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The interaction of fluorosilanes with hydrogen fluoride clusters: strongly blue-shifted hydrogen bonds

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Abstract

The equilibrium structures, binding energies, and vibrational spectra of the complexes formed between hydrogen fluoride clusters (HF)_n (1 ≤ n ≤ 4) and the fluorosilanes SiHF₃, SiH₂F₂, and SiH₃F are investigated within the second-order Møller–Plesset perturbation theory method applying extended basis sets. It is shown that Si–F⋯H–F halogen–hydrogen bonds are formed in the most stable open dimers, SiHF₃–HF, SiH₂F₂⋯HF, and SiH₃F⋯HF. No Si–H⋯F–H hydrogen bonds occur in these dimers. Nevertheless, blue shifts of Si–H stretching frequencies are calculated. All three trimers, fluorosilane–(HF)₂, all three tetramers, fluorosilane–(HF)₃, and two of the pentamers, fluorosilane–(HF)₄, form cyclic structures with strong Si–F⋯H–F halogen–hydrogen bonds and weak Si–H⋯F–H contacts, the latter displaying, nevertheless, strongly blue-shifted Si–H stretching frequencies. These blue shifts are comparable in size to those of the corresponding fluoromethane–(HF)_n complexes and are with about +50 cm^{−1} for the case n=3 among the largest ever calculated and definitely the largest for Si–H bonds. In the title complexes, the formation of the Si–F⋯H–F halogen–hydrogen bonds induces a substantial stretching of this Si–F bond, which in turn leads to a significant contraction of the fluorosilane Si–H bond in the Si–H⋯F–H hydrogen bond. This disposition of the fluorosilane monomers is demonstrated with the aid of suitable potential energy surface scans and appears to be a prerequisite for the formation of strongly *blue-shifted* hydrogen bonds.

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Keywords: Blue-shifted hydrogen bonds; Fluorosilanes; Halogen–hydrogen bond

1. Introduction

An impressively large number of purely theoretical [1–25] and also of experimental studies [26–35] have recently been devoted to the phenomenon of blue-shifting hydrogen bonds, mainly to those of the C–H⋯X-type. In contrast to the well-known behavior of conventional hydrogen bonds, blue-shifting hydrogen bonds C–H⋯X are characterized by a contraction of the C–H bond, a blue shift of its stretching vibrational mode, and a decrease of its infrared intensity. For an up-to-date summary of this topic see Ref. [36]. In a few very recent theoretical investigations [22,23], it was suggested that Si–H⋯X hydrogen bonds are also likely candidates to show the typical features of blue-shifting hydrogen bonds.

In two previous investigations [37,38], large blue shifts up to about 60 cm^{−1} have been predicted for the C–H stretching frequencies in complexes of the fluoromethanes CHF₃, CH₂F₂, and CH₃F with hydrogen fluoride oligomers, (HF)_n (n=2,3). These complexes are cyclic and may be thought of as being constructed by replacing one HF molecule of a (HF)_n ring by a fluoromethane or by inserting a fluoromethane into an already preformed (HF)_n ring. They are held together by a strong C–F⋯H–F *halogen–hydrogen* bond, a much weaker, blue-shifted C–H⋯F–H hydrogen bond, and n−1 conventional F⋯H–F hydrogen bonds between HF molecules. The C–H⋯F–H hydrogen bonds in these cyclic complexes were dubbed as *blue-shifted* instead of *blue-shifting*, because the large blue shifts predicted for these complexes are caused mainly by a specifically coupled, structural relaxation, i.e. a contraction of the C–H bonds which is induced by the much larger lengthening of the C–F bonds upon formation of the much stronger C–F⋯H–F halogen–hydrogen bonds. This particular disposition

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of fluoromethanes, namely the contraction of C–H bonds in fluoromethanes, when stretching a C–F bond, can already be observed by appropriate scans of the fluoromethane monomer potential energy surface [38].

In this work, several ideas put forward in our previous investigations [37,38] are probed further: (i) whether the effect of inserting candidate molecules in cyclic $(\text{HF})_n$ complexes produces exceptionally large blue shifts also for the case of Si–H bonds, and (ii) if so, whether the effect can, as in the case of fluoromethanes, to a large degree be traced back to an *intrinsic property* of the candidate molecules; namely a particular coupling of the intramolecular stretching degrees of freedom, and is thus mainly determined by the intramolecular force field of the candidate molecule. Finally, (iii) to clarify, whether the structures of these complexes are dominated by the formation of a strong $\text{Si-F}\cdots\text{H-F}$ halogen–hydrogen bond and that the formation of the blue-shifted hydrogen bonds plays only a minor role from the energetical point of view. The term *halogen bonding* has frequently been used to describe the interaction of molecules carrying X–Hal bonds with a variety of partner molecules, mainly amines [39–45]. The halogen bond has many features in common with the *conventional* hydrogen bond, particularly, the elongation of the X–Hal distances, the typical red shift of $\nu(\text{X-Hal})$, and the increased infrared intensity of $\nu(\text{X-Hal})$. Adjacent hydrogen and halogen bonds were also encountered in the $\text{C-F}\cdots\text{H-F}$ bonds of fluoromethane– $(\text{HF})_n$ clusters and are expected to play also a leading role in the structures of fluorosilane– $(\text{HF})_n$ clusters.

With these aims in mind, the structures, stabilization energies and vibrational spectra of the complexes of the three fluorosilanes SiHF_3 , SiH_2F_2 , and SiH_3F with $(\text{HF})_n$ ($1 \leq n \leq 4$) clusters are investigated theoretically. All features pertinent to the $\text{Si-F}\cdots\text{H-F}$ halogen–hydrogen bonds and the blue-shifted $\text{Si-H}\cdots\text{F-H}$ hydrogen bonds are monitored and discussed in detail. To the best knowledge of the author, neither theoretical nor experimental results are available for these complexes. The only exception is an SCF/DZP calculation on the $\text{SiH}_3\text{F-HF}$ complex [46].

2. Method of calculation

All calculations reported in the present work were performed with the GAUSSIAN 98 suite of packages [47]. The second-order perturbation Møller–Plesset method (MP2) within the frozen core (fc) approximation has been applied using two extended basis sets: 6-311 + +G(2d,2p) [48–51] and aug-cc-pVTZ [52–53]. Because of the extremely floppy nature of these complexes, all geometry optimizations were carried out with the ‘tight’ option. MP2 harmonic vibrational frequencies were calculated for all complexes in order to allow for a proper characterization of stationary points. The effect of the counterpoise (CP) correction [54] to the basis set superposition error (BSSE) has also been taken into account.

