

Study of the stretching vibrational band intensities of XH_4 molecules employing four-dimensional *ab initio* ($X=C$ and Sn) and *effective* ($X=C$ and Si) dipole moment surfaces

Sheng-Gui He, An-Wen Liu, Hai Lin,^{a)} Shui-Ming Hu,^{b)} Jing-Jing Zheng, Lu-Yuan Hao, and Qing-Shi Zhu

Laboratory of Bond Selective Chemistry, University of Science and Technology of China, Hefei, 230026, People's Republic of China

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Stretching vibrational band intensities of XH_4 molecules were investigated employing four-dimensional *ab initio* ($X=C$ and Sn) and *effective* ($X=C$ and Si) dipole moment surfaces (DMS) in combination with the local mode potential energy surfaces. The *ab initio* DMS of CH_4 and SnH_4 calculated at the coupled cluster CCSD(T) level of theory reproduced most of the observed intensities within a factor of 1.5. The *effective* DMS of CH_4 and SiH_4 were obtained by adjusting some selected high-order terms in the *ab initio* DMS to fit the observed intensities. They were applied to the corresponding deuterated isotopomers yielding better results than the *ab initio* DMS. The intensities of the combination bands are mainly due to the interbond cross terms in the DMS for SiH_4 , GeH_4 , and SnH_4 , while for CH_4 , both diagonal and cross terms are important. The relatively strong combination band that has comparable intensity with the pure overtone was predicted at the fourth local mode manifold for SnH_4 . © 2002 American Institute of Physics. [DOI: 10.1063/1.1520130]

I. INTRODUCTION

The quantum chemistry calculations have shed light on the area of molecular overtone intensity. Many interesting observations have been successfully rationalized using dipole moment surface (DMS) from *ab initio* or density functional calculations. Some examples are (1) the more intense of the first overtone than the fundamental in $CHCl_3$ originates from the nonlinearity of the DMS near molecular equilibrium;^{1,2} (2) the cancellation of transition moments from linear and quadratic terms in the DMS leads to a rapid intensity decrease of Si–H stretching overtones in $SiHD_3$,³ $SiHF_3$,⁴ and $SiHCl_3$;⁵ and (3) large cross terms in the DMS in combination with the cancellation effect result in unusually strong combination bands in the third and fourth stretching manifolds for PH_3 ⁶ and GeH_4 ,⁷ respectively.

However, it has also been found that the DMS from quantum chemistry calculations often gives poor predictions for intensities of high overtones.^{3–10} About 3–10 times over- or underestimation of the observed intensities is common. This is mainly due to inaccurate high-order terms in the DMS, which would make a significant contribution to the transitions in highly excited energy region.^{2,4,9,11} On the other hand, the calculated intensities are found to be less sensitive to the potential energy surface (PES).^{1,8,11–13} Therefore, it is attractive to adjust some selected high-order terms in theoretical DMS to fit the observed intensities. This

method has been adopted to get the *effective* stretching DMS of $SiHF_3$ ⁴ and GeH_4 ⁷ with improved results.

In the present study, we extend our previous intensity studies by applying both *ab initio* and *effective* four-dimensional (4-D) stretching DMS to three group IV hydrides (CH_4 , SiH_4 , and SnH_4), which will provide us another angle of view of the local mode feature about the vibrations in the XH_4 species, in addition to energy levels. It is a fact that SiH_4 , GeH_4 , and SnH_4 are good local mode molecules whose stretching vibrational energy levels are well described by the local mode theory, for instance, the anharmonically coupled anharmonic oscillator (ACAO) model.^{14–16} It is not the case for CH_4 because of the strong Fermi resonance between the bending and stretching vibrations. However, it is still instructive to apply the crude local mode picture to CH_4 so as to compare it with the other XH_4 species. Moreover, a very simple local mode model involving only C–H stretching motions has been successfully applied to predict the overtone intensities for CH_4 employing a DMS calculated from QCISD (quadratic configuration interaction including single and double excitations) method.²⁷ This implies a good zeroth-order approximation that the C–H stretching modes carry the intrinsic intensity in this molecule. This is also consistent with the findings in the study of the C–H chromophore intensities of CHD_3 .²⁴

The experimental intensities of CH_4 ^{17–19} and SiH_4 ^{20,21} can be found in the literature up to the eighth stretching overtone region. For SnH_4 , the experimental intensities in the fundamental and low overtone regions have been reported.^{22,23} On the theoretical aspect, several investigations on the DMS of CH_4 have been presented. Quack's group derived analytical, nine-dimensional (9-D) vector valued

^{a)}Current address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany.

^{b)}Author to whom correspondence should be addressed. Fax: +86-551-3602969; electronic mail: smhu@ustc.edu.cn

DMS from an analysis of the *ab initio* calculated electronic structure and a direct adjustment to the experimental data for the overtone intensities of the CH chromophore in CHD₃.^{24,25} It is somehow questionable to neglect the stretching–stretching coupling terms in the 9-D DMS model. Mourbat, Aboumajd, and Loëte determined the linear and quadratic dipole moment derivatives of CH₄ in terms of the symmetric internal coordinates by use of the experimental spectroscopic parameters.²⁶ This low-order DMS is not expected to give a good description for high overtone intensities of CH₄. We will compute *ab initio* 4-D stretching DMS of CH₄ and SnH₄ in this work. The *effective* DMS for CH₄ and SiH₄ will be determined based on the *ab initio* ones (this work for CH₄ and Ref. 10 for SiH₄).

II. HAMILTONIAN AND DIPOLE MOMENT MODELS

The ACAO II model²⁸ will be adopted in this work for all the XH₄ molecules. The Hamiltonian takes the form

$$H = \sum_{i=1}^4 \left(\frac{1}{2} G_{rr} p_i^2 + D_e y_i^2 \right) + \sum_{i < j}^4 \left(G_{rr'} p_i p_j + \frac{1}{a^2} F_{rr'} y_i y_j \right). \quad (1)$$

Here $y_i = 1 - \exp(-ar_i)$, r_i is the i -th X–H stretching displacement, $G_{rr} = 1/m_H + 1/m_X$, m_H (m_X) is the mass of the H (X) atom, $G_{rr'} = -1/3m_X$, p_i is the momentum conjugate to r_i , D_e and a are Morse parameters, and $F_{rr'}$ is the inter-bond potential coupling coefficient. Replacing $y_i y_j / a^2$ by $r_i r_j$ yields the ACAO I model. Since earlier works^{6,7,10} have demonstrated that ACAO I and II models gave very similar intensity results, we will exclusively use the ACAO II model in this work.

