AB INITIO CALCULATION OF GEOMETRIES AND HFS CONSTANTS
OF CH_3, SiH_3, AND GeH_3 RADICALS

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Structures and hyperfine splitting (hfs) constants of the group IV AH_3 radicals, CH_3, SiH_3, and GeH_3, have been calculated by the pseudo-orbital (PO) theory. The optimized out-of-plane angle of SiH_3 is 16.1° and that of GeH_3 is 18.4°. In the group IV AH_3 radicals, SiH_3 was reported to be the most pyramidal from ESR measurement. In this study, however, GeH_3 is calculated to be the most pyramidal in these three radicals. Calculated hfs constants are in fair agreement with experiments except for GeH_3. Vibrational effect for the hfs constants is calculated to be large at the central element. The spin-polarization effect, considered by the PO theory, has been decomposed into shell contributions (inner shells and valence shells). The inner shell spin-polarizations for CH_3 and SiH_3 are not always small and vary largely with the molecular pyramidality. For GeH_3, the spin-polarization occurs mainly in the 4s valence shell and the inner shell contributions are negligibly small.

1. Introduction

The hyperfine splitting (hfs) constants of the AH_3 radicals, including the group IV elements as the central atom A, have been systematically studied experimentally [1] and, for methyl and silyl radicals, several ab initio studies have been performed [2,3]. The molecular structures of these AH_3 radicals, especially the out-of-plane angles have been discussed on the basis of the central atom s-character obtained from ESR measurements [1]. Gordy et al. reported the out-of-plane angles to be 0°, 15.1° and 13.1° for CH_3, SiH_3, and GeH_3, respectively. This sequence of pyramidality, however, seems to be rather irregular from the general consideration in the Walsh rule [4] and the electrostatic force (ESF) theory [5]. Due to the qualitative consideration based on the ESF theory, the out-of-plane angle will increase as the central element A becomes heavier in the group IV elements, the gap being large between C and Si and small among Si, Ge, and Sn.

In this study we perform ab initio calculations of the molecular geometry and hfs constant of these AH_3 (A = C, Si, Ge) radicals. The hfs constant has been calculated by the pseudo-orbital (PO) theory [6]. The

PO theory is a new open-shell orbital theory based on the symmetry-adapted-cluster (SAC) expansion theory [6] and includes open-shell spin-correlation effects correctly in comparison with the conventional open-shell orbital theories such as the unrestricted HF (UHF) [7] and the spin-extended (SE) HF [8] theory. In the previous studies [9], we applied the PO theory to the calculations of hfs constants of various open-shell atoms and organic and inorganic radicals and obtained fairly good results in comparison with experimental values. Ellinger et al. [3] have shown by ab initio calculation that the effect of vibration [10] is important for hfs constants. In this study, we also consider the effect of vibration on both the hfs constant and the out-of-plane angle. Lastly, inner shell contribution to the spin-polarization effect, which is interesting especially for heavier elements, is analyzed.

In the next section we briefly explain the method of calculation. The calculated molecular structures and hfs constants are given in section 3. The vibrational effect and the shell structure in the spin-polarization effect are discussed in sections 4 and 5 respectively. The conclusion of the present study is given in section 6.

2. Method of calculation

In the previous works [6,9], we have proposed the pseudo-orbital (PO) theory as a new open-shell orbital theory based on the symmetry-adapted-cluster (SAC) expansion theory. The SAC expansion theory and the PO theory have been discussed in detail in refs. [6] and [9], respectively.

The PO wavefunction for doublet radicals studied here is written as follows,

$$|\Psi_{PO3}\rangle = \hat{O}_{1/2} \exp\left[\sum_t \sum_k C_{P,tk} S_{P,tk}^+\right]|0\rangle , \qquad (1)$$

$$S_{P,tk}^+ = 3^{-1/2}\left[2^{-1/2}(a_{t\alpha}^+ a_{k\alpha} - a_{t\beta}^+ a_{k\beta})\right.$$
$$\left. + 2^{1/2} a_{t\alpha}^+ a_{k\beta} a_{m\beta}^+ a_{m\alpha}\right] , \qquad (2)$$

$$|0\rangle = \|\phi_1\alpha\phi_1\beta \dots \phi_k\alpha\phi_k\beta \dots \phi_q\alpha\phi_q\beta\phi_m\alpha\| , \qquad (3)$$

where $S_{P,tk}^+$ is a spin-adapted excitation operator which generates a spin-polarization configuration,

