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Density functional theory study of the $Si_2H_{6-x}F_x$ series of molecules $\stackrel{\text{theorem}}{\to}$

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Abstract

The systematic replacement of hydrogen by fluorine atoms in disilane (Si_2H_6) is investigated using density functional theory (DFT). For every molecule in the $Si_2H_{6-x}F_x$ family, with $0 \le x \le 6$, we find the energetically most favorable configurations. Properties such as chemical potential, chemical hardness, polarizability, electrophilicity and the infrared vibration modes and frequencies are evaluated and analyzed in terms of the fluorine substitution. The molecular response to twisting the silyl groups at each end of the Si–Si axis, relative to each other, is also investigated. A consistent picture emerges which is in good agreement with the available experimental results. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

Fluorinated silanes and disilanes are of interest to electronic device technology, in relation to chemical vapor deposition (which has been used in industry for over three decades) and to the etching of silicon surfaces [1]. The precise knowledge of the molecular properties is thus of basic and applied relevance. In this context, we undertook a detailed study of various physical and chemical properties of $Si_2H_{6-x}F_x$ molecules, where we have considered all the possible compositions ($0 \le x \le 6$) and all the possible configurations and conformations that these molecules can adopt.

Using the atomic numbering of the Si₂F₆ molecule in Fig. 1, the dihedral angle θ (defined as the angle that the plane that contains atoms 6, 1 and 2 makes with the plane containing atoms 3, 1 and 2) is 60°, for the illustrated (stable) staggered configurations. For the eclipsed configurations $\theta = 0^\circ$. The molecular structures displayed in Fig. 1 are all the possible configurations of the Si₂H_{6-x}F_x family, ranging from disilane (x = 0) to the other

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Fig. 1. Optimized geometries for each conformation. H, and F are represented by pale and dark small spheres, respectively; Si is represented by large medium dark spheres. Hexafluordisilane and disilane are at the top and bottom, respectively. The energies increase from top to bottom and from left to right.

extreme case (x = 6), which corresponds to hexafluordisilane (Si₂F₆). For disilane the experimentally determined [2] Si–Si distance is 2.331 Å and the Si–H one is 1.492 Å. Hexafluordisilane has only slightly different Si–Si (2.317 Å) and Si–F (1.564 Å) distances [2]. However, the dependence of properties such as the chemical potential μ and chemical hardness η on the dihedral angle θ is quite different for Si₂H₆ and Si₂F₆ [3–5]. The main purpose of this Letter is to explore and characterize qualitatively and quantitatively the properties of the Si₂H_{6-x}F_x family. The molecules we study in this contribution have low rotational barriers, which are mostly due to bond repulsion. In fact, it was recently shown [3] that for low rotation barrier molecules hyperconjugation does not play an important role. In particular, it was shown that for Si_2H_6 delocalization accounts for at most 10% of the barrier height [6].

This Letter is organized as follows: after this Introduction, in Section 2, the computation method is presented. In Section 3 the geometry is fully characterized. The results for several molecular properties, like dipole moments, chemical potentials, chemical hardness, polarizability and electrophilicity, are given and analyzed in Section 4. The behavior of the stable configurations of the $Si_2H_{6-x}F_x$ family when they are twisted around the Si-Si axis, going from the staggered to the eclipsed conformation, is discussed in detail in Section 5. In Section 6 the chemical reactivity of these systems is analyzed in terms of the HOMO and LUMO orbitals. Next, in Section 7, the infrared vibration modes and frequencies are discussed. Finally, in Section 8 we draw conclusions and close this Letter.

