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Factorial design and principal component analyses of the vibrational frequencies and infrared intensities of methane and silane

Anselmo E. de Oliveira*, Roy E. Bruns

Instituto de Química, Universidade Estadual de Campinas, 13081-970, Campinas, SP, Brazil

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Abstract

A multivariate statistical approach is presented to analyze the changes in calculated harmonic vibrational frequencies and infrared intensities obtained from ab initio calculations for methane and silane. The effects of four wave function modifications on these spectral parameters are investigated using a two-level factorial design and principal component analyses: basis set (6-31G and 6-311G), inclusion of polarization and diffuse functions as well as electron correlation treatment using the second-order Møller–Plesset method. Characteristic group frequencies present similar factorial models for each molecule. However, the intensity factorial models are quite different for these group vibrations. The most important effect values for the methane frequencies are due to a change from the Hartree–Fock to the second-order Møller–Plesset level. However, this effect is secondary to the one provoked by the inclusion of polarization functions in the silane basis set. Published by Elsevier Science B.V.

Keywords: Methane; Silane; Factorial design; Principal component analyses; Wave function

1. Introduction

The molecular property results obtained from ab initio calculations are dependent on the basis set and other factors used in the construction of the wave function employed to solve the Schrödinger equation. A better wave function in a variational sense is one that can provide a lower total energy for a specific molecular or atomic system. Although these wave functions may provide accurate results for some molecular properties, such as geometries and vibrational frequencies, this is not necessarily true for others such as the dipole moments and infrared intensities.

Several research groups have modified wave

functions in attempts to determine how the calculated fundamental vibrational frequencies and infrared intensities of various molecules are changed [1–7]. The inclusion of electron correlation treatment via Møller–Plesset perturbation, as well as the addition of polarization and diffuse functions, has been found to provoke large changes in some calculated frequency and intensity values. The use of the Møller–Plesset perturbation method has been found to consistently cause large decreases in most vibrational frequencies. However, changes in other wave function characteristics do not provoke such regular changes in these frequencies. In these cases it becomes difficult to quantitatively assess how specific wave function modifications affect the vibrational frequency and infrared intensity values.

* Corresponding author.

Table 1

A 2⁴ factorial design for the calculation of the methane and silane vibrational harmonic frequencies and infrared intensities

Factor	Level	
	–	+
1. Basis set	6-31G	6-311G
2. Polarization functions	Absent	Present
3. Diffuse functions	Absent	Present
4. Electron correlation	Hartree–Fock	Møller–Plesset 2

In a recent paper [8] our group has proposed the use of multivariate statistical procedures to determine how various wave function modifications affect the calculated values of the vibrational frequencies and infrared intensities of CH₃F. Prominent among techniques to optimize the results of experimental systems that depend on various factors are factorial design [9] and principal component analyses [10]. Factorial design is important for determining how to adjust several factor levels simultaneously in order to optimize a given property of the system being studied. This scheme allows a more quantitative assessment of how specific wave function modifications change molecular property values. Furthermore, interaction effects involving more than one kind of wave function modification can be evaluated. Ultimately, this analysis can lead to a better understanding of the nature of the wave function used.

Principal component analyses can be used to complement factorial design results and provide a statistical

criterion for determining which wave function, among a group of candidate wave functions, best reproduces the calculated results of several molecular properties. Moreover, this analysis is frequently possible using bidimensional projections that permit convenient visualizations of the optimization processes.

Our main objective in this study is to investigate in a systematic way how changes in wave function characteristics provoke changes in the vibrational frequencies and infrared intensities of methane and silane. The determination of the factorial effects and the principal component results can be expected to lead to a greater understanding of how to optimize wave function characteristics for calculating these properties. Other studies using these methods have concentrated on how the effect and principal component values change with different terminal atoms, H, F and Cl. In this work the substitution of the central atom of the group IV halides is studied, by focusing on carbon–silicon substitution.

