Uniform broadband excitation of crystallites in rotating solids using interleaved sequences of delays alternating with nutation

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Abstract

In solids that are spinning about the magic angle, trains of short pulses in the manner of Delays Alternating with Nutations for Tailored Excitation (DANTE) allow one to improve the efficiency of the excitation of magnetization compared to rectangular pulses. By interleaving $N$ pulse trains with $N > 1$, one obtains DANTE–$N$ sequences comprising $N$ pulses per rotor period that extend over $K$ rotor periods. Optimized interleaved DANTE schemes with $N > 1$ are shorter than basic DANTE-1 sequences with $N = 1$. Therefore, they are less affected by coherent or incoherent decays, thus leading to higher signal intensities than can be obtained with basic DANTE-1 or with rectangular pulses. Furthermore, the shorter length of DANTE-$N$ with $N > 1$ increases the width of the spikelets in the excitation profile, allowing one to cover the range of isotropic chemical shifts and second-order quadrupolar effects typical for side-chain and backbone amide $^{14}$N sites in peptides at $B_0 = 18.8$ T. In DANTE-$N$, spinning sidebands only appear at multiples of the spinning frequency $\nu_{\text{rot}}$, as if the samples were rotating at $N\nu_{\text{rot}}$. We show applications to direct detection of nitrogen-14 nuclei with spin $I = 1$ subject to large quadrupole interactions, using fast magic angle spinning (typically $\nu_{\text{rot}} \geq 60$ kHz), backed up by simulations that provide insight into the properties of basic and interleaved DANTE sequences. When used for indirect detection, we show by numerical simulations that even basic DANTE-1 sequences can lead to a four-fold boost of efficiency compared to standard rectangular pulses.

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1. Introduction

In static solids, nuclear magnetic resonance (NMR) spectra are often very broad, particularly for quadrupolar nuclei with $I > 1/2$, and for spins with $I = 1/2$ in paramagnetic samples. In the early days of continuous-wave excitation, it was straightforward to sweep the radio-frequency (rf) carrier over large bandwidths, and the main challenge of broad spectra arose from the weakness of signals that were spread over wide ranges of frequencies. Although the advent of pulsed excitation and Fourier transformation (FT) [1] heralded decisive advantages for spectra with bandwidths $\Delta \omega$ that are comparable with typical rf intensities $\omega_x$, pulsed excitation is challenging for spectra with larger bandwidths. Various approaches to broadband excitation have been reviewed recently by Shurko et al. [2] with particular emphasis on $^{14}$N spectra of static solids. Broadband excitation may benefit from pulses with very short durations $\tau_p$ that can cover large bandwidths $\Delta \omega \approx 2\pi/\tau_p$, although this usually entails small flip angles $\beta = |\gamma B_1 \tau_p| \ll \pi/2$, and hence poor S/N ratios, since the rf intensities are necessarily limited. Broadband excitation may be improved by recording complementary spectra in (possibly overlapping) segments.

