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RESEARCH NOTE

Density Functional Study of Sulfur Hexafluoride (SF₆) and its Hydrogen Derivatives.

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Abstract

Density functional study has been performed for group of compounds derived from sulfur hexafluoride (SF₆) by consecutively substituting fluorine with hydrogen. SF₆ 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 SF₆ 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_{6-n}H_n (n=0...6) molecules have been obtained and discussed. For comparison, computational results for the SCl₆ 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 (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 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 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, SF_6 is a candidate refrigerant to replace the chlorofluorocarbons (CFC's) which are damaging the ozone layer. For an extensive review of SF_6 technical applications see, for example, [1] and publications therein.

On the theoretical side, SF_6 has become a classic molecule for the study of electron attachment at ultralow electron energies. The attachment of low energy electrons to 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 SF_6 is, in turn, of importance in the design of gaseous insulators and diffuse discharge switchers.

Furthermore, 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 ν_3 as well as ν_4 bands are allowed in absorption [6]. In particular, the region of the ν_3 fundamental near 950 cm^{-1} has very strong absorption. The bond dissociation energy of SF_6 (to $\text{SF}_5 + \text{F}$) is 3.82 eV, but photodissociation is not observed until the photon energy exceeds ~ 10 eV [4].

However, at the same time 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 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 ~ 6 eV, so it is very unlikely that SF_6 will be photodissociated there. Therefore, although the concentration of 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 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 (SF_5CF_3), has been detected in the atmosphere [10,11]. It is supposed that SF_5CF_3 originates as a breakdown product of SF_6 formed by high-voltage discharges in electric industry equipment [10]. Atmospheric lifetime of SF_5CF_3 (~ 800 years) is lower than that of 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): CF_4 , C_2F_6 , C_3F_8 , $\text{c-C}_4\text{F}_8$, SF_6 , NF_3 and 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 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 SF_6 were consecutively replaced with the hydrogen atoms. The aim of the study is to look for potential industrial alternatives to SF_6 as well as to examine mechanisms that can contribute to its faster atmospheric decay. SCl_6 has been also taken into consideration to compare our results with a heavier analogue of the 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 DMol³ code [18,19] available as part of the Materials Studio 4.0 software environment [20]. For an extensive review of the DMol³ 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 DMol³ package in order to get stable and accurate results, as compared to experiment and other calculations.

DMol³ 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 DMol³ 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 calculation with local and non-local functionals yielded that in the case of 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 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 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 SF_6 in the local spin density (LSD) approximation. Delley [22] studied static deformations and vibrations of 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 SF_6 molecule based on DFT methodology. Molecular properties of SF_6 are collected in Table 1.

It can be seen from Table 1 that our results obtained for the 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 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 SF_6 molecule, as well as by the SH_6 and 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 DMol³ 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 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° or

180°, respectively. The most deformed structure is that of SF₂H₄ (a) with low, C_{2v} 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 SCl₆ the chlorine-sulfur distance is significantly larger and equals to 2.1461 Å. Trend in binding energy for the SF_{6-n}H_n (n=0...6) series and SCl₆ is illustrated in Figure 3.

The SF₆ molecule has the highest binding energy as compared to the SF_{6-n}H_n (n=1...6) series. Interestingly enough, the SCl₆ and SH₆ molecules have similar values of binding energies. These results are listed in Table 2. Since the SF₆, SH₆ and SCl₆ molecules have octahedral symmetry, as well as the SF₄H₂ (b) and SF₂H₄ (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_{6-n}H_n 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_{6-n}H_n system (in order to keep the Figure 4 as readable as possible we decided to label eigenstates only for SF₆ and SH₆ molecules). Because of the same molecular symmetry of the SF₆ and SH₆ molecules molecular orbitals have the same symmetry in their case. However, there are fewer electrons in SH₆ than in SF₆, so only 6 first single particle eigenstates in 3 energetically lowest states with symmetries A_{1g}, T_{1u} i E_g are occupied.

