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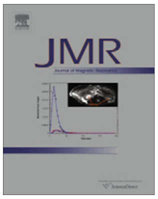

Probing proximities between different quadrupolar isotopes using multi-pulse cross-polarization

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ABSTRACT

We present a novel cross-polarization MAS NMR pulse sequence to probe proximities between half-integer quadrupolar isotopes. This sequence employs a multi-pulse cross-polarization (MP-CP) transfer, instead of the previous continuous-wave CP (CW-CP) transfer. With respect to CW-CP transfers, our sequence is more robust with respect to offsets and Rotary Resonance Recoupling detrimental effects, especially when taking into account rf-inhomogeneity. Moreover, by using a frequency splitter and a single channel MAS probe, this MP-CP sequence may allow analyzing the through-space connectivities between two isotopes with half-integer spin values and close Larmor frequencies.

1. Introduction

Solid-state Nuclear Magnetic Resonance (NMR) is a powerful spectroscopy, which allows probing the short-range order in crystalline, disordered or amorphous solid samples. This short-range order can be determined by the analysis of through-space or through-bond NMR correlation spectra, using coherence transfers via dipolar or *J*-scalar couplings, respectively. Herein, we consider the observation of correlations between different half-integer spin quadrupolar isotopes. Transfers of coherences between quadrupolar isotopes are not efficient owing to: (i) the short relaxation times of these coherences, (ii) the weak *J*-couplings of these nuclei, and (iii) the difficult dipolar recoupling under Magic-Angle Spinning (MAS) condition owing to the intricate spin dynamics of quadrupolar nuclei in the presence of sample rotation and radio-frequency (rf) field.

One-bond connectivities between quadrupolar nuclei have been probed using two-dimensional (2D) *J*-mediated Heteronuclear Multiple Quantum Correlation (*J*-HMQC) spectroscopy in between ^{27}Al and ^{17}O in ^{17}O-enriched crystalline grossite (CaAl$_2$O$_4$) [1], and ^{27}Al and ^{43}Ca in ^{43}Ca-enriched Ca-aluminate or Ca-alumino-silicate glasses [2]. To the best of our knowledge, the observation of heteronuclear correlation (HETCOR) spectra via two-bonds scalar-coupling has been precluded by the small magnitude of these ^{2}J-couplings compared to the transverse relaxation rate, $1/T_2'$, in spin-echo experiments.

Heteronuclear through-space proximities between quadrupolar nuclei (^{27}Al–^{17}O, ^{11}B–^{23}Na, ^{11}B–^{27}Al, ^{27}Al–^{7}Li) have been probed using continuous-wave cross-polarization (CW-CP), first in static samples [3,4], and more recently under MAS [5–9]. In particular, proximities between the different ^{11}B and ^{27}Al sites in magnesium alumino-borate glasses have been probed using 2D ^{11}B–{^{27}Al} dipolar-mediated heteronuclear correlation (*D*-HETCOR) with CW-CP coherence transfer [6,7]. High-resolution along the indirect ^{27}Al spectral dimension has even been achieved by combining in *D*-HETCOR experiment a CW-CP transfer with a multiple-quantum (MQ) quadrupolar filter [8]. However, the efficiency and the robustness of CW-CP transfers are limited owing to the complex spin dynamics during spin-locking, which depends on several parameters, including: (i) the amplitude of the electric field gradient (efg), and (ii) the orientation of its principal axis systems (PAS$_Q$) with respect to a rotor-fixed frame, (iii) the MAS frequency, ν_R, and (iv) the rf-field amplitude, ν_1. First, depending on the orientation of the PAS$_Q$ with respect to the rotor-fixed frame, the instantaneous quadrupolar splitting changes of sign ('zero crossing') twice or four times per rotor period. Second, in CW-CP experiments, the spin-locking of the central transition (CT) of a half-integer quadrupolar nucleus requires the use of weak CT-selective rf-field, at the expense of a high sensitivity to offsets on this channel [10,11]. Third, the Rotary Resonance Recoupling (R^3) conditions [10–13] should be avoided since they have a detrimental effect on the spin-locking efficiency. In the case of CW-CP transfer between two half-integer spin quadrupolar isotopes, twice more energy-level zero-crossings occur every rotor period, and the sensitivity to offsets extends to both channels. As a conclusion, the lack of robustness of CW-CP involving two quadrupolar isotopes has limited its applications.

