



## Density Functional Study of Sulfur Hexafluoride (SF<sub>6</sub>) and its Hydrogen Derivatives

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## RESEARCH NOTE

### Density Functional Study of Sulfur Hexafluoride (SF<sub>6</sub>) and its Hydrogen Derivatives.

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#### Abstract

Density functional study has been performed for group of compounds derived from sulfur hexafluoride (SF<sub>6</sub>) by consecutively substituting fluorine with hydrogen. SF<sub>6</sub> is widely used as the insulating gas in the electrical industry and is recognized as one of the greenhouse gases with extraordinary global warming potential. The aim of the present study is to look for potential industrial alternatives to SF<sub>6</sub> as well as to examine mechanisms that can contribute to its faster atmospheric decay. The ground state geometries, binding energies, vibrational spectra, charge distributions, dipole moments, as well as thermodynamic properties for the series of the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) molecules have been obtained and discussed. For comparison, computational results for the SCl<sub>6</sub> molecule have also been included in the present study.

**Keywords:** sulfur hexafluoride; greenhouse gases; density functional theory;

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## 1. Introduction

Interest in the sulfur hexafluoride ( $\text{SF}_6$ ) system stems both from practical and theoretical considerations. It is one of the most popular (next to air) insulating gases, with a breakdown strength of about 3 times that of air. It has a number of technologically important properties: it is not flammable and non-toxic; at normal temperatures, it is also non-corrosive, and is fairly inert. That is why  $\text{SF}_6$  is commonly used in industry as a gaseous dielectric and as a plasma etching gas in applications such as: circuit breakers, gas-insulated busbar systems, and also for large scale scientific applications such as tandem particle accelerators. Other areas of application of  $\text{SF}_6$  include the magnesium industry to protect molten magnesium from oxidation and potentially violent burning, and semiconductor manufacturing to create circuitry patterns on silicon wafers. Also,  $\text{SF}_6$  is a candidate refrigerant to replace the chlorofluorocarbons (CFC's) which are damaging the ozone layer. For an extensive review of  $\text{SF}_6$  technical applications see, for example, [1] and publications therein.

On the theoretical side,  $\text{SF}_6$  has become a classic molecule for the study of electron attachment at ultralow electron energies. The attachment of low energy electrons to  $\text{SF}_6$  results in formation of a metastable negative ion by the process:  $\text{SF}_6 + e^- \rightarrow \text{SF}_6^-$  [2-5]. An understanding of the thermal electron attachment properties and temperature behaviour of rate constant for  $\text{SF}_6$  is, in turn, of importance in the design of gaseous insulators and diffuse discharge switchers.

Furthermore,  $\text{SF}_6$  has a unique, octahedral symmetry structure, which provides good example of shape resonance phenomena. The infrared active modes of octahedral molecules are of  $F_{1u}$  symmetry and  $\nu_3$  as well as  $\nu_4$  bands are allowed in absorption [6]. In particular, the region of the  $\nu_3$  fundamental near  $950\text{ cm}^{-1}$  has very strong absorption. The bond dissociation energy of  $\text{SF}_6$  (to  $\text{SF}_5 + \text{F}$ ) is 3.82 eV, but photodissociation is not observed until the photon energy exceeds  $\sim 10$  eV [4].

However, at the same time  $\text{SF}_6$  is the most potent greenhouse gas that has been evaluated by the Intergovernmental Panel on Climate Change (IPCC), with a global warming potential (GWP) of 22,800 times that of  $\text{CO}_2$  when compared over a 100 year period [7]. Two main factors contributing to this extraordinary high value of GWP is strong radiative forcing ( $0.52\text{ Wm}^{-2}\text{ppb}^{-1}$ ) and very long atmospheric lifetime (3200 years) [8]. In the stratosphere, the highest energy solar photons have an energy of  $\sim 6$  eV, so it is very unlikely that  $\text{SF}_6$  will be photodissociated there. Therefore, although the concentration of  $\text{SF}_6$  is still relatively low in the Earth's atmosphere (5.21 ppt) [8], it is one of the greenhouse gases that the Kyoto Protocol seeks to control [9], as even small amounts of  $\text{SF}_6$  emissions can constitute a significant carbon-equivalent emission tonnage.

Apart from destroying ozone layer greenhouse gases that can absorb infrared radiation in the so-called "atmospheric window" between the wavelengths of  $800 - 1400\text{ cm}^{-1}$  are of great concern because they are able to trap radiation that would have otherwise been emitted into space — most of the radiation emitted by the earth's surface at wavelengths within in the atmospheric window would have passed through the Earth's atmosphere without heating it.

Recently, another compound with extremely strong radiative forcing (of  $0.59\text{ Wm}^{-2}\text{ppb}^{-1}$ ), identified as trifluoromethyl sulfur pentafluoride ( $\text{SF}_5\text{CF}_3$ ), has been detected in the atmosphere [10,11]. It is supposed that  $\text{SF}_5\text{CF}_3$  originates as a breakdown product of  $\text{SF}_6$  formed by high-voltage discharges in electric industry equipment [10]. Atmospheric lifetime of  $\text{SF}_5\text{CF}_3$  ( $\sim 800$  years) is lower than that of  $\text{SF}_6$ , but its value of GWP ( $\sim 17,700$ ) is one of the highest of all other greenhouse gases [7].

It is worth noting, however, that the greenhouse gases with the greatest GWP values are the fully fluorinated compounds (FFC's):  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{c-C}_4\text{F}_8$ ,  $\text{SF}_6$ ,  $\text{NF}_3$  and  $\text{CHF}_3$ , that are widely used by the semiconductor industry [12]. As for now there is no significant mechanism for their destruction in the natural circulation of the Earth's atmosphere — as a result their atmospheric lifetimes are estimated to be up to 50,000 years for  $\text{CF}_4$  [7].

In case of CFC's a wide variety of alternative compounds has been investigated with the aim

of protecting the ozone layer and reducing the global warming. The basic concept in the process of development of alternative CFC's is the introduction of a hydrogen atom into the CFC molecule to reduce its atmospheric lifetime without detrimenting its properties. In this way, several hydrochlorofluorocarbons (HCFC's) and hydrofluorocarbons (HFC's) have already been developed and have found practical use. The introduction of hydrogen atoms into the molecule raises the compound's reactivity towards OH radicals as the reactivity with OH radicals is related to the stability of the molecule in the troposphere [13].

Motivated by this fact we have studied the series of the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots 6$ ) molecules where the fluorine atoms of  $\text{SF}_6$  were consecutively replaced with the hydrogen atoms. The aim of the study is to look for potential industrial alternatives to  $\text{SF}_6$  as well as to examine mechanisms that can contribute to its faster atmospheric decay.  $\text{SCl}_6$  has been also taken into consideration to compare our results with a heavier analogue of the  $\text{SF}_6$  molecule. To our best knowledge this is the first report on the properties of the  $\text{SF}_{6-n}\text{H}_n$  series of compounds.

The present study is based on density functional theory (DFT) [14,15]. This approach has over the past decade emerged as a tangible and versatile computational method with applications in many subfields of chemistry. The DFT-based methods can provide bond energies, structures and other electronic properties of high accuracy. The method has previously been applied to similar studies on diatomic  $3d$  transition metal monoxides [16,17].

The rest of the paper is organized as follows. Computational details are reported in Section 2. In Section 3 the ground state geometries, bonding energies, vibrational spectra, charge distributions partitioned by Hirshfeld method, dipole moments, as well as thermodynamic properties are presented and analyzed. In Section 4 the main points of this work are summarized and perspectives for future research are outlined.

## 2. Computational details

As mentioned in the introduction, the computational method used for the purpose of the present study is based on DFT as implemented in the DMol<sup>3</sup> code [18,19] available as part of the Materials Studio 4.0 software environment [20]. For an extensive review of the DMol<sup>3</sup> description and its features we refer the reader to [18,19] and references therein. We present here only a summary of the input parameters set up in the DMol<sup>3</sup> package in order to get stable and accurate results, as compared to experiment and other calculations.

DMol<sup>3</sup> uses numerical functions on an atom-centered grid as its atomic basis. For the purpose of the present study the DNP basis set was used for all atoms. The DNP basis set uses double-numerical quality basis set with polarization functions. This means that for each occupied atomic orbital one numerical function is generated and a second set of this functions is given for valence atomic orbitals. It also generates polarization  $d$ -functions on all non-hydrogen atoms and polarization  $p$ -function on all hydrogen atoms. The DNP basis sets are comparable in quality to Gaussian 6-31G\*\* basis sets.

The quality of the integration grid that controls the selection of mesh points for the numerical integration procedure used in the evaluation of the matrix elements was chosen to be FINE. The electron density in DMol<sup>3</sup> is expanded in terms of multipolar partial densities (auxiliary density) used to specify the maximum angular momentum  $L_{\text{max}}$  of the multipolar fitting functions that specify the analytical form of the charge density and the Coulombic potential. This parameter was set to be OCTUPOLE which corresponds to  $L_{\text{max}}$  of 3.

The local density approximation (LDA) can be used to predict the structures and relative energies of covalent and ionic systems quite accurately. However, usually bond energies are overestimated while vibrational frequencies are underestimated than those obtained within other methods and experimental data. These problems with the LDA method can be corrected to large extent by using the so-called gradient-corrected (or nonlocal) functionals. However, extensive test calculation with local and non-local functionals yielded that in the case of  $\text{SF}_6$  it is the LDA method

with Perdew-Wang functional (PWC) that yield the results closer to available experimental data. We have therefore adopted this approach in all calculations performed for the purpose of the present study.

