# Solid-State DNP at 263, 395 and 527 GHz

## DNP-NMR Spectrometers and Microwave Source

Dynamic Nuclear Polarization (DNP) experiments transfer polarization from electron spins to nuclear spins for large gains in sensitivity and dramatic reduction in signal averaging time. Bruker DNP-NMR spectrometers are designed specifically for extended solid-state NMR experiments, delivering unsurpassed sensitivity for exciting new applications in biological solids, material science and pharmaceuticals.

DNP samples are prepared by adding a polarizing agent to a shared solvent or exploiting a native radical on the sample of interest. Experiments are performed under MAS conditions at low temperature, 100-170 K, and with continuous microwave irradiation. The custom-designed gyrotron microwave source operates at 263, 395 or 527 GHz for DNP-enhanced NMR experiments at 400, 600, or 800 MHz.


Fig. 1 Photograph of 527 GHz DNP Spectrometer at the University of Utrecht, The Netherlands. Left to right: 800 WB NMR magnet, microwave transmission line, second-harmonic cryogen-free gyrotron tube and magnet, control system.

## DNP NMR Magnet with Sweep Coils

The DNP/NMR magnets are equipped with sweep coils for studying a range of polarizing agents, direct DNP experiment to non-1H spins and investigating DNP polarization transfer mechanisms.

- 400/89 Ascend DNP 263 GHz
- 600/89 Ascend DNP 395 GHz
- 800/89 USP/RS DNP 527 GHz

## Low Temperature MAS DNP Probes

DNP probes are available in the following configurations to cover a range of applications:

- 3.2 HCN or HX (15 kHz MAS at 100 K) for 400, 600 and 800 MHz
- 3.2 mm low-gamma probe (15 kHz MAS at 100 K) for 400, 600 and 800 MHz
- 1.9 mm HCN (25 kHz MAS at 100 K) for 600 and 800 MHz
- 1.3 mm HCN (40 kHz MAS at 100 K) for 800 MHz

