

^{27}Al nuclear magnetic resonance study of synthetic
and natural corundum ($\alpha\text{-Al}_2\text{O}_3$)
Some experimental aspects of quantitative ^{27}Al nuclear magnetic
resonance spectroscopy

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Abstract

The ^{27}Al nuclear magnetic resonance (NMR) response of a series of natural and synthetic corundum ($\alpha\text{-Al}_2\text{O}_3$) samples is studied quantitatively by short-pulse excitation and frequency-stepped adiabatic half-passage (FSAHP). Using on- and off-resonance nutation NMR, it was established that the quadrupole coupling parameters of visible Al is identical in all samples. Remarkably, the relaxation behavior for the aluminum is very different in the various samples and has a marked effect on the quantitative response. In natural corundum samples the ^{27}Al spin–lattice relaxation is very efficient as these samples contain paramagnetic impurities. As a result, however, the full signal could not be recovered, which is attributed to relaxation broadening of spins in the vicinity of these impurities. In synthetic samples, containing no impurities, the full signal could be recovered, although the relaxation behaviour appeared to depend strongly on the preparation method. We observed differences in the spin–lattice relaxation by a factor 20; the longest T_1 was observed in a crushed single crystal. This implies that $\alpha\text{-Al}_2\text{O}_3$ can only be used as a standard in quantitative analyses if it has been characterized thoroughly. Furthermore, the effective relaxation behaviour for different types of excitation is studied. Finally, a method to measure the spin–lattice relaxation of half-integer quadrupole nuclei is introduced, using a frequency-stepped adiabatic passage (FSAP) to invert the spin system.

Keywords: Solid-state nuclear magnetic resonance; $\alpha\text{-Al}_2\text{O}_3$; Quantification; Relaxation; Frequency-stepped adiabatic (half-)passage; Nutation

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1. Introduction

An important analytical feature of NMR spectroscopy is the proportionality between signal intensity in the NMR spectrum and the number of nuclei giving rise to this signal. This is useful for spectral assignment and interpretation, e.g. to assign crystallographic different sites in crystalline samples or to determine the amount of various functional groups in glassy samples. For spin $I = 1/2$ nuclei this proportionality is observed straightforwardly. For half-integer quadrupole spins the situation is more complicated due to the presence of quadrupolar interaction. For these spins it is very important that the excitation is done correctly, i.e. that short enough pulses are used to excite the system in order to avoid intensity distortions due to different nutation angles of spinpackets experiencing different quadrupole interactions. These aspects of quadrupole effects in solid-state NMR are well known by now and are reviewed clearly by Freude and Haase [1]. As was demonstrated recently, an FSAHP has advantages over short-pulse excitations in that it gives spectra with an increased signal intensity and is less dependent on the exact radiofrequency (rf) field strength [2].

Despite this proportionality between the number of spins and spectral intensity, sometimes situations are encountered where not all of the spins can be accounted for. The “invisibility” of these spins can generally be attributed to a broadening beyond detection due to large quadrupole interaction parameters. A striking example of this was given by Ernst et al. [3] who demonstrated that the ^{27}Al nuclei at dehydrated Brønsted sites in zeolites have a quadrupole coupling constant of 16 MHz and are therefore not observed by direct detection. Another example is the invisibility of surface sites in a number of high-surface aluminum oxide samples [4].

It is clearly useful in many cases to perform NMR experiments in a quantitatively reliable manner. It is therefore important to have a reliable reference compound. As was pointed out by Freude and Haase [1] it is preferable to have a standard compound that has a response similar to that of the actual samples and can thus be mea-

sured under similar conditions. An attractive candidate for ^{27}Al NMR of aluminium in oxygen surroundings, which is a vastly studied area, is $\alpha\text{-Al}_2\text{O}_3$. It is readily available, cheap, and has a high Al content from one well defined crystallographic site. $\alpha\text{-Al}_2\text{O}_3$ has already been studied by Pound [5], its quadrupole parameters were recently accurately redetermined by nuclear quadrupole resonance (NQR) [6] and NMR [7]. Furthermore, it is inert and not hygroscopic or toxic. In fact, in some recent studies, $\alpha\text{-Al}_2\text{O}_3$ was used as a reference compound [4,8]. As our initial experiments using $\alpha\text{-Al}_2\text{O}_3$ gave some erratic results, we decided to study the NMR response of a series of corundum samples from different sources in a systematic way.

In this paper we describe the results of quantitative NMR experiments on two natural and three differently prepared synthetic samples.