Vibrational spectra and Hessians were computed by finite differences of analytic first derivatives. This means that each atom in the system was displaced in each Cartesian direction. The results of Hessian evaluation have been used to compute thermodynamic properties of the molecules. Point group symmetry was used to reduce the total number of displacements. The vibrational analysis was performed at the final geometry. Hirshfeld partitioned charges were defined relative to the deformation density. Finally, the convergence criteria were established to be FINE both for the SCF density convergence (the density convergence threshold for SCF) and for the optimization energy convergence (the threshold for energy convergence during geometry optimization). The numerical values for these thresholds were  $10^{-6}$  Ha and  $10^{-5}$  Ha, respectively.

### 3. Results and discussion

#### 3.1 Geometry optimization

The accuracy of the data obtained in the course of the present study can be compared only in the case of the reference  $\text{SF}_6$  molecule. There have been quite a number of electronic properties calculations for this system, and the predicted properties vary remarkably depending upon the methodology of the computation (see Ref. 31 for the discussion). Therefore we decided to compare results yielded by our calculation with theoretical studies founded on DFT [21-22] that are available for the  $\text{SF}_6$  molecule. The first and the most extensive work (however, without calculated vibrational frequencies) came from Tang and Callaway [21] who performed calculations for  $\text{SF}_6$  in the local spin density (LSD) approximation. Delley [22] studied static deformations and vibrations of  $\text{SF}_6$  with an applied strong static electric field; basic molecular properties in the absence of external electrostatic fields in local as well as gradient corrected approximations to DFT were obtained. To our knowledge these are all numerical studies of the electronic structure of the  $\text{SF}_6$  molecule based on DFT methodology. Molecular properties of  $\text{SF}_6$  are collected in Table 1.

It can be seen from Table 1 that our results obtained for the  $\text{SF}_6$  molecule are in good agreement with those presented in Ref. 21 and Ref. 22. The maximum deviation of calculated frequencies is at  $49\text{ cm}^{-1}$ , that is less than 10% in comparison with experimental values. The LDA PWC approximation thus gives a fairly accurate description of the energy surface near the equilibrium conformation. Surprisingly enough, the gradient corrected functionals perform significantly worse for this molecule, except for the binding energy.

The equilibrium structures as obtained from optimization of geometry of all studied molecules in their ground states are shown in Figure 1. The structures were optimized in imposed symmetry, relevant to each molecule (see the labels under the figure labels). The highest symmetry point group  $O_h$  is adopted by the  $\text{SF}_6$  molecule, as well as by the  $\text{SH}_6$  and  $\text{SCl}_6$  ones. With the substitution of fluorine atoms by the hydrogen ones the symmetry is lowered, but symmetries of the  $\text{SF}_{6-n}\text{H}_n$  ( $n=1\dots5$ ) molecules are consistent with the correlation table of the  $O_h$  group. For molecules  $\text{SF}_{6-n}\text{H}_n$  ( $n=2,3,4$ ) two possible nonequivalent conformations exist: the first one, denoted further as (a), in which one of the hydrogen atoms is perpendicular to other hydrogen atom(s), and the second one, denoted as (b), in which all hydrogen atoms are in the same plane. Subsequent DMol<sup>3</sup> computations of other properties were performed at these final geometries. The point group symmetries were imposed on each molecule in order to reduce the computational time whenever possible.

Closer examination of structural data obtained shows that geometry of the  $\text{SF}_{6-n}\text{H}_n$  ( $n=1\dots6$ ) molecules resembles that of the  $\text{SF}_6$  parent one. Due to large amount of data collected detailed values of bond lengths and angles are available from the authors. For the purpose of the present study only principal trends are summarized. The relevant H-S-F angles are very close to  $90^\circ$  or



180°, respectively. The most deformed structure is that of SF<sub>2</sub>H<sub>4</sub> (a) with low, C<sub>2v</sub> symmetry. The deviation from 180° is about 10°. The molecular distances between sulfur and fluorine atoms increase as the fluorine atoms are substituted by the hydrogen ones, and hydrogen-sulfur distances are smaller than the fluorine-sulfur ones. These trends are illustrated in Figure 2a and 2b. It is worth to mention that in the case of SCl<sub>6</sub> the chlorine-sulfur distance is significantly larger and equals to 2.1461 Å. Trend in binding energy for the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) series and SCl<sub>6</sub> is illustrated in Figure 3.

The SF<sub>6</sub> molecule has the highest binding energy as compared to the SF<sub>6-n</sub>H<sub>n</sub> (n=1...6) series. Interestingly enough, the SCl<sub>6</sub> and SH<sub>6</sub> molecules have similar values of binding energies. These results are listed in Table 2. Since the SF<sub>6</sub>, SH<sub>6</sub> and SCl<sub>6</sub> molecules have octahedral symmetry, as well as the SF<sub>4</sub>H<sub>2</sub> (b) and SF<sub>2</sub>H<sub>4</sub> (b) have tetragonal symmetry, there are no static dipole moments in their case. The values of dipole moments obtained for the molecules under study are listed in Table 3, and its analysis is postponed to Section 3.3.

Closer examination of single particle eigenvalues (depicted in Figure 4) yields that with increasing number of the H atoms in the SF<sub>6-n</sub>H<sub>n</sub> system the number of eigenstates is gradually diminishing, as there are less electrons. Symmetries of the orbitals are changing according to symmetries of the given SF<sub>6-n</sub>H<sub>n</sub> system (in order to keep the Figure 4 as readable as possible we decided to label eigenstates only for SF<sub>6</sub> and SH<sub>6</sub> molecules). Because of the same molecular symmetry of the SF<sub>6</sub> and SH<sub>6</sub> molecules molecular orbitals have the same symmetry in their case. However, there are fewer electrons in SH<sub>6</sub> than in SF<sub>6</sub>, so only 6 first single particle eigenstates in 3 energetically lowest states with symmetries A<sub>1g</sub>, T<sub>1u</sub> i E<sub>g</sub> are occupied.

### 3.2 Optical properties

Normal modes and their frequencies for all the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) molecules are shown in Figure 5, while explicit values, supplemented with data obtained for SCl<sub>6</sub>, are listed in Tables 4 and 5. In Table 6 square of first derivatives of molecular dipole moments wrt infrared active normal modes are shown. Calculated absorption spectra are collected in Figure 6.

The infrared absorption spectrum of SF<sub>6</sub> is composed of two bands. Only ν<sub>3</sub> and ν<sub>4</sub> modes with F<sub>1u</sub> symmetry satisfy dipole selection rules and are allowed in absorption. Their maxima are located at 567.2 and 938.06 cm<sup>-1</sup> with intensity respectively 22.17 and 390.19 km/mol. Both of these normal modes are triple degenerate and correspond to the change of bond lengths and bond angles.

The frequencies of vibrations are expected to increase as hydrogen atoms are substituted for fluorine ones. This effect can be attributed to the extension of reduced masses of these molecules, as well as the decrease of intermolecular interactions (see the Figure 2a and 2b and Table 2): binding energies are decreasing and bond lengths are increasing. As a consequence, with increasing n in SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) spectra are shifted into higher energies. Variations in mass distribution and molecular geometries cause also alterations in symmetries of normal modes. The intensity of absorption for the fundamental vibrational transitions is given by:

$$A = B_{nw} \cdot h \cdot \nu_{nw} \cdot c^{-1} \cdot N_A,$$

where A is the integral coefficient of absorption (measure of absorption in band), ν<sub>nw</sub> is the frequency of transition between n and w levels, and B<sub>nw</sub> is the Einstein coefficient for induced emission, which can be expressed as:

$$B_{nw} = \frac{8\pi^3}{3h^2} \cdot |\mu_{nw}^2|,$$

in which μ<sub>nw</sub> is the transition moment for n and w levels. For the fundamental transitions, this

quantity is proportional to square of first derivatives of molecular dipole moments wrt infrared active normal modes. As it is shown in Table 6, these values are increasing with the increasing rate of replacement of fluorine by hydrogen.

Molecules  $\text{SCl}_6$  and  $\text{SH}_6$  are again quite similar to  $\text{SF}_6$ . As they adopt  $\text{O}_h$  point group symmetry, the infrared spectra are analogous to this of  $\text{SF}_6$ . The difference is in the frequencies of normal modes and intensities of their absorption.  $\text{SCl}_6$ , as a heavier molecule, has lower vibrational transition intensity as well as lower frequencies of normal modes. In contrast to this,  $\text{SH}_6$  has a much higher vibrational transition intensity and higher frequencies of normal modes. This means that  $\text{SH}_6$  absorbs even more radiation than  $\text{SF}_6$ , but in for higher frequencies.  $\text{SH}_6$  has also nearly two times lower binding energy than  $\text{SF}_6$  and, as such, is less stable.

It is also worth to mention that strongest absorption band of  $\text{SF}_6$  at  $\sim 940\text{ cm}^{-1}$  is located in the atmospheric window mentioned in Section 1, and no other molecule studied here has so strong absorption band in this frequency region as  $\text{SF}_6$  has.

