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Spin–orbit effect on the magnetic shielding constant using the ab initio UHF method: silicon tetrahalides

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Abstract

The ^{29}Si NMR chemical shifts of silane, SiH_4, and silicon tetrahalides, SiX_4 (X = F, Cl, Br and I) and $SiXI_3$ (X = Cl and Br), are calculated by the ab initio unrestricted Hartree–Fock/finite perturbation method including the spin–orbit (SO) interaction proposed previously. The SO effect is included through the effective core potentials for the halogens. The chemical shifts calculated with the SO effects show good agreement with experiment for all the compounds studied. The SO effects of the halogen ligands, especially of bromine and iodine, are large and move the chemical shift to higher magnetic field. The inverse halogen dependence on the substitution of F by Cl is derived from the paramagnetic term, but the normal halogen dependence on the substitution from Cl to I is caused mainly by the SO effect.

1. Introduction

The ^{29}Si NMR chemical shifts of various silicon compounds have been extensively studied and summarized in the literature [1–4]. It is known that in silicon tetrahalides substitution of Cl by I causes an anomalous high field shift of the ^{29}Si chemical shift, like those of the main-group metal halides; Kidd called this shift the 'normal halogen dependence' (NHD) [5], while substitution of F by Cl causes a low field shift, called the inverse halogen shift (IHD). However, the electronic origin of the NHD is not yet understood [1].

We have theoretically investigated the metal NMR chemical shifts of various metal complexes in order to elucidate the origins and the mechanisms of the chemical shifts [6–9]. Previously, we studied the ^{29}Si chemical shifts of the compounds, $SiCl_nF_{4-n}$ ($n = 0$–4), and showed that the 'p mechanism' is the origin of the chemical shift; the ^{29}Si chemical shift reflects the change in the valence p-electronic state of Si induced by the halogen substitution [9].

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In the previous paper of this series [10], we formulated the calculation method of the magnetic shielding constant under the influence of the spin–orbit (SO) effect using the unrestricted Hartree–Fock (UHF) wavefunction and the finite perturbation (FP) method. It was applied to the proton, carbon [10], Ga and In [11] chemical shifts in the hydrogen and methyl halides and gallium and indium tetrahalides, and the importance of the SO effect was shown. However, except for these examples, the SO effect on the NMR chemical shift is not well elucidated though it is expected to be quite important. This is perhaps due to the lack of an adequate calculation method except for the third-order perturbation method which is numerically unreliable. Our UHF/FP method is therefore quite useful for studying the SO effect.

In this Letter, we introduce the use of the effective core potentials (ECPs) including the SO effect in the framework of the UHF/FP method. With this method we investigate the SO effect on the ^{29}Si NMR chemical shifts of silane and silicon tetrahalides and clarify the origin of the NHD. The compounds studied here are SiX_4 (X = H, F, Cl, Br and I) and $SiXI_3$ (X = Cl and Br).

2. Method of calculation

In our previous paper, magnetic shielding constants were calculated by the UHF/FP method including the SO interaction [10]. The SO interaction was calculated ab initio with the UHF wavefunction [10]. In this Letter, the SO operator is replaced, together with the core electrons, with the relativistic effective core potential (RECP) presented by Christiansen et al. [12–14]. This RECP is partitioned into the averaged RECP and the SO potentials; the averaged RECP can be used in the same form as the Kahn-type ECP [15], while the SO potential is used in the following SO operator [12]:

$$\hat{H}^{\mathrm{SO}} = \hat{S} \sum_{\mathrm{A}}^{\mathrm{atom}} \sum_{l=1}^{L} \frac{2}{l} \hat{U}_{\mathrm{A}l}^{\mathrm{SO}}(r) \sum_{m} \sum_{m} |l_{\mathrm{A}} m_{\mathrm{A}}\rangle\langle l_{\mathrm{A}} m_{\mathrm{A}}|\hat{l}_{\mathrm{A}}|l_{\mathrm{A}} m'_{\mathrm{A}}\rangle\langle l_{\mathrm{A}} m'_{\mathrm{A}}|, \tag{1}$$

where $\hat{U}_{\mathrm{A}l}^{\mathrm{SO}}(r)$ is the effective SO potential centered on atom A fitted by Gaussian functions, $|l_{\mathrm{A}} m_{\mathrm{A}}\rangle$ is the spherical harmonic basis function centered on A and the prime indicates basis functions with a different exponent. This form is convenient for use with the standard ab initio program since it does not include the total angular momentum ($j = l + s$).

