

Solid-State DNP (Dynamic Nuclear Polarization)

Making the invisible visible

DNP is microwave irradiation that transfers the 660x higher polarization of native or admixed electron spins to nuclear spins in the solvent matrix and sample. Bruker DNP systems enable solid-state NMR with unsurpassed sensitivity gains (>200x typical) as well as excellent cold (<100K) stability (up to 14-days continuously running experiment sets) performance in low-temperature (LT) MAS format that DNP typically utilizes. The full Bruker package allows exciting new applications in biological solids, materials science, and pharmaceuticals.

Gyrotron & Klystron Microwave Sources

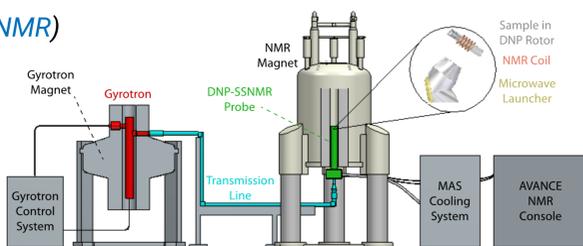
Since 2008: **53 systems** installed or underway

28x 400 MHz (263 GHz)	7x 800 MHz (527 GHz)
17x 600 MHz (395 GHz)	1x 900 MHz (593 GHz)

Gyrotrons (for 400 – 900 MHz NMR)

with CPI Palo Alto

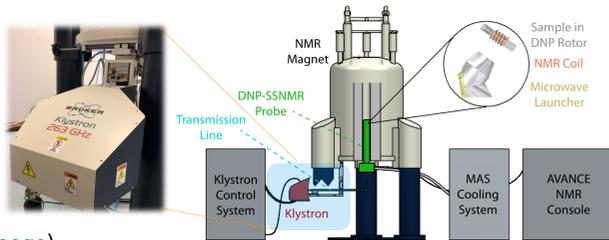
- ✓ 10 – 30 W output
- ✓ CF magnet
- ✓ stable operation
- ✓ up to 10 yr lifetime



Klystrons (for 400 MHz only) 80% DNP performance at ~70% cost!

with CPI Canada

- ✓ 5 W output
- ✓ stable operation
- ✓ small footprint
- ✓ simple facility needs
- ✓ 20k operational hours (up to 5-10 years, dep. on usage)



3rd-generation LT-MAS Cooling Cabinet

- Updated main control unit
 - ✓ integrated *Topspin* control ($\geq 4.1.3, \geq 3.6.5$) → →
 - ✓ improved regulation (pressure, flow and fill)
 - ✓ integrated venturi for fast probes (≤ 1.9 mm)
- MAS-3 controller integration
 - ✓ automated cold insert/eject & spin up/down
 - ✓ best-in-field spin regulation
- Improved cryogenic efficiency
- Touch-panel GUI – duplicates TS functionality



Organized Tabs for various Control & Monitoring Features



HFX LT-MAS DNP probe (work in progress)

^{19}F is a critically valuable probe of biological systems (via selective labels), pharmaceuticals, polymers & materials. HFX DNP brings unprecedented sensitivity, selectivity and resolution to these applications fields.

- 3 indep. channels (^1H , ^{19}F & X); 2 coils (similar to E-free design)
- Improved ^{19}F resolution gain via ^1H decoupling
- Higher ^{19}F sensitivity gain in $^1\text{H}/^{19}\text{F}$ CP-MAS experiment (vs. direct ^{19}F)

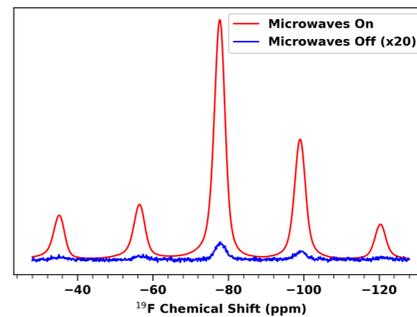
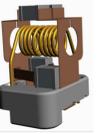


Fig.1 $^1\text{H}/^{19}\text{F}$ CP-MAS spectra, with & without DNP, of NH_4^+ trifluoroacetate. ^1H DNP gain (on/off): 250x. Sample plus 12 mM AMUPol radical in (60/30/10) glycerol- d_8 / $\text{D}_2\text{O}/\text{H}_2\text{O}$, 3.2 mm rotor, 8 kHz MAS, 9.4 T (400 MHz ^1H), $T = 106$ K.

