New opportunities for double rotation NMR of half-integer quadrupolar nuclei

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Abstract

A combined approach is presented which expands the applicability of double rotation (DOR) by overcoming its most prominent disadvantages: spinning stability and sensitivity. A new design using air-bearings for the inner rotor and a computer-assisted start-up procedure allows DOR operation over in principle unlimited time at outer rotor speeds of up to 2000 Hz. Sensitivity enhancement of the DOR experiment is achieved by applying amplitude-modulated adiabatic pulses such as the double frequency sweep (DFS) before pulse excitation. Repeating the DFS enhancement and signal readout several times without allowing for spin–lattice relaxation leads to sensitivity enhancements of a factor 3 for ^{27}Al in various minerals. As a result, it becomes possible to study low sensitivity quadrupolar nuclei and various long duration 2D measurements can be performed routinely. Spinning is adequate to suppress residual homonuclear dipolar couplings in the spectral dimension of typical quadrupolar spin systems. In 2D-exchange spectroscopy, however, homonuclear correlation can still be established through dipolar–quadrupolar cross-terms.
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1. Introduction

High-resolution solid-state nuclear magnetic resonance (NMR) of half-integer quadrupolar ($I > 1/2$) nuclei is a valuable structural analysis tool in materials science. As a result of the non-spherical charge distribution of the nucleus, quadrupolar spins experience both a Zeeman interaction and an interaction with the local electric field gradient. Usually, the central transition ($-1/2 \leftrightarrow 1/2$) is observed as it is affected by the quadrupolar interaction in second-order perturbation theory only [1]. Magic-angle spinning (MAS) is unable to suppress the second-order quadrupolar line broadening. This problem was overcome by introducing sophisticated mechanical reorienta-tion schemes that average both second- and fourth-rank contributions to the linewidth by spinning the sample around two angles, either simultaneously in double rotation (DOR) [2], or at consecutive times in a two-dimensional dynamic angle spinning (DAS) [3] experiment. However, due to its technical simplicity it is the multiple-quantum magic-angle spinning (MQMAS) [4] that has proven most popular in high-resolution NMR of quadrupolar nuclei. MQMAS involves the excitation and conversion of multiple-quantum coherences and therefore its sensitivity is compromised. Satellite-transition magic angle spinning (STMAS) [5] potentially offers better sensitivity, but is very demanding in experimental setup. Of all methods described, only DOR provides high-resolution spectra in real time. A single short pulse can be used for signal excitation, in principle providing the most quantitative results.

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In this manuscript, we present a combined approach which expands the applicability of DOR significantly by overcoming its most prominent disadvantages: spinning stability and sensitivity. Due to the mechanical complexity of an inner rotor stabilized by needle bearings within an outer rotor, early DOR designs were hard to spin over prolonged periods of time. Moreover, the spinning speed of the outer rotor was limited to about 1000 Hz resulting in numerous spinning sidebands. Further developments of the design in the group of one of the authors (A.S.) has overcome this problem, however. By introducing air-bearings for the inner rotor and using a computer-assisted start-up procedure, properly packed samples can now be spun over prolonged periods of time at outer rotor speeds of up to 2000 Hz. Here, we demonstrate that this leads to well-resolved spectra even for samples with large quadrupolar interactions. Furthermore, we show that the sustained spinning stability opens the way for two-dimensional NMR spectroscopy under DOR conditions. This can give insightful spectra that are not easily obtained in any other way.

A further drawback of DOR is that its sensitivity is diminished because of the relatively low filling factor (<3%) of the receiver coil with respect to MAS experiments (filling factor ∼30% for a typical 2.5 mm rotor). Related to this is the fact that the rf-field strength is limited due to the relatively large volume of the coil. Signal enhancements of the central transition of half-integer quadrupolar spin systems in single crystals were pioneered by Vega and Naor [6] using selective amplitude-modulated inversion pulses on the satellites. Haase and Conradi [7] used sequential adiabatic inversions of the satellites to achieve this. A more versatile implementation are the so-called double frequency sweeps (DFSs) which were successfully introduced for the enhancement of static, magic-angle spinning and multiple-quantum magic-angle spinning experiments for half-integer quadrupolar nuclei [8]. The basic idea for introducing the DFS in static and MAS single pulse excitation experiments is to invert the satellite transitions simultaneously by an adiabatic passage so that the population of the outer spin levels is transferred to the central 1/2 and −1/2 levels before this transition is selectively excited, giving a theoretical signal enhancement of 2I. In single crystals, the sweeps can indeed be optimized to reach this maximum signal enhancement [9]. For a general crystallite, the level of enhancement is determined by the adiabaticity of the individual transitions in the spin system. The adiabaticity of a general spin transition $m_i \leftrightarrow m_j$ is quantified by the parameter $A = \frac{\omega^2_{\Delta m, \text{eff}}}{\Delta m \lambda}$ which should be greater than 1 to get an efficient inversion. In a static sample this is controlled by the employed rf-field strength ω_1 and the sweep rate λ. In MAS experiments, it is the combined effect of the time-dependency of the satellite transitions due to the spinning, in combination with the frequency sweeping that determine the adiabaticity of each passage:

