Aspects of Germanium-73 Nuclear Magnetic Resonance Spectroscopy†

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Germanium-73 n.m.r. observations have been extended to a wider range of hydrides, alkyls, and polygermanes, together with further observations on mixed halides. Chemical shifts, coupling constants, linewidths, relaxation times, and derived parameters are reported. The current limits of observability are indicated.

As ^{73}Ge is the most difficult Group 4 isotope for n.m.r. work (gyromagnetic ratio, $\gamma = -0.9332 \times 10^{-7}$ rad T^{-1} s^{-1}, spin $I = \frac{9}{2}$, nuclear electric quadrupole moment, $Q = -0.18 \times 10^{-28}$ m, natural abundance 7.76%), it is not surprising that there have been only limited reports of its observation. In an earlier paper[1] the enhancement of sensitivity in hydrides and alkyls by proton polarization transfer was explored, and fuller results are now presented.

The earliest ^{73}Ge n.m.r. data stem from a survey by Schwenk and co-workers[2] which included T_2 determinations by the Carr-Purcell sequence. Soon after, Kidd and Spinney[3] observed binary and ternary mixtures of germanium tetrahalides, assigning ^{73}Ge shifts to all possible Cl/Br/I species. More recent work has extended ^{73}Ge observations to germatranes,[4,5] carbofunctional tetra-alkyls,[6] shifts and relaxation times of tetrasubstituted germanes[7,8] including methylgermacyclohexanes,[9] and to silicon–germanium hydrides.[10] There are few reports on arylgermanes, apart[7] from $GePh_4$, and Ge directly bonded to a transition metal has not been observed. Comparisons of chemical shifts between pairs of C/Si, Si/Sn, and Sn/Pb analogues[11] have been extended[12] to include the Si/Ge and Ge/Sn pairs, but with fewer than 30 examples available. Very recently, a fuller study of tetra-alkoxygermanes[13] produced a different linear relationship between δ(Ge) and δ(Si) for this class of compound, reinforcing earlier[6,7,12] relations based on limited data.

We now report further ^{73}Ge observations including chemical shifts, linewidths, coupling constants, relaxation times, and derived parameters. Table 1 lists all the compounds examined by ^{73}Ge resonance in this work. A full listing of all published data, for approximately one hundred compounds, will be published elsewhere.[14] The only other available data are a handful of coupling constants measured *via* the bonded element, including ^1J(GeH) = −97.6[15] or −87.8 Hz[16] for GeH_4, ^1J(GeC) = −18.7[17] and ^2J(GeH) = 2.94 Hz[18,19] for $GeMe_4$, ^1J(GeF) = 178.5 Hz for GeF_4[20] and 98 Hz for $[NH_4]_2[GeF_6]$.[21]

Results

The germanium-73 chemical shifts, linewidths, and coupling constants, given in Table 1, were measured on samples ranging in concentration from neat liquids (7—9 mol dm^{-3}), requiring only two or three scans, to about 0.1 mol dm^{-3}, requiring several thousand scans to recognize the signal (signal-to-noise ratio > 2.5). Experimental errors in chemical shifts for clear signals ranged from ±0.1 p.p.m. for sharp signals to ±1 p.p.m. for broad signals, and similarly for the other parameters. The higher polygermanes and methyldigermanes were difficult to free from related species and the results for Ge_3H_8, Ge_4H_{10}, and the two dimethyldigermanes are of lower quality than the others. The ^{73}Ge linewidths were less than 30 Hz except for some polygermanes. Other work has shown wider lines for carbofunctional germanes,[6] up to $W_{\frac{1}{2}}$ = 315 Hz for $GeMe_2(CH_2Cl)_2$. By comparison, $W_{\frac{1}{2}}$ values[22] for tetrahalide ions range up to 60 Hz for ^{27}Al and to 270 Hz for ^{71}Ga. Linewidths increased with viscosity, molar mass, replacement of H by GeH_3 or of Cl by I, and with reduction of symmetry at Ge, all as expected for dominant quadrupolar relaxation (see below).

Chemical Shifts.—As the values collected in Table 2 illustrate, variations of shift with concentration, solvent, and calibration mainly fall within the experimental errors shown above. Other studies are also in agreement within this range. For $GeEt_4$, all observations in weakly interacting media agree within experimental limits and this is typical for all peralkyls, including the use of aromatic solvents or $Cr(acac)_3$ (acac = acetylacetonate). Strong donors, such as pyridine, do not affect the higher tetra-alkyls, though $GeMe_4$ and $GeEt_4$ need further study. For the tetrahalides, as shown for $GeCl_4$, non-donor solvents, concentration, the addition of HCl up to 1 atm, or the presence of methylchlorogermanes caused no changes. Addition of pyridine gave a small but significant shift in the $GeCl_4$ resonance but no further signal. Addition of C_6H_5NHCl to $GeCl_4$ gave no shift in the $GeCl_4$ resonance and no signal from a chloro complex was seen. Other iodides would probably show solvent effects similar to those[2] for GeI_4 (Table 1).

The hydrides show small changes in chemical shift with medium, illustrated by the range of values for GeH_4 from −296.7 ± 0.3 p.p.m. in C_6D_6 to −301.5 ± 1 p.p.m. for dilute solutions in C_6H_{14} or Et_2O. For all the hydrides listed, the range of shifts with solvent and concentration was within 5 p.p.m., and there is a consistent aromatic solvent effect of about +2 p.p.m. One significant anomaly is the values[12] for GeH_4, Ge_2H_6, and Ge_3H_8 measured in a solvent-free germane mixture, which are 10—14 p.p.m. to high field of those in Table 1. Similarly, for neat liquid Ge_3H_8, δ(GeH_3) = −286.0 p.p.m. and δ(GeH_2) = −323.5 p.p.m. Clearly the germanes differ as a medium from their saturated solutions in organic solvents.

