

**Supporting Information for:**

**Exploring the limits of  $^{73}\text{Ge}$  solid-state NMR spectroscopy at ultrahigh magnetic field**

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|  |            |
|--|------------|
| Experimental Section   | Page S2-S5 |
| Figure S1: $^{73}\text{Ge}$ static piecewise-frequency stepped QCPMG NMR spectra of $\text{GeCl}_2 \cdot \text{dioxane}$ at 21.1 T.  | Page S6    |
| Table S1: Calculated $^{73}\text{Ge}$ NMR parameters for $\text{GeCl}_2 \cdot \text{dioxane}$ using CASTEP.  | Page S7    |
| Figure S2: (a) $^{73}\text{Ge}$ MAS NMR spectrum of $\text{GePh}_4$ at 21.1 T.<br>(b) Simulated $^{73}\text{Ge}$ static NMR spectrum of $\text{GePh}_4$ .<br>(c) $^{73}\text{Ge}$ static echo NMR spectrum of $\text{GePh}_4$ at 21.1 T showing satellite transitions (STs). | Page S8    |
| Table S2: Calculated $^{73}\text{Ge}$ NMR parameters for $\text{GePh}_4$ using CASTEP.   | Page S9    |

## Experimental Section:

**Materials.** GeCl<sub>2</sub>•dioxane was synthesized according to literature procedures from GeCl<sub>4</sub>, 1,4-dioxane and tetramethyldisiloxane.<sup>1</sup> GePh<sub>4</sub> was purchased from Alfa Aesar and used as received without further purification.

**Solid-state NMR spectroscopy.** Solid-state <sup>73</sup>Ge NMR experiments were performed on a 900 MHz Bruker Avance II spectrometer at the *National Ultrahigh-field NMR Facility for Solids* in Ottawa, Canada, operating at a frequency of 31.4 MHz. Experimental setup, pulse calibration and referencing were done using 1M GeCl<sub>4</sub> solution ( $\delta_{\text{iso}} = 30.9$  ppm), acting as a secondary standard to neat GeMe<sub>4</sub> at 0.0 ppm.

For GeCl<sub>2</sub>•dioxane, QCPMG NMR experiments<sup>2</sup> were performed for stationary samples using a single-channel Bruker 7 mm MAS probe without proton decoupling. The frequency-stepped technique was used since breadth of the CT spectra exceeded the pulse width excitation profile. The sub-spectra with different frequency offsets were co-added on the frequency scale (Hertz). The resulting spectrum was then treated and referenced as a single spectrum.

For GePh<sub>4</sub>, static <sup>73</sup>Ge NMR experiments with proton decoupling (about 30 kHz rf power) were performed on a home-built 7 mm H/X low-gamma NMR probe for stationary samples with a dual resonator design.<sup>3</sup> A quadrupolar-echo pulse sequence  $[(\pi/2) - \tau_1 - (\pi/2) - \tau_2 - \text{acq}]$ , where  $\tau$  represents inter-pulse delays,  $\tau_1 = 200$   $\mu\text{s}$  and  $\tau_2 = 100$   $\mu\text{s}$ ] was used. The relaxation delay used was 5 s, 10k transients were accumulated. 4-5 kHz MAS experiments were also done on a single-channel Bruker 7 mm MAS probe applying a single-pulse sequence, 256 scans were accumulated with a 5 s relaxation delay.

**NMR spectral simulations.** All NMR parameters including  $C_Q$ ,  $\eta_Q$ ,  $\delta_{\text{iso}}$ ,  $\Omega$ , and  $\kappa$  were determined by analytical simulations of NMR spectra using the WSOLIDS1 simulation package.<sup>4</sup> The experimental error for each measured parameter was determined by visual comparison of experimental spectra with simulations. The parameter of concern was varied bidirectionally starting from the best fit value and all other parameters were kept constant, until noticeable differences between the spectra were observed.

