Reprinted from The Journal of Physical Chemistry, 1995, 99.



# Theoretical Study on Metal NMR Chemical Shifts. Arsenic and Antimony Compounds

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*Received: November 16, 1994; In Final Form: February 28, 1995*[⊗]

The group XV As and Sb chemical shifts of the compounds $AsCl_xF_{6-x}^-$ ($x = 0-6$), $AsO_4^{3-}$, $AsMe_4^+$, $SbCl_xF_{6-x}^-$ ($x = 0-6$), $SbS_4^{3-}$, $SbMe_4^+$, $SbCl_5$, and $Sb(OH)_6^-$ are theoretically investigated by the ab initio Hartree−Fock/finite perturbation method. The calculated values are in good agreement with the experimental ones: large basis sets including FOBFs (first order basis functions) proposed previously are necessary to accomplish this agreement. Theoretical analysis reveals that the As and Sb chemical shifts are mainly dominated by the paramagnetic term and are due to the p-electron mechanism, that is, the shifts are parallel with the number of the valence p-electrons at the As and Sb atoms. As the coordination number increases, the valence p-electron population decreases and the chemical shift shows an upfield shift. In the four-coordinate compounds the major factor of the p-mechanism is the excitation energy. The U-shaped relationship observed for the $MCl_xF_{6-x}^-$ compounds (M = As and Sb; $x = 0-6$) reflects the change in the valence p-electron density of the metal.

## Introduction

In recent years, multinuclear NMR methods, which deal with all kinds of nuclei in the periodic table, have been extensively utilized in the fields of science, technology, biology, and medical science, and much experimental data for almost all nuclei has been accumulated.[1-6] The chemical shift is the property that sensitively reflects the electronic structure near the nucleus and therefore includes much information on the electronic structure of the molecule. For utilizing such information from accumulated experimental data, it is necessary to theoretically clarify the electronic mechanisms of the chemical shifts, which is one purpose of this series of studies.[7-17] A review was published in ref 7c.

In this series of studies, we have investigated the metal NMR chemical shifts of various complexes using the ab initio Hartree−Fock/finite perturbation method. We have found that the origin and the mechanism of the chemical shifts are intrinsic properties of the metal atom itself and therefore are closely related with the position of the metal atom in the periodic table. We have presented so far four distinct mechanisms. First is the p-electron and d-hole mechanism for the complexes of Cu, Ag, Zn, and Cd atoms characterized by $d^{10}s^{1-2}p^0$ configurations,[8] second is the d-excitation mechanism for the complexes of the transition metal atoms Ti,[9] Nb,[10] Mn,[11] and Mo[12] having $d^n$ configurations, third is the p-mechanism (p-electron and p-hole mechanisms) for the complexes of Si,[13] Ge,[14] Sn,[15] and Se[16] having $s^2p^{2,4}$ configurations, and fourth is the diamagnetic mechanism for the complexes of Ga and In[17] having $s^2p^1$ configuration. In other laboratories, Ditchfield *et al.*,[18] Tossell *et al.*,[19] Barfield *et al.*,[20] and Malkin *et al.*[21] have studied the Si, Zn, Mo, and V chemical shifts, respectively, and the basis set dependence of the chemical shift in some Se compounds has also been investigated.[21,22]

One of the groups which has not yet been theoretically investigated is group XV, including arsenic and antimony, whose electronic structure is $s^2p^3$. The elements of this group are very useful; for example, GaAs is widely used as a semiconductor material, and $AsF_5$ and $SbF_5$ are known as superacids. Then, the experimental data for the As and Sb chemical shifts are increasing.[1,2,5,23] In this paper, we theoretically study the NMR chemical shifts of the As and Sb compounds and analyze the electronic mechanism of the As and Sb chemical shifts. We calculate the chemical shifts of the four-, five-, and six-coordinate compounds, $AsCl_xF_{6-x}^-$ ($x = 0-6$), $AsO_4^{3-}$, $AsMe_4^+$, $SbCl_xF_{6-x}^-$ ($x = 0-6$), $SbS_4^{3-}$, $SbMe_4^+$, $SbCl_5$, and $Sb(OH)_6^-$.

## Method of Calculation

We calculate the magnetic shielding constant $\sigma$ of the As and Sb compounds by the ab initio Hartree−Fock/finite perturbation method.[24] The details of this method were described in a previous paper.[8a] The geometries of the As and Sb compounds were optimized at the RHF level, and the excitation energies were calculated at the single-excited CI (SECI) level. The programs used were HONDO7[25] and HONDO8[26] for geometry optimization and GAUSSIAN92[27] for the SECI calculations.

Basis functions used are as follows. For geometry optimizations, the basis sets are taken from the book of Huzinaga *et al.*[28] The triple-$\zeta$ sets plus double polarization functions are used for metals; the (13s10p4d)/[6s5p1d] set plus polarization d functions with the exponent of 0.129 and 0.434 for arsenic and the (16s13p7d)/[7s6p2d] set plus polarization d functions with the exponent of 0.088 and 0.277 for antimony. The double-$\zeta$ sets are used for ligands; the (9s5p)/[3s2p] set for carbon, fluorine, and oxygen, the (11s8p)/[4s3p] set for chlorine and sulfur, and the (4s)/[2s] set with the scale factor 1.2 for hydrogen. For calculating the chemical shifts and the excitation energies, the same basis functions are used for As and Sb and Pople's 6-31G basis set[29] plus first-order higher angular momentum d basis functions (d-FOBFs),[30] which are explained below, are used for C, F, and O, and Pople's 66-31G basis set[31] plus d-FOBFs for Cl and S. For H, which is non-neighboring to the metal, we use the basis set that is the same as the one used for geometry optimization.

The gauge origin is located on the central As and Sb metals. The reason for adding d-FOBFs on the atoms that neighbor the

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⊗ Abstract published in *Advance ACS Abstracts*, April 15, 1995.

