Efficient transfer of DNP-enhanced ^1H magnetization to half-integer quadrupolar nuclei in solids at moderate spinning rate

Hiroki Nagashima,^{1*} Julien Trébosc,^{2,3} Yoshihiro Kon,¹ Olivier Lafon,^{2,4*} Jean-Paul Amoureux^{2,5,6*}

¹ Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, 305-8565 Ibaraki, Japan.

² Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS- Unité de Catalyse et de Chimie du Solide, F-59000 Lille, France.

³ Univ. Lille, CNRS, Centrale Lille, Univ. Artois, FR 2638, Federation Chevreul, F-59000 Lille, France.

⁴ Institut Universitaire de France.

⁵ Bruker Biospin, 34 rue de l'industrie, F-67166 Wissembourg, France.

⁶ Riken NMR Science and Development Division, Yokohama, 230-0045 Kanagawa, Japan.

* Corresponding authors: nagashima-hiroki@aist.go.jp olivier.lafon@univ-lille.fr

jean-paul.amoureux@univ-lille.fr

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Dedicated to Dr. Mélanie Rosay

Abstract: We show herein how the proton magnetization enhanced by dynamic nuclear polarization (DNP) can be efficiently transferred at moderate magic-angle spinning (MAS) frequencies to half-integer quadrupolar nuclei, $S \geq 3/2$, using the through-space refocused INEPT (*D*-RINEPT) technique (Insensitive Nuclei Enhanced by Polarization Transfer), in which a symmetry-based SR4_1^2 recoupling scheme built from adiabatic inversion ^1H pulses reintroduces the ^1H - S dipolar couplings, while suppressing the ^1H - ^1H ones. The use of adiabatic pulses also improves the robustness to offsets and rf-field inhomogeneity. Furthermore, the efficiency of the polarization transfer is further improved by using ^1H composite pulses and continuous-wave irradiations between the recoupling blocks, as well as by manipulating the S satellite transitions during the first recoupling block. Furthermore, in the case of large ^1H - S dipolar couplings, the *D*-RINEPT variant with two pulses on the quadrupolar channel results in an improved transfer efficiency. We compare here the performances of this new adiabatic scheme with those of its parent version with single π -pulses, as well as with those of PRESTO and CPMAS transfers. This comparison is performed using simulations as well as DNP-enhanced ^{27}Al , ^{95}Mo and ^{17}O experiments on isotopically unmodified γ -alumina, hydrated titania-supported MoO_3 , $\text{Mg}(\text{OH})_2$ and L-histidine $\cdot\text{HCl}\cdot\text{H}_2\text{O}$. The introduced RINEPT method outperforms the existing methods, both in terms of efficiency and robustness to rf-field inhomogeneity and offset.

I. Introduction

More than 66% of isotopes detectable by nuclear magnetic resonance (NMR) have a nuclear spin quantum number $S = 3/2, 5/2, 7/2$ or $9/2$.¹ These half-integer spin quadrupolar isotopes are the only NMR-active isotopes for over 60% of the chemical elements of the first six periods of the periodic table. These isotopes are located in the vicinity of protons in many materials, including organic compounds, biomolecules, porous and hybrid materials, nanoparticles and heterogeneous catalysts. NMR experiments, in which the proton polarization is transferred to half-integer quadrupolar nuclei, via their hetero-nuclear dipolar couplings, have been developed to probe the proximities between these isotopes. These methods have notably been applied to observe the proximities between protons and ^{11}B , ^{27}Al and ^{17}O in zeolites,²⁻⁴ mesoporous aluminosilicates,⁵ phyllosilicates,⁶ microporous aluminophosphates,^{7,8} pharmaceuticals,⁹ and

nanoparticles.^{8,10} More recently, these methods have been employed to improve the sensitivity for the detection of half-integer quadrupolar isotopes by transferring the magnetization of protons enhanced by dynamic nuclear polarization (DNP) to these isotopes under magic-angle spinning (MAS) conditions.¹¹ This sensitivity gain has notably been used to detect quadrupolar nuclei, such as ²⁷Al, ¹⁷O, ⁴³Ca, ⁹⁵Mo, ⁶⁷Zn and ^{47,49}Ti, near the surface of mesoporous materials and nanoparticles.^{11–18} It is especially useful to observe isotopes with low natural abundance (NA), such as ¹⁷O (NA = 0.037%) and ⁴³Ca (NA = 0.14%), in isotopically unmodified solids.^{14–21}

The transfer of ¹H magnetization to half-integer quadrupolar isotopes under MAS conditions has first been achieved using cross-polarization (CP).²² However, this CPMAS technique then suffers from several limitations due to the spin-locking of the quadrupolar spin's magnetization.^{23,24} Indeed, during this spin-locking, energy level crossings occur, which can partly destroy the quadrupolar spin's magnetization, thus reducing the transfer efficiency.^{23,25} Moreover, the duration of these crossings depends on the crystallite orientation, and hence the magnetization of some crystallites cannot be spin-locked, which produces line-shape distortions.^{26–28} Furthermore, the polarization loss during these crossings depends on the quadrupolar coupling constant, C_Q , which can prevent the simultaneous spin-lock of nuclei with very different C_Q values. The adiabatic crossings of the energy levels lead to efficient spin-locks, but require large radio-frequency (rf) fields that are usually not compatible with the rf power specifications of most MAS probes. Therefore, the spin-locking of quadrupolar nuclei is generally achieved in the sudden-passage condition, which entails the use of low rf fields, and the selective spin-locking of the central transition (CT) between energy levels $\pm 1/2$. However, this low rf field leads to a high sensitivity to offset and chemical shift anisotropy (CSA).^{24,29,30} In addition, CPMAS transfers involving half-integer quadrupolar nuclei require a careful adjustment of the rf fields in order to fulfill one of the Hartmann-Hahn matching conditions: $(S + 1/2)v_{1S} + \varepsilon v_{1I} = nv_R$, where v_{1S} and v_{1I} denote the amplitudes of the rf fields applied to quadrupolar S spin and protons, I , respectively, $\varepsilon = +1$ (double-quantum CP) or -1 (zero-quantum (0Q) CP), $n = \pm 1$ or ± 2 , and v_R denotes the MAS frequency; while avoiding the rotary resonance recoupling (R^3) conditions, $v_{1S} = pv_R/(S + 1/2)$, with $p = 0, 1, 2, 3, \dots$, as spin-locking of the single-quantum (SQ) coherences of the S spin then fails.^{24,29} These requirements lead to a high sensitivity to rf field inhomogeneity.

In order to circumvent these issues, this transfer of ¹H polarization to half-integer quadrupolar isotopes has been achieved using PRESTO (Phase-shifted Recoupling Effects a Smooth Transfer of Order) technique,^{14,31} and more recently, the through-space refocused INEPT sequence (shortened to RINEPT in the following).^{8,18} In these techniques, no spin-lock is applied to the half-integer quadrupolar nucleus, which limits the polarization losses, and improves the robustness to C_Q value, offset and rf field inhomogeneity. We have recently shown that at high MAS frequencies, $v_R \geq 60$ kHz, and high static magnetic field, B_0 , the RINEPT sequence using the symmetry-based $SR4_1^2$ hetero-nuclear dipolar recoupling scheme (denoted RINEPT- $SR4_1^2$) is more efficient than PRESTO, since it exhibits a higher robustness to rf field inhomogeneity as well as to ¹H offset and CSA (CSA_{1H}), and it does not suffer from dipolar truncation, thus allowing polarization transfers beyond the first neighbors.⁸ Conversely, at moderate MAS frequencies, $v_R \leq 20$ kHz, the transfer efficiency of RINEPT- $SR4_1^2$ drops since (i) the rf field during the $SR4_1^2$ recoupling period, $v_{1I} \approx 2v_R$, is not sufficient to decouple the ¹H-¹H dipolar interactions, and (ii) coherent losses due to residual ¹H-¹H dipolar couplings occur during the windows used to rotor synchronize the non- γ -encoded $SR4_1^2$ blocks (Fig. 1b). These losses increase at lower MAS frequencies, because they lead to longer windows and shorter lifetimes, $T_2'(^1H)$, of ¹H SQ coherences during a spin echo.^{32,33} Conversely, PRESTO is more immune to those losses at moderate MAS frequencies since it uses dipolar recoupling schemes

with higher rf requirements, such as R18₁⁷ and R18₂⁵ with $\nu_{1I} = 9\nu_R$ and $4.5\nu_R$, respectively, and no window to separate the different recoupling blocks (Fig. 1a).

We have recently introduced a variant of RINEPT-SR4₁², which limits the polarization losses due to ¹H-¹H dipolar interactions at moderate MAS frequencies.¹⁸ These losses are reduced by employing on the ¹H channel: (i) a SR4₁² recoupling scheme with high-power tanh/tan (tt) adiabatic inversion pulses, and (ii) continuous wave (CW) irradiations during the windows. The use of composite $\pi/2$ and π ¹H pulses further improves the transfer efficiency of this sequence. This novel sequence, denoted RINEPT-CWc-SR4₁²(tt) hereafter, has been shown to be more efficient than PRESTO and CPMAS at moderate MAS frequencies. The efficient decoupling of ¹H-¹H dipolar interactions is especially useful to detect the signal of quadrupolar nuclei with small dipolar couplings with protons, including those with small gyromagnetic ratios, γ , or located in subsurface regions. For instance, we have leveraged the RINEPT-CWc-SR4₁²(tt) technique to acquire the first DNP-enhanced NMR spectra of ^{47,49}Ti, ⁹⁵Mo and ⁶⁷Zn isotopes with natural abundance $NA \leq 16\%$ and $|\gamma/\gamma(^1\text{H})| \leq 0.065$. We have also demonstrated that this novel indirect DNP technique is more sensitive than both direct DNP and indirect DNP using PRESTO to observe unprotonated ¹⁷O sites.

We compare here the performances of RINEPT variants using SR4₁² and SR4₁²(tt) recoupling schemes with those of PRESTO sequences at moderate MAS frequencies. These schemes are first described using an average Hamiltonian theory. We then analyze their robustness to rf inhomogeneity, offset and ¹H-¹H dipolar interactions using numerical simulations of spin dynamics. Their efficiency and robustness are also assessed by experiments performed on isotopically unmodified samples, in which the DNP-enhanced ¹H polarization is transferred to ²⁷Al and ¹⁷O nuclei in γ -alumina and Mg(OH)₂, respectively. We also demonstrate on hydrated titania-supported MoO₃ (MoO₃/TiO₂) that the efficiency of the ¹H $\rightarrow$ ⁹⁵Mo polarization transfer for indirect DNP experiments can be improved by manipulating the populations of the satellite transitions (ST) of ⁹⁵Mo nuclei during the first half of the defocusing period. Finally, we introduce a new version of the *D*-RINEPT transfer with only two pulses applied to the quadrupolar isotope, which provides an enhanced transfer efficiency in the case of large hetero-nuclear dipolar couplings.

