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Theoretical Study on Metal NMR Chemical Shifts: Germanium Compounds

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Abstract

Germanium chemical shifts were studied theoretically by the ab initio molecular orbital method. The compounds studied were $GeMe_{4-x}Cl_x$ and $GeMe_{4-x}H_x (x = 0-4)$. The calculated values of the germanium chemical shifts agreed well with the available experimental values. The germanium chemical shift is due to the p-electron mechanism that reflects the ligand electronic effect on the $p-p^*$ excitation term in the second-order paramagnetic term. For $GeMe_{4-x}H_x$, the chemical shift is almost linear to the number of the ligand, x. On the other hand, a U-shaped dependence is predicted for the chemical shifts of the $GeMe_{4-x}Cl_x$ series and is shown to be caused by the strong and nonadditive electron-withdrawing ability of the Cl ligand. The diamagnetic contribution is relatively small for the chemical shift and is determined solely by a structural factor. © 1994 John Wiley & Sons, Inc.

1. Introduction

Among the experimental studies of multinuclear magnetic resonance of IVb group elements, germanium is not as popular as are silicon and tin, whose NMR parameters have been vastly accumulated in several review articles [1–4]. The experimental difficulty in observing germanium chemical shifts and other NMR parameters is caused by its electric quadrupole moment, leading to a broadening of the ^{73}Ge resonance [5]. In this paper, the germanium NMR chemical shifts of several germanium compounds are studied theoretically by an ab initio molecular orbital method. We study the mechanism of the germanium NMR chemical shifts to understand the nature of the chemical bonds between germanium and ligands.

In this series of studies [6–16], we have studied systematically the metal chemical shifts of Cu, Ag, Zn, Cd, Sn, Se, Ti, Mn, Nb, Mo, Ga, and In complexes. The calculated metal chemical shifts have been in fairly good agreement with experiments. The electronic mechanisms of the metal chemical shifts of these compounds may be grouped as follows [7]:

1. p-electron and d-hole mechanisms for the Cu, Ag, Zn, and Cd complexes: The electronic configurations of these metals are characterized by $d^{10}s^{1-2}p^0$.

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2. d-excitation mechanism for the Ti, Mn, Nb, and Mo complexes: These metals have open d-subshell, d^n, in their ground state.
3. p-excitation mechanism for the Sn and Si complexes. The electronic configuration is s^2p^2.

In the above three cases, the chemical shifts are due mainly to the paramagnetic term. However,

4. diamagnetic mechanism is important for the Ga and In complexes. The chemical shifts are determined mainly by the structural factor and are insensitive to the detailed electronic structure. The p electron of the s^2p^1 metal is strongly bound to the M–L bond and is insensitive to the external magnetic field.

These results are summarized in a recent review article [7].

The Ge atom has the s^2p^2 configuration and many similarities are expected for the chemical shifts of the Si and Sn compounds. For the Si and Sn compounds, linear and U-shaped dependencies of the chemical shifts on the number of the ligands exist. The linear dependence is found for $\mathrm{MeR}_{4-x}\mathrm{R}'_x$ series with R and R′ being hydrogen, alkyl, phenyl, vinyl, etc., ligands. The U-shaped dependence is found when R′ is an electronegative ligand like a halogen, methoxy, etc. For Ge compounds, the linear dependence is actually observed for the $\mathrm{GeMe}_{4-x}\mathrm{H}_x$ series, but no clear data exist for the U-shaped dependence because of the large nuclear quadruple moment of the Ge nucleus. Thus, it is interesting whether the U-shaped relationship is calculated theoretically for the haloalkyl germanium compounds, and if the relationship is shown, the mechanism of the U-shaped dependence is interesting.

