

Theoretical Study on Metal NMR Chemical Shifts. Electronic Mechanism of the Sn Chemical Shift

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Sn chemical shifts of the complexes $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ ($x = 0-4$) are studied theoretically by an ab initio molecular orbital method using larger basis sets than our previous ones. The calculated values of the Sn chemical shifts agree reasonably with the experimental values. The electronic mechanism of the Sn chemical shifts is analyzed. The Sn chemical shifts are mainly governed by the Sn valence p AO contribution to the paramagnetic term. The diamagnetic term is small and determined solely by the structural factor. The major factor affecting the p AO mechanism is the $\sigma-\sigma^*$ excitation energy and the minor factor the density distribution in the p AO's, and these two factors are canceling. The linear relationship in the $\text{SnMe}_{4-x}\text{H}_x$ series is due to the large change in the excitation energy and the similarity between H and Me. The U-shaped relationship in the $\text{SnMe}_{4-x}\text{Cl}_x$ series is due to the relatively small change in the excitation energy, the existence of the two lower states, and the anisotropic (for $x = 1, 2, 3$) and nonadditive inductive effects of Cl on the 5p AO density.

Introduction

For the studies of metal NMR chemical shifts, Sn is one of the most popular elements. The electronic configuration of the Sn atom is characterized by $4d^{10}5s^25p^2$, and it normally forms four-coordinate compounds. The data of Sn NMR chemical shifts of Sn compounds have been accumulated and published in several review articles.¹⁻³ However, the knowledge on the electronic origin of the chemical shifts is still limited. Furthermore, an interesting point in the Sn chemical shifts is the existence of the linear and U-shaped dependences of the chemical shifts on the number of the ligands. Organotin compounds of the type $\text{SnR}_{4-x}\text{R}'_x$, where both R and R' are organic ligands like H, Me, Ph, vinyl, etc. show linear dependence, but those of the type $\text{SnR}_{4-x}\text{Y}_x$ with Y being electronegative ligands like halogens, alkoxy, amino, etc., show U-shaped dependence. Such twofold dependence is also seen for silicon compounds. For elucidating the electronic mechanism of the Sn chemical shifts and the origins of the linear and U-shaped dependences, we choose the Sn compounds, $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$, in the present study.

In this series of studies on the metal NMR chemical shift, we have studied the complexes of Cu, Ag, Zn, and Cd whose electron configurations are $d^{10}s^1-2p^0$ and the complexes of Ti, Nb, Mn, and Mo which have open d subshells.⁴⁻⁹ The calculated chemical shifts agreed reasonably well with the experimental values and the electronic mechanisms were elucidated.

Previously, we have reported the preliminary result for the Sn chemical shifts¹⁰ for the same compounds as adopted in the present paper. Here, the calculations of the Sn chemical shifts are performed with the use of the larger basis sets which have polarization d functions on Sn and Cl atoms and p function on H atoms, and the geometries taken from more recent experimental results.

Method of Calculations

The Sn chemical shifts are calculated by the ab initio finite perturbation method.^{11,12} The details of the method was described in a previous paper.⁴ For the SCF calculations, a modified version of the HONDOG program is used.¹³ The gauge origin is taken at the position of the Sn nucleus. The geometries of the Sn compounds observed by microwave spectroscopy, electron diffraction method, and Raman and IR vibration-rotation bands are summarized in Table I.¹⁴ The basis sets are taken from the book of Huzinaga et al.¹⁵ For Sn, $(16s13p7d)/[6s5p2d]$ plus polarization d-functions with the exponent of 0.183 are used. For the atoms connected directly to Sn, the basis sets are as follows;

$(9s6p)/[4s3p]$ plus valence d-functions with the exponent of 1.0 for Cl, $(6s3p)/[3s2p]$ for C, and $(3s)/[2s]$ plus polarization p functions with the exponent of 1.0 for H. For the other atoms, the minimal basis sets with the same exponents are used.

