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Resolution enhancement in solid-state MQ-MAS experiments achieved by composite decoupling

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ABSTRACT: It is shown that, in the presence of strong heteronuclear dipolar couplings, resolution can be significantly improved in solid-state multiple quantum magic angle spinning NMR experiments on half integer quadrupolar nuclei by applying composite decoupling schemes during triple quantum evolution and acquisition. Reduction of the effects of heteronuclear dipolar coupling during the multiple quantum evolution period is shown to lead to improved resolution of ^{27}Al sites in crystalline chiolite ($Na_5Al_3F_{14}$) and ^{11}B sites in a polyborazilene sample. © John Wiley & Sons, Ltd.

KEYWORDS: NMR; solid-state NMR; multiple quantum magic angle spinning; decoupling; ^{27}Al; ^{11}B; quadrupolar interaction

INTRODUCTION

The description of the multiple quantum magic angle spinning experiment (MQ-MAS)[1] has revolutionized the field of high-resolution solid-state NMR of quadrupolar nuclei, providing an accessible way of obtaining isotropically resolved spectra. Since the description of the first multiple quantum MAS experiment,[1] a great deal of work has been devoted to extending its capability to obtain two-dimensional isotropic–anisotropic correlation spectra. This can be achieved by tailoring the acquisition conditions: multiple quantum pumping and single quantum back conversion using nutation pulses,[2,3] adiabatic transfer under spin locking,[4] shaped pulses,[5] gradient pathway selection,[6] composite pulses,[7] etc. Numerous efforts have also been made to model and compute the transfer efficiencies under various conditions.[2,8] It quickly became apparent that numerous spinning sidebands exist in the triple quantum dimension which could be summed during acquisition using a synchronized acquisition protocol,[9] allowing shorter acquisition times and simplification of the isotropic spectrum. Showing that the dipolar coupling is multiplied by the coherence order (three times for triple quantum), Duer[10] first proposed ascribing these spinning sidebands to the signature of the enhanced dipolar coupling. Marinelli and Frydman,[11] followed by Amoureux *et al.*,[12] demonstrated that these spinning sidebands are mainly due to the excitation pulse sequence itself. As earlier proposed by Frydman, the MQ-MAS technique has also been used as a resolution block for double resonance experiments such as cross-polarization from ^{1}H or ^{19}F[13] or REDOR with defocusing pulses applied during the final single quantum step[14] or during triple quantum evolution.[15] This later MQ-REDOR experiment, in which the defocusing pulses are applied during the triple quantum t_1 evolution period, takes advantage of the enhanced dipolar interaction during evolution on multiple quantum coherences. While the REDOR-type experiments are aimed at reintroducing the dipolar interaction, supposedly averaged out by MAS high-speed spinning rates, it has been implicitly[13,16] or explicitly shown[17] that the application of continuous wave proton decoupling during MQ evolution and observation might be necessary in the case of proton-bearing systems to obtain a resolved isotropic dimension. The aim of this contribution is to show that the dipolar interactions can even become so large that composite decoupling[18] applied during triple quantum evolution and observation is necessary to obtain a resolved spectrum, as specifically shown for the cases of both fluorine- and proton-bearing inorganic materials.

EXPERIMENTAL

We examined two different samples, both containing direct chemical bonds between the observed quadrupolar nuclei of interest (^{27}Al, ^{23}Na or ^{11}B) and a high gamma spin $\frac{1}{2}$ nucleus (^{19}F or ^{1}H).

The crystalline chiolite sample was provided by Pechiney-France. In the structure of crystalline chiolite ($Na_5Al_3F_{14}$),[19] each of the aluminum and sodium sites

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is surrounded by fluorine atoms forming two different AlF_6 sites in a 1:4 ratio and two different Na sites (NaF_8 and NaF_6) in a 1:2 ratio. $Al_{[1]}F_6$ is at the center of an axially symmetric octahedron with in-plane Al—F distances of 1.795 Å and apex distances of 1.780 Å (d_{avg} = 1.790 Å), whereas $Al_{[2]}F_6$ is located in a more distorted octahedron with in-plane Al—F distances of 1.789 Å and apex distances of 1.826 Å (d_{avg} = 1.801 Å). For $Na_{[1]}F_8$, all Na—F distances are 2.583 Å, whereas for $Na_{[2]}F_6$ the Na—F distances are paired and equal to 2.625, 2.290 and 2.268 Å, giving an average distance d_{avg} to 2.394 Å. Considering these distances, the dipolar coupling is expected to be more important for ^{27}Al than for ^{23}Na.

