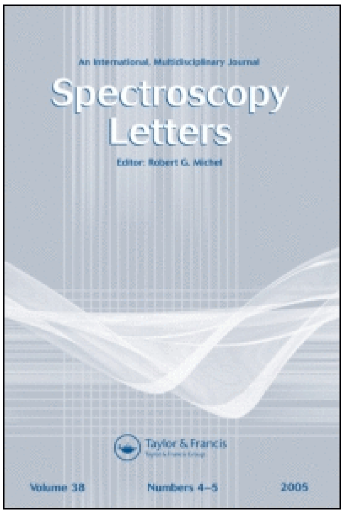

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Structures and Spectral Characteristics of Silylborane, Silylaluminum Hydride, Silylphosphine, and Silyl Mercaptan

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STRUCTURES AND SPECTRAL CHARACTERISTICS OF SILYLBORANE, SILYLALUMINUM HYDRIDE, SILYLPHOSPHINE AND SILYL MERCAPTAN

Key words: Vibrational frequencies, geometry optimization, ab initio, silanes

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ABSTRACT

The vibrational frequencies of several silanes H_3SiX ($X=BH_2$, AlH_2, PH_2 and SH) are determined. The infrared and Raman spectra are plotted. Several scale procedures were use to improve the theoretical spectra. The geometric parameters in the *planar*, *staggered* and *eclipsed* structures of these species are fully optimized and compared with ab initio calculations. Basis set effects on the calculated structures are discussed. A few thermodynamic parameters, net atomic charges, dipole moment and energy are also computed.

INTRODUCTION

The importance of thin film technology has prompted significant interest in silane chemistry throughout the world. Research to discover and develop an inexpensive method of producing efficient amorphous silicon solar cells is being carried out intensively worldwide[1]. The *p*-doped layers of amorphous devices are usually constructed by codeposition of elements (B, Al, F ...) into amorpho-Si during the preparation of such films by chemical vapor deposition (CVD), or by a glow discharge[2,3]. Among the molecular structures identified, several compounds with fluorine were analyzed in a previous paper[4]. Thus, along this line, the present article shows the work carried out on other silanes with great importance H_3Si-X (X=BH_2, AlH_2, PH_2 and SH). Our theoretical calculations collect and analyze the structural data and spectral characteristics of these molecules.

Concernig these compounds, the silylboranes have not been identified by direct observation as an isolated entity, because of the experimental instability of these substances, although the existence of H_3Si-BH_2 has been postulated[5]. Silylphosphine H_3Si-PH_2, originally discovered by Jolly[6] and synthesized by the Normal method[7,8], is the major product of the IR multiphoton-induced decomposition of H_4Si-PH_3 mixtures[9]. Silyl phosphine is a very unstable substance even at -78°C and it apparently reacts with the adsorbed moisture on the metal surface[8]. However, some geometric parameters[8,10] and the Infrared[11] and Raman[12] spectra have been reported. Silyl mercaptan H_3Si-SH, characterized by Glidewell[13,14], may result from the reaction of disilyl sulphide with hydrogen sulphide[15], although no experimental structure is available.

Theoretically, the silanes under investigation form several stable isomers, including forms with X-H-Si bridging bonds. Previous studies using smaller basis sets have reported conformations for some of the species studies here[16-19], although we found that some of them are not stable at high ab initio level. Stable inverted isomers[20], as in SiH_3Li, have also been reported to be possible in the present compounds[18].

COMPUTATIONAL METHODS

The accuracy of the various computational procedures has been discussed and a variety of results presented by Hehre *et al*[21]. In the present research, the molecular geometries were fully optimized with the OPT=TIGHT option, at the restricted Hartree-Fock (RHF) method with the basis sets 6-31G** and 6-31++G**. In addition, electron correlation was included at the level of second-order Moller-Plesset perturbation theory (MP2), MP2/6-31G**. Vibrational frequencies were obtained from analytical second derivatives[22], to assess the character of all stationary points. All molecular orbital calculations were performed with the GAUSSIAN 92 and 94 program packages developed by Pople *et al.*[23]

The Figures obtained were prepared with a Macintosh microcomputer, using the BALL and STICK program[24].

RESULTS AND DISCUSSION

GEOMETRY OPTIMIZATIONS

All minimum-energy conformations computed are shown in Fig. 1 with the labeling of the atoms. In Tables 1-4 the results obtained with several ab

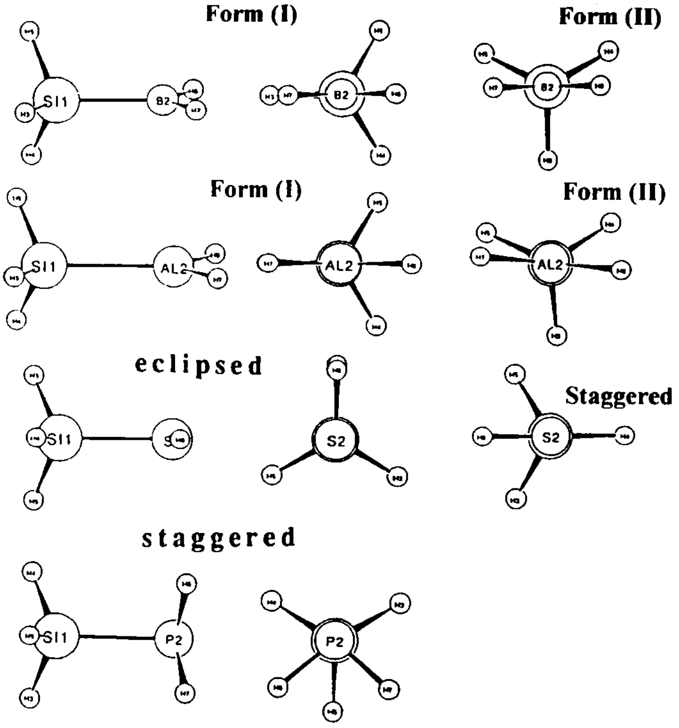

Fig. 1. Optimum geometry and labeling of the atoms in $H_3Si\text{-}BH_2$, $H_3Si\text{-}AlH_2$, $H_3Si\text{-}PH_2$ and $H_3Si\text{-}SH$ molecules.

initio basis set are compiled. The total energy and the dipole moment are also listed. The definition of the parameters κ, ζ and angles ω, ε is drawn in Fig. 2.

$H_3Si\text{-}BH_2$ compound is stable in two possible C_s conformations, called in the present article *forms* (I) and (II). The difference of energy between both forms is very small, so rotation about the Si-B bond should be essentially free. Form (I) is identified as a *saddle* point (one imaginary frequency). The BH_2 bisector of the molecule makes an inversion angle ω with the Si-B axis, which is very small, less than 2.5° (Table 5). Thus no *eclipsed* or *staggered* conformations are found in this compound. In form (I), the repulsion between the hydrogens H3 and H7 makes the intramolecular distances r Si···H6 and r Si···H7 different and the angles Si-B-H6 and Si-B-H7. As a measure of this asymmetry is defined the angle ε (Fig. 2). The intramolecular repulsions of the hydrogens H3 and H7 also produce a tetrahedral character of the $\text{-}SiH_3$ group,

Table 1[a]. Optimized bond lengths in Å, bond angles in degrees and total energies in hartrees, in the forms (I) and (II) of Silylborane (H_3Si-BH_2) at different ab initio levels.

