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Heavy Atom Effect on 14 Group Nuclear Shielding Constant of SiX_4 and $CH_{4-n}X_n$ (X=Cl, Br, I; n=1, 2, 3, 4)

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A sum-over-states third-order perturbation theory using a semiempirical wavefunction parameteric method 3 was applied to ^{29}Si and ^{13}C nuclear magnetic shielding constants of SiX_4 and $CH_{4-n}X_n$ (X=Cl, Br, I; n=1, 2, 3, 4), respectively. The other new spin-orbit (LS) term, $\sigma_{LS}(A)$, was proposed to come from the cross term involving the halogen spin-orbit coupling, Fermi I·S interaction and the external field-(carbon or silicon) orbit interaction. The values using the MO method predicted a substantial contribution (25%) of σ_{LS}(Si or C) to the $\sigma_{LS}(X)$ as already given. The results agreed fairly well with the experimental values, indicating the importance of the spin-orbit effect on the chemical shifts of molecules containing halogen heavier atoms. The dominant contribution of electronic states to the LS shifts is due to the excitations from all occupied MOs to only all vacant $\sigma^*_{\text{Si(or C)}-\text{X}}$ antibonding MOs, since the Fermi interaction intervenes between the shift contributions.

MO calculations of NMR chemical shifts became quite popular and reproduce the experimental values well, making possible theoretical assignment,[1] and clarifications of the electronic mechanisms of the metal chemical shifts.[2] Recently Malkin and co-workers have calculated NMR shielding tensors by the sum-over-states (SOS) density functional perturbation theory.[3] However, the relativistic effect, especially the spin-orbit effect, on the magnetic shielding constant has not been fully investigated despite its expected great importance. A part of the relativistic corrections due to a heavy neighboring atom can be estimated by the third-order perturbation theory with nonrelativistic semiempirical wavefunctions.[4—6] The contribution to shielding was indicated to come from the cross term involving the spin-orbit coupling, I·S interaction, and the external field-orbit interaction.[4] The relativistic theory of the chemical shift has been formulated by Pyper,[7] Pyykko,[8] and Zhang and Webb,[9] but no relativistic ab initio calculations have been done except for the one electron molecule, $H_2{}^+$,[10] though some calculations were reported by the relativistically parameterized extended Hückel method and the second-order perturbation theory.[11]

Recently Nakatsuji and co-workers[12] have proposed a calculational method for the spin-orbit effect on the magnetic shielding constant using an ab initio unrestricted Hartree–Fock (UHF) wavefunction and the finite perturbation method:[13] The method corresponds to considering the ground state wavefunction involving the triplet spin-orbit term using the second-order perturbation theory. The calculations were done for the proton and carbon magnetic shielding constants in hydrogen halides and methyl halides, respectively. The results for hydrogen halides suggested very well the contribution of the LS shift[4] by the third-order perturbation theory with a nonrelativistic semiempirical wavefunction as in the collaboration with one of us. Nakatsuji et al.[14] have also stated that the electronic mechanism of nuclear chemical shieldings for the 14 group (Si, Ge, Sn) complex is p-excitation of the s^2p^2 electronic configuration. This means the NMR chemical shielding of the silicon complex is explained mostly by electronic states in the valence-electron region, since the nuclear shielding of core electrons become nearly constant in the silicon compounds. In this paper, we thus reproduced the SOS states third-order perturbation theory using a semiempirical parameteric method 3 (PM3)[15] to evaluate the spin-orbit effects on the proton magnetic shielding constants of HX (X=Cl, Br, I). Furthermore, we have calculated the spin-orbit effects on the Si and C magnetic shielding constants of SiX_4 and $CH_{4-n}X_n$ (X=Cl, Br, I; n=1, 2, 3, 4), respectively. The main contribution of the electronic states for the LS shift was identified by comparing the SOS calculations with the excitations from all occupied MOs to only all vacant $s\sigma^*_{\text{Si(or C)}-\text{X}}$MOs.