2. Experimental

2.1. Materials

The M_2O_3 structure ($\text{M} = \text{Al}$ for corundum) has been described by Newham and De Haan [9] and Ishizawa et al. [10]. It crystallizes in the hexagonal space group $\text{R}\bar{3}\text{c}$ with $a = 4.754 \text{ \AA}$ and $c = 12.99 \text{ \AA}$. The oxygen atoms are arranged in an almost ideal hexagonal close packing with Al atoms occupying 2/3 of the octahedral interstices. The vacant positions are arranged in an ordered way. The shortest Al–Al distance in corundum is 0.2657 nm, which is one of the shortest distances encountered in oxides. Common impurities in natural corundum are Cr, Fe and Ti. Traces of Cr impurities give corundum a red color (which is called ruby in gem quality). Fe and Ti impurities give the corundum a blue color (blue or any other color is called sapphire).

Two natural and three synthetic samples were studied. The first synthetic sample (corundum A) was prepared by heating 1 g of $\text{Al}(\text{OH})_3$ powder at 1100°C for four days. The second synthetic sample (corundum Verneuil) was a single crystal of about 1 cm^3 prepared by the Verneuil method [11]. Finally a commercially available synthetic

sample Analar (corundum B) purchased from R & L (Slaughter, UK) was used. The natural samples are a number of red-colored crystals from Bamble (Norway) and a number of blue-colored crystals from the isle of Naxos (Greece). The crystals were crushed into fine-grained powders in a tungsten-carbide ball mill.

The corundum structure of all the samples was confirmed by X-ray powder diffraction with a Philips PW 1050/25 diffractometer using $\text{CuK}\alpha$ radiation. The Al content of all samples was checked independently by using X-ray fluorescence spectroscopy (Philips PW 1400/00) and electron microprobe analysis (Jeol Jx-8600 Superprobe). The analyses of all samples were in agreement with the Al_2O_3 stoichiometry. The natural sample from Bamble contained 0.2 wt.-% Fe_2O_3 and 0.3 wt.-% Cr_2O_3 . The Naxos sample contained 0.5 wt.-% Fe_2O_3 and 0.1 wt.-% TiO_2 .

2.2. NMR spectroscopy

Spectra were obtained on a Bruker AM 500 spectrometer, equipped with a solid-state accessory operating at 11.7 T (130.3 MHz for ^{27}Al). Spectra were taken in a home-built magic-angle spinning (MAS) probe equipped with a 5-mm Doty MAS assembly, allowing an rf field strength up to 60 kHz, and a home-built static probehead with a 3-mm solenoid that could be operated at an rf field strength up to 200 kHz. All spectra were recorded without sample rotation.

3. Results and discussion

In order to establish the quantitative response of the α -alumina samples, ^{27}Al spectra of a known amount of a 0.13 M $\text{Al}(\text{NO}_3)_3$ solution were recorded. The spectra were run as a function of pulse length so that an excitation curve was obtained in order to obtain the ^{27}Al response of the solution and the effective rf field strength ($\omega_{\text{rf}} = 28$ kHz) in the solution. Next, short-pulse (1 μs) spectra of the different α -alumina samples were obtained. The rf field strength in the solid (42 kHz) was obtained in a nutation experiment. This allowed us to compare the Al response of the

solids and the solution at the same $\omega_{\text{rf}}\tau_{\text{p}} (< \pi/12)$ value. In these experiments, only the Al response of the synthetic corundum A and B samples were within experimental error ($\pm 5\%$), with the normalized intensity of the solution. In all other samples different responses were obtained with up to 30% of the expected signal intensity missing.

These experiments were conducted in a Doty MAS probehead which is known to have a high quality (Q) factor. Furthermore, the coil in this probehead had four turns only and, thus, the rf homogeneity was not very good. As these factors might influence the outcome of NMR intensity measurements, as was pointed out by Freude and Haase [1], we decided to repeat the experiments in a different probehead. This probehead was home-built with a low Q , allowing an rf field strength of up to 200 kHz. It had a twelve-turn coil which enabled us to keep the sample well within the coil in order to have a homogeneous rf field over the sample volume. The sample volume was kept constant in all experiments. Again, pulse excitation spectra ($\omega_{\text{rf}} = 120$ kHz) were obtained for all samples, and the relaxation delay was chosen to be 5 s. It was established that the signal intensity increased linearly with each transient at this delay. In these carefully conducted experiments we got 94, 92, 78, 76 and 71% of the expected Al signal intensity for corundum A, B, Verneuil, Bamble and Naxos, respectively. Inspection of the excitation curves showed a strongly distorted curve for the Verneuil sample, giving nutation spectra with signal intensities at 3, 6 and $9\omega_{\text{rf}}$, making it clear that the relaxation delay was chosen too short in this case [12]. At this point it was realized that the spin-lattice relaxation for a quadrupole spin system is multi-exponential, in fact $2I T_1$ values are to be expected for a uniformly excited spin I system [1]. It may thus well be that the signal intensity increases linearly with every transient although the relaxation delay is chosen too short.

