Effects of $T_2$ Relaxation and Diffusion on Longitudinal Magnetization State and Signal Build for HOMOGENIZED Cross Peaks

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ISMRM 2004, Poster 2323, Thursday, May 20

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Abstract

An analytical expression has been developed to describe the effects of $T_2$ relaxation and diffusing spatially modulated longitudinal spins during the signal build period of an HOMOGENIZED cross peak. Diffusion of the longitudinal spins results in a lengthening of the effective dipolar demagnetization time, delaying the re-phasing of coupled anti-phase states in the quantum picture. In the classical picture the unwinding rate of spatially twisted magnetization is no longer constant, but decays exponentially with time. The expression is experimentally verified for the HOMOGENIZED spectrum of 100mM TSP in $H_2O$ at 4.7T.

Introduction

HOMOGENIZED$^{[13]}$ and its variants$^{[2,9]}$ and the recently proposed IDEAL$^{[14]}$ sequences have great potential for in-vivo spectroscopy$^{[10]}$. Diffusion weighting in HOMOGENIZED is present both to give intentional diffusion weighting and as a side effect of the various gradients present. Stekjsal-Tanner (ST) diffusion weighting$^{[12]}$ during the $t_1$ (mix) and $t_2$ (build) periods of the sequence can be used to suppress radiation dampening. Enhanced diffusion weighting$^{[15,4,3]}$ is obtained during $t_1$. There is an additional $t_2$ dependent diffusion weighting possible, due to the iZQC gradient $G_{zq}$ and $\beta$ pulse combination. The weighting results from diffusing modulated longitudinal magnetization, and does not behave as ST diffusion weighting. Kennedy et al.$^{[11]}$ have shown recently that this diffusion weighting has the novel property of being insensitive to object motion.

We have concentrated our efforts on the 2d HOMOGENIZED sequence shown in figure$^{[1]}$. The sequence consists of three RF pulses, $\alpha$ for excitation, $\beta$ to convert helical transverse magnetization to $M_z$ modulation, and $\pi$ to form a spin echo. The $G_{a1}$, $G_{a2}$ gradient pair yields ST diffusion weighting and radiation damping suppression during $t_1$. The $G_{b1}$, $G_{b2}$ gradient pair accomplishes the same during $t_2$. The $G_{c1}$, $G_{c2}$ gradient pairs crush transverse magnetization created at $\pi$ due to pulse imperfections and $B_1$ inhomogeneity, as well as introduce some additional diffusion weighting. The $G_{zq}$ gradient selects intermolecular zero quantum coherences (iZQCs) in the quantum picture. In the classical picture the $G_{zq}$ gradient in combination with $\beta$ creates spatially modulated longitudinal magnetization whose magnetic field causes unwinding (and eventually rewinding) of helically twisted transverse magnetization$^{[8]}$.

A 2d HOMOGENIZED experiment (see figure$^{[5]}$) is carried out by incrementing $t_1$ over multiple acquisitions. In a two (or multiple) component system where only one component is present in high concentration
(the solvent $S$), cross peaks with the solute component of interest $I$ will be formed at $(F_1, F_2) = (I - S, I)$ the "p" type iZQC and $(S - I, I)$ the "n" type iZQC. Axial iZQC peaks are formed at $(0, I)$ and $(0, S)$. The equation for peak amplitudes, neglecting radiation damping, $T_2$ relaxation, and diffusion has been described in the literature.[1]

Theory

For the first time, to the authors’ knowledge, an analytical expression, equation (4), for the cross peak amplitude in the presence of diffusion and $T_2$ relaxation has been developed. Some preliminary definitions precede the expression, notation follows Ahn et al.[1]

\[ q_{zq} \equiv \frac{\gamma G_{zq} \delta_{zq}}{2\pi} \]  

(1)

is the spatial frequency of periodic longitudinal magnetization $M_z$ formed by $G_{zq}$ of duration $\delta_{zq}$ and RF pulse $\beta$.

\[ \tau_{Seff} \equiv \tau_S e^{(b_a + b_{zq}) D_S \frac{4}{T_2}} \]  

(2)

$\tau_{Seff}$ has been defined to take account of $T_2$ and diffusion losses (ST b-values, $b_a$ and $b_{zq}$) incurred during $t_1$ before $\beta$ beta forms $M_z$. $\tau_S$ is the dipolar demagnetization time for spin $S$ as per reference[1].

