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Review

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^{73}Ge NMR spectroscopic studies of organogermanium compounds *

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Abstract

The literature, and the authors' own data, on the ^{73}Ge NMR spectra of organogermanium compounds are critically assessed. The experimental techniques for the observation of ^{73}Ge NMR spectra, the mechanisms for ^{73}Ge nuclear relaxation, as well as relationships between the ^{73}Ge chemical shifts and those of other Group 14 elements or substituent electronegativities, are discussed. ^{73}Ge coupling constants and similar couplings, including other Group 14 elements, are compared.

Introduction

Historically, the development of ^{73}Ge NMR spectroscopy can be divided into three periods. The first period covers the early 1950s, when the ^{73}Ge signal had been registered for the first time for $GeCl_4$, followed by the determination of the ^{73}Ge resonance frequency and nuclear magnetic moment [1,2].

The magnetic moment for germanium at 1.48 MHz in a field of 1 T was found to be $\mu = -(0.87678 \pm 0.0001)\mu_N$ for pure $GeCl_4$, without diamagnetic correction [1], which coincides with the value measured 20 years later, viz. $\mu = -(0.87678 \pm 0.00001)\mu_N$ [3]. The resonance frequency for ^{73}Ge in $GeCl_4$ is comparable with absorption frequencies for other nuclei. It has been demonstrated for $GeMe_4$, used as a reference compound in ^{73}Ge NMR experiments, that the resonance frequency for the ^{73}Ge nuclei is $\nu = 3488315 \pm 10$ Hz at a field intensity of 1.807 T [3–6].

The second period started in the 1970s, when chemical shifts were measured for the germanium tetrahalides $GeX_{4-n}Y_n$ [3,7], and for four tetraalkylgermanes GeR_4 [3], along with several spin–spin coupling constants for the last compounds. Spin–spin relaxation times are determined for the ^{73}Ge nuclei [3], and the first review dedicated to ^{73}Ge NMR spectroscopy was published [8].

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* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.

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The third period, unfolding in the 1980s, is characterized by an upsurge of interest in ^{73}Ge resonance studies. The earlier obtained results have been tested [9]. ^{73}Ge NMR spectra have been examined for a number of unsymmetrical derivatives of tetraalkylgermanes [10], germatranes [11,12], and tetraalkoxygermanes [13]. The mechanism of spin-lattice relaxation for the ^{73}Ge nuclei has been explored [14,15], and quadrupole coupling constants for ^{73}Ge nuclei determined [14]. The INEPT technique has been introduced for obtaining ^{73}Ge NMR spectra of alkylgermanes [16]. The applicability of ^{73}Ge NMR spectroscopy to conformational analysis [17] has also been demonstrated.

Until recently, the usefulness of ^{73}Ge NMR spectroscopic studies for analytical purposes has been questioned repeatedly [8]. However, the present situation in this field is rapidly changing. This implies a need for reevaluation of experimental results obtained in ^{73}Ge NMR studies. The present review surveys literature data published up to the year 1987.

The experimental techniques

The only magnetically active isotope of germanium, ^{73}Ge, is highly unfavourable to magnetic resonance studies [18]: low natural abundance (7.6%), very small gyromagnetic ratio ($\gamma = -0.9332 \times 10^7$ rad T^{-1} s^{-1}), large spin quantum number ($I = 9/2$) and comparatively large quadrupole moment ($Q = -0.22$ barn) determine the receptivity of this nucleus being very small: it is only 1.08×10^{-4} relative to ^{1}H, at equal field strength. In addition, the predominance of the quadrupolar relaxation mechanism leads to considerable broadening of resonance signals, amplifying the difficulties of ^{73}Ge observations. Therefore, high concentrations of samples are required to obtain ^{73}Ge NMR spectra.

Historically, the first measurements of ^{73}Ge resonances [1,2] were performed on continuous wave spectrometers. Spectra were recorded as absorption peaks or as dispersion signals under the condition of adiabatic rapid passage. The large linewidths in these studies originate from the small homogeneity of the magnetic field (the half-width of the line being > 25 Hz). The measurements of the chemical shifts were performed employing the calibration of the spectrum by modulation with an audio generator. This caused the low accuracy of the chemical shift measurements under these conditions (± 3 ppm).

The presence of Ge–H scalar couplings in a molecule enables the measurement of ^{73}Ge chemical shifts with the aid of proton resonances, using the heteronuclear INDOR technique, which remarkably increases the sensitivity of stationary methods. This approach was applied to obtain the ^{73}Ge chemical shifts, $\delta(^{73}\mathrm{Ge})$, for some five-coordinate germanium compounds [11].

The introduction of multipulse methods, as well as more reliable magnets, reduced the error in half-width measurements to ±0.4 Hz [3], or lower. In addition, the high relaxation rate of ^{73}Ge nuclei enabled the application of the optimal pulse widths, with very short delays between the pulses.

Since the resonance frequency of ^{73}Ge (3.14 MHz at 2.1 T) is very low, additional difficulties connected with acoustic ringing arise when pulse methods for obtaining ^{73}Ge NMR spectra are used. During the past years, a number of methods have been developed to overcome these difficulties [19]. Nevertheless, owing to fast nuclear relaxation of ^{73}Ge, these methods are not very effective, and decrease additionally the sensitivity for the detection of ^{73}Ge resonances.

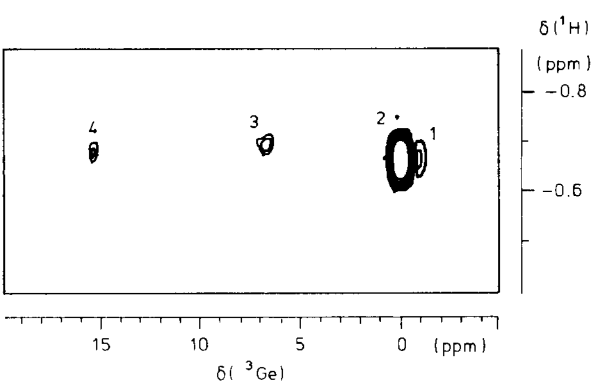


Fig. 1. 2D-Correlation spectrum ^{73}Ge–^{1}H for a mixture of trimethylgermanes: 1, 2-(trimethylgermyl)ethanol; 2, tetramethylgermane; 3, bis(trimethylgermyl)methane; 4, 1-trimethylgermyladamantane.