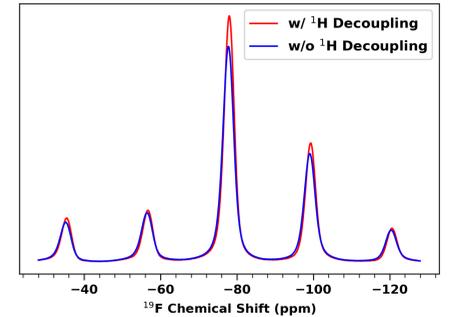


Fig.2 Sample, conditions and experiment as Fig.1 ($^1\text{H}/^{19}\text{F}$ CP-MAS), here with & without ^1H decoupling.

FAST LT-MAS DNP probes (1.3 & 0.7 mm, for 40 & 65 kHz at 100K)

Fast spinning provides state-of-the-art spectral quality in LT-MAS DNP via superior averaging of anisotropic interactions (improved resolution), longer coherence lifetimes, and increased RF field strengths. Fast MAS plus DNP provides the ultimate gains in sensitivity & resolution to enable new applications.

1.3 mm, 40 kHz ^{13}C - ^{13}C spectrum

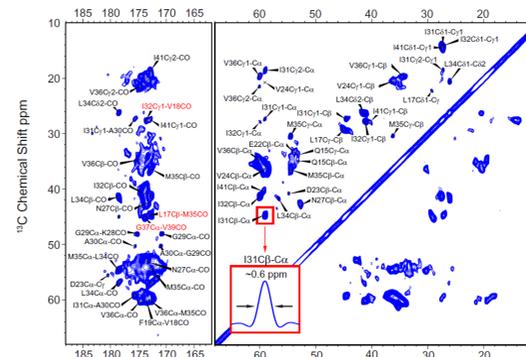


Fig.3 DNP-enhanced ^{13}C - ^{13}C CORD-RFDR spectra of 1,3- $^{13}\text{C}_2/2$ - $^{13}\text{C}/^{15}\text{N}$ -labeled $\text{M}_\beta\text{A}\beta_{1-42}$ amyloid fibrils with 10 mM of the radical M-TinyPol in glycerol- d_8 / $\text{D}_2\text{O}/\text{H}_2\text{O}$ (60/30/10), 1.3 mm rotor at 40 kHz MAS, 800 MHz ^1H (18.8 T) and $T = 115$ K.

0.7 mm, 62.5 kHz ^1H -detected ^1H - ^{13}C

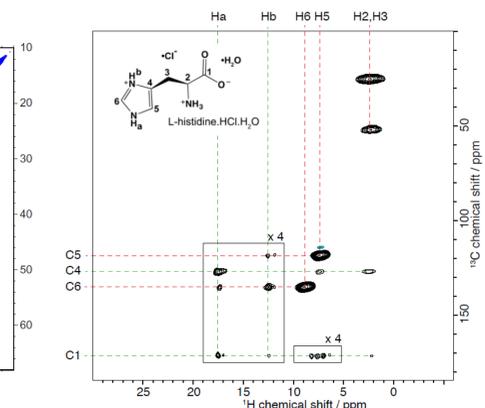


Fig.4 DNP enhanced, ^1H detected ^1H - ^{13}C HETCOR of $[\text{U}-^{13}\text{C},^{15}\text{N}]$ histidine- $\text{HCl}\cdot\text{H}_2\text{O}$ sample impregnated with 32 mM of the radical HyTEK2 in TCE solvent, 0.7 mm rotor at 62.5 kHz MAS, and 900 MHz ^1H (21.1 T) and $T = 105$ K.

Data courtesy of A. Lesage, G. Pintacuda, B. Griffin (Lyon University, France; MIT, USA)
See also, PNAS (2022)

Data courtesy of P. Berruyer, L. Emsley (EPFL Lausanne, Switzerland)
See also, JPC Lett. (2020)

Conclusion

- Bruker offers turn-key solutions for DNP-enhanced solids NMR from 400 – 900 MHz with strong track records for reliability & cutting-edge developments.
- High-power Gyrotron microwave sources meet all needs across bio, materials and pharma Apps.
- Klystron provides a cost- and user-friendly package for near-max DNP performance at 400 MHz
- Low-temperature (100 K) MAS probes optimize DNP enhancement combined with best-in-field spinning.
- High-performance, automated, user-friendly LT-MAS control makes DNP more accessible than ever.

TECHNOLOGY & APPLICATIONS