Solid State Nuclear Magnetic Resonance 36 (2009) 177–181

Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

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

Compensated DRAMA sequence for homonuclear dipolar recoupling under magic-angle spinning

Fang-Chieh Chou, Tim W.T. Tsai, Hsin-Kuan Lee, Jerry C.C. Chan *

Department of Chemistry, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei, Taiwan

ARTICLE INFO

Article history:
Received 27 July 2009
Received in revised form
29 September 2009
Available online 11 November 2009

ABSTRACT

The DRAMA sequence has been considered as the milestone in the development of homonuclear dipolar recoupling. Although it has a high efficiency for double-quantum excitation in spin 1/2 systems, it is seldom used today for real applications because of its susceptibility to the deteriorating effects of chemical shift anisotropy and resonance offsets. We show in this work that the practicability of DRAMA can be greatly enhanced by incorporating four π pulses with XY-4 phases into the basic DRAMA cycles. Average Hamiltonian theory is used to evaluate the performance of the resulting pulse sequence with respect to the compensation of chemical shift anisotropy. Numerical simulations and experimental measurements on hydroxyapatite indeed show that the performance of DRAMA-XY4 is very satisfying for ^{31}P DQ excitation, provided that the resonance offset is within the range of $[-4, 4]$ kHz.

1. Introduction

Development of homonuclear dipolar recoupling has been actively pursued for decades. The very first homonuclear dipolar recoupling method was developed by Tycko and co-workers, which has the acronym DRAMA (dipolar recovery at the magic angle) [19]. Later, Tycko and Smith attempted to improve the practicability of DRAMA on the basis of symmetry arguments [20]. Because the symmetry rules derived therein are only strictly obeyed in the delta-pulse limit, the improved DRAMA remains not very well compensated for chemical shift anisotropy (CSA) and resonance offset. Although DRAMA is not very robust for real applications, it has set the stage for the development of homonuclear dipolar recoupling. Nowadays, there are many elegant methods developed for homonuclear dipolar recoupling [15]. To certain extent, the design principles may be classified into two categories. In the first category, the delta-pulse approximation is used to design a concatenation of toggling states to achieve the desired average Hamiltonian. Typical techniques include DRAMA [19], RFDR [3], and BABA [9]. Alternatively, one may derive the target average Hamiltonian in the interaction frame transformed by the rf pulses of finite width. This class of pulse sequences has been unified in the C and R symmetry frameworks developed by Levitt and co-workers [16,4,5,7].

Currently, the average Hamiltonian associated with DRAMA or BABA has the largest amplitude, or the so-called scaling factor for homonuclear dipolar recoupling [16]. However, their uses for double-quantum (DQ) excitation are susceptible to the deteriorating effects of CSA and resonance offsets. In this work, we have developed a simple strategy to significantly enhance the practicability of DRAMA. The idea is to incorporate four π pulses with XY-4 [10] phases into DRAMA. The resulting pulse sequence is henceforth referred to as DRAMA-XY4. We show by numerical simulations and measurements on hydroxyapatite that the performance of DRAMA-XY4 is superior to finite-pulse RFDR (fp-RFDR) [13] for ^{31}P DQ excitation, provided that the resonance offset is within the range of ± 4 kHz.

2. Theory

2.1. Average Hamiltonian of DRAMA

We first consider the original DRAMA sequence, which has only two $\pi/2$ pulses in one rotor period. For a two-spin homonuclear system under MAS condition, the Hamiltonian is given by

$$H(t) = H_{CS}(t) + H_D(t) \tag{1}$$

$$H_{CS}(t) = \sum_{j=1}^{2} \sum_{m=-2}^{2} \omega^{j}_{CS,m} \exp(im\omega_R t) T^{j}_{10} \tag{2}$$

$$H_D(t) = \sum_{m=-2}^{2} \omega_{D,m} \exp(im\omega_R t) T_{20} \tag{3}$$

where $H_{CS}(t)$ and $H_D(t)$ denote the Hamiltonians due to chemical shifts and homonuclear dipole–dipole couplings, respectively; $\omega^{j}_{CS,m}$ and $\omega_{D,m}$ are the Fourier coefficients of the corresponding

* Corresponding author. Fax: +886 2 2363 6359.
E-mail address: chanjcc@ntu.edu.tw (J.C.C. Chan).