The enhancement of ^{73}Ge signal intensities in some cases may be achieved by applying recently proposed methods [20,21] for polarization transfer from protons to the ^{73}Ge nuclei (INEPT, DEPT). Nothwithstanding the comparatively short relaxation times of ^{73}Ge, these techniques provide considerable signal enhancement for compounds containing hydrogen, methyl, or ethyl groups at germanium. Signal enhancement range from 2- to 6-fold for proton decoupled spectra, and up to 20-fold for *J*-coupled spectra. Reduction in the time required to obtain a ^{73}Ge spectrum ranges from 10-fold to 100-fold, respectively. The best results have been achieved by applying the INEPT sequences. It is necessary to note that, owing to longer relaxation times for ^{1}H nuclei as compared to ^{73}Ge, it is impossible to use fast cycling of INEPT or DEPT pulse sequences. In order to decrease ^{1}H relaxation times, small amounts of paramagnetic relaxant [Cr(acac)$_3$] (up to 10^{-3} *M*; acacH = 2,4-pentanedione) can be added [16]. In some cases this reduces the time necessary for an experiment by up to 10-fold.

The unfavourable relaxation rate of the ^{73}Ge nucleus explains the low efficiency of 2D-correlation methods used for interpretation of $\delta(^{73}\mathrm{Ge})$ and $\delta(^1\mathrm{H})$. Fast relaxation of ^{73}Ge nuclei considerably diminishes cross-peak intensities in 2D-correlation spectra, ^{73}Ge–^{1}H (Fig. 1). Nevertheless, in some cases, such experiments may be performed, and they give unambiguous results.

Spin–lattice and spin–spin relaxation of ^{73}Ge nuclei

^{73}Ge nuclei spin–lattice and spin–spin relaxation times have been discussed elsewhere [3,13,14]. The total spin–lattice relaxation time of any nucleus may be approximated as follows:

$$1/T_1^{\mathrm{T}} = 1/T_1^{\mathrm{DD}} + 1/T_1^{\mathrm{SR}} + 1/T^{\mathrm{CSA}} + 1/T_1^{\mathrm{QR}} \qquad (1)$$

where T_1 contains contributions from separate spin–lattice relaxation mechanisms: DD = dipole–dipole, SR = spin–rotational, CSA = chemical shift anisotropy, and QR = quadrupolar.

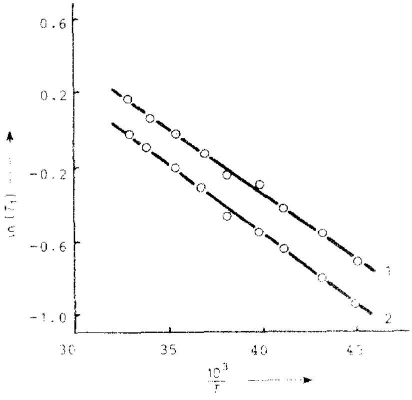


Fig. 2. Temperature dependence for ^{73}Ge nuclei spin–lattice relaxation time in tetramethylgermane: 1, neat sample; 2, solution in $CDCl_3$.

The source of DD relaxation is fluctuations of local magnetic fields, caused by dipolar interaction of the relaxing nucleus with the neighbouring nuclei. The intramolecular DD relaxation rate between ^{73}Ge and ^{1}H is a function of r^{-6} (where r is the distance between the H and Ge atoms). Its value is negligible as compared to the experimental value for $1/T_1^{exp} = 0.9\ s^{-1}$ [14]. Besides, within the limits of experimental error, no nuclear Overhauser effect (NOE) enhancement of ^{73}Ge signals has been found in germanium compounds. As was pointed out earlier, NOE is an indicator of the effectiveness of the DD relaxation mechanism. Contrary to these results, the NOE factor for $GeMe_4$ was determined to be 0.3 [16].

The SR mechanism originates from the interaction between nuclear magnetic moments and rotational magnetic moments of the molecules containing these nuclei. The diagnostic criterion for this mechanism is its characteristic temperature dependence: the relaxation rate increases with temperature [22]. The relationship between $\ln(T_1)$ of ^{73}Ge in $GeMe_4$ and T^{-1} is shown in Fig. 2. When the SR mechanism predominates, the slope of the line $\ln(T_1)$ vs. $1/T$ must be positive, but the contribution of this mechanism will manifest itself as a deviation from linearity at higher temperatures. Results presented in Fig. 2 prove the absence of the SR relaxation mechanism within the explored temperature range.

Recently it has been reported [23] that in $GeCl_4$, $GeBr_4$ and GeH_4, the spin–lattice relaxation time, T_1, of ^{73}Ge nuclei considerably exceeds the spin–spin relaxation time, T_2. In the case of $GeCl_4$ and $GeBr_4$, this difference has been attributed to scalar relaxation of the second kind, and the coupling constant $^{1}J(^{73}Ge–^{35}Cl)$ 24 Hz has been calculated. Dissimilarities of T_2 and T_1 in GeH_4 have been interpreted in terms of chemical exchange in this molecule.

The CSA mechanism may be excluded for the alkyl- and alkoxygermanes which have been studied, because of the symmetric tetrahedral configuration of germanium in these compounds.

^{73}Ge has $I = 9/2$ and therefore quadrupolar relaxation is expected to be dominant. The interaction of the electric quadrupole moment (eQ) with a time-dependent electric field gradient (eq), induced by molecular motions, provide an effective mechanism for spin–lattice relaxation. Within the limits of the extreme narrowing condition ($\omega_0\tau_c \ll 1$) for quadrupolar relaxation rate, we have eq. 2 [24]:

$$\frac{1}{T_1^{\mathrm{QR}}} = \frac{3\pi^2}{10} \cdot \frac{2I+3}{I^2(2I-1)} \cdot \left(1 + \frac{\eta^2}{3}\right) \cdot \left(\frac{e^2qQ}{h}\right)^2 \cdot \tau_c \tag{2}$$

where I is the spin of the quadrupolar nucleus, η is the asymmetry parameter, $(e^2qQ/h)^2$ is the quadrupolar coupling constant (QCC), and τ_c is the rotational correlation time.