Variation of the relaxation delay subsequently showed that the full ^{27}Al signal intensity could be recovered for all three synthetic samples A, B and Verneuil, but not for the natural samples from Bamble and Naxos. In fact, the relaxation of

aluminium in the natural samples appeared to be very efficient. This was attributed to the presence of paramagnetic impurities, such as Fe and Cr, in the samples. These impurities acted as relaxation sinks. The effect was that Al spins in the direct vicinity of these impurities relaxed so fast that they were broadened beyond detection. The “visibility” of Al in Bamble was 76% and 71% for Naxos. The effects of the paramagnetic impurities on the visible fraction of Al was witnessed by an additional line broadening. The line width was 9000 and 10000 Hz for Bamble and Naxos, respectively. For the synthetic samples a line width of 7500 Hz was observed. The fact that every Al spin in the lattice was affected by the presence of the paramagnetic impurities means that there is an efficient spin diffusion between the aluminum spins, at least through the central transition. This is not surprising as the Al–Al distance (0.2657 nm) in α -Al₂O₃ is rather short. This also explains why no quadrupolar lineshape was observed for any of the samples either with or without MAS. The homonuclear dipolar interaction obviously blurred the expected second-order quadrupolar features.

Fig. 1 shows the experimental and theoretical excitation curves of corundum B at rf field

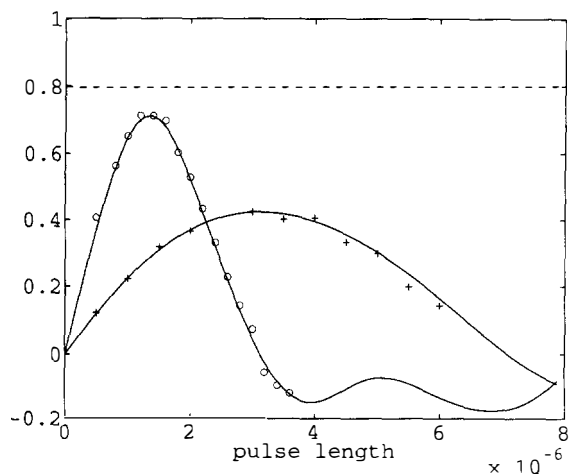


Fig. 1. Excitation curves of ²⁷Al in commercially available α -Al₂O₃ powder (corundum B) at 120 kHz (O) and 30 kHz (+) together with the theoretical calculations using $e^2qQ/h = 2.38$ MHz and $\eta = 0$. The dotted line indicates the intensity obtained in a FSAHP experiment. The intensities are normalized with respect to a non-selective excitation ($I = 1$).

strengths of 30 and 120 kHz. Clearly, the experimental data are in accordance with the theoretical curves. The intensities are normalized with respect to the intensity that can be obtained if the excitation were non-selective. In principle, an FSAHP should give the same intensity as a non-selective excitation [2]. However, the FSAHP intensity, as indicated in Fig. 1, appears to be less. This is due to the fact that the magnetization of the satellite transitions is not brought into the x - y plane. The resonance offset of the satellites as compared to the rf field is very large. Therefore, the passage acts differently on the satellites. The satellites above the central transition resonance are swept below the x - y plane, and those below the resonance reside above the x - y plane at the end of the frequency sweep. This clearly has its effect on the central transition intensity. In fact, the central transition intensity can be strongly influenced by the way the satellite transitions are treated during the sweep. A comprehensive investigation of these effects using frequency stepping methods is under way. Recently Haase and Conradi [13] used frequency sweeps to selectively invert the satellite transitions in order to gain central transition intensity. The relaxation delay used in the pulsed experiments at 120 kHz proved to be sufficiently long for the FSAHP experiments.

