Experimental verification of the exact response of nuclear spins to an exponentially shaped pulse

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This paper presents an experimental determination of the offset dependence of the response of a nuclear spin to an exponentially shaped pulse. There are two limiting cases: If the decay constant, a, is greater than ω_1/π, 100% inversion is not possible. If the decay constant, a, is less than ω_1/π, 100% inversion is possible. In the latter case, the agreement with the theoretically derived response curve is excellent. In the former case, agreement between theory and experiment is very good but not exact. In addition, if the pulse length of a square π pulse of maximum radiofrequency field strength ω_1 is known, then the pulse length of an exponential π pulse with the same maximum field strength may be calculated.

1. Introduction

With the advent of inexpensive and versatile waveform generators, selective excitation in nuclear magnetic resonance has attracted renewed interest [1-3]. The output from the transmitter is modulated in amplitude and/or phase by the waveform generator resulting in a pulse shape that resembles the waveform stored in the waveform generator. Historically, rectangular pulse shapes were the first to be employed in Fourier transform NMR [4], and although adequate for many NMR experiments they have severe limitations [5] when applied to magnetic resonance imaging or NMR experiments requiring selective excitation. These limitations may be alleviated by using alternative pulse shapes.

In the limit of a weak radiofrequency field, the response of a weakly coupled spin system to a single arbitrarily shaped pulse is easy to calculate. The so-called linear response theory predicts the response of a spin system to a pulse is simply the Fourier transform of the pulse shape. The assumptions of linear response theory are, however, rarely satisfied in the typical experiments carried out by NMR spectroscopists. We must resort to non-linear techniques to calculate the excitation response for the most frequently used flip angles, $\pi/2$ and π. Despite enormous advances in instrumentation in the area of selective excitation, the response of a weakly coupled spin system to commonly used pulse shapes has been calculated analytically for only two waveforms, the rectangular waveform and the phase-modulated hyperbolic secant waveform [5,6]. One must resort to perturbative techniques to obtain an approximate solution for pulse shapes such as a Gaussian waveform or a sine waveform [5,7,8].

In this Letter we experimentally verify the theoretically derived response of a weakly coupled spin system to two different cases of exponentially shaped pulses [8]. We demonstrate in both cases an excellent correlation between the experimental results and the predicted response.

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2. Experimental

All experimental data points are acquired with a small sample (smaller than the size of the coil) of 2% H_2O in D_2O lightly doped with $Cr(acac)_3$. All data are collected at 500.1 MHz on a Varian VXR 500 NMR spectrometer. Exponential waveforms are generated on a SUN 4/110 computer and then downloaded to the non-volatile waveform storage of a LeCroy waveform generator (LeCroy, Chestnut Ridge, NY, USA). Prior to the experiment the waveform is recalled to the high-speed memory of the waveform generator and, on receipt of a trigger from the spectrometer, used to modulate a rectangular pulse via a double-balanced mixer.

The degree of inversion of the HOD signal is determined by measuring the transverse magnetization which is created by applying a high-power $\pi/2$ rectangular pulse on resonance immediately following the exponentially shaped pulse. Any transverse magnetization remaining after the exponential pulse is suppressed by cycling the phase of the exponential π pulse and keeping the phase of the rectangular $\pi/2$ pulse and the phase of the receiver constant. The radiofrequency field strength of the exponentially shaped pulse is 0.8 kHz and the rectangular $\pi/2$ pulse is 2.8 kHz.

3. Theoretical background

The Wei–Norman approach [8] is used to find a solution of the quantum Liouville equation for NMR field modulation. The exact analytical solution of the resulting Riccati equation is given by [8]

$$\%\text{spin inversion} = 100 \times \frac{(\pi\omega_1/4a)^2 \exp(-at)}{[\cosh(\Delta\omega\pi/2a)]^2} \times \left| J_{-i\Delta\omega/2a-1/2}\left(\frac{\omega_1}{2a}\right) J_{+i\Delta\omega/2a+1/2}\left(\frac{\omega_1}{2a}\exp(-at)\right) - J_{i\Delta\omega/2a+1/2}\left(\frac{\omega_1}{2a}\right) \times J_{-i\Delta\omega/2a-1/2}\left(\frac{\omega_1}{2a}\exp(-at)\right)\right|^2 \quad (1)$$

This solution is valid at any offset $\Delta\omega$ for an exponential pulse having magnetic field components of

$$H_x(t) = H_y(t) = (\omega_1/\gamma)\exp(-at)\,. \quad (2)$$

When $\Delta\omega \neq 0$, the Bessel functions $J_\alpha(x)$ have complex order. For $\Delta\omega = 0$, the solutions collapse to a rotation matrix. In particular, eq. (1) reduces to the $\Delta\omega = 0$ limit of

$$\%\text{spin inversion} = 100 \times \sin^2\left(\frac{\omega_1}{2a}[1-\exp(-at)]\right). \quad (3)$$

Two different cases are studied in this work:

(a) $\omega_1 > \pi a$. In this regime 100% inversion is possible. As an example of the typical response in this regime several points are calculated for $a = \omega_1/4$ using eq. (1). The π exponential pulse length is calculated from the known pulse length of a rectangular π pulse at the same transmitter power from eq. (84) of Campolieti and Sanctuary [8]

$$t_{exp} = (-1/a)\ln(1 - a\pi/\omega_1)\,, \quad (4)$$

where $a = \omega_1/4 = \pi/4t_{rect}$, t_{exp} is the length of the exponential pulse and t_{rect} is the length of a rectangular pulse at the same maximum field strength as the exponential pulse. The theoretical response of a spin system for this case is shown in fig. 1A.

