

# Effects of $T_2$ -relaxation in MAS NMR spectra of the satellite transitions for quadrupolar nuclei: a $^{27}\text{Al}$ MAS and single-crystal NMR study of alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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Received 15 October 2004; revised 7 December 2004

Available online 22 January 2005

## Abstract

Asymmetries in the manifold of spinning sidebands (ssbs) from the satellite transitions have been observed in variable-temperature  $^{27}\text{Al}$  MAS NMR spectra of alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), recorded in the temperature range from  $-76$  to  $92$  °C. The asymmetries decrease with increasing temperature and reflect the fact that the ssbs exhibit systematically different linewidths for different spectral regions of the manifold. From spin-echo  $^{27}\text{Al}$  NMR experiments on a single-crystal of alum, it is demonstrated that these variations in linewidth originate from differences in transverse ( $T_2$ ) relaxation times for the two inner ( $m = 1/2 \leftrightarrow m = 3/2$  and  $m = -1/2 \leftrightarrow m = -3/2$ ) and correspondingly for the two outer ( $m = 3/2 \leftrightarrow m = 5/2$  and  $m = -3/2 \leftrightarrow m = -5/2$ ) satellite transitions.  $T_2$  relaxation times in the range 0.5–3.5 ms are observed for the individual satellite transitions at  $-50$  °C and 7.05 T, whereas the corresponding  $T_1$  relaxation times, determined from similar saturation-recovery  $^{27}\text{Al}$  NMR experiments, are almost constant ( $T_1 = 0.07$ – $0.10$  s) for the individual satellite transitions. The variation in  $T_2$  values for the individual  $^{27}\text{Al}$  satellite transitions for alum is justified by a simple theoretical approach which considers the cross-correlation of the local fluctuating fields from the quadrupolar coupling and the heteronuclear ( $^{27}\text{Al}$ – $^1\text{H}$ ) dipolar interaction on the  $T_2$  relaxation times for the individual transitions. This approach and the observed differences in  $T_2$  values indicate that a single random motional process modulates both the quadrupolar and heteronuclear dipolar interactions for  $^{27}\text{Al}$  in alum at low temperatures.  
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**Keywords:** Quadrupolar nuclei; Satellite transitions; Transverse relaxation; Quadrupolar coupling; Dipolar interaction

## 1. Introduction

Magic-angle spinning (MAS) NMR of the satellite transitions for half-integer spin quadrupolar nuclei, generating a complete manifold of spinning sidebands (ssbs), has proven to be a strong tool for determination of the quadrupole coupling parameters ( $C_Q$  and  $\eta_Q$ ) for small and intermediate quadrupole couplings [1,2]. For spin nuclei that are only influenced by the quadrupole coupling interaction, the MAS NMR spectrum exhibits

a manifold of ssbs from the satellite transitions, which is symmetric around the central transition when the spectrum is recorded under optimum experimental conditions. However, small variations in ssb linewidths may be observed throughout the ssb manifold as a result of the difference in second-order quadrupolar broadening for the individual satellite transitions [3,4]. Asymmetries in the ssb manifold from the satellite transitions may arise from internal as well as external effects. The internal effects include chemical shift anisotropy (CSA), which results in distinct asymmetries of the ssb intensities that additionally allow determination of the CSA parameters and the relative orientation of the CSA and quadrupole coupling tensors [5]. The external effects

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include small deviations from exact magic-angle setting, which may lead to unique lineshapes for the individual ssbs [6]. Furthermore, RF offsets caused by improper cable lengths for the  $\lambda/4$  cable in the duplexer of the preamplifier and between the probe and the preamplifier (and/or filters in this line) may give a “tilt” of the ssb manifold [7,8]. However, optimization of these external effects (magic-angle and cable lengths) can generally result in a highly symmetric MAS spectrum, if the nucleus under investigation is influenced only by the quadrupole coupling interaction.

In this work, we report the observation of an internal effect that has not been considered earlier and which may result in asymmetries of the manifold of ssbs from the satellite transitions. This effect is related to differences in  $^{27}\text{Al}$  ( $I = 5/2$ ) transverse ( $T_2$ ) relaxation times for the two inner transitions ( $m = 1/2 \leftrightarrow m = 3/2$  and  $m = -1/2 \leftrightarrow m = -3/2$ ) and correspondingly for the two outer transitions ( $m = 3/2 \leftrightarrow m = 5/2$  and  $m = -3/2 \leftrightarrow m = -5/2$ ), which are observed in  $^{27}\text{Al}$  MAS NMR spectra of the satellite transitions for the alum  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , recorded at temperatures in the range  $-76$  to  $92$  °C. The variation in  $T_2$  values for the different satellite transitions is elucidated by consideration of the effects from the fluctuating fields from the quadrupolar interaction and the  $^{27}\text{Al}$ – $^1\text{H}$  dipolar couplings on the  $T_2$  relaxation. The effects of cross-correlation of anisotropic interactions such as CSA–dipole, dipole–dipole, and quadrupole–dipole cross-correlation have been observed and described in detail for transverse relaxation of coupled spins in the liquid-state [9]. An important application of cross-correlation is achieved in the TROSY experiment which utilizes the cross-correlation of CSA and dipolar interactions ( $^1\text{H}$ ,  $^{15}\text{N}$ , and  $^{13}\text{C}$ ) in structural determination of large biological molecules in solution [10]. Moreover, the effect of quadrupole–dipole cross-correlation ( $^2\text{H}$ – $^{13}\text{C}$ ) on the lineshape for the  $^{13}\text{C}$  resonance has been observed and evaluated theoretically for a  $^2\text{H}$ -labelled protein in solution [11].