$$A = \frac{\omega^2_{\text{eff}}}{\frac{\mathrm{d}}{\mathrm{d}t}[\Omega_Q(t) - \Delta\omega(t)]},$$

where $\Omega_Q(t)$ is the position of the satellite transition and $\Delta\omega(t)$ the resonance offset of the sweep components with respect to the satellite transitions. In FAM type experiments introduced by Vega and co-workers [10,11] $\Delta\omega$ is kept constant and one relies on the spinning alone to effectuate the adiabatic passage. A good educational overview of these concepts is given by Wasylishen and co-workers [12].

Intuitively, one would expect DFS type enhancements to be possible in DOR experiments as well, but this has never been studied experimentally. Specific to the DOR experiment are the different trajectories of the satellite transitions compared to MAS, the relatively slow spinning and low rf-fields available. Here, we explore DOR sensitivity enhancements by applying these amplitude-modulated adiabatic pulses. To further optimize sensitivity, we fully deplete the satellite transitions by using these AM pulses in a repetitive way without allowing for relaxation.

2. (Repetitive) DFS enhancement of DOR experiments

The mineral sillimanite is one of the Al_2SiO_5 polymorphs with two crystallographic aluminium sites with sizeable quadrupolar interactions of $C_{\text{qcc}} = 6.77$ MHz and of $C_{\text{qcc}} = 8.93$ MHz for the tetrahedral and octahedral ^{27}Al ($I = 5/2$), respectively. A DOR experiment, spinning at an outer rotor speed of 1600 Hz at 9.4 T, gives a well-resolved spectrum showing the expected resonances accompanied by a set of spinning sidebands due to the limited spinning speed with respect to the central transition linewidth (Fig. 1). The sidebands are well-separated, however, in no way complicating spectral assignment. Using a DFS running from ±1500 kHz to ±100 kHz ($v_1 = 18$ kHz), a S/N enhancement of 2.4 is achieved for a sweep duration of 8 ms. This enhancement is similar to that obtained in a fast MAS study using multiple frequency sweeps simultaneously [13]. This proofs that DOR is amenable to DFS enhancements despite the limitations in spinning speed and rf-field and the different trajectories of the satellites due to double rotation.