$$S_{P,tk}^+|0\rangle$$

$$= 3^{-1/2}(2^{-1/2}\|\phi_1\alpha\phi_1\beta \dots \phi_t\phi_k(\alpha\beta + \beta\alpha)\dots$$

$$\dots \phi_q\alpha\phi_q\beta\phi_m\alpha\|$$

$$+ 2^{1/2}\|\phi_1\alpha\phi_1\beta \dots \phi_k\alpha\phi_t\alpha \dots \phi_q\alpha\phi_q\beta\phi_m\beta\|) , \qquad (4)$$

on applying the reference wavefunction $|0\rangle$, which is restricted HF (RHF) wavefunction. The suffices k, m, and t denote doubly occupied, singly occupied and unoccupied orbitals, respectively. $\hat{O}_{1/2}$ is the projection operator on to the doublet spin space.

We have calculated spin density correct to second order in the coefficients

$$\rho(r) = \rho_{SD}(r) + \rho_{SP}(r) , \qquad (5)$$

$$\rho_{SD}(r) = N_0\langle 0|\hat{\rho}(r)|0\rangle = N_0|\phi_m(r)|^2 , \qquad (6)$$

$$\rho_{SP}(r) = \rho_{SP1}(r) + \rho_{SP2}(r)$$

$$= N_0\left[2\sum_I C_I\langle 0|S_I\hat{\rho}(r)|0\rangle\right.$$

$$\left. + \sum_{IJ} C_I C_J\langle 0|S_I\hat{\rho}(r)S_J^+|0\rangle\right] , \qquad (7)$$

where N_0 is a normalization factor and I denotes the

set of indices, (P, tk) of the wavefunction (1). $\hat{\rho}$ denotes a normalized spin density operator. The subscripts SD and SP mean spin-delocalization and spin-polarization contribution, respectively [11]. ρ_{SD} arises from the delocalization of the radical orbital ϕ_m and is always positive or zero. ρ_{SP} arises from the spin-polarization correction to the RHF wavefunction by the PO theory. It is either positive or negative. ρ_{SP1} is the first-order contribution and ρ_{SP2} is the second-order contribution. The hfs constant a^N in gauss units and the spin density $\rho(r_N)$ in atomic units are connected by the following relation,

$$a^N = (8\pi/3)(g_e/g_0)g_N\beta_N\rho(r_N) , \qquad (8)$$

in standard notation [9]. Specifically $a^H = 1592.2 \times \rho(H), a^C = 400.4\,\rho(C), a^{Si} = -316.3\,\rho(Si)$, and $a^{Ge} = -55.54\,\rho(Ge)$.

The basis set used in this study are contracted Gauss type functions (CGTO) of double-zeta quality. For carbon we used Huzinaga's (9s5p) set [12] contracted to (4s2p) set [2] and for hydrogen (4s) contracted to (2s) [9] with the scale factor 1.2. The silicon basis is Dunning's (6s4p) CGTO [13]. For germanium we used (14s10p6d) set contracted to (6s5p2d) [14].

The vibrational effects on the geometry and hfs constants were studied as follows. The expectation value of an operator $\hat{\Omega}(Q)$, which is a function of nuclear coordinate, for the vibrational wavefunction $\chi(Q)$ is obtained from the equation

$$\bar{\Omega} = \int\int\dots\int \chi^*(Q)\,\hat{\Omega}(Q)\chi(Q)\,dQ_1\,dQ_2\dots dQ_{3N-6} , \qquad (9)$$

where Q is a set of $3N-6$ normal coordinates, $\{Q_k\}_{k=1,3N-6}$. In this study, we constrained the molecular geometry of AH$_3$ to C$_{3v}$. Then the internal coordinates are out-of-plane angle θ and bond length r(AH). The hfs constant of AH$_3$ radical, especially for the central element A, is a sensitive function of the out-of-plane angle but not sensitive to the variation of bond length [3,10]. Here we discuss mainly the vibrational effect on the hfs constant of the central element A and the molecular pyramidality. Then we consider only the bending vibration and neglect the effect of the stretching mode, i.e., we approximate the hfs constant to be represented as a function of only the out-of-plane angle θ, i.e. $a(\theta)$. Then eq. (9) is approximated effectively as

$$\bar{a} = \int \chi^*(\theta)a(\theta)\chi(\theta)\,d\theta . \qquad (10)$$

The out-of-plane angle was also averaged by the equation

$$\bar{\theta} = \int \chi^*(\theta) |\theta| \chi(\theta) \, d\theta .$$ (11)

