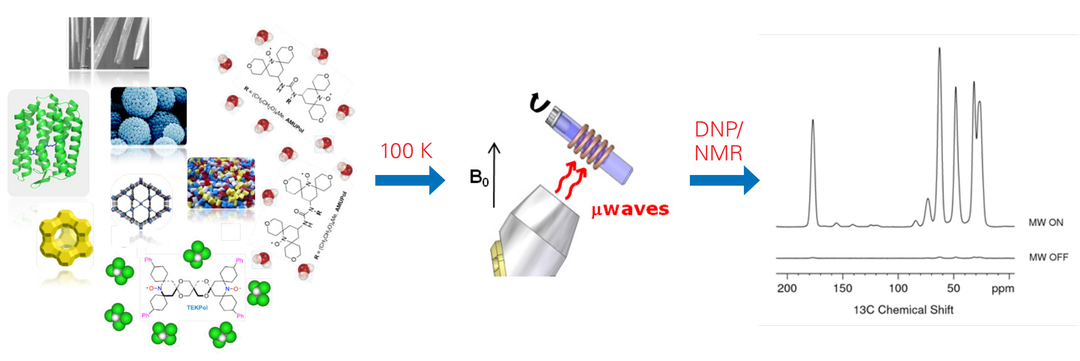
Solid-State DNP at 263-593 GHz

Making the Invisible Visible

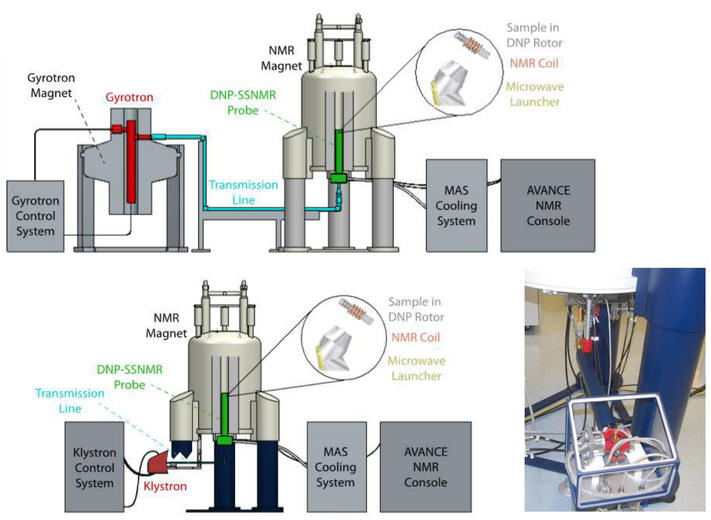
Dynamic Nuclear Polarization (DNP) experiments transfer the high polarization of electron spins to nuclear spins, driven by microwave irradiation of unpaired electron spins. Bruker DNP-NMR spectrometers are designed specifically for extended solid-state NMR experiments, delivering unsurpassed sensitivity and stability for exciting new applications in biological solids, material science and pharmaceuticals.

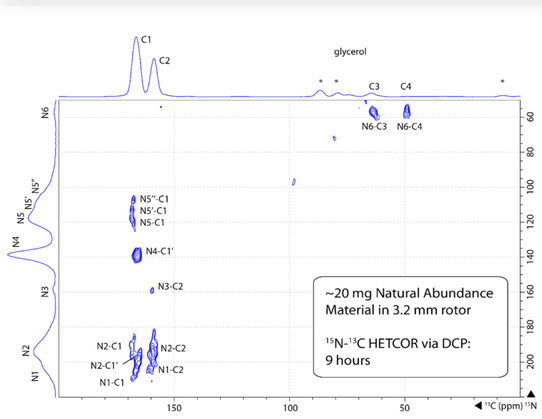


Gyrotron and Klystron Microwave Sources

Bruker's custom-designed gyrotron microwave sources and low-temperature MAS (LTMAS) probes have a proven record of performance with 38 installed systems to date. We also offer a 263 GHz Extended Interaction Klystron (EIK) with 5 W output power and high frequency/power stability. The 263 GHz klystron provides 80-100% of the gyrotron DNP efficiency (depending on the sample) with a lower purchase price, footprint and facility requirements.

Magnetic Field	^{1}H NMR Frequency	EPR/µwave Frequency	Microwave Source
9.4 T	400 MHz	263 GHz	Klystron
14.1 T	600 MHz	395 GHz	Gyrotron
18.8 T	800 MHz	527 GHz	Gyrotron
21.1 T	900 MHz	593 GHz	Gyrotron





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Using the 263 GHz klystron, excellent enhancements can be obtained even for highly challenging samples, such as polymeric carbon nitride materials (photocatalysts for solar H_2 production). With the help of DNP enhancement, 2-dimensional ^{15}N-^{13}C correlation spectra of this material were acquired at natural isotopic abundance in less than 10 hours, allowing the structure of the material to be characterized.

