

Spin-orbit effect on the magnetic shielding constant using the ab initio UHF method: tin tetrahalides

H. Kaneko, M. Hada, T. Nakajima, H. Nakatsuji^{*,1}

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Received 14 June 1996; in final form 22 July 1996

Abstract

The ^{119}Sn NMR chemical shifts of SnX_4 ($X = \text{H}, \text{Cl}, \text{Br}$ and I) and $\text{SnBr}_{4-n}\text{I}_n$ ($n = 1, 2, 3$) are calculated by the ab initio UHF method including the spin-orbit (SO) interaction combined with the finite perturbation method. The calculated Sn chemical shifts are in good agreement with experiment when the SO interaction is included. As the halogen ligand becomes heavier, the SO effect increases and the chemical shift moves to a higher field. The normal halogen dependence by the substitution from Cl to I in tin tetrahalides is reproduced only when the SO interaction is included. The origin of the SO effect is ascribed to the Fermi contact term.

1. Introduction

Tin is one of the common elements in metal NMR studies in organic and inorganic chemistry. The ^{119}Sn chemical shifts of many Sn compounds have been accumulated and published [1–4]. An interesting point in Sn chemical shifts is the existence of both linear and U-shaped dependences on the number of substituted ligands on Sn. The linear dependence appears when the ligands are not electronegative, whereas the U-shaped dependence is observed for electronegative ligands. In our previous paper [5], we have reproduced these dependences by ab initio calculations of $\text{SnMe}_{4-n}\text{H}_n$ and $\text{SnMe}_{4-n}\text{Cl}_n$ ($n = 0–4$) and showed that the U-shaped dependence of the

latter compounds is due to the non-additive induction effect of the halogen atom. Another interesting dependence of the Sn magnetic shielding constants is seen for the compounds having heavier halogen ligands; it increases as the halogen ligand becomes heavier. This dependence is called the normal halogen dependence [6]. In our series of studies on metal NMR chemical shifts [7], we expected that relativistic effects such as the spin-orbit interaction are important in the chemical shifts of compounds containing heavier halogen atoms [8].

Recently, we have proposed a useful and simple method, called the SO-UHF method [9], for calculating the spin-orbit (SO) interaction using the ordinary UHF wavefunction and applied it to calculations of NMR chemical shifts. This method can easily be combined with the effective core potential method including the SO effect [11]. It has been applied to the ^1H , ^{13}C [9], ^{71}Ga , ^{115}In [10], ^{29}Si [11] and ^{27}Al [12] chemical shifts of several halogenated

^{*} Corresponding author.

¹ Also at the Institute for Fundamental Chemistry, 34-4 Takano Nishi-Hiraki-cho, Sakyo-ku, Kyoto 606, Japan.

Table 1

Magnetic shielding constants and their components of the tin compounds with and without spin-orbit effects (ppm)

Compound	Without SO				With SO						δ^{exp}	
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}		$\delta^{\text{cal c}}$
					SD ^a	FC ^b	total					
SnH ₄	5097.86	-1703.03	3424.82	0	5097.67	-1677.02	16.03 ^d	-3.01 ^d	13.02	3433.67	0	0
SnCl ₄	5184.65	-2079.55	3105.10	319.72	5184.65	-2079.65	0.40	43.59	43.99	3148.98	275.84	350
SnBr ₄	5184.56	-2204.16	2977.41	447.41	5177.22	-2205.37	5.43	469.42	474.85	3446.70	-21.88	-138
SnBr ₃ I	5179.39	-2152.75	3026.64	398.18	5175.23	-2243.28	9.16	746.89	756.05	3687.99	-263.17	-416
SnBr ₂ I ₂	5182.85	-2104.84	3078.02	346.80	5173.24	-2278.07	12.94	1025.09	1038.03	3933.20	-508.38	-687
SnBrI ₃	5170.65	-2065.45	3109.90	314.92	5171.25	-2308.95	16.78	1306.69	1323.43	4185.77	-760.95	-947
SnI ₄	5172.45	-2025.45	3147.50	277.32	5169.25	-2335.17	20.59	1587.69	1608.25	4442.36	-1017.54	-1201

^a Spin-dipolar term.^b Fermi contact term^c For the chemical shift, the shielding constant of SnH₄ calculated without the spin-orbit interaction is used as a reference.^d For SnH₄, the results with SO include the SO effect due to the Sn atom; these values are essentially due to the SO effect of the Sn atom.

compounds. These results have shown that the SO effects are large in compounds containing Br and I; even the trends in the experimental chemical shifts cannot be reproduced without the SO effects.