It should be noted that at low rf-fields the enhancement is not very sensitive to the sweep length once it is long enough to ensure the adiabaticity of the sweeps as is exemplified in Fig. 2. At higher rf-fields the sweeps may become adiabatic for double-quantum transitions having a detrimental effect on the enhancement of the central transition [14]. We recorded ^{27}Al DOR spectra of the mineral Amelia albite ($C_{\text{qcc}} = 3.29$ MHz, $\eta = 0.62$ [15]) spinning at an outer rotor speed of 1650 Hz. Using a DFS running from ±1 MHz to ±100 kHz ($v_1 = 25$ kHz), a S/N enhancement of 2.2 is achieved for a sweep duration of 860 μs. Although sizeable, this enhancement is far from the theoretical maximum of 5. For a spinning powder the satellite transitions of each crystallite move around in
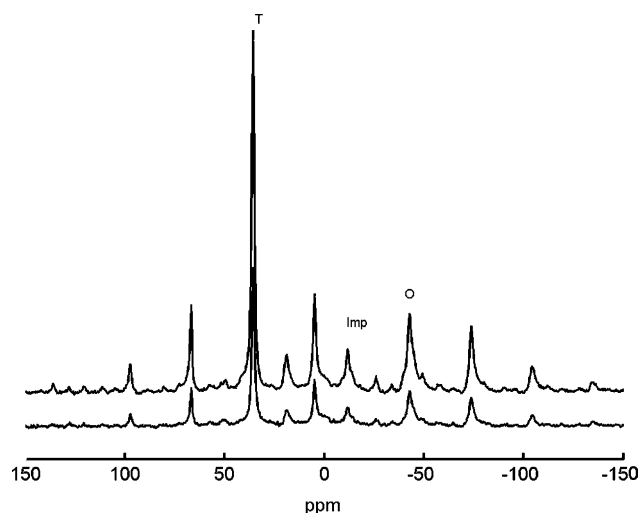
Fig. 1. Single pulse excitation (bottom) ^{27}Al DOR spectrum of sillimanite at 9.4 T spinning at an outer rotor speed of 1600 Hz showing well-resolved resonances for the tetrahedral (T) and octahedral (O) coordinated aluminum along with a set of spinning sidebands. Furthermore, an impurity (imp) signal is present in this natural mineral sample. Applying a DFS before excitation (top) gives a S/N gain of 2.4, proving the viability of the DFS concept in DOR experiments.
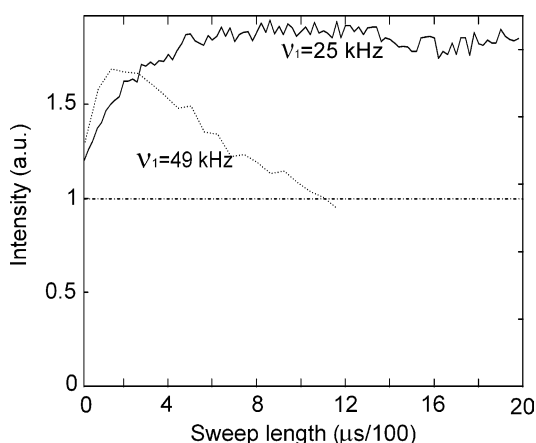

Fig. 2. Optimization of the DFS for γ-Al_2O_3 ($v_{outer} = 1750$ Hz) at two different rf-field strengths. At 25 kHz the maximum enhancement is reached at ∼800 μs and remains constant. At 49 kHz the built-up is much faster but decays at longer times which is attributed to detrimental effects of passing partially adiabatic through higher-quantum transitions [14]. The dash-dotted line indicates the intensity of a single-pulse experiment without enhancement.

different trajectories that are determined by the spinning of the inner and outer rotor, as a result of which it is no longer possible to invert all satellites perfectly. Depending on the adiabaticity and number of passages of the various spin transition in each crystallite, the actual enhancement in MAS experiments varies between 1 and $2I$ for the various crystallites [13]. There appears to be no systematic pattern related to specific orientations, in fact the enhancements appear to be randomly distributed over all possible crystallite orientations on a sphere [13]. Therefore, we explore the possibility to repeat the DFS

enhancement and signal readout several times without allowing for spin–lattice relaxation as there should be enough spin population left in the outer spin levels to be transferred to the central levels. For albite, with an effective Al T_1 of ∼20 s at 9.4 T, strong signals were obtained for a train of repetitive DFS (rDFS) enhancements without relaxation delay as shown in Fig. 3. We observe an approximately exponential decay of the signal intensity in the consecutive scans. As was described by Kwak et al. [16] the enhancement in S/N ratio can be optimized by a weighted sum of the consecutive scans, with each scan scaled by its own intensity, which is comparable to using a matched filter. With a gain G in the first scan and assuming an exponential decay e^{-x} between consecutive scans one can improve the overall S/N by a factor $G\sqrt{\frac{1}{1-e^{-2x}}}$ by repetitive addition of the signals. For the albite we improved the S/N by a factor 2.9 by weighted addition of 8 repetitive acquisitions, which is 1.3 times the enhancement obtained by "multiple RAPT" applied to albite under MAS conditions (cf. Fig. 2 in [16]).