Correlation between Theory and Experiment

The Sn nuclear magnetic shielding constants and the chemical shifts are summarized in Table II for all the compounds studied here. The experimental values are shown in the last column of the table. The Sn chemical shift of the compound M is defined relative to the reference compound, SnMe_4 as

$$\Delta\sigma_M = \sigma(\text{SnMe}_4) - \sigma(M) \quad (1)$$

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

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}} \quad (2)$$

where σ^{dia} and σ^{para} are the first- and second-order terms, respectively, in the perturbation theory.¹⁶ In particular, σ^{para} is given by

$$(\sigma^{\text{para}})_{xy} = -\frac{\mu_0 e^2}{8\pi m^2} \sum_n \frac{1}{E_n - E_0} \left[\langle 0 | \sum_\nu l_{xy} | n \rangle \left\langle n \left| \sum_\nu \frac{l_{yy}}{r_\nu^3} \right| 0 \right\rangle + \text{c.c.} \right] \quad (3)$$

where l_{xy} is an angular momentum operator of electron ν around the x axis and $|0\rangle$ and $|n\rangle$ the wave functions for the ground and excited states, respectively. c.c. denotes complex conjugate. Though we used the finite perturbation method, it is connected to and can be rewritten in the sum-over-states formula as given by eq 3.¹²

The correlations between the theoretical and experimental values of the Sn chemical shifts are shown in Figure 1. The agreement is reasonably good. In comparison with the previous results calculated with a cruder basis set,¹⁰ the correlation is not necessarily improved. However, for the $\text{SnMe}_{4-x}\text{Cl}_x$ series, we found that the d-polarization functions are important for reproducing the U-shaped dependence in a better agreement with experiments.

Mechanism of the Sn Chemical Shifts

The nuclear magnetic shielding constant, σ , is the sum of the diamagnetic term, σ^{dia} , and the paramagnetic term, σ^{para} , and these contributions can be further broken down into core and valence MO contributions.⁴ The results are shown in Table II. The

TABLE I: Geometries of the Tin Compounds in the Present Calculations

compd	Sn-C	Sn-Cl	Sn-H	C-H	\angle CsnC	\angle SnCH	\angle HSnC	\angle ClSnC	\angle HSnH	\angle ClSnCl
SnH ₄			1.7108						109.47	
SnMeH ₃	2.140		1.708	1.083		110.36	109.36		109.58	
SnMe ₂ H ₂	2.150		1.680	1.080	104.8	111.7	108.0		119.20	
SnMe ₃ H	2.147		1.705	1.086	107.5	111.6	111.5			
SnMe ₄	2.144			1.118	109.47	112.0				
SnMe ₃ Cl	2.106	2.351		1.125	114.9	113.4		103.2		
SnMe ₂ Cl ₂	2.109	2.327		1.112	110.0	110.0		109.8		107.5
SnMeCl ₃	2.104	2.304		1.100		107.5		113.9		104.7
SnCl ₄		2.2808								109.47

^aLength in angstroms, and angles in degrees.¹⁵

TABLE II: Diamagnetic and Paramagnetic Contributions, σ^{dia} and σ^{para} , to the Tin Nuclear Magnetic Shielding Constant σ and Their Analyses into Core and Valence MO Contributions (in ppm)

compd	σ^{dia}				σ^{para}				σ^{total}		exptl
	core	valence	total	shift	core	valence	total	shift	total	shift	
SnH ₄	5042	54	5096	125	-38	-1655	-1693	-522	3403	-398	-500
SnMeH ₃	5051	77	5128	93	-63	-1823	-1886	-329	3242	-236	-346
SnMe ₂ H ₂	5059	100	5159	62	-84	-1944	-2028	-187	3130	-125	-225
SnMe ₃ H	5068	122	5190	31	-107	-2042	-2149	-66	3041	-35	-104.5
SnMe ₄	5076	144	5221	0	-129	-2086	-2215	0	3006	0	0
SnMe ₃ Cl	5108	145	5253	-32	-152	-2201	-2353	138	2900	106	154-166
SnMe ₂ Cl ₂	5140	145	5285	-64	-177	-2289	-2466	251	2819	187	132.5
SnMeCl ₃	5173	145	5318	-97	-192	-2276	-2468	253	2850	156	6.03
SnCl ₄	5206	146	5352	-131	-216	-2232	-2448	233	2904	102	-150

TABLE III: Diamagnetic and Paramagnetic Contributions, σ^{dia} and σ^{para} , to the Tin Nuclear Magnetic Shielding Constant σ and Their Analyses into s, p, and d AO Contributions and Ligand Contributions (in ppm)

compd	σ^{dia}								σ^{para}							
	Sn				ligand				Sn ^c				ligand			
	s	p	d	total	Me	Cl	H	total	p	d	total	Me	Cl	H	total	
SnH ₄	2367	1808	898	5073			6	24	-1432	-253	-1686			-2	-8	
SnMeH ₃	2367	1807	898	5072	38		6	56	-1581	-282	-1864	-16		-2	-23	
SnMe ₂ H ₂	2366	1807	898	5071	38		6	88	-1684	-308	-1992	-16		-2	-36	
SnMe ₃ H	2366	1806	898	5070	38		6	120	-1768	-330	-2098	-16		-2	-50	
SnMe ₄	2365	1805	899	5069	38			152	-1795	-356	-2152	-16			-64	
SnMe ₃ Cl	2365	1805	899	5069	38	69		183	-1927	-365	-2292	-16	-13		-61	
SnMe ₂ Cl ₂	2365	1805	900	5070	38	69		214	-2028	-378	-2407	-16	-13		-58	
SnMeCl ₃	2365	1804	901	5070	38	70		248	-2019	-392	-2411	-16	-13		-55	
SnCl ₄	2364	1804	902	5070		70		280	-1973	-421	-2394		-13		-52	

