

Theoretical Study on Metal NMR Chemical Shifts. Gallium Compounds,  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ )

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Ga NMR chemical shifts of tetrahalogenogallates,  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ), are calculated with the Hartree-Fock/finite perturbation method. For the Ga chemical shift, the diamagnetic contribution  $\sigma^{\text{dia}}$  is dominant and the paramagnetic contribution  $\sigma^{\text{para}}$  is small. This means that the Ga chemical shifts in the  $\text{GaCl}_{4-n}\text{Br}_n^-$  series are mainly determined by structural factors such as metal-ligand distance and ligand nuclear charge. This is in sharp contrast to the cases of transition-metal complexes previously reported, in which  $\sigma^{\text{para}}$  gives the dominant contribution. The smallness of  $\Delta\sigma^{\text{para}}$  in the Ga compounds is attributed to the smallness in the change of the valence electronic structure due to the ligand substitution. On the basis of ab initio results for the  $\text{GaCl}_{4-n}\text{Br}_n^-$  series, we also analyze the metal chemical shifts for the series of aluminum, gallium, and indium halides,  $\text{MX}_{4-n}\text{Y}_n^-$  ( $M = \text{Al, Ga, In; X, Y} = \text{Cl, Br, I}$ ).

## Introduction

In this series of studies, we investigate electronic origins of metal NMR chemical shifts by an ab initio molecular orbital method.<sup>1,2</sup> Some useful pictures for understanding the observed trends of metal chemical shifts have been suggested. In this paper, we present a study of the electronic origin of the Ga chemical shifts in the tetrahalogenogallates  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ). We are interested in the factor which determines the "normal halogen dependence (NHD)"<sup>3</sup> observed in this series of compounds, since our previous investigations of the  $\text{Mo}$ ,<sup>2e,f</sup>  $\text{Ti}$ ,<sup>2g</sup> and  $\text{Nb}^{2h}$  complexes are concerned with the "inverse halogen (chalcogen) dependence (IHD)" of the metal chemical shifts.

Kidd reported that there are two types of halogen dependences (the NHD and IHD) in multinuclear NMR chemical shifts, each of which is inherent to the nucleus under consideration.<sup>3</sup> The NHD indicates the trend in which the shift monotonically moves downfield as the ligand is substituted with a more electronegative one, and the IHD means the reverse trend. To the best of our knowledge, there seems to be no study which systematically explains the origin of the NHD, while our previous studies<sup>2e-h</sup> have explained the IHD.

In previous theoretical studies of the chemical shifts, it has generally been recognized that the paramagnetic contribution is dominant for chemical shifts: the diamagnetic term has only a secondary importance.<sup>1-6</sup> This is particularly true for the transition-metal complexes studied in our previous paper.<sup>1,2</sup> We have suggested that the IHD appears when the magnetically allowed excitation energy  $\Delta E$  from bonding molecular orbitals (MOs) to antibonding MOs is important; it appears in the denominator of the sum-over-states perturbation formula for  $\sigma^{\text{para}}$ . Thus, the dependence may be related to the spectrochemical series of ligands. In contrast, it was suggested that the factors which dominate the change in the numerator of the perturbation formula for  $\sigma^{\text{para}}$  are responsible for the NHD.<sup>3</sup> Juranic showed the linear relation between  $\beta/\Delta E$  and Rh chemical shifts for Rh(III) complexes which gives the NHD, where  $\beta$  is a nephelauxetic ratio.<sup>6</sup>

In this paper, we show that, in contrast to the metal chemical shifts previously studied, the diamagnetic term is important, rather than the paramagnetic one, for the Ga chemical shifts. We also investigate whether this is true even for the other group IIIb metal halides,  $\text{MX}_{4-n}\text{Y}_n^-$  ( $M = \text{Al, Ga, In; X, Y} = \text{Cl, Br, I}$ ).

## Method of the Calculations

The unperturbed wave functions are obtained by the HONDO7 program developed by Dupuis et al.,<sup>7</sup> and the magnetic shielding

constants are calculated by the finite perturbation method.<sup>8</sup> The gauge origin is placed at the position of the gallium atom. The details of the theoretical method were given in the first paper of this series.<sup>2a</sup>

The bond distances are taken from the crystallographic data.<sup>9,10</sup> The bond distances are summarized in Table I. The bond angles are assumed to be tetrahedral 109.47° for all the compounds including the mixed ligand ones.

We use the basis sets of Huzinaga and co-workers.<sup>11</sup> In order to check the basis set dependence of the calculated properties, we use four combinations of basis sets A-D

A: Ga(I) + Cl(I), Br(I)

B: Ga(I) + Cl(II), Br(II)

C: Ga(II) + Cl(II), Br(II)

D: Ga(I) + Cl(III), Br(III)

where I, II, and III denote the following basis sets:

Ga (I) (13s10p4d)/[5s4p2d] with two polarization d functions ( $\zeta = 0.336, 0.091$ )

Ga (II) (13s10p4d)/[6s5p2d] with two polarization d functions

Cl (I) (10s7p)/[3s2p]

Cl (II) (10s7p)/[4s3p]

Cl (III) (II) with a polarization d function ( $\zeta = 0.514$ )

Br (I) (13s10p4d)/[4s3p1d]

Br (II) (13s10p4d)/[5s4p1d]

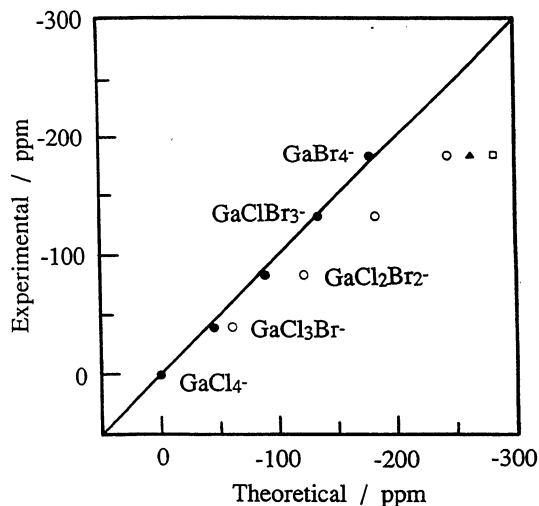
Br (III) (II) with a polarization d function ( $\zeta = 0.389$ )

For the series of compounds  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ), basis sets A and B are used. Basis sets C and D are used only for  $\text{GaCl}_4^-$  and  $\text{GaBr}_4^-$ .

