Pushing the Limits of Ultra-Wideline Solid-State NMR: ^{209}Bi and ^{127}I Signatures in MOFs

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Bismuth- and iodine-containing *metal-organic frameworks* (MOFs) show promise for applications in catalysis, gas adsorption, photoluminescence, and radionuclide capture. Their performance is closely tied to the local environments of Bi^{3+} and I^{-} ions. While ^{209}Bi and ^{127}I solid-state NMR (SSNMR) could provide valuable insights, their use for characterizing MOFs remains limited due to major experimental challenges. Despite high natural abundance and favorable receptivity, ^{209}Bi (I = 9/2) and ^{127}I (I = 5/2) have exceptionally large quadrupole moments (−51.6 and −71.0 fm²), producing extremely broad SSNMR powder patterns. Higher-order quadrupolar effects and closely spaced satellite transitions further complicate spectral acquisition and analysis.

Using SSNMR at ultra-high magnetic fields on the MagLab's 36T Series Connected Hybrid (36T-SCH) magnet and field-stepped acquisition strategies, we successfully acquired ultra-wideline (UW) ^{209}Bi and ^{127}I SSNMR spectra, overcoming long-standing experimental challenges. These spectra allow for direct probes of the local environments of the Bi and I atoms in MOFs. Despite their extreme breadth, the UW NMR signals are highly sensitive to changes in coordination environments induced by dehydration, guest adsorption, phase transitions, and local disorder.

This work establishes ^{209}Bi and ^{127}I UW SSNMR as viable tools for characterizing quadrupolar nuclei with extremely large quadrupole moments. The approach is broadly applicable beyond MOFs and holds significant promise for advancing research fields such as surface science, solar energy conversion, catalysis, and biochemistry, where atomic-scale insights into coordination and bonding environments are essential. The ability to resolve ultra-broad NMR signatures at ultra-high magnetic fields opens new avenues for the rational design of functional materials for targeted applications.

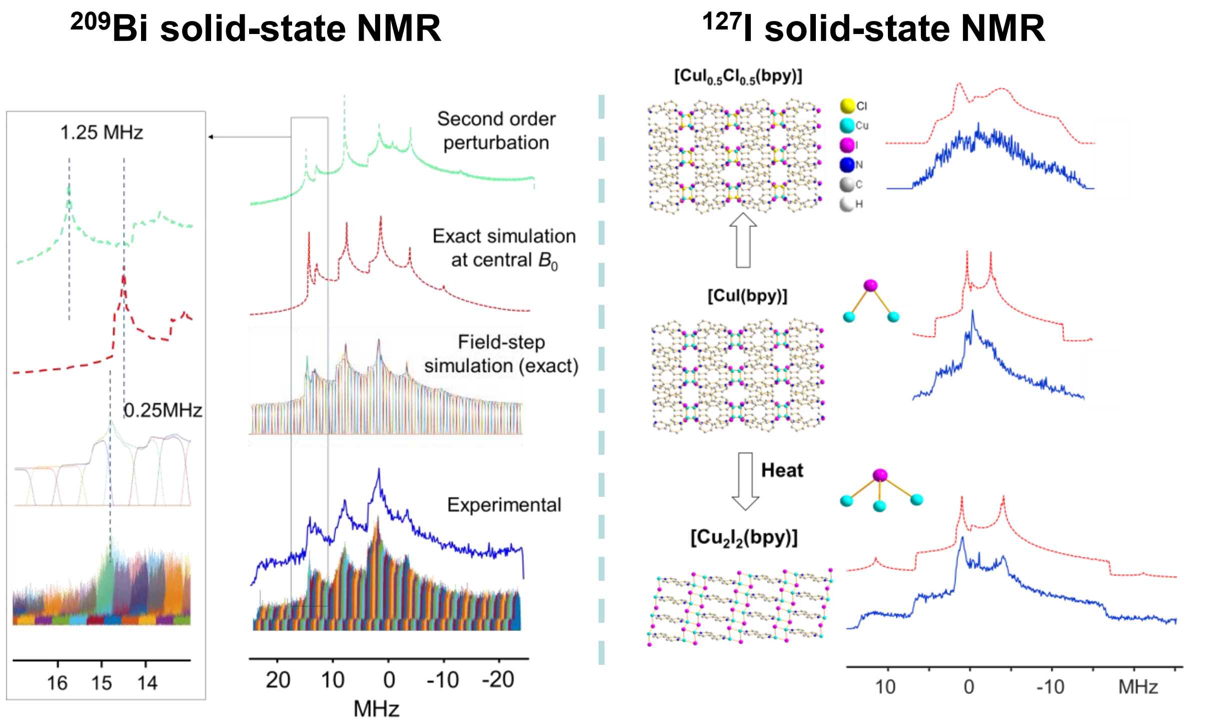

Figure 1. Left: Experimental and simulated ^{209}Bi NMR spectra of MOF IEF-3 using three simulation protocols. The magnified view of the "horn" at *ca*. 15MHz is shown in the inset. **Right:** Schematic illustrations of MOFs [CuI(bpy)], $[Cu_2I_2(bpy)]$ and $[CuI_{0.5}Cl_{0.5}(bpy)]$; experimental (blue) and simulated (red) ^{127}I SSNMR spectra of the three MOFs.

Facilities and instrumentation used: 36 T/40 mm Series Connected Hybrid Magnet (35.2 T/1.5 GHz)

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