An ab initio MO Study of the Gas-Phase Reactions 2 $SF_2 \rightarrow FS{-}SF_3 \rightarrow S{=}SF_4$ − Molecular Structures, Reaction Enthalpies and Activation Energies[‡]

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High level ab initio MO calculations at the G3(MP2) level of theory were employed to study the molecular structures of SF_2, $FSSF_3$, and SSF_4, as well as the dimerization of gaseous SF_2 to $FSSF_3$ and the isomerization of $FSSF_3$ to SSF_4. The dimerization of SF_2 was calculated to be an exothermic process (ΔH°_{298} = −77 kJ·mol^{-1}) with an activation enthalpy ($\Delta H^{\neq}_{298}$) of 65 kJ·mol^{-1}. The transition state of the dimerization reaction is characterized by a bridging fluorine atom that undergoes a 1,2-shift, and a weak sulfur-sulfur single bond. The calculated lowest-energy structure of $FSSF_3$ (**2a**) is in excellent agreement with the experimentally derived structure, with the –SF group in an equatorial position of the distorted pseudo-trigonal-bipyramid at the central sulfur atom. A significantly less stable $FSSF_3$ conformer **2b**, 76 kJ·mol^{-1} higher in energy, has the –SF group in an axial position. Unimolecular rearrangement of $FSSF_3$ (**2a**) to the trigonal-bipyramidal SSF_4 (**3**), by a 1,2-fluorine shift (**TS2**), is endothermic by 37 kJ·mol^{-1} and is inhibited by a large activation barrier of 267 kJ·mol^{-1}. SSF_4 is predicted to be an observable species in the gas phase. Calculated infrared spectra of **2a** and **3** are also reported.

Introduction

Sulfur forms at least eight binary fluorides representing all seven oxidation numbers between 0 and +6:[1]

$$SF_2 \quad SF_4 \quad SF_6 \quad S{=}SF_2 \quad FS{=}SF$$
$$FS{-}SF_3 \quad FS{-}S{-}SF_3 \quad F_5S{-}SF_5$$

In addition, preparation of the chain-like difluorotrisulfane (S_3F_2) and difluorotetrasulfane (S_4F_2) have been reported.[2] While SF_4 and SF_6 are industrial products,[3] the other fluorides are too unstable, toxic, and/or reactive for any large scale production and application. However, these compounds are intermediates in the preparation of the higher sulfur fluorides and are therefore of fundamental interest.

Disproportionation reactions are a characteristic feature in the chemistry of all of the above mentioned species except for SF_4, S_2F_{10}, and SF_6. One of the most intriguing disproportionation reactions is the reversible dimerization of SF_2 to form S_2F_4, which was first observed by Seel et al.[4]

$$2\,SF_2 \rightleftarrows FS{-}SF_3 \tag{1}$$

In this reaction, a sulfur−sulfur bond is formed by combination of two atoms that must be positively charged because of the large difference in electronegativity between fluorine and sulfur. Willner et al. managed to determine the reaction enthalpy [$\Delta H^\circ_{298}(1) = 69 \pm 2$ kJ·mol^{-1}] despite enormous experimental difficulties, and observed that the reaction rate depends on the nature of the walls of the container.[5] The authors also noted that the equilibrium is established only partly because of the irreversible side reaction shown in Equation (2).

$$SF_2 + FS{-}SF_3 \rightarrow S{=}SF_2 + SF_4 \tag{2}$$

Subsequently, another side reaction according to Equation (3) was discovered: $FS{-}S{-}SF_3$ is formed when SF_2 and $S{=}SF_2$ are condensed together.[6]

$$SF_2 + S{=}SF_2 \rightarrow FS{-}S{-}SF_3 \tag{3}$$

The structure of SF_2 has been determined by microwave spectroscopy. The internuclear distances were obtained as 158.7 pm and the bond angle as 98.5° (C_{2v} symmetry).[7] SF_2 is rather unstable and can therefore only be studied in dilute vapour or using matrix isolation at low temperature. Because of reactions in Equation (1) and Equation (2), the formation of SF_2 is usually accompanied by S_2F_2 and S_2F_4. The latter compound is a colourless liquid, which is best prepared by fluorination of elemental sulfur or carbonyl sulfide followed by fractional distillation of the product mixture.[8] This reaction primarily yields gaseous SF_2 that dimerizes to S_2F_4 on condensation. The structure of S_2F_4 was investigated by electron diffraction (ED), microwave spectroscopy (MW), and ab initio MO calculations at the HF level.[9] The instability of the compound, the possible existence of several conformers and by-products, and the