We study theoretically the germanium chemical shifts and their electronic mechanism for the germanium compounds, $\mathrm{GeMe}_{4-x}\mathrm{Cl}_x$ and $\mathrm{GeMe}_{4-x}\mathrm{H}_x$ ($x = 0$–4). In the next section, the calculational method, the basis sets, and the geometries of the compounds are explained. The correlations between the calculated and experimental values are then examined and the mechanism of the germanium chemical shifts is elucidated. We next analyze the origin of the U-shaped relationship in the $\mathrm{GeMe}_{4-x}\mathrm{Cl}_x$ series. Some concluding remarks are given in the last section.

2. Method of Calculation

The germanium chemical shifts are calculated by the ab initio finite perturbation method [17]. The details of the method have been described in a previous paper [8]. For the SCF calculations, a modified version of the HONDOG program is used [18]. The gauge origin is taken at the position of the germanium nucleus. The geometries of the germanium compounds are summarized in Table I [19]. The basis sets are taken from the book of Huzinaga et al. [20]. For Ge, the basis $(13s10p4d)/[5s4p1d]$ plus d-functions with the exponent of 0.246 are used. For the atoms directly connected to Ge, the basis set are as follows: $(9s6p)/[4s3p]$ plus polarization d-functions ($\zeta = 1.0$) for Cl, $(6s3p)/[3s2p]$ for C, and $(3s)/[2s]$ plus polarization p-functions ($\zeta = 1.0$) for H [21]. For the other atoms, the minimal basis sets with the same exponents are used.

TABLE I. Geometries of the germanium compounds used in the present calculations.[a, b]

Compound	Ge—C	Ge—Cl	Ge—H	C—H	∠CGeC	∠GeCH	∠HGeC	∠ClGeC	∠HGeH	∠ClGeCl
GeH_4	—	—	1.5251	—	—	—	—	—	109.47	—
$GeMeH_3$	1.9453	—	1.5290	1.083	—	110.52	109.64	—	109.30	—
$GeMe_2H_2$	1.9500	—	1.5320	1.083	110.00	110.43	109.47	—	109.47	—
$GeMe_3H$	1.9470	—	1.5320	1.095	109.60	110.97	109.34	—	—	—
$GeMe_4$	1.9450	—	—	1.120	109.47	108.20	—	—	—	—
$GeMe_3Cl$	1.9400	2.170	—	1.105	112.62	109.47	—	106.1	—	—
$GeMe_2Cl_2$	1.9260	2.155	—	1.105	121.70	107.79	—	107.0	—	106.10
$GeMeCl_3$	1.9450	2.135	—	1.103	—	110.50	—	112.3	—	106.40
$GeCl_4$	—	2.113	—	—	—	—	—	—	—	109.47

[a] In angstrom for length and in degree for angle.

[b] [19].

3. Correlation between Theory and Experiment

The germanium chemical shift of the compound M is defined relative to the reference compound, $GeMe_4$, as

$$\Delta\sigma_M = \sigma(GeMe_4) - \sigma(M).$$

The nuclear magnetic shielding constant σ is the sum of the diamagnetic term, σ^{dia}, and the paramagnetic term, σ^{para},

$$\sigma = \sigma^{dia} + \sigma^{para}.$$

σ^{dia} and σ^{para} are the first- and second-order terms, respectively, in the perturbation theoretic view.

We summarize in Table II the germanium nuclear magnetic shielding constants and the chemical shifts for all the compounds studied here. The calculated values are broken down into σ^{dia} and σ^{para} and further into valence and core MO contributions. The experimental values are shown in the last column of the table. For $GeMe_{4-x}Cl_x$ ($x = 1-3$), the experimental values are not available, so that the values are estimated from the Ge/Si correlations given by

$$\Delta(Ge)^{(1)} = 1.85\Delta(Si) + 1.52 \qquad (r = 0.970) \tag{1}$$

$$\Delta(Ge)^{(2)} = 2.01\Delta(Si) + 1.11 \qquad (r = 1.00) \tag{2}$$

$$\Delta(Ge)^{(3)} = 3.32\Delta(Si) + 39.9 \qquad (r = 0.967), \tag{3}$$

where r is the correlation factor. Correlation (1) is obtained from the MR_4 (M = Si, Ge; R = Me, Et, Ph, 2-furyl) compounds [22], correlation (2) from MMe_3R' (M = Si, Ge) compounds with R' being substituted alkyl or alkenyl ligand, and correlation (3) from alkyl, alkoxy, and halocompounds [5].