\[ F(t2) \equiv \frac{1 - e^{-t_2(2\pi q_{zq})^2 D_S}}{\tau_{Seff}(2\pi q_{zq})^2 D_S} \]  

(3)

can be thought of as an exponentially slowing "winding" parameter, instead of the linear (in $t_2$) winding parameter $e^{-\frac{t_2}{T_2}}$ when diffusion is negligible. The new analytical expression for the signal amplitude in the presence of diffusion and $T_2$ decay is

\[ M_p = M_0^I e^{-(b_a + b_{zq} + b_c + b_b) D_t} e^{-\frac{(t_1 + t_2)}{T_2} \left[ \cos(\beta) + \frac{1}{2} \right]} J_1 \left[ \sin(\beta) \frac{2}{3} F(t2) \right], \]  

(4)
Figure 2: Plot of theoretical cross peak amplitude $M_p$ vs. $t_2$, for the case of negligible $T_2$ decay. $\beta = 90^\circ$ and $\tau_S = 200ms$. Three situations are shown:

Black - negligible diffusion
Dark Gray - diffusion of $M_z$ has delayed the maximum and stretched the zero crossings to longer times.
Light Gray - $M_z$ modulation has completely diffused away before the maximum can be obtained.

where $M_p$ is the p-type cross peak amplitude. $b_a$, $b_b$, and $b_c$ are the ST b-values due to the $G_a$, $G_b$, $G_c$ gradient pairs, respectively. $G_{zq}$ also introduces some ST diffusion weighting $b_{zq}$ in the short delay before $\beta$.

The effect of $F(t_2)$ is to stretch the time axis when diffusion weighting is significant. Equation (4) is valid as long as $S$ and $I$ are separated by $1/\tau_S$ in frequency, so that only longitudinal $S$ magnetization contributes to signal build. Steady state values ($TR < 5T_1^S$ or $T_1^I$) may be used for $\tau_S$ and $M_0$, as long as diffusion has eliminated residual spatial modulation of longitudinal magnetization. As long as the $a$ and $b$ gradient areas are chosen correctly, radiation dampening is not significant. Three theoretical situations are shown in figure 2. A similar expression has been found for the n-type crosspeak amplitude $M_n$. 

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Figure 3: Representative low resolution 2d HOMOGENIZED spectrum. TSP is referenced to -4.7ppm on F1 axis and 0.0ppm on F2 Axis. Projections are restricted to [0, 4] ppm F2 and [-5, -1] ppm F1.
Figure 4: Data points and theoretical curve of p type TSP peak for three cases. Y axis arbitrary units. Data points and theoretical curve of p type TSP peak for three cases. Y axis arbitrary units.

\[ \alpha = \beta = 90^\circ, \delta_a = \delta_b = \delta_c = 1\text{ms}, \delta_{\text{spoil}} = 5\text{ms} \]

\[ G_a = G_b = G_c = G_{\text{spoil}} = 20 \frac{mT}{m}, \delta_{zq} = 3\text{ms} \]

Upper - \( TR = 20\text{s}, G_{zq} = 10 \frac{mT}{m} \)

Middle - \( TR = 20\text{s}, G_{zq} = 40 \frac{mT}{m} \)

Lower - \( TR = 2\text{s}, G_{zq} = 40 \frac{mT}{m} \)

**Experimental Results**

A series of low resolution (512x64) HOMOGENIZED spectra were obtained with various strengths of \( G_{zq} \) (see figure 3). The solvent (S) is water at room temperature, the solute of interest (I) was TSP at 100mM concentration. Glucose was also present in solution. Field strength is 4.7T yielding nominal \( \tau_S = 200\text{ms} \).

A best fit, adjusting \( M_I^0 \) and \( \tau_S \) to account for pulse imperfections and \( B_1 \) inhomogeneity, was obtained for the top curve, and kept the same for the other curves. Relaxation rates were measured in separate inversion recovery and spin echo experiments with \( T_S^1 = 2.57\text{s}, T_S^2 = 140\text{ms} \) and \( T_I^2 = 1.62\text{s} \). Effects such as \( B_1 \) inhomogeneity and RF pulse error contribute to lengthen \( \tau_{\text{Seff}} \) (reduce available S magnetization).

Comparison of the predicted cross peak amplitude with experiment is shown in figure 4. An analysis of axial peaks and \( T_1 \) effects is in progress[6, 7].