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low symmetry of the molecule resulting in twelve independent geometrical parameters, made the structural analysis using a single experimental method impossible. This molecule was even termed "recalcitrant".[9] The geometry derived from the combination of ED and MW data using force constants computed at HF level is shown in Figure 1.

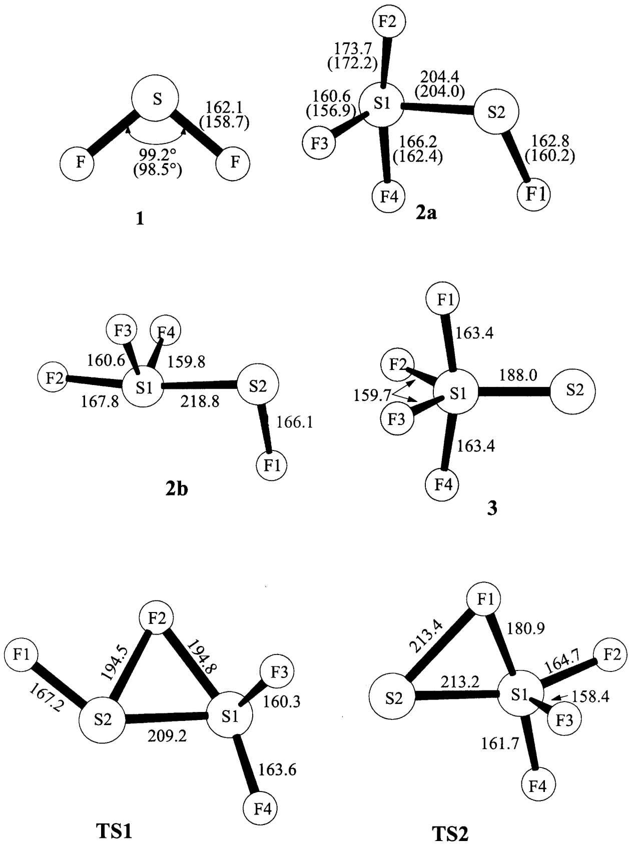

Figure 1. Calculated equilibrium structures of sulfur fluorides SF_2 (**1**), $FSSF_3$ (two conformers, **2a** and **2b**) and SSF_4 (**3**), and the transition states **TS1** and **TS2**. Internuclear distances in pm; experimental values of **1** and **2a** in parentheses. Bond angles and torsion angles are given in Table 1

There are various possible conformations of 1,2-difluorodisulfane-1,1-difluoride ($FSSF_3$). They can be considered as derivatives of the pseudo-trigonal-bipyramidal SF_4 molecule in which one equatorial (*e*) fluorine atom has been substituted by an $-SF$ group. For the gas-phase structure of $FSSF_3$, the F_eSSF torsion angle was determined as 95° and the axial (*a*) F_aSF_a bond angle as 167.0°.[9] The ^{19}F NMR spectrum of liquid $FSSF_3$ recorded at −80° C shows signals for four non-equivalent fluorine atoms.[8] The same holds for gaseous $FSSF_3$ at ambient temperature,[10] in sharp contrast to SF_4 which undergoes rapid pseudo-rotation with an activation enthalpy of only 47 $kJ \cdot mol^{-1}$ at 298 K.[11]