II. Pulse sequences and theory

II-1. PRESTO

In the PRESTO sequence, symmetry-based γ -encoded recoupling schemes applied to the ¹H channel reintroduce the $|m| = 2$ space components and the SQ terms of hetero-nuclear dipolar coupling and CSA_{1H}, while they suppress the contributions to the first-order average Hamiltonian of ¹H-¹H dipolar couplings, ¹H isotropic chemical shifts and hetero-nuclear *J*-couplings with protons.³⁴ We employed here the R42₂¹⁷, R20₁⁸, R18₁⁷ and R18₂⁵ recoupling schemes built with single π square pulses having rf field requirements of $\nu_1/\nu_R = 10.5, 10, 9$ and 4.5 , respectively, which are compatible with the rf power specification of most NMR probes with 3.2 mm rotors when $\nu_R \approx 10$ -15 kHz.

During these schemes, the dipolar coupling between *I* and *S* spins contributes to the first-order Hamiltonian by

$$\bar{H}_{D,IS}^{(1)} = \omega_{D,IS} S_z [I^+ \exp(i2\varphi) + I^- \exp(-i2\varphi)] \quad (1)$$

where $I^\pm = I_x \pm iI_y$ are the shift operators, and the magnitude and phase of the recoupled *I*-*S* dipolar coupling are given by

$$\omega_{D,IS} = -\kappa \frac{\sqrt{3}}{2} b_{IS} \sin^2(\beta_{PR}^{D,IS}) \quad (2)$$

and

$$\varphi = \gamma_{PR}^{D,IS} - \omega_R t^0 \quad (3)$$

respectively, where b_{IS} is the dipolar coupling constant in rad/s, and κ is the scaling factor equal to 0.182 for $R42_2^{17}(\pi)$, $R20_1^8(\pi)$, $R18_1^7(\pi)$ and 0.175 for $R18_2^5(\pi)$, respectively. The Euler angles $\{0, \beta_{PR}^{D,IS}, \gamma_{PR}^{D,IS}\}$ relate the inter-nuclear I - S vector to the rotor frame, $\omega_R = 2\pi\nu_R$, and t^0 refers to the starting time of the symmetry-based irradiation. The recoupling schemes are γ -encoded since the norm of $\bar{H}_{D,IS}^{(1)}$ does not depend on the $\gamma_{PR}^{D,IS}$ angle.^{35,36} This γ -encoding character improves the maximum efficiency of the $^1\text{H} \rightarrow S$ polarization transfer for a ^1H - S spin pair. However, Eq.1 also results in dipolar truncation, which prevents long-range transfers, since $\bar{H}_{D,IS}^{(1)}$ does not commute among different spin pairs.

As mentioned above, the employed hetero-nuclear dipolar recoupling schemes also reintroduce with same scaling factor the CSA_{IH} terms in the first-order Hamiltonian, which do not commute with the recoupled ^1H - S dipolar interactions.

In the case of moderate CSA_{IH} , e.g. at moderate B_0 fields, and large ^1H - S dipolar interactions, such as those between covalently bonded ^1H and ^{17}O nuclei, resulting in short defocusing periods, τ_1 , the CSA_{IH} interferences are limited and the PRESTO-II sequence (Fig.1g,i) with only two pulses applied to the quadrupolar isotope is generally the most efficient variant of the PRESTO scheme since it minimizes the number of pulses on the S channel (see subsection IV.5).^{14,37}

Conversely, either in the case of large CSA_{IH} , e.g. at high B_0 fields, or low ^1H - S dipolar interactions, the PRESTO-III variant is generally more efficient (Fig.1a,e), since the interferences of CSA_{IH} are then partly eliminated by the application of two CT-selective π pulses on S channel at the centers of τ_1 and τ_2 periods and a simultaneous overall phase shift of 180° of the ^1H irradiation. The partial refocusing of the CSA_{IH} as well as the shorter delay between the CT-selective $\pi/2$ pulse and the maximum intensity of the spin echo, which is equal to τ_2 for PRESTO-III instead of $2j\tau_R (\geq 2\tau_2)$ for PRESTO-II, can compensate for the magnetization loss due to the additional CT-selective π pulse applied to the S isotope in the case of the PRESTO-III variant.³⁸

It must be noted that using a phase inversion super-cycle (e.g. $R18_2^5.R18_2^{-5}$) to increase the PRESTO robustness leads to a non γ -encoded sequence.

II-2. RINEPT

In the RINEPT sequence, the hetero-nuclear dipolar couplings with protons are reintroduced by applying to the ^1H channel the SR4_1^2 recoupling sequence,³⁹ using either single or tanh/tan adiabatic inversion π -pulses⁴⁰ as basic element.¹⁸ These two recoupling sequences are denoted hereafter $\text{SR4}_1^2(\pi)$ and $\text{SR4}_1^2(\text{tt})$, respectively. This short high-power adiabatic tanh/tan pulse has been shown to produce broadband inversions in solids and has already been employed as an inversion element in RN_n^V symmetry-based hetero-nuclear dipolar recoupling schemes, such as R2_1^1 , R4_2^1 and REDOR sequences, which recouple the $|m| = 1$ space components and the 0Q terms of hetero-nuclear dipolar coupling.^{18,41-44} During the tanh/tan pulse, the instantaneous rf-amplitude is equal to:

$$\omega_1(t) = \omega_{1,\text{max}} \begin{cases} \tanh\left[\frac{8\xi t}{\tau_R}\right] & 0 \leq t < \tau_R/8 \\ \tanh\left[2\xi\left(1 - \frac{4t}{\tau_R}\right)\right] & \tau_R/8 \leq t < \tau_R/4 \end{cases} \quad (4)$$

where $\omega_{1,\text{max}}$ is the peak amplitude of the rf field, t refers to the time since the start of the pulse, which lasts a quarter of one rotor period, $\tau_R = 1/\nu_R$, when incorporated into the SR4_1^2 recoupling

scheme. The parameter ξ determines the rise and fall times of the pulse. The instantaneous phase of the rf field in radians is given by

$$\phi_I(t) = \frac{\Delta\nu_{0,\max}}{20\tan(\theta)} \ln \left\{ \cos \left[\theta \left(1 - 8 \frac{t}{\tau_R} \right) \right] \right\}. \quad (5)$$

Hence, in the frequency-modulated (FM) frame,⁴⁵ the frequency offset is

$$\Delta\omega_0(t) = \frac{\Delta\omega_{0,\max}}{\tan(\theta)} \tan \left[\theta \left(1 - 8 \frac{t}{\tau_R} \right) \right]. \quad (6)$$

where $\Delta\omega_{0,\max}$ is the peak amplitude of the carrier frequency modulation and θ determines the frequency sweep rate in the center of the pulse. Here, we employed $\xi = 10$ and $\theta = 87^\circ = \text{atan}(20)$.^{18,41,43,44} In this FM frame, the effective rf-field has a magnitude of

$$\omega_{\text{eff}}(t) = \sqrt{\omega_1^2(t) + \Delta\omega_0^2(t)} \quad (7)$$

and is tilted from the z-axis of the FM frame by an angle $\beta_{\text{eff}}(t)$ defined by

$$\cos[\beta_{\text{eff}}(t)] = \frac{\Delta\omega_0(t)}{\omega_{\text{eff}}(t)} \quad \text{and} \quad \sin[\beta_{\text{eff}}(t)] = \frac{\omega_1(t)}{\omega_{\text{eff}}(t)}. \quad (8)$$

An efficient adiabatic inversion requires a large $\nu_{1,\max}/\nu_R$ ratio, but a limited $\Delta\nu_{0,\max}/\nu_R$ one.⁴⁴ However, the size of the $\Delta\nu_{0,\max}$ parameter controls the robustness to offset.

The $R4_1^2$ and $R4_1^{-2}$ symmetries recouple the $|m| = 2$ space components and the 0Q terms of hetero-nuclear dipolar coupling and CSA_{IH} . However, they do not suppress the $|m| = 2$ space components and the SQ terms of the ^1H - ^1H dipolar interactions, as well as the SQ terms of the ^1H isotropic chemical shift and the hetero-nuclear J -couplings with protons. These unwanted terms are eliminated by the $R4_1^2 R4_1^{-2}$ super-cycle, which corresponds to a 180° phase shift between successive $R4_1^{\pm 2}$ blocks. In the $\text{SR}4_1^2$ scheme, a three-step multiple-quantum super-cycle, $[R4_1^2 R4_1^{-2}]_0 [R4_1^2 R4_1^{-2}]_{120} [R4_1^2 R4_1^{-2}]_{240}$, further improves the robustness of the recoupling scheme by eliminating unwanted higher-order terms in the effective Hamiltonian.⁴⁶ Other symmetries, such as $\text{R}12_9^5$, (i) allow the $|m| = 2$ space components and the 0Q terms of hetero-nuclear dipolar coupling and CSA_{IH} , (ii) suppress all ^1H isotropic shift and ^1H - ^1H dipolar interactions, but (iii) have a lower rf field requirement since they consist of less than four inversions during one rotor period.⁴⁷ Nevertheless, the sequences built from these symmetries with π pulses as basic element have a scaling factor of the hetero-nuclear dipolar coupling equal to 0 and hence, are unsuitable as hetero-nuclear dipolar recoupling.

