

Review Article

^{73}Ge Nuclear Magnetic Resonance Spectroscopy of Germanium Compounds

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The field of ^{73}Ge NMR spectroscopy is reviewed in this paper, from early developments in the 1950s to present day research. Specific attention is paid to recent investigations, including the observation of fluxional behavior of hypervalent germanium species having five or six attached ligands by ^{73}Ge NMR spectroscopy, the spectral properties of linear and branched oligogermanes that contain single germanium-germanium bonds, and the relatively new field of solid-state germanium- ^{73}Ge NMR.

1. Introduction

The use of nuclear magnetic resonance (NMR) spectroscopy to characterize and probe the nuclei of the group 14 elements is highly useful, with the notable exception of the central element germanium. Carbon-13 NMR spectroscopy is invaluable for the characterization of organic compounds, and silicon-29 NMR spectroscopy can provide a wealth of structural information for organosilicon compounds [17–20], and allows direct observation of the silicon nucleus itself rather than gaining information regarding the silicon centers indirectly by probing the attached organic substituents. Tin has two NMR-active nuclei, tin-117 and tin-119, which, like carbon-13 and silicon-29, are both spin 1/2 nuclei. These two nuclei have also been extensively used for the characterization of organotin compounds, and ^{117}Sn – ^{119}Sn coupling between the two nuclei can also be readily observed [21]. Lead-207 is the only NMR-active nucleus for this element, and it is also spin 1/2 and has been regularly used to characterize organolead compounds [22]. The relevant NMR parameters for the group 14 nuclei are summarized in Table 1.

In terms of germanium, the only NMR-active nucleus this element possesses is ^{73}Ge [23, 24], which has a spin of 9/2 and a relatively large quadrupole moment of -19.6 fm^2 [25]. This large quadrupole moment leads to the observation of broad lines if the germanium nucleus being observed is not

disposed in a symmetric environment. To further complicate matters, the gyromagnetic ratio of all other observable nuclei in group 14 render them sensitive enough to be observed without considerable difficulty. However, the gyromagnetic ratio for the ^{73}Ge nucleus is $0.9332 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ [26–28] which results in an inherent lack of sensitivity despite the fact that the natural abundance of the ^{73}Ge nucleus is 7.7% which is seven times that of ^{13}C (1.1%). At a magnetic field strength of 11.74 T, the ^{73}Ge nucleus resonates at 17.44 MHz and therefore requires a dedicated low-band probe for its observation. In fact, the gyromagnetic ratio of the ^{73}Ge nucleus is among the lowest on the periodic table, with those of the nuclei ^{41}K , ^{57}Fe , ^{103}Rh , ^{187}Os , ^{191}Ir , ^{193}Ir , and ^{197}Au being lower [26]. Of these seven nuclei, ^{197}Au is very difficult to detect and the two isotopes of iridium have not been studied.

The purpose of this paper is to present a summary of the advances in the field of ^{73}Ge NMR spectroscopy, with a specific focus on some recent investigations including the use of applications of ^{73}Ge solid-state NMR spectroscopy. The field was first reviewed in 1978 where chemical shift data for only 20 compounds were collected [27]. Advances in instrumentation and techniques in the late 1970s and early 1980s expanded the field considerably, and two more comprehensive reviews were published in 1987 [29] and in 1988 [23]. A recent comprehensive review was also published in 2005 [24].

TABLE 1: Nuclear magnetic resonance data for the group 14 elements.

Nucleus	Nuclear spin	Gyromagnetic ratio ($\times 10^7$, $\text{rad s}^{-1} \text{T}^{-1}$)	Natural abundance	Resonance frequency (MHz) ^a	Relative sensitivity ^b
¹³ C	1/2	6.725	1.11	125.7	1.00
²⁹ Si	1/2	-5.314	4.67	99.3	2.10
⁷³ Ge	9/2 ^c	-0.9332	7.76	17.4	0.62
¹¹⁹ Sn	1/2	-9.971	8.60	186.4	25.6
²⁰⁷ Pb	1/2	5.597	22.60	104.6	11.4

^a Values in a 11.74 T magnetic field (¹H = 500 MHz).

^b Sensitivity is given at natural abundance in a constant field.

^c Quadrupole moment = $-0.18 \times 10^{-28} \text{ m}^2$.

2. Observation of the ⁷³Ge Nucleus

As mentioned previously, ⁷³Ge is an extremely challenging nucleus to study, especially when considered relative to the other nuclei of the group 14 elements, and there are two major complications in this regard. First, the low resonance frequency of 17.4 MHz at a field strength of 11.74 T (¹H = 500 MHz) requires that the radiofrequency pulses used to excite the nucleus to be both long and nonhomogeneous, which results in significant acoustic ringing of the probe. Second, the high spin ($I = 9/2$) results in quadrupolar relaxation of the nucleus. Acoustic ringing is most significant during the early portion of the acquisition and thus the most useful part of the FID is complicated by the presence of transient responses in the probe [30]. As a result, baseline distortions will be present especially when spectra are acquired at lower magnetic fields. This can be remedied by using high sample concentrations and is not a significant problem if the signals are sharp. However, broad signals, which are often of significant interest, will often not be resolved due to baseline roll.

Several pulse sequences for the containment of acoustic ringing were developed in the early 1980s that improved the resolution of broad resonances. One of these included implementation of a three-pulse sequence $(\pi/2)$ -(acquisition/add)- π - τ -($\pi/2$)-(acquisition/subtract) shown in Figure 1 that was applied for the observation of ¹⁷O NMR spectra [31] and is a modification of the inversion-recovery sequence. A second technique was directed at the suppression of the effect of ringing in the spectrum itself and consists of the pulse sequence (delay)- θ° -(acquire/add)-delay- π - τ - θ° -(acquire/subtract), which is known as the ACOUSTIC (Alternate Compound One-eighties Used to Suppress Transients In the Coil) technique and also was investigated with respect to the acquisition of ¹⁷O NMR spectra [32]. It was shown in 1984 that proton polarization transfer using INEPT could be applied to the ⁷³Ge nucleus, and significant signal enhancements were shown in the spectra of the germanes GeH₄, GeMe₄, GeEt₄, MeGeH₃ and the digermane Ge₂H₆ [33]. The RIDE (RInG down DELay) sequence was also reported (Figure 2) to suppress acoustic ringing during the acquisition of ³³S NMR spectra [34], and the use of composite pulses [35] increases the size of the spectral window in which the RIDE sequence can be applied for observation of the ⁷³Ge nucleus and results in

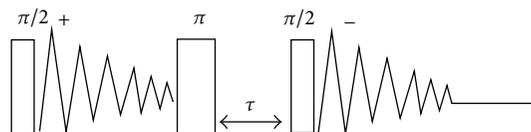


FIGURE 1: The $(\pi/2)$ -(acquisition/add)- π - τ -($\pi/2$)-(acquisition/subtract) pulse sequence. Reproduced from [31].

suppression of the acoustic ringing to a significant extent such that very weak and broad signals could be observed [36]. The EXSPEC (EXtended SPin ECho) sequence [37] also allows for very good signal enhancement and is a combination of RIDE and PHASE (PHase Alternated Spin Echo) (Figure 2), and representative spectra showing the application of these techniques to the ⁷³Ge NMR spectrum of Ph₃GeEt are shown in Figure 3.

Successful acquisition of ⁷³Ge NMR spectra has also resulted from the use of the Carr-Purcell-Meiboom-Gill (CPMG) sequence [38, 39]. This involves a modification of Hahn's spin-echo method [40] where a combination of 90- and 180-degree pulses is used with varying intensity and duration. The radiofrequency pulses are kept coherent and a 90-degree phase shift is incorporated into the first pulse.

3. Early Developments in ⁷³Ge NMR Spectroscopy

Initial NMR investigations on the ⁷³Ge nucleus were reported in 1953 and involved measuring its magnetic moment, which was found to be $-0.87675 \pm 0.00012 \mu$ without diamagnetic correction for pure GeCl₄ [41]. This was later reevaluated to be $-0.87917 \pm 0.00012 \mu$ in 1967, where the Larmor frequency was also determined to be 2.68 MHz in a magnetic field with a strength of 1.80 T [42]. Two values for the ²J_{Ge-H} coupling constant for GeMe₄ were reported in 1963 to be $2.92 \pm 0.02 \text{ Hz}$ [43] and 2.94 Hz [44]. One-bond germanium-fluorine coupling constant data was reported in 1964 for GeF₄ to be ¹J_{Ge-F} = 178.5 Hz [45], while the ¹J_{Ge-H} coupling constant for GeH₄ was determined in two separate studies to be $87.77 \pm 0.03 \text{ Hz}$ [46] or 97.6 Hz [47].

In 1973, the first reports of chemical shift values for the three germanium halides GeX₄ (X = Cl, Br, I) as well as all twelve permutations of the mixed halide species were

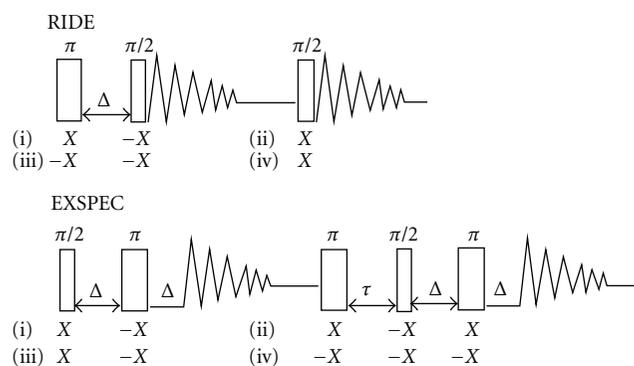


FIGURE 2: The RIDE and EXSPEC pulse sequences. Reproduced from [36].

