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Cite as: J. Chem. Phys. **151**, 154202 (2019); https://doi.org/10.1063/1.5126599 Submitted: 03 September 2019 . Accepted: 01 October 2019 . Published Online: 21 October 2019

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# Efficient and sideband-free <sup>1</sup>H-detected <sup>14</sup>N magic-angle spinning NMR

Cite as: J. Chem. Phys. 151, 154202 (2019); doi: 10.1063/1.5126599 Submitted: 3 September 2019 • Accepted: 1 October 2019 • Published Online: 21 October 2019



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#### ABSTRACT

Indirect detection via sensitive spin-1/2 nuclei like protons under magic-angle spinning (MAS) has been developed to overcome the low spectral sensitivity and resolution of <sup>14</sup>N NMR. The <sup>14</sup>N quadrupolar couplings cause inefficient encoding of the <sup>14</sup>N frequency due to large frequency offsets and make the rotor-synchronization of the evolution time necessary. It is shown that <sup>14</sup>N *rf* pulses longer than the rotor period can efficiently encode <sup>14</sup>N frequencies and generate spinning sideband free spectra along the indirect dimension. Average Hamiltonian and Floquet theories in the quadrupolar jolting frame (QJF) are used to treat the spin dynamics of the spin-1 quadrupolar nucleus under long <sup>14</sup>N *rf* pulses and MAS. The results show that the *rf* action can be described by a scaled and phase-shifted effective *rf* field. The large quadrupolar frequency offset becomes absent in the QJF and therefore leads to sideband-free spectra along the indirect dimension. More importantly, when a pair of long <sup>14</sup>N *rf* pulses are used, the distribution of the phase shift of the effective *rf* field does not affect the <sup>14</sup>N encoding for powder samples; thus, high efficiencies can be obtained. The efficient and sideband-free features are demonstrated for three <sup>1</sup>H/<sup>14</sup>N indirectly detected experiments using long <sup>14</sup>N pulses under fast MAS.

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#### I. INTRODUCTION

<sup>14</sup>N is the abundant isotope (99.6%) of nitrogen, an important element for all branches of chemistry. The large <sup>14</sup>N quadrupole coupling and spin-1 quantum number make acquisition of <sup>14</sup>N solidstate NMR spectra challenging. For static solid samples, <sup>14</sup>N powder spectra are often several megahertz broad; therefore, the acquisition of wide-line spectra usually requires use of multiple-echoes such as the Carr-Purcell Meiboom-Gill (CPMG) sequence.<sup>1,2</sup> Broadband frequency-sweep pulses and stepping of the irradiation frequency offset are also used to cover the large <sup>14</sup>N breadth.<sup>3</sup> For spinning samples, fast and stable sample spinning precisely at the magic-angle can average the large first-order quadrupole interaction. The modulation of the first-order quadrupole coupling, however, results in many spinning sidebands that spread over the same breadth as the static <sup>14</sup>N wide-line pattern.<sup>4</sup> The wide lines and low <sup>14</sup>N gyromagnetic ratios cause low resolution and sensitivity for direct detection of <sup>14</sup>N.

Indirect detection of <sup>14</sup>N via nearby spin-1/2 nuclei such as <sup>1</sup>H and <sup>13</sup>C has been developed to overcome the aforementioned sensitivity and resolution problems. Under magic-angle spinning (MAS), these spin-1/2 "spy" nuclei with higher gyromagnetic ratios have much narrower line widths than that of <sup>14</sup>N and thus provide better resolution and sensitivity in the form of two-dimensional (2D) spectra. Methods based on heteronuclear multiple-quantum correlation (HMQC) and cross-polarization (CP) have been reported.<sup>5-</sup> The correlation and polarization transfer can be established via the residual dipolar splitting and J-coupling that remains under MAS or by using the larger dipolar interaction obtained through recoupling pulse sequences.<sup>10,11</sup> HMQC, in particular, is a simple experiment that uses only a pair of short pulses to encode the <sup>14</sup>N frequency [Fig. 1(a)]. Single-quantum, double-quantum, or even overtone <sup>14</sup>N transitions can be indirectly detected this way.<sup>12–14</sup> By synchronizing the time evolution between the pair of <sup>14</sup>N encoding pulses accurately with the rotor period, the large first-order quadrupole interaction can be refocused, provided that the magic-angle is set



**FIG. 1**. Pulse sequences for 2D <sup>1</sup>H/<sup>14</sup>N correlation: (a) D-HMQC with SR4<sup>2</sup><sub>1</sub> dipolar recoupling<sup>11</sup> applied to <sup>1</sup>H, (b) TRAPDOR-HMQC using long <sup>14</sup>N pulses for both dipolar recoupling and <sup>14</sup>N frequency encoding in the quadrupolar jolting frame, and (c) double cross-polarization (DCP) from <sup>1</sup>H to <sup>14</sup>N and then back to <sup>1</sup>H.

accurately. The rotor-synchronization restricts the indirect spectral window to the spinning frequency, which is equivalent to folding all <sup>14</sup>N spinning sidebands into a single peak along the <sup>14</sup>N dimension. It should be noted that significant  $t_1$ -noise can arise due to fluctuations in spinning frequency, and spinning sidebands appear if a large spectral window is used in the indirect dimension. In addition, the encoding pulses become inefficient for large <sup>14</sup>N quadrupolar couplings. For a rectangular pulse, the excitation profile can be described by a sinc function with frequency nulls that are inversely proportional to the pulse length. Its bandwidth is usually not enough to cover the several megahertz breadth of the complete <sup>14</sup>N pattern. In searching for more efficient pulse schemes, it has been found that longer radio-frequency (rf) pulses approaching the rotor period can increase the efficiency dramatically.<sup>15</sup> This behavior and the term sideband-selective long pulses (SLP)<sup>16</sup> used to describe it are counterintuitive since longer pulses usually have narrower bandwidths. Jarvis et al.<sup>17</sup> have exploited long pulses further by extending the <sup>14</sup>N pulses far beyond the inverse of the dipolar coupling [Fig. 1(b)], reminiscent of the TRAnsfer of Population in DOuble Resonance (TRAPDOR) experiment.<sup>18-20</sup> Interestingly, in this case, the long <sup>14</sup>N pulses are used for encoding and dipolar recoupling at the same time without additional dipolar recoupling on the "spy" nuclei. Recently, Carnevale et al.9 have also obtained efficient <sup>14</sup>N correlation via double cross-polarization (DCP) by adding a <sup>1</sup>H spin-lock rf field simultaneously with the long <sup>14</sup>N pulses [Fig. 1(c)]. Throughout this work, long pulses are defined as being at least a rotor period in duration.

The three aforementioned methods using long <sup>14</sup>N pulses have been demonstrated experimentally and by numerical simulations.

