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Transverse relaxation in the rotating frame induced by chemical exchange

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Abstract

In the presence of radiofrequency irradiation, relaxation of magnetization aligned with the effective magnetic field is characterized by the time constant $T_{1\rho}$. On the other hand, the time constant $T_{2\rho}$ characterizes the relaxation of magnetization that is perpendicular to the effective field. Here, it is shown that $T_{2\rho}$ can be measured directly with Carr–Purcell sequences composed of a train of adiabatic full-passage (AFP) pulses. During adiabatic rotation, $T_{2\rho}$ characterizes the relaxation of the magnetization, which under adiabatic conditions remains approximately perpendicular to the time-dependent effective field. Theory is derived to describe the influence of chemical exchange on $T_{2\rho}$ relaxation in the fast-exchange regime, with time constant defined as $T_{2\rho,\mathrm{ex}}$. The derived theory predicts the rate constant $R_{2\rho,\mathrm{ex}}$ $(= 1/T_{2\rho,\mathrm{ex}})$ to be dependent on the choice of amplitude- and frequency-modulation functions used in the AFP pulses. Measurements of $R_{2\rho,\mathrm{ex}}$ of the water/ethanol exchanging system confirm the predicted dependence on modulation functions. The described theoretical framework and adiabatic methods represent new tools to probe exchanging systems.

Keywords: Transverse relaxation; Rotating frame; Chemical exchange; Adiabatic pulse

1. Introduction

Longitudinal relaxation in the rotating frame during radiofrequency (RF) irradiation, with characteristic time constant $T_{1\rho}$, is an important property of spin systems. Measurements of $T_{1\rho}$ offer a valuable way to assess different types of motion, from slow atomic motions [1] to spin dynamics in viscous liquids and proteins [2–5]. This experimental technique is most sensitive to correlation times of motion τ_c in the range of 10^{-6}–10^{-4} s, which is of the order of the reciprocal of the spin-locking effective field, $\boldsymbol{\omega}_{\mathbf{eff}}^{-1}$. Determinations of the exchange parameters via $T_{1\rho}$ measurements have been described in numerous theoretical and experimental reports, and the theory describing the affects of chemical exchange on $T_{1\rho}$ relaxation is well established.

The rate constant $R_{1\rho}$ $(= 1/T_{1\rho})$ describes the relaxation of magnetization along $\boldsymbol{\omega}_{\mathbf{eff}}$, whereas relaxation in the plane perpendicular to $\boldsymbol{\omega}_{\mathbf{eff}}$ is governed by the transverse relaxation rate constant $R_{2\rho}(= 1/T_{2\rho})$. For the case of fast chemical exchange between identical spins having a chemical-shift difference $\delta\omega$, the rate constant describing exchange-induced $T_{1\rho}$ relaxation is given by [2,6]

$$R_{1\rho,\mathrm{ex}} = P_A P_B \delta\omega^2 \sin^2\alpha \frac{\tau_{\mathrm{ex}}}{1 + (\omega_{\mathrm{eff}}\tau_{\mathrm{ex}})^2}, \tag{1}$$

where

$$\omega_{\mathrm{eff}} = \sqrt{\omega_1^2 + \Delta\omega^2} \tag{2}$$

and

$$\alpha = \tan^{-1}\left[\frac{\omega_1}{\Delta\omega}\right]. \tag{3}$$

Here, ω_1 is the RF field amplitude, $\Delta\omega$ is the difference between the angular frequency of the RF field and the

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exchange-averaged resonance, τ_{ex} is the correlation time for exchange, and P_A and P_B are the normalized equilibrium mole fractions of spins at unique magnetic sites A and B, respectively. Despite much progress in the understanding of $T_{1\rho}$ relaxation in NMR, theoretical descriptions and applications of transverse relaxation in the rotating frame $T_{2\rho}$ have been limited [7–14]. In part, the paucity of previous $T_{2\rho}$ relaxation studies is a consequence of multiple experimental obstacles to making accurate $T_{2\rho}$ measurements. For example, the experimental determination of the $T_{2\rho}$ using the rotary echo method [15] is sensitive to resonance offsets. Furthermore, to the best of our knowledge, the influence of chemical exchange on $T_{2\rho}$ has not previously been described or measured.