Table 2

	Wave function	Factorial designation
1	HF/6-31G	– – – –
2	HF/6-311G	+ – – –
3	HF/6-31G(d,p)	– + – –
4	HF/6-311G(d,p)	+ + – –
5	HF/6-31++G	– – + –
6	HF/6-311++G	+ – + –
7	HF/6-31++G(d,p)	– + + –
8	HF/6-311++G(d,p)	+ + + –
9	MP2/6-31G	– – – +
10	MP2/6-311G	+ – – +
11	MP2/6-31G(d,p)	– + – +
12	MP2/6-311G(d,p)	+ + – +
13	MP2/6-31++G	– – + +
14	MP2/6-311++G	+ – + +
15	MP2/6-31++G(d,p)	– + + +
16	MP2/6-311++G(d,p)	+ + + +

2. Calculations

A factorial analysis design built to investigate how four main factors affect molecular orbital results is presented in Tables 1 and 2. The wave function modifications were investigated at two levels (minus and plus in Table 1) with regard to the following factors: (1) the use of a 6-31G or 6-311G valence basis set; (2) the presence or absence of diffuse functions in the basis set; (3) the inclusion or not of polarization functions; (4) the treatment of the Hartree–Fock (HF) wave function with the second-order Møller–Plesset (MP2) perturbation method. This 2ⁿ factorial design, with the number of factors *n* equal to 4, yields 16 different wave functions as shown in Table 2. These wave functions were used to calculate the ab initio vibrational harmonic frequencies and infrared intensities for methane and silane.

The main effect of each variable is defined as the difference between two averages

$$(ef)_i = (\bar{R}_+)_i - (\bar{R}_-)_i \quad (1)$$

where $(\bar{R}_+)_i$ is the average response for the plus or high level of the *i*th variable (factor) and the $(\bar{R}_-)_i$ is the average response for the minus or low level. For

example, to evaluate the average change in a spectral parameter due to the inclusion of polarization functions in the basis set, the difference in Eq. (1) involves the averages of the results for the eight wave functions in Table 2 with polarization functions and of the eight results without these functions. Analogous to the main effects, the interaction effects are seen to be differences between two averages, half of the 16 results being included in one average and the other half in the other. This can be done by multiplying the signs in the columns of the factors involved in the interaction. The resulting signs are the ones used in Eq. (1) to calculate the interaction effect. Overall, there are four main effects, six second-order, four third-order and one fourth-order interaction effect for each molecular spectral parameter. The main interaction effects are determined for each vibrational mode for both molecules.

To conveniently treat a multidimensional problem, such as the simultaneous study of the calculated vibrational harmonic frequencies of a molecule, the statistical method of principal component analysis (PCA) may be used to represent data in two-dimensional plots, where their axes are the two principal components that explain the most data variance. PCA is an eigenvector rotation problem in which the covariance

Table 3

Calculated and experimental fundamental vibrational frequencies (cm⁻¹) and infrared intensities (km mol⁻¹) for methane. Sign combinations as in Table 2

Wave function	ν_1 A1 CH str	ν_2 E CH bend	ν_3 T ₂ CH str	ν_4 T ₂ CH bend	A ₃ T ₂ CH str	A ₄ T ₂ CH bend
– – – –	3181.89	1708.82	3296.49	1516.97	113.52	64.37
+ – – –	3147.45	1699.89	3257.11	1501.86	149.86	63.51
– + – –	3174.41	1685.49	3285.24	1469.01	118.93	30.68
+ + – –	3150.76	1667.76	3253.98	1453.23	130.26	35.21
– – + –	3178.06	1700.00	3288.12	1511.19	127.37	72.53
+ – + –	3143.79	1698.63	3252.87	1499.46	147.27	68.47
– + + –	3168.85	1673.00	3276.13	1462.44	127.55	36.67
+ + + –	3149.96	1666.67	3252.23	1452.77	125.75	35.92
– – – +	3062.97	1619.95	3194.32	1441.45	89.13	55.18
+ – – +	3002.72	1587.63	3135.31	1425.78	107.50	60.73
– + – +	3132.61	1624.13	3278.55	1404.54	63.94	34.60
+ + – +	3075.92	1579.98	3213.52	1363.67	65.09	41.95
– – + +	3051.33	1586.66	3179.79	1432.56	100.60	65.95
+ – + +	2999.23	1577.27	3131.63	1423.89	106.72	66.35
– + + +	3119.58	1590.40	3264.10	1394.66	69.66	43.40
+ + + +	3073.56	1570.88	3210.75	1362.50	61.57	43.63
Exptl.	3025.5 ^a	1582.7	3156.8	1367.4	69.74 ^b	33.36

^a Estimated harmonic frequencies obtained from observed anharmonic frequencies [13].