The PES parameters of SiH₄ and SnH₄ can be found in Refs. 10, 29. For CH₄, the PES parameters were determined in this work by least-squares fitting to the observed band centers in Ref. 19 ($V=6$ and 7), Refs. 30, 31 ($V=4$ and 5), and Ref. 32 ($V \leq 3$), where V is the total stretching vibrational quantum number and $V = n_1 + n_2 + n_3 + n_4$ [in the local mode notation ($n_1 n_2 n_3 n_4$), n_i is the quantum number of the i th X–H bond stretching].²⁸ The observed values below and above 10000 cm⁻¹ were assigned the weights of 1.0 and 0.5, respectively. In the least-squares fitting (and other calculations throughout this work), the vibrational eigen-values and eigen-functions were calculated variationally,¹⁶ by setting the maximum value of V to 12. The determined parameters is $D_e = 40212(246)$ cm⁻¹, $a = 1.82517(679)$ Å⁻¹, and $F_{rr'} = 2242(279)$ cm⁻¹ Å⁻², where the value in the parentheses is one standard error in the last significant digit. The root-mean-squares of the fitting residual is 11.6 cm⁻¹. This large value is due to the Fermi resonance which is not included in the adopted ACAO model, as expected.

The absolute intensity can be calculated as

$$I = 3K \bar{\nu} |\langle N | M_z | 0 \rangle|^2. \quad (2)$$

Here $|0\rangle$ denotes the wave function of the ground state and $|N\rangle$ the one of the excited state with F_{2z} symmetry of the T_d point group, $\bar{\nu}$ is the band center in cm⁻¹, $K = 4.1623755$

$\times 10^{-19}$ cm² Debye⁻², and M_z is the dipole moment component (in Debye) along one of the S_4 -symmetry axes in the XH₄ molecule.

In an earlier study,¹⁰ M_z was expanded with the symmetry-adapted polynomials in terms of the four bond length displacements (r_i , $i = 1, 2, 3, 4$),

$$M_z(r_1, r_2, r_3, r_4) = \sum_{abcd} C_{abcd}^{F_{2z}} O_{abcd}^{F_{2z}}(r_1, r_2, r_3, r_4), \quad (3)$$

where a , b , c , and d are zero or positive integers, $C_{abcd}^{F_{2z}}$ are expansion coefficients, and $O_{abcd}^{F_{2z}}(r_1, r_2, r_3, r_4)$ are polynomials with F_{2z} symmetry. The method to construct the symmetry-adapted polynomials was described in the original reference.¹⁰ We derive the necessary terms used in this work. They are listed below:

$$O_{a000}^{F_{2z}}(r_1, r_2, r_3, r_4) = (r_1^a + r_2^a - r_3^a - r_4^a)/2, \quad a = 1, 2, 3, 4, \quad (4)$$

$$O_{1100}^{F_{2z}}(r_1, r_2, r_3, r_4) = (r_1 r_2 - r_3 r_4)/\sqrt{2}, \quad (5)$$

$$O_{0111}^{F_{2z}}(r_1, r_2, r_3, r_4) = [r_3 r_4 (r_1 + r_2) - r_1 r_2 (r_3 + r_4)]/2, \quad (6)$$

$$O_{2100}^{1F_{2z}}(r_1, r_2, r_3, r_4) = [(r_1^2 + r_2^2)(r_3 + r_4) - (r_3^2 + r_4^2) \times (r_1 + r_2)]/\sqrt{8}, \quad (7)$$

$$O_{2100}^{2F_{2z}}(r_1, r_2, r_3, r_4) = [r_1 r_2 (r_1 + r_2) - r_3 r_4 (r_3 + r_4)]/2. \quad (8)$$

III. DETERMINATION OF DIPOLE MOMENT COEFFICIENTS

First, *ab initio* calculations were adopted to determine the dipole moment coefficients of CH₄ and SnH₄. The CCSD(T) (coupled cluster theory with all single and double substitutions from the Hartree–Fock reference determinant³³ augmented by a perturbative treatment of connected triple excitations)^{34,35} method was used. For CH₄, the cc-pVQZ (correlation-consistent polarized valence quadruple zeta) basis set^{36,37} was used. For SnH₄, the Hay and Wadt (HW)³⁸ effective core potential was adopted for the heavy Sn atom and accordingly a smaller cc-pVTZ (correlation-consistent polarized valence triple zeta) basis set for H atom was chosen. The valence shell basis set used with the HW pseudo-potential was taken from Table 3 of Ref. 39, where it was deduced from a universal Gaussian basis set.^{40,41}

The calculations employed the GAUSSIAN 98 package⁴² which ran on a PC-cluster in our laboratory. The dipole moment expansion coefficients were determined in this work via central differences of the dipole moments (centered about the optimized geometry). The optimized equilibrium C–H and Sn–H bond lengths are 1.0879 and 1.7030 Å, respectively, which are close to the experimental data (1.0858 and 1.701 Å).^{43,44} The single point dipole moment was calculated as

$$M_z = [E(p_z) - E(-p_z)]/2p_z, \quad (9)$$

where $E(p_z)$ and $E(-p_z)$ are, respectively, the CCSD(T)

TABLE I. Four-dimensional stretching vibrational DMS coefficients^a of XH₄ (X=C, Si, and Sn).