The compounds GeI_4 (−1 081.8 p.p.m.) and $GeCl_4$ (30.9 p.p.m.) represent the bounds of the observed chemical shift range. Halogen-free germanium compounds show a narrower range from −324.6 (H_3GeSiH_3) to 17.8 p.p.m. ($GeEt_4$) with the tetra-alkyls clustered together at higher shift and the polyhydrides near the low-shift limit. The range of ^{73}Ge shifts is five times greater than the range of ^{13}C shifts for MeGe species. Thus the methylgermanes are readily distinguished by δ(^{73}Ge) values, while the range of δ(^{13}C) values is similar to the range of solvent shifts. Comparisons with other Group 4 element shifts have been made elsewhere.[12]

Chemical shifts change as expected with local shielding effects. Thus for H_3GeMH_3 and $H_3GeMMeH_2$, changing M from Si to Ge or to C changes the $^{73}GeH_3$ shift by 15 or by 100

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

Table 1. ^{73}Ge Chemical shifts, linewidths, and coupling constants

Compound	Solvent	δ/p.p.m.	$W_{\frac{1}{2}}$/Hz	J(GeH)/Hz	Other studies
$GeMe_4$	Neat	0.0 ± 0.5	1.0 ± 0.1	2.95 ± 0.03	2, 6, 7, 8
$GeEt_4$	Neat	17.8 ± 0.2	0.9 ± 0.1	3.0 ± 0.6	2,7
$GePr^n{}_4$	Neat	2.4 ± 0.6	3.3 ± 0.2		2
$GeBu^n{}_4$	Neat	6.0 ± 0.6	5.1 ± 0.5		2, 6, 8
$Ge(n\text{-}C_5H_{11})_4$	Neat	6.0 ± 0.6	9.5 ± 0.5		
$Ge(n\text{-}C_6H_{13})_4$	Neat	5.6 ± 0.6	18 ± 2		
$GePh_4$	C_6H_6	−33.2 ± 0.5	5.9 ± 0.5		7
$GeMeH_3$	Bu_2O	−209.2 ± 0.1	1.5 ± 0.2	94.5 ± 0.5 (^1J) 3.48 ± 0.1 (^2J)	
$GeMe_2H_2$	Neat	−127.6 ± 0.1	1.8 ± 0.2	92.3 ± 0.5 (^1J) 3.42 ± 0.2 (^2J)	
$GeMe_3H$	C_6H_{14}	−56.9 ± 0.2	4.0 ± 0.5	93 ± 2	
$GeEtH_3$	Neat	−186.4 ± 0.6	3.4 ± 0.2	92.4 ± 0.5	
$GeEt_2H_2$	Neat	−88.4 ± 1	20 ± 2	88.7 ± 2.0	
$GeEt_3H$	Neat	−15.7 ± 0.8	20 ± 2	88 ± 2	
GeH_4	Bu_2O	−298.7 ± 0.7	1.1 ± 0.7	97.6 ± 0.3	
Ge_2H_6	Bu_2O	−311.8 ± 0.7	12.7 ± 0.5	95.5 ± 0.5	
Ge_3H_8	C_6H_{12}[a]	−298 ± 2	25 ± 5	94 ± 1 (GeH_3)	
		−310 ± 10	40 ± 10	90 ± 10 (GeH_2?)	
Ge_4H_{10}	Neat[a]	−284 ± 2	76 ± 5	(GeH_3)	
		−300 ± 10	100 ± 20	(GeH_2?)	
$H_3GeGeMeH_2$	*b*	−306.2 ± 0.2	2.0 ± 0.2	90.0 ± 0.5 (GeH_3, ^1J) 4.7 ± 0.3 (GeH_3, ^2J)	
		−210 ± 1.5	13 ± 2	($GeMeH_2$)	
$(GeMeH_2)_2$	Neat	−209 ± 1	7 ± 1		
$H_3GeGeMe_2H$	*c*	−296 ± 1	7 ± 1	85 ± 2 (GeH_3)	
		−127 ± 1	3 ± 1	($GeMe_2H$?)	
$H_3GeGeMe_3$	Neat	−295.6 ± 0.7	13.2 ± 1.2	90.7 ± 1 (GeH_3)	
		−47.7 ± 1.0	63 ± 10	($GeMe_3$)	
$(MeH_2Ge)_2GeMeH$	Neat	−206.2 ± 0.8	2.0 ± 0.5	($GeMeH_2$)	
		−125 ± 2	8 ± 4	(GeMeH)	
H_3GeSiH_3	Bu_2O	−324.6 ± 0.7	1.2 ± 0.7	91.5 ± 0.1 (^1J) 2.7 ± 0.2 (^2J)	
$H_3GeSiMeH_2$	C_6H_6	−316.4 ± 1	4 ± 2		
MeH_2GeSiH_3	C_6H_6	−229.7 ± 0.8	4.0 ± 0.5		
$GeCl_4$	Neat	30.9 ± 0.1	2.1 ± 0.1		2, 3, 7
$GeBr_4$	Neat	−311.3 ± 0.1	2.2 ± 0.1		2, 3
GeI_4	CS_2	−1 081.8 ± 0.2	4.1 ± 0.2		2, 3
	C_6H_6	−1 106 ± 4	10 ± 4		2
$GeCl_3Br$	*d, e*	−47.8 ± 0.1	2.2 ± 0.1		3
$GeCl_2Br_2$	*d, e*	−131.3 ± 0.1	2.2 ± 0.1		3
$GeClBr_3$	*d, e*	−219.4 ± 0.1	2.2 ± 0.1		3
$GeCl_3I$	*f*	−235.9 ± 0.2	23 ± 4		3
$GeCl_2I_2$	*f*	−523.7 ± 1	23 ± 4		3
$GeClI_3$	*e, f*	−809.9 ± 1	22 ± 4		3
$GeBr_3I$	*e, g*	−509.3 ± 1	22 ± 4		3
$GeBr_2I_2$	*e, g*	−707.4 ± 1	29 ± 6		3
$GeBrI_3$	*e, g*	−899.8 ± 1	20 ± 4		3
$GeCl_2BrI$	*e*	−326 ± 3	7 ± 3		3
$GeClBr_2I$	*e*	−418 ± 3	20 ± 4		3
$GeClBrI_2$	*e*	−611 ± 1	27 ± 5		3