^b From [14].

matrix, obtained by multiplying $\mathbf{X}^T\mathbf{X}$, where \mathbf{X}^T is the transpose of the \mathbf{X} data matrix, is diagonalized with the first two eigenvectors defining the first two principal components. They are perpendicular to each other and the amount of statistical variance explained by their bidimensional projection is equal to the sum of their eigenvalues.

If the residual variance, that is the variance not explained by the first two eigenvectors, is sufficiently low, the data being treated are said to be adequately modeled in the two-dimensional space. As such, its corresponding graph can be used to determine which of the wave functions investigated is in best agreement with the experimental results.

The \mathbf{X} data matrix for each molecule for which PCA was performed has 16 rows, each one corresponding to the wave functions in the factorial design in Table 2, and four columns, one for each of the distinct vibrational harmonic frequencies. The one doubly-degenerate and two triply-degenerate normal modes (E and T_2) are each represented by one and two columns respectively in the data matrix. Additional columns are not needed since they are all equivalent to other columns already included in the matrix and provide no new statistical information.

Factorial design and principal component calculations were carried out using computer programs developed in our laboratories [11]. The ab initio molecular orbital calculations were performed with the GAUSSIAN 92 computer package [12] on an IBM RISC 6000 workstation at the CENAPAD/SP (UNICAMP). The frequencies and intensities were calculated using optimized equilibrium geometries for each wave function.

3. Results

Tables 3 and 4 show all the vibrational harmonic frequencies and infrared intensities calculated using the wave functions in Table 2. The estimated harmonic frequencies obtained from the observed anharmonic ones and the experimental infrared intensities for both molecules are also reported at the bottom of these tables. Overall, 32 ab initio molecular orbital calculations were performed and 130 min of elapsed CPU time spent. The harmonic frequencies calculated using HF theory tend to be overestimated by about 5–6%. When electron correlation is not neglected at the MP2 level this relative average

Table 4

Calculated and experimental fundamental vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) for silane. Sign combinations as in Table 2

Wave function	ν_1 A1 SiH str	ν_2 E SiH bend	ν_3 T_2 SiH str	ν_4 T_2 SiH bend	A_3 T_2 SiH str	A_4 T_2 SiH bend
– – – –	2273.80	1033.34	2277.32	960.06	677.72	642.04
+ – – –	2273.44	1044.04	2261.83	978.48	402.55	667.96
– + – –	2369.93	1053.44	2360.44	1017.15	640.43	689.19
+ + – –	2350.91	1051.05	2337.75	1018.77	516.32	704.31
– – + –	2279.37	1039.86	2279.30	965.87	614.73	657.32
+ – + –	2247.46	1044.70	2234.50	982.71	415.40	674.85
– + + –	2371.03	1054.64	2360.58	1018.43	626.85	722.66
+ + + –	2350.79	1051.22	2337.14	1019.06	522.23	705.39
– – – +	2185.57	973.36	2206.37	908.06	531.90	513.33
+ – – +	2189.85	991.42	2195.91	926.86	335.96	538.62
– + – +	2339.31	1017.61	2349.88	973.72	489.73	558.36
+ + – +	2330.14	1016.64	2334.79	973.28	405.31	595.27
– – + +	2193.40	976.42	2208.98	913.29	496.51	534.94
+ – + +	2188.04	979.17	2193.18	926.62	345.77	546.88
– + + –	2341.98	1015.82	2350.51	974.39	491.95	594.89
+ + + +	2330.08	1007.87	2334.20	972.98	413.12	597.19
Expt ^a	2187.6 ^a	965.6	2267.4	948.5	320.48 ^b	296.38

^a Estimated harmonic frequencies obtained from observed anharmonic frequencies [15].