An interesting case is γ-Al_2O_3 because this sample displays inherent disorder. Although γ-Al_2O_3 has a well-defined oxygen sublattice, the aluminum sublattice is distorted resulting in average quadrupolar coupling constants of 5 and 4.5 MHz for the Al(IV) and Al(VI), respectively. The disorder in the Al sublattice results in large distributions in the NMR parameters of both sites [17].
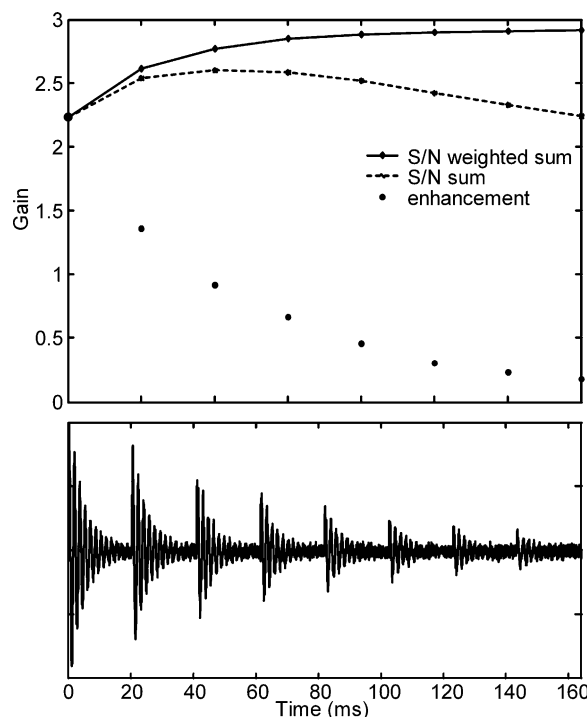

Fig. 3. Repetitive DFS-enhanced data acquisitions for ^{27}Al in Amelia Albite ($T_1 = 20$ s) without any relaxation delay. The dots represent the signal enhancement, relative to single pulse excitation, in each individual scan. The dotted line gives the overall S/N enhancement by summing each acquisition. The solid line is obtained when each scan is weighted by its own intensity (matched filter).
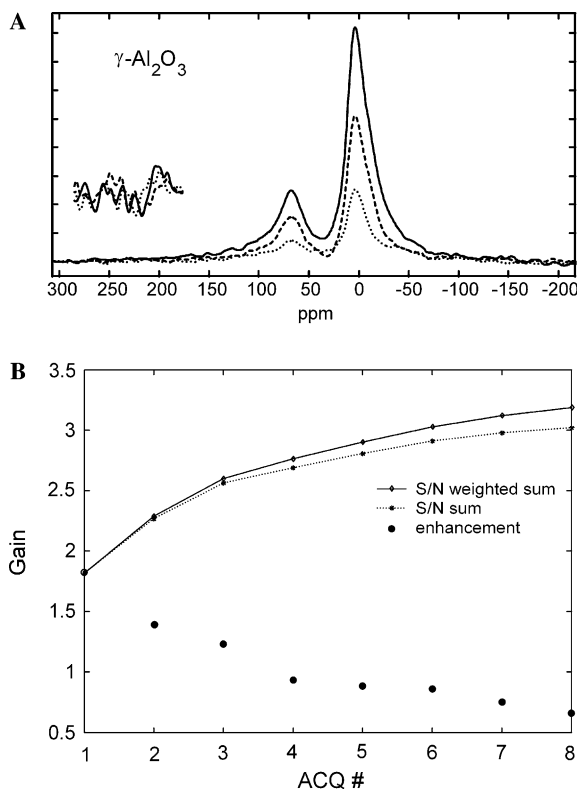
Fig. 4. (A) Single pulse excitation (···) ^{27}Al DOR spectrum of γ-Al$_2$O$_3$ at 9.4 T. Applying a DFS before excitation gives a S/N gain of 1.8 (---). Using eight repetitive DFS enhancements (without relaxation) delay increases the S/N gain to 3.2 (—). (B) S/N enhancements of the individual acquisitions and their cumulative effect.