Recent advances in RF pulse design and experimental capabilities have led to the routine use of sequences based on adiabatic RF pulses, where typical pulse lengths are on the order of one to tens of milliseconds [16]. In classical analyses of adiabatic pulses, it is convenient to consider the vector components of the magnetic fields and magnetization **M** in a reference frame that rotates at the instantaneous frequency of the RF pulse, $\omega_{RF}(t)$. This frame is referred to as the frequency-modulated (FM) frame with axis labeled x', y', z'. In the FM frame, the direction of $\boldsymbol{\omega_1}$ remains fixed during an AFP pulse, and it can be seen that the angle between $\boldsymbol{\omega_{eff}}$ and a perpendicular magnetization component remains close to 90° (Fig. 1A). In other words, when the adiabatic condition is well satisfied, the components of magnetization initially in the transverse plane of the FM frame remain perpendicular to the rotating $\boldsymbol{\omega_{eff}}$ throughout the pulse. This implies that the decay of magnetization during the pulse is governed mainly by $T_{2\rho}$ processes. Because $\omega_{eff}(t)$ is time dependent during the adiabatic pulse, $T_{2\rho}$ is also time dependent and thus is a function of the pulse modulation functions, $\omega_1(t)$ and $\omega_{RF}(t)$.

Spin-echo sequences using multiple AFP pulses (i.e., an adiabatic Carr–Purcell train) offer the possibility to assess directly the chemical exchange process from $T_{2\rho}$ measurements. Following the initial excitation pulse, an even numbers of the AFP pulses refocus dispersion of **M** caused by magnetic field inhomogeneities and chemical-shift evolution [16,17]. When no delays are used between AFPs, the decay of signal is governed solely by time-dependent $T_{2\rho}$ processes.

In this work, the theoretical formalism of $T_{2\rho}$ relaxation due to chemical exchange in fast regime is derived. In addition, $T_{2\rho}$ relaxation during AFP pulses using different modulation functions is investigated. Theoretical predictions are validated by comparisons with experimental measurements of transverse relaxation times of an water/ethanol mixture.

2. Theory

2.1. Transverse relaxation in the rotating frame due to fast chemical exchange

For simplicity, we consider the situation of a two-site chemical exchange process between A and B sites, $A \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} B$. Here k_1 and k_{-1} represent the forward and backward exchange rate constants obeying the relation

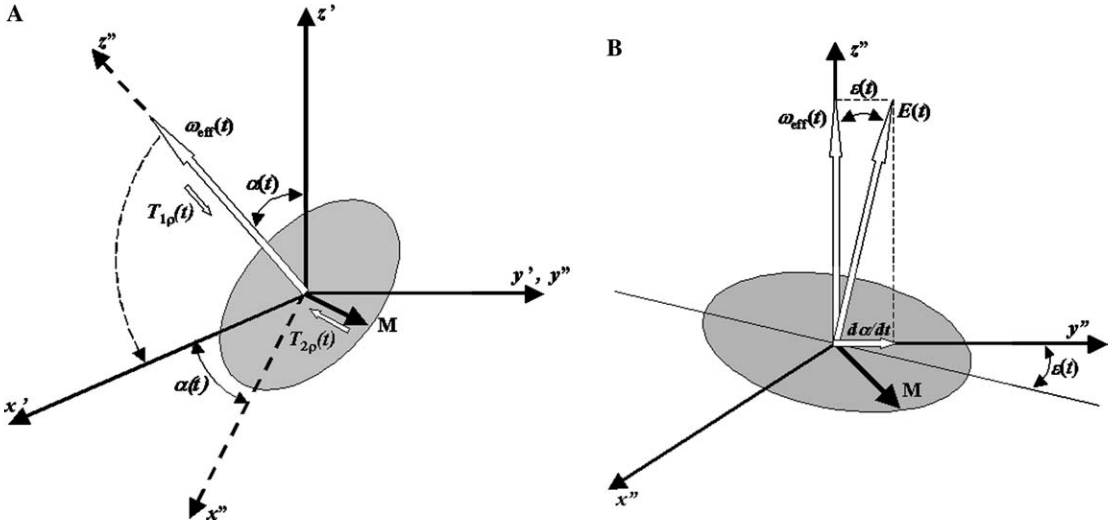

Fig. 1. (A) The effect of an adiabatic full-passage on a magnetization vector initially in the transverse plane, as viewed from the FM reference frame denoted by x', y', z'. During adiabatic rotation, the magnetization **M** remains approximately perpendicular to $\boldsymbol{\omega_{eff}}(t)$. The figure also illustrates the orientation of the tilted double rotating frame (TDRF), denoted by x'', y'', z'', relative to the FM frame. Any component of **M** that is aligned with $\boldsymbol{\omega_{eff}}(t)$ will relax with the time constant $T_{1\rho}(t)$ along the z'' axis, whereas the component perpendicular to $\boldsymbol{\omega_{eff}}(t)$ will relax with the time constant $T_{2\rho}(t)$ in the $x''y''$ plane. (B) Vector diagram showing the effective field $\boldsymbol{E}(t)$ and its components in the TDRF. **M** evolves around $\boldsymbol{E}(t)$ in a plane tilted by the angle $\varepsilon(t)$ relative to the $x''y''$ plane. When the adiabatic condition is satisfied (i.e., $d\alpha/dt \ll \omega_{eff}(t)$), the field component $\mathbf{d\alpha/dt}$ can be neglected and **M** evolves around $\boldsymbol{\omega_{eff}}(t)$.