2. Computational details

The results we provide were obtained within the framework of density functional theory (DFT), using the three parameter Becke parametrization [13] for the Lee et al. [14] exchange-correlation (B3LYP) and a Gaussian basis set. All the computations were performed with the GAUSSIAN 98 package [9] using the 6-311++G* basis, hereafter referred to, in the usual notation, as B3LYP/ 6-311++G*. In a previous Letter [3] we employed the 6-311++G** basis set, which also includes polarization for the hydrogen, but the differences we obtained for Si₂F₆ and Si₂H₆ proved irrelevant. Moreover, the basis set we did use includes a hydrogen diffuse additional s-like function which might be significant when calculating the polarizabilities.

Each particular molecule is fully characterized specifying 18 coordinates; they are the 7 bond lengths, the 6 angles that the H and/or F atoms

form with the Si–Si axis and 5 dihedral angles like the angle θ defined above. This dihedral angle always contains the Si–Si axis and one atom on one silyl group (atoms 3, 4 or 5 in Fig. 1) and one on the other group (atoms 6, 7 or 8 in Fig. 1). The precise structure of each conformation was obtained by full geometric optimization at the B3LYP/6-311++G* level. Fig. 1 illustrates the stable conformations we found for all possible configurations of the *x* fluorine atoms (0 < $x \le 6$).

3. Characterization of the stable configurations

The atomization energies (AE) in Table 1 do not include the zero point contribution, but they are accurate enough to unambiguously identify the most stable configuration for each x-value. This is due to the fact, which we have verified numerically, that the vibrational energy difference between the various structures is quite small. In particular, for a given x value the vibrational contribution is rather insensitive to the specific molecular configuration, and thus does not modify the ground state ordering. For the x-values for which several different atomic arrangements are possible, i.e., for x = 2, 3 and 4, the most stable one corresponds to the F atoms on the same silyl group.

The substitution of H by F atoms in the disilane molecule substantially modifies its geometry. In fact, the symmetry of each of these new molecular arrangements is different and requires a whole set of parameters to be precisely specified. In Table 1 we display the geometrical parameters we consider to be most relevant; moreover, the detailed geometries are available on request. In particular, the Si–H distances vary between $1.471 \le d_{\text{Si}-\text{H}} \le 1.488$ A; the shortest distance corresponds to the $Si_2H_4F_2$ molecule in the (c)-configuration of Fig. 1, and the longest to Si_2H_5F . The latter is very close to the d_{Si-H} distance of disilane which amounts to 1.487 Å. In turn, the Si-F distances vary in the range $1.598 \leq d_{\text{Si}-F} \leq 1.639$ A. The former corresponds to Si_2F_6 , and the latter to $Si_2H_4F_2$ in the (b)-configuration, where the F atoms are in different silyl groups and facing each other. The general trend is that the magnitude of d_{Si-H} is

Table 1

Interatomic distances and angles (θ_{opt}) for the optimized geometries, atomization energies (AE) and dipolar moments (**D**), for all possible Si₂F_xH_{6-x} conformations

