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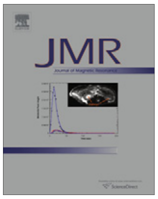

Efficient rotational echo double resonance recoupling of a spin-1/2 and a quadrupolar spin at high spinning rates and weak irradiation fields

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ABSTRACT

A modification of the rotational echo (adiabatic passage) double resonance experiments, which allows recoupling of the dipolar interaction between a spin-1/2 and a half integer quadrupolar spin is proposed. We demonstrate efficient and uniform recoupling at high spinning rates (ν_r), low radio-frequency (RF) irradiation fields (ν_1), and high values of the quadrupolar interaction (ν_q) that correspond to values of $\alpha\ (= \nu_1^2/\nu_q\nu_r)$, the adiabaticity parameter, which are down to less than 10% of the traditional adiabaticity limit for a spin-5/2 ($\alpha = 0.55$). The low-alpha rotational echo double resonance curve is obtained when the pulse on the quadrupolar nucleus is extended to full two rotor periods and beyond. For protons (spin-1/2) and aluminum (spin-5/2) species in the zeolite SAPO-42, a dephasing curve, which is significantly better than the regular REAPDOR experiment (pulse length of one-third of the rotor period) is obtained for a spinning rate of 13 kHz and RF fields down to 10 and even 6 kHz. Under these conditions, α is estimated to be approximately 0.05 based on an average quadrupolar coupling in zeolites. Extensive simulations support our observations suggesting the method to be robust under a large range of experimental values.

1. Introduction

Measuring an accurate distance or obtaining proximity information between atoms in a molecule is one of the basic goals of chemical and physical sciences. It has been realized years ago, that such information can be obtained using magic-angle spinning solid-state NMR of powdered samples by selectively recoupling the magnetic dipolar interaction between two adjacent spins. The REDOR experiment (Rotational Echo Double Resonance [1]) presented by Gullion and Shaefer more than 20 years ago provided an elegant and accurate way to measure the distance between two isolated spin-1/2 nuclei. In this experiment, two π pulses are applied synchronously every rotor period, thus recoupling the dipolar interaction while decoupling the anisotropic chemical shift terms. Problems arising from the existence of multiple coupled spins or motion have been treated by a more complex analysis of the REDOR dephasing curves [2], and by various types of selective REDOR experiments [3–5]. An analytical solution for the REDOR curve also exists [6], and the REDOR curve can be transformed using a special kernel function to produce a spectrum presenting the distribution of the dipolar frequencies [7]. Although REDOR is extremely useful and has been used in hundreds of applications, a large portion of the periodic table consists of atoms with a spin quantum number larger than one-half. Many of these spins are of interest in wide areas of research ranging medical applications, nanomaterials, non-crystalline materials, metalloenzymes and more. Examples are numerous: ^{17}O, ^{27}Al, ^{11}B, ^{51}V, ^{67}Zn, ^{43}Ca, ^{2}H, ^{14}N, ^{23}Na, ^{31}K, and others. All these spins posses a nuclear quadrupole moment and therefore a magnetic quadrupolar interaction (provided that the electric field gradients do not vanish). The quadrupolar interaction splits the $2S + 1$ energy levels of a spin S to a central band and satellites in the case of half integer spins, and to two satellites in the case of a spin-1 (^{14}N, ^{2}H). For the case where the radio-frequency (RF) irradiation ν_1 is larger than the quadrupolar frequency ν_q, the REDOR sequence can be used just as in the case of two isolated spin ½ nuclei. This is the normally achievable for ^{7}Li [8] (spin-3/2) and ^{133}Cs [9] (spin-7/2). However, mostly the RF power is too weak to affect all transitions in a quadrupolar spin uniformly, and thus the REDOR dephasing becomes a complex function of the quadrupolar frequency, the dipolar interaction and their relative orientation. This behavior stems from the fact that the π pulse on the quadrupolar nucleus does not achieve the required inversion of the spin states $|m\rangle$ to $|-m\rangle$, or in a density matrix notation, $S_z \rightarrow -S_z$. Consequently, the dephasing becomes less efficient. It is possible to solve the problem of functional complexity by irradiating selectively on the central transition of a half integer quadrupolar spin ($\nu_1 \ll \nu_q$), inverting the population difference of the quantum states $|1/2\rangle$ and $|-1/2\rangle$ while keeping all other spin states unchanged. However, the extent of dephasing is reduced to $(S + 1/2)^{-1}$, so for a spin $S = 3/2$ only half the signal of the de-