No experimental evidence for the existence of other isomers of S_2F_4, such as $F_2S{=}SF_2$ and $S{=}SF_4$, has so far been reported in the literature. However, these species were investigated by ab initio MO calculations. Oberhammer et al. reported that $S{=}SF_4$ dissociated into SF_4 and S on attempts to optimize its geometry at the HF/3-3-21 level, although the oxygen derivative $O{=}SF_4$ is a well-known compound.[9] The same authors found that the hypothetical molecule $F_2S{=}SF_2$ corresponds to a minimum on the PES, but it lies 440 $kJ \cdot mol^{-1}$ above $FS{-}SF_3$ (HF/3-3-21 level).[9]

In this work, we report high level ab initio MO calculations on the structures and relative stabilities of SF_2, $FS{-}SF_3$, $S{=}SF_4$, and $F_2S{=}SF_2$. In addition, we examine the reaction profiles of the dimerization reaction of SF_2 and the rearrangement $FS{-}SF_3 \rightarrow S{=}SF_4$.

Computational Methods

Standard ab initio MO calculations were performed using the Gaussian 98 series of programs.[12] The energies of various equilibrium structures and transition states were examined using the G3(MP2) level of theory.[13] In brief, the G3(MP2) method is a composite procedure that aims at providing an accurate approximation to the high level of theory at QCISD(T)/GTMP2LARGE//MP2(full)/6-31G(d),

Table 1. Calculated bond angles and torsional angles of SF_2 (**1**), $FSSF_3$ (**2a** and **2b**), SSF_4 (**3**), the transition states (**TS1** and **TS2**), and the experimental data of **2a**

parameter	**2a** (calc)[a]	**2a** (expt)	**2b**[a]	**3** (C_{2v})[a]	**TS1**[a]	**TS2**[a]
α(FSF)	86.7 (F2S1F3)		85.7 (F2S1F3)	85.3 (F1S1F2)	79.7 (F1S2F2)	96.6 (F1S1F2)
	88.6 (F3S1F4)		87.2 (F2S1F4)	106.9 (F2S1F3)	87.0 (F2S1F3)	88.8 (F1S1F3)
	164.9 (F2S1F4)	167.0	101.7 (F3S1F4)	164.2 (F1S1F4)	93.1 (F3S1F4)	170.5 (F1S1F4)
						92.9 (F2S1F4)
						90.4 (F2S1F3)
						91.9 (F3S1F4)
α(FSS)	103.9 (F1S2S1)	105.9	87.1 (F1S2S1)	97.9 (F1S1S2)	137.2 (F1S2S1)	65.0 (F1S1S2)
	74.9 (F2S1S2)	76.0	171.6 (F2S1S2)	126.5 (F2S1S2)	105.1 (F3S1S2)	158.7 (F2S1S2)
	107.4 (F3S1S2)	104.9	86.1 (F3S1S2)		100.4 (F4S1S2)	99.3 (F3S1S2)
	92.8 (F4S2S1)	92.2	92.3 (F4S1S2)			105.5 (F4S1S2)
τ(FSSF)	178.3 (F1SSF2)		173.4 (F1SSF2)		2.4 (F1S2S1F2)	
	96.6 (F1SSF3)		158.5 (F1SSF3)		78.7 (F1S1S2F3)	
	7.3 (F1SSF4)	95±4	-99.9 (F1SSF4)		174.9 (F1S2S1F4)	
					172.5 (F2S1S2F4)	

[a] MP2(full)/6-31G* values (in degrees).

with the incorporation of the zero-point energy and higher level corrections. This level of theory is usually within ± 6 kJ·mol^{-1} of accurate experimental values.[13] Charge density analysis, at the MP2/6-31G* level, was performed using the natural bond orbital (NBO) approach.[14] Unless otherwise noted, all relative energies reported in this publication are given as $\Delta H°_{298}$ and correspond to the G3(MP2) level, while all structural parameters were obtained at the MP2(full)/6-31G* level.

Results and Discussion

Structures and Relative Stabilities

The calculated structures of all investigated molecules are shown in Figure 1, and further geometrical details are given in Table 1.