Theory

The basic derivation of the LS(spin-orbit) shift was already given in our previous paper[4] from the general perturbation-theory expressions. We assume that the exact wavefunctions for the corresponding electronic states in the following Eq. 1 are approximately built from Hartree–Fock MO's. The wavefunctions[6] for the ground and lowest excited states are written as a single determinant of the form, as mentioned previously.[4] The MO is expanded as a linear combination of the atomic orbitals. The shielding constant of the atom A is obtained from the usual third-order perturbation theory

$$\begin{aligned}
\sigma_{\mathrm{k}} = (\partial^2/(\partial\mu_{\mathrm{k}}\partial H_{\mathrm{k}}\{\langle {}^1\Phi_0 \mid h \mid {}^1\Phi_0\rangle \\
-\sum_{i}^{\mathrm{Occ}}\sum_{j}^{\mathrm{Unocc}} (\langle {}^1\Phi_0 \mid h \mid {}^1\Phi_{i\to j}\rangle\langle {}^1\Phi_{i\to j} \mid h \mid {}^1\Phi_0\rangle({}^1E_{ji}-E_0)^{-1}) \\
+\sum_{i}^{\mathrm{Occ}}\sum_{jj'}^{\mathrm{Unocc}} [\langle {}^1\Phi_0 \mid h \mid {}^{1(\mathrm{or}\ 3)}\Phi_{i\to j}\rangle \\
\times\langle {}^{1(\mathrm{or}\ 3)}\Phi_{i\to j} \mid h \mid {}^{1(\mathrm{or}\ 3)}\Phi_{i\to j'}\rangle\langle {}^{1(\mathrm{or}\ 3)}\Phi_{i\to j'} \mid h \mid {}^1\Phi_0\rangle \\
\times\{({}^{1(\mathrm{or}\ 3)}E_{ji}-E_0)({}^{1(\mathrm{or}\ 3)}E_{j'i}-E_0)\}^{-1}] - \langle {}^1\Phi_0 \mid h \mid {}^1\Phi_0\rangle \\
\times\sum_{i}^{\mathrm{Occ}}\sum_{j}^{\mathrm{Unocc}} [\langle {}^1\Phi_0 \mid h \mid {}^{1(\mathrm{or}\ 3)}\Phi_{i\to j}\rangle\langle {}^{1(\mathrm{or}\ 3)}\Phi_{i\to j} \mid h \mid {}^1\Phi_0\rangle \\
\times({}^{1(\mathrm{or}\ 3)}E_{ji}-E_0)^{-2}]\})_{\mu=\mathrm{H}=0}. \qquad (1)
\end{aligned}$$

where h is the total hamiltonian, ${}^1\Phi_0$ denotes the total wavefunction for the ground state, ${}^{1(\mathrm{or}\ 3)}\Phi_{i\to j}$ represents a singlet (or triplet) state; the subscript $i{\to}j$ labels excitation of a single electron from MO φ_i to MO φ_j. We think that if we obtain the exact wavefunctions of the molecules, we can reproduce the experimental NMR chemical shieldings using Eq. 1.

The diamagnetic and paramagnetic terms[17] are written as

$$\begin{aligned}
\sigma_{\mathrm{dia}}{}^{\mathrm{uv}}=(1/2)\alpha^2\sum_{a,b}P_{ab} < \chi_a(\mathrm{k}) \mid (r_{\mathrm{Ak}}^2\delta_{\mathrm{uv}} \\
-r_{\mathrm{u}}r_{\mathrm{Av}})r_{\mathrm{Ak}}^{-3} \mid \chi_{\mathrm{b(k)}} > \qquad (2)
\end{aligned}$$

$$\begin{aligned}
\sigma_{\mathrm{para}}{}^{\mathrm{uv}}=-\alpha^2\langle r_{\mathrm{Ak}}^{-3}\rangle_{\mathrm{np}}\sum_{i}^{\mathrm{Occ}}\sum_{j}^{\mathrm{Unocc}}\{[C_i^{\mathrm{A}}\times C_j^{\mathrm{A}}]_{\mathrm{u}}[C_j^{\mathrm{A}'}\times C_i^{\mathrm{A}'}]_{\mathrm{v}} \\
+[C_i^{\mathrm{A}}\times C_j^{\mathrm{A}}]_{\mathrm{v}}[C_j^{\mathrm{A}'}\times C_i^{\mathrm{A}'}]_{\mathrm{u}}\}({}^1E_{ji}-E_0)^{-1}, \qquad (3)
\end{aligned}$$

where ${}^1E_{ji}-E_0$ is the singlet excitation energy from φ_i to φ_j and the components of the vectors C_i^{A}, $C_i^{\mathrm{A}'}$ are the coefficients of the corresponding p_x, p_y, and p_z AOs of i-th MO in the atom A and atoms X including the atom A, respectively. α is the fine-structure constant.