$$\tau_{\text{ex}} = \frac{P_A}{k_{-1}} = \frac{P_B}{k_1} \tag{4}$$

and for exchange in the fast regime,

$$\tau_{\text{ex}} = \frac{1}{k_{\text{ex}}} \ll \delta\omega^{-1}. \tag{5}$$

In the present theoretical derivation, we follow the general formulation of the problem considered for the determination of exchange rates via $T_{1\rho}$ relaxation. Specifically, the exchange is explicitly introduced into the spin Hamiltonian [6,18]. We consider a homonuclear system of spins I_i in the presence of a Zeeman field ω_0 and a much smaller RF field ω_1, which for the moment is held fixed in amplitude.

The evolution of a spin system of indistinguishable spins in the laboratory frame in the presence of exchange is governed by the following time-dependent Hamiltonian (expressed in frequency units):

$$H(t) = H_0 + H_{\text{RF}}(t) + H^{\text{ex}}(t), \tag{6}$$

where

$$H_0 = \omega_0 I_z, \tag{7}$$

$$H_{\text{RF}}(t) = \omega_1[I_x \cos\omega_{\text{RF}}t + I_y \sin\omega_{\text{RF}}t], \tag{8}$$

$$H^{\text{ex}}(t) = (\omega(t) - \omega_{\text{AV}})I_z. \tag{9}$$

Here H_0 is the time-independent part of the Hamiltonian of the spin system, and $H_{\text{RF}}(t)$ is the RF Hamiltonian. $H^{\text{ex}}(t)$ is the Hamiltonian for a random perturbation due to the chemical exchange. The $\omega(t)$ term describes the variation of the resonance frequency about the population averaged frequency, ω_{AV}, defined as $\omega_{\text{AV}} = P_A\omega_A + P_B\omega_B$, where ω_A and ω_B are resonance frequencies of the spins in the A and B sites, respectively [2].

The analysis is based on the density matrix formulation following standard procedures [2,19,20]. In the interaction representation that includes a time-dependent Hamiltonian $H''(t)$ in the tilted double rotating frame (TDRF) (or in the terminology of adiabatic pulses, the ω_{eff} frame [16]), the evolution of the density matrix $\rho''(t)$ can be approximated up to the second order as

$$\frac{d\rho''(t)}{dt} = \frac{1}{i\hbar}\overline{[H''(t), [H''(t-\tau), \rho''(t) - \rho_{\text{eq}}]}, \tag{10}$$

where

$$H''(t) = U(t)H(t)U(t)^{-1} \tag{11}$$

and

$$\rho''(t) = U(t)\rho(t)U(t)^{-1}. \tag{12}$$

In Eqs. (10)–(12), ρ_{eq} is the equilibrium density matrix, $U(t)$ is a unitary operator, the double primes indicate operators in the TDRF, the bar is used to indicate ensemble averaging, and the change of variables is from t to t', where $t' - t = \tau$.

The Hamiltonian in the TDRF describing spin evolution in the presence of an RF field and chemical exchange is defined as [2,6]

$$H''^{\text{ex}}(t) = (\omega(t) - \omega_{\text{AV}})\left\{ I''_z \cos\alpha - \left(I''^{+} e^{-i\omega_{\text{eff}}t} + I''^{-} e^{i\omega_{\text{eff}}t}\right)\frac{\sin\alpha}{2} \right\}, \tag{13}$$

where $I''^{\pm} = I''_x \pm iI''_y$ are raising and lowering operators in the TDRF. Here, the physical variables $Q'' = I''_x, I''_y, I''_z$ are defined as $Q'' = U(t)QU(t)^{-1}$ in the TDRF.

The expectation value of the operator Q'' is obtained by solving [2,19,20]:

$$\frac{d\langle Q''\rangle}{dt} = -g(\tau)\left\{ \langle [[Q'', I''_z], I''_z]\rangle - \langle [[Q'', I''_z], I''_z]\rangle_{\text{eq}} \right\}, \tag{14}$$

where the correlation function $g(\tau) = \langle\omega(0)\omega(\tau)\rangle$ that describes the two-site fast exchange process is given by [2,21]

$$g(\tau) = P_A P_B \delta\omega^2 e^{-\tau/\tau_{\text{ex}}}. \tag{15}$$

Here, $[A, B] = C$ are commutators of the spin operators. For the case of transverse relaxation, the final interest is in the real part of the operator $Q'' = I''^{\pm}$.

