Open Access MAGNETIC RESONANCE Discussions

Magn. Reson. Discuss., community comment CC4
https://doi.org/10.5194/mr-2021-29-CC4, 2021

Reply on CC2

Jean Paul Amoureux

Community comment on "Improved NMR transfer of magnetization from protons to half-integer spin quadrupolar nuclei at moderate and high magic-angle spinning frequencies" by Jennifer S. Gómez et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2021-29-CC4, 2021

There has been an increasing interest in CPMAS from ^{1}H to half-integer quadrupolar nuclei in order to materialize the high ^{1}H DNP enhancement through efficient spin diffusion for detecting quadrupolar nuclei. This work is practically useful to this effort in addition to the proximity information by optimizing the pulse sequences. The authors have chosen g-alumina as the sample system, which has a fairly large shift dispersion at 800 MHz field. The proton homo-nuclear coupling is relatively weak as compared to rigid organic molecules. They have also chosen 20 and 62.5 kHz spinning speeds and typical rf-fields that 3.2 and 1.3 mm probes can achieve. From previous publications, the authors also have added adiabatic pulses to improve the offset performance and some modifications to the blank rotor period to reduce the ^{1}H T_2' loss. There is no doubt that they have improved the performances, but I am not sure if this optimization is generally applicable to other samples and spin systems. My particular concern is the strong ^{1}H homo-nuclear coupling. It is correct that the first-order ^{1}H homo-nuclear term is not 'recoupled' for the selected hetero-nuclear recoupling sequences. What about the high-order homo-nuclear terms that cause the short T_2', especially at not-so-high spinning speeds? My observation is that ^{1}H T_2' under the recoupling is often very short, and thus can have a strong effect onto the performances.

8) I wonder if the authors could provide some ^{1}H T_2' information under the recoupling sequences, say as compared to a regular spin-echo T_2' decay. We fully agree with Zhehong on this point. We have introduced the T_2' results of these experiments at 62.5 kHz MAS. These values are very interesting, and they highlight many previous experimental limitations we have observed.

9) In addition, is it possible to program the experiment to avoid the blank rotor period to rotor during the CT p-pulse by simultaneous pulses.

The p-pulses have two purposes: eliminate the ^{1}H CSA and keep the ^{1}H-S dipolar coupling. In 2007, we have proposed with Zhehong several methods in JMR, to avoid these p-pulses. However, it was for D-HMQC or RINEPT sequences with R^3 recoupling, and 'inverting the phase of R^3 pulses also reverse the sign of the average Hamiltonians'. This led to sequences in Fig.1d and f of this article. Here, we recouple with $SR4^2_1$ which is an I_zS_z operator, and thus inverting the phases should not change anything. On the contrary, this change of phase is used with PRESTO, which has a transverse operator.

- Trébosc, B. Hu, JP. Amoureux, Z. Gan, Through-space R^3-HETCOR experiments between spin-1/2 and half-integer quadrupolar nuclei in solid-state NMR, *J. Magn. Reson*, 186 **(2007**) 220-227.

We have also shown in Nagashima et. al, 2021, that it is impossible to avoid the blanks close to the ^{1}H p/2 and p-pulses, except with very large rf-fields that are not accessible with conventional MAS probes.

10) I would be interested in the overall transfer efficiency. It seems very low based on the S/N. Of course, only a small portion of g-alumina has ^{1}H in its vicinity. It would help to know where the main loss comes from, for future improvement. We have not quantified this efficiency, because it is uneasy to define. However, we remind here that we are using a 1.3 mm rotor with ca. only 2.5 mL of active volume, and we show now in Fig.9 a 2D HETCOR spectrum with high S/N recorded in only 72 min.

11) The first citation on PRESTO, p2 line-66, should include the paper from the original paper from Levitt's group. Xin Zhao, Wilfried Hoffbauer, Jörn Schmedt auf der Günne, Malcolm Levitt, *Solid State Nucl. Magn. Reson*., 26(2) (**2004**) 57-64, doi: 10.1016/j.ssnmr.2003.11.001 Done.

I would like to recommend this work on the through description of symmetry based recoupling and search for recoupling sequences that are optimal for CPMAS with practically feasible spinning speed and rf field for 3.2 and 1.3 mm probes.