0022-3654/95/2099-7951$09.00/0 

**TABLE 1: Optimized Geometrical Parameters of the Arsenic and Antimony Compounds**

| compd | symmetry | bond length[a] | bond angles[b] |
|---|---|---|---|
| $AsCl_6^-$ | $O_h$ | As−Cl = 2.299 | |
| $AsCl_5F^-$ | $C_{4v}$ | As−Cl = 2.298,[c] 2.287, As−F = 1.743 | ∠ClAsCl = 91.1, ∠ClAsF = 88.9 |
| *cis*-$AsCl_4F_2^-$ | $C_{2v}$ | As−Cl = 2.288,[d] 2.277,[e] As−F = 1.737 | ∠ClAsCl = 91.5,[g] ∠ClAsF = 89.7,[g] ∠FAsF = 89.4 |
| *fac*-$ASCl_3F_3^-$ | $C_{3v}$ | As−Cl = 2.280, As−Cl = 1.731 | ∠ClAsCl = 91.5, ∠ClAsF = 89.4, ∠FAsF = 89.4 |
| *cis*-$AsCl_2F_4^-$ | $C_{2v}$ | As−Cl = 2.270, As−F = 1.733,[e] 1.727[f] | ∠ClAsCl = 91.8, ∠ClAsF = 89.8,[g] ∠FAsF = 90.0[g] |
| $AsClF_5^-$ | $C_{4v}$ | As−Cl = 2.266, As−F = 1.724,[c] 1.728 | ∠ClAsF = 90.1, ∠FAsF = 89.9 |
| $AsF_6^-$ | $O_h$ | As−F = 1.726 | |
| $AsO_4^{3-}$ | $T_h$ | As−O = 1.711 | |
| $AsMe_4^+$ | $T_h$ | As−C = 1.915, C−H = 1.082 | |
| $SbCl_6^-$ | $O_h$ | Sb−Cl = 2.430 | |
| $SbCl_5F^-$ | $C_{4v}$ | Sb−Cl = 2.422,[c] 2.420, Sb−F = 1.928 | ∠ClSbCl = 91.3, ∠ClSbF = 88.7 |
| *cis*-$SbCl_4F_2^-$ | $C_{2v}$ | Sb−Cl = 2.378,[d] 2.380,[e] Sb−F = 1.886 | ∠ClSbCl = 91.8,[g] ∠ClSbF = 89.6,[g] ∠FSbF = 88.9 |
| *fac*-$SbCl_3F_3^-$ | $C_{3v}$ | Sb−Cl = 2.402, Sb−F = 1.919 | ∠ClSbCl = 92.2, ∠ClSbF = 89.7, ∠FSbF = 88.4 |
| *cis*-$SbCl_2F_4^-$ | $C_{2v}$ | Sb−Cl = 2.371, Sb−F = 1.879,[e] 1.887[f] | ∠ClSbCl = 92.2, ∠ClSbF = 89.9,[g] ∠FSbF = 89.3[g] |
| $SbClF_5^-$ | $C_{4v}$ | Sb−Cl = 2.387, Sb−F = 1.910,[c] 1.911 | ∠ClSbF = 90.6, ∠FSbF = 89.4 |
| $SbF_6^-$ | $O_h$ | Sb−F = 1.907 | |
| $SbS_4^{3-}$ | $T_h$ | Sb−S = 2.414 | |
| $SbMe_4^+$ | $T_h$ | Sb−C = 2.124, C−H = 1.082 | |
| $SbCl_5$ | $D_{3h}$ | Sb−Cl = 2.397,[c] 2.351 | |
| $Sb(OH)_6^-$ | $C_1$ | Sb−O = 1.975,[g] O−H = 0.952[g] | ∠HOSb = 117.05[g] |

[a] The bond length is given in angstroms. [b] The angles are in degrees. [c] The bond along the main rotation axis. [d] The bond at the Cl−M−Cl bond (M = As, Sb). [e] The bond at the Cl−M−F bond (M = As, Sb). [f] The bond at the F−M−F bond (M = As, Sb). [g] Given in the average value.

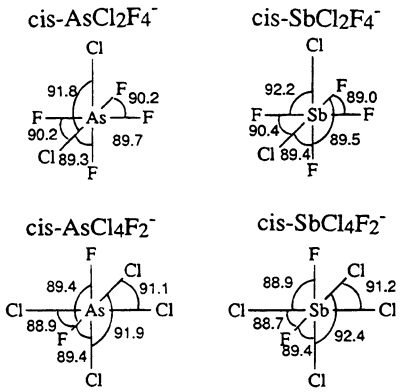


**Figure 1.** The calculated angular parameters (degrees) for some As and Sb compounds. Other details are given in Table 1.

metal is as follows.[30] One of the troubles in calculating chemical shifts is the gauge dependence arising from the basis set incompleteness. To overcome this problem, we may use the gauge invariant atomic orbitals (GIAOs),[32] or we may add the first-order higher angular momentum basis functions (FOBFs) $\{r\chi\}$, which are the first-order terms obtained by expanding the GIAOs.[30] The FOBFs of the valence s and p functions are the p and d functions, respectively. In the Poples 6-31G and 66-31G basis sets the same exponent are used for *n*s, *n*p, and *n*d functions, so that only the FOBFs of the outermost functions must be included. For the ligand atoms that neighbor the metals, the FOBFs for the present compounds are the d functions. Therefore, including these d-FOBFs, we can expect an improvement in the gauge dependence and the basis set dependence.[30,33]

## Geometry Optimizations

The geometrical parameters used in this paper are fully optimized since the experimental geometry has not been reported for most of the compounds and furthermore the six-coordinate compounds containing fluorine may be distorted from the octahedral symmetry. In Table 1 and Figure 1, we summarize the optimized geometrical parameters of the As and Sb compounds adopted in this study. The experimental bond distances[34] are As−F = 1.80 ± 0.05 Å for $AsF_6^-$ and As−Cl = 2.21 Å for $AsCl_6^-$, in comparison with the optimized values 1.726 and 2.299 Å, respectively, suggesting that the optimized geometries are reliable.