On the other hand, narrow-band excitation can be achieved either by using weak rf amplitudes, or equivalently by applying long trains of intense short pulses at regular intervals $\tau_d$. This type of excitation, dubbed Delays Alternating with Nutations for Tailored Excitation (DANTE) [3], has become popular for selective excitation, saturation and inversion in solution-state NMR [4] and in magnetic resonance imaging [5]. During a DANTE sequence, the magnetization vectors in the rotating frame undergo nutation and precession in alternation. If the offset $\Omega = \omega_B - \omega_{\text{rot}}$ between the precession frequency of the spins $\omega_B$ and the carrier frequency $\omega_{\text{rot}}$ coincides with a multiple of the pulse repetition rate, i.e., if $\Omega = 0$ or $\Omega = 2\pi j/\tau_d$, with integer $j$, the spins precess through an
integer number $j$ of full $2\pi$ rotations between two consecutive rf pulses. Therefore, the DANTE sequence causes the magnetization vectors to move along a meridian of the rotating frame. At other offsets, precession robs the pulses of their cumulative effect [4], so that the magnetization vectors undergo a zig-zag trajectory and remain close to the north pole. As illustrated in Fig. 1, a DANTE sequence can be described by a product of an infinite ‘comb’ of equidistant rectangular pulses, each of width $\tau_p$, repeated with a period $\tau_d$, multiplied by a boxcar function of length $K\tau_d$, where $K$ is the total number of pulses [4]. The FT of an infinite train of Dirac delta functions with period $\tau_d$ in time domain leads to an infinite Dirac comb with intervals $1/\tau_d$ in frequency domain (Fig. 1a). The peaks in the excitation profile that occur at frequencies $\omega_{\text{rot}} + 2\pi j/\tau_d$ will be called rf-spikelets in the following. As a convolution in time domain is equivalent to a multiplication in frequency domain, the FT of an infinite comb of rectangular pulses of finite duration $\tau_p$, repeated with the period $\tau_d$, again leads to an infinite comb of Dirac rf-spikelets separated by $1/\tau_d$ in frequency domain, but with an envelope determined by the FT of the individual pulse, which is a sinc function with a width proportional to $1/\tau_p$ (see Fig. 1b). However, the DANTE sequence does not extend forever, since it is multiplied by a boxcar function of length $K\tau_d$. The FT of this boxcar function gives another sinc function with a width proportional to $1/(K\tau_d)$, so that each of the rf-spikelets is broadened accordingly (see Fig. 1c). In the examples discussed below, we have typically $\tau_p = 0.5 \mu s$, and hence $1/\tau_p = 2 \text{ MHz}$. If we interleave $N$ equidistant pulses per rotor period $\tau_{\text{rot}}$ to obtain a ‘DANTE-N’ sequence, the pulse interval is $\tau_d = \tau_{\text{rot}}/N$. For fast spinning, e.g., for $\nu_{\text{rot}} = 62.5 \text{ kHz}$, one therefore obtains $\tau_d = \tau_{\text{rot}}/N = 1/(N\nu_{\text{rot}}) = 16/N \mu s$. If the sequence extends over $K$ rotor periods, the total number of pulses is $NK$, and the total duration $K\tau_{\text{rot}} = 160 \mu s$ if $K = 10$, so that the width of each rf-spikelet is $1/(K\tau_{\text{rot}}) = \nu_{\text{rot}}/K = 6.25 \text{ kHz}$. In summary, as shown in Fig. 1d, the DANTE-N excitation profile comprises a comb of rf-spikelets that has: (i) an

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**Fig. 1.** Fourier transforms of an infinite comb of (a) Dirac pulses, (b) short rectangular pulses, and (c,d) finite DANTE trains of rectangular pulses of duration $\tau_p = 0.5 \mu s$ repeated $K = 7$ times in (c) and $K = 10$ times with a period $\tau_d = 1.5 \mu s$ in (c) and $16 \mu s$ in (d). The conditions used in (d) are appropriate for DANTE-1 at $\nu_{\text{rot}} = 62.5 \text{ kHz}$. Multiplications are denoted by $\times$ and convolutions by $\ast$. In (c,d), $t = 0$ corresponds to the beginning of the DANTE sequence and the lengths of the first and last pulses are halved in order to obtain rf-spikelets in pure absorption. In (d), the frequency domain spikelets are shown over a range $[-5, +5] \text{ MHz}$ and expanded in a window of $[-175, +175] \text{ kHz}$. V. Vitzthum et al. / Journal of Magnetic Resonance 223 (2012) 228–236 229
envelope with a width proportional to \(1/T_p\) (typically 2 MHz if \(T_p = 0.5\) \(\mu s\)), if we disregard bandwidth limitations due to the quality factor of the probe, (ii) a frequency interval between the sidebands equal to \(N\nu_{rot}\) and (iii) each rf-sideband has a width proportional to \(1/(K\nu_{rot}) = \nu_{rot}/K\) (e.g., 6.25 kHz if \(\nu_{rot} = 62.5\) kHz and \(K = 10\)). DANTE sequences may be regarded as special cases of ‘tailored’ excitation profiles, as discussed by Tomlinson and Hill [6].