Polyborazilenes are of particular interest as preceramic polymers to boron nitride, because of their potentially high ceramic yields and their close structural relationship to hexagonal BN. They are composed of linked borazine rings, and boron is thus expected to occupy two types of threefold coordinated sites, BN_2H and BN_3. Polyborazilenes are obtained by dehydropolymerization of the cyclic borazine $(BH—NH)_3$ at moderate temperatures (70–110 °C).[20]

The NMR spectra presented here were acquired using a Bruker DSX400 spectrometer equipped with 4 mm Bruker MAS probeheads. The MQ-MAS experiments were acquired using a Z-filter pulse sequence[21] with triple quantum transfer achieved under high power. The typical triple quantum excitation and conversion pulses were of 5.5/1.25 and 3.0/1.2 μs for ^{11}B and ^{27}Al, respectively. The maximum decoupling powers were 70 and 75 kHz for ^{19}F and ^{1}H, respectively. The TPPM (two pulse phase modulated) composite decoupling pulse sequence[18] was applied with a 20° phase modulation. The maximum efficiency was obtained, as expected, for a π duration of the individual decoupling pulses. Acquisition of multiple quantum experiments was synchronized with the spinning rate[9] (13–15 kHz) in the first dimension and 8–128 t_1 slices were acquired. A 3 ms Z-filter was applied for all experiments, with recycle delays ranging from 3 to 6 s, and 144 (^{27}Al) or 528 (^{11}B) scans were accumulated. The spectra were referenced to $Al(NO_3)_3$, and $BF_3 \cdot OEt_2$ at 0 ppm for ^{27}Al and ^{11}B, respectively. The isotropic dimensions of the MQ-MAS spectra were referenced according to previously described protocols.[3] The NMR parameters reported in Table 1 were fitted to experimental spectra using a modified version of the Bruker Winfit program.[22]

RESULTS AND DISCUSSION

The ^{27}Al spectrum of chiolite ($Na_5Al_3F_{14}$) in Fig. 1 clearly shows two overlapping second-order quadrupolar lineshapes under conditions of high-speed MAS spinning (13 kHz). Significant resolution enhancement is obtained by applying continuous-wave ^{19}F decoupling during observation. This implies that spinning alone does not average out all the heteronuclear coupling

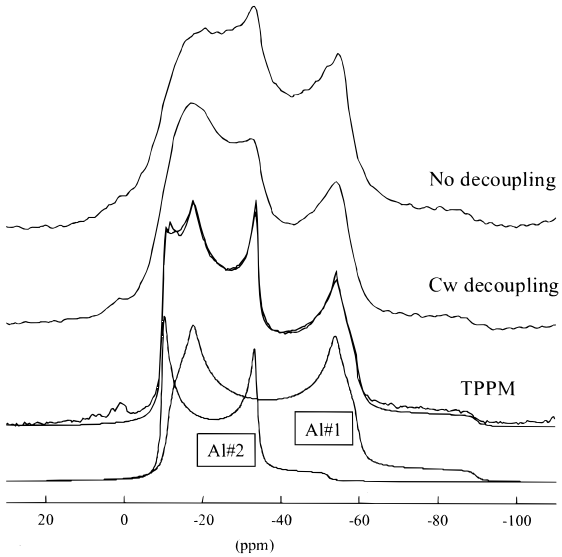

Figure 1. ^{27}Al MAS spectra (9.4 T) of chiolite ($Na_5Al_3F_{14}$) showing the resolution enhancement obtained with various decoupling schemes. Lower traces represent the modeled components according to Table 1.

between the observed nuclei (^{27}Al) and the fluorine bath. In the case of ^{27}Al, the applied 70 kHz decoupling power still does not remove all the residual dipolar interaction and resolution is improved using a TPPM composite decoupling scheme (Fig. 1).

