Comment on mr-2021-22
Anonymous Referee #1

Referee comment on "Non-classical disproportionation revealed by photo-CIDNP NMR" by Jakob Wörner et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-22-RC1, 2021

Research on photolyases and cryptochromes is presently a hot field. Cryptochromes are even considered to be involved in “animal detected magnetic resonance”. Therefore, an update on flavin-related compounds, their capacity to form radical pairs and to build up hyperpolarization is highly desirable. The manuscript revealed the existence of a transient high redox state of 6,7,8-trimethyllumazine by means of photo-CIDNP NMR. The compound is able to form upon illumination radical pairs with its two different protonation states. The experimental isotropic hyperfine coupling constants are obtained and correlate well with DFT data. Combining DFT and CIDNP, the careful analysis of the data on the basis of Kaptein’s sign rule is convincing and allows a remarkable reconstruction of a reaction dynamics involving photochemistry, spin-chemistry as well as proton transfer.

As for the title, I feel that the authors are unnecessarily opening a discussion that is not really helpful. Why should a disproportionation (2A = A⁺ + A⁻) not also be able to be triggered photochemically (A⁺ + A = A⁺ + A⁻)? In the textbook by Klessinger and Michel, photochemically triggered disproportionations are indeed discussed (for example, as a result of Norrish I). One could also ask whether a system A + AH really “disproportionates”, since A and AH are different species. Nevertheless, it seems to me that a very special CIDNP-capable donor-acceptor system is present here, perhaps deserving the term “non-classical”.

Two questions:

- From the Figure 6B, it seems like the H(7α) also enjoys very high amplitude of electron spin density, but in the photo-CIDNP spectrum, there is no polarization at H (7α). How to understand such a contradiction?
- In the supplementary information, Table S2, Table S3, there are three times H(6α), three times H(7α), and three times H(8α). What do they refer to?
Minor comments:

- The "R." of "Rhodobacter sphaeroides" needs to be introduced (line 35).
- "it absorbs at shorter wavelengths" (line 41): Should an antenna not exactly do that? Might be helpful to mention the absorption maxima.
- "operating at 14.1 T and a 1H freq of 600 MHz" (line 66): Sounds to be two different things.
- "fibre" (line 70) = fiber.
- Fig Caption Fig 3: Dashed lines show laser excitation.
- Line 212: radical pair formation from a triplet precursor: Is that surprising considering flavin photo-chemistry?
- Line 244: To what refers the "this"?
- Line 253: The use of the asterisk in a text of photochemical relevance might be misleading.