To derive the contribution to relaxation from chemical exchange, all possible permutations of the double commutations of I''_z, I''^{+}, and I''^{-} in Eq. (14) must be evaluated. After the commutators are analyzed and the trace (*Tr*, sum over the diagonal elements) operator is applied, the real part of $\langle I''^{\pm}\rangle$ is evaluated. Neglecting small rapid oscillating terms, the derived expression for the transverse relaxation rate constant due to chemical exchange is:

$$R_{2\rho,\text{ex}} = P_A P_B \delta\omega^2 \cos^2\alpha\,\tau_{\text{ex}}. \tag{16}$$

From Eq. (16) it can be seen that $R_{2\rho,\text{ex}}$ is smaller than the exchange rate constant under free precession (i.e., in the absence of RF),

$$R_{2,\text{ex}} = P_A P_B \delta\omega^2 \tau_{\text{ex}}, \tag{17}$$

by the scaling factor $\cos^2\alpha$.

2.2. Time dependence of $R_{2\rho,\text{ex}}$ during AFP pulses

In the following analysis of adiabatic pulses, we allow the RF parameters, ω_1 and ω_{RF}, to be time dependent, since we are interested in the time dependence of $R_{2\rho,\text{ex}}$ during the $\omega_{\text{eff}}(t)$ sweep of the pulses. In this work, we investigate the time dependence of $R_{2\rho,\text{ex}}$ during AFP pulses of the HS*n* family with $n = 1$ or 4 [16,22]. In the FM frame, the amplitude and frequency modulated functions for the HS1 pulse are given by:

$$\omega_1(t) = \omega_1^{\max}\operatorname{sech}\left(\beta(2t/T_p - 1)\right) \tag{18}$$

and

$$\omega_{\text{RF}}(t) - \omega_c = A\tanh\left(\beta(2t/T_p - 1)\right). \tag{19}$$

For the HS4 pulse

$$\omega_1(t) = \omega_1^{\max}\operatorname{sech}\left(\beta\left(2t/T_p - 1\right)^4\right) \tag{20}$$

and

$$\omega_{RF}(t) - \omega_c = A\int_0^t \operatorname{sech}^2\left(\beta\left(2t'/T_p - 1\right)^4\right) dt', \tag{21}$$

where $t \in [0, T_p]$, β is a truncation factor ($\operatorname{sech}(\beta) = 0.01$), A is the amplitude of the frequency sweep in rad/s, T_p is pulse length, ω_c is carrier frequency (the center frequency in the bandwidth of interest), and $\omega_1^{\max}$ is the maximum value of $\omega_1(t)$. The shapes of these modulation functions in the FM frame are shown in Fig. 2. During these AFP pulses, $\boldsymbol{\omega}_{\mathbf{eff}}(t)$ changes its orientation at the instantaneous angular velocity, $d\alpha(t)/dt$, with:

$$\alpha(t) = \tan^{-1}\left[\frac{\omega_1(t)}{\Delta\omega(t)}\right], \tag{22}$$

where $\boldsymbol{\Delta\omega}(t) = (\omega_0 - \omega_{RF}(t))\hat{z}'$. Now $\boldsymbol{\omega}_1(t)$ and $\boldsymbol{\Delta\omega}(t)$ are time-dependent and different for pulses with different modulation functions.

As illustrated in Fig. 1B, the rotation of the TDRF frame relative to the FM frame gives rise to an effective field $\boldsymbol{E}(t)$ with a component along y'' $(= y')$ with an instantaneous magnitude $d\alpha(t)/dt$. This shifts the precession of the magnetization, which is initially perpendicular to the $\omega_{\text{eff}}(t)$, to the plane tilted relative to the $x''y''$ plane by the angle $\varepsilon(t)$. In the present derivation, it is assumed that $d\alpha/dt$ can be neglected (i.e., $\boldsymbol{E}(t) = \omega_{\text{eff}}(t)$) since adiabaticity is a requirement (i.e., $\omega_{\text{eff}}(t) \gg d\alpha/dt$ for all t).

To calculate the average effective relaxation rate constant $\overline{R}_{2\rho,\text{ex}}$ during an AFP pulse of length T_p, all instantaneous contributions during the pulse must be taken into account and thus the average relaxation rate constant is determined by:

$$\overline{R}_{2\rho,\text{ex}} = \frac{1}{T_p}\int_0^{T_p} R_{2\rho,\text{ex}}(t)\, dt. \tag{23}$$