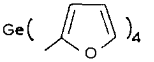
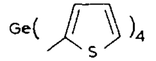
For ^{73}Ge nuclei, it is possible to transform eq. 2 into eq. 3:

$$\frac{1}{T_1^{\mathrm{QR}}} = \frac{\pi^2}{45} \cdot \left(\frac{e^2qQ}{h}\right)^2 \tau_c \tag{3}$$

Data on T_1 for ^{73}Ge are presented in Table 1. In tetraalkylgermanes, the lengthening of the alkyl chain leads to an increase of the relaxation rate. An increase in symmetry (e.g. the decrease of QCC) would lead to greater T_1 values, as has been experimentally observed. T_1 was measured in various solvents for GeMe$_4$. Its value is higher in cyclohexane than in trichloromethane or methanol. If one assumes that the relaxation of ^{73}Ge is ensured by reorientation of solvent dipoles (a function of solvent viscosity), then relaxation will be more efficient in polar solvents, such as trichloromethane or methanol, than in nonpolar cyclohexane, in agreement with experiment.

Table 1

^{73}Ge nuclei spin–lattice (T_1) and spin–spin (T_2) relaxation times, and quadrupole coupling constants (QCC) in organogermanes at 303 K

Compound	T_2 (ms)		T_1 (ms)	QCC (MHz)
	a	b		
GeMe$_4$	550±200	740±80	295 (CDCl$_3$) [c] 350 (CDCl$_3$) [d]	1.7 [e] 2.2 [f]
GeEt$_4$	20.4±0.5	140±20	250 (CDCl$_3$) [c]	
GePr$_4$	23.9±0.4	100±12		
GeBu$_4$	23.1±0.8	65±7	69 (CDCl$_3$) [d]	1.1 [e] 1.2 [f]
GeMe$_3$(CMe$_3$)			42 (CDCl$_3$) [d]	3.9 [e] 4.5 [f]
			20 (dmso) [c]	
			44 (dmso) [c]	
GeCl$_4$	158±8	163±20	287 (CDCl$_3$) [c]	
GeBr$_4$	181±15	196±30		
GeI$_4$	145±23 [g]			
Ge(OMe)$_4$	26±3	30±3		
Ge(OEt)$_4$				4.1 [f]
Ge(OPr)$_4$				3.6 [f]

[a] Ref. 3, T_2 calculated from $\Delta\nu_{1/2}(^{73}\mathrm{Ge})$. [b] Ref. 3, T_2 measured by the spin-echo method. [c] Ref. 15. [d] Ref. 14, at 296 K. [e] Ref. 14, QCC determined from $T_1(^{73}\mathrm{Ge})$. [f] Ref. 14, QCC determined from $\Delta\nu_{1/2}(^{73}\mathrm{Ge})$. [g] At 313 K.

The values of T_2 reported in the literature [3] were measured either by the Carr and Purcell spin-echo technique [25], or calculated from linewidths, according to eq. 4:

$$T_2 + 1/\Delta\nu_{1/2} \quad (4)$$

Within the experimental error, both sets of T_2 values are in good agreement for $GeMe_4$, $GeBr_4$, $GeCl_4$ and $Ge(OMe)_4$. In the early measurements of T_2, values calculated from the linewidths for GeR_4 (R = Et, Pr or Bu) are 3–5 times lower than those obtained by the spin-echo method. We assume that an unresolved spectrum of many NMR lines, instead of the width of a single line, was measured because of limited spectral resolution and the absence of proton decoupling in these experiments. Indeed, if we introduce the value $\Delta\nu_{1/2} = 5.8$ Hz (obtained 10 years later [14] on a high resolution spectrometer), the calculated T_2 for $GeBu_4$ is 60 ms, which is very close to that measured by the spin-echo method. For all studied compounds, $T_2 < T_1$ (Table 1).

The half-widths of the ^{73}Ge NMR signal vary from 1.7 Hz for $GeEt_4$ [16] to 315 Hz for $GeMe_3(CH_2Cl)$ [10]. The expected relationship is observed: increase in the bulk of the molecule tends to broaden the NMR lines. A rise in temperature leads to narrowing of the signals (Fig. 3), due to either decrease in quadrupolar coupling constant (QCC) or decrease in correlation time τ_c of the ^{73}Ge nuclei.

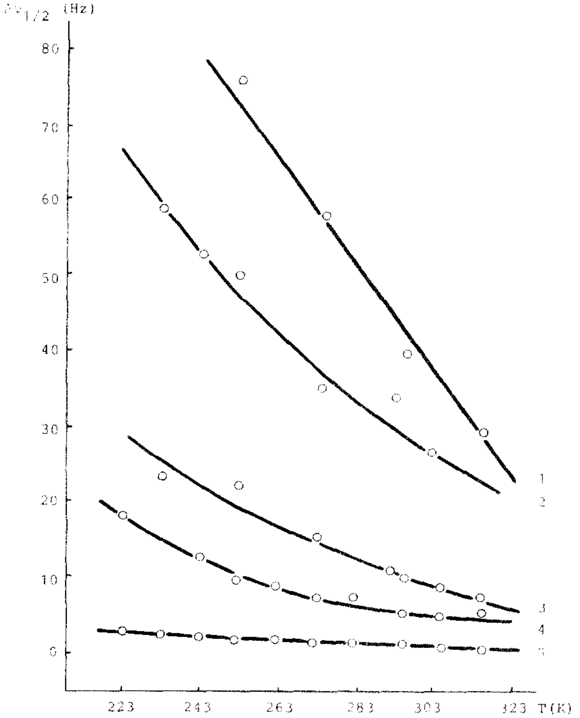


Fig. 3. Temperature dependence for the ^{73}Ge linewidth in $CDCl_3$ solutions: 1, $Ge(OPr)_4$; 2, $Ge(OEt)_4$; 3, $GeMe_3(CMe_3)$; 4, $GeBu_4$; 5, $GeMe_4$.

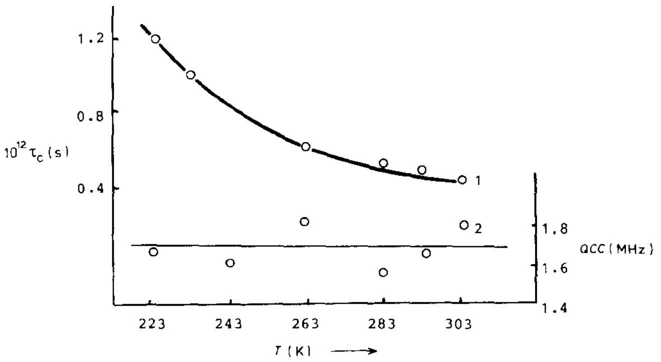


Fig. 4. Temperature dependence for the correlation time (τ_c) and quadrupole coupling constant (*QCC*) for $GeMe_4$ in $CDCl_3$ solution.

