High-resolution NMR spectroscopy in inhomogeneous fields via intermolecular multiple-quantum coherences between spin 1/2 and quadrupolar nuclei

Z. Chen[1], S. Cai[1], and S. Chen[1]

[1]Department of Physics, Xiamen University, Xiamen, Fujian, China, People's Republic of

Introduction

In inhomogeneous fields, high-resolution NMR spectra can be achieved via homonuclear intermolecular multiple-quantum coherences (iMQCs) [1-3]. We ever proposed SEL-HOMOGENIZED, IDEAL and iDQF-HOMOGENIZED pulse sequences for this purpose [2-4]. To simplify the 2D spectra, selective RF pulses were used, which make them not applicable when the chemical shifts of solvent and solute are close to each other. On the other hand, the homonuclear and heteronuclear iMQCs between spin 1/2 nuclei often intermingle with intramolecular *J* coupling, which will result in complex splitting patterns in 2D spectra, thus blocking some of their potential applications. Since deuterated solvents are often injected into samples for field locking in NMR experiments and most of the deuterated solvents are chemically stable and do not react or exchange with solutes, the nuclei ^{2}H may be utilized as a probe to detect heteronuclear iMQCs without confronting above problem [5]. Taking these considerations into account, a modified heteronuclear CRAZED pulse sequence was proposed to obtain high-resolution NMR spectroscopy in inhomogeneous fields in this abstract.

Methods

The pulse sequence is shown in Fig. 1. Channel I is for ^{2}H nuclei, and channel S is for ^{1}H nuclei. Experiments were performed on a Varian NMR System 500 MHz spectrometer. The sample is a mixture of methyl ethyl ketone and cyclohexane in acetone-d_6. The gradient amplitude was $G_1 \approx 0.20$ T/m and the duration $\delta = 1.2$ ms. The magnetic field was intentionally deshimmed to produce a linewidth of about 100 Hz. Both spectral widths of the F1 and F2 dimensions were 1200 Hz. The total experimental time for a 2D spectrum was about 47 min.

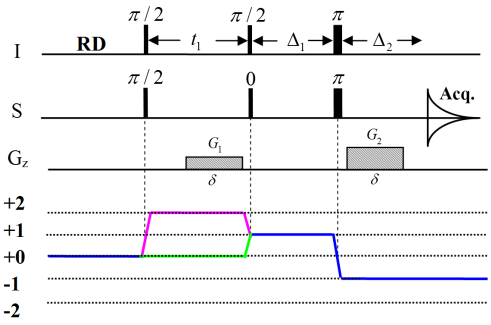

Fig. 1 Heteronuclear CRAZED pulse sequence for high-resolution NMR spectra in inhomogeneous fields via iZQCs or iDQCs between spin 1/2 and quadrupolar nuclei. Related parameters are defined in text.

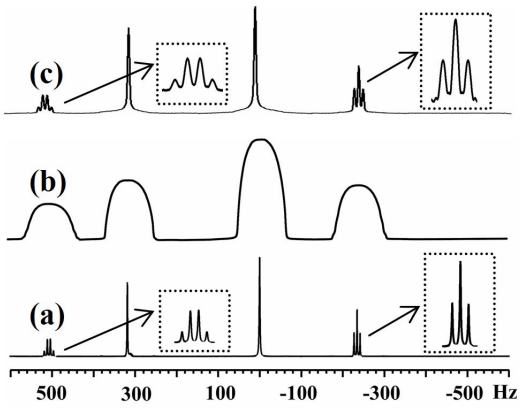

Fig. 2 ^{1}H NMR spectra of the mixture of methyl ethyl ketone and cyclohexane. (a) Conventional 1D high-resolution spectrum acquired in a well-shimmed field, (b) 1D spectrum acquired in an inhomogeneous field of about 100 Hz line-width, (c) accumulated projection of the sheared iZQC experimental spectrum shown in Fig. 3b.

Results and Discussion

Take heteronulcear intermolecular multiple-quantum coherences (iZQCs) for example. The accumulated projection into the F2 dimension of the sheared 2D iZQC experimental spectrum after data processing with SPROM is shown in Fig. 2(c). The linewidth is reduced from 100 Hz to about 5 Hz. Like conventional 1D high-resolution spectrum, the projection spectrum provides the information of chemical shifts, relative peak areas, coupling constants, and multiplet patterns. The only difference is that the *J* splitting distances are about 2-fold magnified, i.e. the scale factor of the *J* coupling constants is ca. 2 (see Fig. 2a & 2c). This makes it more suitable to retrieve multiplet information in spin systems with small *J* coupling constants. Compared to homonuclear iMQC sequences, the sequence proposed herein is more realizable and provides a more compact result containing all information necessary for structural identification.

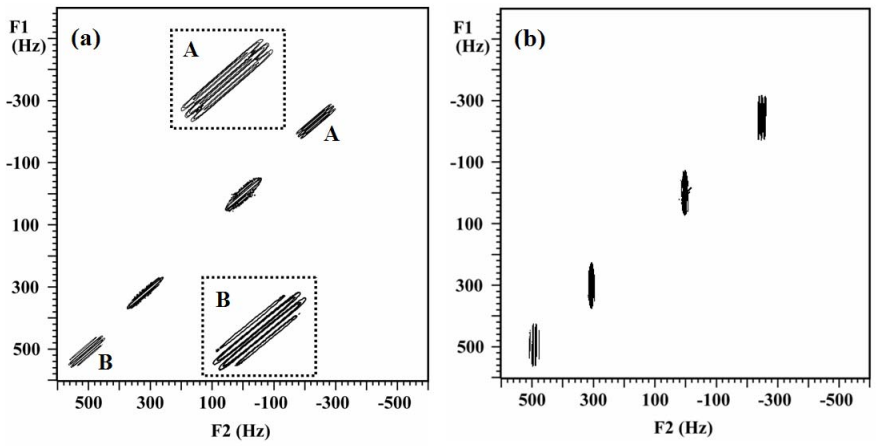

Fig. 3 (a) Heteronuclear iZQC ^{1}H NMR spectra of the mixture of methyl ethyl ketone and cyclohexane; (b) sheared spectrum of (a) after data processing with SPROM.

Acknowledgments

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References

[1] Vathyam S, et al. *Science* 272 (1996) 92.

[2] Chen Z, et al. *Chem. Phys. Lett.* 386 (2004) 200.

[3] Chen Z, et al. *J. Am. Chem. Soc.* 126 (2004) 446.

[4] Chen X, et al. *Phys. Chem. Chem. Phys.* 9 (2007) 6231.

[5] Chen S, et al. *Chem. Phys. Lett.* 458 (2008) 368.