Table 1
Selected MP2-calculated properties of fluorosilane molecules

Molecule	Property	Basis set	
		6-311 + + G(2d,2p)	aug-cc- pVTZ
SiHF_3	Total energy (hartree)	–588.93713	–589.07428
	$r(\text{Si-H})$ (Å)	1.4461	1.4539
	$\nu(\text{Si-H})$ stretch (cm^{-1})	2446	2426
	$A(\text{Si-H})^a$ (km/mol)	59	63
	$r(\text{Si-F})$ (Å)	1.5815	1.5857
	$\nu(\text{Si-F})$ stretch (cm^{-1})	867, 984 ^b	842, 987 ^b
	$A(\text{Si-F})$ (km/mol)	85, 572	79, 528
SiH_2F_2	Total energy (hartree)	–489.74852	–489.84695
	$r(\text{Si-H})$ (Å)	1.4588	1.4659
	$\nu(\text{Si-H})$ stretch (cm^{-1})	2373, 2381	2355, 2365
	$A(\text{Si-H})$ (km/mol)	52, 135	53, 136
	$r(\text{Si-F})$ (Å)	1.5958	1.5994
	$\nu(\text{Si-F})$ stretch (cm^{-1})	854, 910	859, 909
	$A(\text{Si-F})$ (km/mol)	82, 27	76, 9
SiH_3F	Total energy (hartree)	–390.56223	–390.62206
	$r(\text{Si-H})$ (Å)	1.4677	1.4736
	$\nu(\text{Si-H})$ stretch (cm^{-1})	2330, 2331 ^b	2316, 2321 ^b
	$A(\text{Si-H})^a$ (km/mol)	30, 276	34, 282
	$r(\text{Si-F})$ (Å)	1.6124	1.6150
	$\nu(\text{Si-F})$ stretch (cm^{-1})	857	865
	$A(\text{Si-F})$ (km/mol)	86	78

^a Infrared intensity.

^b Doubly degenerate.

3. Results

3.1. The monomers

The most relevant structural and vibrational spectroscopic properties of the isolated fluorosilanes needed for the following discussion are collected in Table 1. The corresponding data for the $(\text{HF})_n$ species may be found in Table 2 of Ref. [37]. Cyclic (HF) clusters have been thoroughly described and discussed in the literature (see [55–60] and references therein). Their structures, stabilities and gas-phase vibrational spectroscopic properties are well known.

3.2. The dimeric complexes $\text{SiHF}_3\text{-HF}$, $\text{SiH}_2\text{F}_2\text{-HF}$, and $\text{SiH}_3\text{F-HF}$

The optimized, most stable structures of these dimeric complexes as obtained at the MP2/aug-cc-pVTZ level are

Table 2
MP2-calculated stabilization energies of the fluorosilane–HF complexes (kcal/mol)

Complex	Basis set	
	6-311 + +G(2d,2p)	aug-cc-pVTZ
$\text{SiHF}_3\text{-HF}$	–3.7 (–2.5) ^a	–3.4 (–2.8)
$\text{SiH}_2\text{F}_2\text{-HF}$	–4.5 (–3.3)	–4.2 (–3.6)
$\text{SiH}_3\text{F-HF}$	–5.4 (–4.2)	–5.1 (–4.4)

^a Counterpoise corrected energies in parentheses.

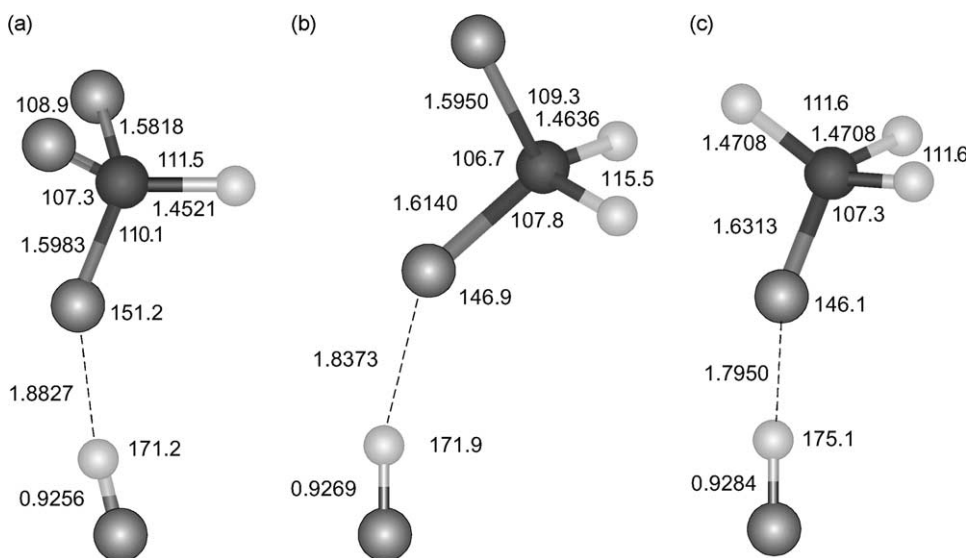


Fig. 1. MP2/aug-cc-pVTZ calculated equilibrium structures of fluorosilane–HF dimers: (a) $\text{SiHF}_3\text{--HF}$, (b) $\text{SiH}_2\text{F}_2\text{--HF}$, and (c) $\text{SiH}_3\text{F--HF}$. Bond lengths in Å and bond angles in degrees.

shown in Fig. 1. As a first important observation, we note that Si–F \cdots H–F halogen–hydrogen bonds are formed in all three complexes. Attempts to find other conceivable minima bound via Si–H \cdots F hydrogen bonds failed. There are none. Only higher-lying saddle points with Si–H \cdots F bonds were found. In all three cases, the complexes are very floppy with two exceedingly low-lying intermolecular vibrational frequencies. The calculated stabilization energies, bond length changes relative to the monomers, and selected vibrational frequencies and frequency shifts are reported in Tables 2–4. In general, the various trends calculated for these complexes parallel those of the corresponding series of fluoromethane–HF complexes. One notable difference is that the global minimum of $\text{CHF}_3\text{--HF}$ is a cyclic structure [37]. The analogous structure for $\text{SiHF}_3\text{--HF}$ is not a minimum.

Table 3
MP2-calculated bond length changes in fluorosilane–HF complexes relative to monomers (Å)

Complex	Bond length change	Basis set	
		6-311 + + G(2d,2p)	aug-cc-pVTZ
$\text{SiHF}_3\text{--HF}$	$\Delta r(\text{Si--H})$	–0.0017	–0.0018
	$\Delta r(\text{Si--F})^a$	0.0135	0.0126
	$\Delta r(\text{Si--F})$	–0.0039	–0.0039
	$\Delta r(\text{H--F})$	0.0032	0.0039
	$\Delta r(\text{H--F})$	0.0040	0.0052
$\text{SiH}_2\text{F}_2\text{--HF}$	$\Delta r(\text{Si--H})$	–0.0022	–0.0023
	$\Delta r(\text{Si--F})^a$	0.0155	0.0147
	$\Delta r(\text{Si--F})$	–0.0042	–0.0044
	$\Delta r(\text{H--F})$	0.0040	0.0052
	$\Delta r(\text{H--F})$	0.0040	0.0052
$\text{SiH}_3\text{F--HF}$	$\Delta r(\text{Si--H})$	–0.0026	–0.0028
	$\Delta r(\text{Si--F})$	0.0172	0.0163
	$\Delta r(\text{H--F})$	0.0057	0.0067

^a Si–F bond involved in the formation of the halogen–hydrogen bond.

