
Relativistic Effects and the Halogen Dependencies in the ^{13}C Chemical Shifts of $\text{CH}_{4-n}\text{I}_n$, $\text{CH}_{4-n}\text{Br}_n$, $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$ ($n = 0-4$)

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Received 24 May 2000; accepted 16 November 2000

ABSTRACT: Linear and nonlinear halogen dependencies of the ^{13}C magnetic shielding constants of $\text{CH}_{4-n}\text{I}_n$, $\text{CH}_{4-n}\text{Br}_n$, $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$ were fairly reproduced by the *ab initio* generalized unrestricted Hartree–Fock (GUHF)/finite perturbation (FP) method including spin-orbit (SO) interaction and spin-free relativistic (SFR) terms. As seen from the experimental trends, the calculated ^{13}C chemical shifts in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$ depend linearly on $n = 0-4$, while those in $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$ depend nonlinearly. We found that both the linear and nonlinear dependencies are due to the relativistic effects, and especially due to the Fermi–Contact (FC) term originating from the SO interaction. © 2001 John Wiley & Sons, Inc. *J Comput Chem* 22: 528–536, 2001

Keywords: relativistic effect; spin-orbit interaction; GUHF method; chemical shift; halogen dependence of methyl halides

Introduction

Because carbon is a key element for constructing most molecules, the ^{13}C NMR chemical shifts of various organic and inorganic compounds have been extensively studied, and much experi-

mental data are accumulated in the literatures.¹⁻³ The substituent effects in the ^{13}C chemical shifts are also investigated for a wide range of substituents, and empirical parameters that predict ^{13}C chemical shifts are given experimentally.³ As seen from the experimental trends, the shifts per one halogen ligand for a given nucleus is almost constant from Cl to I, or from Br to I. Such linear additivity fails down when the substitutions occur from H to Br or from H to I. The deviation from the linearity is observed as U-shaped or sagging curves of

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Contract/grant Sponsor: Grant-in-Aid for the Scientific Research from the Ministry of Education, Science, and Culture

the chemical shifts vs. the number of substituents, which are commonly observed for ^{27}Al , ^{29}Si , ^{119}Sn , and ^{31}P chemical shifts of tetrahedral and/or pyramidal molecules.^{4–7}

In a series of our studies, we have studied the mechanisms of the chemical shifts of various elements, and showed that the major mechanism of the NMR chemical shifts is an intrinsic property of the element itself, and therefore, the mechanism is closely related with the position of the nucleus in the periodic table. The results by 1993 were summarized in ref. 8. Because chemical shifts reflect the valence electron state near the atomic core region at the resonant nucleus, relativistic effect is quite important for molecules including heavy elements.^{9–15}

In our recent reports,^{9–15} we examined the halogen dependencies of the ^1H ,^{9,13} ^{13}C ,⁹ ^{27}Al ,¹² ^{29}Si ,¹¹ ^{119}Sn ,¹⁵ ^{115}In ,¹⁰ and $^{69,71}\text{Ga}$ ¹⁰ chemical shifts in various halogenated molecules. The chemical shifts of these nuclei commonly move to high frequency region, especially when a ligand is replaced with iodine. Kidd called this movement of the chemical shifts as normal halogen dependence (NHD).¹⁶ We have clarified that these halogen dependencies are mainly due to the relativistic effect, and especially due to the Fermi–Contact (FC) term originating from the spin-orbit (SO) interaction. Further, we have calculated the ^{199}Hg ¹⁴ and ^{183}W ¹⁴ chemical shifts of HgX_2 ($X = \text{Cl}, \text{Br}, \text{I}, \text{and } \text{CH}_3, \text{SiH}_3, \text{GeH}_3$), WX_6 ($X = \text{F}, \text{Cl}$), and WO_4 including both spin-orbit interaction and spin-free relativistic (SFR) terms, and shown that not only the SO interaction, but also the SFR terms are important to reproduce these heavy nuclei chemical shifts.

In this report, we present calculations of the ^{13}C magnetic shielding constant of the halogenated molecules, $\text{CH}_{4-n}\text{Br}_n$, $\text{CH}_{4-n}\text{I}_n$, $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$ ($n = 0, 1, 2, 3, 4$) considering both the SO and the SFR terms. We utilized the generalized unrestricted Hartree–Fock (GUHF) method,¹⁷ which describes the spin-dependent part more adequately than the SO-UHF method.⁹ The chemical shifts of the present compounds show two different behaviors: the chemical shifts of $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$ depend linearly on the number of iodines, while those of $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$ nonlinearly on the numbers of iodines and bromines, respectively. The origin of these different dependencies are analyzed by decomposing the calculated values into diamagnetic, paramagnetic, spin-dipolar (SD) and FC terms.⁹

Method of Calculations

The ^{13}C chemical shift δ is defined here by

$$\delta = \sigma(\text{CH}_4) - \sigma \quad (1)$$

where $\sigma(\text{CH}_4)$ is the ^{13}C magnetic shielding constant of CH_4 . The magnetic shielding constant σ is averaged over all directions of the molecule.

