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Magn. Reson. Discuss., referee comment RC1
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Comment on mr-2022-20

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Referee comment on "The effect of the zero-field splitting interaction in light-induced pulsed dipolar EPR spectroscopy" by Andreas Scherer et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2022-20-RC1, 2022

This manuscript considers two pulsed dipolar spectroscopy experiments, LiDEER and LaserIMD, for pairs of consisting of a persistent radical and a transient triplet state. The authors pose the question whether violation of the high-field approximation by the zero-field splitting of the triplet state influences analysis of the data in terms of distance distribution, background decay rate, and modulation depth. They conclude that the effect on distance distributions is minor under typical experimental conditions and provide guidance on minimizing it by choice of the observer field for LiDEER. In contrast, background decay and modulation depth estimates can be affected, in particular at short distances and low magnetic fields.

This work is important for reliable analysis of LiDEER and LaserIMD data and thus of interest for the readers of Magnetic Resonance. Experiments, simulations, and data analysis have been performed according to the current state of the art. The conclusions are largely supported by experimental and computational evidence. However, the authors should state more clearly to what extent analysis with the S = 1/2 DEER kernel works and what its limits are. Referencing should be improved as detailed below and a few typos should be corrected. I consider these necessary revisions as minor.

Details:

1. As I understand it, all analysis in terms of distance distributions in this work has been performed with the DEER kernel (S = 1/2 approximation), while you argue that the kernel should include effects due to the ZFS and provide software for computing such adapted kernels. You analyze in terms of distance distributions with the open-source software DeerLab. Why don't you directly compare analysis by Tikhonov regularization with the DEER kernel and your kernel? This would be particularly valuable for your experimental data.

2. Except perhaps for the case of LiDEER performed at non-canonical orientations in X band, effects of ZFS on the extracted distance distribution are so minor that they are likely overwhelmed by other uncertainties in application work. If you agree with this assessment, you should clearly state this in the Conclusion.

3. I think that the experimental data is underused. Even if you perform only simulations with your own kernel (instead of using it in Tikhonov regularization), you should make an effort to assess the influence that ZFS has on the background decay rate and modulation depth for these examples.

4. Your referencing does not follow established rules. If you provide a reference for a statement, it should be either the first paper where this was found or a review/book chapter. If the statement can be considered as textbook knowledge, no reference is needed. In several cases you rather appear to cite the papers where you first encountered the same statement. For example, you cite me for textbook knowledge (distance dipendence of the dipolar coupling) and for work by Salikhov, Tsvetkov, and Milov (p. 4, l. 11, citation (Jeschke, 2016) for the term "background", if this really needs a citation). There are many more instances, also affecting others. In a very general Introduction as you write it, the absence of citations to the pioneering work from the Novosibirsk lab is problematic.

5. In the Introduction, you come close to considering orientation selection, but you never mention it. You should do so, as neglect of orientation selection is a feature of your treatment.

6. “Please note that we did not consider all non-secular terms and pseudo-secular terms were also ignored.” It is not clear to me, which terms you consider as pseudo-secular and how you selected the terms that you included. Section S1 of the Supplementary Information does not help. Common usage is that terms that you consider on top of the secular terms are pseudo-secular and terms that you drop are (considered as) non-secular.

6. In powder averaging, an equidistant grid over cos β_{dip} would have been more efficient (all grid points would have had the same weight). I do not suggest that you repeat the work. This is just advice for future work.

7. p. 5, l. 10: “The dipolar coupling tensor ð□□□ is axial”. This presumes the point-dipole approximation, which might be questionable for a TPP triplet at the shorter distance of 2.2 nm. In any case you should mention that your treatment uses the point-dipole approximation.

8. p. 12, l. 13: "In X-band the resonator was critically coupled to a Q-value of ≈ 900-2000

for higher sensitivity". Did you check this? A higher Q improves detection sensitivity, but reduces excitation bandwidth. Common wisdom is that, as long as you have sufficient microwave power, you should overcouple. What is different in your case?

9. p. 13, l. 8: “effects of the background were ignored”: You probably want to say that background decay was ignored.

Typos:

p.2, l. 15: “This gives a virtually infinite excitation bandwidths”: remove the surplus “a”

p. 4, l. 1: “reduced Plank constant”: Planck

p. 11, l. 16 “Euler angels”: angles

p. 15, l. 4/5: “The previously mentioned decay is faster for a lower Zeeman frequencies”, l. 18 “such that a stronger ZFS parameters”: remove the two surplus “a”

p. 17, l. 17: “To check to what extend this is true”: extent

p. 19, l. 14: “but are always larger as them”: larger than them

p. 20, l. 3 “Euler angels”: angles

p. 26, l. 9/10: “where the spin systems behaves as if it would consist of two ð□□□ = 1/2 spins”: spin system