

High-resolution MRS in inhomogeneous fields via double-quantum-filtered intermolecular zero-quantum coherences

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Introduction

Intermolecular zero-quantum coherences (iZQCs) are not susceptible to magnetic field inhomogeneities larger than the dipolar correlation distance, and can be used to achieve 1D high-resolution spectra in inhomogeneous fields. However, with the iZQC methods proposed previously [1,2], the residual conventional single-quantum coherences (SQCs) will result in strong t_1 ridge noises. A new pulse sequence with a double-quantum filter (DQF) [3], named DQF-HOMOGENIZED, was designed in this study to eliminate conventional SQC signals and also to suppress the solvent iZQC signal. The results show potential applications in *in vivo* spectroscopy.

Methods

We consider a homogeneous liquid mixture consisting of S component of an AX spin-1/2 system (solute) and I component of a single spin-1/2 system (solvent). The pulse sequence of DQF-HOMOGENIZED is depicted in Fig. 1. Three coherence selection gradients (CSGs) and phase cycling are used to select the desired coherence transfer pathway $0 \rightarrow +2 \rightarrow +1 \rightarrow -1$. After dropping undesired coherence orders and higher order spin terms that are too weak to be observed, the two spin terms $I_{\alpha}I_{\beta}$ and $I_{\alpha}S_{\alpha}$ will evolve under the pulse sequence as:

$$\begin{cases} I_{\alpha}I_{\beta} \\ I_{\alpha}S_{\alpha} \end{cases} \xrightarrow{\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}} \xrightarrow{\alpha I_x} \xrightarrow{\beta I_x} \xrightarrow{\pi I_x, \pi S_x} \begin{cases} -\frac{1}{8} \sin^2 \alpha \sin \beta \cos^2 \frac{\beta}{2} (I_{\alpha}I_{\beta}^{-} + I_{\alpha}^{-}I_{\beta}) \\ -\frac{i}{4} \sin^2 \frac{\alpha}{2} \sin \beta I_{\alpha}S_{\alpha}^{-} \end{cases} \quad (1)$$

The long-range intermolecular interactions will convert the terms $I_{\alpha}I_{\beta}^{-}$ ($I_{\alpha}^{-}I_{\beta}$) and $I_{\alpha}S_{\alpha}^{-}$ into observable terms I^{-} and S^{-} respectively. It can be seen that the conventional SQC signals of both solvent and solute spins will not pass the double-quantum filter and the elimination of residual SQCs by DQF will be insensitive to the imperfection of the pulses. Furthermore, according to Eq. (1), the solvent signal is null when $\alpha = \pi$, while maximal solute signals will be achieved at the same time. And the optimal flip angle of β is $\pi/2$.

Experiments were performed with a Varian Unity plus 500 NMR spectrometer. We used a biologic sample of a piece of grape sarcocarp with intrinsic macroscopic susceptibility gradients and intense water signal. The experiments were all performed without locking and shimming. A 2-step phase cycling was used: the phases for both the third RF pulse and the acquisition were $(x, -x)$. The CSGs with strength $G \approx 0.1$ T/m, $G' \approx -0.02$ T/m, and the duration $\delta = 1.2$ ms were applied.

Results and Discussion

The line-width of the water resonance is about 100 Hz in the conventional 1D NMR spectrum (Fig. 2(a)), from which hardly any spectral information of solute can be resolved. The corresponding 2D spectrum was acquired using the DQF-HOMOGENIZED sequence and the regions of interest after a counterclockwise rotation of $\pi/4$ is shown in Fig. 2(b). After a projection onto the horizontal axis, the line-widths are greatly reduced. Furthermore, the water signal is effectively suppressed so that the two peaks of beta- and alpha-glucose, which are about 0.2 down-field and 0.4 ppm up-field away from the water resonance respectively and are completely concealed in conventional 1D NMR spectra, can be resolved. For comparison, a 1D spectrum of the grape juice was obtained in a homogeneous field and the area between 3.1 to 4.1 ppm is presented in Fig. 2(c). The corresponding area in the sheared 2D DQF-HOMOGENIZED spectrum of grape sarcocarp is shown in Fig. 2(d), with accumulated projections along both dimensions. It can be seen that much spectra information is recovered from regions with severe overlapping. The resulting spectrum of DQF-HOMOGENIZED is quite similar to 1D high-resolution juice spectrum with reasonable SNR. In addition, a weak triplet peak from a methyl group with low concentration at 1.1 ppm is also displayed in Fig. 2(d). The resolution is largely improved in the F1 dimension.

The intensity of the residual solvent iZQC signal is very sensitive to the deviation of the α angle from π . Therefore, in order to apply the techniques for *in vivo* application where spatially selective pulses are used, the highly accurate rotation angles for rf pulses are needed for effective solvent suppression. Further research in this aspect is in progress.

Acknowledgments

This work was partially supported by the NNSF of China under Grants 10375049 and 20573084, and NCET and EYTP of Ministry of Education of China.

Reference

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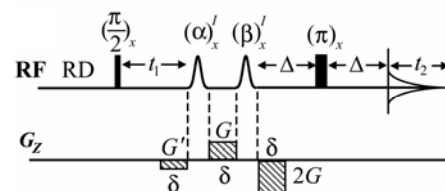


Fig. 1. DQF-HOMOGENIZED pulse sequence.

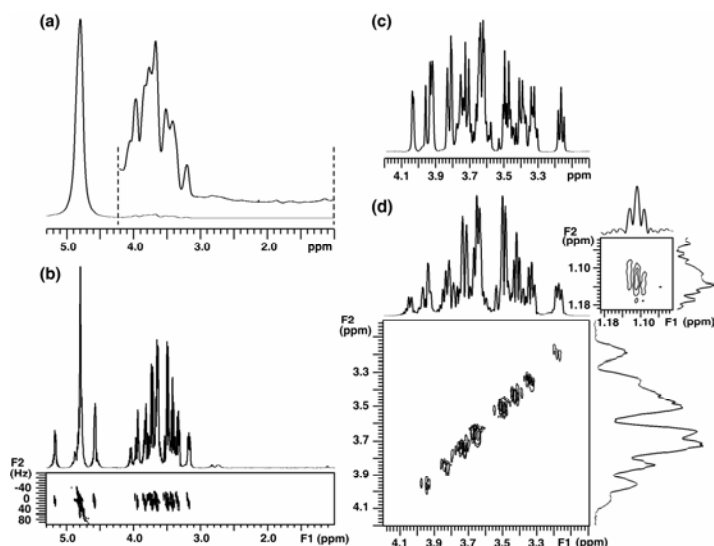


Fig. 2. ¹H NMR spectra of grape. (a) Single-pulse NMR spectrum of a piece of grape sarcocarp, (b) the 2D spectrum obtained from the DQF-HOMOGENIZED sequence after a shearing by $-\pi/4$, (c) the expanded area in a single-pulse NMR spectrum of the grape juice in a well-shimmed field, and (d) two expanded areas in the 2D DQF-HOMOGENIZED spectrum of grape sarcocarp.