

Magn. Reson. Discuss., referee comment RC3
<https://doi.org/10.5194/mr-2022-23-RC3>, 2023
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Comment on mr-2022-23

Anonymous Referee #3

Referee comment on "Paramagnetic relaxivity of delocalized long-lived states of protons in chains of CH₂ groups" by Aiky Razanahoera et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2022-23-RC3>, 2023

Razanahoera *et al.* present the results of experimental investigations into long-lived nuclear spin states (LLSs) excited in delocalized pairs of protons, *i.e.*, CH₂ groups, of several molecules and within the chain of the same molecule. The context of their exploration was relaxivity from the common ¹H d-DNP agent TEMPO dissolved in solution at typical post-dissolution radical concentrations. The manuscript is well-written, well-thought out and contains clear figures. The work is interesting and suitable for publication after minor corrections.

Major comments:

1/ The authors frequently refer to relaxation rates and relaxation times. However, this is not what is gleaned from the experimental results. These are relaxation rate constants and relaxation time constants. This is especially true in this case since mono-exponential decay curves are observed. This comment was also pointed out by Reviewer 1 and should be corrected throughout the manuscript.

2/ In the abstract, the authors note that "...the yield of conversion of observable magnetization into LLS and back are on the order of 10% or less...". This is likely quite an unfair lower bound to use as motivation. Typically, 30-45% of the 2/3 theoretical maximum can be achieved with such a *rf*-pulse sequence. Furthermore, the contribution to signal is given, whilst the conversion yield *vs.* observable magnetization is not. A typical value should be quoted in the manuscript.

3/ There are a number of important works from the LLS community that are not cited.

Ratio of T_{LLS}/T_1 :

Angew. Chem. 2015, **127**, 3811-3814.

J. Am. Chem. Soc. 2012, **134**, 17494-17497.

T₀₀ Filter:

J. Am. Chem. Soc. 2013, **135**, 2120-2123.

These should be incorporated into the manuscript.

Minor comments:

1/ The authors mention that LLSs in homonuclear spin-1/2 pairs are immune to intra-pair dipole-dipole interactions. It is more likely to be correct to say intra-pair dipole-dipole relaxation.

2/ Were the samples degassed? Would the results differ significantly if the samples were degassed?

3/ In Table 1, the ratios of the relaxation rate/time constants would also be nice to see.

4/ It would be nice to know the number of scans used for experiments.

5/ "reconversion" is incorrectly spelt in the caption of Table 1.

6/ "relaxation " is incorrectly spelt in the short summary.