^as AO contribution is zero since it has no angular momentum.

diamagnetic and paramagnetic contributions can also be analyzed into Sn s, p, d AO contributions and ligand contributions.⁴ The results are shown in Table III. In this section, we analyze the mechanism of the Sn chemical shifts using the results of these analyses and study the origin of the linear and the U-shaped relationships in the SnMe_{4-x}H_x and SnMe_{4-x}Cl_x series, respectively.

The importance of the paramagnetic contribution for the metal chemical shifts has been shown in this series of studies.⁴⁻¹⁰ For the Sn chemical shifts, the paramagnetic contribution is certainly more important than the diamagnetic one, but the latter is also important since it amounts to $1/4$ - $1/2$ of the former (except for the sign). We therefore investigate the paramagnetic term first and then the diamagnetic term.

A. Paramagnetic Contribution. We see from the MO analysis shown in Table II that the valence MO contribution to the paramagnetic term is dominant for the Sn chemical shifts. On the other hand, the AO analysis shown in Table III shows that the Sn 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, since the s AO does not have an angular momentum. The ligand contributions are small though they cannot be ignored in the SnMe_{4-x}H_x ($x = 0-4$) series; though the methyl group contribution is only -16 ppm individually, it sums up to -64 ppm in SnMe₄. For the SnMe_{4-x}H_x ($x = 0-4$) series, a substitution of each methyl group with hydrogen results in a shift of 14 ppm to lower field. For the SnMe_{4-x}Cl_x ($x = 0-4$) series, this contribution is not important since the contributions of Me and Cl are similar.

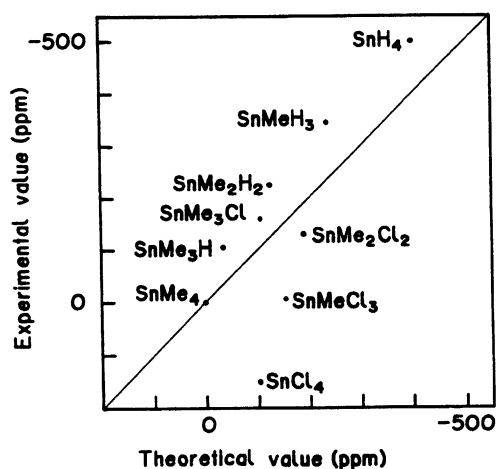


Figure 1. Correlation between experimental and theoretical values of the ¹¹⁹Sn chemical shifts of the Sn compounds.

We thus understand that the valence p AO contribution is the dominant mechanism of the Sn chemical shifts. The reason why the Sn p AO contribution is dominant is understood as follows. The d AO level of the Sn atom is deep: the 4d-5s separation is 22.6 eV, while the 5s-5p separation is 9.5 eV.¹⁷ This is why the d-electron contribution is small; the 4d shell is fully occupied and insensitive to the ligand substitution like an inner core, so that

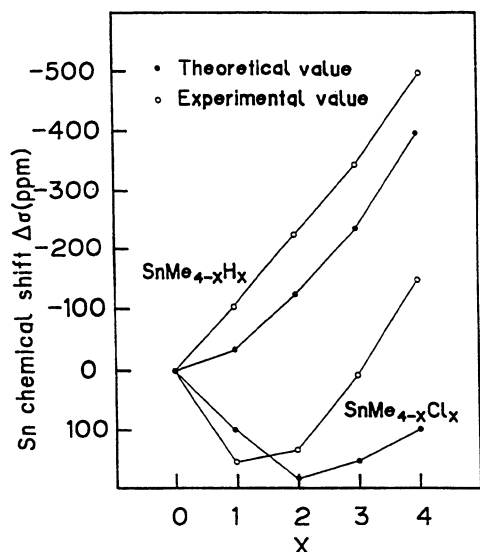


Figure 2. Comparison between theoretical and experimental values for the ^{119}Sn chemical shifts of the $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ series.

