Electric Dipole Moment Derivatives for Methane and Silane Computed by Density Functional Method

Delano I' · Chong* and D. Papoušek

Institute of Atomic und Molecular Sciences, Acudemiu Sinicu, P. 0. Box 23-166, Taipei, Tuiwun 106, R.O.C.

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The first derivatives of the electric dipole moments along the symmetry coordinates were computed for XH_3D and XHD_3 (X = C, Si) by means of the *deMon* density functional program [A. St-Amant and D. R. Salahub, ***Chem. Phys.*** *Letters* **169**, 387-392 (1990)] and transformed into those for XH4, XD4, and XH_2D_2 (X = C, Si) using relations between the symmetry coordinates for T_d, C_{3v} and C_{2v} molecules. Dipole moment derivatives along the normal coordinates of vibration were calculated using the force field of CH_4 and SiH_4 and were compared with the available experimental values.

I. INTRODUCTION

In a previous paper,[1] we used the density functional program *deMon* (Ref. 2; see also references cited in 1 and 3) to compute electric dipole moments for a series of diatomic and small polyatomic molecules at their average or equilibrium structures. In a subsequent paper,[3] we have extended this treatment to calculate the derivatives of the dipole moment function along the symmetry coordinates of vibration for a series of symmetric top molecules of C_{3v} symmetry. In both cases, the results agreed well with the available experimental data.

In the present continuing attempt to assess the reliability of the density functional theory, we calculated the dipole moment derivatives for molecules of T_d symmetry, therefore extending the treatment to molecules without a permanent dipole moment. A suitable candidate for a comparison of the computed values with experimental results is methane and its isotopomers because of previous experimental work on the intensities of infrared bands (cf., e.g. Ref. 4). Besides this, a reliable anharmonic potential function is available for methane' (see also Ref. 6), which makes it possible to transform the computed derivatives along the symmetry coordinates to the derivatives along the normal coordinates of vibration and compare the results with experimental values (including the signs of the dipole moment derivatives).

The results for CH_4 and CD_4 were discussed in our previous paper;[7] here we report full

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details of the computation including the isotopic species CH_3D, CHD_3, and CH_2D_2 and also extension of these calculations to $SiH_{4-n}D_n$ (n = 0 to 4).

II. COMPUTATIONAL DETAILS

With the exception of a slight change in the auxiliary fitting functions for hydrogen,[8*] we used the same technique to compute the dipole moment derivatives along the symmetry coordinates as described in our previous paper.[3]

For XY_4 molecules (X = C, Si, Y = H, D), we used the same conventions for the H or D atoms numbering and the orientation of the molecule fixed system of axes x, y, z as defined in Ref. 5 (see also Fig. 1). The symmetry coordinates are then defined as

$$S_1^{(A_1)} = 2^{-1}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4) \tag{1}$$

$$S_{2a}^{(E)} = 12^{-1/2}(2\Delta\alpha_{12} - \Delta\alpha_{13} - \Delta\alpha_{14} - \Delta\alpha_{23} - \Delta\alpha_{24} + 2\Delta\alpha_{34}) \tag{2a}$$

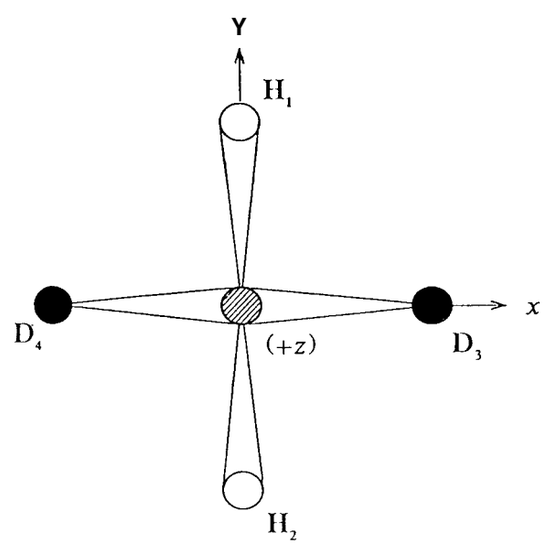

FIG. 1. Orientation of the molecule-fixed axes x, y ,z and the numbering conventions for the H and D atoms in CH_2D_2 and SiH_2D_2. For CH_4 or SiH_4, the axis system should be rotated anticlockwise around the axis z by $\pi/4$.

