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Journal of Magnetic Resonance 185 (2007) 318–325
JMR Journal of Magnetic Resonance
www.elsevier.com/locate/jmr

Spin-locking and recoupling of homonuclear dipolar interaction between spin-3/2 nuclei under magic-angle sample spinning

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Received 14 December 2006; revised 9 January 2007
Available online 12 January 2007

Abstract

Numerical simulations and experiments were used to examine the possibility of employing strong spin-lock fields for recoupling of homonuclear dipolar interactions between spin-3/2 quadrupolar nuclei and to compare it to the rotary-resonance recoupling at weak spin-lock fields. It was shown that strong spin-lock pulses under MAS conditions can lead to recoupling, provided that the electric-field gradient principal axes systems of the coupled nuclei are aligned and that their quadrupolar coupling constants are approximately the same. The phenomenon is based on the fact that strong spin-lock pulses induce adiabatic transfer of magnetization between the central-transition coherence and the triple-quantum coherence with equal periodicity as is the periodicity of the time-dependent dipolar coupling. Because of the synchronous variation of the state of the spin system and of the dipolar interaction, the effect of the latter on the central-transition coherence and on the triple-quantum coherence is not averaged out by sample rotation. The approach is, however, very sensitive to the relative orientation of the electric-field gradient principal axes systems and therefore less robust than the approach based on weak spin-lock pulses that satisfy rotary-resonance condition.

Keywords: Quadrupolar nuclei; MAS; Spin-lock; Homonuclear dipolar recoupling

1. Introduction

Homonuclear correlation spectroscopy [1] is one of the key experiments in nuclear magnetic resonance because it can elucidate the geometry of molecules and frameworks in liquids and in solids. High-resolution NMR in solids requires fast magic-angle sample spinning (MAS) in order to suppress broadening due to chemical shielding anisotropy. Because fast spinning usually also suppresses through-space dipole–dipole interactions that carry the required geometrical information, a number of techniques were developed to reintroduce the homonuclear dipolar interaction between spin-1/2 nuclei under MAS [2–9]. Homonuclear correlation spectroscopy for studying connectivities between half-integer quadrupolar nuclei has also attracted considerable attention recently. As opposed to the dipolar coupling between spin-1/2 nuclei, homonuclear dipolar interaction between quadrupolar nuclei is not entirely averaged out by magic angle spinning because of the interference of this interaction with a strong quadrupolar interaction [10–12]. However, while experiments exploiting the residual couplings are not difficult to design, the efficiency of transfer of magnetization between the coupled quadrupolar nuclei is relatively low, especially if dipolar coupling is weak [13,14]. Therefore several other ways were proposed for increasing the 'non-averaged' part of the dipolar interaction. A very elegant approach is based on experiments in which the dipolar interaction is prevented from 'being averaged out' by spinning the sample away from the regular magic angle [15,16]. Such conditions occur, for example, during double orientation rotation experiment, which is a technically challenging method for high-resolution spectroscopy of quadrupolar nuclei and requires a dedicated probe [17]. Alternative approaches

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doi:10.1016/j.jmr.2007.01.008

include pulse assisted homonuclear dipolar recoupling by symmetry-based R-type pulse sequences [18,19] and rotational resonance [20] and rotary resonance driven recoupling [21–25]. The two approaches [23,19] that enable efficient excitation and selection of two-spin double-quantum coherences are particularly interesting because they allow one to analyze homonuclear dipolar couplings even among nuclei, which occupy equivalent sites within solids and contribute to the same spectral line. The methods employ spin-lock pulses with weak radiofrequency (rf) fields that satisfy rotary-resonance condition. Application of weak rf fields, however, introduces substantial sensitivity to frequency offsets. In this contribution we examine the possibility of using strong spin-lock fields for recoupling of homonuclear dipolar interactions between spin-3/2 quadrupolar nuclei and compare it to the rotary-resonance recoupling at weak spin-lock fields. We demonstrate that recoupling introduced in this way is possible, but its efficiency is extremely sensitive to relative orientation of quadrupolar tensors and therefore usually much lower than the efficiency of rotary-resonance driven recoupling.

2. Experimental

All measurements were performed on a 600 MHz Varian NMR system equipped with a 3.2 mm Varian T3 MAS probehead. In all experiments selective 90-degree pulses of 20 μs were used. Rf-field strength of RIACT pulses was approximately 80 kHz. Rf-field amplitude satisfying rotary-resonance condition was set using a simple spin-lock experiment on the Na_2SO_3 sample itself as described in reference [23]. A precise optimization of parameters for the double-quantum homonuclear correlation experiment was also performed on the sample of sodium sulfite itself. This optimization included only fine adjustment of rf-field strength for the excitation and reconversion spin-lock pulses and of the duration of these pulses. Hypercomplex approach was used to provide pure absorption two-dimensional spectra. Simulations were carried out by SIMPSON simulation package [26].

