Relaxational signal attenuation during selective refocusing pulses

Runchao Li, Laura Castañar, Mathias Nilsson and Gareth A. Morris
Department of Chemistry, The University of Manchester
runchao.li@postgrad.manchester.ac.uk

MANCHESTER 1824

Introduction

In modern NMR spectroscopy, selective pulses[1] are widely used to restrict signal excitation to specified frequency ranges. However, due to the relatively long durations of such pulses, relaxation can affect quantitation. As part of a wider project to investigate quantitation in multiple pulse NMR methods, signal loss during on-resonance selective 180° refocusing pulses of different shapes has been examined.

The practical problem is the lack of analytical results for relaxation during shaped pulses. The full analytical solutions of the Bloch equations for constant *x* radiofrequency (RF) irradiation[2] reduce on-resonance to single exponential decay of M_y with rate constant $(R_1 + R_2)/2$ if the RF amplitude is large compared to $R_1 - R_2$. A heuristic approach to describing relaxation during shaped 180° pulses is thus to use an exponential decay constant which is a pulse shape-dependent linear combination $\alpha R_1 + (1 - \alpha)R_2$.

Selective spin echo experiments (Figure 1) on a range of doped water samples, and corresponding numerical simulations using the experimental T_1 and T_2 values, have been used to test this approach for Gaussian,[3] rSNOB,[4] and REBURP[5] shaped pulses. They yield a single parameter α for each shape that satisfactorily describes the relaxational attenuation produced by on-resonance shaped 180° refocusing pulses, and can be used to correct signal loss due to relaxation during selective pulses in experiments such as pure shift NMR.[6]

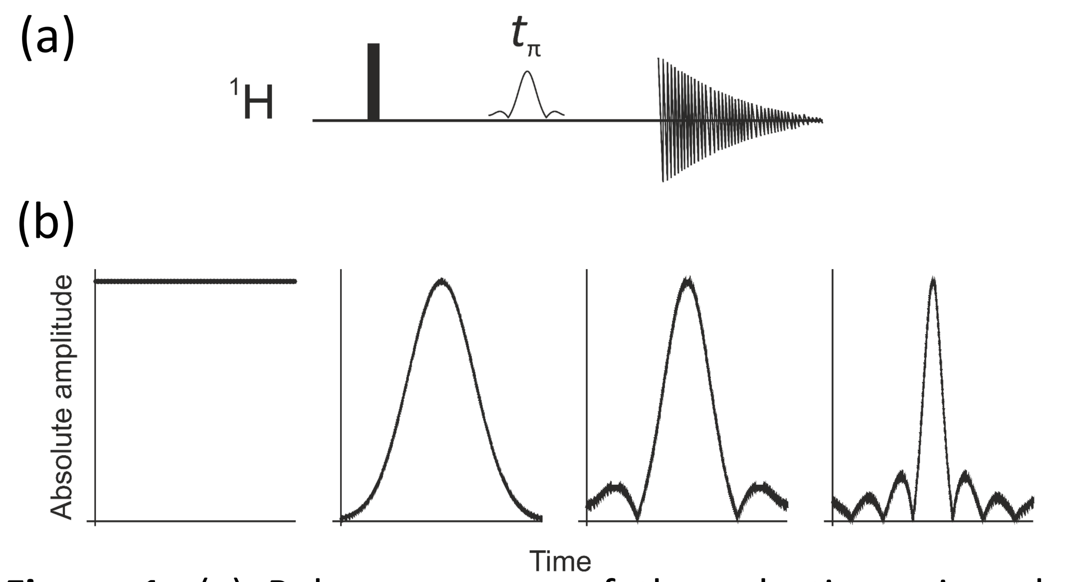

Figure 1. (a) Pulse sequence of the selective spin echo experiment, consisting of a hard π/2 pulse followed by a selective π pulse with a duration of t_π.
(b) Pulse profiles of the four selective pulses used, which are rectangular, Gaussian, rSNOB and REBURP, from left to right, respectively.

