

Interactive comment on “RIDER distortions in the CODEX experiments” by Alexey Krushelnitsky and Kay Saalwächter

Anonymous Referee #1

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The manuscript by Krushelnitsky and Saalwächter contains a quantitative analysis of the RIDER effect and its influences on the analysis of CODEX dephasing data. CODEX (= Centralband Only Detection of EXchange) allows to study millisecond-sec dynamics under MAS, and involves encoding and decoding of anisotropic interactions (CSA/dipole) by a train of 180 pulses on the X-nucleus. RIDER (= Relaxation Induced Dipolar Exchange with Recoupling) is a consequence of dipolar coupling between X and I nuclei during the de- and rephasing periods and results in S_yI_z magnetization which is not reconverted in the course of the experiment. An artifact-free version of CODEX is of great interest to expand the range of correlation times to characterize slow motion (rocking motion) in solid proteins.

The authors state that RIDER might be an issue in the CSA CODEX due to ^{15}N - ^2H

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dipolar interactions. This is not clear to me. If 180 pulses on the X channel are applied every half rotor period, this would refocus the evolution of any anisotropic interaction. Please clarify.

Proton driven spin diffusion among X-nuclei is another source that can potentially affect the CODEX dephasing curves. The authors argue that this effect can be neglected, since the buildup of magnetization between X-nuclei takes typically several seconds, and is suppressed by decoupling during the mixing period. In addition, a Z-filter element is suggested to suppress interfering anti-phase coherences.

On the other hand, it is known that CSA facilitates spin diffusion processes (see e.g. Fry EA, Sengupta S, Phan VC, Kuang S, Zilm KW (2011) CSA-Enabled Spin Diffusion Leads to MAS Rate-Dependent T₁'s at High Field. J. Am. Chem. Soc. 133: 1156-1158). The CODEX scheme recouples anisotropic interactions. Please comment whether re-coupling of anisotropic interactions enhances spin diffusion.

The authors did not consider ABMS (Anisotropic Bulk Magnetic Susceptibility) as a potential source of artifacts (Vanderhart DL, Earl WL, Garroway AN (1981) Resolution in C-13 NMR of organic-solids using high-power proton decoupling and magic-angle sample spinning. J Magn Reson 44:361–401). Depending on the applied CPMG field, a dephasing effect is observed. Is there a chance that ABMS acts similar as CSA, and enhances spin diffusion effects? Please comment. This could be tested e.g. by varying the CPMG field in the de- and rephasing CODEX elements.

Minor: Please indicate explicitly the spacing of the 180 pulses in the CODEX de- and rephasing periods.

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