3.2 Optical properties

Normal modes and their frequencies for all the SF_{6-n}H_n (n=0...6) molecules are shown in Figure 5, while explicit values, supplemented with data obtained for SCl₆, 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 SF₆ is composed of two bands. Only ν₃ and ν₄ modes with F_{1u} symmetry satisfy dipole selection rules and are allowed in absorption. Their maxima are located at 567.2 and 938.06 cm⁻¹ 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_{6-n}H_n (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_{nw} is the frequency of transition between n and w levels, and B_{nw} 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_{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 SCl_6 and SH_6 are again quite similar to SF_6 . As they adopt O_h point group symmetry, the infrared spectra are analogous to this of SF_6 . The difference is in the frequencies of normal modes and intensities of their absorption. SCl_6 , as a heavier molecule, has lower vibrational transition intensity as well as lower frequencies of normal modes. In contrast to this, SH_6 has a much higher vibrational transition intensity and higher frequencies of normal modes. This means that SH_6 absorbs even more radiation than SF_6 , but in for higher frequencies. SH_6 has also nearly two times lower binding energy than SF_6 and, as such, is less stable.

It is also worth to mention that strongest absorption band of 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 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 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 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: SF_6 , SF_4H_2 (b), SF_2H_4 (b), SH_6 and SCl_6 . The SF_5H has almost two times smaller magnitude of dipole moment than SFH_5 , although charges on constituent atoms are larger in SF_5H than in SFH_5 , and both molecules have the same symmetry. One can assume that for SFH_5 the charge and induced dipole contributions have the same polarity that account for its large dipole moment, in contrast to SF_5H . In case of the SF_3H_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 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 SCl_6 are the best of all the molecules studied here, in particular better than these of SF_6 . The industrial usage of SF_6 instead of SCl_6 is due to greater stability of SF_6 than SCl_6 (bonding energy for SF_6 is twice higher than that for 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 SF₆. For other molecules with octahedral symmetry, such as SH₆ and SCl₆, their absorption bands are outside the atmospheric window. On the other hand, for the SF_{6-n}H_n (n=1...5) molecules with lower symmetries, there are more absorptions bands with reduced intensities as compared to SF₆.

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_{6-n}H_n (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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Figure 1. Equilibrium geometries of the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) series and SCl_6 in their ground states: a. SF_6 , O_h symmetry; b. SF_5H , C_{4v} symmetry; c. SF_4H_2 (a), C_{2v} symmetry; d. SF_4H_2 (b), D_{4h} symmetry; e. SF_3H_3 (a), C_{3v} symmetry; f. SF_3H_3 (b), C_{2v} symmetry; g. SF_2H_4 (a), C_{2v} symmetry; h. SF_2H_4 (b), D_{4h} symmetry; i. SFH_5 , C_{4v} symmetry; j. SH_6 , O_h symmetry; k. SCl_6 , O_h symmetry.

Figure 2. Interatomic distances in the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) series and SCl_6 a. fluorine-sulfur distances; b. hydrogen-sulfur distances.

Figure 3. Binding energies for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) series and SCl_6

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Figure 12. Heat capacity for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) molecules and SCl_6 .

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Table 1. Experimental and calculated properties of the SF₆ molecule.

| Parameter | Unit | Present | Ref. 31 | Ref. 32 ^d | Experiment |
|-----------------------------|------------------|---------|---------|----------------------|----------------------|
| Binding energy ^a | 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 ^b |
| ν_1 A _{1g} | cm ⁻¹ | 723.5 | — | 718 | 772.269 ^c |
| ν_2 E _g | cm ⁻¹ | 625.5 | — | 622 | 641.608 ^c |
| ν_3 F _{1u} | cm ⁻¹ | 938.1 | — | 931 | 947.289 ^c |
| ν_4 F _{1u} | cm ⁻¹ | 567.2 | — | 562 | 614.589 ^c |
| ν_5 F _{2g} | cm ⁻¹ | 477.9 | — | 476 | 523.449 ^c |
| ν_6 F _{2u} | cm ⁻¹ | 315.7 | — | 312 | 348.428 ^c |