The stability of the fluorosilane–HF complexes increases progressively in the series from SiHF_3 to SiH_3F . The Si–F bonds, as well as the H–F bonds involved in the formation of the Si–F \cdots H–F halogen–hydrogen bond, are enlarged, the former much more than

Table 4
Selected MP2-calculated harmonic vibrational frequencies ν , frequency shifts, and infrared intensities in fluorosilane–HF complexes

Complex	Assignment	Basis set	
		6-311 + + G(2d,2p)	aug-cc-pVTZ
$\text{SiHF}_3\text{--HF}$	$\nu(\text{Si--H})$	2457 (11) ^a [47] ^b	2438 (12) [49]
	$\nu(\text{Si--F})^c$	835 (–32) [92]	837 (–5) [75]
		961 (–23) [330]	962 (–25) [309]
	$\nu(\text{Si--F})$	997 (13) [281]	999 (12) [258]
	$\nu(\text{F}\cdots\text{H})$	123 [4]	116 [5]
	$\nu(\text{H--F})$	4106 (–58) [417]	4046 (–76) [429]
$\text{SiH}_2\text{F}_2\text{--HF}$	$\nu(\text{Si--H})$	2385 (12) [47]	2367 (12) [47]
		2397 (17) [114]	2383 (18) [115]
	$\nu(\text{Si--F})^c$	839 (–16) [127]	842 (–17) [104]
	$\nu(\text{Si--F})$	905 (–5) [41]	905 (–4) [21]
	$\nu(\text{F}\cdots\text{H})$	138 [2]	128 [4]
	$\nu(\text{H--F})$	4090 (–74) [481]	4017 (–107) [495]
$\text{SiH}_3\text{F--HF}$	$\nu(\text{Si--H})$	2342 (12) [28]	2328 (12) [31]
	$\nu(\text{Si--H})^d$	2350 (19) [228]	2341 (20) [232]
	$\nu(\text{Si--F})$	818 (–39) [143]	828 (–37) [139]
	$\nu(\text{F}\cdots\text{H})$	163 [5]	157 [6]
	$\nu(\text{H--F})$	4051 (–113) [548]	3984 (–140) [584]

Frequencies and frequency shifts with respect to monomers in cm^{-1} ; infrared intensities in km/mol .

^a Frequency shifts in parentheses.

^b Infrared intensities in square brackets.

^c Si–F bond involved in Si–F \cdots H–F halogen–hydrogen bonding participating.

^d Nearly degenerate.

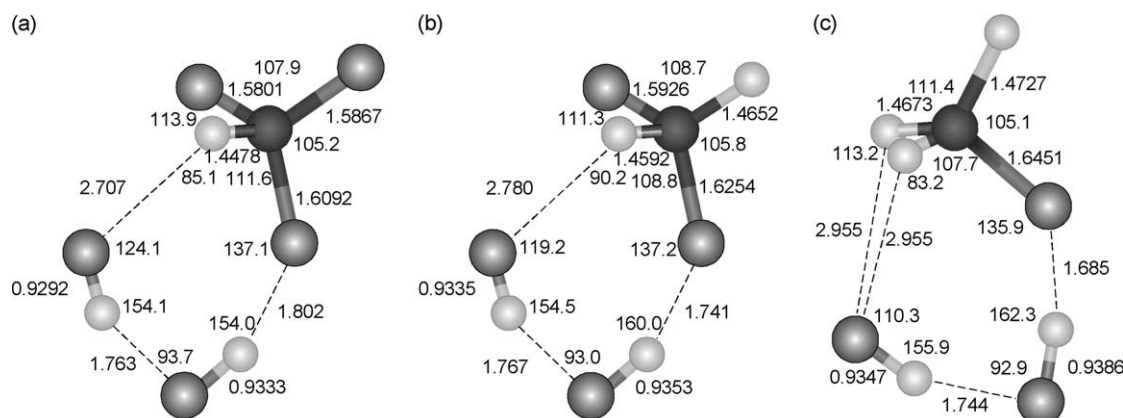


Fig. 2. MP2/aug-cc-pVTZ calculated equilibrium structures of fluorosilane-(HF)₂ trimers: (a) SiHF₃-(HF)₂, (b) SiH₂F₂-(HF)₂, and (c) SiH₃F-(HF)₂. Bond lengths in Å and bond angles in degrees.

the latter. Si–F bonds not involved in intermolecular bonding and all Si–H bonds are slightly contracted upon complex formation. Hence, in spite of the absence of a hydrogen bond involving the Si–H bond, all $\nu(\text{Si–H})$ stretching frequencies are blue shifted, with shifts of 11–20 cm^{−1}. Moreover, the calculated infrared intensities of all $\nu(\text{Si–H})$ stretching frequencies are slightly reduced compared to the fluorosilane monomers (cf. Tables 1 and 4). $\nu(\text{Si–F})$ stretching frequencies with participation of the Si–F bond involved in the Si–F \cdots H–F bond and H–F stretching frequencies are red shifted and their infrared intensities are enhanced.

3.3. The complexes SiHF₃ \cdots (HF)_n, SiH₂F₂ \cdots (HF)_n, and SiH₃F \cdots (HF)_n; (2 ≤ n ≤ 4)

3.3.1. Complexes with (HF)₂

The MP2/aug-cc-pVTZ optimized structures of these trimeric complexes are sketched in Fig. 2. As with the previously treated fluoromethane-(HF)₂ complexes, all three fluorosilane-(HF)₂ trimers have *cyclic* global minima. Open-chain minima do not exist. Starting with open-chain structures with either Si–H \cdots F or Si–F \cdots H–F connections between open C_s-symmetric (HF)₂ and a fluorosilane results invariably in the formation of cyclic structures. The complexes SiHF₃-(HF)₂ and SiH₂F₂-(HF)₂ have C₁ symmetry, SiH₃F-(HF)₂ has C_s-symmetry. A strong Si–F \cdots H–F halogen–hydrogen bond is formed in each trimer, with F \cdots H distances decreasing from 1.80 Å in SiHF₃-(HF)₂ to 1.69 Å in SiH₃F-(HF)₂, whereas the F \cdots H distances of the (HF)₂ moiety remain practically constant in this series. Turning now to the Si–H \cdots F contacts, one observes comparatively large H \cdots F distances which increase from 2.71 Å in SiHF₃-(HF)₂ to 2.96 Å in SiH₃F-(HF)₂, the latter being larger also because of the presence of a bifurcated structure. Choosing accepted values of 1.4 and 1.5 Å for the van der Waals radii of H and F, respectively, the above H \cdots F distances do not differ very much from the sum of 2.9 Å. It appears thus fair to say that the structures of

the trimers are dominated by the presence of the halogen–hydrogen bond and the hydrogen bond between the HF molecules. The intermolecular Si–H \cdots F moiety can at best be described as a very weak hydrogen bond.

The calculated stabilization energies of the trimers are compiled in Table 5. Two sets of stabilization energies are used in the following: ΔE_a , defined relative to infinitely separated fluorosilanes and (HF)_n and ΔE_b , the stabilization energy with respect to isolated monomers, i.e. the fluorosilane and *n* HF molecules. Within the series of fluorosilanes, the trends in intermolecular stabilization energies for the trimers are identical to the dimer case. All three trimers are strongly bound with respect to fluorosilanes and (HF)₂ with values between −5 and −7.5 kcal/mol for ΔE_a (CP). Compared to cyclic (HF)₃, the fluorosilane-(HF)₂ complexes are less stable, SiH₃F-(HF)₂ is, however, quite close in stability, i.e. the combined stabilization gained by forming a halogen–hydrogen bond and a blue-shifted hydrogen bond is a bit less than the energy of two F–H \cdots F hydrogen bonds of (HF)₃.