We note some characteristics in the geometry of these compounds, particularly of $MCl_xF_{6-x}^-$ (M = As and Sb; $x$ = 0−6). First, the ligand−metal−ligand angles are ∠ClMCl > ∠ClMF > ∠FMF, for example, ∠ClAsCl, ∠ClAsF, and ∠FAsF at *cis*-$AsCl_4F_2^-$ are 91.5°, 89.7°, and 89.4°, respectively. This fact is explained by the substituent effect in the ESF (electrostatic force) theory.[35] The distortions of the valence angle from the octahedral one are small and are only 2° or 3°. Second, when F is replaced with Cl, both M−F and M−Cl bonds are elongated. For example, the F−As bond length in the F−As−Cl 3c−4e bond of $AsClF_5^-$, *cis*-$AsCl_2F_4^-$, *fac*-$AsCl_3F_3^-$, *cis*-$AsCl_4F_2^-$, and $AsCl_5F^-$ are 1.724, 1.727, 1.731, 1.737, and 1.743 Å, respectively, showing that as the number of Cl ligands increases instead of F around the As atom, the F−As bond length increases. This may be due to the steric effect. In the case of Sb compounds, the F−Sb bond length in the F−Sb−Cl bond at $SbClF_5^-$, *cis*-$SbCl_2F_4^-$, *fac*-$SbCl_3F_3^-$, *cis*-$SbCl_4F_2^-$, and $SbCl_5F^-$ are 1.910, 1.879, 1.919, 1.886, and 1.928 Å, respectively, showing that the increase in the number of the ligand substitutions is not proportional to the F−Sb bond length, since the Sb atom is large enough.

These characteristics are also related to the electronegativity (F, 4.10; Cl, 2.83; As, 2.20; Sb, 1.82).[36] The differences in electronegativity between ligands and As are $\chi_F - \chi_{As} = 1.90$ and $\chi_{Cl} - \chi_{As} = 0.63$; the former is large and the latter is small. In the case of Sb, on the other hand, $\chi_F - \chi_{Sb} = 2.28$ and $\chi_{Cl} - \chi_{Sb} = 1.01$, both of which are relatively large. Then the metal net charge changes much in the As series (+1.09 for $x = 6$ and +2.75 for $x = 0$), but only little in the Sb series (+2.35 for $x = 6$ and +2.75 for $x = 0$).

## Comparison with the Experimental Chemical Shifts

The chemical shift $\delta$ is defined by

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

where $\sigma^{ref}$ is the magnetic shielding constant of the reference compound. The magnetic shielding constant is the sum of the diamagnetic term $\sigma^{dia}$ and the paramagnetic term $\sigma^{para}$,

$$\sigma = \sigma^{dia} + \sigma^{para} \quad (2)$$

The diamagnetic term represents the structural factor, and the

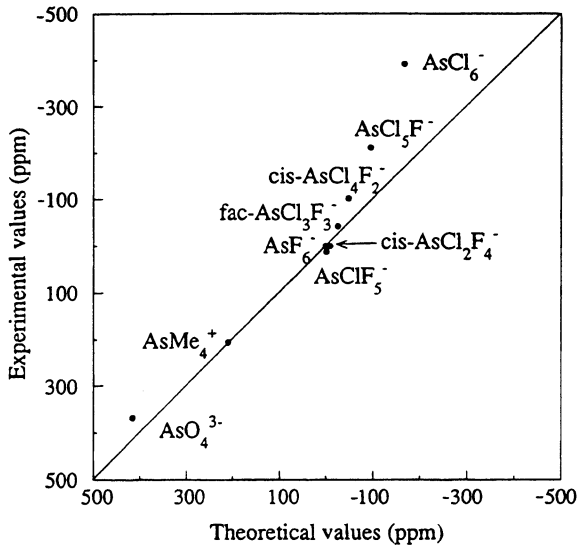


**Figure 2.** Correlation between the experimental and theoretical values of the As chemical shifts.

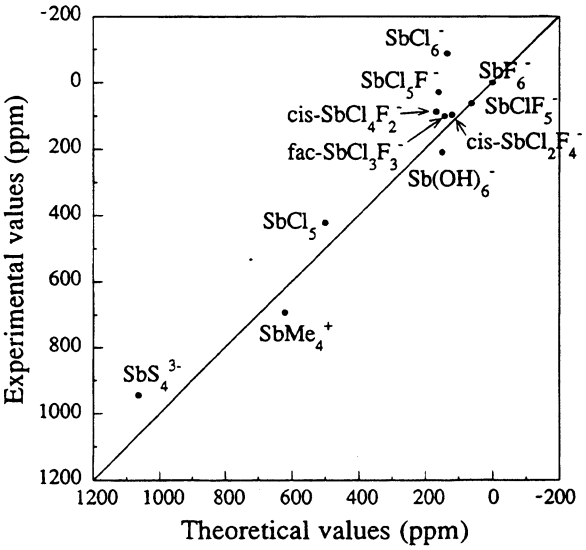


**Figure 3.** Correlation between the experimental and theoretical values of the Sb chemical shifts.

paramagnetic term represents the electronic factor.[7c] In the perturbation theory,[37] $\sigma^{para}$ is given by

$$\sigma^{para}_{N_{xy}} = -\sum_{n}\frac{1}{E_n - E_0}\{\langle 0|\sum_j L_{jx}|n\rangle\langle n|\sum_j L_{N_jy}/r_{N_j}^3|0\rangle + \text{c.c.}\} \quad (3)$$

where $N$ is the nucleus, $x$ and $y$ denote the $x$ and $y$ axes, $L$ is the angular momentum operator, $|0\rangle$ and $|n\rangle$ are the wave functions for the ground and excited states, respectively, with $n$ running over the excited states, and c.c. is the complex conjugate. Since the $\sigma^{para}$ obtained by the finite perturbation method can be written in the form of eq 3, as shown previously,[38] we can analyze $\sigma$ values in terms of the perturbation concept.

