Instrumentation for Solid-State DNP
Melanie Rosay, Ph.D., Hyperpolarization Product Manager

Winter School on Biomolecular SSNMR, Stowe, January 12, 2018
Outline

(1) NMR and sensitivity

(2) Microwave sources
   Gyrotrons for DNP at 263-593 GHz
   263 GHz klystron
   Solid State Sources

(3) Low-temperature DNP MAS probes

(4) NHMFL 395 GHz solids and solution DNP

(5) Grenoble CEA He MAS

(6) UCSB 200 GHz DNP and EPR

(7) Additional references
NMR and Sensitivity: the need for Hyperpolarization

Relatively low sensitivity in NMR and MRI due to small spin polarization at thermal equilibrium

Boltzmann Polarization at 14 T

\[
\frac{P}{2} \approx \frac{\gamma \hbar B_0}{2kT}
\]

in high T limit:
Increasing the Sensitivity of NMR

- Spectrometer and probe optimization
  - Increase magnetic field ($B_0$)
  - Lower temperature ($T$)
  - Improve RF signal pickup and transmission efficiency
  - Reduce thermal noise
- NMR method development
  - FT, magic angle spinning, indirect detection, fast MAS...
Increasing the Sensitivity of NMR

Increase Sensitivity by pushing spins away from thermal equilibrium: *Hyperpolarization*:

- **Dynamic Nuclear Polarization (DNP)**
  - *Solids DNP*
  - *Dissolution DNP*

- Ultra low temperature (ULT/Brute Force)
- Optical pumping (e.g. Xenon)
- Para Hydrogen
Dynamic Nuclear Polarization


**Phys. Rev. (1953) 92, 211**

**Phys. Rev. (1956) 975-980**
**Solids DNP**: Very Brief History

- Magnetic ordering at low temperature (< 1 K) (1970’s)
  - Doped polymers and carbonaceous materials
  - DNP frequency ≤ 40 GHz, introduction of DNP with Magic Angle Spinning (MAS)
- Solids DNP experiments at high field (5-18 T) (R.G. Griffin, 1990’s-ongoing)
  - Technology and method development
  - Applications to biological solids
- Solids DNP experiments 3.4 T/95 GHz for dissolution experiments (J.H. Ardenjkaer-Larsen, K. Golman et. al., 2000’s-ongoing)
  - Solids DNP followed by solution NMR
Dynamic Nuclear Polarization (DNP)

- Transfer polarization from unpaired electron spins to nuclear spins
  \[ \gamma_e \gg \gamma_n \]
- Driven by microwave irradiation at or near EPR frequency

\[
\begin{align*}
\gamma_e &>> \gamma_n \\
\text{DNP signal } \varepsilon &= 130 \\
\text{at } 395 \text{ GHz/600 MHz}
\end{align*}
\]
Requirements for Solid-State DNP-NMR

(1) Millimeter-wave microwave sources: **1-50 watts** in the **250-600 GHz**
regime (*gyrotron sources*)

(2) **Low temperature (100 K)** multiple resonance NMR probes with MAS

(3) Polarizing agents that are widely applicable and stable

(4) Uncompromised NMR performance

<table>
<thead>
<tr>
<th>Magnetic Field</th>
<th>EPR/μwave Frequency</th>
<th>EPR Wavelength</th>
<th>$^1$H NMR Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4 T</td>
<td>263 GHz</td>
<td>1.14 mm</td>
<td>400 MHz</td>
</tr>
<tr>
<td>14.1 T</td>
<td>395 GHz</td>
<td>0.76 mm</td>
<td>600 MHz</td>
</tr>
<tr>
<td>18.8 T</td>
<td>527 GHz</td>
<td>0.57 mm</td>
<td>800 MHz</td>
</tr>
</tbody>
</table>
Microwave Sources: wide array of sources up to 95 GHz (W-band)

Average Atmospheric Absorption of Millimeter Waves

Graph courtesy of R. Weber, Bruker BioSpin EPR
Microwave Sources: High Frequency Options

Vacuum electronic devices (VEDs):

Gyrotron
Klystron (EIO, EIK/A)
Backward wave oscillator (BWO)
Traveling wave tube (TWT)

Solid State devices:

Gunn and IMPATT diodes

For ssNMR applications, also consider: frequency and power stability, spectral purity

Graph courtesy of R. Temkin, MIT
Vacuum Electronic Devices (VED)

**Principle:**
- Conversion of electronic beam energy into radiation (electron bunching)
- Amplifiers or oscillators

**Electron Tube Components:**
- Cathode with heater for electron emission
- Anode to accelerate and focus electron beam
- Magnet to focus electron beam through the tube
- Interaction circuit or cavity
  - Generates microwaves
- Collector for spent electron beam

High-Power Microwave Sources and Technologies, Robert J. Barker (Editor) and Edl Schamiloglu (Editor), Wiley and Sons, New York, NY, 2001.