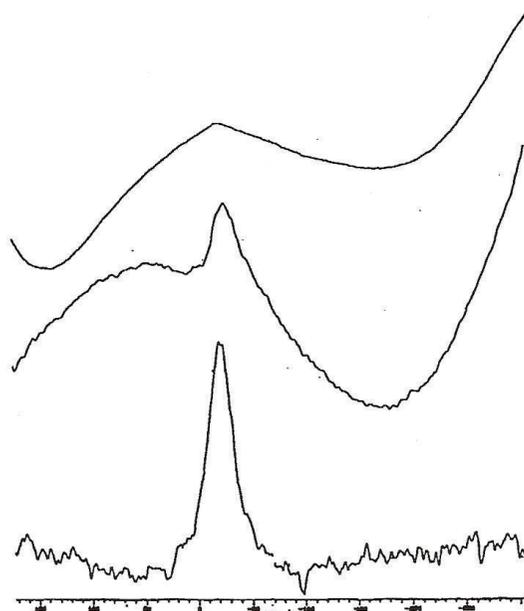


FIGURE 3: The ^{73}Ge NMR spectrum of Ph_3GeEt using a one-pulse experiment (top), the RIDE sequence (middle), and the EXSPEC sequence (bottom). Reprinted [11] with permission. Copyright 1999 Taylor & Francis.

reported [1]. These values are collected in Table 2. As expected, the shielding of the ^{73}Ge nucleus increases in the halogenated compounds GeX_4 in the order $\text{Cl} < \text{Br} < \text{I}$, such that the chemical shift of the ^{73}Ge NMR resonance for these species shifts upfield as the electronegativity of the halogen decreases. The chemical shifts of the fifteen halogermanes tabulated in Table 2 do not show a linear relationship in their chemical shift values, but rather exhibit a second-order dependence that arises from the change that one substituent exerts on the wavefunctions of all of the other substituents present.

TABLE 2: Chemical shift values for the germanium halides GeX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$)^a.

Compound	δ (ppm)
GeCl_4	31
GeCl_2Br	-47
GeCl_2Br_2	-130
GeClBr_3	-219
GeCl_3I	-231
GeCl_2I_2	-518
GeClI_3	-808
GeBr_4	-312
GeBr_3I	-513
GeBr_2I_2	-708
GeBrI_3	-901
GeI_4	-1086
GeCl_2BrI	-316
GeClBr_2I	-407
GeClBrI_2	-601

^aChemical shift values are relative to GeMe_4 . Data taken from [1].

TABLE 3: Chemical shift data for germanes and alkylgermanes^a.

Compound	δ ^{73}Ge (ppm)	Reference
Me_4Ge	0	[2]
Me_3GeH	-56.9	[2]
Me_2GeH_2	-127.6	[2]
MeGeH_3	-209.2	[2]
GeH_4	-299	[2]
Et_4Ge	17.8	[2]
Et_3GeH	-16	[2]
Et_2GeH_2	-88	[2]
EtGeH_3	-186.4	[2]
Pr^n_4Ge	2.4	[2]
Bu^n_4Ge	6.0	[2]
$(\text{C}_5\text{H}_{11})_4\text{Ge}$	6.0	[2]
$(\text{C}_6\text{H}_{13})_4\text{Ge}$	5.6	[2]
Ph_4Ge	-31.6	[3]
Ph_3GeH	-56.0	[3]
Ph_2GeH_2	-108.5	[3]
PhGeH_3	-187.5	[3]
$(p\text{-MeOC}_6\text{H}_4)_3\text{GeH}$	-189.9	[4]
$(p\text{-MeOC}_6\text{H}_4)_2\text{GeH}_2$	-112.0	[4]
$(p\text{-MeC}_6\text{H}_4)_3\text{GeH}$	-190.6	[4]
MesGeH_3	-234.3	[4]

^aData are referenced to Me_4Ge .

4. Correlation of ^{73}Ge NMR Spectra with Other Group 14 Nuclei and Applications to the Conformational Analysis of Organogermanes

The effects on the ^{73}Ge NMR chemical shifts resulting from interchanging relatively neutral substituents are generally predictable, as illustrated by the data collected in Table 3.

In the series of methylgermanes $\text{Me}_x\text{GeH}_{4-x}$, there is a progressive upfield shift of the ^{73}Ge chemical shift as hydrogen atoms are substituted for methyl group, which is observed over a range of approximately 300 ppm [2]. The same pattern is observed in the series of ethylgermanes $\text{Et}_x\text{GeH}_{4-x}$, [2] but the chemical shifts for this series of compounds are shifted further downfield than the corresponding chemical shifts for the methyl series which might be expected to result from the enhanced shielding effects of the ethyl substituents resulting from their being more inductively electron donating.

However, when comparing the ^{73}Ge NMR chemical shifts of the tetraalkyl substituted germanes GeR_4 , very little difference in the chemical shifts of the single resonances for these species was observed, with the exception of GeEt_4 [2]. The chemical shift for this species is anomalously shifted downfield and was observed at δ 17.8 ppm. A similar anomaly was observed for the corresponding silicon compounds in their ^{29}Si NMR data [57]. The ^{73}Ge NMR chemical shifts for the three species Bu^n_4Ge , $(\text{C}_5\text{H}_{11})^n_4\text{Ge}$, and $(\text{C}_6\text{H}_{13})^n_4\text{Ge}$ are all very close to δ 6.0 ppm, despite the increase in the inductive donating properties of the alkyl groups. Similar to the alkyl-substituted germanes, the series of phenyl-substituted species $\text{Ph}_x\text{GeH}_{4-x}$ also exhibit a progressive upfield shift in their ^{73}Ge NMR resonances [3, 4]. However, the deshielding effects of the phenyl substituents, versus their alkyl counterparts, result in a net upfield shift of the chemical shifts of the $\text{Ph}_x\text{GeH}_{4-x}$ germanes versus those of the alkyl-substituted $\text{R}_x\text{GeH}_{4-x}$ compounds.

The quadrupolar coupling constants of six symmetric tetra substituted germanes were measured in solution by obtaining their spin-lattice relaxation times (T_1) and their reorientation correlation times (τ_c) [58]. The quadrupolar coupling constant e^2Qq/h can be obtained from these values using the following equation (in the extreme-narrowing limit):

$$\pi\Delta\nu_{1/2} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{(3\pi^2/10)(2I+3)}{I^2(2I-1)} \times \left(\frac{e^2Qq}{h}\right)^2 \left(1 + \frac{\xi^2}{3}\right) \tau_c. \quad (1)$$

The quadrupolar coupling constants for GeMe_4 , GeEt_4 , GePr^n_4 , GeBu^n_4 , GeCl_4 , and GeBr_4 were determined to be 1.51, 0.97, 1.00, 0.72, 1.45, and 1.25 MHz, respectively.

Several studies have been directed at the correlation of ^{73}Ge NMR chemical shifts with those of the other group 14 elements, specifically ^{29}Si and ^{119}Sn , and several correlation equations have been developed. The comparison of NMR data for 29 pairs of analogous silicon and germanium compounds and 26 pairs of analogous germanium and tin compounds was reported in 1984 [59], and two correlation equations were derived are shown as follows:

$$\begin{aligned} \delta(\text{Ge}) &= 3.32[\delta(\text{Si})] + 39.9 \quad (r = 0.967), \\ \delta(\text{Sn}) &= 1.56[\delta(\text{Ge})] - 87.4 \quad (r = 0.991). \end{aligned} \quad (2)$$

Takeuchi et al. published a series of thirteen papers in the 1980s that focused on the ^{73}Ge NMR of numerous

germanes and correlated their spectral data with those of the analogous silicon and tin compounds [48–50, 60–69]. Molecular mechanics calculations were also used to further explain the experimental data.

One such study that was reported in 1984 [60] involved the acquisition of ^{73}Ge NMR data for six symmetrically substituted germanes, including GeMe_4 , GeEt_4 , GePh_4 , and $\text{Ge}(2\text{-furyl})_4$. The chemical shifts of these species were found to be related to their silicon analogs according to

$$\delta(\text{Ge}) = 2.01[\delta(\text{Si})] + 1.11 \quad (r = 1.00). \quad (3)$$

The ^{73}Ge NMR spectra of $\text{Ge}(2\text{-thienyl})_4$ and GeCl_4 were also recorded which exhibited peaks at δ -95.5 and 30.9 ppm (resp.). The linewidths for these six symmetrical compounds were all sharp, ranging from $\nu_{1/2}$ 1.2 to 11 Hz. The ^{73}Ge spin-lattice relaxation times (T_1) for these six species were also determined and were the first unambiguous determination that the ^{73}Ge nucleus relaxes via a quadrupolar mechanism [60]. The spin-spin relaxation times (T_2) of these compounds as well as the symmetrical germanes GeR_4 ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n$, and Bu^n) were also subsequently measured, and it was found that the unsymmetrical methylgermacyclohexanes exhibited shorter T_1 and T_2 values than the alkylgermanes [63]. Furthermore, it was demonstrated that both of these values also decrease as the molecular radius becomes larger [63]. The spectrum of the unsymmetrical compound $\text{Me}_3\text{GeCH}_2\text{CH}_2\text{COOH}$ was also acquired, and this compound exhibited a resonance at δ 6.3 ppm with a $\nu_{1/2}$ value of 54 Hz, where the line broadening is result of the perturbation of the electric field gradient at the germanium center [60].

It was also shown that ^{73}Ge NMR, when combined with ^{13}C NMR, could be used to determine the conformation of organogermanium compounds [48]. The ^{73}Ge NMR spectrum of 1,4-dimethylgermacyclohexane exhibited two resonances at δ -61.5 and -73.4 ppm, where the resonance at δ -61.5 ppm is assigned to the *trans*-isomer while the other resonance corresponds to the *cis*-isomer (Scheme 1). The signal at δ -73.4 ppm is also more intense which correlates with the observation that the *cis*-isomer is the more abundant conformation. Six other methyl-substituted germacyclohexanes were also characterized, as well as the parent unsubstituted germacyclohexane, and it was determined that the exchange of one hydrogen bound to germanium in germacyclohexane with a methyl group in 1-methyl-1-germacyclohexane not only shifts the ^{73}Ge resonance downfield but reduces the $^1J_{\text{Ge-H}}$ coupling constant [48]. Molecular mechanics calculations combined with ^{73}Ge and ^{13}C NMR spectroscopy also indicated that 1-methyl-1-germacyclohexane slightly prefers the axial conformer (Scheme 1) versus the equatorial isomer [62].