	CH ₄					SiH ₄		SnH ₄
	<i>Ab initio</i>	<i>Effective</i> ^b	Ref. 24 ^c	Ref. 25 ^c	Ref. 26 ^d	<i>Ab initio</i> ^e	<i>Effective</i> ^b	<i>Ab initio</i>
$C_{1000}^{F_{2z}}$	-0.71752	-0.71752	-0.7110	-0.8070	-0.737	-1.50938	-1.50938	-2.10264
$C_{2000}^{F_{2z}}$	-0.89943	-1.198(22)	-1.2001	-1.2597	-1.21	-0.51240	-0.51240	-0.18071
$C_{1100}^{F_{2z}}$	0.32339	0.225(31)	0.231(61) ^f	0.27126	0.27126	0.18425
$C_{3000}^{F_{2z}}$	0.30066	0.190(28)	0.3286	0.5169	...	0.5207	0.412(16)	0.67315
$C_{2100}^{-1F_{2z}}$	-0.57491	-0.179(44)	-0.17018	-0.180(53)	-0.18465
$C_{2100}^{2F_{2z}}$	0.12704	0.12704	0.09808	0.09808	0.08726
$C_{0111}^{F_{2z}}$	0.06987	0.06987	0.06434	0.06434	0.08947
$C_{4000}^{F_{2z}}$	0.183(24)	...

^aThe units are defined such that the dipole moment is in Debye ($=3.33564 \times 10^{-30}$ C m), and the bond length displacement in Å.
^bThe coefficient with no parentheses is constrained to the *ab initio* value, the value in the parentheses is one standard error in last significant digit in the least-squares fitting.
^cThe ‘‘Set I’’ 9-D dipole moment function in Ref. 24 and the 9-D function in Ref. 25 were used to calculate the DMS expansion coefficients up to third order by a finite-difference method, and the steps were set to 0.05 Å.
^dThe DMS expansion coefficients in this work are related to the dipole moment derivatives in Ref. 26 as follows: $C_{1000}^{F_{2z}} = M_3$, and $C_{2000}^{F_{2z}} = (M_{33} + M_{13})/2$, where M_{13} was constrained to zero in the reference.
^eTaken from Ref. 10.
^f $C_{1100}^{F_{2z}}$ was determined by fitting the experimental intensities with $C_{n000}^{F_{2z}}$ ($n=1,2,3$) being constrained to the reference’s values (see the text for details).

energies of the molecule in the electric field with positive and negative strength of p_z along the molecular fixed z axis (see Ref. 10 for definition), and p_z was chosen to be 0.005 atomic units.
 The formula of the central differences were deduced according to the dipole moment expansion in Eqs. (3)–(8). The steps in the central differences were set to 0.1 Å. To deter-

mine the terms up to third order, 14 single point dipole moments were calculated for each molecule. The data are available from the authors upon request. The obtained *ab initio* DMS coefficients of CH₄ and SnH₄ in this work and those of SiH₄ taken from Ref. 10 are, respectively, listed as columns 2, 9, and 7 in Table I. They will be used to calculate the band intensities according to Eq. (2) in the next section.

TABLE II. Observed and calculated stretching vibrational band intensities (in 10^{-22} cm) for CH₄, SiH₄, and SnH₄.

band ^b	CH ₄					SiH ₄			SnH ₄ ^a
	$I_{obs.}^c$	$I_{cal.1}^d$	$I_{cal.2}^e$	$I_{cal.3}^f$	$I_{cal.4}^g$	$I_{obs.}^h$	$I_{cal.1}^d$	$I_{cal.2}^e$	$I_{cal.3}^d$
(1000)	1.11E+5	1.27E+5	1.35E+5	1.34E+5	1.33E+5	4.20E+5	4.94E+5	4.96E+5	9.05E+5
(2000)	6.55E+2	1.96E+1	5.88E+2	7.57E+2	5.75E+2	2.69E+3	2.57E+3	2.57E+3	1.20E+4
(1100)	6.64E+2	4.66E+2	6.31E+2	1.56E+2	5.66E+2	2.49E+2	1.99E+2	1.99E+2	1.72E+2
(3000)	...	9.81E+1	2.30E+2	2.82E+2	2.72E+2	8.33E-1	3.84E+0	8.44E-1	6.25E+1
(2100)	...	6.69E+1	5.58E+1	2.97E+1	5.42E+1	1.36E+1	5.46E+0	5.50E+0	4.28E+0
(4000)	2.37E+1	1.93E+1	3.27E+1	4.10E+1	4.09E+1	2.53E+0	6.22E+0	2.30E+0	4.83E-1
(3100)	3.24E+0	5.17E+0	3.53E+0	2.44E+0	3.68E+0	1.28E-1	2.53E-1	2.33E-1	2.00E-1
(5000)	3.07E+0	3.00E+0	4.40E+0	5.63E+0	5.67E+0	5.77E-1	1.16E+0	3.44E-1	5.27E-1
(4100)	2.57E-1	4.29E-1	2.60E-1	2.15E-1	2.84E-1	...	1.66E-2	1.40E-2	1.26E-2
(6000)	5.32E-1	4.77E-1	6.41E-1	8.36E-1	8.45E-1	2.07E-2	1.72E-1	4.08E-2	1.21E-1
(5100)	2.31E-2	4.24E-2	2.34E-2	1.97E-2	2.50E-2	...	1.38E-3	1.07E-3	1.00E-3
(7000)	1.09E-1	8.27E-2	1.05E-1	1.39E-1	1.41E-1	4.32E-3	2.57E-2	4.88E-3	2.23E-2
(6100)	2.60E-3	4.86E-3	2.46E-3	2.04E-3	2.57E-3	...	1.38E-4	9.86E-5	9.76E-5
(8000)	2.60E-2	1.59E-2	1.94E-2	2.60E-2	2.63E-2	4.95E-4	4.07E-3	6.26E-4	4.05E-3
(7100)	...	6.32E-4	2.87E-4	2.31E-4	2.93E-4	...	1.61E-5	1.07E-5	1.13E-5
(9000)	5.96E-3	3.43E-3	4.04E-3	5.47E-3	5.54E-3	1.36E-4	6.98E-4	8.78E-5	7.68E-4
(8100)	...	9.01E-5	3.52E-5	2.60E-5	3.42E-5	...	2.17E-6	1.35E-6	1.53E-6
Δ	...	1.05 ⁱ	0.21	0.50 ^j	0.32	...	1.28	0.43	0.36

^aThe respective observed intensities (in 10^{-22} cm) for the (1000), (2000), and (3000) bands are 7.37E+5, 1.83E+4, and 9.50E+1 (see the text for details).
^bThe summed intensity of two close-lying bands in each (n 100) manifold is given when $n > 1$.
^cTaken from Refs. 17–19.
^d*Ab initio* DMS used.
^e*Effective* DMS used.
^fOnly $C_{n000}^{F_{2z}}$ ($n=1,2,3$) terms (calculated from the 9-D DMS in Ref. 24) in column 4 of Table I used.
^gAll four terms in column 4 of Table I used (see the text for details).
^hTaken from Refs. 10, 20, 21.
ⁱ $\Delta = 0.41$ if the (2000) band intensity is excluded.
^j $\Delta = 0.26$ if the (n 100) band intensities are excluded.

