

New Pathways in NMR Crystallography: Structural Refinement and Solid-State NMR of the Periodic Table

Robert W. Schurko*, Sean T. Holmes, David A. Hirsh, Austin A. Peach, Christopher A. O’Keefe, Jacqueline E. Gemus, and Stanislav L. Veinberg

Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4

Abstract

NMR crystallography is an emerging discipline that combines solid-state NMR (SSNMR) spectroscopy, X-ray diffraction (XRD) methods, and computational approaches for the purposes of refining and determining molecular-level structures in a wide array of solids, including crystalline, semi-ordered, and amorphous materials.[1-3] SSNMR can be utilized to provide information on interatomic distances, structural assignments, local atomic/molecular symmetries, and/or characterization of structural disorder; these data, when used in combination with XRD and/or computational methods, can elicit structures that rival those determined by neutron diffraction methods.

The majority of modern NMR crystallographic studies rely upon the measurement of chemical shifts (typically from ^1H , ^{13}C , or ^{15}N NMR spectra), and comparison to magnetic shielding values of refined structures obtained from plane-wave density functional theory (DFT) calculations. An increasing number of studies have utilized data from numerous NMR-active nuclides across the periodic table, including metal nuclides with large chemical shift anisotropies and quadrupolar nuclides (i.e., nuclear spin $> 1/2$). Quadrupolar nuclides are of particular interest, since the quadrupolar interactions that influence SSNMR spectra are extremely sensitive to even the smallest structural differences/changes.

In this lecture, first, I will present a discussion of NMR crystallographic studies conducted in my group, with a focus on structural refinements aided by ^{14}N , ^{17}O , ^{35}Cl , ^{111}Cd and ^{195}Pt solid-state NMR data. These nuclides can be classified as unreceptive, due to a number of factors, including: (i) low gyromagnetic ratios, (ii) low natural abundance, (iii) large anisotropic interactions that can lead to substantial line broadening, (iv) inconvenient relaxation characteristics, or (v) combinations of these factors. Then, I will discuss some of the methods designed by my group that allow for rapid acquisition of SSNMR spectra crucial for NMR crystallographic studies.[5] Finally, I will outline a powerful method for refining crystal structures that uses dispersion-corrected plane-wave DFT, which relies upon the accurate measurement and computation of electric field gradient (EFG) tensors.[6]

1. *NMR Crystallography*; Harris, R.K.; Wasylishen, R.E.; Duer, M.J., Eds.; John Wiley & Sons, Ltd.: Chichester, U.K., **2009**.
2. Ashbrook, S.E.; McKay, D. *Chem. Commun.* **2016**, 52, 7186–204.
3. Bryce, D.L.; Taulelle, F. *Acta Crystallogr. C.* **2017**, 73, 126–127.
4. Harper, J.K.; Iuliucci, R.; Gruber, M.; Kalakewich, K. *CrystEngComm* **2013**, 15, 8693–8704.
5. Schurko, R.W. *Acc. Chem. Res.* **2013**, 46, 1985–1995.
6. Holmes, S.T. and Schurko, R.W. *J. Phys. Chem. C.* **2018**, 122, 1809–1820.