The contribution of ^1H -S dipolar coupling to the first-order Hamiltonian is given by:^{8,39,48}

$$\bar{H}_{D,IS}^{(1)} = 2\omega_{D,IS} I_z S_z \quad (9)$$

with

$$\omega_{D,IS} = \kappa b_{IS} \sin^2(\beta_{PR}^{D,IS}) \cos(2\varphi) \quad (10)$$

where φ is given by Eq.3 and $\kappa = 0.25$ for a single π pulse and is given by:^{44,49}

$$\kappa = \frac{1}{2} \int_0^{\tau_R/8} \cos[\beta_{\text{eff}}(t)] \cos\left(8\pi \frac{t}{\tau_R}\right) dt \quad (11)$$

for a tanh/tan pulse achieving an adiabatic inversion; i.e. the ^1H magnetization remains locked along the effective field in the first adiabatic frame tilted by $\beta_{\text{eff}}(t)$ around the y axis of the FM frame. Furthermore, the frequency sweeping range is always much larger than the spinning speed ($\Delta\nu_{0,\max} \gg \nu_R$), and hence the tanh/tan pulse averages out all terms that are not proportional to the 0Q spin operator for the protons. As a consequence, the $R4_1^{\pm 2}$ sequences with tanh/tan adiabatic inversion only recouple in the first-order Hamiltonian the $|m| = 2$ space components and the 0Q terms of hetero-nuclear dipolar coupling and CSA_{IH} , and suppress all

terms related to ^1H - ^1H dipolar interactions, ^1H isotropic chemical shifts and the hetero-nuclear J -couplings with protons.

The κ scaling factor of $\text{SR4}_1^2(\text{tt})$ is $\sqrt{2}$ times smaller than that of other sequences with $\tanh/\tan$ pulses that recouple the $|m|=1$ space components of the hetero-nuclear dipolar coupling, such as $\text{R4}_2^1(\text{tt})$ or $\text{R2}_1^1(\text{tt})$.⁴⁴ However, these schemes do not suppress the ^1H - ^1H dipolar interactions in the first-order average Hamiltonian, and hence they cannot be applied to transfer ^1H magnetization to other isotopes. The scaling factor of $\text{SR4}_1^2(\text{tt})$ depends on several parameters, and e.g. is equal to $\kappa = 0.31$ for $v_{1,\text{max}}/\Delta v_{0,\text{max}} = 0.0685$, $\xi = 10$ and $\theta = 87^\circ$, which is slightly larger than that of $\text{SR4}_1^2(\pi)$: $\kappa = 0.25$. The κ value monotonously decreases for increasing $v_{1,\text{max}}/\Delta v_{0,\text{max}}$ ratios.

As seen in Eqs.3, 9 and 10, the norm of $\bar{H}_{D,IS}^{(1)}$ depends on $\gamma_{PR}^{D,IS}$ angle and hence, the SR4_1^2 recoupling scheme is non- γ -encoded, which results in lower theoretical maximum transfer efficiencies than for PRESTO. However, SR4_1^2 is not affected by dipolar truncation since the recoupled ^1H - S dipolar interactions commute among different spin pairs. Finally, the recoupled ^1H - S dipolar interaction also commutes with the recoupled $\text{CSA}_{1\text{H}}$, which is proportional to I_z . Hence, contrary to PRESTO, $\text{CSA}_{1\text{H}}$ does not interfere with the hetero-nuclear dipolar recoupling scheme for the SR4_1^2 sequence.

In order to transfer the ^1H polarization to S spins, the SR4_1^2 recoupling scheme can be incorporated in the RINEPT sequence, as shown in Figs. **1b,d** and **h,i**. By analogy with the PRESTO-II sequence, we introduce here a RINEPT variant with two pulses applied to the quadrupolar isotope (RINEPT-II shown in Fig. **1h,i**), which is expected to be more efficient in the case of limited $\text{CSA}_{1\text{H}}$ interferences, notably in the case of large ^1H - S dipolar interactions. Conversely, in the case of large $\text{CSA}_{1\text{H}}$ or small ^1H - S dipolar coupling, the conventional RINEPT sequence with three pulses applied to the quadrupolar channel (Fig. **1b,d**) must be preferred. SR4_1^2 is a non- γ -encoded $|m|=2$ recoupling scheme with $\omega_{D,IS}(t^0 + l\frac{\tau_R}{2}) = \omega_{D,IS}(t^0)$, where l is an integer, (according to Eqs.3 and 10), and hence the beginning of the SR4_1^2 blocks, must be separated by an integer number of $\tau_R/2$. In addition, the interval between two successive recoupling blocks must be minimized in order to limit the losses. Furthermore, the $\pi/2$ and π pulses on both channels of the conventional RINEPT sequence (Figs. **1b** and **1e**) must be rotor-synchronized. These synchronizations entail the use of intervals between two consecutive SR4_1^2 blocks equal to either (i) τ_R for complete $\text{R4}_1^{\pm 2}$ cycles, i.e. $\tau_1 = 2k_1\tau_R$ and $\tau_2 = 2k_2\tau_R$, where k_1 and k_2 are integers, or (ii) $\tau_R/2$ for incomplete $\text{R4}_1^{\pm 2}$ cycles, i.e. $\tau_1 = (2k_1+1)\tau_R$ and $\tau_2 = (2k_2+1)\tau_R$.

Even if the $\pi/2$ and π pulses on the ^1H channel are shorter than $5\text{ }\mu\text{s}$, those on the S spins are CT-selective and their lengths range from 5 to $20\text{ }\mu\text{s}$. Therefore, the conventional RINEPT- SR4_1^2 incorporates eight windows on the ^1H channel (Fig. **1b**). However, signal losses related to ^1H - ^1H interactions mainly occur during the first four windows, because the ^1H magnetization is aligned with the z axis during the last four ones. The total length of these four first windows is equal to τ_R or $2\tau_R$ for intervals between the recoupling blocks equal to $\tau_R/2$ or τ_R , respectively, i.e. 100 and $200\text{ }\mu\text{s}$ at $v_R = 10\text{ kHz}$. These total lengths are comparable to the inverse of the ^1H linewidth under these MAS frequencies, which are typically equal to a few kHz.⁵⁰ Hence, significant losses due to ^1H - ^1H dipolar interactions can occur during these windows.

This issue can be circumvented by the application of CW irradiations during these delays (Fig. **1c**). The proton nutation frequency during CW irradiation, $v_{1,\text{CW}}$, must exceed $4v_R$ in order to avoid the first- and second-order R^3 conditions.^{51,52} Note that commensurate $v_{1,\text{CW}}$ and v_R values can then be described as CN_n^0 and RN_n^0 sequences built from rectangular 2π and π pulses, respectively, with $N/n > 4$, which suppress the contribution of ^1H - ^1H dipolar interactions to the

first-order Hamiltonian.^{53,54} An alternative to CW irradiations between the SR4_1^2 blocks would be homo-nuclear dipolar decoupling schemes, such as DUMBO.⁵⁵ However, the cycle times of these schemes are not necessarily commensurate with the delays between the recoupling blocks, and in practice, CW irradiations yielded the highest transfer efficiency. Furthermore, the nutation during these CW irradiations can be eliminated by bracketing the π or $\pi/2$ ^1H pulses by CW irradiations with opposite phases, which are either equal or opposite to the phase of the central π or $\pi/2$ pulses since

$$R_x(\omega_{1,\text{CW}}\tau_{\text{CW}})R_x(q\pi)R_x(-\omega_{1,\text{CW}}\tau_{\text{CW}}) = R_x(q\pi) \quad (12)$$

where $R_x(\psi) = \exp(-i\psi I_x)$ is the rf propagator of a pulse with flip angle ψ and phase x , and $q = 1/2$ or 1 . It must be noted that the CW irradiation during the first delay of Fig. 1b has been skipped in Fig. 1c, because it only acts as a spin-lock of ^1H transverse magnetization.

The robustness to the ^1H rf inhomogeneity can be improved by the use of composite $\pi/2$ and π pulses. Fig. 1d displays the RINEPT variant combining CW irradiations with composite pulses for an interval of τ_R between consecutive SR4_1^2 blocks. This variant is denoted RINEPT-CWc hereafter.

The rf propagator of the composite π pulse is equal to:

$$R_y(\pi/2)R_x(\omega_{1,\text{CW}}\tau_{\text{CW}})R_x(\pi)R_x(-\omega_{1,\text{CW}}\tau_{\text{CW}})R_y(\pi/2) = R_y(\pi/2)R_x(\pi)R_y(\pi/2) \quad (13)$$

i.e., it is identical to that of $\pi/2_{90}\pi_0\pi/2_{90}$, which is a composite π pulse compensated for rf field inhomogeneity.⁵⁶ The application of CW irradiations between the bracketing $\pi/2_{90}$ pulses and the first central π_0 pulse decouples the ^1H - ^1H dipolar interactions. Conversely, no improvement in the transfer efficiency was detected when employing a composite π pulse during the refocusing delay.

The rf propagator of the composite $\pi/2$ pulse is the same as that of $\pi/2_{90}\pi/2_0$,

$$R_y(\pi/2)R_x(\omega_{1,\text{CW}}\tau_{\text{CW}})R_x(-\omega_{1,\text{CW}}\tau_{\text{CW}})R_x(\pi/2) = R_y(\pi/2)R_x(\pi/2) \quad (14)$$

which is a composite $\pi/2$ pulse compensated for rf field inhomogeneity,⁵⁷ and canceling the ^1H - ^1H dipolar interactions.

The coherence transfer from protons to the S quadrupolar spins can also be accelerated by manipulating the satellite transition (ST) populations of the S -spin during the first half of the defocusing period since the ^1H SQ coherences dephase more rapidly under the dipolar coupling with the STs than with the CT. This experiment is denoted population transfer (PT) RINEPT hereafter (Fig. 1f). This faster transfer limits the magnetization losses during the defocusing part and hence, improves the transfer efficiency. This approach has already been employed to improve the efficiency of through-bond and through-space HMQC (hetero-nuclear multiple-quantum coherence) experiments involving half-integer quadrupolar isotopes in solids.^{38,58-60}

III. Numerical simulations

III-1. Simulation parameters

All numerical simulations of spin dynamics were performed with the SIMPSON software (version 4.1.1).⁶¹ The powder average was calculated using 462 and 34000 $\{\alpha_{\text{MR}}, \beta_{\text{MR}}, \gamma_{\text{MR}}\}$ Euler angles consisting of 66 and 2000 $\{\alpha_{\text{MR}}, \beta_{\text{MR}}\}$ angles and 7 and 17 γ_{MR} angles for $^1\text{H} \rightarrow ^{13}\text{C}$ and $^1\text{H} \rightarrow ^{17}\text{O}$ transfers, respectively. The $\{\alpha_{\text{MR}}, \beta_{\text{MR}}\}$ angles, which relate the molecular and rotor frames, were selected according to the REPULSION algorithm,⁶² while the γ_{MR} angles, were equally stepped from 0 to 360° .