TABLE III. Transition moments (in Debye) from the vibrational ground state to the excited state calculated with different terms in the *ab initio* DMS of CH₄.

	(1000)	(2000)	(1100)	(3000)	(2100, 1F _{2z})	(2100, 2F _{2z})
C ₁₀₀₀ ^{F_{2z}}	-5.569E-2	-5.379E-3	-1.904E-3	8.935E-4	2.630E-4	-1.383E-4
C ₂₀₀₀ ^{F_{2z}}	-3.764E-3	6.587E-3	2.565E-3	-1.679E-3	-5.198E-4	2.463E-4
C ₁₁₀₀ ^{F_{2z}}	5.583E-4	-5.790E-4	1.827E-3	4.311E-5	-2.563E-4	-4.285E-5
C ₃₀₀₀ ^{F_{2z}}	4.787E-4	-2.197E-4	-8.738E-5	-2.444E-4	-7.922E-5	5.075E-5
C ₂₁₀₀ ^{1F_{2z}}	3.529E-4	1.325E-4	4.970E-5	4.357E-5	-7.153E-5	3.599E-4
C ₂₁₀₀ ^{2F_{2z}}	6.780E-5	-2.750E-5	5.017E-5	-1.383E-5	6.405E-5	1.430E-5
C ₀₁₁₁ ^{F_{2z}}	-7.878E-7	2.936E-6	-8.630E-6	9.600E-7	-7.818E-6	-3.863E-6
Total ^a	-5.800E-2	5.172E-4	2.492E-3	-9.558E-4	-6.076E-4	4.862E-4
Expt. ^b	5.423E-2	3.011E-3	2.976E-3			

^aCalculated total transition moment.

^bTransition moment calculated with $u = \sqrt{I/3K\bar{\nu}}$, where I is the observed intensity in Refs. 17, 18, $\bar{\nu}$ is the band center in Refs. 14, 32, and K is the same as in Eq. (2).

Second, the *effective* DMS coefficients of CH₄ and SiH₄ were determined in a least-squares procedure, in which

$$\Delta^2 = \frac{1}{n_{\text{data}}} \sum_{i=1}^{n_{\text{data}}} \left[\ln \frac{I_i(\text{cal})}{I_i(\text{obs})} \right]^2 \quad (10)$$

is minimized. Here Δ is the logarithmic deviation,¹² n_{data} is the number of experimental data, $I_i(\text{cal})$ and $I_i(\text{obs})$ are calculated and observed band intensities, respectively. For each (n 100) manifold with $n > 1$, there are two close-lying bands. The summed intensity for the whole manifold is used in this case as justified in Ref. 7.

In the least-squares procedure, some selected high-order DMS coefficients were optimized and all others were constrained to the *ab initio* values (PES parameters kept to the values in this work for CH₄ and Ref. 10 for SiH₄). The *effective* DMS coefficients are collected in columns 3 and 8 of Table I for CH₄ and SiH₄, respectively. The justification to optimize the specific terms in the *ab initio* DMS will be discussed in the next section.

IV. RESULTS

A. CH₄

In this work, the experimental intensity of the (2000) band for CH₄ was obtained by a summation of the individual line intensities measured by Margolis¹⁸ in the range of 5500–6180 cm⁻¹. The intensity of the (1100) band in the same region has been determined¹⁸ and was removed simply by subtraction. Except the (1100) band centered around 6005 cm⁻¹,⁴⁵ the structure of other bands in this region is complicated. Some of them have been assigned.^{32,46} As mentioned in Sec. II, the stretching modes are assumed to carry the intrinsic intensity in CH₄. Thus, we attributed the summed intensity for these bands to the (2000) local mode overtone whose predicted band center is 5856 cm⁻¹.¹⁴

The observed and calculated intensities from the *ab initio* DMS are listed as columns 2 and 3 in Table II for CH₄. It can be seen that the CCSD(T) DMS obtained in this work reproduced most of the observed intensities within a factor of

TABLE IV. Observed and calculated C–H stretching vibrational band intensities (in 10⁻²² cm) of CH_nD_{4-n} ($n = 1, 2, 3$).

Band ^a	$I_{\text{obs.}}(\text{CHD}_3)^b$	$I_{\text{cal. 1}}(\text{CHD}_3)^c$	$I_{\text{cal. 2}}(\text{CHD}_3)^d$	$I_{\text{cal}}(\text{CH}_2\text{D}_2)^c$	$I_{\text{cal}}(\text{CH}_3\text{D})^c$
(100)	3.74E+4	3.59E+4	3.39E+4	7.08E+4	1.04E+5
(200)	2.43E+2	2.60E+2	4.00E+1	4.54E+2	5.80E+2
(110)	9.16E+1	2.76E+2
(300)	7.04E+1	7.00E+1	3.81E+1	1.34E+2	1.90E+2
(210)	6.13E+0	2.22E+1
(400)	8.43E+0	8.73E+0	5.94E+0	1.72E+1	2.52E+1
(310)	3.81E-1	1.38E+0
(500)	1.14E+0	1.06E+0	8.09E-1	2.08E+0	3.14E+0
(410)	2.86E-2	1.03E-1
(600)	5.83E-2	1.35E-1	1.11E-1	2.69E-1	4.14E-1
(510)	2.48E-3	8.93E-3
(700)	...	1.54E-2	1.37E-2	4.96E-2	7.83E-2
(800)	...	2.76E-3	2.28E-3	5.38E-3	8.68E-3
(900)	...	2.84E-4	2.35E-4	1.56E-3	1.55E-3
Δ	...	0.34	0.85

^a($n_1n_2n_3$) for CH₃D, (n_1n_2) for CH₂D₂, and (n_1) for CHD₃. The summed intensity is given for each manifold.