Very remarkable is the difference in effective relaxation time for the synthetic samples. The relaxation delay needed to obtain quantitatively correct spectra was 30 s for corundum A and B and 500 s for Verneuil. These differences in T_1 were confirmed by inversion–recovery measurements which will be discussed below. As none of the synthetic samples has a significant amount of paramagnetic impurities this cannot be the cause for the difference. Furthermore, X-ray diffraction confirmed the crystallinity of the samples. The corundum A and B samples were prepared as fine-grained powders and are likely to contain more lattice defects than the Verneuil sample which was grown as a single crystal and then crushed. Therefore, we think that relaxation in corundum A and B is caused by mobile defects [14], whereas the relaxation in the Verneuil sample is effected by spin phonon couplings.

On- and off-resonance nutation of ^{23}Na in differently prepared NaNO_3 samples showed the presence of sites with deviating quadrupole parameters in a commercial sample as compared with a crushed single crystal [15]. Therefore, similar experiments were conducted for ^{27}Al in the synthetic $\alpha\text{-Al}_2\text{O}_3$ samples. As can be seen in Fig. 2, however, no differences are observed between the on- and off-resonance nutation spectra of the commercial sample and the crushed single crystals. The spectra could be simulated well using the literature values for the quadrupole coupling constant. Thus, there is no clear sign of the presence of defects in the corundum A and B samples. It is not to be expected, however, that a low concentration of mobile defects would show up in the spectra, whereas they might still be responsible for the more effective relaxation in these samples.

As the relaxation behavior is an important factor in quantitative analyses, some further experiments were conducted to get more insight concerning this behaviour under various experimental conditions. The effective relaxation delay of a quadrupole spin strongly depends on how the excitation occurred. It was demonstrated experimentally by Day and Squire [16] that the effective T_1 of a quadrupolar nucleus changes

when the spin system is excited non-selectively, as compared with a selective excitation of the central transition. This was subsequently treated theoretically by Andrew and Tunstall [17]. They calculated that the spin–lattice relaxation can be described by three exponentials for a spin $I = 5/2$. The amplitude of the exponentials depends on the excitation. For pure selective and non-selective excitation the dominant exponentials differ by a factor of 2, if the transition probabilities for single- and double-quantum transitions, W_1 and W_2 , are considered equal. It was demonstrated by Haase et al. [18] that selective irradiation of the central transition in zeolites leads to a single exponential with the minimum T_1 value ($T_{1,\text{min}}$). For quantitative analysis of a spectrum with several lines, selective excitation is obviously not possible. The question is thus to what extent the satellite transitions are excited by practically employed rf field strengths (50–100 kHz).

In order to get an indication of the variation of the effective relaxation behavior we performed inversion–recovery experiments at rf field strengths of 15, 30 and 200 kHz for corundum B. As shown in Fig. 3, in all cases a multi-exponential relaxation behavior was found. It appeared to be impossible to get an efficient inversion of the central transition magnetization, indicating that