DANTE sequences turn out to be useful in solid-state NMR of spin-\(1/2\) nuclei, both for static samples [7], and for samples undergoing MAS [8]. In rotating solids, chemically distinct sites with different isotropic chemical shifts give rise to interlaced families of spinning sidebands that do not overlap, provided the differences in isotropic chemical shifts do not coincide with a multiple of the spinning frequency. Using a DANTE sequence with a carrier frequency \(\nu_{rot}\) that coincides with the centerband (or with one of the sidebands) associated with one of the chemically distinct sites, it is possible to manipulate only one selected family of sidebands [8]. The broadband virtues of DANTE sequences have recently been rediscovered using optimal control methods [9]. Note that most applications to solids stand in contrast to selective manipulations in solution-state NMR, where one usually exploits only the central rf-sideband of the DANTE spectrum, by ensuring that the other sidebands have phases that add constructively if the magnetization builds up in a constructive manner. The DANTE-N sequence is thus comprised of \(N\) interleaved basic DANTE-1 sequences, which lead to \(N\) overlapping combs of rf-sidebands, all separated from the carrier frequency by multiples of the spinning frequency, \(\nu_{rot} + j\nu_{rot}\). These rf-sidebands have phases that depend on the positions of the pulses within the rotor period. If the \(n\)th pulse train with an \(rf\) phase \(\phi_n\) (\(n = 1, \ldots, N\)) is delayed by \(\Delta\nu_{rot} = \nu_{rot}(0 \leq \Delta\nu_{rot} < 1)\) with respect to the first train (\(n = 1\)), the \(j\)th rf-sideband stemming from the \(n\)th pulse train experiences a phase shift

\[
\phi_{nj} = 2\pi\Delta\nu_{rot} + \phi_n
\]

where \(j\) is an integer and \(\phi_n\) is the phase of all pulses of the \(n\)th pulse train. One may choose to apply \(N\) regularly-spaced pulses in each rotor period:

\[
x_n = (n - 1)/N
\]

which leads to

\[
\phi_{nj} = 2\pi(n - 1)/N + \phi_n
\]

The combined effect of the sum of the \(N\) interleaved pulse trains on the complex amplitude of the \(j\)th spinning sideband is therefore:

\[
\exp(i\phi_j) = \sum_{n=1}^{N} \exp(i2\pi(n-1)/N + \phi_n)
\]

In the absence of any phase shifts between the different pulse trains (i.e., if \(\phi_n\) is independent of \(n\)), the \(j\)th spinning sideband is \(N\) times more intense than with the basic DANTE-1 sequence with the same pulse length, as if the spinning speed was enhanced by a factor \(N\). Each of the \(N\) DANTE-1 and DANTE-N usually leads to different \(K\) and \(\tau_p\) values. In practice however, the optimization of DANTE-1 and DANTE-N usually leads to different \(K\) and \(\tau_p\) values.

The signals excited by the \(rf\)-sidebands thus add constructively if \(j\) is a multiple of \(N\). The comb of sidebands of the DANTE-N sequence therefore only comprises frequencies \(\nu_{rot} + j\nu_{rot}\) with integer \(k\). The frequency interval between neighboring spinning sidebands observed with DANTE-N is thus \(N\) times larger than with DANTE-1, as if the spinning speed was enhanced by a factor \(N\). The integral of the comb of sidebands is determined by the first point of the time domain signal, which corresponds to the first pulse. Therefore, reducing the number of \(rf\)-sidebands entails an \(N\)-fold increase of the intensity of each of the remaining \(rf\)-sidebands.

