

# ***Interactive comment on “Analysis of the electronic asymmetry of the primary electron donor of photosystem I of *Spirodela oligorrhiza* by photo-CIDNP solid-state NMR” by Geertje J. Janssen et al.***

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1. You may want to state that the 2020 Artiukhin *et al.* work uses a frozen density embedding approach for improved treatment of the PS-matrix interaction.
2. I understand that ‘bidirectional’ was introduced before as a term for what actually is ‘two-sided’ electron transfer. However, I find this extremely confusing. In all other science and engineering, ‘bidirectional’ means ‘forth and back’, which is not what a PS should do under normal condition. It adds to the con-

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fusion that in your experiments, with reduced  $F_x$ , ET becomes bidirectional in the usual sense of the term. There is precedent on using the proper term 'two-sided' (<https://doi.org/10.1529/biophysj.105.059824>). Please consider using it, too.

3. It is not clear to me how exactly you referenced  $^{13}\text{C}$  shifts (p. 9, l. 7). Do you quote values with the chemical shift of chlorotrimethylsilane set to 0 ppm or do you set TMS to 0 ppm and assume a known shift for chlorotrimethylsilane? If it is the latter, which shift do you assume? It is about 0.4 ppm difference to normal convention.

4. It is imprecise to state that labeling has an influence on the photo-CIDNP mechanisms. It does have an influence on the outcome, i.e., on the observed nuclear spin polarization.

5. I am not sure about the interpretation in terms of relative contribution of the TSM and DD mechanisms. If isotope labeling changes lifetime(s) of the radical pair, the TSM polarization will also be affected. If it does not, DD should not be suppressed by such labeling. You might want to state that your explanation is tentative.

6. That the polarization of the aliphatic carbon at 52 ppm vanishes at low field implies that polarization transfer by spin diffusion to this carbon is negligible at low field, but not high field. It does not strictly imply that the neighboring aromatic carbons do not obtain enhancement. This should also be formulated with more caution.

7. Conclusion: "Our study contributes to converging and convincing evidence" Please leave it for the readers to decide whether the evidence is convincing. It may be also useful to discuss current limitations. The "which is thought to originate" on page 16 reveals that there is no quantitative understanding (yet) of the supposedly dynamic origin of the asymmetry in bacterial reaction centers. It is also somewhat dangerous to draw conclusions on effects of static electronic structure from only ground-state properties. That chemical shifts are similar between the two types of PS in the diamagnetic "resting state" does not necessarily imply that the electronic structure of the donor and acceptor radical states is also similar.

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8. Please number pages in the Supplementary Material.

9. Are you sure that a *short* MD calculation would be sufficient to improve chemical shift computations? In other words, can you exclude that chemical shift changes on longer timescales? Rather long MD trajectories would still correspond to the fast chemical exchange limit in NMR. 10. The title does not appear to reflect your main conclusion

Typos/grammar:

p. 2, Line 32, comma after 'properties' is superfluous

p. 3, Line 47: 'Synechococcus elongates' should be typeset italic

p. 4, Lines 67-69: Please be consistent with notation of PA and PB (either always or never subscript)

p. 7, Line 47: superscript missing in '<sup>13</sup>C'

p. 12, line 60: Please do not jump forth and back between fields and frequencies.

p. 18, line 37: "similar extend" should read "similar extent"

SI, Section 2.5: "calculalted" should read "calculated"

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Interactive comment on Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2020-22>, 2020.

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