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 a 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 in the sample of interest. Experiments are performed under MAS conditions at low temperature, 100-180 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. Bruker DNP spectrometers have a proven record of performance, with 25 systems installed to date.

Materials Science Applications

Studies of small-core CdSe quantum dot (QD) materials:

- QDs exhibit desirable electronic and optical properties that are size-tunable.
- DNP provides enhancements ~80-fold (^{113}Cd) with straightforward sample preparations.
- Core, surface and ligand sites can be readily identified and probed; unlike in larger QDs, core signals show large enhancements, enabling further study of their properties.

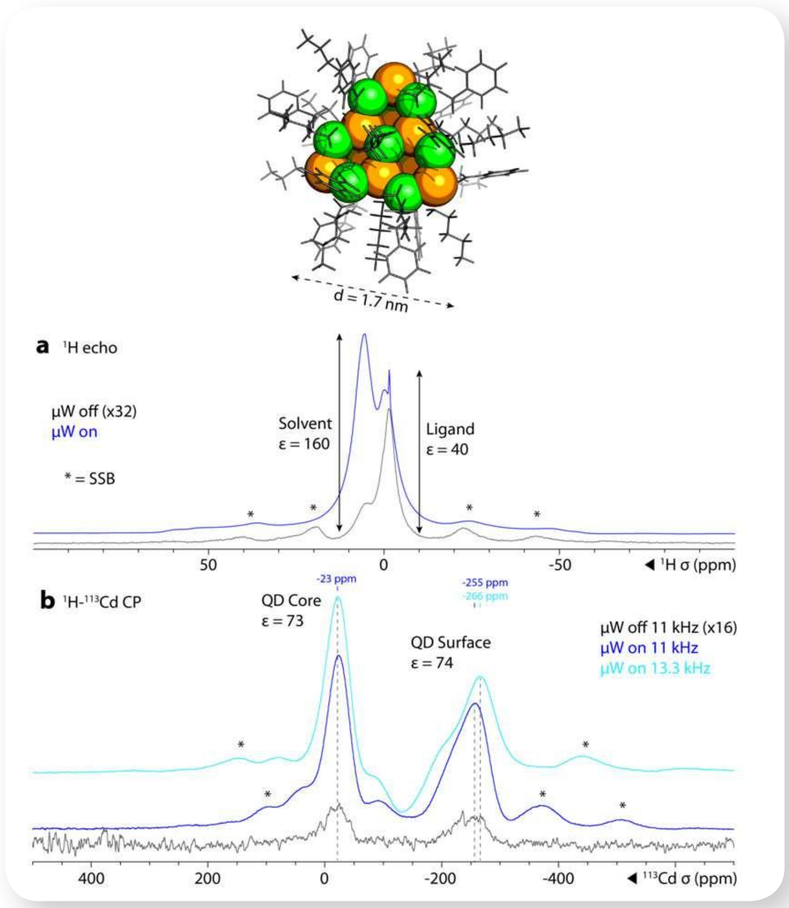

Fig. 1 (a) ^{1}H and (b) ^{113}Cd DNP spectra of 1.7 nm QD colloidal samples show distinct chemical shifts and anisotropies for core and surface cadmium sites. Surface site shifts are sensitive to MAS frequency. In collaboration with J. Owen, Columbia University.

Low Temperature MAS DNP Probes

DNP probes are available in the following configurations to cover a range of applications at 400, 600 and 800 MHz:

- 3.2 HCN, HX or HXY with variety of X/Y combinations (15 kHz MAS at 100 K)
- 3.2 mm low-gamma probe (15 kHz MAS at 100 K)
- 1.9 mm HCN at 600 and 800 MHz (25 kHz MAS at 100 K)
- 1.3 mm HCN at 600 and 800 MHz (40 kHz MAS at 100 K)

Fig. 2 527 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.

Biological Solids Applications

DNP enables rapid characterization of large biological assemblies, such as intact Pf1 virus.

- MAS at 25 kHz (in 1.9 mm rotors) can improve enhancement and resolution for difficult biological samples.
- DNP signal enhancements and non-uniform sampling (NUS) enable rapid acquisition of multidimensional experiments.
- Assignments are simplified by use of long-range transfer sequences (e.g. sequential sidechain correlation, CANCOCA).
- Resolution of uniformly ^{13}C, ^{15}N-labeled protein samples is sufficient to permit assignments and distance measurements.

