

## Characterization of $^{79/81}\text{Br}$ magnetic shielding and electric field gradient tensors in a series of alkaline earth metal bromides and hydrates thereof

Cory M. Widdifield and David L. Bryce

*Department of Chemistry, University of Ottawa, Ottawa, Ontario*

[dbryce@uottawa.ca](mailto:dbryce@uottawa.ca)

Over the past year, we have continued our  $^{79/81}\text{Br}$  solid-state NMR study on inorganic bromine-containing systems, with the goal of establishing such experiments as useful probes of local and extended bromine environments. The systems under study serve as model systems for future studies, as their crystal structures are known, and in several cases,  $^{79}\text{Br}$  nuclear quadrupole resonance (NQR) data exist. The nuclear properties of  $^{79}\text{Br}$  ( $I = 3/2$ ;  $\Xi = 25.053\,980\%$ ; N.A. = 50.54%;  $Q = 3.3 \times 10^{-29}\text{ m}^2$ ) and  $^{81}\text{Br}$  ( $I = 3/2$ ;  $\Xi = 27.006\,518\%$ ; N.A. = 49.46%;  $Q = 2.7 \times 10^{-29}\text{ m}^2$ ) make  $^{79/81}\text{Br}$  solid-state NMR experiments at standard magnetic fields quite difficult for all but the most ideal of scenarios (i.e., tetrahedral or octahedral nuclear site symmetry).

Over the past year, we have supported our previous experimental observations at both  $B_0 = 11.75\text{ T}$  and  $21.1\text{ T}$  with quantum chemical computations using gauge-including projector augmented plane wave (GIPAW) density functional theory (DFT) calculations as implemented within the CASTEP software [1] and powder X-ray diffraction data. Some of these efforts have led to a communication in *PCCP*, in which we demonstrated that  $^{25}\text{Mg}$  and  $^{79/81}\text{Br}$  nuclei could be used as experimental probes of structure in  $\text{MgBr}_2$ , a finding which ultimately led to a revised structure for this ionic system [2].

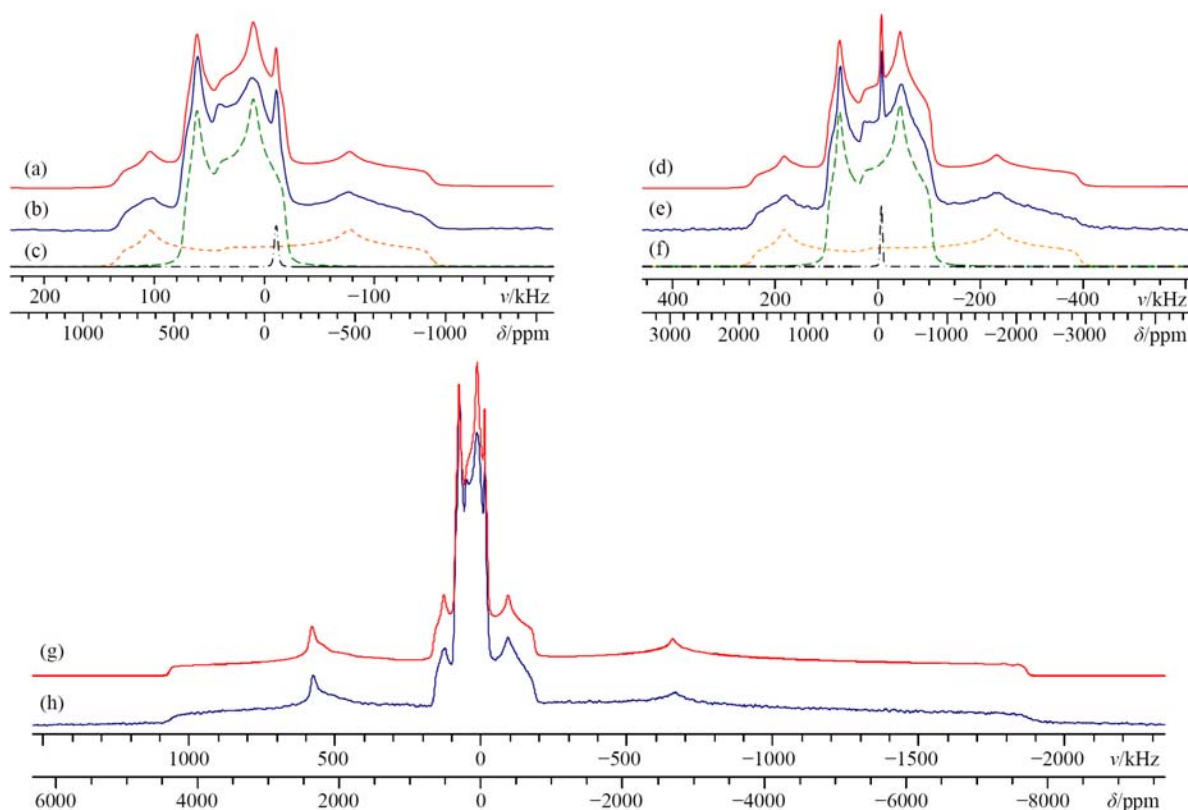
The  $^{79/81}\text{Br}$  solid-state NMR experiments have offered not only an opportunity to confirm or modify prior X-ray and NQR parameters, but they have also allowed us to make proposals regarding crystal structure and characterise sample composition when it is unknown. One such application is briefly described in Figure 1.

