

^{14}N overtone NMR spectroscopy at 21.1 T

Luke A. O'Dell and Christopher I. Ratcliffe

Steacie Institute for Molecular Sciences, National Research Council, Ontario, Canada

luke.odell@nrc-cnrc.gc.ca

Nitrogen is one of the most abundant elements in nature, yet solid-state NMR studies of the 99.6 % naturally abundant ^{14}N nucleus are scarce. This is due to the combination of its quadrupole moment (20.4 mbarn) and integer spin number ($I=1$), which results in large first-order quadrupolar perturbations to the $\Delta m=1$ Zeeman transitions, broadening the resonances over many MHz for the vast majority of nitrogen sites and making standard NMR experiments very difficult [1]. Several decades ago, Bloom & LeGros noted that the first-order quadrupolar perturbation is absent from the $\Delta m=2$, or "overtone" transition and that this transition is weakly allowed when the magnitudes of the quadrupolar and Zeeman interactions are comparable [2]. Shortly after, Tycko & Opella reported the first ^{14}N overtone NMR spectra from single-crystal and powder samples [3], but this technique has not yet become routine due to various associated difficulties.

We have obtained ^{14}N overtone powder patterns from static powder samples at both intermediate and high magnetic field strengths. Such spectra can be obtained using simple single-pulse excitation, and the powder patterns are sensitive to the ^{14}N isotropic shift, the quadrupolar interaction, the CSA, and the relative orientations of these two interaction tensors (Figure 1). Such spectra are therefore more information-rich than the ultra-wideline ^{14}N NMR powder patterns, where perturbations due to the nuclear shielding are too small to resolve from the first-order quadrupolar powder patterns [5]. We are also currently investigating the advantages of magic angle spinning in

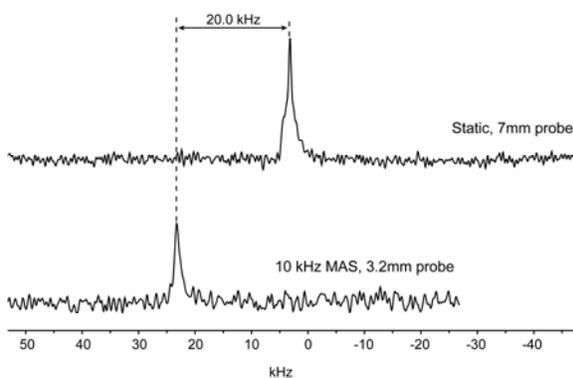


Figure 2: ^{14}N overtone NMR spectra obtained from a powder sample of glycine at 21.1 T under both static and MAS conditions.

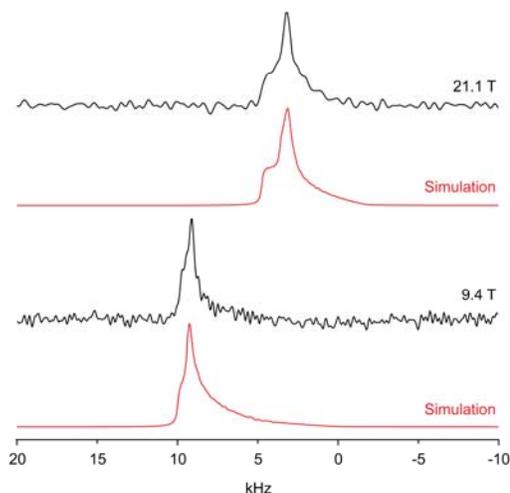


Figure 1: ^{14}N overtone NMR spectra obtained from a powder sample of glycine at two magnetic fields. Simulations made using the RMNSim software [4] are shown in red. These simulations include the ^{14}N quadrupolar parameters, isotropic shift, CSA and Euler angles.

overtone spectroscopy (Figure 2), which results in line-narrowing and a MAS-rate dependent shift in the peak position [6].

References

- [1] L.A. O'Dell, *Prog. Nucl. Magn. Reson. Spec.* (2011) **59** (2011) 295-318.
- [2] M. Bloom, M.A. LeGros, *Can. J. Phys.* **64** (1986) 1522.
- [3] (a) R. Tycko, S.J. Opella, *J. Am. Chem. Soc.* **108** (1986) 3531; (b) R. Tycko, S.J. Opella, *J. Chem. Phys.* **86** (1987) 1761.
- [4] N.M. Trease, P.J. Grandinetti, *J. Chem. Phys.* **128** (2008) 052318.
- [5] L.A. O'Dell, R.W. Schurko, K.J. Harris, J. Autschbach, C.I. Ratcliffe, *J. Am. Chem. Soc.* **133** (2011) 527.
- [6] L.A. O'Dell and C.I. Ratcliffe, *Chem. Phys. Lett.* **514** (2011) 168.