

# Calculation of nuclear magnetic shieldings. XI. Vibrational motion effects

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Nuclear magnetic shieldings in first- and second-row hydrides were calculated with electron correlation taken into account through third order. The calculation was performed using London's gauge-invariant atomic orbitals (GIAOs) and finite-field Møller–Plesset perturbation theory (FF-MPPT). Furthermore, the vibrational motion corrections to the magnetic shieldings were evaluated. It was shown that the calculated isotropic shielding constants at the experimental geometries are higher than the experimental values, but that vibrational corrections are generally negative and improve the calculated shielding constants. © 1996 American Institute of Physics. [S0021-9606(96)00835-5]

## I. INTRODUCTION

In the last few years, several gauge-invariant or at least approximately gauge-invariant calculations of nuclear magnetic shieldings at electron-correlated levels have been presented.<sup>1–12</sup> Until several years ago, it was believed that the coupled Hartree–Fock (CHF) approximation, which includes only first-order electron correlation correction in terms of the Møller–Plesset (MP) perturbation theory, would give sufficiently good results for calculations of nuclear magnetic shielding constants in most cases, e.g., first-row hydrides.<sup>13</sup> Recently we presented the second- and third-order MP correlated calculations for the nuclear magnetic shieldings in four first-row hydrides HF, H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub>, which were performed with the London's gauge-invariant atomic orbitals (GIAO).<sup>8,14</sup> We showed that second- and third-order correlation corrections are not so small as estimated before.<sup>15</sup>

Sugimoto and Nakatsuji<sup>16</sup> recently suggested that the SCF result using GIAOs may show coordinate origin dependence. However, their prediction is incorrect because the CHF calculation with GIAOs has been proved to be independent of any displacement of coordinate origin.<sup>17</sup> A recent development in the calculation indicates that the combination of an electron-correlated method and use of GIAOs can afford the most reliable results for nuclear magnetic shieldings.<sup>1–8</sup>

Sometimes experiments and theoretical calculations are complementary to each other. In fact it is hard work to get experimentally absolute values of the magnetic shielding constants in the condition of an isolated molecule. On the contrary, usual theoretical computations yield the absolute shielding constant of an isolated molecule. Therefore, it is a work of importance to perform accurate calculations for absolute magnetic shielding constants of small and simple molecules which may serve as a standard substance in NMR chemical shift measurements. In this work, we present correlated calculations for the nuclear magnetic shieldings in first- and second-row hydrides and estimate the vibrational corrections to the shielding constants.

## II. RESULTS AND DISCUSSION

### A. Experimental geometry values for the magnetic shieldings

We performed CHF, finite-field self-consistent-field (FF-SCF), finite-field second- and third-order Møller–Plesset (FF-MP2 and FF-MP3) correlation calculations with GIAOs for nuclear magnetic shieldings in four first-row hydrides HF, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> and four second-row hydrides HCl, H<sub>2</sub>S, PH<sub>3</sub>, SiH<sub>4</sub>. The theory for these calculations of magnetic shielding constants is shown in our previous paper.<sup>8</sup> The magnitudes of the finite-field parameters, i.e., magnitudes of magnetic flux density components and nuclear dipole moment components, were chosen appropriately from the condition that the FF-SCF value should reproduce the CHF value corresponding to analytical derivatives of the energy. The CHF value was obtained with the use of the density matrix method proposed by Dodds *et al.*<sup>18</sup> We used the basis sets proposed by Schäfer *et al.*,<sup>19</sup> which were augmented by the addition of polarization functions.

The results for the calculation of nuclear magnetic shieldings in the first- and second-row hydrides at the experimental geometries<sup>20</sup> are shown in Tables I and II, respectively, with other calculated results and experimental values.<sup>13,21–24</sup> Table I shows that our MP3 results agree well with the most recent GIAO coupled-cluster singles and doubles (GIAO-CCSD) results given by Gauss *et al.*<sup>3</sup> The calculated isotropic shielding values  $\sigma_{av}$  for F in HF at the electron-correlated levels are substantially higher than experimental values. The difference may be referred to as rovibrational effects on the magnetic shieldings, which will be discussed in the following subsections.

To our knowledge, the electron-correlated calculations for the magnetic shieldings in the second-row hydrides have not been presented except the GIAO-MP2 shielding calculations for the P atom in PH<sub>3</sub>.<sup>25</sup> Table II shows that the isotropic shielding values decrease with an increasing quality of the basis sets. It is apparent that the basis set used in our MP3 calculations is insufficient for the second-row hydrides, but improvement of our MP3 program will be necessary before we can use bigger basis sets. Tables I and II show that the calculated magnetic shielding constants of the non-

TABLE I. Nuclear magnetic shieldings (in ppm) in first-row hydrides at the experimental geometries.<sup>a</sup>