One cannot obtain *QCC* directly from ^{73}Ge spectra. An independent method to evaluate τ_c is required. This problem may be solved via some other nuclei, e.g. ^{13}C. If molecular tumbling is the source of relaxation both for ^{73}Ge and ^{13}C nuclei, the correlation time τ_c for ^{73}Ge is equal to that for ^{13}C $\{\tau_c(^{73}Ge) = \tau_c'(^{13}C)\}$. The latter can be calculated from the spin–lattice relaxation time, T_1, of ^{13}C.

The spin–lattice relaxation of methyl group carbons proceed via DD and SR mechanisms. By measuring the NOE factor (η), the DD contribution may be estimated [26]:

$$1/T_1^{DD} = 1/T_1^{exp} \cdot \eta/2.0 \tag{5}$$

and further τ_c' can be calculated:

$$1/T_1^{DD} = N\gamma_H^2 \cdot \gamma_C^2 \cdot \hbar^2 \tau_c' \cdot r^{-6} \tag{6}$$

where N is the number of directly bonded hydrogen atoms, γ_H, γ_C are the gyromagnetic ratios of ^1H and ^{13}C nuclei, and r is the mean distance between atoms C and H. Since the rotation of methyl groups along the Ge–C bond proceeds more easily than along C–C bond, one may assume that the total correlation time of $GeMe_4$ molecular amounts to 9 τ_c' [27] *. The results are presented in Table 1. Spin–spin relaxation times were determined from eq. 4, and *QCC* was calculated from eq. 3 employing the condition $T_2 = T_1$.

The effect of solvent on the *QCC* in $GeMe_4$ is negligible. The distortion of symmetry of molecule increases the *QCC*.

The analysis of the *QCC* and τ_c temperature dependence for $GeMe_4$ in $CDCl_3$ solution (Fig. 4) demonstrates that the broadening of the ^{73}Ge signals at low temperatures must be explained by a decrease in τ_c, as the value of *QCC* (within the experimental error) does not alter. If the compound contains molecules with equal geometric size (i.e. equal correlation time), the difference in the half-widths, $\Delta\nu_{1/2}$, may be attributed chiefly to differing *QCC* values. An increase in germanium coordination number increases the *QCC* value [28].

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* The value of 9 is derived from a study of the relaxation of the methyl and backbone carbons of cholesterol chloride (much larger than $GeMe_4$), and so must be treated with some caution.

From the temperature dependence of T_1, the activation energy (E_a) for ^{73}Ge quadrupolar relaxation may be calculated: for $GeMe_4$ it constitutes 6.3 kJ mol^{-1} (neat sample) and 6.7 kJ mol^{-1} (solution in $CDCl_3$). Using the dependence of correlation time upon temperature (obtained from ^{13}C relaxation spectra), it is possible to calculate the activation energy for molecular tumbling. Within the experimental error, both E_a values coincide. Consequently, the quadrupolar relaxation rate may be successfully applied to the intramolecular motion studies.

^{73}Ge Chemical shifts

Magnetic shielding of nuclei is a function of the electronic structure of the molecule. Most semi-empirical methods for the calculation of shielding constants for heavy nuclei take into account only variation in the paramagnetic contribution, σ^{para}. In contrast to silicon nuclei, no σ^{para} calculation data have been reported in the literature for ^{73}Ge nuclei relative to individual compounds. ^{73}Ge shielding constants have been mentioned in publications of a more general character, together with other calculation data [29,30]. The given shielding constant is parabolically related to the nett charge. This may account for the absence of linear correlation between $\delta(^{73}Ge)$ and the inductive constants for substituents in organogermanium compounds (the latter characterize, indirectly, the charge variation on the atom with different substituents).

The pattern of $\delta(^{73}Ge)$ dependence on substituent electronegativity is a complicated one (Fig. 5), therefore it appears worthwhile to analyze $\delta(^{73}Ge)$ for each individual class of compounds in the hope of establishing empirical relationships between substituent effects and ^{73}Ge resonance signal positions for limited series of compounds.

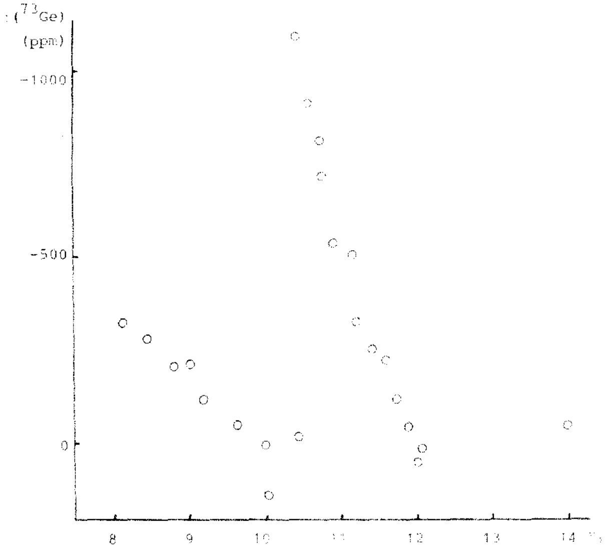


Fig. 5. The dependence of ^{73}Ge chemical shifts on electronegativity of the substituents in organogermanes.

On the other hand, Watkinson and Mackay [9] have proposed eqs. 7 and 8 relating $\delta(^{73}Ge)$ to $\delta(^{29}Si)$ and $\delta(^{119}Sn)$ for alkyl-, halogeno- and alkoxy derivatives of germanium, silicon and tin:

$$\delta(^{73}\mathrm{Ge}) = 3.32\delta(^{29}\mathrm{Si}) + 39.9;\ r = 0.967;\ n = 29 \quad (7)$$

$$\delta(^{119}\mathrm{Sn}) = 1.56\delta(^{73}\mathrm{Ge}) - 87.4;\ r = 0.991;\ n = 26 \quad (8)$$

Exclusion of the points corresponding to oxygen containing compounds from the data set improves the correlation (7):

$$\delta(^{73}\mathrm{Ge}) = 3.29\delta(^{29}\mathrm{Si}) + 13.3;\ r = 0.995;\ n = 26 \quad (9)$$

However, $\delta(^{73}Ge)$ and $\delta(^{119}Sn)$ estimation, with the aid of eqs. 8 and 9 using data from the same authors, results in a fairly large disparity between experimental and estimated δ values, amounting (in some cases) to tens of ppm, or even to 200 ppm for $Ge(OMe)_4$. This suggests that the above equations lack universality. This is another point in favour of studying $\delta(^{73}Ge)$ for individual series of compounds.