Parameters	Form (I)		Form (II)		
	6-31G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**
r Si-B	2.0404	2.0186	2.0400	2.0402	2.0221
r Si-H3	1.4795	1.4753	1.4841	1.4836	1.4826
r Si-(H4,H5)	1.4824	1.4798[b]	1.4802	1.4796	1.4776
r B-H6	1.1903	1.1871	1.1898	1.1903	1.1874
r B-H7	1.1893	1.1860	1.1898	1.1903	1.1874
∠ B-Si-H3	113.58	114.15	107.70	107.68	106.63
∠ B-Si-H4	109.51	108.66	112.44	112.36	112.83
∠ B-Si-H5	109.54	109.56	112.46	112.39	112.82
∠ H3-Si-H4	108.05	108.18	108.06	108.06	107.96
∠ H4-Si-H5	107.93	107.77	108.17	108.17	108.42
∠ Si-B-H6	119.77	119.46	121.33	121.31	121.34
∠ Si-B-H7	122.95	123.24	121.36	121.32	121.33
∠ H6-B-H7	117.28	117.30	117.34	117.34	117.28
∠ H3-Si-B-H7	0.09	4.36	-89.03	-88.98	-88.52
∠ H4-Si-B-H6	59.19	62.93	-29.99	-29.99	-29.66
∠ H5-Si-B-H6	-59.01	-54.57	-152.28	-152.28	-152.96
∠ H5-Si-B-H7	121.01	126.05	29.86	29.86	29.82
Dipole moment (Debyes)	0.4875	0.4819	0.4882	0.5083	0.4860
Total Energy (RHF)	.469060	.468896	.469080	.470585	.468967
(-316 a.u.) (MP2)		.667434			.667476

[a]In Tables 1-4 the last digit shown in the calculated values is to aid in reproduction of the results and is not thought to be physically meaningful. [b]With H4.

calculated through the parameter ζ, remarkably greater in form (I) than in form (II), 0.14 Å at 6-31G** level and 0.18 Å with electron correlation MP2/6-31G**. Deviations of the B-H bonds from planarity and symmetry are very small in each basis set employed; the sum of the angles on boron atom are 360°. In Form (I) a slight torsion of the -BH_2 group is observed at MP2/6-31G** level with an ∠H3-Si-B-H7 angle of 4.36°. This compound is not known experimentally, thus there is currently no experimental geometry with which to compare these theoretical predictions.

Table 2. Optimized bond lengths in Å, bond angles in degrees and total energies in hartrees, in the forms (I) and (II) of Silylaluminum hydride ($H_3Si\text{-}AlH_2$) at different ab initio levels.

Parameters	Form (I)			Form (II)		
	6-31G**	6-31++G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**
r Si-Al	2.4784	2.4816	2.4592	2.4787	2.4815	2.4521
r Si-H3	1.4815	1.4808	1.4792	1.4843	1.4837	1.4812
r Si-H4	1.4836	1.4829	1.4814	1.4826	1.4818	1.4794
r Al-H6	1.5862	1.5854	1.5817	1.5862	1.5853	1.5807
r Al-H7	1.5859	1.5850	1.5813	1.5860	1.5851	1.5806
∠ Al-Si-H3	112.66	112.59	112.90	110.36	110.36	110.30
∠ Al-Si -H4	110.86	110.84	110.84	111.67	111.65	111.74
∠ Al-Si -H5	110.86	110.84	110.84	112.31	112.27	112.46
∠ H3-Si -H4	107.52	107.57	107.49	107.23	107.25	107.12
∠ H4-Si -H5	107.17	107.21	107.03	107.65	107.68	107.66
∠ Si-Al-H6	120.00	119.93	119.88	120.40	120.38	120.38
∠ Si-Al-H7	121.59	121.55	121.70	121.12	121.09	121.16
∠ H6-Al-H7	118.41	118.52	118.42	118.47	118.52	118.45
∠ H3-Si-Al-H7	0.06	0.06	0.06	-99.64	-99.60	-99.68
∠ H4-Si-Al-H6	59.51	59.52	59.41	-39.59	-39.61	-39.59
∠ H5-Si-Al-H6	-59.39	-59.40	-59.29	-160.64	-160.64	-160.80
∠ H5-Si-Al-H7	120.61	120.60	120.71	20.13	20.19	20.06
Dipole moment (Debyes)	0.4068	0.3681	0.4011	0.4090	0.3674	0.3910
Total Energy (RHF)	.704987	.707060	.704905	.704985	.707059	.704834
(-533 a.u.) (MP2)			.886888			.886885

$H_3Si\text{-}AlH_2$ shows a geometry similar to $H_3Si\text{-}BH_2$, Table 2, thus the AlH_2 bisector is nearly zero out of line with the Si-Al axis, $\omega \approx 0.8°$. The Si-Al bond length is longer than the Si-B, thus a smaller repulsion between H3 and H7 is determined in form (I), ε is nearly 0.6°, Table 5. The sum of the angles on Aluminum is also 360°. In form (II) a slight torsion of the $-AlH_2$ group is observed, thus ∠H4-Si-Al-H6 is ca. -39.6° while ∠H5-Si-Al-H7 is ca. 20.1°, because forms (I) and (II) are energetically equivalent; hence rotation is free. No experimental data appear to be available for this compound.

In silylphosphine, Table 3 lists the structural parameters computed in the *staggered* conformation and the experimental data available[8,12]. The calculated Si-P bond length, 2.252 Å at MP2 level, is in good agreement with the

Table 3. Optimized bond lengths in Å, bond angles in degrees and total energies in hartrees, in Silylphosphine ($H_3Si\text{-}PH_2$).

Parameters	*Staggered* Form				*Eclipsed* Form[b]	Experimental[c]
	6-31G**	6-31++G**	MP2 6-31G*	MP2 6-31G**	6-31G**	
r Si-P	2.2665	2.2678	2.2531	2.2522	2.2784	2.250[d]
r Si-H3	1.4759	1.4751	1.4848	1.4741	1.4762	
r Si-H5	1.4765	1.4756	1.4858	1.4750	1.4754	
r P-H6	1.4055	1.4054	1.4166	1.4069	1.4048	1.420
∠ P-Si-H3	107.99	107.95	114.15	107.84	111.47	114.4
∠ P-Si -H5	113.30	113.20		114.10	109.02	114.4
∠ H3-Si -H4	109.36	109.42	109.15	109.17	109.81	
∠ H3-Si -H5	109.07	109.13		108.90	108.27	
∠ Si-P-H6	97.33	97.30	96.54	95.92	96.90	92.8
∠ H6-P-H7	95.74	95.93		94.84	95.16	93.9
∠ H3-Si-P-H6	-169.29	-169.38		-168.86	96.17	
∠ H4-Si-P-H6	72.55	72.43		73.38	-25.53	
∠ H4-Si-P-H7	169.34	169.41		168.89	-121.71	
∠ H5-Si-P-H7	48.42	48.50		47.77	119.46	
Dipole moment (Debyes)	1.0391	1.0251		1.0066	1.0575	0.59[d]
Total Energy (RHF) (-632 a.u.) (MP2)	.543623	.545261	.737641	.543423 .781491	.541602	

[a]From ref. 17. [b]**Transition structure.** [c]From ref. 12. [d]Microwave measurements [8]

experimental[8,25] value 2.250 Å. The bond angles at phosphorus are very small due to the high inversion angle ω; the Si-P-H and H-P-H values, 95.92° and 94.84° respectively at MP2 level, are slightly larger than found experimentally[12] 92.8°, 93.9°, and[8] 92.48°, 93.50°. The *eclipsed* conformation is a stationary point in C_S symmetry and represents a transition structure for the rotation from one *staggered* conformation to another. The calculated barrier of 1.27 kcal mol^{-1} at RHF level corresponding to this *eclipsed* form, is close to the experimental[12] value of 1.51 kcal mol^{-1}.