For the third-order contribution including the spin-orbit coupling interaction, we can obtain four shielding constants[4,5] which intervene in Fermi, spin-dipolar, and electron-spin Zeeman interactions, and the vector potential of nuclear dipole, respectively. We here consider the dominant term involving the Fermi interaction and neglected the other three terms, since these terms are smaller.[4,5] We propose an other new LS shift, $\sigma_{\mathrm{LS}}(\mathrm{A})$, which is indicated to come from the cross term involving the halogen spin-orbit coupling, silicon (or carbon) I·S interaction and external field-silicon (or carbon) orbit, with the previous LS shift,[4] $\sigma_{\mathrm{LS}}(\mathrm{X})$. The expression was rewritten in this case,

$$\begin{aligned}
\sigma_{\mathrm{LS}}{}^{\mathrm{uv}}=\sigma_{\mathrm{LS}}(\mathrm{A})^{\mathrm{uv}}+\sigma_{\mathrm{LS}}(\mathrm{X})^{\mathrm{uv}}=-(4\pi\alpha^2\lambda/3)|S(0)|^2 \\
\times\{\sum_{i}^{\mathrm{Occ}}\sum_{jj'}^{\mathrm{Unocc}}[C_i^{\mathrm{X}}\times C_j^{\mathrm{X}}]_{\mathrm{u}}\{[C_j^{\mathrm{A}}\times C_{j'}^{\mathrm{A}}]_{\mathrm{v}}+[C_j^{\mathrm{X}}\times C_{j'}^{\mathrm{X}}]_{\mathrm{v}}\}C_{sj'}^{\mathrm{A}}C_{\mathrm{si}}^{\mathrm{A}} \\
\times[\{({}^3E_{ji}-E_0)({}^3E_{j'i}-E_0)\}^{-1}+\{({}^1E_{ji}-E_0)({}^3E_{j'i}-E_0)\}^{-1}] \\
+\sum_{i}^{\mathrm{Occ}}\sum_{jj'}^{\mathrm{Unocc}}\{[C_i^{\mathrm{A}}\times C_j^{\mathrm{A}}]_{\mathrm{u}}+[C_i^{\mathrm{X}}\times C_j{}^{\mathrm{X}}]_{\mathrm{u}}\}C_{sj}^{\mathrm{A}}C_{sj'}^{\mathrm{A}}[C_{j'}^{\mathrm{X}}\times C_i^{\mathrm{X}}]_{\mathrm{v}}\{({}^3E_{ji} \\
-E_0)({}^1E_{j'i}-E_0)\}^{-1}-\sum_{ii'}^{\mathrm{Occ}}\sum_{j}^{\mathrm{Unocc}}\{[C_i^{\mathrm{A}}\times C_j^{\mathrm{A}}]_{\mathrm{u}}+[C_i^{\mathrm{X}}\times C_j^{\mathrm{X}}]_{\mathrm{u}}\} \\
\times[C_{i'}^{\mathrm{X}}\times C_i^{\mathrm{X}}]_{\mathrm{v}}C_{sj}{}^{\mathrm{A}}C_{si}{}^{\mathrm{A}}[\{({}^3E_{ji}-E_0)({}^3E_{ji'}-E_0)\}^{-1}+\{({}^1E_{ji} \\
-E_0)({}^3E_{ji'}-E_0)\}^{-1}]-\sum_{ii'}^{\mathrm{Occ}}\sum_{j}^{\mathrm{Unocc}}\{[C_i^{\mathrm{A}}\times C_j^{\mathrm{A}}]_{\mathrm{u}}+[C_i^{\mathrm{X}}\times C_j^{\mathrm{X}}]_{\mathrm{u}}\} \\
\times C_{si'}{}^{\mathrm{A}}C_{si}{}^{\mathrm{A}}[C_j{}^{\mathrm{X}}\times C_{i'}^{\mathrm{X}}]_{\mathrm{v}}\{({}^3E_{ji}-E_0)({}^1E_{ji'}-E_0)\}^{-1} \\
+2\sum_{imm'}^{\mathrm{Occ}}\sum_{j}^{\mathrm{Unocc}}\{[C_i^{\mathrm{A}}\times C_j^{\mathrm{A}}]_{\mathrm{u}}+[C_i^{\mathrm{X}}\times C_j^{\mathrm{X}}]_{\mathrm{u}}\}[C_{m'}^{\mathrm{X}}\times C_m^{\mathrm{X}}]_{\mathrm{v}}C_{sj}^{\mathrm{A}}C_{si}{}^{\mathrm{A}} \\
\times\{{}^3E_{ji}-E_0\}^{-2}\}, \qquad (4)
\end{aligned}$$

