Optimal sensitivity regime for ^{1}H detected relayed DNP

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Dynamic Nuclear Polarization (DNP) is now a well-established hyperpolarization technique that can significantly enhance the sensitivity of magic angle spinning (MAS) solid-state NMR. There has been a lot of interest in combining DNP with high magnetic field and fast MAS to benefit from the significantly improved ^{1}H resolution and high sensitivity and thus allow the implementation of ^{1}H-detected 2D correlation schemes. Recently, demonstrating this, we reported the first DNP MAS experiments at 21.2 T using a 0.7 mm MAS probe that enabled spinning rates of up to 65 kHz, at ~100 K. [1] However, under these conditions, despite the high enhancements observed in the radical solution, in the context of relayed DNP (R-DNP), faster MAS rates have a detrimental effect on the DNP enhancement. This raises the question of whether this decrease in DNP enhancement is also reflected in the sensitivity of the microwave ON experiment. Here we analyze the effect of faster MAS rates on the absolute sensitivity of the experiment recorded under microwave irradiation.

^{1}H-^{1}H spin diffusion is a central component of the hyperpolarization mechanism in MAS DNP, [2] as it conveys hyperpolarization to the bulk of impregnated materials. While faster MAS rates increase ^{1}H sensitivity and resolution, they also reduce the level of hyperpolarization in the polarized materials by reducing the spin diffusion rate. Thus, between these counteracting effects, we predict that there should be an optimal sensitivity regime. Here we perform R-DNP experiments at fast MAS rates using 0.7 mm diameter rotors at 21.2 T to study the trend of the overall sensitivity as a function of MAS rate. We find that at faster MAS rates, the sensitivity gain due to ^{1}H detection overcomes the loss of overall polarization in impregnated materials due to slower spin diffusion.

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[2] Nathan A. Prisco, Arthur C. Pinon, Lyndon Emsley and Bradley F. Chmelka, *Physical Chemistry Chemical Physics*, **2021**, 23, 1006-1020.