**TABLE I: M-L Bond Distances (M = Ga, Al, In; L = Cl, Br, I) Used in the Present Study (in Å)**

| M  | Cl                 | Br                 | I                  |
|----|--------------------|--------------------|--------------------|
| Ga | 2.157 <sup>a</sup> | 2.314 <sup>b</sup> | 2.458 <sup>c</sup> |
| Al | 2.14 <sup>c</sup>  | 2.30 <sup>c</sup>  | 2.44 <sup>c</sup>  |
| In | 2.37 <sup>c</sup>  | 2.48 <sup>d</sup>  | 2.71 <sup>e</sup>  |

<sup>a</sup> Reference 9. <sup>b</sup> Reference 10. <sup>c</sup> Reference 18. <sup>d</sup> Reference 19. <sup>e</sup> Reference 20.



**Figure 1.** Correlation between calculated and experimental values of the Ga chemical shifts in  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ): ●, ○, ▲, and □ show the results by basis sets A, B, C, and D, respectively.

**TABLE II: Total Energies Obtained by the Unperturbed Hartree-Fock Calculations for  $\text{GaCl}_4^-$  and  $\text{GaBr}_4^-$  (in atomic units)**

| basis set | $\text{GaCl}_4^-$ | $\text{GaBr}_4^-$ |
|-----------|-------------------|-------------------|
| A         | -3757.739 681     | -12202.138 763    |
| B         | -3757.783 259     | -12202.160 344    |
| C         | -3757.823 970     | -12202.198 508    |
| D         | -3757.853 818     | -12202.359 437    |

### Comparison with the Experimental Chemical Shifts

Chemical shift is defined as the difference of the magnetic shielding constant  $\sigma$  for a particular compound from that of the reference molecule, i.e.

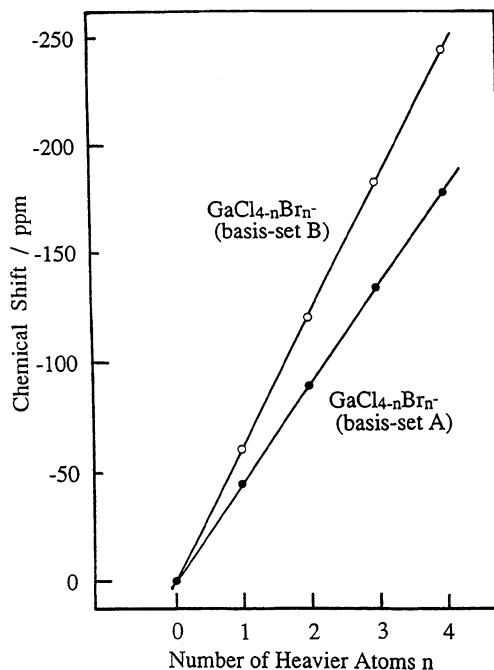
$$\delta = \sigma(\text{ref}) - \sigma \quad (1)$$

where the reference molecule is  $\text{GaCl}_4^-$  in this study. In the experiments by Tarasov et al.<sup>12</sup> and McGarvey et al.,<sup>13</sup> the reference is  $\text{Ga}(\text{H}_2\text{O})_6^{3+}$  in aqueous solution, so the data are converted by using the relation

$$\delta(\text{ref: GaCl}_4^- \text{ in MeCN}) = \delta(\text{ref: Ga}(\text{H}_2\text{O})_6^{3+} \text{ in H}_2\text{O}) - 251.8 \text{ ppm} \quad (2)$$

We use the experimental data observed in MeCN solution for comparison, though the data in some other solvents are available.<sup>4</sup>

We show the correlation between the calculated and experimental results in Figure 1. A good agreement with the experiments is obtained, especially with the use of basis set A, which is a rather crude basis set for the ligands. The results do not show a systematic improvement as the quality of the basis set becomes better. Table II tabulates the unperturbed Hartree-Fock energies calculated by basis sets A-D. As discussed below, such basis set dependence comes from the paramagnetic contribution of the magnetic shielding constant. Since the molecules are highly spherically symmetric, we think that it does not result from the gauge origin problem. Anyway, all the basis sets give



**Figure 2.** Dependence of the Ga chemical shifts calculated with basis sets A and B on the number of bromine atoms in  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ).

good enough agreement with the experiments for discussing the electronic origin of the Ga chemical shift.

Figure 2 illustrates the dependence of the calculated chemical shift of  $\text{GaCl}_{4-n}\text{Br}_n^-$  on the number of Br atoms,  $n$ . For basis sets A and B, the substitution Cl  $\rightarrow$  Br gives a constant shift of  $-45$  or  $-60$  ppm to the higher field, and the  $n$  dependence of the chemical shift is linear. Note that this trend is similar to that observed in  $\text{NbCl}_{6-n}\text{Br}_n^-$  ( $n = 0-6$ )<sup>2b</sup> but that the sign is opposite. Namely, the present results reproduce the so-called "normal halogen dependence (NHD)".<sup>3</sup> Now, what is the origin of this NHD?

### Analysis of the Ga Chemical Shifts

The calculated magnetic shielding constants  $\sigma$  and Ga chemical shifts  $\delta$  are summarized in Table III. It also shows the breakdown into the diamagnetic and paramagnetic contributions and the core and valence MO contributions for each term. Figure 3 shows the dependence of the Ga chemical shift and the contributions from  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  on the number of Br atoms, which are obtained with basis set A.

We find an interesting behavior of  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$ , in sharp contrast to the previous results. The paramagnetic term, which has been shown to be dominant in the metal NMR chemical shifts studied so far,<sup>1,2</sup> gives a smaller contribution to the total chemical shift than the diamagnetic term. Except for the results of basis set D, the sign of  $\Delta\sigma^{\text{para}}$  is opposite to that of the chemical shifts. On the other hand, the contribution from  $\sigma^{\text{dia}}$  is larger and simulates the trend in the total magnetic shielding constant. Therefore, we conclude that  $\sigma^{\text{dia}}$  is the origin of the Ga chemical shift of  $\text{GaCl}_{4-n}\text{Br}_n^-$ .