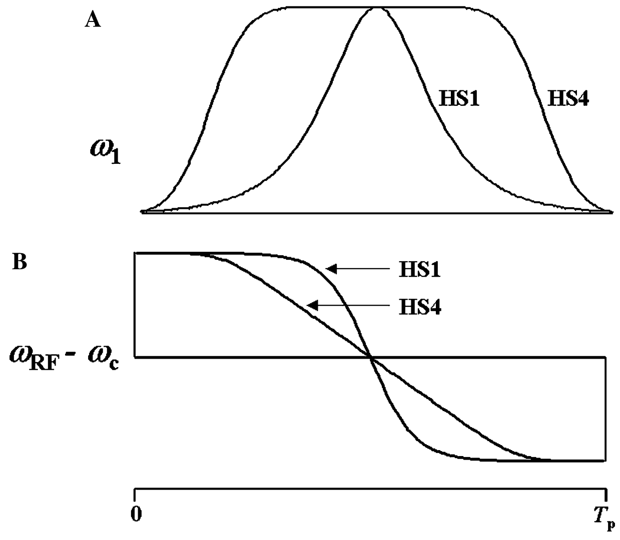

Fig. 2. Amplitude (A) and frequency (B) modulation functions in the FM frame for two different AFP pulses, HS1 and HS4.

2.3. Transverse relaxation due to dipolar interactions during AFP pulses

Transverse relaxation due to dipolar interactions in the rotating frame, characterized by the rate constant $R_{2\rho,\text{dd}}(= 1/T_{2\rho,\text{dd}})$, has been extensively analyzed previously [7,8,13,14,23]. For a system of two equivalent nuclei [7],

$$\begin{aligned} R_{2\rho,\text{dd}} = \frac{1}{(40k_{\text{dd}})}&[3(3\cos^2\alpha - 1)^2 + 30\sin^2\alpha\cos^2\alpha J(\omega_{\text{eff}}) \\ &+ 3\sin^4\alpha J(2\omega_{\text{eff}}) + (20 - 6\sin^2\alpha)J(\omega_0) \\ &+ (8 + 12\sin^2\alpha)J(2\omega_0)], \end{aligned} \tag{24}$$

where $1/k_{\text{dd}} = 2I(I+1)\hbar^2\gamma^4 r^{-6}\tau_c$. Here r is the internuclear distance, $\hbar$ is Planck's constant, and J is the spectral density function. Eq. (24) describes the instantaneous rate constant and can be used to calculate the time-dependence of $R_{2\rho,\text{dd}}$ during AFP pulses. The average value, $\overline{R}_{2\rho,\text{dd}}$, varies with the modulation functions of the AFP pulses.

3. Methods

Measurements were performed using a 4.7 T Oxford magnet interfaced to a Varian console. Transverse relaxation rate constants of water/ethanol were measured using the adiabatic Carr–Purcell (CP) sequence without interpulse delays. The length of the CP train of adiabatic pulses was incremented by adding sets of four AFP pulses cycled according to MLEV4 $(+X + X - X - X)$ [24]. The CP train was composed of HSn pulses ($n = 1$ or 4) of length $T_p = 0.003$ s, with an adiabaticity factor $R = 20$ $(\equiv AT_p/\pi)$ [22,25]. The carrier frequency ω_c was placed on the water/ethanol resonance. RF power was varied to attain $\omega_1^{\max}/2\pi$ values between 2.5 and 9 kHz.

Water/ethanol samples were prepared at the molar ratio ~1.1:0.9. The pH was adjusted by the addition of small amounts of acid or base solutions in the presence of the phosphate buffer and measured with a Thermo Orion pH meter.

The $\overline{R}_{2\rho,\text{ex}}$ values of the water/ethanol samples were calculated from the signal intensities using a linear regression algorithm with a mono-exponential decay function. Numerical calculations and 3D graphs were produced using Mathematica (Version 5.0) from Wolfram Research.

4. Results and discussion

Figure 3 shows theoretical predictions of $R_{2\rho,\mathrm{ex}}(t)$ during HS1 and HS4 pulses as a function of τ_{ex} using different $\omega_1^{\max}$ values. Upon inspection of the plots it can be seen that $R_{2\rho,\mathrm{ex}}(t)$ exhibits a significant dependence on the choice of modulation functions (HS1 versus HS4) and on the choice of $\omega_1^{\max}$. It can also be seen that the time dependence of $R_{2\rho,\mathrm{ex}}$ resembles the modulation functions of the pulses. The exchange contribution to the transverse relaxation rate reaches maxima at the early ($t \approx 0$) and late ($t \approx T_{\mathrm{p}}$) extremes, where $\cos\alpha(t) \approx 1$ and approaches zero near the middle of the pulses where $\cos\alpha(t) \approx 0$ (see Eq. (16)).

