Open Access MAGNETIC RESONANCE Discussions

Magn. Reson. Discuss., referee comment RC2
https://doi.org/10.5194/mr-2021-10-RC2, 2021
© Author(s) 2021. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on mr-2021-10

Thomas Prisner (Referee)

Referee comment on "The decay of the refocused Hahn echo in double electron–electron resonance (DEER) experiments" by Thorsten Bahrenberg et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-10-RC2, 2021

The authors describe in this manuscript the optimization of pulse settings (the original Hahn echo time) of a 4-pulse DEER experiment. Experiments are shown for nitroxide, trityl and Gd paramagnetic centers at W-band frequencies for deuterated and protonated water solvent. They demonstrate that the time interval t1 optimally is optimally set as t2 for short times of t2 and somewhat shorter for long t2 values. These experimental findings could be quantitatively reproduced by computer simulation of the interaction between the radical with 2-5 nuclear spins - similar to an earlier publications where such calculations have been demonstrated for experiments at more common Q- and X-band frequencies. Overall this work demonstrates very impressively that quantitative simulation of the experimental data can be achieved with couled spin clusters (of at least 3).

I have some questions and remarks which might be helpful also for other readers in the final version of the paper:

1) The data are all recorded at W-band. This has of course the advantage that the classical ESEEM effects are reduced. On the other side the authors describe the decoherence of the EPR signal as a nuclear-spin-cluster electron spin decoherence arising from the interference of nuclear coherences arising from the different hyperfine coupling of two nuclear spins. This is an interesting model but would probably also imply a field dependence. It would be interesting to give a statement in this direction. Also, the term SzAzxIx is omitted in this calculations (different from the earlier publication for data at Q-band and X-band). It would be good to also explain this in more detail. The experiments are performed at the maximum of the EPR spectra. Tm for nitroxides at high field is known to be orientation dependent. Again the authors should comment on this aspect.

2) The authors demonstrate that for samples with 25% 50% 75% and 100% protonation this dephasing is efficient but claim that this is not the case for fully deuterated samples. In the cited work by Soetbeer et al. it is shown that dynamic decoupling is also effective

for 100% deuterated samples. It would be nice to discuss this point more carefully. Also in the above mentioned work Tm was analysed by two different components with streched exponential with a 50/50 ratio. It would again be important to discuss this differences to the treatment here which is relying only on one mechanism.

3) The red maxima shown in the 2D datasets should also be presented in 4 6b and 7b for consistancy.