Intermolecular Double-quantum-filtered Zero-quantum Coherence in Liquid NMR

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Introduction

In the CRAZED sequence with $n = 0$ (ZQ-CRAZED) [1], the conventional single-quantum coherences (SQCs) due to imperfection in the first RF flip angle and the recovered longitudinal magnetization during the evolution period cannot be dephased after the second RF pulse, which may obscure the weak intermolecular zero-quantum coherence (iZQC) signals [1-3]. A double-quantum filtered iZQC pulse sequence was proposed to detect pure iZQC signals from isolated spin-1/2 systems. Experimental observations and computer simulations are in good accord with theoretical predictions. Compared to the ZQ-CRAZED sequence, the new sequence is insensitive to the imperfection of flip angles.

Methods

For the three-pulse sequence shown in Fig. 1, the coherence transfer pathways for an isolated spin-1/2 system are listed in Table I. The coherence order before the first RF pulse P_0 is zero. P_1, P_2, and P_3 are the coherence orders during t_0, t_1, and t_2, respectively. For [1]H, quadrature detection selectively detects the (−1)-coherence order, i.e. $P_3 = -1$. Table I indicates that there are zero-quantum (ZQ), ±double-quantum (±2Q), and other higher order coherences during the t_1 period. A four-step phase cycling scheme ($\varphi = x, y, -x, -y$) with receiver phase ($\varphi_{rec} = x, -x, x, -x$) is designed to obtain the signal originating from iZQC only created in the t_1 period. Analytical expression derived from the modified Torrey's equations with dipolar fields can be written as:

Table I. Coherence transfer pathways

P_0	P_1	P_2	P_3
0	−1	−2	−1
0	−2	0	−1
0	−3	+2	−1
…	…	…	…

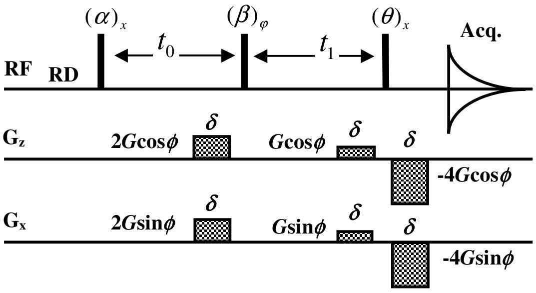

Fig. 1. Pulse sequence designed to detect pure iZQC signals.

$$M^{+}_{\text{iZQC}} \approx -\frac{3}{16}\gamma\mu_0\Delta_s(M_0)^2 t_2 \exp(\mathrm{i}\Delta\omega t_2)\exp(\mathrm{i}2\Delta\omega t_0)\sin^2\alpha\sin^2\beta\sin 2\theta. \quad (1)$$

Most 1H NMR experiments were performed on a Varian INOVA 600 NMR spectrometer at 298 K using a sample of water with 20% D_2O. The two-dimensional (2D) experiments were performed on a Varian Unity+ 500 spectrometer. The resonance offset of spins in rotating frame $\Delta\omega$ was set to 100 Hz.

Results and discussion

The 2D experimental spectrum from the three-pulse sequence without phase cycling displays intermolecular cross-peaks at –2Q- and ZQ-coherence frequencies in the indirectly detected dimension F_1 (Fig. 2(a)). When the four-step phase cycling scheme was used, only iZQC signal is observed (Fig. 2(b)). These results agree with theoretical predictions and are supported by the results of computer simulations shown in Fig. 2 (c) and (d) [4]. The experimental observations and simulated results of the relative signal intensity versus flip angles (α, β, or θ) show that the iZQC signal intensities are proportional to $\sin^2\alpha$ (Fig. 3(a)), $\sin^2\beta$ (Fig. 3(b)), and $\sin 2\theta$ (Fig. 3(c)). When $\alpha = \beta = 90°$ and $\theta = 45°$, maximal iZQC signal created in t_1 is achieved.