* The modification made the auxiliary basis consistent with the so-called one-third rule. Thus the A-HYDROGEN (3,1;3,1) functions now have exponents of: 45.0, 7.5, 1.5, 0.3; 15.0, 2.5, 0.5, 0.1.

$$S_{2b}^{(E)} = 2^{-1}(\Delta\alpha_{13} - \Delta\alpha_{14} - \Delta\alpha_{23} + \Delta\alpha_{24}) \tag{2b}$$

$$S_{3x}^{(F_2)} = 2^{-1}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4) \tag{3a}$$

$$S_{3Y}^{(F_2)} = 2^{-1}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4) \tag{3b}$$

$$S_{3z}^{(F_2)} = 2^{-1}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4) \tag{3c}$$

$$S_{4x}^{(F_2)} = 2^{-1/2}(\Delta\alpha_{24} - \Delta\alpha_{13}) \tag{4a}$$

$$S_{4Y}^{(F_2)} = 2^{-1/2}(\Delta\alpha_{23} - \Delta\alpha_{14}) \tag{4b}$$

$$S_{4z}^{(F_2)} = 2^{-1/2}(\Delta\alpha_{34} - \Delta\alpha_{12}) \tag{4c}$$

For CH_3D and CHD_3 (or SiH_3D and $SiHD_3$), the numbering and coordinate conventions were the same as decribed in our previous paper;[3] here atom 4 is identified with the unique atom, e.g. the D atom in CH_3D. The symmetry coordinates are defined as the following linear combinations of the T_d symmetry coordinates:

$$S_1^{(A_1)} = (3^{1/2}/2)S_1 + 12^{-1/2}(S_{3x} - S_{3y} + S_{3z}) \tag{5a}$$

$$S_2^{(A_1)} = 3^{-1/2}(-S_{4x} + S_{4y} - S_{4z}) \tag{5b}$$

$$S_3^{(A_1)} = 2^{-1}(S_1 - S_{3x} + S_{3y} - S_{3z}) \tag{5c}$$

$$S_{4z}^{(E)} = 6^{-1/2}(S_{3x} + 2S_{3y} + S_{3z}) \tag{6a}$$

$$S_{4Y}^{(E)} = 2^{-1/2}(S_{3x} - S_{3z}) \tag{6b}$$

$$S_{5x}^{(E)} = -8^{-1/2}S_{2a} - (3/24^{1/2})S_{2b} + 12^{-1/2}S_{4x} + 3^{-1/2}S_{4y} + 12^{-1/2}S_{4z} \tag{7a}$$

$$S_{5y}^{(E)} = (3/24^{1/2})S_{2a} - 8^{-1/2}S_{2b} + 2^{-1}(S_{4x} - S_{4z}) \tag{7b}$$

$$S_{6x}^{(E)} = -8^{-1/2}S_{2a} - (3/24^{1/2})S_{2b} - 12^{-1/2}S_{4x} - 3^{-1/2}S_{4y} - 12^{-1/2}S_{4z} \tag{8a}$$

$$S_{6y}^{(E)} = (3/24^{1/2})S_{2a} - 8^{-1/2}S_{2b} - 2^{-1}(S_{4x} - S_{4z}) \tag{8b}$$

For CH_2D_2 and SiH_2D_2, we used the symmetry coordinates defined as the following combinations of the T_d symmetry coordinates (see also Ref. 9).

