High-field liquid-state ^{19}F Overhauser DNP reaches analytical sample volumes

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Fluorine-19 nuclear magnetic resonance (NMR) is widely used to analyze pharmaceuticals, functional materials, and environmentally persistent fluorinated compounds. Its sensitivity, however, often limits measurements at low concentrations.

We demonstrated liquid-state fluorine-19 Overhauser dynamic nuclear polarization (ODNP) at 14.1 tesla at the MagLab. Microwave (μW) irradiation is delivered from a 395 GHz gyrotron into a modified liquid-state NMR probe with a sample volume about 70 microliters (Fig. 1). A sweep coil enables precisely matched ODNP microwave condition for optimal ^{19}F signal enhancement up to 37-fold using BDPA stable radical (1,3-bisdiphenylene-2-phenylallyl) as the polarization source while retaining 0.02 ppm spectral resolution. It was found that aromatic fluorocarbons generally showed larger enhancements than aliphatic compounds.

The work establishes high-field, repeatable fluorine-19 signal enhancement in conventional liquid-state NMR sample volumes. It provides a foundation for faster or lower-concentration analysis of fluorinated pharmaceuticals, polymers, and per- and polyfluoroalkyl substances (PFAS), and it identifies molecular interactions that can guide improved polarizing agents and sample formulations.

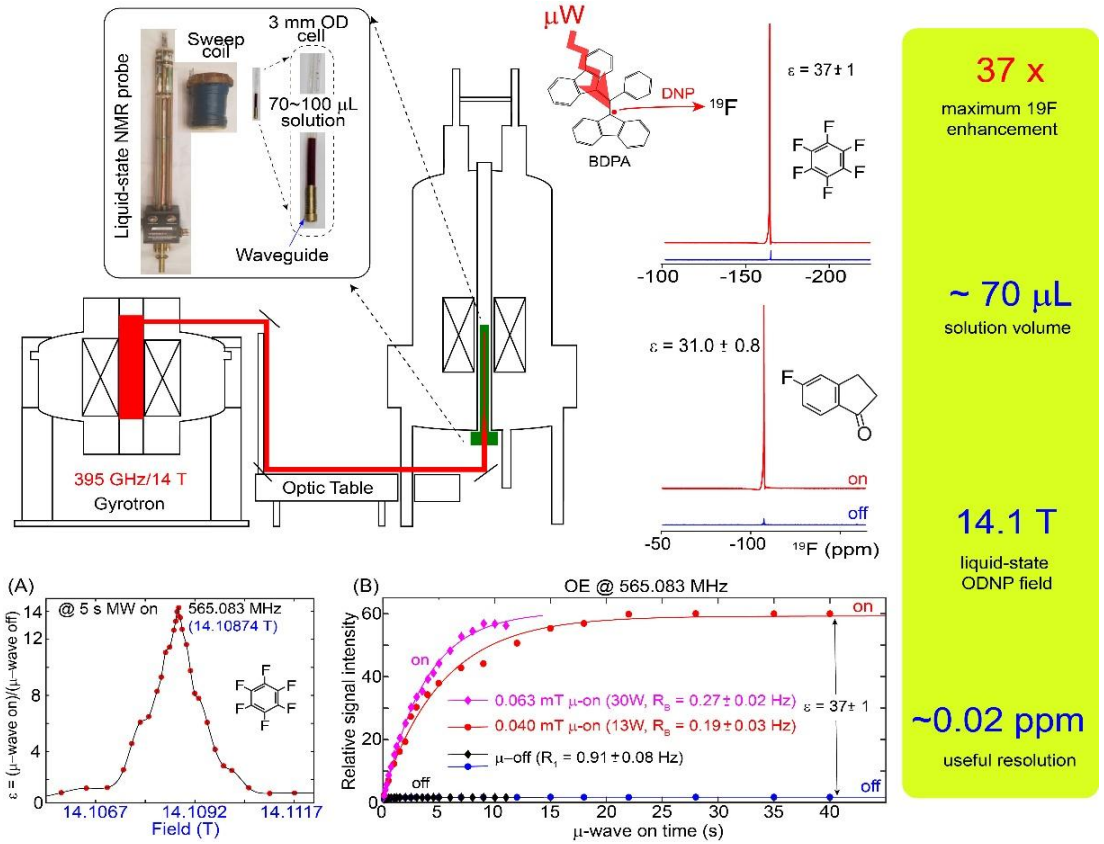


Figure 1. 14.1 T liquid-state ODNP system delivered 395 GHz microwaves to a ~70 μL sample and (A) field tuning and (B) microwave irradiation buildup that produced up to 37-fold ^{19}F signal enhancement.

Facilities and instrumentation used: 14.1 T liquid-state DNP NMR spectrometer (NMR Facility).
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