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Investigation of intermolecular double-quantum off-resonance longitudinal relaxation in the tilted rotating frame

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ABSTRACT

A modified correlation spectroscopy revamped by asymmetric *z*-gradients echo detection (CRAZED) sequence was applied to investigate the behavior of intermolecular double-quantum longitudinal relaxation processes in the tilted rotating frame. Theoretical formalism based on dipolar field theory was presented in detail. Spectroscopic measurements and quantitative analysis demonstrated that the signal intensities and intermolecular double-quantum off-resonance longitudinal relaxation time in the rotating frame ($T^{eff}_{1\rho,DQC}$) are inversely correlated with the tilt angle (θ), while positively correlated with the effective frequency of spin-locking field (ω_e). Magnetic resonance imaging experiments of an agarose phantom also prove the validity of the theoretical analysis and demonstrated the feasibility of imaging based on $T^{eff}_{1\rho,DQC}$. The rotating-frame double-quantum relaxation measurements are useful for probing slow-motion molecules and this study provides the guidance for optimization of the spin-lock experiments.

1. Introduction

Intermolecular multiple-quantum coherence (iMQC) in strongly polarized spin systems arise from residual long-range dipolar interactions in liquid nuclear magnetic resonance (NMR) [1,2]. These phenomena have been described successfully using either classical dipolar field or quantum–mechanical density-matrix approaches [3,4]. Intermolecular dipolar effects have been extensively explored for enhancing contrast in anatomic magnetic resonance imaging (MRI) [5–8], functional imaging [9,10], microscopic structural measurements [11–13], and high-resolution NMR spectroscopy in inhomogeneous magnetic fields [14–16]. The poor sensitivity is the main obstacle of the wider application of iMQC. As an efficient approach, the dynamic nuclear polarization is used to enhance the sensitivity in iMQC experiment [17,18]. Besides that, Levitt found that the sensitivity of iMQC signals was improved in pancake-like samples [19]; Branca utilized square wave dipolar fields to improve nonlinear magnetic resonance signals [20].

We have investigated the behaviors of longitudinal relaxation [21], transverse relaxation [22], and diffusion [23] related to the intermolecular double-quantum coherence (iDQC), as well as their applications in human brain imaging [24]. MRI contrast often results from different relaxation processes within tissues, represented by characteristic time constants of longitudinal relaxation T_1 and/or transverse relaxation T_2. However, a specific contrast mechanism has its own particular range of applications. The single-quantum coherence (SQC) longitudinal relaxation time in the rotating frame, $T_{1\rho}$, has been demonstrated to be effective for probing low-frequency behaviors of molecule mobility in high static fields [25]. Therefore, $T_{1\rho}$-weighting images can possess unique contrast and have been investigated in various biological tissues [26–28]. Intermolecular zero-quantum coherence (iZQC) spin lock sequence has been proposed and investigated [29]. However, the iZQC suffers from inherent low signal to noise ratio (SNR), strong solvent signal and strong noise of indirect dimension [30], which limit its practical application. It has been reported that iDQC possess features similar to those of iZQC but also some distinctive advantages, such as higher SNR (30% higher than iZQC) and nonnecessity of phase cycles [31,23]. Therefore, we have successfully introduced on-resonance and off-resonance spin-locking technique into an iDQC imaging experiment [32,33]. Yet the mechanism of iDQC off-resonance longitudinal relaxation in tilted rotating frame has not been fully discussed.

In this work, a modified correlation spectroscopy revamped by asymmetric *z*-gradients echo detection (CRAZED) sequence was applied to investigate the behaviors of iDQC off-resonance longitudinal relaxation process in the tilted rotating frame. A

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long-duration, low-power, and off-resonance spin-locking pulse was incorporated into the evolution period of the CRAZED sequence. The usual iDQC transverse relaxation process is replaced by that of iDQC off-resonance longitudinal relaxation during the evolution period. Theoretical formalisms related to $T^{eff}_{1\rho,DQC}$ were derived following the dipolar field theory. Detailed discussion of the quantitative relationship between the iDQC and SQC relaxations in the rotating frame was also presented. Spectroscopic measurements of relaxation times and imaging experiments of agarose gel samples are in good agreement with the theoretical predictions.

