Journal of Magnetic Resonance 245 (2014) 94–97

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Communication

COMPOZER-based longitudinal cross-polarization via dipolar coupling under MAS

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ARTICLE INFO

Article history:
Received 17 April 2014
Revised 30 May 2014
Available online 24 June 2014

Keywords:
Cross polarization
Flip–flop exchange
Magic-angle spinning

ABSTRACT

We propose a cross polarization (CP) sequence effective under magic-angle spinning (MAS) which is tolerant to RF field inhomogeneity and Hartmann–Hahn mismatch. Its key feature is that spin locking is not used, as CP occurs among the longitudinal (Z) magnetizations modulated by the combination of two pulses with the opposite phases. We show that, by changing the phases of the pulse pairs synchronized with MAS, the flip–flop term of the dipolar interaction is restored under MAS.

Cross polarization (CP) is a technique often used to overcome the low sensitivity of dilute spins, e.g. ^{13}C, by magnetization transfer from abundant spins, e.g. ^{1}H. In general, CP requires both spin locking and Hartmann–Hahn matching [1,2]. The basic CP sequence employs continuous-wave (CW) radio-field (RF) irradiation for spin locking. Levitt et al. suggested a modification to the spin-locking pulse, known as mismatch-optimized *I–S* transfer (MOIST) [3], to alleviate the effect of RF field inhomogeneities by repeated phase inversions. Later, the phase inversion scheme was combined with magic angle spinning (MAS), leading to a sequence referred to as simultaneous phase-inversion CP (SPICP) [4,5]. Since then, various CPMAS methods with amplitude-, phase- and/or frequency-modulation have been proposed. They include variable-amplitude cross polarization (VACP) [6], amplitude-modulated cross polarization (AMCP) [7], ramped-amplitude cross polarization (RAMP-CP) [8], frequency sweep cross polarization (FSCP) [9], nuclear integrated cross polarization (NICP) [10], and simultaneous adiabatic spin-locking cross polarization (SADIS CP) [11].

Recently, we proposed a CP sequence which does not use the spin-locking pulse but instead employs a series of phase-inverted 2π pulses. This method, called composite zero-degree pulse CP (COMPOZER [12]), induces transfer of longitudinal (*Z*) magnetizations. Even though this unique CP technique was shown to be effective for static samples with tolerance against RF field inhomogeneity and Hartmann–Hahn mismatch, its CP efficiency almost diminishes under MAS where the heteronuclear dipolar interaction gains time dependence.

In this paper, we propose a CP scheme under MAS which retains the merits of COMPOZER, such as tolerance for RF field inhomogeneity and robustness against Hartmann–Hahn mismatch. This method employs phase modulation in such a way that the relevant parts of the dipolar Hamiltonian gain additional time dependence by spin rotation around the *Z* axis in the interaction frame. For this reason, we call the new CP sequence as COMPOZER with *Z* rotation (CPZ).

We consider a heteronuclear two spin system (*I* and *S*), whose dipolar interaction in the conventional rotating frame is given by the Hamiltonian,

$$\mathcal{H}_d = dI_zS_z. \tag{1}$$

d denotes the geometrical part of the heteronuclear dipolar interaction given by

$$d = -\frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}(3\cos^2\theta - 1), \tag{2}$$

where γ_X represents the gyromagnetic ratio for the *X* spin, and r_{IS} and θ are the internuclear $I-S$ distance and the angle between external magnetic field and the $I-S$ vector, respectively. μ_0 is the vacuum permeability, thus the constant $\mu_0/4\pi$ represents Eq. (2) to be in SI units.

The basic sequence of COMPOZER is written as $-(2\pi)_X-(2\pi)_Y-$, where $(2\pi)_\phi$ denotes two 2π pulses with a phase ϕ applied to both *I* and *S* spins simultaneously. The zeroth order average Hamiltonian over two 2π pulse periods is given by [12],

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http://dx.doi.org/10.1016/j.jmr.2014.06.003
1090-7807/

$$\overline{\mathcal{H}_d} = \frac{d}{8}\{4I_zS_z + (I^+S^- + I^-S^+)\}. \tag{3}$$

The flip–flop term, $I^+S^- + I^-S^+$, indicates that CP occurs between the Z magnetizations. Under MAS, however, d becomes time dependent;

$$d \to d(t) = D_1\cos(\omega_r t + \psi) + D_2\cos(2\omega_r + 2\psi), \tag{4}$$

with

$$D_1 = \sqrt{2}\frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\sin 2\beta \tag{5}$$

and

$$D_2 = -\frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\sin^2\beta, \tag{6}$$

where ω_r represents the MAS rate, and β and ψ are a polar angle and an azimuthal angle that orient the I–S vector $\mathbf{r}_{IS}$ with respect to the MAS rotation axis. Eq. (4) indicates that $d(t)$ is averaged out under MAS, leading to inefficient CP.