No signal was observed from the following compounds as neat liquids (except as shown): $GeMeCl_3$, $GeMe_2Cl_2$, $GeMe_3Cl$, $GeMe_2HBr$ (in C_6H_6), $GeMeH_2Br$, $GeEt_2Cl_2$, $GeBu^n{}_2Cl_2$, $(H_3Ge)_2Te$ (in CS_2), $GeMeI_3$ (in C_6H_6), GeI_2 (in C_6H_6), $GeCl_4(C_5H_5N)_2$ (in CCl_4), and $[Ge(OH)_6]^{2-}$ (from GeO_2 in concentrated NaOH).

[a] Small samples: contain some GeH_4 from decomposition during handling. [b] Neat but with $GeMe_2H_2$. [c] *ca.* 80:20 mixture with $(GeMeH_2)_2$. [d] From 1:1 $GeCl_4$:$GeBr_4$. [e] From 1:1:2 $GeCl_4$:$GeBr_4$:GeI_4. [f] From 1:1 $GeCl_4$:GeI_4. [g] From 1:1 $GeBr_4$:GeI_4.

p.p.m., correlating with the electronegativity[23] differences of 0.1 and 0.6 respectively. Most of the tetrahalide shifts vary linearly with the sum of the halogen electronegativities, but the heavy-atom species[24] show the usual addition shielding effects of anisotropic induced fields. This is clearly seen for the iodides, and is present for the bromides and also for the polygermanes.

Chemical shifts for the tetra-alkyls approach a constant value (δ 5—6 p.p.m.) as the chain length of the alkyl ligand increases, but $GeEt_4$ exhibits a significantly higher frequency than the other tetra-alkyls. The δ(^{29}Si) values of SiR_3H compounds[25] display a similar anomaly for R = Et. Replacement of R by H gives shifts to low frequency but with the non-linear relationship illustrated in Figure 1. Such patterns are usually found[26] for compounds of the type $MX_{4-y}Y_y$ (M = ^{29}Si, ^{119}Sn, or ^{207}Pb) when shielding is plotted as a function of y, and are related to the way in which the p-electron imbalance[27] affects the paramagnetic shielding term. Both the alkylgermane and mixed tetrahalide series have δ values which, while in close accord with

Table 2. Effects of media on the ^{73}Ge chemical shifts and linewidths of $GeEt_4$ and $GeCl_4$

Compound	Concentration (volume)	δ/p.p.m.	$W_{\frac{1}{2}}$/Hz	Notes
$GeEt_4$	Neat	17.8 ± 0.2	0.9 ± 0.1	
	Neat	18.1 ± 0.7		Ref. 2
	70% $CDCl_3$	19 ± 2	1.6 ± 0.1	
	$CDCl_3$	17.3	1.7	Ref. 7
	50% in $GeCl_4$	18.2 ± 0.1	1.1 ± 0.5	
	25% $Bu^n{}_2O$	17.7 ± 0.1	1.3 ± 0.1	No change for 75 or 6%
	6% C_6H_{12}	17.8 ± 0.1	0.9 ± 0.05	
	Dilute in $GeEt_3H$	17.7 ± 2		
$GeCl_4$	Neat	30.9 ± 0.1	1.8 ± 0.1	
	Neat or CS_2	30.9 ± 0.5	1.2 to 2.5	Refs. 2, 3, 7. No change on dilution
	Traces HCl	30.8 ± 0.1	2.2 ± 0.1	
	1 atm HCl	30.9 ± 0.5	2.2 ± 0.3	
	50% in $GeEt_4$	31.1 ± 0.1	2.2 ± 0.1	
	20% $MeNO_2$	30.9 ± 0.5	7.8 ± 0.5	
	1:1 C_5H_5NHCl in 50% $MeNO_2$	30.7 ± 1.0	8 ± 2	
	1:1.7 $GeCl_4$:C_5H_5N in 60% CCl_4	27.6 ± 0.7	7.0 ± 0.6	
	In $GeMe_nCl_{4-n}$ mixture	30.5 ± 0.4	6 ± 1	

Table 3. Observed and calculated equilibrium ^{73}Ge intensity distributions (as %) for several mixed halide systems

System		$GeCl_4$	$GeCl_3Br$	$GeCl_2Br_2$	$GeClBr_3$	$GeBr_4$
$SiBr_4$–$GeCl_4$	Obs.	3.1	12.5	28.8	34.4	21.3
	Calc.	10.5	32.6	33.7	19.0	4.2
$SnCl_4$–$GeBr_4$	Obs.	44.1	36.9	15.2	3.8	0.0
	Calc.	7.7	27.7	36.9	22.6	5.1
$HgCl_2$–$GeBr_4$	Obs.	2.8	9.1	25.3	37.7	25.1
	Calc.	0.4	4.8	21.0	42.2	31.7
$HgCl_2$–$GeBr_4$–CS_2	Obs.	6.8	18.9	32.4	29.7	12.2
	Calc.	0.8	7.6	26.5	40.9	24.2

Calculated values assume a statistical distribution with zero enthalpy change.