However, their mechanisms are not completely clear and some questions still remain. For a spin-1/2, long pulses can effectively spin-lock the magnetization as necessary for CP. However, for <sup>14</sup>N, a long pulse can barely do any spin-locking under MAS as the quadrupole coupling is at least an order of magnitude larger than the rf field. To our knowledge, efficient one-step  ${}^{1}H \rightarrow {}^{14}N$  CP transfer has not yet been achieved under MAS; then, why is  ${}^{1}H \rightarrow {}^{14}N \rightarrow {}^{1}H$  two-step CP transfer efficient? For the case of "long-pulse" HMQC [Fig. 1(b)], the intriguing <sup>14</sup>N rf offset and field strength dependences, both observed experimentally and with numerical simulations have not yet been explained.<sup>16</sup> The spin dynamics of the three-level <sup>14</sup>N spin system under rf pulses is more complex than for a spin-1/2, especially in the presence of the very large MAS-modulated quadrupole coupling. In the past, a level-crossing picture between the modulating quadrupole coupling frequency and the rf frequency has been used to describe what happens during the long pulses under MAS. Because of the large frequency offsets, most of the rf action occurs only during the brief level crossings. The effect of these level crossings can be a small perturbation, efficient excitation, or inversion depending on the regime of the so-called adiabaticity parameter  $\omega_1^2/\Delta\omega' \ll 1$ , ~1, or  $\gg 1$ , respectively.<sup>21</sup> Here,  $\omega_1$  represents the rf field strength and  $\Delta \omega'$  is the sweep rate of the crossing. In this work, we present a theory to derive the rf spin dynamics in the so-called jolting frame<sup>22</sup> to describe the long-pulse <sup>14</sup>N experiments and their phenomena quantitatively. The robust theoretical tool presented and physical insights obtained can help understand and further improve correlation experiments, as well as aid the development of new efficient methods to acquire <sup>14</sup>N NMR spectra directly or indirectly.

The jolting frame used to treat long <sup>14</sup>N pulses under MAS is briefly described here. First introduced by Caravatti et al.,<sup>22</sup> the jolting frame is an extension of the well-known rotating frame widely used in NMR spectroscopy. The rotating frame transformation unwinds the time dependence of the radio frequency and reduces the large Zeeman interaction to a small frequency offset term. The action of the rf pulse can then be described simply by a rotation about a static effective rf field. This simple picture of rf pulses forms the basis for almost all NMR experiments.<sup>23</sup> The jolting frame extends this idea further to large modulated spin interactions that remain in the NMR rotating frame. Transformation into a "quadrupolar jolting frame" (QJF) eliminates the large offsets due to MAS modulation of the quadrupole coupling frequency but introduces modulations to the rf Hamiltonian. The large quadrupolar coupling frequency offsets and spinning sidebands become absent when pulses longer than a rotor period are used. The observation of sideband-free <sup>14</sup>N spectra has not been reported before and is experimentally demonstrated here. Under the conditions of fast MAS, average Hamiltonian theory (AHT) can be applied to determine the scaled effective rf Hamiltonian in the QJF. The modulated Hamiltonian in the jolting frame can also be treated more generally using Floquet theory.<sup>24</sup> In particular, the Floquet treatment is used below to derive the recoupling of the heteronuclear dipolar interaction under long <sup>14</sup>N pulses, which is a critical element for indirect <sup>14</sup>N detection through heteronuclear correlation or polarization transfer. Notably, Pell et al. have used the jolting frame to treat large anisotropic paramagnetic shifts under MAS,<sup>25</sup> as well as the <sup>14</sup>N quadrupolar interaction to obtain indirectly detected double-quantum spectra.<sup>26</sup>

Following the theory, three indirectly detected experiments employing long <sup>14</sup>N pulses will be presented: (1) <sup>1</sup>H/<sup>14</sup>N HMQC with dipolar recoupling applied to <sup>1</sup>H, also commonly dubbed D-HMQC; (2) <sup>1</sup>H/<sup>14</sup>N HMQC using a pair of long <sup>14</sup>N pulses that serve for both dipolar recoupling and <sup>14</sup>N frequency encoding, which we call TRAPDOR-HMQC or simply T-HMQC, given its similarity with the TRAPDOR experiment;<sup>18–20</sup> and (3) <sup>1</sup>H/<sup>14</sup>N correlation using <sup>1</sup>H  $\rightarrow$  <sup>14</sup>N  $\rightarrow$  <sup>1</sup>H forward-and-back polarization transfer, namely, double cross-polarization (DCP). The mechanism of each experiment will be described using the theory in the quadrupolar jolting frame, and their frequency offset and *rf* field dependences will be investigated.

In this work, ultrafast 95 kHz MAS is used with <sup>1</sup>H detection to acquire <sup>14</sup>N spectra indirectly. Detection through protons gives high sensitivity due to its high gyromagnetic ratio and natural abundance. Fast MAS helps by narrowing the <sup>1</sup>H resonances and prolonging <sup>1</sup>H  $T_2$  relaxation. The HMQC sequence often uses a long proton spinecho and therefore benefits greatly from longer  $T_2$  constants in addition to narrower line widths. As for <sup>14</sup>N encoding, it will be shown that the faster spinning leads to stronger effective <sup>14</sup>N *rf* fields. It should be noted that the mechanism and principles behind the three presented experiments should also be applicable when using other spin-1/2 "spy" nuclei such as <sup>13</sup>C.

#### **II. THEORY**

Let us consider the following Hamiltonian in the rotating frame for an indirectly detected <sup>14</sup>N experiment under MAS of a two-spin system with <sup>14</sup>N (S) and <sup>1</sup>H (I):

$$H = H_Q + H_D + H_{CS} + H_{rf},$$

$$H_Q = q(t)(S_z^2 - 2/3), \quad H_D = d(t)I_zS_z, \quad H_{CS} = \Delta\omega S_z, \quad H_{rf} = \omega_1 S_x,$$
(1)

where  $H_Q$ ,  $H_D$ ,  $H_{CS}$ , and  $H_{rf}$  are the Hamiltonians for the quadrupolar coupling, dipolar coupling, chemical shift, and rf irradiation, respectively. Here, q(t) and d(t) are the first-order quadrupole coupling and the dipolar coupling frequencies modulated by MAS, respectively. The second-order quadrupole shift is included in the chemical shift offset term  $\Delta \omega$  of  $H_{CS}$ , and  $\omega_1 = \gamma B_1/2\pi$  is the angular frequency of the rf field applied along the *x*-axis. The MASmodulated components of the chemical shift anisotropy (CSA) and second-order quadrupolar shift are much smaller than that of the first-order quadrupole coupling and are thus not considered here.

