

Magn. Reson. Discuss., referee comment RC2
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Comment on mr-2022-12

Frédéric Mentink-Vigier (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-RC2>, 2022

This is an original article by Nino et al. The authors used a coherent DNP pulse sequence to obtain information about the protons surrounding the electron spins. They qualitatively described the effect of deuteration and radical concentration on the decay of the nuclear polarization surrounding the unpaired electrons, as well as used "electron decoupling". The authors prove that the proton polarization decay around the radical is mostly driven by spin diffusion away from the said electron spins. To the best of my knowledge, this is the first time such experiments are carried out. The article is well written and its stimulating content warrants publication in MR. I have minor comments that should be addressed in order to improve the manuscript.

- The introduction states that the experiments could be used for ENDOR and to probe the DNP mechanism which I entirely agree with. However, the discussion is rather succinct. How would the reverse DNP be used for ENDOR? My understanding is that the NOVEL condition requires large mw power, as a consequence would it be possible to have "resolution"? Would an ENDOR require a frequency sweep of a rf pulse?
- In addition, could we imagine using different pulse sequences? e.g. can we use an eNCP (Rizzato, 2013) to generate the nuclear polarization and then carry out the same reverse CP? If yes, this may be more practical for high field? (Bearing in mind that using offset to have HH condition may be similar as doing off-resonance NOVEL).
- Could the first step of the nuclear hyperpolarization be replaced by a long ELDOR pulse? Then read the polarization with reverse NOVEL (or other pulse sequence)? Same question, with DAVIES ENDOR, Iz generated after the rf pi pulse, so DAVIES could also be used?
- In general, having more experimental details, such as the delays used, the timing in the pulse sequence figures, would be appreciated. Since MR is a specialized journal, I do not think this would make the manuscript less valuable.
- "These findings strongly indicate that nuclear polarisation is generated during the first NOVEL block, even without direct proton NMR detection." True but that's like ELDOR, isn't it? So "strongly" is probably not needed.
- Why is the "minimum of the electron spin echo intensity at 184 ns"?
- "Note that even in deuterated solvent, there are still 48 non-exchangeable protons in OX063. We speculate that the transfer efficiency could be improved for less abundant

nuclei, but experiments are needed to test this hypothesis." I am not sure I understand what is meant here. Do you think that a fully deuterated OX063 would enable higher transfer efficiency? If so, could you explain a bit more?

- Figure 2, would it be possible to add on the pulse sequence figure the timings in between the pulses? Not as numerical values, but as variables.
- Figure 3, a, is this deuterated or protonated? In the text it is mentioned but not in the caption. This might improve the readability.
- Figure S9 has an issue
- Figure S13, the caption could be improved. I think it would be better if it was described by a separate paragraph.