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# Spin–orbit effect on the magnetic shielding constant using the ab initio UHF method: gallium and indium tetrahalides

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## Abstract

The spin–orbit effect on the Ga and In NMR chemical shifts of the gallium and indium tetrahalides compounds,  $\text{MX}_4^-$  ( $\text{M} = \text{Ga}$  and  $\text{In}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ), are studied using an ab initio UHF wavefunction and the finite perturbation method as has been proposed previously. The spin–orbit effect of the heavier halogen ligand is large and works to move the chemical shift to higher field, and as a result the calculated shifts show better agreement with experiment. Though the Ga and In chemical shifts are due to the diamagnetic mechanism, the spin–orbit effect appears through the paramagnetic interaction and the dominant term is the metal valence s AO contribution to the Fermi contact term.

## 1. Introduction

We have theoretically investigated the mechanism for the metal NMR chemical shifts of a wide class of metal complexes and clarified that the mechanism is closely related to the electronic configuration of the free atom and therefore with the position of the metal atom in the periodic table [1]. Among these we found that the Ga and In chemical shifts are unique and interestingly due to the diamagnetic mechanism [2], while the other metal chemical shifts are dominated by the paramagnetic term. The diamagnetic term is described quite accurately by ab initio SCF calculation or even by the Flygare–Goodisman equation [3]: it depends only on the structural factor and does not reflect the details of the electronic structure.

For the gallium and indium tetrahalides with the *heavier* halogen ligands, however, the calculated results did not reproduce the experimental chemical shifts well; the calculated values deviated to lower field in comparison with the experimental ones. We have pointed out in our previous paper [2] that the most probable reason, especially in the case of the In compounds,  $\text{InX}_{4-n}\text{I}_n^-$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ), is the spin–orbit effect. Morishima, Endo and Yonezawa [4] have investigated the chemical shifts in hydrogen halides, using the semi-empirical MO method combined with third-order perturbation theory, and found that the abnormal higher field shift of the proton chemical shift in hydrogen halides can be explained by the spin–orbit effect.

In the previous paper of this series [5] we formulated a calculational method for magnetic shielding constants under the influence of the spin–orbit effect using the UHF wavefunction and the finite perturbation method. It was applied to the  $^1\text{H}$  and  $^{13}\text{C}$

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chemical shifts in hydrogen halides and methyl halides, respectively, and its effective usefulness was shown. In this Letter, we study by this method the spin-orbit effect on the Ga and In NMR chemical shifts of tetrahalide compounds, and try to clarify the reason for the discrepancies found previously for heavier halogen ligands [2]. The compounds studied here are  $\text{MX}_4^-$  ( $M = \text{Ga}$  and  $\text{In}$ ,  $X = \text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ).

## 2. Method of calculation

We calculate the Ga and In magnetic shielding constants  $\sigma$  by the UHF/finite perturbation method including the spin-orbit interaction. The details of the method have been reported in the previous paper of this series [5].

The geometries of the Ga and In compounds are taken from the experimental values as used in Ref. [2]. The gauge origin is located on the metal atom, though the magnetic shielding constants of all the compounds studied here are invariant to the choice of gauge because of the  $T_d$  symmetry [6,7].

The basis sets used are taken from the book of Huzinaga et al. [8]. The triple-zeta sets plus double polarization functions are used for the metals: for gallium the (13s10p4d)/[6s5p1d] set plus polarization d functions with exponents of 0.091 and 0.336, and for indium the (16s13p7d)/[7s6p2d] set plus polarization d functions with exponents of 0.069 and 0.231. The double-zeta sets plus first-order higher angular momentum d basis functions (d-FOBFs) [6] are used for the halogen atoms; (10s7p)/[4s3p] plus d-FOBFs for chlorine, (13s10p4d)/[5s4p1d] plus d-FOBFs for bromine, and (16s13p7d)/[6s5p2d] plus

d-FOBFs for iodine. By adding the FOBF, especially to the atoms neighbouring the center metal, we can decrease the basis set dependence and the gauge origin dependence [6,7]. The basis sets used in this study are better than those used in Ref. [3]: we have added the d-FOBFs to the basis set better than the set D which was the largest in Ref. [3]. The d-FOBFs are added to improve the basis set dependence [6,7].

## 3. Results and discussion

Fig. 1 shows the Ga and In chemical shifts in (a) the gallium tetrahalides and (b) the indium tetrahalides, comparing the experimental and theoretical values. The values shown by ( $\square$ ) are due only to the diamagnetic term calculated by the Flygare–Goodisman equation. The values shown by ( $\circ$ ) and ( $\bullet$ ) are due to the diamagnetic and paramagnetic terms without and with the spin-orbit (LS) interaction, respectively. The experimental chemical shifts are taken from Refs. [9,10]. The reference compounds of the chemical shifts are  $\text{GaCl}_4^-$  and  $\text{InCl}_4^-$ . Table 1 shows a detailed comparison between the calculated values without and with the LS interaction. The magnetic shielding constant with the LS interaction is divided into the diamagnetic term, paramagnetic term, spin-dipolar term, and Fermi contact term [5].

