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PRESTO Polarization Transfer to Quadrupolar Nuclei: Implications for Dynamic Nuclear Polarization

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Abstract

We show both experimentally and numerically on a series of model systems that in experiments involving transfer of magnetization from ^{1}H to the quadrupolar nuclei under magic-angle-spinning (MAS), the PRESTO technique consistently outperforms traditionally used cross polarization (CP), affording more quantitative intensities, improved lineshapes, better overall sensitivity, and straightforward optimization. This advantage derives from the fact that PRESTO circumvents the convoluted and uncooperative spin dynamics during the CP transfer under MAS, by replacing the spin-locking of quadrupolar nuclei with a single central transition selective 90° pulse and using a symmetry-based recoupling sequence in the ^{1}H channel. This is of particular importance in the context of dynamic nuclear polarization (DNP) NMR of quadrupolar nuclei, where the efficient transfer of enhanced ^{1}H polarization is desired to obtain the highest sensitivity.

Introduction

The transfer of polarization from one nuclear species to another forms the basis of most nuclear magnetic resonance (NMR) experiments aimed at improving sensitivity and/or probing connectivities between spins. Polarization of quadrupolar spins ($S > 1/2$) under magic angle spinning (MAS) in the solid-state, however, poses a remarkable challenge to this day.[1]

Early attempts at performing cross-polarization (CP) under MAS conditions (CPMAS) on a quadrupolar nucleus had determined a major flaw to the application of this experiment. Namely, that during a spin-locking pulse the identities of the various eigenstates can change a number of times every rotor period through the MAS-induced zero crossings of the quadrupole splitting.[2,3] These level crossings, as well as the spread in nutation rates found across the powder pattern, complicate the spin-lock that is central to the CPMAS experiment.[4,5] For the spins to be efficiently spin-locked, the level crossings need to either proceed adiabatically or suddenly, otherwise the polarization is lost. The adiabatic condition can be satisfied if a very high radio-frequency (RF) magnetic field is used so as to spin-lock all of the transitions,[6] however, this is typically not possible due to the very high RF requirements. The sudden condition entails selective spin-locking of the central transition (CT, m = 1/2 to -1/2 transition) with a very low RF field,[2,7] thereby hampering the CP process which has higher RF requirements. Additionally, even with very low RF fields, some crystallites cannot be spin-locked, leading to lineshape distortions from the depolarization of certain isochromats.[3,4,5,8] This is responsible for causing the well-known attenuation of the low-frequency singularity in CPMAS NMR spectra of quadrupolar nuclei. It is worth noting that all of these issues arise only under MAS conditions and that CP to quadrupolar nuclei in non-spinning samples, or samples spinning away from the magic angle,[9] is quite efficient. This has recently been exploited in the BRAIN-CP experiment that can efficiently polarize the broad patterns of low-γ quadrupolar nuclei.[10]

Because of these limitations, and the fact that quadrupolar nuclei typically have shorter spin-lattice relaxation times than spin-1/2 nuclei, CP has rarely been used as a means to improve the sensitivity in NMR spectroscopy for quadrupolar nuclei.[11] The CP-based experiments have mainly been used to measure spectral-edited data or generate correlations between spin-1/2 and quadrupolar nuclei (or even pairs of quadrupolar nuclei[12,13]) to evaluate atomic connectivities.[14,15,16] Several CP-based 2D correlation experiments utilizing quadrupolar nuclei have then been published, many of which were integrated with multiple-quantum MAS NMR (MQMAS) to achieve higher resolution.[17,18,19,20,21] The low efficiency provided by CP, however, motivated several groups to replace it with dipolar-based heteronuclear multiple-quantum correlation (D-HMQC) experiments,[22,23,24,25,26,27] in which high transfer efficiencies are achieved by applying heteronuclear dipolar recoupling to the spin-1/2 nuclei while limiting the RF irradiation of quadrupolar nuclei to a few pulses.