			[6s4p2d/3s1p]				[8s5p2d/3s2p]				[10s7p3d/4s2p]	Other results <sup>b</sup>	Expt. <sup>c</sup>
			CHF	SCF	MP2	MP3	CHF	SCF	MP2	MP3	CHF		
HF	F	$\sigma_{\perp}$	378.5	378.5	394.9	385.0	379.5	379.5	395.0	385.4	379.3		
		$\sigma_{\parallel}$	482.0	482.2	481.8	482.0	482.0	482.1	481.7	481.8	481.9		
		$\sigma_{av}$	413.0	413.1	423.4	417.3	413.7	413.7	423.9	417.6	413.5	418.1	410±6
	H	$\Delta\sigma$	103.5	103.7	87.5	97.0	102.5	102.6	86.7	96.4	102.6	95.0	93.8 <sup>b</sup>
		$\sigma_{\perp}$	21.61	21.61	22.34	22.61	20.81	20.81	21.70	21.93	20.91		
		$\sigma_{\parallel}$	44.09	44.10	44.24	44.34	44.10	44.09	44.28	44.37	44.09		
H <sub>2</sub> O <sup>d</sup>	O	$\sigma_{xx}$	304.5	304.6	321.6	312.4	306.1	306.4	322.8	313.4	304.8		
		$\sigma_{yy}$	361.1	360.8	370.3	365.7	364.4	363.2	372.7	367.8	364.8		
		$\sigma_{zz}$	311.8	311.4	336.9	325.3	313.6	312.0	336.9	325.1	313.0		
	H	$\sigma_{av}$	325.8	325.6	342.9	334.5	328.0	327.2	344.1	335.4	327.5	336.9	344.0±17.2 <sup>b</sup>
		$\sigma_{av}$	31.32	31.32	31.38	31.63	30.88	30.87	30.99	31.23	30.93	30.9	30.09
		$\Delta\sigma$	273.0	272.8	288.4	282.5	274.6	274.3	289.3	283.1	274.2	269.7	264.5
NH <sub>3</sub>	N	$\sigma_{\perp}$	273.0	272.8	288.4	282.5	274.6	274.3	289.3	283.1	274.2		
		$\sigma_{\parallel}$	235.0	235.2	245.2	240.3	235.9	235.9	245.4	240.4	235.2		
		$\sigma_{av}$	260.3	260.3	274.0	268.4	261.7	261.5	274.7	268.9	261.2	269.7	264.5
	H	$\Delta\sigma$	-38.0	-37.6	-43.2	-42.2	-38.7	-38.4	-43.9	-42.7	-39.0	-43.2 <sup>e</sup>	-40.3 <sup>f</sup>
		$\sigma_{av}$	32.14	32.14	32.01	32.18	31.78	31.78	31.66	31.82	31.80	31.6	30.68 (liq)
		$\sigma_{av}$	194.9	195.3	201.3	199.2	195.3	195.2	200.9		195.0	198.7	197.4
CH <sub>4</sub>	C	$\sigma_{\perp}$	28.69	28.74	28.49	28.64	28.37	28.37	28.12		28.41		
		$\sigma_{\parallel}$	38.36	38.34	38.36	38.29	38.31	38.31	38.32		38.28		
	H	$\sigma_{av}$	31.92	31.94	31.78	31.86	31.69	31.69	31.52		31.70	31.5	30.61
		$\Delta\sigma$	9.67	9.60	9.87	9.65	9.94	9.94	10.21		9.88	10.1	

<sup>a</sup>Taken from Ref. 20.<sup>b</sup>Taken from Ref. 3.<sup>c</sup>Taken from Ref. 13 if not noted otherwise.<sup>d</sup>The z axis is parallel to the C<sub>2</sub> axis. The x axis is perpendicular to the molecular plane.<sup>e</sup>The original value -21.6 ppm in Ref. 3 was doubted.<sup>f</sup>Taken from Ref. 21.

hydrogen atoms rather well reproduce the experimental values, but the agreement between calculations and experiments is rather poor for the proton magnetic shielding constants. We will estimate vibrational corrections to the proton shieldings later.

## B. Rovibrational corrections for the shieldings in diatomic molecules

In diatomic molecules we have one vibration which couples with the rotational motion. We assumed the following interatomic potential function  $V$  for diatomic molecules:

$$V = (1/2)KR_e^2\xi^2(1 + a_1\xi), \quad \xi = (r - r_e)/r_e, \quad (1)$$

where  $K$  is the force constant and  $r_e$  is the equilibrium value for the bond length  $r$ . The averages of  $\xi^n$  can be expressed in terms of the parameter  $a_1$  and the usual molecular constants  $\omega_e$  and  $B_e$ , in cm<sup>-1</sup>.<sup>26</sup> We have<sup>27</sup>

$$\langle \xi \rangle_{vJ} = -3 \left( v + \frac{1}{2} \right) a_1 \left( \frac{B_e}{\omega_e} \right) + 4J(J+1) \left( \frac{B_e}{\omega_e} \right)^2, \quad (2)$$

$$\langle \xi^2 \rangle_{vJ} = 2 \left( v + \frac{1}{2} \right) \left( \frac{B_e}{\omega_e} \right), \quad (3)$$

where  $v$  and  $J$  are the vibration and rotation quantum numbers, respectively. At room temperature we may assume  $v=0$ . The rovibrational correction to the magnetic shielding tensor  $\sigma$  is given by

$$\langle \sigma \rangle_{vJ} - \sigma_e = \left( \frac{\partial \sigma}{\partial \xi} \right)_{\xi=0} \langle \xi \rangle_{vJ} + \left( \frac{1}{2} \right) \left( \frac{\partial^2 \sigma}{\partial \xi^2} \right)_{\xi=0} \langle \xi^2 \rangle_{vJ}, \quad (4)$$

where  $\sigma_e$  is the magnetic shielding tensor at the equilibrium bond length, i.e., at  $\xi=0$ . We calculated the rovibrational corrections to the magnetic shieldings in the HF and HCl molecules at 300 K. The results for HF and HCl are shown in Table III. Table III indicates that the rovibrational correction improves our results for HF and HCl shown in Tables I and II.

## C. Vibrational corrections for the shieldings in C<sub>2v</sub> molecules

For polyatomic molecules we neglected the effects of rotational motions on the magnetic shieldings. It has been shown that the effect of centrifugal distortion due to molecular rotational motions is usually one order of magnitude smaller than the effect due to anharmonic vibrations.<sup>28</sup> We will calculate here only the vibrational effects on the magnetic shieldings at 0 K in the polyatomic molecules.