^a SF₆ → S + 6F^b Table 8 in Ref. 4, p. 280^c Table 7 in Ref. 4, p. 280^d PWC calculation

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

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

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

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

Table 4. Frequencies of normal modes in [cm⁻¹].

| Mode | SF ₆ | SF ₅ H | SF ₄ H ₂ a | SF ₄ H ₂ b | SF ₃ H ₃ a | SF ₃ H ₃ b | SF ₂ H ₄ a | SF ₂ H ₄ b | SFH ₅ | SH ₆ | SCl ₆ |
|------|-----------------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------------------|-----------------|------------------|
| 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⁻¹].

| Mode | SF ₆ | SF ₅ H | SF ₄ H ₂ a | SF ₄ H ₂ b | SF ₃ H ₃ a | SF ₃ H ₃ b | SF ₂ H ₄ a | SF ₂ H ₄ b | SFH ₅ | SH ₆ | SCl ₆ |
|------|-----------------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------------------|-----------------|------------------|
| 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 ₆ | SF ₅ H | SF ₄ H ₂ a | SF ₄ H ₂ b | SF ₃ H ₃ a | SF ₃ H ₃ b | SF ₂ H ₄ a | SF ₂ H ₄ b | SFH ₅ | SH ₆ | SCH ₆ |
|------|-----------------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------------------|-----------------|------------------|
| 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 ₆ | O _h | 0.5801 | -0.0967 | - |
| SF ₅ H | C _{4v} | 0.5013 | -0.1148 | 0.0729 |
| SF ₄ H ₂ a | C _{2v} | 0.4224 | -0.1333 | 0.0553 |
| SF ₄ H ₂ b | D _{4h} | 0.4249 | -0.1419 | 0.0714 |
| SF ₃ H ₃ a | C _{3v} | 0.3396 | -0.1591 | 0.0459 |
| SF ₃ H ₃ b | C _{2v} | 0.3459 | -0.1643 | 0.0490 |
| SF ₂ H ₄ a | C _{2v} | 0.2613 | -0.2078 | 0.0386 |
| SF ₂ H ₄ b | D _{4h} | 0.2776 | -0.1619 | 0.0116 |
| SFH ₅ | C _{4v} | 0.1917 | -0.2248 | 0.0066 |
| SH ₆ | O _h | 0.1361 | - | -0.0227 |
| SCl ₆ | O _h | 0.3411 | - | -0.0568 |

Table 8. Thermodynamic properties.

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

^aZero Point Vibrational Energy.

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M. K. Bruska, J. Piechota

Molecular Simulation

RESEARCH NOTE

Density Functional Study of Sulfur Hexafluoride (SF₆) and its Hydrogen Derivatives.

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Abstract

Density functional study has been performed for a group of compounds derived from sulfur hexafluoride (SF₆) by consecutively substituting fluorine with hydrogen. SF₆ 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 SF₆ 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_{6-n}H_n (n=0...6) molecules have been obtained and discussed. For comparison, computational results for the SCl₆ 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 (SF₆) 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 SF₆ 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 SF₆
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, SF₆ is a candidate refrigerant to replace the chlorofluorocarbons (CFC's) which are damaging
13 the ozone layer. For an extensive review of SF₆ technical applications see, for example, [1] and
14 publications therein.