The vibrational wavefunction $\chi(\theta)$ was calculated on the basis of the one dimensional adiabatic potential obtained from the PO theory. The potential was expanded into polynomial function of the out-of-plane angle θ by the least-squares fitting method. The wavefunction of molecular vibration was approximated by a linear combination of harmonic oscillators and their expansion coefficients were determined variationally. The exponential factors of the harmonic oscillators were determined by minimizing the difference

$$|\langle H^2 \rangle - \langle H \rangle^2| .$$ (12)

The reduced mass, for the approximate inversion coordinate θ, is a function of θ itself. However, we can fix it, to a good approximation, to the value of the planar geometry, since the angular dependence of the reduced mass is small.

3. Energy and hfs constant adiabatic potential

The optimized geometries of CH_3, SiH_3 and GeH_3 radicals are given in table 1. The out-of-plane angles of SiH_3 and GeH_3 are calculated to be $16.1°$ and $18.4°$, respectively, which are larger than those estimated from the ESR measurement. The decrease in the out-of-plane angle from SiH_3 ($\theta = 15.1°$) to GeH_3 ($\theta = 13.1°$) estimated from the ESR measurement [1] was not reproduced.

Figs. 1a, 1b, and 1c show the adiabatic potential for the out-of-plane mode. The bond length was kept fixed to the optimized value shown in table 1. The potential curve of CH_3 is a single well as shown in fig. 1a. The energy lowering, due to the spin-correlation correction by the PO theory, is 4.9 kcal/mole at planar structure and decreases as the out-of-plane angle increases. The effect of the spin-correlation was found to be largest at the planar structure commonly for these AH_3 radicals. (This trend is understood by a simple orbital interaction picture which will be shown below.) The adiabatic potentials for SiH_3 and GeH_3 are double well as shown in figs. 1b and 1c.

Table 1
Structure and hfs constant of AH_3 radicals without vibrational averaging [a]

	CH_3	SiH_3	SiH_3 [b,c]	GeH_3
opt. geom. r (Å)	(1.079) [d]	1.472	1.477	1.554
θ (deg) [e]	0.0	16.1	16.4	18.4
hfs A (G)	39.4	−173.8	−177.6	−156.3
H (G)	−26.5	−10.1	−1.0	−8.4
inversion barrier (kcal/mole)	0.0	3.0	4.0	5.8
exp. geom. [f] r (Å)	1.079	1.48 (SiH$_4$)		1.53 (GeH$_4$)
θ (deg)	0.0	15.1		13.1
exp. hfs [f] A (G)	38.3	190		75 ± 3
H (G)	23.0	8.1 ± 0.5		15 ± 2
total energy (au) planar geometry ($\theta = 0°$) RHF	−39.5373	−290.5586	−290.5571 [g]	−2073.9163
PO	−39.5451	−290.5648	−290.5616 [g,c]	−2073.9248
opt. geom. RHF	−	−290.5673	−290.5663	−2073.9307
PO	−	−290.5696	−290.5680 [c]	−2073.9341