### 3.3 Charge distribution and dipole moments

Charge partitioning as obtained from Hirshfeld method for all the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots 6$ ) molecules and the  $\text{SCl}_6$  one is listed in Table 7. These values are normalized to single atoms, so one should bear in mind that for given  $n$  in  $\text{SF}_{6-n}\text{H}_n$   $q_S = (6-n) \cdot q_F + n \cdot q_H$ . Hirshfeld analysis for  $\text{SF}_6$  indicates positive charge on the sulfur atom and small negative charges on the fluorine atoms. Negative charges on the fluorine atoms increase while positive charge on the sulfur atom decreases as fluorine atoms are gradually substituted with the hydrogen atoms. Although not included here, the results of Mulliken analysis are consistent with the results of Hirshfeld one.

The dipole moment of a molecule is determined by the charges and the induced dipoles on the constituent atoms. Because of symmetric charge distribution, there are no static dipole moments in molecules:  $\text{SF}_6$ ,  $\text{SF}_4\text{H}_2$  (b),  $\text{SF}_2\text{H}_4$  (b),  $\text{SH}_6$  and  $\text{SCl}_6$ . The  $\text{SF}_5\text{H}$  has almost two times smaller magnitude of dipole moment than  $\text{SFH}_5$ , although charges on constituent atoms are larger in  $\text{SF}_5\text{H}$  than in  $\text{SFH}_5$ , and both molecules have the same symmetry. One can assume that for  $\text{SFH}_5$  the charge and induced dipole contributions have the same polarity that account for its large dipole moment, in contrast to  $\text{SF}_5\text{H}$ . In case of the  $\text{SF}_3\text{H}_3$  (a) and (b) molecules the large difference in dipole moments is caused by different symmetry of charge distribution.

### 3.4 Thermodynamical properties

Basic thermodynamic properties such as total entropy, vibrational entropy, free energy, heat capacity and zero point vibrational energy have been also calculated for the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots 6$ ) and  $\text{SCl}_6$  molecules. The results are presented in Table 8 and Figures 7 to 12. Values of heat capacity decrease with molecular mass reduction. As the heat capacity is defined as the amount of heat required to change the temperature of a substance by one degree, larger molecules will need more heat than smaller ones. This suggest that insulating properties of  $\text{SCl}_6$  are the best of all the molecules studied here, in particular better than these of  $\text{SF}_6$ . The industrial usage of  $\text{SF}_6$  instead of  $\text{SCl}_6$  is due to greater stability of  $\text{SF}_6$  than  $\text{SCl}_6$  (bonding energy for  $\text{SF}_6$  is twice higher than that for  $\text{SCl}_6$ ). Total and vibrational entropy decreases as fluorine atoms are substituted with hydrogen ones. On the other hand the free energy and zero point vibrational entropy show opposite tendency. This behaviour is in good relation to changes in molecular mass of studied compounds.

## 4. Conclusions

In the present study the series of the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots 6$ ) molecules have been examined for the first time. Molecular constants such as equilibrium bond distances, binding energies, vibrational frequencies, charge distributions partitioned by Hirshfeld method, dipole moments, as well as thermodynamic properties have been determined and analyzed.



The results of IR spectra simulations confirm that it is fluorine atoms that play crucial role in greenhouse effect of SF<sub>6</sub>. For other molecules with octahedral symmetry, such as SH<sub>6</sub> and SCl<sub>6</sub>, their absorption bands are outside the atmospheric window. On the other hand, for the SF<sub>6-n</sub>H<sub>n</sub> (n=1...5) molecules with lower symmetries, there are more absorptions bands with reduced intensities as compared to SF<sub>6</sub>.

Because of inherent approximations in DFT, computational methods based on this approach are not expected to yield very accurate values of molecular constants, as wavefunction based *ab initio* methods do. Rather, due to their efficiency and robustness DFT-based methods constitute valuable tool in predicting general trends across a wide range of compounds. Therefore, the present study can be regarded as the first step toward more detailed examination of the series of SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) molecules. Further research can cover following areas:

- (1) formation of metastable negative ions;
- (2) reaction paths with OH radicals;
- (3) investigation of excited states.

These topics are outside the scope of the present study, but the need for further *ab initio* calculations for these systems is therefore obvious.

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Table 1. Experimental and calculated properties of the SF<sub>6</sub> molecule.

Parameter	Unit	Present	Ref. 31	Ref. 32 <sup>d</sup>	Experiment
Binding energy <sup>a</sup>	eV	26.81	25.06	26.12	22.06 (20.12)
<i>d</i> (S—F)	Å	1.587	1.584	1.588	1.564 <sup>b</sup>
$\nu_1$ A <sub>1g</sub>	cm <sup>-1</sup>	723.5	—	718	772.269 <sup>c</sup>
$\nu_2$ E <sub>g</sub>	cm <sup>-1</sup>	625.5	—	622	641.608 <sup>c</sup>
$\nu_3$ F <sub>1u</sub>	cm <sup>-1</sup>	938.1	—	931	947.289 <sup>c</sup>
$\nu_4$ F <sub>1u</sub>	cm <sup>-1</sup>	567.2	—	562	614.589 <sup>c</sup>
$\nu_5$ F <sub>2g</sub>	cm <sup>-1</sup>	477.9	—	476	523.449 <sup>c</sup>
$\nu_6$ F <sub>2u</sub>	cm <sup>-1</sup>	315.7	—	312	348.428 <sup>c</sup>

<sup>a</sup> SF<sub>6</sub> → S + 6F<sup>b</sup> Table 8 in Ref. 4, p. 280<sup>c</sup> Table 7 in Ref. 4, p. 280<sup>d</sup> PWC calculation

Table 2. Binding energy in [eV] and [J].

Molecule	Symmetry	Binding energy	
		[eV]	[J]
SF <sub>6</sub>	O <sub>h</sub>	26.810	4.295·10 <sup>-18</sup>
SF <sub>5</sub> H	C <sub>4v</sub>	25.663	4.112·10 <sup>-18</sup>
SF <sub>4</sub> H <sub>2</sub> (a)	C <sub>2v</sub>	24.090	3.860·10 <sup>-18</sup>
SF <sub>4</sub> H <sub>2</sub> (b)	D <sub>4h</sub>	24.508	3.927·10 <sup>-18</sup>
SF <sub>3</sub> H <sub>3</sub> (a)	C <sub>3v</sub>	22.381	3.586·10 <sup>-18</sup>
SF <sub>3</sub> H <sub>3</sub> (b)	C <sub>2v</sub>	22.565	3.615·10 <sup>-18</sup>
SF <sub>2</sub> H <sub>4</sub> (a)	C <sub>2v</sub>	20.670	3.316·10 <sup>-18</sup>
SF <sub>2</sub> H <sub>4</sub> (b)	D <sub>4h</sub>	20.058	3.214·10 <sup>-18</sup>
SFH <sub>5</sub>	C <sub>4v</sub>	18.165	2.910·10 <sup>-18</sup>
SH <sub>6</sub>	O <sub>h</sub>	15.230	2.440·10 <sup>-18</sup>
SCI <sub>6</sub>	O <sub>h</sub>	14.372	2.303·10 <sup>-18</sup>

Table 3. Magnitudes of dipole moments vectors in [Debye] and [C·m].

Molecule	Symmetry	Dipole magnitude	
		[Debye]	[C·m]
SF <sub>6</sub>	O <sub>h</sub>	0.080	0.267·10 <sup>-30</sup>
SF <sub>5</sub> H	C <sub>4v</sub>	1.752	5.844·10 <sup>-30</sup>
SF <sub>4</sub> H <sub>2</sub> a	C <sub>2v</sub>	2.659	8.871·10 <sup>-30</sup>
SF <sub>4</sub> H <sub>2</sub> b	D <sub>4h</sub>	0.001	0.003·10 <sup>-30</sup>
SF <sub>3</sub> H <sub>3</sub> a	C <sub>3v</sub>	3.634	12.122·10 <sup>-30</sup>
SF <sub>3</sub> H <sub>3</sub> b	C <sub>2v</sub>	2.151	7.175·10 <sup>-30</sup>
SF <sub>2</sub> H <sub>4</sub> a	C <sub>2v</sub>	3.392	11.314·10 <sup>-30</sup>
SF <sub>2</sub> H <sub>4</sub> b	D <sub>4h</sub>	0.067	0.223·10 <sup>-30</sup>
SFH <sub>5</sub>	C <sub>4v</sub>	2.610	8.706·10 <sup>-30</sup>
SH <sub>6</sub>	O <sub>h</sub>	0.039	0.131·10 <sup>-30</sup>
SCI <sub>6</sub>	O <sub>h</sub>	0.042	0.141·10 <sup>-30</sup>



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Table 4. Frequencies of normal modes in [cm<sup>-1</sup>].

