Indirect detection of broad spectra in solid-state NMR using interleaved DANTE trains

Yixuan Li, Julien Trebosc, Bingwen Hu, Ming Shen, Jean-Paul Amoureux, Olivier Lafon

Indirect detection of broad spectra in solid-state NMR using interleaved DANTE trains

Yixuan Li,[1,2] Julien Trébosc,[1] Bingwen Hu,[2] Ming Shen,[2] Jean-Paul Amoureux,[1,2,3*] Olivier Lafon,[1,4*]

[1] Univ. Lille, CNRS-8181, UCCS, Unit of Catalysis and Chemistry of Solids, 59000 Lille, France

[2] Shanghai Key Laboratory of Magnetic Resonance, School of Physics and Materials Science, East China Normal University, Shanghai 200062, China.

[3] Bruker France, 34 rue de l'Industrie, F-67166 Wissembourg, France.

[4] Institut Universitaire de France, 1, rue Descartes, 75231 Paris, France.

Email: jean-paul.amoureux@univ-lille1.fr olivier.lafon@univ-lille1.fr

Abstract.

We analyze the performances and the optimization of ^{1}H-{*I*} HMQC experiments using basic and interleaved DANTE schemes for the indirect detection of nuclei I = 1/2 or 1 exhibiting wide lines dominated by chemical shift anisotropy (CSA) or quadrupole interaction, respectively. These sequences are first described using average Hamiltonian theory. Then, we analyze using numerical simulations (i) the optimal lengths of the DANTE pulse and DANTE train, (ii) the robustness of these experiments to offset, and (iii) the optimal choice of the defocusing and refocusing times for both ^{1}H-{*I*} *J*- and *D*-HMQC sequences for ^{195}Pt (I = 1/2) and ^{14}N (I = 1) nuclei subject to large CSA and quadrupole interaction, respectively. These simulations are compared to ^{1}H-{^{14}N} *D*-HMQC experiments on γ-glycine and L-histidine.HCl at B_0 = 18.8 T and MAS frequency of 62.5 kHz. The present study shows that (i) the optimal defocusing and refocusing times do not depend on the chosen DANTE scheme, (ii) the DANTE trains must be applied with the highest rf-field compatible with the probe specifications and the stability of the sample, (iii) the excitation bandwidth along the indirect dimension of HMQC sequence using DANTE trains is inversely proportional to their length, (iv) interleaved DANTE trains increase the excitation bandwidth of these sequences, and (v) dephasing under residual ^{1}H-^{1}H and ^{1}H-*I* dipolar couplings, as well as ^{14}N second-order quadrupole interaction, during the length of the DANTE scheme attenuate the transfer efficiency.

Key words. Solid-state NMR, DANTE, Broadband excitation, fast MAS, ^{14}N, very large CSA.

I. Introduction

In the last decades, the advancement of Magic-Angle Spinning (MAS) [1–4] with presently rotation frequencies up to 150 kHz, magnetic fields up to 35.2 T [5–7], and Dynamic Nuclear Polarization (DNP) at fields up to 21.1 T [8–11], has enabled a considerable improvement in the resolution and/or sensitivity of solid-state NMR spectroscopy. Furthermore, the sensitivity of this technique can be further enhanced by the transfer of polarization from abundant nuclei with high gyromagnetic ratio, such as ^{1}H, to dilute isotopes with lower ratio, such as ^{13}C or ^{15}N, using pulse sequences such as Cross-Polarization under MAS (CPMAS) [12]. The resolution of NMR spectra can be improved by the suppression of dipolar couplings with protons using homo- [13] or hetero-nuclear [14] dipolar decoupling schemes. In the case of half-integer spin quadrupolar nuclei, the sensitivity can be increased by irradiating the satellite transitions [15], whereas the resolution can be improved by

removing the second-order quadrupole broadening using MQMAS or STMAS (Multiple-Quantum or Satellite Transition MAS) [16,17].

In spite of these advances, the detection of broad powder patterns ranging from hundreds of kHz to tens of MHz in breadth is still challenging [18,19]. Such wide spectra can arise from three distinct anisotropic NMR interactions, including (i) the chemical shift anisotropy (CSA), notably for heavy spin-1/2 nuclei [20], (ii) the quadrupole interaction for nuclei with spin values larger than ½ either integer (e.g. ^{14}N and ^{10}B [21–23]) or half-integer, and (iii) the shift resulting from the hyperfine interaction with localized or delocalized electrons in insulating or conductive solids, respectively [24–26].

The difficulties for the detection of wide one-dimensional (1D) spectra include (i) the need to excite a broad spectral width, which can exceed the excitation bandwidth of the radio-frequency (rf) pulses and the detection bandwidth of the probe, (ii) the short decay time of the Free Induction Decay (FID), which is inversely proportional to the line width and often shorter than the pulse dead time, and (iii) the low signal-to-noise (*S*/*N*) ratio since the total integrated intensity of the signal is spread over a broad spectral width. Various techniques have been introduced for the direct detection of wide 1D spectra. The excitation and inversion of wide NMR signals have been achieved using either adiabatic pulses [27–31] or DANTE (Delays Alternating with Nutation for Tailored Excitation) trains of short rotor-synchronized pulses [31–34]. Under MAS, adiabatic inversion can be achieved using SHAPs (Short High-powered Adiabatic-Pulses) [28] or S^{3}APs pulses (Single Sideband-Selective Adiabatic-Pulses) [29,31]. When the breadth of the powder pattern exceeds the excitation bandwidth of the pulses or the detection bandwidth of the probe, the spectrum can be acquired piecewise using the VOCS method (Variable Offset Cumulative Spectrum) [35], which consists in acquiring sub-spectra with different frequency offsets and co-adding them to produce the overall broad powder pattern. The use of VOCS is facilitated by employing NMR probes equipped with automatic tuning/matching robots [36]. Frequency stepping under MAS has also been demonstrated [37,38]. The issue of rapidly decaying FIDs can be circumvented by the use of the spin-echo sequence or its CPMG variant (Carr-Purcell Meiboom-Gill), which is applicable to spin-1/2 [20] and half-integer spin quadrupolar nuclei [39]. The CPMG sequence improves the sensitivity by the acquisition of a train of echoes in every scan, and its excitation bandwidth can be increased using adiabatic pulses, such as WURST (Wideband Uniform-Rate Smooth-Truncation) [27]. Under static conditions, additional sensitivity gains can be achieved using the BRAIN-CP sequence (BRoadband Adiabatic InversioN Cross-Polarization), which efficiently transfers the ^{1}H polarization to spin-1/2 and quadrupolar nuclei exhibiting wide spectra [40,41]. Moreover, the sensitivity of BRAIN-CP experiments can be further enhanced using DNP, which initially transfers the polarization of unpaired electrons to surrounding protons [42–44]. Finally, it has been shown that the resolution of wide 1D spectra can be improved by the acquisition of MATPASS (Magic-Angle Turning and Phase Alternating Sideband Separation) 2D spectra, which allow separating the overlapping sideband patterns and display along the indirect dimension only the isotropic resonances [45–47]. For ^{14}N isotope, the resolution can be dramatically improved by the observation of ^{14}N double-quantum (2Q) coherences, which are only broadened by the second-order quadrupole interaction, whereas the single-quantum (1Q) coherences are broadened by both first- and second-order ones. However, the direct detection of ^{14}N 2Q coherences is usually less sensitive than that of 1Q ones. ^{14}N 2Q coherences can also be directly detected using overtone spectroscopy, which excites and acquires ^{14}N signal at twice its Larmor frequency. Such approach has first been demonstrated for static samples [48,49] and more recently under MAS [50,51]. Its sensitivity can be improved by ^{1}H $\rightarrow$ ^{14}N polarization transfer [52,53] and DNP [53].

For proton-containing samples, an alternative to the direct detection of *I* isotope exhibiting wide spectra is their indirect detection via protons at high MAS frequencies using either *I* $\rightarrow$ ^{1}H or ^{1}H $\rightarrow$ *I* $\rightarrow$ ^{1}H polarization transfers. These methods are advantageous in terms of resolution since (i) the

synchronization of the indirect evolution period, t_1, with the rotor period, $T_R = 1/\nu_R$, refocuses the anisotropic NMR interactions with spatial rank $l = 2$, such as the CSA or the first-order quadrupole interaction, and causes the spinning sidebands to coincide with one of them along the indirect dimension, F_1, (ii) overlapping I signals can potentially be resolved in these 2D I-^{1}H spectra, provided they correlate to distinct ^{1}H isotropic chemical shifts, and (iii) MAS partially averages anisotropic NMR interactions with spatial rank $l > 2$, including the second-order quadrupole interaction and the terms with orders higher than 2 in the average Hamiltonian of multiple dipolar couplings with protons [54]. High MAS frequencies are advantageous for these experiments since they average out the ^{1}H-^{1}H dipolar couplings and hence improve the resolution and the sensitivity of these proton-detected experiments [55,56]. The proton detection of wide spectra has first been demonstrated through the indirect detection of 1Q and 2Q coherences of ^{14}N isotope in solids using the HMQC scheme (Heteronuclear Multiple-Quantum Correlation) [57]. These experiments are denoted ^{1}H-{^{14}N^{1Q}} and ^{1}H-{^{14}N^{2Q}} HMQC hereafter. The ^{1}H-^{14}N coherence transfer has first been demonstrated through a combination of ^{1}H-^{14}N J-coupling and second-order quadrupolar-dipolar cross-terms, also known as residual dipolar splitting, using the conventional J-mediated HMQC (J-HMQC) scheme [57]. Nevertheless, faster and hence more efficient transfers are usually achieved through the larger ^{1}H-^{14}N dipolar interactions, which are reintroduced by the application of heteronuclear dipolar recoupling schemes, such as the symmetry-based $SR4_1^2$ [58], on the ^{1}H channel during the defocusing and refocusing delays of the dipolar-mediated HMQC (D-HMQC) sequence [59,60]. The HSQC sequence (Heteronuclear Single-Quantum Correlation) has also been employed for the indirect detection of ^{14}N nuclei via protons, but it is less sensitive than HMQC [61–63]. Similarly to ^{14}N direct detection, the indirect dimension of ^{1}H-{^{14}N^{2Q}} HMQC spectra may exhibit a higher resolution than that of ^{1}H-{^{14}N^{1Q}} [57,60,64–67]. However, the former experiments are less sensitive than the latter ones [60,66,67]. Proton-detected HMQC experiments have also been employed recently to detect the overtone signal of another integer-spin quadrupole isotope, ^{10}B with $I = 3$ [68].

More recently, it has been demonstrated that proton-detected D-HMQC MAS experiments are more sensitive than WURST-CPMG ones for the detection of wide spectra [69]. The highest sensitivity is achieved using rotor-synchronized t_1 periods since all spinning sidebands then coincide along the F_1 dimension. Nevertheless, the full wide MAS spectra can be indirectly detected via protons using t_1 increments smaller than the inverse of the width of the static powder pattern, even if the sensitivity is decreased by about the number of spinning sidebands along the indirect dimension [69]. When the range of isotropic chemical shifts exceeds the MAS frequency, the resonances along the rotor-synchronized indirect dimension are folded back at frequencies which can differ from the isotropic chemical shifts. Such issue can be circumvented either by incorporating the Magic-Angle Turning (MAT) scheme in the t_1 period [70], or by recording two spectra with different spinning speeds.

The indirect detection via protons of central and satellite transitions (CT and ST) of half-integer spin quadrupolar nuclei exhibiting wide signals has also been recently reported using D-HMQC and D-RINEPT techniques (Dipolar-mediated Refocused Insensitive Nuclei Enhanced by Polarization Transfer) [71,72].