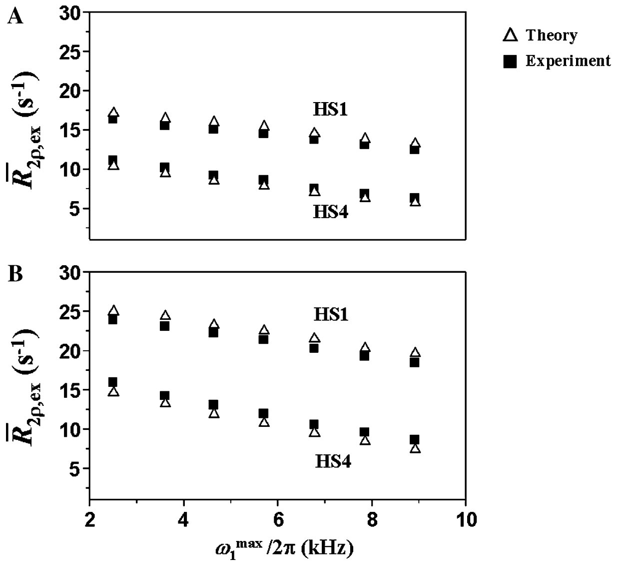

Fig. 4. The $\overline{R}_{2\rho,\mathrm{ex}}$ dependence on the $\omega_1^{\max}$ values used in measurements of a water/ethanol solution at pH 6.12 (A) and pH 7.0 (B). Measurements were performed with the adiabatic CP sequence using HS1 pulse (top) and HS4 pulse (bottom). The black squares are the experimental measurements and the open triangles indicate theoretical predictions based on Eqs. (16) and (23).

It is well documented that in water/ethanol mixtures the separate resonances from the water and ethanol OH groups coalesce and the averaged resonance appears when the relative molecular concentrations are ~1:1 at room temperature. This corresponds to the onset of rapid proton exchange [26]. The proton exchange in ethanol/water solution accelerates in the presence of strong acids or bases [27]. The $\overline{R}_{2\rho,\mathrm{ex}}$ values of the water/ethanol mixture, as measured using HS1 and HS4 pulses with different $\omega_1^{\max}$ values at two different pH values, are presented in Fig. 4. In comparing results obtained with HS1 versus HS4 pulses, a greater decrease of $\overline{R}_{2\rho,\mathrm{ex}}$ was observed when the CP train was composed of HS4 pulses, particularly as $\omega_1^{\max}$ was increased. On the same plots, the theoretical simulations of $\overline{R}_{2\rho,\mathrm{ex}}$ using Eq. (23) are presented. The correlation times for exchange obtained from simulations were $\tau_{\mathrm{ex}} = 81 \pm 7\,\mu\mathrm{s}$ (pH 6.12) and $\tau_{\mathrm{ex}} = 116 \pm 8\,\mu\mathrm{s}$ (pH 7.0). Simulations used $\delta\omega \approx 0.85\,\mathrm{ppm}$ [26] and $P_A P_B = 0.247$. As shown in