Mode	SF <sub>6</sub>	SF <sub>5</sub> H	SF <sub>4</sub> H <sub>2</sub> a	SF <sub>4</sub> H <sub>2</sub> b	SF <sub>3</sub> H <sub>3</sub> a	SF <sub>3</sub> H <sub>3</sub> b	SF <sub>2</sub> H <sub>4</sub> a	SF <sub>2</sub> H <sub>4</sub> b	SFH <sub>5</sub>	SH <sub>6</sub>	SCl <sub>6</sub>
7	315.6	296.3	325.8	276.2	367.2	346.9	337.7	430.8	630.4	1319.5	139.7
8	315.6	346.2	348.2	380.1	367.2	375.9	634.1	430.8	787.3	1319.5	139.7
9	315.6	346.2	399.4	380.1	486.3	422.0	675.0	611.7	787.3	1319.5	139.7
10	477.7	449.0	464.4	418.7	690.7	607.4	774.9	837.5	1112.5	1322.8	205.7
11	477.7	515.3	530.6	584.6	690.7	698.4	890.6	937.2	1220.5	1322.8	205.7
12	477.7	515.3	620.0	642.6	786.5	844.9	956.3	1119.8	1264.9	1322.8	205.7
13	567.0	572.6	718.4	649.4	866.8	941.8	1213.5	1119.8	1264.9	1329.3	230.7
14	567.0	606.5	809.6	860.2	1098.6	1134.9	1228.2	1299.7	1405.5	1329.3	230.7
15	567.0	659.2	875.7	860.2	1098.6	1159.4	1338.8	1423.6	1405.5	1329.3	230.7
16	625.0	832.1	1086.8	1195.5	1347.1	1262.4	1352.8	1423.6	1553.4	1909.2	253.9
17	625.0	902.6	1169.1	1195.5	1361.3	1280.3	1402.4	1651.4	2070.1	1909.2	263.2
18	722.9	902.6	1263.1	1253.2	1361.3	1449.0	2451.8	2174.4	2198.5	2014.5	263.2
19	937.4	1241.0	1391.9	1253.2	2575.2	2523.6	2484.5	2293.1	2198.5	2014.5	400.1
20	937.4	1241.0	2621.4	2649.1	2575.5	2540.9	2501.8	2293.1	2277.0	2014.5	400.1
21	937.4	2707.1	2636.2	2725.0	2575.5	2592.0	2505.1	2354.9	2438.2	2173.2	400.1

Table 5. Intensities of normal modes in [km·mol<sup>-1</sup>].

Mode	SF <sub>6</sub>	SF <sub>5</sub> H	SF <sub>4</sub> H <sub>2</sub> a	SF <sub>4</sub> H <sub>2</sub> b	SF <sub>3</sub> H <sub>3</sub> a	SF <sub>3</sub> H <sub>3</sub> b	SF <sub>2</sub> H <sub>4</sub> a	SF <sub>2</sub> H <sub>4</sub> b	SFH <sub>5</sub>	SH <sub>6</sub>	SCl <sub>6</sub>
7	0	0	1.5	0	0.9	0.8	0.3	20.5	168	0	0
8	0	1.3	0	5.1	0.9	3.8	171.2	20.5	2.4	0	0
9	0	1.3	7.9	5.1	4.5	26.7	186.8	0	2.4	0	0
10	0	0	3.4	0	156.1	13.1	0	361.6	0	0	0
11	0	8.7	8.4	0	156.1	191.5	5	0	30.2	0	0
12	0	8.7	10.2	90.3	188.3	389.1	27.2	0	6.9	0	0
13	22.2	19.1	168.8	0	0	33.1	12.6	0	6.9	49.6	1.3
14	22.2	0	192.2	417.7	20.7	0.1	12.8	11.7	32.2	49.6	1.3
15	22.2	14.9	395.6	417.7	20.7	0	1	40.3	32.2	49.6	1.3
16	0	189.4	25.9	0	5.6	9.1	4.5	40.3	0	0	0
17	0	407.7	0	0	1.7	1.1	0	0	0	0	0
18	0	407.7	0.3	0.5	1.7	2.6	4.6	0	357.3	678.2	0
19	390.2	0.1	1.7	0.5	40.6	33.5	58.5	284.2	357.3	678.2	116.7
20	390.2	0.1	15.1	0	26.4	24.1	44.3	284.2	0	678.2	116.7
21	390.2	0.2	13.6	0.05	26.4	17.6	82.1	0	99.5	0	116.7

Table 6. Square of first derivatives of molecular dipole moments wrt infrared active normal modes in [a.u.].

Mode	SF <sub>6</sub>	SF <sub>5</sub> H	SF <sub>4</sub> H <sub>2</sub> a	SF <sub>4</sub> H <sub>2</sub> b	SF <sub>3</sub> H <sub>3</sub> a	SF <sub>3</sub> H <sub>3</sub> b	SF <sub>2</sub> H <sub>4</sub> a	SF <sub>2</sub> H <sub>4</sub> b	SFH <sub>5</sub>	SH <sub>6</sub>	SCH <sub>6</sub>
7	0	0	0	0	0.001	0.001	0	0.021	0.17	0	0
8	0	0.001	0	0.005	0.001	0.004	0.175	0.021	0.003	0	0
9	0	0.001	0.01	0.005	0.005	0.027	0.191	0	0.003	0	0
10	0	0	0	0	0.159	0.014	0	0.369	0	0	0
11	0	0.009	0.01	0	0.159	0.195	0.005	0	0.03	0	0
12	0	0.009	0.01	0.092	0.192	0.397	0.028	0	0.007	0	0
13	0.02	0.019	0.17	0	0	0.034	0.013	0	0.007	0.05	0.001
14	0.02	0	0.2	0.427	0.021	0	0.013	0.012	0.033	0.05	0.001
15	0.02	0.015	0.4	0.427	0.021	0	0.001	0.041	0.033	0.05	0.001
16	0	0.193	0.03	0	0.006	0.009	0.005	0.041	0	0	0
17	0	0.416	0	0	0.002	0.001	0	0	0	0	0
18	0	0.416	0	0	0.002	0.003	0.005	0	0.364	0.69	0
19	0.4	0	0	0	0.041	0.031	0.06	0.29	0.364	0.69	0.119
20	0.4	0	0.02	0	0.027	0.028	0.045	0.29	0	0.69	0.119
21	0.4	0	0.01	0	0.027	0.018	0.084	0	0.1	0	0.119

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Table 7. Charges partitioned by Hirshfeld method.

Molecule	Symmetry	Charges		
		S	F	H/Cl
SF <sub>6</sub>	O <sub>h</sub>	0.5801	-0.0967	-
SF <sub>5</sub> H	C <sub>4v</sub>	0.5013	-0.1148	0.0729
SF <sub>4</sub> H <sub>2</sub> a	C <sub>2v</sub>	0.4224	-0.1333	0.0553
SF <sub>4</sub> H <sub>2</sub> b	D <sub>4h</sub>	0.4249	-0.1419	0.0714
SF <sub>3</sub> H <sub>3</sub> a	C <sub>3v</sub>	0.3396	-0.1591	0.0459
SF <sub>3</sub> H <sub>3</sub> b	C <sub>2v</sub>	0.3459	-0.1643	0.0490
SF <sub>2</sub> H <sub>4</sub> a	C <sub>2v</sub>	0.2613	-0.2078	0.0386
SF <sub>2</sub> H <sub>4</sub> b	D <sub>4h</sub>	0.2776	-0.1619	0.0116
SFH <sub>5</sub>	C <sub>4v</sub>	0.1917	-0.2248	0.0066
SH <sub>6</sub>	O <sub>h</sub>	0.1361	-	-0.0227
SCl <sub>6</sub>	O <sub>h</sub>	0.3411	-	-0.0568

Table 8. Thermodynamic properties.

Molecule	Symmetry	Total entropy [cal·mol <sup>-1</sup> ·K <sup>-1</sup> ]	Vibrational entropy [cal·mol <sup>-1</sup> ·K <sup>-1</sup> ]	ZPVE [kcal·mol <sup>-1</sup> ]	Free energy [kcal·mol <sup>-1</sup> ]	Heat capacity [cal·mol <sup>-1</sup> ·K <sup>-1</sup> ]
SF <sub>6</sub>	O <sub>h</sub>	77.235	9.128	12.682	-18.776	24.175
SF <sub>5</sub> H	C <sub>4v</sub>	74.798	7.662	17.349	-18.355	21.553
SF <sub>4</sub> H <sub>2</sub> a	C <sub>2v</sub>	71.896	5.977	21.816	-17.829	18.883
SF <sub>4</sub> H <sub>2</sub> b	D <sub>4h</sub>	72.350	6.239	21.906	-17.928	18.933
SF <sub>3</sub> H <sub>3</sub> a	C <sub>3v</sub>	68.412	4.780	26.870	-17.165	16.156
SF <sub>3</sub> H <sub>3</sub> b	C <sub>2v</sub>	68.879	4.337	25.992	-17.262	16.249
SF <sub>2</sub> H <sub>4</sub> a	C <sub>2v</sub>	65.210	2.576	29.664	-16.462	13.770
SF <sub>2</sub> H <sub>4</sub> b	D <sub>4h</sub>	64.384	2.624	29.165	-16.259	13.735
SFH <sub>5</sub>	C <sub>4v</sub>	60.170	1.800	32.541	-15.331	11.263
SH <sub>6</sub>	O <sub>h</sub>	54.932	0.231	34.238	-13.948	9.253
SCl <sub>6</sub>	O <sub>h</sub>	101.464	28.160	5.302	-23.158	34.214

<sup>a</sup>Zero Point Vibrational Energy.