Except for this observation, the other factors mostly follow our previous results: For  $\sigma^{\text{dia}}$ , (1) the core MO contributions are larger than those of valence MOs, (2) the electronegative ligand contributes to the downfield shift, and (3) the values are independent of the basis set quality. For  $\sigma^{\text{para}}$ , (1) the valence MOs determine the trend of this term and (2) the substitution of Br for Cl leads to a stabilization of the second-order energy in the magnetic field (i.e., it makes this term more negative). The  $n$  dependence of  $\Delta\sigma^{\text{dia}}$  and  $\Delta\sigma^{\text{para}}$  is also linear. It seems to imply that the factors affecting each term are the same as those in the

TABLE III: Calculated Magnetic Shielding Constants and Their Breakdown into Core and Valence MO Contributions (in ppm)

| molecule                                       | $\sigma^{\text{dia}}$ |         |        |        | $\sigma^{\text{para}}$ |         |         |       | $\sigma$ total | $\delta$ |                    |  |
|--|-----------------------|---------|--------|--------|------------------------|---------|---------|-------|----------------|----------|--------------------|--|
|  | core                  | valence | total  | shift  | core                   | valence | total   | shift |                | calcd    | exptl <sup>a</sup> |  |
| Basis Set A <sup>b</sup>                       |                       |         |        |        |                        |         |         |       |                |          |                    |  |
| GaCl <sub>4</sub> <sup>-</sup>                 | 2821.0                | 111.1   | 2932.1 | 0.0    | -269.9                 | -618.8  | -888.7  | 0.0   | 2043.4         | 0.0      | 0.0                |  |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 2890.6                | 109.5   | 3000.1 | -68.0  | -262.0                 | -649.7  | -911.7  | 23.0  | 2088.4         | -45.0    | -39.8              |  |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 2960.4                | 108.0   | 3068.4 | -136.4 | -254.6                 | -681.4  | -936.0  | 47.4  | 2132.4         | -89.0    | -83.8              |  |
| GaClBr <sub>3</sub> <sup>-</sup>               | 3029.7                | 106.3   | 3136.1 | -204.0 | -246.2                 | -712.3  | -958.5  | 69.9  | 2177.5         | -134.1   | -132.8             |  |
| GaBr <sub>4</sub> <sup>-</sup>                 | 3099.3                | 104.8   | 3204.1 | -272.0 | -238.3                 | -744.0  | -982.3  | 93.6  | 2221.8         | -178.4   | -183.8             |  |
| Basis Set B <sup>b</sup>                       |                       |         |        |        |                        |         |         |       |                |          |                    |  |
| GaCl <sub>4</sub> <sup>-</sup>                 | 2821.2                | 111.4   | 2932.6 | 0.0    | -287.2                 | -788.2  | -1075.3 | 0.0   | 1857.3         | 0.0      | 0.0                |  |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 2890.8                | 109.8   | 3000.6 | -68.0  | -281.3                 | -801.2  | -1082.6 | 7.4   | 1918.0         | -60.7    | -39.8              |  |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 2960.4                | 108.2   | 3068.6 | -136.0 | -275.4                 | -814.2  | -1089.6 | 14.3  | 1978.9         | -121.7   | -83.8              |  |
| GaClBr <sub>3</sub> <sup>-</sup>               | 3030.0                | 106.6   | 3136.6 | -204.0 | -269.3                 | -827.3  | -1096.6 | 21.2  | 2040.0         | -182.8   | -132.8             |  |
| GaBr <sub>4</sub> <sup>-</sup>                 | 3099.6                | 105.0   | 3204.6 | -272.0 | -263.0                 | -840.4  | -1103.4 | 28.1  | 2101.2         | -244.0   | -183.8             |  |
| Basis Set C <sup>b</sup>                       |                       |         |        |        |                        |         |         |       |                |          |                    |  |
| GaCl <sub>4</sub> <sup>-</sup>                 | 2819.5                | 111.7   | 2931.3 | 0.0    | -309.1                 | -589.5  | -898.6  | 0.0   | 2032.6         | 0.0      | 0.0                |  |
| GaBr <sub>4</sub> <sup>-</sup>                 | 3098.0                | 105.2   | 3203.2 | -271.9 | -275.4                 | -631.9  | -907.3  | 8.6   | 2295.9         | -263.3   | -183.8             |  |
| Basis Set D <sup>b</sup>                       |                       |         |        |        |                        |         |         |       |                |          |                    |  |
| GaCl <sub>4</sub> <sup>-</sup>                 | 2820.6                | 112.2   | 2932.9 | 0.0    | -299.6                 | -832.3  | -1131.8 | 0.0   | 1801.1         | 0.0      | 0.0                |  |
| GaBr <sub>4</sub> <sup>-</sup>                 | 3099.2                | 105.6   | 3204.7 | -271.9 | -269.4                 | -851.6  | -1121.0 | -10.8 | 2083.8         | -282.7   | -183.8             |  |

<sup>a</sup> References 12 and 13. <sup>b</sup> The definition of the basis set is given in the text.

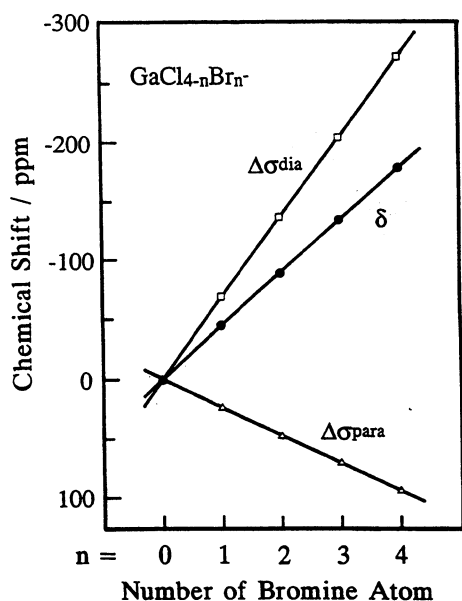


Figure 3. Dependence of the Ga chemical shifts  $\delta$  and the contributions from  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  on the number of bromine atoms in  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ), obtained with basis set A.

previous metal chemical shifts; the relative importance between  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  is reversed in the Ga chemical shift.