^bExperimental data are taken from Ref. 24 and the band strength (G) is converted to intensity (I) by $I = G\bar{\nu}$, where $\bar{\nu}$ is the observed band center (Ref. 47). The intensities of individual components within a polyad are summed.

^c*Effective* DMS used.

^d*Ab initio* DMS used.

1.5. The large logarithmic deviation (1.052) is due to the (2000) band whose intensity is about 25 times underestimated by the calculation. This is caused by the DMS cancellation effect.¹¹

In Table III, one finds that the $C_{1000}^{F_{2z}}$ term plays a dominant role in the fundamental transition moment of CH_4 , which yields a good agreement with observed intensity. As to the (2000) band, the prominent contributions from $C_{1000}^{F_{2z}}$ and $C_{2000}^{F_{2z}}$ terms cancel significantly, resulting in a small total transition moment. This implies that it is reasonable to constrain the $C_{1000}^{F_{2z}}$ to its *ab initio* value, while to adjust $C_{2000}^{F_{2z}}$ to achieve improvements. We also fixed the $C_{2100}^{2F_{2z}}$ because of its strong correlation with $C_{2100}^{1F_{2z}}$ and $C_{0111}^{F_{2z}}$ because of its small contribution to the transition moment. Other coefficients up to third order in the DMS were refined to get the *effective* values, and the corresponding intensity results are listed as column 4 in Table II. The improvement is evident: the logarithmic deviation decreased from 1.05 to 0.21.

We note that the *ab initio* and *effective* DMS coefficients of CH_4 are close to each other for $C_{2000}^{F_{2z}}$, $C_{1100}^{F_{2z}}$, and $C_{3000}^{F_{2z}}$, while for $C_{2100}^{1F_{2z}}$, the *ab initio* value is about three times as large as the *effective* one. It is interesting to compare our *ab initio* and *effective* DMS of CH_4 with those in the literature. Because there are no bond–bond stretching coupling terms in the analytical 9-D DMS derived by Quack's group, we only list the stretching–stretching diagonal terms from Refs. 24–26 in Table I, where the values in columns 4 and 5 are calculated from the analytical 9-D dipole moment functions by the finite-difference method. It can be seen that the first-order term ($C_{1000}^{F_{2z}}$) determined by the *ab initio* method in this work is close to values in Refs. 24 and 26. The *effective* second-order term ($C_{2000}^{F_{2z}}$) is close to all the values in the literature. This implies that it is important to have a very accurate $C_{2000}^{F_{2z}}$ value for predicting overtone intensities of CH_4 .

The *effective* DMS of CH_4 was used to compute the intensities for the deuterated isotopomers. The results are listed in Table IV. The available experimental intensities are given for CHD_3 .^{24,47} It is noticeable that all the C–H chromophore intensities for each Fermi resonance polyad in CHD_3 are reproduced quite well. This corroborates our approximation that the stretching modes of CH_4 carry the intrinsic intensity (Sec. II). On the other hand, the *ab initio* DMS gives a poor prediction again for the first C–H stretching overtone (see column 4), indicating that the *effective* DMS is superior to the *ab initio* one in this work.

B. SiH_4

The same considerations in the previous subsection were applied to SiH_4 in selecting the DMS coefficients for optimization. The logarithmic deviation decreases now from 1.28 to 0.43. In the optimization, an additional fourth-order diagonal term ($C_{4000}^{F_{2z}}$) was included, which reduced the logarithmic deviation significantly ($\Delta = 0.64$ if $C_{4000}^{F_{2z}}$ is constrained to zero). The intensities calculated from the *effective* DMS are presented in Table II as column 9, in comparison

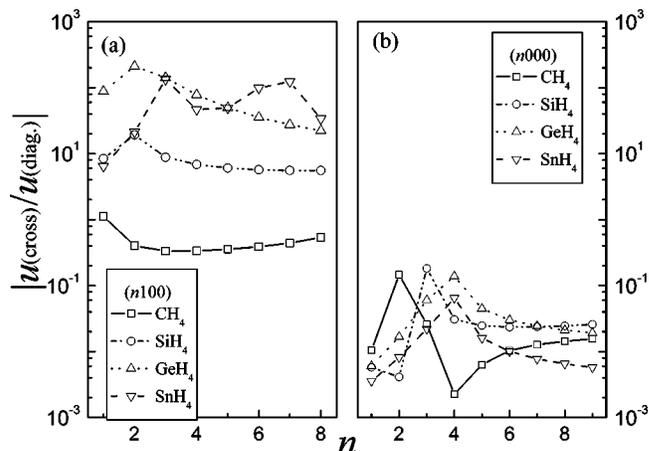


FIG. 1. Calculated ratio (absolute value) of the transition moment from the cross terms to that from the diagonal terms in the DMS for (*n*100) (a) and (*n*000) (b) bands of XH_4 molecules. The *effective* DMS of CH_4 , SiH_4 , and GeH_4 (4-D DMS₃ in Ref. 7) and the *ab initio* DMS of SnH_4 were used. For the (*n*100) manifold with $n > 1$, because there are two close-lying bands, the transition moment is computed as $u(\alpha) = \sqrt{u_1(\alpha)^2 + u_2(\alpha)^2}$, where $\alpha = \text{“cross”}$ or “diagonal” and $u_1(\alpha)$ and $u_2(\alpha)$ are the transition moments of the two bands calculated from the α terms in the DMS.

with those measured in the experiments^{10,20,21} (column 7) and calculated from the *ab initio* DMS¹⁰ (column 8).

It can be seen from Table I (columns 7 and 8) that the *effective* $C_{3000}^{F_{2z}}$ and $C_{2100}^{1F_{2z}}$ values are close to the corresponding *ab initio* ones and an additional fourth-order term ($C_{4000}^{F_{2z}}$, not determined from *ab initio* calculations¹⁰) was well determined in the least-squares procedure.