Recently, with the development of high-frequency gyrotrons, dynamic nuclear polarization (DNP) MAS NMR has been gaining importance as a characterization tool in materials science.[28,29] In DNP MAS NMR, a sample is typically wetted with a biradical solution, spun at low temperature (typically below 105 K), and irradiated near the electron Larmor frequency to transfer polarization from the electrons to the nuclei. This process can yield signal-to-noise enhancements as high as γ_e/γ_n, corresponding to 658 for ^{1}H, and has opened the door to efficiently studying extremely dilute species as well as surfaces.[30,31]

The appearance of MAS-DNP has caused a paradigm shift in the utility of polarization transfer techniques to quadrupolar nuclei in that, for the first time, polarization of these nuclei via the ^{1}H spins can benefit the overall sensitivity.[32] This is the case since the DNP enhancements are largest for high-γ nuclei, such as ^{1}H,[33,34] and the more rapid ^{1}H spin-diffusion combined with the ^{1}H's longer T_1 relaxation times enable for a larger fraction of the sample to become hyperpolarized in the polycrystalline state.[35,36] Numerous reports have demonstrated that the use of CPMAS-DNP can indeed accelerate the acquisition of 1D as well as 2D NMR data for quadrupolar nuclei.[37,38,39,40,41] Further expansion of these studies is contingent upon the improvement of the heteronuclear polarization transfer.

In this paper we propose an alternative approach for the direct transfer of polarization from a spin-1/2 to a quadrupolar nucleus for DNP applications, namely the PRESTO (phase-shifted recoupling effects a smooth transfer of order) experiment introduced by Levitt and coworkers.[42,43,44] Although initially used for recoupling of pairs of spin-1/2 nuclei, PRESTO proved to be competent in recoupling ^{1}H-^{17}O pairs, as well.[43] Much like the recent HMQC-based experiments, PRESTO does not require the use of a spin-lock. In fact, only a simple spin echo pulse sequence needs to be applied to the quadrupolar nucleus, see Figure 1 for the pulse sequence diagram. We have already applied this methodology for acquiring ^{17}O DNP-enhanced NMR spectra, where PRESTO was shown to provide 5 times higher signal intensity than CP for strongly coupled ^{1}H-^{17}O pairs.[45] The present study will demonstrate that PRESTO outperforms CP for a number of quadrupolar nuclei, also when there is no bond linking the recoupled spins.[46]

Similar pulsed polarization transfer experiments have been proposed, including the transferred-echo double resonance (TEDOR)[47] and pulsed-CP[48] methods. However, the utility of these approaches was limited, mostly due to the lack of ^{1}H homonuclear decoupling in TEDOR and the use of a spin-lock (applied stroboscopically) in pulsed-CP. Of note is also the application of a dipolar-INEPT (insensitive nuclei enhanced by polarization transfer) pulse sequence for generating correlation spectra involving quadrupolar nuclei;[49] although this has not been applied as a pre-polarization step. In theory, PRESTO should yield higher performance than dipolar-INEPT since γ-encoded dipolar recoupling is used[50] and fewer pulses are applied to the quadrupolar spin.

The PRESTO Experiment

The pulse sequence diagram for the common Bloch decay and CP experiments, as well as the PRESTO-II and PRESTO-III experiments are shown in Figure 1.[42] In a Bloch decay experiment, the quadrupolar nucleus is directly excited by a single 90° pulse. This simplest NMR pulse sequence will be used as a standard to gauge the performance of the polarization transfer techniques. In the case of a CP experiment, ^{1}H spins are first excited by a 90° pulse and are then spin-locked. Concomitantly, a spin-locking pulse is applied to the quadrupolar spins with an RF power equal to $1/(S + 1/2)$ that of the proton channel so as to satisfy the CT single-quantum Hartmann-Hahn matching condition.[7] The spin-locking pulses enable the transfer of polarization from one nuclear species to the other and free precession can be detected on the quadrupolar nucleus' channel once the locking pulses are turned off.