#### Diamagnetic Contributions

Table IV shows the result of the analysis for the diamagnetic term into atomic orbital (AO) contributions using a method similar to the Mulliken population analysis.<sup>2a</sup> We see that each term is constant: the deviations are less than 5 ppm. Thus, a Pascal-rule like formula also holds for these Ga compounds

$$\sigma^{\text{dia}} = \sigma_{\text{Ga}}^{\text{dia}} + \sum_L n_L \sigma_L^{\text{dia}} \quad (3)$$

where  $n_L$  is the number of the ligand L. The average value of  $\sigma_{\text{Ga}}^{\text{dia}}$  is 2631.5 ppm, which is close to the free atom value given by Malli and Froese, 2638.57 ppm.<sup>14</sup> Therefore, we confirm that  $\sigma^{\text{dia}}$  is fairly insensitive to the bond formation in molecules and the quality of the basis set used. The shifts are entirely due to the ligand contributions.

In our previous studies, we have shown that the values of  $\sigma^{\text{dia}}$  calculated by the Hartree-Fock method is well reproduced by

the Flygare-Goodisman equation<sup>15</sup>

$$\sigma^{\text{dia}} = \sigma_{\text{Ga}}^{\text{dia}} + \frac{e^2}{3mc^2} \sum_L \frac{Z_L}{R_L} \quad (4)$$

where  $R_L$  denotes the distance between Ga and ligand. Equation 4 explains why the linear dependence of  $\sigma^{\text{dia}}$  on the number of Br atoms is observed in Figure 3. Table V compares the results due to eq 4 with our ab initio results. The diamagnetic term depends on the nuclear charge of the ligand and the distance from the resonant nucleus as shown in eq 4. The fact that such an analysis is possible is the merit of the common origin method.

In the experiment by McGarvey et al.,<sup>13</sup> the Ga chemical shifts for  $\text{GaX}_{4-n}\text{I}_n^-$  ( $X = \text{Cl}, \text{Br}$ ) are also reported. For  $\text{GaCl}_{4-n}\text{Br}_n^-$ , the substitution of Br for Cl causes a shift of 40–54 ppm, while for  $\text{GaCl}_{4-n}\text{I}_n^-$ , the shift is 128–220 ppm for the substitution of I for Cl. The fact stated above is the reason why the shift is larger for replacement with a heavier atom. From this viewpoint, we will analyze the chemical shifts of the group IIIb tetrahalides,  $\text{MX}_{4-n}\text{Y}_n^-$  ( $M = \text{Al}, \text{Ga}, \text{In}$ ;  $X, Y = \text{Cl}, \text{Br}, \text{I}$ ), in a later section of this paper.

#### Paramagnetic Contribution

In this section, we discuss why  $\sigma^{\text{para}}$  is less important for the Ga chemical shifts than for the metal chemical shifts studied so far and why it has a linear  $n$  dependence (shown in Figure 3).

We show, in Table VI, the AO analysis of  $\sigma^{\text{para}}$  as is given for  $\sigma^{\text{dia}}$  in Table IV. We see that the Ga atom contribution dominates the paramagnetic term. The contributions from the ligands are negligibly small. The s AO contribution of the Ga atom is not shown: it is identically zero since the s AO does not have an angular momentum. The p AOs of the Ga atom give larger contribution than the d AOs including the polarization functions. Thus, local paramagnetic charge circulation through the p AO of the gallium atom is important for  $\sigma^{\text{para}}$ . This observation is similar to previous observations concerning p orbital contributions in  $\text{Sn}^{2+}$  and  $\text{Ge}^{2+}$  complexes and d orbital contributions in  $\text{Mo}^{2+}$  and  $\text{Nb}^{2+}$  compounds. Therefore, we think that  $\sigma^{\text{para}}$  reflects the magnetically allowed  $\sigma \rightarrow \sigma^*$  excitation energy  $\Delta E$ , as supported by the calculations with basis sets A–C.

Three factors are thought to cooperatively reduce the paramagnetic contribution to the chemical shift. First is the smallness of the change in the 4p population, since  $\sigma^{\text{para}}$  and the AO population are interconnected through the density matrix. Certainly these two quantities have a linear relation as illustrated in Figure 4. Such a relation was also found for  $\text{NbX}_{6-n}\text{Y}_n^-$  ( $X,$

TABLE IV: AO Contributions to the Diamagnetic Term  $\sigma^{\text{dia}}$  (in ppm)

| molecule                                       | gallium |       |       |        | chlorine |      |     |       | bromine |      |      |       | $\sigma^{\text{dia}}$ total |
|--|---------|-------|-------|--------|----------|------|-----|-------|---------|------|------|-------|-----------------------------|
|  | s       | p     | d     | total  | s        | p    | d   | total | s       | p    | d    | total |                             |
| Basis Set A <sup>a</sup>                       |         |       |       |        |          |      |     |       |         |      |      |       |                             |
| GaCl <sub>4</sub> <sup>-</sup>                 | 1394.4  | 930.7 | 305.5 | 2630.6 | 25.6     | 49.8 |     | 75.4  |         |      |      |       | 2932.1                      |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 1395.5  | 930.9 | 304.4 | 2630.8 | 25.6     | 49.8 |     | 75.4  | 32.1    | 70.7 | 40.5 | 143.2 | 3000.1                      |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 1396.7  | 931.0 | 303.3 | 2631.1 | 25.6     | 49.9 |     | 75.5  | 32.1    | 70.6 | 40.5 | 143.2 | 3068.4                      |
| GaClBr <sub>3</sub> <sup>-</sup>               | 1398.0  | 931.2 | 302.2 | 2631.3 | 25.6     | 49.8 |     | 75.3  | 32.1    | 70.6 | 40.5 | 143.1 | 3136.1                      |
| GaBr <sub>4</sub> <sup>-</sup>                 | 1399.2  | 931.4 | 301.0 | 2631.6 |          |      |     |       | 32.1    | 70.6 | 40.5 | 143.1 | 3204.1                      |
| Basis Set B <sup>a</sup>                       |         |       |       |        |          |      |     |       |         |      |      |       |                             |
| GaCl <sub>4</sub> <sup>-</sup>                 | 1397.9  | 933.0 | 302.4 | 2633.4 | 25.3     | 49.5 |     | 74.8  |         |      |      |       | 2932.6                      |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 1398.8  | 933.0 | 301.7 | 2633.6 | 25.3     | 49.5 |     | 74.8  | 31.9    | 70.4 | 40.4 | 142.7 | 3000.6                      |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 1399.7  | 933.1 | 301.0 | 2633.8 | 25.3     | 49.4 |     | 74.8  | 31.9    | 70.3 | 40.4 | 142.6 | 3068.6                      |
| GaClBr <sub>3</sub> <sup>-</sup>               | 1400.5  | 933.1 | 300.4 | 2634.0 | 25.3     | 49.4 |     | 74.7  | 31.9    | 70.3 | 40.4 | 142.6 | 3136.6                      |
| GaBr <sub>4</sub> <sup>-</sup>                 | 1401.3  | 933.1 | 299.7 | 2634.1 |          |      |     |       | 31.9    | 70.3 | 40.4 | 142.6 | 3204.6                      |
| Basis Set C <sup>a</sup>                       |         |       |       |        |          |      |     |       |         |      |      |       |                             |
| GaCl <sub>4</sub> <sup>-</sup>                 | 1396.3  | 931.0 | 301.9 | 2629.2 | 25.7     | 49.9 |     | 75.5  |         |      |      |       | 2931.3                      |
| GaBr <sub>4</sub> <sup>-</sup>                 | 1400.2  | 931.8 | 298.8 | 2630.8 |          |      |     |       | 32.1    | 70.5 | 40.4 | 143.1 | 3203.2                      |
| Basis Set D <sup>a</sup>                       |         |       |       |        |          |      |     |       |         |      |      |       |                             |
| GaCl <sub>4</sub> <sup>-</sup>                 | 1396.4  | 932.2 | 302.3 | 2631.0 | 25.1     | 49.9 | 0.5 | 75.5  |         |      |      |       | 2932.9                      |
| GaBr <sub>4</sub> <sup>-</sup>                 | 1398.0  | 932.1 | 301.2 | 2631.3 |          |      |     |       | 31.7    | 70.8 | 40.9 | 143.4 | 3204.7                      |