The correlation between the theoretical and experimental values of the chemical shift is shown in Figure 1. The theoretical values are in good agreement with the experimental ones. Similar good correlations have been observed for the chemical shifts of many different metal complexes [8–15].

The values estimated from the Ge/Si correlations (1)–(3) are shown in the last column of Table II in parentheses: They spread by as large as 91 ppm. For $GeMe_4$, whose chemical shift should be 0 ppm, the values estimated from correlations (1)–(3) are 1.52, 1.11, and 39.9 ppm, respectively. Therefore, correlations (1) and (2) seem to be more reliable than is correlation (3). However, correlations (1) and (2) are obtained from the compounds of alkyl and alkoxy ligands, which do not include any halocompound. Thus, for the chemical shift of $GeMe_3Cl$, correlations (1) and (2), which give 56.8 and 66.4 ppm, respectively, would be more reliable than correlation (3), but for the shift of $GeMeCl_3$, correlation (3), which gives 80.9 ppm, is expected to be more reliable. Whereas the Ge/Sn correlation

$$\Delta(Ge) = 0.641\Delta(Sn) + 56.0 \qquad (r = 0.991) \tag{4}$$

is also found in the literature [5], the values calculated from Eq. (4) lie in the values calculated from (1) to (3).

TABLE II. Diamagnetic and paramagnetic contributions, σ^{dia} and σ^{para}, to the germanium nuclear magnetic shielding constants σ and their analyses into core and valence MO contributions (in ppm).

	σ^{dia}				σ^{para}				σ^{total}		
Compound	Core	Valence	Total	Shift	Core	Valence	Total	Shift	Total	Shift	Expt.[a]
GeH_4	2716	62	2777	136	−16	−991	−1007	−403	1771	−267	−283.7
$GeMeH_3$	2725	86	2811	102	−24	−1107	−1131	−279	1680	−177	−209.2
$GeMe_2H_2$	2734	111	2845	68	−32	−1209	−1241	−168	1604	−100	−127.6
$GeMe_3H$	2744	135	2879	34	−41	−1286	−1327	−83	1552	−48	−57.2
$GeMe_4$	2753	160	2914	0	−49	−1361	−1410	0	1504	0	0.0
$GeMe_3Cl$	2787	159	2946	−33	−51	−1469	−1520	110	1426	78	(56.8−147.8)[b]
$GeMe_2Cl_2$	2822	159	2981	−67	−54	−1537	−1592	182	1389	115	(60.4−146.7)[b]
$GeMeCl_3$	2857	158	3015	−101	−58	−1539	−1597	187	1418	86	(24.1−81.3)[b]
$GeCl_4$	2893	159	3052	−139	−63	−1544	−1607	197	1446	58	30.9

[a] [3, 4].

[b] Estimated by Eqs.(1)–(3) in the text.