The experimental structure of SF_2 (**1**) is well reproduced by our calculations, although the calculated sulfur-fluorine distances are slightly shorter than the experimental values (see Figure 1). The sulfur atom bears an atomic charge (NBO) of +1.04 units. In the case of $FS-SF_3$, two conformers were located on the potential energy hypersurface. These conformers can be interconverted by pseudo-rotation, i.e. exchange of one equatorial for one axial ligand. As expected, the more stable isomer (**2a**) has the −SF group in an equatorial position and both axial positions occupied by fluorine as the most electronegative atoms in the molecule. In contrast, the less stable form (**2b**) has one axial position occupied by the −SF group. The total and relative energies of these species are given in Table 2.

Conformer **2a** was predicted to be more stable than **2b** by 76 kJ·mol^{-1}. This finding is in agreement with the observed structure of S_2F_4, which corresponds to **2a**. A comparison of the calculated and experimental structures of **2a** shows an excellent agreement for the SS bond length (within 0.4 pm), while the calculated SF bonds are 1.5−3.8 pm longer than the experimentally derived values. The bond angles agree within 3°. Only one torsional angle was reported for the experimental structure [τ(F3−S−S−F1) = 95±4°], in excellent accord with the calculated value (96.6°). The atoms F1−S−S−F4 are almost coplanar (τ = 7.3°). Interestingly, the S−F4 bond (166.2 pm) is significantly shorter than the other axial bond S−F2 (173.7 pm), although one would expect the opposite trend due to the repulsion between the atoms F4 and F1. Atoms F1 and F2 have a practically ideal *trans* position (τ = 178.3°).

The less stable $FS-SF_3$ conformer **2b** is also of C_1 symmetry, although the structure is just slightly distorted from a C_{2v} symmetry. In comparison with the structure of **2a**, the most remarkable differences are the rather long SS bond (218.8 pm) and the F2−S−S−F1 torsion angle of 173.4°. This places the atom F1 on the same side as one usually expects to find the "axial lone pair" at the sulfur atom in this pseudo-trigonal-bipyramidal geometry (Figure 1). These two structural features are probably the main reasons for the lower stability of **2b**. As in the case of **2a**, the axial SF bond (167.8 pm) of **2b** is longer than the two equatorial bonds (159.8 and 160.6 pm). The higher stability of **2a** compared to **2b** is in line with the valence shell electron pair repulsion (VSEPR) model,[15] which predicts that the conformer with the most electronegative substituents in the *axial* positions of a trigonal bipyramid is the most stable one.

A second isomer of S_2F_4, namely thiothionyltetrafluoride $S=SF_4$ (**3**), has a distorted trigonal-bipyramidal structure of C_{2v} symmetry. This derivative of hexavalent sulfur is 37 kJ·mol^{-1} less stable than **2a**, but surprisingly 39 kJ·mol^{-1} more stable than **2b**. The structure of **3** is very similar to that of the oxygen analogue, thionyltetrafluoride $O=SF_4$.[16] All SF bond lengths and bond angles show normal values. The SS bond length of 188.0 pm may be compared with those in the S_2 molecule (189.2 pm), S=S=O (188.2 pm), $S=SF_2$ (186.0 pm), and FS=SF (188.8 pm), which are considered as double bonds on the basis of their bond strength.[17] It is customary to indicate this strength by the symbol S=S, although it is not claimed that there exists a π bond in addition to the σ bond. In the case of **3**, the relatively short SS bond length may be attributed to the significant π interaction between the *d* orbital of S1 and *p* orbital of S2. The plausible description as a "semipolar" S^+S^- bond is only partly supported by the calculated atomic charges of SSF_4, which are given in Table 3. The NBO atomic charges of the central sulfur atoms (S1) in **2a**, **2b**, and **3** are +1.7, +1.8, and +2.4, respectively, while the terminal sulfur atom of **3** bears a rather small negative charge of −0.3 units. The dipole moment of **3** is 0.14 D, while **2a** has a dipole moment of 0.97 D.