<sup>a</sup> The definition of the basis set is given in the text.

TABLE V: Estimate of the Diamagnetic Term from the Flygare-Goodisman Equation Compared with the ab Initio Results (in ppm)

| molecule                                       | Flygare-Goodisman |         |                       | ab initio (basis set A) |         |                       | ab initio (basis set B) |         |                       |
|--|-------------------|---------|-----------------------|-------------------------|---------|-----------------------|-------------------------|---------|-----------------------|
|  | Ga                | ligands | $\sigma^{\text{dia}}$ | Ga                      | ligands | $\sigma^{\text{dia}}$ | Ga                      | ligands | $\sigma^{\text{dia}}$ |
| GaCl <sub>4</sub> <sup>-</sup>                 | 2638.6            | 296.0   | 2934.6                | 2630.6                  | 301.6   | 2932.1                | 2633.4                  | 299.2   | 2932.6                |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 2638.6            | 364.1   | 3002.7                | 2630.8                  | 369.4   | 3000.1                | 2633.6                  | 367.1   | 3000.6                |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 2638.6            | 432.2   | 3070.8                | 2631.1                  | 437.4   | 3068.4                | 2633.8                  | 434.8   | 3068.6                |
| GaClBr <sub>3</sub> <sup>-</sup>               | 2638.6            | 500.3   | 3138.9                | 2631.3                  | 504.6   | 3136.1                | 2634.0                  | 502.5   | 3136.6                |
| GaBr <sub>4</sub> <sup>-</sup>                 | 2638.6            | 568.4   | 3207.0                | 2631.6                  | 572.4   | 3204.1                | 2634.1                  | 570.4   | 3204.6                |

TABLE VI: AO Contributions to the Paramagnetic Term  $\sigma^{\text{para}}$  (in ppm)

| molecule                                       | gallium |        |         | chlorine |       |      |       | bromine |       |       |       | $\sigma^{\text{para}}$ total |
|--|---------|--------|---------|----------|-------|------|-------|---------|-------|-------|-------|------------------------------|
|  | p       | d      | total   | s        | p     | d    | total | s       | p     | d     | total |                              |
| Basis Set A <sup>a</sup>                       |         |        |         |          |       |      |       |         |       |       |       |                              |
| GaCl <sub>4</sub> <sup>-</sup>                 | -694.3  | -168.2 | -862.5  | -2.9     | -3.6  |      | -6.5  |         |       |       |       | -888.7                       |
| GaCl <sub>3</sub> Br <sup>-</sup>              | -721.1  | -163.3 | -884.5  | -2.9     | -3.6  |      | -6.5  | -5.4    | -4.3  | 1.9   | -7.7  | -911.7                       |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | -749.0  | -158.8 | -907.7  | -2.9     | -3.6  |      | -6.5  | -5.4    | -4.2  | 1.9   | -7.7  | -936.0                       |
| GaClBr <sub>3</sub> <sup>-</sup>               | -775.9  | -153.2 | -929.1  | -2.9     | -3.6  |      | -6.5  | -5.4    | -4.2  | 1.9   | -7.7  | -958.5                       |
| GaBr <sub>4</sub> <sup>-</sup>                 | -803.7  | -148.0 | -951.7  |          |       |      |       | -5.3    | -4.2  | 1.9   | -7.6  | -982.3                       |
| Basis Set B <sup>a</sup>                       |         |        |         |          |       |      |       |         |       |       |       |                              |
| GaCl <sub>4</sub> <sup>-</sup>                 | -848.1  | -199.9 | -1048.0 | -2.2     | -4.6  |      | -6.8  |         |       |       |       | -1075.3                      |
| GaCl <sub>3</sub> Br <sup>-</sup>              | -855.5  | -198.7 | -1054.2 | -2.2     | -4.6  |      | -6.8  | -3.7    | -5.0  | 0.7   | -8.0  | -1082.6                      |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | -863.1  | -197.1 | -1060.2 | -2.2     | -4.6  |      | -6.8  | -3.7    | -5.0  | 0.7   | -8.0  | -1089.6                      |
| GaClBr <sub>3</sub> <sup>-</sup>               | -870.9  | -195.1 | -1065.9 | -2.2     | -4.5  |      | -6.8  | -3.7    | -5.0  | 0.7   | -7.9  | -1096.6                      |
| GaBr <sub>4</sub> <sup>-</sup>                 | -878.9  | -192.8 | -1071.7 |          |       |      |       | -3.7    | -4.9  | 0.7   | -7.9  | -1103.4                      |
| Basis Set C <sup>a</sup>                       |         |        |         |          |       |      |       |         |       |       |       |                              |
| GaCl <sub>4</sub> <sup>-</sup>                 | -665.5  | -208.0 | -873.6  | -2.1     | -4.2  |      | -6.3  |         |       |       |       | -898.6                       |
| GaBr <sub>4</sub> <sup>-</sup>                 | -678.0  | -200.4 | -878.4  |          |       |      |       | -3.3    | -4.6  | 0.7   | -7.2  | -907.3                       |
| Basis Set D <sup>a</sup>                       |         |        |         |          |       |      |       |         |       |       |       |                              |
| GaCl <sub>4</sub> <sup>-</sup>                 | -776.7  | -264.6 | -1041.4 | -3.3     | -12.2 | -7.2 | -22.6 |         |       |       |       | -1131.8                      |
| GaBr <sub>4</sub> <sup>-</sup>                 | -779.5  | -246.0 | -1025.5 |          |       |      |       | -1.4    | -12.5 | -10.0 | -23.9 | -1121.0                      |