where the components of the vectors, $C_i{}^{\mathrm{A}}$ and $C_i{}^{\mathrm{X}}$, are the coefficients of the corresponding p_x, p_y, and p_z AOs of i-th MO in the atoms A and X, respectively, C_{sj}^{A} is the coefficient of the s AO of the j-th MO in the atom A, and $|S\ (0)\ |^2$ is the electron orbital probability density of the atom A at $r_{\mathrm{AK}}=0$. λ is the spin-orbital constant.

Results and Discussion

We calculated the H, C, and Si chemical shifts of HX, $CH_{4-n}X_n$, and SiX_4 (X=Cl, Br, I; n=1—4) compounds, respectively.The geometries of (CHX_3, CH_3X), CH_2X_2, and (CX_4, SiX_4) were optimized under their C_{3v}, C_{2v}, and T_d symmetries by the PM3 method.[15] Table 1 shows the optimized values with experimental ones for the bond lengths. In the calculation of the chemical shift, we modified a PM3 program to output the singlet and triplet excitation energies from all occupied MOs to all unoccupied MOs, and considered only the one-electron term of the spin-orbit. This is enough for calculating the isotropic terms for the dia-

Table 1. Bond Lengths of HX, $CH_{4-n}X_n$ and SiX_4 as Optimized by PM3 Method

Compound	Calculated (Å)		Observed (Å)	
	$R_{\mathrm{A(H,C,Si)-X}}$,	$R_{\mathrm{C-H}}$	$R_{\mathrm{A(H,C,Si)-X}}$,	$R_{\mathrm{C-H}}$
HCl	1.2676		1.274	
HBr	1.4707		1.414	
HI	1.6771		1.609	
CH_3Cl	1.7397	1.1167	1.785	1.090
CH_3Br	1.9013	1.1168	1.933	1.086
CH_3I	2.1300	1.1166	2.132	1.084
CH_2Cl_2	1.7575	1.1018	1.765	1.087
CH_2Br_2	1.9400	1.1166	1.924	1.080
CH_2I_2	2.1300	1.1166		
$CHCl_3$	1.7251	1.1118	1.758	1.100
$CHBr_3$	1.8719	1.0941	1.924	1.110
CHI_3	2.0478	1.1168		
CCl_4	1.7470		1.767	
CBr_4	1.9454		1.935	
CI_4	2.1335		2.150	
$SiCl_4$	2.0413		2.019	
$SiBr_4$	2.1530		2.153	
SiI_4	2.4144		2.437	

magnetic, paramagnetic, and the LS terms including Fermi contact interaction. The shielding constant of CX_4 and SiX_4 is gauge-independent because of their T_d symmetry.[18,19] Table 2 showed quantities (the spin-orbit coupling constant of halogen[20] and the hyperfine coupling constant of proton, carbon and silicon atoms)[21] which were required for a calculation of the LS term in Eq. 4.

(a) H Chemical Shifts of HX. We first calculated proton chemical shifts of HX (X=Cl, Br, I) using the semiempirical PM3 program. The principal axis of the molecule was taken to be the z-axis.[4] The gauge origin is located on the halogen atom. The diamagnetic term, σ_{dia}, is given as:

$$\begin{aligned}\sigma_{\mathrm{dia}} = (1/3)\alpha^2 \sum_{i}^{\mathrm{Occ}} \sum_{a,b} C_{ia} C_{ib} \{ & \langle \mathrm{X_a(k)} \mid 1/r_{\mathrm{Hk}} \\ & - R Z_{\mathrm{Hk}}/r_{\mathrm{Hk}}^3 \mid \mathrm{X_b(k)} \rangle \\ & + \langle \mathrm{X_a(k)} \mid 1/r_{\mathrm{Hk}} \mid \mathrm{X_b(k)} \rangle \}, \end{aligned} \tag{5}$$

where the first term contains only wavefunctions that are centered on the halogen nucleus, and the second term contains wavefunctions that are centered on the hydrogen and both halogen and hydrogen atomic orbitals that are centered on the hydrogen. We considered two-center integrals as done in our previous work[4] for the σ_{dia}.