When the resonant nuclei are as heavy as the fifth-row elements, Hg, W, Pb, etc., other relativistic effects such as the mass velocity and Darwin terms become important [13,14]. We have presented a systematic method for calculating such terms as well as the SO term [15] and applied it to the proton [15], Hg [13] and W [14] chemical shifts. The coupling between the SO and the spin-free relativistic terms such as the mass velocity and Darwin terms is found to be quite important [13,14].

In this Letter we study the halogen dependence of the ¹¹⁹Sn chemical shifts δ of the halogenated tin compounds, SnX₄ (X = Cl, Br and I) and SnBr_{4-n}I_n (n = 1, 2, 3) considering the SO effect as a relativistic term. The reference compound is chosen as SnH₄. We aim at clarifying the origin of the normal halogen dependence in this series of compounds.

2. Method of calculation

We calculate the Sn magnetic shielding constants σ using the SO-UHF/finite perturbation (FP) method [9]. The SO interaction is included [11] by

Table 2

MO contributions in the dia-, para-, spin-dipolar and Fermi contact terms of the tin compounds (ppm)

Compound	σ^{dia}				σ^{para}			
	core	valence	total	shift	core	valence	total	shift
SnH ₄ ^d	5037.62	60.23	5097.86	-	-194.49	-1482.53	-1677.02	-
SnCl ₄	5038.47	146.18	5184.65	-86.79	-272.09	-1807.56	-2079.65	402.63
SnBr ₄	5039.34	137.88	5177.22	-79.36	-199.94	-2005.43	-2205.37	528.35
SnBr ₃ I	5039.44	135.79	5175.23	-77.37	-193.11	-2050.17	-2243.28	566.26
SnBr ₂ I ₂	5039.55	133.69	5173.24	-75.38	-185.52	-2089.34	-2274.86	597.84
SnBrI ₃	5039.66	131.59	5171.25	-73.39	-178.01	-2130.94	-2308.95	631.93
SnI ₄	5039.77	129.48	5169.25	-71.39	-169.64	-2315.53	-2335.17	658.15

^a Spin-dipolar term.^b Fermi contact term.^c For the chemical shift, the shielding constant of SnH₄ calculated without the spin-orbit interaction is used as a reference.^d For SnH₄, the SO effect due to the Sn atom is also included.

using the SO effective core potentials proposed by Christiansen et al. [16–18]. For simplicity, the SO interaction on the Sn atomic orbitals is not considered except for SnH₄ since it is estimated to be small and constant for all the compounds studied here. This is verified in the next section. For SnH₄, one-electron SO integrals of Sn and H are included.

The geometries of SnX₄ (X = H, Cl, Br and I) are taken from the experimental values [19–21]. For SnBr_{4–n}I_n, the bond angles are assumed to be tetrahedral and the Sn–Br and Sn–I distances are assumed to be the same as the corresponding distances in SnBr₄ and SnI₄.

The basis set for the Sn atom is taken from the book of Huzinaga et al. [22] plus first-order higher angular momentum p and d basis functions (p and d FOBFs) for the valence orbitals [23]. For the halogen atoms, the core electrons and the SO effects are replaced by the relativistic ECPs [16–18] and the double zeta sets plus p and d FOBFs are used; (4s4p)/[2s2p] set [17] plus p, d FOBFs for chlorine, (3s3p)/[2s2p] set [18] plus p, d FOBFs for bromine and (3s3p)/[2s2p] set [18] plus p, d FOBFs for iodine. For hydrogen, the (4s)/(2s) set of Huzinaga–Dunning [24] plus p FOBFs are used. The gauge origin is placed at the position of the tin atom. By adding the FOBFs, especially to the atoms neighboring the resonant atom, the basis set dependence and the gauge origin dependence are diminished [23,25]. The magnetic shielding constants of the compounds having T_d symmetry are invariant to the choice of the gauge origin, while those having C_{3v} symmetry are not invariant [23,25].