15 Because of its unique structure, unusual spectroscopy, and applied interest, the SF₆ 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 SF₆ provides good example of shape resonance phenomena. The
20 infrared active modes of octahedral molecules are of F_{1u} symmetry and ν₃ as well as ν₄ bands are
21 allowed in absorption [17]. In particular, the region of the ν₃ fundamental near 950 cm⁻¹ has very
22 strong absorption. The bond dissociation energy of SF₆ (to SF₅ + 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, SF₆ has become a classic molecule for the study of electron
25 attachment at ultralow electron energies. The attachment of low energy electrons to SF₆ results in
26 formation of a metastable negative ion by the process: SF₆ + e⁻ → SF₆⁻ [18,21]. An understanding
27 of the thermal electron attachment properties and temperature behaviour of rate constant for SF₆ 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 SF₆ 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 CO₂ 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⁻²ppb⁻¹)
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 SF₆ will be photodissociated there.
35 Therefore, although the concentration of SF₆ 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 SF₆ emissions can constitute a significant carbon-equivalent emission tonnage.

Deleted: Furthermore, SF₆ 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 ν₃ as well as ν₄ bands are allowed in absorption [6]. In particular, the region of the ν₃ fundamental near 950 cm⁻¹ has very strong absorption. The bond dissociation energy of SF₆ (to SF₅ + F) is 3.82 eV, but photodissociation is not observed until the photon energy exceeds ~10 eV [4].¶

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⁻¹ 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⁻²ppb⁻¹),
45 identified as trifluoromethyl sulfur pentafluoride (SF₅CF₃), has been detected in the atmosphere
46 [28,29]. It is supposed that SF₅CF₃ originates as a breakdown product of SF₆ formed by high-
47 voltage discharges in electric industry equipment [28]. Atmospheric lifetime of SF₅CF₃ (~800
48 years) is lower than that of SF₆, 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): CF₄, C₂F₆, C₃F₈, c-C₄F₈, SF₆, NF₃ and CHF₃, 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 CF₄ [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_{6-n}H_n (n=0...6) molecules where the fluorine atoms of SF₆ were consecutively replaced with the hydrogen atoms. The aim of the study is to look for potential industrial alternatives to SF₆ as well as to examine mechanisms that can contribute to its faster atmospheric decay. SCl₆ has been also taken into consideration to compare our results with a heavier analogue of the SF₆ molecule. To our best knowledge this is the first report on the properties of the SF_{6-n}H_n 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 DMol³ code [36,37] available as part of the Materials Studio 4.0 software environment [38]. For an extensive review of the DMol³ 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 DMol³ package in order to get stable and accurate results, as compared to experiment and other calculations.

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DMol³ 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 DMol³ 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 SF₆ 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 SF₆ 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 SF₆ molecule. The first and the most extensive work (however, without calculated vibrational frequencies) came from Tang and Callaway [39] who performed calculations for SF₆ in the local spin density (LSD) approximation. Delley [40] studied static deformations and vibrations of SF₆ 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 SF₆ molecule based on the DFT methodology. Molecular properties of SF₆ are collected in Table 1.

It can be seen from Table 1 that our results obtained for the SF₆ molecule are in good agreement with those presented in Ref. 39, and Ref. 40. The maximum deviation of calculated frequencies is at 49 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), in order to reduce the computational time whenever possible. The highest symmetry point group O_h is adopted by the SF₆ molecule, as well as by the SH₆ and SCl₆ ones. With the substitution of fluorine atoms with the hydrogen ones the symmetry is lowered, but symmetries of the SF_{6-n}H_n (n=1...5) molecules are consistent with the correlation table of the O_h group. For molecules SF_{6-n}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 DMol³ computations of other properties were performed at these final geometries.

Closer examination of structural data obtained shows that geometry of the SF_{6-n}H_n (n=1...6)

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molecules resembles that of the SF₆ 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 SF₂H₄ (a) with low, C_{2v} 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 SCl₆ the chlorine-sulfur distance is significantly larger and equals to 2.1461 Å.