In $H_3C\text{-}PH_2$ compound, several studies are available[10,26]. Thus, comparing the structures of methyl- and silylphosphine, is observed that the values are

Table 4. Optimized bond lengths in Å, bond angles in degrees and total energies in hartrees, in the *Staggered* and *eclipsed* forms of Silyl-mercaptan (H_3Si-SH).

Parameters	*Staggered*			*Eclipsed*		
	6-31G**	6-31++G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**
r Si-S	2.1516	2.1530	2.1392	2.1597	2.1607	2.1469
r Si-(H3,H5)	1.4733	1.4725	1.4728	1.4721	1.4712	1.4713
r Si-H4	1.4704	1.4701	1.4698	1.4729	1.4720	1.4719
r S -H6	1.3289	1.3293	1.3319	1.3272	1.3275	1.3297
∠ S-Si-H3	111.09	110.93	111.63	109.84	109.77	110.20
∠ S-Si -H4	105.09	105.19	104.83	108.10	108.10	108.39
∠ H4-Si -(H3,H5)	110.36	110.40	110.09	110.05	110.09	109.71
∠ H3-Si -H5	108.87	108.95	108.55	108.94	108.99	108.60
∠ Si-S-H6	97.75	97.56	96.14	97.04	96.88	95.16
∠ H3-Si-S-H6	-60.59	-60.61	-60.82	120.12	120.13	120.12
∠ H4-Si-S-H6	-179.95	-179.99	-179.98	0.03	0.02	0.04
∠ H5-Si-S-H6	60.73	60.63	60.87	-120.07	-120.09	-120.04
Dipole moment (Debyes)	1.6759	1.6537	1.6184	1.6967	1.6682	1.6239
Total Energy (RHF)	.779034	.780572	.778885	.777396	.778928	.777249
(-688 a.u.) (MP2)			1.025281			1.023466

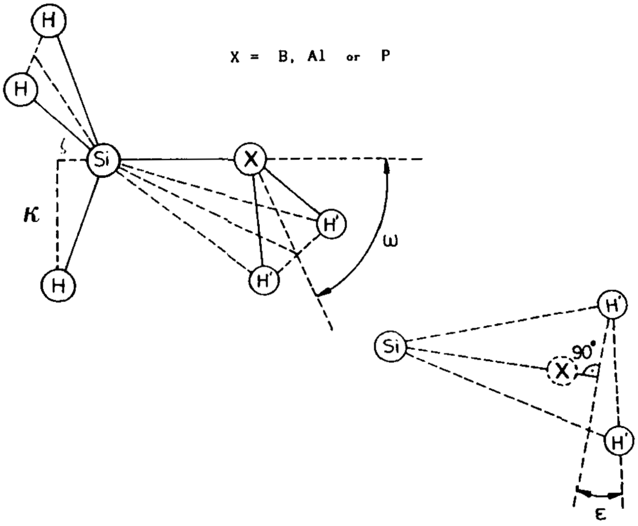

Fig. 2. Definition of the parameters κ and ζ, and the angles ω and ε.

Table 5. Values of κ and ζ parameters in Å, and ω (inversion) and ε angles in degrees, at different ab initio levels.

Parameters	Form (I)			Form (II)		
	6-31G**	6-31++G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**
In H_3Si-BH_2						
κ	1.3560	1.3560	1.3462	1.4138	1.4135	1.4202
ζ	0.5918	0.5918	0.6036	0.4512	0.4506	0.4220
ω	1.63	1.63	2.00	1.74	1.74	2.33
ε	1.20	1.20	1.42	0	0	0
In H_3Si-AlH_2						
κ	1.3671	1.3668	1.3629	1.3916	1.3910	1.3892
ζ	0.5708	0.5695	0.5726	0.5164	0.5162	0.5139
ω	0.81	0.82	0.84	0.75	0.78	0.82
ε	0.59	0.60	0.62	0.27	0.26	0.29
	Staggered			*Eclipsed*		
In H_3Si-PH_2						
κ	1.3561	1.3563	1.3464			
ζ	0.5840	0.5813	0.6023			
ω	79.23	79.06	81.23			
In H_3Si-SH						
κ	1.4197	1.4187	1.4208	1.4000	1.3992	1.3967
ζ	0.3828	0.3852	0.3762	0.4576	0.4573	0.4644
ω	82.25	82.44	83.86	82.96	83.12	84.84

similar, the equilibrium structure in H_3C-PH_2 being also *staggered*. The larger Si-P distance, compared to the C-P bond length, can produce a decrease in the rotational barrier of H_3Si-PH_2.

In silyl mercaptan, the Si-S bond length in the *staggered* form is slightly shorter than in the *eclipsed*, 2.1392 and 2.1469 Å respectively at MP2 level, Table 4. Due to the H4···H6 interaction, the S-Si-H bond angles differ more in the *staggered* conformation (ca. 6°) than in the *eclipsed* form (ca. 2°). The difference of energy between the *eclipsed* (saddle point) and *staggered* (real minima) forms is very small, ca. 1.03 kcal/mol.

In H_3C-SH compound, microwave data have been reported[27,28]. Comparing the structures of methyl- and silyl- compounds, it is observed that they are very similar, the greater bond length to the sulphur (Si-S is ca. 2.15 Å while C-S is ca. 1.81 Å) results in a lower rotational barrier in silyl than in methyl[16] mercaptan. In the angles, the Si-S-H (ca. 97°) is very close to C-S-H, 96.5°.

Comparing the results obtained in the silanes under study (Tables 1-4), the following is observed: In form (I) of H_3Si-BH_2 and H_3Si-AlH_2, the repulsions between H3 and H7 produce, compared to form (II), a remarkable increment in the tetrahedral character of the -SiH_3 group and thus of the parameter ζ. This increment is higher in H_3Si-BH_2 (the value of ζ changes ca. 0.14 Å at 6-31G** level) than in H_3Si-AlH_2 (the change of ζ is ca. 0.054 Å), due to the fact that intramolecular distance r H3···H7 is longer in H_3Si-BH_2, ca. 3.30 Å, than in H_3Si-AlH_2, ca. 3.88 Å.

