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Comment on mr-2022-8

Nino Wili (Referee)

Referee comment on "The effect of spin polarization on double electron–electron resonance (DEER) spectroscopy" by Sarah R. Sweger et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2022-8-RC2, 2022

General comments:

The article “The effect of spin polarization in DEER spectroscopy” by Sweger et al. describes what the title promises. The effect of polarization is usually neglected in the analysis of DEER data, and this paper, en passant, confirms the validity of this assumption for typical measurements (Nitroxides, Q-band, 50 K). Nevertheless, they show that the effect becomes important at high-fields and low enough temperatures. An analytical expression of the intermolecular/background contribution is derived, showing that it also contains an out-of-phase contribution. The analytical expression is confirmed by Monte-Carlo simulations (in the SI), and its functional form is also confirmed experimentally – up to a phenomenological scaling factor. The origin of this factor could not be determined yet, but many possibilities are excluded in the SI, and because the intramolecular contribution fits the theory well.

The work addresses a relevant scientific question and certainly fits the scope of MR very well. It is of course unfortunate that the remaining discrepancy in theory vs. experiment could not be resolved, but I think this is clearly and fairly described, and significant effort was taken to resolve it. This is a common encounter in science and should not be a reason not to publish the work.

The paper is clearly written, and the figures are clear, informative, and also aesthetic. The theory is laid out in simple terms where possible (e.g. fig. 2), and (very!) detailed derivations are given in the SI for the more involved parts. The experiments and data analysis procedures are well described.

The paper shows some overlap with a previous publication (Marko,2013), but – if I see it correctly – arrives at another expression for the intermolecular/background contribution (Eq. (39) in (Marko, 2013) vs. Eq. (8) in the present paper). It is unclear to me what was

missing in the earlier work, and a comment in this regard might be helpful. Was something overlooked? Was there another assumption in the derivation?

Specific comments:

- In Figure 1b, a curve could also be shown for the commonly available W-band.
- S4 shows two traces, recorded with the receiver phase shifted by 90 degrees. It is a bit surprising that the decay is slightly faster for one of the two. Do you have any idea why this could be? Is it also seen in the absolute value?
- Line 126: "The measurements were conducted at the field values that gave the maximum echo amplitudes." I was under the impression that in Q-band, one usually applies the pump pulse rather than the observer frequency on the maximum of the EPR spectrum. Is this what you meant?
- I think the outlook could profit from some short comments about the high-spin case (Gd-Gd, Gd-NO/Trityl. Is the extension obvious or complicated?)
- The background of single-frequency techniques behaves quite differently. Do you expect polarization effects as well in the case of SIFTER/DQC/RIDME/etc. ?
- Just an idea regarding the remaining discrepancy: The value for k contains the pump efficiency. If I calculated correctly, at least your Q-band tubes are filled quite high. I don't know your resonator, but I would expect the microwave inhomogeneity to be quite pronounced (not sure about the G-band setup). Even the frequency-swept pulse would lead to a distribution of inversion efficiencies - and thus to a distribution of k. I wonder if this distribution could affect the in-phase and out-of-phase and the inter- and intra-molecular contributions differently? This could be tested computationally quite quickly I think, by assuming some reasonable distribution in microwave amplitudes.
- I agree with reviewer 1 that you could move some of the theory of the SI into the main text, especially regarding derivations that are new compared to (Marko,2013) but it is mostly a matter of taste.