In evaluating the matrix elements for the $\hat{H}^{\mathrm{SO}}$ operator, we included, for simplicity, only the one-center integrals. The SO potential of the Si atom was not included since it is small. Under this approximation, the matrix elements for the $\hat{H}^{\mathrm{SO}}$ operator appear, in the present case, only over the p and d orbitals on the halogen atoms, and are written as

$$\begin{pmatrix} H_{xx}^{\mathrm{SO}} & H_{xy}^{\mathrm{SO}} & H_{xz}^{\mathrm{SO}} \\ H_{yx}^{\mathrm{SO}} & H_{yy}^{\mathrm{SO}} & H_{yz}^{\mathrm{SO}} \\ H_{zx}^{\mathrm{SO}} & H_{zy}^{\mathrm{SO}} & H_{zz}^{\mathrm{SO}} \end{pmatrix} = \begin{pmatrix} 0 & -\mathrm{i}s_z & \mathrm{i}s_y \\ \mathrm{i}s_z & 0 & -\mathrm{i}s_x \\ -\mathrm{i}s_y & \mathrm{i}s_x & 0 \end{pmatrix} \langle \mathrm{p}|\hat{U}^{\mathrm{SO}}|\mathrm{p}'\rangle \tag{2}$$

$$
\begin{pmatrix}
H^{SO}_{x^2x^2} & H^{SO}_{x^2y^2} & H^{SO}_{x^2z^2} & H^{SO}_{x^2xy} & H^{SO}_{x^2zx} & H^{SO}_{x^2yz} \\
H^{SO}_{y^2x^2} & H^{SO}_{y^2y^2} & H^{SO}_{y^2z^2} & H^{SO}_{y^2xy} & H^{SO}_{y^2zx} & H^{SO}_{y^2yz} \\
H^{SO}_{z^2x^2} & H^{SO}_{z^2y^2} & H^{SO}_{z^2z^2} & H^{SO}_{z^2xy} & H^{SO}_{z^2zx} & H^{SO}_{z^2yz} \\
H^{SO}_{xyx^2} & H^{SO}_{xyy^2} & H^{SO}_{xyz^2} & H^{SO}_{xyxy} & H^{SO}_{xyzx} & H^{SO}_{xyyz} \\
H^{SO}_{zxx^2} & H^{SO}_{zxy^2} & H^{SO}_{zxz^2} & H^{SO}_{zxxy} & H^{SO}_{zxzx} & H^{SO}_{zxyz} \\
H^{SO}_{yzx^2} & H^{SO}_{yzy^2} & H^{SO}_{yzz^2} & H^{SO}_{yzxy} & H^{SO}_{yzzx} & H^{SO}_{yzyz}
\end{pmatrix}
$$

$$
= \begin{pmatrix}
0 & 0 & 0 & -\frac{2}{\sqrt{3}}is_z & \frac{2}{\sqrt{3}}is_y & 0 \\
0 & 0 & 0 & \frac{2}{\sqrt{3}}is_z & 0 & -\frac{2}{\sqrt{3}}is_x \\
0 & 0 & 0 & 0 & -\frac{2}{\sqrt{3}}is_y & \frac{2}{\sqrt{3}}is_x \\
\frac{2}{\sqrt{3}}is_z & -\frac{2}{\sqrt{3}}is_z & 0 & 0 & -is_x & is_y \\
-\frac{2}{\sqrt{3}}is_y & 0 & \frac{2}{\sqrt{3}}is_y & is_x & 0 & -is_z \\
0 & \frac{2}{\sqrt{3}}is_x & -\frac{2}{\sqrt{3}}is_x & -is_y & is_z & 0
\end{pmatrix}
\langle d|\hat{U}^{SO}|d'\rangle . \qquad (3)
$$

H^{SO}_{rs} is the matrix element over p_r and p'_s ($r, s = x, y, z$) AOs or d_r and d'_s ($r, s = x^2, y^2, z^2, xy, zx, yz$) AOs and $\langle p|\hat{U}^{SO}|p'\rangle$ and $\langle d|\hat{U}^{SO}|d'\rangle$ are the integrals of $\hat{U}^{SO}$ over the p and d orbitals, respectively. The merit of using the ECPs is not only a reduction of the calculational dimensions but also to circumvent the gauge dependence originating from the ligand core orbitals. Examination of this point will be published elsewhere.