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*Molecular Simulation*

## RESEARCH NOTE

### Density Functional Study of Sulfur Hexafluoride (SF<sub>6</sub>) and its Hydrogen Derivatives.

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#### Abstract

Density functional study has been performed for a group of compounds derived from sulfur hexafluoride (SF<sub>6</sub>) by consecutively substituting fluorine with hydrogen. SF<sub>6</sub> is widely used as the insulating gas in the electrical industry and is recognized as one of the greenhouse gases with extraordinary global warming potential. The aim of the present study is to look for potential industrial alternatives to SF<sub>6</sub> as well as to examine mechanisms that can contribute to its faster atmospheric decay. The ground state geometries, binding energies, vibrational spectra, charge distributions, dipole moments, as well as thermodynamic properties for the series of the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) molecules have been obtained and discussed. For comparison, computational results for the SCl<sub>6</sub> molecule have also been included in the present study.

**Keywords:** sulfur hexafluoride; greenhouse gases; density functional theory;

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1 1. Introduction

2  
3 Interest in the sulfur hexafluoride (SF<sub>6</sub>) system stems both from practical and theoretical  
4 considerations. It is one of the most popular (next to air) insulating gases, with a breakdown  
5 strength of about 3 times that of air. It has a number of technologically important properties: it is  
6 not flammable and non-toxic; at normal temperatures, it is also non-corrosive, and is fairly inert.  
7 That is why SF<sub>6</sub> is commonly used in industry as a gaseous dielectric and as a plasma etching gas in  
8 applications such as: circuit breakers, gas-insulated busbar systems, and also for large scale  
9 scientific applications such as tandem particle accelerators. Other areas of application of SF<sub>6</sub>  
10 include the magnesium industry to protect molten magnesium from oxidation and potentially  
11 violent burning, and semiconductor manufacturing to create circuitry patterns on silicon wafers.  
12 Also, SF<sub>6</sub> is a candidate refrigerant to replace the chlorofluorocarbons (CFC's) which are damaging  
13 the ozone layer. For an extensive review of SF<sub>6</sub> technical applications see, for example, [1] and  
14 publications therein.

15 Because of its unique structure, unusual spectroscopy, and applied interest, the SF<sub>6</sub> molecule  
16 has been a subject of much interest both experimentally and theoretically. Photoelectron [2-4],  
17 valence-shell [5-7], and inner-shell [8-11] photoionization and valence-shell [12] and inner-shell  
18 [13-16] electron energy-loss experimental measurements have been performed. The unique,  
19 octahedral symmetry structure of SF<sub>6</sub> provides good example of shape resonance phenomena. The  
20 infrared active modes of octahedral molecules are of F<sub>1u</sub> symmetry and v<sub>3</sub> as well as v<sub>4</sub> bands are  
21 allowed in absorption [17]. In particular, the region of the v<sub>3</sub> fundamental near 950 cm<sup>-1</sup> has very  
22 strong absorption. The bond dissociation energy of SF<sub>6</sub> (to SF<sub>5</sub> + F) is 3.82 eV, but  
23 photodissociation is not observed until the photon energy exceeds ~10 eV [18].

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24 On the theoretical side, SF<sub>6</sub> has become a classic molecule for the study of electron  
25 attachment at ultralow electron energies. The attachment of low energy electrons to SF<sub>6</sub> results in  
26 formation of a metastable negative ion by the process: SF<sub>6</sub> + e<sup>-</sup> → SF<sub>6</sub><sup>-</sup> [18,21]. An understanding  
27 of the thermal electron attachment properties and temperature behaviour of rate constant for SF<sub>6</sub> is, in  
28 turn, of importance in the design of gaseous insulators and diffuse discharge switchers.

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29 However, at the same time SF<sub>6</sub> is the most potent greenhouse gas that has been evaluated by  
30 the Intergovernmental Panel on Climate Change (IPCC), with a global warming potential (GWP) of  
31 22,800 times that of CO<sub>2</sub> when compared over a 100 year period [22]. Two main factors  
32 contributing to this extraordinary high value of GWP is strong radiative forcing (0.52 Wm<sup>-2</sup>ppb<sup>-1</sup>)  
33 and very long atmospheric lifetime (800-3200 years) [22-26]. In the stratosphere, the highest energy  
34 solar photons have an energy of ~6 eV, so it is very unlikely that SF<sub>6</sub> will be photodissociated there.  
35 Therefore, although the concentration of SF<sub>6</sub> is still relatively low in the Earth's atmosphere (5.21  
36 ppt) [26], it is one of the greenhouse gases that the Kyoto Protocol seeks to control [27], as even  
37 small amounts of SF<sub>6</sub> emissions can constitute a significant carbon-equivalent emission tonnage.

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38 Apart from destroying ozone layer, greenhouse gases that can absorb infrared radiation in  
39 the so-called "atmospheric window" between the wavelengths of 800 - 1400 cm<sup>-1</sup> are of great  
40 concern because they are able to trap radiation that would have otherwise been emitted into space.  
41 In other words, without greenhouse gases most of the radiation emitted by the earth's surface at  
42 wavelengths within in the atmospheric window would have passed through the Earth's atmosphere  
43 without heating it.

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44 Recently, another compound with extremely strong radiative forcing (of 0.59 Wm<sup>-2</sup>ppb<sup>-1</sup>),  
45 identified as trifluoromethyl sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>), has been detected in the atmosphere  
46 [28,29]. It is supposed that SF<sub>5</sub>CF<sub>3</sub> originates as a breakdown product of SF<sub>6</sub> formed by high-  
47 voltage discharges in electric industry equipment [28]. Atmospheric lifetime of SF<sub>5</sub>CF<sub>3</sub> (~800  
48 years) is lower than that of SF<sub>6</sub>, but its value of GWP (~17,700) is one of the highest of all other  
49 greenhouse gases [22].

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50 It is worth noting, however, that the greenhouse gases with the greatest GWP values are the  
51 fully fluorinated compounds (FFC's): CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, c-C<sub>4</sub>F<sub>8</sub>, SF<sub>6</sub>, NF<sub>3</sub> and CHF<sub>3</sub>, that are widely

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used by the semiconductor industry [30]. As for now there is no significant mechanism for their destruction in the natural circulation of the Earth's atmosphere — as a result their atmospheric lifetimes are estimated to be up to 50,000 years for CF<sub>4</sub> [22].

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In case of CFC's a wide variety of alternative compounds has been investigated with the aim of protecting the ozone layer and reducing the global warming. The basic concept in the process of development of alternative CFC's is the introduction of a hydrogen atom into the CFC molecule to reduce its atmospheric lifetime without detrimenting its properties. In this way, several hydrochlorofluorocarbons (HCFC's) and hydrofluorocarbons (HFC's) have already been developed and have found practical use. The introduction of hydrogen atoms into the molecule raises the compound's reactivity towards OH radicals as the reactivity with OH radicals is related to the stability of the molecule in the troposphere [31].

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Motivated by this fact we have studied the series of the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) molecules where the fluorine atoms of SF<sub>6</sub> were consecutively replaced with the hydrogen atoms. The aim of the study is to look for potential industrial alternatives to SF<sub>6</sub> as well as to examine mechanisms that can contribute to its faster atmospheric decay. SCl<sub>6</sub> has been also taken into consideration to compare our results with a heavier analogue of the SF<sub>6</sub> molecule. To our best knowledge this is the first report on the properties of the SF<sub>6-n</sub>H<sub>n</sub> series of compounds.

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The present study is based on density functional theory (DFT) [32,33]. This approach has over the past decade emerged as a tangible and versatile computational method with applications in many subfields of chemistry. The DFT-based methods can provide bond energies, structures and other electronic properties of high accuracy. The method has previously been applied to similar studies on diatomic 3d transition metal monoxides [34,35].

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The rest of the paper is organized as follows. Computational details are reported in Section 2. In Section 3 the ground state geometries, bonding energies, vibrational spectra, charge distributions partitioned by Hirshfeld method, dipole moments, as well as thermodynamic properties are presented and analyzed. In Section 4 the main points of this work are summarized and perspectives for future research are outlined.

## 2. Computational details

As mentioned in the introduction, the computational method used for the purpose of the present study is based on DFT as implemented in the DMol<sup>3</sup> code [36,37] available as part of the Materials Studio 4.0 software environment [38]. For an extensive review of the DMol<sup>3</sup> description and its features we refer the reader to [36,37] and references therein. We present here only a summary of the input parameters set up in the DMol<sup>3</sup> package in order to get stable and accurate results, as compared to experiment and other calculations.

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DMol<sup>3</sup> uses numerical functions on an atom-centered grid as its atomic basis. For the purpose of the present study the DNP basis set was used for all atoms. The DNP basis set uses double-numerical quality basis set with polarization functions. This means that for each occupied atomic orbital one numerical function is generated and a second set of this functions is given for valence atomic orbitals. It also generates polarization *d*-functions on all non-hydrogen atoms and polarization *p*-function on all hydrogen atoms. The DNP basis sets are comparable in quality to Gaussian 6-31G\*\* basis sets.

The quality of the integration grid that controls the selection of mesh points for the numerical integration procedure used in the evaluation of the matrix elements was chosen to be FINE. The electron density in DMol<sup>3</sup> is expanded in terms of multipolar partial densities (auxiliary density) used to specify the maximum angular momentum  $L_{max}$  of the multipolar fitting functions that specify the analytical form of the charge density and the Coulombic potential. This parameter was set to be OCTUPOLE which corresponds to  $L_{max}$  of 3.