3. Results and discussion

Fig. 1 shows the ¹¹⁹Sn chemical shifts of SnX₄ and SnBr_{4–n}I_n, compared between the experimental and theoretical values. The open and filled circles show the calculated values without and with the SO interaction, respectively. The experimental chemical shifts are taken from Refs. [1,2]. The calculated Sn chemical shifts agree well with the experimental values only when we consider the SO interaction. In particular, the normal halogen dependence in tin tetrahalides cannot be reproduced by the calculations without the SO interaction. These results show that the SO effects are essential not only for accurate calculations but also for even qualitative calculations of these Sn chemical shifts. This result is similar to those reported previously for the other halogenated compounds of the main-group elements [9–12]. When the SO effects are included, the calculated chemical shifts move to a higher field and agree much better with the experimental values.

For SnBr_{4–n}I_n (n = 0–4), the calculated chemical shifts are underestimated from 110 to 180 ppm. We guess that the reason is the use of the ECP and the neglect of the electron correlation and other relativistic effects [13–15].

Table 1 shows a detailed analysis of the calculated shielding constant without and with the SO interaction. The magnetic shielding constant with the SO interaction is divided into the diamagnetic term, paramagnetic term, spin-dipolar term and Fermi contact term [9]. For SnH₄, the calculation with the SO interaction means that the SO operator on Sn is

SD ^a				FC ^b				σ^{tot}	$\delta^{\text{calc c}}$	δ^{exp}
core	valence	total	shift	core	valence	total	shift			
3.28	12.75	16.03	–	–8.92	5.90	–3.01	–	3433.67	0	0
0.09	0.31	0.40	–0.40	2.46	30.95	33.41	–33.41	3148.98	275.84	350
0.88	4.55	5.43	–5.43	18.95	397.74	416.69	–416.69	3446.70	–21.88	–138
1.39	7.77	9.16	–9.16	19.52	418.09	437.61	–437.61	3687.99	–263.17	–416
1.91	11.03	12.94	–12.94	76.41	948.68	1025.09	–1025.09	3933.20	–508.38	–687
1.39	15.39	16.78	–16.78	97.05	1209.64	1306.69	–1306.69	4185.77	–760.95	–947
3.01	17.58	20.59	–20.59	117.11	1470.58	1587.69	–1587.69	4442.36	–1017.54	–1201

Table 3

AO contributions in the dia, para, spin-dipolar and Fermi contact terms of the tin compounds (ppm)

Compound	σ^{dia}					σ^{para}			
	metal			ligand	total	metal		ligand	total
	s	p	d			p	d		
SnH ₄ ^c	2364.32	1803.36	895.41	34.77	5097.67	-1285.56	-372.15	-15.32	-1673.03
SnCl ₄	2362.53	1795.18	899.12	127.83	5184.65	-1557.78	-405.44	-116.44	-2079.66
SnBr ₄	2363.49	1798.84	901.32	113.57	5177.22	-1746.27	-367.17	-91.93	-2205.37
SnBr ₃ I	2363.38	1798.52	900.01	112.32	5175.23	-1795.30	-359.58	-88.41	-2243.28
SnBr ₂ I ₂	2363.26	1798.16	900.71	111.11	5173.24	-1838.19	-351.79	-84.88	-2274.86
SnBrI ₃	2363.17	1797.78	900.38	109.93	5171.25	-1884.66	-343.03	-81.25	-2308.95
SnI ₄	2363.06	1797.40	900.06	108.73	5169.25	-1923.60	-333.99	-77.58	-2335.17

^a Spin-dipolar term.^b Fermi contact term.^c For the chemical shift, the shielding constant of SnH₄ calculated without the spin-orbit interaction is used as a reference.^d The metal p and d AO contributions to the Fermi contact term are identically zero since they have a node at the position of the nucleus.^e For SnH₄, the SO effect due to the Sn atom is also included.

included. The SO effect on H is negligible; the difference between the calculations with and without the SO effect is only 8.85 ppm. This fact indicates that the SO interaction on the Sn atom may be neglected for the chemical shift, a relative value, supporting the assumption mentioned in the preceding section. In the other calculations with SO, the SO interactions of halogen atoms are included. Therefore, the value for SnH₄ without SO interaction is used as the reference value for the chemical shift.

As the halogen ligand becomes heavier, the SO effect becomes larger. The spin-dipolar term is much smaller than the Fermi contact term. It is therefore concluded that the most important contribution of the SO effects on the magnetic shielding constant is the Fermi contact term. This fact is valid for all the compounds studied so far in our laboratory [9–12].