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tected spin will be affected by the dipolar interaction, and for a spin-5/2 this number drops to one third [10]. Obviously for weak couplings, this behavior is a major drawback. It was then realized that by inducing adiabatic level anti-crossings via the combined effect of the RF irradiation, the sample spinning and the quadrupolar interaction [11], efficient dephasing can be achieved. The first experiment to exploit this fact utilized a long dephasing pulse applied to the quadrupolar spin while a regular spin echo experiment is performed on the detected spin-1/2. This experiment is termed TRAPDOR (transfer of populations in double resonance [12,13]) and has also been widely used. In addition to inter-nuclear distance measurements with TRAPDOR (which depends heavily on the size of the quadrupolar frequency and on its orientation with respect to the dipolar vector orientation), the experiment has also been used to indirectly measure the quadrupolar interaction of the S spin via modulation of the RF offset value [14]. It was realized that TRAPDOR has several drawbacks, among them the requirement for very long irradiation times and an induced phase shift on the detected spin-1/2. Gullion presented a modification of TRAPDOR which combined the ideas of level anti-crossing with the REDOR concept [15]. In this new experiment termed REAPDOR (rotational echo adiabatic passage double resonance) the two π pulses are applied every rotor period to the detected spin-1/2, similarly to REDOR, however the middle pulse is omitted and applied to the quadrupolar spin in the form of an adiabatic long pulse of approximately one-third of the rotor period. As a result, efficient dephasing is obtained that overcomes many of the drawbacks of TRAPDOR. It was later shown that if sufficient care is taken in the choice of parameters for the REAPDOR experiment, a universal curve can be devised, that is independent on the quadrupolar interaction and its orientation, and therefore a single fit parameter, the dipolar interaction D, is required to fit the experimental data [16,17]. It was demonstrated for example that for a spin-1/2 coupled to a spin-1, a curve of the form $\frac{\Delta S}{S_0}(\lambda) = 0.6(1 - e^{-(1.47\lambda)^2})$, where $\lambda = nDv_r^{-1}$ describes the dipolar interaction accurately up to a 15% error in D, or 4% error in the inter-nuclear distance r. The limitations on such an experiment are that only the initial rise of the curve can be used for the fit (up to values of $\lambda_{\max} \sim 0.7$) and that the adiabaticity parameter $\alpha = v_1^2/(v_q v_r)$ must be larger than 0.25. Only a rough estimation of v_q is needed for the determination of the experimental parameters, stemming from its appearance in the adiabaticity term α. A similar curve was devised [17] for a quadrupolar spin-5/2, however a different functional dependence was obtained, and the values of α (>0.55) and $\lambda_{\max}$ (<0.5) required are somewhat different. Because the curve is universal, it was shown that performing multiple experiments at various spinning rates provided data points that fit to the universal curve, and therefore increase the reliability of the experiment [17]. A couple of applications have demonstrated the usefulness of this approach [18,19]. Recently, an approach that combines rotary resonance recoupling (R^3) and spin–polarization–inversion (SPI–R^3) with TRAPDOR has been proposed [35]. In this approach, irradiation at the R^3 condition of the central transition ($v_1 = nv_r/(2S+1)$) allows the usage of relatively low RF fields, and a hyperbolic fit of the initial recoupling curve (up to $\lambda \sim 0.2$) allows a fit of the second moment and therefore the dipolar couplings. Data was demonstrated for two representative zeolites and RF values of 3.3 kHz were used at a MAS rate of 10 kHz, pertaining to the R^3 condition $3v_1 = v_r$.

In this manuscript we address the following question: Can the REDOR/REAPDOR approach be utilized when the adiabaticity condition is not fulfilled? When α values decrease, the extent of dephasing using REAPDOR will start deviating from universal behavior and eventually diminish as the sudden-passage ($v_1 \ll v_q$) limit is approached. Here we demonstrate that by significantly extending the $Tr/3$ adiabatic inversion pulse in the REAPDOR experiment, we are able to induce efficient recoupling even under very low values of the adiabaticity parameter α. The recoupling is shown by simulations to be weakly dependent on experimental parameters for a significant range of α, and is not limited to R^3 conditions. Moreover, the recoupling curves approach the universal curve at short times, and overtake it at the longer times.

2. Materials and methods

2.1. Pulse sequence

The pulse sequences for REAPDOR, and its modification Low-Alpha (LA) REDOR, are drawn in Fig. 1. The spin-1/2 excitation is presented by a $\pi/2$ pulse (narrow black rectangle), however, it can be replaced with a suitable cross-polarization scheme if required. The π recoupling pulses are applied every half rotor period (indicated by the horizontal lines) and the single long inversion pulse on the quadrupolar nucleus is indicated in the S channel. For REAPDOR it is an adiabatic pulse extending one-third of the rotor period Tr, and for LA-REDOR, two full rotor periods (at least) are used for recoupling (shadowed area). During this pulse, the π pulses on the spin-1/2 nucleus are still active.

2.2. Experimental parameters

All experiments have been performed on a 600WB Avance-III Bruker spectrometer using a triple-resonance 4 mm WB probe. The probe was shimmed by monitoring the Adamantane ^{13}C linewidth (using 500 ms acquisition, a linewidth of 2.5 Hz was obtained). The RF intensities for the ^{27}Al channel were calibrated using a 50 mM $AlCl_3$ solution. REAPDOR and LA-REDOR experiments were performed at RF power levels ranging 6–50 kHz for ^{27}Al and at 100 kHz for ^1H. The spinning rate was set to 12 or 13 kHz. Data processing was performed using topspin2.1 and further analyzed using MATLAB®.