[a] Result of pseudo-orbital (PO) theory.   [b] Result of double-zeta CGTO in ref. [3a].
[c] Result of first-order-perturbation theory.   [d] Experimental bond length from ref. [15].   [e] Out-of-plane angle.
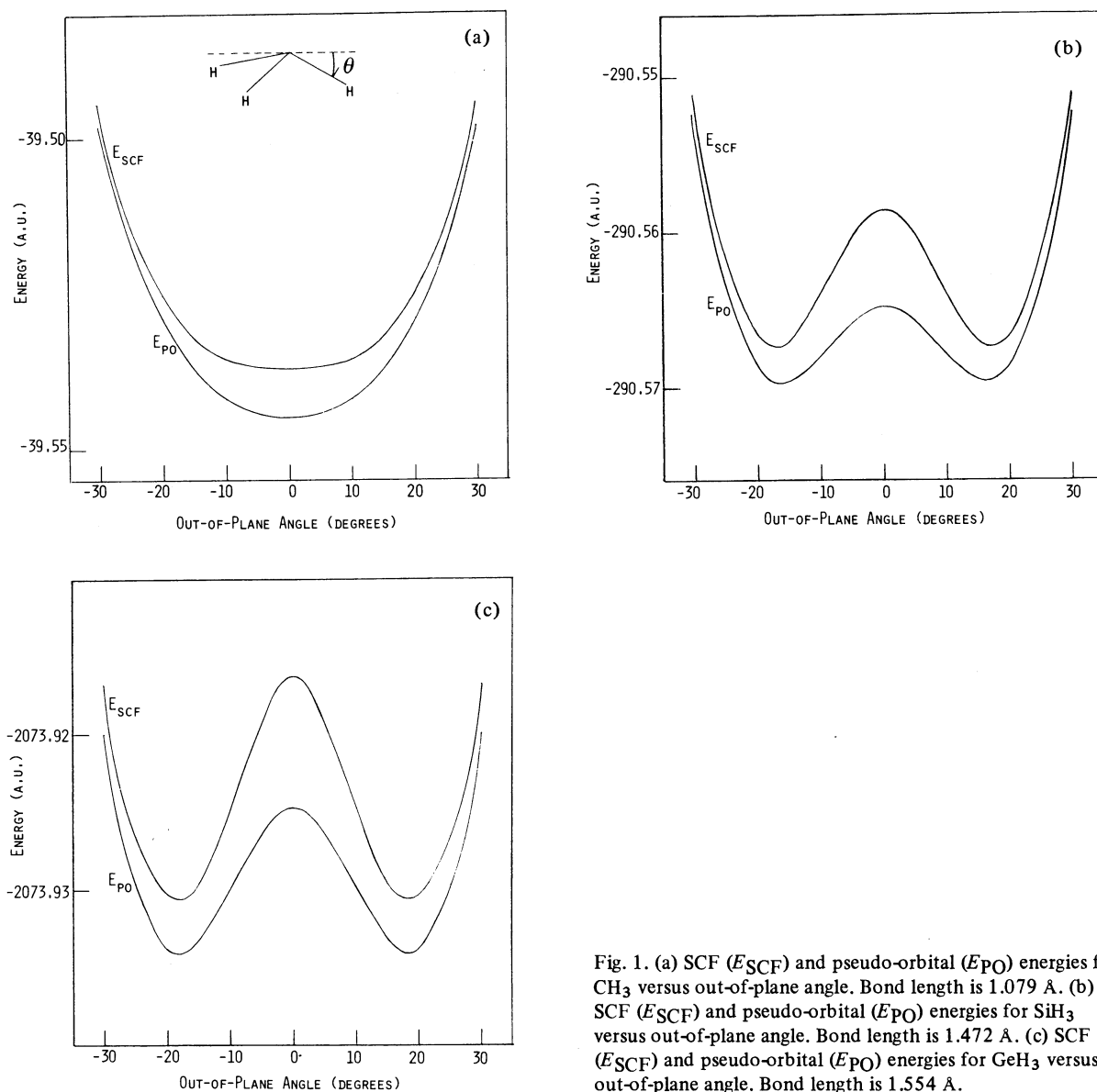[f] Ref. [1].   [g] r (Si–H) = 1.464 Å in ref. [3a].

Fig. 1. (a) SCF (E_{SCF}) and pseudo-orbital (E_{PO}) energies for CH_3 versus out-of-plane angle. Bond length is 1.079 Å. (b) SCF (E_{SCF}) and pseudo-orbital (E_{PO}) energies for SiH_3 versus out-of-plane angle. Bond length is 1.472 Å. (c) SCF (E_{SCF}) and pseudo-orbital (E_{PO}) energies for GeH_3 versus out-of-plane angle. Bond length is 1.554 Å.

The energy lowering due to the spin-correlation is 3.9 kcal/mole for SiH_3 and 5.3 kcal/mole for GeH_3 at planar structure. The inversion barrier is thus reduced to 3.0 kcal/mole for SiH_3 and 5.8 kcal/mole for GeH_3. Because of the small inversion barriers, we except large vibrational effect. Quantitative estimates will be given below.

hfs constants. In table 1, we show the hfs constants calculated by the PO theory at the optimized geome-

try. For CH_3 and SiH_3 radical fairly good results are obtained. On the other hand, the result of GeH_3 is rather poor. The hfs constant of Ge was calculated about twice as large as the experimental value.