Germanium hydrides, and alkyl- and arylgermanes

$\delta(^{73}Ge)$ in compounds of this type vary over a range of more than 200 ppm (Tables 2–6). Alkylgermanes fail to show a linear correlation between $\delta(^{73}Ge)$ and substituent inductive and steric constants. In trimethylalkylgermanes containing bulky substituents, the shielding of germanium nuclei declines with an increase in the total steric and electron-donating influence of substituents. An increase in the number of double bonds in the cyclic substituent enhances the shielding of germanium nuclei (Table 2).

The type and electronic properties of the aromatic ring considerably affect the value of $\delta(^{73}Ge)$ in arylgermanes. $\delta(^{73}Ge)$ tends to increase in the series of substituents: phenyl < 2-thienyl < 3-furyl < 2-furyl (Table 3).

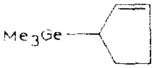
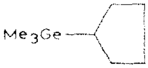
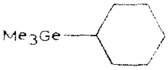
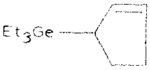
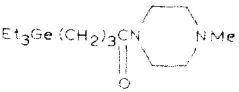
Gradual substitution of hydrogen atoms in GeH_4 by methyl groups (Table 4) leads to nearly additive downfield displacements of the ^{73}Ge signal by 70–80 ppm, whereas substitution by an ethyl group elicits a downfield shift of up to 100 ppm. Downfield shifts brought about by the introduction of a methyl group at the germanium atom are also exhibited in substituted germacyclohexanes (Table 5). Hydrogen substitution for a group containing a silicon or germanium atom [31] results in upfield shifts of the ^{73}Ge resonance signal (Table 6).

As in the case of ^{29}Si and ^{119}Sn, $\delta(^{73}Ge)$ largely depends on the size of the ring incorporating the germanium: e.g., germanium incorporation into a five-membered ring displaces the ^{73}Ge signal to lower fields by 40 ppm, as compared with acyclic molecules, whereas in germacyclohexane, an upfield shift is observed (Table 5). This suggests that interorbital angles play a crucial part in the determination of chemical shift for heavy atoms.

Intriguing results have been gained [17] demonstrating the capabilities of ^{73}Ge NMR methods for the conformational analysis of cyclic organogermanium compounds. Two signals were observed for 1,4-dimethyl-1-germacyclohexane: at -61.5 and -73.4 ppm. Using ^{13}C NMR spectra, it was established that the signal at -61.5 ppm was due to the isomer with an equatorial methyl group at the germanium atom, while the more intense signal at -73.4 ppm corresponds to the isomer with an axial methyl group at germanium.

Table 2

^{73}Ge NMR parameters of alkylgermanes [10]

Compound	$\delta(^{73}Ge)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	Solvent
Me_3GeCMe_3	20.7	20	$CDCl_3$
Me_3GeCH_2Cl	6.9	152	$CDCl_3$
$Me_3Ge(CH_2)_2OH$	−2.6	35	$CDCl_3$
$Me_3GeCH_2CH{=}CH_2$	1.7	36	$CDCl_3$
$Me_3GeCH_2CH{=}CMe_2$	4.7	28	$CDCl_3$
Me_3Ge-Ad	11.2	20	$CDCl_3$
Me_3GeCH_2Ph	3.2	100	$CDCl_3$
	6.6	20	$CDCl_3$
	5.8	22	$CDCl_3$
	−21.9	18	
	8.1	22	$CDCl_3$
	5.4	26	$CDCl_3$
$Me_2Ge(CH_2Cl)_2$	17.5	315	$CDCl_3$
$Me_2Ge(CH_2SiFMe_2)_2$	0.6	175	$CDCl_3$
$MeGe(CH_2CH{=}CH_2)_3$	0.6	60	$CDCl_3$
Et_4Ge	18.1 [a]		neat
	17.3 [b]	1.7	$CDCl_3$
	17.8 [c]		neat
$Et_3Ge(CH_2)_3OH$	15.2	36	$CDCl_3$
$Et_3Ge(CH_3)_3OCOCH_3$	16.4	53	$CDCl_3$
$Et_3Ge(CH_2)_3OCOH$	17.5	36	$CDCl_3$
$Et_3Ge(CH_2)_3COOH$	12.8	40	$CDCl_3$
$Et_3Ge(CH_2)_3Cl$	14.7	60	$CDCl_3$
	11.2	24	$CDCl_3$
	15.2	55	$CDCl_3$
Pr_4Ge	2.1 [a]		neat
	2.4 [d]		
Bu_4Ge	6.0 [d]		
	5.5 [a]		neat
	4.9	15	$CDCl_3$
$Me_3GeCH_2GeMe_3$	7.5	20	$CDCl_3$
$Me_3GeCH_2CH_2GeMe_3$	6.6	25	$CDCl_3$

[a] Ref. 3. [b] Ref. 15. [c] Ref. 16. [d] Ref. 9.

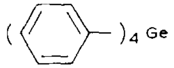
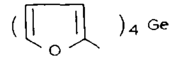
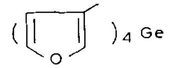
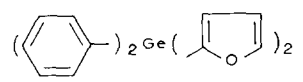
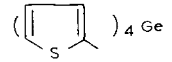
A linear relationship between $\delta(^{73}Ge)$ and $\delta(^{29}Si)$ (eq. 10) or $\delta(^{13}C)$ (eq. 11) was found for trimethylgermanes [10]:

$$\delta(^{73}Ge) = 1.85\delta(^{29}Si) + 1.52;\ r = 0.970;\ n = 6 \tag{10}$$

$$\delta(^{73}Ge) = 3.58\delta(^{13}C) - 107.3;\ r = 0.829;\ n = 6 \tag{11}$$

Table 3

^{73}Ge NMR parameters for arylgermanes and heterocyclic germane derivatives

Compound	$\delta(^{73}Ge)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	Solvent	T (K)	Ref.
	−31.6	6	DMSO	329	15
	−32.9	15	$CDCl_3$	303	[a]
	−112.8	11	DMSO	303	15
	−115.0	30	$CDCl_3$	303	[a]
	−75.8	10	$CDCl_3$	303	[a]
	−43.8	44	$CDCl_3$	303	[a]
	−95.5	8	DMSO	329	15
	−56.5	18	$CDCl_3$	303	[a]

[a] This work: spectra obtained on a Bruker WM-360 spectrometer at 12.56 MHz.

and for tetrasubstituted germanes, R_4Ge (eq. 12) [15]:

$$\delta(^{73}Ge) = 2.01\delta(^{29}Si) + 1.11;\ r = 1.00;\ n = 4 \tag{12}$$

In eqs. 10–12, the ratio $\delta(^{73}Ge)/\delta(^{29}Si)$ departs from that expected from the p-orbital radii of these elements [32]. Consequently, the analysis of δ must take into account, apart from $\langle r^{-3}\rangle_{np}$, the contributions of other factors in σ^{para} variation.