(b) $\omega_1 < \pi a$ where 100% inversion is not possible, as can be seen, for example, when $a = \omega_1/2$,

$$H_1(t) = (\omega_1/\gamma)\exp(-\omega_1 t/2)\,. \quad (5)$$

In this regime the pulse length of a π exponential

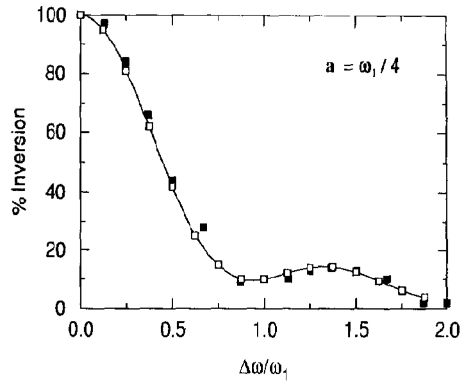

Fig. 1. A comparison of the (A) theoretically calculated (□), (B) experimentally determined (■) spin inversion profile of an $a = \omega_1/4$ exponential pulse.

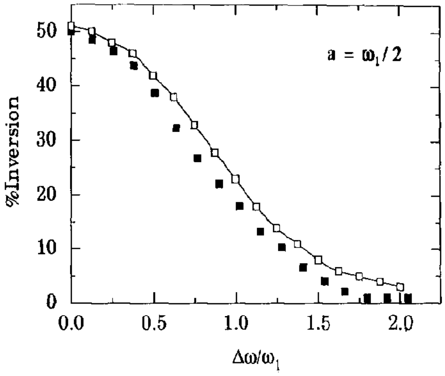

Fig. 2. A comparison of the (A) theoretically calculated (□), (B) experimentally determined (■) spin inversion profile of an $a=\omega_1/2$ exponential pulse.

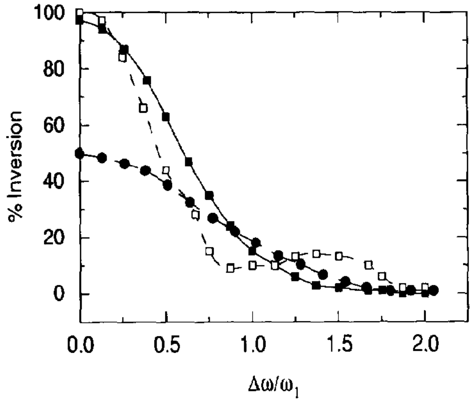

Fig. 3. A comparison of the experimentally determined spin inversion profile of (A) an $a=\omega_1/2$ exponential pulse (●), (B) an $a=\omega_1/4$ exponential pulse (□), (C) a Gaussian pulse (■).

pulse cannot be calculated from the experimentally determined length of a rectangular pulse at the same transmitter power. Hence, the exponential pulse length is arbitrarily chosen to be the same length as the experimentally determined length of a rectangular pulse at the same transmitter power. The theoretical response of a spin system to an exponential pulse described by (5) at several offset values is displayed in fig. 2A [#1].

4. Results and discussion

The response of a spin system to exponential pulses in which $a=\omega_1/2$ and $a=\omega_1/4$ is determined experimentally on the proton signal of 2% H_2O in D_2O. This concentration was chosen to remove any possibility that radiation damping may affect the acquired signal. The offset profile (obtained by stepping the transmitter offset frequency in 200 Hz increments from the HOD line) of an exponential pulse in which $a=\omega_1/2$ is displayed in fig. 2B. The experimentally determined profile compares well with the theoretical response. By comparison, the experimentally determined response profile of the $a=\omega_1/4$ exponential pulse (fig. 1B) agrees exactly (within experimental error) with the calculated response curve. Furthermore, on resonance the inversion is 100%, confirming that eq. (4) can be used to calculate the π pulsewidth of an exponential pulse if the π pulsewidth of a rectangular pulse at the same B_1 field is known. For comparison, we have plotted the experimentally determined inversion response profiles of the $a=\omega_1/2$ and $a=\omega_1/4$ exponential pulses in fig. 3 and compare them to the response curve of a Gaussian pulse shape. (All three pulse shapes have the same maximum field strength as the exponential pulse, i.e. 0.8 kHz.) As expected, the Gaussian closely approximates a Gaussian shape. The $a=\omega_1/4$ exponential pulse inversion profile is narrower than the Gaussian but there are 10% sine-like oscillations at larger offsets.

It is interesting to compare the relative π pulse widths of a Gaussian, an $a=\omega_1/4$ exponentially shaped pulse and a rectangular-shaped pulse at the same maximum field strength. The relative lengths of the three pulse shapes are experimentally found to be

$$t_{rect}=0.51t_{exp}=0.36t_{Gaussian}\,.$$

We have experimentally determined the inversion response profiles of two exponentially ramped pulse

[#1] In ref. [8], a calculation error exists in figs. 2 and 3a. Fig. 2 should be replaced by fig. 2A of this paper. In fig. 3a the sine oscillations are a factor of 2 too big. Also noted are three typographical errors: in eq. (59) the second Bessel function should read $\exp(-\mathrm{i}at)/2a$; in eq. (83) the argument of the last Bessel function should read $-\mathrm{i}\Delta\omega/2a-\frac{1}{2}$ and in eq. (86) the second term on the rhs should be multiplied by i.

shapes and compared them to the theoretical profiles which resulted from an analytical solution of the Bloch equations. We find that in the regime $a<\omega_1/\pi$, the length of a π exponential pulse on resonance can be calculated from the known length of the rectangular π pulse at the same transmitter power. Nonrectangular pulse shapes will inevitably replace rectangular pulses in many magnetic resonance applications. The methodology presented by Campolieti and Sanctuary [8] and the experimentally verification in this paper suggest a framework for predicting the exact response at any offset of spins $I \geqslant 1/2$ that have been excited by an arbitrarily shaped pulse.

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