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Discussions

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Comment on mr-2022-23

Malcolm Levitt (Referee)

Referee comment on "Paramagnetic relaxivity of delocalized long-lived states of protons in chains of CH_2 groups" by Aiky Razanahoera et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2022-23-RC1, 2022

This is a very nice report continuing the interesting research line of long-lived states in chains of CH2 groups, initiated recently by this group. The authors explore the relaxivities of LLS in a variety of CH2 groups, and also different LLS groups within the same molecule, with respect to the common DNP agent TEMPOL. The paper is well-reasoned and well-presented and is highly suitable for publication.

I have a few minor comments:

The introduction on page 1 is slightly misworded, in my view. The singlet-triplet population imbalance for spin-1/2 pairs, also known as singlet order, is just one special case of a long-lived state. Singlet order is indeed immune to intramolecular dipole-dipole relaxation. but that is not necessarily the case for more complex LLS, including some of the ones discussed later on in the paper.

on page 2 it is stated that fast proton relaxation is the reason for d-DNP being performed mainly on 13C and 15N nuclei: This is true in part, but an even more important reason, in some contexts, is the interference from strong proton background signals.

Presumably the buffer solution is aqueous. This should be stated, and if possible, the precise composition of the buffer should be given.

In Fig.3 the signals are presumably normalized such that “100%” is the first point in the decay. This should be stated.

The statement that PRE is less effective for ZQCs than other coherences is usually true, but at least in principle, anti-correlation of the fluctuating fields could cause the opposite relationship.

In common with numerous others, the paper confuses “rates” (which become smaller as a process approaches equilibrium) with “rate constants” which (as the name implies) are time-independent for an exponential decay. So most of the reported “rates” in the paper are actually “rate constants”.

The discussion on the long-lived states in chains of three CH2 groups is particularly interesting. I much appreciated Figure 6.

As the authors state, a random-field model may be used to relate the rate constant of singlet order relaxation to the correlation factor for fluctuating random fields at the two nuclear sites. I wonder what the corresponding expressions would be for the “delocalised” long-lived states explored by the authors. Many pairs of correlated fields could be involved. Are such rate constants dominated by the “least correlated pair” of fluctuating random fields?