Spin–orbit effect on the magnetic shielding constant using the ab initio UHF method. Electronic mechanism in the aluminum compounds, AlX_4^- (X = H, F, Cl, Br and I)

H. Nakatsuji [1], M. Hada, T. Tejima, T. Nakajima, M. Sugimoto

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

Abstract

The ^{27}Al NMR chemical shifts of the compounds AlX_4^- (X = H, F, Cl, Br and I) are studied theoretically by the ab initio UHF/finite perturbation (FP) method including a previously proposed spin–orbit (SO) interaction. When the SO interaction is included, the calculated chemical shifts agree well with experiment. The SO effects become large in the heavier halogen compounds, $AlBr_4^-$ and AlI_4^-. The paramagnetic term and the SO term are important in the chemical shifts of these compounds. The paramagnetic term is governed by the Al valence p electron mechanism and the SO term arises from the Fermi contact interaction in the Al valence s-orbital. The twofold halogen dependences, namely the normal halogen dependence and the inverse halogen dependence, observed for these compounds arise from the SO effect and the p-electron mechanism, respectively.

1. Introduction

Accurate ab initio calculations of NMR chemical shifts have become quite popular for giving assignments of experimental spectra [1], and clarifying the electronic origins of metal chemical shifts, giving some useful pictures for understanding the trends in observed spectra [2,3]. We have investigated theoretically the NMR chemical shifts of various metal complexes and elucidated that the electronic mechanism of the metal chemical shifts are closely related with the positions of the metals in the periodic table [3].

In this Letter, we study the electronic mechanism of the ^{27}Al NMR chemical shift in the compounds AlX_4^- (X = H, F, Cl, Br, I). The NMR chemical shifts of the tetrahaloaluminiate ions have been extensively studied and the data are accumulated in the literature [4]. The aluminum tetrahalides show a higher field shift (normal halogen dependence (NHD)) from $AlCl_4^-$ to AlI_4^-, and, at the same time, a lower field shift (inverse halogen dependence (IHD)) from AlF_4^- to $AlCl_4^-$ [5]: two kinds of halogen dependence appear in the same series of compounds. We are interested in the electronic origins showing these two different halogen dependences.

Previously, we have studied the gallium and indium NMR chemical shifts of the compounds, $GaCl_nBr_{4-n}^-$ ($n = 1$–4) and $InX_nY_{4-n}^-$ ($n = 1$–4; X, Y = Cl, Br, I) [6]. In these compounds, the paramag-

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

netic term is small since the p electron of Ga, whose atomic configuration is $s^2 p^1$, is used for the chemical bond with the ligand. The diamagnetic term, which is calculated using the structural parameters alone, is therefore dominant in the Ga and In chemical shifts. This is in marked contrast with the chemical shifts of other compounds which are mainly controlled by the paramagnetic term [3]. The ^{27}Al chemical shift was somewhat different from the Ga and In shifts. Further, in the same report [6], we suggested that the SO effects should be large in compounds containing Br and I. Recently, we studied the SO effects in the Ga and In chemical shifts and confirmed that the SO effects are certainly quite important for the chemical shifts of Ga and In compounds having heavier halogen ligands [7].

In the previous paper of this series [8] we presented the calculational method of the magnetic shielding constant including the SO effect using the UHF wavefunction and the finite perturbation (UHF/FP) method. We have also calculated the SO effects using the effective core potentials (ECPs) proposed by Christiansen et al. [9] and applied to silicon halides [10]. In this Letter, we apply this method to the ^{27}Al NMR chemical shifts of the aluminum tetrahydride and tetrahalides compounds AlX_4^- (X = H, F, Cl, Br and I). We investigate the diamagnetic, paramagnetic and SO terms and clarify the origins of the IHD and NHD.

2. Method of calculations

The ^{27}Al magnetic shielding constant σ is calculated by the UHF/FP method including the SO interaction [8]. The chemical shift δ is calculated using AlH_4^- as a reference compound. The SO interaction for the halogen ligand is considered using relativistic ECPs [9], while that for Al is neglected
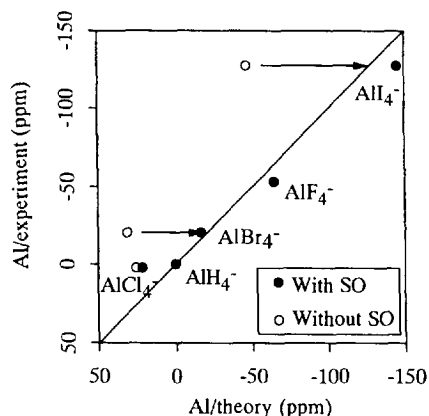

Fig. 1. Correlations between theory and experiment for the ^{27}Al chemical shifts in the aluminum tetrahydride and tetrahalides.

since it is small and almost constant for all the compounds studied in this Letter. Only the one-center integrals for the effective SO potential are added to the imaginary part of the Fock matrices [10]. For AlH_4^- the SO integrals for Al are explicitly calculated [8], though they are small as shown below.