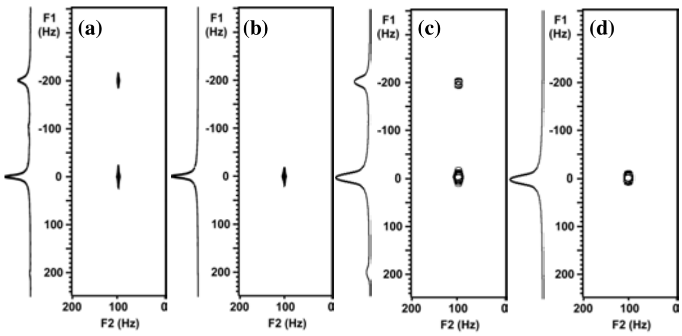

Fig. 2. (a)~(b) 2D experimental spectra (256×1024 data points) of water obtained from the pulse sequence shown in Fig. 1. (a) No phase cycling; (b) with four-step phase cycling; (c) and (d) are simulated results corresponding to (a) and (b), respectively. The flip angles of the pulses were all 80°.

The signal intensity expressed by Eq. (1) is proportional to $\Delta_s = (3\cos^2\phi - 1)/2$. Figure 4(a) shows the iZQC signals with $\alpha = \beta = 90°$ and $\theta = 45°$. The signal is almost null at $\phi = 54.7°$; and the relative amplitude at $\phi = 0°$ is twice as large as that at $\phi = 90°$. These results verify that the signal is indeed originating from intermolecular dipolar interactions. Moreover, when the flip angles are deviated 2/9 from the optimal values, i.e., 90° and 45° are replaced by 70° and 35°, the signal is also almost null at $\phi = 54.7°$, indicating that the sequence for the iZQC detection is insensitive to the precision of the flip angles (Fig. 4(b)). For the ZQ-CRAZED sequence, a two-step phase cycling of the second RF pulse between 45° and 135° has ever been used to remove the residual SQC signal [1]. The result (Fig. 4(c)) shows that the signal is not null at $\phi = 54.7°$, implying that the residual conventional SQC signals are not completely eliminated due to imperfect RF flip angles in practical experiments. When the flip angles are deviated 1/9 from the optimal values, the residual SQC signal at $\phi = 54.7°$ becomes much larger, indicating that the ZQ-CRAZED sequence is much more demanding on the correct setting of the flip angles.

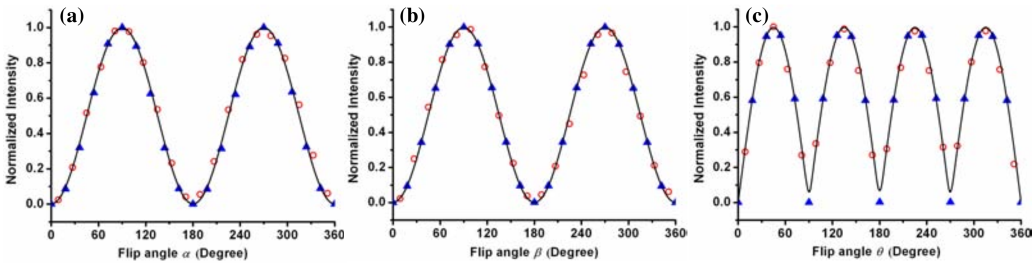

Fig. 3. The variation of iZQC signal amplitude with the flip angle of the (a) first pulse (α), (b) second pulse (β), and (c) third pulse (θ) for the three-pulse sequence, from 0 to 2π in an increment of $\pi/20$. The symbols "○" and "▲" indicate the experimental and simulated data, respectively. The solid line is drawn based on the theoretical expressions.

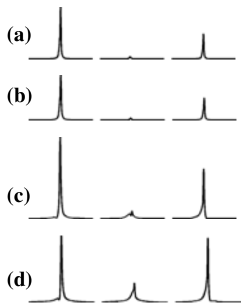

Fig. 4. (a) The iZQC signals obtained from the three-pulse sequence with exact optimal RF flip angles and different gradient orientations: $\phi = 0°$ (left), $\phi = 54.7°$ (middle), and $\phi = 90°$ (right); (b) signals corresponding to (a) with the flip angles deviated by a factor of 2/9 from the optimal values; (c and d) signals obtained from the ZQ-CRAZED sequence: (c) corresponding to (a) with optimal flip angles; (d) corresponding to (c) with the flip angles deviated by a factor of 1/9 from the optimal values.

Acknowledgments

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References

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