Spin thermometry: deuterium NMR spectra allow one to measure millikelvin spin temperatures

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Dissolution DNP at ENS

188 GHz

6.7 T

1.2 K

DNP Polarizer

18.6 T

(800 MHz)

7 T

NMR
Some applications of D-DNP

1- Kinetics of enzymatic reactions *in vitro* and *in cellulo*  
(cancer diagnosis?)

2- Kinetics of *very slow* reactions, using long-lived states  
(fumarate-malate)

3- Signal enhancement of proteins  
(“HYPEX” with hyperpolarized HDO)

4- Drug screening
Multinuclear Hyperpolarization: new probe for frozen bullets

Tuning and matching in superfluid helium

Sina Marhabaie
Behdad Aghelnejad
A Low-Temperature Broadband NMR Probe for Multinuclear Cross-Polarization

Behdad Aghelnejad, Geoffrey Bodenhausen, and Sina Marhabaie


Multinuclear probe immersed in superfluid helium at 1.2 K

$^1$H nutation signals (90 W, 4 K): good rf homogeneity
NMR spectra of various nuclei with/without DNP at 4 K and 6.7 T

Red: no microwave irradiation  
black: positive DNP (187.9 GHz)  
blue: negative DNP (188.38 GHz)

50% ethanol-d$_6$  
40% D$_2$O  
10% H$_2^{17}$O  
1.5 M $^{13}$C-Sodium acetate  
1 M $^{15}$N-Urea  
40 mM TEMPOL

Determine polarization $P(S)$  
or spin temperature $T_{spin}(S)$ from on/off ratio of signal intensities
Asymmetric NMR spectra of $^2$H with/without DNP at 4 K and 6.7 T

Red: no microwave irradiation
black: positive DNP (187.9 GHz)
blue: negative DNP (188.38 GHz)

50% ethanol-d$_6$
40% D$_2$O
10% H$_2^{17}$O
1.5 M $^{13}$C-Sodium acetate
1 M $^{15}$N-Urea
40 mM TEMPOL

Determine polarization $P(S)$
or spin temperature $T_{\text{spin}}(S)$
from ratio of signal intensities
Challenges in preparing, preserving and detecting para-water in bulk: overcoming proton exchange and other hurdles

Daniele Mammoli, Nicola Salvi, Jonas Milani, Roberto Buratto, Aurélien Bornet, Akansha Ashvani Sehgal, Estel Canet, Philippe Pelupessy, Diego Carnevale, Sami Jannin and Geoffrey Bodenhausen


Has this asymmetry been seen before?

Fig. 2 Experimental proton spectra of $\text{H}_2\text{O}$ diluted in DMSO doped with 50 mM TEMPOL and frozen at ca. 1.2 K in a field of 6.7 T,
Proton Spin–Spin and Spin–Lattice Relaxation in CaSO₄·xH₂O below 1 K

P. KUHNS, O. Gonen, AND J. S. WAUGH

Has this asymmetry been seen before?

Figure 3.
Temperature dependence of the asymmetry of the $m = \pm 3/2 \rightarrow \pm 5/2$ transitions for $^{127}I$ in solid ICl.
NMR spectra of $^2$H (spin $S = 1$) with quadrupole coupling in a frozen sample at $T_{\text{spin}} = 0$

Only one “wing” of Pake pattern excited if one uses rf pulses with small nutation angles
Two “wings” of $^2$H Pake pattern excited by rf pulses with increasing nutation angles

$180^\circ - 9^\circ = 171^\circ$

$90^\circ$

$9^\circ$

200 kHz
Our asymmetry: Simulations

$T_{\text{spin}}(^2\text{H}) = 3.5 \text{ mK}$
After 500 s of DNP

\[ T_{\text{spin}}(^2\text{H}) \rightarrow 3.5 \text{ mK} \]

Our asymmetry:
Experimental build-up of DNP
Paris en résonance (2013-2016) at Ecole Normale Supérieure

Hyperdensity:
67.7 T/ 100 m²
Martin Rasmussen (Copernicus) and Bernard Blümich (Ampère)

Open Access
Gold but cheap: 75 €/page
Interactive reviewing
Public reviews
ENS
SU
CNRS
IR-RMN-THC
ANR
EQUIPEX
ERC
Bruker
Thank you for your attention
Spin thermometry: deuterium NMR spectra give a straightforward measure of very low spin temperatures resulting from dynamic nuclear polarization

Behdad Aghelnejad, Sina Marhabaie, Mathieu Baudin, Diego Carnevale and Geoffrey Bodenhausen

Ecole normale supérieure, Paris
Dynamic nuclear polarization of samples at low temperatures, typically between 1.2 and 4.2 K, allows one to achieve spin temperatures as low as 2 mK, so that for many nuclear isotopes the high-temperature approximation is violated. This leads to characteristic asymmetries in powder spectra. We show the lineshapes due to the quadrupolar couplings of deuterium spins that are present in virtually all solvents used for such experiments allows the quick yet accurate determination of the spin temperature, or, equivalently, of the polarization. The observation of quadrupolar echoes excited by short pulses allows one to monitor the build-up and decay of positive or negative hyperpolarization when switching the frequency of the microwave irradiation.
Has this asymmetry been seen before?