Spectroscopic and Imaging Observations of Intermolecular Single-quantum Coherence

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Introduction

When the CRAZED sequence with $n = \pm 1$ is applied to an isolated spin-1/2 sample, the observed signals are composed of intermolecular single-quantum coherence (iSQC) signal and residual conventional SQC signal. The latter is rather difficult to remove [1], especially for isolated spin-1/2 samples such as water, which are very important for *in vivo* MRI and high-resolution NMR [2]. A new pulse sequence with three radio-frequency (RF) pulses was designed to detect pure iSQC signals from isolated spin-1/2 systems. Experimental observations and computer simulations are in good accord with theoretical predictions. Compared to the CRAZED sequence, the new sequence is much less sensitive to imperfection of flip angle.

Methods

The new pulse sequence is shown in Fig. 1, together with the coherence transfer pathway of iSQC of an isolated spin-1/2 system. A four-step phase cycling scheme ($\varphi = x, y, -x, -y$) with the receiver phase ($\varphi_{rec} = x, y, -x, -y$) was designed to obtain pure iSQC signal created in the t_1 period. An analytical expression derived from the modified Torrey's equations with dipolar fields [3] can be written as:

$$M^{+}_{\mathrm{iSQC}} \approx \frac{1}{4}\gamma\mu_0\Delta_s(M_0)^2 t_2 \exp(\mathrm{i}\Delta\omega t_2)\exp(\mathrm{i}\Delta\omega t_1 + \mathrm{i}2\Delta\omega\delta)e^{-t_1/T_2}e^{-2\delta/T_2}e^{-t_2/T_1}e^{-t_2/T_2}$$
$$(1+\cos\alpha e^{-t_1/T_1} - e^{-t_1/T_1})\sin\alpha\sin\beta(1+\cos\beta)\sin\theta(1+\cos\theta) \quad (1)$$

Accordingly, the optimal flip angles of the three RF pulses are $\alpha = 45°$ and $\beta = \theta = 60°$.

Experiments were performed on a Varian INOVA 600 NMR scanner at 298 K. The sample for ^{1}H spectroscopic measurements was water with 20% D_2O. The resonance offset of spins in rotating frame $\Delta\omega$ was set to 100 Hz. Computer simulation [4] was also carried out to verify the theoretical predictions and experimental observations. Images were acquired with a phantom made of 2% (W/V) agarose gel in test tubes. The desirable iSQC signals were excited with the pulse sequence shown in Fig. 1, which was appended to a standard fast spin-echo (FSE) imaging sequence to form images.

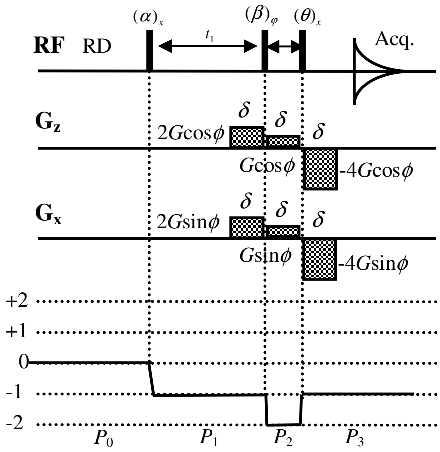

Fig. 1. Pulse sequence designed to detect pure iSQC signals.

Results and discussion

Figure 2(a) shows well-defined cross-peaks at –1Q- and –2Q-coherence frequencies in the indirectly detected dimension F_1 when no phase cycling is used. When the four-step phase cycling is used, the residual unwanted coherences are removed and only pure iSQC signal is observed (Fig. 2(b)). These results agree well with theoretical predictions, which are also supported by the computer simulations (Fig. 2(c) and (d)).

Figure 3(a) shows the iSQC signals with optimal RF filp angles. 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, the signal is still almost null at $\phi = 54.7°$, indicating that the three-pulse sequence for the iSQC detection is insensitive to the precision of the flip angles (Fig. 3(b)). In comparison, for the CRAZED sequence with a two-step phase cycling of the second RF pulse between 45° and 135°, the detected signal is not null at $\phi = 54.7°$ (Fig. 3(c)), 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 CRAZED sequence depends much more on the correct setting of the flip angles.

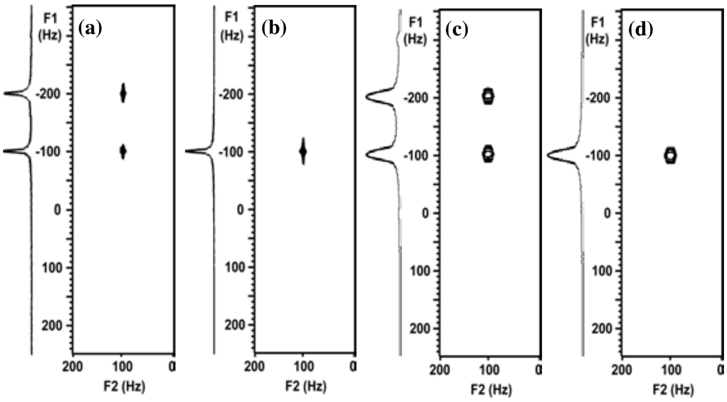

Fig. 2. (a)~(b) 2D experimental spectra (256×1024 data points) of the H_2O obtained from the pulse sequence shown in Fig. 1 with (a) no phase cycling, and (b) four-step phase cycling; (c) and (d) are simulated results corresponding to (a) and (b), respectively. The flip angles of the three pulses were deviated 1/9 from the optimal values.

Images of an agarose phantom are shown in Fig. 4. As predicted by theory, the signal almost vanishes when the coherence selection gradients were applied along the magic angle direction. The images have small ghosting artifacts along the phase direction because the iSQC-encoding gradients have unbalanced the FSE inter-echo spacing requirement. The iSQC images using FSE technique were obtained for the first time. FSE is a viable technique for producing iMQC MR images more quickly than spin echo.

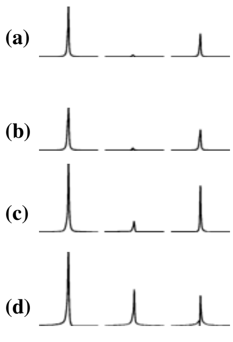

Fig. 3. (a) The iSQC signals obtained from the three-pulse sequence with exact optimal RF flip angles and different gradient orientations: $\phi = 0°$ (left), $\phi = 54.7°$ (middle), and $\phi = 90°$ (right); (b) signals corresponding to (a) with the flip angles deviated by a factor of 2/9 from the optimal values; (c and d) signals obtained from the 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.

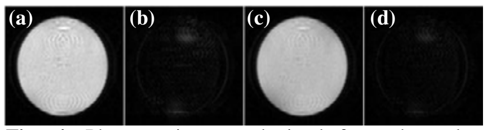

Fig. 4. Phantom images obtained from the pulse sequence shown in Fig. 1 appended to a standard fast spin-echo imaging sequence. (a) and (b) corresponding to exact optimal RF flip angles and different gradient orientations: $\phi = 0°$ (a) and $\phi = 54.7°$ (b), (c) and (d) corresponding to the flip angles deviated by a factor of 2/9 from the optimal values and different gradient orientations: $\phi = 0°$ (c) and $\phi = 54.7°$ (d).

Acknowledgments

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References

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