The unrestricted Hartree–Fock method (UHF) is generalized to describe adequately the spin-dependent part of the wave function. Namely, the generalized (G)UHF wave function is expressed by a single determinant composed of the general spin orbital ψ_k as

$$\psi_k = \phi_k^\alpha \alpha + \phi_k^\beta \beta \quad (2)$$

where the orbital functions ϕ_k^α and ϕ_k^β are complex, because an external magnetic field is involved in our hamiltonian as a finite perturbation (FP). We call this method the SO-GUHF/FP method. The N -electron wave function Φ^{GUHF} is expressed by the Slater determinant of the general spin orbital ψ_k as

$$\Phi^{\text{GUHF}} = ||\psi_1\psi_2\psi_3 \dots \psi_N||. \quad (3)$$

Then, the Fock matrix element $F_{\mu\omega\nu\omega'}$ ($\omega, \omega' = \alpha$ or β) is expressed as follows.

$$F_{\mu\omega\nu\omega'} = (\chi_\mu|h_0|\chi_\nu)\delta_{\omega\omega'} + (\chi_\mu|h^{\text{SO}}|\chi_\nu\omega') + \sum_{\rho\lambda} \left\{ \sum_{\tau} (\mu\nu|\sigma\rho)D_{\rho\lambda}^{\tau\tau}\delta_{\omega\omega'} - (\mu\lambda|\rho\nu)D_{\rho\lambda}^{\omega'\omega} \right\} \quad (4)$$

where,

$$(\mu\nu|\rho\sigma) = \int \int \chi_\mu^*(1)\chi_\nu(1)\chi_\rho^*(2)\chi_\sigma(2)(r_{12})^{-1} d\nu_1 d\nu_2, \quad (5)$$

and $\{\chi_\mu\}$ is a set of basis function, h_0 the spin-independent one-electron operator, h^{SO} the spin-orbit interaction term. τ and τ' run over α and β . $D_{\mu\nu}^{\omega\omega'}$ is the GUHF density matrix defined as

$$D_{\mu\nu}^{\omega\omega'} = \sum_j c_{\mu j}^{\omega\omega'} c_{\nu j}^{\omega\omega'} \quad (6)$$

where $c_{\mu j}^{\omega\omega'}$ the GUHF SCF coefficient. The two-electron spin-orbit integral was neglected in the present article, because it does not so significantly affect the magnetic shielding constant.^{17,33}

We note here about the SO-UHF method,⁹ which we used previously. In the SO-UHF method, the SO interaction is treated in the framework of the UHF theory. This method is based on the fact that the UHF wave function for closed-shell molecules includes triplet states of $m_s = 0$ in the first-order approximation, and they vary in response to the applied external magnetic field. This response generates magnetic shielding constants. This method is an approximate one in the following sense: the

triplet states of $m_s = \pm 1$ cannot be treated simultaneously. Due to this reason, especially, the SO terms (Fermi contact term and the spin-dipolar term) calculated by the SO-UHF method may be modified by the present SO-GUHF method. Because, in the present paper, the effects of the SO term are examined in details, the GUHF method is preferable.

In the present calculations, the SO interaction and the SFR terms for the halogen atoms are evaluated using the relativistic effective core potentials (RECPs) and the SO potentials,^{18–20} respectively. For simplicity, we used only one-center SO integrals on the halogen atoms: this method has been applied successfully to the calculation of the Al, Si, and Sn magnetic shielding constants of various halogenated compounds.^{11, 12, 15}

The calculated magnetic shielding constant is analyzed into the diamagnetic term, paramagnetic term, SD term, and FC term.⁹ The diamagnetic term is the zeroth order term in the perturbation theory, and is determined mainly by the structure of the molecule as reported by Flygare and Goodisman.²¹ The paramagnetic, SD, and FC terms are the first-order terms in the perturbation theory. The latter two terms are due to the SO interaction. The FC term arises from the contact interaction between nuclear and electronic spins, and therefore, the s orbitals of the resonant atom give a dominant contribution. The SD term arises from the interaction between the nuclear and the electronic spin dipoles. The origin of this term is the anisotropy of electronic spin density, and therefore, mainly the p and d orbitals of the resonant atom contribute.

The geometries of $\text{CH}_{4-n}\text{Br}_n$ ($n = 0, 1, 2, 3, 4$), CH_3I and Cl_4 are taken from the experimental

values.²² For CH_2I_2 , CHI_3 , $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$ ($n = 1, 2, 3$), we could not find out the experimental values, so that the bond angles are assumed to be tetrahedral and the C—H, C—Cl, C—Br, and C—I distances are assumed to be equal to those in CH_4 , CCl_4 , CBr_4 , and CI_4 , respectively.

