Inorg. Chem. **1987**, *26*, 3851–3854 **3851**

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Relaxation Mechanism of Germanium-73 Nuclei in Tetrahalogermanes

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Received April 7, 1987

The ^{73}Ge spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) of such tetrahalogermanes as $GeCl_4$, $GeBr_4$, and GeI_4 have been measured as a function of temperature. It has been shown that the germanium nuclei in $GeCl_4$ and $GeBr_4$ relax solely via the quadrupole relaxation mechanism for T_1 and via a combination of the quadrupole and the scalar coupling relaxation mechanisms for T_2. On the other hand, both the spin–lattice and the spin–spin relaxations for germanium nuclei in GeI_4 were solely via the quadrupole relaxation mechanism at room temperature. The viscosities of tetrahalogermane solutions were measured to obtain the reorientational correlation time. The reorientational correlation times (τ_c) of $GeCl_4$ and $GeBr_4$ were 0.78×10^{-11} and 1.8×10^{-11} s at 30 °C, respectively, and the activation energies 9.6 and 11.2 kJ mol^{-1}, respectively. The scalar coupling constant, $J(^{73}\text{Ge}-^{35}\text{Cl})$, was calculated as 24 Hz by using T_2 of ^{35}Cl in $GeCl_4$.

Introduction

The study of the nuclear magnetic relaxation of ^{73}Ge with nuclear spin $^9/_2$ has so far been restricted to those for alkylgermanes[1-5] and halogermanes.[1,4,6,7] The mechanism of the relaxation of alkylgermanes has been determined. Thus, the spin–lattice relaxation of ^{73}Ge in symmetrical alkylgermanes such as $Ge(CH_3)_4$ and $Ge(C_2H_5)_4$ was shown to occur via the quadrupole relaxation mechanism from the temperature dependence of T_1.[2,3] Furthermore, it was shown that the spin–spin relaxation of ^{73}Ge in alkylgermanes, GeR_4 (R = methyl, ethyl, *n*-propyl, *n*-butyl), was also dominated by the quadrupole relaxation mechanism.[8]

As compared with the relaxation of alkylgermanes, the relaxation of germanium nuclei bonded to halogens is expected to be more intriguing in light of the relaxation of nuclei of group IVB (group 14[30]) elements with $I = {}^1/_2$ (i.e., ^{13}C, ^{119}Sn, and ^{207}Pb) that are bonded to halogens.

It has been shown that in CCl_4[9] and $SnCl_4$[10,11] the spin–lattice relaxations of ^{13}C and ^{119}Sn are solely via a spin–rotation mechanism and in tetrahalides such as $SnBr_4$,[11] SnI_4,[10,11] and $PbCl_4$,[12] the spin–lattice relaxation of ^{119}Sn or ^{207}Pb occurs via a combination of two mechanisms, i.e., spin–rotation and scalar coupling, while the spin–spin relaxation of these nuclei in the above tetrahalides occurs solely via the scalar coupling mechanism.

However, very few investigations on the relaxation of ^{73}Ge in tetrahalogermanes have been reported. Tarasov et al. showed that the spin–lattice relaxation of ^{73}Ge in $GeBr_4$ was solely via the quadrupole relaxation mechanism while in $GeCl_4$ the relaxation occurred mostly via the spin–rotation mechanism above the 330 K and mostly via the quadrupole mechanism below 330 K.[13]

In a preliminary communication, we reported the contribution of the scalar coupling pathway to the spin–spin relaxation of ^{73}Ge in $GeCl_4$ and $GeBr_4$.[14] In this paper, we wish to describe the details of our investigation to elucidate the relaxation mechanism of ^{73}Ge nuclei in tetrahalogermanes.

For this purpose we determined the ^{73}Ge spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) of $GeCl_4$, $GeBr_4$, and GeI_4 at various temperatures. Furthermore, as an aid to clarify the relationship between the relaxation times and molecular motions, we also determined the viscosities of the chloroform solutions of these tetrahalogermanes, from which the reorientational correlation times and scalar coupling constants were determined.