The *effective* DMS of SiH_4 was also used to compute the Si–H stretching intensities for the deuterated isotopomers. We found that the ratios of the calculated intensities satisfy almost exactly the following relations, $I_{n000} : I_{n00} : I_{n0} : I_n = 4:3:2:1$ and $I_{n100} : I_{n10} : I_{n1} = 6:3:1$, where the subscripts $n_1 n_2 n_3 n_4$, $n_1 n_2 n_3$, $n_1 n_2$, and n_1 denote the excited Si–H stretching quantum numbers in SiH_4 , SiH_3D , SiH_2D_2 , and SiHD_3 , respectively. The results reflect a local mode feature of the Si–H stretching, which are consistent with an earlier finding in Ref. 10.

Because the band intensities of SiH_3D , SiH_2D_2 , and SiHD_3 calculated from the *effective* DMS can be easily deduced from those of SiH_4 with the above relations, they are not listed in this work. We found that for *effective* DMS, the calculated intensities of these SiH_4 isotopomers agree with the experimental values in Refs. 3, 10 within a factor of *ca.* 2 for all bands with the total stretching vibrational quantum number $V \leq 4$. One can find from Ref. 10 that for *ab initio* DMS, the agreement in $V = 3$ and 4 is much less satisfactory.

It is noticeable that the intensity of $7\nu_1$ in SiH_4 ²¹ was observed to be only one-third of that in SiHD_3 ,⁴⁸ in contrast to the prediction of being 4 times as large. This discrepancy may be introduced by experimental uncertainties in intensity measurement for high overtones. So we tried to exclude the (*n*000) ($n = 7, 8, 9$) experimental data in the *effective* DMS optimization for SiH_4 , but the result was little changed. The calculated intensities employing *effective* DMS are closer to observations for SiH_4 than for SiHD_3 in high overtones. The

TABLE V. Calculated transition moments (in Debye) between the basis of lower and upper states for the (2000) and (1100) bands of CH₄ and SiH₄.^a

	CH ₄			SiH ₄		
	<i>u</i>	Lower basis	Upper basis	<i>u</i>	Lower basis	Upper basis
(2000)						
diag. 1	3.50E-3	[0000] ₀ (99.96)	[2000] ₀ (87.93)	6.84E-3	[0000] ₀ (99.98)	[2000] ₀ (99.78)
2	-1.70E-4	[1100] ₀ (4.0E-2)	[1100] ₀ (11.94)	3.72E-4	[1000] ₀ (1.5E-3)	[2000] ₀ (99.78)
3	-1.58E-4	[1000] ₀ (1.0E-3)	[2000] ₀ (87.93)	-3.67E-4	[0000] ₀ (99.98)	[1000] ₀ (7.4E-4)
cross 1	-4.78E-4	[0000] ₀ (99.96)	[1100] ₀ (11.94)	-9.70E-5	[0000] ₀ (99.98)	[2000] ₀ (99.78)
2	6.94E-5	[0000] ₀ (99.96)	[2000] ₀ (87.93)	8.95E-5	[0000] ₀ (99.98)	[1100] ₀ (1.7E-1)
3	2.18E-5	[1100] ₀ (4.0E-2)	[2000] ₀ (87.93)	-2.32E-5	[1100] ₀ (1.8E-2)	[2000] ₀ (99.78)
(1100)						
diag. 1	1.29E-3	[0000] ₀ (99.96)	[2000] ₀ (11.97)	-5.86E-4	[0000] ₀ (99.98)	[1000] ₀ (1.9E-3)
2	4.61E-4	[1100] ₀ (4.0E-2)	[1100] ₀ (87.95)	4.47E-4	[1100] ₀ (1.8E-2)	[1100] ₀ (99.78)
3	-2.19E-4	[0000] ₀ (99.96)	[1000] ₀ (1.3E-3)	3.65E-4	[1000] ₀ (1.5E-3)	[1100] ₀ (99.78)
cross 1	1.30E-3	[0000] ₀ (99.96)	[1100] ₀ (87.95)	2.16E-3	[0000] ₀ (99.98)	[1100] ₀ (99.78)
2	2.56E-5	[0000] ₀ (99.96)	[2000] ₀ (11.97)	-5.53E-6	[1000] ₀ (1.5E-3)	[1100] ₀ (99.78)
3	8.06E-6	[1100] ₀ (4.0E-2)	[2000] ₀ (11.97)	4.03E-6	[0000] ₀ (99.98)	[2000] ₀ (1.7E-1)

^aThe *effective* DMS of CH₄ and SiH₄ was used in the calculation. The factor in the parenthesis is the absolute square of the coefficient of the basis state in the eigenstate of the total Hamiltonian. Only the top three transition moments calculated, respectively, from the diagonal and cross terms in the DMS are listed.

discrepancy may also be due to some (unknown) contributions excluded in the models in this work.

C. SnH₄

In this work, the experimental absolute intensities of (n000) (*n* = 1,2,3) bands for SnH₄ were determined from the relative intensities of Ref. 23 using the absolute intensity of the fundamental in Ref. 22 as a reference. The values (in 10⁻²² cm) are 7.37 × 10⁵, 1.83 × 10⁴, and 9.50 × 10¹ for *n* = 1, 2, and 3, respectively. It can be seen from column 10 in Table II that the three observed intensities are well predicted ($\Delta = 0.36$) by the *ab initio* DMS. Therefore, it is not necessary to determine the *effective* DMS for SnH₄ at the moment.