The basis set for carbon is the all electron valence triple-zeta (9s5p)/[4s3p] set of Huzinaga et al.²³ plus first-order higher angular momentum p and d basis function (p- and d-FOBFs)^{24, 25} for the valence orbitals. For H the (4s)/[2s] set of Huzinaga-Dunning²⁶ plus p-FOBFs is used. For halogen atoms, the core electrons and the SO operator are replaced by the relativistic ECPs and the double zeta sets plus p- and d-FOBFs are used; (4s4p)/[2s2p] set¹⁸ plus p- and d-FOBFs for chlorine, (3s3p)/[2s2p] set¹⁹ plus p- and d-FOBFs for bromine, and (3s3p)/[2s2p] set²⁰ plus p- and d-FOBFs for iodine. The gauge origin is commonly located on the carbon atom. By adding the FOBFs, especially to the atoms neighboring the resonant atom, the basis set dependence and the gauge origin dependence are expected to be diminished.^{24, 25} We note here that 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.^{24, 25}

Results and Discussion

COMPARISON BETWEEN THEORY AND EXPERIMENT

Figure 1a and b shows the comparisons between theory and experiment for the ^{13}C chemical shifts

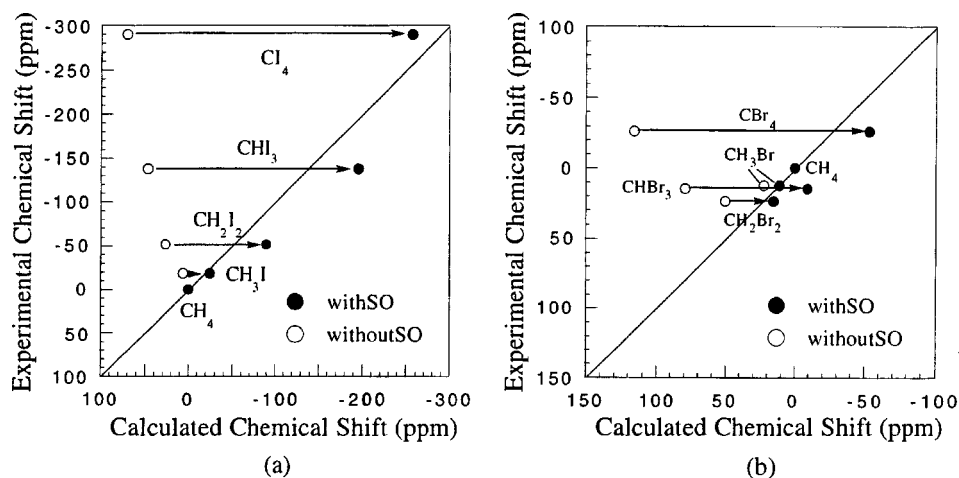


FIGURE 1. Correlation between the calculated and experimental ^{13}C chemical shifts of (a) $\text{CH}_{4-n}\text{I}_n$, (b) $\text{CH}_{4-n}\text{Br}_n$ ($n = 0, 1, 2, 3, 4$).

TABLE I.
¹³C Magnetic Shielding Constants Calculated with and without the SO Interaction and the Analysis into the Diamagnetic, Paramagnetic, and SO Terms for CH_{4-n}I_n, CH_{4-n}Br_n, CCl_{4-n}I_n, and CBr_{4-n}I_n (n = 0, 1, 2, 3, 4) (ppm).

Molecule	Without SO						With SO				σ _{Total}	δ _{calc.}	δ _{exptl.} ^a
	σ _{dia}	σ _{para}	σ _{Total}	δ _{calc.}	σ _{SO}		Total						
					SD	FC							
CH ₄	296.36	-99.32	197.04	0.00	296.36	-0.02	-0.03	-0.05	196.99	0.00	0.0		
CH ₃ I	317.23	-126.75	190.48	6.56	316.82	-7.60	43.82	36.22	221.65	-24.66	-18.4		
CH ₂ I ₂	337.52	-166.80	170.72	26.32	337.60	-17.17	132.80	115.63	286.80	-89.81	-51.7		
CHI ₃	358.49	-208.01	150.48	46.56	358.62	-26.48	264.12	237.64	392.47	-195.48	-137.6		
CI ₄	379.63	-252.82	126.81	70.23	379.80	-29.79	356.88	327.09	454.42	-257.43	-290.2		
CH ₄	296.36	-99.32	197.04	0.00	296.36	-0.02	-0.03	-0.05	196.99	0.00	0.0		
CH ₃ Br	320.38	-146.04	174.35	22.69	320.38	-1.37	12.89	11.52	185.77	11.22	12.3		
CH ₂ Br ₂	344.47	-198.05	146.42	50.62	344.47	-2.06	36.96	34.90	181.24	15.75	23.7		
CHBr ₃	368.96	-251.23	117.73	79.31	368.97	-2.27	90.45	88.18	206.05	-9.06	14.4		
CBr ₄	392.44	-311.49	80.94	116.10	392.46	-2.86	171.88	169.02	250.14	-53.15	-26.2		
CCl ₄	405.24	-332.07	73.18	123.86	405.24	0.04	18.70	18.74	91.91	105.08	98.8		
CCl ₃ I	398.89	-317.85	81.04	116.00	398.92	-12.09	126.52	114.43	197.36	-0.37	—		
CCl ₂ I ₂	392.50	-300.52	91.98	105.06	392.58	-20.92	206.64	185.72	278.44	-81.45	—		
CClI ₃	386.08	-279.07	107.00	90.04	386.20	-27.64	285.53	257.89	365.41	-168.42	—		
CI ₄	379.63	-252.82	126.81	70.23	379.80	-29.79	356.88	327.09	454.42	-257.43	-290.2		
CBr ₄	392.44	-311.49	80.94	116.10	392.46	-2.86	171.88	169.02	250.14	-53.15	-26.2		
CBr ₃ I	389.25	-299.99	89.26	107.78	389.31	-11.45	230.88	219.43	309.20	-112.21	—		
CBr ₂ I ₂	386.06	-286.50	99.57	97.47	386.16	-18.64	279.74	261.10	361.17	-164.18	—		
CBrI ₃	382.85	-270.81	112.04	85.00	382.98	-24.78	321.34	296.56	409.08	-212.09	—		
CI ₄	379.63	-252.82	126.81	70.23	379.80	-29.79	356.88	327.09	454.42	-257.43	-290.2		

