

THEORETICAL STUDY OF METAL NMR CHEMICAL SHIFTS: TIN COMPLEXES

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Received 22 November 1989; in final form 25 December 1989

^{119}Sn chemical shifts have been studied theoretically by an ab initio molecular orbital method. The complexes calculated here are $\text{SnMe}_{4-x}\text{Cl}_x$ and $\text{SnMe}_{4-x}\text{H}_x$ ($x=0-4$). The calculated values of the Sn chemical shifts agree well with the experimental ones. For the $\text{SnMe}_{4-x}\text{H}_x$ compounds, the p mechanism is dominant. For the $\text{SnMe}_{4-x}\text{Cl}_x$ compounds, both the p and d mechanisms are important, and even the structural factor in the diamagnetic term is important. This explains the U-shape of the chemical shifts in the $\text{SnMe}_{4-x}\text{Cl}_x$ series in contrast to the linear relationship in the $\text{SnMe}_{4-x}\text{H}_x$ series.

Many ^{119}Sn NMR parameters have been accumulated in several review articles [1-3]. In spite of a large amount of experimental data, there has been no ab initio theoretical study on ^{119}Sn nuclear shielding constants of tin compounds. In this paper, an ab initio theoretical study on the ^{119}Sn NMR chemical shifts of the compounds $\text{SnMe}_{4-x}\text{H}_x$ and $\text{SnMe}_{4-x}\text{Cl}_x$ is presented.

We have theoretically studied the nuclear shielding constants of Ag, Cu, Cd, Zn, Mn and Mo compounds [4-9]. Our theory has satisfactorily reproduced the experimental chemical shifts. For the Ag, Cu, Cd and Zn atoms, the lowest electronic configurations are characterized by $d^{10}s^{1-2}p^0$ and for the Mn and Mo atoms they are characterized by $d^5s^{1-2}p^0$. For the $d^{10}s^{1-2}p^0$ compounds, the origin of the metal chemical shifts is explained by the p and d mechanisms [4]. The p mechanism is due to the electrons in the valence p orbitals of the metal transferred from the ligands which have an electron-donating nature. The d mechanism is due to the holes in the valence d subshell of the metal produced by the electron-withdrawing ligands [4]. For the $d^5s^{1-2}p^0$ compounds, the d electron contribution is predominant because of the half-filled d subshell configurations of the metals [5,7]. In a perturbation theoretic viewpoint, the metal chemical shifts of the Mn and Mo complexes are predominantly determined by the d-d transitions.

The theory used in the present calculations is the

finite perturbation theory [10,11], as before [4-9]. The geometries of the complexes are summarized in table 1 [12]. The gauge origin is taken on the tin nucleus. The basis sets are Huzinaga's (16s13p7d)/[6s5p3d] set for the tin atom [13], MIDI-1 for the atoms directly bonded to the tin atom and MINI-1 for the other atoms [14]. For SCF calculations, a modified version of the HONDOG program [15] is used.

The chemical shift $\Delta\sigma$ of the compound M is calculated relative to the reference compound, SnMe_4 ,

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

where σ is the ^{119}Sn nuclear shielding constant. The correlation between the theoretical and experimental values of the chemical shift is shown in fig. 1. The open circle for SnH_4 indicates the theoretical value only, since the experimental value is not available. The correlation is good except for some chlorides. The present theory tends to overestimate the nuclear shielding constant. The shielding constant is decomposed in table 2 into diamagnetic and paramagnetic contributions, and they are further analyzed into core and valence MO contributions and into the Sn AO contributions and the ligand contributions.

For the $\text{SnMe}_{4-x}\text{H}_x$ compounds, the chemical shift is dominantly determined by the paramagnetic term. The ratio between the diamagnetic and paramagnetic contributions to the chemical shift is about 1:5. For the $\text{SnMe}_{4-x}\text{Cl}_x$ compounds, on the other hand,

Table 1
Geometries of the Sn complexes ^{a,b,c)}

Compound	Sn-C	C-H	Sn-H	Sn-Cl	∠ CSnC	∠ HCSn	∠ HSnC	∠ ClSnC	∠ HSnH	∠ ClSnCl
SnH ₄	-	-	1.680*	-	-	-	-	-	109.47	-
SnMeH ₃	2.150	1.080*	1.680*	-	-	111.7*	108.0*	-	110.9*	-
SnMe ₂ H ₂	2.153	1.080	1.680	-	104.8	111.7	108.0	-	119.1	-
SnMe ₃ H	2.147	1.086	1.705	-	107.5	111.6	111.5	-	-	-
SnMe ₄	2.134	1.086*	-	-	109.47	111.6*	-	-	-	-
SnMe ₃ Cl	2.108	1.125	-	2.354	114.9	113.4	-	103.2	-	-
SnMe ₂ Cl ₂	2.109	1.100*	-	2.327	114.9	109.47*	-	99.6*	-	104.7*
SnMeCl ₃	2.104	1.100	-	2.306	-	107.5	-	113.9	-	104.7
SnCl ₄	-	-	-	2.281	-	-	-	-	-	109.47

^{a)} The lengths are in Å and the angles in deg. ^{b)} Ref. [12].