We focus here on the excitation and the reconversion at both ends of the t_1 period in HMQC experiments under MAS of 1Q and 2Q coherences of nuclei exhibiting wide spectra. As mentioned above, such excitation and reconversion are difficult since the width of the powder pattern often greatly exceeds the rf-field delivered by the usual NMR probes, notably for nuclei with low gyromagnetic ratios. Nevertheless, several methods have been proposed in recent years to circumvent this issue.

First, in the case of wide spectra, high-power short pulses can achieve broadband excitation of 1Q coherences of either spin-1/2 [66,69,70], ^{14}N [66,73,74] or STs of half-integer spin quadrupolar nuclei

[71]. However, these short hard pulses often tilt the longitudinal magnetization by a small angle, which results in decreased sensitivity.

Second, it has been shown that long rf-pulses can achieve efficient excitation and reconversion of ^{14}N 1Q coherences in ^{1}H-{^{14}N} HMQC experiments [75], and we have recently demonstrated that these selective long pulses (SLP) achieve broadband excitation of wide spectra by frequency-selective excitation of a single spinning sideband [66].

Third, DANTE schemes, including interleaved ones with several pulses per rotor period, have also been employed to excite and reconvert ^{14}N 1Q coherences in ^{1}H-{^{14}N} *D*-HMQC experiments [33,66,76].

Fourth, in the case of ^{14}N isotope, according to theory and spin dynamics simulations, 2Q coherences can be excited either (i) from the quadrupolar order, Q_z, by applying either short hard-pulses [66,77], DANTE trains [33,66] or a SLP [66,75], or (ii) from the *z*-magnetization by applying either SLP [66,78–82] or the XiX (x inverse-x) scheme [30] at the ^{14}N Larmor frequency, or overtone pulses at twice the ^{14}N Larmor frequency [51,52,67]. Experimentally, 2D ^{1}H-{^{14}N^{2Q}} HMQC spectra have been acquired using long pulses at once [57,60,67] or twice the ^{14}N Larmor frequency [64,65,67]. In the latter case, the robustness to offset could be improved by using WURST or composite pulses [64,67,83,84].

Building on our study of direct excitation using DANTE schemes [34], we analyze here the performances and the optimization of ^{1}H-{*I*} HMQC experiments using basic and interleaved DANTE trains for the indirect detection of nuclei with $I = 1/2$ or 1 exhibiting wide lines dominated by CSA or quadrupole interaction, respectively. These sequences are first described using average Hamiltonian theory. Then, we analyze using numerical simulations (i) the optimal lengths of the DANTE pulse and DANTE train, (ii) the robustness of these experiments to offset, and (iii) the optimal choice of the defocusing and refocusing times for both ^{1}H-{*I*} *J*- and *D*-HMQC sequences for ^{195}Pt ($I = 1/2$) and ^{14}N ($I = 1$) nuclei subject to large CSA and quadrupole interaction, respectively. These simulations are compared to ^{1}H-{^{14}N} *D*-HMQC experiments on γ-glycine and L-histidine.HCl at $B_0 = 18.8$ T and MAS frequency of $\nu_R = 62.5$ kHz.

II. Description of the sequences and theory

II-1. The DANTE schemes

We consider hereafter the rotor-synchronized DANTE sequences, also denoted D_N^K, which consist of a train of pulses of rf-amplitude, ν_1, and length, τ_p, having identical phases. A D_N^K train lasts *K* rotor periods and *N* equally spaced pulses are applied during each rotor period, $T_R = 1/\nu_R$. We refer to D_N^K schemes with $N = 1$ and $N \geq 2$ as basic and interleaved DANTE sequences, respectively [33,34,76]. For a D_N^K train with the first pulse applied at $t = 0$, the rf-amplitude for $0 \leq t \leq KT_R$ is equal to:

$$\omega_1(t) = \begin{cases} \omega_1 & \text{if} \quad 0 \leq t \leq \tau_p \bmod \left(\frac{T_R}{N}\right) \\ 0 & \text{if} \quad \tau_p \bmod \left(\frac{T_R}{N}\right) < t \leq \frac{T_R}{N} \bmod \left(\frac{T_R}{N}\right) \end{cases} \tag{1}$$

where $\omega_1 = 2\pi\nu_1$ and mod denotes the modulo operation. This rf-amplitude function can be expanded as a Fourier series [31]

$$\omega_1(t) = \sum_{n=-\infty}^{+\infty} C_n \exp\left[i\left(nN\omega_R t + \zeta_n\right)\right] \tag{2}$$

where $\omega_R = 2\pi\nu_R$ and the amplitude C_n and phase ζ_n of the rf-spikelets are given by

$$C_n = \begin{cases} \bar{\omega}_1 & n = 0 \\ \frac{\omega_1}{n\pi}\left|\sin\left(\frac{nN\omega_R\tau_p}{2}\right)\right| & n \neq 0 \end{cases} \tag{3}$$

$$\zeta_n = -\frac{1}{2} nN\omega_R\tau_p \tag{4}$$

where $\overline{\omega}_1 = \omega_1 N\tau_p/T_R$ is the average rf-amplitude over the DANTE scheme. Eqs. 2 and 3 show that the DANTE scheme excitation profile in the frequency domain consists of a comb of rf-spikelets, all separated from the carrier frequency by a multiple of $N\nu_R$, with amplitude decreasing with n according to a sinc function.

The full width, FW, of a static powder pattern is equal to $\nu_0\delta_{aniso}(3 + \eta_{CSA})/2$ for a spin-1/2 nucleus subject to CSA and $3C_Q/2$ for a spin-1 isotope subject to quadrupole interaction [34]; where ν_0, δ_{aniso}, η_{CSA} and C_Q values denote the Larmor frequency, the reduced CSA, the CSA asymmetry parameter and the quadrupolar coupling constant, respectively. A uniform excitation of such powder pattern can be achieved when $\tau_p \ll 1/(\pi FW)$.

During an on-resonance DANTE irradiation of a spin-1/2 nucleus subject to CSA, if $\overline{\omega}_1 \ll \omega_R$ the first-order average Hamiltonian in the jolting frame is given by [31]

$$\overline{H} = \sum_{n=-\infty}^{+\infty} A_{nN}\, C_n R_z(\zeta_n - \phi_{nN}) I_x R_z(-\zeta_n + \phi_{nN}) \tag{5}$$

where A_{nN} and ϕ_{nN} denote the amplitude and the phase of the sideband of order nN in the spectrum of a crystallite excited by an ideal $\pi/2$-pulse, and $R_z(\Psi)$ is the operator representing the rotation of the spin through angle Ψ about the z-axis.

During an on-resonance DANTE irradiation of a spin-1 nucleus subject to quadrupole interaction, if $\overline{\omega}_1 \ll \omega_R$ the first-order average Hamiltonian in the jolting frame is [30]

$$\begin{aligned}\overline{H} = \sqrt{2} \sum_{n=-\infty}^{+\infty} & A_{nN}\, C_n R_z^{(+1,0)}(\zeta_n - \phi_{nN}) I_x^{(+1,0)} R_z^{(+1,0)}(-\zeta_n + \phi_{nN}) \\ & + A_{-nN} C_n R_z^{(0,-1)}(\zeta_n + \phi_{-nN}) I_x^{(0,-1)} R_z^{(0,-1)}(-\zeta_n - \phi_{-nN})\end{aligned} \tag{6}$$

where A_{nN} and ϕ_{nN} denote the amplitude and the phase of the spinning sideband of order nN for the transition $+1 \leftrightarrow 0$ of a crystallite. As the transitions $+1 \leftrightarrow 0$ and $0 \leftrightarrow -1$ are symmetrical with respect to the center-band, the spinning sideband of order $-nN$ for the transition $0 \leftrightarrow -1$ coincides with that of order nN for the transition $+1 \leftrightarrow 0$ and has an amplitude A_{-nN} and phase $-\phi_{-nN}$. $I_x^{(+1,0)}$ and $I_x^{(0,-1)}$ are the single-transition operators along x axis associated with the transitions $+1 \leftrightarrow 0$ and $0 \leftrightarrow -1$, respectively [79]. The rotation operators $R_z^{(r,s)}(\Psi)$ with $\{r,s\} = \{+1,0\}$ or $\{0,-1\}$ are defined as

$$R_z^{(r,s)}(\Psi) = \exp\left(-\mathrm{i}\Psi I_z^{(r,s)}\right) \tag{7}$$

where $I_z^{(r,s)}$ is the single-transition operator along z axis associated with the transitions $r \leftrightarrow s$.
In the case of the broadband ($\tau_p \ll 1/(\pi FW)$) and basic ($N = 1$) DANTE scheme, it can be shown that [31]

$$\overline{H} = \overline{\omega}_1 I_x \tag{8}$$

for both spins $I = 1/2$ and 1. This equation shows that the density matrix then evolves as during a simple rf-pulse with an rf-field strength $\overline{\omega}_1$. In the absence of losses, the magnetization of the I nucleus along the z-axis is transformed into magnetization along the y-axis as

$$I_z \xrightarrow{D_1^K} I_z\cos(\theta) - I_y\sin(\theta) \tag{9}$$

with $\theta = \overline{\omega}_1 K T_R = \omega_1 K\tau_p$. Hence, after a D_1^K train, in the absence of losses the transverse magnetization is maximal when $\theta = \pi/2$, i.e.

$$K = \frac{1}{4\nu_1\tau_p} \ . \tag{10}$$

Similarly, I_y is converted back to I_z by the application of D_1^K train

$$I_y \xrightarrow{D_1^K} I_y\cos(\theta) + I_z\sin(\theta) \ . \tag{11}$$

Furthermore, for spin-1 nuclei, the D_1^K train transforms Q_z into 2Q coherences along *x*-axis, D_x, and 1Q coherences along y-axis antiphase with respect to the quadrupole interaction, K_y, for which the transitions +1 ↔ 0 and 0 ↔ -1 have opposite phases [77]

$$Q_z \xrightarrow{D_1^K} Q_z \frac{3\cos(2\theta)+1}{4} + D_x \frac{3\cos(2\theta)-3}{4} - \frac{3}{2} K_y \sin(2\theta) \quad (12)$$

and the D_x and K_y operators evolve into

$$D_x \xrightarrow{D_1^K} D_x \frac{3+\cos(2\theta)}{4} + Q_z \frac{\cos(2\theta)-1}{4} - \frac{1}{2} K_y \sin(2\theta) \quad (13)$$

$$K_y \xrightarrow{D_1^K} K_y \cos(2\theta) + \frac{1}{2}(Q_z + D_x)\sin(2\theta) \quad (14)$$

Eqs. 9 to 14 do not take into account the coherent and incoherent losses occurring during the D_1^K train. Such losses decrease inversely to the length of the D_1^K train, i.e. with small *K* value and fast MAS frequency. The incoherent losses are mainly related to dynamics, whereas the coherent ones include the signal decay produced by the second-order quadrupole interaction during the D_1^K train. Such effects are investigated below using numerical simulations of the spin dynamics.

For $N \geq 2$, Eq.8 is not valid since only the spinning sidebands with an order multiple of *N* are excited. Consequently, the evolution during interleaved DANTE schemes differs from that described with Eqs. 9 to 14.

II-2. *J*- or *D*-HMQC schemes

Figs.**1a** and **b** show the ^{1}H-{*I*} *J*- and *D*-HMQC sequences, respectively, using rectangular pulses on the *I* channel, while Figs.**1c** and **d** display the ^{1}H-{*I*} *J*-HMQC sequence, in which the rectangular pulses bracketing the t_1 period are replaced by D_1^K and D_2^K trains, respectively [33,66,76]. Here the t_1 period was rotor-synchronized in order to eliminate the broadening due to CSA or first-order quadrupole interaction along the F_1 dimension.

