Apparent diffusion behaviors modulated by distant dipolar field in solution NMR

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Introduction

Intermolecular multiple quantum coherences (iMQC) have been described to be resulted from intermolecular dipolar interactions and have found wide applications in NMR and MRI. The unique diffusion properties of iMQC may provide a novel MRI contrast mechanism which may improve detection of water molecules associated with ordered structures in soft tissues. However, the diffusion effect on signal attenuation is still not much understood [1-3]. To study this effect, a modified two-pulse CRAZED sequence was designed, where the signal attenuation was weighted by diffusion in mixing period. Experimental and simulation results show that apparent diffusion rate is correlated with the spatial modulation of distant dipolar field, and different orientation of diffusion weighting gradients relative to coherence selection gradients results in different apparent diffusion rate [1].

Materials and Methods

Experiments were carried out on a Varian NMR System 500 MHz spectrometer equipped with a 5 mm actively shielded x, y, z-axis gradients indirect detect probe. Gradient strengths were calibrated with gradient profile experiments. The pulse sequence shown in Fig.1 was for the measurement of signals coming from intermolecular double quantum coherences (iDQC). The diffusion weighting module is a pair of gradients with opposite polarity. For conventional single quantum coherences (SQC), the pulse sequence was a $\pi/2$ RF pulse followed by a diffusion weighting module before acquisition. The sample was a mixture of 80% acetone and 20% acetone-d_6. All ^{1}H NMR spectra were recorded at 298 K. To suppress the effects of radiation damping, the width of $\pi/2$ RF pulse was extended to 52.5 μs by deliberately detuning the probe. A typical set of experimental parameters was as follows: a relaxation delay (RD) of 20 s, to recover the magnetization to its full equilibrium state and prevent any possible stimulated echoes; acquisition time 2.0 s; gradient amplitude $G' = 9$ mT/m and duration $\delta' = 1$ ms; $\tau = 22$ ms; $\Delta = 52$ ms; and $\delta = 2$ ms. The amplitude G of the first diffusion weighting gradient was varied along +z ($\theta = \pi/2$), −z ($\theta = -\pi/2$), and +x ($\theta = 0$) direction to produce a series of diffusion weighting. Numerical simulations were performed to verify experimental observations.

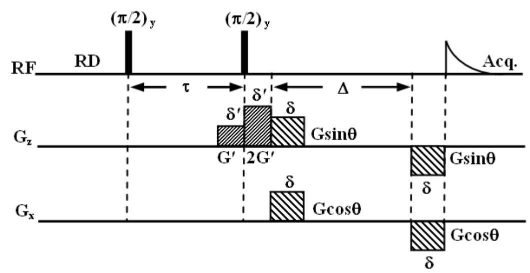

Fig.1 Modified CRAZED pulse sequence for measuring the apparent diffusion rates from iDQC during the mixing period.

Results and Discussion

The variaions of normalized relative singal intensity E with the amplitude G of diffusion weighting gradients are shown in Fig. 2. The experimental results are in excellent agrrentment with simulation ones. According to NMR theory, lnE and G^2 satisfies the relationship $\ln E = -bD_T G^2$ for convientional SQC, where D_T is molecular translational diffusion rate, and b is a diffusion weighting factor related to δ and Δ. Since b is keep constant, the relationship between lnE and G^2 should be linear and the slope of lnE~G^2 line reflects the D_T. In our study, the lnE~G^2 curves are linear for conventional SQC ($\theta=\pi/2$) and SQC from iDQC when the diffusion weighting gradients are along x direction ($\theta=0$). However, their slopes are different. Furthermore, the lnE~G^2 curves are nonlinear for SQC from iDQC when the diffusion weighting gradients are along z direction ($\theta=\pi/2$ and $-\pi/2$). They deviate from the line of $\theta=0$ to different direction. These results indicate that the apparent diffusion rate of SQC from iDQC is influenced by the relative orientation of diffusion weighting gradients to the coherence selection gradients. This may be due to the effects of the distant dipolar field. When $\theta=0$, the directions of diffusion weighting gradients and distant dipolar field are perpendicular to each other. Therefore, the influence of distant dipolar field on signal attenuation is kept constant at various diffusion weighting, resulting in linear relationship of lnE~G^2. However, when $\theta=\pi/2$ or $-\pi/2$, the direction of diffusion weighting gradients is parallel or anti-parallel to the distant dipolar field. This results in enhanced or weakened effect of distant dipolar field on signal attenuation. The stronger the amplitude of diffusion gradient, the larger the influence it introduces. Therefore, the lnE~G^2 curve is nonlinear.

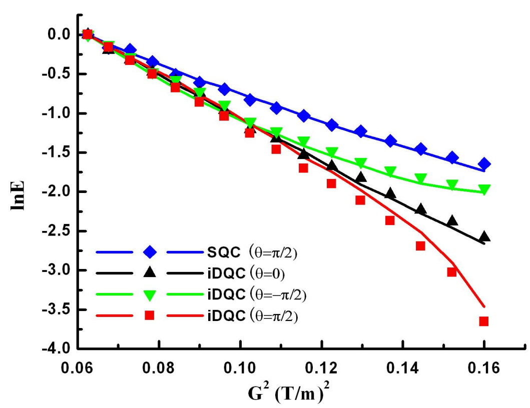

Fig. 2 Experimental and simulation results of signal attenuation due to diffusion of acetone molecules in the mixture of acetone and acetone-d_6. The symbols stand for the experimental data, and the curves represent the simulation results.

Acknowledgments

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References

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