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We have shown that the robustness of CP transfers between spin-1/2 and half-integer quadrupolar nuclei can be improved by replacing the CW irradiation on the quadrupolar channel by a burst of rotor-synchronized rf-pulses [14]. The advantage of this multi-pulse CP (MP-CP) has also been rediscovered in the case of ^{2}H–^{13}C CP transfers using optimal control method [15].

In this article, we propose the use of MP-CP transfers to probe under MAS the proximities between half-integer quadrupolar nuclei. The *D*-HETCOR sequence with MP-CP is more robust with respect to offsets than with CW-CP, because the spin-locking of the two quadrupolar magnetizations is performed with MP-CP using shorter rf-pulses with larger rf-field, instead of a long low-power rf-pulse used with CW-CP. Moreover, the R^3 conditions are much more separated in MP-CP than in CW-CP, also leading to an increased robustness of MP-CP transfer with respect to rf-field homogeneity.

2. MP-CP MAS *D*-HETCOR sequence and extended Hartmann–Hahn conditions

The 2D MP-CP MAS *D*-HETCOR sequence dedicated to half-integer quadrupolar nuclei is shown in Fig. 1. In the following, the indirectly detected isotope is denoted *I*, whereas *S* is the observed isotope. It is based on the conventional CP scheme, in which the two continuous-wave spin-lock irradiations in CW-CP are replaced by two trains of rotor-synchronized rf-pulses in MP-CP [14]. The rotor-synchronization means that the centers of two consecutive rf-pulses applied to a given isotope are separated by an integer number of rotor period, T_R. In the present work, we only employ rf-pulses separated by one rotor period. The phases of rf-pulses on each channel are constant in MP-CP, and they are shifted by 90° relative to the initial 90° CT-selective excitation pulse on the *I* channel. The sequence only uses weak rf-amplitudes in order to selectively manipulate the CTs of both isotopes, which thus behave under this condition as two fictitious spin-1/2 nuclei. Indeed, a low rf-field in the order of a few kHz does not affect satellite transitions and thus avoids uncontrollable transfers to satellite coherences. The signal observed in the *S* channel is the sum of that excited by the pulse train on this channel and that arising from the CP transfer. In order to disentangle these two contributions, we used a 'spin temperature inversion' phase cycling [16]. In this two-step phase cycling, the phases of the receiver and the initial excitation 90° pulse on *I* channel are cycled over 0° and 180°, whereas the phases of rf-pulse trains on *I* and *S* channels are unchanged.

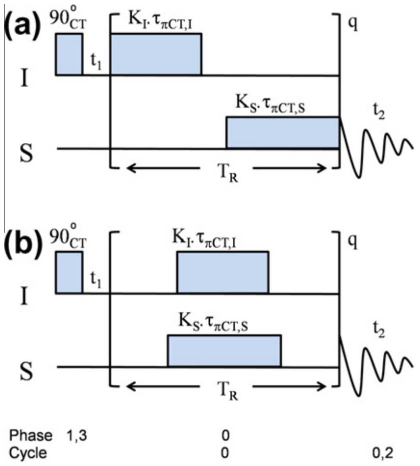

Fig. 1. Pulse sequences for *D*-HETCOR experiments using a MP-CP MAS transfer between two half-integer quadrupolar nuclei. After the initial CT-selective 90° pulse, two rotor synchronized pulse trains are applied on the two channels during $\tau_{CP} = qT_R$. The two pulse trains can be either interleaved (a) or synchronous (b). *K* is the ratio between the actual pulse length and that of a CT-selective π-pulse with same rf-field. When the sum of the two pulse lengths is smaller than one rotor period, there is a spacing between them in (a).