Fig. 4 shows the ^{27}Al DOR ($\nu_{\text{outer}} = 1750$ Hz) spectra of γ-Al$_2$O$_3$, without, with single and repetitive DFS enhancements. A DFS running from ±2 MHz to ±100 kHz at an rf-field of 13 kHz and a sweep length of 1.5 ms gives a signal enhancement of 1.8. Adding 8 rDFS enhanced signals increases the overall signal-to-noise gain to 3.2. Interestingly, the decay in enhancement per scan is much less as compared to the albite case; in fact even after 8 repetitive experiments the effective S/N is rising (Fig. 4B). Although the T_1 of Al in γ-Al$_2$O$_3$ is relatively short ($T_1 \sim 1$ s as determined in a saturation-recovery experiment) it is long with respect to the delay between repetitions (1–2 ms). The slower decay of signal intensity is more likely to be caused by the distribution in quadrupolar parameters. This means that the DFS used is not optimal for the various sites in the distribution. This is compensated for by the repetitions of the sweeps, however. Finally, we checked the efficiency of a fixed frequency amplitude-modulated pulse, which is expected to perform similarly to a FAM type experiment. At a modulation frequency of 900 kHz a steady enhancement is observed fairly insensitive to pulse length at longer times. The optimum is found at 1800 μs giving an overall S/N gain of 2.4 after 8 repetitions, which is two-thirds of the gain in the rDFS enhanced experiment.

3. Two-dimensional DOR experiments

The improved spinning stability opens the way for realistic two-dimensional experiments involving DOR. Practically, we had rotors running for several weeks without problems. The fact that DOR gives isotropic spectra in the direct dimension is of particular value for 2D experiments. DOR allows the implementation of a 2D experiment that cannot be performed in any other way; MQDOR [18,19]. An MQDOR experiment yields truly isotropic spectra in two dimensions where the position of the line is $\delta_{\text{iso}} + \delta_{\text{QIS}}$ in the F2 dimension and $\delta_{\text{iso}} + c \cdot \delta_{\text{QIS}}$ (with $c = -1$, 1/4, 3/5, 3/4 for $I = 3/2$, 5/2, 7/2, and 9/2, respectively) in the (scaled) F1 dimension. This allows the determination of the isotropic chemical shift and the quadrupolar interaction product $P_Q = C_{\text{qcc}}(1 + \eta^2/3)^{1/2}$ of a site from a single measurement. As a model compound powdered Na$_2$SO$_3$ was used. In a 3QDOR spectrum obtained at 9.4 T (not shown) its three sharp ^{23}Na resonances appear at -2.1, -4.9, and -11.0 ppm in the F2-dimension and -1.7, $+1.5$, and -3.8 ppm in the F1 dimension for sites Na(2), Na(1), and Na(3), respectively. This gives for site Na(1) $\delta_{\text{iso}} = -1.7$ ppm, $P_Q = 1.20$ MHz, for site Na(2) $\delta_{\text{iso}} = -1.9$ ppm, $P_Q = 0.30$ MHz and for site Na(3) $\delta_{\text{iso}} = -7.4$ ppm, $P_Q = 1.27$ MHz, which agrees with earlier reported values within the experimental accuracy [20].