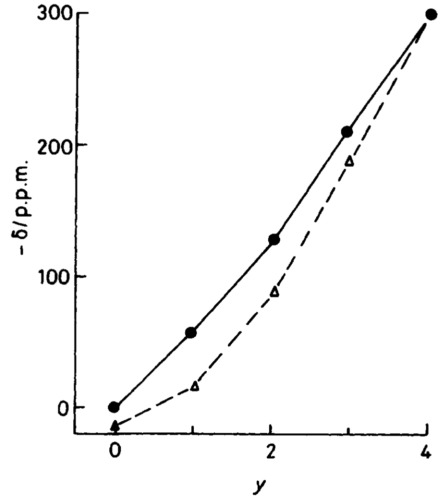

Figure 1. Variation of ^{73}Ge chemical shift, −δ/p.p.m. with y, the number of hydrogens, for $GeMe_{4-y}H_y$ (●) and $GeEt_{4-y}H_y$ (△)

the pairwise model,[28] deviate significantly from a first-order model.[29]

Halogen Redistribution.—In reported[3] redistributions, mixtures of $GeCl_4$ and $GeBr_4$ came to equilibrium in a few days whilst a $SnCl_4$–$SnBr_4$ mixture equilibrated in under a minute,[30] at room temperature and without strict exclusion of water vapour.

Table 3 shows the results of studies of equimolar ratios of GeX_4 and MY_y for M = Si or Sn, $y = 4$ and M = Hg, $y = 2$, each with X, Y = Cl or Br. Because of the smaller linewidths and number of observed signals, ^{73}Ge n.m.r. proved to be a more useful probe than ^{199}Hg, ^{119}Sn, or ^{29}Si n.m.r. spectroscopy in these systems. For M = Hg, it took several days at room temperature to reach equilibrium, probably reflecting the insolubility of $HgCl_2$ and the exclusion of HCl. No ^{199}Hg signal was detected at any stage. By contrast, the $HgCl_2$–$HgBr_2$ exchange is very fast.[30] With M = Sn, redistribution was slower requiring weeks at room temperature or several days at 75 °C. Resonances from ^{119}Sn and ^{73}Ge were monitored, but their substantially greater linewidths made the ^{119}Sn signals less useful. For M = Si, equilibrium was reached only after several months including intermittent heating to 75 °C. The ^{29}Si resonances showed only one silicon species to be present at any point in the reaction: for example, $SiCl_3Br$ when halfway to equilibrium, and with twice the linewidth of the ^{73}Ge signals. Once the exchange was underway, all five germanium tetrahalides could be seen. Table 3 shows how the equilibrium ^{73}Ge intensity distributions compare with the calculated binomial distributions, assuming zero enthalpy change for the halogen redistribution. It is clear that the halogen distribution is more complex than predicted by simple statistics.

Table 4. Germanium-73 nuclear relaxation times

Compound	Solvent	$T_1{}^a$/ms	$T_2{}^*$/ms	T^b/°C	Number of determinations
$GeMe_4$	80% $Bu^n{}_2O$	560 ± 100	290 ± 30	27.0	1
	75% $Bu^n{}_2O$	459 ± 50	(>160)	−14.8	1
		597(12)	320 ± 30	27.0	5
		662 ± 70	400 ± 40	41.3	1
$GeEt_4$	Neat	284 ± 30	(>160)	−14.5	1
		510(15)	350 ± 40	27.0	10
		526 ± 50	(>160)	34.2	1
		598 ± 60	(>160)	47.8	1
		731 ± 70	(>250)	67.5	1
	75% $Bu^n{}_2O$	367(6)	290 ± 30	27.0	3
	25% $Bu^n{}_2O$	298(5)	240 ± 20	27.0	3
	6% C_6H_{12}	905(24)	370 ± 40	27.0	3
$GePr^n{}_4$	Neat	113(2)	96 ± 10	27.0	3
$GeBu^n{}_4$	Neat	71.7(6)	62 ± 6	27.0	3
$Ge(n\text{-}C_5H_{11})_4$	Neat	30.6(2)	29 ± 3	27.0	3
$Ge(n\text{-}C_6H_{13})_4$	Neat	18.7(0.7)	19 ± 2	27.0	3
$GeMeH_3$	0.7 atm $Bu^n{}_2O$	374(11)	250 ± 30	27.0	4
	c	575(12)	220 ± 20	27.0	3
$GeMe_2H_2$	*c*	294(6)	180 ± 20	27.0	3
$GeMe_3H$	*c*	340(60)	190 ± 20	27.0	3
$GeEtH_3$	Neat	95.0(1)	94 ± 10	27.0	5
$GeEt_3H$	Neat	7.4 ± 0.7	8 ± 1	−14.5	1
		9.9 ± 1	10 ± 2	−1.0	1
		12.6(0.8)	12 ± 1	27.0	3
		18.4 ± 2	17 ± 2	47.9	1
		21.4 ± 2	16 ± 3	59.0	1
GeH_4	1.2 atm $Bu^n{}_2O$	863 ± 90	290 ± 30	−14.5	1
		1 300(40)	290 ± 30	27.0	4
		1 290 ± 130	400 ± 40	34.3	1
Ge_2H_6	0.2 atm $Bu^n{}_2O$	22.2(1)	20 ± 2	27.0	3
$H_3GeGeMeH_2$	*c*	264(8)	160 ± 20	27.0	3 (GeH_3)
		50.5(2)	45 ± 5	27.0	6 ($GeMeH_2$
H_3GeSiH_3	0.7 atm $Bu^n{}_2O$	573(6)	270 ± 30	27.0	3
$GeCl_4$	Neat	823 ± 80	110 ± 20	−14.8	1
		1 020(10)	150 ± 20	27.0	4
		1 300 ± 130	110 ± 20	59.0	1
	50% $CDCl_3$	240 ± 20	120 ± 20	27.0	3
$GeCl_4$	*d*	520(5)	140 ± 10	27.0	3
$GeBr_4$	Neat	206(6)	140 ± 10	27.0	3
	d	337(40)	140 ± 10	27.0	3
$GeCl_3Br$	*d*	233(5)	140 ± 10	27.0	3
$GeCl_2Br_2$	*d*	217(4)	140 ± 10	27.0	3
$GeClBr_3$	*d*	278(6)	140 ± 10	27.0	3

[a] The standard deviation of the mean is given in parentheses for all the T_1 values measured at 27.0 °C. For measurements at other temperatures, the ± value is the estimated maximum for random errors. The limit for systematic errors is estimated at 10%. [b] Temperature errors are ±0.2 for 27.0 °C, others ±1.0 °C. [c] In mixtures of methylgermanes. [d] From 1:1 $GeCl_4$:$GeBr_4$.