$$S_1^{(A_1)} = 2^{-1/2}(S_1 + S_{3z}) \tag{9a}$$

$$S_2^{(A_1)} = 2^{-1/2}(S_1 - S_{3z}) \tag{9b}$$

$$S_3^{(A_1)} = 2^{-1/2}(S_{2a} - S_{4z}) \tag{9c}$$

$$S_4^{(A_1)} = 2^{-1/2}(S_{2a} + S_{4z}) \tag{9d}$$

$$S_5^{(A_2)} = S_{2b} \tag{10}$$

$$S_6^{(B_2)} = 2^{-1/2}(S_{3x} + S_{3y}) \tag{11a}$$

$$S_7^{(B_2)} = 2^{-1/2}(S_{4x} + S_{4y}) \tag{11b}$$

$$S_8^{(B_1)} = 2^{-1/2}(S_{3x} - S_{3y}) \tag{12a}$$

$$S_9^{(B_1)} = 2^{-1/2}(S_{4x} - S_{4y}) \tag{12b}$$

There are of course only two independent intensity parameters for methane and silane and once they are calculated for any of the isotopically substituted molecule, all the derivatives for other isotopomers can be obtained by using relations between the three sets of symmetry coordinates. In order to check the reliability of the density functional method, we have calculated all the dipole moment derivatives along the symmetry coordinates of the C_{3v} molecules (CH_3D and SiH_3D) and checked them against relations which follow from symmetry.[3] Using relations between the C_{3v} and T_d symmetry coordinates, we have transformed the computed derivatives from the C_{3v} symmetry coordinates to T_d symmetry coordinates, and checked them against the relations which follow from symmetry for the nonvanishing dipole moment derivatives of molecules of T_d symmetry:

$$\partial\mu_x/\partial S_{tx} = \partial\mu_y/\partial S_{ty} = \partial\mu_z/\partial S_{tz} \qquad (t = 3, 4) \tag{13}$$

Note that in CH_3D and SiH_3D, the z axis coincides with the C_3 symmetry axis while in CH_4 and SiH_4 it coincides with the S_4 symmetry axis (Fig. 1).

Similarly, the derivatives along the symmetry coordinates for CH_2D_2 and SiH_2D_2 were obtained from those for CH_4 and SiH_4 by using relations (9)-(12). In transforming the dipole moment derivatives from the symmetry coordinate to the normal coordinate representation, we used the convention according to which the signs of the normal coordinates are the same as those of the symmetry coordinates to which they approximate for small vibrational amplitudes.

III. RESULTS AND DISCUSSION

XH_4 and XD_4 (X = C, Si)

Because there is no permanent dipole moment in molecules of T_d symmetry, the dipole moment derivatives along the symmetry coordinates, $\partial\mu_z/\partial S_{tz}$, are the same for XH_4 and XD_4 molecules. They are given in Table I. As discussed in our previous papers,[3,7] the computed values for the three nonvanishing dipole moment derivatives for the molecules of T_d symmetry are not exactly identical, nor did we obtain exactly zero values for those derivatives which should vanish by symmetry. This computational inaccuracy can be reduced by choosing extra fine grid points using the density functional program but we feel that we reached an acceptable compromise between the accuracy of the computation and length of the computing time. For CH_4, the variations of the computed values of $\partial\mu_\alpha/\partial S_{3\alpha}$ and $\partial\mu_\alpha/\partial S_{4\alpha}$ are only 1.3% and 3.4%,

TABLE I. Dipole moment derivatives $\partial\mu_z/\partial S_{tz}$ (t = 3, 4) computed for CH_4 and SiH_4 (in units debye/Å)[a]

$\partial\mu_z/\partial S_{tz}$	CH_4	SiH_4
$\partial\mu_z/\partial S_{3z}$	+ 0.666	-1.411
$\partial\mu_z/\partial S_{4z}$	− 0.425	-1.674

[a] computed at the equilibrium geometry r_{CH} = 1.0858 Å (Ref. 5) and r_{SiH} = 1.47418, (Ref. 10)

TABLE II. Dipole moment derivatives $\partial\mu_z/\partial q_{tz}$ (t = 3, 4) for XH_4 and XD_4 (X = C, Si) (in units debye)