II-2-1. Dipolar recoupling

The *D*-HMQC sequence differs from the *J*-HMQC one by the application of a heteronuclear dipolar recoupling scheme during the defocusing and refocusing delays, τ. The $SR4_1^2$ recoupling was employed here [58]. This sequence, during which the protons are irradiated at $\nu_1 = 2\nu_R$, reintroduces the space component $|m| = 1$ of the ^{1}H CSA and heteronuclear dipolar couplings with ^{1}H, whereas it suppresses the ^{1}H-^{1}H dipolar couplings, the ^{1}H isotropic chemical shifts and the heteronuclear *J*-couplings with protons.

The $SR4_1^2$ scheme achieves zero-quantum heteronuclear dipolar recoupling and the contribution of the *I*-*S* dipolar coupling to the first-order average Hamiltonian is equal to [58,85]:

$$\bar{H}_{D,IS}^{(1)} = 2\omega_{D,IS} I_z S_z \quad (15)$$

The magnitude of the recoupled *I*-*S* coupling in Eq.15 is given by

$$\omega_{D,IS} = \frac{1}{4} b_{IS} \sin^2\left(\beta_{PR}^{D,IS}\right)\cos(2\varphi). \quad (16)$$

with

$$\varphi = \gamma_{PR}^{D,IS} + \alpha_{RL}^0 - \omega_R t^0 \quad (17)$$

In Eqs.16 and 17, b_{IS} denotes the dipolar coupling constant in rad.s^{-1}, the Euler angles $\{0, \beta_{PR}^{D,IS}, \gamma_{PR}^{D,IS}\}$, relate the internuclear *I*-*S* direction to the MAS rotor-fixed frame, and t^0 refers to the starting time of the symmetry-based scheme.

The norm of $\overline{H}_{D,IS}^{(1)}$ depends on φ phase and hence, $\gamma_{PR}^{D,IS}$ angle. Therefore, the $SR4_1^2$ scheme is non-γ-encoded and the beginning of the two $SR4_1^2$ schemes in *D*-HMQC sequence must be separated by an integer number of rotor periods. The recoupled Hamiltonian of Eq.15 is not dipolar truncated as it commutes among different *I*-*S* spin pairs, hence allowing to observe long I-S distances. Furthermore, the ^{1}H CSA term recoupled by the $SR4_1^2$ scheme is proportional to I_z and thus commutes with the ^{1}H-*S* dipolar interaction of Eq.15.

II-2-2. ^{1}H-{^{195}Pt} HMQC

In ^{1}H-{^{195}Pt} HMQC experiments, the first π/2-pulse applied to protons with phase *y* creates ^{1}H *x*-magnetization. This magnetization evolves during τ under *J* or dipolar ^{1}H-*I* coupling into:

$$S_x\cos(\omega_{HPt}\tau) + 2S_yI_z\sin(\omega_{HPt}\tau) \tag{18}$$

where the frequency ω_{HPt} is equal either to πJ_{HPt} for *J*-HMQC sequence or to $\omega_{D,IS}$ given by Eq.16 for *D*-HMQC one. $2S_yI_z$ is the *y*-magnetization of proton, in antiphase with respect to the coupling with ^{195}Pt nucleus. The first rectangular pulse on ^{195}Pt channel with phase *y* and tilt angle θ (Figs.**1a** and **b**), or the first D_1^K train with the same phase and producing the same tilt angle (Fig.**1c**), converts it into heteronuclear MQ coherences ($2S_yI_x$) with a coefficient sin(θ) (Eq.9). These coherences evolve under the ^{195}Pt isotropic chemical shift during the t_1 time. The π-pulse applied on ^{1}H channel in the middle of the t_1 period refocuses the evolution of the ^{1}H 1Q coherences under isotropic chemical shift during the τ and t_1 delays as well as its evolution under ^{1}H-^{195}Pt *J*- or dipolar couplings. At the end of t_1, the second rectangular pulse or D_1^K train converts back the MQ coherences into anti-phase ^{1}H magnetization, again with a coefficient sin(θ) (Eq.11) and these coherences evolve during the refocusing τ period into observable transverse ^{1}H magnetization. The signal of this NMR experiment is proportional to

$$S(\tau) \propto \sin^2(\theta)\langle\sin^2(\omega_{HPt}\tau)\rangle \tag{19}$$

where the angular bracket $\langle \dots \rangle$ denotes the powder average over all ^{1}H-^{195}Pt inter-nuclear vectors. The $\langle\sin^2(\omega_{HPt}\tau)\rangle$ term is given by

$$\langle\sin^2(\omega_{HPt}\tau)\rangle = \begin{cases} \sin^2(\pi J_{HPt}\tau) & \text{for } J-\text{HMQC} \\ \frac{1}{2} - \frac{\pi\sqrt{2}}{8} J_{1/4}\left(\frac{b_{IS}\tau}{4}\right) J_{-1/4}\left(\frac{b_{IS}\tau}{4}\right) & \text{for } D-\text{HMQC} \end{cases} \tag{20}$$

where $J_{\pm1/4}(x)$ denotes the Bessel functions of the first kind and ±1/4-order. Eqs.19 and 20 show that τ and θ can be chosen independently for $I = 1/2$. The maximal $S(\tau)$ intensity is obtained for θ = 90°. In the absence of losses, the shorter τ value producing maximal $S(\tau)$ intensity is $\tau^{opt} = 1/(2J_{HPt})$ and $1.5/|b_{IS}|$ for *J*- and *D*-HMQC schemes, respectively (Figs.**2a** and **b**). Eq.20 indicates that *D*-HMQC sequence is ca. 50% less efficient than *J*-HMQC one.

II-2-3. ^{1}H-{^{14}N} HMQC

For ^{1}H-{^{14}N} HMQC experiment, the ^{1}H *x*-magnetization created by the first pulse evolves during the defocusing period into [77]

$$S_x\left(\frac{1+2\cos(2\omega_{HN}\tau)}{3}\right) + S_xQ_z\left(\frac{\cos(2\omega_{HN}\tau)-1}{3}\right) + S_yI_z\sin(2\omega_{HN}\tau) \tag{21}$$

where the frequency ω_{HN} is equal either to πJ_{HN} for *J*-HMQC sequence or to $\omega_{D,IS}$ given by Eq.16 for *D*-HMQC one. S_xQ_z is the *x*-magnetization of proton, leading to a triplet with intensities 1:-2:1 for the coupling with ^{14}N nucleus, and S_yI_z is the *y*-magnetization of proton, leading to a triplet with intensities 1:0:-1. The first rectangular pulse or D_1^K train converts the S_xQ_z operator into S_xK_y one with coefficient

$3\sin(2\theta)/2$ and S_xD_x one with coefficient $(3\cos(2\theta)-3)/2$ (Eq.12) and the S_yI_z operator into S_yI_y with coefficient $\sin(\theta)$ (Eq.9). S_xK_y and S_yI_y operators involve $^{14}N^{1Q}$ coherences, whereas S_xD_x operator involves $^{14}N^{2Q}$ ones. The coherences evolve under isotropic shift during the t_1 time. These terms are converted back into observable transverse ^1H magnetization by the second rectangular pulse or D_1^K train and the evolution during the refocusing period. When both ±1Q ^{14}N coherences are selected during the t_1 period, the signal of the ^1H-$\{^{14}N^{1Q}\}$ HMQC experiment is proportional to

$$S(\tau) \propto \frac{2}{3}\sin^2(\theta)\langle\sin^2(2\omega_{HN}\tau)\rangle + \frac{2}{3}\sin^2(2\theta)\langle\sin^4(\omega_{HN}\tau)\rangle \quad (22)$$

where

$$\langle\sin^2(2\omega_{HN}\tau)\rangle = \begin{cases} \sin^2(2\pi J_{HN}\tau) & \text{for } J-\text{HMQC} \\ \frac{1}{2} - \frac{\pi\sqrt{2}}{8} J_{1/4}\left(\frac{b_{IS}\tau}{4}\right) J_{-1/4}\left(\frac{b_{IS}\tau}{4}\right) & \text{for } D-\text{HMQC} \end{cases} \quad (23)$$

and

$$\langle\sin^4(\omega_{HN}\tau)\rangle = \begin{cases} \sin^4(\pi J_{HN}\tau) & \text{for } J-\text{HMQC} \\ \frac{3}{8} - \frac{\pi\sqrt{2}}{8} J_{\frac{1}{4}}\left(\frac{b_{IS}\tau}{4}\right) J_{-\frac{1}{4}}\left(\frac{b_{IS}\tau}{4}\right) + \frac{\pi\sqrt{2}}{32} J_{\frac{1}{4}}\left(\frac{b_{IS}\tau}{2}\right) J_{-\frac{1}{4}}\left(\frac{b_{IS}\tau}{2}\right) & \text{for } D-\text{HMQC} \end{cases} \quad (24)$$

For ^1H-$\{^{14}N^{1Q}\}$ *J*-HMQC experiment, the maximal signal intensity is 33% less than that of ^1H-$\{^{195}Pt\}$ *J*-HMQC (compare Fig.**2a** and **c**) and is achieved for $J_{HN}\tau$ and θ verifying

$$\left(\frac{\theta-90}{45}\right)^2 + (4J_{HN}\tau - 2)^2 = 1 \quad (25)$$

This equation corresponds to the red dashed ellipse shown in Fig.**2c**. The smaller θ value verifying this equation is 45° for $\tau = 1/(2J_{HN})$, which selects the S_xQ_z operator at the end of the defocusing delay. The shorter τ value verifying Eq.25 is $1/(4J_{HN})$ for θ = 90°, which then selects the S_yI_z operator. The 33% loss in intensity for ^1H-$\{^{14}N^{1Q}\}$ with respect to ^1H-$\{^{195}Pt\}$ *J*-HMQC experiment stems from the fact that the central component of the triplet for a proton coupled to ^{14}N nucleus, which corresponds to the operators $S_x-S_xQ_z$ and $S_y-S_yQ_z$, does not evolve under the ^1H-^{14}N coupling and hence, cannot be transferred to the ^{14}N nucleus.

As seen in Fig.**2d**, in the case of ^1H-$\{^{14}N^{1Q}\}$ *D*-HMQC experiment the maximal transfer efficiency is ca. 0.5 and the smallest θ value and the shortest τ delay yielding such maximal transfer efficiency are ca. 54° and $1.5/|b_{IS}|$, respectively.

When both ±2Q ^{14}N coherences are selected during the t_1 period, the signal of ^1H-$\{^{14}N^{2Q}\}$ HMQC experiment is proportional to

$$S(\tau) \propto \frac{2}{3}\sin^4(\theta)\langle\sin^4(\omega_{HN}\tau)\rangle\,. \quad (26)$$

The maximal transfer efficiency of ^1H-$\{^{14}N^{2Q}\}$ *J*-HMQC experiment (ca. 0.67) is identical to that of ^1H-$\{^{14}N^{1Q}\}$ one, but such optimal transfer is achieved for θ = 90° and $\tau = 1/(2J_{HN})$ (Fig.**2e**). For ^1H-$\{^{14}N^{2Q}\}$ *D*-HMQC experiment, the maximal transfer efficiency only reaches 0.4 and is observed for θ = 90° and ca. $1.5/|b_{IS}|$.

III. Numerical simulations

III-1. Simulation parameters

All numerical simulations of spin dynamics were calculated using SIMPSON software [86]. The powder averages were calculated using 615 $\{\alpha_{MR}, \beta_{MR}\}$ pairs and 4 γ_{MR} angles in order to relate the molecular frame to the rotor one. The $\{\alpha_{MR}, \beta_{MR}\}$ pairs were selected according to the REPULSION algorithm [87], whereas the four γ_{MR} angles were equal to 0, 90, 180 and 270°.

The simulations have been performed for an isolated *I* nucleus and an isolated ^1H-*I* spin pair, in which the *I* nucleus was either a ^{195}Pt nucleus subject to CSA or a ^{14}N one subject to quadrupole interaction.

