

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

In addition, it has been known since the 1970's that ${}^1\text{H}$'s polarize much more rapidly than low- γ species such as ${}^{13}\text{C}$ or ${}^{15}\text{N}$. For example, Hartmann, et al. (*Nuclear Instruments and Methods*, **106**, 9-12 (1973)) showed that ${}^1\text{H}$'s in alcohol samples at 1 K and 5 T could be polarized in <2 minutes to levels of 35-70%.

This paper by Elliott, et al is a description of some of the approaches to implement the ${}^1\text{H} \rightarrow {}^{13}\text{C}$ 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 synchronization of the ${}^1\text{H}$ and ${}^{13}\text{C}$ *rf*-irradiation. The transfer schemes are designed to take advantage of the terms in the expansion of the density matrix that go as $|i_z\rangle\langle j_z|$; a dipolar order term that becomes important at low temperatures. The approach uses a gated microwave field and then different approaches to transfer polarization from ${}^1\text{H}$ to ${}^{13}\text{C}$ in Na-acetate. The paper is largely okay as written. However, I would suggest that the authors consider the following to improve the scholarship of the paper.

The author response is given in italics.

(Q1) 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 ${}^1\text{H}$ at 1-2 K. The *d*DNP 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.

(A1) A reference to Hartmann's 1973 paper has now been included.

(Q2) 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 than a simple triangular waveform.

(A2) The width and rate of the microwave field was optimized in order to give the best ${}^1\text{H}$ polarization during active ${}^1\text{H}$ DNP. A sentence regarding this information has been added to the manuscript: "The sample was polarized by applying microwave irradiation at 197.648 GHz (positive lobe of the EPR line) with triangular frequency modulation of amplitude $\Delta f_{mw} = 120$ MHz (Bornet et al., 2014) and rate $f_{mod} = 0.5$ kHz at a power of c.a. 100 mW, which were optimized prior to commencing experiments to achieve the best possible level of ${}^1\text{H}$ polarization." Detailed information concerning microwave gating is given on page 3/line 100 of the manuscript. More sophisticated AWG's have not been introduced into the experiment at present.

(Q3) 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.

(A3) At present, a concentration of 50 mM of TEMPO radical is used as a "standard sample" within our laboratory, and it is true that the high radical concentration would lead to shorter polarization build-up times. For future experiments, in which the authors plan to dissolve and transfer the sample to a separate superconducting magnet for detection, we will likely use a lower radical concentration c.a. 25 mM TEMPO radical.

(Q4) 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 *d*DNP community use nitroxide biradicals as polarizing agents. Again this could be briefly discussed.

(A4) For ${}^1\text{H}$ nuclei at 1.2 K and 7.05 T the electron-proton transfer will presumably occur through thermal mixing and/or cross-effect. So far, bi-radicals have not shown better performances than TEMPO(L) in our experimental conditions. We prefer to keep this very complicated discussion out of the paper.