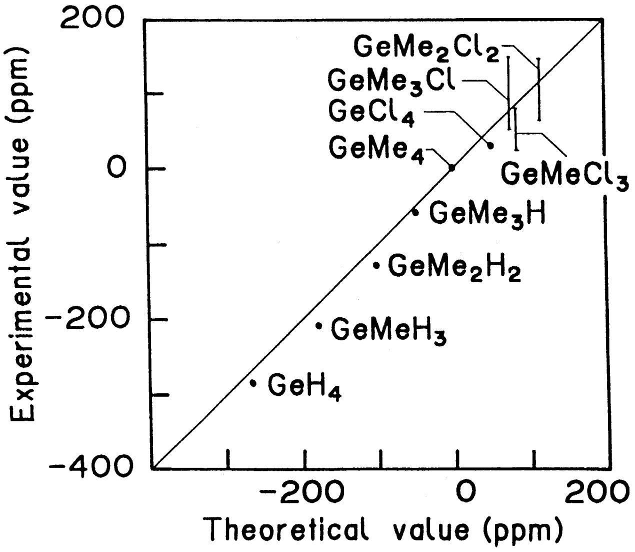

Figure 1. Correlation between the experimental and theoretical values of the ^{73}Ge chemical shifts of the germanium compounds. For $GeMe_{4-x}Cl_x$ ($x = 1-3$) compounds, the experimental values are not available so that the values estimated from the Ge/Si correlations given by Eqs. (1)–(3) are used as the experimental values.

4. Mechanism of the Germanium Chemical Shifts

Referring to Table II, we see that the paramagnetic term σ^{para} is about three times more important than is the diamagnetic term σ^{dia}, though the signs are different. We further note that the shift in the paramagnetic term reflects the valence MO contribution. In Table III, the diamagnetic and paramagnetic terms are further analyzed into germanium AO and ligand contributions. From this analysis, we see that the germanium *p* AO contribution in σ^{para} is dominant for the chemical shifts. The *d* AO contribution is relatively small. The *s* AO contribution vanishes identically, because *s* AO does not have an angular momentum. The ligand contributions are small, though they cannot be ignored in the $GeMe_{4-x}H_x$ ($x = 0-4$) series; e.g., though the individual methyl group contribution in $GeMe_4$ is only -18 ppm, it sums up to -72 ppm. For the $GeMe_{4-x}H_x$ ($x = 0-4$) series, the substitution of each methyl group with hydrogen results in a shift of 16 ppm to higher field. For the $GeMe_{4-x}Cl_x$ ($x = 0-4$) series, the ligand contribution is not important, since the contributions of Me and Cl are similar.

We next consider why the germanium *p* AO contribution is dominant. The atomic orbital energy level of the free Ge atom [23] is illustrated in Figure 2. The 4*s* and 4*p* orbitals of germanium mix to each other to form $sp^{\sim 3}$ hybrid orbitals. The *d* orbital level is much lower, so that the *d* orbitals can hardly mix with the germanium-ligand-bonding orbitals. Therefore, the *d* mechanism due to the angular momentum of the holes produced in the germanium *d* subshell is small.

The electron populations of the germanium 4*p* orbitals are 2.64, 2.23, and 2.07 for GeH_4, $GeMe_4$, and $GeCl_4$, respectively, and this order is understood from the

TABLE III. Analyses into *s*-, *p*-, and *d*-AO contributions and ligand contributions for the diamagnetic and paramagnetic contributions, σ^{dia} and σ^{para}, to the germanium nuclear magnetic shielding constant σ (in ppm).

	Diamagnetic contribution, σ^{dia}								Paramagnetic contribution,[a] σ^{para}						
	Ge								Ge						
Compound	*s*	*p*	*d*	Total	Me	Cl	H	Total	*p*	*d*	Total	Me	Cl	H	Total
GeH_4	1457	980	316	2753	—	—	6	24	−899	−102	−1001	—	—	−1	−4
$GeMeH_3$	1456	979	316	2751	41	—	6	59	−990	−119	−1109	−17	—	−2	−23
$GeMe_2H_2$	1456	979	316	2751	41	—	7	96	−1070	−134	−1204	−17	—	−2	−38
$GeMe_3H$	1455	978	317	2750	41	—	7	130	−1124	−149	−1273	−17	—	−2	−53
$GeMe_4$	1454	978	317	2749	41	—	—	164	−1175	−163	−1338	−18	—	—	−72
$GeMe_3Cl$	1454	977	318	2749	41	75	—	198	−1290	−163	−1453	−18	−14	—	−68
$GeMe_2Cl_2$	1455	976	319	2750	41	75	—	232	−1359	−169	−1528	−18	−14	—	−64
$GeMeCl_3$	1454	976	319	2749	40	75	—	265	−1358	−179	−1537	−17	−14	—	−59
$GeCl_4$	1454	976	320	2750	—	76	—	304	−1356	−194	−1550	—	−14	—	−56

[a] Germanium *s*-AO contribution is identically zero.