^a Neilson, G. C.; Levy, G. L. Carbon-13 Nuclear Magnetic Resonance for Organic Chemists; Wiley-Interscience: New York, 1972.

of $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$, respectively. The open and filled circles indicate the values without and with the SO interaction, respectively. The SFR term is included through the relativistic ECP in both cases. The experimental values are taken from ref. 1. The calculated chemical shifts including the SO interaction fairly reproduce the experimental values, while those calculated without the SO interaction do not explain even qualitatively the experimental trend. This fact is already known from the studies of our⁹⁻¹⁵ and other²⁷⁻³¹ laboratories.

The normal halogen dependence (NHD) of chemical shifts, as shown in the order of $\text{Cl} < \text{Br} < \text{I}$, also reproduced by the present result including the SO interaction, while it is not so even qualitatively when the SO term is not included. Thus, the present result confirms the previous results⁹⁻¹⁵ that the origin of the NHD is the SO effect.

The calculated and experimental ^{13}C chemical shifts of $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$ ($n = 0-4$) show non-linear dependence on the number of halogens. For example, the chemical shift from CH_4 to CH_3I is relatively small in comparison with the shift from CHI_3 to CI_4 . On the contrary, as shown below, the calculated ^{13}C chemical shift in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$ depend quite linearly on the number of iodines, though the experimental data does not exist. These linear and nonlinear dependences are discussed in the following sections.

DECOMPOSITION ANALYSIS

Table I shows the detailed analyses of the magnetic shielding constants calculated without and with the SO interaction. The calculated value is analyzed into the diamagnetic, paramagnetic, SD, and FC terms.⁹ Figure 2a-d is prepared to visualize the trends Table I.

The diamagnetic term σ_{dia} linearly depends on the number of ligands. The σ_{dia} increases constantly by 20 and 24 ppm with the substitutions of $\text{H} \rightarrow \text{I}$ and $\text{H} \rightarrow \text{Br}$, respectively, while it decreases by -6 and -3.2 ppm with the substitutions of $\text{Cl} \rightarrow \text{I}$ and $\text{Br} \rightarrow \text{I}$. This additivity in the diamagnetic term has been reported by Flygare and Goodisman.²¹ The paramagnetic term σ_{para} increases in $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$, and decrease in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$, as predicted by the electronegativities of the ligands. Both σ_{dia} and σ_{para} of the present molecules are not affected by the SO effect.

The SO effect causes two new terms, the SD and FC terms.⁹ When the ligands are light atoms as in CH_4 , both the SD and FC terms are quite small, but on increasing the number n of the ligands I

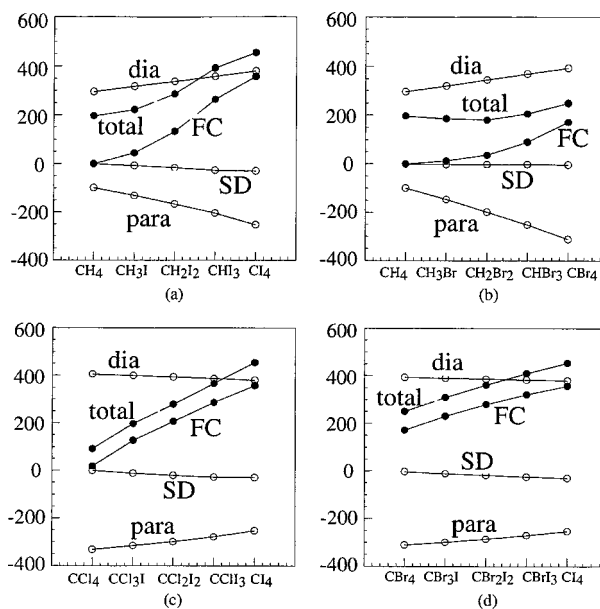


FIGURE 2. The calculated magnetic shielding constants divided into the diamagnetic, paramagnetic, spin-dipolar (SD), Fermi contact (FC) terms of (a) $\text{CH}_{4-n}\text{I}_n$, (b) $\text{CH}_{4-n}\text{Br}_n$, (c) $\text{CCl}_{4-n}\text{I}_n$, and (d) $\text{CBr}_{4-n}\text{I}_n$.

and Br, the SO term becomes large. These terms dominantly contribute to the ^{13}C chemical shifts in all the present molecules.