We find in Fig. 1 that the calculated values without the LS interaction ( $\circ$ ) is nearly parallel to the ones by the Flygare–Goodisman equation ( $\square$ ), indicating that the origin of the Ga and In chemical shifts is the diamagnetic mechanism [2]. Note that the paramagnetic contribution works to deviate fur-

Table 1  
Ga and In chemical shifts in the tetrahalide compounds with and without the spin-orbit effects (ppm)

Compound	Without LS				With LS						$\delta^{\text{exp}}$	
	$\sigma^{\text{dia}}$	$\sigma^{\text{para}}$	$\sigma^{\text{tot}}$	$\delta^{\text{cal}}$	$\sigma^{\text{dia}}$	$\sigma^{\text{para}}$	$\sigma^{\text{LS}}$			$\sigma^{\text{tot}}$		$\delta^{\text{cal}}(\text{LS})$
							SD	FC	total			
$\text{GaCl}_4^-$	2901.13	-1052.08	1849.22	0	2901.29	-1052.41	3.48	25.66	29.14	1878.02	0	0
$\text{GaBr}_4^-$	3173.19	-1069.71	2103.48	-254.26	3173.19	-1070.64	3.84	125.66	129.50	2232.04	-354.02	-187
$\text{GaI}_4^-$	3415.06	-1139.15	2275.91	-426.69	3415.05	-1143.07	4.82	328.39	333.21	2605.19	-727.16	-706
$\text{InCl}_4^-$	5208.51	-1568.77	3639.73	0	5208.45	-1574.61	18.29	75.43	93.72	3727.56	0	0
$\text{InBr}_4^-$	5469.08	-1708.68	3760.40	-120.67	5469.02	-1715.12	19.45	231.56	251.01	4004.92	-277.36	-265
$\text{InI}_4^-$	5673.22	-1773.56	3899.66	-259.93	5673.17	-1784.83	22.07	666.40	688.47	4576.81	-849.25	-1010

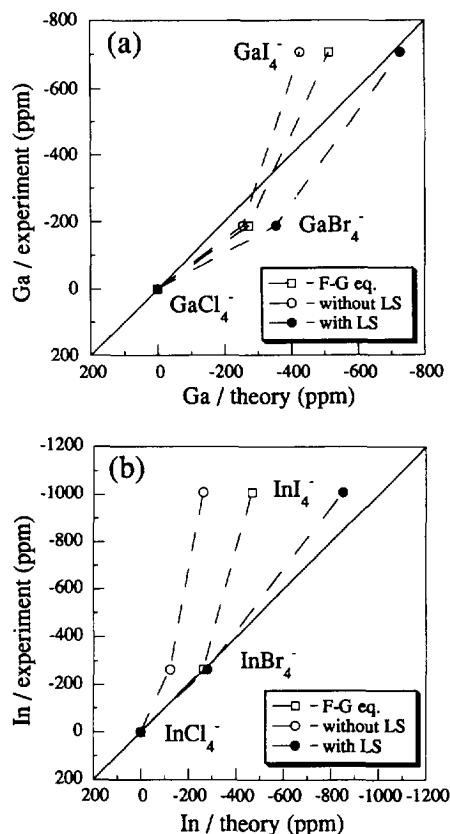


Fig. 1. Correlations between theory and experiment for (a) Ga chemical shifts in gallium tetrahalides and (b) In chemical shifts in indium tetrahalides. The values shown by ( $\square$ ) are due only to the diamagnetic term calculated by the Flygare–Goodisman equation. The values shown by ( $\circ$ ) and ( $\bullet$ ) are due to the sum of the diamagnetic and paramagnetic terms without and with the spin-orbit (LS) interaction, respectively.

ther the calculated values from the experimental ones, if the spin-orbit is not included.

On the other hand, when the spin-orbit effect is

included, the calculated chemical shifts ( $\bullet$ ) show higher field shift and agree much better with the experimental values. This is especially so for the chemical shifts of  $\text{GaI}_4^-$  and  $\text{InI}_4^-$ , showing that the spin-orbit effect is quite important for the chemical shifts of the molecules containing the heavier halogens. We find in Table 1 that the dominant term is the Fermi contact term. In the case of  $\text{InI}_4^-$ , the contribution of the Fermi contact term to the chemical shift is  $-590.97$  ppm, which is about 70% of the calculated chemical shift,  $-849.25$  ppm. The next dominant term is the spin-dipolar term but the value is only several ppm. The others are quite small. Therefore, we conclude that the most important contribution of the spin-orbit effect on the magnetic shielding constant is the Fermi contact term.

For  $\text{GaBr}_4^-$ , the calculated chemical shift with LS deviates more from the experimental value than the one without LS. We think that this is not due to the spin-orbit effect but due to the inaccuracy in the paramagnetic term (basis set incompleteness) and to the electron correlation effect.

