

Characterizing Thermal Mixing Dynamic Nuclear Polarization via Cross-Talk between Spin Reservoirs

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Dynamic Nuclear Polarization (DNP) exploits the transfer of polarization from electron spins to nuclear spins. Several mechanisms of polarization transfer have been identified. Here, we focus on thermal mixing (TM). Already in 1973, Goldman and co-workers¹ demonstrated that TM can lead to a transfer of energy between different types of nuclei in a sample via non-Zeeman electron energy states. In a thermodynamic framework, the polarization transfer can be described as an exchange of heat between different reservoirs, i.e., between different nuclei and electrons. TM relies on the efficiency of triple spin flips embracing two electronic spins S and S' , and different nuclear spins I and I' . To transfer heat from one nuclear bath to another, consecutive triple spin flips involving two different nuclei I and I' are necessary to establish the contact between the electronic reservoir and the two nuclear reservoirs, and enable a flow of heat between different nuclear reservoirs. Optimization of this procedure can assist various DNP applications, such as dissolution-DNP in metabolomics or in-cell studies. To identify the boundaries of the TM regime at $T = 4$ K and $B_0 = 6.7$ T and to quantify the flow of polarization between different heat reservoirs associated with nuclear spins I and I' , we performed experiments on spin systems comprising protons ($I = {}^1\text{H}$) and heteronuclei ($I' = {}^2\text{H}$, ${}^{13}\text{C}$ or ${}^{31}\text{P}$) in the presence of nitroxide radicals at variable concentrations.² We performed two different experiments to probe the effects of TM. In experiment A, we monitored the build-up of the polarization $P(I)$ and $P(I')$ while saturating the EPR spectrum by a microwave field, and subsequently measured their return to thermal equilibrium after interrupting the microwave irradiation (Fig. 1). In experiment B, the heteronuclei I' were saturated after switching off the microwave field, and we monitored the flow of polarization from the protons I to the heteronuclei I' . These two experiments allow one to determine whether TM is the dominant DNP mechanism or not. This depends on the concentrations of radicals and heteronuclei. We find that for the nitroxide TEMPOL, TM is the dominant process at TEMPOL concentrations above 40 mM under our experimental conditions of 4 K and 6.7 T.

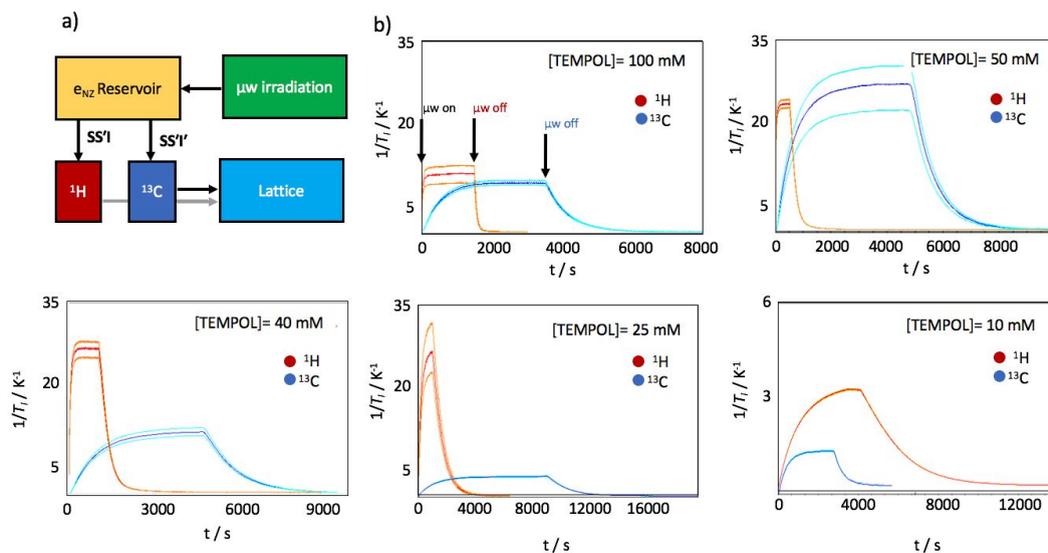


Figure 1. a) Energy reservoirs involved in experiment A that monitors the build-up of the polarizations $P(I = {}^1\text{H})$ and $P(I' = {}^{13}\text{C})$ after switching on the saturation of the EPR spectrum by microwaves (μw), and their decay after interruption of the μw irradiation. The μw irradiation cools down the non-Zeeman dipolar electron reservoir e_{NZ} ; as a result, the ${}^1\text{H}$ and ${}^{13}\text{C}$ spins are polarized simultaneously via heat exchange between the reservoirs. Nuclear relaxation proceeds via dissipation of energy to the lattice. b) DNP build-up curves and decay of polarizations after switching off the μw -field (at the time points indicated by way of example for ${}^1\text{H}$ and ${}^{13}\text{C}$ in the middle panel in the top row for 100 mM TEMPOL) for a sample containing $I = {}^1\text{H}$ and $I' = {}^{13}\text{C}$ nuclei. The polarizations are expressed in terms of inverse spin temperatures, $1/T_i$. Traces shown in lighter color indicate the ranges of experimental errors.

References (1). Cox, S. F. J.; Bouffard, V.; Goldman, M., *J. Phys. C: Solid State Phys.* **1973**, *6*, L100-L103. (2). Guarin, D.; Marhabaie, S.; Rosso, A.; Abergel, D.; Bodenhausen, G.; Ivanov, K.; Kurzbach, D., *J. Phys. Chem. Lett.* **2017**, *8*, 5531–5536.