Tables II and III show the analyses of the four component terms of $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$ into the molecular orbital (MO) and atomic orbital (AO) contributions,³² respectively. The MO analysis clearly shows that valence electron contribution is dominant, and core electron contribution is negligible. The AO analysis shows that both resonant carbon AO and ligand AO contributions are important for the ^{13}C magnetic shielding constants.

In the diamagnetic term, the MO analysis shows that the valence electron contribution to the chemical shift is dominant, and the AO analysis shows that the carbon AO contribution is essentially constant and the ligand contribution increases with $\text{H} \rightarrow \text{I}$ and $\text{H} \rightarrow \text{Br}$, and decreases with $\text{Cl} \rightarrow \text{I}$ and $\text{Br} \rightarrow \text{I}$: the ligand contribution is dominant in the diamagnetic term of the chemical shifts. This again clearly support the Flygare and Goodisman's interpretation.²¹ In the paramagnetic term, the AO analysis shows that both carbon p and ligand AO contributions to the chemical shifts are dominant. The paramagnetic terms in the present molecules increase in absolute value as the ligand electronegativity increases. This is the so-called *inductive effect*, i.e., the resonant atom that bounds directly with

TABLE II. The Core and Valence MO Contributions to the Calculated ^{13}C Magnetic Shielding Constant Including the SO Effect for $\text{CH}_{4-n}\text{I}_n$, $\text{CH}_{4-n}\text{Br}_n$, $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$ ($n = 0, 1, 2, 3, 4$) (ppm).

Molecule	σ_{dia}			σ_{para}			$\sigma_{\text{SO(SD)}}$			$\sigma_{\text{SO(FC)}}$		
	Core	Valence	Total	Core	Valence	Total	Core	Valence	Total	Core	Valence	Total
CH_4	200.8	95.6	296.4	0.0	-99.3	-99.3	0.0	0.0	0.0	0.0	0.0	0.0
CH_3I	200.8	116.4	317.3	0.0	-128.3	-128.3	-0.2	-6.4	-6.6	-6.3	45.0	38.7
CH_2I_2	200.9	136.7	337.6	0.0	-166.4	-166.4	-0.6	-16.6	-17.2	-11.5	144.3	132.8
CHI_3	200.9	157.7	358.6	0.0	-203.8	-203.8	-0.9	-25.6	-26.5	-13.6	277.7	264.1
CI_4	201.0	178.9	379.8	0.0	-252.5	-252.5	-1.0	-28.8	-29.8	5.5	351.4	356.9
CH_4	200.8	95.6	296.4	0.0	-99.3	-99.3	0.0	0.0	0.0	0.0	0.0	0.0
CH_3Br	200.8	119.6	320.4	0.0	-146.1	-146.1	-0.1	-1.3	-1.4	-1.0	13.9	12.9
CH_2Br_2	200.9	143.6	344.5	0.0	-198.1	-198.1	-0.1	-2.0	-2.1	-1.0	37.9	37.0
CHBr_3	200.9	168.1	369.0	0.0	-251.1	-251.1	-0.1	-2.2	-2.3	1.6	88.9	90.5
CBr_4	201.0	191.5	392.5	0.0	-311.3	-311.3	-0.1	-2.8	-2.9	6.8	165.1	171.9
CCl_4	200.9	204.3	405.2	0.0	-332.1	-332.1	0.0	0.0	0.0	0.9	17.8	18.7
CCl_3I	200.9	198.0	398.9	0.0	-316.0	-316.0	-0.4	-11.7	-12.1	-2.1	128.6	126.5
CCl_2I_2	200.9	191.7	392.6	0.0	-299.9	-299.9	-0.7	-20.2	-20.9	-0.7	207.3	206.6
CClI_3	200.9	185.3	386.2	0.0	-278.7	-278.7	-0.9	-26.7	-27.6	1.7	283.8	285.5
CI_4	201.0	178.9	379.8	0.0	-252.5	-252.5	-1.0	-28.8	-29.8	5.5	351.4	356.9
CBr_4	201.0	191.5	392.5	0.0	-311.3	-311.3	-0.1	-2.8	-2.9	6.8	165.1	171.9
CBr_3I	201.0	188.4	389.3	0.0	-299.5	-299.5	-0.4	-11.1	-11.5	6.4	224.5	230.9
CBr_2I_2	201.0	185.2	386.2	0.0	-286.1	-286.1	-0.6	-18.0	-18.6	6.0	273.7	279.7
CBrI_3	201.0	182.0	383.0	0.0	-270.5	-270.5	-0.9	-23.9	-24.8	5.7	315.6	321.3
CI_4	201.0	178.9	379.8	0.0	-252.5	-252.5	-1.0	-28.8	-29.8	5.5	351.4	356.9

TABLE III.
AO Contribution to the Calculated ^{13}C Magnetic Shielding Constant Including the SO Effect for $\text{CH}_{4-n}\text{I}_n$, $\text{CH}_{4-n}\text{Br}_n$, $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$
($n = 0, 1, 2, 3, 4$) (ppm).