The geometries of the Si compounds are taken from the experimental values [16]. For $SiClI_3$ and $SiBrI_3$, the bond angles are assumed to be tetrahedral, and the Si–Cl, Si–Br and Si–I distances are assumed to be equal to the corresponding distances in $SiCl_4$, $SiBr_4$ and SiI_4.

The basis set for the Si atom is the all-electron valence triple-zeta (11s8p)/[5s4p] set of Huzinaga et al. [17] plus first-order higher angular momentum p and d basis functions (p- and d-FOBFs) for the valence orbitals [18]. For the halogen atoms, the core electrons and the SO effect are replaced by the relativistic ECPs [12–14], and the double-zeta sets plus p- and d-FOBFs are used for the halogen atoms: the (4s 4p)/[2s 2p] set [12] plus p- and d-FOBFs for fluorine, the (4s4p)/[2s2p] set [13] plus p- and d-FOBFs for chlorine, the (3s3p)/[2s2p] set [14] plus p- and d-FOBFs for bromine, and the (3s3p)/[2s2p] set [14] plus p- and d-FOBFs for iodine. For hydrogen, the (4s)/[2s] set of Huzinaga–Dunning [19] plus p-FOBFs is used. The gauge origin is placed at the position of the silicon atom. By adding the FOBFs, especially to the atoms neighboring the resonant atom, the basis set dependence and the gauge origin dependence are diminished [18,20]. 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 [18,20]. We applied a finite external magnetic field of 1.0×10^{-3} au.

Table 1
^{29}Si magnetic shielding constants and chemical shifts of silane and silicon tetrahalides calculated with and without the spin–orbit effects (ppm)

Compound	Without spin–orbit				With spin–orbit							δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	SD [a]	FC [b]	total	σ^{tot}	δ^{cal}	
SiH_4	898.96	−414.88	484.08	50.43	898.96	−414.87	−0.05	0.28	0.22	484.31	50.89	99.1
SiF_4	1040.24	−505.74	534.51	0	1040.21	−505.76	−0.06	0.77	0.71	535.16	0	0
$SiCl_4$	1001.25	−611.36	389.89	144.63	1001.25	−612.01	0.06	11.81	11.87	401.11	134.05	89.0
$SiBr_4$	991.77	−630.50	361.27	173.23	991.77	−630.75	0.91	115.65	116.56	477.58	57.58	15.4
$SiClI_3$	983.59	−597.81	385.78	148.73	983.60	−598.89	2.97	304.24	307.21	691.92	−156.76	−136.9
$SiBrI_3$	981.55	−606.04	375.52	158.99	981.56	−607.37	2.54	338.80	341.34	715.53	−180.37	−171.1
SiI_4	977.79	−604.72	373.07	161.44	977.80	−606.37	3.56	446.59	450.16	821.59	−286.43	−237.2

[a] Spin-dipolar. [b] Fermi contact.

3. Results and discussion

Fig. 1 shows the ^{29}Si chemical shifts of silane and silicon tetrahalides, comparing the experimental [1,2] and theoretical values. The open and closed circles indicate the values calculated without and with the SO interaction, respectively. The reference compound of the chemical shifts is SiF_4. Table 1 shows a detailed comparison of the calculated values without and with the SO interaction. The magnetic shielding constants including the SO interaction are divided into the diamagnetic term, paramagnetic term, spin-dipolar term, and Fermi contact term [10].