^{c)} The values with an asterisk are estimated from those of similar compounds.

Table 2
Diamagnetic and paramagnetic contributions, σ^{dia} and σ^{para} , to the Sn nuclear magnetic shielding constant σ and their analyses into core and valence MO contributions and into s, p and d AO contributions of Sn and the ligand AO (in ppm)

Compound	σ^{dia}							total	shift
	MO contributing		AO contribution						
	core	valence	Sn(s)	Sn(p)	Sn(d)	ligands			
SnH ₄	5041	55	2371	1805	892	28	5096	124	
SnMeH ₃	5049	77	2370	1804	892	60	5126	94	
SnMe ₂ H ₂	5058	99	2370	1803	892	92	5157	63	
SnMe ₃ H	5066	122	2369	1802	893	124	5188	32	
SnMe ₄	5075	145	2369	1802	893	156	5220	0	
SnMe ₃ Cl	5106	145	2369	1801	893	188	5251	-31	
SnMe ₂ Cl ₂	5141	142	2369	1802	893	219	5283	-63	
SnMeCl ₃	5171	146	2369	1802	894	252	5317	-97	
SnCl ₄	5204	146	2368	1802	894	286	5350	-130	

Compound	σ^{para}						σ^{total}		Exptl. shift	
	MO contribution		AO contribution ^{a)}			total	shift			
	core	valence	Sn(p)	Sn(d)	ligands	total	shift			
SnH ₄	-85	-1328	-1242	-170	-1	-1413	-599	3683	-475	-
SnMeH ₃	-104	-1464	-1357	-199	-12	-1568	-444	3558	-350	-346
SnMe ₂ H ₂	-123	-1588	-1463	-225	-23	-1711	-301	3446	-238	-225
SnMe ₃ H	-145	-1714	-1571	-252	-36	-1859	-153	3329	-121	-105
SnMe ₄	-179	-1833	-1675	-288	-49	-2012	0	3208	0	0
SnMe ₃ Cl	-184	-1870	-1766	-248	-40	-2054	42	3197	11	154-166
SnMe ₂ Cl ₂	-205	-1850	-1815	-206	-34	-2055	43	3228	-20	137
SnMeCl ₃	-214	-1805	-1818	-173	-28	-2019	7	3298	-90	6
SnCl ₄	-228	-1712	-1763	-158	-19	-1940	-72	3410	-202	-150

^{a)} For the paramagnetic term, the Sn (s) AO contribution vanishes identically because the s electron does not have an angular momentum.

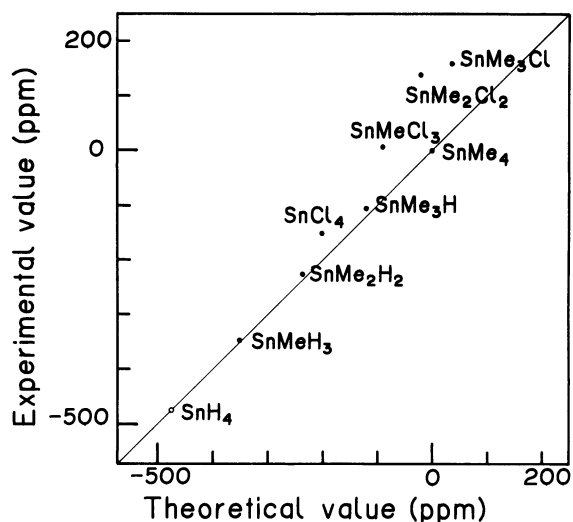


Fig. 1. The correlation between the experimental and theoretical values of the ^{119}Sn chemical shifts of the tin complexes. For SnH_4 , the experimental value is not available so that the open circle shows only the theoretical value.

the diamagnetic and paramagnetic contributions are comparable. It is known that only the structural factor is important for the diamagnetic term [4,5,16]. So, for the chemical shifts of the $\text{SnMe}_{4-x}\text{Cl}_x$ compounds, both the structural and electronic factors are important, though only the latter is important for the $\text{SnMe}_{4-x}\text{H}_x$ compounds.