Experimental Section

Preparation of Compounds. $GeCl_4$, guaranteed reagent grade, was purchased from Sumitomo Metal and Mines Co. Ltd. $GeBr_4$ (bp 82–83 °C (32 mmHg)) and GeI_4 (mp 146 °C) were synthesized by the procedures described in the literature.[15] The purity of the compounds were confirmed by GLC (Shimadzu GC-3BT).

Table I. Measured Values of T_1(IR), T_2(CPMG), and $T_2(\nu_{1/2})$ for ^{73}Ge in Tetrahalogermanes at 303 K

compd	T_1(IR)/ms	T_2(CPMG)/ms	$T_2(\nu_{1/2})$/ms
$GeCl_4$	280	120	120
$GeBr_4$	160	130	130
GeI_4	80	80	80

Germanium-73 NMR Spectra. $GeCl_4$ and $GeBr_4$ were dissolved in $CDCl_3$ (50% v/v) while GeI_4 was dissolved in a 1:1 solution of CS_2 and C_6D_6. Because of the limited solubility of the iodide, the concentration of the solution was 0.46 mol dm^{-3}. The solution placed in an egg-shaped cell and degassed by the freeze-and-thaw method.

The ^{73}Ge NMR spectra were recorded by a JEOL FX-90Q instrument equipped with a low-frequency insert (NM-IT10LF) at 3.10 MHz. T_1 was determined by the inversion–recovery method (T_1(IR)), while T_2 was determined by the Carr–Purcell–Meiboom–Gill (CPMG) method (T_2(CPMG)). The errors in T_1 and T_2 thus determined were estimated to be ≲5%. Other conditions of the measurements have been determined in a previous paper.[8]

Measurement of Viscosity. $GeCl_4$ and $GeBr_4$ were dissolved in $CHCl_3$ (50% v/v), and the procedures of measurement have been described in a previous paper.[8] The radius of a halogermane is defined as the sum of the distance between the germanium and halogen atoms ($Cl_3Ge–Cl$,[16]) $Br_3Ge–Br$[17] plus the van der Waals radius of the halogen atom.

Results and Disucssion

Relaxation Time. As the quadrupole nuclei are generally accepted to relax mostly via the quadrupole pathway, it is expected that the values of T_1 and T_2 are essentially identical. Indded, in the tetraalkylgermanes, T_1 was equal to T_2 within the experimental error, where the relaxation is solely via the quadrupole relaxation

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mechanism.[8] In such a case, the relaxation times can be approximated by $T_2(\nu_{1/2})$ (the relaxation time determined from the line width).

We determined T_1(IR), $T_2(\nu_{1/2})$, and T_2(CPMG) of tetrahalogermanes. Results are given in Table I.

T_2(CPMG) is equal to $T_2(\nu_{1/2})$ for all tetrahalogermanes investigated. However, for $GeCl_4$ and $GeBr_4$, T_1 is longer than T_2 at 303 K. The difference between T_1 and T_2 is particularly substantial for $GeCl_4$. On the other hand, for GeI_4, T_1 is identical with T_2 at 303 K. Tarasov et al.[13] reported the values of $1/T_1$ for $GeCl_4$ and $GeBr_4$ in pure liquid at 1.2 and 7.0 s^{-1}, respectively, while our results of $1/T_1$ for $GeCl_4$ and $GeBr_4$ in 1:1 $CDCl_3$ solutions were 3.6 and 6.3 s^{-1}, respectively. The discrepancy among these values most likely originates from the difference of viscosities of samples. Our experimental results show that the viscosity of $CHCl_3$ ($CDCl_3$) is higher than that of $GeCl_4$ and the viscosity of $GeBr_4$ is higher than that of $CHCl_3$.