2. Theoretical formalism

The spin-locking pulse shown in Fig. 1 (labeled with "$(\omega_1)_y$" associating with a frequency offset $\Delta\omega$) is used to lock the magnetization. The low-power radio-frequency (rf) field $(\omega_1)_y$ and the frequency offset $\Delta\omega$ constitute such an effective spin-locking field along the z' axis of a tilted rotating frame, which has a tilt angle θ with respect to the normal rotating frame [21]. After the $(\alpha)_x$ rf pulse is applied with a flip angle of $\alpha = \theta$, the longitudinal magnetization is flipped along the z' axis of the tilted rotating frame. Therefore, the magnetization is locked along the effective spin-locking field vector and relaxes with the corresponding off-resonance spin–lattice longitudinal relaxation time during the locking period T_{SL}. A pair of gradients $G\delta$ with an area ratio of 1: n (which is referred as coherence selection gradients or CSGs in the following) is utilized to select the desired n-quantum coherence. The subsequent observed signals of n-quantum coherences are then modulated by the off-resonance longitudinal relaxation in the tilted rotating frame.

In the following, the dipolar field treatment will be used to follow the evolution of a one-component N-spin ($I = 1/2$) system with the pulse sequence shown in Fig. 1. The effective spin-locking field is established with an effective frequency $\omega_e = \sqrt{(\omega_1)^2 + \Delta\omega^2}$ and a tilt angle $\theta = \mathrm{a}\tan(\omega_1/\Delta\omega)$ away from the z axis of the normal rotating frame ($\theta = \pi/2$ for an on-resonance spin-locking pulse without the frequency offset). In the experiment, the first $(\alpha)_x$ pulse with the flip angle $\alpha = \theta$ transforms the equilibrium magnetization $M_0\hat{z}$ into the tilted rotating frame, and the magnetization

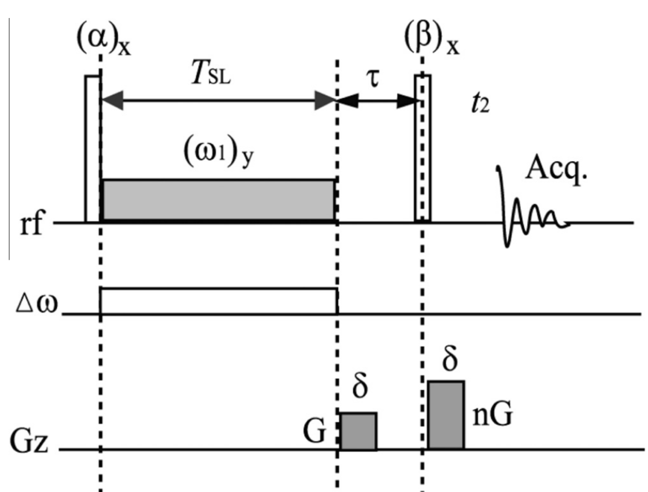

Fig. 1. Pulse sequence for investigation of the behavior of iDQC longitudinal relaxation in the rotating frame. The measurements of the relaxation times were performed by varying T_{SL} and setting τ to the minimum. The off-resonance iDQC longitudinal relaxation was measured when the flip angle of the $(\alpha)_x$ pulse was set to be equal to the tilt angle θ of the effective spin-locking field.

is aligned along the $\hat{z}'$ axis as $\mathrm{M^T} = M_0\hat{z}'$ when seen in the tilted rotating frame, where $\hat{z}' = \hat{z}\cos\theta + \hat{y}\sin\theta$. The component aligned along the effective field ω_e will be retained and relax with a relaxation time constant, defined by $T^{eff}_{1\rho}$. Therefore, the decay of magnetization under the effective spin-locking field during the duration T_{SL} can be approximated as [34,35]