Further investigations also indicated that ^{73}Ge NMR resonances appear upfield for germanium atoms incorporated into germacyclohexanes that bear an axial methyl-substituent in the 3-position [64]. Eight different germacyclohexanes having a *tert*-butyl group bound to germanium that also had methyl groups at various positions around the GeC_5 ring were also characterized in this fashion, and

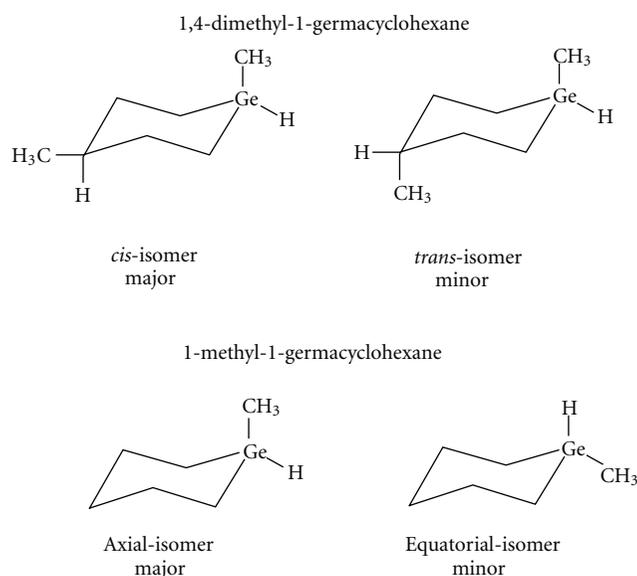
it was ascertained that an upfield shift in the ^{73}Ge NMR resonance for these compounds also resulted when the *tert*-butyl group was in the axial, versus equatorial, position [67]. However, the lines in the *tert*-butyl-substituted compounds were broadened such that features for those species having different *cis*- and *trans*-isomers could not be resolved, which was attributed to the increased molecular masses of these compounds combined with the increase in asymmetry of the electric field gradient at germanium. Similarly, the lines in a series of seven 1-phenylgermacyclohexanes were broadened to the extent that they could not be observed and did not permit resolution of the different signals arising from the *cis*- and *trans*-isomers [66].

A series of 1-germacyclopentanes was also synthesized and characterized by ^{73}Ge and ^{13}C NMR spectroscopy and MDNO calculations [68]. These species show similar effects of methyl substitution at germanium in their ^{73}Ge NMR spectra as found for the methylgermacyclohexanes, in that there is a downfield shift in the resonance upon exchanging a hydrogen atom for a methyl group. Also of interest is that the chemical shift difference between 1,1-dimethylgermacyclopentane and 1,1-dimethylgermacyclohexane is very nearly related to the difference between those of their respective silicon analogues [70].

The ^{73}Ge NMR spectra for several macrocyclic digerman- and tetragermacycloalkanes were also determined (Scheme 2 and Table 12) [49]. The large size of some of these systems suggested that observation of ^{73}Ge NMR signals might prove difficult, as the signal generally becomes broadened as the molecular mass of the compounds increases. However, ^{73}Ge NMR signals for all compounds except the twelve-membered digermacycloalkane were observed. The chemical shift range for all nine compounds that were observed is only 5.0 ppm and there is no apparent correlation between chemical shift and ring size.

Although the ring size has little influence on the ^{73}Ge NMR chemical shift in the aforementioned macrocyclic species, this is not true in systems having smaller rings, where the ring size has a pronounced effect on the ^{73}Ge NMR chemical shift, as indicated by 1,1-dimethyl-1-germacyclopent-3-ene [71] and 1,1-dimethylgermacyclohexane [48] that differ in chemical shift by over 50 ppm. Germanium-73 chemical shift values also appear to reflect the two possible conformations (boat or chair) in 3-germabicyclo[3.1.0]hexanes (Scheme 3 and Table 13) [50]. Considering the progression of chemical shifts of 3,3-dimethyl-3-germabicyclo[3.1.0]hexane (1), 3,3-diethyl-3-germabicyclo[3.1.0]hexane (2), and 3,3-diethyl-1-methyl-3-germabicyclo[3.1.0]hexane (3) relative to that of 1,1-dimethylgermacyclopentane, which has a ^{73}Ge NMR resonance at δ 40 ppm, it was suggested that all three of these compounds had the boat conformation, while the remaining species 3,3-diethyl-1,5-dimethyl-3-germabicyclo[3.1.0]hexane (4) has a chair conformation since the chemical shift of this compound is at higher field than those of compounds 1–3.

The tetraalkoxygermanes $\text{Ge}(\text{OR})_4$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i, \text{and } \text{Bu}^s$) were characterized by ^{73}Ge NMR



SCHEME 1: Conformations of 1,4-dimethyl-1-germacyclohexane and 1-methyl-1-germacyclohexane. Adapted from [48].

spectroscopy in 1986 [5]. The chemical shifts for these species are summarized in Table 4 and range from δ -37.8 to -47.5 ppm. A progressive upfield shift is observed for these compounds as the organic substituent becomes more and more inductively donating, except for the *sec*-butoxy derivative which does not follow this trend. The electron donating ability of an alkyl group can be loosely quantified by the term σ_I [6], and values for these parameters are shown in Table 4. When compared to their silicon analogues, there is a linear relationship between the ^{29}Si [72] and ^{73}Ge NMR chemical shifts of the group 14 element center that follows

$$\delta(\text{Ge}) = 1.6[\delta(\text{Si})] + 88.7 \quad (r = 0.97). \quad (4)$$

It was also noted that the ^{73}Ge NMR signals are more sensitive to changes in the structure of the organic group than the ^{29}Si NMR signals of their lighter congeners [72].

The ^{73}Ge NMR spectra of four methylvinylgermanes were reported in 1989 that have the general formula $\text{Me}_{4-n}\text{Ge}(\text{CH}=\text{CH}_2)_n$ [65]. The chemical shifts for these species, relative to Me_4Ge at δ 0.00 ppm, are δ -15.82 ($n = 1$), -30.61 ($n = 2$), -44.98 ($n = 3$), and -58.73 ppm ($n = 4$). There is therefore a progressive upfield shift in the ^{73}Ge NMR signal over a range of δ 43.1 ppm for these species as methyl groups are exchanged for vinyl groups. Calculations (MDNO) on these molecules indicated that the electron density at the germanium atoms decreased as the number of attached vinyl substituents increased, but an upfield shift in the ^{73}Ge NMR resonance was observed nonetheless, indicating that there is not a correlation between the electron density at germanium and the chemical shift of the ^{73}Ge nucleus in these species. The same trend was observed for the related silicon compounds $\text{Me}_{4-n}\text{Si}(\text{CH}=\text{CH}_2)_n$ although the chemical shift range in the ^{29}Si NMR spectra of these species was only δ 19.6 ppm [73]. The chemical shifts of the

germanium containing species can be correlated to those of their silicon analogues according to

$$\delta(\text{Ge}) = 1.96[\delta(\text{Si})] + 2.37 \quad (r = 0.999). \quad (5)$$

The series of methylethynylgermanes $\text{Me}_{4-n}\text{Ge}(\text{CCH})_n$ were characterized by ^{73}Ge NMR spectroscopy as well, and a progressive upfield shift of the resonance with increasing numbers of ethynyl substituents was also observed [74]. The chemical shift range in this case was 173 ppm, with peaks for the four species being observed at $\delta -34$ ($n = 1$), -77 ($n = 2$), -118 ($n = 3$), and -173 ($n = 4$) ppm. A nearly identical pattern was observed for the tin analogues of these species in their ^{119}Sn NMR spectra [74].

Similarly, the three series of compounds shown in Scheme 4 were investigated using ^{73}Ge NMR spectroscopy [51]. The chemical shift range for the 2-furyl series ranges from $\delta -22.1$ to -115.0 ppm and exhibited a progressive upfield shift of the ^{73}Ge NMR resonance as methyl groups were substituted by 2-furyl groups. The related 2-thienyl series exhibited a similar upfield shift in the chemical shifts of these species, but the range of $\delta -10.1$ to -56.5 ppm was less than that for the 2-furyl series. A nearly identical pattern to the 2-furyl series was observed for the 2-(4,5-dihydrofuryl) series with a chemical shift range of $\delta -22.5$ to -119.1 ppm. These trends are similar to those observed for the aforementioned vinyl series $\text{Me}_{4-n}\text{Ge}(\text{CH}=\text{CH}_2)_n$, and the same upfield progressions were reported for the analogous silicon- and tin-containing 2-furyl [75] and 2-thienyl [76] compounds as well as the analogous 2-(4,5-dihydrofuryl)silanes [77]. Combining these data with the previously described studies of methylvinylgermanes allows a correlation of ^{73}Ge NMR chemical shifts with those of the ^{29}Si and ^{119}Sn nuclei according to the following equations (resp.) [51]:

$$\delta(\text{Ge}) = 2.2[\delta(\text{Si})] + 3.9 \quad (r = 0.975), \quad (6)$$

$$\delta(\text{Sn}) = 2.2[\delta(\text{Ge})] + 11.3 \quad (r = 0.984). \quad (7)$$

5. Effects of Hyperconjugation on the ^{73}Ge NMR Spectra of Germanes

The presence of hypervalency has a dramatic effect on the chemical shift of the ^{73}Ge NMR resonance. In the case of hexacoordinate compounds GeL_6 , which include the bidentate ligands 2,2'-bipyridine or 1,10-phenanthroline in six of the seven examples shown, resonances were observed between $\delta -319.4$ and -442.5 ppm (Table 5) [7]. The addition of 2,2'-bipyridine to GeCl_4 yields (bipy) GeCl_4 , and this species exhibits a ^{73}Ge NMR resonance at $\delta -313.7$ ppm that is shifted far upfield from that observed for GeCl_4 itself at $\delta 30.9$ ppm [78]. As successive chloride ligands are replaced by thiocyanate ligands in the (bipy) $\text{GeCl}_{4-n}(\text{NCS})_n$ derivatives, a progressive upfield shift of the ^{73}Ge NMR resonance was observed. The trend in this case can be explained by the lower electronegativity of the ^-NCS ligand versus that of Cl^- , which leads to increased electron density at germanium and therefore a higher shielding of the ^{73}Ge nucleus. The

TABLE 4: ^{73}Ge NMR data for germanium alkoxide complexes^a.

Compound	δ ^{73}Ge	σ_1 (R) ^b
$\text{Ge}(\text{OMe})_4$	-37.8	0.000
$\text{Ge}(\text{OEt})_4$	-43.9	0.100
$\text{Ge}(\text{OPr}^n)_4$	-45.6	0.130
$\text{Ge}(\text{OPr}^i)_4$	-49.7	0.190
$\text{Ge}(\text{OBu}^n)_4$	-45.6	0.130
$\text{Ge}(\text{OBu}^i)_4$	-45.5	0.125
$\text{Ge}(\text{OBu}^t)_4$	-47.5	0.210

^aData are referenced to GeMe_4 and are taken from [5].