We simulated the $^1\text{H} \rightarrow ^{13}\text{C}$ transfer, instead of the $^1\text{H} \rightarrow ^{27}\text{Al}$ one, in order to accelerate the simulations of transfer efficiency since only CT-selective pulses are applied to the quadrupolar isotope in RINEPT and PRESTO sequences and hence STs only weakly contribute to the signal.

These simulations of the $^1\text{H} \rightarrow ^{13}\text{C}$ transfer were performed for a $^{13}\text{C}^1\text{H}_4$ spin system. This approach has already been employed in the analysis of the PRESTO and RINEPT-SR4 $_1^2(\pi)$ sequences.⁸ Obviously, this simplification is not valid to simulate PT-RINEPT experiments, during which the STs of the quadrupolar isotope are irradiated. The considered $^{13}\text{C}^1\text{H}_4$ spin system consists of four protons located on the vertices of a tetrahedron and a ^{13}C nucleus placed on one symmetry axis of this tetrahedron. All ^1H - ^1H dipolar coupling constants are identical and equal to $|b_{\text{HH}}|/(2\pi) = 7$ kHz, except in Fig. 5, where $|b_{\text{HH}}|/(2\pi)$ was varied from 0 to 20 kHz. The ^{13}C nucleus is dipolar coupled with its closest proton with $|b_{\text{HC}}|/(2\pi) = 2575$ Hz, except in Figs. S2 and S4a, where $|b_{\text{HC}}|/(2\pi) = 368$ Hz. Dipolar coupling constants of 2575 and 368 Hz correspond to ^1H - ^{27}Al distances of 2.3 and 4.4 Å, respectively, which are typical distances between the protons of OH groups and the Al atoms of the first and second surface layers of hydrated γ -alumina.¹³ The CSA $_{\text{IH}}$ value of all protons was equal to 6 kHz, except in Fig. S2a where it was zero, its asymmetry parameter was null, and its principal axis was aligned with the 3-fold rotational axes (C_3) of the $^1\text{H}_4$ tetrahedron. The inversion efficiency of a single tanh/tan pulse was also calculated for an isolated proton with a CSA of 6 kHz (Fig. S1).

On the contrary, the line-shape simulations of the $^1\text{H} \rightarrow ^{17}\text{O}$ 1D RINEPT and PRESTO signals, shown in Figs. 11 and 12, were performed for one ^1H - ^{17}O spin-pair since the ^{17}O CT is broadened by the second-order quadrupolar interaction. The hetero-nuclear dipolar coupling for the ^1H - ^{17}O spin pair was equal to $|b_{\text{HO}}|/(2\pi) = 16.25$ kHz, corresponding to the O-H distance of 0.995 Å in $\text{Mg}(\text{OH})_2$.⁶³ The quadrupolar coupling constant and the asymmetry parameter of the electric field gradient (efg) of the ^{17}O nucleus were 6.835 MHz and zero, respectively. The CSA $_{\text{IH}}$ was equal to 7.5 ppm and its asymmetry parameter was null.⁶⁴ The CSA $_{\text{IH}}$ and ^{17}O efg tensors were coaxial, their principal axes being aligned with the ^1H - ^{17}O inter-nuclear vector, like in $\text{Mg}(\text{OH})_2$ which exhibits a 3-fold crystal symmetry.³⁷

The static magnetic field, B_0 , was equal to 9.4 T and hence, the ^1H , ^{13}C and ^{17}O Larmor frequencies were equal to 400.0, 100.6 and 54.2 MHz, respectively. The MAS frequency was $\nu_{\text{R}} = 12.5$ kHz. These conditions are comparable to those used in experiments (see section IV). For $^1\text{H} \rightarrow ^{13}\text{C}$ transfers, we simulated the signals of PRESTO-III-R42 $_2^{17}(\pi)$, R20 $_1^8(\pi)$, R18 $_1^7(\pi)$, and R18 $_2^5(\pi)$, so that of RINEPT with SR4 $_1^2(\pi)$ and SR4 $_1^2(\text{tt})$, as well as RINEPT-CW and RINEPT-CWc variants using SR4 $_1^2(\text{tt})$. For $^1\text{H} \rightarrow ^{17}\text{O}$ transfers, we simulated the ^{17}O spectra corresponding to the RINEPT-CWc-SR4 $_1^2(\text{tt})$ and PRESTO-III-R18 $_2^5(\pi)$ sequences. We always used identical defocusing and refocusing periods and complete RN_n^v cycles: $\tau_1 = \tau_2 = \tau = 2k\tau_{\text{R}}$, where k is an integer. Furthermore, these periods were fixed to their optimal values: 640 and 4480 μs for $|b_{\text{HC}}|/(2\pi) = 2575$ and 368 Hz, respectively, in the case of SR4 $_1^2(\pi)$ and SR4 $_1^2(\text{tt})$ recoupling schemes, except in Figs. 3a, 4b, S3, S4 and S6. The optimal τ values for R42 $_2^{17}(\pi)$, R20 $_1^8(\pi)$, R18 $_1^7(\pi)$, and R18 $_2^5(\pi)$ recoupling schemes are indicated in the caption of Fig. 5. The delay between two successive recoupling blocks was equal to τ_{R} , except in Fig. S3, where no interval was inserted. The rf field amplitude of the $\pi/2$ and π ^1H pulses, which do not belong to the recoupling sequence, was fixed to 100 kHz, except in Fig. S3, where it was varied, whereas the pulses on the $S = ^{13}\text{C}$ channel were simulated as ideal Dirac pulses. For SR4 $_1^2(\text{tt})$ recoupling, the parameters $\nu_{1,\text{max}}$ and $\Delta\nu_{0,\text{max}}$ were equal to 137 kHz and 2 MHz, except in Figs. 2, 3b and S2. For R42 $_2^{17}(\pi)$, R20 $_1^8(\pi)$, R18 $_1^7(\pi)$, R18 $_2^5(\pi)$ and SR4 $_1^2(\pi)$ recoupling schemes, the rf field amplitudes were fixed to their theoretical values, $\nu_1/\nu_{\text{R}} = 10.5, 10, 9, 4.5$ and 2, respectively. All pulses were applied on resonance. The initial density matrix was $I_{1z} + I_{2z} + I_{3z} + I_{4z}$ and I_{1z} for the CH_4 and OH spin systems, respectively. The efficiencies of $^1\text{H} \rightarrow ^{13}\text{C}$ PRESTO and RINEPT transfers were normalized with respect to the maximal signal intensity for a $^1\text{H} \rightarrow ^{13}\text{C}$ through-bond RINEPT sequence using ideal Dirac pulses in the case of a ^{13}C - ^1H spin system with a J -coupling constant of 150 Hz.

III-2. Optimization of the adiabatic recoupling scheme and build-up curves

Fig. 2 shows the transfer efficiency of the $^1\text{H} \rightarrow ^{13}\text{C}$ RINEPT-SR4₁²(tt) sequence with $\tau = 640 \mu\text{s}$ as function of $v_{1,\text{max}}/v_{\text{R}}$ and $\Delta v_{0,\text{max}}/v_{\text{R}}$ ratios. As this sequence incorporates 64 adiabatic inversion pulses, it requires a larger rf-field and carrier frequency modulation than a single inversion on an isolated ^1H nucleus using a tanh/tan pulse (compare Figs. 2 and S1). The transfer efficiency drops for simultaneous low $v_{1,\text{max}}/v_{\text{R}}$ and large $\Delta v_{0,\text{max}}/v_{\text{R}}$ ratios; conditions under which the tanh/tan pulses do not achieve adiabatic inversions. A small transfer efficiency is also observed for low $\Delta v_{0,\text{max}}/v_{\text{R}}$ ratios, which result in low scaling factors.⁴⁴ In the following, we used $\Delta v_{0,\text{max}}/v_{\text{R}} \approx 160$ and $v_{1,\text{max}}/v_{\text{R}} \approx 11$, i.e. $\Delta v_{0,\text{max}} = 2 \text{ MHz}$ and $v_{1,\text{max}} = 137 \text{ kHz}$, which is compatible with the specifications of the employed 3.2 mm DNP MAS probe. Experimentally, these parameters, indicated with a white star in Fig. 2, allow an adiabatic inversion of the magnetization for all parts of the sample in the rotor, in spite of the distribution of the rf-field displayed as a white vertical line. According to Fig. 2, RINEPT-SR4₁²(tt) requires $v_{1,\text{max}}/v_{\text{R}} \geq 5$, for all parts of this sample with $|b_{\text{HC}}|/(2\pi) = 2575 \text{ Hz}$. In the case of small hetero-nuclear dipolar interactions, higher rf field strengths are necessary since the transfer employs longer recoupling periods and hence, a larger number of adiabatic inversions of the ^1H magnetization.

The build-up curves of $^1\text{H} \rightarrow ^{13}\text{C}$ RINEPT sequences using SR4₁²(π) and SR4₁²(tt) recoupling schemes are compared in Fig. 3a. The maximal transfer efficiency is achieved for the same recoupling time, $\tau \approx 640 \mu\text{s}$. This result is consistent with the similar κ values of those recoupling schemes. However, the maximal transfer efficiency obtained with SR4₁²(tt) is more than twice higher than that of SR4₁²(π). This lower efficiency of SR4₁²(π) stems from losses due to ^1H - ^1H dipolar interactions since in the absence of these interactions, identical build-up curves are obtained for SR4₁²(π) and SR4₁²(tt) recoupling schemes (not shown).

