Journal of Magnetic Resonance 284 (2017) 99–103

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Predicting the effect of relaxation during frequency-selective adiabatic pulses

Annalise R. Pfaff*, Cailyn E. McKee, Klaus Woelk

Department of Chemistry, Missouri University of Science & Technology, 400 West 11th, Rolla, MO 65409-0010, USA

ARTICLE INFO

Article history:
Received 19 July 2017
Revised 8 September 2017
Accepted 28 September 2017
Available online 3 October 2017

Keywords:
Adiabatic pulse
Hyperbolic secant pulse
Relaxation
Solvent suppression
Pulse sequence optimization

ABSTRACT

Adiabatic half and full passages are invaluable for achieving uniform, B_1-insensitive excitation or inversion of macroscopic magnetization across a well-defined range of NMR frequencies. To accomplish narrow frequency ranges with adiabatic pulses (<100 Hz), long pulse durations at low RF power levels are necessary, and relaxation during these pulses may no longer be negligible. A numerical, discrete recursive combination of the Bloch equations for longitudinal and transverse relaxation with the optimized equation for adiabatic angular motion of magnetization is used to calculate the trajectory of magnetization including its relaxation during adiabatic hyperbolic secant pulses. The agreement of computer-calculated data with experimental results demonstrates that, in non-viscous, small-molecule fluids, it is possible to model magnetization and relaxation by considering standard T_1 and T_2 relaxation in the traditional rotating frame. The proposed model is aimed at performance optimizations of applications in which these pulses are employed. It differs from previous reports which focused on short high-power adiabatic pulses and relaxation that is governed by dipole-dipole interactions, cross polarization, or chemical exchange.

1. Introduction

Models to predict the behavior of magnetization during NMR pulse sequences are indispensable for parameter optimizations in a variety of applications such as selective solvent suppression sequences (e.g., BISEP, SWAMP, SSAP, EXCEPT) or *in vivo* imaging with surface coils [1–4]. Many solvent suppression sequences, for example, employ adiabatic pulses to selectively manipulate solvent spins while leaving analyte spins undisturbed. Adiabatic pulses such as the basic hyperbolic secant pulse (HS1) follow radiofrequency (RF) phase and amplitude modulation functions designed to confer uniform excitations (adiabatic half passages, AHP) or inversions (adiabatic full passages, AFP) that, above a given threshold, are independent of B_1 inhomogeneities [5]. During standard hard pulses with durations on the order of five to ten microseconds, standard T_1 and T_2 relaxation is in most cases negligible and can be ignored when optimizing parameters for high-resolution NMR investigations. For the same reason, T_1 and T_2 relaxation has been ignored in previous reports about relaxation during short, high-power adiabatic pulses [6]. However, for applications in which frequency selectivity with bandwidths smaller than 100 Hz is desirable, such as in the solvent suppression sequence EXCEPT [4], adiabatic pulses can last up to hundreds of milliseconds [7]. In this article, we therefore address the effects of T_1 and T_2 relaxation to predict the behavior of magnetization during these slow and selective AHPs or AFPs [2,3,8,9].

Thorough theoretical and empirical treatments of relaxation phenomena in the presence of B_1 fields are provided in the literature for both spin-lock conditions with long, low-power standard pulses and manipulations of magnetization with adiabatic pulses [6,10–12]. The latter works are primarily concerned with short adiabatic pulses (<10 ms) requiring a relatively high RF power to maintain the adiabatic condition ($\omega_{1,max}/2\pi \approx$ several kHz). Relaxation during these pulses is governed primarily by dipolar interaction, cross polarization and chemical exchange. Theoretical treatments of relaxation during these short, high-power adiabatic pulses have led to time-dependent relaxation functions applied collinear and perpendicular to the rotating effective B_1 field (B_{eff}) utilizing a tilted doubly-rotating frame. However, during long, low-power adiabatic pulses applied to non-viscous, small-molecule solutions, standard T_1 and T_2 relaxation becomes the primary effect while dipole-dipole relaxation may be insignificant. Ignoring standard T_1 and T_2 relaxation during frequency-selective (FS) pulses lasting hundreds of milliseconds can lead to inaccurate results and may negatively impact the optimization of