The local density approximation (LDA) can be used to predict the structures and relative energies of covalent and ionic systems quite accurately. However, usually bond energies are

overestimated while vibrational frequencies are underestimated than those obtained within other methods and experimental data. These problems with the LDA method can be corrected to large extent by using the so-called gradient-corrected (or nonlocal) functionals. However, extensive test calculations with local and non-local functionals yielded that in the case of SF<sub>6</sub> it is the LDA method with Perdew-Wang functional (PWC) that yield the results closer to available experimental data. We have therefore adopted this approach in all calculations performed for the purpose of the present study.

Vibrational spectra and Hessians were computed by finite differences of analytic first derivatives. This means that each atom in the system was displaced in each Cartesian direction. The results of Hessian evaluation have been used to compute thermodynamic properties of the molecules. Point group symmetry was used to reduce the total number of displacements. The vibrational analysis was performed at the final geometry. Hirshfeld partitioned charges were defined relative to the deformation density. Finally, the convergence criteria were established to be FINE both for the SCF density convergence (the density convergence threshold for SCF) and for the optimization energy convergence (the threshold for energy convergence during geometry optimization). The numerical values for these thresholds were 10<sup>-6</sup> Ha and 10<sup>-5</sup> Ha, respectively.

### 3. Results and discussion

#### 3.1 Geometry optimization

The accuracy of the data obtained in the course of the present study can be compared only in the case of the reference SF<sub>6</sub> molecule. There have been quite a number of electronic properties calculations for this system, and the predicted properties vary remarkably depending upon the methodology of the computation (see Ref. 39 for the discussion). Therefore we decided to compare results yielded by our calculation with theoretical studies founded on DFT [39,40] that are available for the SF<sub>6</sub> molecule. The first and the most extensive work (however, without calculated vibrational frequencies) came from Tang and Callaway [39] who performed calculations for SF<sub>6</sub> in the local spin density (LSD) approximation. Delley [40] studied static deformations and vibrations of SF<sub>6</sub> with an applied strong static electric field; basic molecular properties in the absence of external electrostatic fields in local as well as gradient corrected approximations to DFT were obtained. To our knowledge these are all numerical studies of the electronic structure of the SF<sub>6</sub> molecule based on the DFT methodology. Molecular properties of SF<sub>6</sub> are collected in Table 1.

It can be seen from Table 1 that our results obtained for the SF<sub>6</sub> molecule are in good agreement with those presented in Ref. 39, and Ref. 40. The maximum deviation of calculated frequencies is at 49 cm<sup>-1</sup>, that is less than 10% in comparison with experimental values. The LDA PWC approximation thus gives a fairly accurate description of the energy surface near the equilibrium conformation. Surprisingly enough, the gradient corrected functionals perform significantly worse for this molecule, except for the binding energy.

The equilibrium structures as obtained from optimization of geometry of all studied molecules in their ground states are shown in Figure 1. The structures were optimized in imposed symmetry, relevant to each molecule (see the labels under the figure labels), in order to reduce the computational time whenever possible. The highest symmetry point group O<sub>h</sub> is adopted by the SF<sub>6</sub> molecule, as well as by the SH<sub>6</sub> and SCl<sub>6</sub> ones. With the substitution of fluorine atoms with the hydrogen ones the symmetry is lowered, but symmetries of the SF<sub>6-n</sub>H<sub>n</sub> (n=1...5) molecules are consistent with the correlation table of the O<sub>h</sub> group. For molecules SF<sub>6-n</sub>H<sub>n</sub> (n=2,3,4) two possible nonequivalent conformations exist: the first one, denoted further as (a), in which one of the hydrogen atoms is perpendicular to other hydrogen atom(s), and the second one, denoted as (b), in which all hydrogen atoms are in the same plane. Subsequent DMol<sup>3</sup> computations of other properties were performed at these final geometries.

Closer examination of structural data obtained shows that geometry of the SF<sub>6-n</sub>H<sub>n</sub> (n=1...6)

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molecules resembles that of the SF<sub>6</sub> parent one. Due to large amount of data collected detailed values of bond lengths and angles are available from the authors [41]. For the purpose of the present study only principal trends are summarized. The relevant H-S-F angles are very close to 90° or 180°, respectively. The most deformed structure is that of SF<sub>2</sub>H<sub>4</sub> (a) with low, C<sub>2v</sub> symmetry. The deviation from 180° is about 10°. The molecular distances between sulfur and fluorine atoms increase as the fluorine atoms are substituted by the hydrogen ones, and hydrogen-sulfur distances are smaller than the fluorine-sulfur ones. These trends are illustrated in Figure 2a and 2b. It is worth to mention that in the case of SCl<sub>6</sub> the chlorine-sulfur distance is significantly larger and equals to 2.1461 Å.

The results obtained for binding energies for the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) series and SCl<sub>6</sub> are listed in Table 2. The SF<sub>6</sub> molecule has the highest binding energy as compared to the SF<sub>6-n</sub>H<sub>n</sub> (n=1...6) series. Interestingly enough, the SCl<sub>6</sub> and SH<sub>6</sub> molecules have similar values of binding energies. Since the SF<sub>6</sub>, SH<sub>6</sub> and SCl<sub>6</sub> molecules have octahedral symmetry, as well as the SF<sub>4</sub>H<sub>2</sub> (b) and SF<sub>2</sub>H<sub>4</sub> (b) have tetragonal symmetry, there are no static dipole moments in their case. The values of dipole moments obtained for the molecules under study are listed in Table 3, and its analysis is postponed to Section 3.3.

Closer examination of single particle eigenvalues (depicted in Figure 3) yields that with increasing number of the H atoms in the SF<sub>6-n</sub>H<sub>n</sub> system the number of eigenstates is gradually diminishing, as there are less electrons. Symmetries of the orbitals are changing according to symmetries of the given SF<sub>6-n</sub>H<sub>n</sub> system (in order to keep the Figure 3 as readable as possible we decided to label eigenstates only for SF<sub>6</sub> and SH<sub>6</sub> molecules). Because of the same molecular symmetry of the SF<sub>6</sub> and SH<sub>6</sub> molecules molecular orbitals have the same symmetry in their case. However, there are fewer electrons in SH<sub>6</sub> than in SF<sub>6</sub>, so only 6 first single particle eigenstates in 3 energetically lowest states with symmetries A<sub>1g</sub>, T<sub>1u</sub> and E<sub>g</sub> are occupied.

### 3.2 Optical properties

Explicit values of the frequencies and intensities of the normal modes for all the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) molecules are listed in Tables 4 and 5, respectively, supplemented with data obtained for SCl<sub>6</sub>. In Table 6 square of first derivatives of molecular dipole moments wrt infrared active normal modes are shown.

The infrared absorption spectrum of SF<sub>6</sub> is composed of two bands. Only ν<sub>3</sub> and ν<sub>4</sub> modes with F<sub>1u</sub> symmetry satisfy dipole selection rules and are allowed in absorption. Their maxima are located at 567.2 and 938.06 cm<sup>-1</sup> with intensity respectively 22.17 and 390.19 km/mol. Both of these normal modes are triple degenerate and correspond to the change of bond lengths and bond angles.

The frequencies of vibrations are expected to increase as hydrogen atoms are substituted for fluorine ones. This effect can be attributed to the extension of reduced masses of these molecules, as well as the decrease of intermolecular interactions (see Figure 2a and 2b, as well as Table 2): binding energies are decreasing and bond lengths are increasing. As a consequence, with increasing n in SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) spectra are shifted into higher energies. Variations in mass distribution and molecular geometries cause also alterations in symmetries of normal modes. The intensity of absorption for the fundamental vibrational transitions is given by:

$$A = B_{nw} \cdot h \cdot \nu_{nw} \cdot c^{-1} \cdot N_A,$$

where A is the integral coefficient of absorption (measure of absorption in band), ν<sub>nw</sub> is the frequency of transition between n and w levels, and B<sub>nw</sub> is the Einstein coefficient for induced emission, which can be expressed as:

Deleted: Trend in binding energy for the SF<sub>6-n</sub>H<sub>n</sub> (n=0...6) series and SCl<sub>6</sub> is illustrated in Figure 3.

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$$B_{nw} = \frac{8\pi^3}{3h^2} \cdot |\mu_{nw}^2|,$$

in which  $\mu_{nw}$  is the transition moment for  $n$  and  $w$  levels. For the fundamental transitions, this quantity is proportional to square of first derivatives of molecular dipole moments wrt infrared active normal modes. As it is shown in Table 6, these values are increasing with the increasing rate of replacement of fluorine by hydrogen.

Molecules  $\text{SCl}_6$  and  $\text{SH}_6$  are again quite similar to  $\text{SF}_6$ . As they adopt  $O_h$  point group symmetry, the infrared spectra are analogous to this of  $\text{SF}_6$ . The difference is in the frequencies of normal modes and intensities of their absorption.  $\text{SCl}_6$ , as a heavier molecule, has lower vibrational transition intensity as well as lower frequencies of normal modes. In contrast to this,  $\text{SH}_6$  has a much higher vibrational transition intensity and higher frequencies of normal modes. This means that  $\text{SH}_6$  absorbs even more radiation than  $\text{SF}_6$ , but in the range of higher frequencies.  $\text{SH}_6$  has also nearly two times lower binding energy than  $\text{SF}_6$  and, as such, is less stable.

It is also worth to mention that strongest absorption band of  $\text{SF}_6$  at  $\sim 940 \text{ cm}^{-1}$  is located in the atmospheric window mentioned in Section 1, and no other molecule studied here has so strong absorption band in this frequency region as  $\text{SF}_6$  has.