**Acknowledgements**

This work and preparation leading to it was carried out under the support of the Flinn Foundation, a State of Arizona Prop. 301 Imaging Fellowship, and NIH 5R24CA083148-05.
Notes

There is an error in the conference abstract on CD for the equation for $M_p$. $\cos(\beta)$ appears in the abstract where $\frac{\cos(\beta) + 1}{2}$ is the correct term as in equation (2).

An extensive DDF/iMQC bibliography can be found at [5].

References

[1] Sangdoo Ahn, Natalia Lisitza, and Warren S. Warren. Intermolecular Zero-Quantum Coherences of Multicomponent Spin Systems in Solution NMR. J. Magn. Reson., 133(2), August 1998.

[2] Zhong Chen, Ting Hou, Zhi-Wei Chen, Dennis W. Hwang, and Lian-Pin Hwang. Selective intermolecular zero-quantum coherence in high-resolution NMR under inhomogeneous fields. Chemical Physics Letters, 386(1-3):200–205, 1 March 2004.

[3] Zhong Chen, Guoxing Lin, and Jianhui Zhong. Diffusion of intermolecular zero- and double-quantum coherences in two-component spin systems. Chemical Physics Letters, 333(1-2):96–102, 5 January 2001.

[4] Zhong Chen and Jianhui Zhong. Unconventional diffusion behaviors of intermolecular multiple-quantum coherences in nuclear magnetic resonance. The Journal of Chemical Physics, 114(13):5642–5653, 1 April 2001.

[5] Curtis A. Corum. DDF/iMQC Page. Web, 2002. Contains bibliography and contact info on groups involved with DDF/iMQC research: http://www.u.arizona.edu/~corum/mq_mri.html.

[6] Curtis A. Corum and Arthur F. Gmitro. Experimental and Theoretical study of TR and T1 Effects on Steady State Mz in Distant Dipolar Field-based Sequences. In Warren S. Warren, editor, 45th ENC Conference. Experimental Nuclear Magnetic Resonance Conference, 21 April 2004. Time Slot/Poster Number: 016.

[7] Curtis A. Corum and Arthur F. Gmitro. Spatially Varying Steady State Longitudinal Magnetization in Distant Dipolar Field-based Sequences. 1 April 2004. submitted to Journal of Magnetic Resonance, http://arxiv.org/abs/physics/0406045.

[8] Curtis A. Corum and Arthur F. Gmitro. Visualizing Distant Dipolar Field and Intermolecular Multiple Quantum Coherence Sequences. In ISMRM 12th Scientific Meeting. International Society of Magnetic Resonance in Medicine, 15 May 2004. ePoster 2711.

[9] Cornelius Faber and David Balla. Water suppression in 2D iZQC spectroscopy for in vivo application. In Warren S. Warren, editor, 45th ENC Conference. Experimental Nuclear Magnetic Resonance Conference, 22 April 2004. Time Slot/Poster Number: 227.

[10] Cornelius Faber, Eberhard Pracht, and Axel Haase. Resolution enhancement in in vivo NMR spectroscopy: detection of intermolecular zero-quantum coherences. Journal of Magnetic Resonance, 161(2):265–274, April 2003.

[11] S. D. Kennedy, B. Razavi, Z. Chen, and J. Zhong. Diffusion Measurements Free of Motion Artifacts Using Intermolecular Dipole-Dipole Interactions. In ISMRM Proceedings, volume 11. International Society for Magnetic Resonance in Medicine, July 2003. talk 0581.

[12] E. O. Stejskal and J. E. Tanner. Spin Diffusion Measurements - Spin Echo in the Presence of a Time Dependent Field Gradient. Journal of Chemical Physics, 42(1):288, 1965.

[13] Sujatha Vathyam, Sanghyuk Lee, and Warren S. Warren. Homogeneous NMR Spectra in Inhomogeneous Fields. Science, 272(5258):92–96, 5 April 1996.

[14] J. Zhong, Zhong Chen, Zhiwei Chen, and S. D. Kennedy. High Resolution NMR Spectra in Inhomogeneous Fields via Intermolecular Double Quantum Coherences. In ISMRM Proceedings, volume 11. International Society for Magnetic Resonance in Medicine, July 2003. talk 0520.

[15] Jianhui Zhong, Zhong Chen, Edmund Kwok, and Scott Kennedy. Enhanced sensitivity to molecular diffusion with intermolecular double-quantum coherences: implications and potential applications. Magnetic Resonance Imaging, 19(1):33–39, January 2001.