Species	Distances (Å)	$\theta_{\rm opt}$ (degrees)	AE (kcal/mole)	D (Debye)
Si ₂ H ₆	$\begin{aligned} SiSi &= 2.354\\ SiH &= 1.487 \end{aligned}$	60.0	576.7	0.0000
Si ₂ FH ₅	$\begin{array}{l} SiSi = 2.354 \\ Si^3F^3 = 1.639 \\ Si^1H^{4,5} = 1.484, Si^2H^{6,8} = 1.485, Si^2H^7 = 1.488 \end{array}$	60.2	617.4	1.7664
$Si_2F_2H_4(a) \\$	$\begin{array}{l} SiSi = 2.351 \\ Si^{1}F^{3,4} = 1.623 \\ Si^{2}H^{6,7} = 1.485, \ Si^{2}H^{8} = 1.483, \ Si^{1}H^{5} = 1.478 \end{array}$	62.0	670.3	2.2881
$Si_2F_2H_4(b) \\$	$ \begin{split} & SiSi = 2.363 \\ & Si^1F^3 = Si^2F^7 = 1.639 \\ & Si^1H^{4,5} = Si^2H^{6,8} = 1.482 \end{split} $	62.0	663.4	0.0061
$Si_2F_2H_4(c) \\$	$\begin{array}{l} SiSi = 2.364 \\ Si^{1}F^{3} = Si^{2}F^{6} = 1.606 \\ Si^{1}H^{4} = Si^{2}H^{7} = 1.473, \ Si^{1}H^{5} = Si^{2}H^{8} = 1.471 \end{array}$	72.4	662.5	2.5375
$Si_2F_3H_3(a) \\$	$\begin{array}{l} {\rm SiSi} = 2.337 \\ {\rm Si}^{1}{\rm F}^{3,4,5} = 1.609 \\ {\rm Si}^{2}{\rm H}^{6,7,8} = 1.482 \end{array}$	60.0	725.8	2.8032
$Si_2F_3H_3(b)\\$	$\begin{array}{l} SiSi = 2.362 \\ Si^1F^3 = 1.620, \ Si^1F^4 = 1.623, \ Si^2F^6 = 1.634 \\ Si^1H^5 = 1.476, \ Si^2H^7 = 1.481, \ Si^2H^8 = 1.480 \end{array}$	72.1	715.7	1.5382
$Si_2F_3H_3(c) \\$	$\begin{split} & \text{SiSi} = 2.362 \\ & \text{Si}^1\text{F}^{3,4} = 1.619, \text{Si}^2\text{F}^8 = 1.630 \\ & \text{Si}^1\text{H}^5 = 1.478, \text{Si}^2\text{H}^{6,7} = 1.482 \end{split}$	58.8	715.1	3.1406
$Si_2F_4H_2(a) \\$	$\begin{array}{l} SiSi = 2.350 \\ Si^{1}F^{3}, Si^{1}F^{4} = 1.609, Si^{1}F^{5} = 1.606, Si^{2}F^{6} = 1.627 \\ Si^{2}H^{7,8} = 1.478 \end{array}$	61.2	770.5	2.4461
$Si_2F_4H_2(b) \\$	SiSi = 2.363 Si ¹ F ^{3,4} = Si ² F ^{6,7} = 1.618 Si ¹ H ⁵ = Si ² H ⁸ = 1.474	64.3	767.6	0.0022
$Si_2F_4H_2(c) \\$	$\begin{array}{l} SiSi = 2.366 \\ Si^{1}F^{3} = Si^{2}F^{7} = 1.619, \ Si^{1}F^{4} = Si^{2}F^{8} = 1.615 \\ Si^{1}H^{5} = 1.474, \ Si^{2}H^{6} = 1.475 \end{array}$	38.8	767.1	2.2652
Si_2F_5H	$\begin{array}{l} SiSi = 2.351 \\ Si^{1}F^{3,4} = 1.604, \ Si^{1}F^{5} = 1.601, \ Si^{2}F^{6,7} = 1.612 \\ Si^{1}H^{8} = 1.471 \end{array}$	63.9	821.6	1.8487
Si ₂ F ₆	SiSi = 2.336 SiF = 1.598	60.0	875.0	0.0000

The superindices refer to the atomic labels in Fig. 1.

reduced when the hydrogens are facing the fluorine atoms.

On the other hand, the Si–Si bond distance of the most stable configuration of $Si_2H_{6-x}F_x$ de-

creases when the F atoms bind to the same Si, increasing the bond population and making the molecular structure more compact. Here and throughout Mulliken analysis was implemented to



Fig. 2. Si–Si bond population versus bond distance. The labels in the graph denote the number (x) of fluorine atoms in the molecule. Here, as well as in the rest of the figures, the solid lines are just a guide to the eye.

obtain bond populations. The dependence of the bond electronic population on the Si–Si distance seems to follow two different linear behaviors, as is observed in Fig. 2. Symmetric systems (x = 0, 3and 6) define a specific linear trend, which is different from the one obeyed by the less symmetric molecular structures (x = 1, 2, 4 and 5). On the contrary, for the systems labeled (b) and (c) in Fig. 1 that have F atoms bonded to two different Si atoms, the bigger electronegativity of F relative to H leads to an increased Si–Si bond distance, due to the additional electronic repulsion.