$\partial\mu_z/\partial q_{tz}$	Calc[a]	Obs	Calc[a]	Obs
	CH_4		CD_4	
$\partial\mu_z/\partial q_{3z}$	+ 0.0661	+ 0.0756[b]	+ 0.0496	+0.0587[c]
$\partial\mu_z/\partial q_{4z}$	− 0.0912	− 0.0795[b]	− 0.0814	− 0.0716'
	SiH_4		SiD_4	
$\partial\mu_z/\partial q_{3z}$	− 0.167	±0.196[d]	− 0.165	±0.146[d]
$\partial\mu_z/\partial q_{4z}$	− 0.325	±0.297[d]	− 0.275	±0.235[d]

[a] from the computed values of $\partial\mu_z/\partial S_{tz}$ in Table I and the force field for CH_4 (Ref. 5) and SiH_4 (Ref. 11)

[b] Ref. 12; the −+ sign relation changed to + −

[c] calculated from the experimental values of $\partial\mu_z/\partial q_{tz}$ for CH_4 in Ref. 12 (see also Ref. 7)

[d] from the experimental intensities in Ref. 13; only absolute values could be determined

respectively; for SiH_4 the variations are 0.2% and 1.1%, respectively. All the computed values of the dipole moment derivatives in this paper are therefore the averaged values from those values which should be identical for symmetry reasons.

The results for CH_4 and CD4 were already discussed in our previous paper.[7] It is interesting to compare the results for methane and silane, because not only the computed values of the dipole moment derivatives are very different but also the sign relations between $\partial\mu_z/\partial S_{3z}$ and $\partial\mu_z/\partial S_{4z}$ are opposite (+ – for CH_4 and – – for SiH_4). There is surprisingly little experimental work available on the infrared intensities in SiH_4 and SiD_4[13,14] but the large absolute values of the computed dipole moment derivatives in silane are in agreement with the available experimental data. This is however not the case of the sign relations between $\partial\mu_z/\partial S_{3z}$ and $\partial\mu_z/\partial S_{4z}$. Levin and King[13] on the basis of the simultaneous analysis of the experimental intensity data for SiH_4 and SiD_4 concluded that these sign relations are the same for SiH_4 and CH_4. Relatively recently, Dudev et *al.*[15] derived the bond polar parameters for SiH_4 using the same assumption.

From the comparison between theory and experiment for other molecules,[3] we have little doubt as for the correctness of our computed sign relations in SiH_4. Thus we hope that our work will help to stimulate further experimental work on the infrared intensities in silane.

CH_3D, CHD_3 and SiH_3D, $SiHD_3$

Because all the dipole moment derivatives for isotopically substituted methanes and silanes of C_{3v} symmetry are obtained from the two independent intensity parameters for CH_4

TABLE III. Nonvanishing dipole moment derivatives $\partial\mu_\alpha/\partial S_i$ for XH_3D and XHD_3 (X = C, Si) (in units debye/Å)

i	Symmetry	CH_3D, CD_3H	SiH_3D, $SiHD_3$
		$\partial\mu_z/\partial S_i$	
1	A_1	– 0.343	+ 0.712
2	Al	– 0.428	_ 1.678
3	A_1	+ 0.584	– 1.248
		$\partial\mu_x/\partial S_{ix}$[a]	
4	E	– 0.661	+ 1.398
5	E	+ 0.304	+ 1.192
6	E	– 0.296	_ 1.175

[a] $\partial\mu_x/\partial S_{ix} = \partial\mu_y/\partial S_{iy}$

TABLE IV. Dipole moment derivatives $\partial\mu_\alpha/\partial q_i$ for CH_3D and CHD_3 (in units debye)[a]

	CH_3D			CHD_3		
i	S_i	ω_i (cm^{-1})[c]	$\partial\mu_\alpha/\partial q_i$	S_i	ω_i (cm^{-1})[c]	$\partial\mu_\alpha/\partial q_i$
			α = z			
1	S_1	3064.1	− 0.0382	S_3	3128.0	+ 0.0589
2	S_3	2282.1	+ 0.0406	S_1	2185.0	− 0.0208
3	S_2	1362.0	− 0.0934	S_2	1042.3	− 0.0810
			a = x			
4	S_{4x}	3156.5	− 0.0651	S_{4x}	2336.3	− 0.0494
5	S_{5x}	1521.7	+ 0.0376	S_{6x}	1335.6	− 0.0526
6	S_{6x}	1206.2	− 0.0787	S_{5x}	1070.0	+ 0.0677

