ENC 2020 Bruker Solid State NMR Workshop: DNP Update

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NMR and MRI

Rich in Information:
- Chemical & structural resolution
- Molecular & chemical dynamics
- Abundant NMR-active nuclei
- Spatial encoding
- Functional tracking
- Non-invasive, no ionizing radiation

But, relatively low sensitivity due to small polarization (P) at thermal equilibrium:

\[ P = \frac{p_+ - p_-}{p_+ + p_-} = \frac{\gamma h B_0}{2kT} \]
Increasing the Sensitivity of NMR

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

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

DNP signal \( \varepsilon = 130 \) at 395 GHz/600 MHz
Bruker DNP Product Line: Gyrotron Microwave Source

<table>
<thead>
<tr>
<th>Magnetic Field</th>
<th>EPR/µwave Frequency</th>
<th>$^2$H NMR Frequency</th>
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<tbody>
<tr>
<td>9.4 T</td>
<td>263 GHz</td>
<td>400 MHz</td>
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<tr>
<td>14.1 T</td>
<td>395 GHz</td>
<td>600 MHz</td>
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<tr>
<td>18.8 T</td>
<td>527 GHz</td>
<td>800 MHz</td>
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<tr>
<td>21.1 T</td>
<td>593 GHz</td>
<td>900 MHz</td>
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</table>
LTMAS DNP Probe Family @ 400, 600, 800 and 900 MHz

- MAS probes
  - 3.2 mm (15 kHz MAS @ 100 K)
    - HCN, HX or HXY with variety of X/Y combinations
    - low-gamma probe
  - 1.9 mm (24 kHz MAS @ 100 K)
  - 1.3 mm (40 kHz MAS @ 100 K)
  - Cold insert/eject capability
- Static probe for aligned samples
- Corrugated probe waveguide
Turbine Assembly and Insert/Eject System for 0.7 mm DNP Probe
Spinning Characteristics at Low Temperature for the 0.7 mm DNP Probe

- $T_{1\text{KBr}}$ @ 10 kHz = 788 ms $\rightarrow T_{\text{Sample}} \approx 98$ K
- $T_{1\text{KBr}}$ @ 25 kHz = 768 ms $\rightarrow T_{\text{Sample}} \approx 98.5$ K
- $T_{1\text{KBr}}$ @ 60 kHz = 730 ms $\rightarrow T_{\text{Sample}} \approx 107$ K

$\mu$-wave heating with KBr ca. 4K
0.7 mm DNP Probe
DNP at 263 GHz/400 MHz
Using a More Compact Source

DNP with Gyrotron

DNP with Klystron
The EIK/EIO converts kinetic energy of electron beam into microwave radiation by interaction with electromagnetic waves in a series of cavities.
263 GHz Klystron in Billerica DNP Demo Lab: 5 W Output Power
(FACTOR OF 10 POWER INCREASE in 10 YEARS!)

System includes:
- 4 kW power supply
- Chiller

263 GHz Klystron with transmission line

Klystron safety shroud removed for visualization

Transmission line

263 GHz Klystron

Klystron ON
Klystron OFF

\[ \varepsilon = 180 \]
263 GHz Klystron Measurements

![Graph showing DNP Signal Enhancement vs. Power at NMR Probe Base (W) for 263 GHz Klystron and 263 GHz Gyrotron.](image)
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
  - Broadband
    - 19 mm ID 263 GHz corrugations
    - 16 mm ID 440 GHz corrugations

\[
\begin{align*}
2a & \\
p & = \lambda/3 \\
d & = \lambda/4 \\
w & < 0.5p \\
\text{Gaussian beam waist} & = 0.64a
\end{align*}
\]

- **Directional coupler** for frequency and power measurement
263 GHz Klystron at the EPFL
Solid State DNP Application Areas

- **Biological Samples**
  - Proteins
  - Membranes proteins
  - Fibrils
  - Whole Cell...

- **Materials**
  - Nanoparticles
  - Catalysts
  - Mesoporous samples
  - Bio-Materials
  - Functionalized silica

- **Small Organic Molecules**
  - Pharmaceutical applications

- **Polymers**
  - Natural
  - Synthetic

- **Solid State DNP**

  - Higher sensitivity and reduction of acquisition time
  - *Opens new application areas for NMR*
DNP Applications: Materials

- **Functionalized materials**
- **Mesoporous silica, alumina**
- **Hybrid organic-silica materials**
- **Nanoparticles**
- **Metal Organic Framework (MOFs)**

**Field of applications**
Photonic, sensors, bio-material, catalyst, drug delivery, separation processes, medical imaging

Detection: $^{13}\text{C}$, $^{29}\text{Si}$, $^{15}\text{N}$, $^{119}\text{Sn}$, $^{27}\text{Al}$, $^{17}\text{O}$, $^{89}\text{Y}$

2D experiments
Characterization of the materials at the molecular level
Organic Thin-Film Semiconducting Devices

