An effective fast acquisition scheme to achieve high-resolution MRS with J-coupling scaling via intermolecular multiple-quantum coherences

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Introduction

Intermolecular zero-quantum coherences (iZQCs) are not susceptible to magnetic field inhomogeneities over distances much larger than the dipolar correlation distance, and can be used to achieve 1D high-resolution spectra in inhomogeneous fields[1]. However, previous iZQC high-resolution methods are 2D spectra with chemical shifts (CSs) of solute evolutions in both F_1 and F_2 dimensions, so they demand a much longer acquisition time than their 1D counterparts. Intense water signal is also a great obstacle in iZQC MRS. In the iDH2, greatly narrowed F_1 spectral width enables a fast acquisition with more than 50-fold speedup. Since the experimental time is reduced dramatically, more phase cycling steps can be used so that the two solvent suppression modules, iDQF[2] and excitation sculpting[3], can be jointly utilized and water suppression efficiency is improved. Furthermore, high-resolution spectra with *J*-coupling scaling can be obtained by the iDH2 via manipulation of the t_1 period.

Methods

The iDH2 sequence (Fig. 1) can be interpreted in the raising and lowing operator formalism:

$$I_z S_z \xrightarrow{\frac{\pi}{2}I_x,\frac{\pi}{2}S_x} \frac{1}{4}I^+S^- \xrightarrow{\pi S_x} \frac{1}{4}I^+S^+ \xrightarrow{\frac{\pi}{2}I_x} \frac{1}{4}I_z S^+ \xrightarrow{\pi I_x,\pi S_x,D_{IS}I_zS_zt_2} \frac{1}{4}S^-, \qquad (1)$$

where *I* spin (corresponding to solvent) and *S* spins (corresponding to solutes) are spin-1/2 systems in a homogeneous liquid mixture. The iDH2 with 2 times scale-up of J-coupling constants (iDH2-2J) achieves fast acquisition by removing the CSs evolutions of solutes in the t_1 period and thus reducing the spectral width in the F_1 dimension. Owing to that all peaks present in a band near diagonal, fast acquisition can be achieved for iDH2 with unaltered *J*-coupling constants (iDH2-1J) by reducing the sampling rate in the t_1 dimension with subsequent foldover correction (FOC)[4] without information loss. The iDH2 with homonuclear decoupling (iDH2-0J) utilizes the constant time scheme and FOC together.

All experiments were performed at 298 K using a Varian NMR System 500 MHz with a 5 mm high-field indirect detection probe with 3D pulsed field gradient (PFG) modules. The W5 composite pulse[5] was used as the water-exclusive reversion pulse. The parameters of coherence selective gradients (CSGs) are $G' = 0.07$ T m^{-1} $\times 1.2$ ms, $G_1 = 0.14$ T m^{-1} $\times 1.2$ ms and $G_2 = 0.2$ T m^{-1} $\times 1.2$ ms, respectively. An 8-step phase cycling was applied: $\phi = (x, y, -x, -y, x, y, -x, -y)$, $\varphi = (x, x, x, x, -x, -x, -x, -x)$ and receiver = $(x, -x, x, -x, x, -x, x, -x,)$. 500×12 points for iDH2-1J and –0J and 1000×12 points for iDH2-2J were acquired with spectral widths of 5000×100 Hz in 7 min. TR / TE = 4 / 0.1 s. A conventional 1D experiment with excitation sculpting was also performed. The parameters of TR, TE and PFGs were the same as those of iDH2, and the number of averages was 32.

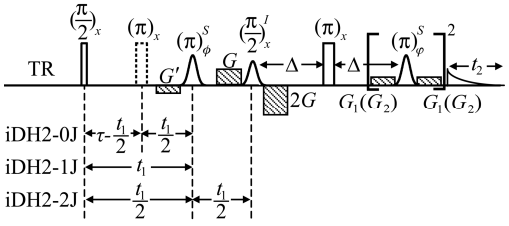

Fig. 1. The iDH2 pulse sequences. The π RF pulse drawn in dashed line is only applied in iDH2-0J sequence.

Results and discussions

In Fig. 2, multiplet patterns of metabolites such as Lac (1.31 ppm), Ala (1.47 ppm), and GABA (2.28 ppm) can be resolved in the iDH2-2J spectrum. On the other hand, the homonuclear decoupled iDH2 spectroscopy achieves higher peak amplitudes for coupled spins as well as better signal separation, both of which benefit the quantification. Several resonances, such as Gln (2.44 ppm), Asp (2.65 and 2.80 ppm) and Tau (3.42 ppm), which are concealed in noise or overlapping in the iDH2-2J and –1J, can be well resolved in the iDH2-0J spectrum.

The fast acquisition scheme shortens the indirect spectral width from 5000 Hz to 100 Hz, thus a 50-fold speedup can be obtained, theoretically. When the same t_{1max} and repetition delay are applied with 2 steps of phase cycling, it will take about 1.5 h to obtain an original iZQC spectroscopy with full F_1 spectral width, while only 2 min to acquire an iDH2 experiment. The intrinsic low SNR of iMQCs is the main obstacle for the speedup of iDH2. On the other hand, since more averages are performed to enhance SNR, more steps of phase cycling can be employed to optimize water suppression in the iDH2.

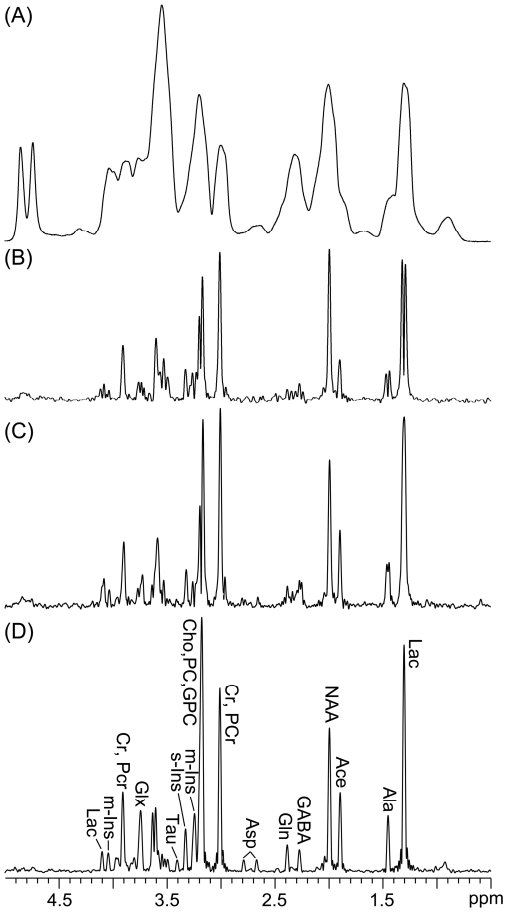

Fig. 2. Spectra of swine brain tissue: (A) 1D conventional spectrum with water suppression, and (B) ~ (D) projection spectra of the iDH2-2J, -1J, -0J, respectively.

Acknowledgments

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Reference

1. Vathyam S., et al., ***Science*** 272, 92, 1996.
2. Chen X., et al., ***Phys. Chem. Chem. Phys.*** DOI: 10.1039/b709154k, 2007.
3. a) Hwang T., et al, ***J. Magn. Reson.*** 112, 275-279, 1995; b) Balla D. Z., et al, ***Chem. Phys. Lett.*** 393, 464, 2004.
4. Nagayama N., et al, ***J. Magn. Reson.*** 40, 321-334, 1980.
5. Liu M. L., et al, ***J. Magn. Reson.*** 132, 125-129, 1998.