the other two sites under the rf-conditions used in this study. Considering that the problem under study is establishing homonuclear correlation for sites with large quadrupolar interaction, we focused on sites 1 and 2 which have a sizable QCC. First, we performed the regular MQMAS exchange experiment on a 2.5 mm Chemagnetics MAS probe with exchange periods up to 1 s (Figure 2b). Although the sites are in close spatial proximity, no significant cross-peaks occur due to averaging of the dipolar interaction.

Similar experiments were performed with the sample spinning at one of the P_4 magic angles. A 3.2 mm Chemagnetics MAS probe was modified to spin at 70.12° . This angle was chosen because the rf-field obtainable is higher as compared to the other P_4 magic angle 30.56° . The sample was spun at 18.2 kHz. The MQMAS exchange spectrum with $10 \mu\text{s}$ mixing time shown in Figure 3a shows sites 1 and 2 well resolved, although the resolution of the spectrum is less as compared to the MQMAS spectrum due to the presence of the CSA. The MQMAS exchange spectrum with mixing time of 1 s (Figure 3b) shows very clear cross-peaks between

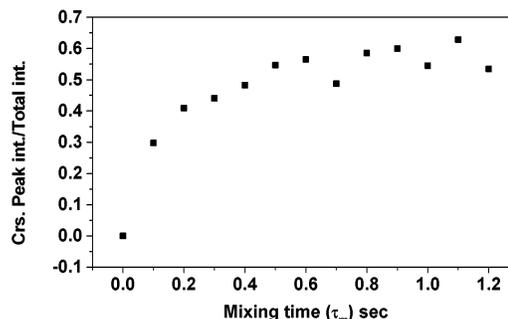


Figure 4. The build-up curve for the MQP₄MAS exchange experiment. The cross-peak integral was calculated by deconvoluting a slice of the 2D spectrum.

the two sodium sites indicative of their close spatial proximity. Clearly, this experiment is capable of giving qualitative information about the proximity of different nuclei. More quantitative information can be obtained by studying the dynamics by running the experiment at different mixing times. A build-up curve of the cross-peak intensity is shown in Figure 4. Sizable cross-peak intensity is obtained for mixing times as short as 100 ms. Extracting distance information from such a curve needs further study. The exchange dynamics of a network of quadrupolar nuclei is not straightforward, with various processes active, as has been pointed out by Frydman and co-workers.¹² Further investigation of these dynamics is in progress and will be discussed elsewhere.

In conclusion, we have presented a very straightforward technique to explore the homonuclear dipolar coupling in half-integer quadrupolar nuclei which can be performed on any routine spectrometer with only minor modification to the MAS probe and would be a very valuable tool for structural studies. Because the CSA is also not averaged out in this experiment, this will be most useful for studying systems with small CSA.

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