3. Spin-locking of spin-3/2 nuclei under MAS

Spin dynamics of half-integer quadrupolar nuclei differs substantially from the dynamics of spin-1/2 nuclei. The major difference stems from the strong quadrupolar interaction, whose magnitude easily reaches MHz range and thus by at least an order of magnitude exceeds the largest achievable rf fields. Behavior of spin-3/2 nuclei under the spin-lock pulse was thoroughly examined by Vega [27]. In the rotating frame, rotating with a frequency of the applied rf field, a Hamiltonian describing a single spin-3/2 nucleus in an on-resonance case can be written as

$$H = 2\pi\tilde{\nu}_{\mathrm{Q}}(t)(3I_z^2 - I(I+1)) - 2\pi\nu_{\mathrm{rf}}I_x. \quad (1)$$

In an axially symmetric electric field gradient (EFG) the time-dependent quadrupole frequency is

$$\tilde{\nu}_{\mathrm{Q}}(t) = \frac{1}{12}\nu_{\mathrm{Q}}(3\cos^2\theta_{\mathrm{Q}}(t) - 1) = \frac{1}{12}\nu_{\mathrm{Q}}(G_1\cos(2\pi\nu_{\mathrm{R}}t) + G_2\cos(4\pi\nu_{\mathrm{R}}t)), \quad (2)$$

with $\nu_{\mathrm{Q}} = 3e^2qQ/2I(2I-1)h$ and

$$G_1 = \frac{3}{2}\sin 2\theta_{\mathrm{m}}\sin 2\beta_{\mathrm{Q}}, \quad G_2 = -\frac{3}{2}\sin^2\theta_{\mathrm{m}}\sin^2\beta_{\mathrm{Q}}. \quad (3)$$

The polar angles $\theta_{\mathrm{Q}}(t)$ and β_{Q} describe the orientation of EFG principal axes system within laboratory and MAS frames, respectively, and θ_{m} is the magic angle. Magic angle spinning causes $\tilde{\nu}_{\mathrm{Q}}$ to oscillate between positive and negative values. As shown in Fig. 1, $\tilde{\nu}_{\mathrm{Q}}$ can experience two or four zero-crossing within one period of rotation. Because of rotation the magnitude of the quadrupolar splitting $|\tilde{\nu}_{\mathrm{Q}}|$ thus continuously varies between very large

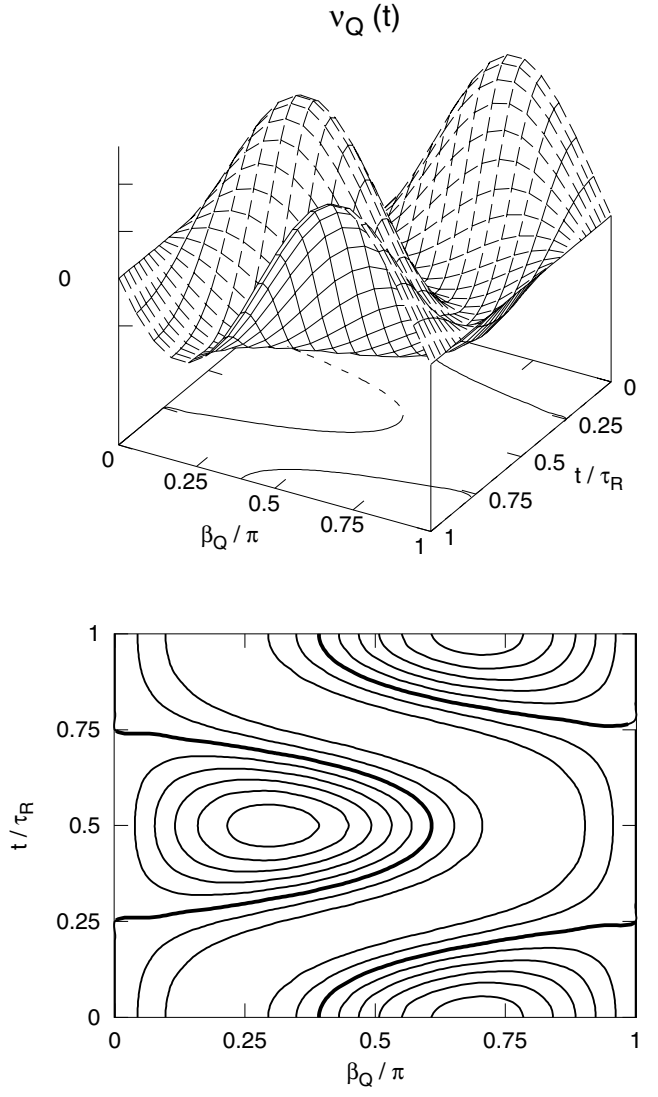

Fig. 1. Time-dependent quadrupolar splitting $\tilde{\nu}_{\mathrm{Q}}(t)$ as a function of time and of the orientation of EFG principal axes system in the MAS frame. Thick lines in the bottom plot connect points with $\tilde{\nu}_{\mathrm{Q}}(t) = 0$. For simplicity only axially symmetric EFG is considered ($\eta_{\mathrm{Q}} = 0$).

and very small values, i.e. it varies between $|\tilde{\nu}_Q| \gg \nu_{rf}$ and $|\tilde{\nu}_Q| \ll \nu_{rf}$. Since eigenstates and eigenvalues of the Hamiltonian (1) depend on the magnitude of the quadrupolar splitting, they also continuously (periodically) vary in the course of sample rotation [27].