For ^{195}Pt, δ_{aniso} = 3880 ppm and η_{CSA} = 0, which correspond to $FW \approx 1$ MHz at B_0 = 18.8 T ($\nu_{0,195Pt}$ = 172 MHz). For the ^{14}N nucleus, C_Q = 1.18 MHz and η_Q = 0.5, which correspond approximately to the quadrupolar parameters of α-glycine [88]. The FW of ^{14}N signal is equal to $1.5C_Q$ = 1.77 MHz.
We used the same couplings of $J_{HI} = |b_{IS}|/(2\pi)$ = 125 Hz for ^{1}H-{I} J- and D-HMQC experiments.
The simulations for I = ^{195}Pt were carried out only at B_0 = 18.8 T, whereas those for I = ^{14}N, were done at 4.7 and 18.8 T in order to investigate the effect of the second-order quadrupole interaction, which is inversely proportional to the B_0 field and hence, four-fold smaller at 18.8 than at 4.7 T. For all simulations, we employed ν_R = 62.5 kHz since fast MAS frequencies improve the resolution and the sensitivity of the ^{1}H-{I} HMQC experiments by averaging out the ^{1}H-^{1}H dipolar interactions. Furthermore, fast MAS frequencies reduce the length of DANTE trains and hence, limit the losses during those schemes. We simulated the projection of the density matrix onto the I_y operator, which corresponds to the total integrated intensity of the spectrum, after the excitation of longitudinal magnetization of isolated ^{195}Pt or ^{14}N nuclei by D_1^K train (Figs.**S4** and **S5**). We also simulated the signal of ^{1}H-{I} J- or D-HMQC experiments with I = ^{195}Pt, ^{14}N^{1Q} and ^{14}N^{2Q} for isolated ^{1}H-^{195}Pt and ^{1}H-^{14}N spin-pairs. The π/2 and π pulses which are applied to the ^{1}H channel and do not belong to the recoupling sequence, were simulated as perfect Dirac pulses. On the I channel, we applied either two perfect Dirac pulses with a tilt angle θ, two rectangular π/2-pulses (Fig.**S1**) or two D_1^K or D_2^K trains with a weak rf-field of ν_1 = 30 kHz, except in Fig.**S6** for which ν_1 = 70 kHz was used. In D-HMQC experiments, the ^{1}H-I dipolar couplings were reintroduced during the τ delays by applying the $SR4_1^2$ scheme with $\nu_1 = 2\nu_R$ = 125 kHz. The efficiency was normalized with respect to the maximum ^{1}H signal produced by ^{1}H-{I} J-HMQC experiment with two perfect Dirac π/2-pulses on I channel and selecting the 1Q coherences during the t_1 period. The rf-pulses were applied on resonance, except in Figs.**3** and **S3C**, where the carrier frequency of the I channel was varied in order to test the robustness to offset. For ^{14}N nucleus, on-resonance irradiation means that the ^{14}N carrier frequency is fixed at the sum of the isotropic chemical shift and the quadrupolar-induced shift (QIS). Additional details about the simulations are given in the figure captions.

III-2. Simulations of ^{1}H-{^{195}Pt} HMQC experiments

III-2-1. Choice of τ delay.

Fig.**S1** shows the simulated signal of ^{1}H-{^{195}Pt} J- and D-HMQC experiments using D_1^K or D_2^K trains on the ^{195}Pt channel as function of τ delay. These simulations show that the optimal τ values are independent of the employed DANTE scheme, and notably of the τ_p and N values, and are equal to $1/(2J_{HPt})$ = 4 ms for J-HMQC and $1.50/|b_{IS}|$ = 12 ms for D-HMQC. Furthermore, the maximal intensity of ^{1}H-{^{195}Pt} D-HMQC is about 30% lower than that of J-HMQC. Such results agree with Figs.**2a** and **b** and hence, Eqs.19 and 20.

III-2-2. Choice of the K value.

Fig.**S2** shows that, provided the individual pulses of D_1^K trains are short enough ($\tau_p \leq 1$ µs) to excite the FW of ^{195}Pt spectrum, the signal of ^{1}H-{^{195}Pt} J- and D-HMQC experiments depends on the $\theta = 360\nu_1 K\tau_p$ angle as $\sin^2(\theta)$ and the maximum signal is obtained for $\theta_{opt} \approx 90°$ for K_{opt} value given by Eq.10. These simulations agree with Figs.**2a** and **b** and Eq.19. For $\tau_p > 1$ µs, the entire ^{195}Pt spectrum is not uniformly excited. As consequence, the maximum signal decreases and θ_{opt} is larger than 90° (Figs.**S2Af** and **S2Bf**) since for large n value, $C_n < \bar{\omega}_1$ (Eq.3), and hence K values larger than that given by Eq.10 are required to excite the spinning sidebands with large offset.

Similar simulations were carried out for ^{1}H-{^{195}Pt} *J*- and *D*-HMQC experiments using D_2^K trains on *I* channel and the results are shown in Fig.**S3A** and **B**. These simulations indicate that the maximal transfer efficiency is then about 30% lower than that achieved using D_1^K trains, and that this maximal signal is achieved for longer θ_{opt} angles which increase from 108 to 130° when τ_p increases from 0.2 to 1.0 µs. These simulations are consistent with the fact that Eqs.8 and 9 do not hold for D_2^K trains. We can also notice that the θ_{opt} values are identical for ^{1}H-{^{195}Pt} *J* and *D*-HMQC experiments and also for the direct excitation of ^{195}Pt 1D spectra (Fig.**S4**). Indeed, the nutation curves, i.e. the signal intensity versus θ angle, for HMQC experiments are the square of those for direct excitation.

III-2-3. Robustness to offset.

Fig.**3** displays the signal of ^{1}H-{^{195}Pt} *J*-HMQC experiments using D_1^{10} and D_2^7 trains as function of the ^{195}Pt offset and it shows that such signal is the square of the excitation profile of those DANTE schemes when applied for the direct excitation of ^{195}Pt nuclei. Hence, the Full Widths at Half Maximum of each rf Spikelet ($FWHM_S$) and of the Envelope of these spikelets ($FWHM_E$) are equal to [34]

$$FWHM_S = \frac{1.09}{KT_R} \text{ and } FWHM_E = \frac{1.09}{\tau_p} \quad (27)$$

The first equation shows that the width of each rf spikelet increases with MAS frequencies and for shorter *K* values. Therefore, D_2^7 trains exhibit a higher robustness to offset than D_1^{10} ones, as seen in Fig.**S3Cd**. Other simulations [not shown] also indicate (i) that the robustness to ^{195}Pt offset of ^{1}H-{^{195}Pt} *D*-HMQC experiments is similar to that of the *J*-HMQC ones using the same trains on the ^{195}Pt channel, and (ii) that the transfer efficiency of ^{1}H-{^{195}Pt} *D*-HMQC experiments using DANTE schemes with $\tau_p < 2$ µs does not depend on the relative orientation between the chemical shift tensor and the H-Pt inter-nuclear vector.

III-3. Simulations of ^{1}H-{^{14}N} HMQC experiments

III-3-1. Signal decay produced by second-order quadrupole interaction.

The nutation curves of ^{14}N *y*-magnetization excited by a D_1^K train are shown in Fig.**S5**. When only the first-order quadrupole interaction (H_{Q1}) is included in the simulations and $\tau_p \leq 0.4$ µs, which permits to excite the full powder pattern, the signal depends on θ as sin(θ) (Fig.**S5a**), in agreement with Eq.9. The signal decreases for larger τ_p values due to limited excitation, but the sin(θ) behavior remains. In the presence of second-order quadrupole interaction, H_{Q2}, the signal deviates from sin(θ) for long *K* values, i.e. large θ angles for short τ_p values (Figs.**S5b** and **c**). The magnitude of H_{Q2} Hamiltonian is inversely proportional to B_0, and hence a larger decay is observed at 4.7 than at 18.8 T. As a result, at 4.7 T the maximum signal is significantly lower than at 18.8 T and the optimal τ_p values result from a compromise between broadband excitation of the powder pattern and limited attenuation of the signal by H_{Q2} dephasing.

III-3-2. ^{1}H-{^{14}N^{1Q}} *J*- or *D*-HMQC with D_1^K train.

Fig.**4** displays the transfer efficiency of ^{1}H-{^{14}N^{1Q}} *J*-HMQC experiments as function of τ_J and θ parameters. When two Dirac pulses are applied on ^{14}N channel and only H_{Q1} is taken into account (Fig.**4a**), the dependence of the maximum efficiency with τ_J and θ parameters is similar to that predicted by Eqs.22-24 and displayed in Fig.**2c**. In particular, the maximum transfer efficiency corresponds to the ellipse described by Eq.25. In agreement with the simulations for the direct

excitation of an isolated ^{14}N nucleus (Fig.**S5**), the substitution of Dirac pulses by D_1^K trains with τ_p = 0.6 µs leads to a reduction in the transfer efficiency of ^{1}H-{^{14}N^{1Q}} *J*-HMQC experiment (Fig.**4b-d**) since these pulses are not short enough to excite the full powder pattern. H_{Q2} further reduces the transfer efficiency for large *K* values, i.e. large θ angles (Figs.**4c** and **d**). Such attenuation increases with the H_{Q2} term, notably at lower B_0 field (Fig.**4d**). These simulations indicate that the conditions θ ≈ 45° and $\tau_J \approx 1/(2J_{HN})$ limit the signal attenuation by H_{Q2} and lead to higher transfer efficiency for the ^{1}H-{^{14}N^{1Q}} *J*-HMQC sequence using D_1^K trains.

Similarly in Fig.**5**, the transfer efficiency of ^{1}H-{^{14}N^{1Q}} *D*-HMQC experiments is plotted versus τ_D and θ parameters. In the case of Dirac pulses (Fig.**5a**), the variation of transfer efficiency with τ_D and θ is similar to that predicted by Eqs.22-24 and displayed in Fig.**2d**. The maximal transfer efficiency is 30% lower than that of ^{1}H-{^{14}N^{1Q}} *J*-HMQC experiments and is obtained for τ = 1.5/125 ≈ 12 ms and θ ≈ 54 and 126°. As for ^{1}H-{^{14}N^{1Q}} *J*-HMQC experiments, the substitution of Dirac pulses by D_1^K trains with τ_p = 0.6 µs decreases the efficiency (Fig.**5b-d**) since these pulses do not achieve uniform excitation of the powder pattern. H_{Q2} attenuates the signal for large θ values, notably at low B_0 field (Fig.**5c**,**d**), and at 4.7 T only the maximum at θ ≈ 54° is detected, whereas that at θ ≈ 126° is not. The comparison of Figs.**5c** and **S6a** shows that a higher efficiency is achieved using D_1^K trains made of shorter pulses (τ_p = 0.25 µs) with higher rf field (ν_1 = 70 kHz), since pulses shorter than 0.4 µs are required to excite the whole ^{14}N powder pattern (Fig.**S5**). However, the use of shorter pulses requires that of higher rf-field in order to keep constant the length of DANTE train and hence, to limit the losses produced by H_{Q2}. The simulations shown in Fig.**S9** show that the efficiency of ^{1}H-{^{14}N^{1Q}} *D*-HMQC experiments does not depend on the relative orientation of the H-N inter-nuclear vector with respect to the efg tensor for τ_D values shorter than the optimal ones.

III-3-3. ^{1}H-{^{14}N^{2Q}} *J*- or *D*-HMQC with D_1^K train.

The simulated dependences of ^{1}H-{^{14}N^{2Q}} *J*- or *D*-HMQC signals with D_1^K trains as function of τ and θ parameters are displayed in Figs.**6** and **S7**, respectively. When Dirac pulses are applied to the ^{14}N channel, these dependences match well those predicted by Eq.26 and Figs.**2e** and **2f**. The maximal transfer efficiencies of ^{1}H-{^{14}N^{2Q}} *J*- or *D*-HMQC experiments are achieved for θ = 90° and τ = 1/(2×125) = 4 and 1.5/125 ≈ 12 ms, respectively. The efficiency of *D*-HMQC sequence is then 60% lower than the *J*-mediated version in that case.

