

Exchange interaction in short lived flavin adenine dinucleotide biradical in aqueous solution revisited by CIDNP and nuclear magnetic relaxation dispersion

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A nice manuscript. Publishable after minor corrections.

Scheme 1 appears on page 2 but is not referred to until page 7. Perhaps it should be moved nearer to the place where it's actually needed.

Lines 35-36: it is an exaggeration to say that the radical-pair mechanism is “generally accepted” as the “explanation of bird navigation”. Although it is clear that migratory birds have a magnetic compass sense, they also use the sun, stars, olfaction, landmarks etc. Additionally, the RPM hypothesis of magnetoreception is not yet “generally accepted”.

Lines 41-42: “In a recently discovered DNA based magnetic sensor FAD was used to repair a DNA lesion by splitting a thymine dimer (Zwang et al., 2018)”. This is a curious way to refer to DNA photolyase. I think the authors should at least say that FADH⁻, the fully reduced form of FAD, acts as the chromophore and electron donor in this light-dependent DNA repair enzyme. It is also far from clear that there should be any magnetic field effect on this reaction (*ACS Cent. Sci.*, **4** (2018) 318-320).

I think the following two articles (at least) should be cited to avoid giving the impression that no-one other than Stob *et al.* (1989) has studied magnetic field effects on FAD photochemistry.

Murakami, M., K. Maeda, and T. Arai. 2005. Dynamics of intramolecular electron transfer reaction of FAD studied by magnetic field effects on transient absorption spectra. *J. Phys. Chem. A* **109**:5793-5800.

Antill, L. M., and J. R. Woodward. 2018. Flavin adenine dinucleotide photochemistry is magnetic field sensitive at physiological pH. *J. Phys. Chem. Lett.* **9**:2691-2696.

Lines 63-64: I was puzzled by the mention of tryptophanyl radicals here. This only became clear in line 98. A few more words of explanation, or references to studies of FAD-Trp photo-reactions, would be helpful.

Line 190: it would be useful to have either a literature reference for this equation or some description of how it was derived.

Lines 211-213: why does hydrogen peroxide cause the spectra to become sharper? Is this because it suppresses the comproportionation reaction, $FAD + FADH^- + H^+ \rightarrow 2FADH^*$?

Lines 249-251: is the pH dependence of the CIDNP intensities evidence for a change in the stacking of the F and A groups?

Lines 272-274: “The high quality of the data left no doubts that only one maximum of CIDNP is detected in the field dependence excluding that two types of biradical with different exchange interaction are formed from FAD.” What evidence do the authors have that there are not, in fact, two unresolved peaks? If there were, their results would not disagree quite so much with Stob, Kemminck and Kaptein.

Table 1: should the units of G be s^{-2} ?