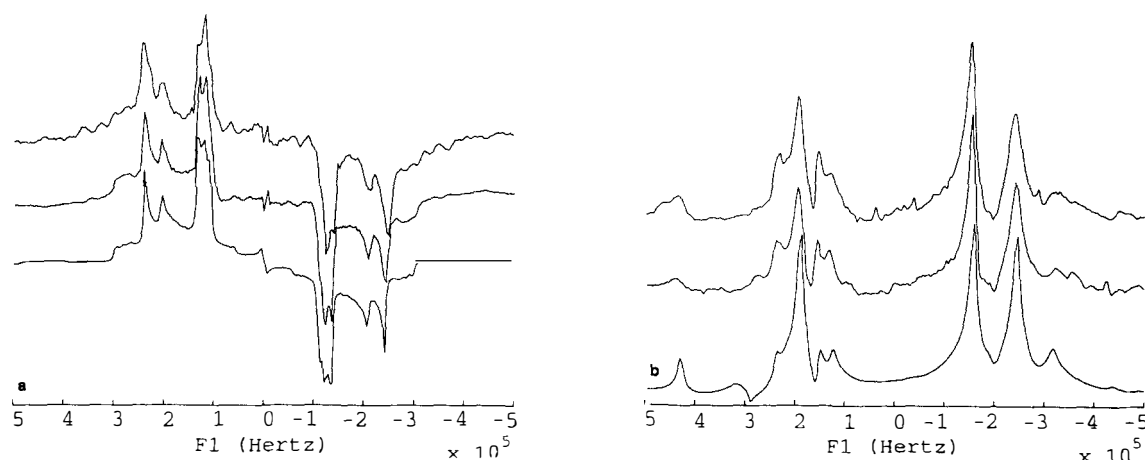


Fig. 2. (a) Phase-sensitive on-resonance nutation spectra, at $\nu_{\text{rf}} = 120$ kHz, of a crushed single crystal of $\alpha\text{-Al}_2\text{O}_3$ (Verneuil, top trace), a commercially available powder (sample B, middle trace) and the simulation ($e^2qQ/h = 2.38$ MHz and $\eta = 0$, lower trace). (b) Magnitude-mode off-resonance nutation spectra ($\nu_{\text{rf}} = 120$ kHz, $\nu_{\text{off}} = 100$ kHz) of a natural sample (Naxos, top trace), a synthetic powder (sample A, middle trace) and the simulation ($e^2qQ/h = 2.38$ MHz and $\eta = 0$, lower trace). In all samples studied the quadrupole parameters are identical, whereas the relaxation behavior differs markedly.

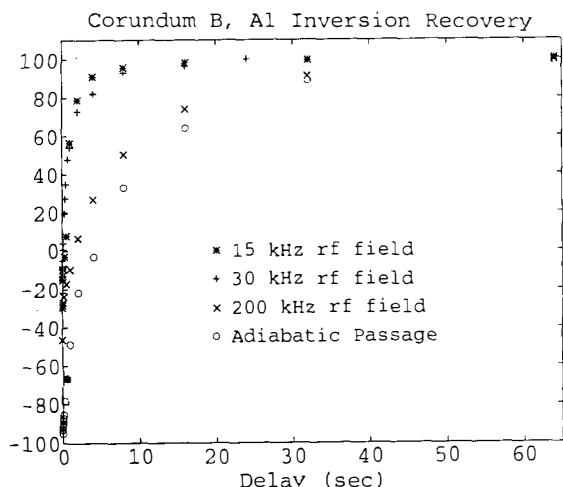


Fig. 3. Inversion–recovery experiments of corundum B under various rf field strengths [$\nu_{\text{rf}} = 15$ kHz (*), $\nu_{\text{rf}} = 30$ kHz (+), $\nu_{\text{rf}} = 200$ kHz (x)], and using an FSAP in order to invert the spin system (o). Only the latter can completely invert the spin system. Intensities are given in percent. In all cases the relaxation is multi-exponential, with the longest T_1 increasing from 4 s (at low rf field strength) to 11 s for the non-selective excitations.

at 15 kHz the excitation is still not completely selective and at 200 kHz is not yet non-selective. Clearly, the use of a strong rf field prolongs the effective relaxation, however, as more of the satellites are excited. A full adiabatic passage using frequency stepping proved to be very efficient in inverting the spin system. In order to do so the frequency was linearly stepped from 2 MHz above resonance to 2 MHz below resonance. The spin–lattice relaxation was then measured by allowing an incrementable delay followed by a short pulse:

$$\text{FSAP} - \tau - \frac{\pi}{n} - \text{ACQ}$$

where ACQ stands for Acquire (data acquisition). As can be seen in Fig. 3, this method gives a full inversion of the signal intensity, making a good T_1 determination of a quadrupolar system possible. The relaxation behavior of the system can be described as [17]:

$$M(t) = M(0) \cdot \left[1 - \sum_{k=1}^3 c_k \cdot \exp(\lambda_k t) \right]$$

Fitting the data with a sum of three exponentials is not very meaningful, however, as this can be done in many different ways. Nevertheless, experiments with different starting values in a simplex fitting procedure showed a good consistency in producing the longest T_1 value, being 4 for the measurement performed at 15 and 30 kHz. For the high-field (200 kHz) experiment and the adiabatic passage inversion experiment, the longest T_1 value was 11 s. This is in accordance with the observation that an FSAHP experiment and a (strong) pulse excitation needed the same repetition rate in order to recover the full magnetization.