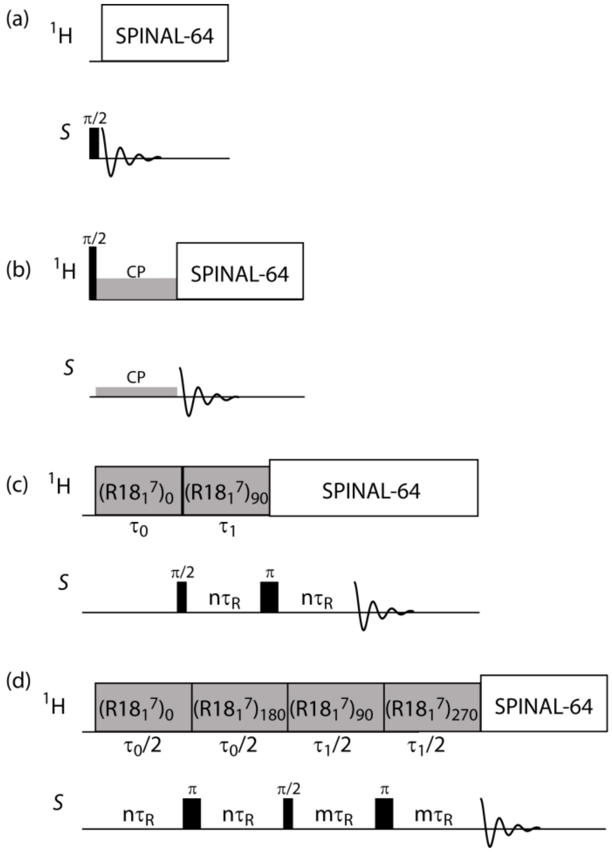

Figure 1. The pulse sequence diagrams for the Bloch decay (a), CP (b), PRESTO-II (c), and PRESTO-III (d) experiments.

The PRESTO-II experiment, on the other hand, does not use a spin locking pulse. γ-encoded, symmetry-based, heteronuclear dipolar recoupling is instead applied to reintroduce heteronuclear dipolar coupling interactions under MAS condition while decoupling ^{1}H-^{1}H dipolar interactions. This recoupling generates ^{1}H polarization which is antiphase to the heteronuclei.[42] A 90° pulse, applied to the quadrupolar nucleus, followed by a second recoupling period converts this ^{1}H magnetization into pure *S* transverse magnetization. Finally, a 180° pulse is applied to refocus the isotropic chemical shifts and second-order quadrupolar coupling of the *S* nuclei, and a spin echo is acquired. A simple improvement of the PRESTO-II sequence can be obtained by separating the recoupling blocks in two as depicted in Figure 1d. This has the effect of refocusing the X spin's chemical shift anisotropy. In this paper, the PRESTO-III sequence is used on all samples because it shows improved performance when compared to the PRESTO-II experiment. The theory describing the PRESTO experiments has been described in detail elsewhere[42] and will not be reiterated here.

For all our experiments, we have used the $R18^7_1$ recoupling sequence[51] since it provides a good RF field at our available spinning speeds (10-15 kHz), however, a number of recoupling sequences can be used in its place if faster spinning is required. A list of possible sequences and a description of the symmetry-based sequence nomenclature has been provided by Levitt.[52]

Results and Discussion

Computational Assessment of the CP and PRESTO Experiments

To compare the scope and performance of the conventional CP and PRESTO experiments, we first performed numerical simulations using the SIMPSON program.[53,54] This numerical framework allows for a smooth variation of the experimental and nuclear parameters in a way that cannot be matched by performing limited experiments on model compounds. A spin system was used consisting of a ^1H and ^{23}Na spin pair with a dipolar coupling of 17 kHz. The ^1H Larmor frequency was set to 400 MHz and the MAS rate to 10 kHz, in accord with our experiments. The PRESTO-II sequence was used for the simulations as no ^{23}Na chemical shift anisotropy was introduced.

The sensitivity to resonance offset, which is often noted as being very high and problematic for quadrupolar nuclei, was first investigated. The offset was smoothly varied from -100 kHz to 100 kHz and the intensity of the ^{23}Na CT, following polarization transfer from the ^1H via PRESTO or CP, was monitored; these data are plotted in Figure 2. The contact and recoupling times were optimized on resonance, assuming that the ^{23}Na nucleus has an axially symmetric EFG tensor with C_Q = 2.5 MHz.