With electron correlation the Si-X bond is remarkably reduced (ca. 0.02 Å) and slightly the Si-H. Also the X-H bond is shorter except with X=P and S, in which the bond slightly increases. The inversion angle ω is always incremented, especially in H_3Si-PH_2, ca. 2°. In form (I) of H_3Si-BH_2 the reduction of the Si-B bond gives rise to a shorter intramolecular distance H3···H7 and thus a slight increase in the value of ζ. However, in form (II) the repulsion H3···H7 is not produced, and thus the reduction of the Si-B bond with MP2 level yields to a shorter intramolecular distance of the boron atom with the hydrogens of the -SiH_3 group, with remarkable decreases of the parameter ζ. These features are also observed in H_3Si-SH, and therefore, the reduction of the Si-S bond with electron correlation produces a lower ζ in the *staggered* conformation and a higher value in the *eclipsed* form. In H_3Si-AlH_2 with a longer Si-Al bond, these interactions are weakened and thus the changes are much decreased. In H_3Si-PH_2, at difference of H_3Si-BH_2 and H_3Si-AlH_2, the shortening of the Si-P bond results in a higher ζ, because in this case the high inversion angle ω of the -PH_2 group leads to a slight interaction of the hydrogens with those of the -SiH_3 group.

When *diffuse* functions are added to the basis set , an enlargement of in the Si-X bond length and a very small decrease in the Si-H bond are observed. The parameter ζ is also slightly diminished.

The total atomic charges from a Mulliken population analysis are collected in Table 6. The hydrogens (except H6 in H_3Si-SH) and X (X=S, P and B at 6-31++G** level) atoms are negatively charged (as in other silanes), with the X atom in the case of sulphur having the highest negative charge. The Si, due to its lower electronegativity, acts as an electron reservoir for its substituents. Adding 3d (Si) functions to the basis set has the effect of reducing the absolute values of all atomic charges, caused[29] by the filling up of the 3d orbitals on Si with electronic charge density from H and X.

The effect of the *diffuse* functions in H_3Si-BH_2 and H_3Si-AlH_2 is to increase the positive atomic charge on the silicon atom (0.078 and 0.117 respectively) and to decrease it on B and Al atoms, 0.124 and 0.036 respectively. However, in H_3Si-PH_2 and H_3Si-SH, the positive charge on Si

Table 6. Values of the total atomic charges calculated at different ab initio levels.

Parameters	Form (I)			Form (II)		
	6-31G**	6-31++G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**
In H_3Si-BH_2						
Si	0.5854	0.6637	0.5848	0.5853	0.6645	0.5847
B	0.0272	-0.0973	0.0276	0.0272	-0.1006	0.0277
H3	-0.1674	-0.1761	-0.1671	-0.1630	-0.1705	-0.1636
H4, H5	-0.1637	-0.1747	-0.1637	-0.1659	-0.1771	-0.1656
H6	-0.0610	-0.0284	-0.0609	-0.0588	-0.0197	-0.0588
H7	-0.0567	-0.0123	-0.0567	-0.0590	-0.0196	-0.0588
In H_3Si-AlH_2						
Si	0.3117	0.4288	0.3150	0.3115	0.4294	0.3164
Al	0.5381	0.5025	0.5345	0.5382	0.5022	0.5331
H3	-0.1604	-0.1576	-0.1605	-0.1603	-0.1568	-0.1605
H4, H5	-0.1602	-0.1585	-0.1604	-0.1602	-0.1590	-0.1604
H6	-0.1855	-0.2338	-0.1852	-0.1849	-0.2311	-0.1846
H7	-0.1835	-0.2230	-0.1831	-0.1839	-0.2259	-0.1836
	Staggered			*Eclipsed*		
In H_3Si-PH_2						
Si	0.6481	0.5408	0.6455			
P	-0.0823	0.0540	-0.0752			
H3, H4	-0.1558	-0.1488	-0.1571			
H5	-0.1576	-0.1556	-0.1575			
H6, H7	-0.0482	-0.0707	-0.0493			
In H_3Si-SH						
Si	0.7381	0.6306	0.7331	0.7400	0.6088	0.7354
S	-0.3388	-0.2644	-0.3290	-0.3522	-0.2649	-0.3425
H3, H5	-0.1571	-0.1450	-0.1578	-0.1529	-0.1371	-0.1543
H4	-0.1500	-0.1290	-0.1517	-0.1559	-0.1285	-0.1569
H6	0.0649	0.0528	0.0631	0.0739	0.0588	0.0727

decrease (0.107 and 0.119 respectively) and increase on P and S atoms, 0.136 and 0.081 respectively. In the hydrogens of the -SiH_3 group, the effect of the *diffuse* functions is to reduce the positive charge ca. 0.010 in H_3Si-BH_2 and to increase 0.002, 0.005 and 0.017 respectively in H_3Si-AlH_2, H_3Si-PH_2 and H_3Si-SH; while in the hydrogens of the -XH_2 (or -XH) group, the positive charge is increased ca. 0.039 in H_3Si-BH_2 and reduced 0.044, 0.022 and 0.014 respectively in H_3Si-AlH_2, H_3Si-PH_2 and H_3Si-SH.

The electron correlation has a very low effect on the atomic charge. Thus the positive charge on Si slightly increases, 0.004 in H_3Si-AlH_2, while 0.003 and 0.005 decrease respectively in H_3Si-PH_2 and H_3Si-SH; in H_3Si-BH_2 the change is very small, 0.001. The variation of the atomic charge on B atom is also insignificant (< 0.001). In P and S atoms the positive charge is slightly increased, 0.007 and 0.010 respectively. In hydrogens no significative change is observed in H_3Si-BH_2 and H_3Si-AlH_2 molecules, while in H_3Si-PH_2 and H_3Si-SH the positive charge is slightly reduced, ca. 0.001.

Compared to H_3C-XH_2 compounds, a shift of electron density away from the -XH_2 group is noted. As expected from electronegativity arguments, the charge on the methyl group is greater than the charge on the silyl group.

VIBRATIONAL FREQUENCIES

In Tables 7 and 8 are collected the harmonic vibrational frequencies calculated in the form (II) of H_3Si-BH_2 and H_3Si-AlH_2 molecules respectively. The second column shows the bands computed at 6-31G** level, their Infrared intensities (the third and fourth columns), their Raman activities (fifth and sixth columns), and the assignment established (the last column). The relative intensities were obtained by dividing the computed value by the intensity of the strongest line. Table 9 lists the vibrational frequencies in H_3Si-PH_2 and Table 10 in the *staggered* form of H_3Si-SH. The calculated frequencies in the other conformations, with one imaginary frequency (*saddle* point), are shown in Table 11. The vibrational modes are numbered according to the order of increasing frequencies. In H_3Si-AlH_2 the frequency calculations at 6-31G** level confirm that the forms (I) and (II) are real minima, whereas at 6-31++G** and MP2 level, form (II) is a *saddle* point with one negative frequency.

The IR and Raman spectra computed for the form (II) in H_3Si-BH_2, form (I) in H_3Si-AlH_2, and *staggered* in H_3Si-PH_2, H_3Si-SH are plotted in Figs. 3-7.

Concerning the values of Tables 9-10, it is noted that the frequencies computed are always higher than those obtained by experiments because of the harmonic approximation, and are in agreement with Hartree-Fock bond lengths, which are expected to be shorter than the experimental ones.