## 2. Experimental

The powder sample of alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) was purchased from Merck (Darmstadt, Germany) and used without further purification. Large crystals of alum were obtained from an aqueous solution by slow evaporation at room temperature. A deuterated powder sample ( $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ ) was prepared by dehydration of alum at  $150$  °C followed by recrystallization in  $\text{D}_2\text{O}$  at room temperature. This process was repeated three times and resulted in 94% deuteration, as estimated by  $^1\text{H}$  MAS NMR. The basic structure and purity of the samples were confirmed by X-ray diffraction.

The  $^{27}\text{Al}$  MAS and single-crystal NMR experiments were performed on a Varian *Unity* INOVA-300 (7.05 T) spectrometer using a homebuilt, narrow-bore, variable-temperature (VT) CP/MAS NMR probe for 7 mm o.d. rotors. The probe is capable of operating in the temperature range from  $-140$  to  $210$  °C by regulation of the temperature for the air-bearing gas, employing a homebuilt VT heater/controller unit as described elsewhere [12]. The temperature gradient across the rotor volume is less than  $2$  °C and the actual sample temperature was determined using  $^{207}\text{Pb}$  MAS NMR of  $\text{Pb}(\text{NO}_3)_2$  as a NMR thermometer [13]. For the MAS NMR experiments, slices of  $\text{NaNO}_3$ , packed above/below the sample of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in the rotor, allowed an accurate adjustment (if necessary) of the magic angle at each temperature by minimization of the linewidths observed for the  $^{23}\text{Na}$  satellite transitions. The  $^{27}\text{Al}$  VT MAS NMR experiments employed single-pulse excitation with a pulse width of  $1.0$   $\mu\text{s}$  for a RF field strength of  $\gamma B_1/2\pi = 40$  kHz,  $^1\text{H}$  decoupling ( $\gamma B_2/2\pi = 45$  kHz), a relaxation delay of 2 s, and a spinning speed of  $\nu_r = 3.0$  kHz regulated to  $\pm 1$  Hz by the Varian spinning-speed controller. The single-pulse  $^{27}\text{Al}$  NMR experiments on the single crystal of alum used a pulse width of  $1.0$   $\mu\text{s}$  for a RF field strength of  $\gamma B_1/2\pi = 40$  kHz,  $^1\text{H}$  decoupling ( $\gamma B_2/2\pi = 50$  kHz), and a relaxation delay of 4 s. The crystal was packed in the middle of a 7 mm zirconia rotor with silica powder in the top and bottom of the rotor and the rotor was fixed in the probe for the VT experiments. The saturation-recovery  $^{27}\text{Al}$  NMR experiments [14] used the same RF field strengths as the single-pulse spectra, 10 saturation pulses with a width of  $4.5$   $\mu\text{s}$  and separated by a delay of 200  $\mu\text{s}$ , and recovery delays in the range 1.0 ms to 0.5 s. The spin-echo  $^{27}\text{Al}$  NMR experiments used high-power  $^1\text{H}$  decoupling ( $\gamma B_2/2\pi = 45$  kHz) but a low RF strength ( $\gamma B_1/2\pi \approx 2.6$  kHz) for the selective  $\pi/2$  and  $\pi$  pulses with pulse widths in the range 36–53  $\mu\text{s}$  and 72–106  $\mu\text{s}$ , respectively. For each transition, the pulse widths for the  $\pi/2$  and  $\pi$  pulses were optimized on the alum crystal for the fixed RF field strength. Moreover, the spin-echo NMR experiments employed echo delays in the range  $\tau = 25$ –3000  $\mu\text{s}$  and a relaxation delay of 4 s. Simulations of the solid-state  $^{27}\text{Al}$  MAS NMR spectra were performed on a SUN ULTRA 5 workstation using the *STARS* solid-state NMR software package [2,5].  $^{27}\text{Al}$  isotropic chemical shifts are in ppm relative to an external sample of  $1.0$  M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .

## 3. Results and discussion

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  belongs to the large family of isotopic compounds called alums,  $\text{A}^+\text{B}^{3+}(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$ ; A = Na, K,  $\text{NH}_4$ , Rb, Cs, and Tl; B = Al, Ga, and Cr; R = S, Se. The crystal structures of alums may be

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