Theory

Starting with the case of a rectangular pulse, we use the Bloch equations[7] [1] in which the RF field B_1 defines the *x* axis of the rotating frame. In a spin echo experiment, the *x* component of magnetization M_x is unaffected by B_1 and decays exponentially with rate constant $R_2 = 1/T_2$, but initial *y* magnetization M_y will experience both spin-spin and spin-lattice relaxation as it is rotated through *z*. It is straightforward to derive the steady state solutions of the Bloch equations on resonance, and solving for the difference between M_y and M_z and their steady-state values gives exponentially damped rotation with an angular frequency ω_{eff} and a decay constant $(R_1 + R_2)/2$. In practical experiments with selective pulses, ω_1 is much larger than the difference of R_1 and R_2, $\omega_1 \sim \omega_{eff}$, and the steady-state magnetization components are negligible. The attenuation function $A(t_\pi)$ for an EXORCYCLEd (or gradient-enforced) spin echo is then For a purely amplitude modulated shaped pulse, which includes all the selective pulses used here, the *x* magnetization contribution to the attenuation is always the same as the second term in [2]. The *y* magnetization again experiences both T_1 and T_2, but for a general shaped pulse we have no analytical solution. A logical choice for a general approximate form for $A(t_\pi)$ [3] for shaped pulses is one in which the spin-lattice contribution to the M_y term in the attenuation is scaled by a shape-specific factor $\alpha < 0.5$.

$$\frac{dM_x}{dt} = -R_2 M_x \qquad \frac{dM_y}{dt} = -R_2 M_y - \omega_1 M_z \qquad \frac{dM_z}{dt} = \omega_1 M_y + R_1(1 - M_z) \qquad [1]$$

Approximation

$$A(t_\pi) = \left[e^{-\frac{(R_1+R_2)t_\pi}{2}} + e^{-R_2 t_\pi}\right]/2 \qquad [2]$$

Extrapolation

$$A(t_\pi) = \left[e^{-t_\pi(\alpha R_1 + (1-\alpha)R_2)} + e^{-R_2 t_\pi}\right]/2 \qquad [3]$$