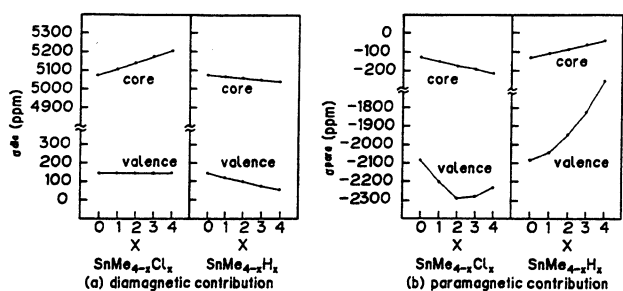


Figure 3. Change as a function of x for (a) diamagnetic and (b) paramagnetic contributions divided into core and valence MO contributions to the Sn magnetic shielding constant in the $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ series.

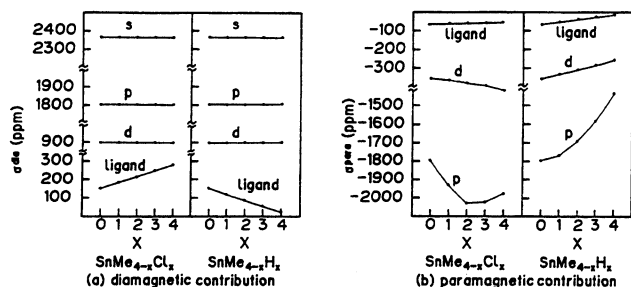


Figure 4. Change as a function of x for (a) diamagnetic and (b) paramagnetic contributions divided into s, p, and d contributions of Sn and ligand contributions to the magnetic shielding constant in the $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ series.

no angular momentum is induced on the d subshell. The 5p orbitals of Sn mix with the 5s orbital to form the sp^3 hybrid σ bond with the ligands: the π bond is unimportant for the class of the compounds studied here. The change of the ligand is therefore mainly reflected through this σ bond, so that the p AO contribution becomes dominant.

B. Diamagnetic Contribution. For the metal chemical shifts studied so far,⁴⁻¹⁰ the diamagnetic contribution has been shown to be relatively unimportant for the metal chemical shifts. For the Sn chemical shifts studied here, we see from Table II that the diamagnetic contribution is not small, especially for the $\text{SnMe}_{4-x}\text{Cl}_x$ series. From the AO analysis shown in Table III, we see that the diamagnetic contribution to the chemical shift is entirely due to the ligand contribution; the Sn contribution is constant for all the molecules studied here. This is also clearly seen from Figure 4a.

TABLE IV: Central Atom and Ligand Contributions to the Diamagnetic Term of the Sn Nuclear Magnetic Shielding Constant (in ppm)

contribution	ab initio	eq 4
$\sigma^{\text{dia}}(\text{Sn})$	5070	5086 ^a
$\sigma^{\text{dia}}(\text{Me})$	38	36
$\sigma^{\text{dia}}(\text{Cl})$	70	68
$\sigma^{\text{dia}}(\text{H})$	6	6

^a From ref 19.

TABLE V: Comparison of the Diamagnetic Terms Calculated by the ab Initio Calculations with Those Calculated from Eq 4 (in ppm)

compd	ab initio		eq 4	
	total	shift	total	shift
SnH_4	5096	125	5110	120
SnMeH_3	5128	93	5140	90
SnMe_2H_2	5159	62	5170	60
SnMe_3H	5190	31	5200	30
SnMe_4	5221	0	5230	0
SnMe_3Cl	5253	-32	5262	-32
SnMe_2Cl_2	5285	-64	5294	-64
SnMeCl_3	5318	-97	5326	-96
SnCl_4	5352	-131	5358	-128

The diamagnetic term is determined by the structural factor. Flygare and Goodisman reported that the diamagnetic term of the nucleus M is expressed to a good approximation as¹⁸

$$\sigma^{\text{dia}} = \sigma^{\text{dia}}(\text{free atom M}) + \frac{e^2}{3mc^2} \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}} \quad (4)$$

where $\sigma^{\text{dia}}(\text{free atom M})$ is the diamagnetic shielding constant for the free atom M, 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 . In a previous paper,⁴ we showed that the diamagnetic term is expressed in the Pascal-rule-like formula,

$$\sigma^{\text{dia}} = \sigma^{\text{dia}}(\text{Sn}) + \sum_L n_L \sigma^{\text{dia}}(\text{L}) \quad (5)$$

which can be derived from eq 4 if r_{α} for each ligand is assumed to be constant. In eq 5, $\sigma^{\text{dia}}(\text{Sn})$ is the sum of the Sn AO contributions, $\sigma^{\text{dia}}(\text{L})$ the ligand contribution, and n_L the number of ligands L.

