Experimental Optimization of Magic Angle Spinning Solid State NMR Spectroscopy at 750 MHz

S. McNeill (UF Electrical and Computer Engineering); P.L. Gor'kov, W.W. Brey (NHMFL/FSU); J.R. Long (UF Biochemistry and Molecular Biology)

Introduction

We have been working on building and optimizing a 750 MHz MAS probe that uses crossed coils, Fig. 1, in a low-E configuration with a ^{1}H loop gap resonator and a ^{13}C solenoid nested inside to achieve RF fields with high homogeneity, high efficiency, and reduced sample heating [1]. In particular, the homogeneity is very good, as Fig. 2 shows. The probe is being used for several applications. Double quantum recoupling experiments, as shown in [1], greatly benefit from the increased homogeneity. Studies of biologically relevant peptide and lipid systems enjoy the reduced RF heating.

Fig.1. A drawing of the stator and coil assembly.

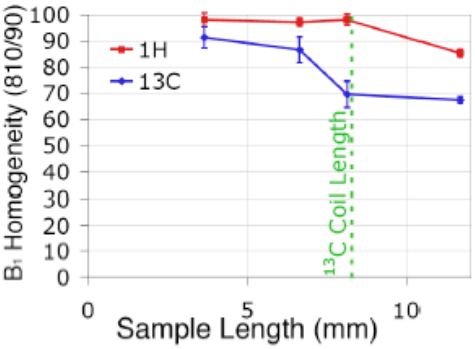

Fig. 2. ^{1}H (red) and ^{13}C (blue) B_1 homogeneity of the probe for different sample lengths.

Methods

We are also attempting to improve pulse sequences for high field applications by designing composite pulses to both invert and refocus magnetization for use in place of standard pulses in ssNMR experiments. This is necessary to compensate for the increased the frequency ranges of isotropic and anisotropic chemical shifts at high fields [2]. Using SPINEVOLUTION [3] to simulate frequency profiles and the Nelder-Mead simplex method as implemented in Matlab to optimize the phases and lengths of composite pulses, we have been able to design several improved composite pulses.

Results and Discussion

Our composite pulses have been verified experimentally using the low-E probe, and it has not been necessary to model RF inhomogeneity since the homogeneity of the probe on both the ^{1}H and ^{13}C channels is so high. This makes the optimization routine simpler and the computations considerably faster. The Nelder-Mead simplex method works well optimizing pulse sequences using small numbers (1-10) of pulses with unconstrained pulse lengths and phase magnitudes at constant RF power; good compensation with realistic experimental parameters can be found as shown in Fig. 3. More constrained optimization and other methods of optimization, such as genetic algorithms, are also being explored to optimize the parameters of windowless pulse sequences we are interested in using with our present hardware constraints.

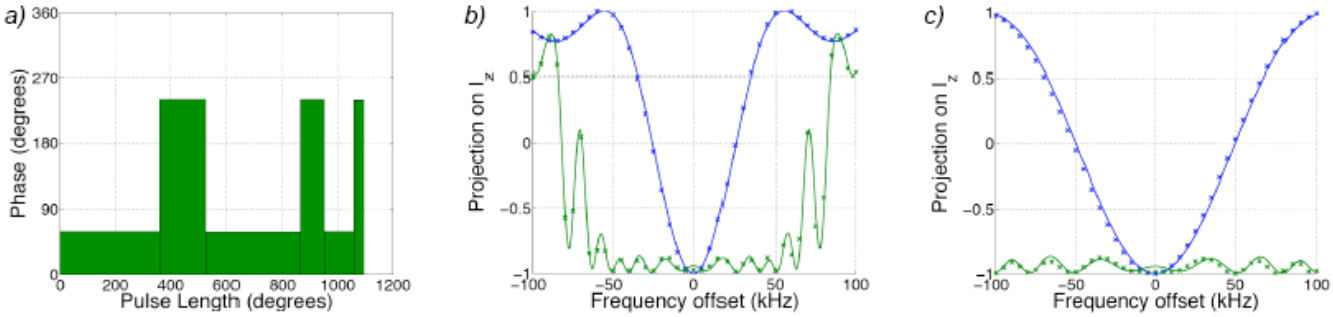

Fig. 3 a) The phases and pulse lengths for a composite ^{13}C inversion pulse optimized for 750 MHz MAS spinning at 10 kHz using constant RF power at 50 kHz. b) Experimental (X's) and simulated (line) data for a single 180º pulse (blue) and the optimized composite pulse (green) at 32 kHz RF power. c) Experimental (X's) and simulated (line) data for a single 180º pulse (blue) and the optimized composite pulse (green) at 63 kHz RF power.

References

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[3] M. Veshtort and R. G. Griffin, *J. Magn. Reson.* **178**, 248-282 (2006).