The data of Table I also indicate that the spin–lattice relaxation time of tetrahalogermanes decreases as the molecular results and the molecular weight increase. The relation between the relaxation time and the molecular size will be discussed later.

Relaxation Mechanism. It is generally accepted that the quadrupole relaxation times, T_1^q and T_2^q, of nuclei with $I > {}^1/_2$ and $\zeta \neq 0$, are related to the reorientational correlation time τ_c at the extreme-narrowing limit as given in eq 1,[18] where e^2Qq/h

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

is the quadrupole coupling constant and ζ is the asymmetry parameter. The correlation time is usually well represented by an Arrhenius-type equation

$$\tau_c = \tau_c{}^{\circ} \exp(\Delta E/RT) \qquad (2)$$

where $\tau_c{}^{\circ}$ is a constant, ΔE an activation energy for the reorientation, and R the gas constant. If the relaxation occurs solely via the quadrupole mechanism, ln $(1/T_1^q)$ and ln $(1/T_2^q)$ are proportional to the reciprocal of the absolute temperature, $1/(T$ (K)). The plot of ln $(1/T_1^q)$ or ln $(1/T_2^q)$ against $1/T$ (K)) should give a straight line with a positive slope, where the superscript q indicates the quadrupole relaxation.

In was found that for the relaxation of ^{73}Ge nuclei in alkylgermanes, GeR_4, the plots of ln $(1/T_1)^{3,8}$ and ln $(1/T_2)^8$ against $1/T$ gave straight lines with positive slopes. These facts indicate that ^{73}Ge in alkylgermanes relaxes exclusively via the quadrupole mechanism.

The situation is somewhat different in the case of tetrahalogermanes. In Figure 1, two plots for $GeCl_4$, ln $(1/T_1)$ vs $1/T$ and ln $(1/T_2)$ vs. $1/T$, are given.

The former plot gave a straight line with a positive slope, which indicates that the spin–lattice relaxation of ^{73}Ge in $GeCl_4$ is predominantly via the quadrupole mechanism. Thus, T_1 of $GeCl_4$ can now be approximated by eq 3.

$$(T_1)^{-1} = (T_1^q)^{-1} \qquad (3)$$

In a previous paper, we have described the reason that the quadrupole relaxation occurs in such highly symmetric tetraalkylgermanes.[8] On the basis of the view of some investigators, we believe that the quadrupole relaxation occurs by the vibration and/or rotation[22] and the collision among molecules.[23] The electric field gradient generated at the germanium nuclei of

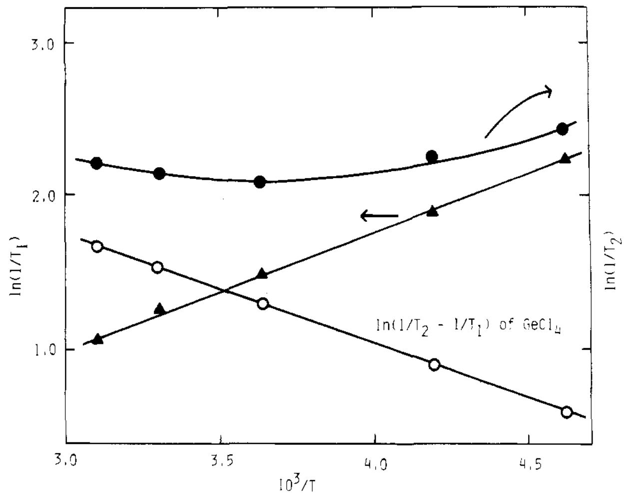

Figure 1. Plots of ln $(1/T_1)$ and ln $(1/T_2)$ vs $1/T$ for tetrachlorogermane.

symmetric tetraalkylgermanes averages to zero, but it has an nonvanishing mean square, i.e., $(e^2Qq/h) \neq 0$. It is expected that, in the case of symmetric tetrahalogermanes, the electric field gradient is also generated at the germanium nucleus.