The quadrupolar coupling is usually the largest interaction among all the terms in the Hamiltonian,  $H_Q > H_{rf}$ ,  $H_{CS}$ ,  $H_D$ . By going to its interaction representation described by the rotation operator  $R = \exp(-i\int_0^t H_Q(t')dt')$ , the *rf* Hamiltonian becomes

$$h_{rf} = RH_{rf}R^{-1} = \frac{\omega_1}{\sqrt{2}} \begin{pmatrix} 0 & e^{i\varphi_Q(t)} & 0\\ e^{-i\varphi_Q(t)} & 0 & e^{-i\varphi_Q(t)}\\ 0 & e^{i\varphi_Q(t)} & 0 \end{pmatrix}.$$
 (2)

The lower case *h* is used to distinguish the Hamiltonians in the QJF from the regular rotating frame. Here,  $\varphi_Q(t)$  is the phase

accumulation from the MAS-modulated first-order quadrupolar coupling frequency,

$$\varphi_Q(t) = \int_0^t \omega_Q(t') dt'.$$
(3)

This periodic phase modulation can be expanded into a Fourier series,

$$e^{i\varphi_Q(t)} = \sum_k s_k e^{ik\omega_r t},\tag{4}$$

$$h_{rf} = \sum_{k} \frac{\omega_{1}}{\sqrt{2}} \begin{pmatrix} 0 & s_{k} & 0\\ s_{-k}^{*} & 0 & s_{-k}^{*}\\ 0 & s_{k} & 0 \end{pmatrix} e^{ik\omega_{r}t},$$
(5)

where the amplitude of the modulated coefficients  $s_k$  satisfies the normalization condition

$$\sum_{k} |s_k|^2 = 1. \tag{6}$$

The phase  $\varphi_Q(t)$  and its Fourier expansion coefficients  $s_k$  are related to the <sup>14</sup>N NMR free-induction-decay signal and the spinning sidebands in <sup>14</sup>N MAS spectra for the +1  $\leftrightarrow$  0 transition. Equation (5) shows that the *rf* Hamiltonian in the QJF becomes modulated. The dipolar coupling and frequency offset Hamiltonians,  $H_D$  and  $H_{CS}$ , both commute with the rotation operator, *R*, and thus remain unchanged. Most importantly, the large quadrupolar coupling is absent in the QJF.

The modulation coefficients  $s_k$  of the *rf* Hamiltonian are of central importance. Let us first look more closely at their phase and magnitude before proceeding. Figure 2 shows simulations of <sup>14</sup>N MAS sidebands  $s_k$  for the +1  $\leftrightarrow$  0 transition of an individual crystallite. The phase of the  $s_k$  sidebands varies widely, even for the same crystallite at different starting rotor positions y. After a powder average over the rotor angle, the spinning sidebands all become absorptive. The sideband amplitudes become  $|s_k|^2$ , which are much smaller than  $s_k$  as a result of phase cancellation from powder averaging.<sup>27</sup> The magnitude of the  $s_k$  terms can be estimated as follows. The spinning sideband intensities  $s_k$  are negligible for  $k\omega_r$  outside the <sup>14</sup>N powder pattern, so the number of sidebands with significant intensities can be estimated to be  $\omega_q/\omega_r$ , where  $\omega_q$  is defined as  $\pi C_0/2$  for <sup>14</sup>N and  $C_0$  is the quadrupole coupling constant in units of Hertz. Hence, from the normalization condition in Eq. (6), we obtain

$$|s_k| \sim \sqrt{\omega_r / \omega_q},\tag{7}$$

where usually  $|s_k| \ll 1$  since  $\omega_q \gg \omega_r$ . It is noteworthy that the scaling parameter  $s_k$  and its phase  $\varphi_k$  pertain to each individual crystallite, which is different from and should not be confused with the "carousel"  $\gamma$ -averaged sideband intensity  $|s_k|^2$ , as shown in Fig. 2.

Under fast spinning, the time evolution of the periodic rfHamiltonian can be approximated using average Hamiltonian theory by keeping only the constant term,

$$\overline{h_{rf}} = \frac{\omega_1}{\sqrt{2}} \begin{pmatrix} 0 & s_0 & 0 \\ s_0^* & 0 & s_0^* \\ 0 & s_0 & 0 \end{pmatrix} = |s_0| \omega_1 \exp(-i\varphi_0 S_z^2) S_x \exp(i\varphi_0 S_z^2).$$
(8)



**FIG. 2.** Simulation of <sup>14</sup>N spinning sidebands at 95 kHz MAS for the +1  $\leftrightarrow$  0 transition of a single crystallite with an orientation ( $\alpha$ ,  $\beta$ ) = (0°, 45°) to the rotor frame at various rotor phases ( $\gamma$ ). Simulations were performed with SIMPSON<sup>28</sup> using quadrupole coupling  $C_Q$  = 1.3 MHz and asymmetry parameter  $\eta_Q$  = 0.3.

The result shows an effective Hamiltonian with the *rf* amplitude scaled by  $|s_0|$  and a phase shift  $\varphi_0$ , i.e.,  $\exp(-i\varphi_0 S_z^2)S_x \exp(i\varphi_0 S_z^2)$ . In powder samples, the phase  $\varphi_0$  varies widely among crystallites due to the different quadrupolar coupling tensor orientations, and powder averaging leads to phase cancellation if a long pulse is applied, for example, in a direct excitation <sup>14</sup>N experiment. However, when a pair of pulses are used, as in the case of the 2D experiments mentioned above, the cancellation does not occur because the relative phase between the two pulses is not affected by the phase  $\varphi_0$ . This is the essence of why indirectly detected experiments are efficient when a pair of long <sup>14</sup>N pulses are used. The second reason for the high efficiencies is that the frequency offset from large quadrupolar couplings is absent in the QJF. Hence, the long pulses exhibit the typical nutation behavior at a scaled *rf* amplitude  $|s_0|\omega_1$ .

The time evolution of a periodically modulated Hamiltonian can also be treated more generally using Floquet theory. The

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Floquet theorem states that the evolution operator can be expressed with a time-independent Hamiltonian Q and a periodic operator P(t),

$$U = P(t)e^{-iQt}P(0)^{-1},$$
  

$$P(t) = \sum_{k} P_{k}e^{ik\omega_{r}t}.$$
(9)

The operators Q and  $P_k$  can be obtained as the eigenvalues and the eigenvectors of the time-independent Floquet Hamiltonian  $H_F$ ,

$$H_F = \sum_{m,n} |m\rangle H_{m-n} + n\omega_r \delta_{nm} \langle n|.$$
<sup>(10)</sup>

Here,  $H_k$  is the Fourier expansion of the modulating Hamiltonian

$$H(t) = \sum_{k} H_k e^{ik\omega_r t}.$$
 (11)

Floquet theory transfers a time-dependent problem into a timeindependent one by an expansion into the Floquet space  $|k\rangle\langle l|$ . Perturbation theory often can be used to diagonalize the matrix of the Floquet Hamiltonian  $H_F$ .