Subsequent experiments recording excitation curves as a function of the rf field strength showed that if the rf field strength exceeded 50 kHz, significant (> 5%) deviations of the expected signal intensity could be observed using relaxation delays of less than 30 s. In other words, at these rf field strengths the satellite transitions are substantially excited so that an effective relaxation delay of three times the non-selective T_1 value (≈ 11 s) is needed. If we use a short-pulse excitation (pulse angle < 30°), as is common in quantitative experiments of quadrupolar nuclei, the relaxation delay may be chosen as short as $1 * T_1$. This means that for quantitative experiments on the corundum B sample a relaxation delay of approximately 10 s should be used for rf field strength exceeding 50 kHz; at lower fields a delay of 4 s suffices. When we inspect calculated nutation NMR spectra for $\alpha\text{-Al}_2\text{O}_3$ as a function of the rf field strength it is seen that at rf field strengths smaller than 50 kHz, the nutation spectrum is dominated by one line at $3\omega_{\text{rf}}$. Well resolved spectra appear at rf field strengths exceeding 50 kHz proving that a significant excitation of the satellites occurs.

In order to confirm the observed difference in repetition rate for the synthetic samples A, B and Verneuil, we performed inversion–recovery experiments for these samples at an rf field strength of 30 kHz. As can be seen in Fig. 4, for samples A and B a similar relaxation behavior is observed (longest $T_1 \approx 4$ s). For the Verneuil sample the effective T_1 is much longer: $T_1 \approx 80$ s. Due to the great time requirements we did not perform an

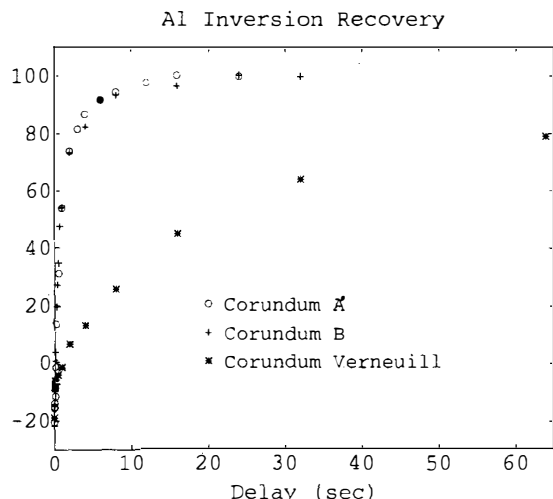


Fig. 4. Inversion–recovery experiments at 30 kHz of corundum A (O), B (+) and Verneuil (*). The crushed single crystal prepared by the Verneuil method shows an increase of the T_1 by a factor of 20. There is no obvious change in the quadrupole parameters, however.

inversion–recovery experiment for this sample using a strong rf field.

The question under what experimental conditions the optimal sensitivity is reached cannot be answered as this will depend on the exact relaxation behavior of the spin system under study. Some general considerations can be made, however. If we consider a fairly selective (s) excitation of the spin system, using 30° -pulses, the relaxation delay can be $1 * T_{1,s}$. Using an FSAHP the full magnetization is brought into the x - y plane, but the relaxation delay has to be $3 * T_{1,ns}$ (ns = non-selective). As was shown by Andrew and Tunstall [17], $T_{1,ns}$ is approximately twice $T_{1,s}$. This would mean that we get the same signal-to-noise ratio in both experiments. For spectra containing several lines it is obviously not possible to use a non-selective excitation. In fact this work shows that, at practically used rf fields, the excitation of spins with moderate quadrupole coupling constants excites the satellite transitions considerably. Furthermore, the frequency stepping is very flexible in that we do not have to make a half-passage. It is also possible to rotate the magnetization over a smaller angle in order to be able

to increase the repetition rate and thus gain the sensitivity.

4. Conclusions

An important conclusion of this work is that synthetic α - Al_2O_3 samples can be used as a standard component for quantitative NMR experiments. However, severe differences in relaxation behavior were observed for differently prepared samples. The samples used should thus be well characterized first. For crushed synthetic single crystals the relaxation delay proved to be inconveniently long. The presence of paramagnetic impurities in natural samples dramatically reduced the spin–lattice relaxation, but this led to a loss of signal as well. These observations again prove very clearly that, generally, the spin–lattice relaxation does not correlate with the static electric field gradient, which is identical in all samples. Probably, the relaxation mechanism is different in the various samples.

For quantitative analyses it should be realised that the rf field used in a pulsed experiment does not only influence the effective pulse angle, but is also of importance for the repetition rate that can be used in the experiments. A strong rf field may excite more of the satellite transitions and thus prolong the effective spin–lattice relaxation. The present study shows, for Al NMR, that this is important for practically employed rf fields.

Finally it was demonstrated that an adiabatic passage accomplished by frequency stepping is an efficient method to invert completely the magnetisation of half-integer quadrupole systems. This gives us a reliable tool for measuring the spin–lattice relaxation of half-integer quadrupole spins.

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