On the other hand, the plot of ln $(1/T_2)$ of $GeCl_4$ against $1/T$ gave a concave line with a minimum, which is evidence that at least two mechanisms with different temperature dependences were involved. Since the plot of ln $(1/T_2 - 1/T_1)$ against $1/T$ gave a straight line with a negative slope, the second contribution has a reverse temperature dependency, opposite that of quadrupole relaxation.

Among the possible relaxation mechanisms with a negative temperature dependency, the only plausible one is the scalar coupling mechanism. Generally, the contribution of scalar coupling is observed for the relaxation of nuclei that are bonded to such quadrupole nuclei as halogens or that exhibit spin–spin coupling with other nuclei.[18,19]

The scalar contributions to T_1 and T_2 of the nucleus I (in this case Ge) bonded to a quadrupole halogen nucleus S can be written as

$$(T_1^{sc})^{-1} = \frac{2}{3}A^2I_S(I_S+1)\,\frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2{}^2}N_S \qquad (4)$$

$$(T_2^{sc})^{-1} = \frac{1}{3}A^2I_S(I_S+1)\left(\tau_1+\frac{\tau_2}{1+(\omega_I-\omega_S)^2\tau_2{}^2}\right)N_S \qquad (5)$$

where I_S is the nuclear spin of halogen atom S, τ_1 and τ_2 are the correlation times for the scalar interaction, ω_I and ω_S are the Larmor frequencies in hertz, and N_S is the number of S nuclei. The superscript sc indicates the scalar coupling relaxation, while A denotes the scalar coupling constant and is equal to $2\pi J$ where J is the coupling constant between the germanium atom and the halogen atom (in hertz).

It is expected that $(T_1^{sc})^{-1}$ is almost negligible as compared with $(T_1^q)^{-1}$ from the experimental result of relaxation times of $GeCl_4$. $(T_2)^{-1}$ is expressed by a combination of two components of the relaxation rates:

$$(T_2)^{-1} = (T_2^q)^{-1} + (T_2^{sc})^{-1} \qquad (6)$$

When

$$1 + (\omega_I - \omega_S)^2\tau_2{}^2 \gg 1 \qquad (7)$$

the difference between $(T_2)^{-1}$ and $(T_1)^{-1}$ $(=1/T_1^q = 1/T_2^q)$ is given by

$$(T_2^{sc})^{-1} = (T_2)^{-1} - (T_1)^{-1} = A^2I_S(I_S+1)\tau_1N_S/3 \qquad (8)$$

Since Cl, Br, and I consist of several isotopes, tetrahalogermanes with ^{73}Ge nuclei are in fact a mixture of isotopomers. The observed relaxation times of $GeCl_4$, $GeBr_4$, and GeI_4 are approximately equal to those of molecules with the average compositions

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Table II. Values of T_1(IR), τ_c, and ΔE for ^{73}Ge in Tetrahalogermanes at 303 K

compd	T_1(IR)/ms	τ_c(30 °C)/10^{-11} s	ΔE/kJ mol^{-1}
$GeCl_4$	280	0.78	9.6
$GeBr_4$	160	1.8	11.2

$^{73}Ge^{35}Cl_{3.04}{}^{37}Cl_{0.96}$, $^{73}Ge^{79}Br_{2.02}{}^{81}Br_{1.98}$, and $^{73}Ge^{127}I_4$, respectively. Furthermore, by use of relations[20]

$$A_{37}/A_{35} = \gamma_{37}/\gamma_{35} = 0.832 \qquad A_{79}/A_{81} = \gamma_{79}/\gamma_{81} = 0.928$$

$$\tau_1{}^{37}/\tau_1{}^{35} = (Q_{35}/Q_{37})^2 = 1.603$$

$$\tau_7{}^{79}/\tau_7{}^{81} = (Q_{81}/Q_{79})^2 = 0.720$$

and the nuclear spin $^3/_2$ of chlorine and bromine isotopes and the nuclear spin $^5/_2$ of iodine, the following relations were obtained:

$$GeCl_4: \quad (T_2{}^{sc})^{-1} = 5.13 A_{35}{}^2 \tau_1{}^{35} \tag{9}$$

$$GeBr_4: \quad (T_2{}^{sc})^{-1} = 4.04 A_{81}{}^2 \tau_1{}^{81} \tag{10}$$

$$GeI_4: \quad (T_2{}^{sc})^{-1} = 11.7 A_{127}{}^2 \tau_1{}^{127} \tag{11}$$

where γ and Q are the gyromagnetic ratio and a quadrupole moment, respectively.

When $(2\pi J) \ll 1/T_2$ or $1/T_1$, $\tau_1{}^{35}$ is equal to T_1 of ^{35}Cl of nucleus of S.[18,19] Since it is reported that T_2 of ^{35}Cl of $GeCl_4$ is 4.1×10^{-5} s,[21] the requirement of eq 7 is satisfied for the relaxation of germanium in $GeCl_4$. Since $1/T_1$ of ^{35}Cl is predominantly via quadrupole, and hence proportional to τ_c (rotational correlation time), the plot of ln $(1/T_2 - 1/T_1)$ of germanium relaxation vs $1/T$ should be a straight line with a negative slope, which is in line with the experimental results. If the scalar coupling relaxation is contained in the T_2 relaxation mechanism, $1/T_1$ is proportional to τ_c, and $1/T_2 - 1/T_1$ to $T_1{}^{Cl}$, i.e., $1/\tau_c$. Then the slopes of ln $(1/T_1)$ and ln $(1/T_2 - 1/T_1)$ vs $1/T$ should be equal in magnitude and opposite in sign. Indeed, the values of ΔE obtained from slopes of ln $(1/T_1)$ and ln $(1/T_2 - 1/T_1)$ are in good agreement: 6.3 and 6.7 kJ/(mol K), respectively.

By substitution of $\tau_1{}^{35}$ by T_2 of ^{35}Cl of $GeCl_4$ into eq 9, the coupling constant $J(^{73}Ge-^{35}Cl)$ was estimated as 24 Hz. As T_2 of ^{35}Cl of $GeCl_4$ should be shorter than T_1 because of the quadrupole effect of ^{73}Ge, i.e., the scalar contribution of T_2 of ^{35}Cl, the coupling constant between ^{73}Ge and ^{35}Cl may be slightly smaller than 24 Hz. Unfortunately, no experimental data for T_1 of ^{35}Cl of $GeCl_4$ are available, and hence it is impossible to refine our coupling constants. To the best of our knowledge, however, this is the first reported experimental value for this coupling.

In GeI_4, T_1 is equal to T_2 at room temperature, as shown in Table I, which suggests that the spin–lattice and spin–spin relaxations occur solely via the quadrupole relaxation mechanism. As anticipated from eq 11, the scalar contribution of the spin–spin relaxation rate of GeI_4 is proportional to $A_{127}{}^2$ and $\tau_1{}^{127}$. If J of GeI_4 is assumed to be 60 Hz on the basis of the fact that J of SnI_4 is larger than that of $SnCl_4$ by a factor of 2.5 and if $\tau_1{}^{127}$ is assumed to be below 10^{-7} s because τ(I) of SnI_4 is 1.5×10^{-7} s at 150 °C, $(T_2{}^{sc})^{-1}$ is negligible compared with $(T_2{}^{q})^{-1}$. Therefore, the experimental result that there is no scalar contribution to T_2 of GeI_4 at room temperature is very reasonable.