Coupling Constants.—The coupling constant $^1J(^{73}Ge–^1H)$ was directly observed for all the germanium hydrides which were available in sufficient abundance. Only the value for GeH_4 has been reported[15,16] from ^1H n.m.r. spectra, while Ge_2H_6 gave[16] no detectable satellites in the proton spectrum. The value found here, 97.6 ± 0.3 Hz, confirms the higher[15] of the two literature values for GeH_4. Similarly, ^2J(GeCH) values for a number of methyl derivatives are now available in addition to the value[18,19] for $GeMe_4$ from ^1H observation. Scalar coupling from germanium to protons ranged from 88.0 to 97.6 Hz for $|^1J(^{73}Ge–^1H)|$ and 2.7 to 3.5 Hz for $|^2J(^{73}Ge–M–^1H)|$ where M = C or Si. By analogy with other Group 4 compounds, ^1J is expected to be negative and ^2J positive. If the contact term is dominant,[30] the magnitude of ^1J or ^2J is expected to increase with increasing *s* character in the bonds. This is reflected in the variation of ^1J when H is replaced by R = Me or Et in the alkylgermanes (Figure 2).

Nuclear Relaxation Times.—All the relatively narrow ^{73}Ge absorption lineshapes were Lorentzian[2] (with the possible exception of those from compounds with unresolved proton coupling), thus the extreme-narrowing condition applies ($\omega_0\tau_c \ll 1$), setting an upper limit[31] on the correlation time, $\tau_c \ll 50$ ns, at the observation frequency of 3.13 MHz. Under this condition, T_1 and T_2 are equal and are given[32] for ^{73}Ge by equations (1) and (2) where χ' is defined as the nuclear quadrupole coupling constant, *q* the electric field gradient, and η the asymmetry parameter, which describes the deviation from cylindrical symmetry.

$$1/T_1 = 1/T_2 = (\pi^2/45)(\chi')^2\tau_c \qquad (1)$$

$$\chi' = (e^2qQ/h)(1 + \eta^2/3)^{0.5} \qquad (2)$$

All ^{73}Ge T_1 experiments using the inversion-recovery tech-

Table 5. Activation energies for molecular reorientation, correlation times, and ^{73}Ge nuclear quadrupole coupling constants

Compound	Solvent	E_a/kJ mol^{-1}	$\tau_c{}^a$/ps	$\chi'(^{73}\text{Ge})^a$/MHz
$GeMe_4$	75% $Bu^n{}_2O$	4.3 ± 0.9	0.79	3.1
$GeEt_4$	Neat	8.4 ± 0.6	1.7	2.3
	75% $Bu^n{}_2O$	—	1.7	2.7
	25% $Bu^n{}_2O$	—	1.6	3.1
$GePr^n{}_4$	Neat	(10 ± 2)	4.9	2.9
$GeBu^n{}_4$	Neat	—	12	2.3
$Ge(n\text{-}C_5H_{11})_4$	Neat	—	18	2.9
$Ge(n\text{-}C_6H_{13})_4$	Neat	—	25	3.1
$GeMeH_3$	0.7 atm $Bu^n{}_2O$	—	0.60	(4.5)
	b	—	0.50	(4)
$GeMe_2H_2$	*b*	—	0.63	(5)
$GeMe_3H$	*b*	—	1.4	(3)
$GeEt_3H$	Neat	11.3 ± 0.9	1.2	(17)
GeH_4	1.2 atm $Bu^n{}_2O$	5.2 ± 0.7	—	—
$H_3GeGeMeH_2$	*b*	—	0.8	(5) (GeH_3)
		—	0.8	(9) ($GeMeH_2$)
$GeCl_4$	Neat	4.4 ± 0.4	—	—

[a] Maximum random errors: χ' (20%); τ_c (10%). Values in parentheses are rough estimates. [b] In mixtures of methylgermanes.

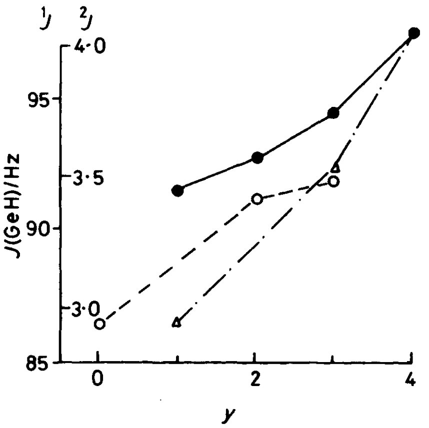

Figure 2. Variation of the absolute value of the coupling constants with *y*, the number of hydrogens, for $GeMe_{4-y}H_y$ [(●) ^1J(GeH), (○) ^2J(GeH)] and $GeEt_{4-y}H_y$ [(△) ^1J(GeH)]

niques exhibited a single exponential decay, supporting the expected extrapolation to $I = \frac{5}{2}$ of T_1 theory[33] as applied to isotopes having $I = \frac{5}{2}$ and $\frac{7}{2}$. These T_1 values and $T_2{}^*$ values ($= \pi W_{\frac{1}{2}})^{-1}$ are listed in Table 4.

