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High-Resolution NMR of Quadrupolar Nuclei Using Mixed Multiple-Quantum Coherences[1]

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A multiple-quantum magic angle spinning (MQMAS) NMR experiment of quadrupolar nuclei is demonstrated, which uses two different multiple quantum coherences in t_1 to refocus the quadrupolar broadening. This experiment has the potential of achieving improved resolution over current techniques.

Key Words: **high-resolution solid-state NMR; MQMAS; quadrupolar nuclei; multiple quantum coherence.**

INTRODUCTION

The nuclear quadrupole interaction of spins greater than $1/2$ with a nonshperically symmetric electrical charge distribution is often much stronger than other spin interactions, such as dipole–dipole and chemical shift, making it necessary to take into account the second order term in a perturbation treatment. The spatial part of this term can be expanded into a sum of spherical harmonics of ranks zero, two, and four, of which only the second rank component can be eliminated by rapid magic angle sample spinning (MAS).

The second and the fourth rank terms can be averaged and correlated by spinning the sample at more than one angle (*1–5*) or by MAS in combination with the creation and conversion of multiple quantum coherence (*6, 7*) (MQMAS). Here, the fact that the ratio of the fourth rank quadrupolar frequency to the chemical shift is different for multiple and single quantum coherences allows one to selectively refocus the effects of one interaction. This refocusing is accomplished by concatenating evolution periods with multiple and single quantum coherences in t_1, while observing the evolution of single quantum coherence in t_2 as depicted in Fig. 1a. The resulting two-dimensional spectra have sharp peaks in ω_1, separated by a scaled isotropic chemical shift and isotropic quadrupolar shift, correlated with anisotropic resonances in ω_2. In experiments where the single quantum coherence does not explicitly evolve during t_1, a shearing transformation brings about this representation. The transformation is tantamount to a shift of the echo time origin to $t_2 = 0$, making both types of experiments formally equivalent (*8, 9*). It should be pointed out, however, that split t_1 experiments may in some cases have significant advantages (*8*).

An alternative approach, which we describe in the present Communication, is to use two different multiple quantum coherences in t_1 in order to refocus the quadrupolar broadening as shown in Fig. 1b. Only a minor modification of the basic experiment is required. The frequency spread in ω_1 of an experiment for a spin $5/2$, which uses five quantum and triple quantum coherence in t_1 (subsequently denoted 5Q3Q) exceeds that of the 5Q1Q experiment by a factor of 1.7 and that of the 3Q1Q experiment by a factor of 7. For a spin $7/2$, the 7Q5Q experiment shows a frequency spread 2.4 greater than for the 7Q1Q experiment, and 24 times greater than for the 3Q1Q experiment.

EXPERIMENTAL

The ^{27}Al NMR spectra were obtained at a Larmor frequency of 130.304 MHz using a Chemagnetics/Varian CMX Infinity 500 (11.7 T) spectrometer equipped with a 4-mm Chemagnetics transmission line MAS probe spinning at 15 kHz. The RF amplitude used for the hard RF pulses was 200 kHz. A continuous 20 kHz decoupling field was applied to the protons. The pulse sequences and desired coherence pathways for the 5Q1Q and 5Q3Q experiments are shown in Fig. 1. The phase cycles for the two experiments are listed in Table 1 and were checked and optimized with the CCCP program (*10*). For the 5Q1Q experiment, the hard RF pulse durations were 7.0 and 1.2 μs, and for the 5Q3Q experiment they were 7.0, 1.98, and 1.24 μs. A soft π pulse (amplitude = 13.3 kHz) was used to selectively invert the $+1$ coherence to a -1 coherence for detection of the full echo (*8, 9*). The dwell times were 12.33 and 33.33 μs (half a rotor period) in t_1 and t_2, respectively, and $\tau = 2$ ms. Ninety-six and 256 data points were collected in t_1 and t_2, respectively. The recycle delay was 0.5 s. Frequencies were referenced to the shift of an $AlCl_3$ solution.