The MQDOR experiment is particularly useful for samples exhibiting a distribution in NMR parameters such as glasses or otherwise disordered materials as a distribution in isotropic chemical shift is mapped out against the distribution in quadrupolar induced shift in the two-dimensional plane. This not only allows the quantification of these distributions but also enables one to establish possible correlations between the two which holds important structural information. An example is the γ-Al$_2$O$_3$ which has a distorted Al sublattice as described above. The ^{27}Al 3QDOR spectrum of γ-Al$_2$O$_3$ is displayed in Fig. 5 showing that the large linewidth in the DOR spectrum is the result of a distribution in both chemical shift and quadrupolar interaction. As the lines do not have a specific pattern there seems to be no apparent correlation between chemical shift and quadrupolar interaction for the various sites. At 9.4 T the resonance of Al(VI) is elongated along the δ_{QIS} direction showing that this distribution, expressed in ppm, dominates over the chemical shift distribution. Spectral simulation (Fig. 5B) shows that the lineshapes can be reproduced satisfactorily assuming a Gaussian distribution in isotropic chemical shift and quadrupole coupling constant for both the octahedral and the tetrahedral coordinated Aluminum. For Al(VI), we find $\delta_{\text{iso}} = 15 \pm 3$ (HWHH) ppm and $C_{\text{qcc}} = 4.5 \pm 1.2$ (HWHH) MHz, for Al(IV) only the average isotropic shift ($\delta_{\text{iso}} = 75$ ppm) and quadrupole coupling constant ($C_{\text{qcc}} = 5$ MHz) could be determined as the S/N was too low to get detailed information about the width of the distributions. The results corroborate values obtained from MQMAS data of this compound [17]. As was described before, however, this
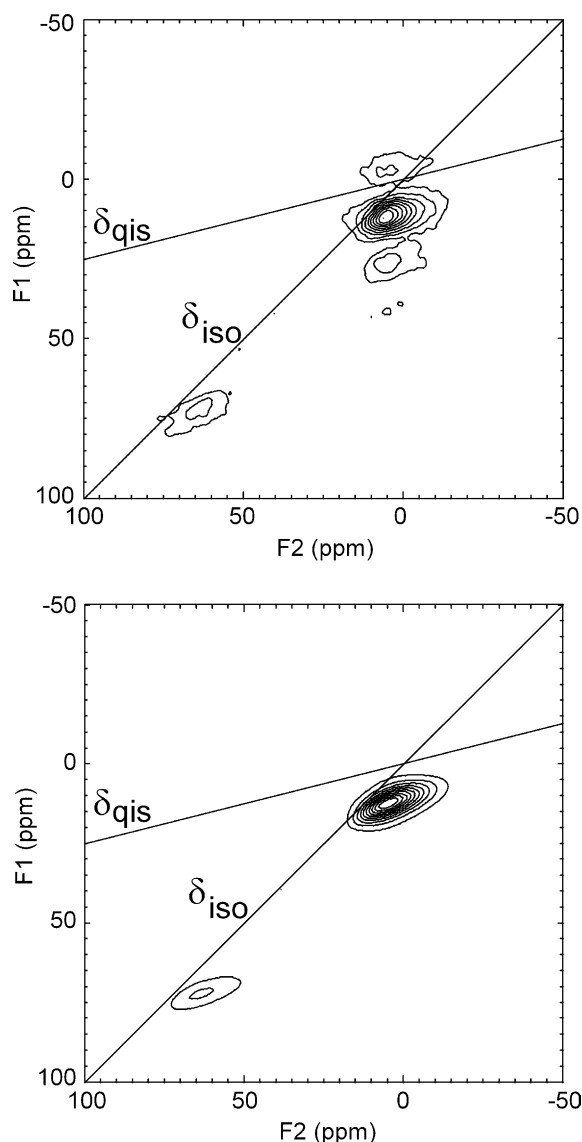
Fig. 5. Experimental (top) and simulated (bottom) ^{27}Al z-filter 3QDOR spectrum of γ-Al$_2$O$_3$ at 9.4 T, giving isotropic resonance lines. The line broadenings can be attributed to a distribution in isotropic chemical shift, parallel to the diagonal, and a distribution in quadrupolar shift, parallel to the quadrupolar induced shift line (see text).

does not imply that Gaussian distributions in the NMR parameters exist. Only simulations based on the structural disorder in γ-Al$_2$O$_3$ can generate the real distributions. Further investigations are needed to establish how sensitive the MQDOR lineshapes are to variations in the actual distribution models that can be expected. In this respect field-dependent measurements can give additional information, as the chemical shift is proportional and the quadrupolar induced shift inversely proportional to the external field, it is possible to attenuate one term with respect to the other by going to either higher or lower field.

A problem of the MQMAS experiment is that it is rather insensitive and this is even more so for the MQDOR experiment. Considerable efforts to improve the efficiency of multiple-quantum experiments were reported concentrat-

ing on the efficiency of the multiple-quantum excitation and multiple to single-quantum conversion [21]. For general spin systems, without previous knowledge of quadrupolar interactions, we propose DFS preparation [22], hard-pulse excitation and DFS conversion [8,9,14] as the optimal scheme. In specific situations, such as $S = 3/2$ spins with similar C_{qcc} values it has been shown that the HS-RIACT-HS pulse scheme gives an astonishingly good performance [23]. So far, due to some technicalities in our setup needing both synchronization of the experiment to the sample rotation and the external device generating the DFS, we implemented an enhanced 3QDOR experiment with only the 3Q-1Q conversion pulse replaced by a DFS. For this DFS it is beneficial to work at higher rf-fields with sweep lengths of tens of μs to avoid problems with relaxation during the experiments. In preliminary experiments using a $v_1 = 85$ kHz rf-field, we obtained an enhancement ~2 for ^{23}Na in Na$_2$SO$_3$ and ^{27}Al ($I = 5/2$) in the mineral sillimanite. Further work is needed to implement the optimally enhanced MQDOR experiment and to quantify its efficiency as a function of quadrupolar frequency over rf-field strength to allow quantitative interpretation of the data.