Molecule	σ^{dia}						σ^{para}						$\sigma^{\text{SO(SD)}}$						$\sigma^{\text{SO(FC)}}$	
	Carbon			Ligand			Carbon			Ligand			Carbon			Ligand			Carbon	
	s	p	d	s	p	d	s	p	d	s	p	d	s	p	d	s	p	s		
CH_4	213.1	40.1	4.7	38.5	-71.8	-3.8	-23.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
CH_3I	213.4	41.6	3.2	58.6	-99.5	-4.8	-27.1	-0.1	-16.4	1.8	7.1	7.1	46.3	-2.5	54.2	78.6	113.5	157.7	157.7	
CH_2I_2	214.6	41.6	2.2	79.2	-121.2	-6.8	-38.4	4.0	-35.3	2.8	11.3	11.3	78.6	54.2	113.5	157.7	157.7	157.7	157.7	
CHI_3	216.9	39.1	3.6	99.1	-128.4	-9.5	-65.9	7.6	-63.0	4.2	24.7	24.7	150.6	113.5	157.7	157.7	157.7	157.7	157.7	
CI_4	220.1	42.0	3.9	113.7	-176.6	-7.1	-68.7	12.0	-36.8	4.1	-9.1	-9.1	199.2	157.7	157.7	157.7	157.7	157.7	157.7	
CH_4	213.1	40.1	4.7	38.5	-71.8	-3.8	-23.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
CH_3Br	212.3	40.6	5.7	61.8	-97.2	-6.4	-42.6	0.2	-1.6	-0.1	0.1	0.1	12.0	0.9	11.7	48.6	179.0	216.5	216.5	
CH_2Br_2	212.5	41.0	7.0	84.0	-129.8	-8.1	-60.3	-0.7	-2.5	0.3	0.9	0.9	48.6	-11.7	179.0	216.5	216.5	216.5	216.5	
CHBr_3	217.7	40.4	7.8	103.1	-162.4	-8.8	-79.9	9.7	-2.0	2.5	-12.5	-12.5	88.6	179.0	216.5	216.5	216.5	216.5	216.5	
CBr_4	220.9	38.9	8.3	124.4	-202.4	-8.6	-100.4	10.3	-3.0	2.2	-12.3	-12.3	44.6	216.5	216.5	216.5	216.5	216.5	216.5	
CCl_4	213.3	32.5	7.0	152.5	-193.3	-11.7	-127.1	0.6	0.5	-0.1	-0.9	-0.9	10.0	8.7	67.5	109.1	142.8	157.7	157.7	
CCl_3I	215.1	33.1	3.3	147.4	-198.1	-13.4	-104.5	1.5	-23.4	2.8	7.0	7.0	59.0	67.5	109.1	142.8	157.7	157.7	157.7	
CCl_2I_2	216.8	36.3	4.9	134.7	-195.3	-10.3	-94.3	5.2	-29.6	4.2	-0.6	-0.6	97.5	109.1	142.8	157.7	157.7	157.7	157.7	
CClI_3	218.6	38.5	4.8	124.3	-187.0	-8.7	-83.0	9.0	-35.2	4.1	-5.5	-5.5	142.8	142.8	157.7	157.7	157.7	157.7	157.7	
CI_4	220.1	42.0	3.9	113.7	-176.6	-7.1	-68.7	12.0	-36.8	4.1	-9.1	-9.1	199.2	157.7	157.7	157.7	157.7	157.7	157.7	
CBr_4	220.9	38.9	8.3	124.4	-202.4	-8.6	-100.4	10.3	-3.0	2.2	-12.3	-12.3	44.6	216.5	216.5	216.5	216.5	216.5	216.5	
CBr_3I	220.4	39.8	6.5	122.7	-199.9	-8.7	-90.9	11.2	-13.6	3.1	-12.2	-12.2	23.3	207.6	207.6	207.6	207.6	207.6	207.6	
CBr_2I_2	220.2	40.5	5.4	120.0	-195.0	-8.4	-82.7	11.5	-22.6	3.6	-11.3	-11.3	85.8	194.0	194.0	194.0	194.0	194.0	194.0	
CBrI_3	220.1	41.3	4.6	117.0	-187.3	-7.8	-75.4	11.7	-30.3	3.9	-10.1	-10.1	144.6	176.7	176.7	176.7	176.7	176.7	176.7	
CI_4	220.1	42.0	3.9	113.7	-176.6	-7.1	-68.7	12.0	-36.8	4.1	-9.1	-9.1	199.2	157.7	157.7	157.7	157.7	157.7	157.7	

electronegative atom shows *low-field* shift. We note that this low-field shift is the trend of the inverse halogen dependence. The light halogens like F and Cl show the inverse halogen dependence (IHD) because this trend is dominant,⁸ while the heavier halogens show the NHD because the SO effect is dominant.