We next examine the AO and MO analyses of the paramagnetic term. For the $\text{SnMe}_{4-x}\text{H}_x$ compounds, the valence p AO contribution of the Sn atom is dominant (p mechanism), and the d electron contribution is small. This is understood since the 4d-5s and 5s-5p level splittings in the Sn ion are 9.5 and 22.6 eV, respectively [17]. The p orbitals of the Sn atom would therefore mix more easily with the metal-ligand bonds than the d orbitals. For the $\text{SnMe}_{4-x}\text{Cl}_x$ series, the valence MO contribution is the main one likewise, but both the p and d electron contributions are important. In other words, the p electron contribution is suppressed in comparison with the $\text{SnMe}_{4-x}\text{H}_x$ series. This relative increase of the d mechanism is attributed to the change in the hybrid bonding nature of the Sn atom from sp^3 to sd^3 with an increasing number of Cl ligands.

For the $\text{SnMe}_{4-x}\text{H}_x$ series, the chemical shift changes linearly with the change in x , but in the

$\text{SnMe}_{4-x}\text{Cl}_x$ series, it changes in a U-shape. The present theoretical results reproduce this general behavior. The U-shape dependence on x in the $\text{SnMe}_{4-x}\text{Cl}_x$ series is attributed to the dual importance of the p and d mechanisms and also to the importance of the diamagnetic structural factor. More details of the present study will be published in a separate paper.

We thank Professor J. Otera for his valuable suggestions given from the experimental side. The calculations have been carried out with the HITAC M680H and FACOM M780 computers at the Institute for Molecular Science and at the Data Processing Center of Kyoto University, respectively. Part of this study has been supported by the Kurata Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

- [1] P.J. Smith and A.P. Tupčiauskas, *Ann. Rept. NMR Spectry.* 8 (1978) 291; B. Wrackmeyer, *Ann. Rept. NMR Spectry.* 16 (1985) 73.
- [2] J.D. Kennedy and W. McFarlane, in: *Multinuclear NMR*, ed. J. Mason (Plenum Press, New York, 1987) p. 305.
- [3] E.A. Williams and J.D. Cargioli, *Ann. Rept. NMR Spectry.* 9 (1977) 231; E.A. Williams, *Ann. Rept. NMR Spectry.* 15 (1983) 235.
- [4] H. Nakatsuji, K. Kanda, K. Endo and T. Yonezawa, *J. Am. Chem. Soc.* 106 (1984) 4653.
- [5] K. Kanda, H. Nakatsuji and T. Yonezawa, *J. Am. Chem. Soc.* 106 (1984) 5888.
- [6] H. Nakatsuji, T. Nakao and K. Kanda, *Chem. Phys.* 115 (1987) 25.
- [7] H. Nakatsuji and M. Sugimoto, *Inorg. Chem.* (1989), in press.
- [8] H. Nakatsuji, in: *Comparisons of ab initio quantum chemistry with experiment: state of the art*, ed. R.J. Bartlett (Reidel, Dordrecht, 1985) p. 409.
- [9] H. Nakatsuji, in: *High resolution NMR spectroscopy, modern chemistry, Supplement 11*, eds. H. Saito and I. Morishima (Tokyo Kagaku Dojin, Tokyo, 1987) p. 237, in Japanese.
- [10] H.D. Cohen and C.C.J. Roothaan, *J. Chem. Phys.* 43 (1965) S34; H.D. Cohen, *J. Chem. Phys.* 43 (1965) 3558; 45 (1966) 10; J.A. Pople, J.W. McIver and N.S. Ostlund, *Chem. Phys. Letters* 1 (1967) 465; *J. Chem. Phys.* 49 (1968) 2960; R. Ditchfield, D.P. Miller and J.A. Pople, *J. Chem. Phys.* 53 (1970) 613;

- H. Nakatsuji, K. Hirao and T. Yonezawa, *Chem. Phys. Letters* 6 (1970) 541.
- [11] H. Nakatsuji, *J. Chem. Phys.* 61 (1974) 3728.
- [12] L.E. Sutton, *Tables of interatomic distances and configuration in molecules and ions* (Chem. Soc., London, 1965);
B. Beagley, K. McAloon and J.M. Freeman, *Acta Cryst. B* 30 (1974) 444;
H. Fujiwara and Y. Sasaki, *J. Phys. Chem.* 91 (1987) 481.
- [13] S. Huzinaga, *Gaussian basis sets for molecular calculations* (Elsevier, Amsterdam, 1984).
- [14] H. Tatewaki and S. Huzinaga, *J. Chem. Phys.* 71 (1979) 4339; *J. Comput. Chem.* 1 (1980) 205;
Y. Sakai, H. Tatewaki and S. Huzinaga, *J. Comput. Chem.* 2 (1981) 100; 3 (1982) 6.
- [15] H.F. King, M. Dupuis and J. Rys, Program Library HONDOG, No. 343, The Computer Center of the Institute for Molecular Science, Okazaki (1979).
- [16] W.H. Flygare and J. Goodisman, *J. Chem. Phys.* 49 (1968) 3122.
- [17] C.E. Moore, *Atomic energy levels, Circular 467* (US GPO, Washington, 1958).