We first set up for the C<sub>2v</sub> molecules the three normal coordinates from the internal coordinates  $\Delta r_1$ ,  $\Delta r_2$ , and  $\Delta\theta$ , i.e., the bond length and bond angle deformations, according to the standard method by Wilson.<sup>29,30</sup> We calculated the normal coordinates iteratively by using experimental values for the normal mode vibration frequencies.<sup>31</sup>

TABLE II. Nuclear magnetic shieldings (in ppm) in second-row hydrides at the experimental geometries.<sup>a</sup>

			[8s6p1d/3s1p]				[8s6p2d/3s2p]				[10s7p3d/4s2p]	Other results	Expt.
			CHF	SCF	MP2	MP3	CHF	SCF	MP2	MP3	CHF		
HCl	Cl	$\sigma_{\perp}$	858.5	859.4	881.1	868.2	853.4	853.6	883.8	869.1	849.5	859.75 <sup>b</sup>	
		$\sigma_{\parallel}$	1149.4	1149.1	1149.1	1149.1	1149.1	1149.1	1148.9	1148.9	1149.1	1148.93 <sup>b</sup>	
		$\sigma_{av}$	955.4	956.0	970.5	961.8	952.0	952.0	972.1	962.3	949.4	956.14 <sup>b</sup>	952 <sup>b</sup>
	H	$\Delta\sigma$	290.9	289.7	268.0	280.9	295.7	295.5	265.1	279.8	299.6	289.18 <sup>b</sup>	298 <sup>c</sup>
		$\sigma_{\perp}$	23.45	23.40	24.04	24.45	23.47	23.39	23.82	24.21	23.34		
		$\sigma_{\parallel}$	45.37	45.37	45.43	45.57	45.61	45.61	45.60	45.74	45.55		
H <sub>2</sub> S <sup>c</sup>	S	$\sigma_{av}$	30.76	30.72	31.17	31.49	30.85	30.80	31.08	31.39	30.75	32.25 <sup>d</sup>	31.5 <sup>d</sup>
		$\Delta\sigma$	21.92	21.97	21.39	21.12	22.14	22.22	21.78	21.53	22.21		
		$\sigma_{xx}$	688.5	689.4	712.2	702.8	678.5	678.4	708.1	696.9	675.0	688.15 <sup>b</sup>	
	H	$\sigma_{yy}$	925.2	925.3	936.5	930.5	929.3	929.6	941.2	934.4	931.0	936.64 <sup>b</sup>	
		$\sigma_{zz}$	570.6	570.7	634.3	617.5	555.6	555.7	635.3	613.8	551.1	570.89 <sup>b</sup>	
		$\sigma_{av}$	728.1	728.4	761.0	750.3	721.3	721.2	761.5	748.4	719.0	731.89 <sup>b</sup>	752 <sup>b</sup>
PH <sub>3</sub>	P	$\sigma_{av}$	31.22	31.22	31.39	31.57	31.16	31.16	31.28	31.44	31.08	32.69 <sup>d</sup>	30.54 <sup>d</sup>
		$\sigma_{\perp}$	608.0	608.0	633.7	627.7	598.9	598.9	631.0	624.0	596.4	629.61 <sup>f</sup>	621.43 <sup>f</sup>
		$\sigma_{\parallel}$	569.9	569.9	580.2	576.4	559.6	559.7	571.5	567.1	557.2	565.07 <sup>f</sup>	556.93 <sup>f</sup>
	H	$\sigma_{av}$	595.3	595.3	615.9	610.6	585.8	585.8	611.2	605.1	583.4	608.09 <sup>f</sup>	599.93 <sup>f</sup>
		$\Delta\sigma$	-38.1	-38.1	-53.5	-51.2	-39.3	-39.3	-59.5	-56.8	-39.2	-64.54 <sup>f</sup>	-64.50 <sup>f</sup>
		$\sigma_{av}$	29.85	29.85	29.89	29.97	29.75	29.75	29.77	29.81	29.71	30.96 <sup>d</sup>	28.3 <sup>d</sup>
SiH <sub>4</sub>	Si	$\sigma_{av}$	489.3	489.8	490.3	489.4	477.8	477.9	476.3		477.4	482.47 <sup>b</sup>	475.3 <sup>b</sup>
		$\sigma_{\perp}$	26.19	26.19	26.16	26.23	26.05	26.05	25.89		26.07		
	H	$\sigma_{\parallel}$	33.31	33.31	33.35	33.33	33.09	33.09	33.07		32.97		
		$\sigma_{av}$	28.56	28.56	28.56	28.60	28.40	28.40	28.28		28.37	29.32 <sup>d</sup>	27.61 <sup>d</sup>
		$\Delta\sigma$	7.12	7.12	7.19	7.10	7.04	7.04	7.18		6.91		

<sup>a</sup>Taken from Ref. 20.<sup>b</sup>Taken from Ref. 22.<sup>c</sup>Taken from Ref. 23.<sup>d</sup>Taken from Ref. 24.<sup>e</sup>The  $z$  axis is parallel to the  $C_2$  axis. The  $x$  axis is perpendicular to the molecular plane.<sup>f</sup>Taken from Ref. 25.

Furthermore, we defined the three internal symmetry coordinates:

$$S_1 = (\Delta r_1 + \Delta r_2)/\sqrt{2}, \quad S_2 = r_e \Delta \theta / \sqrt{2},$$

$$S_3 = (\Delta r_1 - \Delta r_2)/\sqrt{2},$$

where  $r_e$  is the equilibrium bond length. The internal symmetry coordinates  $S$  are expressed in terms of the normal coordinates  $Q$  as  $S = LQ$ . Namely,

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} \alpha & \beta & 0 \\ \gamma & \delta & 0 \\ 0 & 0 & \epsilon \end{bmatrix} \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix}, \quad (5)$$

where  $Q_1$ ,  $Q_2$ , and  $Q_3$  are  $A_1$  stretching,  $A_1$  bending, and  $B_2$  stretching normal coordinates, respectively. Numerical values for the matrix elements of  $L$  are given in Table IV for H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>33</sup>S. Off diagonal elements of the matrix  $L$  are less than one tenth of the diagonal elements.

One of the important applications of the normal coordinates is the calculation of the mean-square values of the internal symmetry coordinates. By ignoring contributions from anharmonic potentials the mean values of the quadratic products of the normal coordinates at 0 K are given by

$$\langle Q_i Q_j \rangle = (\hbar/2\omega_i) \delta_{ij}, \quad (6)$$

where  $\omega_i$  is the angular frequency of the  $i$ th normal mode vibration. The mean values of the quadratic products of the symmetry coordinates  $\langle S_i S_j \rangle$  are readily evaluated with Eqs. (5) and (6).