✓ Organic thin-film semiconducting devices
  • Organic Light-Emitting Diodes (OLEDs)
  • Organic Solar Cells (OSCs)

✓ Properties:
  • Charge carrier mobility
  • Light emission
  • Light out-coupling

✓ Depend on:
  • Intra- and inter-molecular structure
  • Orientation of organic molecules

✓ OLEDs and OSCs are in amorphous state
  • Solid State NMR: limited amount of material, low S/N
  • Enhanced sensitivity by solid state DNP
Organic Thin-Film Semiconducting Devices (OLEDs)

Sample: \textit{POPy}_2

Radical: \textit{bTbK}

Pile of plates and put into \(\Phi 4\) mm glass tube

Place the plates perpendicular to the static field and measure alignment

Total amount of sample: 52 \(\mu\)g \(\times\) 12 plates = 0.62 mg

Suzuki K. \textit{et al.}, \textit{Angewandte} 2017, DOI: 10.1002/anie.201707208
Static DNP Probe 400 MHz/263 GHz
Static DNP Probe 400 MHz/263 GHz
Organic Thin-Film Semiconducting Devices (OLEDs)

- Vacuum deposit \( \text{POPy}_2 \): P=0 perpendicular to SiO\(_2\)
- Drop cast \( \text{POPy}_2 \): isotropic random orientation

Fit by Legendre moment

\[
\langle P_n \rangle = \frac{\int_0^\pi p(\theta)P_n(\cos \theta) \sin \theta \, d\theta}{\int_0^\pi p(\theta) \sin \theta \, d\theta}
\]

Suzuki K. et al., Angewandte 2017, DOI: 10.1002/anie.201707208
263 GHz Klystron $^{15}\text{N}$$-^{13}\text{C}$ Correlation in Photocatalytic Materials

- Polymeric Carbon Nitride: Photocatalysts in solar production of $\text{H}_2$

- With large DNP gain (71), complex correlations can be acquired in reasonable amount of time

Li X. et al., Angew. Chem. Int. Ed., 2018
Batteries: A Complex System

- Performance depends on the interactions between all cell components
- What are the interactions between the components: active material and electrolyte?
Battery Characterization by Solid State DNP

✓ **Stable Solid Electrolyte Interphase (SEI)**
  - Critical for performance and lifetime of rechargeable batteries
  - Properties depend on chemistry of surface layer

✓ Challenging to study by conventional structural tools (X-Ray)
  - Requires molecular level insight
  - NMR: low sensitivity of the organic components of the SEI

✓ SEI: reduced Graphene Oxide (rGO) in a lithium ion cell
  - $^{13}$C DNP experiments

![Before cycling](image1.png)
![After cycling](image2.png)
Battery Characterization by Solid State DNP

In less than 1 hour with DNP...

The organic phase in the SEI

Natural abundance $^{13}$C NMR with DNP

$^{13}$C assignment:
- Li formate
- Li succinate
- Li acetate
- Li ethyl carbonate
- Dimethyl carbonate

Solid-State DNP NMR

- **1980 - 2008**: mostly limited to true specialists
- Now a well-established commercial product – 39 total Bruker systems
Solid-State DNP Spectrometers: 39 Installed Spectrometers

<table>
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<th>400 MHz/263 GHz DNP</th>
<th>600 MHz/395 GHz DNP</th>
<th>800 MHz/527 GHz DNP</th>
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<tr>
<td>Billerica, MA, USA 2008 (Bruker demo)</td>
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<td>Berlin, DE, 2009</td>
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<td>Lausanne, CH, 2009</td>
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<td>Grenoble, FR, 2011, 2017</td>
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<td>Utrecht, NL, 2011</td>
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<td>Wissembourg, FR, 2012 (Bruker demo)</td>
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<td>Lyon, FR, 2013</td>
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<td>Frankfurt, DE 2013</td>
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<td>Darmstadt, DE 2013</td>
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<td>Ames, IA, USA 2014</td>
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<td>KAUST, Jeddah, SA, 2014</td>
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<td>Santa Barbara, CA, USA 15</td>
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<td>Melbourne, AUS 2016</td>
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<td>Rehovot, Israel 2017</td>
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<td>Kyoto, Japan 2017</td>
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<td>Tsukuba, Japan 2017</td>
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<td>Marseille, France 2019</td>
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<td>Billerica, MA, USA, 2012 (Bruker demo)</td>
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<td>Guelph, ON, Canada, 2012</td>
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<td>Tallahassee, FL, USA 2014</td>
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<td>ETH Zurich, CH, 2014</td>
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<td>Columbus, Ohio, USA '15</td>
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<td>Nottingham, UK, 2015</td>
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<td>Dallas, Texas, USA, 2016</td>
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<td>Berlin, DE, 2018</td>
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<td>+ 1 593 GHz, Lausanne, CH (2017)</td>
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Eighteen 263 GHz DNP: 40% biological, 60% material
Fourteen 395 GHz DNP: 75% biological, 25% material
Six 527 GHz DNP (+one 593 GHz): 75% biological, 25% material
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