The Floquet theorem in Eq. (9) can also be expressed in a slightly different form related to the average Hamiltonian  $\tilde{H}$  and periodic operator p(t),

$$U = p(t)e^{-i\tilde{H}t},$$
  
$$\overline{H} = P(0)QP(0)^{-1},$$
  
$$p(t) = P(t)P(0)^{-1} = \sum_{k} p_{k}e^{ik\omega_{r}t}.$$
  
(12)

When the Hamiltonian component  $H_k$  is small compared to the spinning frequency, we have only one significant term in the diagonalization process, i.e.,  $p_0 \sim \mathbb{I}$  and  $p_{k\pm 0} \ll 1$ . We can then take the following approximation for the periodic operator p(t) and its inverse:

$$p(t) = \mathbb{I} + \sum_{k=\pm 1,\ldots\pm\infty} p_k e^{ik\omega_r t},$$
  

$$p(t)^{-1} = \mathbb{I} - \sum_{k=\pm 1,\ldots\pm\infty} p_k e^{ik\omega_r t}.$$
(13)

We apply the Floquet theorem to the general case with the <sup>14</sup>N frequency placed near the *n*th spinning sideband position, the frequency offset  $n\omega_r S_z$  in  $H_{CS}$  merely shifts the indices by *n* in the Floquet space for the modulating *rf* Hamiltonian  $H_k$  in Eq. (11). Consequently, it changes the spinning sideband indices from  $s_0$  to  $s_n$  in Eq. (8) for the effective *rf* Hamiltonian

$$\overline{h_{rf}} = \frac{\omega_1}{\sqrt{2}} \begin{pmatrix} 0 & s_n & 0\\ s_{-n}^* & 0 & s_{-n}^*\\ 0 & s_n & 0 \end{pmatrix}.$$
 (14)

The shift by  $n\omega_r S_z$  reduces the frequency offset to the nearest sideband position to  $\Delta \omega - n\omega_r$ , resulting in the following rotation operator for the jolting frame and the average Hamiltonian:

$$R = \exp\left(-i \int_0^t H_Q(t') dt' S_z^2 - in\omega_r t S_z\right), \tag{15}$$

$$\overline{h_{rf}} = \left| \frac{s_n + s_{-n}}{2} \right| \omega_1 \exp\left(-i\varphi_{\Sigma}S_z^2\right) S_x \exp\left(i\varphi_{\Sigma}S_z^2\right) \\ + \left| \frac{s_n - s_{-n}}{2} \right| \omega_1 \exp\left(-i\varphi_{\Delta}S_z^2\right) [S_z S_x + S_x S_z]$$
(16)  
$$\times \exp\left(i\varphi_{\Delta}S_z^2\right) + (\Delta\omega - n\omega_r) S_z.$$

Here,  $s_n$  and  $s_{-n}$  are the complex intensities of the spinning sidebands near the <sup>14</sup>N *rf* frequency for the +1  $\leftrightarrow$  0 and 0  $\leftrightarrow$  -1 transitions that are mirror images of each other, and  $\varphi_{\Sigma}$  and  $\varphi_{\Delta}$ are the phases for the sum and difference of the two sidebands  $s_n$ and  $s_{-n}$ , respectively. This general solution encompasses the onresonance case in Eq. (8) with n = 0, noting that two-spin operator term  $S_z S_x + S_x S_z$  becomes absent for the case of on-resonance <sup>14</sup>N pulses.

The Floquet formalism allows us to look further into the dipolar recoupling during a long <sup>14</sup>N pulse. The heteronuclear dipolar coupling is usually averaged by fast MAS, as the modulating dipolar coupling frequency averages to zero, i.e.,  $\langle d(t) \rangle = 0$ . The <sup>14</sup>N rf irradiation introduces additional modulation to the <sup>14</sup>N  $S_z$  spin operator, which interferes with the MAS averaging of the dipolar coupling Hamiltonian causing recoupling. Described by the population transfer during the level-crossings of <sup>14</sup>N pulses, such a mechanism has been used in the TRAPDOR experiment for distance measurements with quadrupolar nuclei. Here, we derive the dipolar recoupling using the Floquet formalism in Eq. (12),

$$H_D = d(t)I_z p(t) \exp\left(-i\overline{h_{rf}}t\right) S_z \exp\left(i\overline{h_{rf}}t\right) p(t)^{-1}.$$
 (17)

Considering that the *rf* Hamiltonian  $\overline{h_{rf}}$  is usually much larger than the dipolar coupling term, it is sufficient to keep only the commuting component in the dipolar coupling Hamiltonian as the noncommuting terms are effectively truncated by the *rf* Hamiltonian,

$$\exp\left(-i\overline{h_{rf}}t\right)S_z\exp\left(i\overline{h_{rf}}t\right) \to \frac{Tr\left(S_z\overline{h_{rf}}\right)}{Tr\left(\overline{h_{rf}}^2\right)}\overline{h_{rf}}.$$
 (18)

From the p(t) operator in Eq. (13), we obtain the following form of average dipolar Hamiltonian under the <sup>14</sup>N pulses:

$$\overline{H_D} = \sum_{k=\pm 1,2} \frac{Tr\left(S_z \overline{h_{rf}}\right)}{Tr\left(\overline{h_{rf}}\right)} d_k I_z \Big[\overline{h_{rf}}, p_{n-k}\Big].$$
(19)

The dipolar Hamiltonian contains the product between the modulating dipolar coupling frequency  $d_k$  and the periodic Floquet operator  $p_{n-k}$ .

#### **III. EXPERIMENTAL**

All <sup>1</sup>H/<sup>14</sup>N experiments were carried out at  $v_0(^{1}\text{H}) = 800.1$  MHz and  $v_0(^{14}\text{N}) = 57.8$  MHz using an 800 MHz Bruker Avance III HD spectrometer and a 0.75 mm MAS probe developed at the NHMFL using a spinning assembly and rotors provided by JEOL. The 0.75 mm rotor holds approximately 290 nl of L-histidine·HCl·H<sub>2</sub>O and can spin up to a frequency of 100 kHz. A spinning frequency of 95 kHz was used for measurements. The spinning speed was regulated to within ±5 Hz, and the recycle delay was 2 s. The magic-angle setting was calibrated by narrowing the <sup>14</sup>N line width along the indirection dimension of a 2D  $^{1}$ H/ $^{14}$ N *J*-HMQC spectrum of the sample with small second-order quadrupolar broadening. Other experimental parameters are included in the figure captions.