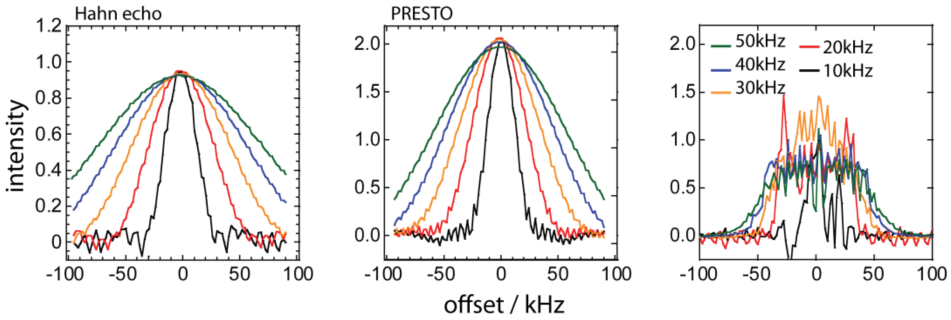

Figure 2. A comparison of the spin echo, PRESTO, and CP offset sensitivities are shown for five RF field strengths for a ^{23}Na-^{1}H spin pair described in the text (black = 10 kHz, red = 20 kHz, orange = 30 kHz, blue = 40 kHz, and green = 50 kHz); the curves are plotted on the same vertical axis which is normalized to the intensity of the directly excited ^{23}Na central transition signal.

As can be seen in Figure 2, the bandwidth of PRESTO is only marginally narrower than that obtained using a conventional spin echo experiment. Surprisingly, the bandwidth of CP on is similar to that of an echo, using low RF field strengths. However, it remains nearly invariant as the RF field is increased and exhibits very irregular patterns as a function of offset, in agreement with earlier studies.[7] It is also interesting to note that the use of a spin-locking field that is too weak or too strong results in a loss on intensity whereas only the bandwidth of PRESTO is affected when the RF field is changed.

We have also calculated the signal intensity of CP and PRESTO experiments as a function of C_Q, under otherwise the same conditions. The results, plotted in Figure 3, show that the signal intensity from a PRESTO experiment is consistently superior to that of a CP experiment, at least under the conditions used in our simulations. Notably, once a certain threshold is passed ($C_Q > 0.25$ MHz), so that the pulses are CT-selective, the efficiency of PRESTO is independent of the strength of the quadrupolar coupling. In the extreme case of $C_Q = 0$, the pulses correspond to non-selective 45° and 90° pulses instead of CT-selective 90° and 180° pulses; the use of these flip angles doesn't lead to any PRESTO polarization transfer. As expected based on the arguments made in the introduction, CP proves critically dependent on the exact EFG tensor parameters of the spin system, which causes distortions of the lineshapes and their intensities, and, in extreme circumstances, may render some of the resonances unobservable.

Taken together, these simulations indicate that not only is a CP experiment less efficient, but its optimization is potentially much more demanding than PRESTO, as it includes the spin-locking field and is also largely depends on C_Q. This can be very problematic when studying an unknown sample or a sample containing multiple sites, where the CP parameters measured on model compounds would be of little value and the variation of the CP conditions as a function C_Q would result in severe spectral distortions.

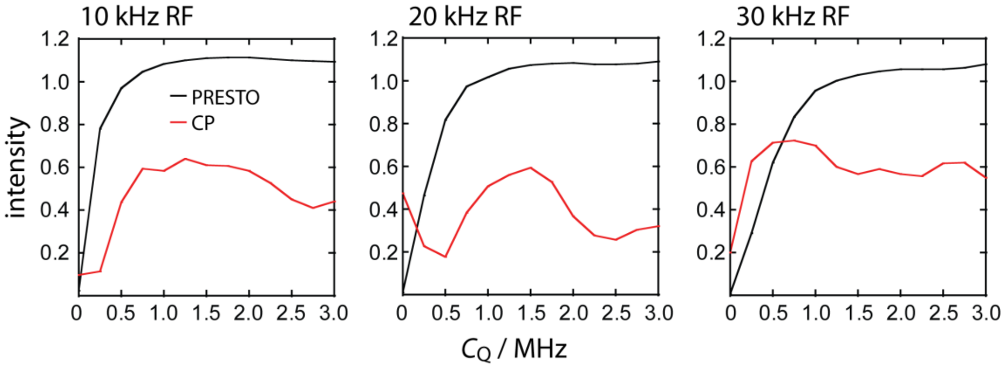

Figure 3. The simulated NMR signal intensity of a ^{23}Na-^{1}H spin pair subjected to a CP (red) or PRESTO (black) pulse sequence is plotted as a function of C_Q for ^{23}Na RF fields of 10, 20, and 30 kHz.