### 3.3 Charge distribution and dipole moments

Charge partitioning as obtained from Hirshfeld method for all the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots 6$ ) molecules and the  $\text{SCl}_6$  one is listed in Table 7. These values are normalized to single atoms, so one should bear in mind that for given  $n$  in  $\text{SF}_{6-n}\text{H}_n$   $q_S = (6-n) \cdot q_F + n \cdot q_H$ . Hirshfeld analysis for  $\text{SF}_6$  indicates positive charge on the sulfur atom and small negative charges on the fluorine atoms. Negative charges on the fluorine atoms increase while positive charge on the sulfur atom decreases as fluorine atoms are gradually substituted with the hydrogen atoms. Although not included here, the results of Mulliken analysis are consistent with the results of Hirshfeld one.

The dipole moment of a molecule is determined by the charges and the induced dipoles on the constituent atoms. Because of symmetric charge distribution, there are no static dipole moments in molecules:  $\text{SF}_6$ ,  $\text{SF}_4\text{H}_2$  (b),  $\text{SF}_2\text{H}_4$  (b),  $\text{SH}_6$  and  $\text{SCl}_6$ . The  $\text{SF}_5\text{H}$  has almost two times smaller magnitude of dipole moment than  $\text{SFH}_5$ , although charges on constituent atoms are larger in  $\text{SF}_5\text{H}$  than in  $\text{SFH}_5$ , and both molecules have the same symmetry. One can assume that for  $\text{SFH}_5$  the charge and induced dipole contributions have the same polarity that account for its large dipole moment, in contrast to  $\text{SF}_5\text{H}$ . In case of the  $\text{SF}_3\text{H}_3$  (a) and (b) molecules the large difference in dipole moments is caused by different symmetry of charge distribution.

### 3.4 Thermodynamical properties

Basic thermodynamic properties such as total entropy, vibrational entropy, free energy, heat capacity and zero point vibrational energy have been also calculated for the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots 6$ ) and  $\text{SCl}_6$  molecules. The results are presented in Table 8. Additionally, entropy as a function of temperature for all the molecules studied here is depicted in Figure 4. Values of heat capacity decrease with molecular mass reduction. As the heat capacity is defined as the amount of heat required to change the temperature of a substance by one degree, larger molecules will need more heat than smaller ones. This suggest that insulating properties of  $\text{SCl}_6$  are the best of all the molecules studied here, in particular better than these of  $\text{SF}_6$ . The industrial usage of  $\text{SF}_6$  instead of  $\text{SCl}_6$  is due to greater stability of  $\text{SF}_6$  than  $\text{SCl}_6$  (bonding energy for  $\text{SF}_6$  is twice higher than that for  $\text{SCl}_6$ ). Total and vibrational entropy decreases as fluorine atoms are substituted with hydrogen ones. On the other hand the free energy and zero point vibrational entropy show opposite tendency. This behaviour is in good relation to changes in molecular mass of studied compounds.

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#### 4. Conclusions

In the present study the series of the  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots6$ ) molecules have been examined for the first time. Molecular constants such as equilibrium bond distances, binding energies, vibrational frequencies, charge distributions partitioned by Hirshfeld method, dipole moments, as well as thermodynamic properties have been determined and analyzed.

The results of IR spectra simulations confirm that it is fluorine atoms that play crucial role in greenhouse effect of  $\text{SF}_6$ . For other molecules with octahedral symmetry, such as  $\text{SH}_6$  and  $\text{SCl}_6$ , their absorption bands are outside the atmospheric window. On the other hand, for the  $\text{SF}_{6-n}\text{H}_n$  ( $n=1\dots5$ ) molecules with lower symmetries, there are more absorptions bands with reduced intensities as compared to  $\text{SF}_6$ .

Because of inherent approximations in DFT, computational methods based on this approach are not expected to yield very accurate values of molecular constants, as wavefunction based *ab initio* methods do. Rather, due to their efficiency and robustness DFT-based methods constitute valuable tool in predicting general trends across a wide range of compounds. Therefore, the present study can be regarded as the first step toward more detailed examination of the series of  $\text{SF}_{6-n}\text{H}_n$  ( $n=0\dots6$ ) molecules. Further research can cover following areas:

- (1) formation of metastable negative ions;
- (2) reaction paths with OH radicals;
- (3) investigation of excited states.

These topics are outside the scope of the present study, but the need for further *ab initio* calculations for these systems is therefore obvious.

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Table 1. Experimental and calculated properties of the SF<sub>6</sub> molecule.

Parameter	Unit	Present	Ref. 39	Ref. 40 <sup>d</sup>	Experiment
Binding energy <sup>a</sup>	eV	26.81	25.06	26.12	22.06 (20.12)
d(S—F)	Å	1.587	1.584	1.588	1.564 <sup>b</sup>
ν <sub>1</sub> A <sub>1g</sub>	cm <sup>-1</sup>	723.5	—	718	772.269 <sup>c</sup>
ν <sub>2</sub> E <sub>g</sub>	cm <sup>-1</sup>	625.5	—	622	641.608 <sup>c</sup>
ν <sub>3</sub> F <sub>1u</sub>	cm <sup>-1</sup>	938.1	—	931	947.289 <sup>c</sup>
ν <sub>4</sub> F <sub>1u</sub>	cm <sup>-1</sup>	567.2	—	562	614.589 <sup>c</sup>
ν <sub>5</sub> F <sub>2g</sub>	cm <sup>-1</sup>	477.9	—	476	523.449 <sup>c</sup>
ν <sub>6</sub> F <sub>2u</sub>	cm <sup>-1</sup>	315.7	—	312	348.428 <sup>c</sup>

<sup>a</sup> SF<sub>6</sub> → S + 6F

<sup>b</sup> Table 8 in Ref. 18, p. 280

<sup>c</sup> Table 7 in Ref. 18, p. 280

<sup>d</sup> PWC calculation

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Table 2. Binding energy in [eV] and [J].

Molecule	Symmetry	Binding energy	
		[eV]	[J]
SF <sub>6</sub>	O <sub>h</sub>	26.810	4.295·10 <sup>-18</sup>
SF <sub>5</sub> H	C <sub>4v</sub>	25.663	4.112·10 <sup>-18</sup>
SF <sub>4</sub> H <sub>2</sub> (a)	C <sub>2v</sub>	24.090	3.860·10 <sup>-18</sup>
SF <sub>4</sub> H <sub>2</sub> (b)	D <sub>4h</sub>	24.508	3.927·10 <sup>-18</sup>
SF <sub>3</sub> H <sub>3</sub> (a)	C <sub>3v</sub>	22.381	3.586·10 <sup>-18</sup>
SF <sub>3</sub> H <sub>3</sub> (b)	C <sub>2v</sub>	22.565	3.615·10 <sup>-18</sup>
SF <sub>2</sub> H <sub>4</sub> (a)	C <sub>2v</sub>	20.670	3.316·10 <sup>-18</sup>
SF <sub>2</sub> H <sub>4</sub> (b)	D <sub>4h</sub>	20.058	3.214·10 <sup>-18</sup>
SFH <sub>5</sub>	C <sub>4v</sub>	18.165	2.910·10 <sup>-18</sup>
SH <sub>6</sub>	O <sub>h</sub>	15.230	2.440·10 <sup>-18</sup>
SCl <sub>6</sub>	O <sub>h</sub>	14.372	2.303·10 <sup>-18</sup>

Table 3. Magnitudes of dipole moments vectors in [Debye] and [C·m].

Molecule	Symmetry	Dipole magnitude	
		[Debye]	[C·m]
SF <sub>6</sub>	O <sub>h</sub>	0.080	0.267·10 <sup>-30</sup>
SF <sub>5</sub> H	C <sub>4v</sub>	1.752	5.844·10 <sup>-30</sup>
SF <sub>4</sub> H <sub>2</sub> a	C <sub>2v</sub>	2.659	8.871·10 <sup>-30</sup>
SF <sub>4</sub> H <sub>2</sub> b	D <sub>4h</sub>	0.001	0.003·10 <sup>-30</sup>
SF <sub>3</sub> H <sub>3</sub> a	C <sub>3v</sub>	3.634	12.122·10 <sup>-30</sup>
SF <sub>3</sub> H <sub>3</sub> b	C <sub>2v</sub>	2.151	7.175·10 <sup>-30</sup>
SF <sub>2</sub> H <sub>4</sub> a	C <sub>2v</sub>	3.392	11.314·10 <sup>-30</sup>
SF <sub>2</sub> H <sub>4</sub> b	D <sub>4h</sub>	0.067	0.223·10 <sup>-30</sup>
SFH <sub>5</sub>	C <sub>4v</sub>	2.610	8.706·10 <sup>-30</sup>
SH <sub>6</sub>	O <sub>h</sub>	0.039	0.131·10 <sup>-30</sup>
SCl <sub>6</sub>	O <sub>h</sub>	0.042	0.141·10 <sup>-30</sup>



Table 4. Frequencies of normal modes in  $[\text{cm}^{-1}]$ .