The changes of hfs constants versus the out-of-plane angle are shown in figs. 2a, 2b, and 2c. In these figures, SD is the spin-delocalization contribution and SP is the spin-polarization contribution. Total hfs is the sum of these two contributions. Though the inversion
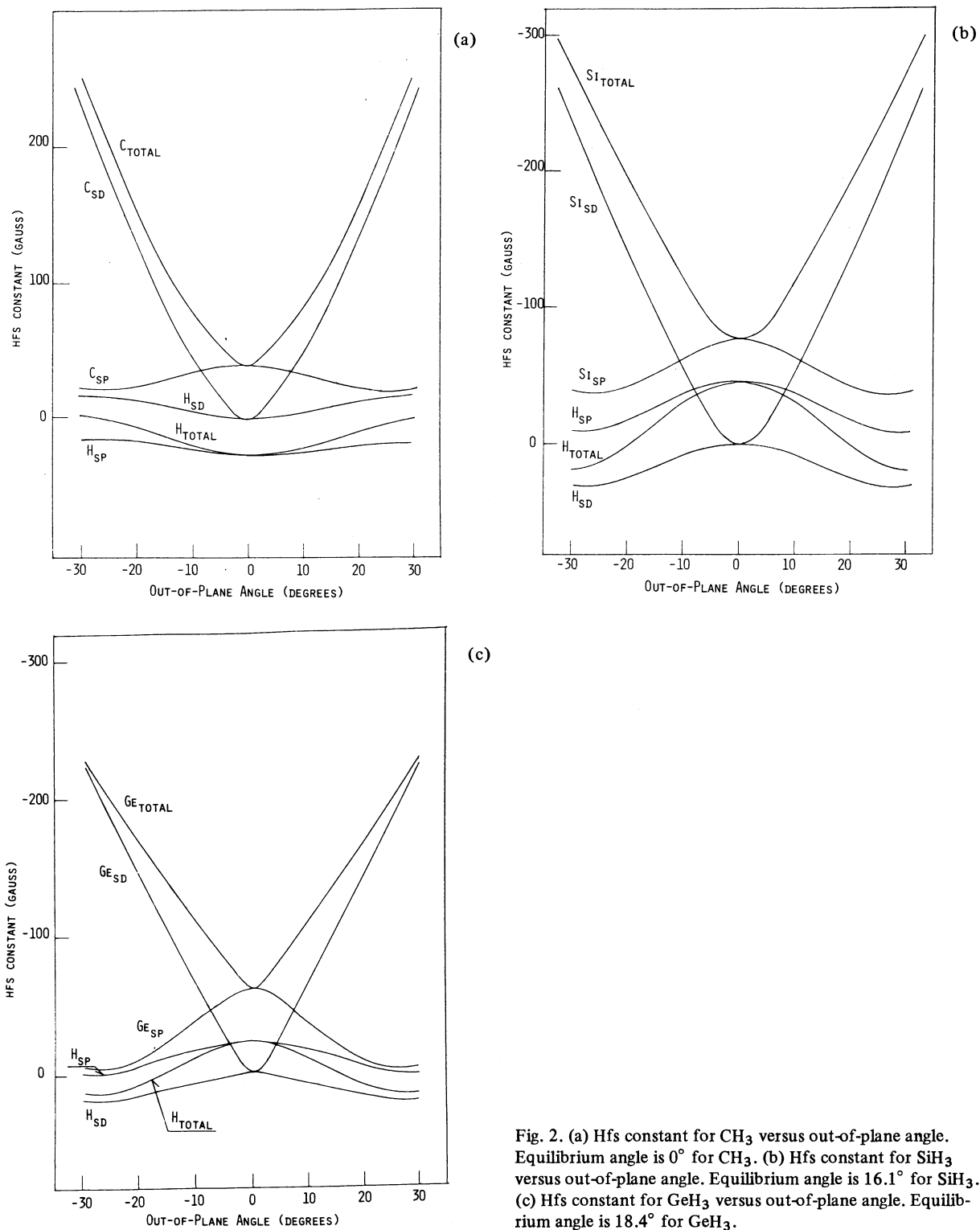
Fig. 2. (a) Hfs constant for CH_3 versus out-of-plane angle. Equilibrium angle is $0°$ for CH_3. (b) Hfs constant for SiH_3 versus out-of-plane angle. Equilibrium angle is $16.1°$ for SiH_3. (c) Hfs constant for GeH_3 versus out-of-plane angle. Equilibrium angle is $18.4°$ for GeH_3.

potentials have different features, such as single or double well, the hfs curves are very similar in these radicals. Since the hfs constant is a direct reflection of the electronic wavefunction, these AH_3 radicals are considered to have very similar electronic and spin structures.

For the central element A, the SD contribution is very sensitive to the out-of-plane angle and increases rapidly. At the planar structure, these radicals become π radicals ($^2A''$) and the total hfs constants are determined only by the SP contribution. Though the SP contribution is less sensitive to the out-of-plane angle than the SD contribution, it also varies with the out-of-plane angle and becomes largest at the planar geometry. This is the same trend as in the case of the spin-correlation correction for the energy in the previous section.

