Referee #1

The tutorial by Smelko et al. gives an analytical description of magnetization transfer in a two-spin system during the cross-polarization (CP) process. The emphasis is mainly on the effect of ramp and tangential CP in the presence of radio-frequency (RF) inhomogeneity along the z-axis of solenoid coils. This is a very detailed and clear description of the phenomenon that shows how shaping the irradiation profile improves the efficiency of CP in all cases however interestingly both show the same overall efficiency if the shape is properly optimized. In all cases, efficiency drops with increases spinning speed, a result that poses a challenge for performing CP at high spinning speeds > 100 kHz and small couplines (e.g. ^{13}C-^{15}N). The authors end suggesting that better polarization transfer techniques are designed to compensate for the loss of signal due to RF inhomogeneity (although no suggestion is made as yet).

We want to communicate that RF inhomogeneities should be part of the pulse sequence design from the beginning. In some works, RF inhomogeneity effects are explored after the sequence is developed, and only within a limited range of RF amplitudes, typically covering $\pm$10%. We have not seen many studies that consider RF field profile of a full solenoid, that is the range 50% to 100%.

The manuscript is suitable for publication in MR after some minor revisions are taken care of.

Line 55 – negative intensities in DQ CP – please provide reference.

We added the reference to the work of Meier [B.H. Meier, Cross polarization under fast magic angle spinning—thermodynamical considerations, Chem. Phys. Lett. 188 (1992) 201–207] who describes the DQ CP conditions at MAS frequency of 10 kHz.

Line 57 – "Developments in NMR hardware and pulse sequences are largely driven by biomolecular applications" – I don't think this is a correct statement. All applications, not just bio, drive development of new hardware and sequences (e.g. MQMAS, surface DNP etc).

Line 69 -reference is missing ("It has been noticed that restriction …")

We agree. In addressing these two comments, we removed controversary statements and re-formulated the paragraph (original lines 57-72) to better communicate our opinion that RF field inhomogeneity should be treated in its full range of the whole available sample volume. This becomes an issue for ultrafast MAS rotors that contain only small amounts of material that should not be wasted by volume-selective behavior of CP transfers.

The paragraph is replaced by this text (new lines 76-89):

RF field inhomogeneity is a concern for the performance of virtually all NMR experiments. Specifically, it affects the sensitivity of the cross-polarization experiment, since the Hartmann-Hahn matching is violated at different positions within the sample as a consequence of the modulation of the RF amplitudes due to inhomogeneity. An experimental example of this volume-selective behavior of the cross-polarization experiment is presented, for example, in the work of Tošner et al. (Tošner et al., 2018). In biomolecular applications, it is difficult to prepare large quantities of isotopically labelled samples, and only limited amounts of material are available that do not allow to completely fill the MAS rotor. To yield the highest possible sensitivity, samples are typically center packed around the center of the coil, and the problem of RF field distribution is reduced. However, the rotors for ultrafast MAS are small and can be completely filled with sample. Under these conditions, RF inhomogeneity comes up as a concern in its full range. With faster MAS and correspondingly smaller rotors that contain less material, we are again facing sensitivity issues. It is obviously desirable that the whole sample contributes to the NMR signal. At this point, it appears that the inhomogeneity of the RF field is the prevailing challenge for the development of new solid-state NMR methods.

*Line 100 – for bij, given that the gyromagnetic ratio is in units of rad*s-1*T-1, in order to get units of Hz, I think you must multiply by hbar and divide by another factor of 2p. Please recheck, or define the constants in a different way.*

We thank the Referee for pointing out this error. The formula is corrected. $b_{IS} = -\frac{\mu}{4\pi}\frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}\frac{1}{2\pi}$

Line 134-5 – what does it mean about the efficiency? You cannot have all orientations satisfy the HH condition at the same time since cos(dt)=-1 will hold only for a single orientation.

The HH condition refers to the matching of RF amplitudes, it does not involve any crystallite orientation dependence. To avoid confusion, and to add the answer about efficiency, we modify the paragraph as follows (new lines 154-157).