In Table IV are shown the values of $\sigma^{\text{dia}}(\text{Sn})$ and $\sigma^{\text{dia}}(\text{L})$ for the compounds studied here. Two values are given for $\sigma^{\text{dia}}(\text{L})$, one calculated from the present ab initio results by a least-squares fitting method and the other from the second term of eq 4. The $\sigma^{\text{dia}}(\text{Sn})$ value of 5086 ppm in the last column is the diamagnetic shielding constant calculated for a free Sn atom.¹⁹ These two values are very close to each other. In Table V, the diamagnetic contributions calculated from eq 4 by using the structural factors of the Sn compounds are summarized and compared with the straightforward ab initio values. It is confirmed that the diamagnetic term of the Sn chemical shifts is accurately determined solely by the structural factors; ab initio calculations are entirely unnecessary for this term.

C. Factors Affecting the p Mechanism. A particularly interesting behavior in the Sn chemical shifts is the existence of the linear and U-shaped dependences on the number of the ligands. For example, the chemical shifts of the compounds $\text{SnMe}_{4-x}\text{Cl}_x$ ($x = 0-4$) show a U-shaped dependence against x . This dependence is also found for other Sn compounds with electronegative ligands like F and OMe, etc. However, for alkyl compounds like $\text{SnMe}_{4-x}\text{H}_x$, the dependence is not U-shaped but linear.

In Figure 2, the experimental and theoretical values of the chemical shifts for the $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ series are plotted against x . We see that the $\text{SnMe}_{4-x}\text{Cl}_x$ series definitely shows the U-shaped relationship both theoretically and experimentally, but the $\text{SnMe}_{4-x}\text{H}_x$ series scarcely does and the dependence is almost linear. For the $\text{SnMe}_{4-x}\text{Cl}_x$ series, the bottom compound is $x = 1$ experimentally but $x = 2$ theoretically. Experimentally, the chemical shift of the $x = 4$ compound is at lower frequency than the $x = 0$ compound, but the calculation does not

reproduce this ordering. For the $\text{SnMe}_{4-x}\text{H}_x$ series, the calculated values are at higher frequency than the experimental ones.

Figures 3 and 4 are prepared in order to clarify the origin of these dependences. Parts a and b of Figure 3 show the core and valence MO contributions to the diamagnetic and paramagnetic terms, respectively. Both the core and valence contributions to the diamagnetic term are linear (Figure 3). The core contribution to the paramagnetic term is linear but the valence contribution shows nonlinearity (Figure 3b); in particular, that of the $\text{SnMe}_{4-x}\text{Cl}_x$ series shows a strong U shape. From the fact that the sum of linear functions is linear, the U shape cannot be obtained by a sum of several linear functions. Hence, the valence MO contribution to the paramagnetic term is the origin of the U-shaped relationship in the $\text{SnMe}_{4-x}\text{Cl}_x$ series.

In Figure 4a,b the Sn AO and ligand contributions to the diamagnetic and paramagnetic terms are shown. We see that most curves are linear except for the p AO contributions to the paramagnetic term. Again, that of the $\text{SnMe}_{4-x}\text{Cl}_x$ series shows a strong U dependence. Combining the implications of Figures 3 and 4, we conclude that the U-shaped dependence for the $\text{SnMe}_{4-x}\text{Cl}_x$ series arises from the valence 5p contribution to the Sn chemical shift. We note that the valence 5p contribution is different from the 5p Gaussian basis contribution, since this behavior comes from the inner amplitude (2p Gaussian AO region) of the valence 5p orbital. Though the 5p Gaussian basis is nodeless and nonorthogonal with the 4p and inner p Gaussians, the actual valence 5p orbital has nodes and some amplitudes at the inner np ($n \leq 4$) regions, since this is necessary for the 5p orbital being orthogonal with the inner p orbitals. In ref 4, we have discussed this subject in more detail.