4. Homonuclear correlation experiments

Homonuclear correlation spectroscopy for mapping out connectivities between quadrupolar nuclei has attracted some attention lately as it is one of the last areas in solid-state NMR that is not so well established. Under MAS conditions spontaneous recovery of homonuclear interactions can occur by interference between quadrupolar and dipolar interactions [24–29] or due to the presence of nearby protons [30,31]. Although such experiments are easy to implement, MQMAS-based 3D-experiments have to be introduced to maintain site specific resolution [32,33]. A good alternative is offered by exchange type experiments, where the dipolar interaction is retained during the mixing time by spinning the sample at angles other than the regular magic angle (54.7°) [34–36]. Using DOR, however, homonuclear correlation can be achieved using a simple 2D-exchange experiment as is shown in Fig. 6 displaying the ^{23}Na homonuclear correlation of Na$_2$SO$_3$. As was described in the previous section this compound has three crystallographically inequivalent sites whose resonances can be assigned on the basis of the MQDOR spectrum. From the spectrum taken with a mixing time of 1 s it is obvious that spontaneous recoupling occurs between all three Na-sites which are all in close proximity in the crystal. Spontaneous recoupling of the three sites has been reported before for this compound [24] and is attributed to quadrupolar-driven recoupling due to dipolar–quadrupolar cross-terms in the Hamiltonian.

As was pointed out by Edén and Frydman [24] it might prove difficult to extract internuclear distances from these data as the recoupling can also be very sensitive to relative tensor orientations. Furthermore, the spontaneous
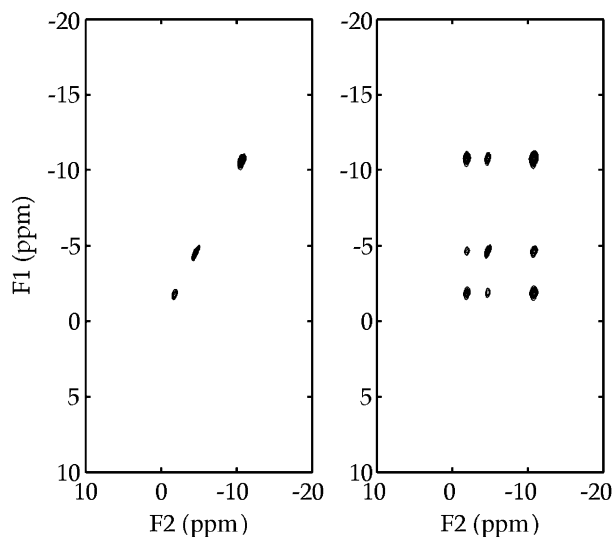
Fig. 6. Two-dimensional DOR exchange spectra of Na_2SO_3 for a mixing time of 10 ms (left) and 1 s (right). The averaging of NMR parameters due to spinning gives well-resolved spectra. At longer mixing times dipolar interactions are still effective (through dipolar–quadrupolar cross-terms in the Hamiltonian) allowing a straightforward determination of homonuclear correlations between the various sites.

recoupling is likely to be quenched if the frequency offsets between the different resonances increases. In that case, one has to resort to rotational resonance [37] or use rf-driven recoupling such as the rotary resonance recoupling which was demonstrated to be successful for quadrupolar nuclei [38–40]. A very promising approach is the recent work by Edén and co-workers [41] showing that it is possible to use pulse-assisted homonuclear dipolar recoupling using symmetry-based R-type pulse sequences [42] in the limit of small rf amplitudes ($v_1 \ll v_Q$). The applicability and efficiency of rf-assisted recoupling in DOR experiments as well as the possibility to extract distance information from DOR exchange spectra will be investigated in detail.

In these correlation experiments, the great advantage of the DOR approach over MQMAS is its higher sensitivity because only single quantum excitations are involved. Furthermore, the lines are isotropic which, besides the desired resolution, gives higher peak intensities. This easily overcomes the drawback of the lower filling factor. Indeed, the overall experiment time of our 2D-exchange experiment compared favorably with our MAS- and OMAS-based experiments for the same compound [35,36]. Finally it can be remarked that, as only the central transition is involved, this experiment lends itself to (repetitive) DFS enhancements as described in the first section.

5. Conclusions

In conclusion, we have demonstrated the great potential of an improved DOR design in combination with sensitivity enhancements using DFSs. The DFS works very well in the operating regime of DOR, needing only low rf-field strengths to bring about substantial S/N improvements.

