

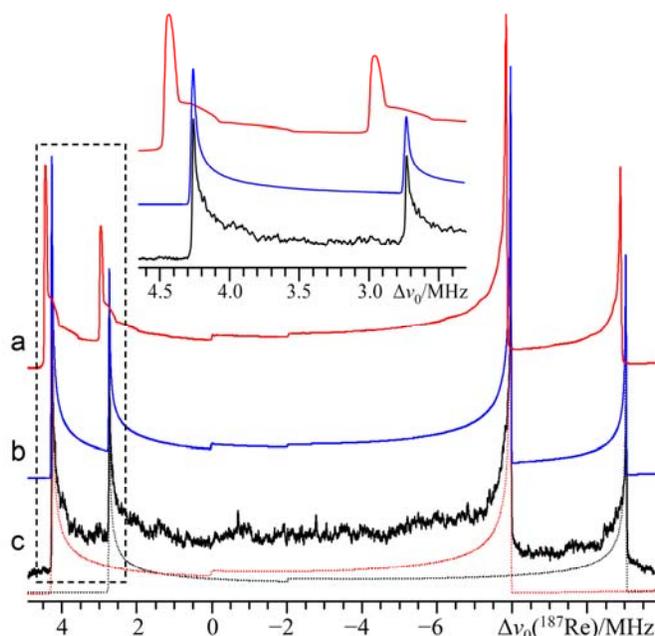
## Investigation of high-order quadrupole-induced effects: rhenium-185/187 solid-state NMR

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Recently, our research group has made significant progress in developing and highlighting the applications of  $^{35/37}\text{Cl}$ ,  $^{79/81}\text{Br}$ , and  $^{127}\text{I}$  solid-state nuclear magnetic resonance (SSNMR) experiments [1]. All the above-mentioned nuclei possess relatively large nuclear electric quadrupole moments ( $Q$ ), and thus the SSNMR signals associated with these probe nuclei are subject to a substantial degree of broadening due to the interaction between the  $Q$  and the electric field gradient (EFG) at the nucleus. While a significant amount of chemical information may be extracted by the proper analysis of the observed line shapes of quadrupolar nuclei, this broadening also decreases the sensitivity and resolution of the SSNMR experiment. Hence, there exists the need to constrain the quadrupolar broadening to the point where the SSNMR experiments are feasible. As the second-order line shape broadening associated with the  $Q$ /EFG interaction scales inversely with  $B_0$ , it is beneficial to obtain the SSNMR spectra of these nuclides within very high magnetic fields. Hence, the National Ultrahigh-Field NMR Facility for Solids has been critical in advancing the SSNMR methods for these large  $Q$  quadrupolar nuclides.



**Figure 1:** Second-order perturbation theory simulation (a), exact simulation (b), and experimental static VOCS Solomon echo (c)  $^{185/187}\text{Re}$  SSNMR spectra of powdered  $\text{NaReO}_4$ , acquired at  $B_0 = 21.1$  T. Below (c), the signals associated with each of  $^{185}\text{Re}$  and  $^{187}\text{Re}$  are deconvoluted: the dotted red trace is  $^{187}\text{Re}$ , while the dotted black trace is  $^{185}\text{Re}$ . The inset above the spectra corresponds to the region contained within the dashed-line box, but excludes the deconvolutions to enhance clarity.

During a previous  $^{127}\text{I}$  SSNMR study “high-order” quadrupole-induced effects (HOQIE) were observed at  $B_0 = 11.75$  and  $21.1$  T [1e]. As expected, these effects cannot be accounted for using commonly-available simulation software, which includes quadrupole broadening effects to second order only. To correctly analyze the observed line shapes, the  $Q$ /EFG interaction was treated exactly [2]. Due to the increasing number of reports involving quadrupolar nuclei with large quadrupole moments and/or very broad central-transition powder patterns, it is