As mentioned above for ^{1}H-{^{14}N^{1Q}} HMQC experiments, the use of D_1^K trains with τ_p = 0.6 µs also reduces the transfer efficiency of ^{1}H-{^{14}N^{2Q}} *J*- or *D*-HMQC experiments (Fig.**6b-d** and **S7b-d**) due to restricted excitation bandwidth. The transfer efficiency is also further reduced with the H_{Q2} dephasing, and such attenuation is especially large at 4.7 T. As for ^{1}H-{^{14}N^{1Q}} *D*-HMQC experiments, shorter pulses increase the excitation bandwidth of D_1^K trains, and hence, also result in higher transfer efficiency for ^{1}H-{^{14}N^{2Q}} *D*-HMQC experiments (Fig.**S6b**).

Fig.**S8** displays the transfer efficiency of ^{1}H-{^{14}N^{1Q+2Q}} *J*-HMQC experiments, during which both 1Q and 2Q coherences are selected during the t_1 period. The transfer efficiency of this sequence is the sum of those of ^{1}H-{^{14}N^{1Q}} and ^{1}H-{^{14}N^{2Q}} variants.

II-3-4. ^{1}H-{^{14}N} *J*- or *D*-HMQC with D_2^K train.

Figs.**7** and **S10-S12** show the variation of the transfer efficiency of ^{1}H-{^{14}N^{1Q}} and ^{1}H-{^{14}N^{2Q}} *J*- or *D*-HMQC sequences using D_2^K trains as function of τ and θ parameters. Those plots are globally similar to those simulated for HMQC experiments using D_1^K trains (Figs.**4-6** and **S6**). A first difference is the lower transfer efficiency in the case of D_2^K trains. For instance, at 18.8 T the transfer efficiency with

D_2^K trains is about 30-40% lower than with D_1^K ones. Furthermore, the maximum transfer efficiencies are reached for θ angles slightly larger for D_2^K schemes than for D_1^K ones. For example, for ^{1}H-{^{14}N^{2Q}} *J*- or *D*-HMQC sequences at 18.8 T, the maximal transfer efficiency is achieved for θ ≈ 120°. Such value agrees with that found for ^{1}H-{^{195}Pt} *J*-HMQC sequences using D_2^K schemes. Nevertheless, the simulations shown in Figs.**7** and **S10-S12** indicate that D_2^K trains are less affected than D_1^K ones by H_{Q2} dephasing, owing to their shorter length, i.e. shorter *K* values. As for D_1^K trains, D_2^K trains made of shorter pulses with higher rf-field achieve more uniform excitation of the ^{14}N powder pattern and hence, increase the efficiency of ^{1}H-{^{14}N} HMQC sequences (Fig.**S6b**).

IV. Experimental demonstration for ^{1}H-{^{14}N} *D*-HMQC sequence

IV-1. Samples and experimental conditions

All solid-state NMR experiments were performed on an 800 MHz (18.8 T) Bruker BioSpin narrow-bore magnet equipped with an Avance-III console. 1D ^{1}H-{^{14}N^{1Q}} and ^{1}H-{^{14}N^{2Q}} *D*-HMQC spectra of L-histidine.HCl monohydrate (Hist) and 1D ^{1}H-{^{14}N^{1Q}} *D*-HMQC ones of γ-glycine were acquired with 1.3 mm double-resonance HX MAS probe. The samples were spun at ν_R = 62.5 kHz.
The ^{1}H-{^{14}N} *D*-HMQC sequences were employed since they are more sensitive than the *J*-HMQC variants for solids. These experiments were acquired using the sequences depicted in Fig.**1c** and **d** with D_1^K or D_2^K trains, respectively. The SR4$_1^2$ recoupling with $\nu_1 = 2\nu_R$ = 125 kHz was applied on ^{1}H channel during the τ_D delays to reintroduce the ^{14}N-^{1}H dipolar couplings. The rf-field of the ^{1}H π/2 and π pulses was 200 kHz. To acquire *D*-HMQC 1D spectra, the t_1 delay was fixed to its minimum rotor-synchronized value equal either to $2T_R$ for rectangular pulses or KT_R for D^K_N trains. The 2D ^{1}H-{^{14}N} *D*-HMQC spectrum of γ-glycine exhibits a single cross-peak between ammonium ^{1}H and ^{14}N nuclei, whereas those of Hist exhibit four cross-peaks: (i) one between pros ^{1}H and ^{14}N nuclei, close to the side chain in the imidazole ring, denoted ^{1}H$^\pi$ and ^{14}N$^\pi$ according to IUPAC, (ii) one between tele ^{1}H and ^{14}N nuclei, far from the side chain in the imidazole ring, denoted ^{1}H$^\tau$ and ^{14}N$^\tau$ according to IUPAC, (iii) one between ammonium ^{1}H and ^{14}N nuclei (NH_3^+), and (iv) one between aliphatic protons, denoted H$^\alpha$ and H$^\beta$, and NH_3^+ nucleus [89]. Fig.**8** displays the integrated intensity of ^{1}H$^\pi$ 1D signal of Hist, corresponding to the ^{1}H$^\pi$-^{14}N$^\pi$ cross-peak, whereas Figs.**9** and **10** display the integrated intensity of ^{1}H 1D signal of γ-glycine. The ^{14}N C_Q and η_Q parameters in γ-glycine are equal to 1.18 MHz and 0.53, respectively [88], whereas those of ^{14}N$^\pi$ nucleus in Hist are 1.29 MHz and 0.94 [64]. The ^{14}N carrier frequency was on-resonance with ^{14}N$^\pi$ resonance of Hist in Fig.**8** and ^{14}NH$_3$ one of γ-glycine in Fig.**9**. In Fig.**10**, the ^{14}N carrier frequency was varied. The 1D spectra were acquired using a recycle delay, τ_{RD} = 5 s, and *NS* = 128 scans. The other experimental parameters are indicated in the figure captions.

IV-2. Experimental results and discussion

Fig.**8** displays the integrated intensity of ^{1}H$^\pi$ signal in 1D ^{1}H-{^{14}N^{1Q}} and ^{1}H-{^{14}N^{2Q}} *D*-HMQC spectra of Hist as function of τ_D and the total on-resonance tilt angle, $\theta = 360kN\nu_1\tau_p$, when D^K_N trains with *N* = 1 or 2 and ν_1 = 75 kHz are applied on the ^{14}N channel. The maximum signal is observed around a recoupling time of τ_D ≈ 150-200 μs, which is comparable to the theoretical one $1.5/|b_{IS}| \approx 200$ μs with $|b_{IS}|/(2\pi) \approx 7.3$ kHz between ^{1}H$^\pi$ and ^{14}N$^\pi$ nuclei. Experimentally, we observe a rapid attenuation of the signal for long τ_D values, whereas such attenuation is not observed for simulations with an isolated ^{1}H-^{14}N spin-pair (compare Figs.**8** with **S6**). Such decrease stems from the rapid decay of the ^{1}H 1Q coherences produced by the residual ^{1}H-^{1}H dipolar interactions during the SR4$_1^2$ scheme, which only suppresses these interactions in the first-order average Hamiltonian, but not in the higher-

order terms. These experimental results also confirm that (i) ^{1}H-{^{14}N^{2Q}} *D*-HMQC experiments are less efficient than the ^{1}H-{^{14}N^{1Q}} ones and (ii) D_1^K trains provides a 10-15% gain in signal intensity with respect to D_2^K ones for ^{14}N nucleus with $C_Q \approx 1.3$ MHz.

Fig.**9** shows the on-resonance integrated intensity of ammonium protons in 1D ^{1}H-{^{14}N^{1Q}} *D*-HMQC spectra of γ-glycine, when using D_1^K trains with ν_1 = 32 or 75 kHz. Given the small dephasing under H_{Q2} for $^{14}NH_3^+$ site in γ-glycine at 18.8 T, the achieved experimental intensities are similar for both rf-fields since the decrease of rf-strength can be compensated by an increase of the DANTE length (KT_R) with little additional intensity losses. Nevertheless, the rise of the DANTE length results in an increased sensitivity to offset (vide supra). In the case of larger H_{Q2} dephasing, for a sample exhibiting bigger C_Q value or experiments at lower magnetic fields, sending a higher rf-field is advantageous in terms of sensitivity since it allows the use of shorter DANTE trains.

Previous experimental results have been obtained for on-resonance irradiation of the investigated ^{14}N nuclei. Fig.**10** shows the integrated intensity of ammonium protons in ^{1}H-{^{14}N^{1Q}} *D*-HMQC 1D spectra of γ-glycine versus ^{14}N offset, when using D_1^K or D_2^K trains with ν_1 = 32 or 75 kHz. For the sake of comparison, the integrated intensity for the variant using selective long pulses (SLP) [66] with ν_1 = 32 kHz instead of DANTE trains is also displayed. For both D_1^K or D_2^K trains, the *K* values were optimized to maximize the on-resonance intensity. For D_1^K trains, the optimal *K* values were equal to 12 and 6 for ν_1 = 32 or 75 kHz, respectively. These values corresponds to θ angles of about 90°, in agreement with Fig.**9**. For D_2^K trains, the optimal *K* values were equal to 9 and 4 for ν_1 = 32 or 75 kHz, respectively. These values corresponds to θ angles of about 125°, in agreement with Fig.**8b**.

On resonance, the most efficient DANTE schemes are those using ν_1 = 75 kHz. These increased efficiencies are related to their shorter trains: D_2^4 versus D_2^9 and D_1^6 versus D_1^{12}, which limit the dephasing under H_{Q2} as well as under the residual ^{1}H-^{1}H and ^{1}H-^{14}N dipolar interactions. For ν_1 = 75 kHz, D_2^4 efficiency is about 15% lower than that of D_1^6. For ν_1 = 32 kHz, D_1^{12} and D_2^9 trains exhibit the same on-resonance efficiencies since for such long trains, the dephasings are non-negligible, and they are smaller for the shorter D_2^9 train than for D_1^{12} one. Therefore, for D_2^9 train the smaller signal attenuation compensates the smaller efficiency.

In agreement with Eq.27, the $FWHM_S$ measured from Fig.**10** are inversely proportional to the *K* value. For example, it is equal to 18 kHz for D_2^4, a value which is 2.25 times larger than $FWHM_S$ = 8 kHz of D_2^9, in agreement with the ratio of the *K* values. These $FWHM_S$ values correspond to 311 and 138 ppm at 18.8 T, respectively.

The broadest excitation bandwidth is achieved using two selective long pulses. Indeed, its width is of $FWHM_S \approx 35$ kHz, which corresponds to 820 ppm. However, this excitation (i) is slightly less efficient on-resonance that the D_1^6 and D_2^4 trains with ν_1 = 75 kHz, but (ii) it requires less rf field and only little experimental optimization.

V. Conclusions

We have analyzed the performances and the optimization of ^{1}H-{*I*} HMQC experiments using basic and interleaved DANTE trains to manipulate *I* nuclei exhibiting wide spectra. We have considered the two cases of *I* = 1/2 nucleus, ^{195}Pt, subject to CSA, and *I* = 1 one, ^{14}N, subject to quadrupole interaction. We have investigated using spin dynamics simulations both *J*- and *D*-HMQC experiments, even if experimentally the through-space variant exhibits usually higher efficiency owing to the larger magnitude of dipolar with respect to *J* couplings. For ^{14}N nuclei, the indirect detection of 1Q coherences is more efficient than that of 2Q ones, even if the 2Q spectrum may exhibit higher resolution since these coherences are not broadened by first-order quadrupole interaction.