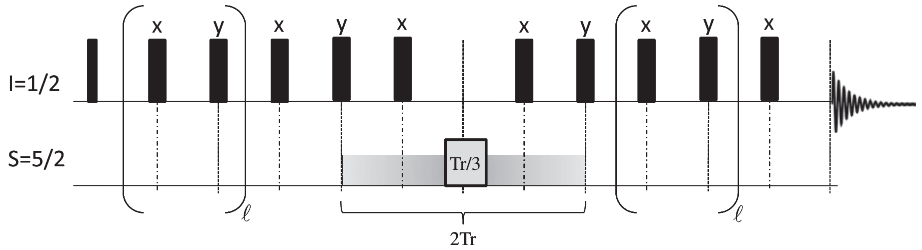

Fig. 1. Rotational echo adiabatic passage double resonance and the low-alpha version of the experiment LA-REDOR. The $\pi/2$ pulse excitation of the $I = 1/2$ spin is presented by the narrow bar, and may be replaced with a proper cross-polarization scheme. The π pulses on this channel follow the XY8 scheme [38] and are applied every half rotor period, with the exception of the middle pulse. This pulse is replaced with a long inversion pulse with a constant phase on the quadrupolar spin ($S = 5/2$). Its length is $Tr/3$ in the case of REAPDOR, and at least $2Tr$ in the case of LA-REDOR.

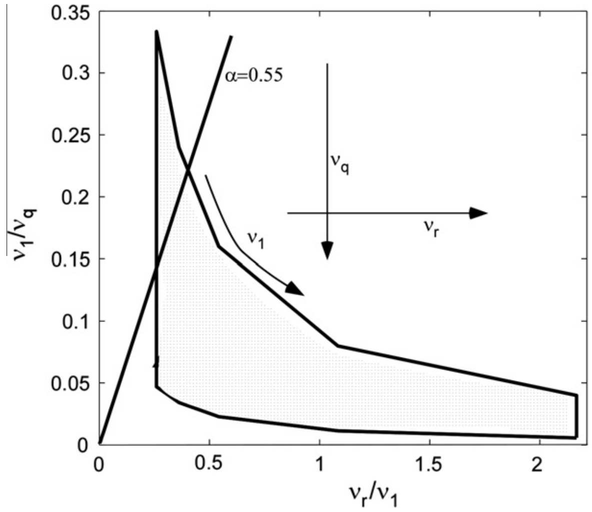

Fig. 2. Experimental and simulation parameters used in this study. The region on the left of the $\alpha = 0.55$ line represents the usable parameters of the REAPDOR experiment. The enclosed area represents the demonstrated range for the modified experiment LA-REDOR. Trends for modifications of the quadrupolar coupling, rotor spinning speed and RF irradiation frequency are indicated by the arrows.

2.3. Materials

All data were collected on a SAPO-42 sample. This sample was kindly provided to us from the group of Prof. Daniella Goldfarb (Weizmann Institute of Science). SAPO-42 is a Silicoaluminophosphate molecular sieve and like other SAPO-*n* materials it is composed of PO_2^+, AlO_2^-, and SiO_4 tetrahedra connected through the bridging oxygen atoms [20]. Since the number of AlO_2^- moieties is larger than that of PO_2^+, there are many cations in the network, among them sodium and protons. SAPO-42 is isostructural with zeolite A. The powder diffraction and ^{27}Al MAS NMR spectra of this sample appear in the supplementary material.

2.4. Simulations

All simulations were performed using the SIMPSON program [21] version 2.0.1. For values of the quadrupolar interaction $\chi = e^2qQ/h \leqslant 4$ MHz, 256 angles were used for powder averaging using the REPULSION [22] algorithm. For higher values of χ, more orientations were used. The convergence of the dephasing curve was validated by increasing the number of orientations for various values of χ. A single spin-1/2–spin-5/2 pair was considered in all simulations, and the dipolar interaction was taken as 150 Hz at all times. The pulse sequence design in the simulation mimicked the experimental setup as shown in Fig. 1 but used ideal π pulses during the long recoupling pulse.

3. Results and discussion

The theoretical explanations for the dephasing behavior of REDOR and REAPDOR have been presented in many pervious papers [6,10,23] and will not be discussed here. For REAPDOR to follow the universal behavior, the adiabaticity parameter α must obey a certain condition, and normally the term $\nu_1^2/\nu_q\nu_r$ must be larger than some number close to 1, as discussed in the Introduction. Since the quadrupolar frequency $\nu_q = \frac{3\chi}{2S(2S-1)}$ is determined by the