Table 7. Harmonic vibrational frequencies (cm^{-1}), IR intensities (km/Mol), Raman scattering activities (Å^4/AMU), Raman depolarization ratios and force constants (mDyne/Å) in form (II) of $H_3Si\text{-}BH_2$

No	6-31G**					Depolarization ratios	6-31++G**			MP2/6-31G**			Force constants	Characterization
	Frequency	IR intensity		Raman activity			Frequency	IR intensity	Raman activity	Frequency	IR intensity			
		Absolute (km mol^{-1})	Relative (%)	absolute (Å^4/AMU)	Relative (%)			Absolute (km mol^{-1})	Absolute (Å^4/AMU)		Absolute (km mol^{-1})	Relative (%)		
1	60	0.1	0	7.9	4.5	0.75	38	0.1	10.1	59	0	0	0	$\tau(BH_2) + \tau(SiH_3)$
2	482	20.4	7.6	1.6	0.9	0.75	482	21.6	2.2	439	36.6	20.2	0.13	$\Gamma(SiH_3) + \Gamma(BH_2)$
3	485	51.1	19.0	8.9	5.1	0.75	487	55.9	9.6	464	16.0	8.8	0.13	$\gamma(BH_2) + \gamma(SiH_3)$
4	653	2.1	0.8	21.4	12.2	0.24	653	2.4	24.4	654	2.1	1.2	0.99	$\nu(Si\text{-}B)$
5	823	22.4	8.3	7.6	4.3	0.75	820	24.1	4.4	797	18.8	10.4	0.49	$\Gamma(BH_2) + \Gamma(SiH_3)$
6	989	29.1	10.8	6.7	3.8	0.73	987	18.8	8.1	947	181.5	100.0	0.60	$\gamma(BH_2)$
7	1005	268.7	100	5.4	3.1	0.68	1005	284.5	4.4	969	48.8	26.9	0.72	$\delta_s(Si\text{-}H)$
8	1026	65.5	24.4	25.9	14.8	0.75	1027	66.9	25.1	986	48.9	26.9	0.59	$\delta_{as}(Si\text{-}H)$
9	1049	92.8	34.5	21.0	12.0	0.75	1050	93.5	21.4	1013	73.5	40.5	0.64	$\delta_{as}(Si\text{-}H)$
10	1295	41.4	15.4	4.2	2.4	0.38	1287	40.8	3.6	1263	39.0	21.5	1.07	$\Delta(BH_2)$ scissor
11	2316	181.4	67.5	114.0	65.2	0.38	2313	181.2	148.4	2293	94.6	52.1	3.21	$\nu_s(Si\text{-}H)$
12	2335	210.2	78.2	79.8	45.6	0.75	2331	206.9	110.7	2318	109.0	60.1	3.27	$\nu_{as}(Si\text{-}H)$
13	2343	115.0	42.8	174.9	100	0.05	2340	113.5	233.1	2322	153.4	84.5	3.34	$\nu_{as}(Si\text{-}H)$
14	2693	107.1	39.9	116.8	66.8	0.10	2690	115.4	158.5	2696	83.9	46.2	4.51	$\nu_s(B\text{-}H)$
15	2767	132.4	49.3	74.0	42.3	0.75	2761	147.2	90.1	2785	96.3	53.1	5.14	$\nu_{as}(B\text{-}H)$

Table 8. Harmonic vibrational frequencies (cm^{-1}), IR intensities (km/Mole), Raman scattering activities (Å^4/AMU), Raman depolarization ratios and force constants (mDyne/Å) in form (I) of $H_3Si\text{-}AlH_2$

No	6-31G**					Depolarization ratios	6-31++G**			MP2/6-31G**			Force constants	Characterization
	Frequency	IR intensity		Raman activity			Frequency	IR intensity	Raman activity	Frequency	IR intensity			
		Absolute (km mol^{-1})	Relative (%)	Absolute (Å^4/AMU)	Relative (%)			Absolute (km mol^{-1})	Absolute (Å^4/AMU)		Absolute (km mol^{-1})	Relative (%)		
1	15	0.1	0	6.3	3.3	0.75	11	0.2	13.4	14	0.1	0	0	τ(structure)
2	352	48.1	7.8	0.6	0.3	0.57	352	54.0	0.7	335	38.3	6.9	0.07	$\Gamma(SiH_3) + \Gamma(AlH_2)$
3	410	4.0	0.7	32.8	17.3	0.21	407	4.1	33.6	407	4.3	0.8	0.70	ν(Si-Al)
4	419	94.9	15.5	4.6	2.4	0.75	421	108.0	8.5	393	72.4	13.0	0.10	$\gamma(AlH_2) + \gamma(SiH_3)$
5	594	3.6	0.6	13.4	7.1	0.75	592	3.5	8.8	570	4.3	0.8	0.23	$\Gamma(AlH_2) + \Gamma(SiH_3)$
6	637	133.3	21.7	0	0	0.75	636	139.7	2.6	615	120.8	21.7	0.27	$\gamma(AlH_2)$
7	835	613.0	100	13.5	7.1	0.70	834	623.4	11.5	807	557.5	100.0	0.41	$\Delta(AlH_2)$ scissor
8	985	171.1	27.9	4.8	2.5	0.30	984	181.4	6.2	935	115.7	20.8	0.57	δ_s(Si-H)
9	1031	68.3	11.1	26.7	14.1	0.75	1032	68.6	25.5	990	53.7	9.6	0.60	δ_{as}(Si-H)
10	1036	76.0	12.4	25.5	13.4	0.75	1036	76.7	26.3	993	60.0	10.8	0.60	δ_{as}(Si-H)
11	1998	218.5	35.6	190.0	100	0.10	2000	264.5	219.4	1983	176.6	31.7	2.38	ν_s(Al-H)
12	2000	314.5	51.3	90.2	47.5	0.56	2001	298.2	173.6	1994	267.1	47.9	2.48	ν_{as}(Al-H)
13	2327	152.4	24.9	170.3	89.6	0.16	2327	150.1	228.0	2292	82.8	14.9	3.17	ν_s(Si-H)
14	2311	197.9	32.3	119.3	62.8	0.75	2311	200.9	146.6	2300	137.6	24.7	3.27	ν_{as}(Si-H)
15	2315	159.1	26.0	166.5	87.6	0.21	2315	164.5	215.2	2312	138.9	24.9	3.30	ν_{as}(Si-H)

Table 9. Harmonic vibrational frequencies (cm^{-1}), IR intensities (km/Mole), Raman scattering activities (Å^4/AMU), Raman depolarization ratios and force constants (mDyne/Å) in the *staggered* conformation of $H_3Si\text{-}PH_2$