Table 2. Total energies (in Hartrees), zero-point energies (ZPE, in kJ·mol^{-1}), and relative enthalpies (in kJ·mol^{-1}) of the sulfur fluorides SF_2, S_2F_4, SSF_4, and the transition states **TS1** and **TS2**

Species	Total energy[a]	ZPE[b]	$H°_{298} - H°_0$[a]	$\Delta H°_{298}$[a]	$\Delta G°_{298}$[a]
SF_2 (**1**)	−597.21504	13.4	11.3	76.7[c]	23.2[c]
$FS-SF_3$ (**2a**)	−1194.45819	37.8	19.6	0.0	0.0
$FS-SF_3$ (**2b**)	−1194.42973	36.5	20.7	75.8	71.0
$S=SF_4$ (**3**)	−1194.44320	43.7	17.6	37.3	43.4
TS1	−1194.40401	33.2	19.4	142.0	141.9
TS2	−1194.35631	34.6	19.4	267.3	266.0

[a] G3(MP2) level. − [b] HF/6-31G* values. − [c] Data for 2 mol SF_2 with respect to **2a**.

Table 3. Calculated NBO atomic charges and dipole moments (μ, Debyes) of the S_2F_4 isomers **2a**, **2b**, and **3**, and the transition states **TS1** and **TS2**

Atom	$FSSF_3$ (**2a**)	$FSSF_3$ (**2b**)	SSF_4 (**3**)	**TS1**	**TS2**
NBO atomic charges[a]					
S1	+1.68	+1.84	+2.40	+1.52	+2.13
S2	+0.58	+0.32	−0.30	+0.73	+0.07
F1	−0.51	−0.53	−0.55	−0.55	−0.60
F2	−0.64	−0.61	−0.49	−0.64	−0.54
F3	−0.51	−0.52	−0.49	−0.50	−0.50
F4	−0.60	−0.51	−0.55	−0.57	−0.56
dipole moments[a]					
μ	0.97	0.56	0.14	2.43	1.05

[a] MP2/6-31G* level.

In contrast to the earlier findings,[16] we were unable to locate any stable equilibrium structure for the hypothetical isomer $F_2S{=}SF_2$, both on the HF/6-31G* and MP2/6-31G* levels of theory. It collapses to a weakly-bound SF_2 dimer upon geometry optimization (without symmetry constraints). The optimized C_{2h} structure has a short SS distance, but it corresponds to a second-order saddle point on the S_2F_4 potential energy surface.

Reaction Enthalpies and Transition States

As seen in Table 1, the calculated enthalpy of the dimerization reaction of Equation (1) is $-77\ kJ{\cdot}mol^{-1}$, slightly larger than the experimental value[5] of $-69{\pm}2\ kJ{\cdot}mol^{-1}$ which is probably less accurate due to the difficulties mentioned in the Introduction. The dimerization reaction proceeds by an interaction between the positively charged sulfur atom of one molecule and one of the negatively charged fluorine atoms of a neighbouring molecule, while the internuclear SS distance simultaneously decreases. In other words, the process occurs via an SS bond formation and a simultaneous 1,2-fluorine shift, which is readily reflected in the transition state **TS1** (Figure 1): the S1, F2, and S2 atoms form an almost symmetrical (C_{2v}) triangle with SF distances of 194.5 and 194.8 pm and an SS separation of 209.2 pm. The latter value corresponds approximately to a single bond.[17] The F1−S2−S1−F2 atoms are almost coplanar (τ = 2.4°) while the F1−S−S−F3 and F1−S−S−F4 torsion angles are 78.7° and 174.9°, respectively.