^b From [16].

error lowers appreciably to about 2%. For the ν_3 and ν_4 normal modes of silane, these errors are even lower (about 0.2%). In these cases neglect of electron correlation seems to be a major deficiency in the wave functions treated here. This is consistent with the results of other studies [1,4–7].

3.1. Factorial design of vibrational harmonic frequencies

The main and interaction effects of the 16 wave functions in Table 2 on the frequencies of methane and silane are presented in Table 5. Effects with absolute values less than 10 cm^{-1} have not been included. The substitution of carbon by silicon results in very different effect values for all the wave function modifications studied here except for the use or not of diffuse functions. For both methane and silane the addition of diffuse functions causes only minor changes in the calculated frequencies. The most important effect values for methane are those for MP2 correlation treatment (-69 to -97 cm^{-1}) whereas this modification has much lower effect values for silane. This may have been anticipated since the valence electrons of the carbon atom can be expected to be more highly correlated than those of the silicon atom. The most important effect values for silane are due to the inclusion of polarization orbitals (23 to 119 cm^{-1}) whereas these effects are of less importance for methane. Certainly, one would expect polarization functions to be more important in describing accurately the electronic densities of SiH bonds than CH bonds. Furthermore, the addition of the polarization orbitals strengthens the SiH bonds more than they

do for the CH bonds since the SiH stretching frequencies increase by 119 and 113 cm^{-1} for ν_1 and ν_3 , respectively. These values are about three times the effect values calculated for these stretching frequencies of methane. It should be noted that the MP2 electron correlation effects are also much more important for all the CH_3F calculated frequencies than are the polarization function effects.

The CH stretching frequencies have similar effects indicating that their calculated values have similar dependencies on the wave function modifications studied. This is confirmed by inspection of the ν_1 and ν_3 values in Table 3. They are highly correlated with a correlation coefficient of 0.974 . As such, one may expect that wave function modifications resulting in higher ν_1 stretching frequency values will also result in higher ν_3 values for methane. Correlation coefficients for all the methane and silane calculated frequencies are shown in Table 6. High correlation coefficients for the calculated values of the frequencies of different normal modes indicate that wave function modifications resulting in more accurate frequency results for one of these normal modes will also provide more accurate results for the other modes.

Similar effect values are also observed for the two SiH stretching frequencies. The calculated values of these frequencies for the wave functions in Table 2 are also seen to be highly correlated, as can be confirmed in Table 6.

The polarization orbital effect values for the silane bending frequencies are not as large as for the stretching frequencies. Whereas the addition of polarization orbitals increases the silane bending frequencies by 23

Table 5
Main and interaction effects of wave function modifications on the fundamental methane and silane vibrational harmonic frequencies (cm^{-1})^a

Effects	Methane				Silane			
	ν_1 CH str	ν_2 CH bend	ν_3 CH str	ν_4 CH bend	ν_1 SiH str	ν_2 SiH bend	ν_3 SiH str	ν_4 SiH bend
Basis set	-40.79	-17.47	-44.42	-18.71	-11.71	-	-20.51	-
Polarization functions	34.78	-15.07	37.36	-48.79	119.16	23.25	113.49	50.60
Diffuse functions	-	-13.77	-	-	-	-	-	-
MP2 correlation	-97.16	-95.42	-69.28	-77.23	-52.29	-49.25	-34.38	-48.79
Basis set–Correlation	-12.98	-	-11.97	-	-	-	-	-
Polarization–Correlation	36.58	13.54	44.11	-	27.01	11.14	27.75	-

^a Effects with absolute values less than 10 cm^{-1} are not included in this table.

Table 6
Correlation coefficients for the calculated frequencies of methane and silane

Methane			
	ν_1	ν_2	ν_3
ν_1	–		
ν_2	0.904	–	
ν_3	0.599	0.853	–
ν_4	0.466	0.745	0.974
Silane			
	ν_1	ν_2	ν_3
ν_1	–		
ν_2	0.921	–	
ν_3	0.899	0.748	–
ν_4	0.826	0.656	0.989

and 51 cm^{-1} , it decreases those of methane by 15 and 49 cm^{-1} . The polarization orbital–MP2 correlation energy interaction effects are important for the ν_1 , ν_2 and ν_3 frequencies of both methane and silane (see Table 5).