Halogenogermanes

$\delta(^{73}Ge)$ for halogenogermanes cover a range of more than 1000 ppm (Table 7). As in the case of the silicon [33,34] and carbon [35,36] analogues, the iodine atom exerts the strongest shielding effect of the halogen atoms on the resonance signal of

Table 4

^{73}Ge chemical shifts of germanium hydrides

Compound	$\delta(^{73}Ge)$ (ppm)	Ref.
GeH_4	−298.9	16
	−283.7	9
$MeGeH_3$	−209.2	16
Me_2GeH_2	−127.6	16
	−127.6	9
Me_3GeH	−57.2	9
$EtGeH_3$	−186.4	9
Et_2GeH_2	−88	9
Et_3GeH	−15.7	9

Table 5

^{73}Ge NMR parameters for germacyclanes

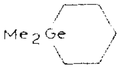
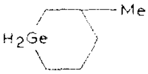
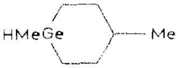
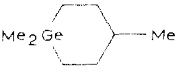
Compound	$\delta(^{73}Ge)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	Ref.
	39.8	75	10
	−131.2	16.4	17
	−65.3	22.3	17
	−13.7	15.6	17
	−131.2		17
	−134.3	21.0	17
	−61.5 (*trans*) −73.4 (*cis*)		17
	−12.2		17
	−17.2	18.3	17

Table 6

^{73}Ge chemical shifts of compounds containing Ge–Ge and Ge–Si bonds

Compound	$\delta(^{73}Ge)$ (ppm)	Solvent	Ref.
$H_3Ge–GeH_3$	−311.8	Bu_2O	16
	−300.5		9
$H_3Ge–GeMeH_2$	−306.2 (GeH_3)	neat	16
	−211.0 ($GeMeH_2$)		
$Et_3Ge–GeEt_3$	−34.7	C_6D_6	this work
Me_3SiGeH_3	−315.5	neat	31
$Me_2Si(GeH_3)_2$	−290.6	neat	31
$MeSi(GeH_3)_3$	−277.0	neat	31
$H_3Si–GeH_3$	−324.6		9

Table 7

^{73}Ge chemical shifts of germanium tetrahalides

Compound	$\delta(^{73}\mathrm{Ge})$ (ppm)	Ref.
$GeCl_4$	30.9	3, 9, 15
	29.7	this work
$GeCl_3Br$	−47.8	9
	−47.1	7
$GeCl_2Br_2$	−131.3	9
	−130.1	7
$GeClBr_3$	−219.4	9
	−219.1	7
$GeBr_4$	−311.3	9
	−312.1	3, 7
$GeBr_3I$	−509.3	9
	−513.1	7
$GeBr_2I_2$	−707.4	9
	−708.1	7
$GeBrI_3$	−899.8	9
	−901.1	7
GeI_4	−1081.8	9
	−1108.1	3
	−1086.1	7
$GeCl_3I$	−235.9	9
	−231.1	7
$GeCl_2I_2$	−523.7	9
	−518.1	7
$GeClI_3$	−809.9	9
	−808.1	7
$GeCl_2BrI$	−326.2	9
	−316.1	7
$GeClBr_2I$	−417.6	9
	−407.1	7
$GeClBrI_2$	−613.5	9
	−601.1	7

the central element. An equation, (13), for $\delta(^{73}\mathrm{Ge})$ prediction for the halogenogermanes [7] was derived on the basis of the pairwise additivity model [37]:

$$\delta(^{73}\mathrm{Ge}) = a + \sum_{i} b_i \delta_i + \sum_{ij} c_{ij} \delta_{ij} \tag{13}$$

where $\delta(^{73}\mathrm{Ge})$ is relative to $GeCl_4$; δ_i represents the direct effect of the i-th halogen substituent and the pair interaction; δ_{ij} accounts for the combined effect of two halogens i and j; b_i and c_{ij} are simple population factors; a is a constant factor.

The study of ^{73}Ge NMR spectra allowed the deduction that the halogen redistribution in halogenogermanes proceeds at a much slower rate than in the analogous tin halides [38].

Quantum chemical calculations have been performed for halogenogermanes, and eq. 14 has been deduced [39], relating $\delta(^{73}\mathrm{Ge})$ to atomic charges on the germanium atom in $GeCl_nBr_{4-n}$ ($n = 0$–4), calculated with the CNDO/2 method:

$$\delta(^{73}\mathrm{Ge}) = -116.1 q_{\mathrm{Ge}} + 1615.4 \tag{14}$$

The validity of calculations was examined by comparison with isostructural carbon compounds. The charge on the central element increases in the two series of compounds with increasing n, i.e., an increase in the number of the more electronegative substituent (chlorine) logically decreases electron density at the germanium atom, which, in its turn, leads to a downfield shift of the ^{73}Ge resonance signal (Table 7).

$\delta(^{73}\text{Ge})$ and $\delta(^{29}\text{Si})$ have been compared for isostructural halides (Fig. 6): the curve can be described by the second-order equation (15):

$$\delta(^{73}\text{Ge}) = 102.1 + 4.7\,\delta(^{29}\text{Si}) + 3.7(\delta(^{29}\text{Si}))^2;\ r = 0.999;\ n = 14 \qquad (15)$$

The ^{73}Ge chemical shifts are more sensitive than the ^{29}Si chemical shifts to variation in halogen substituents, due to a wider range of chemical shift variation, and possibly to the greater polarizability of germanium–halogen bonds than of silicon–halogen bonds. A similar correlation can be obtained by comparing $\delta(^{73}\text{Ge})$ and $\delta(^{119}\text{Sn})$ in isostructural halides.

Thus, no linear correlation exists between $\delta(^{73}\text{Ge})$ and those of other Group 14 elements in halogen-containing derivatives.

