

## ***Interactive comment on “Geminal Parahydrogen-Induced Polarization: Accumulating Long-Lived Singlet Order on Methylene Proton Pairs” by Laurynas Dagys et al.***

**Laurynas Dagys et al.**

l.dagys@soton.ac.uk

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Response to referee #1 We would like to thank anonymous Referee #1 for the kind remarks, and we are happy to answer the important comments given in the review.

“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.”

The target species I slowly decompose at elevated temperatures losing one carboxylic group. As a result, the chemical inequivalence of the two methylene protons is lost and

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the sharp line caused by this can be seen in Figure A1 around 3.5 ppm. We have not carried out a complete measurement to assess the rate of such process but based on our experience it seems that it takes some tens of minutes in the experimental conditions set for PHIP experiments. The decomposition is negligible over the timescale of a single NMR experiment. However, it does interfere with the generation of a reproducible series of experiments. We have added details on the nature and timescale of the decomposition in the Supporting Information.

“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.”

Thank you for the suggestion. Probing short time points would be a very interesting experiment. However, there are several major difficulties which are hard to avoid. The setup with which the experiments were done consists of mechanically controlled valves which are actuated by a user. The time precision required for small changes in time points would be a hard thing to attain without full automation. An automatic setup is under construction but not yet ready for use.

Additionally, we would like to stress an interesting point about the spin dynamics which we imposed into our trajectories. The theoretical expressions involve assumptions about the projections of spin operators which do not apply strictly for short times. We have added explanations and clarifications in the revised text.

R values have now been provided for the fits. Thank you for bringing this to our attention.

“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

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accordingly.”

The additional peak in the spectrum at 3.5 ppm can be assigned to the product of the decomposition of the chemical species I. This has now been indicated in the text.

The discrepancies in the chemical shifts are due to the different temperatures at which the two sets of experimental data were taken. These temperatures are now indicated in the figure captions.

The language flaws in the appendices have been corrected.

Response to referee #2 We thank the referee for his/her appreciative comments.

The referee asks: " The only puzzling fact is more than a factor of 2 difference between  $T_s$  measured at room temperature and at PHIP conditions. The authors mention temperature as a potential reason for discrepancy...Would it be possible to conduct a singlet state lifetime measurement with the synthesized molecule at elevated temperature to support this statement?"

As commented in the manuscript, the singlet decay rate measurement at elevated temperature is made more difficult by the chemical instability of the compound. More details on the chemical instability and its time scale are given in the revised manuscript.

The referee also wishes for a reference to be included. We were not aware of this article and we have now included it.

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Interactive comment on Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2020-16>, 2020.