No	6-31G**									6-31++G**			Depolarization ratios	Force constants	Raman frequencies^d	IR frequencies^e	Characterization
	Frequency					IR intensity		Raman activity		Frequency	IR intensity	Raman activity					
	Calculated	scaled^a	% error^b	scaled^c	% error^b	absolute (Km mol^{-1})	Relative (%)	absolute (Å^4/AMU)	Relative (%)		absolute (Km mol^{-1})	absolute (Å^4/AMU)					
1	175	115		158	5.9	1.7	0.4	0.8	0.4	176	1.6	0.3	0.75	0.02	168^g	219	τ(structure)
2	485	401		437	3.3	4.5	1.1	32.6	17.4	483	4.6	34.8	0.27	1.26	452 m		ν(Si-P)
3	519	432		467	-	43.8	10.7	0.6	0.3	519	47.8	0.5	0.75	0.17	602 vw		$\Gamma(SiH_3) + \Gamma(PH_2)$
4	537	449		483	-	27.6	6.7	6.3	3.4	536	27.7	8.1	0.73	0.18			γ(structure)
5	809	700	3.0	728	0.8	24.2	5.9	18.0	9.6	803	27.4	7.8	0.54	0.45	722 vw	730	$\gamma(PH_2) + \gamma(SiH_3)$
6	862	749	2.7	776	0.8	2.2	0.5	22.3	11.9	857	1.9	16.1	0.75	0.49	770 vw	696^j	$\Gamma(PH_2) + \Gamma(SiH_3)$
7	1007	883	1.9^f	906	0.7	409.0	100	5.5	2.9	1006	423.1	5.4	0.75	0.65	900^h		δ_s(Si-H)
8	1032	906	5.1	929	2.7	91.0	22.2	28.6	15.2	1032	91.5	27.8	0.75	0.65	955 vw^i		δ_{as}(Si-H)
9	1044	917	4.0	940	1.6	73.6	18.0	25.7	13.7	1045	74.4	27.4	0.75	0.67	955 vw^i		δ_{as}(Si-H)
10	1219	1078	0.2	1097	0.3	26.4	6.5	39.1	20.8	1216	23.3	22.5	0.74	0.91	1100 vw^i	1092	$\Delta(PH_2)$ scissor
11	2354	2125	2.9	2119	3.2	178.9	43.8	121.1	64.4	2355	174.6	154.4	0.33	3.41	2189 m		ν_{as}(Si-H)
12	2361	2131	2.6	2125	2.9	175.1	42.8	87.9	46.8	2362	169.0	116.0	0.75	3.45	2189 m		ν_{as}(Si-H)
13	2361	2131	1.6	2125	1.9	129.1	31.6	172.0	91.5	2362	123.7	215.9	0.05	3.37	2166 s		ν_s(Si-H)
14	2567	2321	0.7	2310	0.3	73.4	17.9	188.0	100	2564	98.2	156.4	0.12	4.02	2304 m	2305	ν_s(P-H)
15	2567	2321	0.1	2310	0.3	103.4	25.3	133.2	70.9	2564	74.1	201.5	0.75	4.05	2318 w	2309	ν_{as}(P-H)

[a] Using a scaling equation[36]. [b] 100 $|\nu_{exp.} - \nu_{ab\ initio\ scaled}| / \nu_{exp.}$. [c] Using a scaling factor of 0.9. [d] In gas fase[12]. [e] In the gas phase[37] of $H_3C\text{-}PH_2$. [f] ν_{exp} is from ref. 11. [g] Calculated. [h] In the IR spectrum[11]. [i] In liquid state. [j] In the solid state[37]

Table 10. Harmonic vibrational frequencies (cm^{-1}), IR intensities (km/Mol), Raman scattering activities (Å^4/AMU), Raman depolarization ratios and force constants (mDyne/Å) in the *staggered* conformation of H_3Si-SH

No	6-31G**									6-31++G**			Depolarization ratios	Force constants	IR frequencies		Characterization
	Frequency					IR intensity		Raman activity		Frequency	IR intensity	Raman activity					
	Calculated	scaled^a	%$_b$ error	scaled^c	%$_b$ error	absolute (km mol^{-1})	Relative (%)	absolute (Å^4/AMU)	Relative (%)		absolute (km mol^{-1})	absolute (Å^4/AMU)			(d)	(e)	
1	201	139		181		19.0	5.1	5.9	3.2	202	19.1	1.2	0.75	0.02			τ(S-H) + τ(SiH_3)^f
2	541	453		487	5.2	39.8	10.6	18.5	10.1	538	41.4	19.8	0.30	1.92	514 m		ν(Si-S)
3	597	505	3.6	537	2.5	49.1	13.0	3.1	1.7	596	50.6	3.8	0.52	0.22	524 m	803	Γ(S-H) + Γ(SiH_3)
4	688	589	-	619	-	38.3	10.2	13.9	7.6	688	36.3	10.3	0.75	0.31			γ(SiH_3)
5	900	784	3.0	810	-	5.3	1.4	18.4	10.0	897	5.7	14.6	0.69	0.54	761 w	1074	δ(S-H) +Γ (SiH_3)^f
6	1026	900	1.7	923	0.8	91.4	24.3	21.0	11.4	1027	87.4	22.0	0.75	0.65	916 vs		δ_{as}(Si-H)
7	1029	903	4.0	926	1.6	376.4	100	16.2	8.8	1028	394.2	16.5	0.71	0.67	941 vs		δ_s(Si-H)
8	1060	932	3.3	954	1.0	155.0	41.2	21.9	11.9	1059	151.4	23.4	0.74	0.69	964 s		δ_{as}(Si-H)
9	2371	2141	1.8	2134	2.1	199.0	52.9	76.2	41.4	2372	186.1	104.1	0.75	3.49	2180 s		ν_{as}(Si-H)
10	2376	2145	2.1	2138	2.4	133.0	35.3	184.1	100	2377	131.1	211.0	0.06	3.42	2190 s		ν_s(Si-H)
11	2395	2163	1.5	2156	1.8	146.3	38.9	108.1	58.7	2393	138.5	137.3	0.28	3.52	2196 s		ν_{as}(Si-H)
12	2883	2613	-	2595	-	4.2	1.1	146.0	79.3	2881	3.1	152.9	0.36	5.08		2572	ν(S-H)

[a] Using a scaling equation[36]. [b] $100 \,|\nu_{exp.} - \nu_{ab\ initio\ scaled}| / \nu_{exp.}$ [c] Using a scaling factor of 0.9. [d] From [14]. [e] In H_3C-SH molecule[38,39] [f] Weak contribution of this mode.

Table 11. Harmonic vibrational frequencies (cm^{-1}), in the form (I) of H_3Si-BH_2, form (II) of $H_3Si-AlH_2$, and in the *eclipsed* form of H_3Si-SH

No	X = B (form I)			X = Al (form II)			X = S (*Eclipsed*)			Characterization
	6-31G**	6-31++G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**	6-31G**	6-31++G**	MP2/6-31G**	
1	-40	-60	-91	15	-6	-52	-202	-204	-227	$\tau(XH_2) + \tau(SiH_3)$
2	472	471	445	354	354	333	635	636	603	$\Gamma(SiH_3) + \Gamma(XH_2)^a$
3	504	506	462	422	423	384	699	697	671	$\gamma(XH_2)^a + \gamma(SiH_3)$
4	651	651	656	405	403	414	538	535	537	$\nu(Si-X)$
5	822	819	795	594	592	568	880	876	823	$\Gamma(XH_2)^a + \Gamma(SiH_3)$
6	990	987	948	637	636	614	-	-	-	$\gamma(XH_2)$
7	1003	1003	964	985	984	934	1035	1034	995	$\delta_s(Si-H)$
8	1030	1031	988	1031	1032	989	1026	1026	980	$\delta_{as}(Si-H)$
9	1048	1049	1010	1036	1036	992	1060	1059	1020	$\delta_{as}(Si-H)$
10	1295	1287	1262	834	834	807	-	-	-	$\Delta(XH_2)$ scissor
11	2321	2317	2307	2309	2308	2295	2377	2378	2354	$\nu_{as}(Si-H)$
12	2325	2321	2315	2319	2319	2308	2384	2385	2358	$\nu_{as}(Si-H)$
13	2341	2338	2333	2325	2325	2315	2378	2379	2344	$\nu_s(Si-H)$
14	2697	2693	2702	1998	2000	1986	2897	2895	2847	$\nu_s(X-H)$
15	2771	2764	2791	1999	2001	1997	-	-	-	$\nu_{as}(X-H)$

[a] In H_3Si-SH correspond to (XH).

