A flexible iMQC method for accurate determination of J-coupling constants in inhomogeneous fields

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Introduction

Exact values of *J* coupling constants and chemical shifts are often required for spectral fitting in *in vivo* spectral analysis [1]. However, it is difficult to obtain these values under inhomogeneous fields, especially for spin systems with small *J* coupling constants where spectral overlapping occurs often. Intermolecular multiple-quantum coherences (iMQCs), which derive from intermolecular dipolar interactions among spins in different molecules, provide a possible way for obtaining high-resolution spectra in inhomogeneous fields [2-3]. The pulse sequence in reference [4] based on iMQC acquisition was developed to scale up apparent *J* coupling constants, defined as apparent peak separations in unit of Hz in a reconstructed spectrum for a coupled spin system, for obtaining precise *J* coupling constants and chemical shifts under inhomogeneous fields. In this report, an improved pulse sequence is presented, which can scale apparent *J* coupling constants by a scaling factor (SF) ranging theoretically from zero (complete decoupled) to infinity.

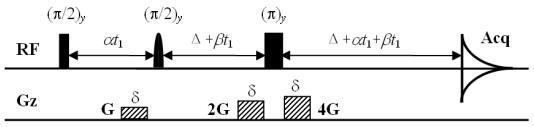

Fig. 1. Pulse sequence for high-resolution MRS under inhomogeneous fields via iMQC acquisition.

Methods

The pulse sequence is shown in Fig. 1. The first and last RF pulses are non-selective, and the second RF pulse is selective for solvent. There are three parts of indirect evolution periods. The variables of α and β are limited by $\alpha > 0$ and $\beta \geq -1.5\alpha$. The scaling factor of *J* coupling constant is SF = $3+2\beta/\alpha$, i.e. the resulting apparent *J* coupling constants are equal to the true values times SF. To test the re-scaling ability of the pulse sequence, we carried out some experiments with (α, β) = (1/6, -1/4), (1/4, -1/4), and (1/4, 1/4), respectively. For the cases of β small than zero, Δ equals $-\beta t_1^{max}$. The experiments were performed at 298K using a 500 MHz Varian NMR system spectrometer and a 5 mm indirect detection probe with three-dimension gradient coils. A sample of mixture of methyl ethyl ketone and cyclohexane was used. The magnetic field was intentionally deshimmed to produce a line width of ~30 Hz (phased mode). The resulting 1D spectrum was shown in Fig. 2b. Radiation damping effect was suppressed effectively by deliberately detuning the probe.

To verify the theoretical predictions and experimental observations, the modified Bloch equations were used to simulate the same sample based on a simulation algorithm presented in reference [5].

Results and Discussion

The 1D accumulated projection spectra of the acquired 2D iMQC spectra after a counterclockwise rotation of peaks with appropriate angles are shown in Fig. 2. It can be seen that the projection spectra maintain chemical shifts, relative peak areas, and multiplet patterns (except for SF=0) while inhomogeneous broadening is suppressed. Moreover, the *J* splitting distances are 5- and 1-fold magnified for Fig. 2e and Fig. 2d compared to Fig. 2a, in good agreement with the theoretical predictions. The magnification of *J* splits allows more accurate measurement of small *J* coupling constants. In view of its ability in scaling apparent *J* coupling constants and extracting high-resolution spectra from inhomogeneous fields, the technique proposed herein may be used in localized spectroscopy and *in situ* analysis of chemical systems. In addition, a completely decoupled homonuclear spectrum with SF=0 can be of considerable help for improving signal separation and thus peak assignment in localized MRS.

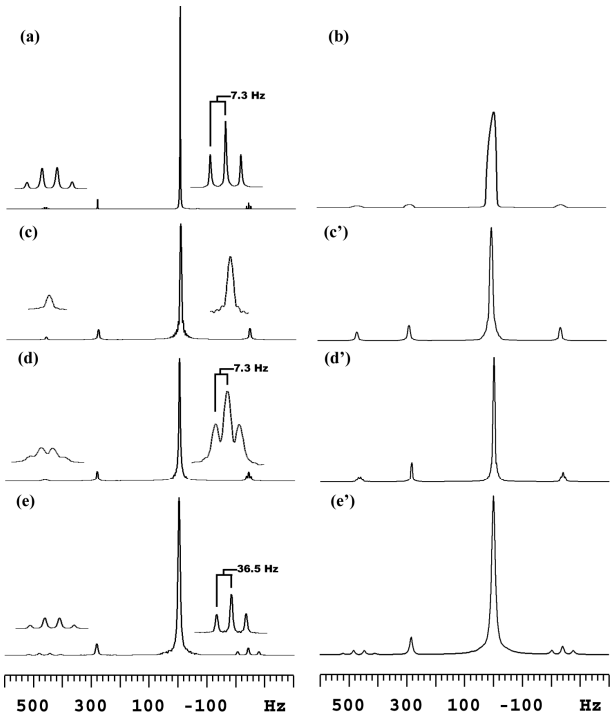

Fig. 2. 1D ^{1}H NMR spectra of the mixture of methyl ethyl ketone and cyclohexane. (a) Conventional 1D high-resolution spectrum in a well-shimmed field; (b) 1D spectrum acquired in an inhomogeneous field of about 30 Hz line-width; (c~e) 1D accumulated projections of 2D iMQC spectra under the same shimming as for (b) with SF = 0 (c), SF = 1 (d), and SF = 5 (e); (c'~e') are simulation results corresponding to (c~e).

Acknowledgments

This work was supported by the NNSF of China (10774125) and NCET of Ministry of Education of China.

References

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