Time-changing of eigenstates and eigenvalues of Hamiltonian (1) has a profound effect on the spin locking of the central-transition coherence. As discussed by Vega [27], a central-transition coherence can be described as a population of appropriate wave functions, eigenstates of Hamiltonian (1) for $|\tilde{\nu}_Q| \gg \nu_{rf}$. When eigenstates change because of MAS, other wave functions become populated, which means that the initial central-transition coherence is transferred to other coherences and that spin-locking can be lost. The efficiency of the spin locking is crucially determined by the rate at which eigenstates change, that is by the rate of the passages from positive to negative $\tilde{\nu}_Q$. The rate of the passages is described by the parameter $\alpha = \nu_{rf}^2/\nu_Q\nu_R$. When $\alpha \gg 1$, i.e. when the applied rf field is strong, the zero crossings are slow and described as adiabatic. In this limit the eigenstates of the Hamiltonian adiabatically change in time and the initial central-transition coherence is periodically demagnetized and remagnetized, giving rise to an echo-like time dependence of the spin-locking signal. The reduced density matrix oscillates between the central-transition (I_x^{23}) and the triple-quantum coherence (I_x^{14}):

$$\sigma(t) \rightarrow I_x^{23} \rightarrow I_x^{14} \rightarrow I_x^{23} \rightarrow I_x^{14} \rightarrow . \quad (4)$$

This rotor-driven interconversion is the basis of the RIACT (Rotation-Induced Adiabatic Coherence Transfer) phenomenon used for the excitation and reconversion of multiple-quantum (MQ) coherences in some MQMAS experiments [28]. When $\alpha \ll 1$, i.e. when the applied rf field is weak, the passages are characterized as sudden. In this limit zero crossings are so fast that the eigenstates cannot follow changes in the Hamiltonian (1) and the initial central-transition coherence is not affected by sample rotation:

$$\sigma(t) \rightarrow I_x^{23} \rightarrow I_x^{23} \rightarrow I_x^{23} \rightarrow I_x^{23} \rightarrow . \quad (5)$$

In the intermediate regime the spin-locking efficiency is reduced.

Characteristics of spin-locking of quadrupolar spin-3/2 nuclei are experimentally demonstrated for ^{23}Na nuclei of Na_2SO_3 and presented in Fig. 2. As we can see, the signal of the central-transition coherence is highest when very weak spin-lock pulses with $\nu_{rf} < \nu_R$ are used. When the strength of spin-lock field is comparable to the sample rotation frequency, the signal amplitude is the lowest. At stronger rf fields the spin-lock signal again starts to increase, but it does not reach the signal that was obtained by weak spin-lock fields. The evolution of the central-transition coherence in the presence of a strong and a weak spin-lock pulse confirms predictions of expressions (4) and (5), respectively. Whereas in case of a weak spin-lock pulse the central-transition coherence decays slowly and smoothly, in case of a strong spin-lock pulse it exhibits oscillatory behavior.

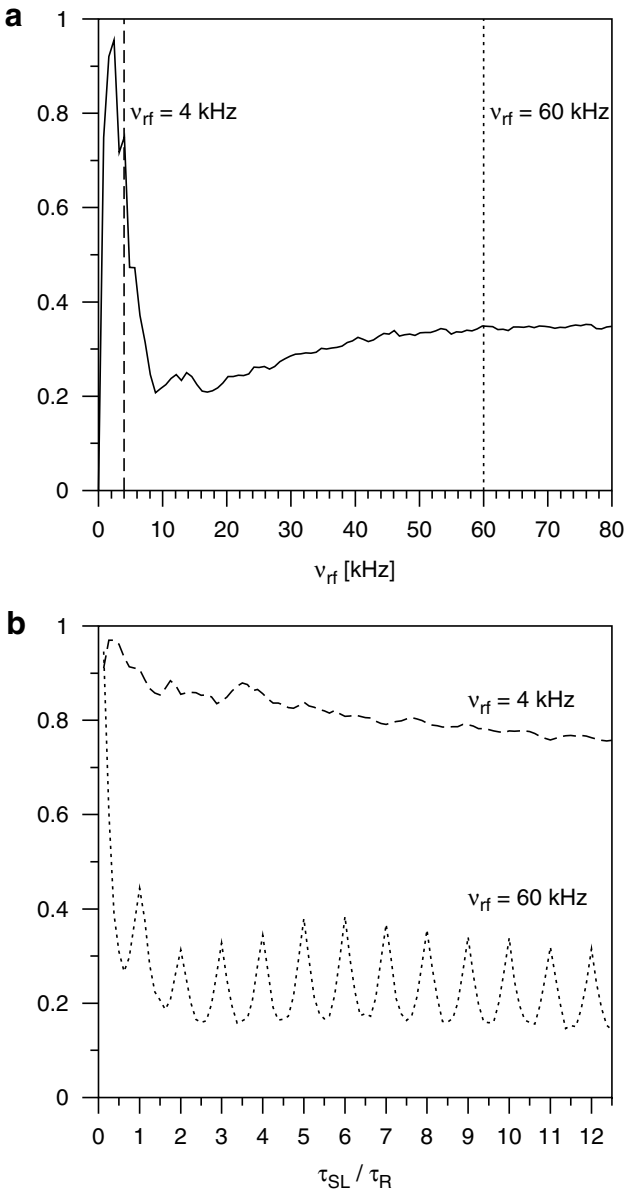

Fig. 2. Results of ^{23}Na spin-lock experiments in Na_2SO_3: (a) amplitude of the central-transition coherence signal as a function of the strength of 1.2 ms long spin-lock pulse, and (b) evolution of spin-locked central-transition coherence signal in time recorded by employing variable-duration spin-lock pulses with either strong (dotted) or weak (dashed) rf field. Strengths of weak and strong spin-lock pulses that were employed in (b) are indicated in plot (a) by a dashed and a dotted vertical line, respectively. Sample rotation frequency was 12.5 kHz. Signal amplitude 1 corresponds to the amplitude of a signal obtained by a single-pulse experiment (or spin-lock experiment with $\tau_{SL} = 0$).