III-3. Robustness to rf inhomogeneity

A MAS NMR coil produces an rf field which depends on the position inside the sample volume.^{65–69} For the 3.2 mm sapphire rotors we employed, the minimal rf field within the sample volume was approximately 70% of its maximum value (see section IV-2). In Fig. 3b, the simulated transfer efficiencies of $^1\text{H} \rightarrow ^{13}\text{C}$ RINEPT sequences using SR4₁²(π) and SR4₁²(tt) are plotted versus the ratio between the applied and the theoretical rf fields, $v_{1\text{max}}/v_{1\text{max,th}}$. These simulations indicate that the SR4₁²(tt) recoupling scheme is much more robust to rf inhomogeneities than SR4₁²(π). For instance, when $v_{1\text{max}} = 0.9v_{1\text{max,th}}$ the transfer efficiency is two-fold lower than its maximal value in the case of SR4₁²(π), whereas it is only reduced by less than 5% with SR4₁²(tt). This high robustness to rf inhomogeneity stems from the tolerance of adiabatic pulses to variations in rf field amplitude, as long this field is sufficient, and has also been reported for other symmetry-based hetero-nuclear dipolar recoupling schemes.^{41,42,44}

For the SR4₁²(π) recoupling scheme, a good transfer efficiency is also achieved when $v_1 = 1.5v_{1\text{max,th}} = 3v_{\text{R}}$ (Fig. 3b), as previously observed.^{8,70,71} Under this condition, the recoupling sequence corresponds to a train of $3\pi/2$ pulses, and hence is not a RN_n^v sequence. However, as the consecutive $3\pi/2$ pulses have opposite phases, the sequence can then be described as a C2_1^0 recoupling scheme built from a $3\pi/2_0 3\pi/2_{180}$ cyclic basic element. This symmetry recouples the ^1H isotropic chemical shifts as well as the $|m| = 2$ space components of hetero-nuclear dipolar coupling with protons and $\text{CSA}_{1\text{H}}$. The contribution of ^1H -S dipolar coupling to the first-order Hamiltonian is given by Eqs. 9 and 10 with $\kappa = 0.19$ (instead of $\kappa = 0.25$ for $v_1 = 2v_{\text{R}}$), while only the 0Q terms of the ^1H isotropic chemical shift and CSA have a non-zero scaling factor. The evolutions under these two recoupled interactions are refocused by the π pulses applied to the ^1H channel. The RINEPT build-up curve corresponding to $v_1 = 3v_{\text{R}}$ is displayed

in Fig. 3a and exhibits the same optimal recoupling time and similar oscillations as the curve simulated for $\nu_1 = 2\nu_R$.

For $|b_{\text{HC}}|/(2\pi) = 2.575$ kHz and $\nu_1 = 2\nu_R$, the optimal τ value is 640 μs and each recoupling block of $\tau/2$ lasts four rotor periods at $\nu_R = 12.5$ kHz, i.e. corresponds to the $[\text{R}4_1^2\text{R}4_1^{-2}]_0[\text{R}4_1^2\text{R}4_1^{-2}]_{120}$ sequence. Conversely, for smaller hetero-nuclear dipolar couplings, longer τ recoupling periods are required and the full $\text{SR}4_1^2$ three-steps multiple-quantum super-cycle can be employed. In that case, this super-cycle improves the robustness to rf inhomogeneity of $\text{SR}4_1^2(\text{tt})$ recoupling, as seen in Fig. S2, and was thus employed when the recoupling blocks were long enough.

III-4. CW irradiation and composite pulses

$\text{SR}4_1^2$ being a non- γ -encoded $|m| = 2$ scheme, the recoupling blocks need to be separated by multiples of $\tau_R/2$, except when using very large rf-fields for the $\pi/2$ and π ^1H pulses (Fig. S3). As shown in Figs. 4 and S4, the transfer efficiency of the RINEPT sequences can be enhanced by applying CW irradiations with opposite phases before and after the $\pi/2$ and π pulses with an rf field amplitude, $\nu_{1,\text{CW}} \geq 4\nu_R$, to avoid the first- and second-order R^3 conditions.⁵¹ Conversely, CW irradiations with $0 < \nu_{1,\text{CW}} \leq 2\nu_R$ reduce the transfer efficiency since the R^3 recoupling conditions, $\nu_{1,\text{CW}} = p\nu_R$, reintroduce the homo- ($p = 1/2$ or 1) and hetero-nuclear ($p = 1$ or 2) dipolar couplings. Fig. S4 indicates that losses due to ^1H - ^1H dipolar couplings occur during the $\text{SR}4_1^2(\text{tt})$ blocks, even if they eliminate the contribution of these couplings to the first-order average Hamiltonian (compare the continuous curves). These losses increase for longer recoupling times, i.e. smaller hetero-nuclear couplings. Fig. S5 confirms that the highest robustness to rf inhomogeneity is obtained by using CW irradiations with opposite phases, one of them being equal to that of the bracketed pulse.

Fig. S6 compares two implementations of composite pulses incorporating CW irradiations. The highest transfer efficiency is obtained when the evolution during the second CW irradiation compensates that during the first one so that the rf propagator during the CW irradiations does not affect the amplitude of the signal (Eqs. 12-14).

III-5. Robustness to ^1H - ^1H dipolar interactions

The robustness to ^1H - ^1H dipolar interactions of PRESTO-III and RINEPT sequences was compared by simulating the $^1\text{H} \rightarrow ^{13}\text{C}$ transfer efficiencies with the $^{13}\text{C}^1\text{H}_4$ spin system as function of the ^1H - ^1H dipolar coupling constant. For PRESTO-III, ^1H - ^{13}C hetero-nuclear couplings were reintroduced using the commonly employed $\text{R}18_1^7(\pi)$ and $\text{R}18_2^5(\pi)$ recoupling schemes with $\nu_1 = 112.5$ and 56.25 kHz, respectively, as well as $\text{R}42_2^{17}(\pi)$ and $\text{R}20_1^8(\pi)$ schemes with $\nu_1 = 131.25$ and 125 kHz, respectively, i.e. an rf field amplitude similar to $\nu_{1,\text{max}} = 137$ kHz employed for the $\text{SR}4_1^2(\text{tt})$ recoupling sequence. For both large and small ^1H - ^{13}C dipolar coupling constants, the RINEPT-CWc- $\text{SR}4_1^2(\text{tt})$ sequence exhibits the highest robustness to ^1H - ^1H dipolar couplings (Fig. 5). This sequence is more robust than the conventional RINEPT- $\text{SR}4_1^2(\pi)$ owing to the higher rf field used during the recoupling blocks, as well as the CW irradiation between them. Furthermore, the higher robustness of the RINEPT-CWc- $\text{SR}4_1^2(\text{tt})$ sequence with respect to the PRESTO-III- $\text{R}42_2^{17}(\pi)$ and $-\text{R}20_1^8(\pi)$ schemes must stem from a better elimination of ^1H - ^1H dipolar couplings by the $\text{SR}4_1^2(\text{tt})$ scheme, since the applied rf field amplitudes on the ^1H channel for these sequences are comparable. The high robustness of the RINEPT-CWc- $\text{SR}4_1^2(\text{tt})$ sequence is especially useful for polarization transfers through small hetero-nuclear dipolar couplings (Fig. 5b). Counterintuitively, the

robustness of PRESTO-III sequences to ^1H - ^1H dipolar interactions is nearly independent of the rf field amplitude, except for large hetero-nuclear dipolar interactions (Fig. 5a), where the $\text{R18}_2^5(\pi)$ recoupling with the lowest rf field requirement is more robust than the $\text{R42}_2^{17}(\pi)$, $\text{R20}_1^8(\pi)$ and $\text{R18}_1^7(\pi)$ recoupling schemes. This better robustness of the $\text{R18}_2^5(\pi)$ scheme is consistent with the smaller root-mean square (rms) of the scaling factors of the symmetry-allowed second-order cross-terms between two terms of the ^1H - ^1H dipolar interaction, which is equal to 1.25×10^{-3} for $\text{R18}_2^5(\pi)$, instead of 1.42×10^{-3} for $\text{R42}_2^{17}(\pi)$, $\text{R20}_1^8(\pi)$ and $\text{R18}_1^7(\pi)$ recoupling schemes. These rms scaling factors have been calculated by using the ‘C and R symmetries’ Mathematica package.^{46,70}

IV. NMR experiments

IV-1. Samples and experimental conditions

Isotopically unmodified γ -alumina, $\text{Mg}(\text{OH})_2$, L-histidine·HCl·H₂O, TCE (1,1,2,2-tetrachloroethane) and TEKPol samples were purchased from Sigma-Aldrich, Fujifilm Wako Pure Chemical Corporation, Sigma-Aldrich, Tokyo Chemical Industry Co. Ltd, and Cortecnet, respectively, and used without any labeling. $\text{MoO}_3/\text{TiO}_2$ containing about 10 wt% of MoO_3 was prepared as previously reported.¹⁸ For DNP-NMR experiments, about 20.5 mg of γ -alumina, 27 mg of $\text{Mg}(\text{OH})_2$, 32 mg of L-histidine·HCl·H₂O and 40 mg of 10 wt% $\text{MoO}_3/\text{TiO}_2$ were impregnated in the air with 30, 30, 20 and 20 μL of TEKPol solutions in TCE with concentration of 5, 16, 16 and 110 mM, respectively, and packed into a 3.2 mm sapphire rotor closed with zirconia caps.

All experiments were performed at 9.4 T on a Bruker BioSpin Avance NEO DNP-NMR spectrometer equipped with a 263 GHz gyrotron and a double-resonance $^1\text{H}/\text{X}$ 3.2 mm low-temperature MAS probe.⁷¹ The microwave irradiation was transmitted through a corrugated waveguide to the probe, and its power delivered to the sample was ca. 6 W. For all experiments, the B_0 field was optimal for DNP applied to protons using TEKPol as polarizing agent, which corresponds to a ^1H Larmor frequency of 400.536 MHz. The samples were spun at MAS frequencies of $\nu_R = 12.5$ kHz, except in Fig. S7. The DNP-NMR spectra were acquired at a temperature of ca. 105 K, which was stabilized using a Bruker BioSpin MAS cooling system.

The build-up time of the DNP-enhanced ^1H polarization was measured using saturation-recovery experiments employing a burst of 31 pre-saturation $\pi/2$ -pulses separated by 0.1 ms, followed by a relaxation delay, τ_{RD} , ranging from 0.1 to 128 s. The signal intensity of these experiments was fitted versus τ_{RD} , which yielded the effective build-up time of the DNP-enhanced ^1H polarization, $T_{\text{B,on}}(^1\text{H}) = 5.7, 0.5, 3.1$ and 48 s for γ -alumina, 10 wt% $\text{MoO}_3/\text{TiO}_2$, $\text{Mg}(\text{OH})_2$ and L-histidine·HCl·H₂O, respectively. The DNP enhancement of the ^1H signal, $\epsilon_{\text{on/off}}(^1\text{H})$, was measured as the ratio between the ^1H signals of TCE in Hahn-echo spectra with and without microwave irradiation and was equal to 122, 48, 220 and 102 for these samples, respectively.

