Supplementary Information

Electron-driven spin diffusion supports crossing the diffusion barrier in MAS DNP

Johannes J. Wittmann,[1] Michael Eckardt,[2,3]
Wolfgang Harneit,[2,3] Björn Corzilius[1,*]

[1] *Institute of Physical and Theoretical Chemistry, Institute of Biophysical Chemistry, and Biomolecular Magnetic Resonance Center (BMRZ), Goethe University Frankfurt, Max-von-Laue-Str. 7-9, 60438 Frankfurt, Germany*

[2] *Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10–14, 55099 Mainz, Germany*

[3] *Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany*

* corresponding author: corzilius@em.uni-frankfurt.de

Supplementary Figures

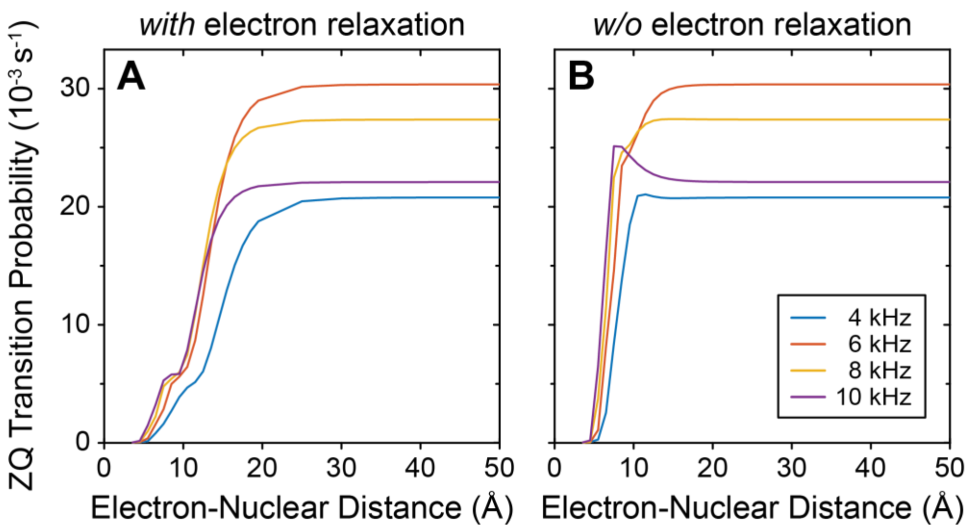

Figure S1. Dependence of the C–C ZQ transition probability [*i.e.*, the contribution of the ZQ line to the nuclear SD rates, summation term in equation (10)] on the distance to an electron spin calculated under the assumption of CSA- and electron-driven SD in the presence of an electronic relaxation superoperator (A, same as Fig. 5A) and without electronic relaxation (B). No explicit relaxation on the nuclear spins has been introduced in both models.

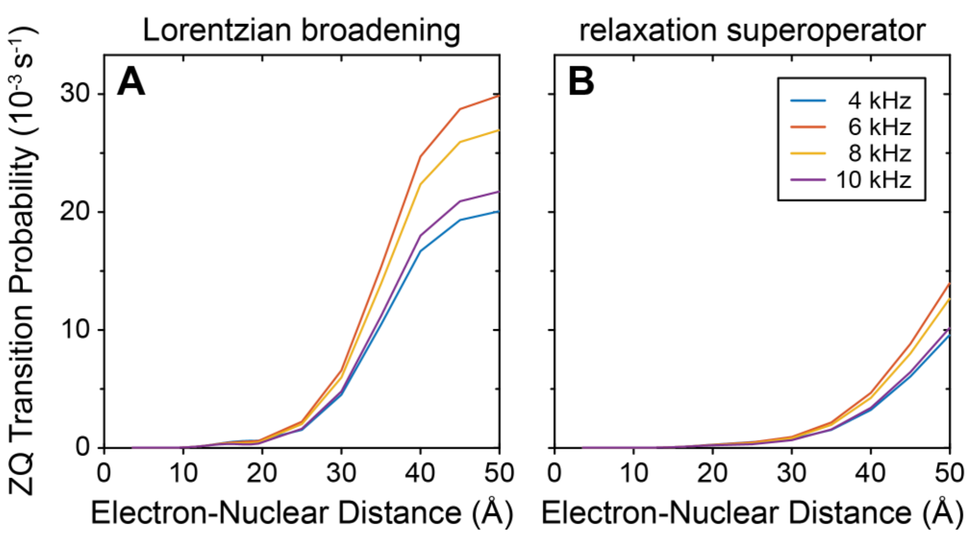

Figure S2. Dependence of the C–C ZQ transition probability [*i.e.*, the contribution of the ZQ line to the nuclear SD rates, summation term in equation (10)] on the distance to an electron spin calculated under the assumption of purely CSA-driven SD. Nuclear relaxation was introduced by Lorentzian broadening of ZQ spectrum after quantum-mechanical calculation (A, same as Fig. 5B) and by application of a relaxation superoperator during propagation in Liouville space (B). No explicit HFI has been introduced in both models.