Mode	SF <sub>6</sub>	SF <sub>5</sub> H	SF <sub>4</sub> H <sub>2</sub> a	SF <sub>4</sub> H <sub>2</sub> b	SF <sub>3</sub> H <sub>3</sub> a	SF <sub>3</sub> H <sub>3</sub> b	SF <sub>2</sub> H <sub>4</sub> a	SF <sub>2</sub> H <sub>4</sub> b	SFH <sub>5</sub>	SH <sub>6</sub>	SCl <sub>6</sub>
7	315.6	296.3	325.8	276.2	367.2	346.9	337.7	430.8	630.4	1319.5	139.7
8	315.6	346.2	348.2	380.1	367.2	375.9	634.1	430.8	787.3	1319.5	139.7
9	315.6	346.2	399.4	380.1	486.3	422.0	675.0	611.7	787.3	1319.5	139.7
10	477.7	449.0	464.4	418.7	690.7	607.4	774.9	837.5	1112.5	1322.8	205.7
11	477.7	515.3	530.6	584.6	690.7	698.4	890.6	937.2	1220.5	1322.8	205.7
12	477.7	515.3	620.0	642.6	786.5	844.9	956.3	1119.8	1264.9	1322.8	205.7
13	567.0	572.6	718.4	649.4	866.8	941.8	1213.5	1119.8	1264.9	1329.3	230.7
14	567.0	606.5	809.6	860.2	1098.6	1134.9	1228.2	1299.7	1405.5	1329.3	230.7
15	567.0	659.2	875.7	860.2	1098.6	1159.4	1338.8	1423.6	1405.5	1329.3	230.7
16	625.0	832.1	1086.8	1195.5	1347.1	1262.4	1352.8	1423.6	1553.4	1909.2	253.9
17	625.0	902.6	1169.1	1195.5	1361.3	1280.3	1402.4	1651.4	2070.1	1909.2	263.2
18	722.9	902.6	1263.1	1253.2	1361.3	1449.0	2451.8	2174.4	2198.5	2014.5	263.2
19	937.4	1241.0	1391.9	1253.2	2575.2	2523.6	2484.5	2293.1	2198.5	2014.5	400.1
20	937.4	1241.0	2621.4	2649.1	2575.5	2540.9	2501.8	2293.1	2277.0	2014.5	400.1
21	937.4	2707.1	2636.2	2725.0	2575.5	2592.0	2505.1	2354.9	2438.2	2173.2	400.1

Table 5. Intensities of normal modes in  $[\text{km}\cdot\text{mol}^{-1}]$ .

Mode	SF <sub>6</sub>	SF <sub>5</sub> H	SF <sub>4</sub> H <sub>2</sub> a	SF <sub>4</sub> H <sub>2</sub> b	SF <sub>3</sub> H <sub>3</sub> a	SF <sub>3</sub> H <sub>3</sub> b	SF <sub>2</sub> H <sub>4</sub> a	SF <sub>2</sub> H <sub>4</sub> b	SFH <sub>5</sub>	SH <sub>6</sub>	SCl <sub>6</sub>
7	0	0	1.5	0	0.9	0.8	0.3	20.5	168	0	0
8	0	1.3	0	5.1	0.9	3.8	171.2	20.5	2.4	0	0
9	0	1.3	7.9	5.1	4.5	26.7	186.8	0	2.4	0	0
10	0	0	3.4	0	156.1	13.1	0	361.6	0	0	0
11	0	8.7	8.4	0	156.1	191.5	5	0	30.2	0	0
12	0	8.7	10.2	90.3	188.3	389.1	27.2	0	6.9	0	0
13	22.2	19.1	168.8	0	0	33.1	12.6	0	6.9	49.6	1.3
14	22.2	0	192.2	417.7	20.7	0.1	12.8	11.7	32.2	49.6	1.3
15	22.2	14.9	395.6	417.7	20.7	0	1	40.3	32.2	49.6	1.3
16	0	189.4	25.9	0	5.6	9.1	4.5	40.3	0	0	0
17	0	407.7	0	0	1.7	1.1	0	0	0	0	0
18	0	407.7	0.3	0.5	1.7	2.6	4.6	0	357.3	678.2	0
19	390.2	0.1	1.7	0.5	40.6	33.5	58.5	284.2	357.3	678.2	116.7
20	390.2	0.1	15.1	0	26.4	24.1	44.3	284.2	0	678.2	116.7
21	390.2	0.2	13.6	0.05	26.4	17.6	82.1	0	99.5	0	116.7

Table 6. Square of first derivatives of molecular dipole moments wrt infrared active normal modes in [a.u.].

Mode	SF <sub>6</sub>	SF <sub>5</sub> H	SF <sub>4</sub> H <sub>2</sub> a	SF <sub>4</sub> H <sub>2</sub> b	SF <sub>3</sub> H <sub>3</sub> a	SF <sub>3</sub> H <sub>3</sub> b	SF <sub>2</sub> H <sub>4</sub> a	SF <sub>2</sub> H <sub>4</sub> b	SFH <sub>5</sub>	SH <sub>6</sub>	SCl <sub>6</sub>
7	0	0	0	0	0.001	0.001	0	0.021	0.17	0	0
8	0	0.001	0	0.005	0.001	0.004	0.175	0.021	0.003	0	0
9	0	0.001	0.01	0.005	0.005	0.027	0.191	0	0.003	0	0
10	0	0	0	0	0.159	0.014	0	0.369	0	0	0
11	0	0.009	0.01	0	0.159	0.195	0.005	0	0.03	0	0
12	0	0.009	0.01	0.092	0.192	0.397	0.028	0	0.007	0	0
13	0.02	0.019	0.17	0	0	0.034	0.013	0	0.007	0.05	0.001
14	0.02	0	0.2	0.427	0.021	0	0.013	0.012	0.033	0.05	0.001
15	0.02	0.015	0.4	0.427	0.021	0	0.001	0.041	0.033	0.05	0.001
16	0	0.193	0.03	0	0.006	0.009	0.005	0.041	0	0	0
17	0	0.416	0	0	0.002	0.001	0	0	0	0	0
18	0	0.416	0	0	0.002	0.003	0.005	0	0.364	0.69	0
19	0.4	0	0	0	0.041	0.031	0.06	0.29	0.364	0.69	0.119
20	0.4	0	0.02	0	0.027	0.028	0.045	0.29	0	0.69	0.119
21	0.4	0	0.01	0	0.027	0.018	0.084	0	0.1	0	0.119

Table 7. Charges partitioned by Hirshfeld method.

Molecule	Symmetry	Charges		
		S	F	H/Cl
SF <sub>6</sub>	O <sub>h</sub>	0.5801	-0.0967	-
SF <sub>5</sub> H	C <sub>4v</sub>	0.5013	-0.1148	0.0729
SF <sub>4</sub> H <sub>2</sub> a	C <sub>2v</sub>	0.4224	-0.1333	0.0553
SF <sub>4</sub> H <sub>2</sub> b	D <sub>4h</sub>	0.4249	-0.1419	0.0714
SF <sub>3</sub> H <sub>3</sub> a	C <sub>3v</sub>	0.3396	-0.1591	0.0459
SF <sub>3</sub> H <sub>3</sub> b	C <sub>2v</sub>	0.3459	-0.1643	0.0490
SF <sub>2</sub> H <sub>4</sub> a	C <sub>2v</sub>	0.2613	-0.2078	0.0386
SF <sub>2</sub> H <sub>4</sub> b	D <sub>4h</sub>	0.2776	-0.1619	0.0116
SFH <sub>5</sub>	C <sub>4v</sub>	0.1917	-0.2248	0.0066
SH <sub>6</sub>	O <sub>h</sub>	0.1361	-	-0.0227
SCl <sub>6</sub>	O <sub>h</sub>	0.3411	-	-0.0568

Table 8. Thermodynamic properties.

Molecule	Symmetry	Total entropy [cal·mol <sup>-1</sup> ·K <sup>-1</sup> ]	Vibrational entropy [cal·mol <sup>-1</sup> ·K <sup>-1</sup> ]	ZPVE [kcal·mol <sup>-1</sup> ]	Free energy [kcal·mol <sup>-1</sup> ]	Heat capacity [cal·mol <sup>-1</sup> ·K <sup>-1</sup> ]
SF <sub>6</sub>	O <sub>h</sub>	77.235	9.128	12.682	-18.776	24.175
SF <sub>5</sub> H	C <sub>4v</sub>	74.798	7.662	17.349	-18.355	21.553
SF <sub>4</sub> H <sub>2</sub> a	C <sub>2v</sub>	71.896	5.977	21.816	-17.829	18.883
SF <sub>4</sub> H <sub>2</sub> b	D <sub>4h</sub>	72.350	6.239	21.906	-17.928	18.933
SF <sub>3</sub> H <sub>3</sub> a	C <sub>3v</sub>	68.412	4.780	26.870	-17.165	16.156
SF <sub>3</sub> H <sub>3</sub> b	C <sub>2v</sub>	68.879	4.337	25.992	-17.262	16.249
SF <sub>2</sub> H <sub>4</sub> a	C <sub>2v</sub>	65.210	2.576	29.664	-16.462	13.770
SF <sub>2</sub> H <sub>4</sub> b	D <sub>4h</sub>	64.384	2.624	29.165	-16.259	13.735
SFH <sub>5</sub>	C <sub>4v</sub>	60.170	1.800	32.541	-15.331	11.263
SH <sub>6</sub>	O <sub>h</sub>	54.932	0.231	34.238	-13.948	9.253
SCl <sub>6</sub>	O <sub>h</sub>	101.464	28.160	5.302	-23.158	34.214

<sup>a</sup>Zero Point Vibrational Energy.