The detailed bond length changes in the trimeric complexes relative to the monomers are collected in Table 6. For all three complexes the Si–H bonds involved in the blue-shifted Si–H \cdots F hydrogen bonds are contracted

Table 5
MP2-calculated stabilization energies of the fluorosilane-(HF)₂ complexes (kcal/mol)

Complex		Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiHF ₃ -(HF) ₂	ΔE_a	−6.1 (−4.6) ^a	−6.0 (−5.1)
	ΔE_b	−12.1 (−8.9)	−11.8 (−10.1)
SiH ₂ F ₂ -(HF) ₂	ΔE_a	−7.2 (−5.4)	−7.1 (−6.0)
	ΔE_b	−12.0 (−9.1)	−11.8 (−10.2)
SiH ₃ F-(HF) ₂	ΔE_a	−8.6 (−6.8)	−8.5 (−7.5)
	ΔE_b	−13.4 (−10.6)	−13.2 (−11.7)
(HF) ₃	ΔE_b	−15.7 (−12.7) ^b	−15.5 (−14.1) ^b

^a Counterpoise-corrected energies in parentheses.

^b From Ref. [37].

Table 6
MP2-calculated bond length changes in fluorosilane-(HF)₂ complexes relative to monomers (Å)

Complex	Bond length change	Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiHF ₃ -(HF) ₂	$\Delta r(\text{Si-H})$	−0.0060	−0.0062
	$\Delta r(\text{Si-F})^a$	0.0236	0.0254
	$\Delta r(\text{Si-F})$	−0.0054, 0.0012	−0.0059, 0.0
	$\Delta r(\text{H-F})$	0.0113, 0.0104	0.0127, 0.0116
SiH ₂ F ₂ -(HF) ₂	$\Delta r(\text{Si-H})^b$	−0.0064	−0.0064
	$\Delta r(\text{Si-H})$	−0.0004	−0.0019
	$\Delta r(\text{Si-F})^a$	0.0259	0.0260
	$\Delta r(\text{Si-F})$	−0.0065	−0.0068
SiH ₃ F-(HF) ₂	$\Delta r(\text{H-F})$	0.0103, 0.0119	0.0118, 0.0136
	$\Delta r(\text{Si-H})^b$	−0.0060	−0.0063
	$\Delta r(\text{Si-H})$	−0.0008	−0.0009
	$\Delta r(\text{Si-F})$	0.0299	0.0301
	$\Delta r(\text{H-F})$	0.0112, 0.0146	0.0130, 0.0169

^a Si-F bond involved in the formation of the halogen-hydrogen bond.

^b Si-H bond involved in the formation of the Si-H...F hydrogen bond.

by about 6 mÅ, whereas *free* Si-H bonds are only marginally contracted. The largest changes occur for the Si-F bonds in the Si-F...H-F halogen-hydrogen bonds. These are lengthened by about 25–50 mÅ, whereas free Si-F bonds are either slightly contracted or unchanged.

The calculated harmonic vibrational frequencies and frequency shifts, compiled in Table 7, faithfully mirror the structural trends just discussed. The $\nu(\text{Si-H})$ stretching frequencies assigned to Si-H...F hydrogen bonds are calculated to be blue shifted by 36 cm^{−1} in the SiHF₃ and SiH₂F₂ complexes, and even up to 43 cm^{−1} in the SiH₃F complex. Stretching frequencies of free Si-H groups are also slightly blue shifted in a range from 7 to 14 cm^{−1}, comparable to the dimers just discussed. Sizable red shifts, given the large mass, are calculated for $\nu(\text{Si-F})$ stretchings of Si-F bonds involved in the Si-F...H-F halogen-hydrogen bonds. These red shifts amount to about −80 cm^{−1} in SiH₃F-(HF)₂.

3.3.2. Complexes with (HF)₃ and (HF)₄

All said so far on energetic, structural and vibrational spectroscopic trends is reencountered in the larger complexes. The calculated data for the fluorosilane-(HF)₃ complexes are presented in Tables 8–10, those for the complexes with (HF)₄ in Tables 11–13. The MP2/aug-cc-pVTZ-optimized structures are shown in Figs. 3 and 4. SiHF₃-(HF)₃ has C₁ symmetry, SiH₂F₂-(HF)₃ and SiH₃F-(HF)₃ have C_s symmetry. The optimized H...F distances in the Si-H...F hydrogen bonds of these larger rings are only slightly shorter than for the fluorosilane-(HF)₂ case. Thus, again only weak Si-H...F hydrogen bonds occur. The calculated stabilization energies ΔE_a for the fluorosilane-(HF)₃ complexes are comparable in size to the complexes with (HF)₂. The SiH₂F₂-(HF)₄ and SiH₃F-(HF)₄ complexes are just on the border of being bound with respect to (HF)₄

Table 7
Selected MP2-calculated harmonic vibrational frequencies ν , frequency shifts, and infrared intensities in fluorosilane-(HF)₂ complexes

Complex	Assign- ment	Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiHF ₃ -(HF) ₂	$\nu(\text{Si-H})$	2482 (36) ^a [38] ^b	2463 (36) [40]
	$\nu(\text{Si-F})^c$	825 (−42) [62]	825 (−17) [37]
		946 (−38) [243]	946 (−41) [221]
	$\nu(\text{Si-F})$	988 (14) [280]	991 (14) [257]
SiH ₂ F ₂ -(HF) ₂	$\nu(\text{H-F})$	3920 (−244) [284]	3848 (−256) [298]
		3997 (−167) [594]	3930 (−194) [636]
	$\nu(\text{Si-H})$	2380 (7) [85]	2363 (8) [90]
	$\nu(\text{Si-F})^{c,d}$	2417 (36) [71]	2401 (36) [76]
SiH ₃ F-(HF) ₂		832 (−22) [13]	841 (−18) [20]
		783 (−71) [280]	791 (−68) [285]
	$\nu(\text{Si-F})$	904 (−6) [39]	906 (−3) [20]
	$\nu(\text{H-F})$	3915 (−249) [297]	3835 (−289) [325]
		3982 (−182) [676]	3910 (−214) [717]
	$\nu(\text{Si-H})$	2337 (7) [90]	2268 (14) [67]
	$\nu(\text{Si-H})$	2362 (31) [61]	2292 (29) [65]
	$\nu(\text{Si-F})$	2373 (42) [102]	2306 (43) [90]
	$\nu(\text{Si-F})$	779 (−78) [266]	786 (−79) [256]
	$\nu(\text{H-F})$	3866 (−298) [424]	3773 (−351) [475]
		3954 (−210) [687]	3876 (−248) [724]

Frequencies and frequency shifts with respect to monomers in cm^{−1}; infrared intensities in km/mol.

^a Frequency shifts in parentheses.

^b Infrared intensities in square brackets.

^c Si-F bond involved in Si-F...H-F halogen-hydrogen bonding participating.

