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Comment on mr-2022-12

Marina Bennati (Referee)

Referee comment on "Reverse dynamic nuclear polarisation for indirect detection of nuclear spins close to unpaired electrons" by Nino Wili et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2022-12-RC3, 2022

The manuscript by Wili et al describes a new polarization transfer experiment between electron and nuclear spins that consists of two steps. The first step has been reported in the literature and is based on electron-nuclear cross-polarization at the NOVEL condition. The second step is a reverse transfer of polarization from nuclei to electron spins at the same NOVEL condition. The experiment is very interesting as it provides a tool to monitor the dynamics of nuclear polarization after a pulse DNP step, which is otherwise difficult to access. The manuscript is overall clearly written, the experimental effects are robust and seem rationalized. Sometimes details are missing. I would recommend publication in MR after adding the following details.

- The first step of the sequence contains a subtle difference to the DNP experiment proposed by the Griffin group, (Can 2015, Mathies 2016). In Figure 2, the NOVEL step is repeated only once, whereas in DNP it is repeated n times (n >~ 1000). In my understanding, this multiple contact is required as one electron spin polarizes a large number of nuclear spins. The question is how much the nuclear spins are polarized in average after only one contact and what is expected then in the reverse polarization step. The authors observe an increase in the intensity of 'repolarized' electron spin in deuterated solvent, indicating that the number of nuclear spins plays indeed a role, see also comment on page 5 ('we speculate that the transfer efficiency could be improved for less abundant nuclei….'). Could the contact time be repeated, which might enhance the efficiency, or are there any hardware constraints to perform this check?
- In context of point (1), in SI 9 the authors report an experiment in which the NOVEL sequence is repeated several times. Perhaps I have missed this, but I could not find a reference to this figure in the main text. This experiment is called 'saturation behavior during depolarization' but it is not entirely clear. Please give the sequence and explain better, also in the main text, what is normalized to 'one' and why the echo is larger than 1 only in the deuterated sample.
- Electron polarization decays as a function of waiting times. The authors write (page 6) that the decay is 'supposably' assigned to proton polarization decay. It would be nice to know what other competitive pathways they suspect.
- Figure 4 shows a clear effect by the solvent deuteration on the 'electron' spin re-polarization dynamics. The effect is tentatively assigned to the faster proton

polarization decay in protonated solvent. It is not clear whether we can learn about the nuclear T1n, which would be very important also for ENDOR.

- Effect of 'decoupling sequence' on the polarization decay. The effect of 'decoupling' is interesting but it would be good to see the sequence in Figure 5 and have a rationale of the chosen parameters (length, intensity, repetition rate, setting of adiabatic pulses) also based on the hyperfine couplings (how large are they ?)

Finally, the authors should add some comments about how this experiment could be beneficial for ENDOR, particularly whether it could be extended to radicals with (much) larger hyperfine interaction and the feasibility at higher fields.