Experiments and simulations

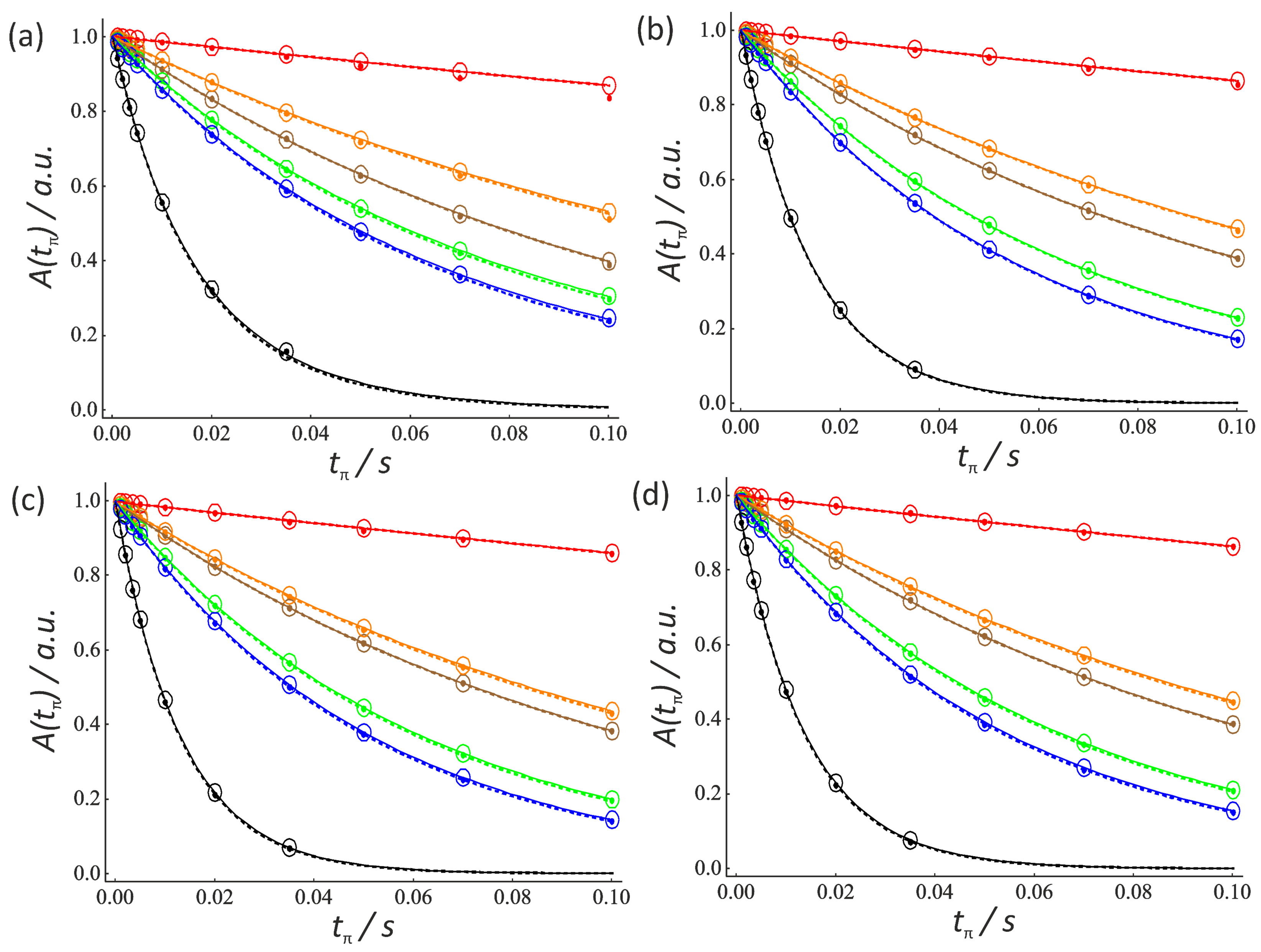

Figure 2. Experimental (small filled circles) and simulated (open circles) data for the relaxational attenuation on resonance $A(t_\pi)$ in a selective spin echo experiment using a shaped selective 180° pulse, for (a) rectangular, (b) Gaussian, (c) rSNOB and (d) REBURP pulse shapes. Solid and dashed lines show the result of global fitting of the simulated and experimental data to Equation [3], with α as the only adjustable parameter.

Selective spin echo experiments with a 90° hard pulse followed by a 180° selective pulse were used to investigate the parameter *α* for rectangular, Gaussian, rSNOB and REBURP pulses. Signal integral attenuation as a function of t_π was measured for six samples of HDO in D_2O doped with Cu^{2+} and/or Mn^{2+} to give different combinations of T_1 and T_2.

Table 1. Relaxation times of HDO in D_2O doped with Cu^{2+} and Mn^{2+} at 25°C nominal temperature.

Sample	6.3 mM $CuSO_4$	1.64 mM $CuSO_4$	0.072 mM $MnCl_2$	0.144 mM $MnCl_2$	1.64 mM $CuSO_4$ + 0.263 mM $MnCl_2$	0.41 mM $CuSO_4$ + 0.066 mM $MnCl_2$
T_1 / s	0.127	0.903	2.413	1.341	0.233	0.959
T_2 / s	0.104	0.667	0.116	0.059	0.013	0.049

For comparison, numerical simulations using the Bloch equations were carried out with the same parameters as experiment, and measured values of T_1 and T_2. The experimental and simulated data were fitted independently to Equation [3], with *α* as the only variable parameter. Figure 2 summarises the experiments, simulations and fits, showing both excellent agreement between experiment and simulation, and excellent consistency with Equation [3]. The values of *α* obtained are summarised in Table 2. The quality of fit for a range of ratios T_1/T_2 gives confidence that Equation [3] could be used to correct experimental data obtained using shaped pulses for the effects of T_1 and T_2 relaxation on resonance during such pulses.

	rectangular	Gaussian	rSNOB	REBURP
Experimental	0.487	0.231	0.122	0.049
Simulated	0.509	0.240	0.147	0.080

Table 2. Values of the pulse shape-specific parameter α obtained by fitting the experimental and simulated data of Figure 1 to Equation [3].

Conclusions

During selective refocusing pulses in practical echo experiments, using phase cycling or gradient pulses to select refocused signals, magnetizations necessarily follow trajectories that can leave the transverse plane of the Bloch sphere. The signal loss in such experiments therefore depends on both T_1 and T_2. The relative importance of the two contributions depends on the shape of the selective pulse, the contribution of T_1 decreasing as the proportion of the pulse duration for which the magnetization remains close to the transverse plane increases. For experiments on resonance, it has been shown both experimentally and by numerical simulation that the signal attenuation is well described by the average of two equal exponential contributions, one of which decays with T_2 and the other of which has a decay constant that is a shape-dependent mixture of T_1 and T_2. It should therefore be possible to make accurate corrections for relaxational signal loss in quantitative NMR experiments using on-resonance selective refocusing pulses.

References

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Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council (grant number EP/R018790).