The period of oscillations is equal to the period of sample rotation.

4. Recoupling of homonuclear dipolar interaction during spin-lock pulse

Let us now consider a pair of dipolar-coupled quadrupolar spin-3/2 nuclei. The dipolar interaction between them can be described by

$$H_{\mathrm{D}} = 2\pi\tilde{\nu}_{\mathrm{D}}(t)(3I_zS_z - \vec{I}\cdot\vec{S}), \tag{6}$$

where a time-dependent magnitude of the dipolar coupling has a similar time dependence as the quadrupolar splitting:

$$\tilde{\nu}_{\mathrm{D}}(t) = \nu_{\mathrm{D}}(G_1\cos(2\pi\nu_{\mathrm{R}}t) + G_2\cos(4\pi\nu_{\mathrm{R}}t)). \tag{7}$$

Here $\nu_{\mathrm{D}} = \mu_0\gamma^2\hbar/16\pi^2r_{IS}^3$ is the dipole frequency, and G_1 and G_2 are constants that depend on the polar angle β_{D} describing the angle between the internuclear vector $\vec{r}_{IS}$ and the MAS axis.

The spin-lock experiment presented in the previous section suggests that quadrupolar nuclei behave very similar to spin-1/2 nuclei when only pulses of weak rf fields are used. Pulses of weak rf fields manipulate only central transitions of quadrupolar nuclei and thus allow us to describe them as fictitious spin-1/2 nuclei. Such a description is for example valid for the rotary-resonance approach to homonuclear correlation experiment for half-integer quadrupolar nuclei. This approach predicts that the dipolar interaction within the rf interaction frame becomes time-independent when strength of the rf field during spin-lock pulse satisfies the following condition:

$$\nu_{\mathrm{nutation}} = (I + 1/2)\nu_{\mathrm{rf}} = \nu_{\mathrm{R}}/2. \tag{8}$$

In other words this means that under the rotary-resonance conditions homonuclear dipolar interaction is recoupled. A more detailed discussion can be found in references [21–23].

In the presence of strong rf fields the description of a spin system can no longer be limited to central transitions only, therefore an exact consideration of a quadrupolar interaction, rf field and dipolar interaction is very demanding. Qualitatively, however, we can gain an insight into the spin dynamics of the pair of coupled spin-3/2 nuclei in the presence of MAS and a strong spin-lock pulse simply by taking a look at Fig. 3. The figure shows evolution of central-transition and triple-quantum coherences in the presence of a strong spin-lock pulse, and time dependency of the two oscillatory components of the dipolar coupling, $\cos(2\pi\nu_{\mathrm{R}}t)$ and $\cos(4\pi\nu_{\mathrm{R}}t)$. If we assume that the dipolar coupling is weak compared to the quadrupolar interaction and the magnitude of the rf field, which is usually the case, we can expect that the evolution of the reduced density matrix $\sigma(t)$ shall still be predominantly governed by the latter two interactions. As we have already learned, they will introduce a periodic transfer of spin-population between the central-transition and the triple-quantum coherences

$$\sigma(t) \rightarrow I_x^{23} + S_x^{23} \rightarrow I_x^{14} + S_x^{14} \rightarrow I_x^{23} + S_x^{23} \rightarrow . \tag{9}$$

Dipolar coupling will act as a weak time-dependent perturbation to the evolution of the spin system and because the perturbation will change in time with the same period as the density matrix, its action on the central-transition coherence $I_x^{23} + S_x^{23}$ (and on the triple-quantum coherence $I_x^{14} + S_x^{14}$) will not be averaged out over a rotation period.

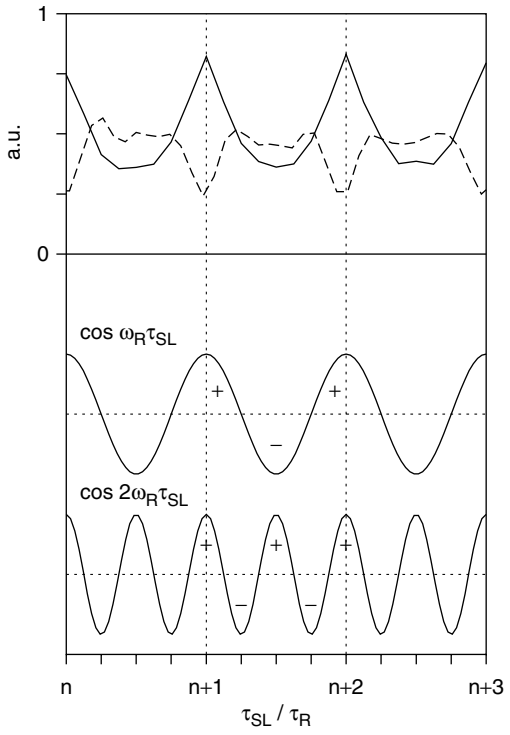

Fig. 3. Evolution of ^{23}Na central-transition (solid) and triple-quantum (dashed) coherences under adiabatic spin-lock conditions (powder average, $\nu_{\mathrm{Q}} = 590$ kHz, $\eta_{\mathrm{Q}} = 0$) and time dependency of two components of the homonuclear dipolar interaction.