High-Power Microwave Sources, Victor Granatstein (Editor) and Igor Alexeff (Editor), Artech House, Norwood, MA, 1987.
Vacuum Electronic Devices (VED)

**Linear (slow-wave) devices:**
- Klystrons, helix TWTs, coupled-cavity TWTs, etc...
- Circuit walls used to modify dispersion of EM wave to create resonance
- Circuit sizes scale with wavelength
  - Very small at high frequencies
  - Reduced power capabilities
  - Reduced beam current capabilities

**Fast wave devices:**
- Gyrotrons, peniotrons, carms
- Beam dispersion modified by magnetic field to achieve synchronism between beam and wave (high order modes)
- Typical transverse circuit dimensions are many times larger than free space wavelength
- Cathode with heater for electron emission
- Larger sizes lead to higher power capabilities
  - Higher beam current
  - Reduced wall loading ($W/cm^2$)
Gyrotrons: Typical Operation

- Most commercial gyrotrons are designed for plasma fusion, military, and radar applications.
- Typically 140 GHz maximum frequency.
- Very high power (kW-MW).
- Occasional use only.
- Short pulses.
- No stability requirements: 1% or larger frequency drift common.
- No frequency accuracy requirements.

CPI 900 kW 140 GHz Gyrotron Tube
Gyrotrons for DNP Applications

• Continuous-wave gyrotrons first introduced for DNP applications by Griffin and Temkin at MIT, USA.
  – Initial design and experiments at 140 GHz*
  – Followed by 250 and 460 GHz

• Also developed in Japan by Idehara (Fukui) with Fujiwara and Matsuki (Osaka)
  – 395 and 460 GHz

Dynamic Nuclear Polarization with a Cyclotron Resonance Maser at 5 T

Lino R. Becerra,1 Gary J. Gerfen,1 Richard J. Temkin,2 David J. Singel,3 and Robert G. Griffin1

1Francis Bitter National Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
2Plasma Fusion Center, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
3Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
(Received 26 July 1993)

DNP (dynamic nuclear polarization) experiments at 5 T are reported, in which a cyclotron resonance maser (gyrotron) is utilized as a 20 W, 140 GHz microwave source to perform the polarization. MAS (magic angle spinning) NMR spectroscopy with DNP has been performed on samples of polystyrene doped with the free radical BDPA (α,γ-bisdiphenylene-β-phenylallyl) at room temperature. Maximal DNP enhancements of ~10 for 1H and ~40 for 13C are observed and are considerably larger than expected. The DNP and spin relaxation mechanisms that lead to these enhancements at 5 T are discussed.

- DNP with gyrotron microwave source
- Magic Angle Spinning
- BDPA in polystyrene
- DNP signal enhancements “considerably larger than expected”
Gyrotrons for DNP-NMR applications

**Gyrotron Schematic**

- Second harmonic design for all Bruker gyrotrons
- Cryogen-free magnets for short distance from cavity to window

\[ \omega_{RF} \sim n \omega_c, \quad n = \text{harmonic} \]

\[ \omega_c = \frac{eB_0}{mc\gamma} \quad (28 \text{ GHz/Tesla}) \]
395 GHz Tube Design: Cavity Beam Pattern

In collaboration with CPI

\[
TE_{10,3} \text{ cavity mode}
\]
395 GHz Tube Design: Cavity Modes

- **Collector**
- **Window**
- **Mode Converter**
- **Cavity**
- **Electron Gun**

**Graph:**
- **Normalized Magnetic Field**
- **Start Current (A)**
- **Cavity Modes**
- **TE2,3,1 194.9 GHz**
- **TE-7,4,1 2nd 398.7 GHz**
- **TE5,2,1 205.7 GHz**
- **TE10,3,1 2nd 395.2 GHz**
395 GHz Tube Design: Mode Converter

Transform gyrotron TE cavity mode to a Gaussian beam
Gyrotron Beam IR Images

Output Gaussian Beam

Beam Waist (cm)

measured width (x)
measured width (z)

theoretical expansion of design beam
Gyrotron Final Test and Tuning

Microwave power and frequency depend on:
- Electron beam current
- Cathode voltage
- Cavity dimensions
- Magnetic field at the cavity
- Magnetic field at the gun
Frequency and Power Stability

- Gyrotron power and frequency must be stable for extended ssNMR experiments
- Aim < 1% fluctuation in DNP-enhanced signal intensity
Most gyrotrons have limited frequency tuning or at least limited tuning with constant output power.