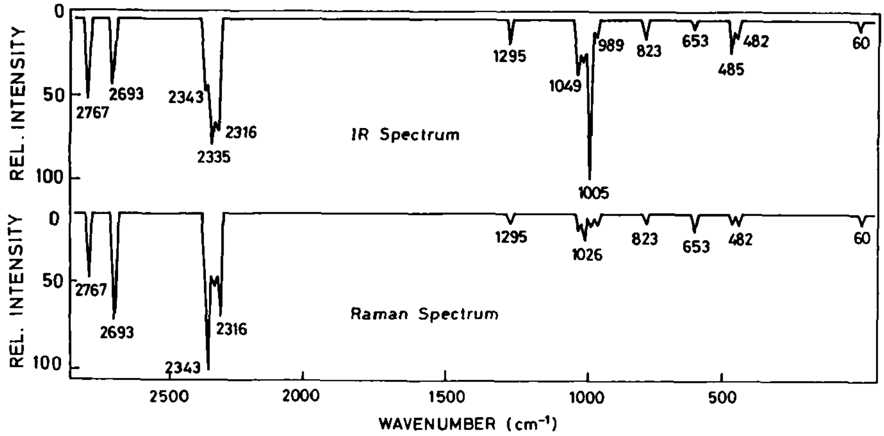

Fig. 3. Infrared and Raman spectra calculated in the form (II) of $H_3Si\text{-}BH_2$

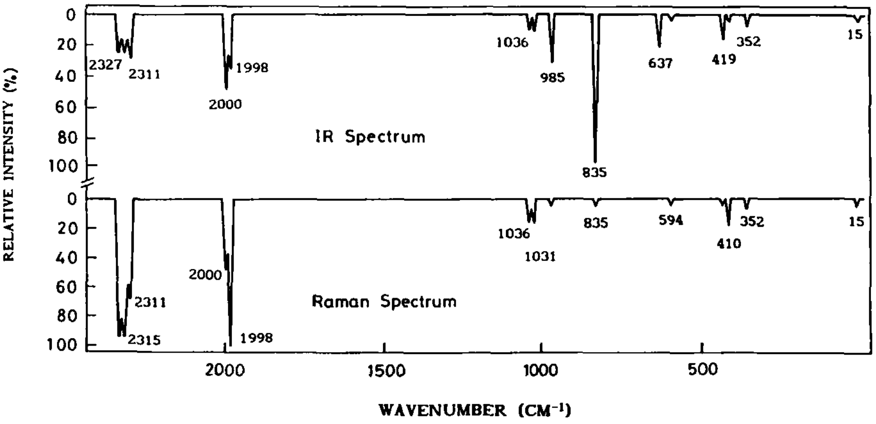

Fig. 4. Infrared and Raman spectra calculated in the form (I) of $H_3Si\text{-}AlH_2$

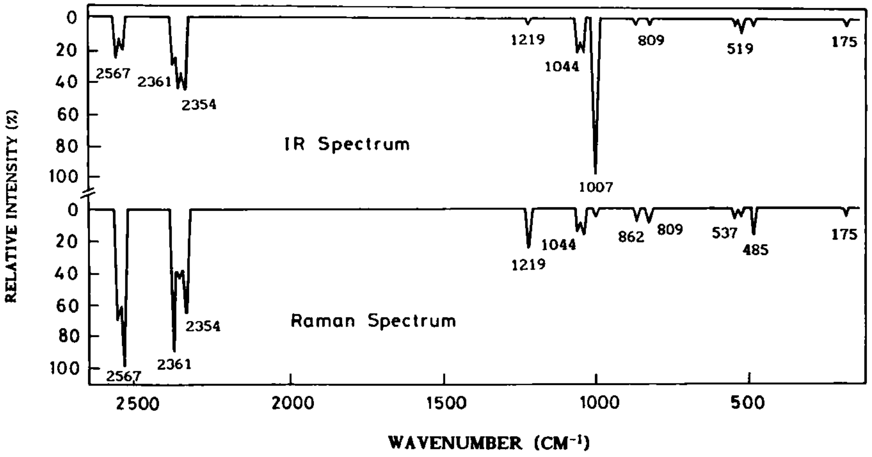

Fig. 5. Infrared and Raman spectra calculated in the *staggered* form of H_3Si-PH_2

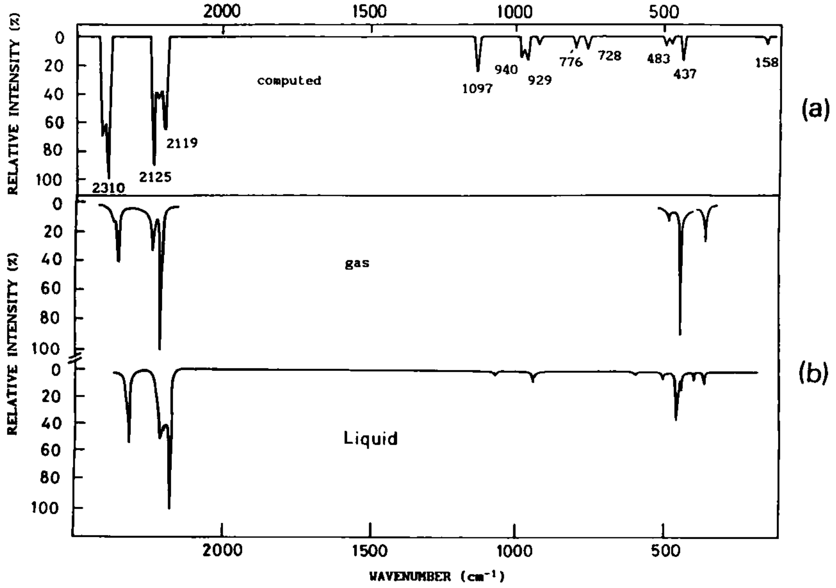

Fig. 6. (a) Raman spectrum of H_3Si-PH_2 calculated at 6-31G** level with scaled frequencies. (b) Raman spectra[12] in the gas and liquid phases.