We may therefore expect that a simple strong spin-lock pulse could also induce recoupling of homonuclear dipolar interaction.

A more informative analysis of the influence of a strong spin-lock pulse on the homonuclear dipolar coupling can be obtained by numerically simulating spin dynamics of a pair of coupled spin-3/2 nuclei. The results of simulations are shown in Fig. 4. In all simulations the initial state was I_x^{23} and the transfer of magnetization to S_x^{23} was studied (i) in the presence of a strong spin-lock pulse (a RIACT pulse) and (ii) in the presence of a weak spin-lock pulse that satisfies rotary-resonance condition (a RR pulse). In simulations the quadrupolar parameters of the coupled spin pair were first limited to $\nu_{\mathrm{Q}}^I = \nu_{\mathrm{Q}}^S$ and $\beta_{\mathrm{Q}}^I = \beta_{\mathrm{Q}}^S$ (aligned principal axes systems of the two EFG tensors). We can see that within these limitations the transfer amplitude of the RIACT pulse is as high as the transfer amplitude of the RR pulse. Moreover, the magnitude of the recoupled dipolar interaction, indicated by the slope of the buildup of the S_x^{23} magnetization, is even by a factor of 2 larger for the RIACT pulse than for the RR pulse. However, the above described conditions are exceptional, because quadrupolar parameters of the coupled nuclei are rarely (nearly) identical. By inspecting Fig. 1 we can expect that the efficiency of recoupling during the RIACT pulse will depend a lot on the relative orientation of the two principal axes systems of the two EFG tensors. If these two systems

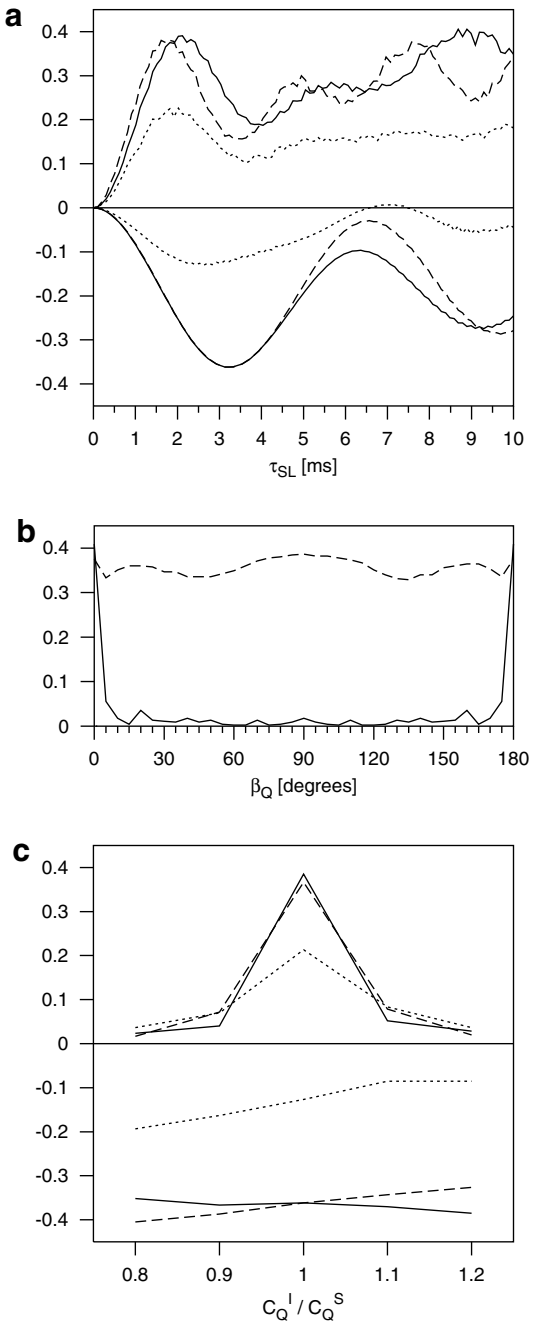

Fig. 4. Numeric simulations of the transfer of magnetization from spin I to spin S in a dipolar-coupled $I-S$ spin system ($I=S=3/2$, $b_{IS}=-158$ Hz, $\nu_R=10$ kHz). (a) Transfer amplitude, $\mathrm{Tr}\{\sigma(t)S_x^{23}\}/\mathrm{Tr}\{\sigma(0)I_x^{23}\}=\mathrm{Tr}\{\sigma(t)S_x^{23}\}/\mathrm{Tr}\{(I_x^{23})^2\}$, as a function of the length of a RIACT pulse (positive amplitudes, $\nu_{rf}=100$ kHz) or of a RR pulse (negative amplitudes, $\nu_{rf}=2.5$ kHz). The EFG principal axes systems of spin I and S were assumed to be colinear and quadrupole coupling constants to be equal ($\nu_Q^{I,S}=0.5$ MHz, solid line; 1 MHz, dashed line; 1.5 MHz, dotted line, $\eta_Q^{I,S}=0$). (b) Transfer amplitude as a function of β_Q that describes relative orientation of EFG principal axes systems of spin I and S (RIACT-driven, solid line; RR-driven, dashed line). (c) Dependency of the transfer amplitude to the mismatch in the quadrupolar coupling constants. Positive values correspond to RIACT-driven transfer and negative values to RR-driven transfer ($\nu_Q^S=0.5$ MHz, solid line; 1 MHz, dashed line; 1.5 MHz, dotted line). EFG systems were colinear.