The paramagnetic term $\sigma_{\mathrm{para}}{}^{\mathrm{uu}}$ is obtained as

$$\begin{aligned}\sigma_{\mathrm{para}}{}^{\mathrm{uu}} = -2\alpha^2 \mathrm{Re}[\sum_{abcd} \{ & \langle \mathrm{X_a(k)} \\ & \times \mid [(r_{(\mathrm{k})} - R) \times \nabla]_{\mathrm{u}}/r_{\mathrm{Hk}}^3 \mid \mathrm{X_b(k)} \rangle \\ & \times \langle \mathrm{X_c(k)} \mid [r_{\mathrm{k}} \times \nabla]_{\mathrm{u}} \mid \mathrm{X_d(k)} \rangle \} \\ & \times \sum_{i}^{\mathrm{Occ}} \sum_{j}^{\mathrm{Unocc}} ({}^1E_{ji} - E_0)^{-1} C_{ai} C_{bj} C_{cj} C_{di}]. \end{aligned} \tag{6}$$

We here retained one-center integrals as done in our previous work,[4] although the two-center integrals may contribute substantially to this term.

For the LS term, we used the $\sigma_{\mathrm{LS}}(\mathrm{X})$ as already given. We compared in Fig. 1 the proton chemical shifts calculated with and without the LS term to the experimental values.[22] The chemical shift values are given relative to the HCl molecule. Our calculated shifts including the LS term agree well with experimental values: The spin-orbit effects are significant for HBr and HI.

(b) C Chemical Shifts of $CH_{4-n}X_n$. Table 3 and Fig. 2 showed the calculated C chemical shieldings of $CH_{4-n}X_n$ (X=Cl, Br, I) with the experimental values.[23,24] In $CH_{4-n}X_n$ molecules other than CX_4, the gauge origin is on the halogen atom. Our calculated values agree fairly well with the experimental ones. The agreement is obtained by considering the LS terms. Our evaluated largest LS shielding was given as the contribution of 330.6 ppm ($\sigma_{\mathrm{LS}}(\mathrm{X})$ 271.5 and $\sigma_{\mathrm{LS}}(\mathrm{C})$ 59.1) to the total shielding for CI_4.

In $CH_{4-n}X_n$ compounds, the contribution of the electronic states to the LS shielding can be considered, as is done in the following section of SiX_4.

(c) Chemical Shifts of SiX_4. In SiX_4 compounds, the origin of the ^{29}Si chemical shifts

Table 2. Quantities for a Calculation of Third-Order Perturbation Term

Atom	λ (a.u.)	$\mid S(0) \mid^2$ (a.u.)
Cl	0.002674	
Br	0.01128	
I	0.02323	
H		0.338
C		2.04
Si		2.06

Table 3. The H Chemical Shift of HX and C Chemical Shift of $CH_{4-n}X_n$ (ppm unit)

	σ_{dia}	σ_{para}	σ_{LS}		σ_{total}	σ_{calcd}	σ_{obsd}
			$\sigma_{\mathrm{LS}}(\mathrm{x})$	$\sigma_{\mathrm{LS}}(\mathrm{A})$			
HCl	14.9	−3.8	0.4		11.5	0	0
HBr	16.0	−3.1	2.9		15.8	4.3	3.9
HI	18.5	−2.3	11.3		27.5	16.0	12.8
CH_3Cl	35.2	−168.6	3.1	0.8	−129.5	0	0
CH_3Br	38.6	−173.7	13.2	2.2	−119.7	9.8	15.1
CH_3I	40.1	−190.0	35.6	12.9	−101.4	28.1	45.8
CH_2Cl_2	40.5	−179.8	4.7	1.0	−133.6	−4.1	−29.1
CH_2Br_2	47.2	−191.9	22.3	7.8	−114.6	14.9	3.5
CH_2I_2	49.9	−215.4	80.7	32.3	−52.5	77.0	78.9
$CHCl_3$	46.1	−192.3	6.8	1.2	−138.2	−8.7	−52.6
$CHBr_3$	56.1	−205.5	33.2	7.0	−109.2	20.3	12.8
CHI_3	60.1	−241.8	145.3	47.0	10.6	140.1	164.8
CCl_4	51.5	−211.9	10.4	2.3	−147.7	−18.2	−71.6
CBr_4	64.8	−252.5	53.8	11.9	−122.0	7.5	53.6
CI_4	69.9	−340.0	271.5	59.1	60.5	190.0	317.4

