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ON THE RELATION BETWEEN GERMANIUM-73 AND OTHER MAIN GROUP IV ELEMENT NMR CHEMICAL SHIFTS

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Summary

Close correlations exist between chemical shifts for germanium-73 versus silicon-29 ($r = 0.967$; 29 species) and versus tin-119 ($r = 0.991$; 26 species). Like earlier Si/Sn and Sn/Pb correlations, the slopes for the correlation lines involving Ge correspond closely to the $\langle r^{-3} \rangle_{np}$ ratios for the element pairs.

Mitchell [1] has recently discussed the relation between the chemical shifts of the Main Group IV elements in the pairs C/Si, Si/Sn and Sn/Pb, finding the correlations 1–3 where N was the number of compounds compared:

$$\delta(\mathrm{Si}) = 0.787\delta(\mathrm{C}) - 61.7;\ r = 0.825\ (N = 43) \quad (1)$$

$$\delta(\mathrm{Sn}) = 5.119\delta(\mathrm{Si}) - 18.5;\ r = 0.990\ (N = 48) \quad (2)$$

$$\delta(\mathrm{Pb}) = 2.424\delta(\mathrm{Sn}) + 74.8;\ r = 0.975\ (N = 35) \quad (3)$$

Our recent studies of germanium-73 parameters [2], supplementing earlier observations [3,4] allow us to extend Mitchell's correlations to include this central element. We have measured ^{73}Ge shifts on 14 analogues of the Si species listed by Mitchell [1] and on 11 analogues of his Sn species. Adding further values from the literature extends the number of comparable pairs to 29 for Ge/Si and to 26 for Sn/Ge. These sets are smaller and more limited than those available [1] for the other pairs of Group IV elements, mainly reflecting the scarcity of germanium-73 data.

There are general limitations on germanium observation [2], reflecting its low gyromagnetic ratio and large nuclear spin. One particularly limiting factor is the failure, so far [2–4], to observe germanium-73 resonance from any mixed haloalkylgermane, R_nGeX_{4-n} or halogermane H_nGeX_{4-n}, and no data from arylgermanes * have been reported. However, the germanium data do range widely from tetrahalides to alkyl species, so the more limited range of comparisons is still a valid one.

* *Note added in proof.* The ^{73}Ge shift for $GePh_4$ has recently been determined as -31.6 ppm (Prof. Y. Takeuchi, personal communication). Inclusion of XPh_4 does not significantly alter eqs. 4 and 5.

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The data used are listed in Table 1. Our measurements for germanium-73 are used as far as possible, for consistency and because they are a little more precise, but there is close agreement with earlier reports for the tetrahalides [4] and for the tetraalkyls [3]. Literature values are used for $Ge(OMe)_4$ [3] $Ge(SMe)_4$ [5] and $ROGe(OCH_2CH_2)_3N$ (R = Me, Pr) [6], these last observed by double resonance. For Si and Sn, we have used Mitchell's values supplemented by additional silicon [7] and tin [8] values from the literature.

Results and discussion

The germanium-73 data fit the relationships

$$\delta(\mathrm{Ge}) = 3.32\delta(\mathrm{Si}) + 39.9;\ r = 0.967(N = 29) \quad (4)$$

$$\delta(\mathrm{Sn}) = 1.56\delta(\mathrm{Ge}) - 87.4;\ r = 0.991(N = 26) \quad (5)$$

TABLE 1

GROUP IV CHEMICAL SHIFT DATA (ppm vs. XMe_4)

