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Interactive comment

Interactive comment on "Heteronuclear and Homonuclear Finite Pulse Radio Frequency Driven Recoupling" *by* Evgeny Nimerovsky et al.

Anonymous Referee #1

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The paper by Nimerovsky and coworker describes fp RFDR applied to homonuclear and heteronuclear coupled dipolar spin systems.

My first impression after reading the manuscript was, that there is no clear focus and clear message of the paper draft. Is the main message a theoretical framework to analyze such sequences (in this case, it is not clear to me what is new) or is it the use of simultaneous RFDR-like sequences on heteronuclear spins systems to achieve heteronuclear polarization transfer. The second point is that the theory part and the first part of the simulations part seems to be very much detached and unconnected to the main part of the paper. I must admit that the manuscript left me a bit at a loss how things are connected and what the authors want to tell.

The theory part is quite lengthy and discusses the details of time slicing used in nu-

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Discussion paper

merical simulations. There is nothing new in this part and it could be left away with any loss of information. But since it is here, I was wondering about two things: (1) Why is the pulse and the remaining rotor period divided into an equal number of time slices. Typically, one would implement time slicing such that the rotor period is divided into a certain number of slices and the pulse occupies whatever time it takes. Here it says explicitly: "The numerical calculations split each of these two parts into N sub parts with the lengths tp/N and (TR – tp)/N, respectively." If SIMPSON was used for the simulations, this is most likely not correct. And why would one do this and have a higher sampling rate during the pulse? (2) Eq. (2.4) is only correct if the Hamiltonian H(t) commutes with itself over the time period Delta of the integration. This is however not how numerical simulations are typically implemented when doing time slicing. Usually, it is assumed that the Hamiltonian is constant over the time interval used for the calculations and I am pretty sure that this is how SIMPSON implements it. I think the statements and the equation at the end of page 5 are wrong.

In the simulation part, first different approximations for the Hamiltonian are used to understand which part of it is responsible for the polarization transfer under different conditions. The Hamiltonian of Eq. 2.1 makes sense (full rotating-frame truncated dipolar Hamiltonian) but it would be nice to rewrite the second part with 2zz instead of 3zz-zz but the ones selected in Eq. 2.2 do not really make sense or are wrong. The zz only Hamiltonian should have a coefficient of 1 and not 1.5! The second one is a J coupling Hamiltonian which makes no sense in this context while the third one is the ZQ part which is sensible. If these are indeed the Hamiltonians used for the simulations, I would put a big question mark on the conclusions presented in Figs. 3-5. This is implied in the figure labeling but of course I cannot judge what was used in the simulations. On page 11, the heteronuclear Hamiltonian is discussed: "The main difference to the heteronuclear full dipolar Hamiltonian with a homonuclear model Hamiltonian (Eq. 2.1a) is a factor of 1.5." This is clearly not correct. The heteronuclear Hamiltonian has just the zz terms and is exactly the same as a homonuclear (weak-coupling) dipolar Hamiltonian. There is no factor of 1.5 difference between the two.

Where we can find a factor of 1.5 is in the transition frequencies after diagonalisation. All these statements that are clearly wrong make me worry about the results presented in this paper. There is another statement that worries me (page 13): "For negligible offset differences with respect to the MAS rate, the evolution of the operators of IS and I2 spin systems are the same at specific time points." What are negligible offset differences in a heteronuclear spin system when the two spins are in different rotating frames? And further on: "With increase of offset difference the IS spin system passes through specific rotor resonance condition (the difference between offsets equal to half of the MAS rate), under which the transfer does not occur. For the I2 spin system the velocity of the transfer increases with increased offset difference." This cannot be. Either the authors mix up homo- and heteronuclear spin systems or this is plain wrong. There are no MAS resonance conditions in heteronuclear spin systems that depend on any offsets (what offset differences are there?).

Even if some of the problems are just a mix up, all of these mistakes make me wonder how carefullthe rest of the work is done. I have not and will not look at the rest of the manuscript before all these problems are corrected or explained.

Some minor remarks that should be cleaned up:

(1) The introduction has a long list of references to homonuclear and heteronuclear recoupling experiments that is clearly incomplete. Instead of such an incomplete list, it would be much better to have a reference to a review. There is for example a recent review about dipolar resoupling by N.C. Nielsen, L.A. Strassø, A.B. Nielsen, (Top. Curr. Chem. 306 (2012) 1–45) as well as older reviews on this topic. I think it would be more appropriate as a reference than an incomplete list.

(2) page 5 line 99/100: Liovuille-von Neumann equation is much more common. Why hbar=1? Usually the Hamiltonian in NMR is in frequency units and then there is no hbar in front of the commutator.

(3) Equation numbering should be continuous from (1) to (N) without chapter subdivi-

sions.

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