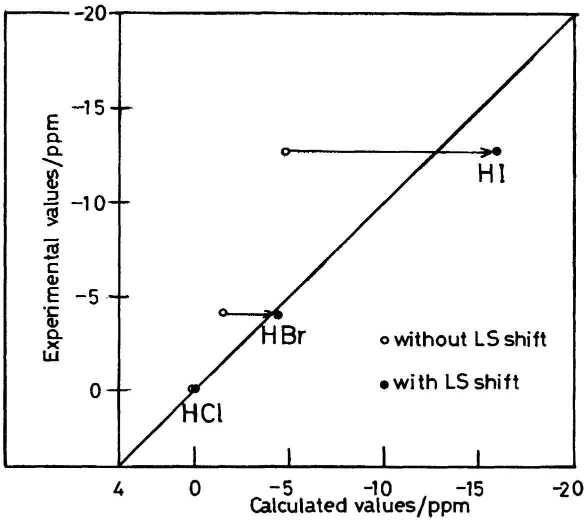

Fig. 1. ^1H chemical shifts in HX (X=Cl, Br, I) compared between the experimental and the calculated values with and without the spin-orbit (LS) shift.

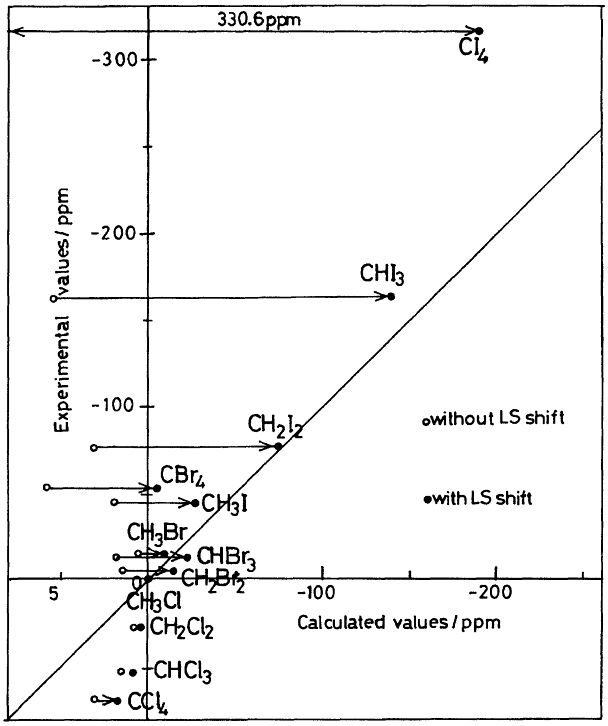

Fig. 2. ^{13}C chemical shifts in $CH_{4-n}X_n$ (X=Cl, Br, I; n=1—4) compared between the experimental and the calculated values with and without the spin-orbit (LS) shift.

has not been explained theoretically, although some investigators[25)] observed the high-field shifts of $SiBr_4$ and SiI_4. We show in Table 4 a comparison between the calculated and the experimental values. Our calculated values of the LS shielding for SiI_4 predicted a substantial contribution as 510.9 ppm (σ_{LS}(X) 420.9 and σ_{LS}(Si) 90.0) to the total shielding. Figure 3 showed the silicon chemical shifts with and without LS shifts together with experimental ones. The calculated values match well with the experimental ones. Thus, we can see that the origin of the high-field shift was interpreted by the LS term.

Table 4. The Si Chemical Shifts of SiX_4 (ppm unit)

	$SiCl_4$	$SiBr_4$	SiI_4
σ_{dia}	54.2	66.0	74.6
σ_{para}	−431.5	−403.5	−669.2
σ_{LS}(X)	10.6	40.9	420.9
σ_{LS}(Si)	2.4	9.5	90.0
$\sigma_{(total)}$	−364.3	−287.1	−83.7
$\sigma_{(calcd)}$	0	77.2	280.6
$\sigma_{(obsd)}$	0	73.6	326.2

Let's examine the contributions of the electronic states to the LS shift of the SiX_4 using the PM3 method. We calculated the two LS shifts of SiX_4 from all occupied MOs to only all s$\sigma^*_{\text{Si–X}}$ antibonding MOs in Table 5. The values of the contribution agree with the SOS values (the values of parenthesis in the table). This indicates that the main contribution of the electronic states to the LS shifts is due to the excitations from all occupied MOs to only all vacant s$\sigma^*_{\text{Si–X}}$ MOs, since the Fermi interaction intervenes between the shift contributions. In Fig. 4, we showed an example of the transitions for the LS shifts of $SiCl_4$.

