

The measurement of residual dipolar coupling between quadrupolar nuclei in double-rotation NMR

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Measuring internuclear distances using dipolar coupling constants (R_{DD}) is a particular challenge in the case of heteronuclear quadrupolar spin pairs. When the quadrupolar interaction is too large, the entire spectrum cannot be excited in a single piece and double resonance methods cannot be used. A second possibility is to use residual dipolar coupling (RDC) to extract R_{DD} as RDCs are amplified when the quadrupolar interaction increases. RDCs are often seen in the magic angle spinning (MAS) NMR spectra of spin-1/2 nuclei that are dipolar coupled to a quadrupolar nucleus although they are more elusive in the case of quadrupolar spin pairs because the quadrupolar interaction typically dwarves all other interactions. In order to resolve these RDCs and measure R_{DD} s it is advantageous to remove the second-order quadrupolar broadening using a high-resolution method such as double-rotation (DOR).

The RDC theory of Menger and Veeman [1] was modified to include two quadrupolar nuclei. In this case, all the terms in the dipolar alphabet (not only A, C, and D) have non-zero expectation values. We then noticed that if the quadrupolar interaction at the observed nucleus is large enough, it will not only affect the quadrupolar broadening but the RDC as well.

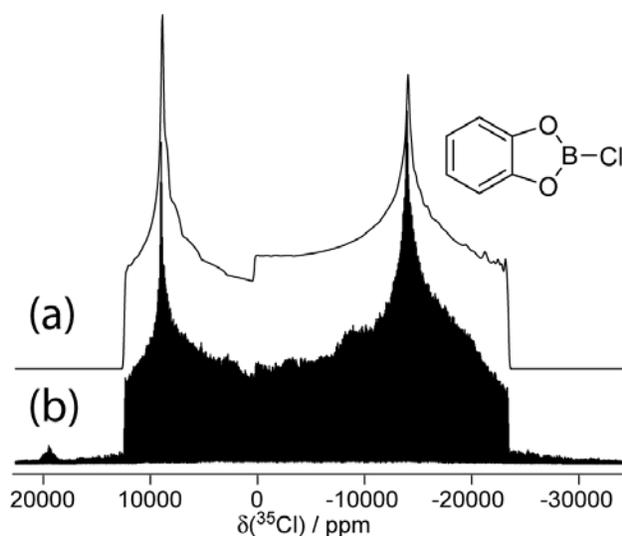


Figure 1: ^{35}Cl WURST-QCPMG NMR spectrum of B-chlorocatecholborane acquired at 21.1 T
(a) Simulation (b) Experiment.

Although these residual splittings can also be observed using multiple quantum magic angle spinning MQMAS [2], there are advantages to the DOR approach as there are no site-specific intensity losses and the DOR experiment is essentially quantitative [3].

B-chlorocatecholborane was chosen as a model sample to test this theory as the potentially large chlorine quadrupolar coupling constant (C_Q) and smaller ^{11}B C_Q would help the observation of RDC. As the RDC not only depends on the R_{DD} but also the chlorine C_Q and asymmetry parameter (η_Q), it was necessary to obtain those parameters independently using

$^{35/37}\text{Cl}$ NMR. As the C_Q for terminal halogens are often very large, it was necessary to use the National Ultrahigh-Field NMR Facility for Solids in order to reduce the second-order quadrupolar broadening which depends inversely on the magnetic field strength. The spectrum is shown in Figure 1.

On the other hand, the ^{11}B DOR spectrum (Figure 2) was acquired at a low field (4.7 T) in order to observe the largest possible RDC. A lopsided doublet was obtained, because of the higher-order quadrupolar effects on $^{35/37}\text{Cl}$ at that field. This made it possible to obtain the sign of the chlorine C_Q , which was negative.

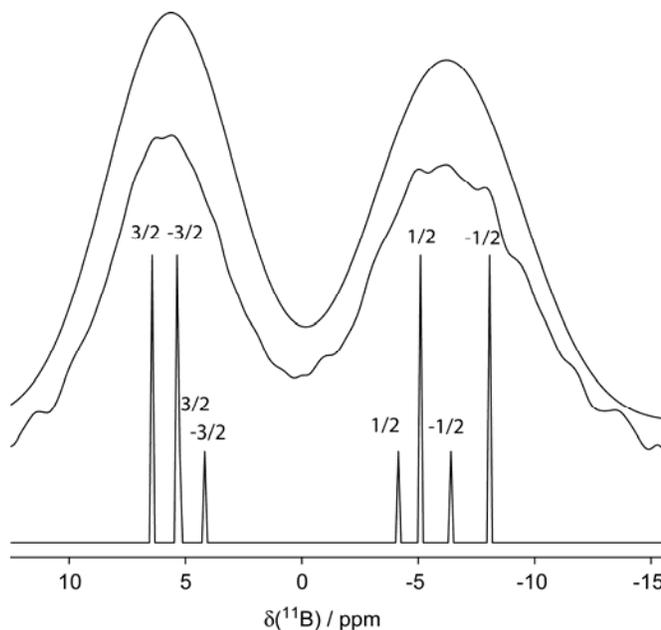


Figure 2: ^{11}B DOR NMR spectrum (middle trace) of B-chlorocatecholborane at 4.7 T. The sidebands have been folded into the centerband to obtain the correct intensities. The bottom trace shows the eight isotropic resonances when no line broadening is used.

As the ^{11}B MAS spectra were also affected by the RDC, it was also possible to obtain both the magnitude and relative orientation of the EFG tensors which can be easily tied to the molecular frame due to the symmetry of the molecule.

When RDCs are observable it is then relatively easy to obtain the sign of C_Q and relative orientation of the EFG tensors in favourable cases. These values were subsequently confirmed with the use of projector augmented wave (PAW) density functional theory (DFT) calculations as implemented in CASTEP. These calculations reproduce the experimental magnitude, sign, and orientation of the EFG tensors nearly quantitatively [3].

We are currently looking into expanding the use of RDCs in DOR between quadrupolar nuclei for obtaining connectivity information which would otherwise be difficult or impractical.

References

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- [2] G. Wu, K. Yamada, *Chem. Phys. Lett.* **313** (1999) 519-524.
- [3] F.A. Perras and D.L. Bryce, "Residual Dipolar Coupling Between Quadrupolar Nuclei Under Magic-Angle Spinning and Double-Rotation Conditions," *Journal of Magnetic Resonance* **213** (2011) 82-89. <http://dx.doi.org/10.1016/j.jmr.2011.08.043>