Qualitative Polarization Build-up Model

The below model qualitatively demonstrates how a linear MAS-dependence of EDSD near a paramagnetic center in combination with inversely linear MAS-dependence of bulk CSA-driven spin diffusion can lead to the experimentally observed DNP parameters.

Due to the complexity of the sample system we demonstrate this principle on a linear chain of 4 nuclear spins. In this chain, the polarization of the first spin is invariably coupled to that of the electron spin. The propagation of polarization from that first (core) spin to the next neighboring spin is subject to EDSD where an increase of the diffusion constant, $k_{\mathrm{SD}}^{(\mathrm{c})}$, with MAS frequency would be expected, according to the simulations discussed in the main text. The subsequent pair-wise (nearest neighbor only) propagation through the chain is assumed to occur with a common diffusion constant, $k_{\mathrm{SD}}^{(\mathrm{b})}$, being inversely scaling with MAS frequency. Longitudinal relaxation is assumed to be faster on the first (electron-coupled) nucleus, but this is not a crucial condition for reproduction of the general behavior. This resulted in the build-up behavior as shown in Fig. S3 for the 4$^{\mathrm{th}}$ spin in the chain.

A qualitatively similar effect is observed as has been shown in Fig. 3A. For the red trace the core spin diffusion rate is reduced while the bulk rate is increased with respect to the green line (i.e., slower MAS). This leads to a faster effective build-up with leveling off at smaller polarization. In contrast, for increased core and reduced bulk diffusion (i.e, faster MAS), the blue curve shows slower effective build-up but larger equilibrium polarization. In panels 3B and 3C one of the diffusion rates is assumed to be invariant with changed in the other, serving as evidence that the core diffusion rate is responsible for determining the final bulk polarization (by modulating the effective transfer of spin polarization from the electron spin to the observable bulk) while the bulk diffusion constant determines the rate with which this polarization is spread over the observable bulk nuclei.

By locking the polarization of the first (electron-coupled nucleus) to 1 we can also qualitatively simulate the effect of paramagnetic relaxation limited by bulk spin diffusion. We found a very similar behavior, where effective saturation recovery rates are increasing with decreasing bulk spin diffusion rate (i.e., faster MAS) but, of course, independent of the core diffusion rate all curves level off at the same thermal nuclear polarization.

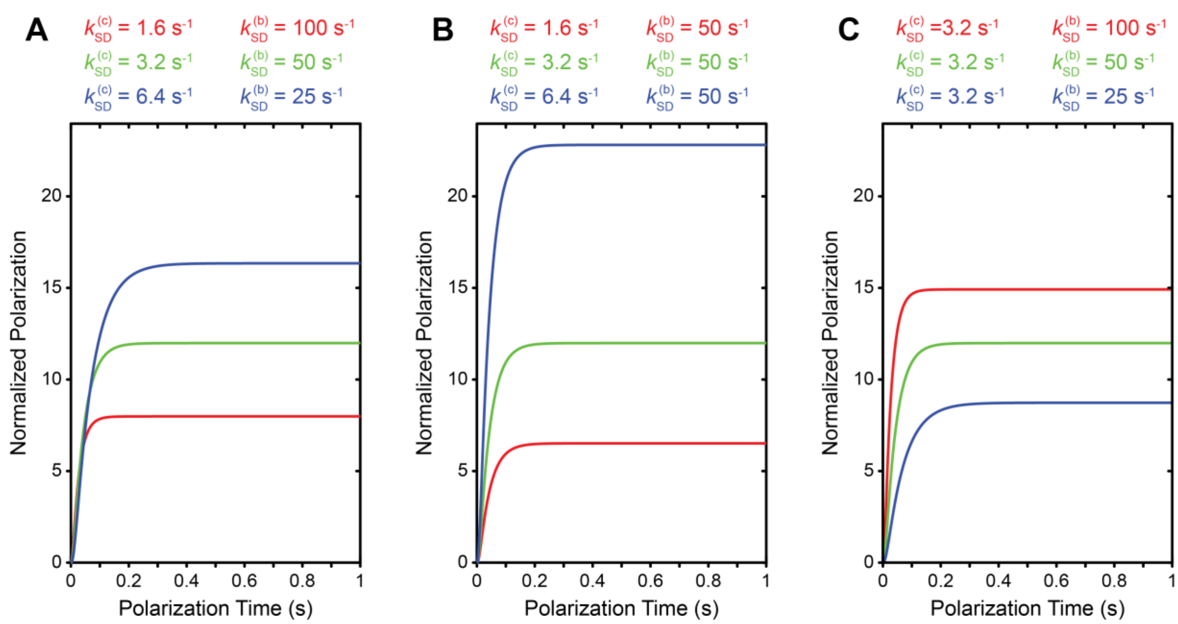

Figure S3. Qualitative model of spin diffusion in a linear chain as described in the text. The polarization build-up on the last spin is shown for three different scenarios: (A) core (c) spin diffusion rate is showing opposite scaling behavior with respect to bulk (b) spin diffusion rate; in (B) and (C) the bulk and the core spin diffusion rate, respectively, are assumed to be invariant while the other rate is scaling equally as in (A).