The basic idea of modification is to add rotation around the Z axis to the spin part of the Hamiltonian,

$$\begin{aligned}\overline{\mathcal{H}_d} &= d(t) \times e^{i\omega(I_z - S_z)t}(I^+S^- + I^-S^+)e^{-i\omega(I_z - S_z)t} \\ &= d(t) \times (e^{-i2\omega t}I^+S^- + e^{i2\omega t}I^-S^+).\end{aligned} \tag{7}$$

It becomes possible to interfere the MAS averaging by matching the Z rotation rate ω to $\omega_r/2$ or ω_r. In this work, we rotate the phase of the RF pulses to realize the Z rotation. The basic sequence of CPZ consists of pairs of phase alternating two pulses $\theta_\phi - \theta_{\bar{\phi}}$ (Fig. 1a), where θ_ϕ denotes a pulse with the flip angle of θ and a phase of ϕ. Similar to COMPOZER, the $\theta_\phi - \theta_{\bar{\phi}}$ pulse pair is applied to both I and S spins simultaneously.

The CPZ sequence consists of N pairs of the phase-alternated pulse blocks for every two rotor periods. The RF irradiation phase of the nth pair, $\Phi_n = (\phi_n^I, \phi_n^S)$ $(n = 1, \cdots, N)$, is set to be

$$\phi_n^I = -2\pi \times \frac{n}{N} + (n-1)\pi, \tag{8}$$

$$\phi_n^S = 2\pi \times \frac{n}{N}, \tag{9}$$

where ϕ_n^X denotes the RF phase for the X (X = I or S) spin. Note that the opposite sign for ϕ_n^I and ϕ_n^S reflects the opposite direction of the Z rotation for I and S in Eq. (7). The propagator for the RF irradiation with the phase Φ_n, $U_{RF}^{\Phi_n}(t)$, is written as

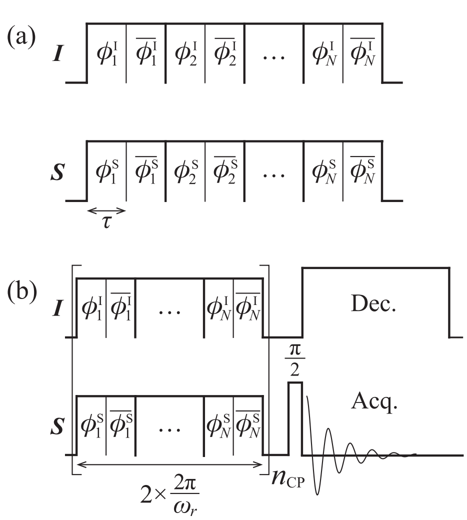

Fig. 1. Pulse sequences for CPZ: (a) pairs of two pulses with phase alternation and (b) the CPZ sequence followed by a single pulse sequence with I-spin decoupling. The inverted phase $\overline{\phi_n^X} = \phi_n^X + \pi$ denotes the RF phase for the X (X = I or S) spin.

$$\begin{aligned}U_{RF}^{\Phi_n}(t) &= e^{-i\omega_{1I}(I_x\cos\phi_n^I - I_y\sin\phi_n^I)t}e^{-i\omega_{1S}(S_x\cos\phi_n^S - S_y\sin\phi_n^S)t} \\ &= e^{-i\phi_n^I I_z}e^{-i\omega_{1I}I_x t}e^{i\phi_n^I I_z}\cdot e^{-i\phi_n^S S_z}e^{-i\omega_{1S}S_x t}e^{i\phi_n^S S_z},\end{aligned} \tag{10}$$

where ω_{1I} and ω_{1S} are RF nutation frequencies of I and S spin, respectively. The dipolar Hamiltonian in the interaction frame of RF irradiation is given by

$$\begin{aligned}\widetilde{\mathcal{H}}_d^{\Phi_n}(t) &= \left\{U_{RF}^{(n)}(t)\right\}^{-1}\mathcal{H}_d U_{RF}^{(n)}(t) = \frac{d(t)}{2} \times \{I_zS_z(\cos\Delta t + \cos\Sigma t) \\ &\quad + (\sin\phi_n^I\sin\phi_n^S I_xS_x - \sin\phi_n^I\cos\phi_n^S I_xS_y - \cos\phi_n^I\sin\phi_n^S I_yS_x \\ &\quad + \cos\phi_n^I\cos\phi_n^S I_yS_y)(\cos\Delta t - \cos\Sigma t) \\ &\quad + (-\sin\phi_n^I I_xS_z + \cos\phi_n^I I_yS_z)(\sin\Delta t + \sin\Sigma t) \\ &\quad - (-\sin\phi_n^S I_zS_x + \cos\phi_n^S I_zS_y)(\sin\Delta t - \sin\Sigma t)\},\end{aligned} \tag{11}$$