The present study indicates that the optimal defocusing and refocusing times in *D*-HMQC experiments do not depend on the employed DANTE trains and are about 1.5 time the inverse of the ^{1}H-*I* dipolar coupling constant when using the SR4$_1^2$ recoupling. For experiments using D_1^K trains, the optimal tilt angle is 90° for ^{195}Pt and $^{14}N^{2Q}$, and theoretically about 54° (and 126°) for $^{14}N^{1Q}$. D_2^K trains require larger tilt angles.

Furthermore, the length of the DANTE trains determines the robustness to offset of the rf-spikelets. Hence, short DANTE trains, including the interleaved ones, benefit from higher robustness to offset. Nevertheless, HMQC experiments using DANTE trains are less robust than those using selective long pulses, at least for moderate quadrupole interactions.

Short DANTE trains also benefit from improved efficiency since they limit the signal decays under ^{1}H-^{1}H and ^{1}H-*I* residual dipolar couplings as well as second-order quadrupole attenuation for *I* = ^{14}N. The length of DANTE trains can be shortened by the use of high MAS frequency and large rf-field, since the length of the individual pulses composing the DANTE train is determined by the width of the static powder pattern. Therefore, the highest rf-field, compatible with the probe specifications, must be employed for the DANTE trains. Similarly, high static magnetic field is advantageous to decrease the signal decay under the second-order quadrupole interaction. Interleaved DANTE trains are shorter than the basic ones and hence, are less affected by signal decays. However, such schemes remain less efficient for spin *I* = 1/2 and ^{14}N ones with $C_Q \leq 1.3$ MHz. Additional simulations and experiments are required to compare the performances of various excitation schemes for ^{14}N nuclei subject to large quadrupole interactions.

Acknowledgements. This work was supported by: *Fédération de Recherche* CNRS (FR-3050) Infrastructure de recherche *RMN à Très Hauts Champs*. JT, OL, and JPA are grateful for funding provided by Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Hauts-de-France, FEDER and CortecNet. They also acknowledge contract CEFIPRA No. 85208-E, PRC CNRS-NSFC and ANR 17-ERC2-0022 (EOS). OL acknowledges financial support from Institut Universitaire de France (IUF). MS and BH are grateful for supports form the National Natural Science Foundation of China (21522303, 21703068). MS also thanks funding provided from the China Postdoctoral Science Foundation (2017M611491). YL is grateful for the financial support from China Scholarship Council.

Fig.1. ^{1}H-{*I*} (a,c,d) *J*- and (b) *D*-HMQC sequences using for the excitation and the reconversion of the *I*-spin coherences: (a,b) square pulses, (c) D_1^K or (d) D_2^K trains. (c,d) *J*-schemes can be transformed into *D* ones by introducing a dipolar recoupling during τ delays.

Fig.2. Transfer efficiency of ^{1}H-{*I*} (a,c,e) *J*- and (b,d,f) *D*-HMQC sequences using Dirac pulses or D_1^K trains for *I* = (a,b) ^{195}Pt, (c,d) $^{14}N^{1Q}$ and (e,f) $^{14}N^{2Q}$ calculated without any loss using Eqs. 19-20, 22-24 and 26, respectively. The maximal transfer efficiency is 1 (a) and 0.67 (e) for {θ, Jτ} = {90°, 0.5}, 0.67 along the dashed red line representing Eq.25 in (c), 0.5 for {θ, $|b_{IS}|\tau$} = {90°,1.5} in (b), 0.5 for {54° or 126°,1.5} in (d), and 0.4 for {90°, 1.5} in (f).

Fig.3. Simulated ^{1}H-{^{195}Pt} *J*-HMQC signal using D_1^{10} or D_2^7 trains on ^{195}Pt channel versus ^{195}Pt offset with τ_p = 0.8 μs, $\tau_J = 1/(2J)$ and θ ≈ 90° for D_1^{10} (Fig.S2Ad) or 120° for D_2^7 trains (Fig.S3Ad). All curves have been scaled to the same on-resonance intensity to facilitate the comparison of their excitation bandwidths. The square of the integrated intensity of 1D spectra excited by D_1^{10} or D_2^7 trains versus offset is also displayed and it coincides with the intensity versus offset for 2D experiments.

Fig.4. Simulated ^{1}H-{$^{14}N^{1Q}$} *J*-HMQC transfer efficiency versus τ_J and θ when one applies on ^{14}N channel: (a) two Dirac pulses with only H_{Q1}, (b-d) two D_1^K trains with τ_p = 0.6 μs and $K = \theta/(360\nu_1\tau_p)$ with (b) only H_{Q1} or (c,d) $H_{Q1} + H_{Q2}$ at (c) 18.8 or (d) 4.7 T.

Fig.5. Simulated ^{1}H-{^{14}N^{1Q}} *D*-HMQC transfer efficiency versus τ_D and θ when one applies on ^{14}N channel: (a) two Dirac pulses with only H_{Q1}, (b-d) two D_1^K trains with τ_p = 0.6 μs and $K = \theta/(360\nu_1\tau_p)$ with (b) only H_{Q1} or (c,d) $H_{Q1} + H_{Q2}$ at (c) 18.8 or (d) 4.7 T.

Fig.6. Simulated ^{1}H-{^{14}N^{2Q}} *J*-HMQC transfer efficiency versus τ_J and θ when one applies on ^{14}N channel: (a) two Dirac pulses with only H_{Q1}, (b-d) two D_1^K trains with τ_p = 0.6 μs and $K = \theta/(360\nu_1\tau_p)$ with (b) only H_{Q1} or (c,d) $H_{Q1} + H_{Q2}$ at (c) 18.8 or (d) 4.7 T.

Fig.7. Simulated ^{1}H-{^{14}N^{1Q}} *J*-HMQC transfer efficiency versus τ_J and θ when one applies on ^{14}N channel: (a) two Dirac pulses with only H_{Q1}, (b-d) two D_2^K trains with τ_p = 0.6 μs and $K = \theta/(720\nu_1\tau_p)$ with (b) only H_{Q1} or (c,d) $H_{Q1} + H_{Q2}$ at (c) 18.8 or (d) 4.7 T.

Fig.8. Experimental integrated intensity of H^{π} signal of (a,b) ^{1}H-{^{14}N^{1Q}} and (c,d) ^{1}H-{^{14}N^{2Q}} *D*-HMQC spectra of Hist, versus τ_D and θ. In (a) and (c), two D_1^K trains are applied on ^{14}N channel, whereas in (b) and (d), they are replaced by two D_2^K trains.

Fig.9. Experimental integrated intensity of ammonium ^{1}H signal in 1D ^{1}H-{^{14}N^{1Q}} *D*-HMQC spectra of γ-glycine at 18.8 T and ν_R = 62.5 kHz, versus τ_D and θ. Two D_1^K trains are applied on ^{14}N channel with ν_1 = (a) 32 or (b) 75 kHz.

Fig.10. Integrated intensity of ammonium ^{1}H signal in 1D ^{1}H-{^{14}N^{1Q}} *D*-HMQC spectra of γ-glycine at 18.8 T, ν_R = 62.5 kHz and τ_D = 160 μs, versus ^{14}N offset. ^{14}N nuclei were manipulated using two DANTE trains with τ_p = 0.6 μs and ν_1 = 32 (D_1^{12} (+) or D_2^9 (×)) or 75 (D_1^6 (*) orD_2^4 (□)) kHz or two selective long-pulses (SLP: ▬) with ν_1 = 32 kHz and τ_p = 24 μs. The curves are only guidelines for the eyes between experimental data points.

References

[1] M. Deschamps, Ultrafast Magic Angle Spinning Nuclear Magnetic Resonance, in: G.A. Webb (Ed.), *Annu. Rep. NMR Spectrosc.*, Academic Press, **2014:** 109–144. doi:10.1016/B978-0-12-800185-1.00003-6.

[2] V. Agarwal, S. Penzel, K. Szekely, R. Cadalbert, E. Testori, A. Oss, J. Past, A. Samoson, M. Ernst, A. Böckmann, B.H. Meier, De novo 3D structure determination from sub-milligram protein samples by solid-state 100 kHz MAS NMR spectroscopy., *Angew. Chem. Int. Ed Engl*. 53 (**2014)** 12253–6. doi:10.1002/anie.201405730.

[3] Y.Q. Ye, M. Malon, C. Martineau, F. Taulelle, Y. Nishiyama, Rapid measurement of multidimensional 1H solid-state NMR spectra at ultra-fast MAS frequencies, *J. Magn. Reson.* 239 (**2014**) 75–80. doi:10.1016/j.jmr.2013.12.010.

[4] L.B. Andreas, K. Jaudzems, J. Stanek, D. Lalli, A. Bertarello, T. Le Marchand, D. Cala-De Paepe, S. Kotelovica, I. Akopjana, B. Knott, S. Wegner, F. Engelke, A. Lesage, L. Emsley, K. Tars, T. Herrmann, G. Pintacuda, Structure of fully protonated proteins by proton-detected magic-angle spinning NMR, *Proc. Natl. Acad. Sci*. 113 (**2016**) 9187–9192. doi:10.1073/pnas.1602248113.

[5] K. Hashi, S. Ohki, S. Matsumoto, G. Nishijima, A. Goto, K. Deguchi, K. Yamada, T. Noguchi, S. Sakai, M. Takahashi, Y. Yanagisawa, S. Iguchi, T. Yamazaki, H. Maeda, R. Tanaka, T. Nemoto, H. Suematsu, T. Miki, K. Saito, T. Shimizu, Achievement of 1020MHz NMR, *J.*

Magn. Reson. 256 (**2015**) 30–33. doi:10.1016/j.jmr.2015.04.009.

[6] H. Maeda, T. Yamazaki, Y. Nishiyama, M. Hamada, K. Hashi, T. Shimizu, H. Suematsu, Y. Yanagisawa, Development of Super-High-Field NMR Operated Beyond 1 GHz Using High-Temperature Superconducting Coils, in: eMagRes, *American Cancer Society*, **2016**: 1109–1120. doi:10.1002/9780470034590.emrstm1492.

[7] Z. Gan, I. Hung, X. Wang, J. Paulino, G. Wu, I.M. Litvak, P.L. Gor'kov, W.W. Brey, P. Lendi, J.L. Schiano, M.D. Bird, I.R. Dixon, J. Toth, G.S. Boebinger, T.A. Cross, NMR spectroscopy up to 35.2T using a series-connected hybrid magnet, *J. Magn. Reson*. 284 (**2017**) 125–136. doi:10.1016/j.jmr.2017.08.007.

[8] T.V. Can, Q.Z. Ni, R.G. Griffin, Mechanisms of dynamic nuclear polarization in insulating solids., *J. Magn. Reson.* 253 (**2015**) 23–35. doi:10.1016/j.jmr.2015.02.005.

[9] A.S. Lilly Thankamony, J.J. Wittmann, M. Kaushik, B. Corzilius, Dynamic nuclear polarization for sensitivity enhancement in modern solid-state NMR, *Prog. Nucl. Magn. Reson*. *Spectrosc.* 102–103 (**2017**) 120–195. doi:10.1016/j.pnmrs.2017.06.002.

[10] W.-C. Liao, B. Ghaffari, C.P. Gordon, J. Xu, C. Copéret, Dynamic Nuclear Polarization Surface Enhanced NMR spectroscopy (DNP SENS): Principles, protocols, and practice, *Curr. Opin. Colloid Interface Sci.* 33 (**2018**) 63–71. doi:10.1016/j.cocis.2018.02.006.

[11] S. Björgvinsdóttir, B.J. Walder, A.C. Pinon, J.R. Yarava, L. Emsley, DNP enhanced NMR with flip-back recovery, *J. Magn. Reson.* 288 (**2018**) 69–75. doi:10.1016/j.jmr.2018.01.017.