When the SO effect is included, the calculated chemical shifts move to a higher magnetic field and agree much better with the experimental values. As the halogen becomes heavier, the SO effect in the chemical shift increases and the Fermi contact term becomes dominant in the ^{29}Si chemical shift. For the heaviest silicon tetrahalide, SiI_4, the contribution of the Fermi contact term to the total magnetic shielding constant amounts to more than 50%. Though the next dominant term is the spin-dipolar term, its value is small. It is, therefore, concluded that the most important contribution of the SO effect on the magnetic shielding constant arises from the Fermi contact term.

Fig. 2 shows the ^{29}Si chemical shifts of SiX_4 (X = F, Cl, Br and I). The experimental values show a U-shaped dependence; the substitution from Cl to I causes higher magnetic field shifts (NHD), while the substitution of F by Cl causes a lower field shift (IHD). The origin of the IHD is mainly due to the paramagnetic

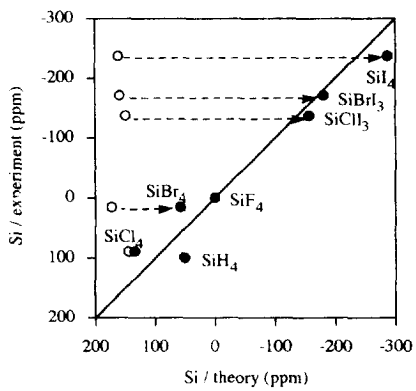

Fig. 1. Correlations between theory and experiment for the ^{29}Si chemical shifts of silane and silicon tetrahalides. The values shown by (○) and (●) are calculated without and with the spin–orbit interaction, respectively.

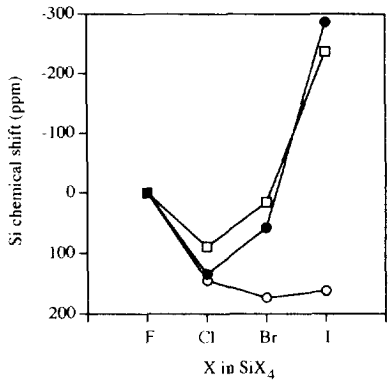

Fig. 2. Comparison between theory and experiment for the ^{29}Si chemical shifts of SiX_4 (X = F, Cl, Br and I). The values shown by (○) and (●) are the theoretical values calculated without and with the spin–orbit interaction, respectively. The experimental value is shown by (□).

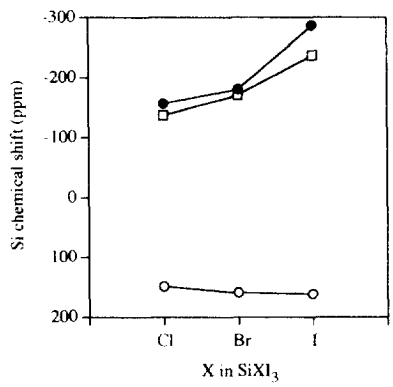

Fig. 3. Comparison between theory and experiment for the ^{29}Si chemical shifts of $SiXI_3$ (X = Cl, Br and I). The values shown by (○) and (●) are the theoretical values calculated without and with the spin–orbit interaction, respectively. The experimental value is shown by (□).

term, as seen in Table 1. This has been pointed out in our previous studies [6,8]. When the SO effect is included, this U-shaped dependence is well reproduced. However, when the SO effect is not included, the NHD for the substitution from Cl to I is not reproduced as seen from the calculated chemical shifts marked by (○).

Fig. 3 shows the ^{29}Si chemical shifts of the $SiXI_3$ series (X = Cl, Br and I). When the SO effect is not included, the NHD for the substitution from Cl to I is not reproduced as seen for the calculated chemical shifts marked by (○). The calculated ones with the SO effect (●), on the other hand, dramatically reproduce the experimental one and show the NHD. Thus, we attribute the main origin of the NHD to the SO effect.