* Corresponding author.
E-mail addresses: arpvdc@mst.edu (A.R. Pfaff), cemy8b@mst.edu (C.E. McKee), woelk@mst.edu (K. Woelk).

https://doi.org/10.1016/j.jmr.2017.09.014
1090-7807/

performance parameters for sequences in which these pulses are utilized [1,8]. To facilitate performance optimizations of sequences employing FS adiabatic pulses, we developed a model that accounts for relaxation during these pulses in a different way. The method predicts angular motion and relaxation of magnetization after a FS adiabatic pulse using a semi-empirical knowledge of the time-dependent angular motion of B_{eff} during the adiabatic passage, the T_1 and T_2 values for the species of interest and the adiabatic pulse duration. The model makes it possible to quickly and effectively predict relaxation of magnetization during FS adiabatic passages for non-exchanging spins in non-viscous, small-molecule solutions.

2. Theory

2.1. Adiabatic pulses and B_1 insensitivity

For an adiabatic pulse such as the basic hyperbolic secant pulse HS1 [5], B_{eff} changes orientation throughout the duration of the pulse at an angular velocity $d\alpha/dt$, where $\alpha(t)$ is the angle between the longitudinal axis of the rotating frame (z axis) and the B_{eff} axis:

$$\alpha(t) = \tan^{-1}\left(\frac{\omega_1(t)}{\Delta\omega_0(t)}\right) = \tan^{-1}\left(\frac{B_1(t)}{\Delta B_0(t)}\right) \quad (1)$$

When $\alpha(t)$ changes continuously from 0° to 90°, an adiabatic excitation (AHP) is achieved, while a continuous change of $\alpha(t)$ from 0° to 180° leads to an adiabatic inversion (AFP). As long as the frequency ω_{eff} associated with B_{eff} is much greater than the frequency of the angular motion of B_{eff}, the adiabatic condition is fulfilled [7,13].

$$|\omega_{eff}(t)| \gg |d\alpha/dt| \quad (2)$$

Under adiabatic conditions, the net magnetization M will follow B_{eff}, and a uniform excitation or inversion is achieved across the frequency bandwidth of the adiabatic pulse [3,13]. To test the validity of the adiabatic condition for the pulse used in the following investigations, a series of experiments was conducted with a 200 MHz Bruker AVANCE DRX spectrometer, measuring the longitudinal magnetization M_z with a 90° observe pulse following the application of a 500 ms, 60 Hz bandwidth AFP HS1 pulse with varying RF power. Fig. 1 shows that inversion of magnetization is reasonably effective across at least one order of magnitude in RF pulse power. In this figure, RF power is expressed in terms of a dampening factor in decibels (dB) applied to the maximum pulse power available for the spectrometer. For comparison, a rectangular hard pulse (90° pulse) at 3 dB dampening required a pulse width of 11.54 μs.

A model that utilizes the standard relaxation time constants T_1 and T_2 to predict the behavior of magnetization during adiabatic pulses must combine three time-dependent parametric equations: the Bloch equations for longitudinal and transverse magnetization [14] and the equation for the angular motion of magnetization (Eq. (1)). It is therefore important not only to know T_1 and T_2 but also the position of magnetization at any time during the pulse. However, $d\alpha/dt$ is only constant for very specific sets of time-dependent pulse amplitude and phase modulations. In the work described here, the modulation functions result in slower angular motion at the beginning ($\omega_{eff} \approx \Delta\omega_{0,max}$) and end ($\omega_{eff} \approx -\Delta\omega_{0,max}$) of the pulse as compared to the middle of the pulse ($\omega_{eff} \approx \omega_{1,max}$). Achieving a constant $d\alpha/dt$ is rather difficult in an actual NMR investigation and will generally require extensive fine-tuning of the RF power level. On the contrary, it is quite unnecessary to go through the laborious process of fine-tuning because the adiabatic condition is fulfilled over a wide range of RF power levels (see Fig. 1). For the remainder of the work described here, a dampening factor of 65 dB was used for the HS1 pulse, resulting in $\omega_{1,max}/2\pi$ around 20 Hz. The actual angular motion of magnetization was monitored in a series of experiments, and the angle $\alpha(t)$ determined from independent measurements of longitudinal and transverse magnetizations at different time points throughout the HS1 pulse (see Section 3.2). The experimental results for $\alpha(t)$ were compared to predicted values obtained from a least-squares optimization of Eq. (1), refining the relative amplitudes of $\omega_{1,max}$ and $\Delta\omega_{0,max}$ by a constant best-fit factor (f_{bf}). The optimized equation of angular motion, therefore, is given by Eq. (3):

