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# First observation of high-resolution solid-state $^{73}$Ge NMR spectra of organogermanium compounds

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**High-resolution solid-state MAS $^{73}$Ge NMR spectra of organogermanium compounds have been observed for the first time; the chemical shifts and half-widths of tetraphenylgermane and tetrabenzylgermane were recorded with and without high-power decoupling.**

Though the natural abundance is comparaable with the $^{29}$Si isotope, recording of $^{73}$Ge resonances is known to be very difficult because of the low value of $\gamma$, along with its nuclear spin of −9/2 and large quadrupolar moment. These cause distortion of the electric field gradient around the germanium nucleus leading to excessive broadening of the signals. In solution $^{73}$Ge NMR spectroscopy, it was observed that when the symmetry of the structure around the germanium atom is high, a sharp signal can be observed (as found for $^{14}$N NMR) while the signal tends to broaden as the symmetry is lost. For instance the half-width of tetramethylgermane, a compound with the highest symmetry, is only 1,4 Hz[1] while corresponding values of germacyclohexane, 1-methylgermacyclohexane and 1,1-dimethylgermacyclohexane are 15.4, 22.3 and 15.6 Hz, respectively.[2] It was also observed that when either halogen or oxygen atoms are unsymmetrically substituted, as found in 1-bromo-1-methylgermacyclohexane, an excessive broadening took place to such an extent that observation of signals was impossible.

Given these factors, it has generally been accepted that observation of $^{73}$Ge signals in the solid state would be even more difficult, and to the best of our knowledge, there have been no reports on $^{73}$Ge signals of organogermanium compounds in the solid state.

In a series of papers on solution $^{73}$Ge NMR spectra over the last 15 years we have accumulated data for a variety of organogermanium compounds.[3] We noted that the rapid development of NMR hard- and soft-ware has made observation of $^{73}$Ge signals more feasible. We thought that by an appropriate modification of hardware it might be possible to observe solid-state high-resolution $^{73}$Ge NMR spectra of organogermanium compounds with the aid of high-field instruments. Thus, we initiated an investigation to observe $^{73}$Ge NMR spectra of solid-state samples.

**Table 1** Chemical shifts and half-width of $^{73}$Ge signals for **1** and **2** in the solid state [a]

| Compound | $\delta$[b] | Half-width/Hz |
|---|---|---|
| **1** (proton decoupled) | −31.0 (−3.6)[c] | 40 (6)[c] |
| **1** (proton coupled) | −31.0 | 49 |
| **2** (proton decoupled) | 0.14 (0.04) | *ca.* 350 (24) |

[a] Values in parentheses are solution data for the same compounds. [b] We measured the $^{17}$Ge NMR spectrum for tetraethylgermane (liquid) filled in a cell without rotation and assumed that the chemical shift under this measurement condition was $\delta$ 17.3 (the same value as in solution). The chemical shifts of **1** and **2** in the solid state were referenced to this value. [c] Data taken from ref. 1.

We chose tetraphenylgermane **1** and tetrabenzylgermane **2** for over first attempt because of their high symmetry.[4] To our surprise, **1** gave an unexpectedly sharp signal, even without high-power proton decoupling, after an accumulation of a few hundred FIDs. Under similar measurement conditions, the half-width of the signal of 2 is much broader, and required much more accumulation for signal recording. $^{73}$Ge chemical shifts and the half-width of the signals for **1** and **2** are given in Table 1. There is a small shift, in comparison to values in solution, arising from a solid-state effect. When high-power proton decoupling was applied to **1**, the half-width became slightly smaller. Fig. 1 shows the$^{73}$Ge NMR spectra of **1** and **2**.

As is always the case for NMR signals for low-$\gamma$nuclei, there is some possibility that the observed signal may be an artifact. We eliminated this possibility by several means: (i) the FID shows a clear ringing pattern; (ii) a systematic change of irradiation frequency yields a corresponding change of resonance frequency; (iii) removal of the sample tube caused the disappearance of the signal.

It is unusual that there is such a large difference in the half-width for the two compounds since X-ray crystallographic analysis indicated a very high symmetry around germanium atom for both **1** and **2**.[6] There is, however, a small difference in the structures (**2** exhibits four independent phenyl rings while **1** exhibits only one in the asymmetric unit), which may be the reason for the difference in half-width.

Given the above encouraging results it will be important and interesting to delineate the scope and limitation of high-resolution solid-state $^{73}$Ge NMR spectroscopy for organogermanium compounds. We believe that most if not all

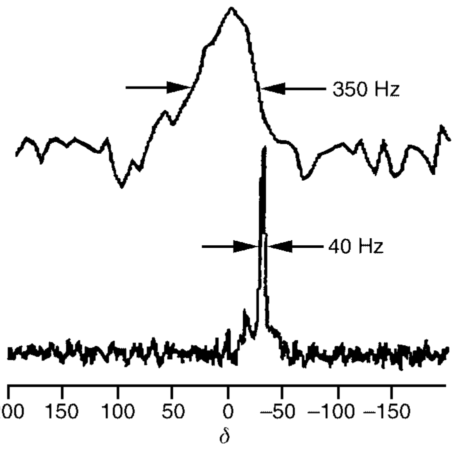

**Fig. 1** Solid-state high-resolution $^{73}$Ge NMR spectra of **1** (lower) and **2** (upper).

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symmetrically substituted germanes will give signals. It will also be of interest whether asymmetrically substituted germanes can also rise to signals. A study along such lines is under progress in our laboratories.

## Notes and references

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4 The $^{73}$Ge NMR spectra were recorded with JEOL ECP 300 spectrometer operating at 10.48 MHz, equipped with a probe modified for this purpose. The design of the probe is essentially the same as that used for observation of $^{107}$Ag. To obtain the best matching, a dummy condenser was attached in series. Cross polarization was not applied. Typically, 208 mg of **1** was packed in a 7 mm (o.d.) cell which was rotated at 4600 kHz. Pulse width, 45°; pre-delay, 1 s; delay; 5 s; number of accumulation, 1000 for **1** and 400 000 for **2**; sweep width, 20 kHz; high-power decoupling, 30 W.

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