Experimental Lineshapes Obtained from PRESTO and CP Experiments

To validate experimentally some of the results from our numerical calculations we have acquired CP and PRESTO NMR spectra of a series of model compounds containing ^{23}Na, ^{27}Al, and ^{11}B nuclei. We firstly decided to compare the quality of the lineshapes, as it determines the reliability of the extracted chemical shift and EFG tensor parameters. To this end, we acquired the ^{23}Na NMR spectra of sodium citrate dihydrate, which has been used as a benchmark compound for heteronuclear correlation (HETCOR) experiments involving quadrupolar nuclei by Goldbourt and coworkers.[20] The Bloch decay, PRESTO and CP spectra of this compound are shown in Figure 4.

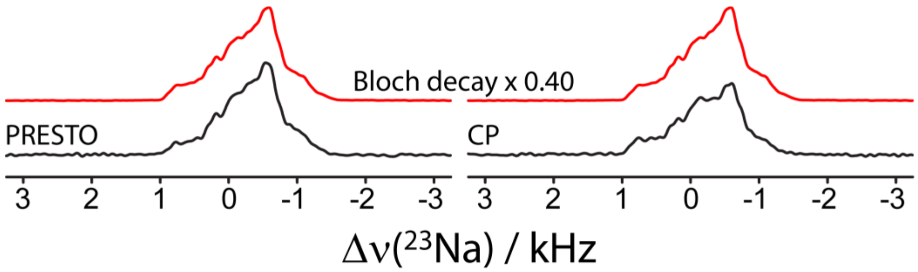

Figure 4. A comparison of the Bloch decay (red overlay), PRESTO-III, and CP ^{23}Na spectra of sodium citrate dihydrate.

It can be seen in Figure 4 that the signal intensity is stronger with PRESTO but, most importantly, the lineshape of the PRESTO experiment is indistinguishable from that of the Bloch decay. On the other hand, CP leads to an intensity loss at the low-frequency end of the spectrum, as is well documented.[3,4,5,8] It can also be seen that the use of population transfer from ^{1}H to ^{23}Na, either by PRESTO or CP, does not yield a sensitivity advantage when compared to Bloch decay unless DNP is used. This is likely the case because of T_2 relaxation during the PRESTO recoupling time. Nevertheless, a 40% relative signal intensity by PRESTO is quite satisfactory.

We have subsequently compared CP and PRESTO for acquiring ^{27}Al MAS NMR spectra of Al(acac)$_3$ (see Figure 5), which features a single site with a nearly axially symmetric EFG tensor.[55] The CP process in this sample has been previously investigated by Barrie.[4] The difference between PRESTO and CP is much more striking in this sample. The spin-locking leads to nearly complete eradication of the low-frequency singularity, whereas PRESTO produced an undistorted spectrum with roughly 4 times higher overall intensity. These results are in agreement with the numerical results and with the previously published ^{17}O data;[45] both nuclides possessing spin quantum numbers of 5/2. The signal intensity from PRESTO is only reduced by 39%, when compared to the Bloch decay experiment.

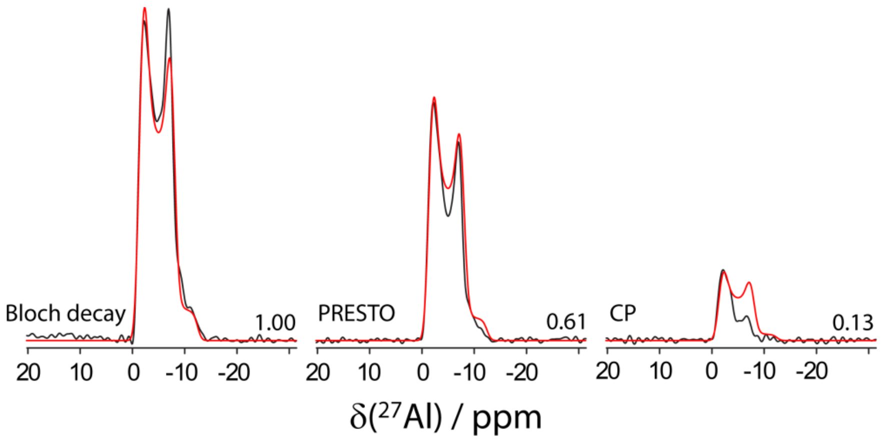

Figure 5. The Bloch decay, PRESTO-III, and CP ^{27}Al spectra of Al(acac)$_3$ (black), and 'ideal' lineshapes obtained from simulations using known NMR parameters[55] (red). The relative integrated intensity of the three spectra is indicated in the figure.