In a triple quantum MQ-MAS ^{27}Al experiment, without fluorine decoupling, the isotropic projection shows very broad unresolved lines (Fig. 2). The use of continuous-wave fluorine decoupling during evolution and acquisition only slightly enhances the resolution in the isotropic dimension without yielding a well resolved spectrum. Clearly, the enhanced Al–F dipolar coupling during the triple quantum evolution is the source of this broadening. A resolved spectrum is ultimately obtained only when composite pulse decoupling[18] is applied during the triple quantum evolution and acquisition period. Under TPPM decoupling, we observe a sharpening of the isotropic lines by a factor of >8 and still a factor of 6.5 compared with continuous-wave (cw) decoupling (Fig. 2). This corresponds to an improvement in terms of r.m.s. signal-to-noise ratio (for identical acquisition conditions) from 23 to 28 and 77 for no decoupling, cw decoupling and TPPM, respectively. It is not fully clear whether we achieved complete decoupling in the latter case. Similarly, we obtain a gain of a factor 5–5.5 in the isotropic linewidth for the ^{23}Na MQ-MAS experiments (not shown). This lower resolution improvement is directly linked to the weaker dipolar coupling due to larger Na—F distances compared with Al—F. It is important to note that in the case of ^{23}Na, where the TPPM decoupling was not necessary to obtain a fully decoupled MAS spectrum, it still provides resolution enhancement when applied during the triple quantum evolution period.

The case of the polyborazilene polymer, containing direct bonds between ^{11}B and ^{1}H, is different in that no

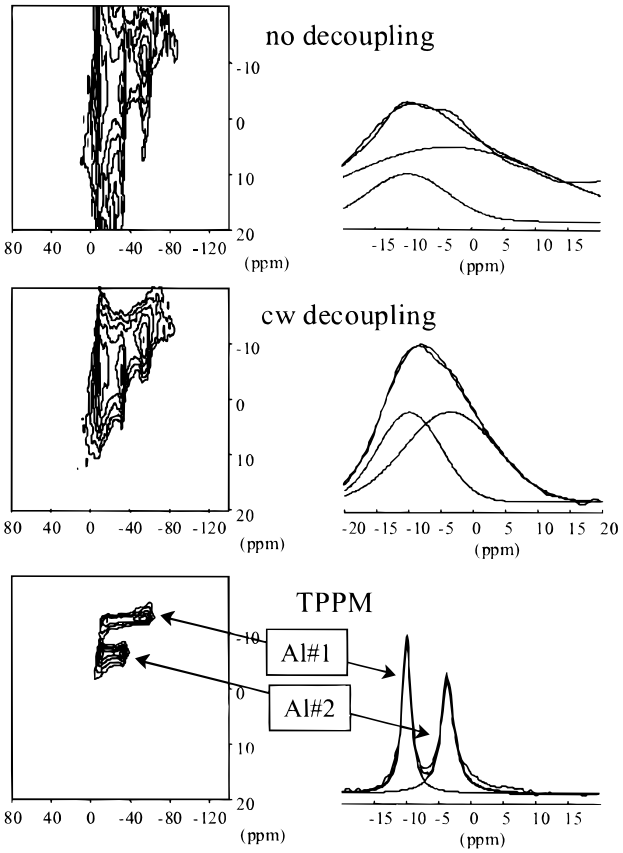

Figure 2. ^{27}Al 3Q MQ-MAS spectra (9.4 T) of chiolite ($Na_5Al_3F_{14}$) showing the resolution enhancement obtained with various decoupling schemes during both triple quantum and acquisition periods. Lower traces represent the modeled components according to Table 1.