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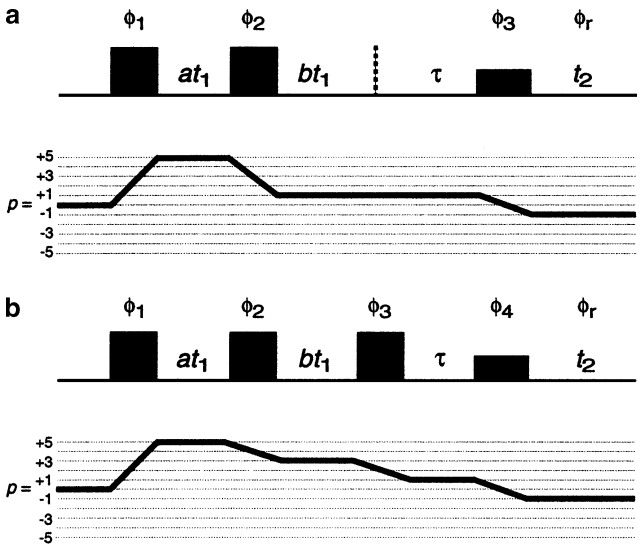

FIG. 1. (a) Pulse sequence for the 5Q1Q experiment. The first pulse excites the 5Q coherence. The second pulse converts the 5Q coherence to single quantum coherence. The third pulse is a soft inversion pulse selectively inverting the central transition to acquire a full echo. The coefficients a and b are calculated to null the overall effect of the fourth rank component of the quadrupolar frequencies (*6*). Here they are $a = 12/37$, $b = 25/37$. (b) Pulse sequence for the 5Q3Q experiment. An additional conversion pulse is needed in this experiment to transform the 5Q to 3Q coherence. Here the coefficients are $a = 19/44$, $b = 25/44$.

The sample of AlPO-41 was dried prior to data acquisition. The spectra were taken after rotating the sample in a pencil rotor overnight, which induced additional dehydration of the sample.

TABLE 1
Phase Cycles for the 5Q1Q and 5Q3Q Experiments

Experiment	Pulse(s)/receiver	Phase list
5Q1Q	ϕ_1	$(0, 18, 36, 54, 72, 90, 108, 126, 144, 162, 180, 198, 216, 234, 252, 270, 288, 306, 324, 342)_8$
	ϕ_2	$[(0)_{20}, (90)_{20}, (180)_{20}, (270)_{20}]_2$
	ϕ_3	$(0)_{80}, (180)_{80}$
	ϕ_r	$(0, 270, 180, 90)_{40}$
5Q3Q	ϕ_1	$(0, 18, 36, 54, 72, 90, 108, 126, 144, 162, 180, 198, 216, 234, 252, 270, 288, 306, 324, 342)_{32}$
	ϕ_2	$[(0)_{20}, (90)_{20}, (180)_{20}, (270)_{20}]_8$
	ϕ_3	$(0)_{80}, (45)_{80}, (90)_{80}, (135)_{80}, (180)_{80}, (225)_{80}, (270)_{80}, (315)_{80}$
	ϕ_4	$(0)_{640}$
	ϕ_r	$\{[(0, 270, 180, 90)_5, (180, 90, 0, 270)_5]_2, [(90, 0, 270, 180)_5, (270, 180, 90, 0)_5]_2, [(180, 90, 0, 270)_5, (0, 270, 180, 90)_5]_2, [(270, 180, 90, 0)_5, (90, 0, 270, 180)_5]_2\}_2$

Note. The labels $\phi_{1,2,3,4,r}$ denote the phases of the pulses in the corresponding pulse sequence or the receiver phase. Subscripts indicate the number of times the phase cycle in the brackets, parentheses, or braces must be repeated. There are 160 steps in the 5Q1Q phase cycle and 640 steps in the 5Q3Q phase cycle.