Experimental Quantitativity of PRESTO and CP Experiments

The quantitative accuracy of the CP and PRESTO methods was tested using two samples featuring multiple sites with varying NMR parameters, AlPO-CJ2[56] (^{27}Al, Figure 6) and borax[57] (^{11}B, Figure 7). As in the case of Al(acac)$_3$, there is a large advantage to using PRESTO instead of CP for ^{27}Al in AlPO-CJ2. The PRESTO spectrum is again approximately 4 times more sensitive and nearly quantitative. Indeed, it differs by only 8% from the expected intensity ratio between the two peaks representing six- and five-coordinate Al sites. The intensity ratio is accurately represented in the DPMAS spectrum. The CP spectrum, on the other hand yields the relative intensities with a 35% error. This discrepancy is a result of the large difference in quadrupolar coupling constants C_Q for the two sites (3.3 and 1.5 MHz for the five- and six-coordinated sites, respectively).[58]

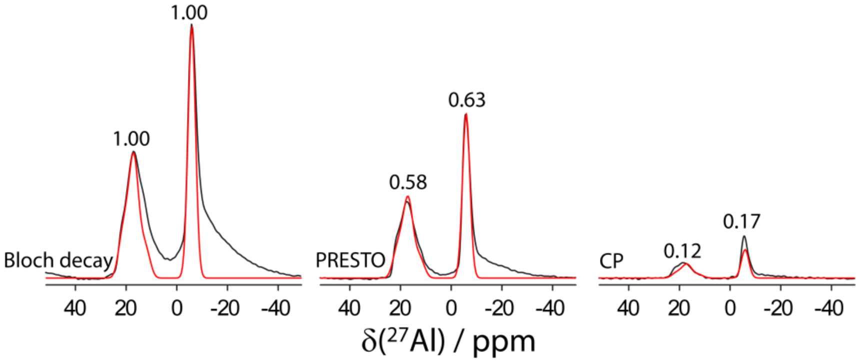

Figure 6. The Bloch decay, PRESTO-III, and CP ^{27}Al spectra of AlPO-CJ2 are shown (in black), along with the relative intensities of the two sites in the spectra. An idealized simulation is overlaid in red to highlight the degree to which the spectra are quantitative.

Similarly to ^{27}Al, a strong disparity between C_Q values is very common in ^{11}B SSNMR spectroscopy.[57] The four-coordinate boron sites have an almost tetrahedral chemical environment and a near-zero quadrupolar coupling, whereas three-coordinate borons reside in a trigonal planar arrangement and have C_Q's of several MHz. Borax (sodium tetraborate decahydrate) possesses both a three- and four-coordinate site; as is very common. Similarly to what was seen for AlPO-CJ2, both sites are well polarized using PRESTO; the difference in integration being of only 7%, whereas this difference is of 37% when using CP. Additionally, as is evident in Figure 7, the lineshape for the tri-coordinate boron site in the CP spectrum is highly distorted, whereas the lineshapes in the PRESTO spectrum are nearly indistinguishable from the Bloch decay result. Both experiments were optimized to yield the highest intensity for the three-coordinate boron site.

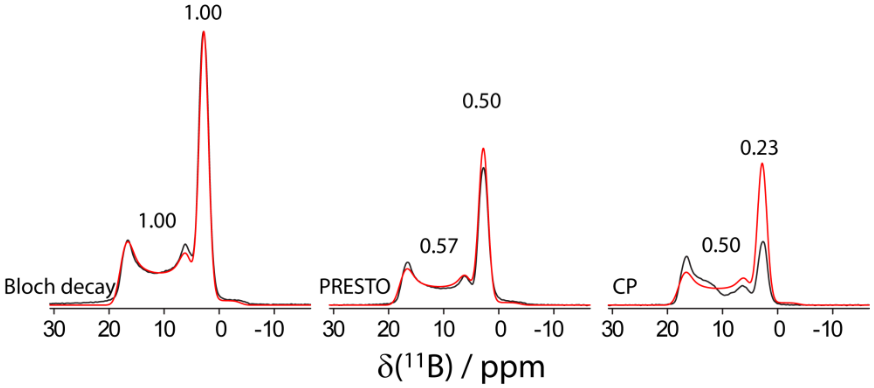

Figure 7. The Bloch decay, PRESTO-III, and CP ^{11}B spectra of borax are shown (in black), along with the relative intensities of these sites in the spectra. An idealized simulation is overlaid in red to highlight the lineshape distortions and the degree to which the spectra are quantitative.