Since this project was proposed in March of 2008,  $^{79/81}\text{Br}$  solid-state NMR data have now been acquired for a range of bromine-containing inorganic salts ( $\text{MgBr}_2$ ,  $\text{CaBr}_2$ ,  $\text{SrBr}_2$ ,  $\text{BaBr}_2$ ), stable hydrates ( $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ ) and the mixture " $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$ ". In addition to our recent publication in *PCCP*, this work has been presented at the 50<sup>th</sup> Rocky Mountain Conference on Analytical Chemistry [3], the 92<sup>nd</sup> Canadian Chemistry Conference [4], and MOOT XXI [5]. We are nearing completion of a comprehensive manuscript which will distill our many observations into important conclusions.

As well, we would like to inform the interested reader of our group's two recent reviews on  $^{35/37}\text{Cl}$ ,  $^{79/81}\text{Br}$  and  $^{127}\text{I}$  solid-state NMR, one which is in *Annual Reports on NMR Spectroscopy* [6]; the other is in *Progress in Nuclear Magnetic Resonance Spectroscopy* [7].

## References

- [1] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson, M.C. Payne, *Z. Kristallog.* **220** (2005) 567-570.
- [2] C.M. Widdifield, D.L. Bryce, *Phys. Chem. Chem. Phys.* **11** (2009) 7120-7122.
- [3] C.M. Widdifield, D.L. Bryce, "Characterization of  $^{79/81}\text{Br}$  Magnetic Shielding and Electric Field Gradient Tensors in a Series of Alkaline Earth Metal Bromides and Hydrates Thereof", 50<sup>th</sup> Rocky Mountain Conference on Analytical Chemistry, 2008, Breckenridge, Colorado, USA.
- [4] D.L. Bryce, R.P. Chapman, C.M. Widdifield, "Chlorine, Bromine and Iodine Solid-State NMR Spectroscopy", the 92<sup>nd</sup> Canadian Chemistry Conference and Exhibition, 2009, Hamilton, Ontario, Canada.
- [5] C.M. Widdifield, D.L. Bryce, "Applications of  $^{79/81}\text{Br}$  and  $^{127}\text{I}$  Solid-State Nuclear Magnetic Resonance", MOOT XXI NMR Symposium, 2008, University of Windsor, Windsor, Ontario, Canada.
- [6] C.M. Widdifield, R.P. Chapman, D.L. Bryce, (G. A. Webb, Ed.), *Ann. Rep. Nucl. Magn. Reson. Spectrosc.* **66** (2009) 195-326.
- [7] R.P. Chapman, C.M. Widdifield, D.L. Bryce, *Prog. Nucl. Magn. Reson. Spectrosc.* **55** (2009) 215-237.



**Figure 1:** Analytical simulations (**a**, **g**) and experimental (**b**, **h**) static Solomon echo  $^{81}\text{Br}$  SSNMR spectra of  $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$ , acquired at  $\mathbf{B}_0 = 21.1$  T. Analytical simulation (**d**) and experimental (**e**)  $^{81}\text{Br}$  SSNMR spectrum of the three central signals, acquired at  $\mathbf{B}_0 = 11.75$  T. In (**c**) and (**f**), a deconvolution of the central three sites is provided. The interpretation is as follows: the very broad signal in (**h**) is assigned to anhydrous  $\text{CaBr}_2$ , and the very narrow peak (black dot/dash trace in (**c**) and (**f**)) is assigned to  $\text{NaBr}$ . After carefully considering the various possible hydrates, it was determined that the bromine NMR signals, deconvoluted as the green and yellow dashed traces in (**c**) and (**f**), are likely due to  $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ , respectively.