The SD and FC terms are due to the relativistic effect. In the SD term, both the carbon p and the ligand contributions are dominant, though the SD term itself is relatively small. The FC term increases significantly as the ligand becomes heavier. It is due to the valence electron contribution, and originates from the core 1s AO of the resonant atom. The valence orbital generally has the core 1s AO component, and this 1s AO component of the valence orbitals contributes to the nuclear magnetic shielding constant.^{8,32} The ligand AO's also contribute to the FC and SD terms: the ligand valence AOs extend to the carbon nuclear region and give large contributions to the FC and SD terms. This effect is additive to the carbon s AO contribution in the FC terms of $\text{CH}_{4-n}\text{I}_n$, $\text{CCl}_{4-n}\text{I}_n$, and $\text{CBr}_{4-n}\text{I}_n$, but cancelling in $\text{CH}_{4-n}\text{Br}_n$.

LINEAR AND NONLINEAR DEPENDENCIES

As seen clearly from Figure 2, the halogen dependencies of the shifts are fairly linear in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CCl}_{4-n}\text{Br}_n$, while they are nonlinear in $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$. Namely, the dependence from H to I in $\text{CH}_{4-n}\text{I}_n$ sagged, and that from H to Br in $\text{CH}_{4-n}\text{Br}_n$ is slightly U-shaped. The calculated nonlinear dependencies are supported by the experiments, while the linear ones are not due to the absence of the experimental data. However, the dependencies from Cl to I and from Cl to Br are reported to be commonly linear for other main-group elements,^{7,16} which supports the present calculated dependence. We analyze here the origin of this nonlinear dependence.

The analysis given in Figure 2 shows that the paramagnetic term decreases linearly with the number of Br or I in $\text{CH}_{4-n}\text{Br}_n$ and $\text{CH}_{4-n}\text{I}_n$, while it increases linearly with the number of I in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$. The diamagnetic term increases linearly in $\text{CH}_{4-n}\text{Br}_n$ and $\text{CH}_{4-n}\text{I}_n$, while it decreases slightly in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$. The SD term also depends linearly. On the other hand, in $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$, the FC term depends nonlinearly on the number of ligands, while in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$, it depends linearly. Thus, it is clearly shown from Figure 2 that the origin of the nonlinear dependence

in $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$ is the FC term due to the relativistic SO effect.

The FC term is closely related with the spin population near the carbon nucleus and, thus, we interpret the origin of this nonlinearity of the FC term as follows. In the T_d symmetry, like in CH_4 or Cl_4 , the maximum point of the spin density exist identically on the resonant carbon nucleus, while in $\text{CH}_{4-n}\text{I}_n$ and $\text{CH}_{4-n}\text{Br}_n$ ($n = 1, 2, 3$), this spin-density cloud is pulled in the direction of the electronegative halogen atom, and the maximum point of the spin density moves out slightly from the carbon nucleus. On the other hand, in $\text{CCl}_{4-n}\text{I}_n$ and $\text{CBr}_{4-n}\text{I}_n$, this anisotropic effect almost cancels because of the similarity of the two different halogen ligands, and therefore, the maximum point of the spin density exists almost on the carbon nucleus. Thus, we explain the nonlinear dependence of the FC term as being due to the shift of the spin-density cloud out from the resonant nucleus. As an evidence of the above interpretation, we note that the total density on the carbon of $\text{CH}_{4-n}\text{I}_n$ increases nonlinearly with n , being 7.307 for CH_4 , 7.312 for CH_3I , 7.314 for CH_2I_2 , 7.319 for CHI_3 , and 7.334 for Cl_4 , and the change from CHI_3 to Cl_4 is the largest.

Summary

The ^{13}C chemical shifts of $\text{CH}_{4-n}\text{I}_n$, $\text{CH}_{4-n}\text{Br}_n$, $\text{CCl}_{4-n}\text{I}_n$, $\text{CBr}_{4-n}\text{I}_n$ ($n = 0, 1, 2, 3, 4$) are calculated by the *ab initio* GUHF/FP method including the spin-orbit (SO) interaction and the SFR terms. The results are summarized as follows: (1) the calculated chemical shifts show good agreement with experiment when the SO effect is included. The values calculated without the SO interaction do not reproduce the experimental values when the halogen ligand is heavy. The SO effects are quite important for describing the ^{13}C chemical shifts for the molecules containing heavier halogens. (2) The MO analysis shows that the valence electrons dominantly contribute to the chemical shifts. The AO analysis shows that the diamagnetic term depends on the number of the halogen ligands, and the paramagnetic term dominantly originates from the carbon 2p orbitals. The FC and SD terms originate from the carbon 1s and 2p spin densities, respectively. The contributions from the tails of the valence AOs of the ligands are also important for those terms. (3) The origin of higher field shifts (i.e., NHD) of the ^{13}C chemical shift of the series of the compound studied here is mainly attributed to the relativistic SO effects caused by the heavy halogen ligands.

The dominant contribution in the SO effect is the FC term. (4) The linear and nonlinear dependencies of the chemical shifts observed in this study reflect the similar trends in the FC term. It is explained to be due to the asymmetry of the spin-density distribution at the resonant nucleus caused by the electronegativity difference of the halogen ligands.

