

Magn. Reson. Discuss., community comment CC1
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Comment on mr-2022-12

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Community 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-CC1>, 2022

This is a very interesting paper from Wili et al, which discussed the effect of pulsed DNP from the EPR perspective, which could shed light on important information that is not easily obtainable from the NMR side. The article is definitely publishable on MR. I have a few minor points that the authors might consider addressing.

About RA-NOVEL. Are the shapes used in repolarization/depolarization symmetrical opposite? i.e., if you adiabatically sweep upward in the first step, one should sweep downward in the second step.

About electron decoupling. It is not clear during which period electron decoupling is applied. Is it during the 'T' period before saturation? It is easier for readers if you can label that in Fig. 2. Is there a reason why 30 microseconds yields an optimum result? Is it empirical or does there exist theoretical reasoning behind it? 30 us corresponds to roughly ~ 30 kHz coupling size, which is much smaller than the anticipated size of hyperfine interaction. The fact that the period inversion resulted in the same depolarisation curve for both concentrations in Fig. 5b appears to me that the periodic inversion is performing an electron-electron decoupling rather than electron-nuclear decoupling (at least not directly). In my opinion, a better proof that the electron decoupling speeds up nuclear spin diffusion would be to repeat this on solvents with different ¹H concentrations, i.e. Gly-d8 with different H₂O: D₂O ratios. Also, can you comment on the Rabi field used for the periodic inversion? Is it much lower than the NOVEL condition?

Other minor points:

Line 20: Fix the symbol '>='

Line 28 & 31: Technically speaking, 'electron-nuclear' and 'nuclear-electron' essentially refer to the same thing. I suggest using a different symbol to highlight the context, i.e., use an arrow symbol. For instance, 'electron-> nuclear' and 'nuclear-> electron' to highlight the direction of transfer.

Line 39: A trivial suggestion. Replace 100 uM with 0.1 mM for easy comparison.

Fig 2. How long is the period T before electron saturation? Can you indicate it in a caption or on the figure? This will determine how much ¹H polarisation is diffused to the bulk.

Echo intensity as a function of T?

Line 95-96: Can you comment if the RA-NOVEL experimental parameters are the same or different for both solvents?

Line 98: One can in principle repeat the experiment in Finland trityl, where both protonated and per-deuterated trityl species exist (see TSSE paper).

Fig 5: The legend label is not clear for different concentrations and with/without dec. State it clearly in the caption which corresponds to dotted and solid lines. I know it is mentioned in the main text. It is easier for the readers to see that in the caption rather than in the main text.