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doi:10.1016/j.ssnmr.2009.11.002

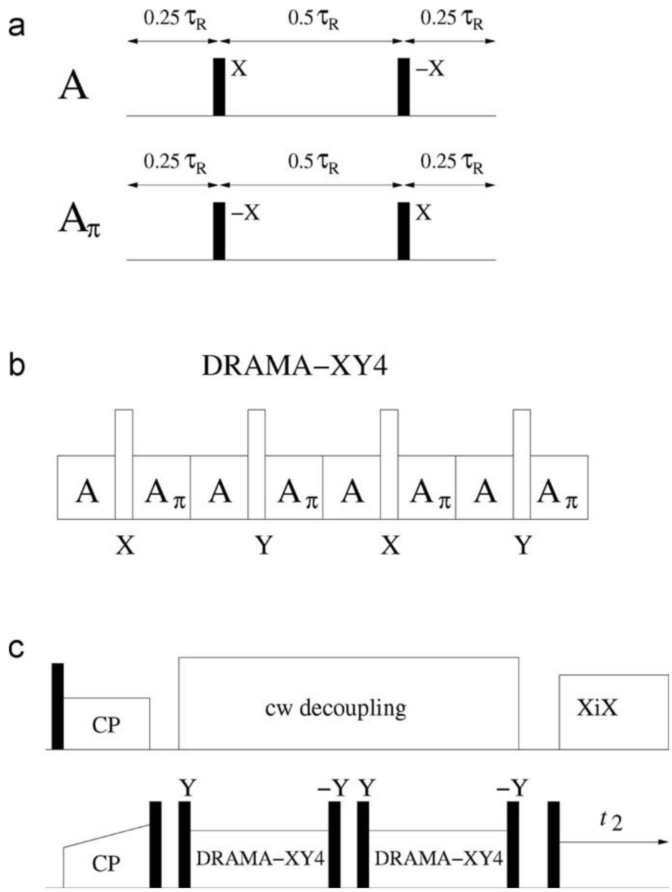

Fig. 1. Pulse sequence used in this work. (a) The basic cycle of DRAMA and its π-shifted cycle are denoted by A and A_π, respectively. The filled rectangles represent $\pi/2$ pulses. (b) By concatenating the cycles of A and A_π, one can generate a supercycle of eight rotor periods. Four π pulses with XY-4 phases (denoted by open rectangles) are then inserted on top of the supercycle to form the DRAMA-XY4. (c) The pulse sequence used for the ^{31}P DQ filtered experiments.

interactions; T^j_{10} and T_{20} are the first- and second-rank tensors, respectively, transformed by the z-components of the spin angular momentum operators. With reference to Fig. 1a, under the delta-pulse approximation, the time evolution operator of the basic DRAMA sequence can be calculated as

$$U(\tau_R)=U(\tau_R;\tfrac{3}{4}\tau_R)P_{-x}U(\tfrac{3}{4}\tau_R;\tfrac{1}{4}\tau_R)P_xU(\tfrac{1}{4}\tau_R;0) \tag{4}$$

where

$$U(\tau_2;\tau_1)=\hat{T}\exp[-i\int_{\tau_1}^{\tau_2}H(t)\,dt] \tag{5}$$

and

$$P_{\pm x}=\exp\left(\mp i\frac{\pi}{2}I_x\right) \tag{6}$$

Then the lowest-order average Hamiltonian can be calculated as

$$\overline{H}^{(1)}=\frac{1}{\tau_R}\left\{\int_0^{\tau_R/4}H(t)\,dt+\int_{\tau_R/4}^{3\tau_R/4}P_{-x}H(t)P_x\,dt+\int_{3\tau_R/4}^{\tau_R}H(t)\,dt\right\} \tag{7}$$