In order to obtain the mean values of the  $S_1$  and  $S_2$  coordinates with  $A_1$  symmetry we express the potential energy  $V$  for the nuclear motions in the molecule in terms of internal symmetry coordinates  $S$  by the relation

$$2V = \sum_i \sum_j F_{ij} S_i S_j + \sum_i \sum_j \sum_k F_{ijk} S_i S_j S_k, \quad (7)$$

where the  $F_{ij}$  and  $F_{ijk}$  represent quadratic and cubic force constants. The equilibrium potential  $V_e$  is set here to be 0. The mean values of the symmetry coordinates  $\langle S_i \rangle$  are determined by the equilibrium conditions<sup>32</sup>

$$\left\langle \frac{\partial V}{\partial S_i} \right\rangle = 0. \quad (8)$$

The vibrational correction to the magnetic shielding tensor is given by

$$\begin{aligned} \langle \sigma \rangle_{0 \text{ K}} - \sigma_e &= \sum_i \left( \frac{\partial \sigma}{\partial S_i} \right)_e \langle S_i \rangle \\ &+ 1/2 \sum_i \sum_j \left( \frac{\partial^2 \sigma}{\partial S_i \partial S_j} \right)_e \langle S_i S_j \rangle. \end{aligned} \quad (9)$$

TABLE III. Rovibrational corrections to the isotropic shielding constants and shielding anisotropies in  $\text{H}^{19}\text{F}$  and  $\text{H}^{35}\text{Cl}$  at 300 K.

$\text{H}^{19}\text{F}$		
$\omega_e^a$ ( $\text{cm}^{-1}$ )		4183.5
$B_e^a$ ( $\text{cm}^{-1}$ )		20.939
$a_1^a$		-2.211
$(\partial\sigma_{av}/\partial\xi)_{\xi=0}$ (ppm) <sup>b</sup>	F	-390.0
	H	-40.90
$(\partial^2\sigma_{av}/\partial\xi^2)_{\xi=0}$ (ppm) <sup>b</sup>	F	-1205.2
	H	122.9
$(\partial\Delta\sigma/\partial\xi)_{\xi=0}$ (ppm) <sup>b</sup>	F	580.2
	H	-49.10
$(\partial^2\Delta\sigma/\partial\xi^2)_{\xi=0}$ (ppm) <sup>b</sup>	F	1831.2
	H	83.10
$\langle\xi\rangle^b$		$1.78\times 10^{-2}$
$\langle\xi^2\rangle^b$		$5.06\times 10^{-3}$
$\langle\sigma_{av}\rangle_{300\text{ K}} - \sigma_{av}^e$ (ppm) <sup>b</sup>	F	-10.0
	H	-0.42
$\langle\Delta\sigma\rangle_{300\text{ K}} - \Delta\sigma^e$ (ppm) <sup>b</sup>	F	14.9
	H	-0.66
$\text{H}^{35}\text{Cl}$		
$\omega_e^a$ ( $\text{cm}^{-1}$ )		2989.7
$B_e^a$ ( $\text{cm}^{-1}$ )		10.59
$a_1^a$		-2.341
$(\partial\sigma_{av}/\partial\xi)_{\xi=0}$ (ppm) <sup>c</sup>	Cl	-877.8
	H	-41.62
$(\partial^2\sigma_{av}/\partial\xi^2)_{\xi=0}$ (ppm) <sup>c</sup>	Cl	-2949.6
	H	119.3
$(\partial\Delta\sigma/\partial\xi)_{\xi=0}$ (ppm) <sup>c</sup>	Cl	1314.7
	H	-46.61
$(\partial^2\Delta\sigma/\partial\xi^2)_{\xi=0}$ (ppm) <sup>c</sup>	Cl	4434.8
	H	73.10
$\langle\xi\rangle^c$		$1.34\times 10^{-2}$
$\langle\xi^2\rangle^c$		$3.54\times 10^{-3}$
$\langle\sigma_{av}\rangle_{300\text{ K}} - \sigma_{av}^e$ (ppm) <sup>c</sup>	Cl	-17.0
	H	-0.35
$\langle\Delta\sigma\rangle_{300\text{ K}} - \Delta\sigma^e$ (ppm) <sup>c</sup>	Cl	25.5
	H	-0.50

<sup>a</sup>Taken from Ref. 26.<sup>b</sup>CHF calculations with the [8s5p2d/3s2p] basis used.<sup>c</sup>CHF calculations with the [8s6p2d/3s2p] basis used.

We calculated the vibrational corrections to the isotropic shielding constants in  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{33}\text{S}$ . We made calculation of the potential values at 125 points using the SCF method and determined the force constants by the least-square method. The equilibrium conditions, Eq. (8), yielded  $\langle S_1 \rangle$  and  $\langle S_2 \rangle$ . The shielding derivatives were calculated as the numerical derivatives of the shielding values obtained with the CHF method.

The results for  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  are listed in Tables V. Table V shows that the total vibrational correction to the isotropic O shielding in  $\text{H}_2\text{O}$  due to the three vibrational motions is -12.1 ppm and our vibrationally corrected value

TABLE IV. Internal symmetry coordinates (in atomic mass units).

	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$
$\text{H}_2^{17}\text{O}$	1.0213	0.0331	-0.0893	1.0323	1.0361
$\text{H}_2^{33}\text{S}$	1.0143	0.0199	-0.0498	1.0144	1.0156

for  $\sigma_{av}(\text{O})$  becomes 323.3 ppm. Our vibrationally corrected value is a little lower than the experimental lower limit shown by the error bar. We note that the  $A_1$  stretching vibration has the largest effect in the three vibrational motions. Our value for the vibrational correction, -12.1 ppm, is slightly smaller than the value reported by Fowler and Raynes,<sup>33</sup> -13.1 ppm. The vibrational correction for the S atom, -19.6 ppm, is about twice as large as that for the O atom. The vibrationally corrected value for  $\sigma_{av}(\text{S})$  becomes 728.8 ppm, which is considerably lower than the experimental value 752 ppm.