The ^1H nutation frequency was measured using 2D nutation experiments without B_0 field gradient and corresponds to the average nutation frequency over the volume of the sample. The spatial distributions of the rf fields at the ^1H and ^{13}C Larmor frequencies were assessed using 2D nutation experiments on PDMS (polydimethylsiloxane) and adamantane, respectively, in the presence of a B_0 field gradient.^{67,68} This experiment uses the pulse-acquire sequence, in which the length of the pulse, t_1 , is incremented and forms the indirect evolution period of the 2D experiment. During this experiment, the B_0 field gradient is generated using the room-temperature shim coil. The ^1H and ^{13}C 2D nutation spectra result from averaging 2 and 8

transients for each of the 200 and 100 t_1 -increments with $\Delta t_1 = 2.1$ and $3.4 \mu\text{s}$, respectively, resulting in 14 and 29 min experimental times.

We also compared the efficiency and the robustness to rf inhomogeneity and offset of the various RINEPT variants shown in Fig. 1 using $\text{SR4}_1^2(\pi)$ or $\text{SR4}_1^2(\text{tt})$ recoupling schemes with those of CPMAS, PRESTO-III- $\text{R18}_1^7(\pi)$ and $-\text{R18}_2^5(\pi)$ sequences in the case of $^1\text{H} \rightarrow ^{27}\text{Al}$ polarization transfers in γ -alumina. We also compared the efficiency of the $^1\text{H} \rightarrow ^{95}\text{Mo}$ RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ transfer with its PT variant in the case of the 10 wt% $\text{MoO}_3/\text{TiO}_2$ sample. The sensitivity of these experiments was enhanced by using the QCPMG (quadrupolar Carr-Purcell-Meiboom-Gill) signal recycling scheme.⁷² Finally, the line-shape distortions were assessed by acquiring the ^{17}O NMR spectra of $\text{Mg}(\text{OH})_2$ enhanced by indirect DNP using the PRESTO- $\text{R18}_2^5(\pi)$ and RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ sequences with two or three pulses on the ^{17}O channel. For all these DNP experiments, we used $\tau_{\text{RD}} = 1.3T_{\text{B,on}}(^1\text{H})$ in order to maximize the sensitivity,⁷³ and $\tau_1 = \tau_2 = \tau = 2k\tau_{\text{R}}$, except in Fig. S7 where $\tau = k\tau_{\text{R}}$, and in Fig. 13b, where $\tau = \tau_{\text{R}}/2$ in order to sample the maximum of the build-up curves of the H_2O signal. The delay between two successive recoupling blocks was equal to τ_{R} , except in Figs. S7b and 13b where this delay was equal to $\tau_{\text{R}}/2$. We used $\nu_{1,\text{max}} = 137, 34, 98$ and 56 kHz , for $\text{SR4}_1^2(\text{tt})$, $\text{SR4}_1^2(\pi)$, $\text{R18}_1^7(\pi)$ and $\text{R18}_2^5(\pi)$ recoupling schemes, respectively, except in Figs. 6a, 9, S9 and S11b, where the strength of the recoupling rf-field was varied. For the $\text{SR4}_1^2(\text{tt})$ scheme, we employed $\Delta\nu_{0,\text{max}} = 2 \text{ MHz}$, except in Fig. S11a. For RINEPT experiments, the rf field of the ^1H $\pi/2$ and π pulses, which do not belong to the recoupling scheme, was equal to 137 kHz . For RINEPT-CW and -CWc experiments, $\nu_{1,\text{CW}} = 87 \text{ kHz}$. SPINAL-64 decoupling with a rf-field of 100 kHz and a pulse length of $4.6 \mu\text{s}$ was applied during the acquisition.⁷⁴ The pulses on the ^1H channel were applied on resonance, and those on the S channel at the frequency position corresponding to the barycenter of the signal, except in Figs. 6b and 8b. The rf-field of the CT-selective $\pi/2$ and π pulses was equal to $5.6, 7.2$ and 10.4 kHz for ^{17}O , ^{27}Al and ^{95}Mo isotopes, except in Fig. 9b. During the $^1\text{H} \rightarrow ^{27}\text{Al}$ CPMAS transfer, the rf-fields on ^1H and ^{27}Al channels were constant and equal to 31 and 6.8 kHz , respectively, equivalent to the $n = 1$ Hartmann-Hahn condition, except in Figs. 9 and S12. The ^{27}Al spectra enhanced by indirect DNP of γ -alumina impregnated with 5 mM TEKPol solution typically result from averaging 16 transients. For $^1\text{H} \rightarrow ^{95}\text{Mo}$ PT-RINEPT experiment (Fig. 10), the populations of the STs were manipulated during the first $\tau_1/2$ period by applying a DFS pulse lasting $160 \mu\text{s}$ and using a maximal rf field amplitude of 30 kHz . During this pulse, the two rf carrier sidebands were linearly swept from 400 to 60 kHz in a symmetric manner. The $^1\text{H} \rightarrow ^{17}\text{O}$ PRESTO and RINEPT spectra of $\text{Mg}(\text{OH})_2$ and L-histidine·HCl· H_2O typically result from averaging 256 (Fig. 12) and 1024, 176, 112 transients, (Fig. 13b-d respectively). Simulations of 1D ^{17}O NMR spectra of L-histidine·HCl· H_2O have been performed using the solid lineshape analysis (SOLA) module v2.2.4 included in the Bruker Topspin version 4.0.8 software.

The isotropic chemical shifts were referenced at 0 ppm to that of: (i) liquid H_2O for ^{17}O , (ii) 2 mol/L aqueous solution of Na_2MoO_4 for ^{95}Mo , and (iii) 1 mol.L^{-1} $\text{Al}(\text{NO}_3)_3$ solution for ^{27}Al .

IV-2. Improving the efficiency and the robustness of RINEPT

Fig. S7 shows the build-up of $^1\text{H} \rightarrow ^{27}\text{Al}$ RINEPT-CW- $\text{SR4}_1^2(\text{tt})$ signal intensity as function of τ recoupling time. Positive sidebands are only observed when the π and central $\pi/2$ pulses on both channels are rotor-synchronized, i.e. when $\tau = 2k\tau_{\text{R}}$ and $(2k+1)\tau_{\text{R}}$ for the delay between successive $\text{SR4}_1^2(\text{tt})$ blocks equal to τ_{R} and $\tau_{\text{R}}/2$, respectively.

The 2D nutation spectra of protons in PDMS and ^{13}C nuclei in adamantane in the presence of a B_0 field gradient are shown in Fig. S8. These spectra display the distribution of rf nutation frequency along the F_1 dimension and the signal frequency, including the frequency shift

produced by the B_0 gradient along the F_2 dimension. The ^{13}C 2D nutation spectrum displays two distinct signals around 38 and 28 ppm ascribed to CH and CH_2 sites of adamantane. At both ^1H and ^{13}C Larmor frequencies, the minimal rf field at the edge of the sample volume was approximately 70% of its maximal value. This rf inhomogeneity is smaller than that measured for conventional 3.2 mm MAS probes in agreement with the restricted sample volume of 3.2 mm sapphire rotors. Furthermore, the 2D nutation spectra indicate that the rf field amplitude decreases in the middle of the sample. This reduction is consistent with the increased pitch of the sample coil at its center in order to launch microwaves between the turns of the coil and to minimize their diffraction by the coil.^{75,76}

As seen in Fig.S9, the experimental optimal rf field for the $\text{SR4}_1^2(\text{tt})$ recoupling sequence using $\Delta\nu_{0,\text{max}} = 2$ MHz is comparable to the value predicted by numerical simulations and ca. 4-times higher than that of $\text{SR4}_1^2(\pi)$. The higher rf field requirement of the $\text{SR4}_1^2(\text{tt})$ recoupling scheme stems from the need to fulfill the adiabaticity condition. Note that the optimal rf-field of the $\text{SR4}_1^2(\pi)$ scheme is intermediate between $2\nu_R$ and $3\nu_R$, the two rf recoupling conditions shown in Fig.3b, owing to the rf-field inhomogeneity of the probe. The $\text{SR4}_1^2(\text{tt})$ recoupling scheme based on adiabatic pulses is more robust to rf-field inhomogeneity and offset than $\text{SR4}_1^2(\pi)$ (Fig.6), although the amplitude-modulated $\text{SR4}_1^2(\pi)$ recoupling sequence already exhibits high robustness to rf-field inhomogeneity for moderate ^1H - ^1H dipolar interactions, as in the case of γ -alumina.⁸

Furthermore, the use of composite π pulses incorporating CW irradiations improves the transfer efficiency and the robustness to rf-field inhomogeneity (Fig.S10). As shown in Fig.7a, the adiabatic recoupling scheme, CW irradiations and composite pulses improve the transfer efficiency of $^1\text{H} \rightarrow ^{27}\text{Al}$ RINEPT experiments on γ -alumina impregnated with TEKPol solution. The improvement in transfer efficiency stems from the decoupling of ^1H - ^1H dipolar interactions by CW irradiations and the higher robustness to rf-field inhomogeneity for the composite pulses. Furthermore, with respect to $\text{SR4}_1^2(\pi)$, the $\text{SR4}_1^2(\text{tt})$ recoupling scheme benefits from improved robustness to ^1H - ^1H dipolar couplings and rf inhomogeneity, which enhances the transfer efficiency. For γ -alumina, the signal of $^1\text{H} \rightarrow ^{27}\text{Al}$ RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ experiment is 16-fold higher than that of the RINEPT- $\text{SR4}_1^2(\pi)$ variant, i.e. an acceleration factor of 256 in acquisition time.