Sweep coils on DNP NMR magnets for investigation of different polarizing agents.

See also Griffin lectures.

Graph courtesy of R. Griffin (MIT)
Tunable Gyrotrons and Amplifiers in development @ MIT (R. Griffin, R. Temkin)
See also Griffin lecture notes
DNP Gyrotron Developments


See also DNP gyrotron developments from:

- Idehara/Fujiwara/Matsuki (395 GHz *2, 460 GHz)
- Barnes (200 GHz, frequency agile http://pages.wustl.edu/barneslab/instrumentation)
- Glyavin (263 GHz)
- Alberti (263 GHz)
Bruker Solid-State DNP Spectrometer

Gyrotron Output Power as a Function of Frequency

- 263 GHz, 100 mA
- 395 GHz, 140 mA
- 527 GHz, 130 mA
Microwave Transmission to NMR Sample

- **Corrugated waveguide:**
  - Negligible ohmic loss for Gaussian beam
  - Loss possible due to mode conversion in case of tilt or offset
  - Somewhat broadband
    - 19 mm ID 263 GHz corrugations
    - 16 mm ID 440 GHz corrugations

\[
\begin{align*}
\text{2a} & \quad p \quad d \\
\text{W} & \quad \text{OD}
\end{align*}
\]

\[
p = \lambda/3 \\
d = \lambda/4 \\
w < 0.5p \\
\text{Gaussian beam waist} = 0.64a
\]

- **Directional coupler** for frequency and power measurement
Microwave Transmission Line: corrugated waveguide

- 19 mm ID 263 GHz corrugations
- 16 mm ID 440 GHz corrugations

Gyrotron output: 100%

Probe base:
- 90% (395 GHz)
- 85% (527 GHz)

End of probe waveguide and double miter bend:
- 65% (395 GHz)
- 70% (527 GHz)
DNP Power Curves
AMUPol binitrooxide in glycerol/water @ 100 K, 8 kHz MAS
Low temperature for DNP NMR applications

**DNP Temperature Dependence**

AMUPol binitroxide in glycerol/water

Sample temperature calibrated with KBr $T_1$ measurements: Thurber and Tycko *JMR*, *(2009)*, *196*, 84.
Low-Temperature MAS Probes

Sample, MAS stator, NMR coil (and rf circuit) at cryogenic temperatures
- Higher Q/less noise
- Higher Boltzmann polarization compared to room temperature
- Variable temperature possible (phase transitions, relaxation studies, etc...)

- Yannoni, et al. ... 1990 He
- Griffin, et al. ... 1997 ... He, N₂, He/N₂
- Samoson, et al. ... 2005 ... He
- Levitt, et al. ... 2007 ... He
- Tycko, et al. ... 2008 ... He/N₂

*Commercialized by Revolution NMR*

- Engelke, et al. ... 2007... N₂
- Doty, et al. ... 2007... N₂/He
- Barnes, et al. ... 2013... N₂/He
- DePaepe, et al. ... 2015... He
Low-Temperature MAS Probes

- 10 µl rotor, 3 m³/h helium gas, 2-3 l/hr liquid helium
- 7 K at 5 kHz, 13 K at 10 kHz and 20 K at 20 kHz
- Example: low-temperature MAS of H₂ trapped inside a fullerene cage
- Continued development ongoing

![Variable-temperature $^1$H MAS spectra of H₂@ATOCF at 360 MHz, 10 kHz sample spinning speed. The spectrum at 279 K consists of a broad line from the protons at the fullerene opening region and of a sharp line corresponding to the hydrogen molecule which is rotating nearly freely inside the fullerene cage. The span of spinning sidebands is caused by the residual dipolar interaction between the protons of the hydrogen molecule. Below 100 K the sideband pattern broadens with decreasing temperature. Saturation of this broadening below 20 K indicates the freezing of the molecular rotation.](image-url)
Low-Temperature MAS Probes