RESULTS AND DISCUSSION

Figure 2 shows the 5Q1Q and 5Q3Q spectra obtained from the AlPO-41 sample. The peak labeled A is clearly resolved into three peaks in the 5Q3Q spectrum. The origin of the broad peak B in the 5Q1Q spectrum, similar to the peak observed by Wimperis and co-workers for an aluminum methylphosphonate sample (*11*), is currently unknown. The broad features may result from residual heteronuclear couplings, which could be unobservable in the 5Q3Q experiment due to the greater broadening and the lower efficiency. Assuming three sites present (A1, A2, A3) the parameters were extracted using the center-of-gravity peak positions (indicated by lines). The chemical shifts and quadrupolar parameters were $\delta_{cs} = 32.9, 34.4, 34.6$ ppm, and $Q\sqrt{1+\eta^2/3} = 2.79, 2.31, 3.19$ MHz. Caldarelli and co-workers (*12*) have likewise considered three sites for a calcined AlPO-41 sample in a 5Q1Q experiment and good qualitative agreement is found (our signals A1, A2, A3 correspond to the signals labeled 1, 2, 3 in their work). It should be noted that at the field strength used in our work, resolving the three sites becomes very difficult with a 5Q1Q experiment as the frequency spacing of adjacent peaks in ω_1 is only on the order of 200 Hz. The spectra presented in Fig. 2 were truncated in t_1 ($t_1^{\max} \approx 1.2$ ms), resulting in convolution broadening (*13*) in the isotropic dimension on the order of 400 Hz at half height. Under these conditions, resolution of the three resonances does not emerge from our 5Q1Q experiment.

The authenticity of the resonance peaks in the 5Q3Q experiment was tested using an extensive phase cycle, verifying that the resonance positions in ω_1 shift by the correct amount with a resonance offset and by repeating the experiment at a different spinning speed. The signal-to-noise ratio normalized by the number of scans in the two experiments was approximately a factor of 6 worse in the 5Q3Q experiment. The total acquisition times were 4.3 and 8.6 h for the 5Q1Q and 5Q3Q experiments, respectively. The sensitivity of all experiments can be improved roughly by a factor of two using two fast amplitude modulated

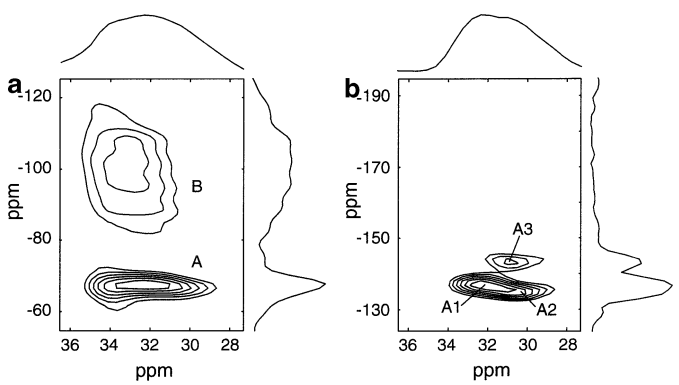

FIG. 2. (a) 5Q1Q spectrum of AlPO-41, (b) 5Q3Q spectrum of AlPO-41. The three sites A1, A2, and A3 correspond to the sites labeled 1, 2, and 3 in Ref. (*12*).

pulses (*14*, *15*) for the conversion from 5Q to 3Q coherence, and from 3Q to 1Q coherence.

Recently, Wimperis and co-workers (*13*) have shown that the resolution may be increased by using the highest-possible multiple quantum coherence in MQ1Q experiments, even when the data are not truncated in t_1. Other authors have observed similar trends (*16*). We anticipate that the resolution can be further increased in an MQNQ experiment when the two highest multiple quantum coherences are combined. The same technique can, in principle, be used for any spin larger than one. A detailed analysis of different line-broadening mechanisms and their scalings is under investigation and will be described in a later publication.

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