#### IV. RESULTS AND DISCUSSIONS

#### A. Dipolar-HMQC

The HMQC experiment with dipolar recoupling applied on the <sup>1</sup>H channel is shown in Fig. 1(a). The pair of <sup>14</sup>N pulses first rotate the  $S_z$  term of the two-spin order generated by the dipolar recoupling into the *xy* plane and then rotate the transverse polarization after the  $t_1$  evolution period back to *z*-axis. The <sup>14</sup>N frequency encoded in the two-spin coherence is converted back to  $I_x$  for proton detection after the second half of the spin-echo. Short and strong <sup>14</sup>N pulses are usually used in order to cover the large frequency offsets due to the quadrupolar coupling. The efficiency is often low as the <sup>14</sup>N quadrupolar coupling is an order of magnitude larger than the typically achievable *rf* field strength. Here, rotor-period long pulses are used for the <sup>14</sup>N frequency encoding.

Figure 3(a) shows the D-HMQC experimental efficiency as a function of the <sup>14</sup>N irradiation frequency. The efficiency is measured as the intensity ratio between the first  $t_1$ -increment of the 2D experiment and a 90°-pulse excitation spectrum. The frequency profile for L-histidine·HCl·H<sub>2</sub>O is nearly flat at around 15% with peaks approximately at the <sup>14</sup>N spinning sideband positions. Three factors contribute to this overall efficiency: the proton  $T_2$  relaxation under dipolar recoupling, the <sup>14</sup>N encoding efficiency, and the interconversion between single- and double-quantum two-spin order, i.e., the powder average of  $(\sin^2[\pi D_{\text{eff}}(\theta,\varphi)\tau])$ , where  $D_{\text{eff}}$  is the effective dipolar coupling and  $\tau$  is the mixing time. Assuming that  $\langle \sin^2[\pi D_{\text{eff}}(\theta, \varphi)\tau] \rangle \sim 1/2$  in the long mixing time regime and the relaxation factor is about 63% measured for a total mixing time of 252  $\mu$ s, the <sup>14</sup>N encoding efficiency is estimated to be about 48%, which is remarkably high for a <sup>14</sup>N quadrupolar pattern spanning ~2 MHz. The long pulses and the scaled effective rf field can achieve large flip-angles as long as the large quadrupolar coupling frequency is absent in the QJF. Most importantly, the phase spread by  $\varphi_0$  [Eq. (8)] does not affect the relative phase between the two pulses and therefore causes no cancellation between the encoding pulses. This is the main reason why high encoding efficiency can be achieved with long <sup>14</sup>N pulses.

It is noteworthy that for a pair of rotor-period long encoding pulses, the effective  $t_1$  evolution is equal to one rotor period for the first  $t_1$ -increment. The time evolution with frequency offset causes cosine and sine modulation of the hypercomplex 2D data as shown by the dashed and dotted lines in Fig. 3(a). It appears that the cosine signal may have been improperly used in the past to measure the frequency profile of the encoding efficiency.<sup>16</sup> The magnitude of the two should be used, and it shows a broad and flat offset profile.

The 2D  ${}^{1}$ H/ ${}^{14}$ N D-HMQC spectrum shown in Fig. 4 has an indirect spectral window larger than the spinning frequency, and shows no  ${}^{14}$ N sidebands. This is striking at first sight since the single-quantum  ${}^{14}$ N coherence is subjected to the large first-order quadrupolar coupling. This result becomes clear in the QJF in which



FIG. 3. Dependence of  $^{14}N$  encoding efficiency for the  $^{1}H_{N\delta1}$  site in Lhistidine HCl·H<sub>2</sub>O as a function of <sup>14</sup>N *rf* irradiation frequency ( $\omega_{irr}$ ) for the (a) D-HMQC, (b) T-HMQC, and (c) DCP experiments. The efficiency is measured by the ratio of the proton peak intensity between the first  $t_1$  increment of the 2D experiments and a  $\pi/2$  one-pulse spectrum. The irradiation frequency is given in units of the MAS frequency ( $\omega_r/2\pi = 95$  kHz), and zero denotes the center band position. In (a), the duration of each D-HMQC SR421 dipolar recoupling block was ~126  $\mu$ s (12 rotor periods), and the <sup>14</sup>N pulse lengths used were 10.5  $\mu$ s (one rotor period). The offset dependence of the cosine and sine (or real and imaginary) of the hypercomplex signals is shown as red dashed and blue dotted lines, respectively. The solid black line shows the magnitude of the two as the measure for the experiment efficiency. For T-HMQC in (b), the <sup>14</sup>N pulse lengths used were each 1 ms. The efficiency is shown for <sup>14</sup>N rf fields of 30 and 60 kHz as red dashed and solid black lines, respectively. For the (c) DCP experiment, the duration of each <sup>1</sup>H  $\leftrightarrow$  <sup>14</sup>N contact time was 4 ms with <sup>1</sup>H and <sup>14</sup>N *rf* field strength described in the main text

the large quadrupolar coupling is absent. This outcome can also be viewed using the level crossing picture. During the long <sup>14</sup>N pulses, the *rf* action occurs mainly during the brief level crossings between the modulating quadrupolar coupling frequency and the <sup>14</sup>N *rf* pulse. The level crossings occur periodically with the rotor period. When the evolution time is increased by a fraction of a rotor period, the timing of the level crossings between the two pulses remains unchanged for most spins. Only the spins with level-crossings occurring at the beginning of the first pulse have level crossings shifted during the second pulse but by a complete rotor period. Thus, the time evolution between the two pulses is not modulated by

the first-order quadrupolar coupling and does not create spinning sidebands.

Figure 4 also shows a stack of <sup>14</sup>N slices from 2D experiments acquired by varying the <sup>14</sup>N irradiation frequency  $\omega_{irr}$ . When <sup>14</sup>N rf is placed in the middle between two neighboring sidebands, two peaks at the neighboring sideband positions of the irradiation frequency appear with similar intensity. This behavior is different from typical <sup>14</sup>N spinning sideband manifolds that spread over the whole span of the powder pattern; only sidebands neighboring the <sup>14</sup>N irradiation frequency have significant intensity. These sidebands originate from the modulating *rf* Hamiltonian in the QJF or, more specifically, from the periodic evolution operator p(t) in the Floquet theory solution. Hence, we call them "Floquet sidebands" in the QJF. When the  $^{14}$ N frequency is placed near the *n*th sideband, only the  $p_n$  Fourier component of p(t) is dominant, resulting in a single <sup>14</sup>N peak at the *n*th sideband position. When <sup>14</sup>N is placed between two sidebands, both  $p_k$  components for the two sideband indices are significant with approximately equal magnitude, giving rise to two peaks. In practice, the <sup>14</sup>N offset is usually placed near the center band or sideband positions such that the  $^{14}$ N peaks appear in the middle of the  $f_1$  window. The 2D spectrum in Fig. 4 was acquired under such a condition and is indeed sideband-free.