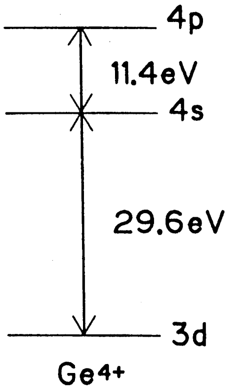

Figure 2. Atomic energy levels for the Ge ion.

order of the electronegativity H < CH_3 < Cl. They are smaller than 3.0, which is just the half-occupation of the p orbitals. It indicates that the p mechanism here is due to the angular momentum of the p-electrons, not to that of the p-holes. However, the order of the p-population is reverse to the order of the lower-field shift in the paramagnetic term, $GeH_4 < GeMe_4 < GeCl_4$, so that it does not explain the order of the chemical shift. However, in the previous study for the Sn chemical shift, we have shown that the similar order in the lower-field shift is explained by the difference in the $\sigma-\sigma^*$ excitation energy, which is $SnH_4 > SnCl_4 > SnMe_4$ in the case of the Sn chemical shift. Though we could not find the experimental excitation energy for the Ge complexes, we believe that the order is $GeH_4 > GeMe_4 > GeCl_4$ and that the Ge chemical shift is due to the $p-p^*$ mechanism. We note that the order between $GeMe_4$ and $GeCl_4$ is reverse to that of the tin complexes. Detailed analysis of the mechanism is given for the Sn complexes in [12] and we do not repeat it again in this paper.

For the metal chemical shifts so far studied [6–15], the diamagnetic term has been shown not to be important for the metal chemical shifts, except for the Ga and In chemical shifts. The same is true for the present germanium chemical shifts as already seen from Table III. Furthermore, the diamagnetic term is determined solely by the structural factors, as we have frequently pointed out. Flygare and Goodisman [24] reported that the diamagnetic term is expressed to a good approximation as

$$\sigma^{dia} = \sigma^{dia}(\text{free atom M}) + \frac{e^2}{3mc^2}\sum_{\alpha}\frac{Z_\alpha}{r_\alpha}, \tag{5}$$

where σ^{dia}(free atom M) is the diamagnetic shielding susceptibility for the free atom M [25], α, runs over all nuclei except for M, Z_α is the atomic number of the nuclei α and r_α is the distance between M and α. Equation (5) does not depend on any detailed information on the electronic structure of the complex except for the structural one.

5. U-shaped Relationship for the $GeMe_{4-x}Cl_x$ (x = 0–4) Series

The U-shaped dependence of the metal chemical shifts on the number x of electronegative ligands is well known for the Si and Sn chemical shifts in series like

$SiMe_{4-x}Cl_x$ and $SnMe_{4-x}Cl_x$. We therefore expect a similar U-shaped relationship for the $GeMe_{4-x}Cl_x$ series, as we wrote in the Introduction. However, the relationship has not yet been confirmed experimentally because of the high nuclear quadrupole moment of ^{73}Ge.

In Figure 3, our theoretical results for the $GeMe_{4-x}Cl_x$ and $GeMe_{4-x}H_x$ ($x = 0-4$) series are plotted against x. We see and predict then that the $GeMe_{4-x}Cl_x$ series certainly shows the U-shaped relationship, but the $GeMe_{4-x}H_x$ series does not, as expected. The experimental values for $GeMe_{4-x}Cl_x$, $x = 1,2,3$ are the values estimated with the use of Eqs. (1)–(3).