V. DISCUSSION

An earlier work⁷ has demonstrated that some strong local mode combination band intensities of GeH₄ mainly arise

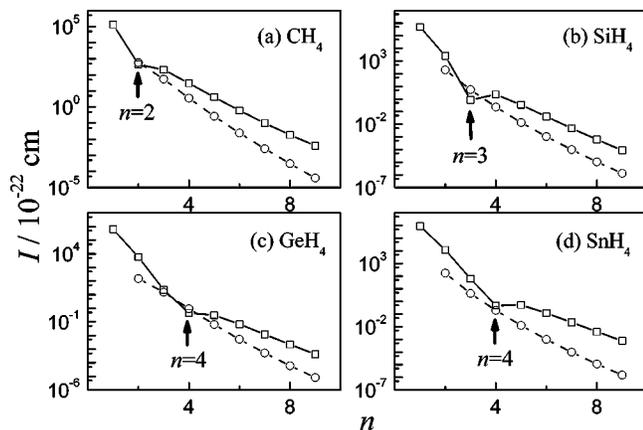


FIG. 2. Calculated intensities of (n000) (hollow squares with solid line) and (n-1100) (hollow circles with a dashed line) bands for XH₄ molecules. The *effective* DMS of CH₄, SiH₄, and GeH₄ (4-D DMS₃ in Ref. 7) and the *ab initio* DMS of SnH₄ were used. The summed intensity of two close-lying bands in each (n100) manifold with *n* > 1 is shown.

from the bond-bond cross terms in the DMS. The DMS in the present study enables us to examine the contributions from diagonal and cross terms in a systematic manner for XH₄ (X=C, Si, Ge, Sn) molecules. For CH₄, we can also check whether the neglect of the stretching coupling terms in the 9-D DMS^{24,25} is reasonable or not. The ratio of the transition moment from the cross terms to that from the diagonal terms in the DMS is plotted in Fig. 1(a) for (n100) and 1(b) for (n000) bands. The *effective* DMS of CH₄, SiH₄, and GeH₄ (4-D-DMS₃ in Ref. 7) and the *ab initio* DMS of SnH₄ were used, respectively. The following three points can be concluded from the figure:

- (1) For all the four group IV hydrides, the cross terms in the DMS are not important for the (n000) overtone transition moments. The transition moments from cross terms are 5–10 times smaller than those from diagonal terms in the cases where the DMS cancellation effect is significant^{7,10} (*n* = 2, 3, 4 for X=C, Si, Ge, respectively), and more than about 20 times smaller in other cases. It is consistent with the well known simple bond dipole model,^{28,49} which neglects the bond-bond stretching coupling terms in the DMS.
- (2) For local mode molecules (SiH₄, GeH₄, and SnH₄), the cross terms in the DMS are much more important than the diagonal ones for the (n100) combination transition moments. The transition moments from the former are 6–20, 20–200, and 6–150 times larger than those from the latter for SiH₄, GeH₄, and SnH₄, respectively. It can be used to explain why the bond dipole model underestimates the combinational band intensities by several orders of magnitude for local mode molecules, for example, AsH₃,⁵⁰ SiH₄, and GeH₄.²⁰
- (3) For the (n100) combination bands of CH₄, the ratio of transition moment from the DMS cross terms to that from the diagonal terms varies from 1/3 to 1, so diagonal terms are more important but the cross terms cannot be neglected. Column 5 of Table II lists the intensities of

CH_4 calculated from three diagonal terms ($C_{n000}^{F_{2z}}$, $n = 1, 2, 3$; see column 4 of Table I) derived from the 9-D DMS.²⁴ It can be seen that all the ($n000$) overtone intensities are well reproduced ($\Delta = 0.26$), but the agreement between calculated and observed intensities is less satisfactory for ($n100$) combinations, especially for the (1100) band. The overall logarithmic deviation is 0.50. If we add one cross term, $C_{1100}^{F_{2z}}$ in the DMS and use the observed intensities to optimize its value (column 4 of Table I), column 6 of Table II shows that the calculated ($n000$) overtone intensities are little changed but all the observed ($n100$) combination intensities are now significantly better reproduced ($\Delta = 0.32$). So we conclude that the analytical 9-D dipole moment functions of CH_4 in Refs. 24, 25 should be improved by introducing some stretching–stretching coupling terms when describing the stretching combination band intensities.

As an example to discuss the problem of “intensity borrowing” (via wave function mixing) in XH_4 molecules, Table V lists a decomposition of transition dipole moments into contributions from different transitions between zeroth order states indicated here by $[n_1n_2n_3n_4]_0$, which is a symmetry-adapted¹⁶ product state $\prod_{i=1}^4 \varphi_{n_i}$, where φ_{n_i} is the eigenstate of a Morse oscillator used in the sum of Eq. (1). Only the two lower overtone bands are discussed. It can be seen that for the (1100) combination band of CH_4 , the transition moment from $[0000]_0 \rightarrow [2000]_0$ (via DMS diagonal terms) is as large as that from $[0000]_0 \rightarrow [1100]_0$ (via DMS cross terms). In (1100) there is thus significant intensity borrowing from a diagonal contribution in the DMS ($[0000]_0 \rightarrow [2000]_0$). In comparison, we find that for the (1100) band of SiH_4 , the prominent transition moment is only from $[0000]_0 \rightarrow [1100]_0$ (via DMS cross terms). The reason is that the wave function mixing in CH_4 (nonlocal mode molecule) is much stronger than that in SiH_4 (local mode molecule). It can also be found that for the (2000) local mode overtone of both CH_4 and SiH_4 , there is no significant intensity borrowing, the prominent transition moment is from $[0000]_0 \rightarrow [2000]_0$ (via DMS diagonal terms).

Finally, we comment briefly on the relative intensities between the ($n-1100$) combinations and ($n000$) overtones. Figure 2 plots the ($n000$) and ($n-1100$) intensities for the four molecules. The intensity of all the ($n-1100$) sequences decreases smoothly as n increases. The ($n000$) sequences show sharp decreases until reaching $n = 2, 3, 4$, and 4 for $\text{X} = \text{C}, \text{Si}, \text{Ge}$, and Sn , respectively, owing to the DMS cancellation effect.^{4,7,10} This results in a relatively strong absorption of (1100), (2100), (3100), and (3100) for CH_4 , SiH_4 , GeH_4 , and SnH_4 , respectively. This has been observed for the first three molecules. For SnH_4 , further experimental investigations are necessary to check this point.