<sup>a</sup> The definition of the basis set is given in the text.

Y = F, Cl, Br;  $n = 0-6$ ).<sup>2h</sup> Table VII summarizes the Mulliken population analysis. For the results of basis set A, the Cl  $\rightarrow$  Br substitution leads to a constant increase of ca. 0.031 for the 4p population and of ca. -28 ppm for  $\sigma^{\text{para}}$  (Ga p component). In the case of Nb complexes, the Cl  $\rightarrow$  Br substitution leads to an increase of ca. 0.092 for the 4d population and of ca. -141 ppm for  $\sigma^{\text{para}}$  (Nb d component). We have performed a unitary transformation of MOs to eliminate the s component in the polarization d functions. The resultant populations on the 4s and polarization d functions show only a slight change. Second is the largeness of the magnetically allowed  $\sigma \rightarrow \sigma^*$  transition energy  $\Delta E$  of the Ga complexes. The transition in the Ga complexes is the  $\sigma \rightarrow \sigma^*$  ( $p \rightarrow p^*$ ) transition of the Ga-X bonds, so it is larger than the  $d \rightarrow d^*$  transitions in the transition-metal complexes.<sup>1,2</sup> Third,

the energy levels of the bonding and antibonding MOs do not change much as the ligand is substituted. Figure 5 depicts the orbital energy levels of the Ga compounds obtained with basis set B. We assign  $2t_2$  and  $5t_2$  MOs as  $\sigma$  and  $\sigma^*$  MOs between the Ga 4p and ligand  $np$  orbitals. The change in the orbital energy is small in comparison with that observed for the Mo complexes,<sup>2c</sup> for example.

Finally, we note the basis set dependence of the paramagnetic term: generally, a better basis set tends to reduce the shift of the paramagnetic term when a ligand is replaced, thereby resulting in an overestimation of the chemical shift. For basis set D,  $\sigma^{\text{para}}$  of GaCl<sub>4</sub><sup>-</sup> becomes more negative than that of GaBr<sub>4</sub><sup>-</sup>, though this is not the case for the other basis sets. As seen in Table VI, the dependence is attributed to the Ga p contributions, though

TABLE VII: Mulliken AO Population Analyses for  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ )

| molecule                                       | gallium                  |       |                    |            | chlorine |       |       |            | bromine |       |       |            |
|--|--------------------------|-------|--------------------|------------|----------|-------|-------|------------|---------|-------|-------|------------|
|  | 4s <sup>a</sup>          | 4p    | pol d <sup>a</sup> | net charge | 3s       | 3p    | pol d | net charge | s       | p     | pol d | net charge |
|  | Basis Set A <sup>b</sup> |       |                    |            |          |       |       |            |         |       |       |            |
| GaCl <sub>4</sub> <sup>-</sup>                 | 0.565 (0.021)            | 1.323 | 0.770 (1.313)      | 0.439      | 1.922    | 5.449 |       | -0.360     |         |       |       |            |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 0.602 (0.161)            | 1.353 | 0.767 (1.208)      | 0.392      | 1.923    | 5.444 |       | -0.355     | 1.929   | 5.404 |       | -0.326     |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 0.641 (0.307)            | 1.384 | 0.766 (1.099)      | 0.343      | 1.923    | 5.440 |       | -0.351     | 1.930   | 5.398 |       | -0.320     |
| GaClBr <sub>3</sub> <sup>-</sup>               | 0.681 (0.460)            | 1.415 | 0.764 (0.985)      | 0.292      | 1.923    | 5.435 |       | -0.347     | 1.930   | 5.392 |       | -0.315     |
| GaBr <sub>4</sub> <sup>-</sup>                 | 0.722 (0.618)            | 1.447 | 0.763 (0.868)      | 0.239      |          |       |       |            | 1.930   | 5.387 |       | -0.310     |
|  | Basis Set B <sup>b</sup> |       |                    |            |          |       |       |            |         |       |       |            |
| GaCl <sub>4</sub> <sup>-</sup>                 | 0.653 (0.368)            | 1.606 | 0.703 (0.988)      | 0.187      | 1.910    | 5.414 |       | -0.297     |         |       |       |            |
| GaCl <sub>3</sub> Br <sup>-</sup>              | 0.695 (0.481)            | 1.618 | 0.707 (0.922)      | 0.140      | 1.911    | 5.410 |       | -0.292     | 1.918   | 5.353 |       | -0.263     |
| GaCl <sub>2</sub> Br <sub>2</sub> <sup>-</sup> | 0.734 (0.589)            | 1.630 | 0.714 (0.859)      | 0.092      | 1.911    | 5.405 |       | -0.288     | 1.918   | 5.348 |       | -0.258     |
| GaClBr <sub>3</sub> <sup>-</sup>               | 0.771 (0.693)            | 1.642 | 0.721 (0.799)      | 0.045      | 1.911    | 5.401 |       | -0.284     | 1.919   | 5.343 |       | -0.254     |
| GaBr <sub>4</sub> <sup>-</sup>                 | 0.805 (0.794)            | 1.654 | 0.731 (0.741)      | 0.000      |          |       |       |            | 1.919   | 5.338 |       | -0.250     |
|  | Basis Set C <sup>b</sup> |       |                    |            |          |       |       |            |         |       |       |            |
| GaCl <sub>4</sub> <sup>-</sup>                 | 0.662 (0.302)            | 1.242 | 0.626 (0.986)      | 0.639      | 1.949    | 5.488 |       | -0.410     |         |       |       |            |
| GaBr <sub>4</sub> <sup>-</sup>                 | 0.823 (0.799)            | 1.399 | 0.659 (0.683)      | 0.331      |          |       |       |            | 1.950   | 5.390 |       | -0.333     |
|  | Basis Set D <sup>b</sup> |       |                    |            |          |       |       |            |         |       |       |            |
| GaCl <sub>4</sub> <sup>-</sup>                 | 0.542 (0.188)            | 1.509 | 0.526 (0.879)      | 0.529      | 1.865    | 5.493 | 0.046 | -0.382     |         |       |       |            |
| GaBr <sub>4</sub> <sup>-</sup>                 | 0.649 (0.382)            | 1.519 | 0.525 (0.792)      | 0.430      |          |       |       |            | 1.896   | 5.425 | 0.116 | -0.358     |