The constructive interference of the two interleaved sequences is shown schematically in Fig. 3a–c for DANTE-2. For \(n = 1\) (Fig. 3a) all sidebands have the same phase, while for \(n = 2\) (Fig. 3b) their phases alternate. Their sum (Fig. 3c) leads to \(rf\)-sidebands that are spaced by \(2\nu_{rot}\). One can achieve different interference effects by changing the \(rf\) phases of the pulses. If the two interleaved pulse trains have the same phases (\(\phi_1 = \phi_2 = 0\)), all spinning sidebands with an odd index \(j\) are cancelled out (Fig. 3d), while alternating
phases ($\phi_1 = 0$ and $\phi_2 = \pi$, i.e., $\phi_n = (n-1)\pi$) in Eqs. (1), (3), (4) result in

$$\exp\{i\phi_j\} = 1 + \exp\{i(\pi j + \pi)\} = 1 - (-1)^j$$

which causes the centerband and all even sidebands to vanish (Fig. 3e).

At first sight, it might appear that the length of DANTE-N sequences, $K\tau_{\text{rot}}$, should not depend on $N$. In actual fact, as shown by simulations and experiments, the optimal number of rotor periods, $K^{\text{opt}}$, decreases as $N$ increases, so that the total duration $K^{\text{opt}}\tau_{\text{rot}}$ of the sequence becomes shorter. This has two advantages: (i) losses due to homogeneous decay and second-order quadrupolar dephasing are reduced, and (ii) the width of the rf-spikelets and hence the tolerance to offsets is increased.

3. Experimental offset profiles for direct observation

While a rectangular $\pi/2$ pulse with an rf-amplitude $v_1 = 100$ kHz and a duration $\tau_p = 2.5$ $\mu$s can barely excite an $^{14}$N spectrum over a frequency range $1/\tau_p = 400$ kHz, a DANTE-N pulse train with $\tau_p = 0.5$ $\mu$s can efficiently excite sidebands over a range $1/\tau_p = 2$ MHz, limited in practice only by the Q factor of the probe. The resulting sideband patterns therefore faithfully reflect the entire breadth of the line-shape of the static sample.

It is of interest to investigate the effect of $v_1$, $v_{\text{rot}}$, $\tau_p$, $N$ and $K$ on the envelope of the rf-spikelets generated by a DANTE-N sequence. To complement the offset profiles recorded previously at $B_0 = 18.8$ T with $v_{\text{rot}} = 31.25$ kHz by rotor-synchronized indirect detection (see Fig. 4 in [13]), Fig. 4 shows experimental offset profiles for $^{14}$N in $\gamma$-glycine ($\gamma_0 = 1.18$ MHz and $\eta_0 = 0.5$) obtained by direct excitation at $B_0 = 18.8$ T with a spinning frequency $v_{\text{rot}} = 62.5$ kHz.

In a first step, the pulse length $\tau_p$ has been optimized for different $K$ and two rf amplitudes $v_1 = 44$ kHz and 88 kHz, with the carrier frequency set on the centerband of the $^{14}$N spectrum ($v_{\text{rf}} = v_0$). Then, offset profiles near the central spikelet were recorded by changing the carrier frequency over a range $v_0 - 5 < v_{\text{rf}} < v_0 + 5$ kHz in steps of 0.4 kHz for DANTE-1 (Fig. 4a and b), and $v_0 - 32 < v_{\text{rf}} < v_0 + 32$ kHz in steps of 4 kHz for DANTE-N (Fig. 4c and d) using either $v_1 = 44$ (Fig. 4a and c) or 88 kHz (Fig. 4b and d). As explained before, the efficiency is approximately twice as large on-resonance with DANTE-2 than with DANTE-1. When $K$ increases, the width of the rf-spikelets decreases as $\Delta v \approx 1/(K\tau_{\text{rot}})$, which corresponds to $\Delta v \approx 8.9$ and 5.7 kHz for $K = 7$ and 11 for DANTE-1 and to $\Delta v \approx 62, 31, 21, 16, and 12$ kHz for $K = 1, 2, 3, 4$, and 5 for DANTE-2. These predictions are qualitatively confirmed by the observations in Fig. 4. More generally, due to the smaller number $K^{\text{opt}}$ of rotor periods, the offset profiles of the central spikelet are much broader for DANTE-N than for DANTE-1, which explains why the signals of the two nitrogen nuclei $N^0$ and $N^\prime$ of histidine are much stronger with DANTE-2 ($K = 2$) than with basic DANTE-1 ($K = 8$) in Fig. 6 of our earlier work [13].