Figures 4 and 5 are prepared to analyze the mechanism and the origin of these shapes. Figure 4(a) and (b) show, respectively, the core and valence MO contributions to the diamagnetic and paramagnetic terms vs. the number of Cl ligands, x. Most of the curves shown in Figure 4 show linear dependence on x, except for the valence MO contributions to the paramagnetic term. In particular, that of the $GeMe_{4-x}Cl_x$ series shows a strong nonlinear dependence. Since the sum of linear functions is linear, the U-shaped dependence cannot be accounted for by a sum of several linear functions. Hence, we attribute the U-shaped relationship in the $GeMe_{4-x}Cl_x$ series as being due to the valence MO contributions to the paramagnetic term.

In Figure 5(a) and (b), the germanium AO and ligand contributions to the diamagnetic and paramagnetic terms, respectively, are shown. We again see that most curves are linear except for those of the p AO contributions to the paramagnetic term. In particular, that of the $GeMe_{4-x}Cl_x$ shows a strong nonlinear dependence. We therefore conclude that the U-shaped dependence of the $GeMe_{4-x}Cl_x$ series arises from

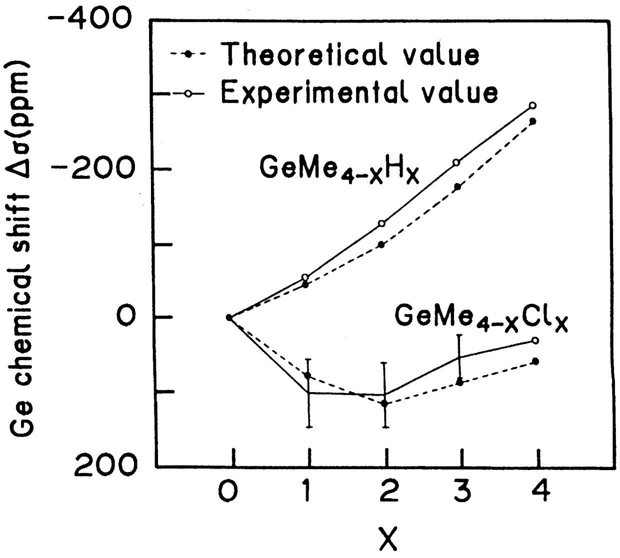

Figure 3. The dependence of the Ge chemical shift on the number of ligands x in the $GeMe_{4-x}H_x$ and $GeMe_{4-x}Cl_x$ series. The values estimated from Eqs. (1)–(3) are used for the experimental values of the $GeMe_{4-x}Cl_x$ ($x = 1-3$) compounds.

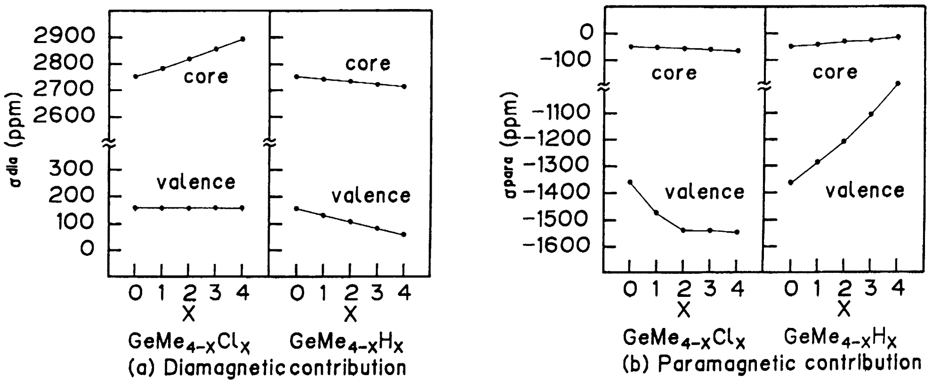

Figure 4. The x-dependencies of the core and valence MO contributions in the (a) diamagnetic and (b) paramagnetic terms of the germanium magnetic shielding constants for the $GeMe_{4-x}H_x$ and $GeMe_{4-x}Cl_x$ compounds.