3.2. Factorial design for the infrared intensities

Table 7 presents the main and interaction effects for the calculated infrared intensities of Tables 3 and 4. Effect values less than 1 km mol^{-1} are not included in the table. The A_3 and A_4 intensities of methane and

silane all present strikingly different effect values. The A_3 silane intensity has extremely large basis set (6-31G–6-311G) and electron correlation effects, -151.6 and $-113.3 \text{ km mol}^{-1}$, respectively. These values are about 30 to 50% of the experimentally observed value of 320 km mol^{-1} . The A_4 calculated intensity has an electron correlation effect value of -123 km mol^{-1} , 40% of the observed experimental value of 296 km mol^{-1} . The absolute values of the methane intensity effects are much smaller. This is not surprising since its A_3 and A_4 observed intensities, 69.7 and 33.3 km mol^{-1} , are much smaller than the silane intensities.

Even though the absolute effect values obtained for the methane intensities due to the inclusion or not of polarization functions are much smaller than for the silane intensities, they represent 30 and 80% of the observed experimental methane values for A_3 and A_4 , respectively. In addition, the inclusion of MP2 correlation treatment lowers the calculated A_3 value for methane by almost 70% of its experimental value. On comparing effect values in Table 6 it should be remembered that both the silane experimental intensities are much larger than those for methane.

On average, the effect of the addition of diffuse functions in the basis sets of methane and silane is much less important than the inclusion of polarization orbitals or the use of MP2 electron correlation treatment. However, their use in the basis set of methane

Table 7
Main and interaction effects of wave function modifications on the methane and silane infrared intensities (km mol^{-1})^{a,b}

Effects	Methane		Silane	
	A_3 CH str	A_4 CH bend	A_3 SiH str	A_4 SiH bend
Basis set	10.42(14)	1.55	-151.64(47)	14.72
Polarization functions	-22.40(32)	-26.88(80)	35.67(11)	48.92(16)
Diffuse functions	3.53	5.84(17)	-9.17	15.63
MP2 correlation	-47.04(67)	–	-113.25(35)	-123.03(41)
Basis set–Polarization	-9.77(14)	1.29	53.65(17)	-5.45
Basis set–Diffuse	-6.38	-2.59	18.26	-11.09
Basis set–Correlation	-6.03	1.84	24.16	4.39
Polarization–Diffuse	-1.96	-1.54	9.76	2.62
Polarization–Correlation	-13.52(19)	5.72(17)	-13.18	4.07
Diffuse–Correlation	–	–	5.28	1.45
Basis set–Polarization–Diffuse	–	–	-12.00	-5.66
Basis set–Polarization–Correlation	1.91	–	-7.79	5.95
Basis set–Polarization–Diffuse–Correlation	–	–	2.09	–

^a Effects with absolute values less than 1 km mol^{-1} are not included in this table.

^b Values in parentheses correspond to the percentage of the experimental intensity.