This trend in the spin-correlation effect for the AH_3 radicals is understood qualitatively by a simple orbital picture based on the first-order perturbation theory. The first-order SP contribution, SP1 in eq. (7), comes from the matrix element of the RHF reference wavefunction and the spin-polarized configuration $S_{P,tk}^+|0\rangle$. The expansion coefficient of $S_{P,tk}^+|0\rangle$ can be expressed approximately by the first-order perturbation theory as

$$C_{P,tk} = \langle 0|HS_{P,tk}^+|0\rangle/(E_0 - E_{P,tk})$$

$$= -(3/2)^{1/2}(km|mt)/(E_0 - E_{P,tk}). \tag{13}$$

Thus, the SP1 contribution depends on the exchange type integral $(km|mt)$ which represents the interaction between the doubly occupied orbital k and the unoccupied orbital t through the radical orbital m. In fig. 3, we showed a schematic picture of a_1-HOMO (k), a_1-LUMO (t) and the radical orbital m (SOMO).

The most important spin-polarized configuration is constructed by these three orbitals. When the out-of-plane angle increases and the s—p hybridization ratio in these orbitals becomes larger, the differential overlaps between k and m and m and t become smaller, as expected from fig. 3, and the exchange integral $(km|mt)$ decreases. This is the reason why the spin-correlation effect decreases as the out-of-plane angle increases in these AH_3 radicals.

For the hfs constant of hydrogen, the SD contribution is less sensitive to the out-of-plane angle than that of the central element A. The SP contribution curve is almost parallel with that of the central element and it is also largest at the planar geometry.

4. Effect of molecular vibration

Since the hfs constants depend largely on the out-of-plane angle θ, and the inversion barriers are small (0—6 kcal/mole), the effect of the bending vibration is considered to be very important for the hfs constants, especially for the central element A. In this section, we average the calculated hfs constants over the zero-point vibrational wavefunction. We also consider the vibrational effect on the out-of-plane angle of these AH_3 radicals. The effects of vibration on the hfs constants of AH_3 radicals are calculated for the zero-point vibrational level of bending mode and they are given in table 2. The changes in the hfs constants are 9.6, 9.0, and 4.2 G for C, Si, and Ge, respectively. The carbon hfs constant became larger by the contribution from the more pyramidal structure since the equilibrium geometry of CH_3 is planar. For SiH_3 and GeH_3, however, their equilibrium geometry is pyramidal. Then, the contribution from the more pyramidal

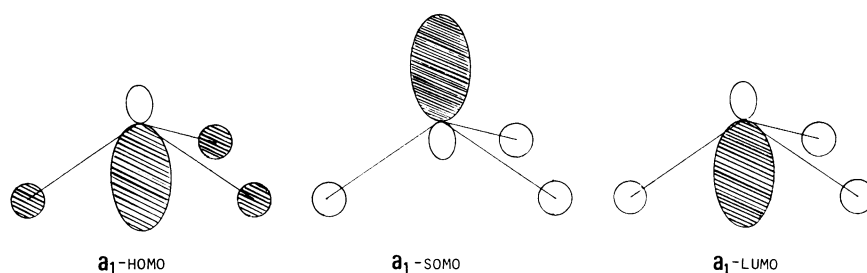a_1-HOMO a_1-SOMO a_1-LUMO

Fig. 3. Schematic picture of three orbitals which make main contribution to spin-polarization effect.

Table 2
Bending vibrational effect on the hfs constant and molecular structure [a]

		CH_3	SiH_3	GeH_3
averaged hfs	A	49.0 (9.6)	−164.8 (9.0)	−152.1 (4.2)
(G)	H	−24.8 (1.7)	−12.3 (−2.2)	6.9 (−1.5)
most probable out-of-plane angle θ [b] (deg)		4.13 (4.13)	15.1 (−1.0)	17.7 (−0.7)
exp. [c] θ [b] (deg)		0.0	15.1	13.1
exp. [c] hfs				
A (G)		38.3	190	75 ± 3
H (G)		23.0	8.1 ± 0.5	15 ± 2

[a] Calculated by zero-point vibration wavefunction in the bending mode. The effect of vibration is given in parentheses.
[b] Out-of-plane angle.   [c] Ref. [1].

structure makes the hfs values of Si and Ge more negative and that from the planar structure makes them less negative. In this study, the contribution from the planar structure was larger than that from the pyramidal structure and the averaged hfs values of Si and Ge became less negative. On the other hand, the vibrational effect on the hydrogen hfs constant is small and is ≈2 G for these radicals.

