Field Reversal in ^{14}N Overtone NMR Under Magic-Angle Spinning

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Introduction

NMR is normally insensitive to the direction of the field or sample spinning. In this report, we present a rare case that the field direction matters to ^{14}N overtone NMR under magic-angle spinning. We reverse the magnetic field direction which can be easily done using the Series-Connected-Hybrid (SCH) magnet at the NHMFL to confirm this phenomenon in overtone NMR experimentally. Overtone NMR is the direction excitation and detection at twice the nuclear spin Larmor frequency. The double-quantum transition is normally "forbidden" at high magnetic fields but can become observable under perturbation from large quadrupolar interactions. For spin-1 nuclei like ^{14}N, overtone NMR has the advantage of the absence of large first-order quadrupolar broadening. Under magic-angle spinning for higher spectral resolution, the quadrupolar interaction is modulated by the sample rotation inducing a shift to overtone NMR peaks. It has been shown by perturbation and Floquet theory that the main overtone peaks shift at the twice the spinning frequency at a direction determined by the relative direction of the magnetic field and spinning axis [1].

Experimental

^{14}N overtone NMR spectra were acquired at 216.70 MHz on the SCH, corresponding to twice the ^{14}N Larmor frequency at 35.2 T field, using a Bruker NEO NMR console and a 3.2mm magic-angle spinning probe developed at the NHMFL. Field reversal comparison was performed back-to-back by ramping the field in opposite directions. The magnetic field was regulated using the Bruker field-frequency lock on a ^{7}Li signal of a paramagnetic doped LiCl solution sample externally [2].

Results and Discussion

Figure 1 shows the ^{14}N overtone spectra of glycine under magic-angle spinning with the spinning and magnetic field directions as depicted. The results clearly show that the overtone peak is shifted at twice of the spinning frequency. Reversing the field direction changes the shift to the opposite direction. This observation agrees with theoretical prediction. In conclusion, we have used the SCH magnet to carry out field-reversal measurement of ^{14}N overtone NMR under magic-angle spinning. The results confirm experimentally a rare case of high field NMR where the magnetic field direction matters.

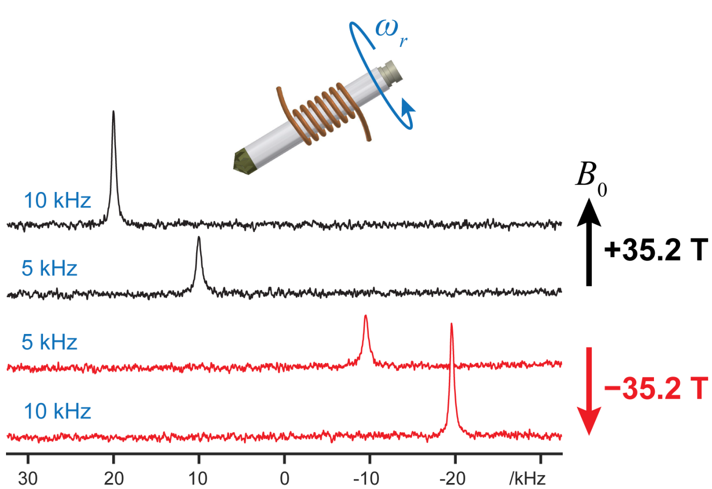

Fig 1 ^{14}N MAS NMR spectra of glycine recorded at 35.2 T using the series-connected-hybrid (SCH) with a 400 μs excitation pulse, 0.1 s recycle delay and 8192 scans. Two sets of spectra were acquired back-to-back by reversing the direction of the magnetic field for $\omega_R/(2\pi)$ = 5 and 10 kHz spinning frequencies.

Acknowledgements

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References

[1] Gan, Z., *et al.,* J. Chem. Phys., **149**, 6, 64201 (2018).
[2] Gan, Z., J. Magn. Reson., **284**, 125-136 (2017).