[12] F. Engelke, S. Steuernagel, Cross Polarization in Rotating Solids: Spin-1/2 Nuclei, **(2011**) 1–8. doi:10.1002/9780470034590.emrstm0102.pub2.

[13] K.R. Mote, V. Agarwal, P.K. Madhu, Five decades of homonuclear dipolar decoupling in solid-state NMR: Status and outlook, *Prog. Nucl. Magn. Reson. Spectrosc*. 97 (**2016**) 1–39. doi:10.1016/j.pnmrs.2016.08.001.

[14] P.K. Madhu, Heteronuclear Spin Decoupling in Solid-State Nuclear Magnetic Resonance: Overview and Outlook, *Isr. J. Chem*. 54 (**2014**) 25–38.

[15] F.A. Perras, J. Viger-Gravel, K.M.N. Burgess, D.L. Bryce, Signal enhancement in solid-state NMR of quadrupolar nuclei, *Solid State Nucl. Magn. Reson*. 51–52 (**2013**) 1–15. doi:10.1016/j.ssnmr.2012.11.002.

[16] C. Fernandez, M. Pruski, Probing Quadrupolar Nuclei by Solid-State NMR Spectroscopy : Recent Advances, *Top. Curr. Chem.* 306 (**2012**) 119–188. doi:10.1007/128.

[17] S.E. Ashbrook, S. Sneddon, New Methods and Applications in Solid-State NMR Spectroscopy of Quadrupolar Nuclei, *J. Am. Chem. Soc*. 136 (**2014**) 15440–15456. doi:10.1021/ ja504734p.

[18] R.W. Schurko, Acquisition of Wideline Solid-State NMR Spectra of Quadrupolar Nuclei, *eMagRes*. (**2011**). doi:10.1002/9780470034590.emrstm1199.

[19] R.W. Schurko, Ultra-wideline solid-state NMR spectroscopy., *Acc. Chem. Res*. 46 (**2013**) 1985–1995. doi:10.1021/ar400045t.

[20] A.W. MacGregor, L.A. O'Dell, R.W. Schurko, New methods for the acquisition of ultra-wideline solid-state NMR spectra of spin-1/2 nuclides., *J. Magn. Reson*. 208 (**2011)** 103–13. doi:10.1016/j.jmr.2010.10.011.

[21] L.A. O'Dell, Direct detection of nitrogen-14 in solid-state NMR spectroscopy, *Prog. Nucl. Magn. Reson. Spectrosc.* 59 (**2011**) 295–318. doi:10.1016/j.pnmrs.2011.04.001.

[22] M. Faaborg, K. Goranson, N. Barnes, E. Troendle, R. Rice, M. Chace, L. Montgomery, A. Koehler, Z. Lindeberg, D. Holland, M.E. Smith, M. Affatigato, S. Singleton, S. Feller, A 10B NMR study of trigonal and tetrahedral borons in ring structured borate glasses and crystals, (**2015**).
http://www.ingentaconnect.com/content/sgt/ejgst/2015/00000056/00000005/art00001 (accessed June 7, 2018).

[23] E. Dib, T. Mineva, B. Alonso, Chapter Three - Recent Advances in 14N Solid-State NMR, in: G.A. Webb (Ed.), *Annu. Rep. NMR Spectrosc.*, Academic Press, **2016**: pp. 175–235. doi:10.1016/bs.arnmr.2015.08.002.

[24] M. Knight, I. Felli, R. Pierattelli, Magic angle spinning NMR of paramagnetic proteins, *Acc. Chem*. Ldots. 46 (2013) 2108–2116. doi:10.1021/ar300349y.

[25] G. Pintacuda, G. Kervern, Paramagnetic Solid-State Magic-Angle Spinning NMR Spectroscopy, Mod. NMR Methodol. *Top. Curr. Chem*. 335 (**2013**) 157–200. doi:10.1007/128_2011_312.

[26] M. Bertmer, Paramagnetic solid-state NMR of materials, *Solid State Nucl. Magn. Reson.* 81 (**2017**) 1–7. doi:10.1016/j.ssnmr.2016.10.006.

[27] L.A. O'Dell, R.W. Schurko, QCPMG using adiabatic pulses for faster acquisition of ultra-wideline NMR spectra, *Chem. Phys. Lett.* 464 (**2008**) 97–102. doi:10.1016/j.cplett.2008.08.095.

[28] G. Kervern, G. Pintacuda, L. Emsley, Fast adiabatic pulses for solid-state NMR of paramagnetic systems, *Chem. Phys. Lett.* 435 (*2007*) 157–162. doi:10.1016/j.cplett.2006.12.056.

[29] A.J. Pell, G. Kervern, L. Emsley, M. Deschamps, D. Massiot, P.J. Grandinetti, G. Pintacuda, Broadband inversion for MAS NMR with single-sideband-selective adiabatic pulses., *J. Chem. Phys.* 134 (**2011**) 24117. doi:10.1063/1.3521491.

[30] A.J. Pell, K.J. Sanders, S. Wegner, G. Pintacuda, C.P. Grey, Low-power broadband solid-state MAS NMR of ^{14}N, *J. Chem. Phys*. 146 (**2017**) 194202. doi:10.1063/1.4983220.

[31] A.J. Pell, G. Pintacuda, Broadband solid-state MAS NMR of paramagnetic systems, *Prog. Nucl. Magn. Reson. Spectrosc.* 84–85 (**2015**) 33–72. doi:10.1016/j.pnmrs.2014.12.002.

[32] D. Carnevale, V. Vitzthum, O. Lafon, J. Trébosc, J.-P. Amoureux, G. Bodenhausen, Broadband excitation in solid-state NMR of paramagnetic samples using Delays Alternating with Nutation for Tailored Excitation ('Para-DANTE'), *Chem. Phys. Lett*. 553 (**2012**) 68–76. doi:10.1016/j.cplett.2012.09.056.

[33] (a) V. Vitzthum, M.A. Caporini, S. Ulzega, G. Bodenhausen, Broadband excitation and indirect detection of nitrogen-14 in rotating solids using Delays Alternating with Nutation (DANTE)., *J. Magn. Reson*. 212 (**2011**) 234–239. doi:10.1016/j.jmr.2011.06.013; (b) M. Murakami, H. Arai, Y. Uchimoto, Z. Ogumi, Selective observation of a spinning-sideband manifold of paramagnetic solids by rotation-synchronized DANTE, *J. Magn. Reso*n., 231 (**2013**) 66-71.

[34] X. Lu, J. Trébosc, O. Lafon, D. Carnevale, S. Ulzega, G. Bodenhausen, J.-P. Amoureux, Broadband excitation in solid-state NMR using interleaved DANTE pulse trains with N pulses per rotor period., *J. Magn. Reson.* 236 (**2013**) 105–116. doi:10.1016/j.jmr.2013.09.003.

[35] D. Massiot, I. Farnan, N. Gautier, D. Trumeau, A. Trokiner, J.-P. Coutures, ^{71}Ga and ^{69}Ga nuclear magnetic resonance study of beta-Ga_2O_3: resolution of four- and six-fold coordinated Ga sites in static conditions., *Solid State Nucl. Magn. Reson.* 4 (**1995**) 241–8.

[36] O. Pecher, D.M. Halat, J. Lee, Z. Liu, K.J. Griffith, M. Braun, C.P. Grey, Enhanced efficiency of solid-state NMR investigations of energy materials using an external automatic tuning/matching (eATM) robot, *J. Magn. Reson*. 275 (**2017**) 127–136. doi:10.1016/j.jmr.2016. 12.008.

[37] S.W. Sparks, P.D. Ellis, Platinum-195 shielding tensors in potassium hexachloroplatinate(IV) and potassium tetrachloroplatinate(II), *J. Am. Chem. Soc*. 108 (**1986**) 3215–3218. doi:10.1021/ja00272a009.

[38] A.J. Pell, R.J. Clément, C.P. Grey, L. Emsley, G. Pintacuda, Frequency-stepped acquisition in nuclear magnetic resonance spectroscopy under magic angle spinning., *J. Chem. Phys.* 138 (**2013**) 114201. doi:10.1063/1.4795001.

[39] F.H. Larsen, H.J. Jakobsen, P.D. Ellis, N.C. Nielsen, Sensitivity-Enhanced Quadrupolar-Echo NMR of Half-Integer Quadrupolar Nuclei. Magnitudes and Relative Orientation of Chemical Shielding and Quadrupolar Coupling Tensors, *J. Phys. Chem*. A. 101 (**1997**) 8597–8606.

[40] K.J. Harris, A. Lupulescu, B.E.G. Lucier, L. Frydman, R.W. Schurko, Broadband

adiabatic inversion pulses for cross polarization in wideline solid-state NMR spectroscopy., *J. Magn*. *Reson.* 224 (**2012**) 38–47. doi:10.1016/j.jmr.2012.08.015.

[41] K.J. Harris, S.L. Veinberg, C.R. Mireault, A. Lupulescu, L. Frydman, R.W. Schurko, Rapid Acquisition of ^{14}N Solid-State NMR Spectra with Broadband Cross Polarization, *Chem. – Eur. J.* 19 (**2013)** 16469–16475. doi:10.1002/chem.201301862.

[42] T. Kobayashi, F.A. Perras, T.W. Goh, T.L. Metz, W. Huang, M. Pruski, DNP-Enhanced Ultrawideline Solid-State NMR Spectroscopy: Studies of Platinum in Metal–Organic Frameworks, *J. Phys. Chem. Lett*. 7 (**2016**) 2322–2327. doi:10.1021/acs.jpclett.6b00860.

[43] D.A. Hirsh, A.J. Rossini, L. Emsley, R.W. Schurko, ^{35}Cl dynamic nuclear polarization solid-state NMR of active pharmaceutical ingredients, *Phys. Chem. Chem. Phys*. 18 (**2016)** 25893–25904. doi:10.1039/C6CP04353D.

[44] T. Kobayashi, F.A. Perras, A. Murphy, Y. Yao, J. Catalano, S.A. Centeno, C. Dybowski, N. Zumbulyadis, M. Pruski, DNP-enhanced ultrawideline ^{207}Pb solid-state NMR spectroscopy: an application to cultural heritage science, *Dalton Trans*. 46 (**2017**) 3535–3540. doi:10.1039/ C7DT00182G.

[45] I. Hung, T. Edwards, S. Sen, Z. Gan, MATPASS/CPMG: A sensitivity enhanced magic-angle spinning sideband separation experiment for disordered solids, *J. Magn. Reson*. 221 (**2012**) 103–109. doi:10.1016/j.jmr.2012.05.013.

[46] I. Hung, L. Zhou, F. Pourpoint, C.P. Grey, Z. Gan, Isotropic high field NMR spectra of Li-ion battery materials with anisotropy >1 MHz., *J. Am. Chem. Soc.* 134 (**2012**) 1898–1901. doi:10.1021/ja209600m.

[47] R.J. Clément, A.J. Pell, D.S. Middlemiss, F.C. Strobridge, J.K. Miller, M.S. Whittingham, L. Emsley, C.P. Grey, G. Pintacuda, Spin-transfer pathways in paramagnetic lithium transition-metal phosphates from combined broadband isotropic solid-state MAS NMR spectroscopy and DFT calculations., *J. Am. Chem. Soc.* 134 (**2012**) 17178–85. doi:10.1021/ja306876u.

[48] M. Bloom, M.A. LeGros, Direct detection of two-quantum coherence, *Can. J. Phys.* 64 (**1986**) 1522–1528. doi:10.1139/p86-271.

[49] R. Tycko, S.J. Opella, High-resolution nitrogen-14 overtone spectroscopy: an approach to natural abundance nitrogen NMR of oriented and polycrystalline systems, *J. Am. Chem. Soc*. 108 (**1986**) 3531–3532. doi:10.1021/ja00272a071.

