Exchange-Induced Relaxations in the Presence of Fictitious Fields

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Introduction

Bendall et al [1] and Garwood et al [2] have described RF pulses with *sin/cos* amplitude ($\omega_1(t)$ and frequency ($\Delta\omega(t)$ modulation functions, respectively, which produce a ***fictitious*** RF field component in a second rotating frame due to a fast sweep of the effective RF field, $\omega_{eff}(t)=(\omega_1(t)^2+ \Delta\omega(t)^2)^{1/2}$. The spin is unable to follow the RF field during its rotation and undergoes precession around the RF magnetic field component out of the plane of rotation of the circularly polarized RF field. Recently we introduced a rotating frame method producing fictitious RF field components operating in even higher rotating frames, entitled RAFFn (Relaxation Along a Fictitious Field, whereby n indicates the rank of the rotating frame). With RAFFn, the final effective field $\omega_{eff}^{(n)}$ is a vector sum of $\Delta\omega^{(n)}(t)$ and $\omega_1^{(n)}(t)$, having fictitious magnetic field components. The amplitude of $\omega_{eff}^{(n)}$ remains stationary in the rotating frame of rank n [3,4]. Here, an analytical solution for exchange during RAFFn was derived and compared with Bloch-McConnell formalism.

Methods:

The analytical solution for two site exchange (2SX) during the RAFFn pulses was derived using density matrix formalism which is valid in the fast exchange regime (FXR). The relaxations were treated upon transformation to the nth rotating frame. The derived equations as well as the method of the derivation can be used to obtain equations for the description of exchange-induced relaxations in higher rotating frames (n > 2). A train of RAFFn pulses assembled into $PP^{-1}P_\pi P_\pi^{-1}$ packets was simulated using Bloch-McConnell formalism, as described in detail in [5].

Results and Discussion

The results of theoretical calculations of the relaxation rate constants during RAFF2 pulses are shown in Fig. 1. The description presented is limited to one particular case when the angle λ defining the initial orientation of $\boldsymbol{M}$ relative to the z' axis of the first rotating frame (FRF) is set to zero (Fig 1, A). When $\lambda = \varepsilon$, the relaxation is governed solely by $R_{1\rho,E}$ (=1/$T_{1\rho,E}$) mechanisms. When $\lambda = 90^{o} - \varepsilon$, $\boldsymbol{M}$ undergoes precession in the plane perpendicular to $\omega_{eff}^{(2)}$, and thus the relaxation is solely $R_{2\rho,E}$ (=1/$T_{2\rho,E}$) (Fig 1, B). Figure 1 (C and D) shows theoretical calculations of $R_{1\rho,E}(t)$ and $R_{2\rho,E}(t)$ during the application of RAFF2 pulses for ε=45^o. It can be seen that the time dependence of the exchange-induced relaxation rate constants resembles the modulation functions of the pulses which oscillate differently for the $R_{1\rho,E}(t)$ and $R_{2\rho,E}(t)$, respectively.