[a] from the computed values of $\partial\mu_\alpha/\partial S_i$ in Table III and force field for CH_4 in Ref. 5
[b] symmetry coordinate which dominates in a particular normal mode
[c] wavenumbers corrected for anharmonicity (Ref. 5)

or SiH_4 in Table I, comparison of the computed and experimental data for C_{3v} molecules can be expected to give results analogous to those for T_d molecules. The results for C_{3v} molecules (Table III-V) can be nevertheless useful because they give information on the sense of the in-

TABLE V. Dipole moment derivatives $\partial\mu_\alpha/\partial q_i$ for SiH_3D and $SiHD_3$ (in units debye)[a]

	SiH_3D			$SiHD_3$		
i	S_i	ω_i (cm^{-1})[c]	$\partial\mu_\alpha/\partial q_i$	S_i	ω_i (cm^{-1})[c]	$\partial\mu_\alpha/\partial q_i$
			α = z			
1	S_1	2298	+ 0.094	S_3	2298	− 0.164
2	S_3	1652	− 0.144	S_1	1635	+ 0.082
3	S_2	933	− 0.323	S_2	687	− 0.278
			a = x			
4	S_{4x}	2299	+ 0.181	S_{4x}	1661	+ 0.165
5	S_{5x}	973	+ 0.174	S_{6x}	869	− 0.219
6	S_{6x}	800	− 0.255	S_{5x}	695	+ 0.196

[a] from the computed values of $\partial\mu_\alpha/\partial S_i$ in Table III and force field for SiH_4 in Ref. 11
[b] symmetry coordinate which dominates in a particular normal mode
[c] wavcnumbers calculated from the force field in Ref. 11

TABLE VI. Nonzero $\zeta^{y}_{s,tx}$ Coriolis coefficients for CH_3D, CHD_3, SiH_3D and $SiHD_3$[a]

q_i \ q_{tx}	q_{4x}	q_{5x}	q_{6x}	q_{4x}	q_{5x}	q_{6x}
		CH_3D			CHD_3	
41	+ 0.030	− 0.163	− 0.579	− 0.094	+ 0.861	− 0.240
q_2	− 0.089	+ 0.128	+ 0.635	+ 0.080	− 0.282	+ 0.117
q_3	− 0.717	− 0.571	+ 0.236	− 0.753	− 0.155	− 0.559
		SiH_3D			$SiHD_3$	
41	+ 0.006	− 0.075	− 0.549	− 0.032	+ 0.875	− 0.085
q_2	− 0.031	+ 0.072	+ 0.675	+ 0.034	− 0.351	+ 0.052
q_3	− 0.710	− 0.605	+ 0.210	− 0.729	+ 0.004	− 0.614

[a] calculated for CH_3D and CHD_3 from the force field in Ref. 5, for SiH_3D and $SiHD_3$ from the force field in Ref. 11

TABLE VII. Dipole moment derivatives $\partial\mu_\alpha/\partial S_i$ computed for CH_2D_2 and SiH_2D_2 (in units debye/Å)[a]

i	Symmetry	$\partial\mu_\alpha/\partial S_i$ CH_2D_2	SiH_2D_2
		$\alpha = z$	
1	A_1	+ 0.471	− 0.983
2	A_1	− 0.478	+ 1.014
3	A_1	− 0.302	− 1.161
4	A_1	+ 0.310	+ 1.191
5	A_2	(− 0.001)[b]	(− 0.007)[b]
		$\alpha = y$	
6	B_2	+ 0.654	− 1.391
7	B_2	− 0.422	− 1.697
		$\alpha = x$	
8	B_1	+ 0.674	− 1.430
9	B_1	− 0.421	− 1.665