4. Molecular properties

In this section we describe the results for the molecular properties that we computed. However, from now on we limit our attention to the lowest energy, (a)-type configuration, of each system illustrated in Fig. 1.

4.1. Dipolar moment

The way that the dipolar moment **D** evolves as a function of fluorine concentration is illustrated in Fig. 3a. As expected from symmetry considerations both for disilane and hexafluordisilane the dipolar moment vanishes. However, for 0 < x < 6 the value of $\mathbf{D} \neq 0$, and reaches its maximum



Fig. 3. (a) Dipolar moment **D**, (b) chemical potential μ , (c) chemical hardness η and (d) average polarizability $\langle \alpha \rangle$, normalized to the disilane value $\langle \alpha^* \rangle$, as a function of fluorine concentration *x*.

strength for the lowest energy configuration $Si_2H_3F_3$, i.e., when one of the silyl groups is made up by three hydrogens and the other by three fluorines. In this case, the dipolar moment points from the negatively charged F (Mulliken charge -0.274) towards the H (Mulliken charge -0.042) atoms, which is consistent with larger electronegativity of F relative to H.

4.2. Chemical potential

The chemical potential μ , a global property that characterizes the energy required to add an electron to the system in equilibrium, is defined by the derivative of the energy with respect to the number of electrons N at constant external potential v(r). Analytically

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)},\tag{1}$$

where *E* is the energy and *N* the number of particles. In finite systems, like molecules, μ is related with the escaping tendency of electrons. μ can be computed numerically [12] by a discretized finite difference approximation (that is by adding or removing single electrons), or as half the difference between the lowest unoccupied and the highest occupied molecular orbital (LUMO and HOMO, respectively). The corresponding expressions read as follows:

$$\mu \approx \frac{1}{2} [E(N+1) - E(N-1)]$$
$$\approx \frac{1}{2} [E(\text{HOMO}) - E(\text{LUMO})], \qquad (2)$$

where E(N+1) and E(N-1) are the energies of the ions obtained by adding or removing one electron from the neutral molecule. We have obtained μ using both computation schemes indicated in Eq. (2), with fairly consistent results. In Fig. 3b we display the dependence of μ on F concentration. obtained from the HOMO-LUMO energies; it is seen that μ decreases monotonously as x increases. The presence of several jumps in the chemical potential is interesting to notice. In fact, when changing the composition from $x = 0 \rightarrow x = 1$ the chemical potential decreases by about 10 kcal/mol, and the same occurs for the transitions $x = 2 \rightarrow x = 3$, $x = 3 \rightarrow x = 4$ and $x = 5 \rightarrow x = 6$, indicating that in these systems substitution is accompanied by significant electronic reordering, that may induce structural changes. This picture is consistent with the behavior of the dipole moment as a function of x. Moreover, since the electronegativity $\gamma = -\mu$ changes in response to the partial charge induced by the substituent fluorine atoms, this makes the resulting molecule more electronegative and consequently, more reactive to nucleophilic species.

4.3. Chemical hardness

The chemical hardness η , defined as

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)},\tag{3}$$

can be approximated as follows [12]:

$$\eta \approx \frac{1}{2} [E(N+1) + E(N-1) - 2E(N)]$$
$$\approx \frac{1}{2} [E(\text{HOMO}) + E(\text{LUMO})]. \tag{4}$$