The Al–H and Al–X (X = F, Cl, Br, and I) distances are taken from the experimental values [11] and are summarized in Table 1. The molecular symmetry is assumed to be T_d. The gauge origin is located on the metal atom, however, the magnetic shielding constants of the compounds with T_d symmetry are invariant to the choice of gauge origin [12,13].

The basis set for Al is the (11s8p)/[5s4p] set of Huzinaga et al. [14] and the valence orbitals are augmented by the first-order higher angular momentum p and d basis functions (p- and d-FOBFs) [12]. For the halogen atoms, the core electrons are replaced by the relativistic effective core potentials (ECPs) [9,15,16], and the valence double-zeta sets plus p- and d-FOBFs are used; namely, the (4s4p)/[2s2p] set plus p- and d-FOBFs are used for F and Cl [9], the (3s3p)/[2s2p] set plus p and d-FOBFs for Br [15] and I [16]. We have already reported that by adding the FOBFs to the atoms neighboring the resonant atom, the basis set dependence and the gauge origin dependence decrease [12,13].

Table 1
Al–X bond distances used in the present study (Å)

X				
H	F	Cl	Br	I
1.59	1.69	2.14	2.30	2.44

3. Correlation between theory and experiment

Fig. 1 shows a comparison between the experimental [4,5] and theoretical values of the ^{27}Al NMR chemical shifts of the aluminum tetrahydride and tetrahalides. The values shown by (O) and (●) are the chemical shifts calculated without and with the SO interaction, respectively. The reference compound of the chemical shift is AlH_4^-. For AlF_4^- and AlH_4^- the open and filled circles are at the same positions since the SO effects are small. The calculated results with the SO interaction well reproduce the experimental ones. The lower-field shift (IHD) from F to Cl and the higher-field shift (NHD) from Cl to I are both well reproduced. The results without the SO interaction are poor for $AlBr_4^-$ and AlI_4^- and do not reproduce the NHD for the Cl and Br ligands.

4. Diamagnetic and paramagnetic terms

Table 2 shows a detailed analysis of the calculated values without and with the SO interaction. The total magnetic shielding constant is divided into the diamagnetic term, paramagnetic term, spin-dipolar term, and Fermi contact term [8]. The last two terms are derived from the SO interaction. Fig. 2 shows the halogen dependences of δ^{dia}, δ^{para}, δ^{SO} and the sum of them δ^{calc} using AlH_4^- as a reference compound.

The diamagnetic term shown in Table 2 decreases monotonically from AlF_4^- to AlI_4^- within the range of 50 ppm. This decrease is small and therefore the diamagnetic contribution is relatively unimportant for the ^{27}Al chemical shifts: the result common to most metal chemical shifts studied so far [2], but
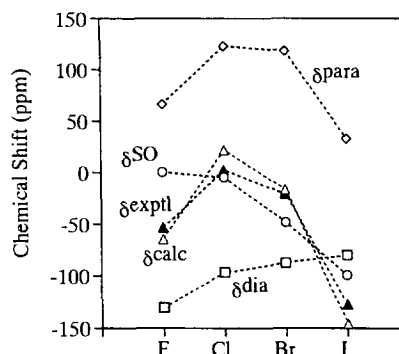

Fig. 2. Halogen dependence of the ^{27}Al chemical shifts relative to AlH_4^-. Total shifts δ^{calc} are decomposed into δ^{dia}, δ^{para} and δ^{SO}.

different from the other 13 group metal (Ga, In) chemical shifts. The diamagnetic term with the SO interaction is essentially the same as that without it, showing that the diamagnetic term is not sensitive to the SO interaction.

The paramagnetic term shown in Table 2 increases (in absolute value) from AlF_4^- to $AlCl_4^-$, but decreases from $AlBr_4^-$ to AlI_4^-. This trend in the paramagnetic term is parallel to that of the experimental chemical shifts as clearly seen from Fig. 2, though the numerical agreement is not good for $AlBr_4^-$ and AlI_4^- without the SO effect. The paramagnetic term is also insensitive to the SO interaction similarly to the diamagnetic term.