Table 2
MO contributions in the spin-dipolar and Fermi contact terms of the Si compounds (ppm)

Compound	σ^{dia}	σ^{para}	Spin-dipolar				Fermi contact				σ^{tot}	δ^{cal}	δ^{exp}
			core	valence	total	shift	core	valence	total	shift			
SiH_4	898.96	−414.87	0.01	−0.06	−0.05	−0.01	−0.34	0.62	0.28	0.47	484.31	50.89	99.1
SiF_4	1040.21	−505.76	−0.01	−0.05	−0.06	0	0.00	0.77	0.77	0	535.16	0	0
$SiCl_4$	1001.25	−612.01	−0.02	0.08	0.06	−0.12	0.48	11.33	11.81	−11.04	401.11	134.05	89.0
$SiBr_4$	991.77	−630.75	−0.06	0.97	0.91	−0.97	4.89	110.76	115.65	−114.88	477.58	57.58	15.4
$SiClI_3$	983.60	−598.89	0.20	2.97	2.97	−3.03	12.96	291.28	304.24	−303.47	691.92	−156.76	−136.9
$SiBrI_3$	981.56	−607.37	0.16	2.38	2.54	−3.00	14.53	324.27	338.80	−338.03	715.53	−180.37	−171.1
SiI_4	977.80	−606.37	0.04	3.52	3.56	−3.62	19.27	427.32	446.59	−445.82	821.59	−286.43	−237.2

Table 3
AO contributions in the spin-dipolar and Fermi contact terms of the Si compounds (ppm)

Compound	σ^{dia}	σ^{para}	Spin-dipolar					Fermi contact			σ^{tot}	δ^{cal}	δ^{exp}
			Si			ligand	total	Si [a]	ligand	total			
			s	p	d			s					
SiH_4	898.96	−414.87	0.00	−0.05	0.00	0.00	−0.05	0.27	0.00	0.28	484.31	50.89	99.1
SiF_4	1040.21	−505.76	0.00	−0.06	−0.00	0.00	−0.06	0.73	0.04	0.77	535.16	0	0
$SiCl_4$	1001.25	−612.01	0.03	0.08	0.02	−0.06	0.06	12.96	−0.81	11.81	401.11	134.05	89.0
$SiBr_4$	991.77	−630.75	0.26	0.93	0.29	−0.57	0.91	139.35	−23.70	115.65	477.58	57.58	15.4
$SiClI_3$	983.60	−598.89	0.44	3.73	0.19	−1.39	2.97	339.20	−34.96	304.24	691.92	−156.76	−136.9
$SiBrI_3$	981.56	−607.37	0.49	3.38	0.17	−1.49	2.54	380.27	−41.47	338.80	715.53	−180.37	−171.1
SiI_4	977.80	−606.37	0.56	4.38	0.39	−1.77	3.56	493.86	−47.26	446.59	821.59	−286.43	−237.2

[a] The Si p and d AO contributions to the Fermi contact term are identically zero since they have a node at the position of the nucleus.

We finally study the molecular orbital (MO) and atomic orbital (AO) contributions in the Fermi contact and spin-dipolar terms. This analysis is done similarly to our method for the diamagnetic and paramagnetic terms [7]. The MO contributions of the spin-dipolar and Fermi contact terms in the ^{29}Si magnetic shielding constants are shown in Table 2. The valence electron contribution is dominant and the core contribution is quite small. The AO contributions are listed in Table 3. The Si s AO contribution is dominant to the Fermi contact term. The Si p and d orbital contributions to the Fermi contact term are identically zero, since these orbitals have a node at the nucleus. Thus, from Figs. 2 and 3 the SO effect on the ^{29}Si magnetic shielding constants is due to the Si valence s AO contribution to the Fermi contact term.

4. Conclusion

The spin–orbit (SO) effects on the ^{29}Si NMR chemical shifts of silane and silicon tetrahalides, SiX_4 (X = H, F, Cl, Br and I) and $SiXI_3$ (X = Cl and Br) are calculated by the ab initio UHF/FP method proposed previously [10]. The SO effect is included through the ECPs [12–14]. The calculated chemical shifts show good agreement with experiment when the SO effects are included. The calculated shifts without the SO effect cannot reproduce the experimental ones for the cases of the heavier halogen ligands, bromine and iodine. The SO effects are important for describing the ^{29}Si chemical shifts of the molecules containing heavier halogens. The origin of the normal halogen dependence (NHD) is clarified to be the SO effect. The inverse halogen dependence (IHD), on the other hand, is due to the paramagnetic term, as shown previously.

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