Of note also is the fact that, although it has been stated that PRESTO is mainly sensitive to short internuclear distances,[42,59] we have found it to be efficient in recoupling long range dipolar coupling. For example, the nearest protons were 2 bonds away from the probed nucleus in borax, AlPO-CJ2, and sodium citrate dihydrate and, in the case of Al(acac)$_3$, they were situated 4 bonds away from the ^{27}Al center.

DNP-enhanced NMR

Although the field is very young, to date the most important application of DNP to quadrupolar nuclei is for the characterization of surface sites on γ-Al_2O_3, an important catalyst support.[37,38,40] This approach has been termed DNP surface-enhanced NMR spectroscopy (DNP-SENS)[29] as well as *primostrato*[40] DNP NMR. Cross-polarization has been used in all instances. We have thus acquired DNP-enhanced ^{27}Al NMR data of bare γ-Al_2O_3 using both the PRESTO and CP methods. The TEKPol biradical,[60] dissolved in tetrachloroethane, was used as a polarization source. The spectra are shown in Figure 8.

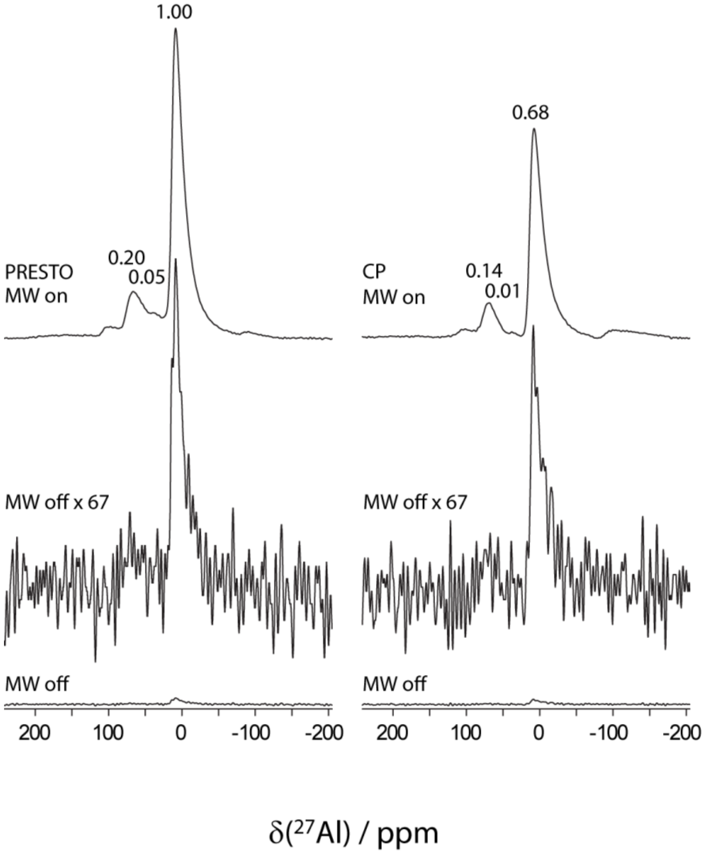

Figure 8. The PRESTO-III (left) and CP (right) ^{27}Al spectra of γ-Al_2O_3 taken with (top) and without (bottom) microwave irradiation for DNP are shown. The relative intensity of the three

sites is indicated in the figure; note that the five-coordinate aluminum site is scarcely polarized by CP.