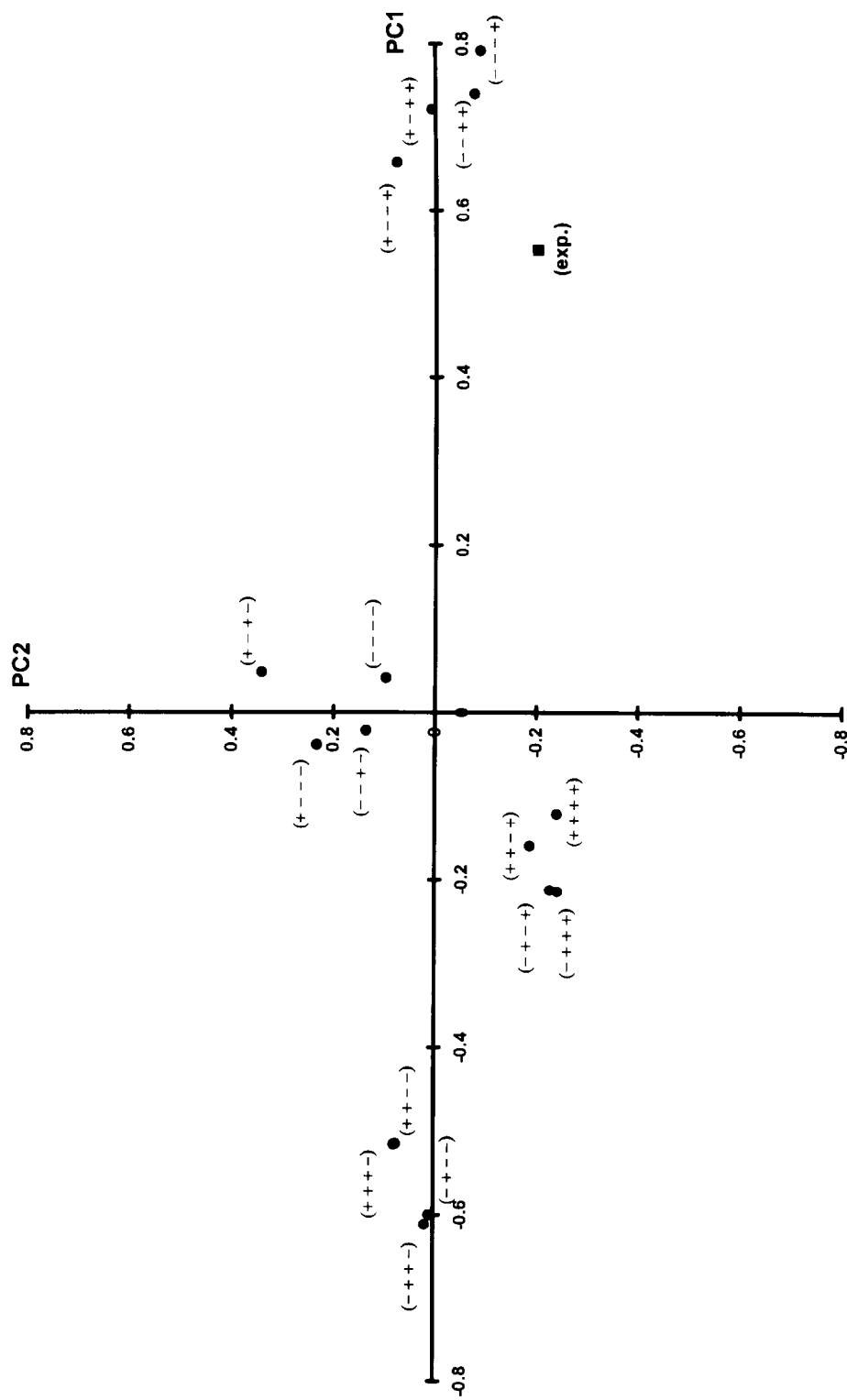


Fig. 2. Principal component score graph for the autoscaled vibrational harmonic frequencies for silane. These two principal components explain 99.0% of the total data variance.

raises the calculated A_4 intensity value by 17% of the experimental value.

The data in Table 7 are helpful in understanding why the vibrational intensities are much more difficult to be estimated by *ab initio* calculations than are the harmonic frequency values. The calculated intensities for each normal mode have factorial design effects that are much different from those of the other modes. Furthermore, this tendency is probably more aggravated for silane than for methane. Several third-order interactions have values larger than 1 km mol^{-1} for silane whereas only one of these effects is observed for methane. Again, this is not surprising since the silane fundamental bands are much more intense than the methane ones.

The differences in the vibrational intensity values between methane and silane are proportional to the squares of their dipole moment derivatives with respect to the normal coordinates. These values for silane are almost two to three times the ones for methane for the non-degenerate vibrational normal modes [17,18]. In addition, for A_3 the inclusion of d functions on the central atoms changes the calculated intensity values: $-22.40 \text{ km mol}^{-1}$ for methane and $35.67 \text{ km mol}^{-1}$ for silane (but reduces its percentage value). In contrast, the inclusion of s and p functions in the basis set has effect values of opposite signs: $10.42 \text{ km mol}^{-1}$ for methane to $-151.64 \text{ km mol}^{-1}$ for silane (increasing its percentage value). These results illustrate the sensitivity of the calculated silane intensity values on the use of additional basis set functions to construct the molecular wave function.