IV-3. Comparison of CPMAS, (PT)-RINEPT- $\text{SR4}_1^2(\text{tt})$ and PRESTO-R18₁⁷ or -R18₂⁵

As seen in Fig.S11, the rf-field requirement of $\text{SR4}_1^2(\text{tt})$ is significantly higher than those of $\text{R18}_1^7(\pi)$ and $\text{R18}_2^5(\pi)$ schemes. The optimal build-up times of PRESTO and RINEPT experiments are similar and ca. 1.5 shorter than that of CPMAS (Fig.8). The $^{27}\text{AlO}_6$ signal of γ -alumina is 1.8 and 1.9 times higher with $^1\text{H} \rightarrow ^{27}\text{Al}$ RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ than with PRESTO-III- $\text{R18}_1^7(\pi)$ and - $\text{R18}_2^5(\pi)$, respectively (Fig.7b). These improvements in the transfer efficiency are lower than those previously reported for quadrupolar isotopes with low gyromagnetic ratio, such as ^{95}Mo (see below), because the dipolar interaction is large in this case ($|b_{\text{HAl}}|/(2\pi) = 2575$ Hz). Indeed, as shown in Fig.5, the higher robustness of $\text{SR4}_1^2(\text{tt})$ recoupling sequence to ^1H - ^1H dipolar couplings is especially useful for small hetero-nuclear dipolar couplings. The RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ transfer also enhances the $^{27}\text{AlO}_6$ signal of γ -alumina by 20% with respect to the CPMAS transfer corresponding to the $n = 1$ Hartmann-Hahn condition, $\nu_{1,\text{H}} - 3\nu_{1,\text{Al}} \approx \nu_R$, with $\nu_{1,\text{H}} \approx 31$ and $\nu_{1,\text{Al}} \approx 6.8$ kHz (Fig.S12). Fig.7b indicates that the transfer efficiency of the CPMAS scheme is higher than that of PRESTO-III- $\text{R18}_2^5(\pi)$. This observation contrasts with previous results reported by Perras *et al.* under similar B_0 field and MAS frequency.³¹ However, Perras *et al.* used a CPMAS transfer corresponding to the $n =$

0 Hartmann-Hahn condition, whereas we used the $n = 1$ Hartmann-Hahn condition, which is significantly more efficient as seen in Fig. S12b.

Furthermore, Figs. 8b and 9a show that RINEPT-CWc-SR4₁²(tt) is much more robust to ¹H offset and rf-field inhomogeneity than the other sequences. CPMAS transfers using long spin-lock on the ²⁷Al channel are also less robust to ²⁷Al rf inhomogeneity than RINEPT and PRESTO sequences using short rectangular pulses (Fig. 9b). In summary, the RINEPT-CWc-SR4₁²(tt) transfer is more efficient and more robust than those observed with PRESTO and CPMAS schemes. Its high robustness facilitates its optimization, which only requires the adjustment of the recoupling time, whereas CPMAS is highly sensitive to rf-field values and offsets. This simplified optimization is a great help in the case of signals with small S/N ratios, as observed with S isotopes with either low natural abundance or small dipolar couplings with ¹H nuclei. Moreover, it must be reminded that this sequence allows for long distance transfers, e.g. to the subsurface in DNP, because it is not dipolar truncated, whereas PRESTO and CPMAS schemes are.

Fig. 10 shows that the transfer of populations from the S -spin STs during the first recoupling period of RINEPT sequence enhances by 15% the efficiency of the ¹H → ⁹⁵Mo transfer of 10 wt% MoO₃/TiO₂ sample impregnated with 110 mM TEKPol solution. This PT variant is mainly useful in the case of small ¹H- S dipolar interactions. In that case, PT-RINEPT-CWc-SR4₁²(tt) is 7.7 more efficient than PRESTO-III-R18₂⁵(π).

IV-4. Quadrupolar line-shape distortions

Fig. 11 shows the ¹⁷O line-shape of isotopically unmodified Mg(OH)₂ acquired using the ¹H→¹⁷O RINEPT-CWc-SR4₁²(tt) and PRESTO-III-R18₂⁵(π) sequences as function of the τ recoupling time. The line-shape is less dependent on this time for RINEPT experiments than for the PRESTO ones. This experimental observation is confirmed by numerical simulations of these spectra for one ¹H-¹⁷O spin pair using NMR parameters of Mg(OH)₂.^{14,37} The lower dependence of the ¹⁷O line-shape with τ recoupling value in the case of RINEPT stems from the non- γ -encoding of SR4₁² recoupling scheme, whereas R18₂⁵ is γ -encoded. The simulation of the RINEPT spectrum recorded with $\tau = 80$ μ s yields ¹⁷O NMR parameters that are consistent with those reported in the literature (Fig. 12).^{37,63}

IV-5. Large hetero-nuclear dipolar interactions

Fig. 12 shows a comparison of ¹H→¹⁷O PRESTO and RINEPT spectra of isotopically unmodified Mg(OH)₂ acquired with the variants of these sequences, in which two and three pulses are applied to the quadrupolar isotope. For both PRESTO and RINEPT techniques, the variants with two pulses are approximately 50% more efficient than those with three pulses since (i) ¹⁷O CT-selective π pulse produces losses³⁸ and (ii) the CSA_{1H} is five-fold smaller than the ¹H-¹⁷O dipolar interactions and hence, weakly interferes with the polarization transfer.^{37,63,64} Furthermore, the RINEPT-II-CW-SR4₁²(tt) transfer is more efficient than the PRESTO-II-R18₂⁵(π) scheme owing to its larger scaling factor, leading to shorter recoupling time, as well as its higher robustness to ¹H-¹H dipolar couplings and rf field inhomogeneity.

We also used the RINEPT-II-CW-SR4₁²(tt) sequence to detect the ¹⁷O CT powder pattern, centered at -128 ppm, of H₂O molecules in L-histidine·HCl·H₂O (Fig. 13a).⁷⁷ The ¹⁷O nucleus of water molecules is subject to an effective dipolar coupling constant of 25.3 kHz with protons, when only considering those distant by less than 3 Å from the O atom in the structure obtained from neutron diffraction.⁷⁸ Because of the large effective ¹H-¹⁷O dipolar coupling, the ¹H polarization is transferred to ¹⁷O nucleus of water in a short recoupling time of 40 μ s. For longer recoupling time, the ¹⁷O signal of H₂O molecules vanishes. In particular, this signal could not be detected using the RINEPT variant with three pulses applied to the quadrupolar isotope, for

which the minimal recoupling period is 80 μs at $\nu_R = 12.5$ kHz. Nevertheless, the RINEPT-CWc-SR4₁²(tt) variant with $\tau = 160$ and 640 μs allows the detection of the ¹⁷O signals of the COO⁻ group. These spectra were simulated using NMR parameters (indicated in the caption of Figure 13) similar to those reported for O₂ and O₁ sites of the COO⁻ group.⁷⁷ The shorter optimal recoupling times for O₂ site compared to O₁ is consistent with its larger effective dipolar coupling, which is equal to 5.2 kHz when considering protons distant by less than 3 Å, instead of 2.7 kHz for O₁.

V. Conclusions

We have shown in this article how the efficiency of polarization transfers between protons and half-integer quadrupolar isotopes at the moderate MAS frequencies typically used in MAS DNP experiments, can be improved by limiting the losses due to ¹H-¹H dipolar coupling during the RINEPT transfer and improving the robustness of this sequence to offset and rf-field inhomogeneity. These improvements have been achieved by combining a symmetry-based hetero-nuclear recoupling scheme with: (i) adiabatic inversion pulses, (ii) CW decoupling periods, and (iii) composite pulses. Furthermore, the RINEPT efficiency can be further improved by accelerating the coherence transfer via a manipulation of the STs populations during the first recoupling block. We have also shown that the RINEPT-CWc-SR4₁²(tt) sequence is more efficient and more robust than CPMAS and PRESTO transfers, which have mainly been employed so far for indirect DNP experiments. The RINEPT technique is notably advantageous for polarization transfers through small dipolar couplings owing to its high robustness and the absence of dipolar truncation. Moreover, the RINEPT spectra exhibit less distortions than their CPMAS counterparts, and they allow a reliable determination of the NMR parameters of the observed quadrupolar nuclei. Furthermore, in the case of large hetero-nuclear dipolar interactions we have introduced a new variant of the RINEPT scheme with only two pulses applied to the quadrupolar isotope, which is more efficient than its PRESTO counterpart. Nevertheless, owing to its high rf-field requirement, the SR4₁²(tt) adiabatic recoupling scheme is not compatible with high MAS frequencies, and hence this technique is mainly useful at moderate MAS rates.

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Figure captions

Fig.1. Pulse sequences of ¹H → S PRESTO and RINEPT experiments. The sequences applied to ¹H and S channels are shown in (a-d,g,h) and (e,f,i), respectively. The sequences with three and two pulses on the S channel are displayed in (a-f) and (g-i) subfigures, respectively. The narrow and broad black bars represent $\pi/2$ and π -pulses, respectively. Except for the PT pulse in (f), the pulses applied to the S channel are CT-selective. For the RINEPT sequences, the

dipolar recoupling can be $\text{SR4}_1^2(\pi)$ or $\text{SR4}_1^2(\text{tt})$. The beginning of the FID is represented by the vertical blue line. The acquisition of the FID starts at the end of the $(\text{R18}_2^5)_{270}$ block for PRESTO-III (a) and on top of the echo shifted by $\tau_R/2$ or $\tau_R/4$ with respect to the end of the last $\text{SR4}_1^2(\pi)$ or $\text{SR4}_1^2(\text{tt})$ block for RINEPT sequences (b-d), in which the delays between successive recoupling periods are equal to τ_R or $\tau_R/2$, respectively. As explained in subsection IV.5, PRESTO-II and RINEPT-II sequences are employed in the case of large ^1H -S dipolar couplings. In order to sample finely the build-up curves of RINEPT-II-CW- SR4_1^2 in that case, the recoupling periods τ_1 and τ_2 can be incremented by $\tau_R/2$, while the two recoupling SR4_1^2 blocks are rotor-synchronized by using a delay between them equal to $\tau_R/2$ and τ_R for $\tau = (k+1/2)\tau_R$ and $k\tau_R$, respectively, where k is an integer. In addition, the echo delay on the ^{17}O channel for PRESTO-II and RINEPT-II sequences is equal to $j\tau_R$ with $j = \text{ceiling}(\tau_2/\tau_R)$.

Fig.2. Simulated transfer efficiency of $^1\text{H} \rightarrow ^{13}\text{C}$ RINEPT- $\text{SR4}_1^2(\text{tt})$ sequence (Fig.1b) for a $^{13}\text{C}^1\text{H}_4$ spin system as function of $v_{1,\text{max}}/v_R$ and $\Delta v_{0,\text{max}}/v_R$ for $\tau = 640 \mu\text{s}$, $|b_{\text{HC}}|/(2\pi) = 2.575$, $|b_{\text{HH}}|/(2\pi) = 7$, $\text{CSA}_{1\text{H}} = 6$ and $v_R = 12.5 \text{ kHz}$. The white star corresponds to $v_{1,\text{max}} = 137 \text{ kHz}$ and $\Delta v_{0,\text{max}} = 2 \text{ MHz}$.