^bValues from [6].

chemical shift of the $[\text{Ge}(\text{NCS})_6]^{2-}$ anion lies very far upfield at $\delta -442.5$ ppm [7, 79], which contrasts strongly with the chemical shifts observed for the tetracoordinate $\text{Ge}(\text{NCO})_4$ at $\delta -88.9$ ppm and the amide compounds $\text{Ge}(\text{NR}_2)_4$ ($\text{R}_2 = \text{Me}_2, \text{Et}_2, \text{Pr}_2, \text{or HPr}$) that range from $\delta 22.0$ to 55.8 ppm [79].

Similar to the exchange study of the germanium halides GeX_4 [1], GeCl_4 was combined with different stoichiometric ratios of KSCN in acetone and the ^{73}Ge and ^{14}N NMR spectra were recorded of the resulting mixed chloride/thiocyanate species formed in solution [80]. In addition to $[\text{Ge}(\text{NCS})_6]^{2-}$, the formation of hexacoordinate species $[\text{GeCl}_2(\text{NCS})_4]^{2-}$ was detected as evidenced by the observation of an upfield feature at $\delta -434.8$ ppm. Three different resonances for the tetracoordinate species $\text{GeCl}_x(\text{NCS})_{4-x}$ were observed at $\delta 25.0, 20.0,$ and 14.0 as the ratio of GeCl_4 to KSCN was varied from 2:1 to equimolar to 1:2, but individual features could not be resolved. The upfield progression of this peak as the stoichiometric amount of KSCN was increased suggested that more chloride ligands are being replaced by thiocyanate ligands in the tetracoordinate species. Curiously, the formation of the heptacoordinate species $[\text{Ge}(\text{NCS})_7]^{3-}$ was postulated to have occurred when the ratio of GeCl_4 to KSCN was 1:10, as a signal in the ^{14}N NMR spectrum at $\delta -201.5$ ppm was observed. However, no feature in the ^{73}Ge NMR spectrum of this mixture was reported.

The linewidth at half-height ($\nu_{1/2}$) has been shown to vary with the presence or absence of hypercoordination in germanes. For example, the species shown in Scheme 5 are expected to contain a hypervalent germanium center resulting from the attachment of the oxygen atom of the organic side chain. The $\nu_{1/2}$ values for **5** and **6** are 370 and 580 Hz, respectively [3], indicating that the hypercoordinative interaction in **6** is stronger than that in **5**. Compound **6**, which contains a longer side chain than **5**, allows the formation of a five-membered ring in the six-coordinate compound, whereas in **5** only a four-membered ring would be possible.

The breadth of the ^{73}Ge NMR resonance is therefore correlated to the strength of the interaction. For example, the two compounds shown in Scheme 6 exhibit $\nu_{1/2}$ values of 30 and 165 Hz for **7** and **8**, respectively [52]. In this case, nitrogen is a stronger donor than oxygen and the

corresponding linewidth of the germane **8** is larger than that observed for **7** which contains only oxygen atoms as potential donors. Similarly, in the triaryl-substituted germanes **9–11** (Scheme 7), the strength of the donor interaction is expected to decrease with the identity of the donor atom in the order $N > O > S$ [53], and the order of $\nu_{1/2}$ values of these compounds follows the expected trend, measuring 900 Hz (**9**), 350 Hz (**10**), and 270 Hz (**11**). In addition, the steric bulk of the substituent in the oxygen substituted species has little effect on the observed $\nu_{1/2}$ values in these compounds, as the $\nu_{1/2}$ values for **9**, **12**, and **13** are all 350 Hz [53].

The ^{73}Ge NMR spectra of a series of oxygen- and sulfur-substituted germanes having tetrahedral molecular symmetry were acquired in order to investigate the effects of ligand structure on the chemical shift and lineshape of the ^{73}Ge resonances [8]. These data are collected in Table 6. Germanes having tetrahedral symmetry at germanium typically exhibit sharp lines that are easy to observe, but a loss of tetrahedral symmetry at germanium can result in significant broadening of the signal, even to the extent that no resonance is observed. In the data for compounds **14–24**, no resonances were observed for the two species **14** and **15** and it was assumed that some, but not all four, nitrogen atoms of the pendant $-\text{NMe}_2$ groups coordinate to the central germanium atom, resulting in a distortion of the tetrahedral symmetry and therefore loss of the ^{73}Ge NMR signal. Compounds **16** and **17** do have an observable resonances at $\delta -45$ and -44 ppm (resp.) that are significantly broadened with $\nu_{1/2}$ values of 103 and 101 Hz (resp.). The fact that **16** and **17** have observable ^{73}Ge NMR signals, while **14** and **15** do not, can be attributed to the fact that the longer alkyl groups separating the germanium-bound oxygen atoms in the former two compounds from the terminal $-\text{NMe}_2$ groups do not allow the $-\text{NMe}_2$ groups to approach the central germanium atom as closely as is possible in **14** and **15**, preserving the tetrahedral symmetry.

The identity of the terminal basic site, as well as that of the atom directly bound to germanium, also has observable effects on the ^{73}Ge NMR chemical shifts for the germanium atoms in these species. The $\nu_{1/2}$ values for the alkoxy-terminated compounds **19** and **20** are diminished relative to the amine-terminated species **14–17** since oxygen is a less basic, and therefore weaker coordinating, atom than nitrogen. No resonance was observed for $\text{Ge}[\text{O}(\text{CH}_2)_2\text{NMe}_2]$ (**15**) but a signal at δ 141 ppm for its sulfur-substituted analogue $\text{Ge}[\text{S}(\text{CH}_2)_2\text{NMe}_2]$ (**24**) was observed with a $\nu_{1/2}$ value of 79 Hz. This is due to the fact that the sulfur atoms in **24** that are bound to germanium render the germanium atom less electron deficient than the more electronegative oxygen atoms in **15**, such that hyperconjugation involving the terminal $-\text{NMe}_2$ groups in **24** is not as significant as that in **15**. These findings indicate that weak hyperconjugative interactions at the germanium center can result in broadening of the ^{73}Ge NMR resonance. However, these interactions are not sufficient enough to cause significant downfield shifting of the resonances as was observed for the hexacoordinate bipyridine germanes described in Table 5 [7]. Therefore, hyperconjugation in these molecules results in disruption of the tetrahedral symmetry at germanium which

TABLE 5: ^{73}Ge NMR data for hexacoordinate germanium complexes^a.

Compound	δ ^{73}Ge (ppm)
$\text{GeCl}_4(\text{bpy})$	-313.7
$\text{GeCl}_3(\text{NCS})(\text{bpy})$	-319.5
$\text{GeCl}_2(\text{NCS})_2(\text{bpy})$	-327.1
$\text{GeCl}(\text{NCS})_3(\text{bpy})$	-340.2
$\text{Ge}(\text{NCS})_4(\text{bpy})$	-351.8
$\text{GeCl}_4(\text{phen})$	-319.4
$[\text{Ge}(\text{NCS})_6]^{2-}$	-442.5

^a Data are referenced to GeMe_4 and are taken from [7]; bpy: 2,2'-bipyridine, phen: 1,10-phenanthroline.

TABLE 6: ^{73}Ge NMR spectral data for tetrahedrally substituted germanes $\text{Ge}(\text{OR})_4$ and $\text{Ge}(\text{SR})_4$ ^a.

Compound	δ ^{73}Ge (ppm)	$\nu_{1/2}$ (Hz)
$\text{Ge}[\text{O}(\text{CH}_2)_3\text{NEt}_2]_4$ (14)	n/r	
$\text{Ge}[\text{O}(\text{CH}_2)_3\text{NMe}_2]_4$ (15)	n/r	
$\text{Ge}[\text{O}(\text{CH}_2)_3\text{NMe}_2]_4$ (16)	-45	103
$\text{Ge}[\text{O}(\text{CH}_2)_4\text{NMe}_2]_4$ (17)	-44	101
$\text{Ge}[\text{O}(\text{CH}_2)_2\text{Pr}^i]_4$ (18)	-41	51
$\text{Ge}[\text{O}(\text{CH}_2)_3\text{OMe}]_4$ (19)	-43	75
$\text{Ge}[\text{O}(\text{CH}_2)_2\text{OMe}]_4$ (20)	-51	68
$\text{Ge}[\text{O}(\text{CH}_2)_2\text{CN}]_4$ (21)	-50	95
$\text{Ge}[\text{SBU}^n]_4$ (22)	120	39
$\text{Ge}[\text{SPR}^i]_4$ (23)	138	37
$\text{Ge}[\text{S}(\text{CH}_2)_2\text{NMe}_2]_4$ (24)	141	79

^a Data are referenced to Me_4Ge and are taken from [8]. n/r: no resonance observed. n/a: not reported.

TABLE 7: ^{73}Ge NMR data for the arylgermanes $\text{Ge}(\text{C}_6\text{H}_4\text{X})_4$ ^a.

X	δ ^{73}Ge (ppm)	$\nu_{1/2}$ (Hz)
H	-33.0	30
<i>o</i> -OMe	-41.6	75
<i>p</i> -OMe	-27.1	29
<i>o</i> -OEt	-39.6	86
<i>m</i> -OEt	-31.1	81
<i>p</i> -OEt	-24.6	33
<i>p</i> -Bu ^t	-29.5	26
<i>p</i> -Cl	-36.2	32
<i>m</i> -CF ₃	-30.4	28
<i>p</i> -CF ₃	-33.3	22
<i>m</i> -CH ₃	-32.9	11
<i>p</i> -CH ₃	-31.6	11

^a Data are referenced to Me_4Ge and are taken from [9].

in turn broadens the resonances for the germanium atom. This occurs before the coordination of the pendant ligand atoms can become sufficient enough to shift the ^{73}Ge NMR resonance downfield.

Similarly, the ^{73}Ge NMR spectra for series of aryl-substituted germanes were obtained to investigate the effects

TABLE 8: One-bond (1J) coupling constants for organogermanes.