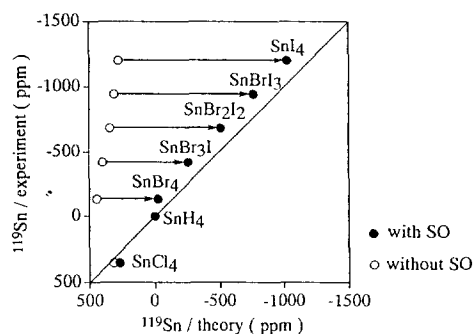


Fig. 1. Correlation between theory and experiment for ¹¹⁹Sn chemical shifts in tin tetrahydride and tetrahalides.

A comparison of the results with and without the SO effects shows that the diamagnetic terms are close, as expected, but the paramagnetic terms are somewhat different; the difference arises when the iodine ligand is introduced. This shows that a coupling between the paramagnetic and spin-orbit terms exists. Such a coupling has also been observed in calculations including both spin-free relativistic and spin-orbit terms [13,14].

Tables 2 and 3 show an analysis of the four terms in the Sn magnetic shielding constants into MO and AO contributions. These analyses are made similarly to our method for the diamagnetic and paramagnetic terms [26].

In the diamagnetic term, Table 2 shows that the valence electron contribution is dominant, while the core electron contribution is almost constant and therefore negligible for the chemical shift. Table 3 shows that the ligand contribution is dominant and that it decreases as the ligand becomes heavier since the Sn–X distance increases; this is understood from the Flygare and Goodisman equation [27]. On the contrary, in the all-electron calculations reported previously [8–10], the diamagnetic contribution increases as the ligand becomes heavier. This is because in the present ECP calculations a complete shielding of the nuclear charge by the inner core orbitals is assumed, but this is not actually true as the previous all-electron calculations show. We believe that the ligand contribution should increase as the previous all-electron calculations showed. This im-

SD ^a			FC ^b			σ^{tot}	$\sigma^{\text{calc c}}$	δ^{exp}		
metal		ligand	total	metal	ligand				total	
s	p	d	s ^d							
0.03	15.10	0.91	0.00	16.03	-3.50	0.49	-3.01	3433.67	0	0
-0.01	0.40	0.02	-0.01	0.40	43.64	-0.04	43.60	3148.98	275.84	350
1.06	5.94	0.01	-1.58	5.43	491.91	-22.49	469.42	3446.70	-21.88	138
1.02	9.76	0.11	-1.73	9.16	771.03	-24.14	746.89	3687.99	-263.17	-416
1.04	13.64	0.19	-1.93	12.94	1062.06	-28.74	1033.32	3933.20	-508.38	-687
1.13	17.56	0.24	-2.15	16.78	1342.89	-36.20	1306.69	4185.77	-760.95	-947
1.25	21.48	0.28	-2.42	20.59	1634.23	-46.54	1587.69	4442.36	-1017.54	-1201

proves the agreement of the present result with experiment.

For the paramagnetic term, the MO contribution analysis shows that the valence electron contribution is dominant, while the AO contribution analysis shows that the Sn p AO contribution is dominant. The p AO contribution increases in absolute value as the electronegativity of the halogen ligand decreases. This is reasonable since the 5p-subshell populations are smaller than three [7].

In both the spin-dipolar and Fermi contact terms, the valence electron contribution is dominant and the core electron contribution is small. In the AO contribution, the metal AO contribution dominates the Fermi contact term, while the metal p AO contribution dominates the spin-dipolar term. All these values increase as the halogen ligand becomes heavier. In the Fermi contact term the metal p and d orbital contributions are identically zero, since these orbitals have a node at the nucleus. It is clear that the SO effect on the Sn magnetic shielding constants is due to the metal valence s AO contribution to the Fermi contact term.

4. Conclusions

The SO effects in the ^{119}Sn NMR chemical shifts of SnX_4 (X = H, Cl, Br and I) and $\text{SnBr}_{4-n}\text{I}_n$ ($n = 1, 2, 3$) are calculated by the ab initio SO-UHF/FP method proposed previously [9]. The results may be summarized as follows.

(1) The calculated chemical shifts show good agreement with experiment when the SO effects are included. The calculated values without the SO inter-

action do not reproduce the experimental values when the halogen ligand is heavy. The SO effects are quite important for describing the Sn chemical shifts for the molecules containing heavier halogens.