The expected dominance of the quadrupolar relaxation mechanism in ^{73}Ge nuclear relaxation was confirmed in work on $GeMe_4$,[7,8] $GeEt_4$,[7] and on other tetra-alkylgermanes and tetra-alkoxygermanes.[8] A further test, suggested by Marks and Shimp,[34] is based on the usual observation that $\tau_c \approx \eta^1/T$, where η^1 is the macroscopic viscosity of the solution and T is the absolute temperature. Since T_1 and τ_c are the only variables for a given compound, equation (1), changes in τ_c arising through dilution or temperature change will affect the T_1 values. The data in Table 4 demonstrate that T_1 increases on dilution in an inert solvent, and with increasing sample temperature (Figure 3), as expected for a quadrupolar relaxation mechanism.[35] The condition $T_1 \geqslant T_2{}^*$ is obeyed for all ^{73}Ge measurements. Relaxation times (see Table 4) increase with an increase in symmetry at germanium (*q* decreases), or a decrease in viscosity (τ_c decreases), as expected for the quadrupolar mechanism. Thus symmetry changes can be invoked to rationalize the T_1 values for $GeEt_3H$ (12.6 ms) and $GeEt_4$ (510 ms), whilst the differences between $H_3GeGeMeH_2$ (T_1 = 264 and 50.5 ms) and H_3GeGeH_3 (T_1 = 22.2 ms) reflect a change in viscosity (b.p.[36] = 54.7 and 29.0 °C respectively).

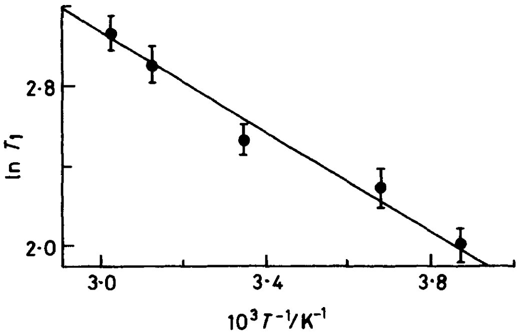

Figure 3. Variation with temperature of the ^{73}Ge relaxation time in neat $GeEt_3H$

Nuclear Quadrupole Coupling Constants.—By inspection of equation (1) it is seen that χ' can be calculated if $T_1(^{73}\text{Ge})$ and an independent value of τ_c are available. The correlation time is obtainable from the ^{13}C dipolar relaxation of ligand methylene or methyl carbons. The general form of this dual spin-probe technique has been used for a variety of nuclei.[37] Applying the equation for dipolar relaxation in the extreme region of motional narrowing to carbon and hydrogen, and using a representative value of the average C–H bond distance, yields equation (3), where N_H is the number of directly bonded hydrogens.

$$\tau_c = (44.2)/T_1(^{13}\text{C})N_H \qquad (3)$$

$$\chi'(^{73}\text{Ge}) = 2.135/[T_1(^{73}\text{Ge})\tau_c]^{0.5} \qquad (4)$$

Together with equation (1) this yields equation (4) when τ_c is expressed in ps, χ' in MHz, and T_1 in seconds. These equations are used to calculate the τ_c and χ' values listed in Table 5.

Neat tetra-alkyls have a small range of χ' values, and these generally increase slightly as the chain length increases. Thus, as the chain length increases, the large reduction in $T_1(^{73}\text{Ge})$ is mainly due to an increase in viscosity (τ_c) rather than to a decrease in effective symmetry at germanium. In the same medium, $GeMe_4$ and $GeEt_4$ have similar effective symmetry at germanium which is lowered by the addition of $Bu^n{}_2O$.

Activation Energy Parameters.—Equation (5) yields[31] activation parameters for molecular reorientation where T_1^0 is the value of T_1 at infinitely high temperature.

$$T_1 = T_1^0 \exp(-E_a/RT) \qquad (5)$$

Using the data of Table 4, linear plots of $\ln(T_1)$ *vs.* $1/T$ were obtained, yielding the activation energies listed in Table 5.

Discussion

The pattern of chemical shifts found here is amplified by published data. The $Ge(OR)_4$ species[2,4–6] show shifts in the range −35 to −75 p.p.m., carbofunctional ligands[6,7] from −5 to +40 p.p.m., pergermylsilanes[10] from −275 to −315 p.p.m., 2-furyl[7] at −113 p.p.m., and 2-thionyl[7] at −96 p.p.m. The highest reported shift is +155 p.p.m., an indirect value for $Ge(SMe)_4$.[38]

It is clear from the larger data set now available that all the recent linear relationships[5–7,12,13] between δ(Si) and δ(Ge) are compatible but oversimplified. A good fit to all data is given by two lines, one close to the general relation[12] for the majority of compounds, and the other covering compounds with four oxygen ligands[13] and a few[6] similar compounds. For the main set the gradient[12] is 3.3, equal to that expected[27] from the *p*-orbital radius ratios and implying the same shielding mechanisms at Si and Ge. For the oxygen set the gradient is substantially smaller at 1.6,[13] 2.01,[7] or 1.85[6] depending on the compounds chosen. For this sub-set, there is a difference between the shielding at Si and Ge which is readily explained by the much greater tendency of silicon to be involved in extra π bonding to oxygen and similar elements. There are insufficient common pairs fully to establish this extra relation for Si/Sn or to examine Ge/Sn for any residual effect. Overall, there are now excellent grounds for believing that an accurate prediction of a ^{73}Ge shift may be made from ^{29}Si or ^{119}Sn data.

Redistribution reactions of halogens between different alkyl-substituted Group 4 elements were monitored[39,40] by ^{1}H n.m.r. spectroscopy in a number of classic studies. The preliminary studies reported here indicate that ^{73}Ge will be the more useful nucleus for studying Si/Ge or Ge/Sn exchange in the tetrahalides. The data in Table 3, and the very slow reactions observed, are in accord with earlier observations[40] on mono- and di-methyl systems. A fuller study over a higher temperature range is underway which will allow an interesting test of general[41] predictions for equilibria of redistributions.