3.3. Principal components for the harmonic frequencies

The principal component plots for the autoscaled harmonic frequencies for the methane and silane molecules are shown in Figs. 1 and 2. The first two principal components of each plot explain 99% of the total data variance. The principal component equations are presented in Table 8. The first principal components (PC1) for both molecules are essentially averages of the autoscaled frequency values. The second components (PC2) are contrasts between the stretching and bending frequencies.

Fig. 1 shows the distribution of the calculated methane frequencies relative to the harmonic values

Table 8
Principal component equations for the calculated harmonic frequencies for methane and silane

	Explained variance/%
Methane	
PC1 = $-0.525\nu_1 - 0.533\nu_2 - 0.489\nu_3 - 0.448\nu_4$	82.1
PC2 = $-0.363\nu_1 + 0.276\nu_2 - 0.551\nu_3 + 0.699\nu_4$	16.9
Silane	
PC1 = $-0.517\nu_1 - 0.470\nu_2 - 0.494\nu_3 - 0.517\nu_4$	88.1
PC2 = $-0.364\nu_1 + 0.693\nu_2 - 0.561\nu_3 + 0.270\nu_4$	10.9

calculated from the observed frequencies. The first principal component discriminates between results obtained from wave functions at the MP2 level (right side of Fig. 1) and those at the HF level (left side). This is consistent with the factorial design results. Since the electron correlation effect has the largest absolute values of the effects for methane in Table 5, one expects that the first and most important principal component would discriminate between these values. The wave function results at the MP2 level are on the right side of this graph since the electron correlation effect values are all negative and all the PC1 loadings shown in Table 8 are also negative. The second component discriminates between wave functions with polarization functions in the basis set (negative PC2 score values) and those without these functions (top half of Fig. 1). The factorial design results also indicated that the calculated methane frequency results are very sensitive to the inclusion or not of polarization orbitals in the basis sets. It should be noted that the distribution of points in Fig. 1 has a pairwise structure, the two points of each pair representing identical wave functions except for the presence or not of diffuse functions in the basis set. This is consistent with the fact that diffuse functions have negligible factorial effect values.

The experimental point representing the harmonic frequencies is in closest agreement with the (+++++) or MP2/6-311++G(d,p) function followed by the MP2/6-311++G and MP2/6-31++G wave functions. These wave functions have relative standard errors of 27.7, 33.7 and 36.9 cm^{-1} , respectively, relative to the harmonic frequency values.

The wave function results for the calculated silane frequencies compared to the harmonic values

obtained from the observed frequencies are shown in Fig. 2. The first principal component discriminates between results for wave functions with polarization orbitals in their basis sets and those without these functions. The polarization function factorial effects were seen to be the most important in the factorial analyses of the silane frequencies. The second principal component shows a partial discrimination between results obtained with wave functions at the HF and MP2 levels. The electron correlation effects were also seen to be important for the calculated silane frequencies.

The harmonic frequency score point in Fig. 2 is closest to the (- - + +) or MP2/6-31++G and (- - - +) and MP2/6-31G wave functions. These functions presented calculated frequencies with relative standard errors of 34.7 and 36.8 cm^{-1} respectively.

4. Conclusions

The factorial design and principal component analyses clearly point out one essential difference in the construction of wave functions for the calculation of methane and silane vibrational frequencies. Of all the wave function modifications studied here, the calculated methane frequencies are most sensitive to the level of electron correlation treatment used, Hartree–Fock or second-order Møller–Plesset. Similar observations have been made for the CH_3F calculated frequencies, as reported previously [8], and for CH_2F_2 and difluoro- and dichloroethylene, presently being studied by our research group. On the other hand, the silane frequencies are most sensitive to the inclusion of polarization orbitals in the basis set. Additional calculations on other molecules containing third-row central atoms are necessary to determine whether this difference in behavior is general or not.

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