**Theoretical calculations.** First-principles (*ab initio*) calculations based on plane wave-pseudo potential Density Functional Theory were conducted using CASTEP (version 4.3) program<sup>5,6</sup> setup by the Materials Studio graphical user interface, running on a single dual core Pentium 2.6 GHz CPU with 4 GB of memory. The NMR module<sup>7-9</sup> was used to calculate the  $^{73}\text{Ge}$  EFG and CSA tensors. The gauge-including projector augmented-wave (GIPAW) method which uses pseudo potentials and plane wave basis sets to describe three-dimensional lattices in crystalline materials was utilized. Unit cell parameters and atomic coordinates were taken from corresponding crystal structures.<sup>10,11</sup> The calculations were performed using ultra soft pseudopotentials generated from the “on-the-fly” method implemented within the CASTEP. The Generalized Gradient Approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) functional was used for all calculations.<sup>12,13</sup> A plane-wave cut-off energy of 450 eV (coarse basis set accuracy) was applied to  $\text{GeCl}_2\cdot\text{dioxane}$ , while 350 eV (fine basis set accuracy) was used for  $\text{GePh}_4$ .

The principal components of the EFG tensor ( $V_{XX}$ ,  $V_{YY}$ ,  $V_{ZZ}$ ) were converted to quadrupolar coupling constant  $C_Q$  and asymmetry parameter  $\eta_Q$  according to the

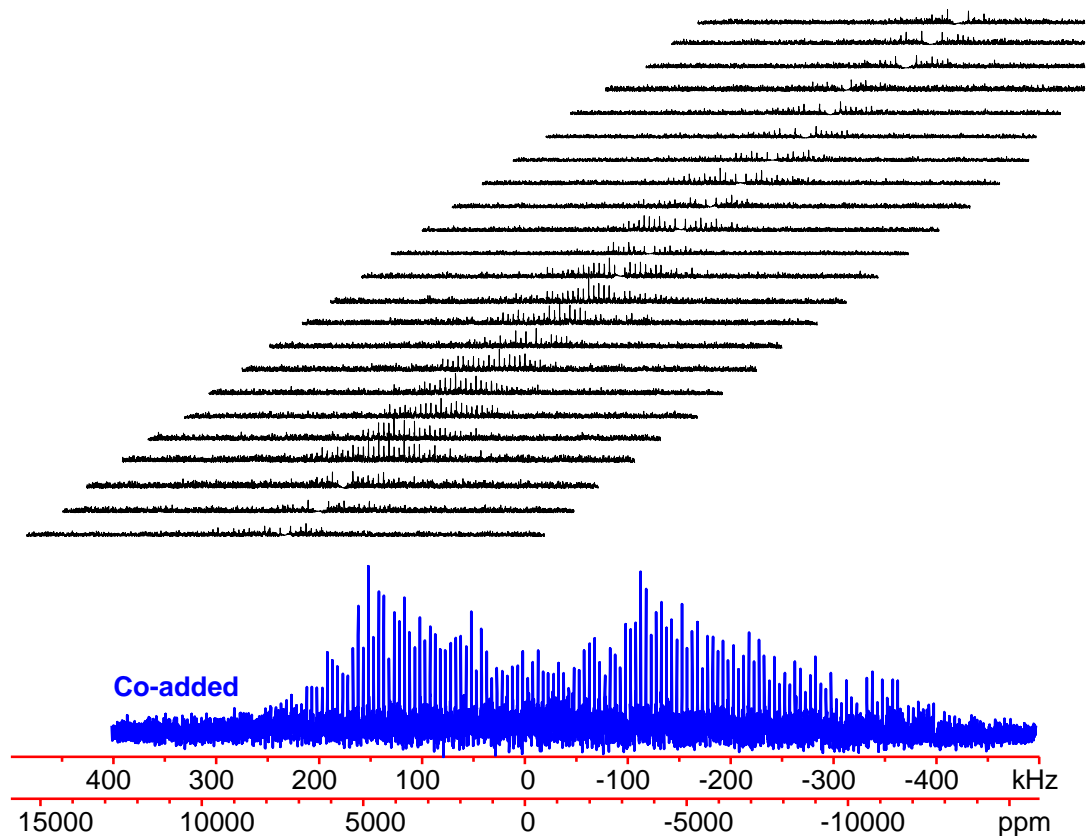
following definition:  $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$ ;  $C_Q$  (in Hz) =  $(eV_{ZZ}Q/h) \times 9.71736 \times 10^{21} \text{ V}\cdot\text{m}^{-2}$ ;  
 $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$ , where  $e$  is the electric charge;  $Q$  is the nuclear quadrupole moment.  
The  $C_Q$  value of  $^{73}\text{Ge}$  was calculated automatically from CASTEP and adjusted accordingly using the more accurate quadrupole moment [ $Q(^{73}\text{Ge}) = -0.196 \text{ barn}$ ].<sup>14</sup>

