

Interactive comment on “High sensitivity Gd³⁺-Gd³⁺ EPR distance measurements that eliminate artefacts seen at short distances” by Hassane El Mkami et al.

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Received and published: 28 August 2020

The authors demonstrate convincingly that by using a high-power W-band spectrometer with an only weakly resonant shorted waveguide end instead of a microwave resonator, the problem of level-mixing related perturbation of large dipolar frequencies can be avoided. This problem makes extraction of distance distributions between Gd(III) labels precarious at distances shorter than 3 nm. Hence, the new approach solves an important problem for broader application of Gd(III)-Gd(III) distance measurements. Furthermore, the authors show convincingly that it can be advantageous to avoid excitation of the central transition of Gd(III) altogether in DEER experiments, which comes

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as a surprise. The manuscript is mostly clear and concise, the data is of high quality, and its analysis is mostly adequate. However, there are a few minor problems that require revision.

General:

1. The text refers mostly to frequency offsets when discussing different excitation schemes, but the Figures use PnOn codes. Please give frequency offsets directly in figures.
2. The claim on similar data quality as with nitroxide labels would have been much more convincing at intermediate distances, where nitroxide labels can convincingly resolve an asymmetry of the distance distribution that is related to flexibility of the ruler backbone. For that, the 2.1 nm may be too short and the 6 nm slightly too long (at the maximum dipolar evolution time achieved here).
3. section 65: Gd(III)-Gd(III) RIDME was first demonstrated and the overtone problem noticed in 2014 (DOI: 10.1021/jz502129t)
4. section 70: “applying the wormlike chain model”. I do not find this in either the results section, discussion, or Supplementary Material.
5. section 155: Why did you measure T_m , T_1 only at the maximum of the Gd(III) spectrum? These relaxation times are known to differ between central and satellite transitions and you focus on satellite transitions. Please make at least a remark that differences are to be expected and cite literature for that.
6. section 205: For systems other than Gd(III), T_m also can rarely be fitted with a single exponential function. Please rephrase to avoid the impression that this is a peculiar feature of Gd(III).
7. section 210: Why did you use fixed exponents 1 and 2 for fitting? I do not see a good theoretical reason for that. Fit quality is hard to ascertain in Fig. S2a (please use a representation as in Figure 3a, black versus red line), However, looking closely I

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am not convinced that it is good. Please check if the fit residual is reasonably close to white noise.

8. Figure 3a: The fits for P1O1 and P2O2 do not compare favorably to the one shown by Dalaloyan et al. for the same compound (DOI: 10.1039/c5cp02602d). Do you have any idea why that may be the case?

9. section 265: “We do not expect any orientation selection and so the Pake pattern spectra reported in Fig. 6a show strong distortions”. This sentence is unclear. Please rephrase.

10. section 310: I recommend more cautious wording regarding the origin of the second component, as you do not have a comparison with a sample with only a single Gd(III).

11. Figure S3: How can you have a rising background for P3O3? This needs to be commented.

Interactive comment on Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2020-19>, 2020.

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