Now, we investigate what factors of the p mechanism lead to the linear relationship for the $\text{SnMe}_{4-x}\text{H}_x$ series and to the U-shaped relationship for the $\text{SnMe}_{4-x}\text{Cl}_x$ series. Referring to eq 3, we see that σ^{para} is determined by the excitation energy denominator and by the numerator which involves angular momentum integrals. For a qualitative analysis, it is convenient to use the formula derived by Karplus and Das²⁰ from eq 3 by adopting the average excitation energy approximation. They showed that the p AO contribution to the paramagnetic term is written as

$$\sigma^{\text{para}} = -\text{const} \frac{1}{\Delta E} \left\langle \frac{1}{r^3} \right\rangle_p \left\{ (D_{xx} + D_{yy} + D_{zz}) - \frac{1}{2}(D_{zz}D_{yy} + D_{xx}D_{yy} + D_{xx}D_{zz}) + \frac{1}{2}(D_{yz}D_{zy} + D_{xy}D_{yx} + D_{xz}D_{zx}) \right\} \quad (6)$$

where ΔE is the average excitation energy, $\langle 1/r^3 \rangle_p$ is the average value of $1/r^3$ over the p_x , p_y , and p_z orbitals of Sn, and D_{xy} , etc., means the density matrix elements between two p AO's. We now neglect the off-diagonal terms D_{yz} , etc., assume $D_{xx} = D_{yy}$, which holds for the present compounds, and introduce the isotropic term I and the anisotropic term A as

$$I = D_{xx} + D_{yy} + D_{zz} \quad (7)$$

$$A = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) \quad (8)$$

Then, eq 6 is rewritten as

$$\sigma^{\text{para}} = -\text{const} \frac{1}{\Delta E} \left\langle \frac{1}{r^3} \right\rangle_p \left(I - \frac{1}{6}I^2 + \frac{1}{6}A^2 \right) \quad (9)$$

Equation 9 is of course very crude for calculations of the paramagnetic term, but it is instructive for understanding the mechanism. This equation implies that three factors are important for the Sn chemical shift. They are (1) excitation energy ΔE , (2) the p-electron density distribution around the Sn nucleus expressed by the terms I and A , and (3) the integral $\langle 1/r^3 \rangle_p$. Among these, we neglect the change of the integral $\langle 1/r^3 \rangle_p$, since it is the integral for the Sn 5p AO. In the following, we examine the other two factors.

We first investigate the density factor. It implies (1) when the anisotropy A is zero, σ^{para} increases monotonously from $I = 0$ (occupation p^0) to $I = 3$ (p^3 , half occupied), it is maximum at

TABLE VI: Mulliken Population for the Sn p AO's

compd	p_x	p_y	p_z	$I(\text{total})^a$	A^a
SnH_4	0.817	0.817	0.817	2.452	0.0
SnMeH_3	0.809	0.809	0.699	2.317	-0.110
SnMe_2H_2	0.742	0.742	0.703	2.187	(-0.039)
SnMe_3H	0.655	0.655	0.750	2.061	0.095
SnMe_4	0.654	0.654	0.654	1.963	0.0
SnMe_3Cl	0.717	0.717	0.490	1.924	-0.227
SnMe_2Cl_2	0.636	0.636	0.607	1.878	(-0.029)
SnMeCl_3	0.557	0.557	0.737	1.837	0.180
SnCl_4	0.620	0.620	0.620	1.859	0.0

^aThe isotropic term I and the anisotropic term A are defined by eqs 7 and 8, respectively.

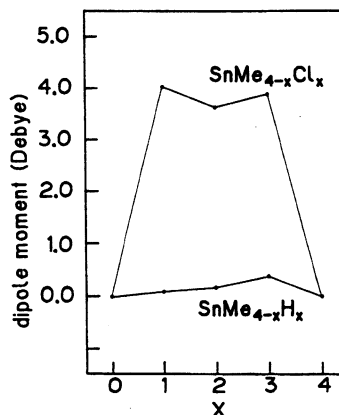


Figure 5. Dipole moment for the $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ series.

$I = 3$, and decreases monotonously up to $I = 6$ (p^6 , fully occupied); at p^0 and p^6 , σ^{para} vanishes identically, and (2) for a given isotropic density I , σ^{para} increases as the anisotropy A in the density increases. For example, for the two p-electron case, the most anisotropic distribution $(p_x)^0(p_y)^0(p_z)^2$ gives 1.5 times larger value of σ^{para} than the isotropic distribution $(p_x)^{2/3}(p_y)^{2/3}(p_z)^{2/3}$. We note that the isotropic term I is invariant for coordinate transformation, but the anisotropic term A is variant. Therefore, for the latter, we have to define it for the most convenient axis of the local density matrix.

In Table VI, we show the Mulliken population analysis for the 5p GTO's of the Sn atom of the complexes $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$. Strictly speaking, Mulliken population is different from density matrix element, and the nodeless 5p GTO is similar to the 5p AO only in the outermost region, but these two quantities should be parallel. Further, we give the sum of the two double ζ quantities. For the C_{2v} compounds, SnMe_2H_2 and SnMe_2Cl_2 , the values of A are not for the coordinate axis along the Sn-Me and Sn-Cl bonds, respectively, and therefore enclosed in parentheses.