- Room temperature N\\textsubscript{2} gas for drive and bearing, cold He VT gas

Fig. 1. (a) Cross-section of MAS unit of helium-cooled low temperature solid state NMR probe. Cold helium (red arrow) enters the MAS unit through the tube labeled A. The sample (green) sits in the sample space region defined by two Teflon pieces (yellow), which fit together to hold the NMR coil and separate the helium-cooled sample space from the nitrogen gas. Helium gas exits the sample space in the small gap around the circumference of the rotor. Both the nitrogen gas, used for the air bearings (B) and for spinning, and the helium gas can vent from the MAS unit on either side of each of the bearings (blue arrows). For stable spinning, the rotor requires a “pointer” (C) which acts to dampen vibration of the rotor. (b) Photograph of the probe head, with outer aluminum can removed. Arrows indicate the helium entry tube (1), optical fibers for MAS tachometer (2), fiber optic temperature sensor (3), hinged pointer for stabilizing spinning (4), shim coil (5), bearing gas supply tubes (6), MAS angle adjust rod (7), Teflon baffle (8), tuning and matching capacitors for \textsuperscript{13}C channel (9). (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

See also Tycko’s lecture notes
Bruker LTMAS DNP Probe Family @ 400, 600, and 800 MHz

- Dry low-temperature nitrogen gas supply
  - 3 gas lines at 100 K: bearing, drive and VT
  - Pressurized heat exchanger chambers
  - Automatic refill of liquid nitrogen supply
- Cold insert/eject capability
- 3.2 mm (15 kHz MAS @ 100 K)
  - HCN, HX or HXY with variety of X/Y combinations
  - low-gamma probe
- 1.9 mm HCN (25 kHz MAS @ 100 K)
- 1.3 mm HCN (40 kHz MAS @ 100 K)
- Corrugated waveguide

1.9 mm DNP probe head
Stability Measurement: CPMAS signal intensity with gyrotron on and off

- DNP-enhanced signal intensity variation < ±1% over 36 hour run (0.31% standard deviation)
- After gyrotron off duration, DNP-enhanced signal stabilizes back to within ±1% of 36 hour value in less than 5 minutes
- 16 scans, 6 s recycle delay, 8 kHz MAS, 1.5 ms 55 kHz CP with 100 kHz Spinal 64 dec., 100 K, 0.1M U-\(^{13}\)C-\(^{15}\)N Proline in glycerol-d\(_8\)/D\(_2\)O/H\(_2\)O (60/30/10) with 10 mM TOTAPOL
593 GHz/900 MHz DNP

- 593 GHz gyrotron development for Lyndon Emsley (EPFL)
  - 10.9 T gyrotron magnet
  - Gyrotron tube design
  - System test and optimization

- Enabled by key improvements at 263-527 GHz
  - Improved launcher and mode converter
  - Improved gyrotron tube and magnet alignment
593 GHz Factory Test at CPI
593 GHz Factory Test at CPI

Output power and frequency as a function of cathode voltage and magnet current

\[ I_0 = 180 \text{ mA} \]

\[ I_g = -2.0 \text{ A} \]

\[ I_m = 160.40 \text{ A} \]

Cav Cool Temp = 22.5°C

0.030” shim at +x axis
Gyrotron Beam IR Images

Output Gaussian Beam

-measured width (x)
-measured width (z)
-theoretical expansion of design beam
Power Measurements @ 593 GHz with 440 GHz Transmission Line and 527 GHz probe waveguide

TL input: 33 W

26 W

30 W
593 GHz/900 MHz DNP Installation at EPFL
DNP Measurements at 593 GHz/900 MHz @ EPFL
Solid-State DNP NMR

- **1980 - 2008**: mostly limited to true experts
- **Now**, a well-established commercial product, **34 total Bruker systems**

![Map of DNP Installations around the world](image-url)
DNP at 263 GHz/400 MHz
Can we use a more compact source?

DNP with Gyrotron

DNP with Klystron
263 GHz klystron, Thurber and Tycko JMR 2016

Output power 1.5 W

See also Tycko’s lectures for more detail

Also, Kemp et. al, (Warwick) gyrotron amplifier at 187 GHz/284 MHz, JMR 2016.
The EIK/EIO converts kinetic energy of electron beam into microwave radiation by interaction with electromagnetic waves in a series of cavities. Each cavity represents a short piece of the resonant slow-wave structure (SWS) based on a ladder geometry. Ladder could be manufactured to operate in fundamental mode up to 300 GHz.
## EIO Capabilities