Fig. 1: Polymeric carbon nitride materials doped with 15 mM AMUPol in aqueous solvent yield excellent DNP signal enhancements of 71 with ~5 W of microwave power, allowing ^{15}N-^{13}C correlation spectra to be acquired rapidly even at natural isotopic abundance.

1.3 and 1.9 mm MAS DNP Probes

The DNP LTMAS probes operate in the 100-200 K temperature range with cold insert/eject capabilities. They are offered with HCN, HX, HXY (with variety of X/Y combinations) or low gamma RF configuration and the following rotor sizes to cover a range of applications at 400 to 900 MHz:

- 3.2 mm: 15 kHz MAS @ 100 K
- 1.9 mm: 24 kHz MAS @ 100 K
- 1.3 mm: 40 kHz MAS @ 100 K

The 1.3 mm probe has optimized microwave coupling into the sample, providing high DNP efficiency with fast MAS.

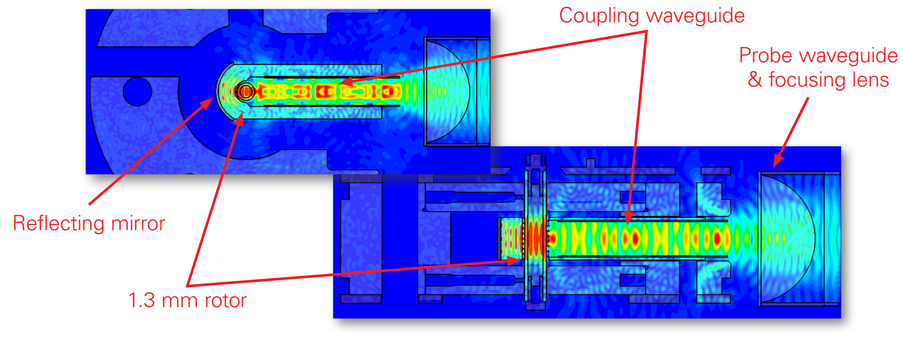

Fig. 2: EM simulations for 1.3 mm optimized DNP stator and waveguide at 263 GHz.

Fast MAS + DNP

As in conventional solid-state NMR, fast magic angle rotation enables superior decoupling of dipolar interactions, often provides favorable relaxation properties and can even allow for ^{1}H-detection. Combined with large signal enhancements from DNP, this has opened up new applications in structural biology and materials science.

1.3 mm DNP probes provide ideal sensitivity for limited-quantity samples. As in the case of a ^{13}C,^{15}N-specifically amino acid labeled dihydrofolate reductase, 4 µL of sample at a concentration of 0.65 mM were sufficient to acquire a ^{1}H-^{13}C heteronuclear correlation spectrum in just 26 minutes.

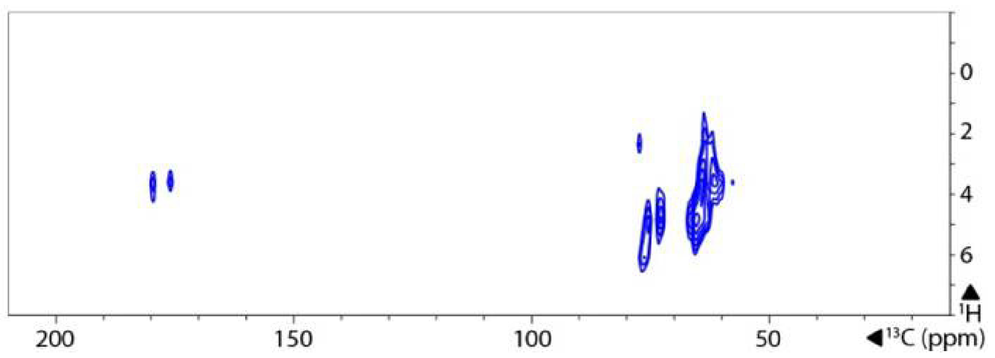

Fig. 3: ^{1}H-^{13}C HETCOR spectrum of specifically-^{13}C,^{15}N-labeled dihydrofolate reductase at a concentration of only 0.65 mM (2.6 nanomoles of protein in rotor), enhanced with 20 mM TOTAPOL in a 3:7 v/v glycerol-d_8/D_2O buffer, 40 kHz MAS.

Summary

- Turn-key solution for DNP-enhanced solids NMR experiments at high field.
- Unique high power CW gyrotron microwave sources at 263, 395, 527, 593 GHz.
- Klystron microwave source option at 263 GHz for increased DNP accessibility.
- Low-temperature (100 K) MAS probe technology with built-in waveguide and cold spinning gas supply.
- High DNP signal enhancements on wide range of samples.