The anisotropy terms A for the compounds $\text{SnMe}_{4-x}\text{Cl}_x$ are about twice as large as those for the compounds $\text{SnMe}_{4-x}\text{H}_x$. Since the Cl ligand is a very strong electronegative ligand, it causes a very large anisotropy A in the electron distribution of the Sn 5p AO's and therefore results in an increase (in absolute value) of σ^{para} for $x = 1, 2$, and 3 of the $\text{SnMe}_{4-x}\text{Cl}_x$ series. For $x = 0$ and 4, A vanishes identically. This is a reason for the U shape observed for the $\text{SnMe}_{4-x}\text{Cl}_x$ series. Radeaglia and Engelhardt²¹ first pointed out this possibility. Further, we notice in Table VI that the dependence of the isotropic density I on the number of the Cl ligands is not linear for the $\text{SnMe}_{4-x}\text{Cl}_x$ series. This is especially so for $x = 2, 3$, and 4. This nonlinear dependence of I is due to the nonadditivity of the effect of the Cl substitution; this is understood because the electronegative effect of Cl is very large. This non-additivity is also a reason of the U-shape.

A large difference in the inductive effects of the $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ series may be seen from the dipole moment dependence on x in these series, which are shown in Figure 5. Though the dipole moment changes largely in the $\text{SnMe}_{4-x}\text{Cl}_x$ series, it changes only little in the $\text{SnMe}_{4-x}\text{H}_x$ series. This figure

TABLE VII: Observed Excitation Energy of the Sn Compounds

compd	nature	excitation energy (eV)
SnH ₄	3t ₂ → 3a ₁ ; p → σ*	8.86
SnMe ₄	3t ₂ → 3a ₁ ; p → σ*	6.63
SnCl ₄	3t ₂ → 3a ₁ ; n(L) → σ*	6.23
	2t ₂ → 3a ₁ ; p → σ*	7.80

shows how large is the anisotropy effect in the SnMe_{4-x}Cl_x series.

However, the interpretation based on the density factor alone is limited. For instance, if the density factor is dominant, σ^{para} should increase (in absolute value) with increasing density *I* if *I* is less than 3, but referring to Tables II, III, and VI, this is not the case. The general tendency is just the reverse: the absolute value of the Sn p AO contribution to σ^{para} shown in Table III increases with decreasing p AO population as shown in Table VI. Therefore, the density factor alone does not explain the trend in the chemical shifts. There should be another opposing factor.

We next investigate the remaining factor which is the excitation energy. In Table VII we show the excitation energy for the compounds SnH₄, SnMe₄, and SnCl₄.^{22,23} For the first two compounds they are the lowest transitions characterized as 3t₂ → 3a₁ which are the transitions from the Sn-L σ bonding MO to the MO which has the mixed nature of the Sn-L antibonding MO and the 6s Rydberg orbital. For SnCl₄, the lowest transition 3t₂ → 3a₁ is the transition of the lone-pair electron on Cl to the orbital of the mixed character as above. The transition pertinent to the 5p mechanism is the next 2t₂ → 3a₁ transition, which is from the Sn-Cl bonding orbital.²² Though these excitations are not magnetically allowed, they should be parallel to them at least qualitatively.

The excitation energy shown in Table VII is useful for understanding the general trend in the Sn chemical shift. The ordering in the excitation energy is SnH₄ > SnCl₄ > SnMe₄, which explains the reverse order of the experimental chemical shift, SnH₄ < SnCl₄ < SnMe₄, though the present calculation does not reproduce the ordering between SnCl₄ and SnMe₄. Figure 6 is a plot for the experimental Sn chemical shift versus the p-σ* excitation energy. We see a rough linearity when we take for SnCl₄ the p-σ* (2t₂ → 3a₁) transition instead of the n(Cl) → σ* (3t₂ → 3a₁) transition. This linearity supports that the Sn chemical shift is mainly due to the p-p* excitation mechanism.

We have already shown that for the dⁿ transition-metal complexes, like Ti, Nb, Mo, and Mn complexes, the metal chemical shifts are due to the d-d* excitation mechanism. We showed a beautiful linearity between the observed chemical shifts and the inverses of the d-d* excitation energies for the Mo complexes.⁶ The p-p* excitation mechanism for the p² Sn complexes is similar to the d-d* excitation mechanism for these dⁿ complexes.