#### D. Vibrational corrections for the shieldings in $\text{C}_{3v}$ molecules

The  $\text{NH}_3$  and  $\text{PH}_3$  molecules have six vibrational motions. We used as the bases for the normal coordinates the following six internal symmetry coordinates:  $S_1 = (\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}$ ,  $S_2 = r_e(\Delta\theta_{12} + \Delta\theta_{23} + \Delta\theta_{31})/\sqrt{3}$ ,  $S_3 = (\Delta r_2 - \Delta r_3)/\sqrt{2}$ ,  $S_4 = r_e(\Delta\theta_{31} - \Delta\theta_{12})/\sqrt{2}$ ,  $S_5 = (\Delta r_2 + \Delta r_3 - 2\Delta r_1)/\sqrt{6}$ ,  $S_6 = r_e(\Delta\theta_{12} + \Delta\theta_{31} - 2\Delta\theta_{23})/\sqrt{6}$ . The symmetry coordinates  $S_1$  and  $S_2$  have the  $A_1$  symmetry, but the coordinates  $S_3$  to  $S_6$  have the E symmetry. Furthermore, the coordinates  $S_3$  and  $S_4$  are equivalent to the coordinates  $S_5$  and  $S_6$ , and the  $S_3$  and  $S_4$  have no cross terms between the  $S_5$  and  $S_6$  in any energy functions. The internal symmetry coordinates  $S$  are expressed in terms of the normal coordinates  $Q$  as  $S = LQ$ . The matrix  $L$  has the structure represented by

$$L = \begin{bmatrix} a & 0 \\ & b \\ 0 & b \end{bmatrix}, \quad (10)$$

where both  $a$  and  $b$  are the  $2\times 2$  matrices. We write here the  $a$  and  $b$  as

$$a = \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix}, \quad b = \begin{bmatrix} \epsilon & \zeta \\ \eta & \vartheta \end{bmatrix}. \quad (11)$$

Numerical values for the matrix elements of  $L$  are given in Table VI for  $^{15}\text{NH}_3$  and  $^{31}\text{PH}_3$ .

We calculated the vibrational corrections to the isotropic shielding constants and the shielding anisotropies in  $^{15}\text{NH}_3$  and  $^{31}\text{PH}_3$ . We made calculations of the potential values at 225 points using the SCF method and determined the force constants by the least-squares method. The equilibrium conditions yielded  $\langle S_1 \rangle$  and  $\langle S_2 \rangle$ . The shielding derivatives were calculated as the numerical derivatives of the shielding values obtained with the CHF method. The results are shown in Tables VII and VIII. Table VII shows that the total vibrational correction to the isotropic N shielding in  $\text{NH}_3$  due to the six vibrational motions is -7.0 ppm. Our value is a little smaller than the value reported by Jameson and de Dias,<sup>34</sup> -8.8 ppm at 300 K. Our value for the vibrational correction to the isotropic P shielding in  $\text{PH}_3$  is -7.3 ppm, which is much smaller than the value by Jameson and de Dias,<sup>35</sup> -12.78 ppm at 300 K. Our calculation gave -8.51 ppm as the  $(\partial\sigma_{av}/\partial S_1)_e \langle S_1 \rangle$  contribution, which is comparable to

TABLE V. Shielding derivatives and vibrational corrections to the isotropic shielding constants in H<sub>2</sub><sup>17</sup>O<sup>a</sup> and H<sub>2</sub><sup>33</sup>S<sup>b</sup> at 0 K.

	H <sub>2</sub> <sup>17</sup> O		H <sub>2</sub> <sup>33</sup> S	
	<sup>17</sup> O	<sup>1</sup> H	<sup>33</sup> S	<sup>1</sup> H
(∂σ <sub>av</sub> /∂S <sub>1</sub> ) <sub>e</sub> (ppm/Å)	-372.9	-29.94	-597.6	-20.26
(∂σ <sub>av</sub> /∂S <sub>2</sub> ) <sub>e</sub> (ppm/Å)	-8.795	-5.503	-68.07	-3.057
(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>1</sub> <sup>2</sup> ) <sub>e</sub> (ppm/Å <sup>2</sup> )	-987.6	70.00	-1113.4	29.09
(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>2</sub> <sup>2</sup> ) <sub>e</sub> (ppm/Å <sup>2</sup> )	285.2	-5.801	388.1	-3.665
(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>3</sub> <sup>2</sup> ) <sub>e</sub> (ppm/Å <sup>2</sup> )	-1041.8	26.69	-1414.7	9.477
(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>1</sub> S <sub>2</sub> ) <sub>e</sub> (ppm/Å <sup>2</sup> )	4.026	-0.5608	-28.54	1.601
(∂σ <sub>av</sub> /∂S <sub>1</sub> ) <sub>e</sub> (S <sub>1</sub> ) (ppm)	-8.78	-0.705	-14.09	-0.477
(∂σ <sub>av</sub> /∂S <sub>2</sub> ) <sub>e</sub> (S <sub>2</sub> ) (ppm)	0.00	0.001	-0.03	-0.001
1/2(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>1</sub> <sup>2</sup> ) <sub>e</sub> (S <sub>1</sub> <sup>2</sup> ) (ppm)	-2.38	0.169	-3.70	0.097
1/2(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>2</sub> <sup>2</sup> ) <sub>e</sub> (S <sub>2</sub> <sup>2</sup> ) (ppm)	1.61	-0.033	2.85	-0.027
1/2(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>3</sub> <sup>2</sup> ) <sub>e</sub> (S <sub>3</sub> <sup>2</sup> ) (ppm)	-2.51	0.064	-4.68	0.031
(∂ <sup>2</sup> σ <sub>av</sub> /∂S <sub>1</sub> S <sub>2</sub> ) <sub>e</sub> (S <sub>1</sub> S <sub>2</sub> ) (ppm)	-0.00	0.000	0.00	-0.000
Total correction (ppm)	-12.1	-0.50	-19.6	-0.38

<sup>a</sup>[8s5p2d/3s2p] basis used.<sup>b</sup>[8s6p2d/3s2p] basis used.

their value, -9.16 ppm. However, our value for the (∂σ<sub>av</sub>/∂S<sub>2</sub>)<sub>e</sub>(S<sub>2</sub>) was 1.40 ppm, which disagrees in sign with their value, -3.29 ppm. Our vibrationally corrected shielding constants for N and P are 261.9 ppm and 597.8 ppm, respectively. Calculated values are improved by adding the vibrational corrections. The vibration effects were also evaluated for the isotropic proton shielding constants. The protons have only the local symmetry lower than the molecular symmetry, C<sub>3v</sub>. However, the average magnetic shielding for the three protons has the same symmetry as the molecule.