Alkoxygermanes and germatranes

^{73}Ge resonance signals can be registered only for tetraalkoxygermanium derivatives, their values occupying a relatively narrow range (11 ppm, Table 8). Substituting methyl for hydrogen in the 2-position, like for alkylgermanes, results in the increased shielding of the germanium nuclei, though this effect in alkoxygermanes is less significant [$\delta(^{73}\text{Ge})_{\text{GeEt}_4} - \delta(^{73}\text{Ge})_{\text{GePr}_4} = +16$ ppm; $\delta(^{73}\text{Ge})_{\text{Ge(OMe)}_4} - \delta(^{73}\text{Ge})_{\text{Ge(OEt)}_4} = +6$ ppm]. The ^{73}Ge signal is shifted to higher fields with increas-

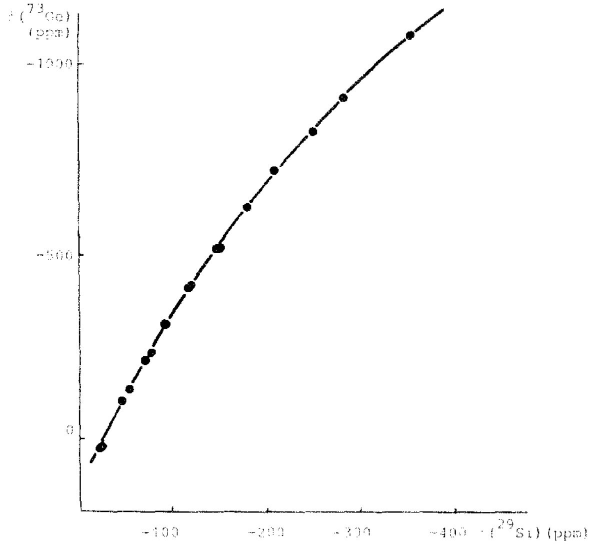


Fig. 6. Correlation of ^{73}Ge chemical shifts in germanium tetrahalides with ^{29}Si chemical shifts in their silicon analogues.

Table 8

^{73}Ge NMR parameters for compounds containing Ge–O, Ge–N and Ge–S bonds

Compound	$\delta(^{73}\mathrm{Ge})$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	Ref.
$\mathrm{Ge(OMe)_4}$	−37.8	10	13
	−36.0		3
$\mathrm{Ge(OEt)_4}$	−43.9	30	13
$\mathrm{Ge(OPr)_4}$	−45.6	40	13
$\mathrm{Ge(O\text{-}i\text{-}Pr)_4}$	−49.7	25	13
$\mathrm{Ge(OBu)_4}$	−45.6	40	13
$\mathrm{Ge(O\text{-}i\text{-}Bu)_4}$	−45.5	30	13
$\mathrm{Ge(OBu^s)_4}$	−47.5	45	13
$\mathrm{Ge(OCH_2CH{=}CH_2)_4}$	−43.8	32	13
$\mathrm{Ge(OSiMe_3)_4}$	−91.9	20	this work
$\mathrm{MeOGe(OCH_2CH_2)_3N}$	−60.6		11
	−63.1		this work
$\mathrm{EtOGe(OCH_2CH_2)_3N}$	−67.7	165	12
$\mathrm{PrOGe(OCH_2CH_2)_3N}$	−63.4		11
$\mathrm{HOGe(OCH_2CH_2)_3N}$	−55.2		11
$\mathrm{Me_3SiOGe(OCH_2CH_2)_3N}$	−73.8	13	12
$\mathrm{Me_3GeOGe(OCH_2CH_2)_3N}$	−55.2		11
	−58.4	95	12
$\mathrm{Me_3SnOGe(OCH_2CH_2)_3N}$	−53.4		11
$\mathrm{Ge(NEt_2)_4}$	47.0	130	41
$\mathrm{Ge(NMe_2)_4}$	49.4	35.3	41
$\mathrm{Ge(NCO)_4}$	−88.9	17.3	41
$\mathrm{Ge(SMe)_4}$	153		9
$\mathrm{K_2[Ge(NCS)_6]}$	−443.0	50	41

ing length of the alkyl chain in alkoxy group, the individual shifts being greater than in the silicon-containing analogues [40].

A linear correlation has been found between $\delta(^{73}\mathrm{Ge})$ and $\delta(^{29}\mathrm{Si})$ in germanium and silicon tetraalkoxy derivatives [13]:

$$\delta(^{73}\mathrm{Ge}) = 88.7(\pm 13.3) + 1.6(\pm 0.2)\delta(^{29}\mathrm{Si});\ r = 0.97;\ n = 10 \tag{16}$$

This line provides a satisfactory fit also for points corresponding to the alkoxy derivatives of five-coordinate germanium.

As in the case of the organosilicon compounds, silatranes, a rise in the coordination number of the germanium atom in germatranes brings about a slight upfield shift of the ^{73}Ge signal relative to alkoxy derivatives.

If $\delta(^{73}\mathrm{Ge})$ and $\delta(^{29}\mathrm{Si})$ in alkoxy derivatives are ascribed exclusively to changes in the paramagnetic shielding contribution, the angular coefficient in eq. 16 would be equal to the ratio of p-orbital radii of the two nuclei, which for the pair Ge/Si has been calculated, to be 3.3 ± 0.5 [32]. However, the angular coefficient value in eq. 16 does not correspond to the ratio of p-orbital radii for silicon and germanium. This may reflect a different degree of double-bonding for the germanium and silicon atoms in compounds of this type.

The silicon atom possesses a greater capacity for additional p_π–d_π bonding with oxygen lone-pairs in the substituent, as compared to germanium atom. This phenomenon can apparently explain the fact that alkoxy compounds form an ad-

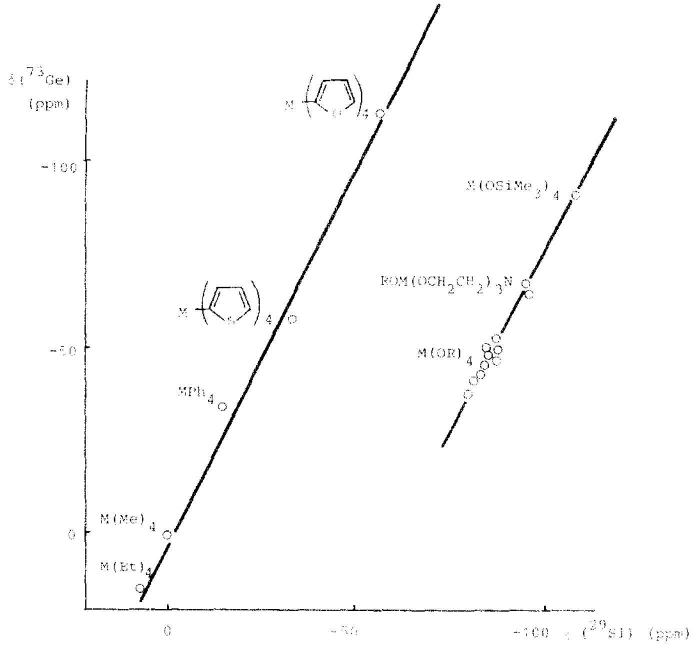


Fig. 7. Correlation of ^{73}Ge chemical shifts in alkyl-, aryl- and alkoxygermanes with ^{29}Si chemical shifts in their silicon analogues.

ditional correlation line which departs considerably from that for alkyl and aryl derivatives of silicon and germanium (Fig. 7).