The correlations between the theoretical and experimental values of the As and Sb chemical shifts are shown in Figures 2 and 3, respectively. We choose $AsF_6^-$ and $SbF_6^-$ as the reference compounds, respectively, so that we can easily compare the As and Sb chemical shifts. Our calculated values are in fair agreement with the experimental ones. We found that the FOBFs are important for obtaining better agreement with experiments. The average deviation from the experimental values for some Sb compounds was 192 ppm before including FOBFs on the ligands, while it is 89 ppm after including the FOBFs. For $SbF_6^-$ and $SbCl_6^-$ which have $O_h$ symmetry, the calculated shielding constant is gauge-origin independent because the rotational irreducible representation is different from the translational one. Therefore, the important role of the FOBFs is to expand the variational space of the basis functions more effectively and thereby improve the calculated values. The theory and the detailed analysis of the roles of the FOBFs were given in the previous papers.[30,33]

Figure 4 shows the comparison between theoretical and experimental values of $MCl_xF_{6-x}^-$ ($x = 0-6$) for M = As (a) and M = Sb (b). The U-shaped relationship for the halogen substitution is reproduced in both cases. There are trans and meridional isomers in the case of $x = 2$, 4, and 3, but they are not specified in the experimental data.[23d] Our calculated average differences of the total energies and of the total magnetic shielding constants between isomers are 1.76 kcal/mol and 6.94 ppm, respectively, which are quite small. Therefore, we consider only the cis and facial isomers in the following sections.

## The Origin and the Mechanism of the As and Sb Chemical Shifts

We now analyze the origin and the mechanism of the As and Sb chemical shifts. The calculated chemical shifts are partitioned into the diamagnetic and paramagnetic terms, and both terms are further divided into the core and valence MO contributions. Here, the valence MOs represent the higher occupied MO's composed of the metal valence *n*s, *n*p and (*n* − 1)d AOs and the ligand valence *m*s and *m*p AOs.

Table 2 shows the core and valence electron contributions to the chemical shifts and Figure 5 is the illustration for the halogen-substituted compounds. The horizontal axis denotes the number of Cl atoms, the vertical axis the change in the magnetic shielding constant ($\Delta\sigma$). We see that the variation in the chemical shift is dominated by the core orbital contributions to the diamagnetic term and the valence orbital contributions to the paramagnetic term. Figure 5 clearly shows that the U-shaped relationship originates from the valence MO contributions to the paramagnetic term.

Table 3 shows the analysis of the As and Sb magnetic shielding constants into the AO contributions; the metal s, p, and d orbitals contributions and the ligand contributions. Since the metal s orbital has no angular momentum, its paramagnetic contribution is identically zero. The paramagnetic contributions of the metal p orbitals show the largest variation due to the ligand substitution and therefore the largest contribution to the chemical shift. On the other hand, the metal d contribution and the ligand contribution to $\sigma^{para}$ are comparatively small, and the $\sigma^{dia}$ contributions of the metals are almost zero. We then conclude that the As and Sb chemical shifts are mainly dominated by the metal p orbital contributions to the paramagnetic term. We note that the ligand contribution to the diamagnetic term is also appreciable, because our compounds involve the variations in six ligands. From the AO contributions shown in Figure 6 for the compounds $MCl_xF_{6-x}^-$ for M = As (a) and M = Sb (b) we see that the major factors of the chemical shifts are the ligand contribution to $\sigma^{dia}$ and the metal p orbital contribution to $\sigma^{para}$. These two contributions show opposite dependence on the number of the ligands. On the other hand, the origin of the U-shaped dependence is the metal p orbital contribution to $\sigma^{para}$.

We find in Table 2 and Figure 4 that the change in the diamagnetic term is nearly the same in the As and Sb chemical

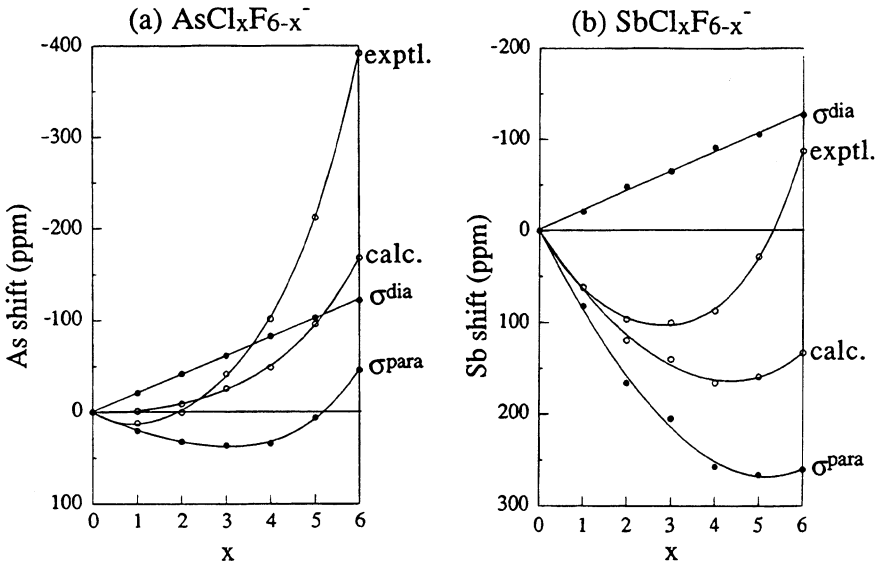


**Figure 4.** Origin of the U-shaped relationship in the chemical shifts of (a) $AsCl_xF_{6-x}^-$ and (b) $SbCl_xF_{6-x}^-$ compounds.