Reorientational Correlation Time. The reorientational correlation time τ_c is given by eq 12[24] which introduces a microviscosity

$$\tau_c = 4\pi r^3 \eta f/3kT \tag{12}$$

f into the Stokes–Einstein–Debye equation, where r is the molecular radius, η the solution viscosity, k the Boltzmann constant, and T the absolute temperature. f is defined by eq 13, where a_s

$$f = [6(a_s/a) + (1 + a_s/a)^{-3}]^{-1} \tag{13}$$

and a are the solvent and solute radii, respectively. τ_c at 30 °C and the activation energies are given in Table II. The activation energies were obtained from the temperature dependence of τ_c, i.e., the slope of ln τ_c vs $\Delta E/RT$, in which τ_c was calculated from eq 12. In Figure 2, plots of ln τ_c of $GeCl_4$ and $GeBr_4$ against $1/T$ are given. The plots using τ_c thus obtained are straight lines; ΔE was estimated on the basis of eq 2. Table III shows, for the sake of comparison, the correlation times of the tetrahalides of IVB elements, which were calculated from the line width of signals (method a) and the viscosities of solutions (method b), and the activation energies. Methods a and b give τ_c values different from each other by a factor of 10. For $GeCl_4$, however, τ_c values are of the same order regardless of the method used.

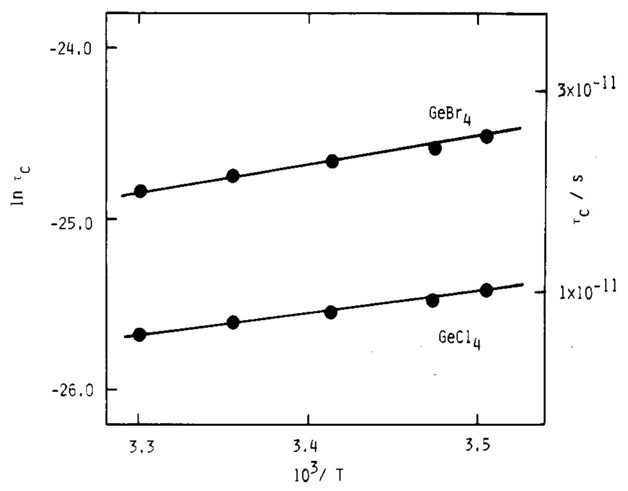

Figure 2. Plots of ln τ_c vs $1/T$ for tetrahalogermanes.

Table III. Correlation Times for the Various Methods of Measurement and Activation Energies of Tetrahalides for Reorientational Motion

compd	$\tau_c{}^a/10^{-11}$ s (t/°C)	$\tau_c{}^b/10^{-11}$ s (t/°C)	$\tau_c{}^c/10^{-11}$ s (t/°C)	ΔE/kJ mol^{-1}	ref
CCl_4	0.17 (30)			7.57	9
	0.153 (26)	1.9 (26)			21
$SiCl_4$	0.193 (26)	1.3 (26)			21
$GeCl_4$	0.233 (26)	2.1 (26)			21
		3.5 (30)	0.78 (30)	9.6	this work
$GeBr_4$		7.5 (30)	1.8 (30)	11.2	this work
$SnCl_4$	0.50 (26)	3.3 (26)		7.78	21
$SnBr_4$	0.31 (21)				11
SnI_4	0.367 (150)				10
$PbCl_4$	1.72 (25)			21.6	12

[a] Calculated from $(^5/_2\pi^2 T_2)(e^2Qq/h)^{-2}$ for the halogen nucleus. [b] Calculated from $4\pi\eta r^3/3kT$. [c] Calculated from $4\pi\eta r^3 f/3kT$.

It was shown that in tetraalkylgermanes, the correlation times become longer and the activation energies increase as the molecular radius increases. It was also shown that a plot of ln τ_c vs the molecular radius (r) and a plot of the activation energy of reorientation ΔE vs. r give excellent correlation coefficients.[8]

When the data of tetrahalogermanes are added to those of tetraalkylgermanes, these plots remain linear except for that of $GeBr_4$. A plot of ln τ_c vs r is given in Figure 3. The correlation coefficient R is 0.980. In Figure 4 a plot of ΔE vs r is given (R = 0.950). The deviation of the $GeBr_4$ plot from linearity seems to indicate that not only the molecular radius but also the molecular weight take part in determining the magnitude of the activation energy of reorientation.