^{73}Ge Spin–spin couplings

Spin–spin coupling constants to ^{73}Ge nuclei have received only scant attention. Quite recently, several $^{1}J(^{73}\mathrm{Ge}-^{1}\mathrm{H})$ coupling constants have been measured for some germanium hydrides (Table 9).

It has been found that the predominant contribution to $^{1}J(^{29}\mathrm{Si}-^{1}\mathrm{H})$ coupling constants is provided by the Fermi contact term [33,34]. For this reason, it is of interest to compare the above coupling values in isostructural compounds. A linear correlation eq. 17 is observed between the $^{1}J(\mathrm{M}-^{1}\mathrm{H})$ coupling for the series $\mathrm{Me}_{4-n}\mathrm{H}_n$ (n = 1–4; M = Si or Ge).

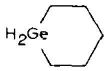
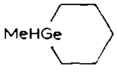
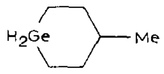
$$^{1}J(^{73}\mathrm{Ge}-^{1}\mathrm{H}) = 0.34\ ^{1}J(^{29}\mathrm{Si}-^{1}\mathrm{H}) + 28.2 \qquad (17)$$

This allows the assumption that the Fermi contact term prevails also in $^{1}J(^{73}\mathrm{Ge}-^{1}\mathrm{H})$ coupling constant variation. The value of angular coefficient in eq. 17 approaches the gyromagnetic ratio for silicon and germanium nuclei. This also suggests that the contribution of the Fermi contact term to $^{1}J(^{73}\mathrm{Ge}-^{1}\mathrm{H})$ is predominant.

The linear correlation (Fig. 8) observed between $^{1}J(^{73}\mathrm{Ge}-^{1}\mathrm{H})$ and $\delta(^{73}\mathrm{Ge})$ in germanium hydrides demonstrates that the contribution of the Fermi contact term to the coupling constant and to $\delta(^{73}\mathrm{Ge})$ is governed by s-electron density on the ^{73}Ge nucleus.

Table 9

Spin–spin coupling constants ${}^{n}J$(Ge–E)

Compound	E	n	${}^{n}J$ (Hz)	Ref.
GeH_4	H	1	97.6±0.3	16
H_3GeMe	H	1	94.3±0.3	16
	H	2	3.5±0.1	16
$GeMe_4$	H	2	2.99±0.03	3
			2.95±0.03	16
			2.92±0.02	45
	C	1	−18.7	42
$GeEt_4$	H	2	3±0.6	16
$GeBu_4$	H	2	2.7	10
Ge_2H_6	H	1	95.5±0.5	16
	H	1	92.8	17
	H	1	90.8	17
	H	1	94.0	17
$Me_2Si(GeH_3)_2$	H	1	90.8	31
$MeSi(GeH_3)_3$	H	1	90.5	31
$Ge(OMe)_4$	H	3	−1.9±0.3	3
$Ge(SMe)_4$	H	3	−2.5	8
GeF_4	F	1	178.5	43
$[NH_4]_2[GeF_6]$	F	1	98	44

The value ${}^{2}J({}^{73}$Ge–^{1}H) decreases with increasing number of methyl groups in compounds of the type Me_nGeH_{4-n} (Table 9).

Spin–spin coupling across three bonds including ^{73}Ge nuclei remains practically unexplored. The known values (Table 9) are unreliable, because they were determined by using approximate ^{73}Ge NMR line shape analysis.

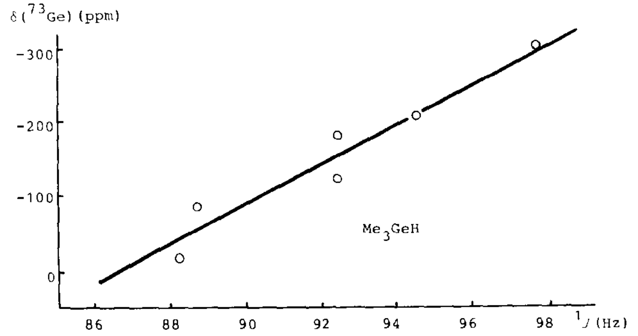


Fig. 8. Correlation of ^{73}Ge chemical shifts and spin–spin coupling constants ${}^{1}J({}^{73}$Ge–^{1}H) in germanium hydrides.

The only $^{1}J(^{73}Ge-^{13}C)$ coupling constant (equal to -18.7 Hz) is for $GeMe_4$ [42]. Its comparison with the value $^{1}J(^{29}Si-^{13}C)$ permits the assumption that the main contribution to this coupling, too, is provided by the Fermi contact term.

Two $^{1}J(^{73}Ge-^{19}F)$ coupling constants equal to 178.5 Hz [43] and 98 Hz [44] have been measured for GeF_4 and $[NH_4]_2[GeF_6]$, respectively. An increase in the coordination number of germanium lowers this coupling constant, its decrease being consistent with theoretical predictions.

The analysis of the collected data prove that ^{73}Ge NMR spectroscopy is finding rapidly its application in the chemist's everyday practice. It is reasonable to hope that experimental difficulties of recording ^{73}Ge NMR spectra will be overcome by the introduction of spectrometers with higher resonance frequencies and superconducting magnets. The authors assume that the near future of ^{73}Ge NMR spectroscopy is connected with: (1) investigations of the electronic and steric influence of substituents in the secondary coordination sphere of the germanium nucleus; and (2) the study of the relationship between $\delta(^{73}Ge)$ and the germanium coordination number. In addition, to date, there are no data in literature on $\delta(^{73}Ge)$ for germanium(II) compounds. The authors of this review are also convinced that the valuable information obtained in ^{73}Ge NMR studies will outweigh all the experimental difficulties of this method.

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