Maximizing Sensitivity in Bulk Hyperpolarization Experiments by MAS Rate Modulation

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We have recently shown how dynamic nuclear polarization can be used to hyperpolarize the bulk of proton-free solids, resulting in significant signal enhancements in MAS experiments.[1] The method relies on hyperpolarization of nuclei near the surface by impregnation DNP and subsequent relay of polarization towards the bulk through slow spontaneous spin diffusion between weakly magnetic nuclei. Pulse cooling is an efficient variant of this strategy that uses a multiple contact cross-polarization sequence for bulk hyperpolarization to achieve overall sensitivity gains of up to a factor 50 for the ^{119}Sn spectrum of powdered SnO_2.[1]

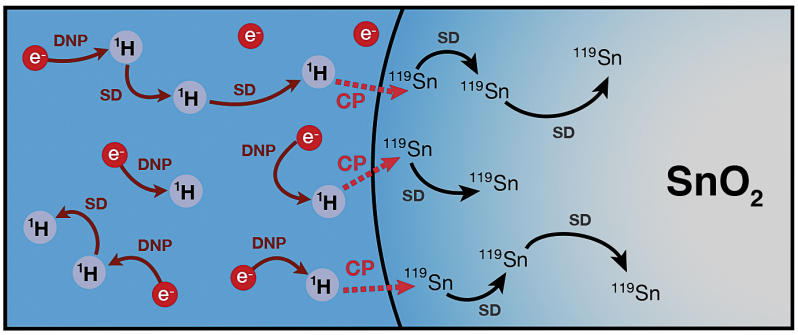

Figure 1. Pulsed cooling of powdered SnO_2. Hyperpolarization is generated on ^{1}H nuclei in a wetting phase and transferred to ^{119}Sn nuclei at the surface of the material with repeated cross-polarization contacts. Slow spin diffusion between tin nuclei transports the polarization towards the bulk.

Here, we show how to optimize the pulse parameters and delays in the pulse cooling method, and how spin rate modulation can be used to maximize sensitivity gains in these experiments. Specifically, we show that when the sample is polarized at a slow spin rate, where spin diffusion is faster, and the MAS rate is then increased before detection to benefit from increased line narrowing, we obtain an additional increase in the sensitivity of ^{119}Sn spectra of SnO_2 up to a factor of 3.5, as compared to a constant MAS rate experiment.

We also show how the spin diffusion pathways in these experiments can be probed with multidimensional experiments, and how the scope of bulk hyperpolarization of inorganic solids can be broadened by looking at compounds with multiple chemical shifts, and by extending the method to other nuclei.

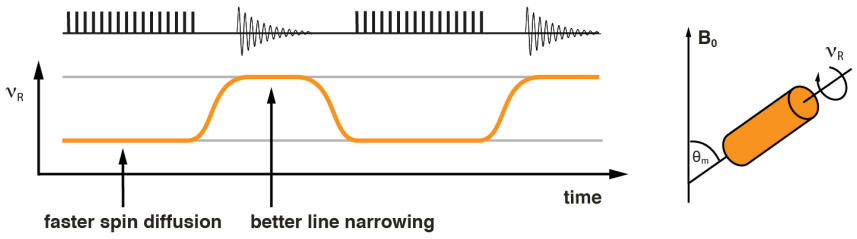

Figure 2. Schematic representation of how the MAS rate is modulated during the experiment. Hyperpolarization and spin diffusion towards the bulk happen at a slow spin rate. The MAS rate is then increased before acquisition of the FID.

1. Bjorgvinsdottir, S.; Walder, B. J.; Pinon, A. C.; Emsley, L., Bulk Nuclear Hyperpolarization of Inorganic Solids by Relay from the Surface. *Journal of the American Chemical Society* **2018,** *140* (25), 7946-7951.