Coupling Constants. Jameson and Gutowsky[27] showed that the coupling constant J_{xn} could be related to the reduced coupling constant K_{xn}, which depended only on the molecular electronic structure; thus, $K_{xn} = (1/h\gamma_x\gamma_n)J_{xn}$. In Table V are given the coupling constants J, $|J/\gamma|$, and the absolute values of reduced

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Table IV. Relaxation Mechanisms for the Central Nuclei in Tetrahalides and Quadrupole Coupling Constants and Correlation Times for Scalar Coupling for the Specified Halogens

compd (MX_4)	relaxn mechanism[a] T_1	T_2	solvent	$e^2Qq/h(X)^{25}$/MHz	$\tau(X)/10^{-6}$ s (t/°C)	ref
$^{13}C^{35}Cl_4$	SR		neat	81.3^{26}	21.3 (25) 25.1 $(26)^{21}$	9
$^{29}Si^{35}Cl_4$				40.8	79 $(26)^{21}$	21
$^{73}Ge^{35}Cl_4$	QD	QD, SC	$CDCl_3$ (50% v/v)	51.4	41 $(26)^{21}$	this work
$^{73}Ge^{81}Br_4$	QD	QD, SC	$CDCl_3$ (50% v/v)			this work
$^{73}Ge^{127}I_4$	QD (30 °C)	QD (30 °C)	$CS_2 + C_6D_6$ (1:1)			this work
$^{119}Sn^{35}Cl_4$	SR	SC	neat	48.2	22 $(26)^{21}$	10, 11
$^{119}Sn^{81}Br_4$	SR, SC	SC	neat	330	0.748 (21)	11
$^{119}Sn^{127}I_4$	SR, SC	SC	neat	1390	0.15 (150)	10, 11
$^{207}Pb^{35}Cl_4$	SR, SC	SC	concd H_2SO_4		7.15 (25)	12

[a] SR = spin–rotation; QD = quadrupole; SC = scalar coupling.

Table V. γ(M), J, $|J/\gamma|$, and $|K|$ for M–H of Group IVB Nuclei[27]

MH	compd	$\gamma(M)^a$/ 10^3 G^{-1} s^{-1}	J/Hz	$\lvert J/\gamma \rvert$/ 10^{-3} G	$\lvert K \rvert$/ 10^{20} cm^{-3}
$^{13}CH^{28}$	CH_4	1.071	125	117	41.4
^{29}SiH	SiH_4	−0.846	202	239	84.6
^{73}GeH	GeH_4	−0.149	97.6	655	232
^{119}SnH	SnH_4	−1.588	1931	1216	431
^{207}PbH	HMe_3Pb	0.888	2379	2679	949

[a] $\gamma(H) = 4.360 \times 10^3$ s^{-1} G^{-1}.

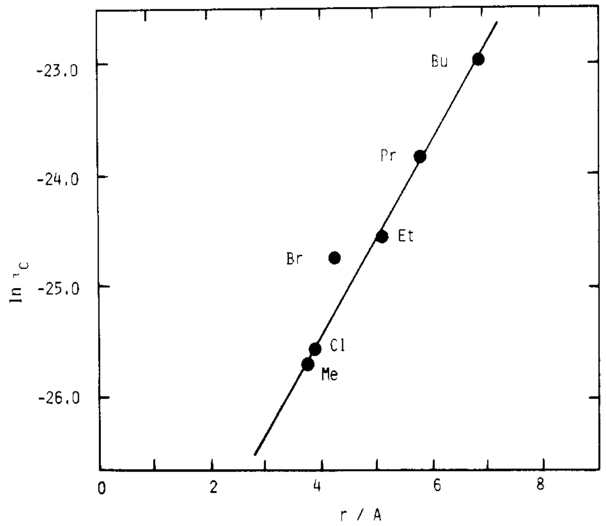

Figure 3. Plot of ln τ_c vs radii of GeR_4.

coupling constants K of M–H bonds of group IVB nuclei. The magnitudes of all the coupling constants listed markedly increase as the atomic number of M increases.