Compound	1J (Hz)	Reference
MeGeH ₃	94.5	[2]
Me ₂ GeH ₂	92.3	[2]
Me ₃ GeH	93	[2]
EtGeH ₃	92.4	[2]
Et ₂ GeH ₂	88.7	[2]
Et ₃ GeH	88	[2]
GeH ₄	97.6	[2]
Ge ₂ H ₆	95.5	[2]
Ge ₃ H ₈	94 (GeH ₃) 90 (GeH ₂)	[2]
MeH ₂ GeGeH ₃	90.0	[2]
Me ₂ HGeGeH ₃	85	[2]
Me ₃ GeGeH ₃	90.7	[2]
(<i>p</i> -MeOC ₆ H ₄)GeH ₃	97	[4]
(<i>p</i> -MeOC ₆ H ₄) ₂ GeH ₂	n/a	[4]
(<i>p</i> -MeC ₆ H ₄)GeH ₃	96	[4]
MesGeH ₃	95	[4]
PhGeH ₃	98	[4]
Ph ₂ GeH ₂	94	[4]
Ph ₃ GeH	98	[4]

of hyperconjugation in these systems, and the data are collected in Table 7 [9]. These findings indicate that the amount of hyperconjugation occurring in this series of compounds is not as significant as in the alkoxy and thioalkoxy species **14–24**. The *ortho*-alkoxy derivatives Ge(C₆H₄-*o*-Me)₄ and Ge(C₆H₄-*o*-Et)₄ exhibit upfield chemical shifts and broader resonances than the other compounds listed in Table 7 which is attributed to the interaction of the oxygen atoms of the *ortho*-substituents with the central germanium atom.

6. One-Bond Coupling of Germanium to Hydrogen in ^{73}Ge NMR Spectra

As mentioned above, the 1J value for GeH₄ was determined to be 87.77 ± 0.03 [46] or 97.6 Hz [47]. In 1987, coupling constant data for thirteen additional compounds were reported and these data are collected in Table 8 [2]. The higher 1J coupling constant for GeH₄ was also confirmed as this species was reported to have a one-bond coupling constant of 97.6 ± 0.3 Hz. The 1J coupling constants reported by Wilkins et al. [2] range from 85 ± 2 to 97.6 ± 0.3 Hz. In comparing the series of methylgermanes Me_{*x*}GeH_{4-*x*} and ethylgermanes Et_{*x*}GeH_{4-*x*}, it was observed that the magnitude of the coupling constant increases as the number of hydrogen atoms increases that is a result of the increasing amount of s-character present in the Ge–H bonds. This study also represents the first dissemination of coupling constant data for oligogermanium compounds, which are catenated species that in this case have single Ge–Ge bonds.

TABLE 9: ^{73}Ge NMR spectral data for linear oligogermanes^{a,b}.

Compound	δ ^{73}Ge (ppm)	$\nu_{1/2}$ (Hz)	Reference
Ge ₂ H ₆ (25)	–312	13	[10]
Ge ₃ H ₈ (26)	–298 –310	25 40	[10]
Ge ₄ H ₁₀ (27)	–284 –300	76 100	[10]
MeH ₂ GeGeH ₃ (28)	–306 –210	2 13	[10]
MeH ₂ GeGeH ₂ Me (29)	–209	7	[10]
Me ₂ HGeGeH ₃ (30)	–296 –127	7 3	[10]
Me ₃ GeGeH ₃ (31)	–296 –48	13 63	[10]
MeH ₂ GeGe(MeH)GeH ₂ Me (32)	–206 –125	2 8	[10]
Me ₂ ClGeGeH ₃ (33)	–281	39	[11]
Ge ₂ Me ₆ (34)	–59	n/r	[11]
Ge ₂ Et ₆ (35)	–35	n/r	[12]
Ge ₂ Ph ₆ (36)	–67	90	[11]
Et ₃ GeGePh ₃ (37)	–64	270	[13]
Pr ^{<i>i</i>} ₃ GeGePh ₃ (38)	–56 –65	80 240	[13]
Bu ^{<i>n</i>} ₃ GeGePh ₃ (39)	–58 –65	100 340	[13]
Bu ^{<i>s</i>} ₃ GeGePh ₃ (40)	–52	30	[13]
PhMe ₂ GeGePh ₃ (41)	–65	90	[13]
Ph ₃ GeGeBu ^{<i>n</i>} ₂ L (42)	–57 –64	90 330	[13]
Ph ₃ GeGeBu ^{<i>n</i>} ₂ GeBu ^{<i>n</i>} ₂ L (43)	–57 –63	310 310	[13]
Ph ₃ GeGeBu ^{<i>n</i>} ₂ GePh ₂ L (44)	–54 –65	120 390	[13]
LBu ^{<i>n</i>} ₂ GeGePh ₂ GeBu ^{<i>n</i>} ₂ L (45)	–111	180	[13]
LPh ₂ GeGePh ₂ GePh ₂ L (46)	–121	170	[13]

^aData are referenced to Me₄Ge.

^bL: CH₂CH₂OEt.

TABLE 10: ^{73}Ge NMR data for branched oligogermanes.

Compound	δ ^{73}Ge (ppm)	Reference
PhGe(GeBu n) $_3$ (47)	-33	[13]
	-195	
PhGe(GePh $_3$) $_3$ (48)	-202	[13]
HGe(GePh $_3$) $_3$ (49)	-56	[14]
	-311	
Ge(GeMe $_3$) $_4$ (50)	-38	[15]
	-339	
PhGe(GeBu n) $_2$ CH $_2$ CH $_2$ OEt) $_3$ (51)	-43	[13]
	-203	
PhGe(GeBu n) $_2$ Bu n) $_2$ CH $_2$ CH $_2$ OEt) $_3$ (52)	-38	[13]
	-209	

In comparing the series of parent oligogermanes Ge $_n$ H $_{2n+2}$, the $^1J_{\text{Ge-H}}$ coupling constants become successively smaller as the degree of catenation increases.

The $^1J_{\text{Ge-H}}$ coupling constants for seven different arylgermanes were reported in 1999 and are collected in Table 8, and the ^{73}Ge NMR spectra of PhGeH $_3$, Ph $_2$ GeH $_2$, Ph $_3$ GeH, and MesGeH $_3$ (Mes = 2,4,6-trimethylphenyl) are shown in Figure 4 [4]. The chemical shifts for these species show the expected trend, in that as hydrogen atoms are exchanged for aryl groups in the general formula Ar $_x$ GeH $_{4-x}$ the resonances for these species shift progressively upfield (Table 3). The ^{73}Ge NMR spectra of each of these species, with the exception of (*p*-MeOC $_6$ H $_4$) $_2$ GeH $_2$ that was observed as a single line, show the appropriate number of lines, as resonances for the ArGeH $_3$ compounds were all observed as quartets, that for Ph $_2$ GeH $_2$ was observed as a triplet, and that for Ph $_3$ GeH was found to be a doublet. The coupling constants in these species all fall into the range of ca. 85–100 Hz found for the simple germanes mentioned above.

7. ^{73}Ge NMR Spectra of Oligogermanes

As part of our extensive investigations on the chemistry of discrete oligogermanes [13–15, 81–89], we recently reported an investigation of the ^{73}Ge NMR spectra of several oligogermanes [13], which furthers the studies conducted by Wilkins et al. [2] and Thomson et al. [11]. The data from these three studies are shown in Table 9. In all cases it has been determined that the presence of hydrogen attached to a germanium center results in a significant upfield shift of the resonances for these compounds.

The parent germanes Ge $_n$ H $_{2n+2}$ (25–27) exhibit resonances with chemical shifts ranging from δ -284 to -312 ppm [2], where resonances for the terminal -GeH $_3$ germanium atoms appear downfield from those of the internal -GeH $_2$ - atoms. For the mixed methyl/hydrogen-substituted oligogermanes 28–32, resonances for germanium atoms bearing methyl substituents appear downfield from those having only hydrogen atoms bound to germanium [2].

For example, in MeH $_2$ GeGeH $_3$ (28) the resonance for the -GeH $_3$ atom appears at δ -306 ppm while that for the -GeH $_2$ Me atom was observed at δ -210 ppm. In the more highly methyl substituted oligogermane Me $_2$ HGeGeH $_3$ (30) the resonance for the -GeHMe $_2$ atom appears at δ -127 ppm and in Me $_3$ GeGeH $_3$ (31) the resonance for the -GeMe $_3$ atom appears at δ -48 ppm [2]. Only one resonance was observed in the ^{73}Ge NMR spectrum of Me $_2$ ClGeGeH $_3$ (33) at δ -281 ppm arising from the -GeH $_3$ atom [11]. No resonance was observed for the -GeMe $_2$ Cl atom due to the presence of the single chlorine atom that results in excessive broadening of the signal for the germanium atom to which it is attached.

The presence of aryl substituents in place of alkyl substituents also affects an upfield shift of the ^{73}Ge NMR resonance, albeit to a significantly lesser extent than what is observed for hydrogen substituents. The single resonance for the permethyl- and perethyl-substituted digermanes Ge $_2$ Me $_6$ (34) [11] and Ge $_2$ Et $_6$ (35) [12] was observed at δ -59 and -35 ppm (resp.) while that for Ge $_2$ Ph $_6$ (36) [11] was observed upfield at δ -67 ppm. This was also observed in several oligogermanes of the general formula R $_3$ GeGePh $_3$ (37–42) [13]. In cases where a resonance was observed for both the phenyl-substituted germanium -GePh $_3$ and the alkyl-substituted germanium -GeR $_3$, the resonance for the -GePh $_3$ group was consistently observed upfield from that of the -GeR $_3$ group. This can be seen in the two compounds Pr $_3$ GeGePh $_3$ (38) and Bu $_3$ GeGePh $_3$ (39) where the resonance for the phenyl-substituted germanium atom both appeared at δ -65 ppm while those for the alkyl-substituted atom were observed at δ -56 and -58 ppm (resp.).

A resonance for the alkyl-substituted germanium atom in Et $_3$ GeGePh $_3$ (37) and PhMe $_2$ GeGePh $_3$ (41) was not observed [13]. In the case of 37, it is unclear why this was so, but it can be argued in 41 the different electronic nature of the single phenyl and two methyl substituents bound to germanium result in a significant enough distortion of the electric field gradient to affect rapid quadrupolar relaxation resulting in a broad, unobservable resonance. These effects are subtle, however, as shown by Ph $_3$ GeGeBu n) $_2$ CH $_2$ CH $_2$ OEt (42) that contains two *n*-butyl substituents and an ethoxyethyl group as ligands at the -GeR $_3$ atom [13]. Two resonances were observed for 42 at δ -57 and -64 ppm corresponding, respectively, to the alkyl- and phenyl-substituted germanium atoms. Here, the electronic nature of the *n*-butyl and ethoxyethyl groups is relatively similar, at least in the proximity of the germanium atom, and therefore it is likely that the electronic field gradient at germanium in this case is symmetric enough to allow observation of a resonance. Curiously, we have found no evidence for hypercoordination in 42 or in its related long-chain analogues (*vide infra*), despite the fact that the oxygen atom of the -CH $_2$ CH $_2$ OEt substituent could coordinate to the germanium atom to form a germaoxacyclobutane (Scheme 8).