Next, we study the MO and AO contributions in the Fermi contact and spin-dipolar terms. This analysis is done similarly to our method for the diamagnetic and paramagnetic terms [11]. The MO contributions of the spin-dipolar and Fermi contact terms in the Ga and In magnetic shielding constants are listed in Table 2. We see that the valence electron contribution is dominant and the core contribution is quite small in both terms. The AO contributions are listed in Table 3. We see that the metal s AO contribution is dominant in the Fermi contact term. The metal p and d orbital contributions to the Fermi contact term are identically zero since these orbitals have a node at the nucleus. In the spin-dipolar term, on the other hand, the metal p orbital contribution is important

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

Compound	$\sigma^{\text{dia}}$	$\sigma^{\text{para}}$	$\sigma^{\text{LS}}(\text{SD})$				$\sigma^{\text{LS}}(\text{FC})$				$\sigma^{\text{tot}}$	$\delta^{\text{cal}}(\text{LS})$	$\delta^{\text{exp}}$
			core	valence	total	shift	core	valence	total	shift			
$\text{GaCl}_4^-$	2901.29	-1052.41	0.46	3.02	3.48	0	0.92	24.74	25.66	0	1878.02	0	0
$\text{GaBr}_4^-$	3173.19	-1070.64	0.59	3.25	3.84	-0.36	9.95	115.71	125.66	-100.00	2232.04	-354.02	-187
$\text{GaI}_4^-$	3415.05	-1143.07	0.72	4.10	4.82	-1.34	27.24	301.15	328.39	-302.73	2605.19	-727.16	-706
$\text{InCl}_4^-$	5208.45	-1574.61	2.72	15.57	18.29	0	-2.04	77.47	75.43	0	3727.56	0	0
$\text{InBr}_4^-$	5469.02	-1715.12	2.65	16.80	19.45	-1.16	10.39	221.17	231.56	-156.13	4004.92	-277.36	-265
$\text{InI}_4^-$	5673.17	-1784.83	3.07	19.00	22.07	-3.78	43.18	623.22	666.40	-590.97	4576.81	-849.25	-1010

Table 3

AO contributions to the spin-dipolar and Fermi contact terms of the Ga and In compounds (ppm)

Compound	$\sigma^{\text{dia}}$	$\sigma^{\text{para}}$	$\sigma^{\text{LS(SD)}}$						$\sigma^{\text{LS(FC)}}$			$\sigma^{\text{tot}}$	$\delta^{\text{cal(LS)}}$	$\delta^{\text{exp}}$	
			metal			ligand			total	metal <sup>a</sup>					
			s	p	d	s	ligand	total							
GaCl <sub>4</sub> <sup>-</sup>	2901.29	-1052.41	0.03	3.23	0.24	-0.02	3.48	26.18	-0.52	25.66	1878.02	0	0		
GaBr <sub>4</sub> <sup>-</sup>	3173.19	-1070.64	-0.09	3.61	0.20	0.12	3.84	126.82	-1.16	125.66	2232.04	-354.02	-187		
GaI <sub>4</sub> <sup>-</sup>	3415.05	-1143.07	-0.54	4.50	0.21	0.65	4.82	328.83	-0.44	328.39	2605.19	-727.16	-706		
InCl <sub>4</sub> <sup>-</sup>	5208.45	-1574.61	-0.06	17.15	1.17	0.03	18.29	74.81	0.62	75.43	3727.56	0	0		
InBr <sub>4</sub> <sup>-</sup>	5469.02	-1715.12	-0.25	18.32	1.28	0.11	19.45	228.92	2.64	231.56	4004.92	-277.36	-265		
InI <sub>4</sub> <sup>-</sup>	5673.17	-1784.83	-0.18	21.05	1.33	-0.12	22.07	661.46	4.94	666.40	4576.81	-849.25	-1010		

<sup>a</sup> 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.

and the others are small. In summary, the spin-orbit effect on the Ga and In shielding constants is due to the metal valence s AO contribution to the Fermi contact term.

We should note that though the Ga and In chemical shifts are due to the diamagnetic mechanism, as shown previously [2], the spin-orbit effect hardly affects the diamagnetic term itself, but it appears through the paramagnetic interaction. Even the largest LS effect on the diamagnetic term is 0.16 ppm in GaCl<sub>4</sub><sup>-</sup> as shown in Table 1.

#### 4. Concluding remarks

The spin-orbit effects on the Ga and In NMR chemical shifts of the gallium and indium tetrahalides, MX<sub>4</sub><sup>-</sup> (M = Ga and In, X = Cl, Br and I) are calculated by the ab initio UHF method as proposed previously [5]. The calculated chemical shifts show good agreement with experiment when the spin-orbit effects are included. The spin-orbit effects are important for describing the Ga and In chemical shifts of the molecules containing the heavier halogens. Though the Ga and In chemical shifts are due to the diamagnetic mechanism, the spin-orbit effect appears through the paramagnetic interaction and the dominant term is the Fermi contact term.

Since the spin-orbit effect is so large, we expect that the normal halogen dependence (NHD) [12] observed in some typical metal halides should be caused by the spin-orbit interaction. Such a study is currently under way.

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