Adiabatic half-passage pulses for measuring the polarization of highly non-equilibrium spin-systems

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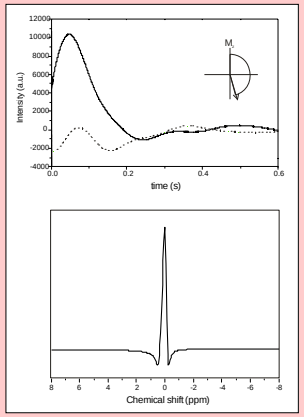
Introduction

The use of highly non-equilibrium, or hyperpolarized, spin species offers a number of challenges that are not normally encountered in nuclear magnetic resonance. Notably the nature of the signal is non-renewable in the sense that after having applied a 90º radio frequency (RF) pulse the magnetization recovers to the thermal equilibrium polarisation and *not* to it's hyperpolarized state. Furthermore radiation damping effects become increasingly problematic since the large bulk magnetic field generated by the sample results in an additional non-linear feedback through the RF coil that drives the magnetization back to equilibrium and can dominate the spin-dynamics (1).

We consider the use of adiabatic half-passage pulses as a simple technique for overcoming the need for pulse calibration (2). Numerous approaches have been described in other fields of NMR for achieving uniform excitation or inversion in the case of incorrectly calibrated RF pulses or where the RF field is inhomogeneous. These pulses yield a full excitation provided the pulse amplitude is above a certain threshold value making the response independent of pulse duration. The influence of radiation damping, a phenomenon that is frequently observed for concentrated samples at high magnetic field strength or for otherwise highly polarized samples, is shown not to adversely affect the method provided the pulse amplitude is above this threshold value. We apply this method to measure the degree of polarization for a hyperpolarized sample of gaseous ^{129}Xe in a clinical scanner at 1.5 T (3).

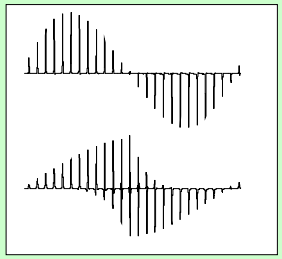
Observation of radiation damping at 1.5 T

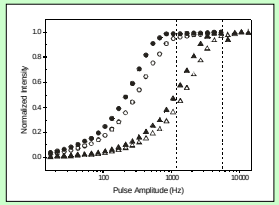
The influence of radiation damping is best appreciated after an inversion pulse where characteristic phase distortions arise in the spectrum due to the non-linear feedback field. The figure (right) shows a representative FID and corresponding spectrum of a gaseous sample of 80 µmol of ~10% hyperpolarized ^{129}Xe at 1.5 T following an imperfect inversion pulse. The envelope of the FID and phase distortion in the spectrum are typical of a signal returning to equilibrium under the non-linear effects of radiation damping, see vector diagram inset. These effects are less pronounced than those observed for water signal at high field strengths, however the influence of radiation damping can still be clearly observed.



Pulse calibration in the presence of RD

The figure (right) shows a typical pulse calibration experiment at 500 MHz for a square pulse as a function of the pulse duration. Spectra are recorded with a 1µs interval. The two samples are $CHCl_3$ and H_2O, respectively. Note that in the presence of radiation damping severe phase distortions are observed and the response of the magnetization is no longer the simple sine function that is expected in the absence of radiation damping. The pulse angle cannot be readily derived.



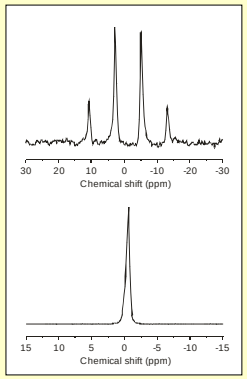


The figure (left) shows the response of the magnetization to an adiabatic tanh RF pulse as a function of the pulse amplitude $\omega_{max}/2\pi$ for 1 ms (circles) and 200 µs (triangles) pulse lengths and in the presence (open symbols) or absence (closed) of radiation damping. The pulse yields a maximum excitation provided the pulse amplitude is set to be greater than the threshold value (dashed lines).

Polarization measurements

To calculate the polarization, P, of the hyperpolarized ^{129}Xe, the signal intensity, *S*, for a known quantity, *n*, of ^{129}Xe is compared to the signal intensity given by a known quantity of a reference sample at thermal equilibrium. In the case of gaseous ^{129}Xe the signal from a thermally polarized sample at 1.5T is extremely time consuming to record. This is in part due to the low spin density in a gaseous sample and partly due to a rather long T_1 (≈ 20 min) for this system. We calculate the polarization with respect to the thermal ^{13}C signal in toluene with the same RF coil at the same B_0 field strength using the following equation

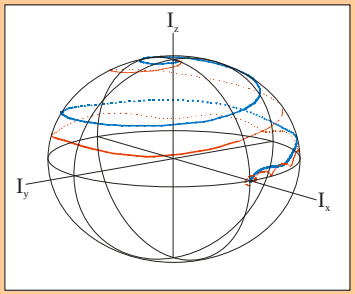
$$\frac{S(^{129}Xe)}{S(^{13}C)} = \frac{P(^{129}Xe)}{P(^{13}C)} \frac{n(^{129}Xe)}{n(^{13}C)} \frac{\gamma_{Xe}^2}{\gamma_C^2} \frac{Q(\omega_0^{Xe})}{Q(\omega_0^C)}$$



The figure (above) shows representative spectra for the ^{13}C signal in toluene and the hyperpolarized ^{129}Xe signal. Both are recorded with a single acquisition employing a 256 µs adiabatic half-passage tanh pulse. The intensity axis is scaled down by a factor of 400 with respect to the ^{13}C signal. From the ratio of these two signals and employing Eq. (5) the polarization level of ^{129}Xe was found to be 9.4 % whereas the equilibrium polarization of ^{129}Xe at 298 K and 1.5 T is 1.43 x 10^{-6}. The polarized signal that we observe therefore corresponds to an enhancement factor of 6.6 x 10^4.

Adiabatic half-passage pulses

The figure below shows two representative magnetization trajectories employing a phase modulated hyperbolic tangent pulse. Simulations were carried out in MATLAB. The duration of the RF pulse was 1 ms. The trajectories are calculated by integrating the Liouville von-Neumann equation in a stepwise fashion and in the absence of relaxation. The blue trajectory corresponds to a maximum pulse amplitude, i.e. the asymptotic value of the tanh curve, of $\omega_{max}/2\pi$ = 5 kHz whereas the red trajectory corresponds to a maximum pulse amplitude of $\omega_{max}/2\pi$ = 10 kHz. Both amplitudes are set above the threshold value. Note that despite the same pulse duration the destination of the magnetization vector yields a maximum in the transverse plane.



Conclusion

We have demonstrated the use of adiabatic half-passage radio frequency pulses for exciting the magnetization of a hyperpolarized sample of ^{129}Xe and thus for calculating the degree of polarization. The method has been shown to overcome problems with pulse calibration and simplifies experiments that are acquired within a single acquisition. Furthermore these pulses are less sensitive to B_1 field inhomogeneity and are less affected by the influence of radiation damping in highly polarized spin systems.

Acknowledgements

This work was supported by the Council for Research Councils Basic Technology Programme grant number GR/S23612/01 and by Cancer Research UK [CUK] grant number C1060/A808.

References

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