4. Simulations of indirect detection

The DANTE-N sequences were originally shown to provide a more efficient excitation and reconversion of nitrogen-14 single-
and double-quantum coherences in indirect detection using $^{1}H$-$^{14}N$-$^{1}H$ D-HMQC [10–12]. Instead of standard rectangular pulses (Fig. 5a), we inserted DANTE-\(N\) sequences with \(N = 1, 2\) or \(8\) (Fig. 5b, c, d) to achieve more efficient excitation and reconversion [13]. The sequences begin with the excitation of transverse magnetization of ‘spy’ nuclei \(S\), typically \(^{13}\)C or \(^{1}H\). The coherence \(T_{S1}^{1}\) of the ‘spy’ nucleus is then transformed into a superposition of coherences \(T_{S1}^{1},T_{S1}^{6},T_{S1}^{11}\) during the first recoupling interval \(\tau_{rec}\), where the \(^{1}H\)–\(^{14}N\) dipolar interactions are recoupled by means of a symmetry-based SR4\(^{2}\) sequence [14–16]. The combination of SR4\(^{2}\) sequences with high spinning frequencies allows a near-complete suppression of \(^{1}H\)–\(^{1}H\) dipolar interactions. The \(^{14}N\) coherence can be excited either by a rectangular pulse, or by a DANTE-\(N\) sequence. The \(^{14}N\) coherence is then allowed to evolve freely during the evolution period \(t_{1}\). In the middle of this period, a \(\pi\) pulse is applied to the \(^{1}H\) channel. At the end of the evolution period \(t_{1}\), one can again apply either a rectangular pulse or a DANTE-\(N\) sequence to the \(^{14}N\) channel, in a symmetrical manner. Finally, the resulting \(T_{S1}^{1},T_{S1}^{6},T_{S1}^{11}\) terms are converted back to coherence \(T_{S1}^{1}\) of the ‘spy’ nucleus by inserting another SR4\(^{2}\) sequence during the second recoupling interval \(\tau_{rec}\). The signal of the spy nucleus is then recorded in the detection interval \(t_{2}\). In conventional 2D experiments using either two rectangular pulses or two DANTE-1 sequences, the \(t_{1}\) period must be incremented in integer numbers of rotor periods (\(D\)\(t_{1} = 1/s_{rot}\)). The use of an interleaved DANTE-\(N\) sequence with \(N > 1\) makes it possible: (i) to multiply by \(N\) the spectral width in the indirect dimension, and (ii) to improve the \(S/N\) ratio [13] by oversampling in the indirect dimension [21], with increments decreasing from \(s_{rot}\) to \(s_{rot}/N\). Note that one should avoid truncation and continue sampling until the signals

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**Fig. 3.** (a–c) A DANTE-2 sequence can be considered as a superposition of two basic DANTE-1 sequences with \(n = 1\) and \(2\) that are shifted in time by \(\tau_{rot}/2\). This time shift induces a phase shift of \(\pi(n - 1)\) for the \(j\)th spikelet in the \(rf\) spectrum arising from the \(n\)th comb. (a) All \(rf\)-spikelets associated with \(n = 1\) have a common phase \(\phi_{n=1} = 0\). (b) For the sequence with \(n = 2\), the phases alternate \(\phi_{n=2} = 0, \pi, 0, \pi, \ldots\) (c) The sum leads to the cancellation of all odd \(rf\)-spikelets. More generally, in the case of DANTE-\(N\) the superposition of \(N\) trains of \(rf\)-spikelets leads to their cancellation except for those that are separated by multiples of the spinning frequency \(N_{rots}\). For identical pulse lengths, the remaining \(rf\)-spikelets are \(N\) times more intense than those appearing for \(N = 1\). Experimentally, the phase shifts can be observed by recording two separate \(^{14}N\) on-resonance spectra of \(\gamma\)-glycine where the \(rf\) phases of the second comb are either \(\phi_{n=2} = 0\) (d) or \(\phi_{n=2} = \pi\) (e). In (d), only sidebands with even \(j\) appear, whereas only those with odd \(j\) appear in (e). Static field \(B_{0} = 18.8\) T, \(\nu_{rots} = 62.5\) kHz, \(\tau_{rot} = 16\) \(\mu\)s, \(K = 2\), \(\nu_{1} = 88\) kHz and \(\tau_{p} = 1.2\) \(\mu\)s.
have decayed. To keep the same $t_{\text{max}}$, one obviously must record $N$ times more increments. Non-linear sampling schemes might improve the sensitivity without sacrificing any resolution, in contrast to our earlier work [13].