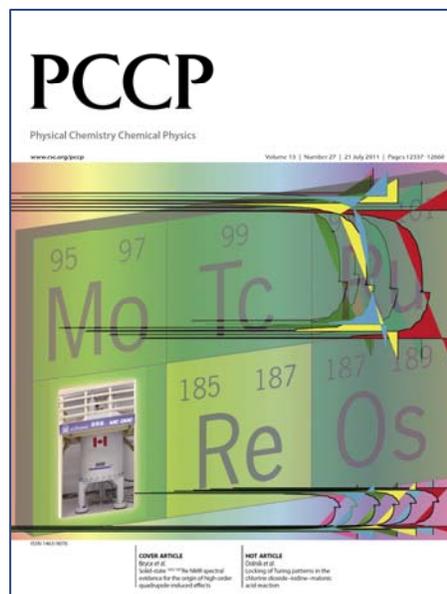
important and relevant to investigate HOQIE in a more general sense. Presently, we chose  $^{185/187}\text{Re}$  (both spin 5/2) nuclei in distorted tetrahedral and other high-symmetry environments to quantify HOQIE in SSNMR spectra of powdered samples. Both NMR-active rhenium nuclei possess very large  $Q$  values,  $Q(^{185}\text{Re}) = 2180$  mb;  $Q(^{187}\text{Re}) = 2070$  mb, and therefore even small deviations from tetrahedral/octahedral symmetry result in a large  $Q/\text{EFG}$  interaction and substantial line shape broadening.

Using  $^{185/187}\text{Re}$  SSNMR experiments at 11.75 and 21.1 T we have convincingly demonstrated the presence of HOQIE for a sample of  $\text{NaReO}_4$ . At the lower applied field, HOQIE manifest as additional fine structure (i.e., discontinuities), while at the higher applied field, HOQIE lead to non-uniform frequency-dependent shifts in the discontinuity positions only (Figure 1). Additional rhenium SSNMR experiments have also been performed on  $\text{NH}_4\text{ReO}_4$  and were used to place bounds on the value of rhenium chemical shift anisotropy for this compound ( $\Omega < 80$  ppm). The findings based upon the above  $^{185/187}\text{Re}$  SSNMR experiments, when coupled with corresponding  $^{185/187}\text{Re}$  nuclear quadrupole resonance (NQR) data, were able to very precisely measure the rhenium EFG tensors, as well as isotropic rhenium chemical shifts (the first time such values have been measured in the solid state). For a more complete account, see ref. [3], which was recently featured as a cover article in *Phys. Chem. Chem. Phys.* (Figure 2).

Motivated by these exciting results, we are presently using the National Ultrahigh-Field NMR Facility for Solids to extend our  $^{185/187}\text{Re}$  SSNMR studies to include a larger number of rhenium-containing compounds. It is hoped that careful line shape analysis (i.e., including HOQIE), coupled with quantum chemical calculations, will allow us to exploit the very sensitive rhenium  $Q/\text{EFG}$  interaction in future "NMR crystallography"-like structural refinements.

#### References

- [1] (a) R.P. Chapman, D.L. Bryce, *Phys. Chem. Chem. Phys.* **11** (2009) 6987; (b) C.M. Widdifield and D.L. Bryce, *Can. J. Chem.* **89** (2011) 754; (c) C.M. Widdifield, D.L. Bryce, *Phys. Chem. Chem. Phys.* **11** (2009) 7120; (d) C.M. Widdifield, D.L. Bryce, *J. Phys. Chem. A* **114** (2010) 2102; (e) C.M. Widdifield, D.L. Bryce, *J. Phys. Chem. A* **114** (2010) 10810.
- [2] A.D. Bain, *Mol. Phys.* **101** (2003) 3163.
- [3] C.M. Widdifield, A.D. Bain, and D.L. Bryce, *Phys. Chem. Chem. Phys.* **13** (2011) 12413. (**cover article**)



**Figure 2:** Cover article in *Phys. Chem. Chem. Phys.* Volume 13, Issue 27 (2011)