The calculated chemical shielding parameters are described using the Herzfeld-Berger convention.<sup>15</sup> The chemical shielding tensors are described by three principal components, ordered such that  $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$ . Isotropic chemical shift is the average of the three chemical shift tensor components [ $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ ]. Span is the difference between the most and the least shielded component [ $\Omega = \sigma_{33} - \sigma_{11}$ ]. Skew describes the shape of the powder pattern and is related to the axial symmetry of the CS tensor [ $\kappa = 3(\sigma_{iso} - \sigma_{22})/\Omega$ ]. In order to compare the calculated nuclear magnetic shielding constants with the experimentally measured chemical shifts, the calculated  $^{73}\text{Ge}$  absolute isotropic chemical shielding values were converted to the corresponding relative isotropic chemical shift values using the calculated chemical shielding values of a reference compound,  $\text{GeMe}_4$  (1494 ppm), via the equation:  $\delta_{iso} = 1494 \text{ ppm} - \sigma_{iso}$ . The molecular structure of  $\text{GeMe}_4$  was derived from proton magnetic resonance studies at low temperature.<sup>16</sup> A plane-wave cut-off energy of 350 eV (fine basis set accuracy) was used for  $\text{GeMe}_4$ . The convergence of the chemical shielding with respect to cutoff energy was not studied systematically in this work because of the limited access to CASTEP software. Previously the chemical shielding constant of  $^{73}\text{Ge}$  in  $\text{GeMe}_4$  was calculated by the *ab initio* molecular orbital method as 1504 ppm.<sup>17</sup>

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Figure S1.  $^{73}\text{Ge}$  static piecewise-frequency stepped QCPMG NMR spectra of  $\text{GeCl}_2 \cdot \text{dioxane}$  at 21.1 T