The magnitude of the effective field in the QJF  $\omega_1^{\text{eff}} \sim |s_n|\omega_1$  can be estimated using Eq. (7) and expressed in terms of the spinning frequency and the so-called adiabaticity parameter  $\alpha$  that was introduced to categorize level-crossings induced by MAS,<sup>21</sup>

$$\omega_1^{\rm eff} \sim \sqrt{\alpha} \omega_r, \alpha = \frac{\omega_1^2}{\omega_q \omega_r}.$$
 (20)

For fast spinning and large quadrupolar interactions, the adiabaticity parameter is usually in the small perturbation regime,  $\alpha \ll 1$ . Figure 5 shows how the efficiency changes with the <sup>14</sup>N *rf* field strength for the D-HMQC experiment. For one-rotor period long pulses, the efficiency peaks when the flip-angle reaches ~90° with the <sup>14</sup>N *rf* field,

$$\omega_1 = \frac{1}{4} \sqrt{\omega_q \omega_r}.$$
 (21)

Thus, an adiabaticity parameter of  $\alpha \sim 1/16$  is expected. The curve in Fig. 5 for D-HMQC agrees well with the observed maximum of  $\omega_1/2\pi \sim 40$  kHz; noting that  $\omega_q$  is defined as  $\pi C_Q/2$  for <sup>14</sup>N with  $C_Q = 1.3$  MHz for the N<sub> $\delta 1$ </sub> site.

#### **B. TRAPDOR-HMQC**

The TRAPDOR-HMQC (or T-HMQC) experiment in Fig. 1(b) introduces two modifications to the D-HMQC experiment. First, the dipolar recoupling sequence is switched from the <sup>1</sup>H to the <sup>14</sup>N channel, bearing strong similarities to the TRAPDOR experiment.<sup>18–20</sup> Second, the long <sup>14</sup>N pulses also serve the purpose of <sup>14</sup>N frequency encoding. In order to better understand this experiment, let us first consider the hypothetical case of a heteronuclear *J*-coupled spin pair in liquids. The long *rf* pulses spin-lock the <sup>14</sup>N polarization allowing the two-spin order  $I_y S_{z'}$  to develop under *J*-coupling. Here, z' is the direction of the tilted effective *rf* field



**FIG. 4**. 2D <sup>1</sup>H/<sup>14</sup>N D-HMQC spectrum of L-histidine-HCI-H<sub>2</sub>O with 250 kHz spectral window in *F*<sub>1</sub> (left). The stack plot on the right shows the *F*<sub>1</sub> slices at the <sup>1</sup>H<sub>N81</sub> site acquired with <sup>14</sup>N irradiation frequencies denoted by arrows set at 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0 times the MAS frequency ( $\omega_r/2\pi = 95$  kHz) with respect to the <sup>14</sup>N81 center band position. The result shows no spinning sideband in the *f*<sub>1</sub> dimension.

due to frequency offset. The build-up of two-spin order is proportional to the J-coupling, which is scaled by the offset of the <sup>14</sup>N rf field. During the  $t_1$  evolution when the <sup>14</sup>N pulse is turned off, the projection of  $S_{z'}$  along the transverse plane starts to evolve according to the <sup>14</sup>N peak frequency. The evolved component after  $t_1$  is then spin-locked again for conversion back to  $I_x$  for <sup>1</sup>H signal detection during the second half of the pulse sequence. The angle of the effective rf field with respect to the z-axis  $\theta$  affects this experiment in two important ways. First, the encoding efficiency depends on  $\sin^2\theta$ , so an on-resonance rf field with  $\theta = \pi/2$  gives the highest efficiency for <sup>14</sup>N frequency encoding. Second, the J-coupling is scaled by  $\cos\theta$ , so excitation and conversion of two-spin order in the short mixing time regime are proportional to  $\cos^2\theta$ . Therefore, on-resonance irradiation acts as decoupling and prevents creation of two-spin order and a null should be observed. The overall signal intensity is proportional to  $\sin^2\theta \cdot \cos^2\theta$  and tapers off away from reson ance, with an optimal effective rf field that should be at  $45^{\circ}$  to the z-axis.

The T-HMQC pulse sequence works the same way as the hypothetical experiment described above. The long <sup>14</sup>N pulses provide (1) dipolar recoupling and (2) <sup>14</sup>N frequency encoding via spinlocking with a scaled effective rf field in the QJF. On-resonance <sup>14</sup>N



**FIG. 5.** Dependence of the <sup>1</sup>H/<sup>14</sup>N efficiency for the <sup>1</sup>H<sub>N\delta1</sub> site in Lhistidine-HCI-H<sub>2</sub>O as a function of <sup>14</sup>N *rf* field strength ( $\omega_1$ ) for the D-HMQC and T-HMQC experiments. The efficiency was measured the same way as in Fig. 3, and the total mixing times for the D-HMQC and T-HMQC experiments were 253  $\mu$ s and 2 ms, respectively.

irradiation should be avoided as the effective rf Hamiltonian in the transverse plane can truncate the dipolar Hamiltonian completely as in the hypothetical case of J-coupling. Indeed, the efficiency profile in Fig. 3(b) shows a significant on-resonance null flanked by higher intensity that decreases away from resonance but starts increasing again as the <sup>14</sup>N irradiation frequency nears the first <sup>14</sup>N sideband positions. A small dip is seen at exactly the sideband positions but not as deep as the on-resonance null. This is likely due to the fact that the effective rf Hamiltonian in Eq. (14) has an additional twospin operator term. The inclusion of this term avoids complete truncation of the dipolar recoupling when the <sup>14</sup>N irradiation frequency is placed exactly at the spinning sidebands. Therefore, one of the <sup>14</sup>N sideband positions is recommended for use in T-HMQC, with the shift reference of the  $f_1$  axis adjusted accordingly. The comparison between two different <sup>14</sup>N rf fields [Fig. 3(b)] shows increased efficiency at higher <sup>14</sup>N rf fields, mostly due to better dipolar recoupling. Higher rf fields also affect how the angle of the effective rf field depends on frequency offset and leads to less tapering toward off-resonant regions, but the on-resonance null remains the same.

The T-HMQC experiment is highly efficient and sideband-free due to the same reasons as noted above for D-HMQC (spectra not shown). There are a few practical differences between the two experiments worth mentioning. First, when heteronuclear dipolar recoupling is applied to the observed nucleus as for D-HMQC, it automatically recouples <sup>1</sup>H chemical shift anisotropy (CSA). The D-HMQC experiment relies on the spin-echo to refocus the CSA, which is sensitive to the timing between the excitation and conversion periods. Small fluctuations of the spinning speed can affect the refocusing and cause  $t_1$ -noise. In the case of T-HMQC, the recoupling is applied to the indirect <sup>14</sup>N channel, which makes the experiment less susceptible to spinning speed fluctuations and  $t_1$ -noise. A comparison of their 2D spectra in Fig. 6 illustrates the difference in  $t_1$ noise. Second, for D-HMQC, the finite <sup>14</sup>N pulse length needs to be taken into account in the first  $t_1$ -increment and compensated with a large first-order phase correction along the indirect dimension. The T-HMQC does not have this restriction since no  $t_1$ -evolution occurs during the long <sup>14</sup>N pulses. Furthermore, the efficiency curves in both Figs. 3 and 5 show a higher efficiency for T-HMQC. These differences make T-HMQC preferred over the D-HMQC experiment.



