

Solid-state ^{73}Ge NMR characterization of organogermanium compounds

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Although NMR spectroscopy is a routine characterization technique for other group 14 elements, it is very rarely used in the case of germanium. This is due to the unfavourable NMR properties of ^{73}Ge including a moderate quadrupole moment (-0.196 Barn), low natural abundance (7.76%) and extremely low gyromagnetic ratio ($=-0.9332 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$, corresponding to a Larmor frequency of only 31.6 MHz at 21.1 T). We are interested in developing ^{73}Ge solid-state NMR spectroscopy as a method of structural characterization due to the availability of ultrahigh magnetic fields.

We were initially interested in exploring the NMR properties of a germanium dication trapped in a molecular cage. Although attempts to obtain an NMR spectrum of this compound were ultimately unsuccessful, we were able to obtain a spectrum of $\text{GeCl}_2 \cdot \text{dioxane}$, a valuable germanium(II) precursor. This relatively low symmetry compound yielded the largest germanium quadrupolar coupling constant $C_Q=44 \text{ MHz}$ recorded to date [1].

We also investigated a series of organogermanium compounds. While tetraphenylgermane exhibited the expected single sharp line under MAS conditions, the static spectrum had a surprising line shape (Figure 1). This was attributed to the first observation of the chemical shielding anisotropy (CSA) in a ^{73}Ge NMR spectrum. Examination of two other tetraarylgermanes under MAS condition revealed appreciable quadrupolar lineshape. We attributed this to slight deviations from ideal tetrahedral

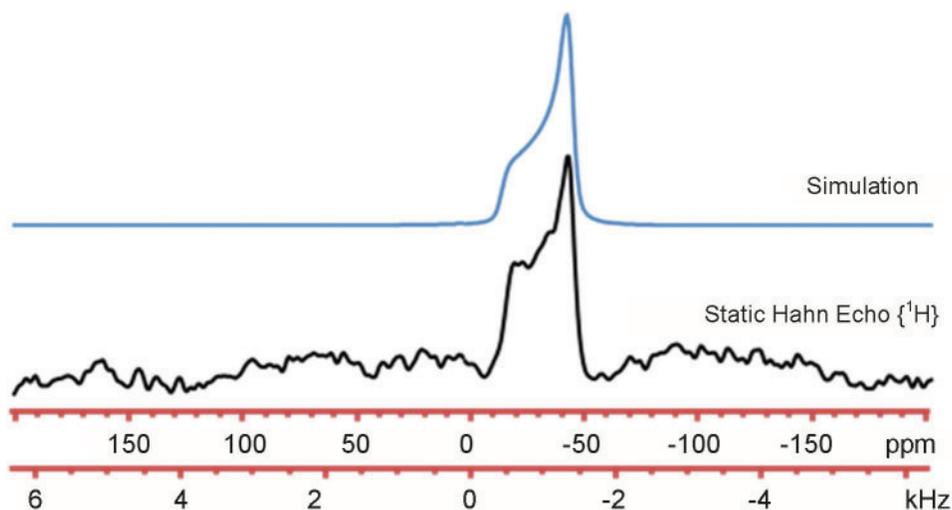


Figure 1: Static ^{73}Ge NMR spectrum of tetraphenylgermane at 21.1 T.

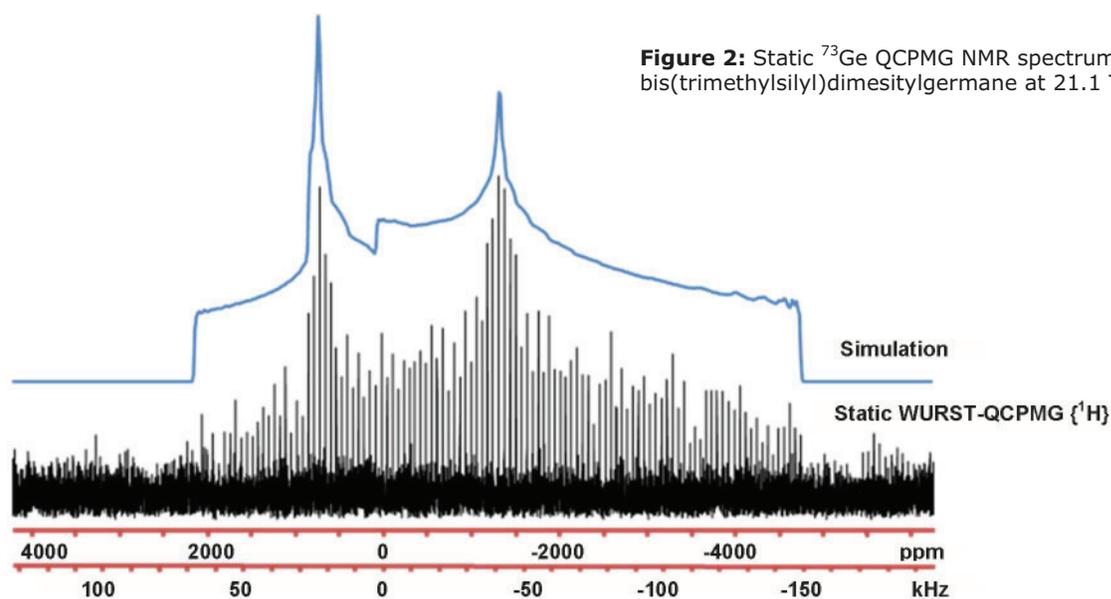


Figure 2: Static ^{73}Ge QCPMG NMR spectrum of bis(trimethylsilyl)dimesitylgermane at 21.1 T.

symmetry in the solid state. We were also able to obtain a static spectrum of tetra(4-methylphenyl)germane which showed greater CSA than in the case of tetraphenylgermane.

In the interest of determining the feasibility of recording ^{73}Ge SSNMR spectra of non-ideal systems, we also examined several lower symmetry organogermanes. Dimesitylgermane and trimesitylgermane both exhibited surprisingly narrow MAS spectra with less quadrupolar interaction than was seen in the case of tetra(4-methylphenyl)germane and tetra(4-methoxyphenyl)germane. Examination of these compounds under static conditions revealed the dominant interaction to be CSA, with dimesitylgermane exhibiting the greatest span of all the compounds studied. Only bis(trimethylsilyl)dimesitylgermane exhibited lineshape dominated by the second-order quadrupolar interaction (Figure 2).

We have found that, at ultrahigh magnetic fields, germanium CSA is actually fairly common to observe. Additionally, the quadrupolar interactions have proven to be sensitive to small changes in structure. More importantly, we have demonstrated that it is possible to obtain ^{73}Ge NMR spectra of non-ideal systems, which is important to the eventual use of the technique for diagnostic purposes. We are continuing to explore the scope and limitations of ^{73}Ge SSNMR spectroscopy at 21.1 T.

References

- [1] A. Sutrisno, M.A. Hanson, P.A. Rugar, V.V. Terskikh, K.M. Baines, and Y. Huang, "Exploring the limits of ^{73}Ge solid-state NMR spectroscopy at ultrahigh magnetic field," *Chemical Communications* **46** (2010) 2817-2819.