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Interactive comment on "Optimising broadband pulses for DEER depends on concentration and distance range of interest" *by* Andreas Scherer et al.

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This manuscript tries to tackle experimentally the question how the pump efficiency of broadband microwave pulses influences the quality of DEER data. Broadband mw pulses become available for pulsed EPR experiments by fast arbitrary waveform generators recently, allowing to adopt broadband excitation pulses known since a long time in the field of NMR for EPR experiments. For DEER experiments it has been shown that broadband pulses achieve larger modulation depth of the dipolar coupled bi-radical sample. On the other hand the larger pump efficiency also leads to a stronger decay arising from intermolecular interactions to the other spin labeled molecules in the

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Discussion paper

sample. In this manuscript the interplay of modulation depth and decay arising from a series of broadband pulses (sech/tanh, WURST, linear chirp with rectangular amplitude shape) have been compared to excitation by rectangular or Gaussian monochromatic pulses. The experimental work performed at a commercial Q-band spectrometer is of good quality and compares the effect of different pump pulses with respect to a MNR (modulation to noise ratio) merit function. This function is defined as the ratio of the modulation depth to the over the time trace averaged noise level. The later part of this function depends on the length of the observer time window, because the noise which is constant per time in the original time trace, increases by the division procedure usually used to remove the intermolecular part. This problem has already been discussed in a recent paper by Fábregas et al., where other procedures to obtain distance distributions from the original data were proposed. Nevertheless, because these other simulations methods are not standard so far, the approach discussed here to optimize the experimental time traces is important and worthwhile to be published after several issues are addressed. 1) For me it is not perfectly clear if the merit function defined here (MNR) is really the most important point. Usually the distance information is encoded in the first part of the time trace and the longer times are only necessary to fit well the intermolecular background function – a necessary procedure to obtain reliable distance information. The question is how large the increasing noise at the end of the time trace is important for this purpose. This point should be discussed and clarified. 2) The manuscript talks about the intermolecular background function but for the larger spin concentration, where most of the experiments are performed and most of the conclusions are taken from, the original time traces including this background function are not shown! This has to be included! It is not enough to show the background density k as in Figure S11. 3) In Figure S10 an unexpected large suppression of the echo intensity by longer broadband pump pulses is shown. This is totally unexpected for the given bandwidth of these pulses and contrary to own experiences, where longer pulses show better frequency shapes! If the pulses are generated by the Bruker software some care has to be taken to use the right amplitude setting, especially when

the frequency runs over the carrier frequency (from minus offsets to plus offsets). The pulse profiles shown in Figure S7 are probably only calculated pulses and not really measured ones? Experimentally recording them including the resonator profile (which also seems somewhat suspicious to me) might give some hints on what is going on here! This issue is rather important for the conclusions drawn here from the shaped pulses! 4) The concentration dependence of the behavior is only discussed in a rather trivial and non-quantitative manner, despite the fact that it showed to be the major parameter influencing the improvement by the broadband pulses (comparison Figure 6 and 7). That lower concentrations of spins are advantageous, especially for larger distances or broader distance distributions is well known in the community. Because broadband pulses might be especially interesting for these kind of systems, this should be discussed more quantitatively! The discussion in the SI including Figure S13 and the text after it is only very qualitative and rather trivial. 5) Minor point: In the supporting information equation (2) is wrong. After that there is a spelling error (ration).

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