In order to study the effect of molecular vibration on the out-of-plane angle itself, we calculated the most probable out-of-plane angle by eq. (9). The calculated results are given in table 2. For these three radicals, the out-of-plane angle changed ≈1° by averaging with the vibrational wavefunction. The out-of-plane angle of CH_3 is calculated 4.13° and it is the mean-square amplitude. The equilibrium geometry is, of course, planar. For both of SiH_3 and GeH_3 the optimized geometries are more pyramidal than those of the experimental results. When we consider the effect of vibration, the SiH_3 and GeH_3 became more planar and the out-of-plane angle of SiH_3 agreed with the experimental value, 15.1°. Again, the decrease in the pyramidality from SiH_3 to GeH_3 estimated from the ESR measurement was not reproduced in these most probable geometries.

5. Shell structure of spin-polarization effect

We analyze here the spin-polarization (SP) term in the hfs constant as the sum of the shell contributions.

For heavier elements like Si and Ge, which have multishell structure, the contributions of inner shells are of interest. In table 3, we showed the shell structure of the first-order spin-polarization contibution ρ_{SP1} for the central element at the equilibrium geometry. It is found that all of the 1s shells give negative contributions and that the total spin-polarization effect is primarily determined by two shells, valence shell and the next lower shell. The contribution of deeper shells in SiH_3 and GeH_3 seems to be small and cancelling. In these AH_3 radicals, the nature of the radical orbital changes largely when the out-of-plane angle changes. Thus, the inner shell contribution to the spin-polarization effect will change largely through the coupling with the radical orbital. In figs. 4a, 4b, and 4c, we plotted the shell contribution versus the out-of-plane angle for CH_3, SiH_3, and GeH_3, respectively. The 1s inner shell and 2s valence shell of CH_3 are spin-polar-

Table 3
Shell analysis for the SP1 contribution of spin density at the central element in equilibrium geometry (bohr^{-3})

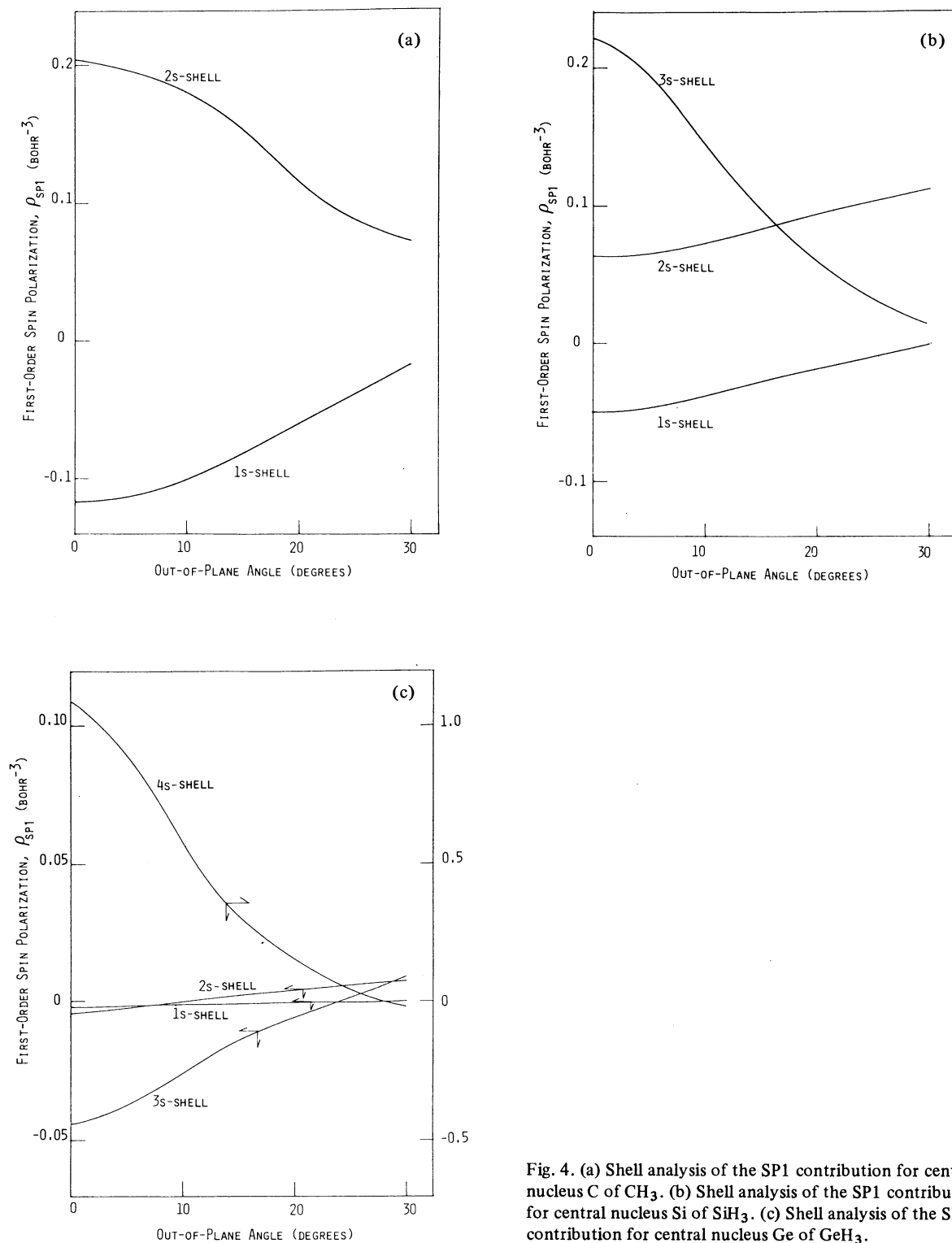|	CH_3	SiH_3	GeH_3
total	0.0867	0.1456	0.1932
	2s(0.2038)	3s(0.0854)	4s(0.1982)
	1s(−0.1171)	2s(0.0861)	3s(−0.0080)
		1s(−0.0258)	2s(0.0035)
			1s(−0.0005)