The results obtained for binding energies for the SF_{6-n}H_n (n=0...6) series and SCl₆ are listed in Table 2. The SF₆ molecule has the highest binding energy as compared to the SF_{6-n}H_n (n=1...6) series. Interestingly enough, the SCl₆ and SH₆ molecules have similar values of binding energies. Since the SF₆, SH₆ and SCl₆ molecules have octahedral symmetry, as well as the SF₄H₂ (b) and SF₂H₄ (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_{6-n}H_n 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_{6-n}H_n system (in order to keep the Figure 3 as readable as possible we decided to label eigenstates only for SF₆ and SH₆ molecules). Because of the same molecular symmetry of the SF₆ and SH₆ molecules molecular orbitals have the same symmetry in their case. However, there are fewer electrons in SH₆ than in SF₆, so only 6 first single particle eigenstates in 3 energetically lowest states with symmetries A_{1g}, T_{1u} and E_g are occupied.

3.2 Optical properties

Explicit values of the frequencies and intensities of the normal modes for all the SF_{6-n}H_n (n=0...6) molecules are listed in Tables 4 and 5, respectively, supplemented with data obtained for SCl₆. In Table 6 square of first derivatives of molecular dipole moments wrt infrared active normal modes are shown.

The infrared absorption spectrum of SF₆ is composed of two bands. Only ν₃ and ν₄ modes with F_{1u} symmetry satisfy dipole selection rules and are allowed in absorption. Their maxima are located at 567.2 and 938.06 cm⁻¹ 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_{6-n}H_n (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_{nw} is the frequency of transition between n and w levels, and B_{nw} is the Einstein coefficient for induced emission, which can be expressed as:

Deleted: Trend in binding energy for the SF_{6-n}H_n (n=0...6) series and SCl₆ is illustrated in Figure 3.

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

in which μ_{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 SCl_6 and SH_6 are again quite similar to SF_6 . As they adopt O_h point group symmetry, the infrared spectra are analogous to this of SF_6 . The difference is in the frequencies of normal modes and intensities of their absorption. SCl_6 , as a heavier molecule, has lower vibrational transition intensity as well as lower frequencies of normal modes. In contrast to this, SH_6 has a much higher vibrational transition intensity and higher frequencies of normal modes. This means that SH_6 absorbs even more radiation than SF_6 , but in the range of higher frequencies. SH_6 has also nearly two times lower binding energy than SF_6 and, as such, is less stable.

It is also worth to mention that strongest absorption band of 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 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 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 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: SF_6 , SF_4H_2 (b), SF_2H_4 (b), SH_6 and SCl_6 . The SF_5H has almost two times smaller magnitude of dipole moment than SFH_5 , although charges on constituent atoms are larger in SF_5H than in SFH_5 , and both molecules have the same symmetry. One can assume that for SFH_5 the charge and induced dipole contributions have the same polarity that account for its large dipole moment, in contrast to SF_5H . In case of the SF_3H_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 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 SCl_6 are the best of all the molecules studied here, in particular better than these of SF_6 . The industrial usage of SF_6 instead of SCl_6 is due to greater stability of SF_6 than SCl_6 (bonding energy for SF_6 is twice higher than that for 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 SF_6 . For other molecules with octahedral symmetry, such as SH_6 and 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 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.

Acknowledgements

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List of Figures

Figure 1. Equilibrium geometries of the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) series and SCl_6 in their ground states: a. SF_6 , O_h symmetry; b. SF_5H , C_{4v} symmetry; c. SF_4H_2 (a), C_{2v} symmetry; d. SF_4H_2 (b), D_{4h} symmetry; e. SF_3H_3 (a), C_{3v} symmetry; f. SF_3H_3 (b), C_{2v} symmetry; g. SF_2H_4 (a), C_{2v} symmetry; h. SF_2H_4 (b), D_{4h} symmetry; i. SFH_5 , C_{4v} symmetry; j. SH_6 , O_h symmetry; k. SCl_6 , O_h symmetry.

Figure 2. Interatomic distances in the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) series and SCl_6 a. fluorine-sulfur distances; b. hydrogen-sulfur distances.