Table VIII shows that the vibrational motions have large effects on the magnetic shielding anisotropies in NH<sub>3</sub> and PH<sub>3</sub>. Our vibrationally corrected shielding anisotropies are considerably smaller than the experimental values, especially for the Δσ(P) in PH<sub>3</sub>. This disagreement may be due to large contributions of high-order correlations in the shielding anisotropies.

### E. Vibrational corrections for the shieldings in T<sub>d</sub> molecules

A T<sub>d</sub>-type molecule like CH<sub>4</sub> has ten internal coordinates, i.e., four bond length displacements and six bond angle deformations. However, the number of degrees of freedom of vibrational motions is nine and the ten internal coordinates are evidently redundant. In fact, the sum of the six bond angle deformations is zero. We have to drop a redundant coordinate without spoiling the symmetry of the coordinates. We can construct the nine internal symmetry coordinates with a use of the well-known method of the group theory.

The nine internal symmetry coordinates are as follows: S<sub>1</sub>(A<sub>1</sub>) = (Δr<sub>1</sub> + Δr<sub>2</sub> + Δr<sub>3</sub> + Δr<sub>4</sub>)/2, S<sub>2</sub>(E) = r<sub>e</sub>(2Δθ<sub>12</sub> - Δθ<sub>13</sub> - Δθ<sub>14</sub> - Δθ<sub>23</sub> - Δθ<sub>24</sub> + 2Δθ<sub>34</sub>)/√12, S<sub>3</sub>(E) = r<sub>e</sub>(Δθ<sub>13</sub> - Δθ<sub>14</sub> - Δθ<sub>23</sub> + Δθ<sub>24</sub>)/2, S<sub>4</sub>(T<sub>2</sub>) = (Δr<sub>1</sub> - Δr<sub>2</sub> + Δr<sub>3</sub> - Δr<sub>4</sub>)/2, S<sub>5</sub>(T<sub>2</sub>) = r<sub>e</sub>(-Δθ<sub>13</sub> + Δθ<sub>24</sub>)/√2, S<sub>6</sub>(T<sub>2</sub>) = (Δr<sub>1</sub> - Δr<sub>2</sub> - Δr<sub>3</sub> + Δr<sub>4</sub>)/2, S<sub>7</sub>(T<sub>2</sub>) = r<sub>e</sub>(-Δθ<sub>14</sub> + Δθ<sub>23</sub>)/√2, S<sub>8</sub>(T<sub>2</sub>) = (Δr<sub>1</sub> + Δr<sub>2</sub> - Δr<sub>3</sub> - Δr<sub>4</sub>)/2, S<sub>9</sub>(T<sub>2</sub>) = r<sub>e</sub>(-Δθ<sub>12</sub> + Δθ<sub>34</sub>)/√2. The three pairs of coordinates, i.e., (S<sub>4</sub>, S<sub>5</sub>), (S<sub>6</sub>, S<sub>7</sub>), and (S<sub>8</sub>, S<sub>9</sub>), are equivalent to each other. The three pairs of coordinates have no cross terms among them in any energy functions. This greatly reduces the number of independent force constants.

The internal symmetry coordinates *S* are expressed in terms of the normal coordinates *Q* as *S* = *LQ*. The matrix *L* has the structure represented by

$$L = \begin{bmatrix} \alpha & & & & & & & & \\ & \beta & & & & & & & 0 \\ & & \beta & & & & & & \\ & & & a & & & & & \\ & & & & a & & & & \\ & & & & & a & & & \\ & 0 & & & & & & & \\ & & & & & & & & \\ & & & & & & & & a \end{bmatrix}, \quad (12)$$

where *a* is the 2×2 matrix. We write here the *a* matrix as

TABLE VI. Internal symmetry coordinates (in atomic mass units).

	α	β	γ	δ	ε	ζ	η	θ
<sup>15</sup> NH <sub>3</sub>	1.0141	0.0080	-0.0847	1.1805	1.0419	-0.0171	0.1367	1.5932
<sup>31</sup> PH <sub>3</sub>	1.0140	0.0193	-0.0864	1.4130	1.0169	-0.0120	0.0527	1.4483

TABLE VII. Shielding derivatives and vibrational corrections to the isotropic shielding constants in  $^{15}\text{NH}_3$ <sup>a</sup> and  $^{31}\text{PH}_3$ <sup>b</sup> at 0 K.

	$^{15}\text{NH}_3$		$^{31}\text{PH}_3$	
	$^{15}\text{N}$	$^1\text{H}$	$^{31}\text{P}$	$^1\text{H}$
$(\partial\sigma_{av}/\partial S_1)_e$ (ppm/Å)	-218.6	-23.12	-274.0	-12.91
$(\partial\sigma_{av}/\partial S_2)_e$ (ppm/Å)	-13.51	-3.216	-142.7	-1.924
$(\partial^2\sigma_{av}/\partial S_1^2)_e$ (ppm/Å <sup>2</sup> )	-336.4	37.21	-215.9	13.68
$(\partial^2\sigma_{av}/\partial S_2^2)_e$ (ppm/Å <sup>2</sup> )	118.7	-0.2681	164.4	-0.9073
$(\partial^2\sigma_{av}/\partial S_1\partial S_2)_e$ (ppm/Å <sup>2</sup> )	-38.42	-0.3409	-78.20	0.6595
$(\partial^2\sigma_{av}/\partial S_3^2)_e$ (ppm/Å <sup>2</sup> )	-540.7	12.15	-646.9	5.460
$(\partial^2\sigma_{av}/\partial S_4^2)_e$ (ppm/Å <sup>2</sup> )	66.60	-1.959	79.21	-1.813
$(\partial^2\sigma_{av}/\partial S_3\partial S_4)_e$ (ppm/Å <sup>2</sup> )	-7.436	-0.05094	0.2297	0.8634
$(\partial\sigma_{av}/\partial S_1)_e\langle S_1 \rangle$ (ppm)	-6.59	-0.697	-8.51	-0.401
$(\partial\sigma_{av}/\partial S_2)_e\langle S_2 \rangle$ (ppm)	0.12	0.028	1.40	0.019
$1/2(\partial^2\sigma_{av}/\partial S_1^2)_e\langle S_1^2 \rangle$ (ppm)	-0.87	0.097	-0.80	0.051
$1/2(\partial^2\sigma_{av}/\partial S_2^2)_e\langle S_2^2 \rangle$ (ppm)	1.47	-0.003	2.80	-0.015
$(\partial^2\sigma_{av}/\partial S_1\partial S_2)_e\langle S_1S_2 \rangle$ (ppm)	0.01	0.000	0.01	-0.000
$(\partial^2\sigma_{av}/\partial S_3^2)_e\langle S_3^2 \rangle$ (ppm)	-2.90	0.065	-4.66	0.039
$(\partial^2\sigma_{av}/\partial S_4^2)_e\langle S_4^2 \rangle$ (ppm)	1.76	-0.052	2.50	-0.057
$2(\partial^2\sigma_{av}/\partial S_3\partial S_4)_e\langle S_3S_4 \rangle$ (ppm)	-0.01	-0.000	0.00	0.000
Total correction (ppm)	-7.0	-0.56	-7.3	-0.36