Enhancements can be increased further by applying the DFS repetitively without allowing for relaxation to occur. Typically, this improves the initial DFS gain by a further factor 1.5. Therefore, DOR experiments become viable for insensitive nuclei.

The increased spinning stability also allows the implementation of two-dimensional NMR experiments that can again be enhanced using amplitude-modulated pulses. The fully isotropic MQDOR experiment allows the determination of chemical shift and quadrupolar product from a single experiment without having to resort to various experiments at different external field strengths. This experiment is especially useful, however, to study the distribution of chemical shift and quadrupolar interaction in disordered compounds as was demonstrated for γ-Al_2O_3. In that case, field-dependent measurements can be of value to verify specific distributions and their possible correlations.

The fact that DOR is the only experiment giving isotropic spectra in real time is of particular value for the implementation of homo- and hetero-nuclear correlation experiments. This saves one dimension and avoids the necessity to go through a multiple-quantum excitation and conversion process to get spectral resolution. As a result, two-dimensional DOR correlation spectra rival the sensitivity of MAS-based experiments as has been demonstrated in a homonuclear correlation experiment for ^{23}Na in Na_2SO_3.

6. Experimental

Na_2SO_3 (Aldrich) and γ-Al_2O_3 (Johnson–Matthey) were commercially obtained and used without any further treatment. Spin–lattice relaxation times (T_1) were determined to be approximately 5 and 1 s for ^{23}Na in Na_2SO_3 and ^{27}Al in γ-Al_2O_3, respectively, as determined by saturation-recovery experiments. The minerals Sillimanite and Amelia Albite were natural samples obtained from the National History museum. The ^{27}Al T_1 in these samples was estimated to be 4.5 and 20 s, respectively.

The DOR system comprised of 9.3 mm outer rotor and 3 mm inner rotor with 23 μL sample volume. The system was operated by four PC controlled compressed gas channels. A proprietary real-time software was interfaced to the controller unit by a standard parallel interface.

DFS enhanced DOR and MQDOR experiments were carried out on a Chemagnetics CMX-400 infinity spectrometer operating at 105.8 MHz for ^{23}Na and 104.2 MHz for ^{27}Al. A PC-based arbitrary waveform generator from National Instruments (DAQArb PCI5411) was used to generate the amplitude modulation for the desired DFSs on a carrier frequency of 14 MHz with a time resolution of 25 ns. This frequency is mixed into the spectrometer as described elsewhere [9,14]. Details of the sweep parameters are given in the text.

For the MQDOR experiments on Na_2SO_3, 102 t_1 experiments were recorded with an increment of 15 μs averaging 192 scans for each t_1 value with a recycle delay of 10 s. A

3-pulse sequence was used, employing a DFS from 0 to 750 kHz with a sweep length of 9.36 μs for 3Q–1Q conversion. The outer rotor was spinning at 1800 Hz and the inner rotor at 7760 Hz. Rotor-synchronized acquisition was implemented in both t_1 and t_2 dimension to suppress odd order sidebands [19,43]. The rf-field strength for the excitation pulse and the DFS was 87 and 13 kHz for the selective refocusing pulse.

The MQDOR experiment on γ-alumina was obtained using a z-filter MQ sequence the excitation and conversion pulse were of 3.5 and 1.25 μs duration, using an rf-field strength of 94 kHz while the z-filter pulse was 3.8 μs at 13 kHz strength. Phase sensitive detection in t_1 was obtained using the States scheme. For each t_1 value 2*960 scans were obtained with a recycle delay of 0.25 s, each time preceded by 24 dummy scans. 100 t_1 experiments were recorded in steps of 10 μs. To suppress odd-order spinning sidebands, the start of t_1 and t_2 were both synchronized with the rotor and alternated by 180°, as is customary in DOR [43].

DOR exchange measurements of Na_2SO_3 were obtained on a Bruker AMX-360 spectrometer operating at 95.2 MHz for ^{23}Na. 96 t_1 experiments were obtained with an increment of 50 μs with 16 scans for each t_1 value using a 10 s of recycle delay. The outer rotor was spinning at 1500 Hz and the inner rotor at 6778 Hz. The acquisition in the t_1 and t_2 dimension were rotor synchronized as described in [19,43]. All processing was done using matNMR [44].

Acknowledgments

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