The results of Fig. 3c were obtained from the HOMO-LUMO energies. In contrast to μ , the η versus x plot has clear cut maxima at x = 0, 3 and 6 that correspond to the higher symmetry systems among the set depicted in Fig. 1. The principle of maximum hardness (PMH) [15-20] states that molecules arrange themselves so as to achieve the largest hardness that is possible. Within this context hard molecules are expected to be less reactive than soft molecules. It is interesting to notice that for the set of the hardest molecules, Si_2H_6 , $Si_2H_3F_3$ and Si₂F₆, $\eta(x)$ seems to obey a linear relation as a function of F substitution (x): $\eta(x) \propto x$. The same type relation, with a slope of the same order of magnitude, is also obeyed by the other four molecules (x = 1, 2, 4 and 5). Thus, symmetry seems to be the factor which determines the behavior of molecular hardness, upon fluorine substitution. The only difference that results from using the discretized expression in Eq. (4) is a slightly lower $\eta(x=0)$ value.

4.4. Electrophilicity

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Parr et al. [7] defined the electrophilicity index ω , which measures the stabilization of a chemical system as it is saturated by electronic charge transferred from the environment, as

$$\omega = \frac{\mu^2}{2\eta}.$$
(5)

Using the μ and η values discussed above, we obtain numerical results for the electrophilicity and find that ω increases with the addition of one F atom from 52.20 to 67.92 kcal/mol. The latter remains quite constant upon the addition of the second and third fluorine atoms on the same silicon. However, the fourth F atom strongly increases the value of ω , which grows from 67.56 for Si₂H₃F₃ to 97.72 kcal/mol for Si₂H₂F₄, but thereafter remains quite constant upon addition of the fifth and sixth fluorine atoms. This underlines the fact that addition of fluorine atoms is accompanied with electronic rearrangements that generate important electronic property changes. Using the μ and η values obtained from the discretized forms of Eqs. (2) and (4), generates little changes, except for a slight increase of $\omega(x = 1)$.

4.5. Polarizability

Above we have reported the results of the evaluation of the response of the system, as measured for example by μ and η , to changes in composition (fluorine replacement in Si_2H_6). The latter substitution primarily changes the number N of electrons of the molecule. On the other hand, since a complete characterization of an Nparticle wavefunction [8] only requires to know N and the external potential $v(\vec{r})$, the polarizability α contributes to the understanding of the response of the system to external fields, while the number of electrons is kept fixed. In Fig. 3d we illustrate the average polarizability $\langle \alpha \rangle$, normalized to the disilane value $\langle \alpha^* \rangle$, as a function of x, the number of F atoms in the molecule. The polarizability is calculated as the average of the trace of the polarizability tensor, that is

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$
 (6)

where the tensor components are obtained as $\alpha_{ii} = [\partial^2 E / \partial \mathscr{E}_i^2]_{\mathscr{E}=0}$, the second derivatives of the energy respect to the Cartesian components of the applied electric field \mathscr{E}_i , evaluated at zero field. A monotonously decreasing behavior of α , as F atoms replace H in disilane, is obtained. Since α is quite sensitive to electron delocalization Fig. 3d suggests that the addition of fluorine atoms increases localization, leading to increased packing and reduced reactivity.

Since polarizability has been found to be inversely proportional to hardness [21,22] the trend illustrated in Fig. 3d is the expected one if we assume an average linear relation between hardness and fluorine number x (see Fig. 3c). On the other hand, it is observed that the less polarizable molecule, namely Si₂F₆, is the hardest one, in agreement with the PMH and the minimum polarizability principle [23].

5. Molecular torsion

In this section we study the effect of torsion on the $Si_2H_{6-x}F_x$ molecules. That is, we investigate what happens when a silyl group at one end of the molecule is twisted rigidly around the Si-Si axis, keeping fixed the silvl group at the other end of the axis. The angular displacement is specified by the dihedral angle $\beta \equiv \theta - \theta_{opt}$, where θ was defined in Section 1. As illustrated in Fig. 4a we increased β in steps of 10° , from the minimum energy E value that defines the angle θ_{opt} , which lies close to the staggered configuration, to reach a maximum energy in the vicinity to the eclipsed configuration. In general, the energy does not change significantly as a function of molecular composition. In other words, we distinguish three families of torsional energy profiles: x = 0 and 1, x = 2, 3 and 4, and x = 5 and 6, and the energy difference between them amounts, at most, to a few tenths kcal/mol. The splittings between these families occur when a pair of F atoms is formed on the same silvl group.