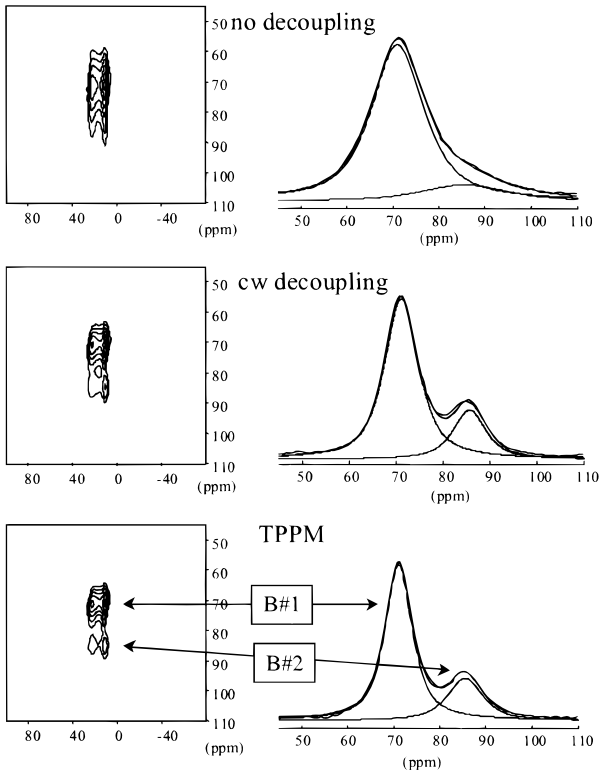

Figure 3. ^{11}B 3Q MQ-MAS spectra (9.4 T) of polyborazilene polymer showing the resolution enhancement obtained with various decoupling schemes during both triple quantum and acquisition periods. Lower traces represent the modeled components according to Table 1.

resolution improvement was observed on applying cw ^{1}H decoupling during acquisition of the high-speed MAS spectrum. This does not imply that dipolar interactions are completely averaged out by spinning, because we are now dealing with a disordered system in which the distribution of chemical shift and quadrupolar interactions can be expected to become dominant. Nevertheless, the ^{11}B MQ-MAS of the polymer gives a nearly featureless isotropic dimension spectrum. The resolution is improved under cw ^{1}H decoupling but we still observe slight resolution enhancement for the peak at $\delta_{F_1} = 73$ ppm under TPPM decoupling (Fig. 3). The limited effect of TPPM decoupling can be understood by examining the shape of the lines in the two-dimensional contour plots. The horizontal lineshape shows that a small distribution of quadrupolar parameters exists with an important distribution of isotropic chemical shift, clearly visible in the TPPM decoupled spectrum. From the modeling of the slices extracted from the two-dimensional chart, it is possible to measure the chemical shift position δ_{CS} and quadrupolar interaction parameters C_Q and η_Q for these two types of sites (Table 1). The parameters obtained are close to those expected for a planar BN_3 configuration.[23,24] The line B#2 can be ascribed to the expected BN2H-type sites, and the line B#1 can be assigned to BN3-type sites, in agreement with the solution-state NMR

Table 1. NMR parameters obtained from modeling the experimental spectra

Site	δ_{cs} (δ_{F1})[a] (ppm)	C_Q (MHz)	η_Q	$\Delta\nu_{\frac{1}{2}}$ (Hz)		
				No decoupling	cw	TPPM
Al#1	−1.5 (−9.9)	8.0	0.13	1500	1200	170
Al#2	−2.8 (−3.5)	6.0	0.04	3900	1750	270
B#1	27 (71.0)	2.7	~0.1	1800	1100	950
B#2	31 (85.5)	2.9	~0.1	2400	1100	1100

[a] δ_{CS} is the isotropic chemical shift position; δ_{F1} is the position of the peak in the isotropic dimension of the MQMAS spectrum, calibrated according to Ref. 3

spectrum of the polyborazilene,[25] which shows two signals, a doublet at 30.4 ppm [^1J(B,H) = 135 Hz] assigned to BN_2H-type sites and a singlet at 26.0 ppm assigned to BN_3-type sites.

CONCLUSION

Following the work of Hanaya and Harris,[17] we have shown that heteronuclear dipolar interaction is not averaged out by high-speed MAS spinning. As the heteronuclear dipolar interaction is multiplied by the coherence order during the triple quantum evolution of an MQ-MAS experiment, its effects can be large enough to reduce the spectral resolution significantly. This can be circumvented by the use of a composite TPPM decoupling pulse sequence during the multiple quantum (and single quantum) evolution, which results in narrower lines by a factor of more than six in the isotropic dimension of the ^{27}Al MQ-MAS spectrum of chiolite.

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