[a] obtained from the computed values of the dipole moment derivatives in Table V

[b] infrared inactive vibration

TABLE VIII. Dipole moment derivatives $\partial\mu_\alpha/\partial q_i$ for CH_2D_2 and SiH_2D_2 (in units debye)[a]

i	Symmetry	S_i	CH_2D_2 ω_i (cm^{-1})[c]	$\partial\mu_\alpha/\partial q_i$	SiH_2D_2 ω_i (cm^{-1})[d]	$\partial\mu_\alpha/\partial q_i$
				a = z		
1	A_1	S_1	3098	+ 0.0497	2297	− 0.128
2	A_1	S_2	2232	− 0.0307	1641	+ 0.116
3	A_1	S_4	1486	+ 0.0554	964	+ 0.215
4	Al	S_3	1068	− 0.0688	692	− 0.208
5	A_2	S_5	1371	(− 0.0002)[e]	861	(+ 0.003)[e]
				a = y		
6	B_2	S_6	3156	+ 0.0640	2295	− 0.181
7	B_2	S_7	1134	− 0.0827	754	− 0.295
				α = x		
8	B_1	S_8	2336	+ 0.0510	1657	− 0.165
9	B_1	S_9	1287	− 0.0897	875	− 0.303

[a] from the dipole moment derivatives in Table VII and the force field for CH_4 in Ref. 5 and SiH_4 in Ref. 11

[b] the symmetry coordinate which dominates in a particular vibrational mode

[c] wavenumber corrected for anharmonicity (Ref. 5)

[d] calculated from the force field in Ref. 11

[e] infrared inactive (average from the computed values of $\partial\mu_x/\partial q_5$, $\partial\mu_y/\partial q_5$, and $\partial\mu_z/\partial q_5$)

tensity perturbations in the infrared spectra due to the Coriolis interactions between the vibrational levels of species A and E. As discussed by diLauro and Mills,[16] the sense of the observed intensity perturbations in the infrared spectrum depends on only the sign of the product of the Coriolis coupling coefficient $\zeta^y_{s,tx}$ and the dipole moment derivatives $\partial\mu_z/\partial q_s$, $\partial\mu_x/\partial q_{tx}$,

$$(\zeta^y_{s,tx})(\partial\mu_z/\partial q_s)(\partial\mu_x/\partial q_{tx}). \tag{14}$$

The density functional method seems to provide reliable sign relations between the computed dipole moment derivatives. Thus the sign relations between the computed Coriolis coupling coefficients $\zeta^y_{s,tx}$ and the dipole moment derivatives in Table VI can be a useful prediction for further experimental work. In some cases, these predictions can be compared with the experimental results. For example, Chackerian and Guelachvili[17] found that for CH_3D, $|\partial\mu_z/\partial q_2|$ = 0.0419 D, which is in very good agreement with our computed value of -0.0406 D in Table IV

Dupre-Maquaire and Tarrago[18] found for CHD_3 that $(\partial\mu_z/\partial q_3)/(\partial\mu_x/\partial q_{6x}) = (-1.15 \pm 0.10)$ while we have -1.196. Dupre-Maquaire *et al.*[19] found for CHD_3 that $\partial\mu_x/\partial q_{5x} = \pm 0.0452$ D which is in reasonable agreement with our computed value of -0.0526 D.

CH_2D_2 and SiH_2D_2

The results of our computations are given in Tables VII-VIII. They should be considered as predictions which might be useful for future experimental work.

IV. CONCLUSIONS

Density functional theory seems useful for the study of the dipole moment functions of polyatomic molecules. Especially the sign relations between the dipole moment derivatives seem to be determined reliably. Because signs relations are important in determining the character of intensity perturbations in the spectra of axially symmetric molecules, a combination of the density functional calculation and an experimental study of the intensities should give very reliable results important for the determination of a good dipole moment function as well as analytical applications of infrared spectroscopy.

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* On leave from: Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, B.C., Canada V6T 1Zl.

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