Number	Compound	$\delta(^{29}Si)$	$\delta(^{73}Ge)$	$\delta(^{119}Sn)$
1	XMe_4	0.0	0	0
2	XMe_3H	−15.5	−57.2	−105
3	XMe_2H_2	−37.3	−127.6	−227
4	$XMeH_3$	−65.2	−209.2	−346
5	XH_4	−93.1	−283.7	
6	X_2H_6	−104.8	−300.5	
7	X_3H_8 (XH_2)	−116.5	−324	
8	GeH_3SiH_3	−98.0	−324.6	
9	XEt_4	7.1	17.8	−6.7
10	XEt_3H	0.15	−15.7	−40.0
11	XEt_2H_2		−88	−231
12	$XEtH_3$		−186.4	−282
13	X(n-Pr)$_4$		2.4	−16.8
14	X(n-Bu)$_4$		6.0	−12
15	$X(OMe)_4$	−79.2	−36.0	
16	$X(SMe)_4$	38.6	153	160
17	$X(OMe)(OCH_2CH_2)_3N$	−95.4	−60.6	
18	$X(OPr)(OCH_2CH_2)_3N$	−95.0	−63.4	
19	XCl_4	−20.0	30.9	−150
20	XCl_3Br	−34.3	−47.8	−263
21	XCl_2Br_2	−50.7	−131.3	−385
22	$XClBr_3$	−69.8	−219.4	−508
23	XBr_4	−92.7	−311.3	−638
24	XBr_3I	−149.5	−509.3	−916
25	XBr_2I_2	−212.3	−707.4	−1187
26	$XBrI_3$	−280.1	−899.8	−1447
27	XI_4	−346.2	−1081.8	−1701
28	XCl_3I	−75.4	−235.9	−557
29	XCl_2I_2	−151.5	−523.7	−955
30	$XClI_3$	−245.9	−809.9	−1342
31	XCl_2BrI	−98.9	−326.2	−672
32	$XClBr_2I$	−122.8	−417.6	−796
33	$XClBrI_2$	−181.9	−613.5	−1068

If only the Si and Sn analogues common to the available Ge species are compared, the data fit the relation

$$\delta(\mathrm{Sn}) = 5.10\delta(\mathrm{Si}) - 87.2;\ r = 0.991\ (N = 22) \qquad (2a)$$

As (2) and (2a) are very close (the displacement of the intercept is about 10% of the range), this suggests that the germanium relationships (4) and (5) can be validly compared with the rest of the Group, (1) to (3), despite the narrower range of compounds, and other pairs such as Ge/Pb may be validly calculated.

If the local paramagnetic shielding involving the valence level p orbitals dominates the chemical shift, then the slopes of (4) and (5) should match the ratios of Jameson and Gutowsky's $\langle r^{-3} \rangle_{np}$ values [9]. The calculated ratios are 3.3 ± 0.5 for Ge/Si and 1.3 ± 0.1 for Sn/Ge which compare well with the experimental gradients of 3.32 ± 0.17 and 1.56 ± 0.04 respectively.

In the Ge/Si relation, the positions of the oxygen species 15, 17 and 18 is anomalous, paralleling Mitchell's [1] note that a low field shift of δ(C) corresponds to a high field shift of δ(Si) for parallel pairs of analogues. If these three compounds are excluded, the regression analysis improves to $r = 0.995$ yielding $\delta(\mathrm{Ge}) = 3.29\delta(\mathrm{Si}) + 13.3$. The unusual values of the metallatranes, 17 and 18, is almost certainly a reflection of contributions from pentacoordination, and the $X(OMe)_4$ ratio may also indicate increased coordination.

Clearly, since the species are relatively small in number and of only three main types, these linear correlations involving germanium-73 may be spuriously good. The values for halides with 3 or 4 iodine atoms fit better to a curve, for example. However, the simple linear correlations noted by Mitchell [1] are clearly extendable to include germanium: any more sophisticated analysis must await the availability of a much larger data set. From the point of view of ^{73}Ge work, we can use the much more abundant ^{29}Si and ^{119}Sn data as a guide with considerable confidence.

Experimental

The ^{73}Ge chemical shifts were measured with respect to neat $GeCl_4$ and converted by $\delta(GeMe_4) = \delta(GeCl_4) + 30.9$; negative values are to low frequency of $GeMe_4$ ($\delta = 0$). Absolute frequencies, relative to the ^{1}H signal of $SiMe_4 = 100$ MHz, were $3\,488\,423 \pm 10$ Hz for $GeCl_4$ (ref. [3] $3\,488\,423 \pm 10$ Hz) and $3\,488\,318 \pm 20$ Hz for $GeMe_4$ (ref. [3] $3\,488\,315 \pm 10$ Hz). Measurements were made on a JEOL FX 90Q spectrometer equipped with the low frequency insert.

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