Response to Comments by Stefan Stoll

This manuscript describes DEER distance measurements on rigid Gd-Gd rulers in a high-power W-band spectrometer with a weakly resonant probe. Excellent sensitivity is demonstrated. It is shown that short-distance artifacts due to dipolar state mixing are suppressed by using a large pump-observe separation and by avoiding the central transition.

The work is well executed. The manuscript is well written. It provides novel and important insights. I recommend publication, after the following comments are addressed.

We would like to thank Prof Stoll for his careful reading of the manuscript and many insightful comments, which we address below.

1. **Some of DEER experiments are performed outside the central transition, but Tm and T1 values are reported only for the central transition. What are Tm and T1 for the pump and observer positions on the non-central transitions?**

   We completely agree it would have been useful and appropriate to measure Tm away from the central transition at the offsets used. At the time of the experiments it was an oversight. Unfortunately, immediately after these experiments the spectrometer was rebuilt to incorporate a wideband AWG and then the lab was locked down when COVID hit and so at the moment it is not possible to incorporate this data (at W-band). We have Q-band data and we will refer to this and other references. We would point out that T_M is expected to get shorter away from the central transition but we still achieve excellent S/N despite this.

2. **Line 111: Is it possible to give G/W^1/2 conversion efficiencies for the shorted waveguide used in this work, and for a standard cylindrical cavity as reference?**

   It is possible to quote an effective conversion efficiency based on the typical length of the $\pi/2$ pulse (6 ns for a s=1/2 sample) in the waveguide, although of course the B_1 field varies significantly across the sample. For a fair comparison one should really quote this based on the power incident on the sample holder, which is not always clear or known when comparing systems, and of course it depends on the chosen bandwidth of the standard cavity. This type of comparison thus requires many caveats, which we are not keen to enter into in this paper. However, in the interest of discussion, a reasonable estimate in our system might be to assume 625 W at the sample, giving c ~ 0.6 $G/W^{1/2}$. This conversion efficiency is comparable to an X-band commercial cavity (optimised for concentration sensitivity) used in pulsed operation and with a comparable sample volume and comparable kW input power. As sensitivity scales with ω_0^2, very substantial sensitivity gains become possible as long as linewidth does not get very significantly broader. A critically coupled W-band cylindrical cavity might have a conversion efficiency that is approximately 15 x larger than the waveguide sample-holder here (but with a much smaller sample volume and effective bandwidth).

3. **Line 272: How significant do the authors think are the differences between the data obtained at 840 MHz and 900 MHz offset? Are they within or outside the expected run-to-run scatter of the experiment?**

We think there are differences, but we agree they are not large, and they were included partly as we had the data sets. The point of including measurements with seemingly similar offsets is that at 840 MHz and 900 MHz offset we are very close to the maximum bandwidth available from the EIK, where the power output starts to significantly degrade at band edges.

4. **Line 245: A pump-observe offset of 900 MHz is mentioned for the 6 nm ruler, but the data show 120 and 420 MHz offset only (Fig.3,4,S3a,S4).**

   Many thanks – we have corrected this typo.

5. **Figs.4 and 6: What do the shaded areas in a) and b) indicate?**

   It is essentially a guide to the eye, but we will add notes in the caption explaining.

6. **Fig.5d and 7b: What does the black arrow indicate?**

The arrow indicates 94 GHz, the nominal centre frequency of our W-band EIK amplifier, which has a bandwidth of just less than 1 GHz. We will add a footnote to make this clear.

7. Fig.S3a: What is the reason the background in the P3O3 measurement is rising, as opposed to decaying?

The underlying reason is that the oscillations have not decayed fully by the end of the time trace and so it is difficult to determine the background accurately. We chose to show this background (with a note it was not physical) to be consistent about the way we determined backgrounds for all the other traces. i.e. by optimising the resulting Pake pattern. We have now changed this to give a slightly decaying background. This now gives a marginally worse Pake pattern, but essentially exactly the same distance and distance distribution.

8. Table S3: What is T1 in the last column? Footnote 1 is not clear.

We agree and we will change the footnote.

9. Table S1: Separate last column into two, one with the linewidths, and with references.

We have done this.

10. Line 313ff: I don't quite understand the author's arguments concerning intra- molecular instantaneous diffusion contribution to dephasing. The modulation depth is only a few percent, so only a few percent of spins get excited by each pulse. Simultaneous excitation of both spins within the same molecule therefore has very low probability. Some clarification would be useful.

As per the discussion with Prof Jeschke we will remove this statement as perhaps it is speculative, but we would point out that we are measuring at the central transition and the presence of pseudosecular interactions shows that we cannot treat it as a simple dilute system.

11. **Line 391ff: What are "backshort positions", and what does it mean to "match out the echo signal"?**

In common microwave terminology a backshort is a short circuit termination in a waveguide whose position can be adjusted with respect to some reference plane. The reflection from the top of the sample and this termination can create a weak resonant circuit, which can significantly enhance the magnitude of the cross-polar signal. Thus sensitivity (echo signal) is thus maximised for certain positions of the backshort. We will add a line of explanation.

12. **Line 397: Claiming that sub-µM concentrations are technically feasible is a bit overly speculative. That would correspond to a ca. 50-fold reduction in concentration compared to the presented data, and a 2500-fold extension of the measurement time, for example from 1 hour to 3 months. Doubling the repetition rate to 6 kHz (more is not feasible given the T1) shortens this to 1.5 months, still not feasible. I suggest removing the statement about sub-µM concentrations.**

The 1.5 month (or 3 month) time-scale suggested for a measurement at sub-µM concentrations would be correct if we needed to maintain the same S/N to extract useful information from the spectra. But the echo S/N after ~ 1.5 hours for 2.1 nm ruler is 8300. Even with only 2.1 % modulation, one would still have acceptable S/N if we reduced S/N by a factor of 10 reducing averaging time by a factor of 100, bringing averaging times < 1 day for sub-uM concentrations. Many published measurements are made with this averaging time. So we thus stand by our statement that practical measurements at sub-µM concentrations are feasible (right now).

To further emphasize this point we will also now include additional comparative Q-band measurements in the SI. In one example, where both pump and probe are offset from the central transition (but on the same side), if we compare to our P3O data for 2.1 nm sample, we have a lower (echo) sensitivity by a factor of ~ 24 and a lower modulation depth by a factor of 3, leading to an effective reduction in S/N of 72. Satisfactory S/N was still obtained by averaging for approximately one day. We would suggest that S/N would still be acceptable with somewhat lower averaging times.

In the discussion, we also point out there are realistic ways to further improve sensitivity. Higher sensitivity would be expected with Gd-complexes with smaller zero-field splittings. There is scope to achieve higher sensitivity by using a wideband AWG to increase both pump and probe excitation bandwidths. Although not discussed in the paper, we also believe there is also scope to improve the conversion factor of the sample holders, whilst maintaining all their other advantages. We thus believe the sub-µM claim will ultimately prove to be relatively conservative.

We will add a sentence or two to make these points clearer, and have included Q-band data in the SI.