

Characterization of $^{79/81}\text{Br}$, $^{35/37}\text{Cl}$, and ^{127}I electric field gradient and chemical shift tensors in a series of phosphonium halide salts and solvates

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Phosphonium halides are a class of compounds containing a tetrahedral phosphorus cation with a halogen acting as a counter ion. Analogues bearing the alkyl triphenylphosphonium (TPP) cation have been employed as reagents in organic synthesis and as fertilizers, they are known to inhibit mitochondrial function specifically in cancerous cells, and their role as surfactants in polymer-cellulose and polymer-clay nanocomposites has been explored. The revelations made above make it essential to fully characterize the different components of phosphonium halides including the local electronic environment surrounding the halogen nuclei and how this relates to the different packing motifs in the crystal structures. Solid-state nuclear magnetic resonance (SSNMR) is a tool developed for this type of analysis for halogen nuclei and has been explored by our group frequently in recent years [1].

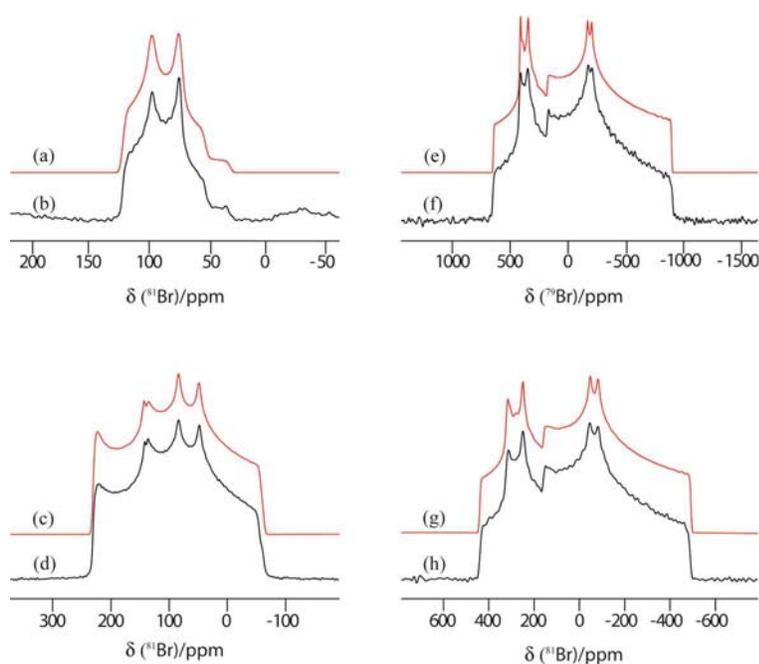


Figure 1: ^{79}Br and ^{81}Br solid-state NMR spectra of a powdered BrBuPPh_3 sample. **(b)** Experimental ^{81}Br 31.25 kHz MAS NMR spectrum acquired at 21.1 T. **(f)** Static ^{79}Br NMR spectrum acquired at 11.75 T. **(d, h)** Static ^{81}Br spectra acquired at 21.1 T (d) and 11.75 T (h). Analytical simulations including CSA and EFG effects are shown in red and were performed using WSolids.

We report here on our initial efforts to completely characterize the $^{79/81}\text{Br}$ electric field gradient (EFG) and chemical shift (CS) tensors for phosphonium bromides bearing the TPP moiety. The National Ultrahigh-Field NMR Facility for Solids was paramount in this undertaking as it permitted (i) the more accurate measurement of CS anisotropy since this subtle effect is accentuated at higher magnetic fields, and (ii) performing ^{81}Br MAS experiments ($\nu_{\text{rot}} = 31.25$ kHz and 62.50 kHz), as the second-order quadrupolar broadening is diminished significantly compared to spectra obtained with our 11.75 T magnet at the University of Ottawa.