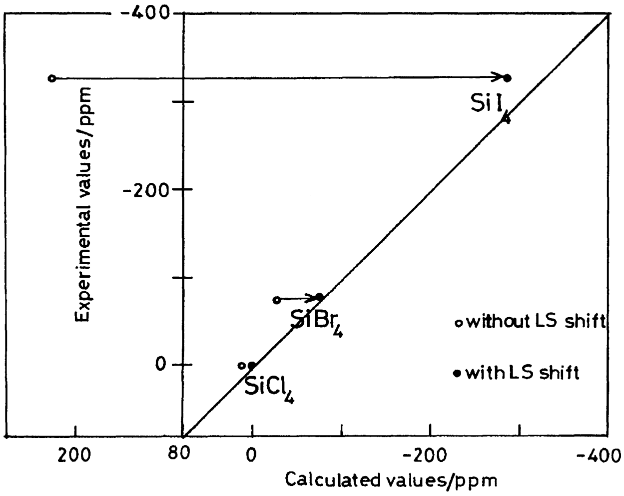

Fig. 3. ^{29}Si chemical shifts in SiX_4 (X=Cl, Br, I) compared between the experimental and the calculated values with and without the spin-orbit (LS) shift.

Table 5. LS shifts of SiX_4 by Consideration of All Occupied MOs and Only All Vacant $\sigma^*_{\text{Si–X}}$ MOs

	$SiCl_4$	$SiBr_4$	$SiCl_4$
σ_{LS}(X)	423	41.3	10.7
	(421)	(40.9)	(10.6)
σ_{LS}(Si)	92	9.5	2.5
	(91)	(9.6)	(2.4)

Parenthesis is the SOS values.

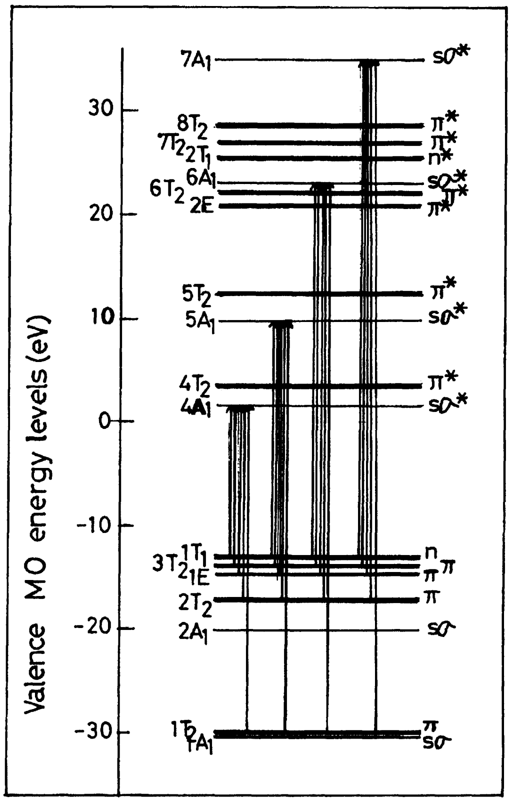

Fig. 4. Valence MO energy levels of $SiCl_4$ and the main contribution to the LS shifts due to the excitations from all occupied MOs to only all vacant $s\sigma^*$ antibonding MOs.

Conclusion

We have formulated an other new LS shift $\sigma_{\mathrm{LS}}(\mathrm{A})$ coming from the cross term involving the halogen spin-orbit coupling, Fermi I•S interaction, and the external field-(C or Si) orbit interaction. The values for SiX_4 and $CH_{n-4}X_n$ using the MO method gave a substantial contribution (25%) of $\sigma_{\mathrm{LS}}(\mathrm{A})$ to the $\sigma_{\mathrm{LS}}(\mathrm{X})$ as already stated. Our results agreed well with the experimental values and at the same time pointed out the importance of the LS shift in the chemical shift of the molecule containing heavier halogen atoms. The dominant contribution of the electronic states to the LS shifts is due to the excitations from all occupied MOs to only all vacant $s\sigma^*_{\mathrm{Si(or\ C)-X}}$ MOs.

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