Fig. 4. (a) Shell analysis of the SP1 contribution for central nucleus C of CH_3. (b) Shell analysis of the SP1 contribution for central nucleus Si of SiH_3. (c) Shell analysis of the SP1 contribution for central nucleus Ge of GeH_3.

ized by the odd electron on the central carbon. The 2s valence shell contribution decreases rapidly as the out-of-plane angle increases. This is the result of rapid decrease of orbital interaction between a_1-HOMO and a_1-LUMO through the radical orbital, the same reason as for the energy lowering due to the spin-correlation discussed in section 3. The contribution of the 1s shell, which is nearly spherical and localized to carbon, does not change so rapidly as the 2s shell contribution and it increases monotonously as shown in fig. 4a. The change of the SP1 contribution of Si in SiH_3 radical is also shown in fig. 4b. The 3s shell is valence shell and its contribution decreases rapidly. It is interesting that, though the potential curve is very different between CH_3 and SiH_3 radical, the valence shell spin-polarization curve is very similar. The inner shell contribution, 1s and 2s shell in SiH_3, increases monotonously as in the case of CH_3 radical. For these two radicals, the shell structure of the spin-polarization varied largely with the change in the out-of-plane angle and inner shell contribution is not always small. The shell analysis for GeH_3 is given in fig. 4c. The valence shell contribution decreases very rapidly. The inner shell contribution, however, is relatively small and does not change so much as in the case of CH_3 or SiH_3.

6. Conclusion

Structures and hfs constants of CH_3, SiH_3, and GeH_3 radicals have been calculated by the pseudo-orbital (PO) theory. In these group IV AH_3 radicals, SiH_3 was reported to be the most pyramidal through the s-character estimation from ESR measurement. It was found in this study, however, that GeH_3 is most pyramidal and the decrease in the out-of-plane angle from SiH_3 to GeH_3 was not reproduced even if we consider the effect of molecular vibration. Hfs constants of CH_3 and SiH_3 calculated by the PO theory were in fair agreement with the experimental values, but for GeH_3 rather poor result was obtained in this calculation. The small inversion barrier and the strong dependence of the hfs constant of the central element A on the out-of-plane angle caused large vibrational effect in these AH_3 systems. The hfs constant of the central element A changed by 9.6, 9.0, and 4.2 G for C, Si, and Ge elements, respectively.

Finally, the spin-polarization effect, considered by the PO theory, has been decomposed into valence and inner shell contributions. For CH_3 and SiH_3, the inner shell spin-polarization effect for the hfs constants of the central element is not always small and varied largely with the change in the molecular pyramidality. For GeH_3, the inner shell contribution is negligibly small and does not change so large as in the case of CH_3 or SiH_3 radical.

Acknowledgement

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