Thus,

$$\overline{H}^{(1)}_{CS}=\sum_{j=1}^{2}\left(\sum_{m=\pm1}\frac{2}{\pi}\omega^j_{CS,m}+\frac{\overline{\omega}^j_{CS}}{2}\right)(I_{jz}-I_{jy}) \tag{8}$$

and

$$\overline{H}^{(1)}_{D}=\sum_{m=\pm1}\frac{2}{\pi}\omega_{D,m}\frac{1}{\sqrt{6}}[(3I_{1z}I_{2z}-I_1\cdot I_2)-(3I_{1y}I_{2y}-I_1\cdot I_2)]$$

$$=\frac{3}{\pi\sqrt{2}}\left(-\frac{\mu_0}{4\pi}\frac{\gamma^2}{r^3_{12}}\right)\hbar\sin(2\beta_{PR})\cos(\gamma_{PR})(I_{1z}I_{2z}-I_{1y}I_{2y}) \tag{9}$$

As discussed by Tycko and co-workers [19,20], the lowest-order average Hamiltonian of DRAMA has large scaling factors for both the homonuclear dipolar interaction and the chemical shift interaction.

2.2. Compensated DRAMA

In this section, we describe how one can selectively suppress the effect of the chemical shift interaction. In the most general case, the original DRAMA has the following average Hamiltonian for the chemical shift:

$$\overline{H}_{CS}=aI_x+bI_y+cI_z \tag{10}$$

where the parameters a, b, and c depend on the crystallite orientation, the particulars of the pulse sequence, and the experimental imperfections. To reduce the size of the parameters a and b, we concatenate the regular DRAMA cycle by another π-shifted cycle to form an extended cycle. Without loss of generality, we rewrite the resultant average Hamiltonian as

$$\overline{H}_{CS}=a'I_x+b'I_y+cI_z \tag{11}$$

where a' and b' are the residual components due to the higher order effects. Next, we inserted four π pulses with the XY-4 phases as shown in Fig. 1b. The new cycle time of the resultant supercycle is equal to eight rotor periods, comprising four toggling states defined by the four π pulses. The Hamiltonian in each of the toggling state is written as

$$\overline{H}_1=a'I_x+b'I_y+cI_z \tag{12}$$

$$\overline{H}_2=a'I_x-b'I_y-cI_z \tag{13}$$

$$\overline{H}_3=-a'I_x-b'I_y+cI_z \tag{14}$$

$$\overline{H}_4=-a'I_x+b'I_y-cI_z \tag{15}$$

Consequently, the first-order average Hamiltonian of the supercycle becomes

$$\overline{H}^{(1)}=(\overline{H}_1+\overline{H}_2+\overline{H}_3+\overline{H}_4)/4=0 \tag{16}$$

and the second-order term is calculated as

$$\begin{aligned}\overline{H}^{(2)}&=-\frac{i}{2(8\tau_R)}\int_0^{8\tau_R}dt\int_0^t dt'[H(t),H(t')]\\&=-\frac{i}{2(8\tau_R)}\left\{\int_0^{2\tau_R}dt'[\overline{H}_1,H(t')]+\int_0^{4\tau_R}dt'[\overline{H}_2,H(t')]\right.\\&\quad\left.+\int_0^{6\tau_R}dt'[\overline{H}_3,H(t')]+\int_0^{8\tau_R}dt'[\overline{H}_4,H(t')]\right\}(2\tau_R)\\&=-\frac{i}{8}\{[\overline{H}_2,\overline{H}_1]+[\overline{H}_3,\overline{H}_1]+[\overline{H}_3,\overline{H}_2]+[\overline{H}_4,\overline{H}_1]+[\overline{H}_4,\overline{H}_2]\\&\quad+[\overline{H}_4,\overline{H}_3]\}(2\tau_R)=a'b'I_z\tau_R\end{aligned} \tag{17}$$

The second-order effect is also negligible when a' and b' are vanishingly small or when the spinning frequency is very fast. In the subsequent discussion, this compensated DRAMA is referred to as DRAMA-XY4. As shown in Eq. (9), the average Hamiltonian of DRAMA-XY4 with respect to homonuclear dipolar recoupling is a mixture of ZQ and DQ Hamiltonian. To obtain a pure DQ Hamiltonian, the sequence of DRAMA-XY4 can be flanked by a pair of $\pi/2$ pulses and the hence obtained DQ Hamiltonian has the