

# Detecting proximities between quadrupolar nuclei by double-quantum NMR

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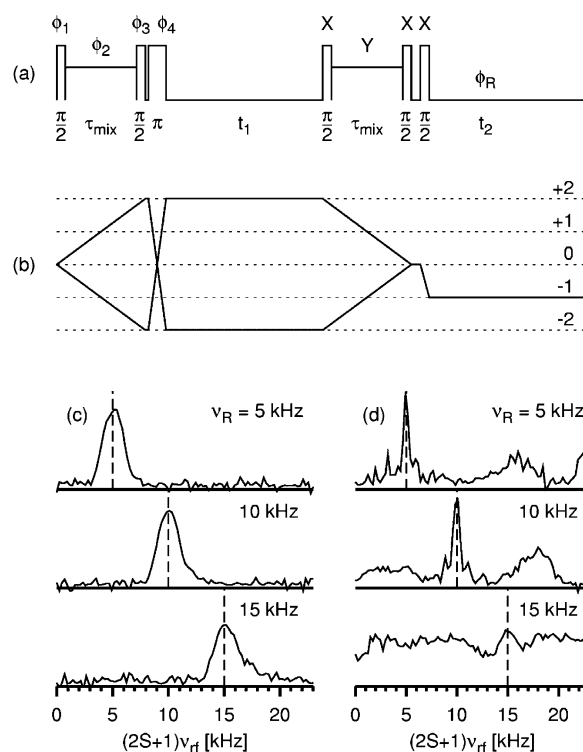
A robust, easy to optimize, and efficient homonuclear correlation NMR experiment for half-integer quadrupolar nuclei in solids is described and has been experimentally tested on anhydrous Na<sub>2</sub>HPO<sub>4</sub> (<sup>23</sup>Na, *S* = 3/2 nucleus) and as-synthesized AlPO<sub>4</sub>-14 (<sup>27</sup>Al, *S* = 5/2 nucleus), an aluminophosphate molecular sieve.

Homonuclear correlation spectroscopy<sup>1</sup> is one of the key experiments in nuclear magnetic resonance because it can elucidate the geometry of molecules and frameworks in liquids and in solids. High resolution NMR in solids demands fast magic-angle spinning (MAS) of the sample in order to suppress broadening due to chemical shielding anisotropy. Since this procedure usually also suppresses through-space dipole–dipole interactions that carry the required geometrical information, a number of techniques were developed to reintroduce the dipolar interaction between spin 1/2 nuclei under MAS.<sup>2–9</sup> Among them, very successful homonuclear correlation techniques are those for which average Hamiltonians contain only double-quantum spin-operator terms. Examples of such techniques are HORROR,<sup>5</sup> C7,<sup>6</sup> and R14.<sup>7</sup> They efficiently excite double-quantum coherence (2QC), which is a specific property of two or more coupled spins of 1/2 and can be distinguished from other coherences on the basis of its symmetry properties under phase shifts of a radio frequency (rf) magnetic field.<sup>1</sup>

Although nuclei with half-integer spin quantum numbers, 3/2, 5/2, 7/2, etc., are also frequently found in solids, only few isolated attempts at homonuclear correlation NMR spectroscopy among those nuclei have been reported so far.<sup>10–14</sup> Nuclei with spin quantum numbers larger than 1/2 are exposed to strong anisotropic quadrupolar interaction, because of which most techniques developed for spin 1/2 systems cannot be directly translated to systems of quadrupolar nuclei. Unlike spin 1/2, 2QC of quadrupolar nuclei can be excited even within the energy levels of a single quadrupolar nucleus. None of the experiments proposed so far have been able to distinguish between a 2QC arising from two coupled identical nuclei and a 2QC excited within a single nucleus.

In this communication, we describe a relatively robust and efficient HORROR-like homonuclear correlation experiment for half-integer quadrupolar nuclei in which 2QC that arises from dipolar coupling is retained and 2QC from single spin is suppressed. The experiment is based on rotary resonance recoupling.<sup>10,15</sup> It employs only weak, central transition-selective rf pulses, for which half-integer quadrupolar nuclei behave as fictitious spin 1/2 nuclei.<sup>16</sup> As shown schematically in Fig. 1, the experiment starts with a spin-lock pulse that is preceded and followed by selective  $\pi/2$  pulses. The average Hamiltonian corresponding to such a 'bracketed' spin-lock pulse contains only double-quantum spin-operator terms and thus efficiently excites 2QC. A selective  $\pi$  pulse at the beginning of the *t*<sub>1</sub> evolution period differentiates the coherence transfer pathways of 2QC arising from dipolar-coupled spins and from a single spin, so that the latter can be efficiently filtered out by phase cycling. The pulse interchanges a two-spin +2QC with a –2QC, whereas single-spin  $\pm$ 2QC are interchanged with  $\pm$ 1Q satellite-transition coherences.<sup>17</sup> The two-spin 2QC is then allowed to evolve for time *t*<sub>1</sub> before it is converted to 0QC with a second 'bracketed' spin-lock pulse. The signal is acquired after a selective  $\pi/2$  pulse.