$$\begin{aligned}\mathbf{M}^{\mathrm{T}} &= \left\{(M_0 - M_{eq})e^{-T_{SL}/T^{eff}_{1\rho}} + M_{eq}\right\}\hat{z}' \\ &= M_0\left\{\left(1 - T^{eff}_{1\rho}\cos\theta/T_1\right)e^{-T_{SL}/T^{eff}_{1\rho}} + T^{eff}_{1\rho}\cos\theta/T_1\right\}\hat{z}',\end{aligned} \quad (1)$$

where $M_{eq} = M_0 T^{eff}_{1\rho}\cos\theta/T_1$, in which M_0 and M_{eq} are the equilibrium magnetization without and with a spin-locking pulse, respectively [35]. For the off-resonance case, the magnetization relaxes and approaches a non-zero equilibrium value M_{eq}. Noted that for the near on-resonance spin lock case (namely, $\theta \approx \pi/2$), M_{eq} approaches zero, $T^{eff}_{1\rho}$ is reduced to the on-resonance relaxation time $T_{1\rho}$, and $\mathrm{M^T} = M_0 e^{-T_{SL}/T_{1\rho}}$. Taking into account of relaxation, the magnetization just before the first CSG of strength G and duration δ in the normal rotating frame can be rewritten as

$$\begin{aligned}\mathbf{M} &= M_0\left(\hat{z}\cos\theta + \hat{y}\sin\theta\right)\left\{(1 - T^{eff}_{1\rho}\cos\theta/T_1)e^{-T_{SL}/T^{eff}_{1\rho}} + T^{eff}_{1\rho}\cos\theta/T_1\right\} \\ &= M_0\left(\hat{z}\cos\theta + \hat{z}\sin\theta\right)f(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}),\end{aligned} \quad (2)$$

where $f\left(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}\right)$ is a function related to the off-resonance relaxation $T^{eff}_{1\rho}$ for a given tilt angle θ. The magnetization is modulated by the first correlation gradient and just before the β pulse it becomes

$$\mathbf{M}(\beta^-) = M_0\left[\hat{z}\cos\theta + (\hat{y}\cos\varphi_G + \hat{x}\sin\varphi_G)\sin\theta\right]f\left(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}\right), \quad (3)$$

where $\varphi_G = \gamma G\delta z$ is the dephasing angle at position z attributed to the first CSG, and γ is the gyromagnetic ratio. The superscript "–" of β in Eq. (3) represents the time just before the β pulse. It should be noted that, since the longitudinal component in Eq. (3) is not modulated by the correlation gradient, it will be spoiled by the second gradient and does not contribute to the finial observable iMQC signal. Therefore, we ignore the contribution of the longitudinal component in the following. Moreover, the weak intermolecular dipolar couplings do not affect the evolution of iMQCs during the evolution period until the final detection period t_2 [36]. The $(\beta)_{+x}$ pulse transforms the transverse components in Eq. (3) into

$$\begin{aligned}\mathbf{M}(\beta^+) = M_0[&\hat{y}\cos\varphi_G\sin\theta\cos\beta - \hat{z}\cos\varphi_G\sin\theta\sin\beta \\ &+ \hat{x}\sin\varphi_G\sin\theta]f\left(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}\right).\end{aligned} \quad (4)$$

The effective dipolar field B_d attributing to the modulated longitudinal component in Eq. (4) has the form [3,4]

$$\mathbf{B}_d = -\mu_0 M_0\hat{z}\cos\varphi_G\sin\theta\sin\beta f\left(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}\right), \quad (5)$$

where μ_0 is the magnetic permeability constant. The transverse components in Eq. (4) continue to evolve under this effective dipolar field and the second CSG. Using properties of Bessel functions, we can write the resulting complex transverse magnetization as [1]

$$\begin{aligned}M^+(t_2, \theta) = i^{-(n+1)}M_0\{&nJ_n(\xi)/\xi - 0.5[J_{n-1}(\xi) - J_{n+1}(\xi)] \\ &\times\cos\beta\}\sin\theta f\left(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}\right)e^{-t_2/T_2},\end{aligned} \quad (6)$$

where $\xi = \gamma\mu_0 M_0 t_2\sin\theta\sin\beta f\left(\theta, e^{-T_{SL}/T^{eff}_{1\rho}}\right)$ and J_n is the nth order Bessel function. Since most experiments satisfy the condition of