Figure 3. Single particle eigenvalues for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) series. For readability only eigenstates for SF_6 and SH_6 molecules are labelled.

Figure 4. Entropy as a function of temperature for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) molecules and SCl_6 .

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Figure 6. Calculated absorption spectra for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) molecules and SCl_6 in their ground states: a. SF_6 , O_h symmetry; b. SF_5H , C_{4v} symmetry; c. SF_4H_2 (a), C_{2v} symmetry; d. SF_4H_2 (b), D_{4h} symmetry; e. SF_3H_3 (a), C_{3v} symmetry; f. SF_3H_3 (b), C_{2v} symmetry; g. SF_2H_4 (a), C_{2v} symmetry; h. SF_2H_4 (b), D_{4h} symmetry; i. SFH_5 , C_{4v} symmetry; j. SH_6 , O_h symmetry; k. SCl_6 , O_h symmetry.

Figure 7. Total entropy for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) molecules and SCl_6 .

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Deleted: Figure 9. Vibrational entropy for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) molecules and SCl_6 .

Figure 10. Zero Point Vibrational Energy (ZPVE) for the $\text{SF}_{6-n}\text{H}_n$ ($n=0\dots6$) molecules and SCl_6 .

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Table 8. Thermodynamic properties.

Table 1. Experimental and calculated properties of the SF₆ molecule.

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

^a SF₆ → S + 6F

^b Table 8 in Ref. 18, p. 280

^c Table 7 in Ref. 18, p. 280

^d PWC calculation

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

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

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

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

Table 4. Frequencies of normal modes in [cm⁻¹].

| Mode | SF ₆ | SF ₅ H | SF ₄ H ₂ a | SF ₄ H ₂ b | SF ₃ H ₃ a | SF ₃ H ₃ b | SF ₂ H ₄ a | SF ₂ H ₄ b | SFH ₅ | SH ₆ | SCl ₆ |
|------|-----------------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------------------|-----------------|------------------|
| 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⁻¹].

| Mode | SF ₆ | SF ₅ H | SF ₄ H ₂ a | SF ₄ H ₂ b | SF ₃ H ₃ a | SF ₃ H ₃ b | SF ₂ H ₄ a | SF ₂ H ₄ b | SFH ₅ | SH ₆ | SCl ₆ |
|------|-----------------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------------------|-----------------|------------------|
| 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 ₆ | SF ₅ H | SF ₄ H ₂ a | SF ₄ H ₂ b | SF ₃ H ₃ a | SF ₃ H ₃ b | SF ₂ H ₄ a | SF ₂ H ₄ b | SFH ₅ | SH ₆ | SCl ₆ |
|------|-----------------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|------------------|-----------------|------------------|
| 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 ₆ | O _h | 0.5801 | -0.0967 | - |
| SF ₅ H | C _{4v} | 0.5013 | -0.1148 | 0.0729 |
| SF ₄ H ₂ a | C _{2v} | 0.4224 | -0.1333 | 0.0553 |
| SF ₄ H ₂ b | D _{4h} | 0.4249 | -0.1419 | 0.0714 |
| SF ₃ H ₃ a | C _{3v} | 0.3396 | -0.1591 | 0.0459 |
| SF ₃ H ₃ b | C _{2v} | 0.3459 | -0.1643 | 0.0490 |
| SF ₂ H ₄ a | C _{2v} | 0.2613 | -0.2078 | 0.0386 |
| SF ₂ H ₄ b | D _{4h} | 0.2776 | -0.1619 | 0.0116 |
| SFH ₅ | C _{4v} | 0.1917 | -0.2248 | 0.0066 |
| SH ₆ | O _h | 0.1361 | - | -0.0227 |
| SCl ₆ | O _h | 0.3411 | - | -0.0568 |

Table 8. Thermodynamic properties.

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

^aZero Point Vibrational Energy.