<table>
<thead>
<tr>
<th>Oscillator (EIO)</th>
<th>Power</th>
<th>Tuning Range</th>
<th>Pulsed/CW</th>
<th>Achieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 GHz</td>
<td>20 W</td>
<td>5,000 MHz</td>
<td>CW</td>
<td>✓</td>
</tr>
<tr>
<td>263 GHz</td>
<td>5 W</td>
<td>9,000 MHz</td>
<td>CW</td>
<td>✓</td>
</tr>
<tr>
<td>263 GHz</td>
<td>10 W</td>
<td>9,000 MHz</td>
<td>CW</td>
<td>–</td>
</tr>
</tbody>
</table>

2017.07.27

CPI Canada 49
263 GHz Klystron in Billerica DNP Demo Lab: 5 W Output Power (**FACTOR OF 10 INCREASE in 10 YEARS**)
DNP with 263 GHz Klystron: Measurements on Dilute Protein Samples

$^2\text{H}, ^{13}\text{C}, ^{15}\text{N}$-DHFR 0.5 mM with 1:1 TMP, 20 mM TOTAPOL, in 3:6:1 glycerol-d$_8$/D$_2$O/H$_2$O

$^{13}\text{C}$-$^{13}\text{C}$ correlation: 6 hours
$^{15}\text{N}$-$^{13}\text{C}$ correlation: 3 hours

DNP at 263 GHz:
*Is 5 W really enough microwave power?*

- Dense opaque organic polymer CNHS with impregnated AMUPol

---

5 W is not enough power for saturation, but there is also a trade off between lifetime and output power
Current DNP Sources:

**Solid State**

- IMPATT, Gunn diodes
- 9 – 20 GHz synthesizers or source followed by series of multipliers
  - [www.vadiodes.com](http://www.vadiodes.com)
- Advantages of solid state sources
  - Compact
  - Easy to use
  - Inexpensive
  - No special facilities required
- Disadvantages of solid state sources
  - Not capable of producing much power
  - But... quickly changing field
  - For example, 200 GHz, 70 mW → 0.5 W in 8 years! (See Han slides)
  - Currently, 100 mW @ 263 GHz (from VDI)
Acknowledgements

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Emile de Rijk

Werner Maas
One Gyrotron, two DNP Instruments

14.1 T – 600 MHz Overhauser DNP

395 GHz Gyrotron

600 MHz MAS DNP

Quasi-optics

Joanna Long
Thierry Dubroca
F. Mentink-Vigier
Microwave management system

Designed and built by Thierry Dubroca, Hans van Tol, Bianca Trociewitz at National High Magnetic Field Lab and Kevin Pike, Richard Wylde at Thomas Keating company

Based on work by Lesurf, Millimetre-Wave Optics, Devices and Systems, CRC press (1990)
Overhauser Dynamic Nuclear Polarization at 600 MHz – 395 GHz

Sample: triphenylphosphine with 100 mM BDPA, in d6-benzene. Sample volume 50 μL (i.e. 3 mm tube). Temperature about 300 K. Microwave power 2 W.

ε = 160

Liquid DNP at high field in high volumes work by Thierry Dubroca, Stephen Hill et al. Submitted to JMR

For more info about our liquid DNP instrument or quasi-optics contact Thierry at dubroca@magnet.fsu.edu

NSF MRI Grant CHE-1229170
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National MAGLAB User Program for MAS DNP
Contact Fred Mentink for time:
Fred Mentink fmentink@magnet.fsu.edu

600 MHz 89 mm MAS DNP System

This instrument is located at the MagLab’s Tallahassee headquarters.

The increased sensitivity of MAS DNP allows high resolution solid state NMR spectroscopy to be used for many previously inaccessible systems. Our Bruker DNP spectrometer utilizes a 394 GHz gyrotron to produce a strong microwave field to enhance NMR polarization.

Request time for this magnet.

Details

Field: 14.1 tesla
Bore diameter: 89 mm
±1% field sweep range (±128 mT)
Console: Bruker Avance III running TOPSPIN 3.2
3 rf channels, 1 kW amplifier for 1H/19F, and two 1 kW amplifiers for X and Y-nuclei
3.2 mm magic-angle spinning probe
Cooling cabinet with continuous liquid N2 supply
Gyrotron microwave source with quasi-optic stable
Funded in part by NIH S10 OD018519 (magnet and console), and NSF CHE-1229170 (gyrotron)
• Independent control of the flow on the three lines.
• Insert / eject capability + Ind. warming of the probe
• Design compatible with small diameter rotors
• Need a very efficient heat exchanger!