It is interesting to notice that successive addition of fluorine atoms increments the electronic



Fig. 4. (a) Electronic energy, (b) chemical potential, and (c) chemical hardness variations, as a function of torsion angle $\beta \equiv \theta - \theta_{opt}$. Each curve corresponds to a different composition, specified by the legend.

population of the Si–Si bond, although the potential barrier decreases, from a small but significant value of 0.94 kcal/mol for Si₂H₆, to ~0.5 kcal/ mol for Si₂F₆. Moreover, already for Si₂H₆ \rightarrow Si₂H₄F₂ the potential barrier decreases considerably, and for $x \ge 2$ quasi free rotational motion sets in. In fact, the lowest barriers correspond to x = 5 and x = 6 and Fig. 2 shows that these molecules have a large electronic population of the Si– Si bond, in contrast with Si₂H₆ and Si₂H₅F₁, which have large potential barriers and the lowest bond population. This constitutes an indication that the torsional motion is basically induced by electrostatic through space interactions.

The close parallel between the variations of the chemical potential $\Delta \mu$ and the chemical hardness $\Delta \eta$ as a function of β , displayed in Figs. 4b and c, is quite remarkable and was previously pointed out by us [3]. We notice that not only the shape of the $\Delta \mu$ and $\Delta \eta$ versus β plots is quite similar to each other, but also the magnitudes are almost identical. This is in sharp contrast with the composition dependence (μ and η versus x displayed in Figs. 4b and c). The different shape of the x = 0 (disilane) and the rest of the plots is quite noticeable, with two inflection points and a maximum distinctly away from the $\beta = 0^{\circ}$ and 60° torsion angles. This peculiar behavior disappears as soon as a single F atom is incorporated in the molecule. It is also worth remarking that the largest change in both quantities occurs for x = 2, that is for Si₂H₄F₂.

Inspection of Figs. 4a and c shows that the behavior of ΔE and $\Delta \eta$, as a function of β , are opposite and thus satisfy the PMH: minimum (maximum) hardness is associated with maximum (minimum) energy. On the other hand, it is observed that Si₂H₄F₂ has both the largest changes in $\Delta \mu$ and $\Delta \eta$, and also an almost barrier-free torsional motion. Thus, in general we notice that variations in electronic properties do not induce significant changes of the torsional potential energy.

The above observations suggest that for these systems it is possible to write the following expression for the torsional potential energy:

$$\Delta E(\beta) = Q_{\eta} \Delta \mu(\beta) + Q_{\mu} \Delta \eta(\beta), \qquad (7)$$

where $\{Q_{\mu}, Q_{\eta}\}$ are parameters related to the electronic charge redistribution during internal

rotation [11]. Since $Q_{\mu} < 0$ for systems that obey the PMH, the energy dependence on β is the result of the quasi cancellation of chemical potential and hardness contributions.

6. HOMO and LUMO orbitals

Fig. 5 displays the shape of the frontier HOMO and LUMO molecular orbitals. The HOMO or-



Fig. 5. HOMO (left) and LUMO (right) orbitals. The number of F atoms increases, by one unit every row, from top (Si_2H_6) to bottom (Si_2F_6) .

bitals do not change significantly with fluorine substitution, as $Si_2H_6 \rightarrow Si_2F_6$; for all these molecules the HOMO orbitals are mainly located on the central Si–Si bond, indicating that all of them should behave quite similarly under electrophilic attack.