The dipolar coupling is an orientation dependent interaction. To yield the magnetization transfer dynamics for a powder sample, the ensemble of all possible crystallite orientations has to be accounted for. The powder averaged inversion efficiency is lower since the condition of a complete transfer, $\cos d_{IS}t = -1$, will hold only for a single orientation.

Line 151 – geometric identities

We suggest using "trigonometric identities".

Figure 8 – please add labels to the axes that are similar to figure 7, not just the values of the ramp. Same in Figure 9.

We add labels I_x^{ZQ}, I_y^{ZQ} I_z^{ZQ} to the axis wherever it will not interfere with the other labels, Figures 7, 8, 9, 11, and 12.

General comment – there is no discussion at all on the effect of a multi-spin system that almost always exists is such experiments. Can 1H-1H coupling be ignored to a sufficient approximation when spinning very fast? Perhaps one simulation can be added that considers a H2X spin system in order to get some initial insight whether RF inhomogeneities are at least partially compensated by homonuclear couplings.

This is a relevant point. What happens if we consider additional spin interactions? Including more spins breaks the simple model of rotations in a 3D ZQ subspace and brings other interference effects. Such a treatment is beyond the scope of this paper. Our main concern expressed in this paper is about the perspective of the 13C-15N CP transfer at ultrafast MAS. For this particular case, two-spin approximation should suffice.

The effects in a HnX spin system are treated, for example, in the work of Marks and Vega [Marks, D.; Vega, S. (1996). A Theory for Cross-Polarization NMR of Nonspinning and Spinning Samples. Journal of Magnetic Resonance, Series A, 118 (2), 157–172. https://doi.org/10.1006/jmra.1996.0024]. Additional homonuclear interactions lead to a manifold of energy levels that makes it easier to fulfill the HH match. The HH matching profile is broader, and it can partially compensate RF amplitude mismatch introduced by RF field inhomogeneity. At the same time, the energy spread of the manifold decreases for increasing spinning speed, leading to a set of isolated resonances that do not help much in compensating the continuous RF field inhomogeneity. Similar conclusion was presented in the work by Emsley and coworkers [Laage, S., Sachleben, J. R., Steuernagel, S., Pierattelli, R., Pintacuda, G., Emsley, L. (2009). Fast acquisition of multi-dimensional spectra in solid-state NMR enabled by ultra-fast MAS. J Magn Reson, 196 (2), 133–141. https://doi.org/https://doi.org/10.1016/j.jmr.2008.10.019]

We add this sentence to the beginning of Theory section (new lines 110-116).

A more general description that considers the surrounding spins and homonuclear interactions within an $I_N S$ spin system can be found, for example, in the work of Vega and coworkers (Marks and Vega, 1996; Ray et al., 1998). This issue has been reviewed in the context of ultrafast MAS by Emsley and coworkers (Laage et al., 2009), concluding that the perturbation effects of homonuclear interactions diminish with increasing spinning rate. The authors infer that the behavior of the CP experiment at very fast spinning in a $I_N S$ spin system is reminiscent of a 13C-15N spin pair, which we would like to analyze in the following in detail.

Referee #2

The manuscript by Smelko et al discusses the important issue of the efficiency of cross polarization in a powder sample, under MAS, in presence of RF inhomogeneity. The authors re-derive transfer efficiencies for ZQ and DQ CP under MAS, and then analytically include the effects of RF inhomogeneity in these equations. They demonstrate that we should expect the transfer efficiencies to drop significantly as MAS frequencies increase, especially for N<->C tranfers. I think this is an important piece of work as we develop faster spinning hardware expecting better performance of existing seqeunces. The effects that they anticipate at 200 kHz MAS frequencies are quite dramatic. I recommend that the manuscript be accepted for publication at Magnetic Resonance

Some comments that may be addressed prior to publication:

1. The authors comment that the development of pulse sequences have so far ignored issues related to rf-inhomogeneity. This may be somewhat true for CP, but rf-inhomogeneity and its deleterious effects have been looked at in other areas, in particular homonuclear decoupling and symmetry based recoupling seqeunces.

We removed the controversary statement and re-formulated the paragraph (original lines 57-72) to better communicate our opinion that RF field inhomogeneity should be treated in its full range of the whole available sample volume. This becomes an issue for ultrafast MAS rotors that contain only small amounts of material that should not be wasted by volume-selective behavior of CP transfers. The updated text (new lines 76-89) can be found in the response to Referee #1.