Here, we compare by simulations the efficiency of the two-way transfer ($^1$H → $^{14}$N → $^1$H) obtained with square pulses (Fig. 5a) and with DANTE-1 sequences (Fig. 5b). The MATLAB simulations include scalar and dipolar couplings, and quadrupole interactions up to third order. In the simulations, we have used the quadrupolar parameters of $\gamma$-glycine ($C_Q = 1.18$ MHz, $\eta_Q = 0.5$) [17]. The orientation of the principal axis system of the electric field gradient (EFG) tensor with respect to the rotor frame is described by $(\alpha, \beta, \gamma)$ Euler angles.

Numerical simulations allow one to clarify the advantages achieved for indirect detection when standard rectangular pulses

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**Fig. 4.** Experimental signal integrals obtained by direct excitation of $^{14}$N in $\gamma$-glycine as a function of the number of rotor periods $K$ and the offset between the rf carrier and the centerband in the $^{14}$N spectrum, recorded (a, b) with basic DANTE-1 using $K = 7$ or 11, and (c, d) with DANTE-2 using $K = 1, 2, 3, 4$ and 5, with rf amplitudes of $\nu_1 = 44$ (a, c) or 88 kHz (b, d). The offset was varied in (a, b) from $-5$ to $+5$ kHz in steps of 400 Hz and in (c, d) from $-32$ to $+32$ kHz in steps of 4 kHz. Static field $B_0 = 18.8$ T, $\nu_{\text{rot}} = 62.5$ kHz, $\tau_{\text{rot}} = 16$ $\mu$s. With an rf amplitude $\nu_1 = 44$ kHz, the best pulse lengths for DANTE-1 were $\tau_p = 1.1$ and 0.7 $\mu$s for $K = 7$ and 11. Those for DANTE-2 were $\tau_p = 1.6, 1.8, 1.5, 1.0$, and 0.9 $\mu$s for $K = 1, 2, 3, 4$ and 5, respectively. With $\nu_1 = 88$ kHz, the best pulse lengths for DANTE-1 were $\tau_p = 0.8$ and 0.5 $\mu$s for $K = 7$ and 11. Those for DANTE-2 were $\tau_p = 1.7, 1.1, 0.6, 0.4$, and 0.4 $\mu$s for $K = 1, 2, 3, 4$ and 5, respectively.