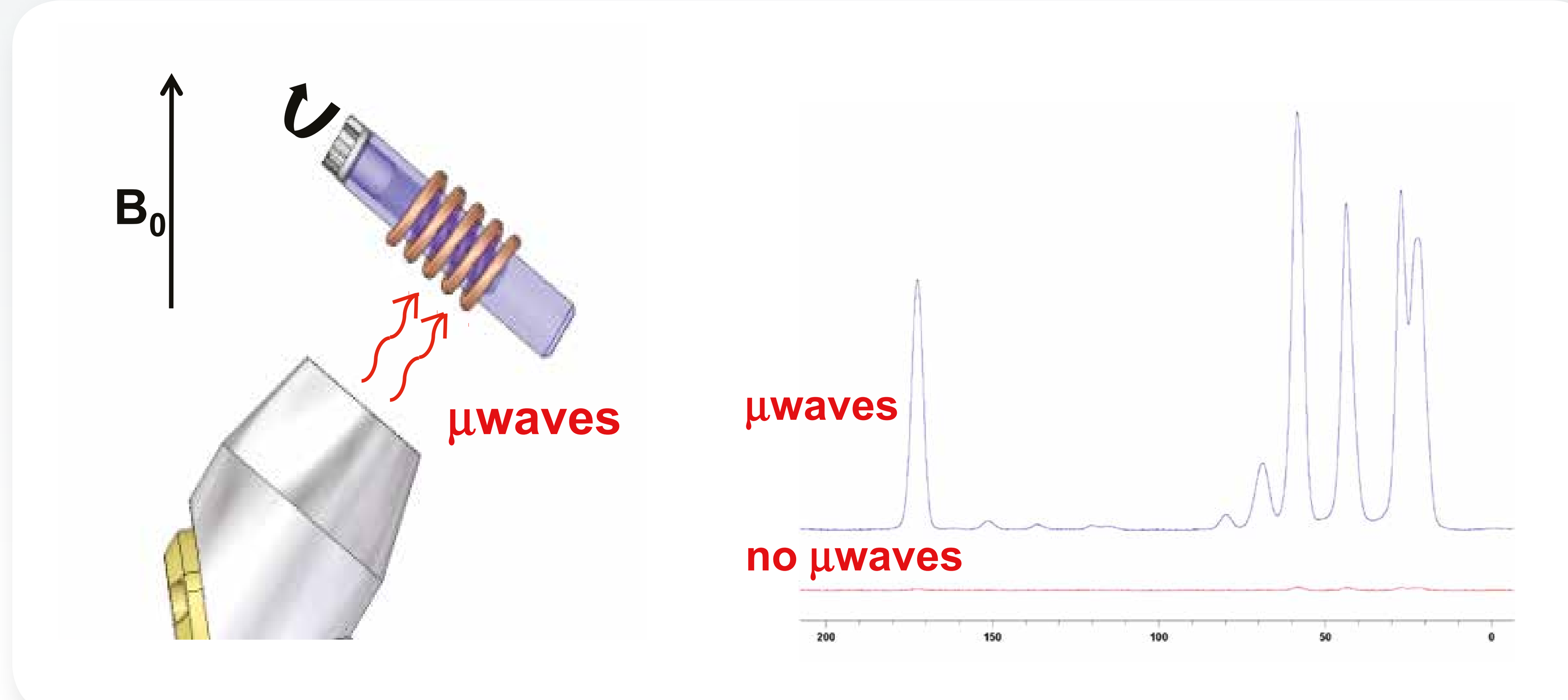
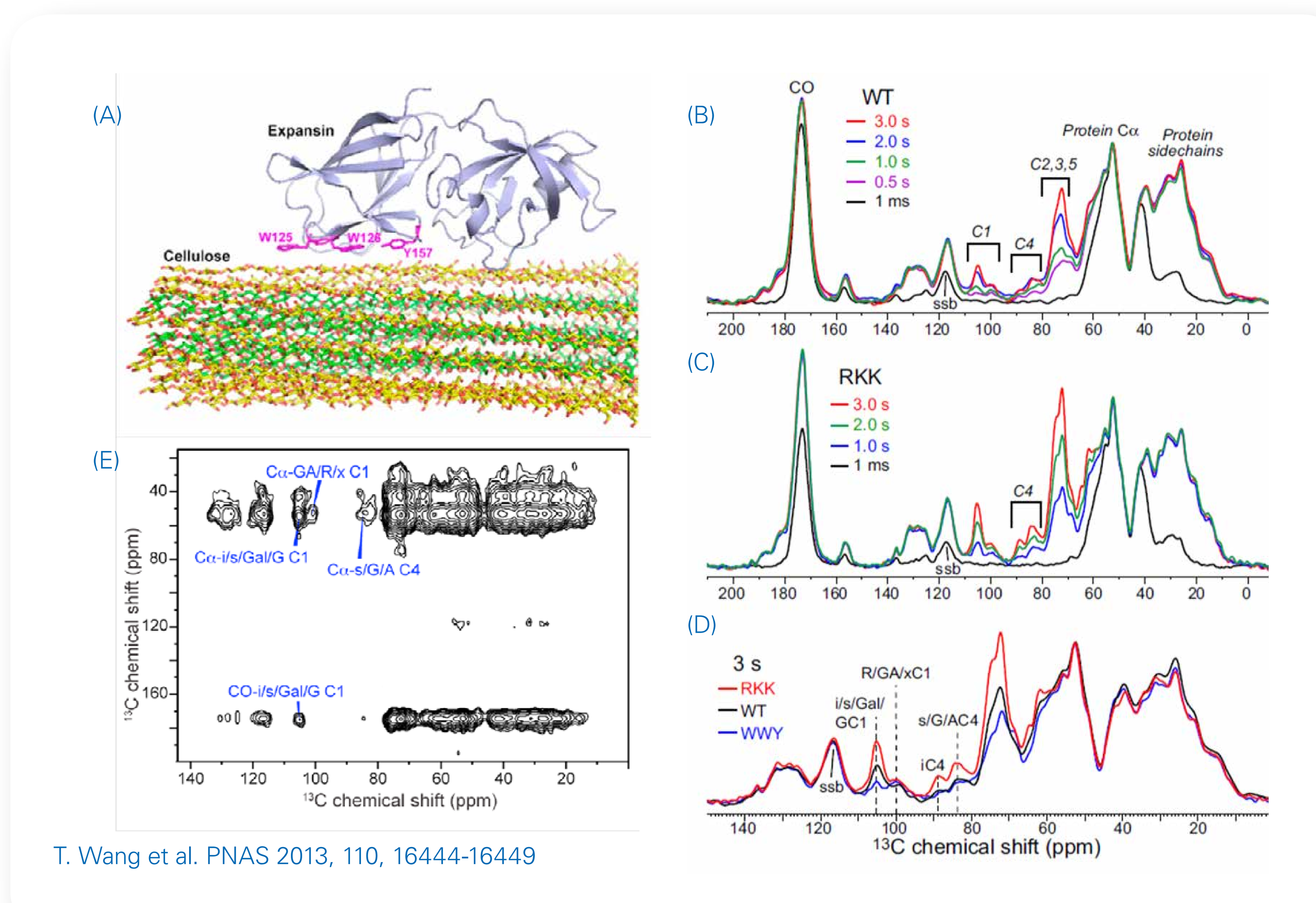



Fig. 2 Schematic of DNP sample in MAS rotor. $^{13}C$ CPMAS spectra of 0.25 M $^{13}C$ proline with 10 mM AMUPol in frozen glycerol/water at 14 kHz MAS and 100 K, with and without 395 GHz µwave irradiation.

## Applications to Biological Solids

Improved sensitivity from DNP allows the characterization of expansin protein binding to plant cell walls.

- DNP experiments allow rapid detection of ~1% U-$^{13}C$, $^{15}N$ expansin mixed with plant cell walls.
- REDOR filter selects only signals from the expansin $^{13}C$ signals.
- Spin diffusion mixing following the REDOR filter reveals correlations between expansin and the cell-wall polysaccharides.
- Comparison of the wild-type protein with two mutants indicate that site-specific cellulose binding is correlated with strong wall-loosening activity.




T. Wang et al. PNAS 2013, 110, 16444-16449

Fig. 3 (A) Graphic depicting expansin binding to plant cell walls. WT (B) and RKK mutant (C) spin diffusion spectra showing the buildup of signals from the protein to the cell-wall polysaccharides. (D) Comparison of signals transferred from the WT and two mutants to the plant cell walls. (E) 2D $^{13}C$-$^{13}C$ spectrum showing direct evidence of protein-polysaccharide correlations through spin diffusion.

## Summary

- Turn-key solution for DNP-enhanced solids NMR experiments at high field
- Unique high power CW gyrotron microwave sources and waveguide
- Low-temperature (100 K) MAS probe technology with built-in waveguide and cold spinning gas supply
- Sweep coils on DNP NMR magnets