The importance of a selective  $\pi$  pulse can be evaluated by comparing two similar experiments that show the intensity of aluminium 2QC in the aluminophosphate molecular sieve AlPO<sub>4</sub>-31 as a function of rf field amplitude (Fig. 1). In the first experiment, a complete pulse sequence as shown in Fig. 1 is employed, while in the second experiment, the selective  $\pi$  pulse is omitted. When the selective  $\pi$  pulse is employed at the beginning of the *t*<sub>1</sub> evolution period, 2QC is 'detected' only when the rf field amplitude is close to the rotary resonance condition. At higher or lower rf fields, 2QC is not detected. In contrast, when the selective  $\pi$  pulse is omitted from the pulse sequence, 2QC can be detected even far away from the rotary resonance condition. Obviously, this 2QC is due to single-spin contributions, which cannot be resolved

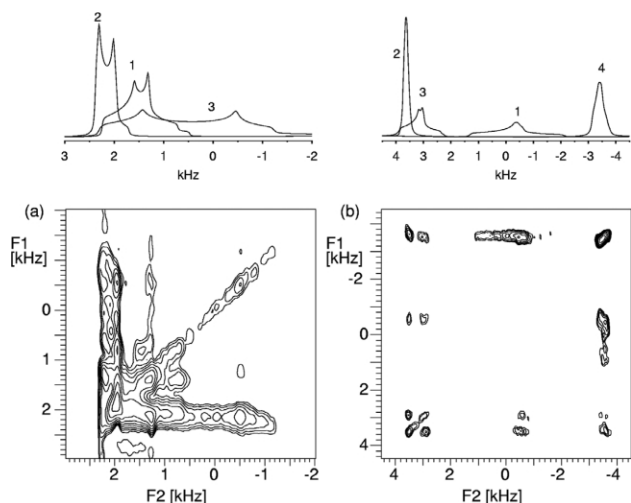


**Fig. 1** Double-quantum homonuclear correlation experiment for half-integer quadrupolar nuclei. The pulse sequence (a) uses 'bracketed' spin-lock pulses for the excitation of 2QC and for its conversion to 0QC. All  $\pi/2$  pulses are central transition-selective pulses and amplitudes of spin-lock pulses satisfy a rotary resonance condition,  $v_{rf} = v_R/(2S + 1)$ . Phase cycling with  $\phi_1 = (0, 90, 180, 270)_4$ ,  $\phi_2 = \phi_1 + 90^\circ$ ,  $\phi_3 = \phi_1$ ,  $\phi_4 = (0^\circ)_4, (90^\circ)_4, (180^\circ)_4, (270^\circ)_4$ , and  $\phi_R = (0^\circ, 180^\circ)_8$  selects the coherence transfer pathway of two-spin 2QC (b) and rejects coherence transfer pathways of single-spin contributions. The traces in (c) and (d) show experimentally determined <sup>27</sup>Al 2QC in AlPO<sub>4</sub>-31 as a function of spin-lock amplitude. Experiments were performed using pulse sequence (a) with and without a selective  $\pi$  pulse, respectively. For each curve, a series of 1D measurements was performed, where the spin-lock amplitude was incrementally increased stepwise from experiment to experiment, while *t*<sub>1</sub> remained fixed to one rotation period. From each 1D experiment, only the amplitude of the recorded <sup>27</sup>Al signal was extracted. Vertical dashed lines in (c) and (d) indicate the position of the rotary resonance condition.

from the two-spin 2QC unless the selective  $\pi$  pulse is applied. The amount of unwanted coherences increases with the sample rotation frequency and at a rotation frequency of 15 kHz, the signal of the two-spin contributions is hardly detected in the strong 'background' of single-spin contributions.