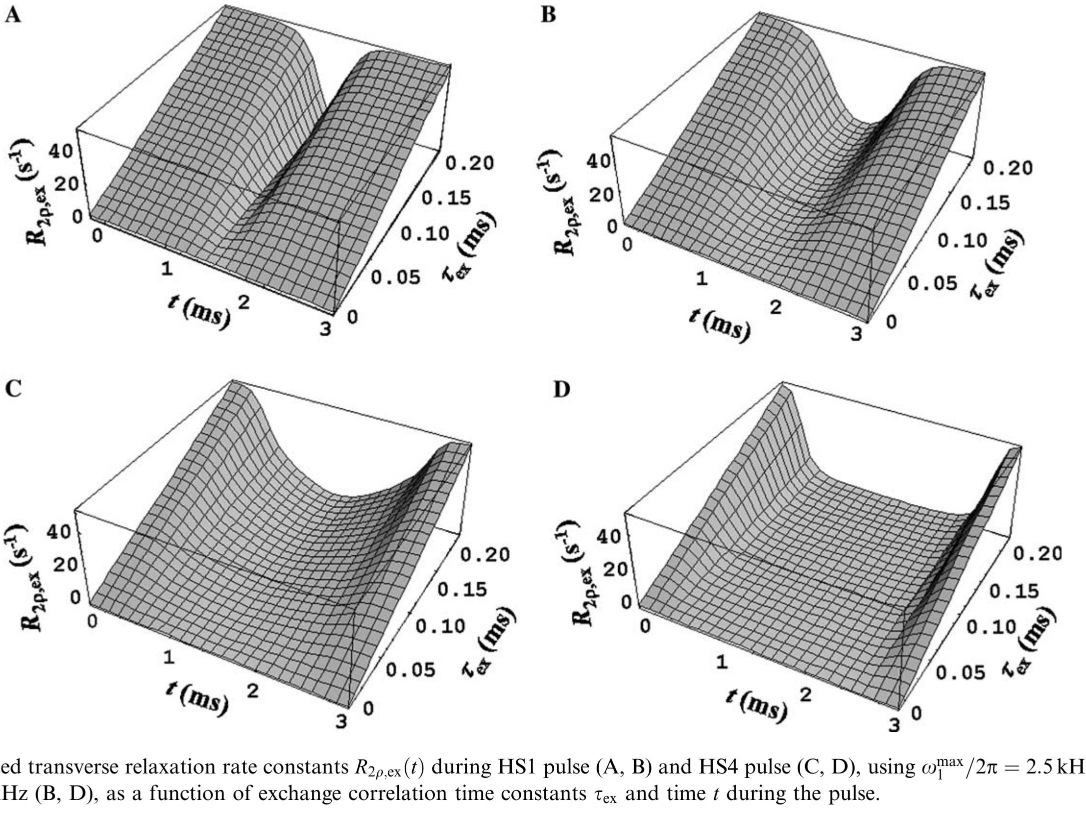

Fig. 3. Calculated transverse relaxation rate constants $R_{2\rho,\mathrm{ex}}(t)$ during HS1 pulse (A, B) and HS4 pulse (C, D), using $\omega_1^{\max}/2\pi = 2.5\,\mathrm{kHz}$ (A, C) and $\omega_1^{\max}/2\pi = 10\,\mathrm{kHz}$ (B, D), as a function of exchange correlation time constants τ_{ex} and time t during the pulse.

Fig. 4, the $\omega_1^{\max}$ dependence of the experimental data is well described by the theoretical $\overline{R}_{2\rho,\mathrm{ex}}$ values. This agreement supports the validity of the theoretical description presented here. Because the modulation functions are different, HS1 and HS4 pulses exhibit different sensitivity to chemical exchange.

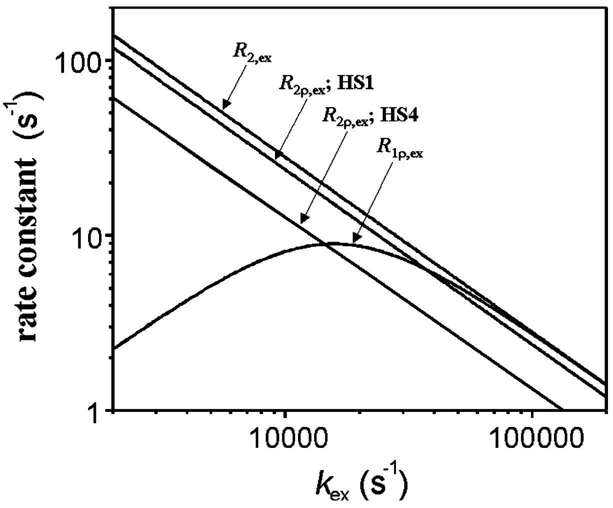

Fig. 5. Theoretical comparison between $R_{2,\mathrm{ex}}$, $R_{1\rho,\mathrm{ex}}$, and $\overline{R}_{2\rho,\mathrm{ex}}$ during HS1 and HS4 pulses. For calculation, $\omega_1^{\max}/2\pi = 2.5\,\mathrm{kHz}$, $\delta\omega = 0.85\,\mathrm{ppm}$, and $P_A P_B = 0.247$.

In Fig. 5, a theoretical comparison between $R_{2,\mathrm{ex}}$ (free precession), $R_{1\rho,\mathrm{ex}}$, and $\overline{R}_{2\rho,\mathrm{ex}}$ during HS1 and HS4 pulses is presented. The $R_{1\rho,\mathrm{ex}}$ curve was calculated from Eq. (1). It can be seen that the exchange rates under free precession are larger than $\overline{R}_{2\rho,\mathrm{ex}}$ and coincide with $R_{1\rho,\mathrm{ex}}$ for the fast exchange rates. This plot shows a difference between the $\overline{R}_{2\rho,\mathrm{ex}}$ during the HS1 and HS4 pulses, and thus further demonstrates the dependence of the $\overline{R}_{2\rho,\mathrm{ex}}$ on the modulation functions of the different adiabatic pulses.

For dipole–dipole interactions, Fig. 6 shows calculated plots of $R_{2\rho,\mathrm{dd}}$ as a function of the rotational correlation time τ_c and time during the pulses. Calculations were performed using modulation functions of the HS1 and HS4 pulses (Eqs. (18)–(22), and 24) for proton spins separated by $r = 1.58\,\text{Å}$. These plots illustrate the difference between $R_{2\rho,\mathrm{dd}}(t)$ values for HS1 and HS4 pulses, as well as the $R_{2\rho,\mathrm{dd}}(t)$ dependence on $\omega_1^{\max}$. This difference becomes apparent for $\tau_c > 10^{-9}$ s, both for the HS1 and HS4 pulses, which suggests a sensitivity of HS1 and HS4 pulses to dipolar interactions for slow moving spins. As compared with chemical exchange, the dipole–dipole contributions to transverse relaxation in the water/ethanol samples are negligible. From the Stokes–Einstein relation, τ_c is estimated to be $<10^{-12}$ s. For these correlation times the contribution of the dipole–dipole relaxation mechanism to the transverse relaxation of water/ethanol can be neglected.