Fig.3. Simulated transfer efficiency of $^1\text{H} \rightarrow ^{13}\text{C}$ RINEPT- $\text{SR4}_1^2(\pi)$ and $\text{SR4}_1^2(\text{tt})$ sequences for a $^{13}\text{C}^1\text{H}_4$ spin system with $|b_{\text{HC}}|/(2\pi) = 2.575$, $|b_{\text{HH}}|/(2\pi) = 7$, $\text{CSA}_{1\text{H}} = 6$ and $v_R = 12.5 \text{ kHz}$. The curves are shown as function of (a) τ (build-up curves) with $v_1 = 2v_R = 25$ (green) or $3v_R = 37.5 \text{ kHz}$ (orange) for $\text{SR4}_1^2(\pi)$ and $v_{1,\text{max}} = 137$ and $\Delta v_{0,\text{max}} = 2000 \text{ kHz}$ for $\text{SR4}_1^2(\text{tt})$ (in black), and (b) the peak rf field amplitude of the recoupling normalized to its theoretical value, $v_{1\text{max}}/v_{1\text{max,th}}$, with $\tau = 640 \mu\text{s}$.

Fig.4. Simulated transfer efficiency of $^1\text{H} \rightarrow ^{13}\text{C}$ RINEPT-CW- $\text{SR4}_1^2(\text{tt})$ sequence, with (x,-x) CW phases, as function of (a) $v_{1,\text{CW}}$ with $\tau = 640 \mu\text{s}$ and (b) τ (build-up curves) with $v_{1,\text{CW}} = 0$, 60 and 87 kHz. The simulations were carried out for a $^{13}\text{C}^1\text{H}_4$ spin system with $|b_{\text{HC}}|/(2\pi) = 2.575$, $|b_{\text{HH}}|/(2\pi) = 7$, $\text{CSA}_{1\text{H}} = 6$ and $v_R = 12.5 \text{ kHz}$.

Fig.5. Relative evolution of the simulated transfer efficiency of $^1\text{H} \rightarrow ^{13}\text{C}$ PRESTO-III- $\text{R42}_2^{17}(\pi)$, $\text{R20}_1^8(\pi)$, $\text{R18}_1^7(\pi)$, $\text{R18}_2^5(\pi)$, and RINEPT- $\text{SR4}_1^2(\pi)$, or -CWc- $\text{SR4}_1^2(\text{tt})$ sequences for a $^{13}\text{C}^1\text{H}_4$ spin system as function of $|b_{\text{HH}}|/(2\pi)$, for $|b_{\text{HC}}|/(2\pi) = 2575$ (a) and 368 Hz (b), with $\text{CSA}_{1\text{H}} = 6$ and $v_R = 12.5 \text{ kHz}$. The vertical dashed lines correspond to $|b_{\text{HH}}|/(2\pi) = 7 \text{ kHz}$ used in other simulations. The τ values for PRESTO-III- $\text{R42}_2^{17}(\pi)$, $\text{R20}_1^8(\pi)$, $\text{R18}_1^7(\pi)$ and $\text{R18}_2^5(\pi)$ sequences are equal to their optimal values: 0.64, and 5.76 ms for $|b_{\text{HC}}|/(2\pi) = 2575$ and 368 Hz respectively.

Fig.6. Variation of the signal normalized to its maximum value of DNP-enhanced $^1\text{H} \rightarrow ^{27}\text{Al}$ RINEPT-CWc- $\text{SR4}_1^2(\pi)$ (blue) and $\text{SR4}_1^2(\text{tt})$ (red) experiments on γ -alumina impregnated with 5 mM TEKPol solution as function of (a) the ratio between $v_{1\text{max}}$ and its theoretical value, and (b) offset of the recoupling schemes at $B_0 = 9.4 \text{ T}$ using $\tau = 400 \mu\text{s}$, $v_R = 12.5 \text{ kHz}$ and $v_{1\text{max,th}} = 34$ and 137 kHz for $\text{SR4}_1^2(\pi)$ and $\text{SR4}_1^2(\text{tt})$, respectively.

Fig.7. ^{27}Al MAS spectra of γ -alumina impregnated with 5 mM TEKPol solution recorded at $B_0 = 9.4 \text{ T}$ with $v_R = 12.5 \text{ kHz}$ using DNP-enhanced $^1\text{H} \rightarrow ^{27}\text{Al}$ polarization transfer achieved with (a) RINEPT variants using $\text{SR4}_1^2(\pi)$ and $\text{SR4}_1^2(\text{tt})$ recoupling schemes and incorporating or not CW irradiation and (b) PRESTO-III- $\text{R18}_1^7(\pi)$ and $\text{R18}_2^5(\pi)$, CPMAS and RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ sequences using $\tau = 400$ and $320 \mu\text{s}$ for RINEPT and PRESTO experiments and $\tau_{\text{CP}} = 640 \mu\text{s}$ for CPMAS experiment.

Fig.8. Experimental (a) build-up curves and (b) robustness to ^1H offset of DNP-enhanced $^1\text{H} \rightarrow ^{27}\text{Al}$ transfers with RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ (red), PRESTO-III- $\text{R18}_1^7(\pi)$ (purple) and $\text{R18}_2^5(\pi)$ (blue), and CPMAS (black) sequences on γ -alumina impregnated with 5 mM TEKPol solution at $B_0 = 9.4 \text{ T}$ with $v_R = 12.5 \text{ kHz}$, $\tau_{\text{CP}} = 640 \mu\text{s}$ for CPMAS experiment, and $\tau = 400$

and 320 ms for RINEPT and PRESTO, respectively. The rf fields were equal to their nominal values. The experimental signal is normalized to its maximal value.

Fig.9. Variation of the signal normalized to its maximum value of DNP-enhanced $^1\text{H} \rightarrow ^{27}\text{Al}$ RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ (red), PRESTO-III- $\text{R18}_1^7(\pi)$ (purple) and $\text{R18}_2^5(\pi)$ (blue), and CPMAS (black) experiments on γ -alumina impregnated with 5 mM TEKPol solution as function of the ratio between the applied rf field and the optimal one on (a) ^1H and (b) ^{27}Al channels at $B_0 = 9.4$ T with $\nu_R = 12.5$ kHz, $\tau_{\text{CP}} = 640$, $\tau = 400$ and 320 μs for RINEPT and PRESTO, respectively. The optimal rf fields on ^1H and ^{27}Al channels were equal in kHz to $\{137, 7.2\}$ for RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$, $\{98, 7.2\}$ for PRESTO-III- $\text{R18}_1^7(\pi)$, $\{56, 7.2\}$ for PRESTO-III- $\text{R18}_2^5(\pi)$ and $\{31, 6.8\}$ for CPMAS. The increased intensity at $\nu_1/\nu_{1,\text{th}} = 50\%$ for CPMAS experiments corresponds to the $n = 2$ Hartmann-Hahn condition for 0Q CP transfer.

Fig.10. ^{95}Mo QCPMG spectra of 10 wt% $\text{MoO}_3/\text{TiO}_2$ at $B_0 = 9.4$ T and $\nu_R = 12.5$ kHz, enhanced by indirect DNP using $^1\text{H} \rightarrow ^{95}\text{Mo}$ PRESTO-III- $\text{R18}_2^5(\pi)$ (black), RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ (blue) and PT-RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ (red) transfers, with $\{\tau$ (ms), N_S , T_{exp} (min) $\} = \{2.56, 512, 12.8\}$, $\{1.92, 512, 12.8\}$, and $\{1.92, 512, 12.8\}$, respectively. Spectra are the Fourier transforms of the sums of the echoes.

Graphical abstract. ^{95}Mo DNP spectra of 10 wt% $\text{MoO}_3/\text{TiO}_2$, recorded at 9.4 T and 12.5 kHz MAS with PRESTO (black), RINEPT (blue) and PT-RINEPT (red).

Fig.11. Simulated (left) and experimental (right) $^1\text{H} \rightarrow ^{17}\text{O}$ RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ and PRESTO-III- $\text{R18}_2^5(\pi)$ spectra for different τ values indicated on the figure. The spectra were simulated for one ^1H - ^{17}O spin pair with parameters corresponding to those of $\text{Mg}(\text{OH})_2$ (section III.1). The experimental spectra were recorded for isotopically unmodified $\text{Mg}(\text{OH})_2$ impregnated with 16 mM TEKPol solution enhanced by indirect DNP at $B_0 = 9.4$ T with $\nu_R = 12.5$ kHz.

Fig.12. ^{17}O MAS spectra of isotopically unmodified $\text{Mg}(\text{OH})_2$ impregnated with 16 mM TEKPol solution at $B_0 = 9.4$ T with $\nu_R = 12.5$ kHz recorded using RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ and PRESTO- $\text{R18}_2^5(\pi)$ with three (Figs. **1a,d,e**) or two (Figs. **1g-i**) pulses on the ^{17}O channel. The spectra in (a), (b), (c) and (d) are obtained with $\tau = 160, 142, 80$ and 80 μs , respectively and result from averaging 256 transients, i.e an experimental time $T_{\text{exp}} = 17.6$ min. The top figure displays the ^{17}O CT line-shape excited by a Dirac pulse simulated using the NMR parameters shown at the top right of the figure.

Fig.13. L-histidine·HCl·H₂O. (a) Structure obtained from neutron diffraction.⁷⁸ (b-d) $^1\text{H} \rightarrow ^{17}\text{O}$ DNP signals at $B_0 = 9.4$ T with $\nu_R = 12.5$ kHz of this isotopically unmodified compound impregnated with 16 mM TEKPol solution. ^{17}O signal: (b) RINEPT-II-CW- $\text{SR4}_1^2(\text{tt})$ of water molecules and (c,d) RINEPT-CWc- $\text{SR4}_1^2(\text{tt})$ of COO^- groups, with $\tau = 40, 160$ and 640 μs , respectively. For the spectrum recorded with $\tau = 40$ μs , the * symbols indicate spinning sidebands. The spectrum (b) has been simulated with parameters given in Table 2 of ref [79], and spectra (c) and (d) were simulated using (c) $\delta_{\text{iso}} = 262$ ppm, $C_Q = 6.9$ MHz, $\eta_Q = 0.73$ and $\text{CSA}_{17\text{O}} = 0$ and (d) $\delta_{\text{iso}} = 307$ ppm, $C_Q = 8.0$ MHz, $\eta_Q = 0.31$, $\text{CSA}_{17\text{O}} = 5.4$ kHz and $\eta_{\text{CSA},17\text{O}} = 0.1$. The spectra (b)-(d) result from averaging 1024, 176 and 112 transients, respectively.

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