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Solid-state NMR indirect detection of nuclei experiencing large anisotropic interactions using spinning sideband-selective pulses

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ABSTRACT

Under Magic-Angle Spinning (MAS), a long radio-frequency (rf) pulse applied on resonance achieves the selective excitation of the center-band of a wide NMR spectrum. We show herein that these rf pulses can be applied on the indirect channel of Hetero-nuclear Multiple-Quantum Correlation (HMQC) sequences, which facilitate the indirect detection via spin-1/2 isotopes of nuclei exhibiting wide spectra. Numerical simulations show that this indirect excitation method is applicable to spin-1/2 nuclei experiencing a large chemical shift anisotropy, as well as to spin-1 isotopes subject to a large quadrupole interaction, such as ^{14}N. The performances of the long pulses are analyzed by the numerical simulations of scalar-mediated HMQC (*J*-HMQC) experiments indirectly detecting spin-1/2 or spin-1 nuclei, as well as by dipolar-mediated HMQC (*D*-HMQC) experiments achieving indirect detection of ^{14}N nuclei via ^{1}H in crystalline γ-glycine and N-acetyl-valine samples at a MAS frequency of 60 kHz. We show on these solids that for the acquisition of *D*-HMQC spectra between ^{1}H and ^{14}N nuclei, the efficiency of selective moderate excitation with long-pulses at the ^{14}N Larmor frequency, $\nu_0(^{14}\mathrm{N})$, is comparable to those with strong excitation pulses at $\nu_0(^{14}\mathrm{N})$ or $2\nu_0(^{14}\mathrm{N})$ frequencies, given the rf field delivered by common solid-state NMR probes. Furthermore, the *D*-HMQC experiments also demonstrate that the use of long pulses does not produce significant spectral distortions along the ^{14}N dimension. In summary, the use of center-band selective weak pulses is advantageous for HMQC experiments achieving the indirect detection of wide spectra since it (i) requires a moderate rf field, (ii) can be easily optimized, (iii) displays a high robustness to CSAs, offsets, rf-field inhomogeneities, and fluctuations in MAS frequency, and (iv) is little dependent on the quadrupolar coupling constant.

1. Introduction

Nuclear magnetic resonance (NMR) is a powerful spectroscopy that provides precious insights into the structure and the dynamics of solids. Contrary to diffraction methods, NMR is suitable for well crystallized samples, but also for amorphous or glass compounds. In particular, two-dimensional (2D) hetero-nuclear correlation (HETCOR) experiments are key tools of the solid-state NMR spectroscopy to probe through-bond connectivities or through-space proximities between distinct isotopes [1–4]. The connectivities and the proximities are revealed by coherence transfers via *J*- or dipolar couplings, respectively.

However, 2D HETCOR experiments are still challenging for isotopes exhibiting wide spectra that are spread over hundreds or thousands of kHz. This situation is encountered in paramagnetic and conductive samples [5,6], in which the NMR spectra are broadened by the interactions between the nuclei and the unpaired or conduction electrons. It is also encountered in diamagnetic samples since: (i) about 75% of all NMR active nuclides have a spin $I \geq 1/2$ and can thus be subject to a large quadrupole interaction [3,4], and (ii) the spin-1/2 'heavy' isotopes, such as ^{119}Sn, ^{195}Pt, ^{199}Hg and ^{209}Pb, are subject to large chemical shift anisotropies (CSA) [7]. HETCOR experiments for nuclei displaying wide spectra face many challenges. First, the detection bandwidth of the probe can be narrower than the 1D spectrum, which hence requires the piecewise acquisition of the 2D HETCOR spectrum. Second, even when the 1D spectrum does lie into the probe detection bandwidth, the radio-frequency (rf) fields delivered by usual solid-state NMR probes are often insufficient to achieve efficient and uniform excitation of wide powder patterns, in particular for nuclei with low gyromagnetic ratios (γ). Third, the

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uniform excitation of quadrupolar nuclei with several energy levels in a static magnetic field is difficult due to the intricate spin dynamics in the simultaneous presence of rf fields and sample rotation.

Several methods have been proposed recently for wide-line HETCOR experiments. Very short small-flip angle pulses allow the excitation of wide spectra. However, this is at the expense of a decreased sensitivity. For instance, they have been used in $^{1}H \rightarrow {}^{13}C$ dipolar-mediated INEPT (*D*-INEPT) for paramagnetic samples [8], and in *D*-HMQC experiments, such as ^{13}C–{^{14}N} for peptides [9,10], and ^{1}H–{^{23}Na} or ^{31}P–{^{23}Na} with STMAS quadrupolar filter (*D*-HMQC-ST) [11]. However, longer pulses are also used for the excitation of nuclei experiencing large anisotropic interactions. For instance, HETCOR experiments involving half-integer spin quadrupolar nuclei often employ pulses selective for the central transition, which last about 10 μs, since this transition is not broadened by the first-order quadrupole interaction [12–18]. The excitation of ^{14}N nuclei in HMQC experiments on solids is typically achieved using rf pulses lasting from 10 to 20 μs with amplitude of $\nu_1 \approx 50$ kHz [19–24]. These long ^{14}N pulses, which correspond to flip angles ranging from 180° to 360°, instead of 90° for HMQC applied to liquid samples, have been found using experimental optimization, but the reason of their efficiency is not known yet, and the influence of their length and strength on the transfer efficiency has not been investigated in details. Note also that ^{13}C–{^{14}N} *J*-HMQC experiments have recently been achieved by applying very long ^{14}N rf pulses of 1–2 ms at rf amplitude of $\nu_1 \approx 40$ kHz [25].