Prior to our investigations, the only linear oligogermanes having more than two catenated germanium atoms in the chain to be investigated by ^{73}Ge NMR spectroscopy were Ge $_3$ H $_8$ (26), Ge $_4$ H $_{10}$ (27), and MeH $_2$ GeGe(MeH)GeH $_2$ Me

TABLE 11: Solid state and solution ^{73}Ge NMR data for organogermanes^a.

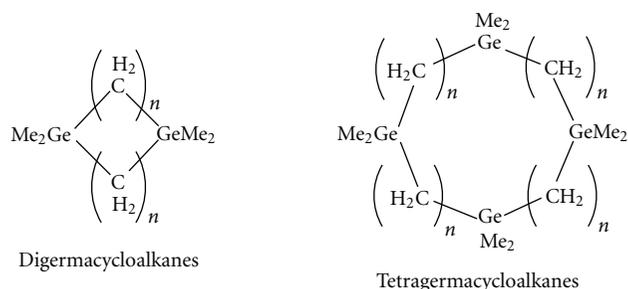
Compound	Solid state		Solution	
	δ ^{73}Ge (ppm)	$\nu_{1/2}$ (Hz)	δ ^{73}Ge (ppm)	$\nu_{1/2}$ (Hz)
Ph_4Ge	-32.9	15	-31.6	6.0
$(p\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Ge}$	n/o		-10.3	28
$(p\text{-MeOC}_6\text{H}_4)_4\text{Ge}$	10.8	48	-11.3	34
$(o\text{-MeC}_6\text{H}_4)_4\text{Ge}$	-28.2	342	-33.1	18.5
$(m\text{-MeC}_6\text{H}_4)_4\text{Ge}$	-32.2	391	-32.9	11.4
$(p\text{-MeC}_6\text{H}_4)_4\text{Ge}$	-32.4	400	-31.6	11.3
$(p\text{-PhC}_6\text{H}_4)_4\text{Ge}$	-32.1	78	-31.5	12.5
$(p\text{-FC}_6\text{H}_4)_4\text{Ge}$	-30.5	300	nss	
$(\text{C}_6\text{F}_5)_4\text{Ge}$	-22.0	225	-27.8	12.7
$(\text{PhCH}_2)_4\text{Ge}$	0.14	350	0.04	24.0
$(1\text{-adamantyl})_4\text{Ge}$	-24.6	260	nss	
$\text{Ph}_2\text{Ge}(p\text{-Tol})_2$	-28.8	450	-31.9	35.6
$\text{Ph}_3\text{Ge}(p\text{-Tol})$	-26.0	430	-32.5	22.4
$(o\text{-Tol})_3\text{GeH}$	n/o		-84	70
$(o\text{-MeOCH}_2\text{C}_6\text{H}_4)_3\text{GeH}$	n/o		-85	350

^a Referenced to GeMe_4 , data from [16]. n/o: not observed, nss: not sufficiently soluble.

TABLE 12: Data for Scheme 2.

n	Ring size	δ ^{73}Ge (ppm)	$\nu_{1/2}$ (Hz)
Digermacycloalkanes			
$n = 4$	10	6.2	67
$n = 5$	12	n/a	
$n = 6$	14	5.0	35
$n = 8$	18	3.5	45
$n = 10$	22	1.9	100
Tetragermacycloalkanes			
$n = 4$	20	5.0	60
$n = 5$	24	6.2	100
$n = 6$	28	1.9	70
$n = 8$	36	1.2	130
$n = 10$	44	5.0	120

(32) [2], and we have obtained ^{73}Ge NMR spectra for four additional linear oligogermanes [13] as well as six branched oligogermanes [13–15, 88]. Data for the linear oligogermanes **43**–**46** are collected in Table 9. Two resonances, instead of the expected three, were observed for the trigermanes **43** and **44** [13]. Based on the chemical shifts of these peaks, these are assigned to the two terminal germanium atoms since a resonance for the central $-\text{GeBu}^n-$ atom in **43** and **44** would be expected to appear between δ -110 to -125 ppm. Specifically, the features at δ -63 (**43**) and -65 (**44**) ppm are due to the terminal $-\text{GePh}_3$ atom, while those at δ -57 (**43**) and -54 (**44**) ppm are assigned to the $-\text{GeR}_2\text{L}$ atom. For the trigermanes **45** and **46**, resonances for only the central germanium atoms were observed at δ -111 (**45**) and -121 (**46**) ppm [13]. These data suggest that the central germanium atoms in **45** and **46** have a symmetric electronic environment at germanium, as they each have a ligand set consisting of two phenyl



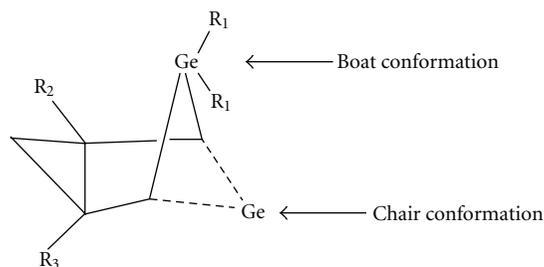
SCHEME 2: Structures of germanium-containing macrocycles. Adapted from [49].

substituents and two $-\text{GeR}_2\text{L}$ groups. However, the different germyl substituents attached to the central germanium atoms in **43** and **44** appear to render the electronic environment at the central germanium atom significantly unsymmetrical to broaden the resonances for these atoms.

The ^{73}Ge NMR spectra of the branched oligogermanes $\text{PhGe}(\text{GeR}_3)_3$ (**47**: $\text{R} = \text{Bu}^n$; **48**: $\text{R} = \text{Ph}$) [13], $\text{HGe}(\text{GePh}_3)_3$ (**49**) [14, 88], $\text{Ge}(\text{GeMe}_3)_4$ (**50**) [15], $\text{PhGe}(\text{GeBu}^n_2\text{CH}_2\text{CH}_2\text{OEt})_3$ (**51**) [13], and $\text{PhGe}(\text{GeBu}^n_2\text{Bu}^n_2\text{CH}_2\text{CH}_2\text{OEt})_3$ (**52**) [13] have been reported, and these data are collected in Table 10. In these compounds, the central germanium atom is formally germanium(I) with the exception of **50**, where it is formally germanium(0). Therefore, resonances corresponding to these Ge atoms are expected to appear upfield from those for the internal germanium atoms of linear tri- and higher oligogermanes. The ^{73}Ge NMR for **49** was reported in 1999, where the resonance for the central germanium atom appeared as a singlet at δ -314 ppm and a feature for the three peripheral germanium atoms was not observed [11].

TABLE 13: Data for Scheme 3.

Compound	R ₁	R ₂	R ₃	δ ⁷³ Ge (ppm)
1	Me	H	H	57
2	Et	H	H	76
3	Et	Me	H	82
4	Et	Me	Me	46

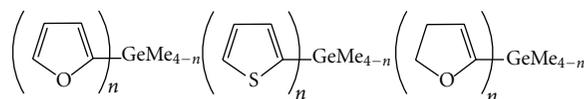


SCHEME 3: Conformations of substituted germacyclohexanes. Adapted from [50].

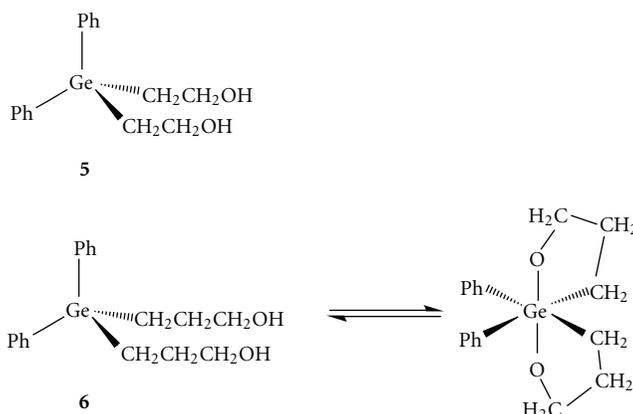
The resonance in this case was broad, with a half-height linewidth of 200 Hz.

We acquired the proton-decoupled ⁷³Ge NMR spectrum of **49** that contained a doublet centered at δ -311 ppm with a ¹J coupling constant of 191 Hz [14]. A second resonance at δ -56 ppm ($\nu_{1/2}$ = 35 Hz) was also observed for the peripheral -GePh₃ atoms. The doublet at δ -311 ppm converges a broad singlet with a $\nu_{1/2}$ value of 210 Hz when the proton-coupled ⁷³Ge NMR spectrum was acquired. The coupling constant observed for **49** is on the order of twice that observed for all other compounds (*vide supra*) including those for linear oligogermanes. To our knowledge no other coupling constant data for branched compounds like **50** has been reported, and therefore the presence of branching at the central germanium atom in **50** might be due to the larger coupling constant observed for this species relative to other systems.

The resonance for the central germanium atom in **49** is significantly shifted upfield by over 100 ppm relative to that in the related systems **47** and **48** that were observed at δ -195 and -202 ppm (resp.) [13]. The upfield shift observed for the central germanium atom of **49** is similar to data reported for linear oligogermanes. As mentioned above, the resonance for the hydrogen-substituted germanium atom in MeH₂GeGeH₂Me (**29**) is shifted upfield from that in Ge₂Me₆ (**34**) by 150 ppm [2]. A sharp resonance for the central germanium atom in Ge(GeMe₃)₄ (**50**) was observed at δ -339 ppm with a $\nu_{1/2}$ value of 9 Hz [15]. The sharpness of this resonance can be attributed to the highly symmetric geometric environment at the central germanium atom, which is expected to closely approach the ideal tetrahedral environment in solution. This is not true for **48** [86], for which the X-ray crystal structures have been determined, and likely would not be the case for the *n*-butyl-substituted compound **47** that has not been crystallographically characterized. Compounds **47** and **48** have $\nu_{1/2}$ values of 240



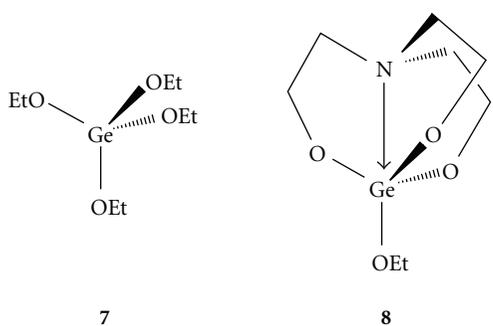
SCHEME 4: Structures of heterocycle-substituted methylgermanes. Adapted from [51].