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- ¹M. Lewerenz and M. Quack, Chem. Phys. Lett. **123**, 197 (1986).
- ²H. Lin, L. F. Yuan, S. G. He, X. G. Wang, and Q. S. Zhu, J. Chem. Phys. **112**, 7484 (2000).
- ³H. Lin, H. Bürger, S. G. He, L. F. Yuan, J. Breidung, and W. Thiel, J. Phys. Chem. A **105**, 6065 (2001).
- ⁴H. Lin, H. Bürger, E. B. MKadmi, S. G. He, L. F. Yuan, J. Breidung, W. Thiel, T. R. Huet, and J. Demaison, J. Chem. Phys. **115**, 1378 (2001).
- ⁵S. G. He, H. Lin, H. Bürger, W. Thiel, Y. Ding, and Q. S. Zhu, J. Chem. Phys. **116**, 105 (2002).
- ⁶S. G. He, J. J. Zheng, S. M. Hu, H. Lin, Y. Ding, X. H. Wang, and Q. S. Zhu, J. Chem. Phys. **114**, 7018 (2001).
- ⁷S. G. He, H. Lin, W. Thiel, and Q. S. Zhu, Chem. Phys. Lett. **349**, 131 (2001).
- ⁸H. Lin, L. F. Yuan, S. G. He, and X. G. Wang, J. Chem. Phys. **114**, 8905 (2001).
- ⁹S. G. He, L. F. Yuan, H. Lin, Q. S. Zhu, and X. G. Wang, J. Phys. Chem. A **105**, 8428 (2001).
- ¹⁰H. Lin, S. G. He, X. G. Wang, L. F. Yuan, H. Bürger, J. F. D’Eu, N. Reuter, and W. Thiel, Phys. Chem. Chem. Phys. **3**, 3506 (2001).
- ¹¹H. G. Kjaergaard and B. R. Henry, J. Chem. Phys. **96**, 4841 (1992).
- ¹²T. K. Ha, M. Lewerenz, R. R. Marquardt, and M. Quack, J. Chem. Phys. **93**, 7097 (1990).
- ¹³J. R. Fair, O. Votava, and D. J. Nesbitt, J. Chem. Phys. **108**, 72 (1998).
- ¹⁴L. Halonen and M. S. Child, Mol. Phys. **46**, 239 (1982).
- ¹⁵L. Halonen and M. S. Child, J. Chem. Phys. **79**, 4355 (1983).
- ¹⁶L. Halonen and M. S. Child, Comput. Phys. Commun. **51**, 173 (1988).
- ¹⁷K. Kim, J. Quant. Spectrosc. Radiat. Transf. **37**, 107 (1987).
- ¹⁸J. S. Margolis, Appl. Opt. **27**, 4038 (1988).
- ¹⁹L. P. Giver, J. Quant. Spectrosc. Radiat. Transf. **19**, 311 (1978).
- ²⁰H. Lin, D. Wang, X. Y. Chen, X. G. Wang, Z. P. Zhou, and Q. S. Zhu, J. Mol. Spectrosc. **192**, 249 (1998).
- ²¹R. A. Bernheim, F. W. Lampe, J. F. O’Keete, and J. R. Qualey III, J. Chem. Phys. **80**, 5906 (1984).
- ²²A. M. Coats, D. C. McKean, and D. Steele, J. Mol. Struct. **320**, 269 (1994).
- ²³M. Halonen, L. Halonen, H. Bürger, and S. Sommer, J. Phys. Chem. **94**, 5222 (1990).
- ²⁴H. Hollenstein, R. R. Marquardt, M. Quack, and M. A. Suhm, J. Chem. Phys. **101**, 3588 (1994); and references therein.
- ²⁵R. Signorell, R. Marquardt, M. Quack, and M. A. Suhm, Mol. Phys. **89**, 297 (1996).
- ²⁶A. Mourbat, A. Aboumajd, and M. Loëte, J. Mol. Spectrosc. **190**, 198 (1998).
- ²⁷H. G. Kjaergaard, C. D. Daub, and B. R. Henry, Mol. Phys. **90**, 201 (1997).
- ²⁸M. S. Child and L. Halonen, Adv. Chem. Phys. **57**, 1 (1984).
- ²⁹X. Zhan, M. Halonen, H. Halonen, H. Bürger, and O. Polanz, J. Chem. Phys. **102**, 3911 (1995).
- ³⁰A. Campargue, D. Permogorov, and R. Jost, J. Chem. Phys. **102**, 5910 (1995).
- ³¹A. Campargue, M. Chenevier, and F. Stoeckel, Chem. Phys. Lett. **183**, 153 (1991).
- ³²E. Venuti, L. Halonen, and R. G. D. Valle, J. Chem. Phys. **110**, 7339 (1999); and references therein.
- ³³G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
- ³⁴M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).
- ³⁵K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
- ³⁶T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
- ³⁷D. E. Woon and T. H. Dunning, J. Chem. Phys. **98**, 1358 (1993).
- ³⁸P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).
- ³⁹A. E. de Oliveira, P. H. Guadagnini, R. Custodio, and R. E. Bruns, J. Phys. Chem. A **102**, 4615 (1998).
- ⁴⁰G. L. Malli and A. B. F. Da Silva, Phys. Rev. A **47**, 143 (1993).
- ⁴¹M. Giordan, R. Custodio, and N. H. Morgon, Chem. Phys. Lett. **279**, 396 (1997).
- ⁴²M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.3, Gaussian, Inc., Pittsburgh, PA, 1998.

- ⁴³D. L. Gray and A. G. Robiette, *Mol. Phys.* **37**, 1901 (1979).
- ⁴⁴L. E. Sutton and E. D. Phil, *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Special Publication, No. 18, the Chemical Society Burlington House, London, 1965.
- ⁴⁵B. Bobin, *J. Phys. (Paris)* **33**, 345 (1972).
- ⁴⁶R. Georges, M. Herman, J. C. Hilico, and O. Robert, *J. Mol. Spectrosc.* **187**, 13 (1998).
- ⁴⁷M. Lewerenz and M. Quack, *J. Chem. Phys.* **88**, 5408 (1988); and references therein.
- ⁴⁸A. Campargue, M. Chenevier, and F. Stoeckel, *Chem. Phys.* **137**, 249 (1989).
- ⁴⁹I. Schek, J. Jortner, and M. L. Sage, *Chem. Phys. Lett.* **64**, 209 (1979).
- ⁵⁰M. Halonen, L. Halonen, H. Bürger, and P. Moritz, *J. Phys. Chem.* **96**, 4225 (1992).