$$\alpha_{opt}(t) = \arctan\left[f_{bf} \times \frac{\sin(\alpha_{th}(t))}{\cos(\alpha_{th}(t))}\right] \quad (3)$$

where $\alpha_{opt}(t)$ represents the angle of B_{eff} at any time t during the pulse and $\alpha_{th}(t)$ the angle assuming constant angular motion. The optimized angle $\alpha_{opt}(t)$ is then used for the discrete recursive computer calculation of magnetization during the adiabatic pulse (see Supplementary Materials). Fig. 2 shows experimentally derived

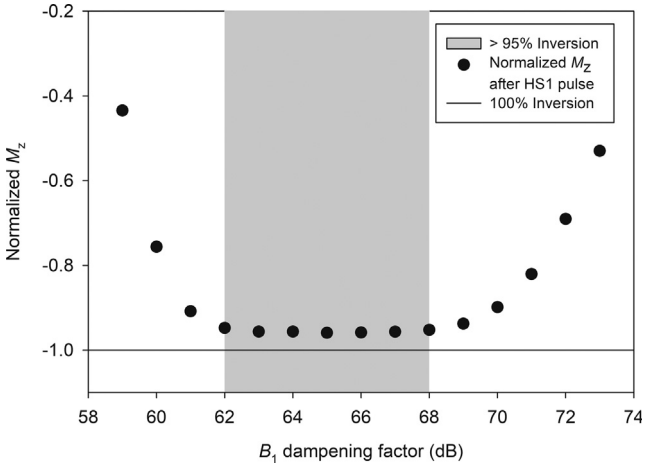

Fig. 1. B_1 insensitivity of an adiabatic HS1 inversion pulse. The ^{1}H NMR signal at 4.7 ppm from a 10% H_2O sample in D_2O (with a small amount of $CuSO_4$ added to achieve T_1 = 1.95 s) was used to determine longitudinal magnetization after a 500 ms HS1 AFP with various power-level dampening factors. The experiments were performed on a 200 MHz Bruker AVANCE DRX spectrometer with a standard 5-mm broad-band probe. Incomplete inversion in the optimum range of 62–68 dB is attributed to relaxation during the HS1 pulse.

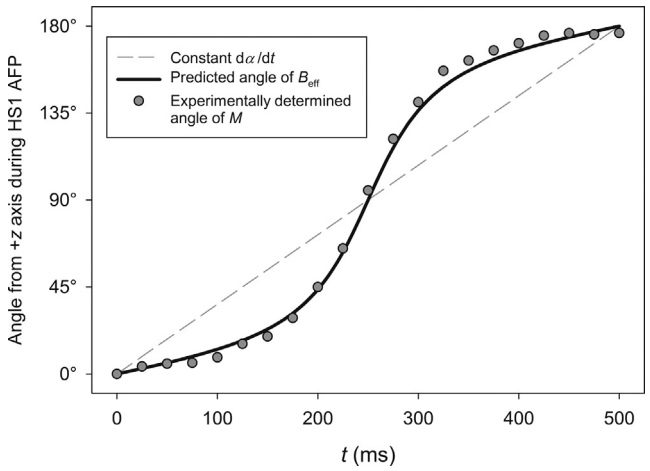

Fig. 2. Orientation of B_{eff} during a 500 ms HS1 AFP as a function of pulse duration. The filled circles indicate the orientation of magnetization derived from independent measurements of transverse and longitudinal magnetization components. The solid line shows the orientation calculated by a least-squares best-fit optimization of Eq. (1) to the experimental data ($f_{bf} = \omega_{1,max}/\Delta\omega_{0,max}$ = 0.3106). For reference, the dashed line represents constant angular motion.