SCHEME 5: Fluxional behavior of *n*-propanol-substituted germanes. Adapted from [3].

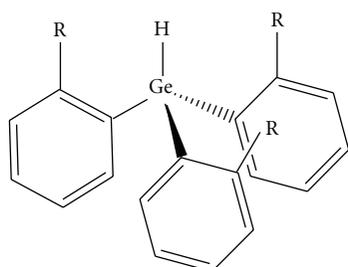
and 290 Hz (resp.) for the resonances corresponding to their central germanium atoms [13].

8. Solid-State ⁷³Ge NMR Spectroscopy (⁷³Ge SSNMR Spectroscopy)

The difficulties encountered in solution ⁷³Ge NMR spectroscopy stemming from the low gyromagnetic ratio and large quadrupole moment of the ⁷³Ge nucleus are expected to be compounded in solid-state ⁷³Ge NMR (⁷³Ge SSNMR) spectroscopy. As a result, the first report of a solid-state magic angle spinning (MAS) ⁷³Ge NMR investigation did not appear until 2000 [90], where the two organogermanes Ph₄Ge and (PhCH₂)₄Ge were investigated due to their high symmetry in their X-ray crystal structures [91, 92]. The proton-decoupled MAS spectrum of Ph₄Ge exhibited a single resonance at δ -31.0 ppm with a $\nu_{1/2}$ value of 40 Hz, while the proton-coupled spectrum contained a single resonance also at δ -31.0 ppm that was slightly broader ($\nu_{1/2}$ = 49 Hz). This is shifted slightly from the solution state chemical shift of δ -33.2 ppm and is expectedly broader than the resonance observed solution ($\nu_{1/2}$ = 5.9 Hz) [2, 60]. For (PhCH₂)₄Ge, the chemical shift was observed at δ 0.14 ppm ($\nu_{1/2}$ = 350 Hz) in the proton-decoupled MAS ⁷³Ge SSNMR spectrum, where the chemical shift value is again similar to the solution state value of δ 0.04 ppm. It was postulated that the resonance in the ⁷³Ge SSNMR for (PhCH₂)₄Ge is significantly broadened compared to Ph₄Ge since the latter species has idealized S₄ symmetry (*T_d* point group symmetry) and thus has only one crystallographically unique phenyl ring [91] in the crystalline state while then benzyl derivative does not [92].

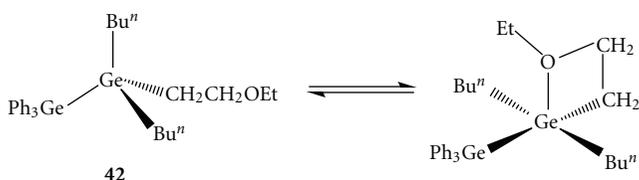


SCHEME 6: Structures of compounds 7 and 8. Adapted from [52].



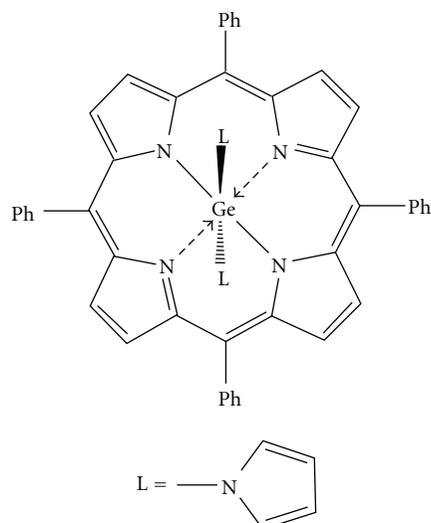
- (9) R = CH₂SMe
- (10) R = CH₂NMe₂
- (11) R = CH₂OMe
- (12) R = CH₂OEt
- (13) R = CH₂OBu^t

SCHEME 7: Structures of triaryl-substituted germanes. Adapted from [53].



SCHEME 8: Fluxional behavior of ethoxyethyl-substituted oligogermanes.

The spin-lattice relaxation times (T_1) of Ph₄Ge and (*p*-C₆H₅C₆H₄)₄Ge in the solid state were also determined [93]. Obtaining a T_1 value for (PhCH₂)₄Ge was precluded due to its large $\nu_{1/2}$ value. The T_1 value for Ph₄Ge, obtained by the inversion-recovery method, was found to be 2.6 s, which is significantly longer than the solution phase T_1 of 0.42 s. The T_1 for (*p*-PhC₆H₄)₄Ge was determined to be 1.2 s. The T_1 value for powdered germanium was also measured to be 10.6 s with MAS [93] which was similar to the previously reported value of 11.0–12.4 s that was obtained without MAS [94]. The use of MAS also results in a sharper resonance for powdered germanium of $\nu_{1/2} = 18$ Hz versus $\nu_{1/2} = 60$ Hz that was obtained without MAS. The $\nu_{1/2}$ value with MAS for germanium powder also was found to increase to 230 Hz [93]

SCHEME 9: Structure of bis(1-pyrrolyl)(*meso*-tetraphenylporphyrinato)germanium. Adapted from [54].

when isotopically enriched germanium (>98% ⁷³Ge) was used with no change in T_1 due to the homonuclear dipolar interaction occurring between identical isotopes [60].

An attempt to obtain the MAS ⁷³Ge SSNMR spectra of eight other tetrahedrally substituted germanes, as well as four other compounds having lower symmetry, resulted in success in all but three of the cases, and the results are collected in Table 11 [16]. The chemical shifts of all compounds that could be observed were the same as those observed in solution within ± 6 ppm, with the exception of (*p*-MeOC₆H₄)₄Ge that exhibited a resonance at δ 10.8 ppm in the solid state versus δ -11.3 ppm in solution. Of the fifteen compounds that were investigated by ⁷³Ge SSNMR, Ph₄Ge exhibited the sharpest resonance while (*p*-MeOC₆H₄)₄Ge and (*p*-C₆H₅C₆H₄)₄Ge had $\nu_{1/2}$ values of less than 100 Hz. However, the $\nu_{1/2}$ for Tol₄Ge (Tol = *p*-CH₃C₆H₄) was 400 Hz, which is on the order exhibited by the nonsymmetric species Ph₂GeTol₂ and PhGeTol₃ of 450 and 430 Hz (resp.). The crystal structure of Tol₄Ge has Ge–C_{ipso} bond lengths ranging from 1.941(4) to 1.958(5) Å [95] and therefore lacks the idealized S₄ symmetry of Ph₄Ge. This was the first suggestion that ⁷³Ge SSNMR is highly sensitive to the local environment at the germanium center. Furthermore, the observation of resonances for Ph₂GeTol₂ and PhGeTol₃, which contain only slightly different substituents at germanium, suggested that ⁷³Ge SSNMR studies on compounds with less than full symmetry should be possible.

The first report on the ⁷³Ge SSNMR of hexacoordinate germanium compounds was published in 2004 [54]. The first investigation focused on GeI₂, which was shown to have six iodine atoms disposed around germanium in an octahedral environment [96]. The ⁷³Ge SSNMR spectrum for GeI₂ exhibited a single resonance at δ -213.4 ppm with $\nu_{1/2} = 270$ Hz. A resonance for GeI₂ in solution could not be observed. The ⁷³Ge SSNMR spectrum of GeI₄ exhibited a single resonance at

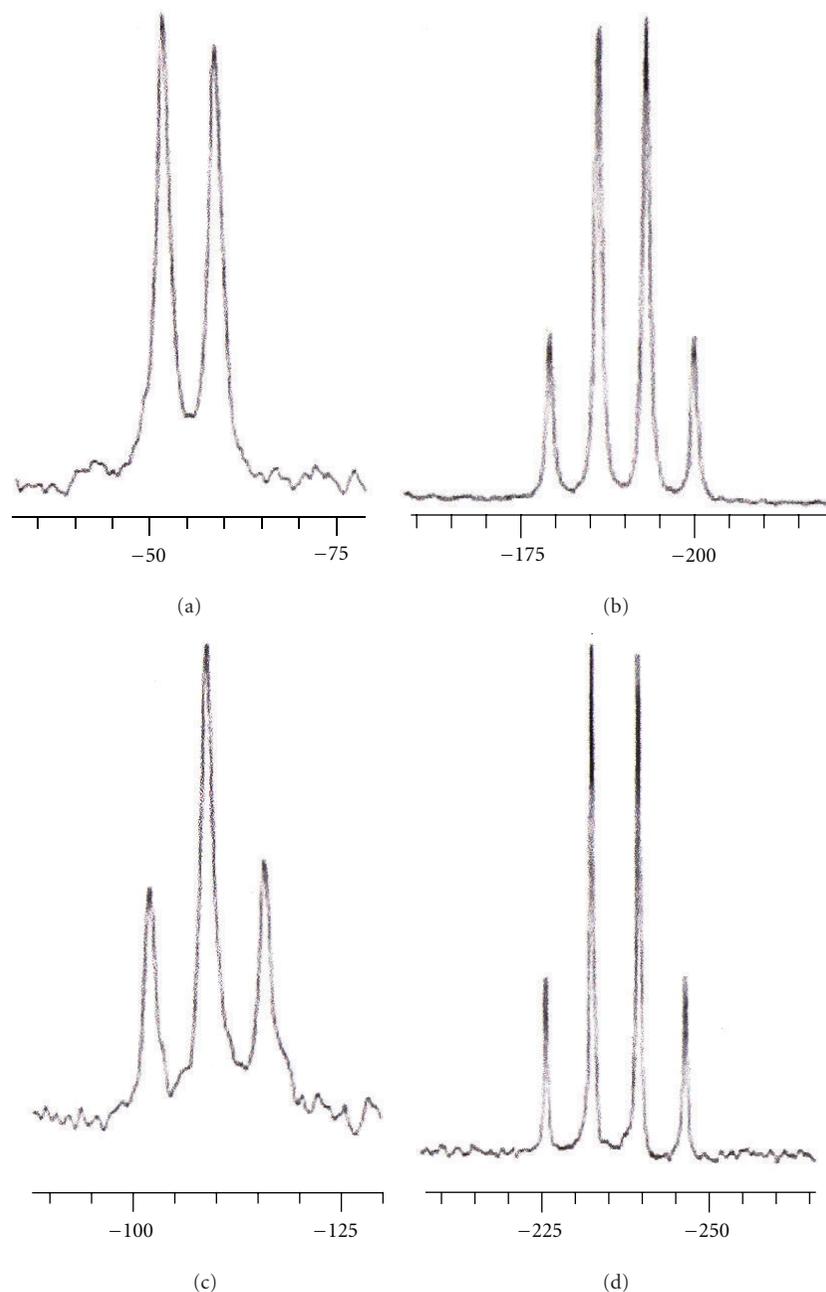


FIGURE 4: Proton-coupled ^{73}Ge NMR spectra of Ph_3GeH (a), PhGeH_3 (b), Ph_2GeH_2 (c), and MesGeH_3 (d). Reproduced with permission from [4]. Copyright 1999 American Chemical Society.