are not aligned, the $I_x^{23}\rightarrow I_x^{14}$ and $S_x^{23}\rightarrow S_x^{14}$ transfers will not occur synchronously and we can expect that the recoupling efficiency will be reduced. Indeed simulations, in which different orientations of the EFG PAS systems or different quadrupolar couplings are inspected, show that recoupling based on the RIACT pulse is extremely sensitive to the orientation and in a slightly smaller extent also to the mismatch in the quadrupolar coupling constants. On the contrary, recoupling based on RR proves to be very robust, almost independent on the relative orientation of the two systems and also much less affected by the mismatch in the quadrupolar coupling constants.

Experimentally, the performance of the RIACT and the RR pulse was tested on the sample of Na_2SO_3. Sodium ions within Na_2SO_3 occupy three inequivalent sites, Na_1, Na_2, and Na_3 with ν_Q of 530, 230, and 590 kHz, respectively [29]. Measured and simulated ^{23}Na MAS spectra are shown in Fig. 5. Crystal symmetry requires that quadrupolar asymmetry parameter η_Q is equal to zero for all three sites and, moreover, that all three EFG principal axes systems are equally oriented [29]. The pulse sequences that we had used are presented in Fig. 6. In all experiments the transverse magnetization associated with the central-transition coherence was first excited and allowed to evolve for time t_1. Before the detection of the signal, a mixing period with either RR or RIACT pulse enabled the exchange of magnetization among the coupled nuclei. A z-filter removed unwanted coherences. The rf-driven transfer of magnetization was compared also to the transfer of magnetization because of spontaneous recoupling. For this purpose, after the t_1 evolution, the transverse magnetization was stored as longitudinal magnetization and the spontaneous transfer of longitudinal magnetization occurred during the subsequent mixing period.

The resulting two-dimensional spectra obtained by the three different pulse sequences are shown in Fig. 7 and the traces selected from these spectra are presented in Fig. 8. With a mixing time of 2.4 ms, RR-based recoupling is the most efficient among the three different approaches. The corresponding two-dimensional spectrum exhibits two cross-peaks, Na_1–Na_3 and Na_2–Na_3, with negative amplitudes. A Na_1–Na_2 cross-peak cannot be detected,

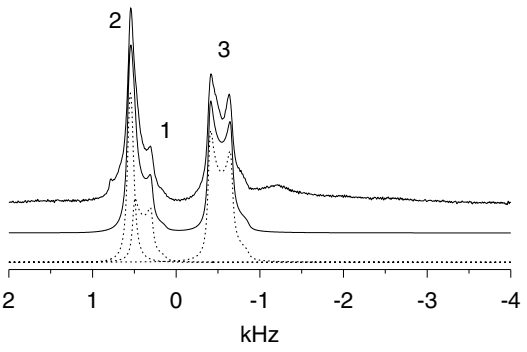

Fig. 5. Measured and simulated ^{23}Na MAS spectra of Na_2SO_3.

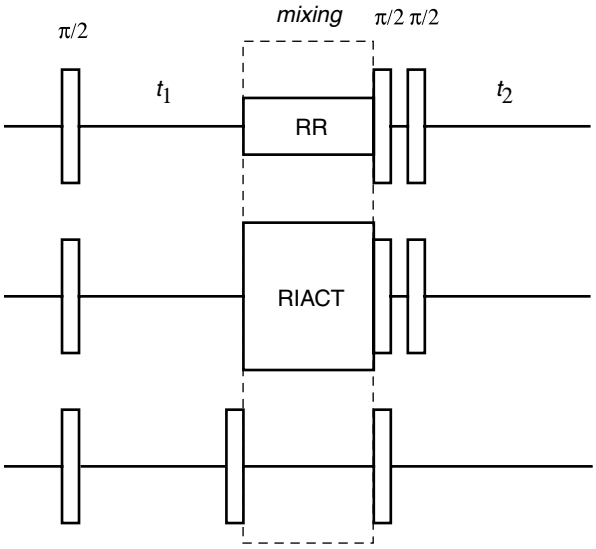

Fig. 6. Pulse sequences that were used for the investigation of the rf-driven (RR and RIACT) and spontaneous homonuclear dipolar recoupling. The first two sequences employ a z-filter to remove unwanted coherences.

because it overlaps with much stronger diagonal peaks of Na_1 and Na_2 nuclei. The two-dimensional correlation spectrum obtained by RIACT-based recoupling exhibits only Na_1–Na_3 cross-peak. Quadrupolar coupling constants for sites Na_2 and Na_3 are quite different so, according to the numerical analysis presented in Fig. 4, the efficiency of recouplig and thus the efficiency of transfer of magnetization between Na_2 and Na_3 is expected to be severely reduced. The traces in Fig. 8 show that the relative intensity of the Na_1–Na_3 cross-peak, compared to the diagonal peak, in the RIACT-based correlation experiments increases with mixing times increasing from 0.4 to 4.8 ms. Spontaneous recoupling in Na_2SO_3 is relatively strong. In case of 2.4 ms long mixing time the cross-peak cannot be detected yet, but with 10 times longer mixing time the cross-peak is noticeable.

