This manuscript is interesting as it aims at the development of an alternative pathway (transfer via ^{1}H) to enhance ^{13}C polarization under dDNP conditions. The proposed ^{1}H-^{13}C transfer mechanism is different from that in the conventional Hartmann-Hahn CP, which is based on the idea of spin-locking on both the channels. The new RF scheme requires non-simultaneous RF irradiation on the two channels.

Although the optimum RF power is not lower (compared to that in conventional CP), the duration of RF on ^{1}H is significantly reduced. However that on ^{13}C channel becomes significantly longer and the transfer efficiency also decreases by a factor of 2. Overall, the new approach might still be better than Hartmann-Hahn CP for technical reasons as the authors claim.

I have a few questions regarding the ^{1}H-^{13}C transfer mechanism (*the authors responses are given in italics*):

1. On page 2 line 31, the authors talk about conversion of ^{1}H Zeeman polarization to $I_{1z}.I_{2z}$ "dipolar order" using RF. How can the proposed RF on ^{1}H convert I_z to $I_{1z}.I_{2z}$ term, can authors provide some more insights?

In the spin-lock frame, the magnetization shrinks to a value which is small relative to that produced by the static magnetic field (for the same sample) during the demagnetization process. This effect has been extensively covered in a number of other papers:

J. Jeener and P. Broekaert, *Phys. Rev.*, **1967**, 157, 232-240.
H.-M. Vieth and C. S. Yannoni, *Chem. Phys. Lett.*, **1993**, 205, 153-156.
J. Jeener, R. Du Bois and P. Broekaert, *Phys. Rev.*, **1965**, 139, A1959-A1961.
A. G. Redfield, *Science*, **1969**, 164, 1015-1023.
J.-S. Lee and A. K. Khitrin, *J. Chem. Phys.*, **2008**, 128, 114504.

However, this is not the main focus of our current paper. Clearly, our spin system of choice is much more complicated than those in the above references (due to the presence of paramagnetic radicals etc.). Multiple dipolar orders or higher spin orders could also exist, as eluded to in our current paper. We aim to analyse these processes in greater detail in our future works.

2. For transfer of polarization from I to S, there has to be an effective ZQ or DQ IS dipolar Hamiltonian. Since there are RF pulses on both the channels, such Hamiltonian terms can be generated. But they seem to be of higher order perturbation term in the Hamiltonian. Maybe that's the reason why transfer rate is very slow. Can authors shed some light on this?

We surmise that since the dCP transfer is slower than conventional cross-polarization it involves a different transfer mechanism. However, we do not have sufficient insights into the true polarization transfer mechanism for this sample under dDNP conditions at present.

3. For the given RF scheme, generating a purely ZQ or a purely DQ (IS) dipolar Hamiltonian might be challenging. This in turn may lead to phase distortion of the ^{13}C signal if there are multiple ^{13}C resonances. Can authors provide some 13C spectra?

^{13}C Chemical Shift / ppm
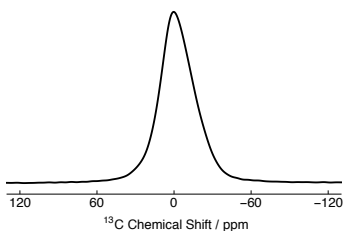
The recorded ^{13}C NMR spectra do not show significant phase distortion and are detected with a good level of signal-to-noise. Please see the attached ^{13}C NMR spectrum. Additional ^{13}C NMR spectra will be provided in a following publication on a similar topic.

4. Since the method is based on ^{1}H "dipolar order", what kind of spin-system is required for it to be efficient. Can the transfer mechanism be elucidated using a simple three-spin ^{1}H-^{1}H-^{13}C model? How would ^{1}H concentration in glassy matrix influence this transfer?

We have started simulations on a simple 3-spin-1/2 ^{1}H-^{1}H-^{13}C model system. However, agreement between simulated and experimental data has not yet been reached. It is this fact which provides a hint to the authors that a similar reservoir of non-Zeeman spin order may be used instead. There are also preliminary data to support this

conclusion. Increasing the proton concentration of the glassy matrix dramatically decreases the polarization transfer time and increases its efficiency.