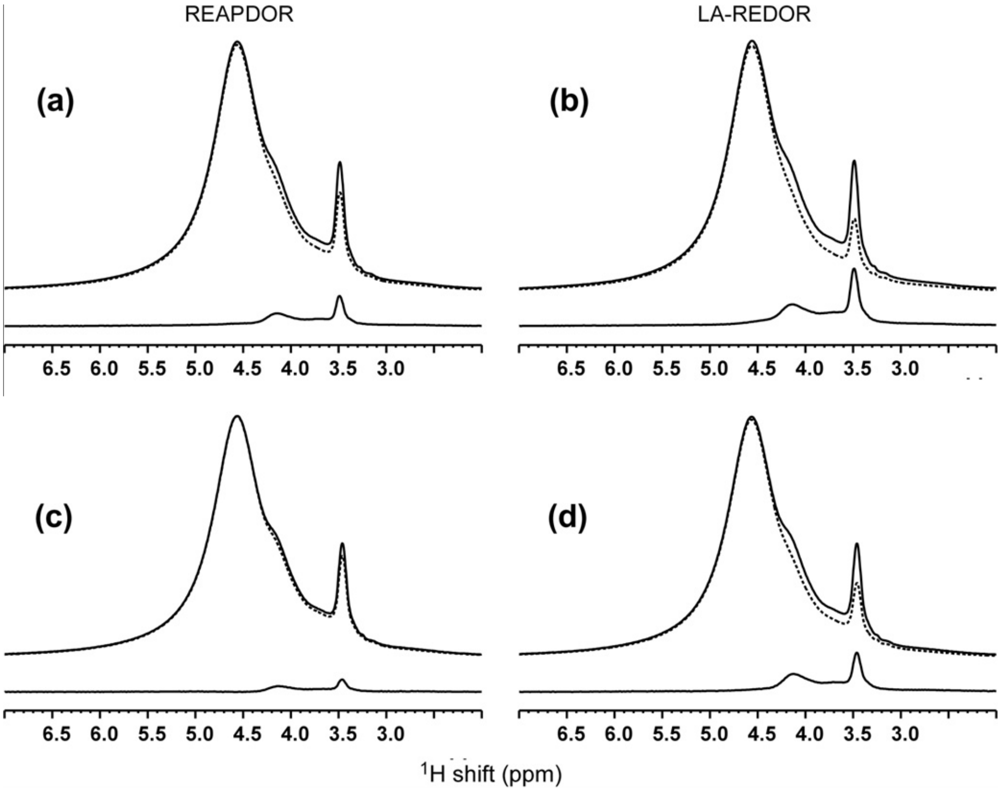

Fig. 3. S, S_0 and ΔS spectra for the ^{1}H–^{27}Al REAPDOR (a and c) and LA-REDOR (b and d) experiments on SAPO-42. The total dephasing time lasted eight rotor periods. The solid lines present the S_0 and ΔS spectra, ΔS being the bottom spectrum. The dash lines present the dephased (S) spectra. The inversion pulse on the quadrupolar ^{27}Al nucleus was two rotor periods in the case of the LA-REDOR experiment, and one-third rotor period for the REAPDOR experiment. The top spectra (a and b) show results from experiments taken at 13 kHz spinning (Tr = 76.9 μs) using ^{27}Al RF power of $\nu_{1,Al}$ = 25 kHz (total dephasing time τ_{exp} = 615 μs). For the bottom spectra ν_r = 12 kHz, $\nu_{1,Al}$ = 12.5 kHz (τ_{exp} = 667 μs).

system under study, the experimentalists have control (somewhat limited) over the intensity of the radio-frequency power $\nu_1 = -\gamma B_1$, and the rotor frequency ν_r. The range of experimental parameters in which we performed ^{1}H ($I = 1/2$)–^{27}Al ($S = 5/2$) recoupling experiments and simulations is demonstrated in Fig. 2 by a plot of the ratio ν_1/ν_q vs. ν_r/ν_1. The diagonal line at $\alpha = 0.55$ separates regions where universal behavior and ideal performance of REAPDOR occurs. Once experimental parameters are below this line, reduced recoupling efficiency is observed for a $Tr/3$ recoupling pulse. Variations in ν_q and ν_r for a constant ν_1 value are represented by the vertical and horizontal arrows, respectively. Variations in ν_1 when ν_r and ν_q are kept constant are indicated by the curved arrow. We performed experiments at $\nu_r = 13$ kHz, and varied ν_1 between 6 and 50 kHz. The area enclosed by the curved line represents this range of experimental parameters if one considers a quadrupolar coupling range of $\chi \approx 1$–7 MHz (an average range for ^{27}Al sites in zeolites [24–26]). This range includes conditions above and significantly below the adiabaticity parameter.