Results of experiments confirm the predictions based on qualitative arguments and numerical analysis. Recoupling of homonuclear dipolar interaction between spin-3/2 quadrupolar nuclei in the presence of a RIACT pulse is possible, but it is extremely sensitive to the orientation of quadrupolar tensors and to the magnitude of the quadrupolar coupling. The experiments performed are very simple and the two-dimensional correlation spectroscopy is very fast. With the exception of the RR based experiment, the presented homonuclear correlation spectroscopy required no optimization. The total experimental time of a typical two-dimensional experiment was 85 min. A known drawback of the type of experiments presented here, however, is their inability to detect homonuclear correlations between nuclei that occupy crystallographically equivalent sites, i.e. Na_1–Na_1, Na_2–Na_2, and Na_3–Na_3 correlations. As already mentioned,

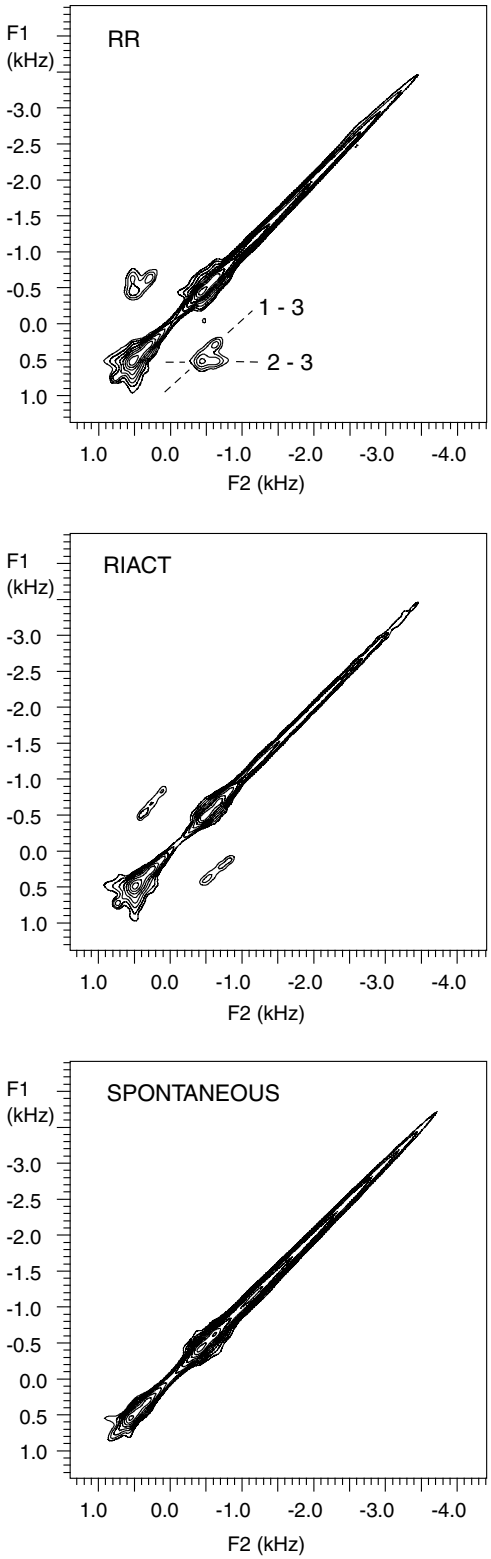

Fig. 7. ^{23}Na homonuclear correlation spectra of Na_2SO_3 measured by the three different pulse sequences of Fig. 6. Mixing time for all three experiments was 2.4 ms, number of scans was 16, number of increments in the indirectly detected dimension was 320, the repetition delay was 0.5 s, and sample rotation frequency was 12.5 kHz.

the problem can be circumvented by the double-quantum correlation experiment based on the rotary-resonance excitation and reconversion [23,19]. The experiment is