<sup>a</sup> The values after eliminating the s component of d polarization function. The values in parentheses are the original values. <sup>b</sup> The definition of the basis set is given in the text.

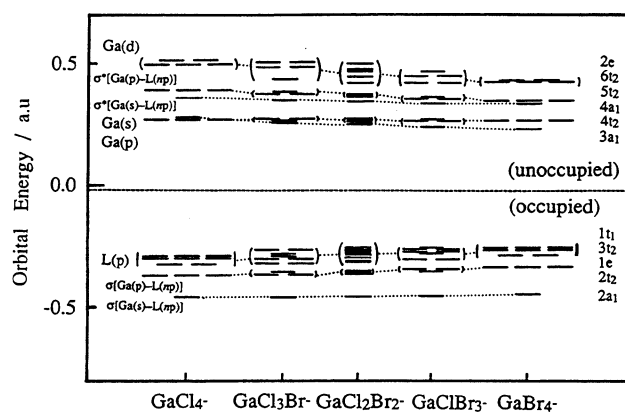


Figure 4. Dependence of the Ga p component of the paramagnetic term on the Ga 4p population.

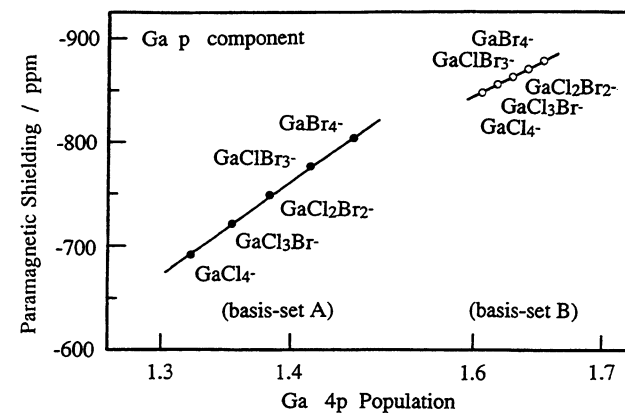


Figure 5. Orbital energy levels of  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ) calculated with basis set B.

we did not necessarily improve the basis set of the Ga atom. There exists some parallelism between  $\sigma^{\text{para}}$  and the AO population in the basis set dependence.

#### Importance of the Diamagnetic Term for the Group IIIb Tetrahalides

It is interesting to examine whether the conclusion that  $\sigma^{\text{dia}}$  determines the Ga chemical shift can be extended to related compounds. Here, we investigate the metal chemical shifts of the group IIIb elements aluminum, gallium, and indium as

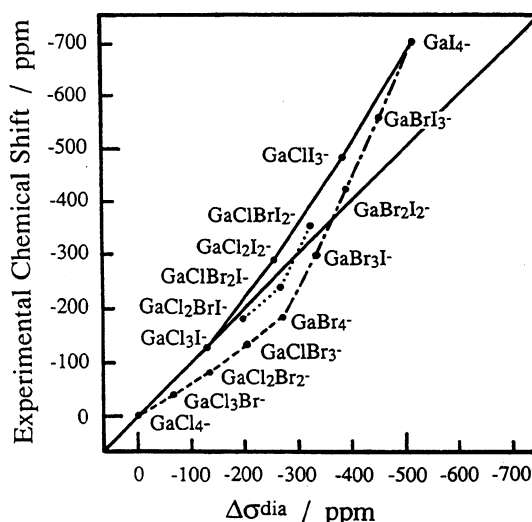


Figure 6. Correlation between  $\Delta\sigma^{\text{dia}}$  and the experimental chemical shift<sup>12,13</sup> for  $\text{GaX}_{4-n}\text{Y}_n^-$  ( $X, Y = \text{Cl, Br, I}$ ).

TABLE VIII: Ligand Contribution to the Diamagnetic Shielding Constant in  $\text{MX}_{4-n}\text{Y}_n^-$  ( $M = \text{Ga, Al, In}$ ;  $X, Y = \text{Cl, Br, I}$ ;  $n = 0-4$ ) Estimated from the Flygare-Goodisman Equation (in ppm)

| ligand | $\text{GaX}_{4-n}\text{Y}_n^-$ | $\text{AlX}_{4-n}\text{Y}_n^-$ | $\text{InX}_{4-n}\text{Y}_n^-$ |
|--------|--------------------------------|--------------------------------|--------------------------------|
| Cl     | 74.0                           | 74.6                           | 67.4                           |
| Br     | 142.1                          | 142.9                          | 132.6                          |
| I      | 202.5                          | 204.0                          | 183.7                          |

tetrahalides,  $\text{MX}_{4-n}\text{Y}_n^-$  ( $M = \text{Al, Ga, In}$ ;  $X, Y = \text{Cl, Br, I}$ ). Figures 6–8 show the correlation between the  $\Delta\sigma^{\text{dia}}$  calculated with the Flygare-Goodisman equation (eq 4) and the experimental metal chemical shift  $\delta^{\text{expd}}$  for Ga,<sup>13</sup> In,<sup>16</sup> and Al<sup>17</sup> compounds, respectively. The experimental bond distances<sup>9,10,18–20</sup> summarized in Table I are used in the calculation of  $\Delta\sigma^{\text{dia}}$ . Table VIII gives the calculated ligand contribution to the diamagnetic term.