These authors[27] suggested that the magnitude of the coupling constants primarily depended on the Fermi contact contribution, which in turn depended on the nature of the bonding orbitals employed by each atom to form the bond in question. Thus, the coupling constants are eventually governed by the electron density at the nuclei involved. As the coupling constant increases, the reduced coupling constant increases.

Table VI shows the coupling constants, $|J/\gamma|$, and reduced coupling constants, $|K|$, of M–X bonds of group IVB nuclei (X = ^{35}Cl, ^{81}Br, ^{127}I). There is a marked increase in J, $|J/\gamma|$, and K in tetrachlorides as the atomic number of M increases. Tzalmona[29] described this in tetramethyl compounds of the type $M(CH_3)_4$; $|J/\gamma|$ was a function of $bZ^{1.3}$, where Z and b were the atomic number of M and a constant, respectively. In MH_4 the value of $bZ^{1.2}$ is calculated from the relevant values in Table V, and in MCl_4 $bZ^{1.7}$ is calculated.

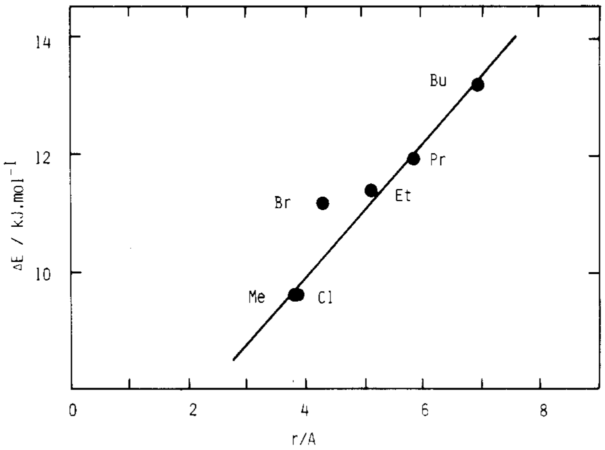

Figure 4. Plot of ΔE vs. radii of GeR_4.

Table VI. J, $|J/\gamma|$, and $|K|$ for M–X of Group IVB Nuclei

compd	J/Hz	$\lvert J/\gamma \rvert$/ 10^{-3} G	$\lvert K \rvert$/ 10^{20} cm^{-3}	ref
$^{73}Ge^{35}Cl_4$	24 (max)[a]	162	585	this work
$^{119}Sn^{35}Cl_4$	375	236	855	10, 11
$^{119}Sn^{81}Br_4$	920	579	760	11
$^{119}Sn^{127}I_4$	940	592	1049	10, 11
$^{207}Pb^{35}Cl_4$	705	794	2874	12

[a] Calculated by substituting τ_c with T_2 of ^{35}Cl of $GeCl_4$.

Acknowledgment. We wish to thank Professor H. Watanabe (Department of Chemistry, The University of Tokyo) for his help in measurement of viscosity, Professor I. Ando and Woo-Sik Jung (Tokyo Institute of Technology) for valuable discussions. Thanks also due to the ASAI Germanium Research Institute and the Ministry of Education for financial support.

Registry No. $GeCl_4$, 10038-98-9; $GeBr_4$, 13450-92-5; GeI_4, 13450-95-8; ^{73}Ge, 15034-58-9.

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(29) Tzalmona, A. *Mol. Phys.* **1964**, *7*, 497.

(30) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)