References

- Nelson, G. C.; Levy, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience: New York, 1972.
- (a) Breitmaier, E.; Voelter, W. *¹³C NMR Spectroscopy: Methods and Applications, Monographs in Modern Chemistry*; Verlag Chemie: Weinheim, Germany, 1974, vol. 15; (b) Johnson, J. F.; Jankowski, W. C. *¹³C NMR Spectra: A Collection of Assigned Coded and Indexed Spectra*; Wiley-Interscience: New York, 1972.
- (a) Nelson, G. C.; Stothers, J. B. *¹³C NMR Spectroscopy*; Academic Press: New York, 1972; (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *¹³C NMR Spectroscopy*; Wiley: New York, 1980.
- Letcher, J. H.; Van Wazer, J. R. *Top Phosphorus Chem* 1967, 5, 75.
- Schraml, J.; Bellama, J. M. *Determination of Organic Structures by Physical Methods*; Nachod, F. C.; Zuckerman, J. J.; Randall, E. W., Eds.; Academic Press: New York, 1976, p. 203, vol. 6.
- Grimmer, A. R. *Z Anorg Allg Chem* 1973, 400, 105.
- Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Manson, J., Ed.; Plenum Press: New York, 1987.
- Nakatsuji, H. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossell, J. A., Ed.; Kluwer: Dordrecht, 1993 p. 263.
- Nakatsuji, H.; Takashima, H.; Hada, M. *Chem Phys Lett* 1995, 223, 95.
- Takashima, H.; Hada, M.; Nakatsuji, H. *Chem Phys Lett* 1995, 235, 13.
- Nakatsuji, H.; Nakajima, T.; Hada, M.; Takashima, H.; Tanaka, S. *Chem Phys Lett* 1995, 247, 418.
- Nakatsuji, H.; Hada, M.; Tejima, T.; Nakajima, T.; Sugimoto, M. *Chem Phys Lett* 1996, 249, 284.
- Ballard, C. C.; Hada, M.; Kaneko, H.; Nakatsuji, H. *Chem Phys Lett* 1996, 254, 170.
- (a) Nakatsuji, H.; Hada, M.; Kaneko, H.; Ballard, C. C. *Chem Phys Lett* 1996, 255, 195; (b) Hada, M.; Kaneko, H.; Nakatsuji, H. *Chem Phys Lett* 1996, 261, 7; (c) Wan, J.; Fukuda, R.; Hada, M.; Nakatsuji, H. *J Phys Chem A*, to appear.
- Kaneko, H.; Hada, M.; Nakajima, T.; Nakatsuji, H. *Chem Phys Lett* 1996, 261, 1.
- Kidd, R. G. *Annu Rep NMR Spectrosc* 1980, 10A, 1.
- Fukuda, R.; Hada, M.; Nakatsuji, H., to be submitted.
- Pasios, L. F.; Christiansen, P. A. *J Chem Phys* 1985, 82, 2664.
- Hurley, M. M.; Pacious, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J Chem Phys* 1986, 84, 6840.
- LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J Chem Phys* 1987, 87, 2812.
- Flygare, W. H.; Goodisman, J. *J Chem Phys* 1968, 49, 3122.
- (a) Callomon, J. H.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Lafferty, W. J. In *Landort-Bornstein New Series Supplement II/15*; Madelung, O.; Hellwege, K.-H.; Hellwege, A. M., Eds.; Springer: Berlin, 1987; (b) Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A.; Pote, C. S. In *Landort-Bornstein New Series Supplement II/7*; Hellwege, K.-H.; Hellwege, A. M., Eds.; Springer: Berlin, 1987; (c) Cruickshank, D. W. J.; Viervoll, H. *Acta Chem Scand* 1949, 3, 560; (d) Akishin, P. A.; Vikov, L. V.; Takaevskii, V. M. *Vestn Mask Univ Ser Mater Merkhan Astron Fiz i Khim* 1957, 12, 143.
- Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. In *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.
- Sugimoto, M.; Nakatsuji, H. *J Chem Phys* 1995, 102, 285.
- Higashioji, T.; Hada, M.; Sugimoto, M.; Nakatsuji, H. *Chem Phys* 1996, 203, 159.
- Dunning, T. H. *J Chem Phys* 1970, 53, 7, 2823.
- Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem Phys Lett* 1996, 261, 335.
- Kaupp, M.; Malkina, O. L.; Malkin, V. G. *Chem Phys Lett* 1997, 265, 55.
- Schreckenbach, G.; Ziegler, T. *Int J Quantum Chem* 1996, 60, 753.
- Schreckenbach, G.; Ziegler, T. *Int J Quantum Chem* 1996, 61, 899.
- Wolf, S. K.; Ziegler, T. *J Chem Phys* 1998, 109, 895.
- Nakatsuji, H.; Kanda, K.; Endo, K.; Yonezawa, T. *J Am Chem Soc* 1984, 106, 4653.
- Malkina, O. L.; Schimmelpfennig, B.; Kaupp, M.; Hess, B. A.; Chandra, P.; Wahlgren, U.; Malkin, V. G. *Chem Phys Lett* 1998, 296, 93.