On the contrary, the LUMO orbitals vary considerably. As $Si_2H_6 \rightarrow Si_2H_{6-x}F_x$ the F atom allows a delocalization of the LUMO density, which leaves the molecule more reactive to nucleophilic chemical species. This result agrees with our observations in relation to the electrophilicity index, which increases as the number (*x*) of F atoms increases. Thus, we conclude that substitution of hydrogen by fluorine changes the reactivity pattern of the resulting molecule.

7. Vibration modes and frequencies

In this section we focus our attention on the molecular vibration modes of the stable configurations of the whole $Si_2H_{6-x}F_x$ family. In Table 2 we list the values of the frequencies that were calculated. For Si_2H_6 and Si_2F_6 they are in excellent agreement with the results obtained by Gy-

Table 2

Infrared (IR) vibration frequencies, in cm^{-1} , for each one of the species

Species	Frequencies (cm ⁻¹)
$\mathrm{Si}_{2}\mathrm{H}_{6}$	136*, 381, 423*, 637*, <u>856</u> , 931*, 946*, 960, 2206, 2213*, 2215*, 2223
Si_2H_5F	99, 164, 368, 409, 523, 620, 737, 812, <u>853</u> , 912, 945, 950, 968, 2206, 2221, 2222, 2223, 2234
$Si_2H_4F(a) \\$	79, 147, 203, 302, 414, 517, 541, 810, 818, <u>825</u> , 896, 913, 945, 947, 2222, 2232, 2239, 2255
$Si_2H_3F_3(a)\\$	86*, 146, 291, 295, 485, 539, <u>805</u> , 905, 915, 948, 2237, 2252
$Si_2H_2F_4(a) \\$	34, 100, 140, 202, 288, 291, 320, 486, 528, 726, <u>804</u> , 834, 909, 922, 928, 954, 2254, 2267
Si_2HF_5	198, 200, 287, 307, 315, 351, 493, <u>788</u> , 814, 817, 893, 922, 937, 941, 937, 941, 2295
Si_2F_6	22*, 101, 190*, 209*, 292, 323*, 384, 521*, 788, 886*, 945*, <u>958</u>

The largest intensity mode is underlined. The frequencies tagged with * are IR inactive.

eong et al. [10] using B3LYP/6-31G*, and with experiment [10].

The most active disilane infrared (IR) mode can be described as an in phase vibration of all the H atoms, with the two Si remaining almost fixed. On the opposite end (x = 6) the most active Si₂F₆ mode consists in the motion of the two Si with two F atoms remaining almost immobile. For intermediate x values ($1 \le x \le 5$) the most active mode is similar to the former case, with the silyl groups moving in phase and the two Si atoms oscillating as a rigid unit 180° out of phase; certainly, since the F mass is so much larger than the H, they oscillate with a reduced amplitude and drag along the Si to which they are bound.

8. Summary and conclusion

In summary, we have studied in detail the $Si_2H_{6-x}F_x$ family of molecules, for $0 \le x \le 6$. We obtained, from first principle DFT calculations, the optimized geometries as well as numerical values for the ground state energies, dipolar moment, chemical potential and chemical hardness, both as a function of fluorine content (*x*) and as function of the torsion angle (β). In addition, we obtained the vibration modes and frequencies.

The lowest energy configurations correspond to arrangements where the F atoms are on the same silvl group. As function of the torsion angle the most stable configuration is always quite close to the staggered conformation, deviating from it by less than 4°, that is $60^{\circ} \leq \theta_{opt} \leq 60^{\circ} \pm 4^{\circ}$. It is also interesting to notice that, as illustrated in Fig. 4a, the energy as a function of $\beta = \theta - \theta_{opt}$ shows only small variations after the addition of a fluorine atom to Si₂H₆ \rightarrow Si₂H₅F and Si₂HF₅ \rightarrow Si₂F₆, but exhibits a jump when Si₂H₅F \rightarrow Si₂H₄F₂ and Si₂H₂F₄ \rightarrow Si₂HF₅, i.e., when a pair of fluorines forms on the same silvl group.

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