**Fig. 5.** Sequence for indirect detection by $^1$H-$^{14}$N-$^1$H dipolar heteronuclear multiple quantum correlation (D-HMQC), where the $^{14}$N coherences are excited and reconverted by (a) two rectangular pulses, (b–d) two DANTE-N sequences lasting $K$ rotor periods with $N = 1, 2$ or 8. Both the pulse length $\tau_p$ and the number $K$ of rotor periods must be optimized for each $N$ value.
with an rf-amplitude $v_1 = 60 \text{ kHz}$ and a pulse length $\tau_p = 0.55 \mu s$. We clearly observe that every pulse contributes constructively to the coherence $T_{1,1}'$ while the initial longitudinal magnetization $T_{1,0}'$ is gradually depleted. We have used $K = 12$, the optimum transfer being observed for $K^{\text{opt}} = 11$ (see Fig. 6b), where one notices a quasi-ideal conversion of $T_{1,0}'$ into $T_{1,1}'$, as for a perfect $\pi/2$ rotation of the $^{13}$N magnetization. The simulations show that the creation of $T_{1,1}'$ during the first DANTE-1 sequence does not follow a sinusoidal pattern as would be expected for a Rabi nutation, but reaches a flat maximum. The subsequent free evolution period $t_1$, which is equal to $2t_{\text{rot}}$ in Fig. 6a, is represented by empty squares and dots. A second DANTE-1 sequence is then applied to the $^{14}$N spins, leading to the reconversion of coherences $T_{1,1}'$ into populations $T_{1,0}'$. The evolution of the density operator during the two SR$^2$ recoupling intervals was not taken into account in the simulations. This approximation is justified in ultra-fast MAS where the rotor periods are short so that losses are minimized, but second-order quadrupole interactions, homogeneous decay and relaxation play an increasing role if the number of rotor periods increases or if the spinning frequency is slowed down.

The excitation-reconversion efficiency of the DANTE-1 sequences in $D$-HMOC experiments (Fig. 5b with $t_1 = 0$) is illustrated in Fig. 6b for rf amplitudes $v_1 = 30, 45, 60, 75 \text{ kHz}$ as a function of the number $K$ of rotor periods. In these simulations, the pulse length was fixed to $\tau_p = 0.4 \mu s$, which is the optimal value for $v_1 = 75 \text{ kHz}$ and $K^{\text{opt}} = 11$ (Fig. 6c). The optimal number of rotor periods does not have a pronounced dependence on the rf-amplitude, i.e., $K^{\text{opt}} = 11$ for $45 < v_1 < 75 \text{ kHz}$ and $K^{\text{opt}} = 12$ for $v_1 = 30 \text{ kHz}$. For $K > 14$, the efficiencies are similar regardless of the rf-amplitude. Similarly, for $K^{\text{opt}} = 11$, the cumulative flip angle, corresponding to the sum of all $K^{\text{opt}}$ pulses each of duration $\tau_p$, is $\theta_{\text{tot}} = 71^\circ$ for $v_1 = 45 \text{ kHz}$, $\theta_{\text{tot}} = 95^\circ$ for $v_1 = 60 \text{ kHz}$ and $\theta_{\text{tot}} = 119^\circ$ for $v_1 = 75 \text{ kHz}$. Nevertheless, the efficiency only increases slightly from $v_1 = 45$ to 75 kHz. This is in agreement with the broad maximum of Fig. 6a. The highest efficiency is obtained for cumulative flip angles 70° < $\theta_{\text{tot}}$ < 120°. Thus if $\tau_p = 0.4 \mu s$, $v_1 = 75 \text{ kHz}$ and $K^{\text{opt}} = 11$, one obtains $\theta_{\text{tot}} \approx 120^\circ$. The efficiency achieved using standard rectangular pulses with various rf-amplitudes was also calculated using a total pulse length $K^{\text{opt}}\tau_p = 4.4 \mu s$, which corresponds to the sum of all pulses in a DANTE-1 sequence with $K^{\text{opt}} = 11$ and $\tau_p = 0.4 \mu s$ (see points enclosed by a dashed circle in Fig. 6b). For the same total area of the rf pulses, the DANTE-1 sequence leads to a four-fold boost of efficiency compared to standard rectangular pulses.

Thus the use of basic DANTE-1 sequences leads to more efficient excitation and reconversion than standard rectangular pulses. Experimental comparisons between rectangular pulses and
DANTE-N sequences show that for fast MAS ($v_{\text{rot}} \geq 60$ kHz) significant sensitivity improvements are indeed observed [13]. At moderate spinning speeds ($30 < v_{\text{rot}} < 35$ kHz), the advantages are less significant.