2. Figure 4: this loss of efficiency seems to be unavoidable irrespective of the condition used, if ZQ CP with ramp is used in presenece of rf inhomogeneity. However, if DQ CP with n=1 is used, is this avoidable? The authors hint at something similar on line 373, but it is not clear what conditions are used to do this.

We believe the referee points towards HH mismatch at the peripheral regions of the coil/sample which causes loss of the overall CP efficiency. Yes, this is unavoidable irrespective of the condition used, ZQ or DQ. There is another detrimental phenomenon that we demonstrate in Figure 4C, which is the simultaneous ZQ and DQ transfer occurring in the sample at different places. This situation can be avoided using appropriate values of RF amplitudes. We hope this clarification is sufficient and we do not modify the main text.

3. Combined with lower efficiencies of CP and increasing T2' with MAS > 150 kHz, would INEPT based experiments (especially for 15N-13C transfers) be a more attractive proposition as one spins faster? Or TEDOR-based approaches (the high rf requirements notwithstanding) which would be less sensitive to rf inhomogeneiety?

In our opinion, recoupling techniques that are based on hard pulses are more robust towards RF inhomogeneity and can be improved by phase cycling. TEDOR is a possible candidate, but it has other drawbacks (mainly its vulnerability to t1 noise due to MAS fluctuations). Making use of scalar-based sequences like INEPT still suffers by relaxation losses. Dipolar-based elements can be an order of magnitude shorter. We hope that our paper will stimulate development of improved dipolar recoupling methods specifically designed for coherence transfers at ultrafast MAS. We already work along these lines using optimal control approach.

4. It would be great if the authors share simpson simulation files and the rf profiles used for their numerical simulations.

The paper is not based on SIMPSON simulations. Therefore, the input files are not included. Numerical simulations were used solely to verify the analytical model. The complexity of our SIMPSON input files does not go beyond basic exercises published elsewhere (see, for example, Juhl, D. W., Tosner, Z., Vosegaard, T. (2020). Versatile NMR simulations using SIMPSON. In G. A. Webb (Ed.), Annual Rep. on Nmr Spectr., VOL 100, pp. 1–59, https://doi.org/10.1016/bs.arnmr.2019.12.001).

Other minor comments
*1. Line 502-503: ...Figure 2 and *the variation* is the same for both RF channels*

We correct the sentence as suggested (inserting the words “the variation”).

Referee #3

The article „Performance of cross-polarization experiment at conditions of radiofrequency field inhomogeneity and slow to ultrafast MAS" by Andrej Šmelko et al. presented very elegant and comprehensive analytical description of cross polarization (CP) usinh AHT aproaches. Article is very well written and fully described very important effect of RF inhomogeneity in case CP experiment. Authors vary carefully analyzed effect of distribution of RF and in addition effect of applying shape pulse (linear ramp or tangential) one of the RF channel. In my opinion article is suitable to publishing Magnetic Resonance without any changes. I have only one question, in section 3.1. authors have written "Both the width and the maximal transfer efficiency are independent of the MAS frequency." I am little surprised about this effect – from previous publications (eg. Emsley, Journal of Magnetic Resonance 196 (2009) 133–141) and experimental results it is clear that width of the CP matching profile depends of spinning speed and becomes sharper when spinning speed is increased (more precisely is inversely proportional to vR2, and directly proportional to bIS3). What is the reason of this inconsistence between results? Is it due to consideration of only two spin system or just AHT is not suitable to predict such behavior and different treatment (Floquet theory) is required?

We thank the Referee for these positive comments. Regarding the statement in question, it is valid within the limits of an isolated spin pair. The behavior described in the work of Emsley is valid for an InS spin system with many homonuclear interactions. These effects, as pointed out, are eliminated with faster sample spinning, leading to a situation reminiscent of a relatively isolated 13C-15N spin pair, which is in the focus of our analysis. We modified the text at the beginning of the Theory section to include this reference. The modified text (new lines 110-116) is described in the response to the last comment of Referee #1.