Experimental demonstration of the usability of the extended pulse is demonstrated in the spectra presented in Fig. 3. The ^{1}H spectrum of SAPO-42 exhibits three major peaks. Two proton sites show clear coupling to aluminum sites (at 3.5 and 4.2 ppm), while the signal at 4.6 ppm shows no coupling or very weak coupling. The reference signals S_0 (for a dephasing time τ of eight rotor periods, or 615 μs), obtained by running the experiment without the recoupling pulse on the quadrupolar nucleus, appears as a solid line, has the strongest peak intensities, and accounts for interactions other than the dipolar couplings (relaxation, pulse imperfections, etc.). The dephased signals S (dash), and the difference signals ΔS (solid) then indicate the extent of dipolar recoupling. Spectra are shown for two different RF values and are compared for REAPDOR and low-alpha REDOR. Spinning rates in all cases are $\nu_r = 13$ kHz. At $\nu_1 = 25$ kHz, a regular REAPDOR recoupling pulse of $Tr/3$ causes some dephasing (a) while the long recoupling pulse of two rotor periods induces a much more significant dephasing (b). The difference between the two pulses is even more pronounced in the bottom part of the figure, where an RF field of 12.5 kHz was used. A pulse of length $Tr/3$ shows minimal dephasing (c, 10%) but for the long recoupling pulse 35% of the signal has already decayed (d). The spectrum at 12.5 kHz presents a reduction by a factor of four for α, and with a rough estimation for the quadrupolar coupling of $\chi \approx 3(\pm 1)$ MHz, or $\nu_q \approx 450(\pm 150)$ kHz, we obtain values of $\alpha = 0.12 \pm 0.04$ in the first case ($\nu_1 = 25$ kHz), and $\alpha = 0.03 \pm 0.01$ in the second case ($\nu_1 = 12.5$ kHz). Furthermore, we compare in Fig. 4 the full $\Delta S/S_0$ dephasing curves for a regular REAPDOR experiment and for the low-alpha experiment. At $\nu_1 = 50$ kHz (4a), they are comparable since α is estimated to be ~0.3–0.6. However, at 25 kHz (4b) and 12.5 kHz (4c), a clear difference can be observed in the dephasing behavior of the two experimental approaches. The performance of the long pulse is unchanged, however the performance of REAPDOR deteriorates significantly. The robustness of the method is demonstrated in 4d, where an overlay of dephasing curves for ν_1 values ranging 6–50 kHz are shown to produce similar behavior when a long recoupling pulse is used.

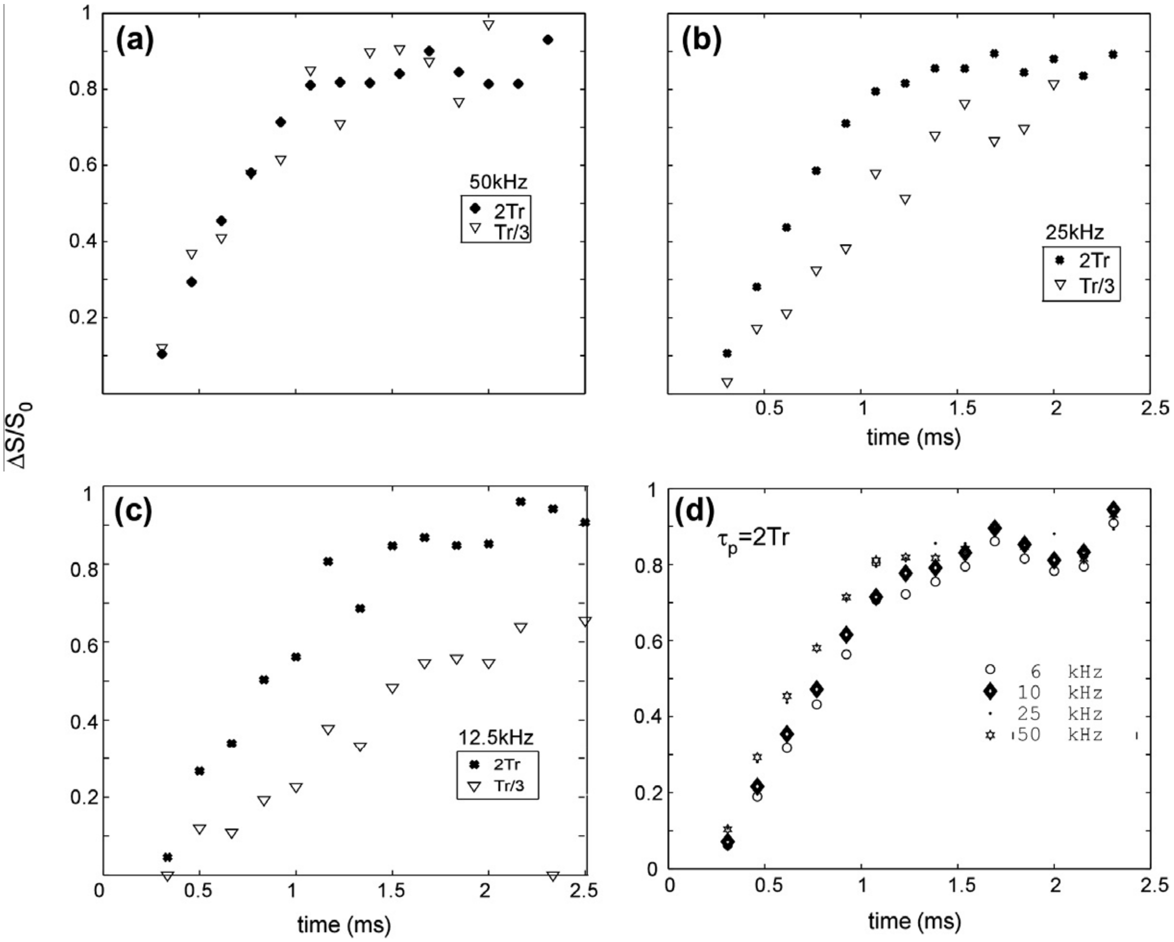

Fig. 4. $\Delta S/S_0$ experimental curves for the REAPDOR and LA-REDOR experiments. The long inversion pulse on the quadrupolar ^{27}Al nucleus was two rotor periods ($\tau_p = 154$ μs in a and b; 166 μs in c). Experiments were performed with a ^{27}Al RF field and spinning rates of (a) $\nu_1 = 50$ kHz, $\nu_r = 13$ kHz (b) $\nu_1 = 25$ kHz, $\nu_r = 13$ kHz (c) $\nu_1 = 12.5$ kHz, $\nu_r = 12$ kHz. (d) Overlay of LA-REDOR $\Delta S/S_0$ curves using RF values of 6, 10, 25, 50 kHz.