In Fig. 1a, all rf-pulses are interleaved to avoid any simultaneous irradiation on the two channels. This is mandatory when using an over-coupled resonator that provides two tuning and matching conditions in a single channel in order to cross-polarize two nuclei with close Larmor frequencies [17]. On the contrary, the sequence shown in Fig. 1b uses two synchronous pulse trains, and hence can only be utilized, with selective filters, when both Larmor frequencies are very different. During the two CT-selective pulse trains, the dephasings related to first-order anisotropic interactions are averaged out by MAS over full rotor periods, while rotor-synchronized pulses act in average as spin-lock irradiations. Indeed, in both channels the successive rf-pulses rotate the CT magnetizations about the rf-fields. The projections of the magnetizations along these two rf-fields are therefore constant, which lead to their spin-locking. Of course, this is true only: (i) if non-refocusable transverse relaxation times (instead of longitudinal relaxation times in the rotating frame, $T_{1\rho}$, in CW-CP) are long enough to avoid signal decay during the spin-lock period, $\tau_{CP} = qT_R$, where *q* is the number of rf-pulses in the MP-CP pulse trains, (ii) if R^3 conditions are avoided, and (iii) if dephasings produced by offsets are not too large. Globally, the continuous spin-locking of both magnetizations in CW-CP is thus replaced in MP-CP by a spin-locking 'in average' obtained by rotating each CT magnetization about its applied effective rf-field.

The lengths of MP-CP pulses on *I* and *S* channels, τ_I and τ_S, respectively, can be defined with respect to those of the CT-selective π-pulses using the same rf-field, $\tau_{\pi CT,I}$ and $\tau_{\pi CT,S}$, respectively:

$$\tau_I = K_I \tau_{\pi CT,I} \quad \text{and} \quad \tau_S = K_S \tau_{\pi CT,S} \tag{1}$$

with

$$\tau_{\pi CT,I}\ [\mu s] = 500/\{(I+1/2)\nu_{1,I}\} \quad \text{and}$$
$$\tau_{\pi CT,S}\ [\mu s] = 500/\{(S+1/2)\nu_{1,S}\} \tag{2}$$

where $\nu_{1,I}$ and $\nu_{1,S}$ are the actual nutation rf-fields given in kHz, measured in the absence of quadrupole interaction, e.g. in a liquid sample. As example, for a spin-5/2 nucleus, if the rf-pulse specifications are: $\tau_I = 8.33$ μs and $\nu_{1,I} = 10$ kHz ($\tau_{\pi CT,I} = 16.67$ μs), then $K_I = 0.5$.

The original CW-CP Hartmann–Hahn (H–H) matching condition for spin-1/2 nuclei in static solids [18], has been first extended to samples under MAS rotation [19], and then to half-integer quadrupolar nuclei submitted to weak CT-selective pulses [20]:

$$(S+1/2)\nu_{1,S} = \varepsilon(I+1/2)\nu_{1,I} + J\nu_R \tag{3}$$

where $\varepsilon = +1$ for the zero-quantum (ZQ: 'flip–flop') or $\varepsilon = -1$ for the double-quantum (DQ: 'flop–flop') terms of heteronuclear dipolar interaction [21,22]. These terms lead to CP transfers of opposite signs. The last term, with $J = 0, \pm1, \pm2, \pm3, \ldots$, is related to the sample rotation, and at ultra-fast MAS, transfers related to $J = \pm1$ or ±2 are the most efficient. Eq. (3) has been adapted to MP-CP MAS transfers including one spin-1/2 and one half-integer quadrupolar nuclei [14]. To do so, the continuous rf-field in CW-CP has been replaced in MP-CP by the effective rf-field which takes into account the rf pulse lengths described in Eq. (1) [14]. It can easily be extended to include two half-integer quadrupolar nuclei submitted to weak CT-selective pulses:

$$K_S = \varepsilon K_I + 2J \tag{4}$$

A partial signal cancelation occurs when there is one CT-selective π-pulse sent in each channel every rotor period (Eq. (1): $K_I = K_S = 1$) because simultaneous transfers via zero-quantum ($\varepsilon = +1$, $J = 0$) and double-quantum ($\varepsilon = -1$, $J = 1$) coherences occur and the