^d Assignment ambiguous due to mixing with different bending coordinates.

and both have C₁ symmetry only. Fig. 4 shows quite clearly that SiH₂F₂ and SiH₃F are almost expelled from the (HF)₄ ring. The cyclic SiHF₃-(HF)₄ complex is not stable anymore. This is interpreted best as a mere consequence of the well-known high stability of cyclic (HF)₄ and (HF)₅ [55–60]. The calculated $\nu(\text{Si-H})$ blue shifts reach their maximal value of about 50 cm^{−1} for SiH₂F₂-(HF)₃ and SiH₃F-(HF)₃ and are still of the order of 40 cm^{−1} for the complexes with (HF)₄. These shifts are considerably

Table 8
MP2-calculated stabilization energies of the fluorosilane-(HF)₃ complexes (kcal/mol)

Complex		Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiHF ₃ -(HF) ₃	ΔE_a	−6.2 (−3.5) ^a	−6.1 (−4.6)
	ΔE_b	−21.8 (−16.8)	−21.6 (−18.6)
SiH ₂ F ₂ -(HF) ₃	ΔE_a	−7.7 (−5.3)	−7.8 (−6.5)
	ΔE_b	−23.3 (−18.3)	−23.3 (−20.6)
SiH ₃ F-(HF) ₃	ΔE_a	−7.3 (−5.3)	−7.5 (−6.3)
	ΔE_b	−22.9 (−18.3)	−23.0 (−20.5)
(HF) ₄	ΔE_b	−28.2 (−24.5) ^b	−29.1 (−28.5) ^b

^a Counterpoise-corrected energies in parentheses.

^b From Ref. [37].

Table 9
MP2-calculated bond length changes in fluorosilane-(HF)₃ complexes relative to monomers (Å)

Complex	Bond length change	Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiHF ₃ -(HF) ₃	$\Delta r(\text{Si-H})$	−0.0070	−0.0075
	$\Delta r(\text{Si-F})^a$	0.0266	0.0272
	$\Delta r(\text{Si-F})$	−0.0051, 0.0016	−0.0055, −0.0016
	$\Delta r(\text{H-F})$	0.0143, 0.0171, 0.0185	0.0172, 0.0192, 0.0221
SiH ₂ F ₂ -(HF) ₃	$\Delta r(\text{Si-H})^b$	−0.0072	−0.0075
	$\Delta r(\text{Si-F})^a$	0.0357	0.0320
	$\Delta r(\text{Si-F})$	0.0013	0.0019
	$\Delta r(\text{H-F})$	0.0166, 0.0168, 0.0200	0.0202, 0.0202, 0.0241
SiH ₃ F-(HF) ₃	$\Delta r(\text{Si-H})^b$	−0.0070	−0.0075
	$\Delta r(\text{Si-H})$	−0.0003	−0.0005
	$\Delta r(\text{Si-F})$	0.0319	0.0323
	$\Delta r(\text{H-F})$	0.0147, 0.0186, 0.0199	0.0177, 0.0225, 0.0238

^a Si-F bond involved in the formation of the halogen-hydrogen bond.

^b Si-H bond(s) involved in the formation of the Si-H...F hydrogen bond.

Table 10
Selected MP2-calculated harmonic vibrational frequencies ν , frequency shifts, and infrared intensities in fluorosilane-(HF)₃ complexes

Complex	Assign-ment	Basis set	
		6-311++ + G(2d,2p)	aug-cc-pVTZ
SiHF ₃ -(HF) ₃	$\nu(\text{Si-H})$	2488 (42) ^a [37] ^b	
	$\nu(\text{Si-F})^c$	815 (−49) [103]	
		941 (−43) [140]	
	$\nu(\text{Si-F})$	987 (13) [279]	
	$\nu(\text{H-F})$	3754 (−410) [607]	
		3862 (−302) [1042]	
SiH ₂ F ₂ -(HF) ₃	$\nu(\text{Si-H})$	2408 (35) [32]	2388 (33) [34]
		2430 (49) [100]	2414 (49) [100]
	$\nu(\text{Si-F})^c$	804 (−50) [172]	808 (−51) [160]
	$\nu(\text{Si-F})$	889 (−21) [156]	894 (−15) [120]
	$\nu(\text{H-F})$	3718 (−446) [531]	3586 (−538) [590]
		3842 (−322) [1305]	3733 (−391) [1579]
SiH ₃ F-(HF) ₃		3870 (−294) [521]	3761 (−363) [475]
	$\nu(\text{Si-H})$	2334 (4) [104]	2322 (6) [103]
	$\nu(\text{Si-H})^d$	2367 (36) [48]	2354 (33) [56]
		2379 (48) [99]	2370 (49) [99]
	$\nu(\text{Si-F})$	785 (−72) [216]	793 (−72) [224]
	$\nu(\text{H-F})$	3718 (−446) [625]	3587 (−537) [723]
		3832 (−332) [1178]	3719 (−405) [1304]
		3878 (−286) [604]	3777 (−347) [677]

Frequencies and frequency shifts with respect to monomers in cm^{−1}; infrared intensities in km/mol.

^a Frequency shifts in parentheses.

^b Infrared intensities in square brackets.

^c Si-F bond involved in Si-F...H-F halogen-hydrogen bonding participating.

^d Si-H bonds involved in bifurcated SiH₂...F hydrogen bonds.

Table 11
MP2-calculated stabilization energies of the fluorosilane-(HF)₄ complexes (kcal/mol)

Complex		Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiH ₂ F ₂ -(HF) ₄	ΔE_a	−4.1 (−2.6) ^a	−3.8 (−2.3)
	ΔE_b	−32.4 (−25.3)	−32.6 (−29.0)
SiH ₃ F-(HF) ₄	ΔE_a	−3.8 (−1.8)	−3.5 (−2.2)
	ΔE_b	−32.1 (−25.7)	−32.3 (−28.9)
(HF) ₅	ΔE_b	−38.4	−39.6

^a Counterpoise-corrected energies in parentheses.

larger than those reported for the complex of SiHF₃ with H₂O (22 cm^{−1}) [22].

4. Discussion

4.1. Comparison with fluoromethane-(HF)_n complexes

The trends in the binding energies ΔE_a of fluorosilane-(HF)_n and fluoromethane-(HF)_n complexes [37,38] are shown in Fig. 5. With the exception of SiH₂F₂ the most stable complexes, are formed with (HF)₂, the fluorosilane complexes being about as stable as the fluoromethane complexes. In general, the contractions of the Si-H bonds in the Si-H...F hydrogen bonds are distinctly larger than those of the C-H bonds in the C-H...F hydrogen bonds, whereas the elongations of Si-F and C-F in the halogen-hydrogen bonds are of comparable magnitude. In both cases, these elongations are by far the largest structural changes in the fluorosilanes and methanes upon complex formation. The blue shifts of the $\nu(\text{Si-H})$ stretching frequencies reach a maximum close to +50 cm^{−1} in case

Table 12
MP2-calculated bond length changes in fluorosilane-(HF)₄ complexes relative to monomers (Å)

Complex	Bond length change	Basis set	
		6-311++ G(2d,2p)	aug-cc-pVTZ
SiH ₂ F ₂ -(HF) ₄	$\Delta r(\text{Si-H})$	−0.0072, −0.0072	−0.0078, −0.0065
	$\Delta r(\text{Si-F})^a$	0.0301	0.0318
	$\Delta r(\text{Si-F})$	0.0013	0.0019
	$\Delta r(\text{H-F})$	0.0193, 0.0235, 0.0235, 0.0181	0.0237, 0.0290, 0.0290, 0.0225
SiH ₃ F-(HF) ₄	$\Delta r(\text{Si-H})^b$	−0.0059, −0.0059	−0.0073, −0.0065
	$\Delta r(\text{Si-H})$	−0.0005	−0.0006
	$\Delta r(\text{Si-F})$	0.0270	0.0305
	$\Delta r(\text{H-F})$	0.0173, 0.0229, 0.0240, 0.0190	0.0225, 0.0279, 0.0296, 0.0242

^a Si-F bond involved in the formation of the halogen-hydrogen bond.