DNP provides a large enhancement of 67, when compared to the conventional PRESTO and CP spectra. This enhancement is lower than that reported in other studies using the TEKPol biradical since we used a zirconia rotor, instead of a sapphire one, to eliminate background signals from the rotor. It can be seen that PRESTO affords higher sensitivity than CP for all sites, which is important when considering that insensitive MQMAS or DQ-SQ spectra are often desired.[37,38,40] Most importantly, however, the five-coordinate aluminum site is nearly absent in the CP spectrum. Five-coordinate aluminum sites are far less-symmetrical than their tetrahedrally- or octahedrally-coordinated counterparts and thus have larger C_Q values,[61] and different optimal CP conditions. In agreement with the data on AlPO-CJ2 and $Al(acac)_3$, this site is approximately 5 times stronger in the PRESTO spectrum.

Conclusions

We have demonstrated both computationally and experimentally that in experiments performed under MAS the polarization transfer from ^1H to quadrupolar nuclei by the PRESTO technique outperforms conventional CP on all fronts: (1) it is more efficient, (2) provides more quantitative spectra (3) yields undistorted lineshapes, and (4) is easier to optimize. These results suggest that CP can be superseded by PRESTO as a method of choice for polarization transfer from ^1H to quadrupolar nuclei, especially in samples containing multiple sites with different quadrupolar parameters. This finding is particularly important in the context of DNP of quadrupolar nuclei, which usually relies on polarization transfer from the hyperpolarized ^1H spins.

Experimental

SIMPSON Calculations

All numerical calculations were performed using SIMPSON (ver. 4.1.1).[53,54] A ^{23}Na-^{1}H spin pair was inferred with a dipolar coupling constant of 17 kHz, and a C_Q value for ^{23}Na of 2.5 MHz (unless varied, Figure 3) and an asymmetry parameter of zero. The ^{23}Na transmitter was set to the second-order quadrupole induced shift so as to be on resonance. The spinning rate was 10 kHz and the RF field was set to that indicated in Figures 2 and 3. Powder averaging was accomplished using 100 orientations from the REPULSION scheme.[62] The ^{1}H spin-locking field was set to twice that of ^{23}Na, to which the spin rate was subsequently subtracted to be on the most efficient $\varepsilon = +1$ Hartmann-Hahn condition,[7] and the recoupling field strength was of 90 kHz for $R18_1^7$ recoupling.[51,52] The optimal contact and recoupling times were determined on this sample to being 300 μs and 2 rotor cycles, respectively. The offset sensitivity was determined by calculating the total transferred magnetization from ^{1}H to the CT of ^{23}Na in steps of 2 kHz and the C_Q sensitivity was trialed in steps of 250 kHz; the transmitter was always set on resonance.

NMR Experiments

The experiments were all performed on a Bruker AVANCE III 400 DNP-NMR spectrometer equipped with a triple-resonance 3.2 mm LTMAS probe. The samples were purchased from Aldrich with the exception of AlPO-CJ2, which was kindly provided by Prof. Francis Taulelle, and used without further treatment. The samples were powdered and packed into either sapphire or zirconia MAS rotors and spun at 10 kHz. The γ-Al_2O_3 sample was further impregnated with a 16 mM solution of TEKPol dissolved in TCE for DNP measurements. The experiments on sodium citrate dihydrate, AlPO-CJ2, and borax were performed at room temperature whereas the data on $Al(acac)_3$ and γ-Al_2O_3 were acquired at 105 K. In all CP experiments the ^1H RF field and the *effective* X RF field was set to 50 kHz (i.e. 25 kHz for ^{11}B and ^{23}Na and 16.6 kHz for ^{27}Al), although this was further optimized experimentally to provide the highest sensitivity. The PRESTO experiments generally did not require any optimization and the X CT-selective excitation pulse was simply set to 10 μs. The contact times used for CP were of 1.5, 2.0, 1.5, 0.2, and 0.95 ms for sodium citrate dihydrate, Al(acac), AlPO-CJ2, borax, and γ-Al_2O_3, respectively. Similarly, the total PRESTO-III recoupling lasted 8 rotor periods for sodium citrate dihydrate, borax, and γ-Al_2O_3 and 12 rotor periods for $Al(acac)_3$ and AlPO-CJ2. In all experiments the recycle delays were set to 5 times the T_1 relaxation time, in order to have reliable intensity comparison, and between 8 and 32 scans were accumulated. The supercycle $R18^7_1R18^{-7}_1$ was used to stabilize the long recoupling times.[42,46] A simple π pulse was used as the *R* element although it may be possible to improve the efficiency with the use of a composite element.[63]

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