**TABLE 2: Core and Valence Orbital Contributions to the As and Sb Magnetic Shielding Constants (in ppm)**

| | $\sigma^{dia}$ | | | | $\sigma^{para}$ | | | | $\sigma^{total}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | core | valence | total | shift[a] | core | valence | total | shift[a] | total | shift[a] | exptl[b] |
| $AsCl_6^-$ | 2727 | 558 | 3285 | −122 | −69 | −1262 | −1331 | −46 | 1954 | −168 | −392 |
| $AsCl_5F^-$ | 2698 | 568 | 3266 | −103 | −70 | −1313 | −1383 | 6 | 1882 | −96 | −212 |
| *cis*-$AsCl_2F_4^-$ | 2668 | 577 | 3246 | −83 | −70 | −1341 | −1411 | 34 | 1835 | −49 | −102 |
| *fac*-$AsCl_3F_3^-$ | 2638 | 587 | 3225 | −62 | −68 | −1344 | −1413 | 36 | 1812 | −26 | −42 |
| *cis*-$AsCl_2F_4^-$ | 2608 | 597 | 3205 | −42 | −67 | −1342 | −1409 | 32 | 1796 | −9 | 0 |
| $AsClF_5^-$ | 2578 | 607 | 3184 | −21 | −65 | −1332 | −1397 | 20 | 1787 | −1 | 12 |
| $AsF_6^-$ | 2547 | 616 | 3163 | 0 | −63 | −1315 | −1377 | 0 | 1786 | 0 | 0 |
| $AsO_4^{3-}$ | 2526 | 530 | 3056 | 107 | −72 | −1613 | −1685 | 308 | 1371 | 415 | 369 |
| $AsMe_4^+$ | 2521 | 507 | 3028 | 135 | −67 | −1384 | −1451 | 74 | 1577 | 209 | 206 |
| $SbCl_6^-$ | 5172 | 433 | 5605 | −127 | −116 | −2031 | −2147 | 260 | 3458 | 133 | −87 |
| $SbCl_5F^-$ | 5144 | 440 | 5584 | −106 | −114 | −2038 | −2153 | 266 | 3432 | 159 | 28 |
| *cis*-$SbCl_2F_4^-$ | 5118 | 451 | 5569 | −91 | −114 | −2030 | −2144 | 257 | 3425 | 166 | 87 |
| *fac*-$SbCl_3F_3^-$ | 5087 | 456 | 5543 | −65 | −110 | −1982 | −2092 | 205 | 3451 | 140 | 100 |
| *cis*-$SbCl_2F_4^-$ | 5059 | 466 | 5526 | −48 | −108 | −1945 | −2053 | 166 | 3472 | 119 | 96 |
| $SbClF_5^-$ | 5028 | 471 | 5499 | −21 | −103 | −1866 | −1969 | 82 | 3530 | 61 | 62 |
| $SbF_6^-$ | 4999 | 479 | 5478 | 0 | −100 | −1787 | −1887 | 0 | 3591 | 0 | 0 |
| $SbS_4^{3-}$ | 5096 | 371 | 5467 | 11 | −138 | −2802 | −2940 | 1053 | 2527 | 1064 | 945 |
| $SbMe_4^+$ | 4976 | 380 | 5355 | 123 | −112 | −2274 | −2386 | 499 | 2969 | 621 | 693 |
| $SbCl_5$ | 5138 | 406 | 5544 | −66 | −123 | −2330 | −2454 | 567 | 3091 | 500 | 422 |
| $Sb(OH)_6^-$ | 4997 | 467 | 5464 | 14 | −106 | −1915 | −2021 | 134 | 3443 | 148 | 209 |

[a] $AsF_6^-$ and $SbF_6^-$ are chosen as the reference compounds: $SbF_6^-$ is chosen in order to compare easily with the As chemical shift (experimentally $SbCl_6^-$ is the reference compound). [b] References 1, 2, 5, and 23.

shifts, as expected from the Flygare and Goodisman's equation,[39] while the change in the paramagnetic term is larger in the Sb compounds than in the As compounds. The paramagnetic contribution to the chemical shift is more important in the Sb chemical shift than in the As chemical shift.

We will now discuss more details of the diamagnetic and paramagnetic contributions.

### Diamagnetic Contributions

The diamagnetic term is almost entirely determined by the structural factors alone, as shown in the previous papers of this series.[7c,15a,17] Using Flygare and Goodisman's equation,[39] we can reproduce the diamagnetic terms in good agreement with the ab initio values. All we need there are the molecular geometry and the nuclear species involved. We have also confirmed this for the present compounds but omit the data to avoid duplication. Because most of the present molecules are six-coordinate compounds, the diamagnetic term becomes somewhat important, though the most important one is the paramagnetic term.

### Paramagnetic Contributions

For the As and Sb chemical shifts, the metal valence p orbital contribution to the paramagnetic term is dominant in every case for the four-, five-, and six-coordinate compounds. The paramagnetic term given by eq 3 can be much simplified when we introduce the average excitation energy approximation,[40,41] and we have previously shown[15a] that the p AO contribution to $\sigma^{para}$ is written as

$$\sigma^{para} = -(\text{constant})\frac{1}{\Delta E}\left\langle\frac{1}{r^3}\right\rangle_p\left(I - \frac{1}{6}I^2 + \frac{1}{6}A^2\right) \quad (4)$$

where $\Delta E$ is the average excitation energy, $\langle 1/r^3\rangle_p$ represents the expectation value of $r^{-3}$ over the p orbitals of the metal, and the isotropic term $I$ and anisotropic term $A$ are defined as

$$I = D_{xx} + D_{yy} + D_{zz} \quad (5)$$

$$A = D_{zz} - 1/2(D_{xx} + D_{yy}) \quad (D_{zz} \geq D_{xx}, D_{yy}) \quad (6)$$

