

Calcium-43 chemical shift tensors as spectroscopic probes of inorganic and bioinorganic systems

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Calcium is a key element in diverse biochemical and inorganic systems. It would therefore be very desirable to further develop Ca-43 NMR spectroscopy as a probe of the local calcium environment. To date, there has been a handful of solid-state ^{43}Ca NMR studies [1-4]. The NMR spectroscopic properties of Ca-43 ($I = 7/2$; $\Xi = 6.739$ MHz; N.A. = 0.135 %; $Q = -4.08$ fm²) are generally favourable with the exception of the very low natural abundance of this isotope and the low resonance frequency. Isotopic enrichment is very expensive. Furthermore, central-transition signal enhancement methods such as the use of hyperbolic secant pulses seem to become less efficient for higher spins. QCPMG methods are also of little use for accurate quantification of the NMR interaction tensors since the ^{43}Ca lineshapes are relatively narrow. The signal-to-noise afforded by the 21.1 T instrument has therefore been critical for the results achieved in the present study.

Previous Ca-43 solid-state NMR studies have yielded isotropic chemical shifts and some quadrupolar coupling constants. However, to our knowledge, only one chemical shift tensor span has been reported [1], and no complete chemical shift tensors (*i.e.*, including orientational information) have been determined for calcium. We have begun to develop natural-abundance ^{43}Ca solid-state NMR spectroscopy at 21.1 T and gauge-including projector-augmented-wave (GIPAW) DFT calculations as tools to provide insight into calcium binding environments, with special emphasis on the calcium CS tensor. We have reported the first complete analysis of a ^{43}Ca solid-state NMR spectrum, including the relative orientation of the CS and electric field gradient (EFG) tensors, for calcite (Fig. 1) [5].

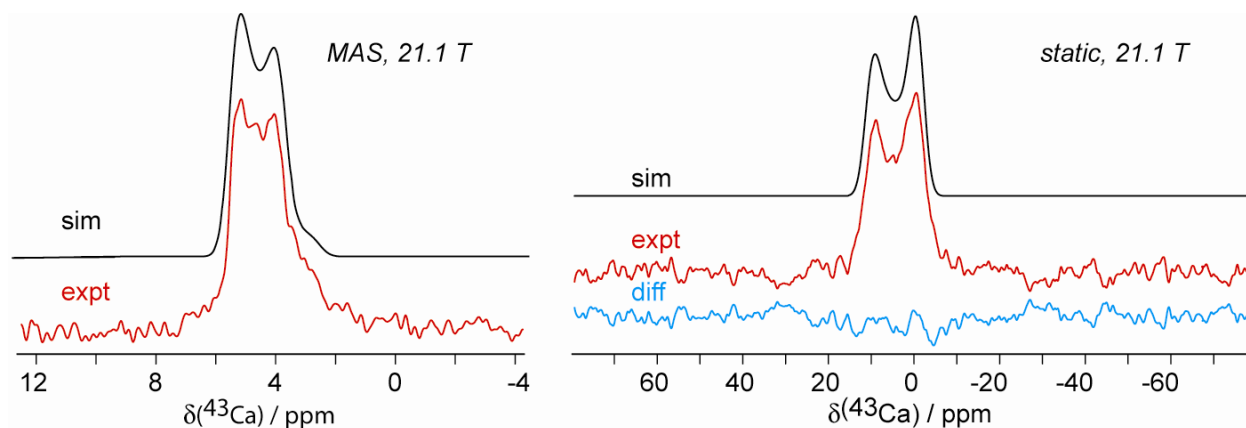


Figure 1: Natural abundance solid-state calcium-43 NMR spectra of powdered calcite. Left: under MAS conditions at 21.1 T; right: under stationary conditions.

The span of the CS tensor is 8 ± 2 ppm, in distinct contrast to the value of 57 ± 4 ppm reported for the aragonite polymorph [1]. We have also shown that GIPAW calculations of the ^{43}Ca CS and EFG tensors for a series of small molecules reproduce experimental trends; for example, the trend in available solid-state chemical shifts is reproduced with a correlation coefficient of 0.983 (Fig. 2). The results suggest the utility of the calcium CS tensor as a novel probe of calcium binding environments in a range of calcium-containing materials.

On the basis of the excellent agreement between experimental and calculated calcium NMR interaction tensors achieved during the first part of this study, we have pursued the application of a combined experimental-theoretical ^{43}Ca NMR approach to provide insight into the structure of the vaterite polymorph of calcium carbonate. Experimentally, orthorhombic and hexagonal structural representations have been proposed on the basis of powder X-ray diffraction experiments. We have concluded that the hexagonal $P6_3/mmc$ space group provides a better representation of the structure than does the orthorhombic $Pbnm$ space group, thereby demonstrating the utility of ^{43}Ca solid-state NMR as a complementary tool to X-ray crystallographic methods [5].

Future work on this project will examine the relationship between calcium CS tensors and local structure in a wider range of materials, including organic calcium compounds which are models for biological calcium binding environments.

References

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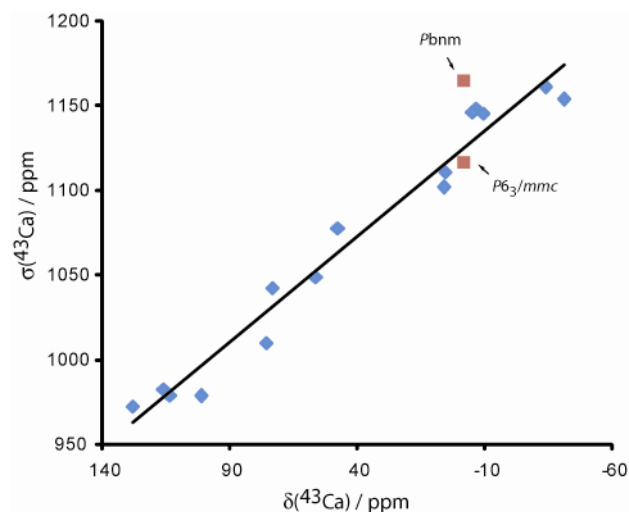


Figure 2: Correlation between calculated (GIPAW) ^{43}Ca shielding constants and experimental chemical shifts. The data points for the two possible structures of vaterite ($Pbnm$ and $P6_3/mmc$) were excluded from the fit. Partly on this basis, we conclude that the $P6_3/mmc$ structure is favoured for vaterite.