δ -1171 ppm with $\nu_{1/2} = 950$ Hz [54] where the chemical shift was similar to the value obtained in solution at δ -1117 ppm ($\nu_{1/2} = 4.8$ Hz) [23]. The ^{73}Ge SSNMR spectrum of the germanium porphyrin bis(1-pyrrolyl)(*meso*-tetraphenylporphyrinato)germanium (Scheme 9) revealed a single resonance at δ -259 ppm ($\nu_{1/2} = 156$). The germanium center in this species is surrounded by six pyrrolyl moieties and the porphyrin ring bears four identical phenyl substituents therefore rendering a symmetric environment at germanium. Replacing the two axial pyrrole substituents with other ligands, including chloride, methyl, or phenyl, did

not allow the observation of a signal in the solid state nor in solution.

Increases in sensitivity have been realized by the use of ultrahigh field magnets that have become more readily available in recent years. Several new pulse sequences have also assisted in the acquisition of meaningful ^{73}Ge SSNMR spectra. This includes the quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) sequence that involves acquisition of a quadrupolar echo spectrum during the Carr-Purcell-Meiboom-Gill sequence and results in a two- to thirtyfold increase in sensitivity when compared to results when a

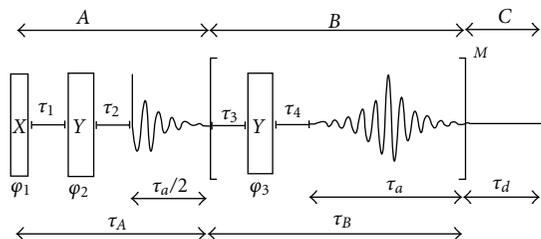


FIGURE 5: The QCPMG pulse sequence. Reproduced from [55] with permission. Copyright 1997 American Chemical Society.

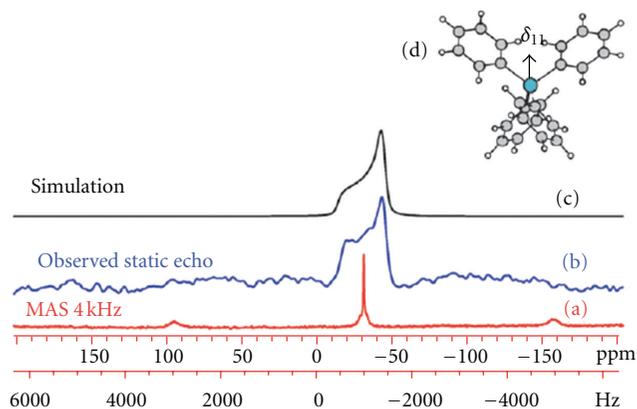


FIGURE 6: ^{73}Ge SSNMR spectra of GePh_4 using ^{73}Ge MAS (a) and static-echo (b) techniques. The simulated spectrum is shown in (c). Reproduced from [56] with permission. Copyright 2010 Royal Society of Chemistry.

normal quadrupolar echo sequence is applied [55]. The pulse sequence is shown in Figure 5. Other modified QCPMG pulse sequences have been developed that are of use in this regard as well, including the double-frequency sweep (DFS-QCPMG) and rotor-assisted population transfer (RAPT-QCPMG) sequences [97]; combination of a hyperbolic-secant π -inversion pulse to the QCPMG sequence [98], and application of the WURST-QCPMG (WURST = wideband uniform-rate smooth truncation) sequence [99] have also led to improved spectra.

The ^{73}Ge NMR spectrum of GeO_2 had been initially determined in neutral aqueous solution and displayed a single resonance at -16.7 ppm with a $\nu_{1/2}$ value of 22 Hz despite the low solubility of GeO_2 in water. The addition of triethylamine increased the solubility of GeO_2 but also resulted in the appearance of a resonance at -269.1 ppm that was assigned to the formation of the $[\text{Ge}(\text{OH})_6]^{2-}$ anion [100]. The ^{73}Ge spin-echo SSNMR of GeO_2 was successfully collected at a field strength of 18.8 T where the ^{73}Ge nucleus resonates at 27.9 MHz ($^1\text{H} = 800$ MHz) and isotropic chemical shift (δ_{iso}) was found to be in the range of 50 to -100 ppm [101]. The quadrupolar coupling constant (C_Q) was determined to be between 8 and 10 MHz. The isotopic disorder in crystalline GeO_2 has been investigated using ^{73}Ge SSNMR spectroscopy as well [102].

The ^{73}Ge SSNMR spectra of $\text{GeCl}_2 \cdot \text{dioxane}$ and GePh_4 were acquired at a field strength of 21.1 T, where the resonance frequency of the ^{73}Ge nucleus is 31.4 MHz ($^1\text{H} = 900$ MHz) [56]. The $\text{GeCl}_2 \cdot \text{dioxane}$ complex does not have high symmetry at the germanium center since it is formally bound to two chlorine atoms and datively bound to the two oxygen atoms of the coordinated dioxane molecule. It does, however, possess *pseudo*-octahedral coordination due to the presence of two additional nonbonded chlorine atoms from neighboring molecules [103]. Nevertheless, the low symmetry at the germanium center rendered acquisition of its ^{73}Ge SSNMR spectrum tedious, requiring the acquisition of 23 piecewise frequency-stepped QCPMG subspectra and a total acquisition time of 115 hours.

The ^{73}Ge quadrupolar coupling constant was determined to be 44(2) MHz and is the largest such value to be determined at the time the spectrum was determined, resulting from the lack of a spherical environment at the germanium center in $\text{GeCl}_2 \cdot \text{dioxane}$. The δ_{iso} was determined to be 1110 ppm with a rather large uncertainty of 250 ppm, indicating that the divalent ^{73}Ge nucleus in this species is more deshielded than that of GeI_2 that has a chemical shift of $\delta -213$ ppm [54]. Both $\text{GeCl}_2 \cdot \text{dioxane}$ and GeI_2 are more deshielded than their corresponding tetravalent germanium analogues GeCl_4 ($\delta 30.0$ ppm) [22] and GeI_4 ($\delta -101.8$ ppm) [22] due to the lower formal oxidation state of germanium.

The acquisition of the ^{73}Ge SSNMR spectrum of GePh_4 at high field was considerably more facile, again due to the high S_4 symmetry at germanium in this species. The δ_{iso} of GePh_4 was determined to be -30 ppm [56] which is nearly identical to the value of $\delta -31.0$ ppm determined by MAS ^{73}Ge SSNMR spectroscopy [90]. The use of a high field spectrometer also permitted, for the first time, direct observation of the ^{73}Ge NMR chemical shift anisotropy (CSA). The measurement of CSA is not possible for quadrupolar nuclei at low field since the magnitude of the second-order quadrupolar interaction is large compared to the CSA. However, at high field, this problem is diminished and the CSA can be extracted from the spectrum. The spectral results, as well as the simulated spectrum, are shown in Figure 6. A value for the span (Ω) was determined to be 30(3) ppm and the skew (κ) has a value of -1 indicating the presence of an axially symmetric ^{73}Ge chemical shift tensor, as it should be at a germanium center having S_4 symmetry. The quadrupolar coupling constant (C_Q) is not zero and had an upper limit of 0.3 MHz, which is also indicated in the MAS spectrum by the presence of spinning side bands that arise from satellite transitions. The CS tensor contains one unique component δ_{11} that was shown to be oriented along the 2-fold axis at the germanium center that bisects the $C_{\text{ipso}}-\text{Ge}-C_{\text{ipso}}$ bond angle. The $C_{\text{ipso}}-\text{Ge}-\delta_{11}$ angle is 54.59° in this system.

These recent findings suggest that ^{73}Ge SSNMR spectroscopy can become a viable and useful tool for the study of a diverse array of germanium compounds. From these types of investigations a variety of structural and bonding information can be obtained. Further advances in instrumentation and software will likely continue to make such investigations more facile.

Acknowledgment

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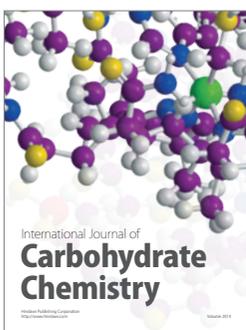
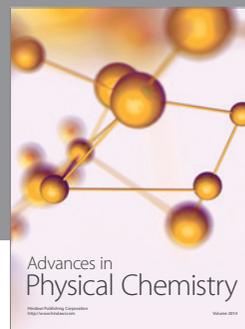
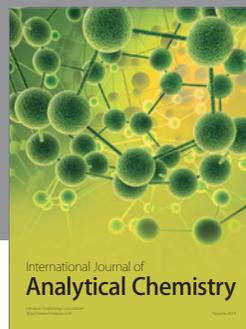
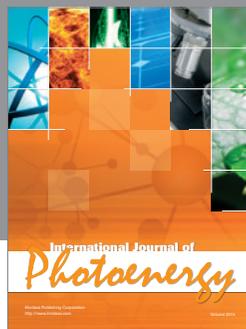
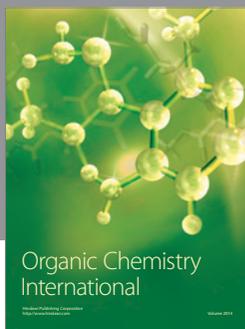
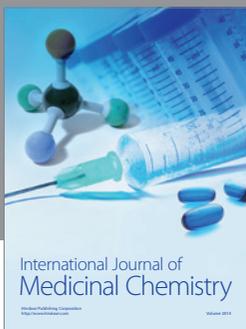
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