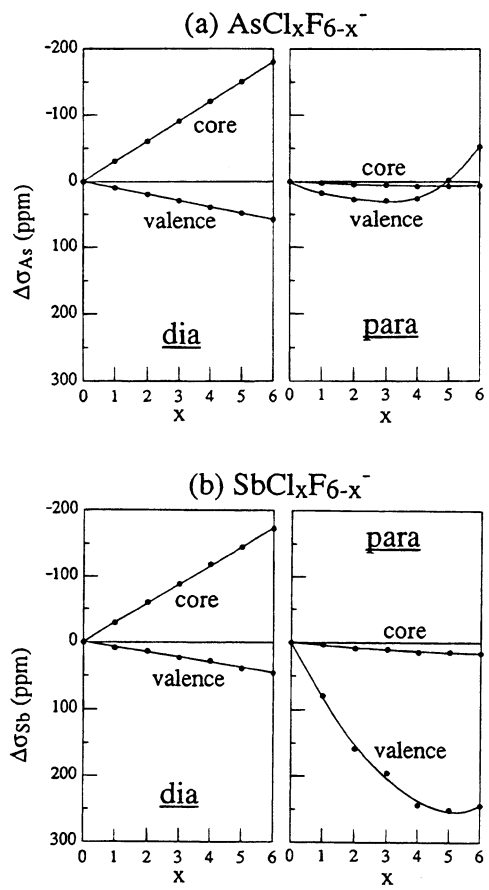


**Figure 5.** Core and valence electron contributions to the diamagnetic (left) and paramagnetic (right) terms for (a) $AsCl_xF_{6-x}^-$ and (b) $SbCl_xF_{6-x}^-$ compounds.

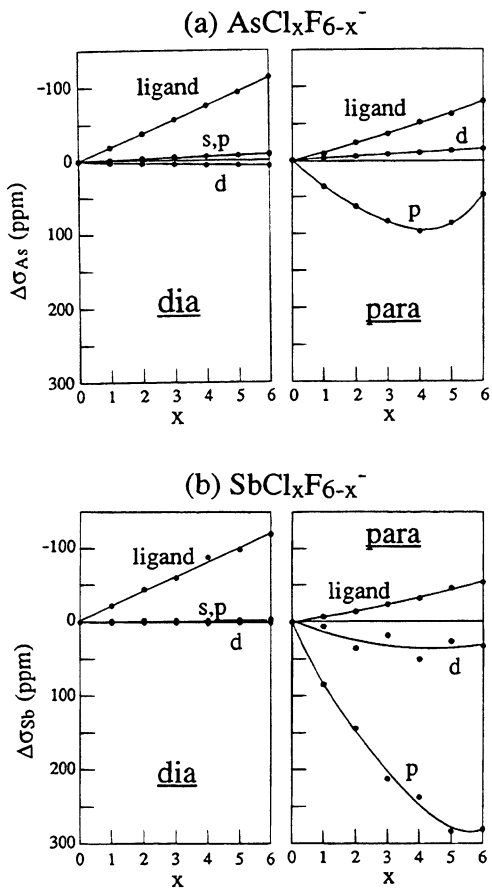


**Figure 6.** AO contributions to the diamagnetic (left) and paramagnetic (right) terms for (a) $AsCl_xF_{6-x}^-$ and (b) $SbCl_xF_{6-x}^-$ compounds.

**TABLE 3: AO Contributions to the As and Sb Magnetic Shielding Constants (in ppm)**

| | $\sigma^{dia}$ | | | | | $\sigma^{para}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | metal | | | | ligand | metal | | | | ligand |
| compd | s | p | d | total | total | s[a] | p | d | total | total |
| $AsCl_6^-$ | 1502 | 1014 | 342 | 2858 | 432 | 0 | −960 | −201 | −1171 | −168 |
| $AsCl_5F^-$ | 1500 | 1013 | 343 | 2856 | 412 | 0 | −999 | −203 | −1202 | −183 |
| *cis*-$AsCl_4F_2^-$ | 1499 | 1012 | 343 | 2854 | 394 | 0 | −1010 | −206 | −1216 | −194 |
| *fac*-$AsCl_3F_3^-$ | 1498 | 1010 | 344 | 2852 | 375 | 0 | −996 | −208 | −1204 | −210 |
| *cis*-$AsCl_2F_4^-$ | 1496 | 1008 | 345 | 2849 | 356 | 0 | −976 | −211 | −1187 | −222 |
| $AsClF_5^-$ | 1494 | 1007 | 346 | 2847 | 337 | 0 | −949 | −213 | −1162 | −237 |
| $AsF_6^-$ | 1492 | 1005 | 348 | 2845 | 318 | 0 | −913 | −216 | −1129 | −246 |
| $AsO_4^{3-}$ | 1496 | 1015 | 348 | 2859 | 196 | 0 | −1331 | −202 | −1533 | −152 |
| $AsMe_4^+$ | 1495 | 1019 | 340 | 2854 | 172 | 0 | −1204 | −138 | −1342 | −108 |
| $SbCl_6^-$ | 2414 | 1847 | 933 | 5194 | 408 | 0 | −1530 | −447 | −1977 | −168 |
| $SbCl_5F^-$ | 2413 | 1846 | 935 | 5194 | 387 | 0 | −1533 | −441 | −1974 | −176 |
| *cis*-$SbCl_4F_2^-$ | 2412 | 1845 | 936 | 5193 | 376 | 0 | −1487 | −465 | −1952 | −190 |
| *fac*-$SbCl_3F_3^-$ | 2413 | 1844 | 936 | 5193 | 348 | 0 | −1462 | −433 | −1895 | −198 |
| *cis*-$SbCl_2F_4^-$ | 2413 | 1843 | 936 | 5192 | 332 | 0 | −1394 | −450 | −1844 | −208 |
| $SbClF_5^-$ | 2413 | 1843 | 935 | 5191 | 310 | 0 | −1334 | −421 | −1755 | −215 |
| $SbF_6^-$ | 2414 | 1843 | 934 | 5191 | 288 | 0 | −1250 | −415 | −1665 | −222 |
| $SbS_4^{3-}$ | 2417 | 1855 | 934 | 5206 | 260 | 0 | −2519 | −316 | −2835 | −104 |
| $SbMe_4^+$ | 2414 | 1850 | 932 | 5196 | 156 | 0 | −1978 | −302 | −2280 | −104 |
| $SbCl_5$ | 2413 | 1848 | 934 | 5195 | 350 | 0 | −1909 | −407 | −2316 | −140 |
| $Sb(OH)_6^-$ | 2413 | 1843 | 938 | 5194 | 264 | 0 | −1341 | −470 | −1811 | −204 |

[a] The metal s orbital contribution is identically zero since the s orbital has no angular momentum.

with the use of the density matrix $D_{xx}$ etc. Though eq 4 is a very crude approximation of the paramagnetic term, we can qualitatively understand the behavior of $\sigma^{para}$ using this equation. For example, the paramagnetic value increases monotonously from $I = 0$ ($p^0$) to $I = 3$ ($p^3$, half-occupied) and decreases monotonously from $I = 3$ to $I = 6$ ($p^6$, fully occupied) as far as the anisotropic term A is small. The mechanisms of the Sn ($s^2p^2$) and Se ($s^2p^4$) chemical shifts, which are due to the p-mechanism (p-electron mechanism for the former[15] and the p-hole mechanism for the latter[16]), are understood with this idea. Using this equation we first examine the relationship between the chemical shift and the coordination number and then investigate the electronic origin of the chemical shift for each coordination number.