<sup>a</sup>[8s5p2d/3s2p] basis used.<sup>b</sup>[8s6p2d/3s2p] basis used.

$$a = \begin{bmatrix} \gamma & \delta \\ \epsilon & \zeta \end{bmatrix}. \quad (13)$$

Numerical values for the matrix elements of  $L$  are given in Table IX for  $^{13}\text{CH}_4$  and  $^{29}\text{SiH}_4$ .

We calculated the vibrational corrections to the isotropic shielding constants in  $^{13}\text{CH}_4$  and  $^{29}\text{SiH}_4$ . We made calculation of the potential values at 135 points using the SCF method and determined the force constants by the least-square method. The equilibrium condition yielded  $\langle S_i \rangle$ . The shielding derivatives were calculated as the numerical de-

TABLE VIII. Shielding derivatives and vibrational corrections to the magnetic shielding anisotropies in  $^{15}\text{NH}_3$ <sup>a</sup> and  $^{31}\text{PH}_3$ <sup>b</sup> at 0 K.

	$^{15}\text{NH}_3$	$^{31}\text{PH}_3$
	$^{15}\text{N}$	$^{31}\text{P}$
$(\partial\Delta\sigma/\partial S_1)_e$ (ppm/Å)	61.79	132.0
$(\partial\Delta\sigma/\partial S_2)_e$ (ppm/Å)	-36.36	42.24
$(\partial^2\Delta\sigma/\partial S_1^2)_e$ (ppm/Å <sup>2</sup> )	254.2	10.39
$(\partial^2\Delta\sigma/\partial S_2^2)_e$ (ppm/Å <sup>2</sup> )	-140.2	-215.0
$(\partial^2\Delta\sigma/\partial S_1\partial S_2)_e$ (ppm/Å <sup>2</sup> )	31.46	210.0
$(\partial^2\Delta\sigma/\partial S_3^2)_e$ (ppm/Å <sup>2</sup> )	179.6	259.1
$(\partial^2\Delta\sigma/\partial S_4^2)_e$ (ppm/Å <sup>2</sup> )	147.9	350.5
$(\partial^2\Delta\sigma/\partial S_3\partial S_4)_e$ (ppm/Å <sup>2</sup> )	121.4	292.0
$(\partial\Delta\sigma/\partial S_1)_e\langle S_1 \rangle$ (ppm)	1.86	4.10
$(\partial\Delta\sigma/\partial S_2)_e\langle S_2 \rangle$ (ppm)	0.31	-0.42
$1/2(\partial^2\Delta\sigma/\partial S_1^2)_e\langle S_1^2 \rangle$ (ppm)	0.66	0.04
$1/2(\partial^2\Delta\sigma/\partial S_2^2)_e\langle S_2^2 \rangle$ (ppm)	-1.74	-3.66
$(\partial^2\Delta\sigma/\partial S_1\partial S_2)_e\langle S_1S_2 \rangle$ (ppm)	-0.01	-0.04
$(\partial^2\Delta\sigma/\partial S_3^2)_e\langle S_3^2 \rangle$ (ppm)	0.96	1.87
$(\partial^2\Delta\sigma/\partial S_4^2)_e\langle S_4^2 \rangle$ (ppm)	3.90	11.06
$2(\partial^2\Delta\sigma/\partial S_3\partial S_4)_e\langle S_3S_4 \rangle$ (ppm)	0.10	0.07
Total correction (ppm)	6.1	13.0

<sup>a</sup>[8s5p2d/3s2p] basis used.<sup>b</sup>[8s6p2d/3s2p] basis used.

derivatives of the shielding values obtained with the CHF method. The results are shown in Table X. Table X shows that the total vibrational correction to the isotropic C shielding in  $\text{CH}_4$  due to the nine vibrational motions is  $-4.7$  ppm. Our vibrationally corrected value, 194.5 ppm, is a little lower than the experimental value, 197.4 ppm. Table X shows that the vibrational correction to the Si atom is small, i.e.,  $-2.0$  ppm. Our MP3 value for the isotropic Si shielding at the experimental geometry is 489.4 ppm with the [8s6p1d/3s1p] basis, which is too high compared with the experimental value 475.3 ppm. However, the use of the [8s6p2d/3s2p] basis lowers the SCF and MP2 values by 12 to 14 ppm from the [8s6p1d/3s1p] values. So we may expect that the MP3 value of larger bases would be around 477 ppm. The vibrational correction  $-2.0$  ppm may be a reasonable value.

To our knowledge, the present article is the first report on the vibrational effect calculation for the magnetic shieldings in  $T_d$ -symmetry molecules. Jameson and Osten<sup>36</sup> assumed in the calculation of the vibrational corrections to the  $^{19}\text{F}$  shieldings in  $\text{CH}_n\text{F}_{4-n}$ -type molecules that for the nearly tetrahedral molecules the contribution of the bond angle deformations and the second-order derivative contribution of the bond lengths can be neglected. On the other hand, Enevoldsen and Oddershede<sup>37</sup> asserted that for  $\text{CH}_3\text{F}$  shieldings the second-order derivative contributions of the bond

TABLE IX. Internal symmetry coordinates (in atomic mass units).

