Introduction

We have recently demonstrated that directly bonded $^{27}$Al/$^{17}$O pairs can be correlated with $J$-coupling in solids under magic-angle spinning [1]. Both $^{27}$Al and $^{17}$O are half-integer quadrupolar nuclei, therefore their frequencies under MAS are shifted by the second-order quadrupolar interaction. The resulting two-dimensional powder patterns are sensitive to the relative orientation between the electric-field-gradient (EFG) tensors of $^{27}$Al and $^{17}$O. We report here extracting orientation information from $^{27}$Al/$^{17}$O HMQC spectra by comparing experimental data with simulations based on quantum chemical calculations of $^{27}$Al and $^{17}$O EFG tensors.

Experimental

The $^{27}$Al/$^{17}$O HMQC experiment was performed on the 900MHz wide bore magnet at the NHMFL equipped with a Bruker Avance console. A 3.2mm triple-resonance magic-angle spinning probe from Bruker was used for the measurement.

Results and Discussion

Figure 1 shows the pulse sequence and the $^{27}$Al/$^{17}$O correlation spectrum of crystalline mineral Grossite (CA2-CaAl4O7) acquired using the 900MHz magnet. The sample was spinning at 20kHz slightly off the magic-angle (~1°) for a prolonged $T_2$. The HMQC based experiment consists of a long spin-echo, therefore the magic-angle offset increases the signal-to-noise significantly (more than factor of 2 for Grossite) [1, 2]. At 21.1T, the two $^{27}$Al peaks show large second-order quadrupolar broadening. The four $^{17}$O sites have relatively small quadrupolar coupling, nevertheless features of two-dimensional 2nd-order quadrupolar powder patterns like tilted line shape are evident from the experimental data. These features fit qualitatively with the simulations using the relative EFG tensor orientations obtained from quantum chemical calculations.

Conclusions

Two-dimensional correlation spectra between two quadrupolar nuclei provide not only information on connectivity but on the relative EFG tensor orientation as well.

References