**A. Relationship between Chemical Shift and Coordination Number.** Table 4 lists the Mulliken AO population analysis for the As and Sb compounds, where d denotes the polarization d functions located on the metals. The electronic configurations of As and Sb metals are $s^2p^3d^0$ in the ground states. In the six-coordinate compounds, the valence p-electrons of the metals are pulled by the electron-withdrawing ligands, but in the four-coordinate compounds, the electrons in the s orbitals are strongly pulled. This is explained as follows. In the six-coordinate compounds, all ligands are bound to the central metal by the three-center, four-electron bond (3c−4e bond; the bond order is $^1/_2$) using metal *m*p orbitals so that the metal p-electrons are easily transferred to the ligands, while in the four-coordinate compounds the metal atoms form the $sp^3$ hybrid orbital (the bond order is 1) and both metal s- and p-electrons are pulled out. The calculated bond orders listed in Table 4 support this bonding picture. The 5p populations of the five-coordinate compound $SbCl_5$ is 1.74, which is the median between those of $SbF_6^-$ and $SbS_4^{3-}$, since the binding in the axial bond is the 3c−4e type and that in the equatorial bond is due to the $sp^2$ hybrid orbital.

The above analysis shows that the valence p-electron population decreases as the coordination number increases, which results in the upfield shift of $\sigma^{para}$ in this order, since the As

**TABLE 4: Mulliken Valence AO Population Analysis for the As and Sb Compounds**

| compd | coord no. | s | p | d[a] | net | bond order[b] | $\sigma^{para}$ (ppm) |
|---|---|---|---|---|---|---|---|
| $AsF_6^-$ | 6 | 0.111 | 0.955 | 1.250 | +2.745 | 0.67 | −1377 |
| $AsClF_5^-$ | 6 | 0.365 | 1.170 | 1.016 | +2.513 | 0.65−0.79 | −1397 |
| *cis*-$AsCl_2F_4^-$ | 6 | 0.631 | 1.404 | 0.797 | +2.350 | 0.63−0.86 | −1409 |
| *fac*-$AsCl_3F_3^-$ | 6 | 0.878 | 1.651 | 0.606 | +1.934 | 0.61−0.89 | −1413 |
| *cis*-$AsCl_4F_2^-$ | 6 | 0.992 | 1.833 | 0.596 | +1.651 | 0.59−0.94 | −1411 |
| $AsCl_5F^-$ | 6 | 1.116 | 1.981 | 0.615 | +1.361 | 0.61−0.93 | −1383 |
| $AsCl_6^-$ | 6 | 1.242 | 2.101 | 0.643 | +1.091 | 0.93 | −1331 |
| $AsO_4^{3-}$ | 4 | 0.411 | 2.169 | 1.537 | +0.965 | 1.52 | −1685 |
| $AsMe_4^+$ | 4 | 0.452 | 2.359 | 0.252 | +2.037 | 0.93 | −1451 |
| $SbF_6^-$ | 6 | 0.628 | 0.991 | 0.644 | +2.720 | 0.68 | −1887 |
| $SbClF_5^-$ | 6 | 0.512 | 1.001 | 0.794 | +2.670 | 0.65−0.73 | −1919 |
| *cis*-$SbCl_2F_4^-$ | 6 | 0.406 | 1.011 | 0.919 | +2.647 | 0.65−0.69 | −2053 |
| *fac*-$SbCl_3F_3^-$ | 6 | 0.340 | 1.147 | 1.016 | +2.470 | 0.69−0.70 | −2092 |
| *cis*-$SbCl_4F_2^-$ | 6 | 0.287 | 1.273 | 0.936 | +2.480 | 0.65−0.72 | −2144 |
| $SbCl_5F^-$ | 6 | 0.379 | 1.458 | 0.730 | +2.410 | 0.62−0.70 | −2153 |
| $SbCl_6^-$ | 6 | 0.553 | 1.617 | 0.466 | +2.348 | 0.65 | −2147 |
| $Sb(OH)_6^-$ | 6 | 0.441 | 1.093 | 1.300 | +2.142 | 0.84 | −2021 |
| $SbCl_5$ | 5 | 0.347 | 1.740 | 0.689 | +2.196 | 0.80−0.85 | −2454 |
| $SbS_4^{3-}$ | 4 | 0.741 | 2.970 | 0.830 | +0.451 | 1.36 | −2940 |
| $SbMe_4^+$ | 4 | 0.412 | 1.760 | 0.528 | +2.302 | 0.92 | −2386 |

[a] The letter d denotes the polarization d functions. [b] The bond order is the calculated value at RHF level.

**TABLE 5: Correlation between $\sigma^{para}$ and the $p_\sigma$−$p_\sigma$* Excitation Energy**

| compd | $\sigma^{para}$ (ppm) | $\Delta E$ (eV)[a,b] |
|---|---|---|
| $AsMe_4^+$ | −1451 | 11.43, 13.44 |
| $AsO_4^{3-}$ | −1685 | (8.63), 9.07, 9.80 |
| $SbMe_4^+$ | −2386 | 9.98, 12.30 |
| $SbS_4^{3-}$ | −2940 | (4.67), (7.02), 7.45, 7.65 |

[a] The excitation energy is calculated at the SECI level. Only the magnetically allowed excited states having the $T_1$ state are shown. [b] The data in parentheses are the (ligand n) → $\sigma$* excitation energies.

and Sb chemical shifts are due to the p-mechanism. This trend is very clearly seen in Figures 2 and 3.