where Σ and Δ are the sum $\Sigma = \omega_{1I} + \omega_{1S}$ and the difference $\Delta = \omega_{1I} - \omega_{1S}$ of the RF amplitudes, respectively. For the phase-inverted pair of pulses, the Hamiltonian, $\widetilde{\mathcal{H}}_d^{\overline{\Phi_n}}(t)$, can be obtained in the same manner, and we assume that the zeroth order average Hamiltonian for $\theta_{\Phi_n} - \theta_{\overline{\Phi_n}}$ is given simply by

$$\overline{\widetilde{\mathcal{H}}_d^{(n)}} = \frac{1}{2\tau}\left\{\int_{2(n-1)\tau}^{(2n-1)\tau}\widetilde{\mathcal{H}}_d^{\Phi_n}(t)\,dt + \int_{(2n-1)\tau}^{2n\tau}\widetilde{\mathcal{H}}_d^{\overline{\Phi_n}}(t)\,dt\right\}, \tag{12}$$

where τ is the pulse width. Note that the pulse width τ is given by

$$\tau = \frac{\tau_r}{N}, \tag{13}$$

with τ_r being the rotor period ($\tau_r = 2\pi/\omega_r$). The flip angle of the pulse θ_X (X = I or S) is therefore written as

$$\theta_X = \omega_{1X}\frac{\tau_r}{N}. \tag{14}$$

We found that for the case of a rotor cycle divided into eight (Fig. 1b), i.e., $N = 8$, the "$\sin\Delta t$" and "$\sin\Sigma t$" terms in Eq. (11) vanish after averaging over the 16 pulse periods (two rotor cycles). The total average Hamiltonian for the 8 pulse pairs is given by

$$\overline{\widetilde{\mathcal{H}}_d} = \frac{1}{8}\sum_{n=1}^{8}\overline{\widetilde{\mathcal{H}}_d^{(n)}} = f(\Delta,\Sigma)I_zS_z + g_1(\Delta,\Sigma)I^+S^- + g_2(\Delta,\Sigma)I^-S^+, \tag{15}$$

where $f(\Delta,\Sigma)$, $g_1(\Delta,\Sigma)$ and $g_2(\Delta,\Sigma)$ are functions of Δ and Σ. The exact formulae for f and g as well as detailed calculation of the above derivations will be reported elsewhere.

At $\Delta = 0$, Eq. (15) becomes

$$\overline{\widetilde{\mathcal{H}}_d} = \frac{\sqrt{2}D_1}{8\pi}\cdot e^{i\frac{3}{4}\pi S_z}(I^+S^- + I^-S^+)e^{-i\frac{3}{4}\pi S_z}, \tag{16}$$

with ignoring the Σ terms, whose contribution will be negligible when $\Sigma \gg \omega_r$. Eq. (16) shows that with the CPZ irradiation the flip–flop term is restored under MAS, which enables CP between the Z magnetizations. The $\Delta = 0$ condition means the equal pulse flip angle for I and S, $\theta_I = \theta_S$. It is true that the recoupling mechanism is not directly related to the original Hartmann–Hahn matching, but we shall call the condition as the Hartmann–Hahn condition in the following for ease of legibility.

We demonstrated the CPZ experiment for the ^{1}H-^{13}C system using adamantane. All NMR spectra were obtained at room temperature in a magnetic field of 9.4 T with Larmor frequencies of 400.2 MHz and 100.6 MHz for the ^{1}H and ^{13}C nuclei, respectively, on an OPENCORE spectrometer [13]. A Chemagnetics T3 MAS probe for a 3.2 mm rotor was used. The MAS frequency $\omega_r/2\pi$ was set to 20.00 kHz. The RF amplitudes for both ^{1}H and ^{13}C 90° pulses were about 100 kHz and that for the ^{13}C CPZ pulses was 50 kHz. The ^{1}H RF amplitude for CPZ was used as an experimental parameter as shown below. The pulse width and phase-modulation angle for TPPM decoupling with the RF amplitude of ca. 70 kHz were 11 µs and ±17.5°, respectively. The recycle delay used was 4 s in all