^b Si-H bond(s) involved in the formation of the Si-H...F hydrogen bond.

Table 13
Selected MP2-calculated harmonic vibrational frequencies ν , frequency shifts, and infrared intensities in fluorosilane–(HF) $_4$ complexes

Complex	Assignment	Basis set, 6-311 + + G(2d,2p)
SiH ₂ F ₂ –(HF) ₄	$\nu(\text{Si–H})$	2405 (32) ^a [37] ^b
		2427 (46) [99]
	$\nu(\text{Si–F})^c$	809 (–45) [98]
	$\nu(\text{Si–F})$	892 (–18) [156]
	$\nu(\text{H–F})$	3607 (–557) [614]
		3728 (–436) [1894]
		3794 (–370) [618]
SiH ₃ F–(HF) ₄	$\nu(\text{Si–H})$	3835 (–329) [587]
		2335 (5) [102]
	$\nu(\text{Si–H})^d$	2361 (30) [55]
		2371 (40) [103]
	$\nu(\text{Si–F})$	794 (–63) [87]
	$\nu(\text{H–F})$	3612 (–552) [728]
		3733 (–431) [1696]
		3818 (–346) [552]
		3828 (–336) [724]

Frequencies and frequency shifts with respect to monomers in cm^{–1}; infrared intensities in km/mol.

^a Frequency shifts in parentheses.

^b Infrared intensities in square brackets.

^c Si–F bond involved in Si–F···H–F halogen–hydrogen bonding participating.

^d Si–H bonds involved in bifurcated SiH₂···F hydrogen bonds.

of the fluorosilane–(HF)₃ complexes. These are the largest reported so far for blue-shifted Si–H···X hydrogen bonds. A similar pattern, with blue shifts of the $\nu(\text{C–H})$ stretching frequencies close to +60 cm^{–1}, was calculated for the fluoromethane–(HF)₃ complexes. Despite the larger mass, the red shifts of the $\nu(\text{Si–F})$ stretching frequencies are, with about –40 to –80 cm^{–1}, only slightly smaller than the corresponding red shifts of the $\nu(\text{C–F})$ stretching frequencies of the fluoromethane–(HF)_{*n*} (2 ≤ *n* ≤ 4) complexes.

Overall, the structures, stabilities and vibrational frequency shifts in the two series are very similar indeed.

4.2. Similarities in the intramolecular coupling of fluorosilanes and fluoromethanes

In the recent investigations on the series of fluoromethanes [37,38], the coupling between C–H and C–F stretching modes of a given fluoromethane molecule has been discussed in some detail and was found to be at least partially responsible, if not the main source, for the large blue shifts in the fluoromethane–(HF)_{*n*} complexes. As with the fluoromethane–(HF)_{*n*} complexes, the contractions $\Delta R(\text{Si–H})$ in the blue-shifted Si–H···F hydrogen bonds correlate very well with the elongations $\Delta R(\text{Si–F})$ in the Si–F···H–F halogen–hydrogen bonds. Fig. 6 shows a simple plot of $\Delta R(\text{Si–H})$ vs. $\Delta R(\text{Si–F})$ for all optimized fluorosilane–(HF)_{*n*} structures as obtained at the MP2/aug-cc-pVTZ level. In view of the floppy character of the complexes with several large-amplitude motions and additional complications due to non-additivities, bifurcated hydrogen bonds, and different deviations from idealized planar ring structures, the interdependence of these two structural parameters is evident and is remarkably regular.

This behavior has, however, a deeper, intramolecular origin. This was already discussed for the fluoromethanes [38]. The forced elongation of a C–F bond in a fluoromethane molecule results in a contraction of the available C–H bonds when complete geometry relaxation is allowed. The very same motif is observed for the fluorosilanes as well. Fig. 7 shows the response of the remaining bonds of a fluorosilane, when either one Si–H or one Si–F bond is scanned. In these scans, complete geometry optimizations were carried out. In the relevant regions, i.e. about ±50 mÅ around

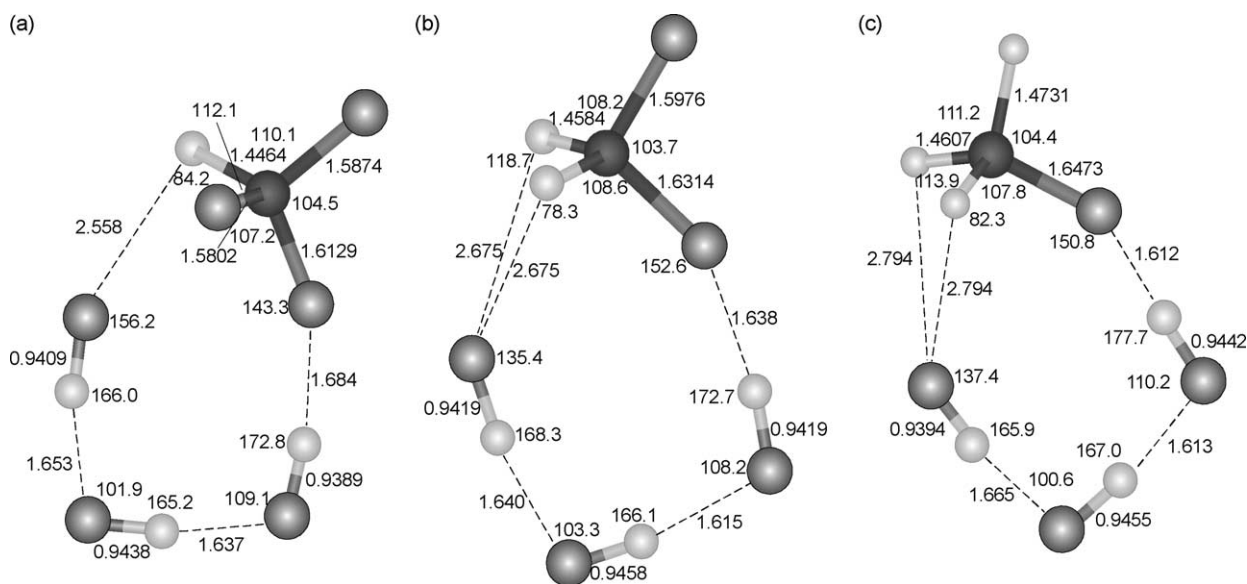


Fig. 3. MP2/aug-cc-pVTZ calculated equilibrium structures of fluorosilane–(HF)₃ tetramers: (a) SiHF₃–(HF)₃, (b) SiH₂F₂–(HF)₃, and (c) SiH₃F–(HF)₃. Bond lengths in Å and bond angles in degrees.