Adiabatic pulses with modulation of the rf field amplitude and frequency have also been demonstrated to effectively increase the excitation bandwidth of cross-polarization (CP) transfer for static samples [26,27]. The adiabatic CP has also been applied under Magic-Angle Spinning (MAS) conditions [28–32], but to the best of our knowledge, adiabatic CP transfers have not yet been used to acquire HETCOR MAS 2D spectra with a wide-line spectral dimension. Indeed, interferences between frequency swept adiabatic pulses and spin interactions modulated under MAS limit the bandwidth of the CP transfer [32]. Trains of rotor-synchronized short pulses in the manner of Delays Alternating with Nutation for Tailored Excitation, DANTE [33,34], have been recently employed for broadband excitation of quadrupolar nuclei in 2D HETCOR MAS experiments using HMQC [35–37] or CP pulse sequences [38–42].

Here, we investigate the conditions under which pulses lasting tens of microseconds efficiently excite wide-line spectra in the indirect dimension of HMQC experiments. We focus on the HMQC sequence because it is one of the most simple, efficient and robust HETCOR method to correlate spin-1/2 and quadrupolar nuclei. In particular, HMQC sequences using indirect detection via protons are advantageous in terms of sensitivity at high MAS frequencies, ν_R [43]. Note that besides HMQC, long rectangular pulses have been used for other NMR experiments, including: (i) the selective saturation of an entire family of spinning sidebands to simplify the spectrum [34], (ii) the "FAst Spinning gives Transfer Enhancement at Rotary resonance" (FASTER) method in MQMAS experiment [44–46], (iii) the Rotational-Echo Saturation-Pulse Double-Resonance (RESPDOR) [47–52] and Low-Alpha/Low-Amplitude Rotational-Echo DOuble-Resonance (LA-REDOR) [53–55] methods to quantify the dipolar dephasing of one spin-1/2 nucleus coupled to one isotope experiencing large anisotropic NMR interactions, and (iv) techniques for selectively exciting under MAS a subset of crystallites from a powder sample [56]. In RESPDOR and LA-REDOR experiments, it has been demonstrated that long rf pulses scramble the magnetization of nuclei that are subject to large anisotropic NMR interactions. For powder samples, this scrambling results in an apparent saturation, i.e. the cancellation of all powder-averaged populations and coherences [34,50,54].

The present article analyzes the performances of rf pulses for the indirect excitation of wide-line spectra in HMQC experiments. We compare the efficiency and the robustness of rectangular pulses applied to the indirectly detected nuclei with or without DANTE rotor-synchronized repetition. In particular, we show that in both cases the indirectly detected nuclei experiencing large anisotropic NMR interactions can be manipulated efficiently using either short pulses achieving broadband excitation or long pulses producing spinning sideband-selective excitation. The first regime is in principle the most efficient but it requires high rf field strengths that may not be compatible with the specifications of the probe, especially for low-γ isotopes. In that case, we demonstrate that an efficient alternative is the use of long center-band-selective pulses, which require moderate rf field strengths and benefit from good robustness to rf field inhomogeneity, offset and MAS instabilities.

The analysis will be performed for an indirectly detected *I* nucleus with a spin value of either 1/2 or 1. In the first case we have chosen ^{195}Pt, which is known to be often subject to a very large CSA, whereas for the second case, we have chosen ^{14}N which is subject to a large quadrupole interaction. In order to simplify the discussion, in the following the detected nucleus will always be ^{1}H, but obviously the same results should apply to any spin-1/2 nucleus.

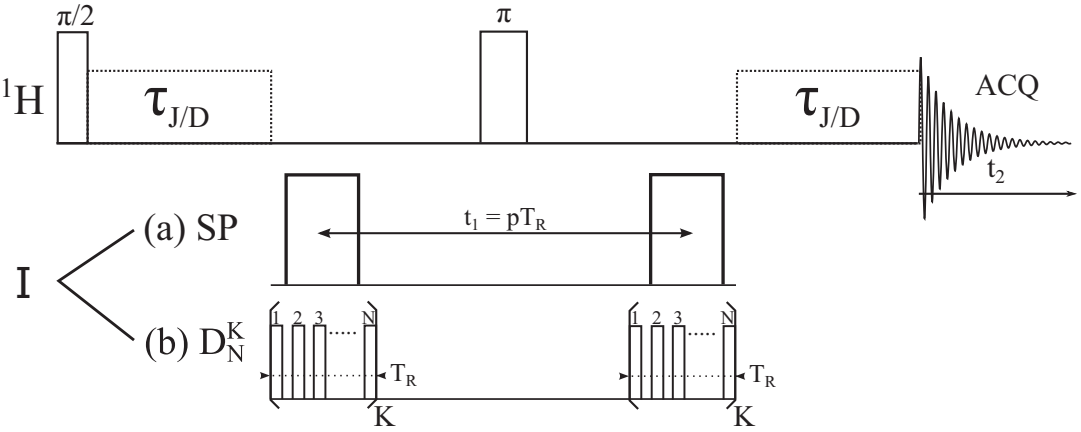

Fig. 1. ^{1}H–{*I*} HMQC pulse sequences. Lines (a) and (b) describe the two optional irradiations that are sent on the *I* channel for the excitation and reconversion of heteronuclear MQ coherences: either (a) two rectangular single pulses (SP) or (b) two D_N^K DANTE schemes. In the case of *J*-HMQC, no rf irradiation is applied during $\tau_{J/D}$ delays, whereas a dipolar recoupling sequence, such as $SR4_1^2$, is applied during $\tau_{J/D}$ in case of *D*-HMQC sequence.