	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\zeta$
$^{13}\text{CH}_4$	1.0000	1.7321	1.0396	-0.1476	0.4099	1.4974
$^{29}\text{SiH}_4$	1.0000	1.7321	1.0205	-0.0668	0.1861	1.4660

TABLE X. Shielding derivatives and vibrational corrections to the isotropic shielding constants in  $^{13}\text{CH}_4$ <sup>a</sup> and  $^{29}\text{SiH}_4$  at 0 K.<sup>b</sup>

	$^{13}\text{CH}_4$		$^{29}\text{SiH}_4$	
	$^{13}\text{C}$	$^1\text{H}$	$^{29}\text{Si}$	$^1\text{H}$
$(\partial\sigma_{av}/\partial S_1)_e$ (ppm/Å)	-104.0	-17.34	-41.50	-8.784
$(\partial^2\sigma_{av}/\partial S_1^2)_e$ (ppm/Å <sup>2</sup> )	-34.46	19.90	-79.32	5.151
$(\partial^2\sigma_{av}/\partial S_2^2)_e$ (ppm/Å <sup>2</sup> )	17.52	-2.236	5.535	-1.042
$(\partial^2\sigma_{av}/\partial S_4^2)_e$ (ppm/Å <sup>2</sup> )	-180.5	7.817	-257.9	3.969
$(\partial^2\sigma_{av}/\partial S_5^2)_e$ (ppm/Å <sup>2</sup> )	49.17	0.2369	61.38	-0.381
$(\partial^2\sigma_{av}/\partial S_4S_5)_e$ (ppm/Å <sup>2</sup> )	5.508	0.1553	3.914	0.4701
$(\partial\sigma_{av}/\partial S_1)_e\langle S_1 \rangle$ (ppm)	-5.65	-0.942	-2.50	-0.529
$1/2(\partial^2\sigma_{av}/\partial S_1^2)_e\langle S_1^2 \rangle$ (ppm)	-0.10	0.057	-0.31	0.020
$(\partial^2\sigma_{av}/\partial S_2^2)_e\langle S_2^2 \rangle$ (ppm)	0.58	-0.074	0.29	-0.054
$3/2(\partial^2\sigma_{av}/\partial S_4^2)_e\langle S_4^2 \rangle$ (ppm)	-1.71	0.074	-3.14	0.048
$3/2(\partial^2\sigma_{av}/\partial S_5^2)_e\langle S_5^2 \rangle$ (ppm)	2.20	0.011	3.69	-0.229
$3(\partial^2\sigma_{av}/\partial S_4S_5)_e\langle S_4S_5 \rangle$ (ppm)	-0.01	-0.000	-0.00	-0.000
Total correction (ppm)	-4.7	-0.87	-2.0	-0.54

<sup>a</sup>[6s4p2d/3s2p] basis used.<sup>b</sup>[8s6p2d/3s2p] basis used.

lengths should not be ignored. We note that bond angle vibration contributions nearly cancel each other and note that the second-order derivative contribution of  $S_1$  is very small. Our results show that the assumption by Jameson and Osten may be a reasonable approximation.

### F. Comparison between calculations and experiments

Tables I and II show that the MP3 values for the isotropic shieldings of the heavier atoms (C to Cl) at the experimental geometries are higher than the experimental values. However, the vibrational corrections are negative and improve the calculated shieldings of the heavier nuclei except  $^{17}\text{O}$  and  $^{33}\text{S}$ . In  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  the MP3 shieldings are lower

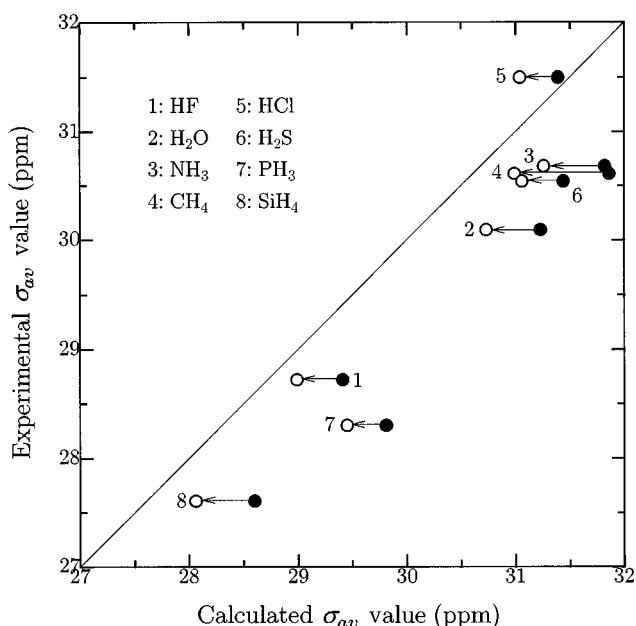


FIG. 1. Calculated and experimental proton shieldings. (O) vibrationally corrected shieldings; (●) MP3 shieldings at the experimental geometries.

than the experimental shieldings and the vibrational corrections further deteriorate agreement with the experimental values. Gauss suggested that the experimental value  $344.0 \pm 17.2$  ppm for the isotropic O shielding in  $\text{H}_2\text{O}$  may also be too high.<sup>38</sup> The experimental value for the isotropic S shielding in  $\text{H}_2\text{S}$  may also be too high.

Tables I and II show that the MP3 values for the isotropic proton shieldings in the experimental geometry molecules are higher than the experimental shieldings except HCl. The vibrational corrections to the isotropic proton shieldings are negative and improve the calculated values. The calculated MP3 proton shieldings at the experimental geometries and the vibrationally corrected proton shieldings are plotted against the experimental values in Fig. 1. Figure 1 shows that the vibrationally corrected proton shieldings are yet higher than the experimental shieldings. The higher-order correlation corrections and rotational motion corrections may be necessary for obtaining better agreement with experimental proton shieldings.

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