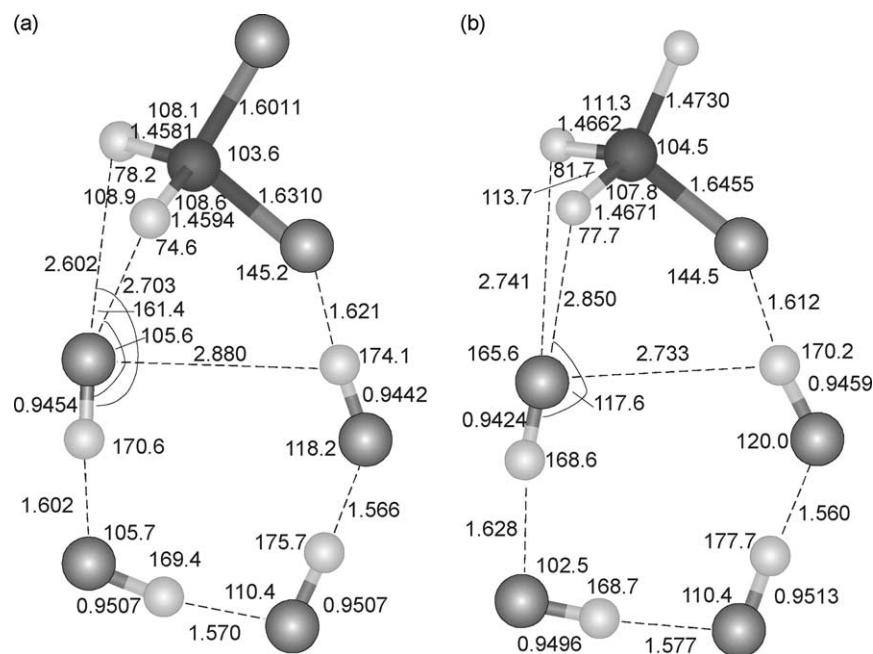


Fig. 4. MP2/aug-cc-pVTZ calculated equilibrium structures: (a) $\text{SiH}_2\text{F}_2-(\text{HF})_4$, and (b) $\text{SiH}_3\text{F}-(\text{HF})_4$. Bond lengths in Å and bond angles in degrees.

the equilibrium value of a given Si–H or Si–F bond distance, the relaxation of all bond angles is entirely negligible. The figure clearly demonstrates that stretching of $R(\text{Si–H})$ results in a contraction of $R(\text{Si–F})$ and $R(\text{Si–H})$ (see Fig. 7a,b). Even more importantly (see Fig. 7c), the forced elongation of $R(\text{Si–F})$ results in the contraction of $R(\text{Si–H})$ for all three fluorosilanes. This disposition of the fluorosilanes is completely identical to that of the fluoromethanes and it seems to be a necessary prerequisite for the appearance of *large* blue shifts in the complexes with $(\text{HF})_n$, where the formation of the halogen–hydrogen bond leads to an elongation of $R(\text{Si–F})$ and thereby induces just this particular structural relaxation. The behavior or the response of those free fluorosilane bonds which are not part of the ring are more difficult to interpret because of a compensation effect.

In this and previous work [37,38], the large blue shifts are attributed to the combined action of $\text{Si–F}\cdots\text{H–F}$

halogen–hydrogen bond formation and the thereby induced Si–H bond length contractions in the $\text{Si–H}\cdots\text{F}$ hydrogen bonds based on specific couplings between intramolecular stretching degrees of freedoms in the fluorosilanes. To cast this interpretation into more quantitative terms is a task that remains still to be done. The alternative point of view, to make only the $\text{Si–H}\cdots\text{F}$ hydrogen bonds responsible for the large blue shifts appear less plausible. Isolated $\text{Si–H}\cdots\text{F}$ hydrogen bonds are simply not formed.

4.3. Limited NBO analysis

The most important results of a NBO population analysis are reported in Table 14. This analysis was performed using the MP2/6-311++G(2d,2p) density and the MP2/6-311++G(2d,2p) optimized fluorosilane monomer

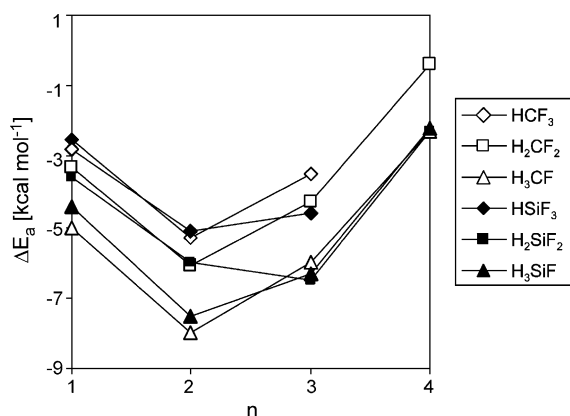


Fig. 5. MP2/aug-cc-pVTZ calculated trends in the stabilization energies ΔE_a of fluorosilane and fluoromethane complexes with $(\text{HF})_n$.

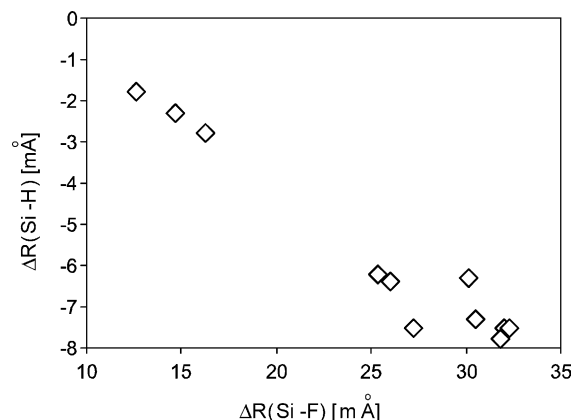


Fig. 6. MP2/aug-cc-pVTZ calculated interdependence of $\Delta R(\text{Si–H})$ and $\Delta R(\text{Si–F})$ in $\text{Si–H}\cdots\text{F}$ hydrogen bonds and $\text{Si–F}\cdots\text{H–F}$ halogen–hydrogen bonds of fluorosilane– $(\text{HF})_n$ complexes.

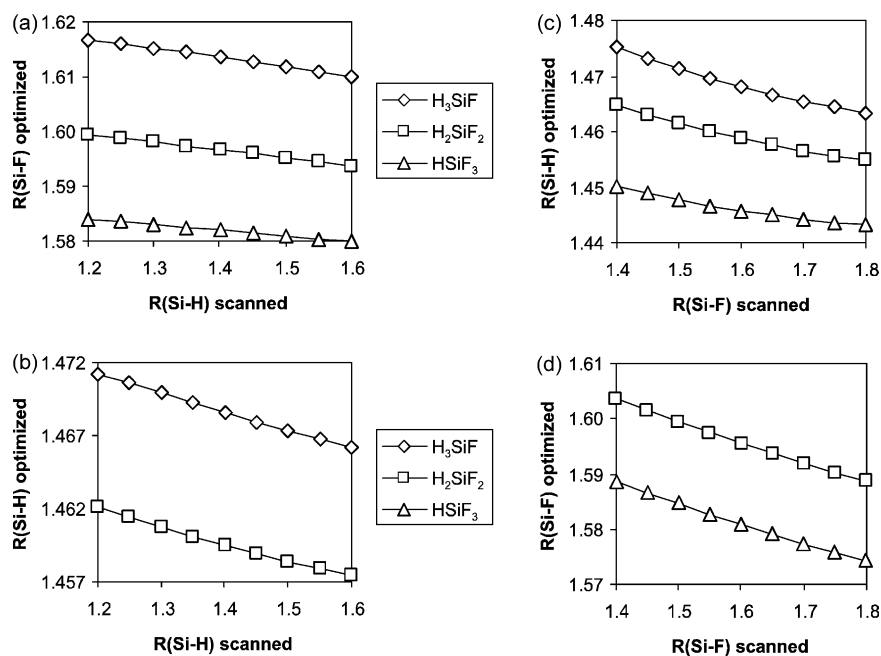


Fig. 7. MP2/6-311 + +G(2d,2p) calculated intramolecular response to selected scans of fluorosilane energy surfaces.

