

Polenova, Gronenborn and co-workers provide a detailed investigation into the competing transfer pathways active in biomolecular under MAS DNP. Here, three different pathways are currently known, namely CP-based indirect DNP, direct DNP, as well as a spontaneous contact between  $^1\text{H}$  and  $^{13}\text{C}$  magnetization mediated through heteronuclear cross-relaxation (SCREAM-DNP). The authors excellently provide a short review about these pathways and introduce the reader to the topic under investigation.

Understanding the interplay between the three transfer pathways is of crucial importance to successfully apply MAS DNP towards different questions by choosing the optimal conditions for the task at hand. While some control may be exerted by choice of the pulse sequence, the disentanglement of the pathways is not trivial. In this regard, this work gives very useful information about the dynamics of each transfer pathway and their dependence on the polarizing agent concentration. Furthermore, line broadening is discussed for various distinct resonances under the different experimental conditions.

The manuscript is well written and of good scientific quality. All experimental data is well presented and documented, and reproduction seems possible given the provided information. The content is of general interest to a broad magnetic resonance community and therefore suitable for publication in MR. Before publication, however, I ask the authors to comment on several specific points and perform minor revisions of the manuscript accordingly.

In line 40, the authors state that “modest gains have been detected for membrane proteins with  $\epsilon=4-10$  (Wylie et al., 2015)”. This statement reads like a general observation, however, the referenced work covers a rather special case of membrane proteins labeled with single nitroxide tags which come into dipolar contact. In my experience, DNP enhancement of 40-60 can be routinely achieved for membrane proteins.

The following sentence (“Recently, large DNP signal...”) is confusing. The first part deals with impregnated microcrystalline histidine, the second part is in no way generally applicable and seems to be specifically limited to the highest available field. Even in this regard, the sentence is misleading because it implies that no soluble polarizing agents are available for biological systems.

The authors use “build-up time,  $T_b$ ” interchangeably for both the time constant as well as the experimentally chosen polarization time period (c/f lines 127, 129, 142, and Figure 2). These two different parameters have to be clearly distinguished by an unambiguous choice of symbol and naming.

In Figure 2, it is not clear, which graphs the subpanels abc are referring to. Also, in the lower left graph,  $\epsilon(-)$  seems to be missing a negative sign (-4).

When discussing the build-up dynamics in Figure 2, it should be clarified that SCREAM-DNP magnetization is emerging from the methyl groups and the spreading through the  $^{13}\text{C}$  network by spin diffusion. This explains the quick inversion of Ile resonances, and the delayed response of the other resonances.

On the bottom of page 5, it is stated that “Heteronuclear decoupling has no effect...”. I am wondering by what means turning off the decoupling is expected to effect a sign inversion? Heteronuclear decoupling is used when the  $^{13}\text{C}$  magnetization is already in the transverse plane, so it is unclear to me how this can influence the sign of polarization. For SCREAM-DNP  $^1\text{H}$  saturation during the build-up period mostly destroys the incoherent pathway, but this is independent from decoupling. This part should be revised, it should either be explained why decoupling may be expected to change the outcome of the experiment, or it should be clarified if indeed decoupling is mistaken for saturation.

In line 204, “with the with line...” seems to contain an additional “with”.