4. Numerical calculations

In order to support our observations and to determine a useful range of experimental parameters for which our approach is useful, we performed numerical simulations using the SIMPSON simulation program [21], where a spin system of a spin-1/2 coupled to a spin-5/2 was considered. In order to set a reference point for the success of our dephasing sequence, we compare our calculations to the spin-5/2 universal curve [17] and to the behavior of a regular REAPDOR pulse of length *Tr*/3. The maximal dephasing that can be reached using experimental parameters corresponding to the universal curve, using $\alpha > 0.55$, is $\Delta S/S_0 = 0.83$, pertaining to the formula $S_{univ}(\lambda) = \frac{\Delta S}{S_0} = 0.63(1 - e^{-(3.0\lambda)^2}) + 0.2(1 - e^{-(0.7\lambda)^2})$. It should be noted however, that the curve is accurate only up to a value of $\lambda = 0.5$ ($S_{univ} = 0.62$). Here again $\lambda = D\tau$ is a dimensionless parameter that equals the product of the dipolar interaction (in Hz) $D = \frac{1}{2\pi}\frac{h\gamma_I\gamma_S}{r_{IS}^3}$ ($\gamma_{I/S}$ – gyromagnetic ratios of spins *I*/*S*, r_{IS} – inter-nuclear *I*–*S* distance in meters) and the dephasing time $\tau = n\nu_r^{-1}$ (*n*: number of rotor periods). In Fig. 5, we examine the extent of dephasing at $\lambda = 0.3$, when the parameter α is varied via a change in ν_1 and ν_r while $\nu_q = 0.6$ MHz ($\chi = 4$ MHz) is kept constant. We also examined the dependence on the pulse length at two representative values of α, one well within the adiabatic limit ($\alpha = 1.125$) and the other at a value of $\alpha = 0.1$.

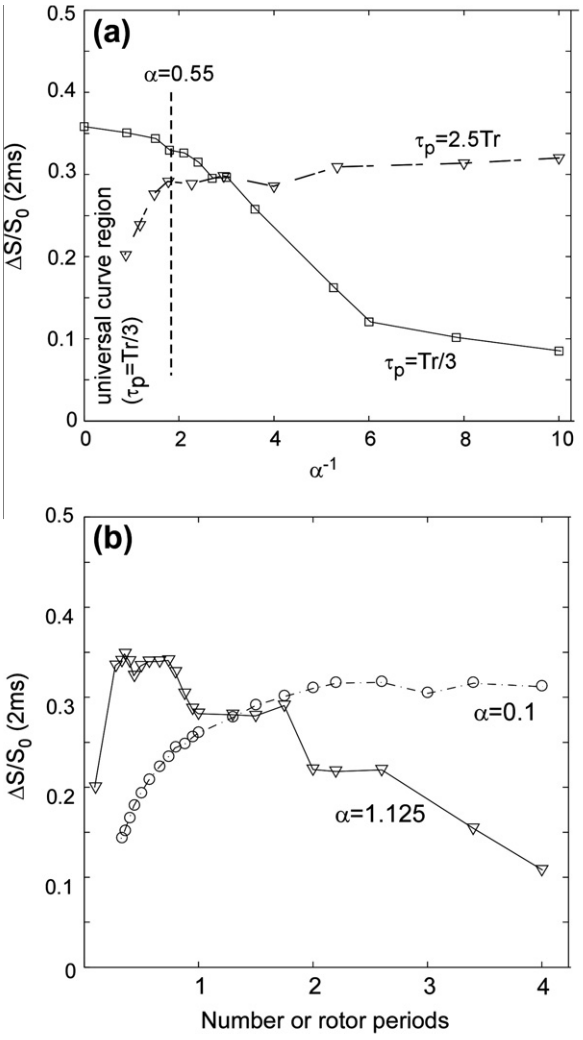

Fig. 5. (a) Dependence of the dipolar dephased signal $\Delta S/S_0$ ($\lambda = D\tau = 0.3$) on the adiabaticity parameter α for various values of ν_1 and ν_r, where ν_q was kept constant at 0.6 MHz. Explicitly, the values (in kHz) were as follows: ν_1/ν_r = 45/3, 45/4, 45/6, 40/6, 35/6, 30/6, 30/8, 30/12, 30/15. The dashed line indicates a value of $\alpha = 0.55$. The solid line is used for the REAPDOR experiment ($\tau_p = Tr/3$) and the dash line for LA-REDOR ($\tau_p = 2.5Tr$). (b) The dependence of the dephased signal $\Delta S/S_0$ ($\lambda = 0.3$) on the recoupling pulse length $\tau = n\nu_r^{-1}$ (in rotor periods, *n*) for $\alpha = 1.125$ (in kHz, $\nu_q = 600$, $\nu_1 = 45$, $\nu_r = 3$) and for $\alpha = 0.1$ ($\nu_q = 600$, $\nu_1 = 30$, $\nu_r = 15$).