**FIG. 6.** Comparison of 2D <sup>1</sup>H/<sup>14</sup>N spectra of L-histidine-HCI-H<sub>2</sub>O acquired using the (a) D-HMQC, (b) T-HMQC, and (c) DCP pulse sequences in Fig. 1. The 2D experiments were acquired with a spectral width of 50 kHz and an acquisition time of 10 ms in  $f_2$  and 47.5 kHz and 5 ms in  $f_1$ ; each spectrum took a total experimental time of 2.2 h. The base contours are set at 3% of the maximum intensity in each of the 2D spectra.

Figure 5 compares the efficiency vs. rf field strength curves between the D-HMQC and T-HMQC experiments. Both increase with the rf field initially. The D-HMQC efficiency peaks and starts to fall after the flip-angle by the effective rf field passes 90°. The T-HMQC efficiency increases due to better dipolar recoupling with an increased rf field, as implied by Eq. (17). This trend can also be viewed in the picture of periodic level-crossings under MAS and the transfer of population that contributes to recoupling. The population transfer starts from small perturbations when the  ${}^{14}N$   $r\bar{f}$  field is weak and achieves more efficient inversion as the adiabatic regime is reached. Once the rf field is high enough to reach the adiabatic regime, population transfer is maximized and the T-HMQC efficiency plateaus (Fig. 5). The efficiency/sensitivity of T-HMQC is significantly higher at all rf fields compared to D-HMQC. A major contributor to the difference comes from the <sup>1</sup>H signal attenuation during the spin-echo portion of the two experiments. When applying recoupling sequences to <sup>1</sup>H nuclei, the  $T_2'$  relaxation usually becomes much shorter than that observed with a conventional spin-echo.

### C. <sup>1</sup>H/<sup>14</sup>N double cross-polarization

The HMQC type experiments utilize the z-Hamiltonian, i.e., the  $I_zS_z$  term in the J and dipolar couplings to generate two-spin order. Heteronuclear correlation can also be established through the *xy*-Hamiltonian that contains the flip and flop terms via direct polarization transfer. In solution NMR, this can be done by completely suppressing chemical shift differences, for example, with isotropic mixing in the TOCSY experiment.<sup>29,30</sup> In the solidstate, cross-polarization is typically used, by applying spin-lock *rf* fields simultaneously to both nuclei. The so-called zero-quantum  $I_+S_- + I_-S_+$  or double-quantum  $I_+S_+ + I_-S_-$  dipolar coupling Hamiltonian can be reintroduced under MAS when the *rf* fields satisfy the modified Hartman-Hahn condition under MAS,

$$\omega_{1H} - \omega_{1N} = n\omega_r \text{ for ZQ}, \quad \omega_{1H} + \omega_{1N} = n\omega_r \text{ for DQ}, \quad n = \pm 1, \pm 2.$$
(22)

Figure 2(c) shows the pulse sequence used for  ${}^{1}H/{}^{14}N$  heteronuclear correlation through double cross-polarization (DCP). The key question is how the large  ${}^{14}N$  frequency offsets affect spin-locking and polarization transfer.

For <sup>14</sup>N, applying a long *rf* pulse cannot maintain efficient spinlock under the MAS modulation of the quadrupolar coupling, which is an order of magnitude larger than the *rf* field strength. The theory and previous two experiments have shown that the quadrupole frequency offset is indeed removed when viewed in the QJF, and the *rf* field is scaled by  $s_n$  and its phase spread that depends on crystallite orientation. Without the modulating frequency offsets, spin-locking can be achieved but along the direction determined by the phase of  $s_n$ . This phase spread causes signal cancellation and is the reason for the poor spin-lock efficiency in the regular rotating frame. However, the phase cancellation does not occur if two long pulses are used. This is the essence of why high efficiency can be achieved for all three indirectly detected <sup>1</sup>H/<sup>14</sup>N correlation experiments including the DCP method.

Proper *rf* fields and Hartman-Hahn conditions are critical to cross-polarization. Figure 7 shows how a 1 ms <sup>1</sup>H spin-lock behaves with *rf* field strength. The rotary resonance conditions to the spin-lock are evident at  $\omega_{1H} = 0.5\omega_r$  and  $\omega_r$  from the homonuclear dipolar coupling and  $\omega_{1H} = \omega_r$  and  $2\omega_r$  from the chemical shift anisotropy. A high-order secondary resonance at  $\omega_{1H} = 1.5\omega_r$  is also visible.<sup>31</sup> These conditions need to be avoided to have efficient spin-locking for cross-polarization. Considering that a strong effective <sup>14</sup>N *rf* field is difficult to generate due to the low <sup>14</sup>N gyromagnetic ratio and the



**FIG. 7.** Proton intensities as a function of *rf* field strength  $\omega_1$  of a 1 ms spin-lock showing the various resonant conditions at integer and half-integer multiples of the spinning frequency  $\omega_r/2\pi = 95$  kHz. The arrow points to the <sup>1</sup>H *rf* field used for <sup>1</sup>H/<sup>14</sup>N DCP experiments.

 $s_n$  scaling in the QJF, the  $\omega_{1H} + \omega_{1N}^{\text{eff}} = \omega_r DQ$  matching condition with  $\omega_{1H} \sim 0.8\omega_r$  was chosen for DCP experiments. Restricted by a limited effective <sup>14</sup>N *rf* field in the QJF, it is essential to use fast MAS such that <sup>1</sup>H *rf* fields with good spin-lock can be found to match the Hartman-Hahn condition in the gaps among these resonance conditions.

Figure 3(c) shows that the efficiency for the DCP experiment is comparable to D-HMQC and T-HMQC. A ±10% linear ramp was applied to the <sup>1</sup>H *rf* field amplitude to compensate for mismatch of the Hartman-Hahn condition due to *rf* field inhomogeneity and the distribution of  $s_n$  scaling to the effective <sup>14</sup>N *rf* fields in the QJF. The offset dependence shows that efficient DCP also occurs when the frequency of the <sup>14</sup>N spin-lock is applied at the spinning sideband positions with even slightly higher intensity than at the center band position.