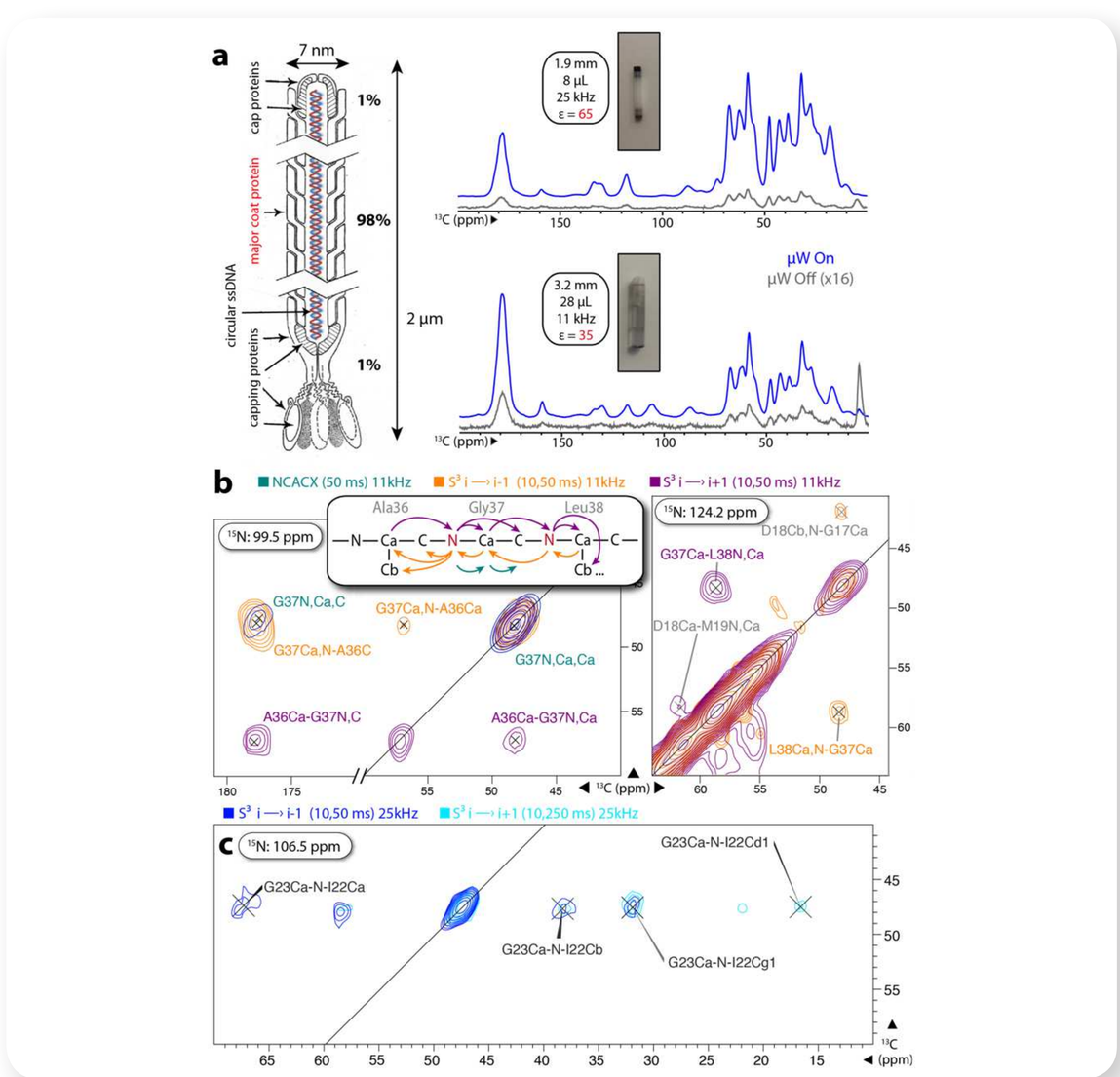

Fig. 3 (a) Intact Pf1 bacteriophage samples yield promising DNP enhancements in both 3.2 mm and 1.9 mm rotors. (b) Assignments of the Pf1 major coat protein are simplified using the sequential sidechain-sidechain correlation (S^3) technique. (c) 25 kHz MAS improves the resolution of DNP spectra, enables long-range inter-residue polarization transfers, and is helpful for extending assignments. I. Sergeyev et al. 2016 PNAS submitted.

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.