the valence $4p$ contribution to the Ge chemical shift. We note that this contribution originates from the inner amplitude of the $4p$ orbital, as noted in [8]. This result is very natural since we have shown in the preceding section that the Ge $p-p^*$ excitation mechanism is the origin of the chemical shift. Since the Cl atom is very strongly electron-withdrawing, the effect may not be linear because the number of electrons on the Ge atom is limited. If such electronic ability is small like those of H and CH_3, the effect can be almost linear so that the linear dependence is obtained. We have also pointed out in the previous paper for the Sn chemical shift [12] that the existence of the $n \rightarrow p^*$ excitation in the $GeMe_{4-x}Cl_x$ series, where n denotes the lone-pair orbital of the Cl ligand, is another reason for the U-shaped dependence: A mixing between the $p-p^*$ and $n \rightarrow p^*$ excitations occurs in the $GeMe_{4-x}Cl_x$ series. Thus, the origin of the U-shaped dependence lies in the nonadditivity of the electronic

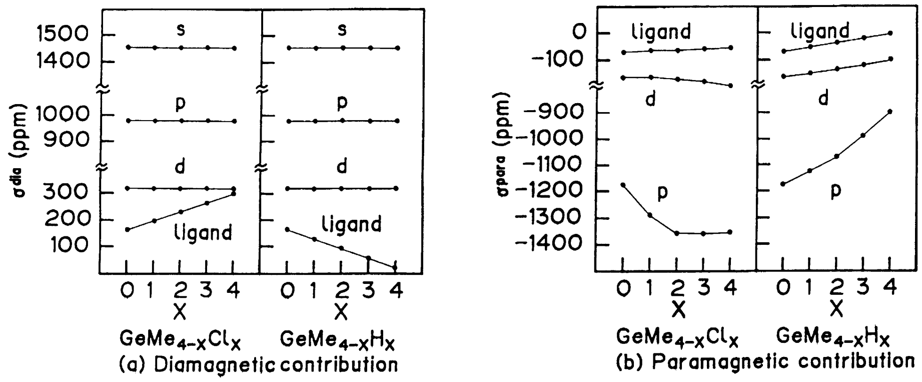

Figure 5. The x-dependencies of the s, p, d, and ligand contributions of the (a) diamagnetic and (b) paramagnetic contributions of the germanium magnetic shielding constant for the $GeMe_{4-x}H_x$ and $GeMe_{4-x}Cl_x$ compounds.

effect of Cl on the $4p$ orbital of Ge as the number x in the complexes, $\mathrm{GeMe}_{4-x}\mathrm{Cl}_x$ ($x = 0-4$), increases.

6. Conclusion

The germanium chemical shifts of the germanium compounds, $\mathrm{GeMe}_{4-x}\mathrm{H}_x$ and $\mathrm{GeMe}_{4-x}\mathrm{Cl}_x$ ($x = 0-4$), were studied theoretically. The calculated values of the germanium chemical shifts agree well with the experimental values. The chemical shifts are caused mainly by the germanium valence p AO contribution to the paramagnetic term. From the analogy to the Sn chemical shifts studied previously, the $p-p^*$ excitation term seems to dominate the second-order paramagnetic term. The diamagnetic contribution is relatively small for the chemical shift and is determined solely by the geometry and the number of the ligands. A U-shaped dependence is expected for the chemical shifts of the complexes, $\mathrm{GeMe}_{4-x}\mathrm{Cl}_x$, and the origin is the nonadditivity of the inductive effect of the strongly electron-withdrawing Cl ligand on the Ge p orbital.

Note

This study was done for the partial fulfillment of the Doctor Thesis of T. N. submitted to the Faculty of Engineering of Kyoto University [26]. After completion of the manuscript, we noticed the poster presentation on the calculations of the Ge chemical shifts, which were given at VIIth International Congress on Quantum Chemistry in Menton held on July 2–5, 1991 [27].

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