**B. Four-Coordinate Compounds.** It is widely accepted that the metal chemical shifts of many transition metal compounds are governed by the d−d* excitation mechanism: Co,[42] Ti,[9] Nb,[10] Mn,[11] Mo[12] chemical shifts. We show in Table 5 the excitation energies of the four-coordinate As and Sb compounds calculated at the SECI level. All compounds have $T_d$ symmetry, so that only $T_1$ states are magnetically allowed. These excitations are from the $p_\sigma$-bonding orbitals to the $p_\sigma$-antibonding orbitals and may be referred to as the p−p* excitations. From this table we see that the orders of the excitation energies are $AsMe_4^+$ > $AsO_4^{3-}$ and $SbMe_4^+$ > $SbS_4^{3-}$. This order accords with the order of the paramagnetic term shown in Table 5, so that the origin of the chemical shift within the four-coordinate compounds may be considered to be the p-p* excitation energy difference. Note that the valence p-electron population shown in Table 4 does not explain the chemical shift. The reason is that the term $(I - {}^1/_6I^2 + {}^1/_6A^2)$ has the maximum value at $I = 3$, so the change of $\sigma^{para}$ is small when $I$ is close to 3. For example, the 4p populations in $AsMe_4^+$ and $AsO_4^{3-}$ are 2.359 and 2.169, respectively, and the difference is only 0.190. On the other hand, the 5p populations in $SbMe_4^+$ and $SbS_4^{3-}$ are 1.760 and 2.90, respectively, so this explains the order of $\sigma^{para}$ since the difference 1.210 is very large.

**C. U-Shaped Relationship in the Six-Coordinate Compounds.** Kidd reported[43] that the metal chemical shift shows monotonously downfield or upfield shifts on substitutions of the halogen ligand by heavier ones. He named the former the IHD (inverse halogen dependence) and the latter the NHD (normal halogen dependence). In group XV, Sb shows the NHD; for example, in the compounds $SbBr_xCl_{6-x}^-$, the chemical shift shows an upfield shift of about 400 ppm on the substitution of Br for Cl.[23c] Furthermore, he described that fluorine does not obey the NHD; for example, the orders of the downfield shifts are Cl > F > Br in the $^{11}B$ chemical shifts and Br > F > I in the $^{27}Al$, $^{29}Si$, and $^{119}Sn$ chemical shifts. The chemical shifts of the compounds $MCl_xF_{6-x}^-$ (M = As and Sb; $x = 0-6$) show a strong U-shaped relationship, and this is also the reason why fluorine does not obey the NHD.

For the Sn chemical shift, we have previously clarified the origin of the U-shaped relationship.[15a] In the As and Sb cases, the origin is not very clear. The density term $(I - {}^1/_6I^2 + {}^1/_6A^2)$ of eq 4 does not show a linear dependence. As the electronegativity change of the ligand is large in the $MCl_xF_{6-x}^-$ (M = As and Sb), the effect should not be linear, since the electronegative ligand pulls p-electrons from the metal p orbital which has only a limited number of electrons. The excitation energy term $\Delta E$ seems not to be an origin, in this case, because $(\Delta E)^{-1}$ calculated by the SECI method showed almost linear dependence on X.

We have recently found that the abnormal upfield shift in the some heavier halogen containing compounds is due to the spin−orbit effect.[44] We therefore expect that the chemical shifts for the heavier halogen substituted As and Sb compounds would be improved by considering the spin−orbit effect. Such a study is now underway.

Recently, Gauss reported that the electron correlation affects the $^{13}CF_4$ chemical shift significantly.[45] It is also interesting to investigate the correlation effect on the NHD and the U-shaped relationship.

For the IHD, we have already clearly shown that the Ti, Nb, and Mo chemical shifts are dominated by the $(\Delta E)^{-1}$ term for the d−d* transitions.[9-12]

## Summary

The As and Sb chemical shifts of the compounds $AsCl_xF_{6-x}^-$ ($x = 0-6$), $AsO_4^{3-}$, $AsMe_4^+$, $SbCl_xF_{6-x}^-$ ($x = 0-6$), $SbS_4^{3-}$, $SbMe_4^+$, $SbCl_5$ and $Sb(OH)_6^-$ have been investigated with the Hartree−Fock/finite perturbation method. The calculated values are in good agreement with the experimental ones. The first-order higher angular momentum basis functions (FOBFs) proposed previously[30] were important for obtaining such good agreement. We investigated the electronic mechanism of the chemical shifts, and the results may be summarized as follows.

(1) The As and Sb chemical shifts are mainly due to the p-mechanism. The metal valence p orbital contribution to the paramagnetic term is the origin of the chemical shift. It shows a downfield shift as the number of the valence p-electrons of the As and Sb atoms increases. This p-electron mechanism is common with the Ge and Sn chemical shifts.[14,15] For Se the chemical shift, the mechanism was the p-hole mechanism.[16] The p-electron mechanism is for the atoms having the configuration $s^2p^n$ with $n \leq 3$, and the p-hole mechanism is for $n > 3$.

(2) The valence p-electron population decreases as the coordination number increases, so that as a result of the p-electron mechanism, the chemical shift shows an upfield shift as the coordination number increases.

(3) Within the four-coordinate compounds, the change in the excitation energy is the major factor for the change in the paramagnetic term.

(4) The U-shaped relationship is due to a similar behavior of the paramagnetic term, which is caused by a nonlinear change of the As and Sb valence p-electron density derived caused by a substitution between the ligands whose electronegativity difference is very large. The spin−orbit effect would also be important for the U-shaped relationship.

**Acknowledgment.** We thank Mr. T. Higashioji for many helpful discussions. Part of the calculations have been carried out with the computers at the Institute for Molecular Science. Part of this study has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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