For the Ga compounds shown in Figure 6, the points distribute along the 45° line, which means a good correlation between  $\Delta\sigma^{\text{dia}}$  and  $\delta^{\text{expd}}$ . Therefore, the diamagnetic term  $\Delta\sigma^{\text{dia}}$  is considered to be the origin of the Ga chemical shift even for the compounds containing iodine atom. Figure 7 indicates that, for the  $\text{InCl}_{4-n}\text{Br}_n^-$  series, the agreement with  $\delta^{\text{expd}}$  is excellent, but the In complexes with iodine ligand give large deviations from the 45° line. The points spread on the upper side of the figure, showing underes-

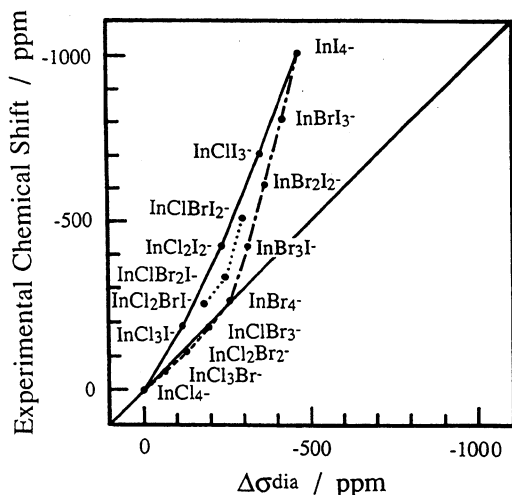


Figure 7. Correlation between  $\Delta\sigma^{\text{dia}}$  and the experimental chemical shift<sup>16</sup> for  $\text{InX}_{4-n}\text{Y}_n^-$  (X, Y = Cl, Br, I).

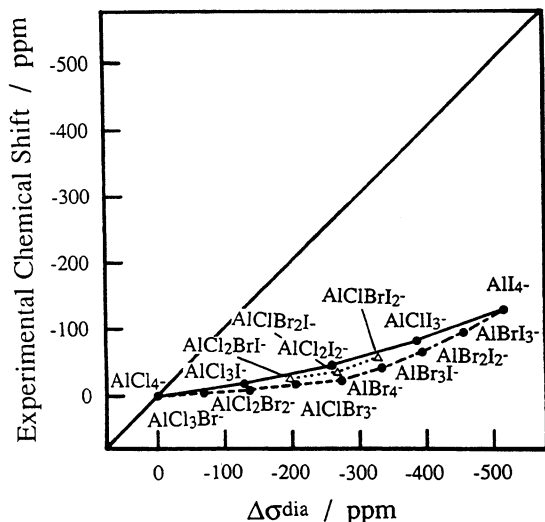


Figure 8. Correlation between  $\Delta\sigma^{\text{dia}}$  and the experimental chemical shift<sup>17</sup> for  $\text{AlX}_{4-n}\text{Y}_n^-$  (X, Y = Cl, Br, I).

timation of the experimental values. In Figures 6 and 7, the I-containing molecules are largely out of the 45° line, suggesting a strong relativistic effect of the iodine ligand. For the Al compounds, the distribution is on the lower side, and the calculated  $\Delta\sigma^{\text{dia}}$  no longer explains the chemical shifts: the Al chemical shifts cannot be explained without calculating  $\sigma^{\text{para}}$ . However, it should be stressed that, for all the compounds,  $\Delta\sigma^{\text{dia}}$  qualitatively simulates the observed trends of the NHD.

We also note some interesting features observed in these figures. All three plots give a similar pattern. The increment becomes larger in the order of the series  $\text{MCl}_{4-n}\text{Br}_n^- < \text{MBr}_{4-n}\text{I}_n^- < \text{MCl}_{4-n}\text{I}_n^-$ . In particular, the difference of the increments between two series of compounds seems to be amplified as the metal M becomes heavier. In both theory and experiment, the shift becomes larger in the order  $\text{Cl} \rightarrow \text{Br} < \text{Br} \rightarrow \text{I} < \text{Cl} \rightarrow \text{I}$ , which is readily understandable through eq 4. Based on our ab initio results, it is reasonable to expect that the dependence of  $\sigma^{\text{para}}$  on ligand substitution is similar to that in the Ga compounds. Although, for the Al compounds,  $\Delta\sigma^{\text{dia}}$  overestimates the experimental value,  $\sigma^{\text{para}}$  would cause the lower field shift. However, for the In compounds,  $\Delta\sigma^{\text{dia}}$  underestimates the experimental chemical shift, but the inclusion of  $\sigma^{\text{para}}$  would further enlarge this trend, and the calculated chemical shifts would become much worse. Therefore, some effects such as the spin-orbit interaction must be explicitly considered, particularly for the In

compounds,  $\text{InX}_{4-n}\text{I}_n^-$  (X = Cl, Br), to obtain results comparative with experiments.

We think that such heavy ligand shifts may be related to the "abnormal" higher field shift of proton chemical shift in hydrogen halides, which was theoretically investigated by Morishima, Endo, and Yonezawa.<sup>21</sup> They examined the spin-orbit effect for the chemical shift by a semiempirical MO method combined with third-order perturbation theory and showed that the spin-orbit contribution is a source of the larger upfield shift.

### Summary

We have studied the electronic origin of the Ga chemical shifts in  $\text{GaCl}_{4-n}\text{Br}_n^-$  ( $n = 0-4$ ) by the Hartree-Fock/finite perturbation method. The Ga chemical shift is determined by the diamagnetic contribution  $\sigma^{\text{dia}}$  rather than the paramagnetic one  $\sigma^{\text{para}}$ . This is in sharp contrast to the metal chemical shifts previously investigated. Since  $\sigma^{\text{dia}}$  is calculated by the Flygare-Goodisman equation to a good approximation, we conclude that the Ga chemical shifts in the  $\text{GaCl}_{4-n}\text{Br}_n^-$  series reflect the structural factors of the ligands: bond distance and nuclear charge. This explains the normal halogen dependence observed in these Ga compounds. The reason the paramagnetic contributions are so small may be attributed to the small variations in the valence electronic structure. We have also examined, using the Flygare-Goodisman equation, whether  $\sigma^{\text{dia}}$  is important for the metal chemical shifts of the group IIIb metal tetrahalides  $\text{MX}_{4-n}\text{Y}_n^-$  (M = Al, Ga, In; X, Y = Cl, Br, I). We have shown that  $\Delta\sigma^{\text{dia}}$  qualitatively explains the normal halogen dependence experimentally observed for these compounds.

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