Two sets of T_2 values have been determined[2,42] by the Carr–Purcell method, and are in good agreement with the T_2^* values in Table 4 for GeR$_4$, R = H, Cl, Br, Pr, or Bu, with Schwenk's values[2] for GeBr$_4$, but high compared with Takeuchi's values[42] or with T_2^*. Values[2] for R = Me or Et do not match the T_2^* values in Table 4 nor the earlier[2] T_2^*, and probably reflect the experimental difficulties of the T_2 measurement. For the larger molecules, with relaxation times of 100 ms or less, the T_1 values match T_2^* within experimental error. For molecules with $T_1 >$ 100 ms there is increasing divergence as expected.

From study of the temperature variation of T, it was concluded that spin–lattice relaxation occurred by a quadrupole mechanism for GeMe$_4$,[7,8] GeEt$_4$,[7] and for other tetra-alkyls and tetra-alkoxides.[8] The data of Table 4 are in accord with these observations and suggest this mechanism applies also to GeEt$_3$H. Takeuchi and co-workers[42] have produced evidence for an additional scalar coupling mechanism for ^{73}Ge spin–spin relaxation in GeH$_4$, GeCl$_4$, and GeBr$_4$, and the more limited data of Table 4 are in accord with these results. Finally, the very marked effect of solvent and concentration on T_1 for the smaller species is worth noting, with a range of room-temperature T_1 values for GeMe$_4$ from 1 110[8] to 295 ms,[7] for GeEt$_4$ from 905 to 205 ms,[7] for GeH$_4$ from 1 300 to 570 ms,[42] and for GeCl$_4$ from 1 020 to 280 ms.[42] Where similar systems have been examined, the values obtained by different authors are in agreement. Such values have earlier been queried when compared with T_2^*.

The activation energies for molecular reorientation of 5.6 and 5.8 kJ mol^{-1} found[31] for ^{47}Ti and ^{49}Ti, respectively, in TiCl$_4$ (80% v/v in toluene) are not very different from the value of 4.4 kJ mol^{-1} determined here for neat GeCl$_4$. The linearities of the present plots of ln T_1 *vs.* $1/T$, as measured by r (-0.999 to -0.983), compare well with those obtained in the study on TiCl$_4$ (-0.995 to -0.977).

Nuclear quadrupole coupling constants for quadrivalent organogermanium compounds were typically 3 MHz, whereas χ' for GeF$_6^{2-}$ was estimated as 5.8 MHz by Tarasov and Buslaev.[43] Hao *et al.*[31] calculated $\chi'(^{49}$Ti) in TiF$_6^{2-}$ as 1.6 MHz, and felt that their value was more reliable than the larger value of 4.5 MHz given by Tarasov and Buslaev, due to their own more direct measurement of relaxation and correlation times. This same argument could be used when comparing the present χ' values with those of Tarasov and Buslaev. The correlation times in Table 5 compare reasonably with values[8] for GeMe$_4$ ranging from 0.45 ps in CD$_3$OD to 0.70 ps in C$_6$H$_{12}$ and for GeBu$_4$ of 6.8 ps in CDCl$_3$.

Limits of ^{73}Ge *Observation.*—No ^{73}Ge signal was detected from the compounds listed in Table 1, although ^{13}C and ^{1}H signals were found where appropriate. It is common to find resonances which are too broad for detection from quadrupolar nuclei with medium-to-large line-broadening factors in environments of low symmetry (*e.g.* no ^{71}Ga resonance was observed[22] from Ga$_2$Cl$_6^{2-}$). For Ge, substituents may be divided into two groups: (*a*) H, GeR$_3$, SiR$_3$, alkyl, and substituted alkyl; (*b*) halogen, OR, and SR. Resonances have been observed from germanes containing mixtures of substituents within either group, but no signal was found from species with mixtures of ligands (*a*) and (*b*).[1,2,5,13] A signal was found for GePh$_4$, but not[6] for GePhEt$_3$. For carbofunctional tetra-alkyls, quadrupolar α substituents are often limiting: thus GeMe$_2$(CH$_2$Cl)$_2$ was observed[6] but GeMe$_3$(CHCl$_2$) was not. No signal has yet been observed for Ge directly bonded to Mn, Fe, or Co.

At present, it appears that ^{73}Ge resonance from germanium in significantly unsymmetrical environments is not observable, and the formation of five- or six-co-ordinate complexes in solution may not be detectable.

Experimental

Compounds.—The solvents CS$_2$, C$_6$H$_6$, C$_6$H$_{14}$, and Bu$^n{}_2$O were dried and degassed. The gases GeH$_4$, Ge$_2$H$_6$, GeMeH$_3$, and H$_3$GeSiH$_3$ were distilled into the solvent to give about 1 atm pressure in the sealed tube. The tetra-alkylgermanes were used as supplied by T.N.O. The hydrides, polygermanes, and silylgermanes were prepared[44] using standard techniques.

Methyldigermane was prepared by the action of a silent electric discharge on GeMeH$_3$ and GeH$_4$ followed by separation by gas chromatography or vacuum-line distillations. The compounds MeH$_2$GeSiH$_3$ and H$_3$GeSiMeH$_2$ were prepared by addition of iodine or SnCl$_4$, respectively,[45] to silylgermane followed by addition of MgMeI in Bu$_2$O.

All these compounds showed appropriate i.r. and ^{1}H n.m.r. spectra. The following δ(^{13}C) values (±0.5 p.p.m.) were determined: GeMe$_4$, 0.0; GeEt$_4$, 4.0, 9.3; GePr$_4$, 16.4, 19.0, 19.6; GeBu$_4$, 13.3, 14.4, 27.6, 28.4; Ge(C$_5$H$_{11}$)$_4$, 13.5, 14.7, 23.2, 25.8, 36.9; Ge(C$_6$H$_{13}$)$_4$, 13.6, 14.9, 23.7, 26.2, 32.6, 34.4; GeMeH$_3$, -1.5; GeMe$_2$H$_2$, -7.0; GeMe$_3$H, -3.1; GeEtH$_3$, 1.5, 12.2; GeEt$_2$H$_2$, 0.0, 8.3; GeEt$_3$H, 4.2, 10.5; Ge$_2$MeH$_5$, -8.1; (GeMeH$_2$)$_2$, -9.3; Me$_3$GeGeH$_3$, 0.8; (MeH$_2$Ge)$_2$GeMeH, -3.9, -9.8; and MeH$_2$GeSiH$_3$, -9.9. The δ(^{29}Si) values (p.p.m.) were: H$_3$GeSiH$_3$, -98.0 ± 0.1, $W_{\frac{1}{2}} = 1.0 \pm 0.2$; MeH$_2$GeSiH$_3$, -95.1 ± 0.1, $W_{\frac{1}{2}} = 4.0 \pm 0.5$ Hz.