Between the compounds SnH₄ and SnMe₄, the difference in the excitation energy is large and the nature of the excitations is the same, but between the compounds SnMe₄ and SnCl₄, the difference is small and further, as explained above, the excitation somewhat different in nature arises in this energy region of SnCl₄. For the SnMe_{4-x}H_x series, this fact and the fact that the density factor changes linearly are the reason of the linear dependence of the chemical shift. For the SnMe_{4-x}Cl_x series, the energy levels and the natures of the lower excitations as a function of *x* are very interesting, but we have the experimental values only for the two limiting compounds. However, we think that the relatively small change in the excitation energy in this series and the rather opposing behaviors of the two lowest transitions, and further the large anisotropic and nonadditive effects in the density factor, are the reason for the U-shaped dependence in the SnMe_{4-x}Cl_x series. For a definite conclusion, however, we need the excitation energies and their natures of the lower transitions for the rest of the compounds.

Conclusion

The Sn chemical shifts of the Sn compounds SnMe_{4-x}H_x and SnMe_{4-x}Cl_x (*x* = 0-4) are studied by ab initio quantum theory for elucidating the underlying electronic mechanism. The cal-

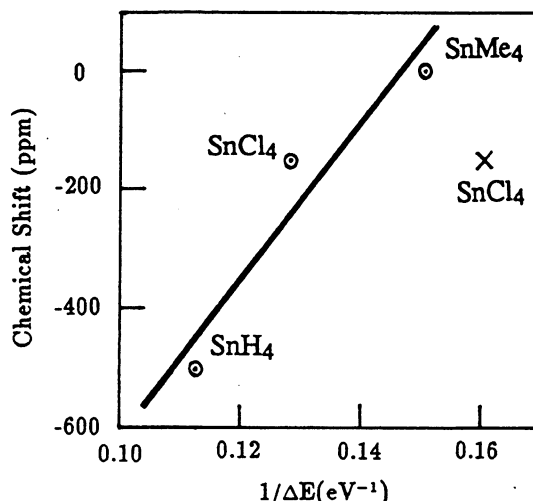


Figure 6. Plot of the experimental Sn chemical shifts vs the inverse of the p-σ* excitation energies for SnH₄, SnCl₄, and SnMe₄. The cross for SnCl₄ is for the n(Cl)-σ* excitation shown in Table VII.

culated values of the Sn chemical shifts agree well with the experimental values. Therefore, the ab initio method adopted in this study is reliable for analyzing the mechanism of the Sn chemical shifts. The elucidated mechanism is as follows.

- (1) The Sn chemical shifts are mainly governed by the Sn valence p AO contribution to the paramagnetic term.
- (2) The diamagnetic term, which is determined solely by the structural factor, is certainly a minor factor, but is not small especially for the SnMe_{4-x}Cl_x series. The trend of this term is opposite to that of σ^{para}.
- (3) The 5p AO mechanism in Sn σ^{para} is determined by the two rather competing factors. One is related to the energy denominator and the other to the numerator in the perturbation theoretic formula. The larger factor is the excitation energy from the Sn-L σ bonding MO to the antibonding MO (p-p* excitation mechanism) and the smaller factor is the density distribution in the Sn 5p AO's (density anisotropy factor). The excitation energy change is large in the SnMe_{4-x}H_x series but small in the SnMe_{4-x}Cl_x series. The ordering of the experimental chemical shift, SnH₄ < SnCl₄ < SnMe₄, is understood from the ordering of the pertinent excitation energies.
- (4) The linear relationship in the SnMe_{4-x}H_x series is understood from the large change in the excitation energy and the similarity between H and Me group. Their chemical shifts are primarily due to the p-p* excitation mechanism.
- (5) The U-shaped relationship in the SnMe_{4-x}Cl_x series is understood from the opposite and competitive nature of the two factors, namely the p-p* excitation mechanism and the density anisotropy factor. The smaller change in the excitation energy, the opposite behaviors of the two lower transitions of different natures, and a large nonadditive inductive effect of the Cl ligand on the Sn p AO density and the resultant anisotropic distribution among the Sn p_x, p_y, and p_z AO's in partial Cl substitutions are the origin of the U-shaped dependence of the chemical shifts of the SnMe_{4-x}Cl_x series.

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Registry No. SnH₄, 2406-52-2; SnMe₃H, 1631-78-3; SnMe₂H₂, 2067-76-7; SnMe₃Cl, 1631-73-8; SnMe₄, 594-27-4; SnMe₃Cl, 1066-45-1; SnMe₂Cl₂, 753-73-1; SnMeCl₃, 993-16-8; SnCl₄, 594-27-4.

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