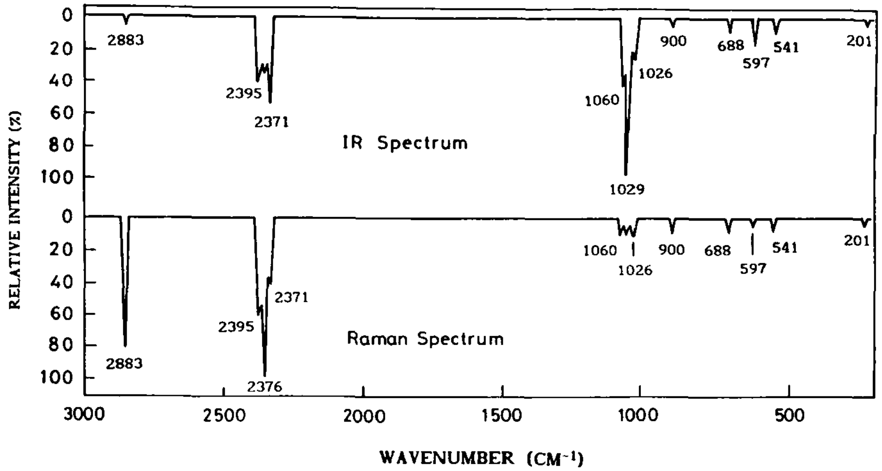

Fig. 7. Infrared and Raman spectra calculated in the *staggered* conformation of H_3Si-SH

The symmetric ν_s(Si-H) stretching vibration is observed in general at a higher frequency than the antisymmetric one, Tables 7-11. This is a usual error in ab initio and semiempirical methods when the frequencies are very close[30]. In monoalkylsilanes the frequencies of the asymmetric and symmetric -SiH_3 modes have been reported so close as to be indistinguishable[31]. In silanes these Si-H stretching frequencies are considerably closer together than the comparable C-H frequencies because of the heavier mass of the silicon atom. In H_3Si-PH_2 molecule (Table 9), three Si-H stretching vibrations are computed (two at the same frequency) in agreement with the only two bands observed in the Raman spectra[12] of the gaseous H_3Si-PH_2. The computed Si-H deformations show strong IR bands, in analogy with the C-H deformations.

To get the desired degree of accuracy in the prediction of a spectrum is not always possible because the experimental frequencies depend on effects that are not included in the theory, such as solvent shifts, anharmonicity effects, Fermi resonance, etc. Also the theoretical frequencies are known to be overestimated[21,32] by approximately 10%. To correct this deficiency, three possibilities have been reported to be used on the computed frequencies. In the first procedure, sets of specific scaling factors (or correction factors) described in ab initio (at 3-21G* level[33,34]) and semiempirical methods (AM1[30,35]) are used for each vibrational mode. Although with this procedure a lower error is obtained than with the other two procedures that are described below, specific scaling factors have not been reported in silanes[4]. Another procedure is the use of a scaling equation to correct in general all the theoretical frequencies, which in the case of 6-31G** level has been established[36] as:

$$\nu(\text{scaled}) = -45.99 + 0.92227\ \nu(\text{theor.})\ (\text{cm}^{-1})$$

This equation was used in the present paper with the 6-31G** frequencies of H_3Si-PH_2 and H_3Si-SH compounds (Tables 9 and 10), in which experimental frequencies have been recorded[12,14]. The % error obtained in the scaled frequencies is very small, in general less than 5%, except in the low frequency range (< 650 cm^{-1}).

The third procedure is to use one uniform correction factor of 0.9 in all the computed frequencies[21]. The results obtained in the frequencies of H_3Si-PH_2 and H_3Si-SH compounds are shown in the fifth and sixth columns of Tables 9 and 10 respectively. The scaled Raman spectrum of H_3Si-PH_2 is plotted in Fig. 6 together with the experimental Raman spectra[12]. A very good agreement is observed between theory and experiment, with only a slight disagreement in the scaled frequency at 700 cm^{-1}, characterized as $\gamma(PH_2)+\gamma(SiH_3)$, while the corresponding band at 722 cm^{-1} has been assigned[12] as $\gamma(PH_2)$ wagging mixed with $\Gamma(SiH_3)$. In general, with this procedure a lower error is obtained than by using the scaling equation (2nd procedure), which gives smaller desviations in the frequency range (> 2000 cm^{-1}).

The Raman frequencies reported[12] in the gas phase of H_3Si-PH_2 are very close to the IR data reported in the parent H_3C-PH_2 molecule[37] which are included in Table 9 for comparison purposes. The computed frequencies of H_3Si-SH are also in agreement with the IR data of methyl mercaptan[38,39], included in Table 10.

The zero-point vibrational energies, thermal energies, rotational constants and entropies, and in the most stable conformations, are listed in Table 12. In the ZPE energies, a scaling factor of[32] 0.89 and[40] 0.93 has been recommended to be used to correct the known overestimation obtained by using Hartree-Fock theory. In H_3Si-PH_2, experimental values of the rotational constants (51.8617, 5.58148 and 5.55650) have been reported[12], which are in agreement with our calculations.

SUMMARY AND CONCLUSIONS

Two optimum structures called form (I) and (II) were obtained in H_3Si-BH_2 and H_3Si-AlH_2 molecules, while *eclipsed* and *staggered* forms were identified in H_3Si-SH. Only a *staggered* conformation was found as minimum in H_3Si-PH_2. The calculated inversion angle ω was very small, ca 2° in H_3Si-BH_2 and ca. 0.8° in H_3Si-AlH_2, thus could not be identified *eclipsed* or *staggered* conformations in these molecules.

Table 12. HF/6-31G** computed zero-point vibrational energies (kcal mol^{-1}), sum of thermal energies (kcal mol^{-1}), rotational constants (GHz), and entropies (cal mol^{-1} K^{-1}).

Parameter	BH2 Form (II)	AlH2 Form (I)	PH2 *staggered*	SH *staggered*
Zero-point energy (ZPE)	28.97	24.68	28.45	22.97
Thermal energy (TC)	31.86	27.93	31.17	25.49
Rotational constants	64.21	53.20	52.51	67.11
	10.48	4.80	5.51	6.22
	10.05	4.64	5.47	6.09
Entropy				
Total	66.34	72.78	66.14	64.59
Translational	37.27	38.19	38.39	38.39
Rotational	21.39	23.12	22.83	22.36
Vibrational	7.68	11.46	4.92	3.85

The agreement between the calculated and experimental structure of H_3Si-PH_2 was satisfactory, with all of the calculated structural values well within the uncertainties of the experimentally determined bond lengths and bond angles.

The difference of energy between forms (I) and (II) in H_3Si-BH_2 and H_3Si-AlH_2, and between the *eclipsed* and *staggered* forms of H_3Si-SH, was very small, so rotation about the Si-X bond should be essentially free.

In a comparison analysis, the structure of the present silanes were computed very close to those of the respective methanes. The values of the total atomic charge, rotational constant and other thermodynamics parameters were coherent.

The agreement between computed frequencies and available experimental values seemed reasonable. By using one uniform correction factor of 0.9 a very low error in general was obtained (less than 3.5%), although in the frequency range (> 2000 cm^{-1}) a slightly better agreement was established with a scaling equation. These procedures although studied in H_3Si-PH_2 and H_3Si-SH, could be applied to H_3Si-BH_2 and H_3Si-AlH_2 molecules for an accurate prediction of their theoretical spectra, since they have not been determined experimentally. It should be noted that the computation of a vibrational infrared spectrum of a molecule is cheaper than the synthesis of the molecule and the experimental determination of its spectrum.

SUPPLEMENTARY MATERIAL

Supplementary material available: A list of the z-matrix optimized geometries, cartesian coordinates and force constant matrixes for all the compounds. Ordering information is given on any current masthead page.

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