The magnetic shielding constants are partitioned into the MO and AO contributions [2] in Tables 3 and 4, respectively. Table 3 shows that the variations in the core-orbital contributions are quite small in both the diamagnetic and paramagnetic terms, while the valence-orbital contributions determine the trends

Table 2

Analysis of the Al chemical shifts in AlX_4^- (X = H, F, Cl, Br and I) with and without the 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}	δ^{cal}		
							SD	FC	total				
AlH_4^-	817.66	−301.64	516.02	0	817.66	−301.59	0.00	0.20	0.20	516.27	0		0
AlF_4^-	948.13	−367.89	580.24	−64.22	948.13	−367.89	−0.05	0.02	−0.03	580.21	−63.94		−53.1
$AlCl_4^-$	914.30	−423.90	490.40	25.62	914.31	−424.61	−0.02	4.98	4.96	494.66	21.61		2.3
$AlBr_4^-$	904.73	−420.18	484.55	31.47	904.73	−420.18	0.15	47.89	48.04	532.59	−16.32		−20.5
AlI_4^-	897.13	−334.30	562.83	−46.81	897.11	−334.53	0.18	98.95	99.13	661.71	−145.44		−127.2

Table 3
MO contributions in the dia-, para-, spin-dipolar and Fermi contact terms of AlX_4^- (X = H, F, Cl, Br and I) (ppm)

Compound	σ^{dia}			σ^{para}			$\sigma^{SO}(SD)$			$\sigma^{SO}(FC)$			σ^{tot}	δ^{calc}	δ^{exp}
	core	valence	total	core	valence	total	core	valence	total	core	valence	total			
AlH_4^-	764.03	53.63	817.66	-36.23	-265.36	-301.59	0.01	-0.01	0.00	-0.22	0.42	0.20	516.27	0	0
AlF_4^-	763.96	184.17	948.13	-21.76	-346.13	-367.89	-0.01	-0.04	-0.05	-0.02	0.04	0.02	580.21	-63.94	-53.1
$AlCl_4^-$	764.22	150.09	914.31	-36.26	-388.35	-424.61	-0.02	0.00	-0.02	0.26	4.72	4.98	494.66	21.61	2.3
$AlBr_4^-$	764.30	140.43	904.73	-40.00	-380.18	-420.18	-0.07	0.22	0.15	2.75	45.14	47.89	536.59	-16.32	-20.5
AlI_4^-	764.28	132.83	897.11	-36.66	-297.87	-334.53	-0.14	0.32	0.18	5.62	93.33	98.95	661.71	-145.44	-127.2

Table 4
AO contributions in the dia-, para-, spin-dipolar and Fermi contact terms of AlX_4^- (X = H, F, Cl, Br and I) (ppm)

Compound	σ^{dia}					σ^{para}				$\sigma^{SO}(SD)$					$\sigma^{SO}(FC)$			σ^{tot}	δ^{calc}	δ^{exp}
	metal			ligand	total	metal		ligand	total	metal			ligand	total	metal	ligand	total			
	s	p	d			p	d			s	p	d								
AlH_4^-	539.23	248.23	-0.71	30.90	817.66	-269.60	-7.64	-24.35	-301.59	0.00	-0.04	0.00	0.04	0.00	0.20	0.00	0.20	516.27	0	0
AlF_4^-	533.76	239.94	1.81	172.62	948.13	-192.42	-9.56	-165.91	-367.89	0.00	-0.05	0.00	0.00	-0.05	-0.01	0.02	0.02	580.21	-63.94	-53.11
$AlCl_4^-$	535.39	242.01	1.21	135.70	914.31	-282.40	-10.13	-132.08	-424.61	0.01	-0.02	0.00	-0.01	-0.02	4.98	0.00	4.98	494.66	21.61	2.3
$AlBr_4^-$	536.31	246.57	3.57	118.28	904.73	-301.76	-10.82	-107.60	-420.18	0.04	0.16	0.04	-0.09	0.15	48.19	-0.30	47.89	532.59	-16.32	-20.5
AlI_4^-	535.78	243.92	2.96	114.46	897.11	-269.60	-8.07	-56.86	-334.53	0.52	1.20	0.26	-1.80	0.18	127.42	-28.47	98.95	661.7	-145.44	-127.2

of the diamagnetic and paramagnetic terms as reported previously for almost all the compounds [3]. Table 4 shows that the diamagnetic term is mainly determined by the ligand (halogen) contributions as expected [2], while in the paramagnetic terms the Al p-orbital contribution and the ligand contribution are important. This is analyzed as follows.

