

Reviewer Report

Manuscript Number: mr-2020-16

Title: "Geminal Parahydrogen-Induced Polarization: Accumulating Long-Lived Singlet Order on Methylene Proton Pairs"

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The manuscript introduces an extension of hydrogenative PHIP allowing to hyperpolarize long-lived singlet states of CH₂-groups and models the reaction kinetics and spin dynamics using a rate equation system. Even though in the system under study the polarization level turns out to be rather low, the method is intriguing and may lead to fascinating applications. Altogether, the manuscript is coherently written and is well suited for publication. There are a few points listed below that the authors should reconsider.

Page 5, line 87: here, "chemical instability" of target species **I** is shortly mentioned. A more specific information on the life-time is needed to ensure that this instability doesn't interfere with the observed time evolution.

Page 7, Figure 5: The first experimental points are given for $\tau_2=5$ s (with certain deviation from the model curve), while for shorter time only the model functions are shown. In my opinion, additional data measured at earlier time would make the agreement more compelling. At least for case c there is no reason to skip $\tau_2=0$. Also, the R value for the quality of the fit should be given.

Page 17, Figure A1: The spectrum of molecule **I** does not agree with that shown in Figure 2. Chemical shift and number of lines are different. These differences should be commented. Also, the Appendices should be checked for language flaws and corrected accordingly.