2D homonuclear correlation  $^{23}\text{Na}$  and  $^{27}\text{Al}$  spectra recorded for anhydrous  $\text{Na}_2\text{HPO}_4$  and as-synthesized  $\text{AlPO}_4\text{-14}$  (Fig. 2) demonstrate the performance of the proposed experiment on real samples containing spin 3/2 and spin 5/2 quadrupolar nuclei, respectively. In both materials there are several quadrupolar sites, offering a variety of quadrupolar coupling constants, isotropic chemical shifts, and homonuclear distances.<sup>18–20</sup> In the  $^{23}\text{Na}$  spectrum of  $\text{Na}_2\text{HPO}_4$ , the central transition signals broadened by the second-order quadrupolar interaction overlap severely and thus make the analysis of the homonuclear correlation spectrum relatively difficult. Nevertheless, in the 2D spectrum, we can clearly resolve very strong cross-peaks between sodium sites 2 and 3, a slightly weaker diagonal cross-peak due to the interaction between identical sodium nuclei occupying neighboring sites 3, and still weaker cross-peaks between sites 1 and 3. Cross-peaks between sodium sites 1 and 2 are also detected, but are more difficult to analyze since they overlap with strong 2–3 cross-peaks. The observed cross-peaks and the qualitative information on their intensities agree with the structure of  $\text{Na}_2\text{HPO}_4$  as determined from X-ray diffraction and solid-state NMR analysis.<sup>18</sup>

In the  $^{27}\text{Al}$  spectrum of  $\text{AlPO}_4\text{-14}$ , central transition signals overlap negligibly. All aluminium dipolar couplings with internuclear distances between 2.9 and 5.5 Å are detected. The dipolar



**Fig. 2**  $^{23}\text{Na}$  and  $^{27}\text{Al}$  2D homonuclear correlation experiments on anhydrous  $\text{Na}_2\text{HPO}_4$  (a) and as-synthesized  $\text{AlPO}_4\text{-14}$  (b), respectively. Both pure absorption 2D spectra were recorded using the hypercomplex approach, a magnetic field of 14.1 T, and a sample rotation frequency of 12.5 kHz. The carrier frequency was set in the middle of the spectra and the spectral width in the indirectly detected dimension was equal to sample rotation frequency. In (a), the mixing time was 760  $\mu\text{s}$ , the number of scans 128, the repetition delay 5 s, and the number of increments along the indirectly detected dimension 24. The total acquisition time was 8 h. In (b), the mixing time was 560  $\mu\text{s}$ , the number of scans 2400, the repetition delay 0.25 s, and the number of increments along the indirectly detected dimension 28. The total acquisition time was 10 h. Both 2D spectra are sheared; therefore, they can be read as more familiar RFDR spectra. Because of shearing, spectral widths along the F1 and F2 dimensions are equal and folding of spectral lines in the F1 dimension is easily prevented. Decompositions of the corresponding  $^{23}\text{Na}$  and  $^{27}\text{Al}$  MAS spectra are shown above the 2D spectra. The labeling of individual lines corresponds to the crystallographic notation for the Na and Al sites of  $\text{Na}_2\text{HPO}_4$  and  $\text{AlPO}_4\text{-14}$ .

coupling between two nearest  $\text{Al}_1$  nuclei, which are 6.7 Å apart, is not detected. The cross-peak intensities clearly show that the  $\text{Al}_1\text{-Al}_4$  and  $\text{Al}_4\text{-Al}_4$  distances are by far the shortest and thus, in full agreement with the X-ray diffraction data,<sup>19</sup> demonstrate that there are direct  $\text{Al}_1\text{-O-Al}_4$  and  $\text{Al}_4\text{-O-Al}_4$  connectivities present in  $\text{AlPO}_4\text{-14}$ , in addition to the more common  $\text{Al}_i\text{-O-P-O-Al}_j$  connectivities.

Although both 2D experiments used weak spin-lock fields, frequency offset didn't affect their performance critically. With a spin-lock amplitude of 2.1 kHz, 2QC were efficiently excited in an 8 kHz wide  $^{27}\text{Al}$  spectrum of  $\text{AlPO}_4\text{-14}$ . The experiment on  $^{23}\text{Na}$  nuclei in  $\text{Na}_2\text{HPO}_4$  was even less exposed to offset problems, since the resonant spin-lock amplitude, characterized by  $v_{\text{rf}} = v_{\text{R}}/(2S + 1)$ ,<sup>11,13,15</sup> was larger for  $^{23}\text{Na}$  nuclei with  $S = 3/2$  than for  $^{27}\text{Al}$  nuclei with  $S = 5/2$ . Perhaps the most serious problem that one might encounter when applying the experiment to a large variety of samples would be fast relaxation of double-quantum coherences during spin-lock pulses. Apart from these possible limitations, however, the proposed experiment presents most of the qualities needed: it efficiently excites and reconverts double-quantum coherences, its optimization is quite simple, and it is not highly dependent on the exact rotary resonance condition. As with the homonuclear correlation experiments for spin 1/2 nuclei mentioned above,<sup>5–7</sup> the proposed experiment for half-integer quadrupolar nuclei also allows quantitative determination of internuclear distances by analyzing cross-peak intensities as functions of spin-lock duration.

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