We can see in Fig. 5a that as long as the experimental parameters are within the adiabaticity limit, i.e. $\alpha > 0.55$ (on the left of the dash line, $1/\alpha = 1.82$), a pulse of length *Tr*/3 is superior, as discussed by Gullion and Vega [10], however, when the values of α start to decrease, the dephasing efficiency of a *Tr*/3 pulse decreases sharply while the application of a long pulse ($\tau_P = 2.5$ rotor periods) reaches a plateau at a value of $\Delta S/S_0 \approx 0.32$. A pulse length of 2.5*Tr* is not unique. In Fig. 5b it can be clearly seen that up to a pulse length of about two rotor periods, there is a gradual increase in the recoupling efficiency for small values of α. Beyond this value, the behavior reaches a plateau, and therefore further extension of the pulse is not always necessary.

In order to show the complete dephasing behavior of the new approach, we demonstrate in Fig. 6 the full dephasing behavior of various representative pulses using $\alpha = 0.1$. It can be seen that the long recoupling pulse reaches within 10% of the universal behavior up to ~4 ms ($\lambda = 0.6$), and then improves at longer recoupling times. For the regular pulse of length *Tr*/3 and for a normal REDOR experiment with central-transition selective π pulses, the performance is clearly inferior.

Using values of α down to 0.1 already allow us to perform recoupling experiments not only in unfavorable conditions such as high quadrupolar coupling constants or low RF power levels, but also to choose much higher spinning rates than was customary for this type of experiments (3–5 kHz). For example, if a pulse of 50 kHz is available, and the quadrupolar coupling constant is that of an aluminum site in a zeolite (~5 MHz), $\alpha = 0.55$ demands that we use a spinning rate only up to 6.1 kHz. If a power of only 25 kHz is available, this value reduces to only 1.5 kHz. At these spinning rates not only the accuracy of the spin controller affects significantly the signal-to-noise [16,27] but perhaps the main problem is that MAS becomes less efficient, and many sidebands may interfere with the spectra. Also, coupling to other spins is inefficiently removed. If for the system above one can use a value of $\alpha = 0.1$, the same experiment can be performed at a spinning rate of 33 kHz using RF power of only 8.3 kHz, thus making this experimental approach useful for ultrafast spinning/low RF experiments. Performing experiments at high MAS rates and low RF fields has been found extremely useful for applications of solid-state NMR

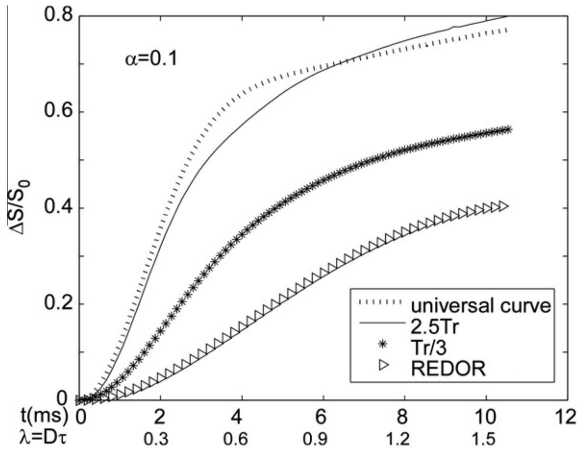

Fig. 6. Build-up curves for a ^{1}H–^{27}Al spin pair at a dipolar interaction $D = 150$ Hz. The parameters $\nu_1 = 30$ kHz, $\nu_r = 15$ kHz, and $\nu_q = 600$ kHz were used, pertaining to $\alpha = 0.1$. Simulated curves for REAPDOR, LA-REDOR, central-transition selective REDOR and the universal curve are shown for mixing times up to $\tau = 10$ ms, i.e. $\lambda = D\tau = 1.5$. In the case of the REDOR simulations, selective π pulses were carried out using a nutation frequency $\nu_{nut} = (S + 1/2)\cdot\nu_1 = 45$ kHz ($\nu_1 = 15$ kHz).

