Large Volume Liquid State Scalar Overhauser Dynamic Nuclear Polarization at High Magnetic Field

Thierry Dubroca¹*, Sungsool Wi¹, Johan van Tol¹, Lucio Frydman¹,², Stephen Hill¹,³*

Authors affiliations:
1) National High Magnetic Field Laboratory, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310 (USA)
2) Department of Chemical and Biological Physics, Weizmann Institute of Science, 76100 Rehovot (Israel)
3) Department of Physics, Florida State University, Tallahassee, Florida 32306 (USA)

*corresponding authors. dubroca@magnet.fsu.edu and shill@magnet.fsu.edu

Supporting Information

Table of contents

a) Temperature calibration
b) Supplemental NMR-DNP spectra
c) Microwave B₁ field
d) NMR-DNP hardware and scheme
a) Temperature calibration

During DNP experiments, a fair amount of microwave power is used and, therefore, it is typical to see some temperature effects on the NMR spectra. In particular, in our work, we use one of those temperature effects to estimate the temperature in our samples. The NMR $^{13}$C chemical shift of chloroform is very sensitive to temperature, while the chemical shift for carbon tetrachloride is essentially independent of temperature (in the range of our experiments). Using the relative change in chemical shift between these two compounds, one can estimate the sample temperature during DNP experiments. In order to calibrate the temperature, that is, relate precisely the change in chemical shift to the temperature, we first conducted a series of experiments in a Bruker liquid NMR spectrometer (18.8 T). The spectrometer temperature system was first calibrated using ethylene glycol following the work of Raiford et al. (Anal. Chem. Vol 51, No 12, pages 2050-2051, 1979) Using the variable temperature system of the spectrometer we collected NMR spectra of carbon tetrachloride and chloroform as function of the temperature, see figure SI-1. We then plotted the relative chemical shift between these two compounds as a function of the temperature, see inset Figure SI-1. A 2$^{nd}$ order polynomial function is used to model the temperature with a correlation coefficient of 0.998, thus allowing us to estimate the sample temperature during DNP experiments using the difference in chemical shift between carbon tetrachloride and chloroform.
Figure SI-1: $^{13}$C NMR spectra of labeled carbon tetrachloride and chloroform measured at 18.8 T as function of the temperature. The natural abundance $^{13}$C peaks from the solvent, n-pentane-d$_{12}$, are also visible. Inset: temperature plotted as a function of the relative chemical shift between carbon tetrachloride and chloroform (large dots). A 2$^{nd}$ order polynomial function is used to model the temperature (fine dots). Sample information: $^{13}$CCl$_4$ (9% vol.) & $^{13}$C-chloroform (1% vol.) in n-pentane-d$_{12}$ with 10 mM TEMPO (oxygen was removed by freeze pump thaw), 100 µL volume.
b) Supplemental NMR-DNP spectra

Figure SI-2 and SI-3 display the NMR spectra of phenylacetylene-2-$^{13}$C and deuterated chloroform, respectively, with and without microwaves.

**Figure SI-2:** NMR spectra of carbon tetrachloride, universally $^{13}$C labeled (5% vol.), and labeled phenylacetylene-2-$^{13}$C (5% vol.) in n-pentane-d$_{12}$ solvent with 10 mM TEMPO, with and without microwaves. The "microwave on" spectrum was acquired using 13 W of microwave power for 1.4 s before each NMR scan.

**Figure SI-3:** NMR spectra of universally $^{13}$C labeled carbon tetrachloride (7% vol.) and deuterated chloroform (7% vol.) in n-pentane-d$_{12}$ solvent with 10 mM TEMPO, with and without microwaves. The "microwave on" spectrum was acquired using 13 W of microwave power for 2.6 sec before each NMR scan.
c) Microwave $B_1$ field

In order to estimate the microwave $B_1$ field at the sample during a DNP experiment, we calculate its relationship to the power of a microwave beam using the energy density definition for an electromagnetic wave.

Energy density ($J/m^3$) equation:

$$ U = \frac{\varepsilon E^2}{2} + \frac{B^2}{2\mu} \quad (1) $$

where $E$ and $B$ are the electric and magnetic fields associated with the microwave beam, $\varepsilon$ is the permittivity and $\mu$ is the permeability (essentially equal to $\mu_0$ here, since the sample and sample holders are diamagnetic).

Using the relationship between $E$ and $B$:

$$ E = \frac{cB}{n} \quad (2) $$

Where $c$, is the speed of light in vacuum and $n$ in the index of refraction in the traveling material (in our case the NMR sample tube containing mostly $n$-pentane-$d_{12}$ solvent).

Assuming no losses in the sample and sample tube (pentane is transparent to microwaves, as is FEP, the plastic used for our sample tubes), the permittivity can be written as:

$$ \varepsilon = \varepsilon_r\varepsilon_0 \quad (3) $$

$$ \varepsilon_r = n^2 \quad (4) $$

where $\varepsilon_r$ is the relative permittivity and $\varepsilon_0$ is the permittivity in vacuum.

Combining equations (1), (2), (3) and (4) gives us:

$$ U = \frac{B^2}{\mu_0} \quad (5) $$

The power, in watts, of the microwave beam is then defined as:

$$ P = \frac{U \times V}{t} \quad (6) $$

Where $t$ is the time and $V$ is the volume of interaction. The volume of interaction is defined as:

$$ V = \frac{\pi d^2 c}{4n} t \quad (7) $$

Where $d$ is the diameter of the sample tube in which the microwaves are confined.

Note: the interaction volume is a cylinder (our sample volume geometry). The cross section is a disk of area $\frac{\pi d^2}{4}$ and the length is equal to the speed of the microwave in the sample, $\frac{c}{n}$, multiplied by the interaction time, $t$.

Using equations (6) and substituting $U$, the energy density (5) and $V$, the interaction volume (7) we obtain:
\[ P = \frac{\pi d^2 c}{4n\mu_0} B^2 \quad (8) \]

using \( d = 3 \text{ mm} \) (i.e. the sample tube diameter) and \( n = 1.5 \), in SI units, we obtain:

\[ P = 1.1 \times 10^9 B^2_1 \quad (9) \]

Note: for 30 W of microwave power we obtain \( B_1 = 0.16 \text{ mT} \)

d) NMR-DNP hardware and scheme

The NMR-DNP instrumentation is composed of a commercial spectrometer, namely an Agilent direct drive console with two channels (600MHz for proton and broadband for other nuclei), an Oxford 600AS superconducting magnet operating at 14.1T, and a modified Varian HCN probe. The probe was modified by replacing the Dewar used to flow cooling/heating gas with a microwave guide to provide microwave irradiation of the sample. An adaptor was added to allow gases to flow via the microwave guide to cool the sample down during microwave irradiation experiments. For DNP experiments, a Bruker 395 GHz gyrotron was used to generate microwaves. The generated microwaves were transmitted to the probe via a quasi-optical table, that is, a set of mirrors and grids used to control the microwave beam path, polarization and power. The complete details about quasi-optical system can be found in reference 13, i.e. Dubroca et al. JMR 289 (2018). Finally, the quasi-optical table is equipped with a mechanical shutter triggered by the NMR console, allowing control of the microwave irradiation within pulse sequences (see scheme below).

```
Microwave

\[ ^{13}\text{C} \]

Recycling
delay

\[ \pi/2 \]

acquisition
```

irradiation