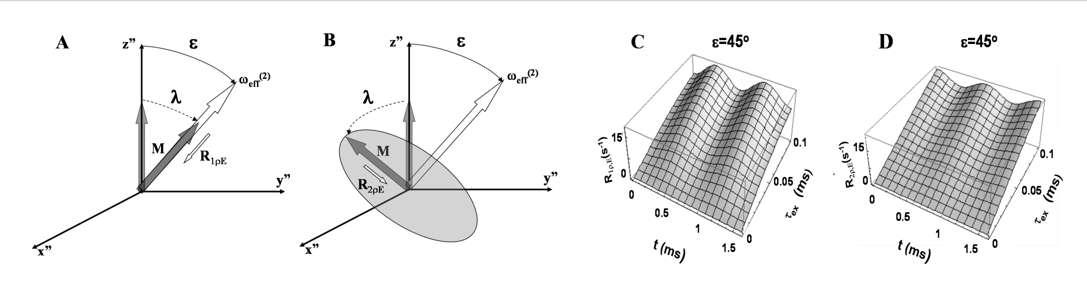

Figure 1. Relaxation during RAFF2 pulse. $\omega_{eff}^{(2)}$ = effective field of the rotating frame of rank n, ε= angle between $\omega_{eff}^{(2)}$ and z'', λ= angle at which magnetization is tilted before application of the RAFF2 pulse relative to z''. A) When $\lambda=\varepsilon$, magnetization is aligned with $\omega_{eff}^{(2)}$ in the second rotating frame, and it relaxes along the $\omega_{eff}^{(2)}$ with rate constant $R_{1\rho,E}$(t). B) When λ = 90^o-ε, magnetization rotates in a plane perpendicular to $\omega_{eff}^{(2)}$, and relaxes with $R_{2\rho,E}$(t). (C and D) Calculated longitudinal $R_{1\rho,E}(t)$ and transverse $R_{2\rho,E}(t)$ relaxation rate constants during the RAFF2 pulses as a function of exchange correlation times τ_{ex} for ε=45^o. For calculation, $\omega_1^{max}/(2\pi)$ =625 Hz, $\delta\omega$=0.85 ppm, and the fractional populations of sites A and B: $p_A p_B$=0.25.

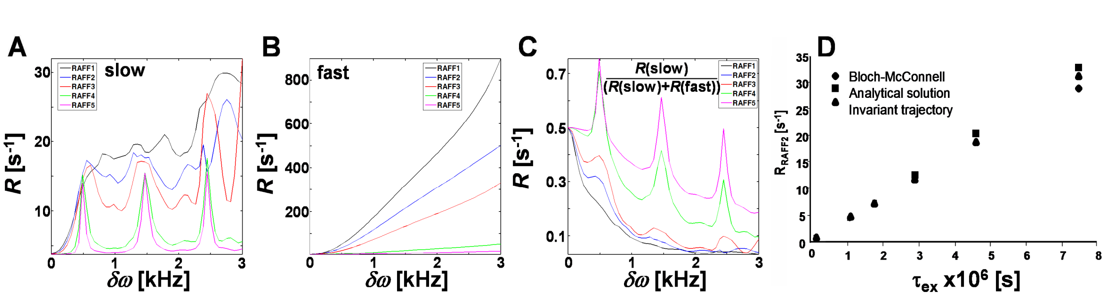

Figure 2. Plots of $\boldsymbol{R_{ex}}$ for RAFF1, RAFF2, RAFF3, RAFF4 and RAFF5 as a function of chemical-shift difference $\delta\omega$ for 2SX, as deteremined from Bloch-McConnell simulations using exchange rate constant k_{ex} equal to A) 100 Hz and B) 10000 Hz. C) The fraction of slow motion induced relaxation from panel A compared to fast exchange induced relaxation from panel B. p_A=0.9 and p_B=0.1; D) Theoretical simulation of R_{ex} with RAFF2 using Bloch-McConnell formalism (squares), analytical solution (triangle) and invariant trajectory method (circle), for ε=45^o for different exchange correlation times. Exchange parameters: $\delta\omega$=085 ppm, p_A=p_B=0.5, $\omega_1^{max}/(2\pi)$ = 625 Hz.

In Fig. 2, simulation results for 2SX during the RAFFn pulse trains are shown. With the increase of the rank n of the rotating frame, the sensitivity to slow exchange increases and is maximal for RAFF4 and RAFF5. Fourier transformation of RAFFn pulses reveals specific frequency bands of high intensity (sidebands) which lead to an increase of the rate constants at specific chemical shifts (Figs. 2, A and C). This may allow “relaxation tuning” of RAFFn pulses to specific frequencies of interest. The analytical solution for exchange-induced relaxations during RAFFn is in good agreement with the description of exchange given by Bloch-McConnell and invariant trajectory formalisms [6].

Conclusion: In the presence of the fictitious fields, with the increase of rank n of the rotating frames, the sensitivity to slow exchange increases.

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References: [1] Bendall, M. and D. Pegg, J Magn Reson 1986 [2] M. Garwood and L. DelaBarre, J Magn Reson. 2001 [3] T. Liimatainen et al. MRM 2010 [4] T. Liimatainen et al. ISMRM 2012 [5] Liimatainen et al., J Magn Reson. 2011.