The halogen contribution to the diamagnetic term mainly reflects the variation in the Al–X distance in the Flygare–Goodisman equation [17]. The difference between hydrogen and halogen lies in the nuclear charge. The ligand (halogen) contribution to the paramagnetic term monotonically decreases from AlF_4^- to AlI_4^-. This trend again reflects the variations in the Al–X distance, as σ^{para} includes the operator $1/r_{Al}^3$, in which r_{Al} measures the distance between Al and the electron cloud on the halogen. The ratio of R_{Al-F}/R_{Al-I} is ≈ 1.44 and this value reasonably explains the decrease of the ligand contribution [18]. We note, therefore, that the ligand contributions in σ^{dia} and σ^{para} are based on similar origins so that they closely cancel each other as seen in Table 4. The iodine ligand is an exception for the diffuseness of its valence orbitals. As a result, only the p-orbital contribution in σ^{para} becomes important. We show in Fig. 3 the Mulliken population of the Al 3p AO. The p orbital contribution in Table 4 and the Mulliken population in Fig. 3 are closely parallel: the population becomes maximum at X = Br just as the p-AO contribution to σ^{para}. This strongly support that the chemical shift without including the SO term is dominated by the p-mechanism, as expected from
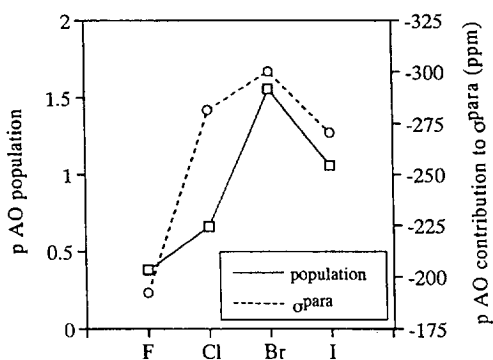
our series of studies on metal NMR chemical shifts [3,19].

5. Spin–orbit interaction term

The SO interaction term is divided into the Fermi contact term and the spin-dipolar term [8]. Table 2 shows that the Fermi contact term is dominant in the SO effects; it is large for X = Br and I and comparable with the paramagnetic term. The Fermi contact term becomes larger in the order F < Cl < Br < I as seen from Fig. 2. The MO contributions of the spin-dipolar and Fermi contact terms in the [27]Al magnetic shielding constants are shown in Table 3. The valence electron contribution is dominant, while the core contribution is quite small in both terms. The AO contributions are listed in Table 4. The metal s AO contribution is dominant to 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.

We note here the SO interaction of Al. For AlH_4^- we explicitly calculated the one-electron SO integrals, so that the Al SO interaction is included for AlH_4^-. Table 1 shows that the SO effect is small in AlH_4^-, and, therefore, the SO interaction of Al should also be small in the other compounds studied here, which justifies the neglect of the SO interaction of Al.

When the SO effect is not included, the calculated chemical shifts O do not agree well with the experimental values (Fig. 1). The calculated chemical shifts (●) including the SO effect move to higher field and agree much better with the experimental values for $AlBr_4^-$ and AlI_4^-. As the halogen becomes heavier, the SO effect increases as seen from Fig. 2. As a result, the substitution from Cl to I causes a higher field shift (NHD), while the substitution from F to Cl causes a lower field shift (IHD). This tendency is consistent with the experiment. Thus, the origin of the NHD in the aluminum tetrahalides (X = Cl, Br, I) is the SO effect, while the origin of the IHD is mainly due to the p-electron mechanism in the paramagnetic term. This result is consistent with the previous result for the Si, Ge and Sn chemical shifts [10,19].

Fig. 3. Halogen dependence of the Al p AO population and the p AO contibution to σ^{para}.

6. Summary

The SO effects in the ^{27}Al NMR chemical shifts of the aluminum tetrahydride and tetrahalides, AlX_4^- (X = H, F, Cl, Br and I) are calculated by the ab initio UHF/FP method proposed previously [8]. The SO interaction is calculated using the effective SO potential [10].

(1) The calculated chemical shifts show a good overall agreement with experiment when the SO interaction is included. The SO effects are important for describing the ^{27}Al chemical shifts of compounds containing heavier halogen ligands.

(2) The trend in the sum of the diamagnetic and paramagnetic terms are understood by the p-electron mechanism. The ligand contributions in σ^{dia} and σ^{para} reflect the same origins and closely cancel each other, except for the iodine ligand.

(3) In the SO effects, the Fermi contact term owing to the metal s AO contribution is dominant. It increases monotonically from AlF_4^- to AlI_4^-, and therefore causes the NHD from Cl to I, where the paramagnetic term is also cooperative (see Fig. 2). On the contrary, the IHD for X = H, Cl, F is due mainly to the p-electron mechanism in the paramagnetic term.

Acknowledgements

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