**Table S1. Calculated  $^{73}\text{Ge}$  NMR parameters for  $\text{GeCl}_2\cdot\text{dioxane}$  using CASTEP.**

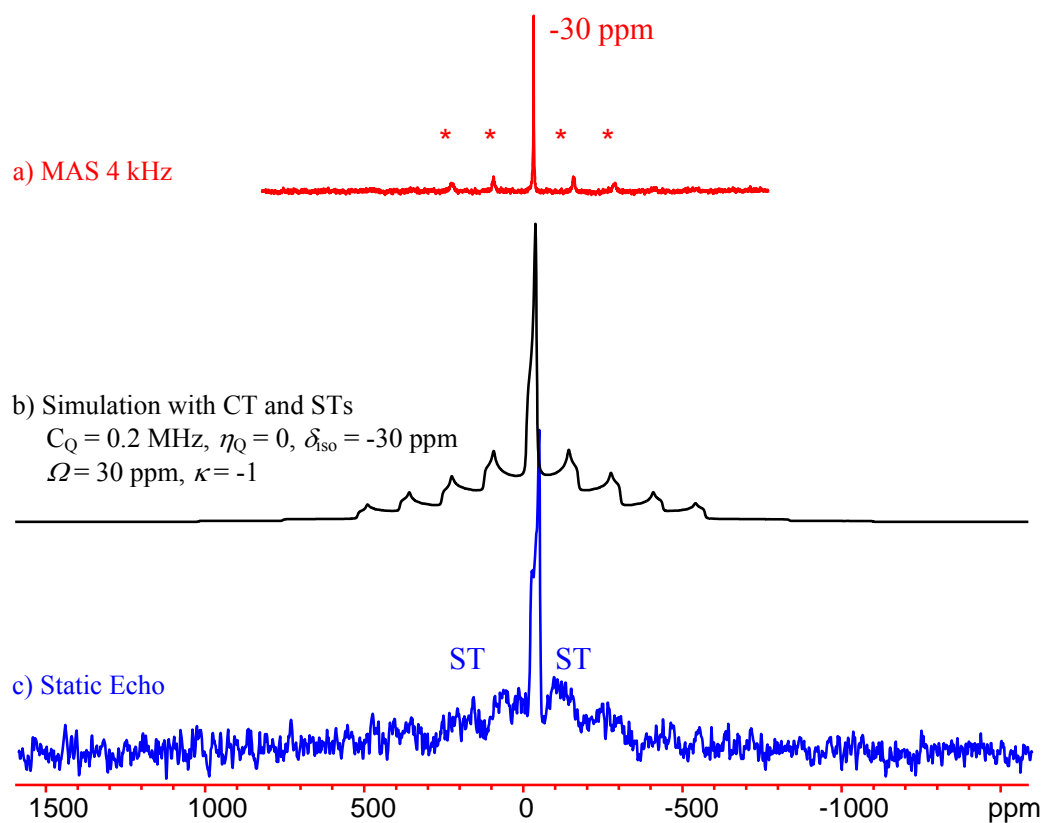
| Compound                           | Method                  | $ C_Q $ (MHz) | $\eta_Q$ | $\delta_{iso}$ (ppm) |
|------------------------------------|-------------------------|---------------|----------|----------------------|
| $\text{GeCl}_2\cdot\text{dioxane}$ | <i>Experimental</i>     | 44(2)         | 0.5(1)   | 1100(250)            |
|                                    | Calculated <sup>a</sup> | 69.0          | 0.87     | -                    |
|                                    | Calculated <sup>b</sup> | 69.8          | 0.85     | -                    |
|                                    | Calculated <sup>c</sup> | 70.3          | 0.85     | -                    |

<sup>a</sup> Calculations were performed by using the crystal structure data<sup>11</sup> without structure optimization.

<sup>b</sup> Calculations were performed with only H and C positions being optimized.

<sup>c</sup> Calculations were performed with fully optimized structure.

Figure S2. (a)  $^{73}\text{Ge}$  MAS NMR spectrum of  $\text{GePh}_4$  at 21.1 T  
(b) Simulated  $^{73}\text{Ge}$  static NMR spectrum of  $\text{GePh}_4$   
(c)  $^{73}\text{Ge}$  static echo NMR spectrum of  $\text{GePh}_4$  at 21.1 T showing  
satellite transitions (STs)





**Table S2. Calculated  $^{73}\text{Ge}$  NMR parameters for  $\text{GePh}_4$  using CASTEP.**

| Compound        | Method                  | $ C_Q $ (MHz) | $\eta_Q$ | $\delta_{iso}$ (ppm) | $\Omega$ (ppm) | $\kappa$ |
|-----------------|-------------------------|---------------|----------|----------------------|----------------|----------|
|                 | <i>Experimental</i>     | $< 0.30$      | 0        | -30(2)               | 30(3)          | -1       |
| $\text{GePh}_4$ | Calculated <sup>a</sup> | 1.65          | 0        | -8                   | 30             | -1       |
|                 | Calculated <sup>b</sup> | 0.15          | 0        | -30                  | 29             | -1       |
|                 | Calculated <sup>c</sup> | 0.15          | 0        | -30                  | 29             | -1       |

<sup>a</sup> Calculations were performed by using the crystal structure<sup>10</sup> without structure optimization.

<sup>b</sup> Calculations were performed with only H and C positions being optimized.

<sup>c</sup> Calculations were performed with fully optimized structure.