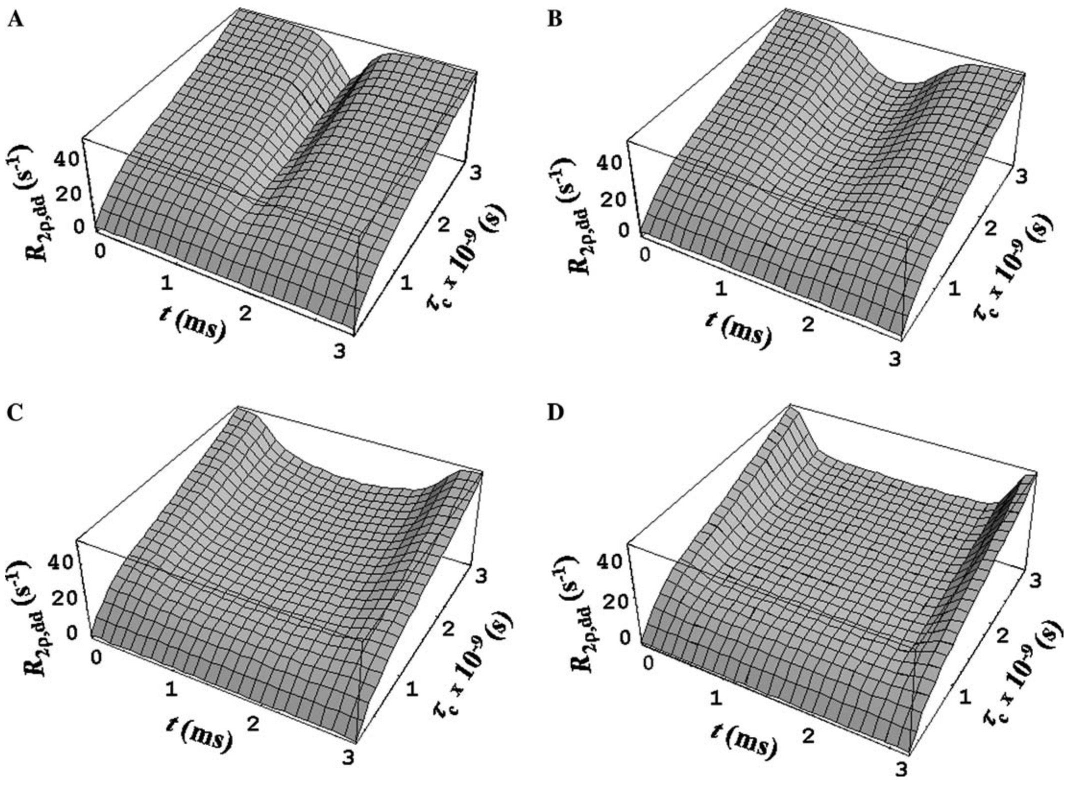

Fig. 6. Calculated transverse relaxation rate constants $R_{2\rho,\mathrm{dd}}(t)$ during HS1 pulse (A, B) and HS4 pulse (C, D), using $\omega_1^{\max}/2\pi = 2.5\,\mathrm{kHz}$ (A, C) and $\omega_1^{\max}/2\pi = 10\,\mathrm{kHz}$ (B, D), as a function of rotational correlation times τ_c and time during the pulse t.

5. Conclusion

The goal of this work was to introduce a theoretical description of transverse relaxation in the rotating frame in the presence of chemical exchange in the fast regime. The developed theory was applied for the quantification of relaxation due to chemical exchange during the AFP pulses in a Carr–Purcell spin-echo sequence. It was shown that transverse relaxation in the rotating frame is the dominant relaxation mechanism during AFP pulses of the CP pulse train when the adiabatic condition is well satisfied.

Two types of AFP pulses that are driven by different modulation functions, HS1 and HS4, exhibited different sensitivity to chemical exchange. Predictions based on the derived theory compared well with transverse relaxation measurements of the water/ethanol, when using HS1 and HS4 pulses. The dependence of dipole–dipole interactions between identical spins was also considered. Simulations predicted differences between the transverse relaxation rates measured with HS1 and HS4 pulses for correlation times $\tau_c > 10^{-9}$ s.

Utilization of the adiabatic pulses provides a unique way to measure $T_{2\rho}$ and offers a novel method for determining chemical exchange rates and rotational correlation times. The derived theory and experimental procedure are applicable to a broad range of different adiabatic pulses and provide a description of the nontrivial spin behavior that takes place during adiabatic pulse sequences.

Acknowledgments

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