Traces of HCl and HBr were removed from GeCl$_4$ (BDH) and GeBr$_4$ (Koch-Light) respectively, by vacuum distillation. Germanium tetraiodide was prepared by standard procedures,[46] and purified by vacuum sublimation at 110 °C.

Dry-box techniques were used with involatile compounds like GeBr$_4$, and volatile compounds were degassed and handled *in vacuo*. Most samples were contained in sealed glass tubes (outside diameter 5 mm), although a few were sealed into tubes of 3 or 8 mm outside diameter. These tubes were concentrically located in a 10-mm n.m.r. tube containing D$_2$O for the lock.

Methods.—Measurements were made as described earlier,[1] with the inclusion of a JEOL-JES-VT-3 variable-temperature unit. Chemical shifts were measured relative to neat GeCl$_4$, and referenced to GeMe$_4$ according to the relationship

Table 6. Observed signal enhancements using i.n.e.p.t.

		Maximum enhancement		Average $E/\%^a$	
Compound	Solvent^b	Coupled^c	Decoupled	Coupled	Decoupled
$GeMe_4$	Bu_2O	5.2, 12	5.4	73	67
	C_6H_6	—	5.4	—	67
	C_6H_6	—	5.2	—	65
	C_6H_5Cl	—	3.7	—	39
$GeEt_4$	$CDCl_3$	2.2^d	2.2	20	33
$GeMe_2H_2$	Neat	7.8	2.8	103	73
	Neat^c	2.2	2.0	30	35
$GeMe_3H$	C_6H_{14}	—	3.4	—	89
	C_6H_{14}^{e}	—	2.3	—	33
$GeEtH_3$	Neat	2.4	3.0	44	69
$GeEt_3H$	Neat	—	1.4	—	37
H_3GeSiH_3	Bu_2O	3.0, 8.3	4.2	77	96
	Bu_2O^{e}	1.8, 4.6	2.7	44	62

[a] Percentage fraction of theoretical enhancement actually attained. [b] Solutions *ca.* 20%. [c] The smallest non-zero enhancement of the inner multiplets and the largest of the outermost multiplets are listed. [d] Average value for partially resolved spectrum. [e] Based on ^2J, all other values from ^1J.

$\delta(GeMe_4) = \delta(GeCl_4) + 30.9$. Negative values are to low frequency of $GeMe_4$. Absolute frequencies, relative to the ^1H signal of $SiMe_4$ (100 000 000 Hz), were 3 488 423 ± 10 Hz for $GeCl_4$ (lit.,[2] 3 488 423 ± 10 Hz) and 3 488 318 ± 20 Hz for $GeMe_4$ (lit.,[2] 3 488 315 ± 10 Hz). Coupling constants were measured directly from ^{73}Ge n.m.r. spectra, and in the case of GeH_4 also from ^1H n.m.r. spectra. Linewidths were obtained directly from high-resolution spectra, recorded under conditions where the magnetization recovered fully between scans.

A standard 180°–τ–90° phase-alternated sequence was used to obtain ^{13}C and ^{73}Ge T_1 data, where τ represents the interval between the given events. A waiting time of at least $5T_1$ was employed before repeating the sequence. Typically, a T_1 determination required 5 τ measurements spanning $0.1T_1$ to $1.4T_1$. Standard JEOL software[47] was used to calculate T_1 from a least-squares fit to a plot of $\ln(M_0 - M_\tau)$ *versus* τ, where M_0, M_τ are magnetisations at time = 0 and τ, respectively.

Since the error in a single T_1 determination may be up to 20%, the $GeEt_4$ study was based on 10 measurement cycles giving 510 ms with a standard deviation of 15 ms. Other determinations used between three and six measurements. Additional single determinations on the same compounds under different conditions (for example at different temperatures or concentrations) were regarded as sufficient for comparisons. For ^{13}C T_1 values, the average of two independent determinations was used.

Details of insensitive nuclei enhancement by proton polarization transfer (i.n.e.p.t.) sequences used are given elsewhere.[1] Other proton polarization transfer (p.t.) sequences, distortionless enhancement by p.t.(d.e.p.t.)[48] and universal p.t.(u.p.t.),[49] have been used experimentally, but were less advantageous than i.n.e.p.t. Since inter-pulse sequence times are smaller for i.n.e.p.t. than for u.p.t., especially for a nucleus with a large spin like ^{73}Ge, the loss of p.t. during the sequence due to relaxation is less for i.n.e.p.t. than for u.p.t. U.p.t. delivered up to 80% (GeH_4) and 30% ($GeMe_4$) of the signal-to-noise ratio of i.n.e.p.t. The range of compounds receiving enhancement *via* i.n.e.p.t. has been extended from those reported earlier.[1] Table 6 lists these later results.

Acknowledgements

We thank the New Zealand University Grants Committee for doctoral and post-doctoral scholarships (to P. J. W.), and, together with the Golden Kiwi Lottery Fund, for grants towards the purchase of the spectrometer. We acknowledge the Germanium Research Committee (now defunct) which provided the germanium tetra-alkyls, through T.N.O. We are also grateful to Professor Takeuchi who provided results prior to their publication.

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Received 13*th November* 1986; *Paper* 6/2173