(2) The origin of the normal halogen dependence of the Sn chemical shifts is the SO effect of the halogen ligand.

(3) The main contribution in the SO effect is the Fermi contact term, to which the metal valence s AO contribution is dominant.

(4) The spin-orbit effect due to the Sn atom is small.

Acknowledgements

We thank Mr. S. Tanaka for valuable discussions. Part of the calculations have been carried out by use of the computers at the Computer Center at the Institute for Molecular Science. This study has partially been supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture and by a grant from the New Energy and Industrial Technology Development Organization (NEDO).

References

- [1] R.K. Harris, J.D. Kennedy and W. McFarlane, in: NMR and the periodic table, eds. R.K. Harris and B.E. Mann (Academic Press, New York, 1978) p. 309.
- [2] J.D. Kennedy and W. MacFarlane, in: Multinuclear NMR, ed. J. Mason (Plenum, New York, 1987) p. 305.

- [3] P.J. Smith and A.P. Tupciausk, in: *Annu. Rep. NMR Spectrosc.* 8 (1978) 291.
- [4] B. Wrackmeyer, in: *Annu. Rep. NMR Spectrosc.* 16 (1985) 73.
- [5] H. Nakatsuji, T. Inoue and T. Nakao, *J. Phys. Chem.* 96 (1992) 7953.
- [6] R.G. Kidd, *Ann. Rept. NMR Spectrosc.* 10A (1980) 1.
- [7] H. Nakatsuji, in: *Nuclear magnetic shielding and molecular structure*, ed. J.A. Tossell (Kluwer, Dordrecht, 1993) p. 263.
- [8] M. Sugimoto, M. Kanayama and H. Nakatsuji, *J. Phys. Chem.* 97 (1993) 5868.
- [9] H. Nakatsuji, H. Takashima and M. Hada, *Chem. Phys. Lett.* 233 (1995) 95.
- [10] H. Takashima, M. Hada and H. Nakatsuji, *Chem. Phys. Lett.* 235 (1995) 13.
- [11] H. Nakatsuji, T. Nakajima, M. Hada, H. Takashima and S. Tanaka, *Chem. Phys. Lett.* 247 (1995) 418.
- [12] H. Nakatsuji, M. Hada, T. Tejima, T. Nakajima and M. Sugimoto, *Chem. Phys. Lett.* 249 (1996) 284.
- [13] H. Nakatsuji, M. Hada, H. Kaneko and C.C. Ballard, *Chem. Phys. Lett.* 255 (1996) 195.
- [14] M. Hada, H. Kaneko and H. Nakatsuji, *Chem. Phys. Lett.* in press.
- [15] C.C. Ballard, M. Hada, H. Kaneko and H. Nakatsuji, *Chem. Phys. Lett.* 254 (1996) 170.
- [16] L.F. Pacios and P.A. Christiansen, *J. Chem. Phys.* 82 (1985) 2664.
- [17] M.M. Hurley, L.F. Pacios, P.A. Christiansen, R.B. Ross and W.C. Ermler, *J. Chem. Phys.* 84 (1986) 6840.
- [18] L.A. LaJohn, P.A. Christiansen, R.B. Ross, T. Atashroo and W.C. Ermler, *J. Chem. Phys.* 87 (1987) 2812.
- [19] H.W. Kattenberg and A. Oskam, *J. Mol. Spectrosc.* 51 (1974) 377.
- [20] H. Fujii and M. Kimura, *Bull. Chem. Soc. Jpn.* 43 (1970) 1933.
- [21] L.E. Sutton, *Table of interatomic distances and configurations in molecules and ions* (Chem. Soc., London, 1965).
- [22] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki, *Gaussian basis sets for molecular calculations* (Elsevier, Amsterdam, 1984).
- [23] M. Sugimoto and H. Nakatsuji, *J. Chem. Phys.* 102 (1995) 285.
- [24] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293; T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [25] T. Higashioji, M. Hada, M. Sugimoto and H. Nakatsuji, *Chem. Phys.* 203 (1996) 159.
- [26] H. Nakatsuji, K. Kanda, K. Endo and T. Yonezawa, *J. Am. Chem. Soc.* 106 (1984) 4653.
- [27] W.H. Flygare and J. Goodisman, *J. Chem. Phys.* 49 (1968) 3122.