and fluorosilane-(HF) $_n$ structures. What is shown there are the difference atomic charges defined as $\Delta q = q(\text{complex}) - q(\text{monomer})$. Only the Δq values of the atoms of the fluorosilane moieties are given, those of the HF molecules are omitted. In full accord with the above discussion on structure changes accompanying cluster formation, larger changes (larger than 0.015 in absolute value) of the atomic charges are obtained only for those atoms which are directly involved in the formation of Si-F \cdots H-F halogen-hydrogen bonds or blue-shifted Si-H \cdots F hydrogen bonds.

These values are reported in italics. Fluorine atoms in Si-F \cdots H bonds acquire negative charge, hydrogen atoms in blue-shifted hydrogen bonds acquire positive charge. The Δq values are largest in absolute value for $n=2$ and 3.

5. Summary and conclusions

In this work, the results of high-level ab initio calculations of the complexes formed between fluorosilanes

Table 14
MP2/6-311 + +G(2d,2p) derived NBO atomic charge differences of fluorosilane-(HF) $_n$ clusters relative to fluorosilane monomers

	HSiF ₃		H ₂ SiF ₂		H ₃ SiF	
$n=1$	H	0.0109	H	0.0107	H	0.0120
	Si	<i>0.0043</i>	Si	<i>-0.0006</i>	Si	<i>-0.0068</i>
	F	<i>-0.0186</i>	F	<i>-0.0177</i>	F	<i>-0.0165</i>
	F	0.0050	H	0.0107	H	0.0111
	F	0.0050	F	0.0054	H	0.0111
$n=2$	H	0.0241	H	0.0247	H	0.0203
	Si	<i>0.0022</i>	Si	<i>-0.0012</i>	Si	<i>-0.0089</i>
	F	<i>-0.0264</i>	F	<i>-0.0241</i>	F	<i>-0.0217</i>
	F	0.0056	F	0.0071	H	<i>0.0203</i>
	F	<i>-0.0018</i>	H	0.0040	H	0.0042
$n=3$	H	<i>0.0279</i>	H	<i>0.0221</i>	H	<i>0.0216</i>
	Si	<i>0.0041</i>	Si	<i>-0.0037</i>	Si	<i>-0.0039</i>
	F	<i>-0.0258</i>	F	<i>-0.0280</i>	F	<i>-0.0236</i>
	F	<i>-0.0022</i>	F	<i>-0.0027</i>	H	0.0021
	F	0.0050	H	<i>0.0221</i>	H	<i>0.0216</i>
$n=4$			H	<i>0.0229</i>	H	<i>0.0185</i>
			Si	<i>-0.0030</i>	Si	<i>-0.0046</i>
			F	<i>-0.0233</i>	F	<i>-0.0188</i>
			F	<i>-0.0021</i>	H	0.0185
			H	<i>0.0172</i>	H	<i>0.0042</i>

For atoms involved in the formation of Si-F \cdots H halogen-hydrogen bonds and of Si-H \cdots F blue-shifted hydrogen bonds the values are given in italics.

and $(\text{HF})_n$ species were presented. To date, no spectroscopic data are available for these complexes, nor any previous theoretical studies. All fluorosilane–HF dimers have open, non-cyclic structures with $\text{Si-F}\cdots\text{H-F}$ halogen–hydrogen bonds. No minima with $\text{Si-H}\cdots\text{F}$ hydrogen bonds could be detected for the dimers. The larger fluorosilane– $(\text{HF})_n$ clusters are all cyclic. All trends observed in the series are completely analogous to the trends calculated for the related series of fluoromethane– $(\text{HF})_n$ complexes. Surprisingly large blue shifts of $\nu(\text{Si-H})$ stretching frequencies between $+40$ and $+50\text{ cm}^{-1}$ are predicted for fluorosilane– $(\text{HF})_3$ complexes and only somewhat smaller blue shifts are calculated for the complexes with $(\text{HF})_2$ and $(\text{HF})_4$. These are by far the largest blue shifts calculated to date for $\text{Si-H}\cdots\text{X}$ hydrogen bonds. The $\text{H}\cdots\text{F}$ distances in these $\text{Si-H}\cdots\text{F}$ hydrogen bonds are, however, only slightly shorter than the sum of the van der Waals radii of H and F, and they must therefore be classified as very weak hydrogen bonds. The equilibrium structures and the stabilization energies are dominated by the presence of strong, short $\text{Si-F}\cdots\text{H-F}$ halogen–hydrogen bonds. These give rise to strong red shifts of the Si-F stretching frequencies, reaching values close to -80 and -70 cm^{-1} in $\text{SiH}_3\text{F}-(\text{HF})_2$ and $\text{SiH}_3\text{F}-(\text{HF})_3$, respectively.

In each of these complexes, the formation of a $\text{Si-F}\cdots\text{H-F}$ halogen–hydrogen bond results in a significant lengthening of the Si-F bond, which in turn induces the contraction of the Si-H bond in the $\text{Si-H}\cdots\text{F}$ hydrogen bond. This specific coupling is already visible when the Si-F bond of an isolated fluorosilane is scanned, while fully optimizing all remaining internal coordinates. Elongating a selected $R(\text{Si-F})$ bond results in a shortening of the $R(\text{Si-H})$ bond(s). This disposition of the fluorosilanes, a property of their intramolecular force field, is in full analogy to the intramolecular couplings in fluoromethanes and occurs also in other halomethanes.

Needless to say, the above fluorosilane monomer force field couplings are not sufficient to fully explain each and every detailed property of the complexes or all the intramolecular structure changes taking place upon complex formation. All other conventional mechanisms of the theory of intermolecular interaction, electrostatics, polarization, dispersion, exchange, and charge-transfer, are operative, too, and complicate the analysis of these strongly non-additive intermolecular complexes. The existence of this specific kind of intramolecular coupling in molecules, which are likely candidates for giving rise to blue shifting of different X-H stretching frequencies in $\text{X-H}\cdots\text{Y}$ hydrogen bonds, is, however, an ingredient which appears to be of central interest and deserves to be investigated in much greater detail in the future. Work along these lines is in progress. Quite apart from these detailed aspects of analysis, the insertion of fluoromethanes, fluorosilanes and other candidate molecules in cyclic $(\text{HF})_n$ clusters appears to be a promising route to generate complexes in which

the blue shifts are high, and in which they can theoretically be studied and controlled by varying the cluster size.

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