Decoupled proton NMR spectroscopy in modest to severe inhomogeneous fields via distant dipolar interactions

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Introduction

Decoupled proton NMR spectroscopy provides an important tool to simplify the spectra and eliminate the peak overlap, which benefits the resonance assignment and quantification. However, broadened peaks due to magnetic field inhomogeneities can severely degrade the resolution of decoupled proton spectra. Intermolecular multiple-quantum coherences (iMQCs) provide a feasible way to obtain high-resolution spectra [1]. In this abstract, intermolecular single-quantum coherence (iSQC) signals originated from ^{1}H-^{1}H homonuclear and ^{2}H-^{1}H heteronuclear distant dipolar interactions were employed to obtain high-resolution decoupled proton spectra in inhomogeneous fields with high acquisition efficiency.

Methods

The pulse sequences for high-resolution decoupled spectra via ^{1}H-^{1}H homonuclear and ^{2}H-^{1}H heteronuclear iSQCs are presented in Fig. 1a and 1b, respectively. The iSQC evolution during $t_1$period in the sequences are intrinsically insensitive to field inhomogeneities and a constant-time (CT) scheme [2] is utilized to achieve *J* decoupling during t_1 (the minimum value for the echo time Δ is $-0.5t_1^{max}$), so high-resolution 1D decoupled spectra can be recovered from inhomogeneous fields. In the homonuclear iSQC sequence, the first and the third RF pulses are solvent-selective while the second RF pulse is solute-selective. The distant dipolar field is produced from the solvent spin [3]. In the heteronulcear iSQC sequence, RF pulses are applied for the deuterated solvent spin ^{2}H and solute spins ^{1}H, respectively. The distant dipolar interaction is produced from the ^{2}H spin. The foldover correction [4] is used to improve acquisition efficiency.

Experiments were performed at 298 K using a Varian NMR System 500 MHz spectrometer, equipped with a 5 mm indirect detection probe with three-dimensional gradient coils. A sample of solution of butyl methacrylate in methanol was placed in an inhomogeneous field with 200 Hz line-width to test the feasibility of the homonuclear sequence. The molar ratio of butyl methacrylate and methanol was 1:10. 350 × 35 points were acquired with a spectral width of 3500 × 300 Hz (F1 × F2) in 2.3 min. In addition, a sample of solution of 20% butyl methacrylate in 80% acetone-d_6 was placed in an inhomogeneous field with 3.5 KHz line-width to test the capability of the heteronuclear sequence in large inhomogeneous fields. 64×105 points were acquired with a spectral width of 5000 × 3500 Hz (F1 × F2) in 7 min.

Results and Discussion

The results of butyl methacrylate in methanol are presented in Fig. 2. It is noticed that hardly any spectral information can be obtained from the conventional SQC spectrum. In the 1D decoupled spectrum obtained from the accumulated projection of the 2D iSQC spectrum, the line-widths are reduced from 200 Hz to 10 Hz. Since the solvent spin ^{1}H should be selected solely for the distant dipolar field, this sequence is not suitable for large field inhomogeneities.

The results of butyl methacrylate in acetone-d_6 are presented in Fig. 3. All the peaks are severely overlapped in the conventional SQC spectrum. The 1D decoupled spectrum is recovered from the very inhomogeneous field and the line-widths are reduced from 3.5 KHz to 50 Hz. Since deuterated solvents are often injected into samples for field locking in NMR experiments and most of them do not react or exchange with solutes, this sequence is more applicable in practical applications under severe inhomogeneous fields.

Acknowledgment

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References

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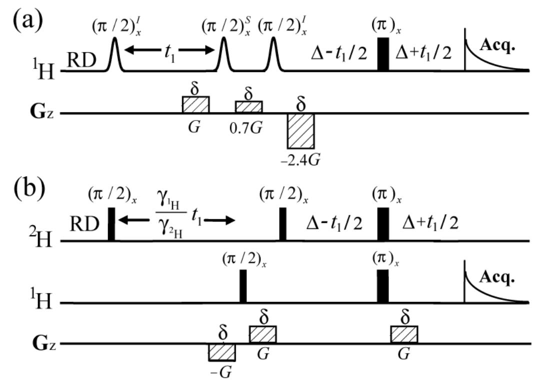

Fig. 1 Pulse sequences for high-resolution decoupled spectra via: (a) ^{1}H-^{1}H homonuclear and (b) ^{2}H-^{1}H heteronuclear iSQCs.

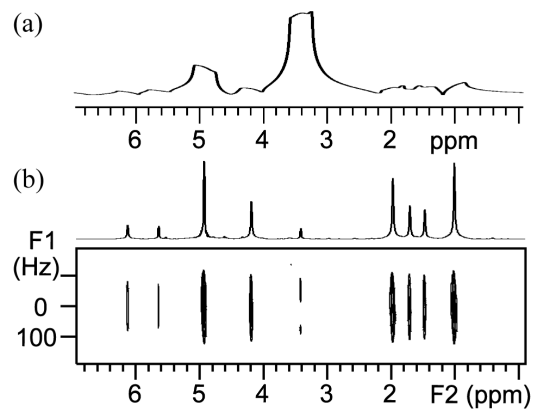

Fig. 2 (a) 1D conventional SQC spectrum, and (b) decoupled spectrum via homonuclear iSQCs.

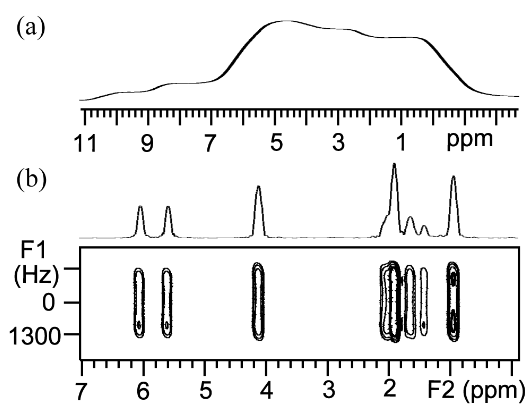

Fig. 3 (a) 1D conventional SQC spectrum, and (b) decoupled spectrum via heteronuclear iSQCs.