[50] L.A. O'Dell, C.I. Ratcliffe, 14N magic angle spinning overtone NMR spectra, *Chem. Phys. Lett*. 514 (**2011**) 168–173. doi:10.1016/j.cplett.2011.08.030.

[51] L.A. O'Dell, A. Brinkmann, ^{14}N overtone NMR spectra under magic angle spinning: Experiments and numerically exact simulations, *J. Chem. Phys*. 138 (**2013**) 64201.

doi:10.1063/1.4775592.

[52] I. Haies, J.A. Jarvis, H. Bentley, I. Kuprov, P.T.F. Williamson, M. Carravetta, ^{14}N Overtone NMR under MAS: signal enhancement using symmetry-based sequences and novel simulation strategies, *Phys. Chem. Chem. Phys.* 17 (**2015**) 6577–6587. doi:10.1039/C4CP03994G.

[53] A.J. Rossini, L. Emsley, L.A. O'Dell, Dynamic nuclear polarisation enhanced 14N overtone MAS NMR spectroscopy, *Phys. Chem. Chem. Phys*. 16 (**2014**) 12890–12899. doi:10.1039/C4CP00590B.

[54] C. Filip, M. Bertmer, D.E. Demco, B. Blümich, Application of the Floquet theory to multiple quantum NMR of dipolar-coupled multi-spin systems under magic angle spinning, *Mol. Phys.* 99 (**2001**) 1575–1587. doi:10.1080/00268970110060118.

[55] Y. Ishii, R. Tycko, Sensitivity Enhancement in Solid State ^{15}N NMR by Indirect Detection with High-Speed Magic Angle Spinning, J. Magn. Reson. 142 (2000) 199–204. doi:10.1006/ jmre.1999.1976.

[56] Y. Ishii, J.P. Yesinowski, R. Tycko, Sensitivity enhancement in solid-state ^{13}C NMR of synthetic polymers and biopolymers by ^{1}H NMR detection with high-speed magic angle spinning., *J. Am. Chem. Soc.* 123 (**2001**) 2921–2922.

[57] S. Cavadini, S. Antonijevic, A. Lupulescu, G. Bodenhausen, Indirect detection of nitrogen-14 in solids via protons by nuclear magnetic resonance spectroscopy., *J. Magn. Reson.* 182 (**2006)** 168–72. doi:10.1016/j.jmr.2006.06.003.

[58] A. Brinkmann, A.P.M. Kentgens, Magic-Angle-Spinning Solid-State NMR Spectroscopy for the Determination of Hydrogen Bond Lengths, *J. Am. Chem. Soc.* 128 (**2006**) 14758–14759.

[59] Z. Gan, J.-P. Amoureux, J. Trébosc, Proton-detected ^{14}N MAS NMR using homonuclear decoupled rotary resonance, *Chem. Phys. Lett*. 435 (**2007**) 163–169. doi:10.1016/j.cplett. 2006.12.066.

[60] S. Cavadini, A. Abraham, G. Bodenhausen, Proton-detected nitrogen-14 NMR by recoupling of heteronuclear dipolar interactions using symmetry-based sequences, *Chem. Phys. Lett*. 445 (**2007)** 1–5. doi:10.1016/j.cplett.2007.07.060.

[61] S. Cavadini, A. Abraham, G. Bodenhausen, Coherence transfer between spy nuclei and nitrogen-14 in solids., *J. Magn. Reson*. 190 (**2008**) 160–164. doi:10.1016/j.jmr.2007.10.008.

[62] S. Antonijevic, N. Halpern-Manners, Probing amide bond nitrogens in solids using ^{14}N NMR spectroscopy., *Solid State Nucl. Magn. Reso*n. 33 (**2008**) 82–87. doi:10.1016/j.ssnmr. 2008.04.006.

[63] O. Lafon, Q. Wang, B. Hu, F. Vasconcelos, J. Trébosc, S. Cristol, F. Deng, J.-P. Amoureux, Indirect Detection via Spin-1/2 Nuclei in Solid State NMR Spectroscopy: Application to the Observation of Proximities between Protons and Quadrupolar Nuclei, *J. Phys. Chem*. A. 113 (**2009**) 12864–12878. doi:10.1021/jp906099k.

[64] L.A. O'Dell, R. He, J. Pandohee, Identifying H–N proximities in solid-state NMR using ^{14}N overtone irradiation under fast MAS, *CrystEngComm.* 15 (**2013**) 8657–8667. doi:10.1039/ c3ce40967h.

[65] Y. Nishiyama, M. Malon, Z. Gan, Y. Endo, T. Nemoto, Proton – nitrogen-14 overtone two-dimensional correlation NMR spectroscopy of solid-sample at very fast magic angle sample spinning, *J. Magn. Reson.* 230 (**2013**) 160–164. doi:10.1016/j.jmr.2013.02.015.

[66] M. Shen, J. Trébosc, O. Lafon, Z. Gan, F. Pourpoint, B. Hu, Q. Chen, J.-P. Amoureux, Solid-state NMR indirect detection of nuclei experiencing large anisotropic interactions using spinning sideband-selective pulses, *Solid State Nucl. Magn. Reson*. 72 (**2015**) 104–117. doi:10.1016/j.ssnmr.2015.09.003.

[67] M. Shen, J. Trébosc, L.A. O'Dell, O. Lafon, F. Pourpoint, B. Hu, Q. Chen, J.-P. Amoureux, Comparison of various NMR methods for the indirect detection of nitrogen-14 nuclei via protons in solids, *J. Magn. Reson*. 258 (**2015**) 86–95. doi:10.1016/j.jmr.2015.06.008.

[68] N.T. Duong, I. Kuprov, Y. Nishiyama, Indirect detection of 10B (I = 3) overtone NMR at very fast magic angle spinning, *J. Magn. Reson.* 291 (**2018**) 27–31. doi:10.1016/j.jmr.2018. 04.004.

[69] A.J. Rossini, M.P. Hanrahan, M. Thuo, Rapid acquisition of wideline MAS solid-state NMR spectra with fast MAS, proton detection, and dipolar HMQC pulse sequences, *Phys. Chem. Chem. Phys*. 18 (**2016**) 25284–25295. doi:10.1039/C6CP04279A.

[70] F.A. Perras, A. Venkatesh, M.P. Hanrahan, T.W. Goh, W. Huang, A.J. Rossini, M. Pruski, Indirect detection of infinite-speed MAS solid-state NMR spectra, *J. Magn. Reson*. 276 (**2017**) 95–102. doi:10.1016/j.jmr.2017.01.010.

[71] M.K. Pandey, H. Kato, Y. Ishii, Y. Nishiyama, Two-dimensional proton-detected 35Cl/^{1}H correlation solid-state NMR experiment under fast magic angle sample spinning: application to pharmaceutical compounds, *Phys. Chem. Chem. Phys*. 18 (**2016**) 6209–6216. doi:10.1039/ C5CP06042G.

[72] A. Venkatesh, M.P. Hanrahan, A.J. Rossini, Proton detection of MAS solid-state NMR spectra of half-integer quadrupolar nuclei, *Solid State Nucl. Magn. Reson*. 84 (**2017**) 171–181. doi:10.1016/j.ssnmr.2017.03.005.

[73] Z. Gan, Measuring amide nitrogen quadrupolar coupling by high-resolution ^{14}N/^{13}C

NMR correlation under magic-angle spinning., *J. Am. Chem. Soc*. 128 (**2006**) 6040–6041. doi:10.1021/ja0578597.

[74] Z. Gan, $^{13}C/^{14}N$ heteronuclear multiple-quantum correlation with rotary resonance and REDOR dipolar recoupling., *J. Magn. Reson.* 184 (**2007**) 39–43. doi:10.1016/j.jmr.2006.09.016.

[75] S. Cavadini, A. Lupulescu, S. Antonijevic, G. Bodenhausen, Nitrogen-14 NMR Spectroscopy Using Residual Dipolar Splittings in Solids, *J. Am. Chem. Soc*. 128 (**2006**) 7706–7707. doi:10.1021/ja0618898.

[76] V. Vitzthum, M.A. Caporini, S. Ulzega, J. Trébosc, O. Lafon, J.-P. Amoureux, G. Bodenhausen, Uniform broadband excitation of crystallites in rotating solids using interleaved sequences of delays alternating with nutation., *J. Magn. Reson.* 223 **(2012**) 228–236. doi:10.1016/j.jmr.2012.05.024.

[77] D. Merlet, M. Sarfati, B. Ancian, J. Courtieu, P. Lesot, Description of natural abundance deuterium 2D-NMR experiments in weakly ordered liquid-crystalline solvents using a tailored cartesian spin-operator formalism, *Phys. Chem. Chem. Phys*. 2 (**2000**) 2283–2290.

[78] S. Vega, A. Pines, Operator formalism for double quantum NMR, *J. Chem. Phys*. 66 (**1977**) 5624–5644.

[79] A. Wokaun, R.R. Ernst, Selective excitation and detection in multilevel spin systems: application of single transition operators, *J. Chem. Phys*. 4 (**1977**) 1752–1758.

[80] P. Brunner, M. Reinhold, R.R. Ernst, Double quantum cross polarization. Heteronuclear excitation and detection of NMR double quantum transitions in solids, *J. Chem. Phys*. 73 (**1980**) 1086–1094. doi:10.1063/1.440258.

[81] M. Reinhold, P. Brunner, R.R. Ernst, Double quantum cross polarization via dipolar order, *J. Chem. Phys.* 74 (**1981**) 184–188. doi:10.1063/1.440861.

[82] T.K. Pratum, M.P. Klein, Heteronuclear Cross Polarization of Solid-State 14N NMR Powder Patterns, *J. Magn. Reson*. 55 (**1983**) 421–437.

[83] M. Shen, Q. Chen, J.-P. Amoureux, B. Hu, Broad-band excitation in indirectly detected ^{14}N overtone spectroscopy with composite pulses, *Solid State Nucl. Magn. Reson.* 78 (**2016**) 5–8. doi:10.1016/j.ssnmr.2016.05.001.

[84] A. Brinkmann, L.A. O'Dell, Optimisation of excitation schemes for 14N overtone MAS NMR using numerically exact simulations, *Solid State Nucl. Magn. Reson.* 84 (**2017**) 34–40. doi:10.1016/j.ssnmr.2016.12.006.

[85] X. Lu, O. Lafon, J. Trébosc, G. Tricot, L. Delevoye, F. Méar, L. Montagne, J.-P.

Amoureux, Observation of proximities between spin-1/2 and quadrupolar nuclei: which heteronuclear dipolar recoupling method is preferable?, *J. Chem. Phys.* 137 (*2012*) 144201. doi:10.1063/ 1.4753987.

[86] M. Bak, J.T. Rasmussen, N.C. Nielsen, SIMPSON: a general simulation program for solid-state NMR spectroscopy., *J. Magn. Reson*. 147 (**2000**) 296–330. doi:10.1006/jmre.2000.2179.

[87] M. Bak, N.C. Nielsen, REPULSION, A Novel Approach to Efficient Powder Averaging in Solid-State NMR, *J. Magn. Reson*. 125 (**1997**) 132–139.

[88] S.L. Veinberg, Z.W. Friedl, A.W. Lindquist, B. Kispal, K.J. Harris, L.A. O'Dell, R.W. Schurko, ^{14}N Solid-State NMR Spectroscopy of Amino Acids, *ChemPhysChem*. 17 (**2015**) 4011–4027. doi:10.1002/cphc.201600873.

[89] M. Shen, J. Trébosc, O. Lafon, F. Pourpoint, B. Hu, Q. Chen, J.-P. Amoureux, Improving the resolution in proton-detected through-space heteronuclear multiple quantum correlation NMR spectroscopy., *J. Magn. Reson*. 245 (**2014**) 38–49. doi:10.1016/j.jmr.2014.05.006.