Shown in Figure 1 are the experimental ^{79}Br and ^{81}Br NMR spectra at 11.75 T in our NMR facility at the University of Ottawa and the stationary and MAS ^{81}Br spectra at 21.1 T for a powdered sample of butyltriphenylphosphonium bromide (BrBuPPh_3). Along with the methyl and propyl analogues, the $C_Q(^{81}\text{Br})$ s were within 1 MHz of each other with an average of 9.25 MHz. For BrEtPPh_3 , $C_Q(^{81}\text{Br})$ was higher at 14.0 MHz. This type of observation could also be made for the CS tensor span, Ω , where this was on average 100 ppm for the butyl, methyl, and propyl adducts and 160 ppm for BrEtPPh_3 . This suggested that BrBuPPh_3 , BrPrPPh_3 , and BrMePPh_3 may share the same space group while BrEtPPh_3 does not. This was confirmed by our own single-crystal X-ray diffraction studies, thereby demonstrating the power of SSNMR to detect small structural changes between seemingly identical compounds.

In order to relate the NMR parameters and the solid-state structure, we have performed gauge-including projector-augmented-plane-wave (GIPAW) density functional theory (DFT) calculations of NMR parameters for both the phosphorus and bromine nuclei and have found that $C_Q(^{81}\text{Br})$ s are well predicted within experimental error in most cases but difficulties in optimizing the hydrogen positions in the X-ray crystal structure due to the large unit cell sizes limits the precision. Nonetheless, it was found that the orientation of the largest component of the $^{79/81}\text{Br}$ CS tensor, δ_{11} , is perpendicular to the P-Br vector in these compounds. Furthermore, as the P-Br length is decreased, the magnitude of δ_{11} increases, which is consistent with Ramsey's theory on paramagnetic shielding. GIPAW DFT calculations on BrBuPPh_3 when the bromine atom is displaced towards or away from the phosphorus atom show that σ_{11} is the most sensitive to this action (Figure 2).

A manuscript discussing in more detail these themes along with other findings is currently in preparation. A next step would be in applying this form of analysis to phosphonium iodides, as these are expected to exhibit smaller than usual ^{127}I quadrupolar interactions, as seen here for $^{79/81}\text{Br}$ in the phosphonium bromides.

References

- [1] (a) D.L. Bryce, E.B. Bultz, *Chem. Eur. J.* **13** (2007) 4786; (b) R.P. Chapman, D.L. Bryce, *Phys. Chem. Chem. Phys.* **9** (2007) 6219; (c) C.M. Widdifield, D.L. Bryce, *J. Phys. Chem. A* **114** (2010) 2102.

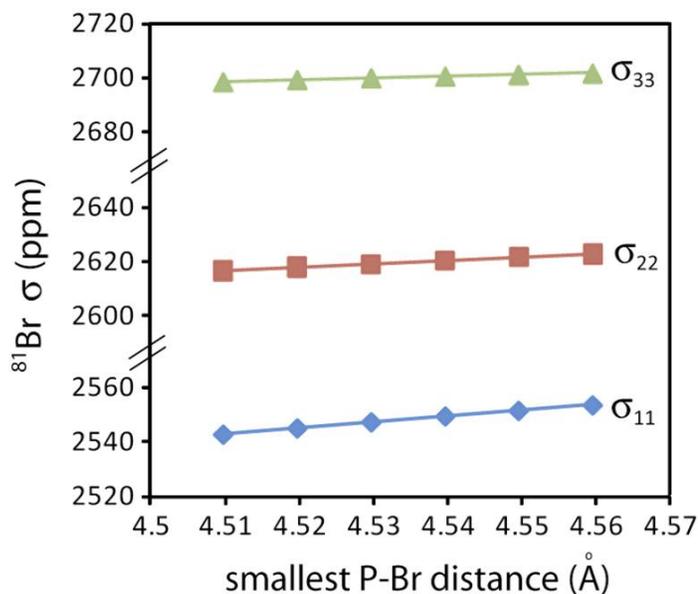


Figure 2: GIPAW DFT calculations for BrBuPPh_3 demonstrating that $\sigma_{11}(^{81}\text{Br})$ is the most sensitive to the P-Br distance component of the chemical shielding tensor.