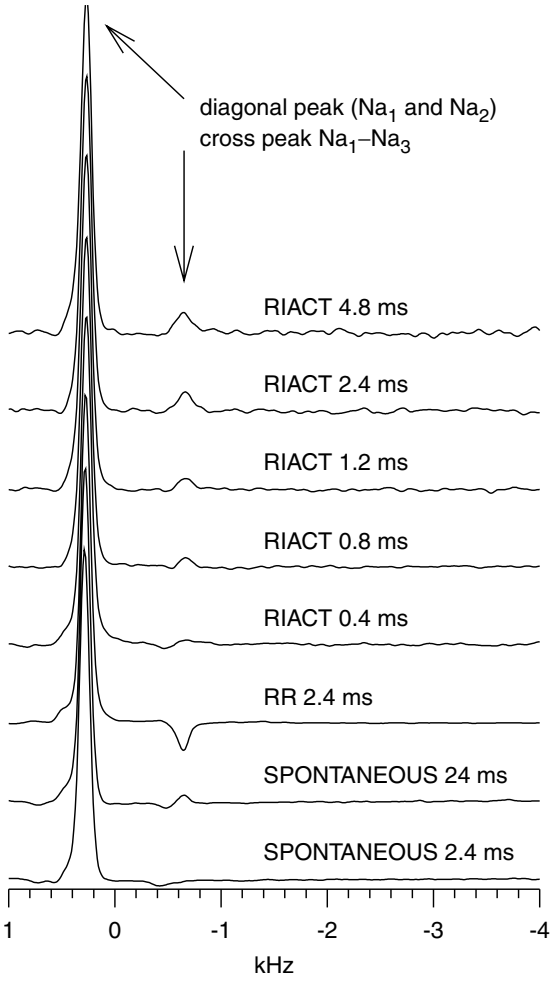

Fig. 8. Selected traces extracted from two-dimensional ^{23}Na homonuclear correlation spectra of Na_2SO_3. The length of mixing times and the type of experiment are indicated.

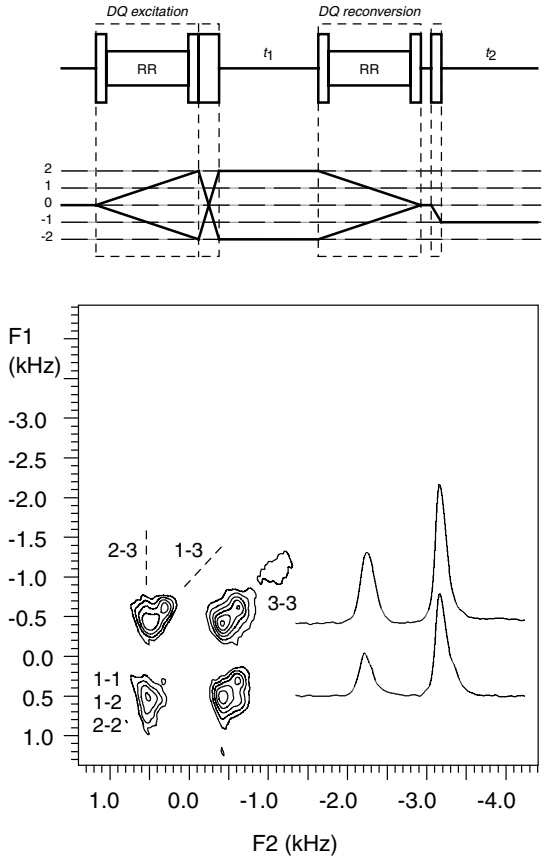

Fig. 9. Pulse sequence for the double-quantum homonuclear correlation experiment and corresponding ^{23}Na two-dimensional spectrum of Na_2SO_3. Number of scans was 128, number of increments in indirectly detected dimension was 256, repetition delay was 1 s, sample rotation frequency was 12.5 kHz, and duration of spin-lock pulses for the excitation and reconversion of double-quantum coherences was 640 μs.

technically more demanding and more time consuming, but clearly superior for studying homonuclear correlations. 'Diagonal peaks' of double quantum spectra appear only when nuclei that occupy equivalent sites are coupled. Furthermore, in these spectra intensities of all peaks at least qualitatively reflect the effective dipolar couplings between the nuclei.

An example of ^{23}Na double-quantum homonuclear correlation spectrum of Na_2SO_3 is presented in Fig. 9. For easier comparison to the two-dimensional spectra that were presented above, the double-quantum spectrum is sheared. The intensities of peaks within the spectrum indicate that couplings between Na_1–Na_3, Na_2–Na_3, and Na_3–Na_3 are strong, and couplings between Na_1–Na_1, Na_1–Na_2, and Na_2–Na_2 are weak. This is in agreement with known structure of Na_2SO_3—with the distances between the sodium nuclei and with the number of neighbors surrounding a particular crystallographic site. Thus the double-quantum experiment indeed provides a better and easier analysis of couplings and proximities in the network of spin-3/2 nuclei.

5. Conclusions

Application of strong spin-lock pulses under MAS conditions can lead to recoupling of the homonuclear dipolar interaction between quadrupolar spin-3/2 nuclei, provided that the EFG principal axes systems of the coupled nuclei are aligned and that their quadrupolar coupling constants are approximately the same. The phenomenon is based on the fact that strong spin-lock pulses induce adiabatic transfer of magnetization between the central-transition coherence and the triple-quantum coherence with equal periodicity as is the periodicity of the time-dependent dipolar coupling. Because of the synchronous variation of the state of the spin system and of the dipolar interaction, the effect of the latter on the central-transition coherence and on the triple-quantum coherence is not averaged out by sample rotation. The approach is, however, not very useful for the application in homonuclear recoupling experiments, except if one wants to verify the alignment of the EFG principal axes systems, because it is too sensitive to the relative orientation of these systems. A much more robust approach is

the one that is based on weak spin-lock pulses satisfying rotary-resonance condition, which can be employed also in elegant double-quantum homonuclear correlation experiments.

Acknowledgment

This work was supported by the Slovenian Research Agency research program J1-6350.

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