The main difference between the DCP and HMQC experiments is the  $T_2$  contribution from the observed spin (i.e., <sup>1</sup>H) to the <sup>14</sup>N line width along the indirect dimension. The comparison in Fig. 6 shows clearly narrower line widths along the <sup>14</sup>N dimension for the DCP experiment. Multiple-pulse <sup>1</sup>H decoupling was applied during the  $t_1$ -period to remove broadening from the *J*-coupling. Figure 6 also shows more cross peaks due to relayed <sup>1</sup>H-<sup>1</sup>H transfer via spindiffusion during the <sup>1</sup>H spin-lock. Relayed transfer is undesired as it affects the direct relationship between cross-peak intensity and <sup>1</sup>H/<sup>14</sup>N distance. It has been shown recently that the spin-diffusion can be reduced by setting the <sup>1</sup>H spin-lock off-resonance at the Lee-Goldburg condition.<sup>32-34</sup>

## **V. CONCLUSIONS**

In summary, we have shown both theoretically and experimentally that long pulses can efficiently encode spin-1 nuclei like <sup>14</sup>N with large quadrupolar couplings under MAS. The theory derived in the quadrupolar jolting frame (QJF) has successfully explained the mechanism that yields high efficiency and sideband-free features of the three 2D  $^{1}$ H/ $^{14}$ N experiments. Average Hamiltonian and Floquet theories provide a clear and simple picture for spin dynamics of long  $^{14}$ N pulses under MAS: a scaled effective *rf* field with a phase spread and the elimination of large modulating  $^{14}$ N quadrupolar couplings in the QJF. For experiments using a pair of encoding pulses, the phase spread for powder samples does not cause cancellation and high efficiencies can be obtained. This idea and the efficient and sideband-free features can likely be extended to other half-integer quadrupolar nuclei to design more efficient indirect detection and correlation methods. Work along this direction is under way.

#### ACKNOWLEDGMENTS

This work was supported by the National High Magnetic Field Laboratory through National Science Foundation Cooperative Agreement (No. DMR-1644779) and by the State of Florida.

#### REFERENCES

<sup>1</sup>F. H. Larsen, H. J. Jakobsen, P. D. Ellis, and N. C. Nielsen, J. Phys. Chem. A **101**, 8597 (1997).

<sup>2</sup> F. H. Larsen, H. J. Jakobsen, P. D. Ellis, and N. C. Nielsen, Chem. Phys. Lett. 292, 467 (1998).

<sup>3</sup>K. J. Harris, S. L. Veinberg, C. R. Mireault, A. Lupulescu, L. Frydman, and R. W. Schurko, Chem. Eur. J. **19**, 16469 (2013).

<sup>4</sup>T. J. Bastow, D. Massiot, and J. P. Coutures, Solid State Nucl. Magn. Reson. 10, 241 (1998).

<sup>5</sup>Z. Gan, J. Am. Chem. Soc. **128**, 6040 (2006).

<sup>6</sup>S. Cavadini, A. Lupulescu, S. Antonijevic, and G. Bodenhausen, J. Am. Chem. Soc. 128, 7706 (2006).

<sup>7</sup>S. Cavadini, S. Antonijevic, A. Lupulescu, and G. Bodenhausen, J. Magn. Reson. 182, 168 (2006).

<sup>8</sup>Z. H. Gan, J. P. Amoureux, and J. Trebosc, Chem. Phys. Lett. 435, 163 (2007).

<sup>9</sup>D. Carnevale, X. Ji, and G. Bodenhausen, J. Chem. Phys. 147, 184201 (2017).

<sup>10</sup>X. Zhao, M. Edén, and M. H. Levitt, Chem. Phys. Lett. **342**, 353 (2001).

<sup>11</sup> A. Brinkmann and A. P. M. Kentgens, J. Am. Chem. Soc. **128**, 14758 (2006).

<sup>12</sup>S. Cavadini, Prog. Nucl. Magn. Reson. Spectrosc. 56, 46 (2010).

<sup>13</sup>Y. Nishiyama, M. Malon, Z. H. Gan, Y. Endo, and T. Nemoto, J. Magn. Reson. 230, 160 (2013).

<sup>14</sup>L. A. O'Dell, R. L. He, and J. Pandohee, CrystEngComm 15, 8657 (2013).

<sup>15</sup>M. Shen, J. Trébosc, O. Lafon, Z. Gan, F. Pourpoint, B. Hu, Q. Chen, and J.-P. Amoureux, Solid State Nucl. Magn. Reson. 72, 104 (2015).

<sup>16</sup>A. G. M. Rankin, J. Trébosc, P. Paluch, O. Lafon, and J.-P. Amoureux, J. Magn. Reson. **303**, 28 (2019).

<sup>17</sup>J. A. Jarvis, I. M. Haies, P. T. F. Williamson, and M. Carravetta, Phys. Chem. Chem. Phys. 15, 7613 (2013).

<sup>18</sup>E. Vaneck, R. Janssen, W. Maas, and W. Veeman, Chem. Phys. Lett. **174**, 428 (1990).

<sup>19</sup>C. P. Grey, W. S. Veeman, and A. J. Vega, J. Chem. Phys. **98**, 7711 (1993).

<sup>20</sup>C. P. Grey and A. J. Vega, J. Am. Chem. Soc. **117**, 8232 (1995).

<sup>21</sup> A. J. Vega, J. Magn. Reson. **96**, 50 (1992).

<sup>22</sup>P. Caravatti, G. Bodenhausen, and R. R. Ernst, J. Magn. Reson. 55, 88 (1983).

<sup>23</sup> R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford University Press, New York, 1987).

<sup>24</sup> J. H. Shirley, Phys. Rev. **138**, B979 (1965).

<sup>25</sup> A. J. Pell, G. Kervern, L. Emsley, M. Deschamps, D. Massiot, P. J. Grandinetti, and G. Pintacuda, J. Chem. Phys. **134**, 024117 (2011).

<sup>26</sup> A. J. Pell, K. J. Sanders, S. Wegner, G. Pintacuda, and C. P. Grey, J. Chem. Phys. 146, 194202 (2017).

<sup>27</sup> M. H. Levitt, J. Magn. Reson. 82, 427 (1989).

<sup>28</sup>M. Bak, J. T. Rasmussen, and N. C. Nielsen, J. Magn. Reson. 147, 296 (2000).

<sup>29</sup>L. Braunschweiler and R. R. Ernst, J. Magn. Reson. **53**, 521 (1983).

<sup>30</sup>D. G. Davis and A. Bax, J. Am. Chem. Soc. 107, 2820 (1985).

<sup>31</sup>I. Scholz, B. H. Meier, and M. Ernst, J. Chem. Phys. 127, 204504 (2007).

<sup>32</sup>A. Venkatesh, I. Hung, K. C. Boteju, A. D. Sadow, P. L. Gor'kov, Z. Gan, and A. J. Rossini, "Suppressing 1H Homonuclear Spin Diffusion in Fast MAS 1H-X NMR Experiments," Solid State Nucl. Magn. Reson. (submitted).

<sup>33</sup>W. I. Goldburg and M. Lee, Phys. Rev. Lett. 11, 255 (1963).

<sup>34</sup>M. Lee and W. I. Goldburg, Phys. Rev. 140, A1261 (1965).