Fig. 6c demonstrates that the optimum pulse length $t_{\text{opt}}$ is always inversely proportional to $K$ and that the cumulative flip angle is always in the range $70^\circ < \theta_{\text{rot}} < 120^\circ$. The increased efficiency of D-HMQC using DANTE-N sequences rather than rectangular pulses can be ascribed to the larger number of crystallite orientations that are efficiently excited. To confirm this hypothesis, further simulations were carried out to investigate the excitation and reconversion efficiency as a function of the crystallite orientations. The experimental parameters were $v_1 = 60$ kHz, $t_{\text{opt}} = 0.55$ $\mu$s, $K_{\text{opt}} = 11$, and the carrier frequency was set on resonance. Fig. 7 represents the relative efficiency $e/e_{\text{max}}$ of the two-step transfer ($^1$H $\rightarrow ^{14}$N $\rightarrow ^1$H) in D-HMQC as a function of the crystallite orientations, ranked in decreasing order. Two histograms are shown, one for DANTE-1 sequences and one for rectangular pulses. The DANTE-1 scheme leads both to a higher overall efficiency and to a more uniform excitation of the crystallites.

In order to depict the uniformity of the excitation that can be achieved with the DANTE-1 scheme, the relative efficiency $e/e_{\text{max}}$ associated with various crystallite orientations has been represented in Fig. 8 by a vector with polar angles $(\alpha, \beta)$ and a modulus proportional to $e/e_{\text{max}}$, where $e_{\text{max}}$ is the maximum achievable efficiency. The $z$-axis in the figure corresponds to crystallites where the $V_{zz}$ component of the EFG tensor is aligned with the rotor axis. For DANTE-1 sequences, the spatially uniform distribution of the vectors allows one to fit their extremities with a 3D surface that resembles a ‘doughnut’. Note that the efficiency is close to one near the equator and dips in the vicinity of the poles. The efficiency decreases if the quadrupole interaction increases.

For rectangular pulses, the erratic efficiencies are represented by red dots that do not lie on a smooth surface (Fig. 8b), thus confirming the haphazard distribution of crystallite orientations excited by rectangular pulses. This chaotic behavior is due to the lengths of the two rectangular pulses ($\tau_p = 20$ $\mu$s each) while $\tau_{\text{rot}} = 16$ $\mu$s. The fluctuating quadrupole interactions are too large during a fraction of the rotor cycle for the rf pulses to be effective.

This is not the case for DANTE-1 sequences, which only use very short pulses.

Simulations of DANTE-1 sequences combined with $^1$H-$^{14}$N-$^1$H D-HMQC experiments have been performed for various quadrupole interactions. They show that the optimum pulse length $t_{\text{opt}}$ that allows one to excite all crystallites uniformly is inversely proportional to $C_0$ and that the optimum number of rotor periods $K_{\text{opt}}$ must be proportional to $C_0$ in order to obtain a cumulative flip angle $70^\circ < \theta_{\text{rot}} < 120^\circ$. However, it must be remembered that these simulations do not take into account homogeneous losses and bandwith limitations due to the quality factor $Q$ of the probe.

5. Conclusions

We have analyzed and compared signal intensities of $^{14}$N spectra ($I = 1$) with quadrupole interactions of several MHz in samples that are spinning about the magic angle. The $^{14}$N coherences have been excited with rectangular pulses, basic DANTE-1 and interleaved DANTE-N sequences ($N > 1$). Comparisons have been made not only for experimental $^{14}$N spectra observed by direct detection, but also for simulations of indirect $^1$H-$^{14}$N-$^1$H D-HMQC experiments. We have shown that with very fast spinning, a significant increase in sensitivity can be obtained with DANTE-N sequences compared to rectangular pulses, owing to the much larger number of crystallite orientations that can be excited efficiently. The main limitation of the basic DANTE-1 sequence lies in its sensitivity to offsets, which may hinder applications to samples that contain several $^{14}$N nuclei with very different isotropic chemical shifts or second-order quadrupole interactions. This limitation can be overcome with DANTE-N sequences ($N > 1$), which may be combined with non-linear oversampling of the signal in the indirect dimension of 2D experiments, thus providing a significant gain in sensitivity.

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