The Grenoble design - Helium spinning

- 3 gas lines forms a closed-loop circuit
- Cooling = cryogenic fluid or cryocooler
ULT-MAS-DNP is sustainable...!

100 €/hour LHe vs Cryogen Free!!!

NUMOC vs SACRYPAN
Helium spinning MAS-DNP at \( T << 100 \, K \)

\[ \mu W_{\text{ON}} \]
\[ \mu W_{\text{OFF}} \times 100 \]

\[ \nu \text{H} \varepsilon_{\text{ON/OFF}} = 677 \]

\[ \begin{align*}
\text{1H chemical shift / ppm} \\
80 & \quad 60 & \quad 40 & \quad 20 & \quad 0 & \quad -20 & \quad -40 & \quad -60 & \quad -80 \\
\end{align*} \]

\[ \begin{align*}
\text{Temperature / K} \\
0 & \quad 20 & \quad 40 & \quad 60 & \quad 80 & \quad 100 & \quad 110 \\
\end{align*} \]

2M \(^{13}\text{C}\)-urea, \(^{2}\text{H}_8\text{glycerol}, \text{D}_2\text{O}, \text{H}_2\text{O}, 4 \text{ mM AMUPOL} \]

Bouleau et al., Chem. Sci. 2015
Lee et al., JMR, 2016

Coll. Engelke et al.
Sensitivity improvement

$\gamma$-Al$_2$O$_3$

$^1$H Hahn echo

- x9 time-savings by lowering the temp. from 100 to 36 K

[D6]-DMSO, D$_2$O, and H$_2$O (78/14/8, w/w/w) containing 10 mM of AMUPol
Sensitivity improvement

γ-Al₂O₃

Surface selective CP

78 K
21 kHz MAS

36 K
13 kHz MAS

$^{27}$Al chemical shift / ppm

$^{1}$H$\varepsilon_{on/off} = 65$

$^{1}$H$\varepsilon_{on/off} = 140$

• Low power CP at fast spinning frequency = no sign of arcing!

• Larger Cq can easily be excited by CP at faster spinning

[D6]-DMSO, D₂O, and H₂O (78/14/8, w/w/w) containing 10 mM of AMUPol
Sensitivity improvement

50 K
17.5 kHz MAS

High Power dec. 30 ms
No sign of arcing!

50 K
12.5 kHz MAS

τ_{DNP} = 4 s

Bouleau et al., Chemical Science 2015

108 K
12.5 kHz MAS

τ_{DNP} = 3 s

x 6.5 enhancement in sensitivity

More than x 50 in time-savings ...!

by going from 100 K to 30-50 K
• 2D experiments = possible!

Lee et al., JMR, 2016
Acknowledgments

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Funding Agency
High-level manipulations of electron spins at 200 GHz and 7 T
Towards sensitivity-enhanced, integrated and time-domain DNP-NMR and EPR

Kaminker, Leavesley, Siaw & Han, UCSB
At 200 GHz and 7 Tesla, now < 0.5 Watt of microwave power available

New VDI source

EPR nutation curve with Gd$^{3+}$ (spin S = 7/2)  
$\pi/2$ from 380 ns to 190 ns

- 0.5W AMC
- 0.15W AMC

What about higher fields?

scalable to 400 GHz, but ...

Limitations will be the source and amplifier technology

However, concept of pulse shaping will greatly benefit high-field DNP

Songi Han, UCSB
Next generation integrated DNP hardware with dual AWG capabilities for modular pump and probe channels

Upgrade AWG DAC board from 16 kB to 8 MB memory
Maximum waveform length has increased from ~16 μs to 3.3 ms

Ilia Kaminker

Songi Han, UCSB

- Kaminker et al. unpublished work
Implementation of pulsed EPR with phase-locked solid-state source and heterodyne and phase-sensitive detection

Shaping the electron spin polarization potential by AWG shaping of microwaves

**Conventional CW pump mapped by ELDOR**

\[ V_{\text{pump}} \]

**AWG chirp-enhanced pump mapped by ELDOR**

\[ V_{\text{pump}} \]

Songi Han, UCSB

Additional References (not comprehensive)

• Background/early work


  V.A. Atsarkin, M.I. Rodak Sov. Phys.-USPEKH 15, **251** (1972)


• Solids DNP/NMR at 40 GHz & 95 GHz, review papers and dissolution experiment


- **Gyrotron references**
  


