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Interactive comment on "Dipolar Order Mediated ^{1}H->^{13}C Cross-Polarization for Dissolution-Dynamic Nuclear Polarization" *by* Stuart J. Elliott et al.

Anonymous Referee #2

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Following the introduction of dissolution-DNP (dDNP) by Golman and Ardenkjær-Larsen, there have been discussions of approaches to shorten the hours long times required for the e-âđİ13C polarization transfer process. This step is limited by the slow 13C-13C spin diffusion process. Improvements are impeded by the fact that GE/Oxford/etc. does not permit investigators to modify their dDNP equipment – for example, by adding an 1H tuning circuit to the single resonance 13C circuit present in their probes.

In addition, it has been known since the 1970's that 1H's polarize much more rapidly than low-ðİŻĎ species such as 13C or 15N. For example, Hartmann, et al. (Nuclear

Instruments and Methods 106, 9-12 (1973)) showed that 1H's in alcohol samples at 1K and 5 T could be polarized in <2 minutes to levels of 35-70

This paper by Elliot, et al is a description of some of the approaches to implement the 1Hâđİ13C transfers that utilize low powers to avoid arcing in the helium atmosphere. The schemes are based on: (i) Less (or low) rf-power; (ii) less overall rf-energy; (iii) simple rf-pulse shapes; and (iv) no synchronized of the 1H and 13C rf-irradiation.

The transfer schemes are designed to take advantage of the terms in the expansion of the density matrix that go as $I_{izx}I_{jz}, adipolarordertermthatbecomesimportantatlowtemperatures.Theapproachesuseagat$

The paper is largely okay as written. However, I would suggest that the authors consider the following to improve the scholarship of the paper.

(1) I would include the reference to Hartmann (1973) above that, as far as I am aware, was the first to report the short polarization times of 1H at 1-2 K. The dDNP community pretty much ignores the extensive DNP physics literature from the 1960-2000 era and starts by quoting Golman and Ardenkjær-Larsen in 2003. In fact, I would suggest that they do a literature search to see if others have also reported these short polarization times.

(2) They also mention that the microwaves are gated and swept with a triangular frequency modulation. It would be good to discuss this in more detail. Why was the width of 120 MHz and a rate of 500 Hz chosen ? There are AWG's available these days that can easily produce more interesting waveforms. Have any of these been introduced into the experiment ? For example, the waveform could be adiabatic which might be more efficient that a simple triangular waveform.

(3) Why was the TEMPO concentration set at 50 mM ? This is about 3 times that used in MAS experiments and x3 the 15 mM concentration of trityl often employed by Ardenkjær-Larsen and coworkers in their experiments. Does the higher concentration

lead to the shorter polarization periods ? A fair comparison of polarization levels and build up times and would compare 15mM trityl to 15 mM TEMPO.

(4) Is the transfer mechanism established to be thermal mixing or the cross effect ? Although this is not the focus of the paper, it should be mentioned and discussed at least briefly. If the cross effect is involved then why doesn't the dDNP community use nitroxide biradicals as polarizing agents. Again this could be briefly discussed.

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