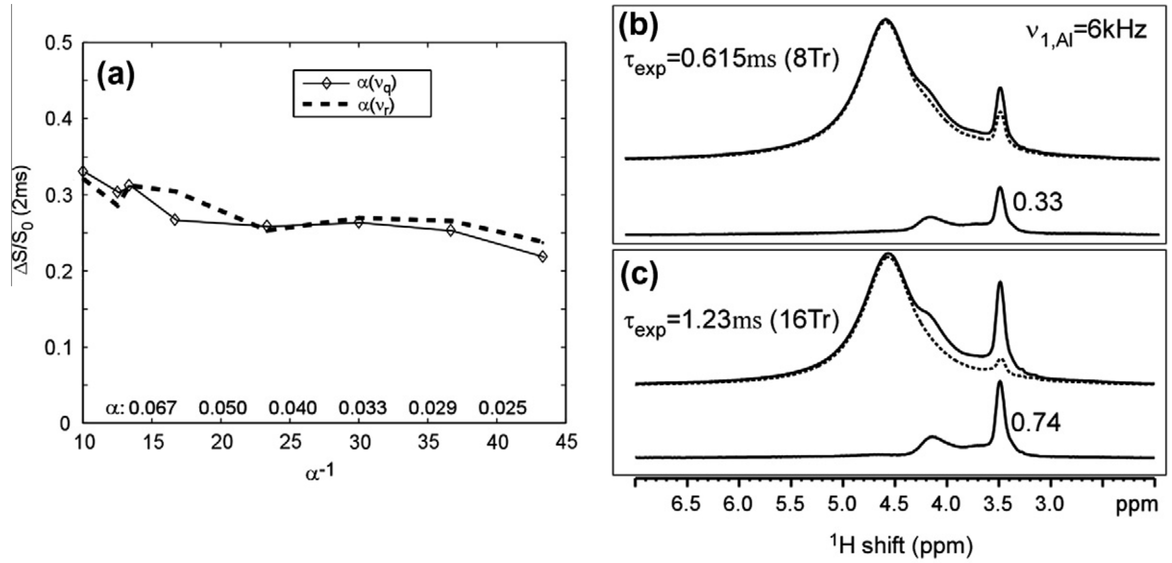

Fig. 7. Extent of dephasing at low adiabaticity values. (a) Simulations extending Fig. 5b (D = 150 Hz, τ_{exp} = 2 ms, λ = 0.3): The solid line indicates various ν_q values ranging 0.6–1.95 MHz (χ = 4–13 MHz), with the spinning rate set to 20 kHz. The dash line indicates various ν_r values ranging 20–65 kHz, with the quadrupolar frequency set to 600 kHz. (b and c) Experimental results from SAPO-42 ^{1}H–^{27}Al LA-REDOR with $\nu_{1,Al}$ = 6 kHz, ν_r = 13 kHz and dephasing times of eight rotor periods (b) and 16 rotor periods (c). A very rough estimation for the value of $\lambda = D\tau$ gives 0.4 for the top spectrum. Experimental $\Delta S/S_0$ values are indicated in each of the spectra.

to biological systems [28,29] and therefore our approach may be especially suitable for studies of metalloenzymes. While these conditions are a significant improvement over previously available experimental schemes, we show here that even further improvement can be obtained, and recoupling can still be observed down to much lower values of α. In Fig. 7a we show the extent of dephasing beyond the value of $\alpha = 0.1$. Dephasing is monitored as the spinning rate is increased significantly, or the quadrupolar coupling interaction is made larger, so the ratio ν_1/ν_q decreases. Even at values of $1/\alpha = 43.3$ (or $\alpha = 0.023$), our calculations suggest that we can expect a $\Delta S/S_0(\lambda = 0.3)$ value of ~0.22, which amounts to ~70% of the values reached for $\alpha = 0.1$, however at such values a pulse of length $Tr/3$ will exhibit a negligible dephasing, probably below detection threshold.

The experimental evidence for the success of the sequence at very low RF values is demonstrated as well (Fig. 7b and c). We performed experiments at ^{27}Al RF power levels of only 6 kHz (calibrated using a 50 mM $AlCl_3$ solution). Even at such low RF power levels, significant dephasing of the proton signal can be detected. Representative S, S_0 and ΔS spectra are shown for two experimental times corresponding to $8Tr$ (b) and $16Tr$ (c).

5. Conclusions

The study of atoms having a nuclear spin larger than one-half has become an important tool for the study of many materials such as zeolites, glasses, hybrid materials and biological macromolecules. Detecting high-resolution spectra of nuclei such as ^{17}O, ^{27}Al, and ^{11}B, has become an extremely useful tool with the advent of MQMAS [30] and other high-resolution detection methods [31]. Structural information than becomes available many times in conjunction with DFT calculations [32,33] and proved helpful even in the case of metaloenzymes [34]. A more complete structural picture can be obtained if correlations to adjacent spins can be efficiently probed using experiments such as REAPDOR, TRAPDOR and others [35–37]. In this manuscript we managed to significantly improve the experimental regime (by more than an order of magnitude in α), in which one can obtain such correlations. Our modification of the REAPDOR experiment, in which the recoupling pulse on the quadrupolar spin is extended to approximately two rotor periods, allows the experimentalists to use much higher spinning rates and much lower RF values than was required before, without significantly compromising the recoupling efficiency. In comparison to the R^3–SPI approach [35], LA-REDOR recoupling is more efficient at similar dipolar-scaled recoupling times $nD\nu_r^{-1}$. The maximal dephasing values reached at long times ($\Delta S/S_0 > 0.8$) also suggest that population exchange of energy levels |±3/2> and |±5/2> must take place during the experiment, and the source of this observation is currently under investigation. The approach presented here therefore opens the way to the study of many new systems involving weak couplings, low-γ nuclei and nuclei have relatively strong quadrupolar coupling values. We therefore believe that this experiment will make the detection of dipolar couplings to quadrupolar spins easier and more applicable.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmr.2010.05.019.

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