The calculated activation enthalpy of $65\ kJ{\cdot}mol^{-1}$ ($\Delta H^{\neq}_{298}$) for the dimerization of SF_2 suggests that this equilibrium is unlikely to be rapidly established at room temperature (see Figure 2). In fact, it has been observed that the reaction rate depends on the surface of the container,[5] which may act as a catalyst. Since **TS1** has a larger dipole moment (2.43 D; Table 3) than **2a** (0.97 D), polar surface sites may support its formation. The calculated activation enthalpy for the dissociation of $FSSF_3$, i.e. the reverse of reaction of Equation (1), is $142\ kJ{\cdot}mol^{-1}$. The observed activation enthalpies $\Delta H^{\neq}_{298}$ (12.5 and $52\ kJ{\cdot}mol^{-1}$ in two experiments) are much lower, obviously because of the surface catalysis mentioned above.[5]

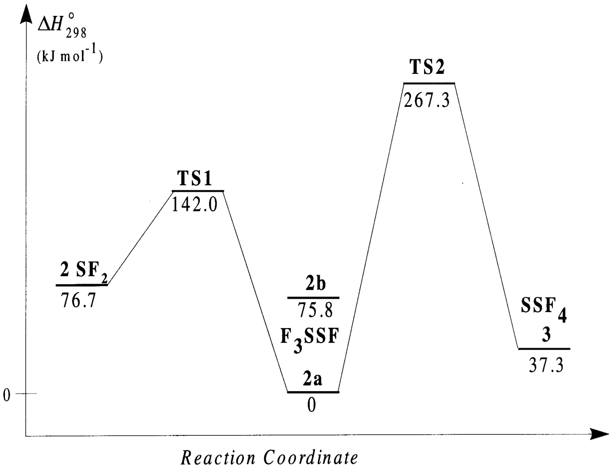

Figure 2. Schematic energy level diagram for the dimerization of SF_2 to $FSSF_3$ (**2a**) via transition state **TS1**, and for the isomerization of $FSSF_3$ (**2a**) to SSF_4 (**3**) via **TS2**. Calculated relative energy of the less stable conformer of $FSSF_3$ (**2b**) is also included

In the industrial production of SF_6 from elemental sulfur and fluorine, which is a highly exothermic process, the formation of SF_2 as an intermediate is very likely. Its exothermic dimerization to $FSSF_3$ explains the formation of the extremely toxic side-product S_2F_{10}; this species has the connectivity $F_5S{-}SF_5$ and is likely to originate from $FS{-}SF_3$ by partial fluorination.

The unimolecular isomerization of $FS{-}SF_3$ (**2a**) to $S{=}SF_4$ (**3**), by a 1,2-fluorine shift via transition state **TS2**, requires an activation enthalpy $\Delta H^{\neq}_{298}$ of $267\ kJ{\cdot}mol^{-1}$. This means that **3** is protected by an energy barrier of $230\ kJ{\cdot}mol^{-1}$ against rearrangement back to **2a** (Figure 2). Thus we predict that species **3** is experimentally accessible, presumably in a matrix isolation experiment. The calculated vibrational wavenumbers of **3** are given below. The structure of the transition state **TS2** for the interconversion of **2a** and **3** (Figure 1) is of C_1 symmetry with a fluorine atom (F1) bridging the SS bond in an asymmetrical manner. This SS bond (213.2 pm) is longer than a typical single bond (205 pm)[17] and the bridging SF distances of 180.9 and 213.4 pm are also significantly longer than SF single bonds (160 pm). The other three SF bonds are of normal single bond lengths.

We have also computed the thermodynamic data of the formation of $SSF_2 + SF_4$ from $SF_2 + FSSF_3$, i.e. for reaction of Equation (2). The calculated reaction enthalpy is $-6\ kJ{\cdot}mol^{-1}$ (ΔH°_{298}) at the G3(MP2) level.

Harmonic Fundamental Vibrations

The calculated wavenumbers of the harmonic fundamental vibrations of $FSSF_3$ and SSF_4 were calculated at the MP2/6-311+G(2d) level of theory and are given in Table 4 together with the reported infrared absorptions[8] of $FSSF_3$.

Table 4. Fundamental harmonic vibrations [MP2/6-311+G(2d) level] of $FSSF_3$ (**2a**) and SSF_4 (**3**), and observed infrared spectrum of **2a**. Wavenumbers in cm^{-1} and absolute infrared intensities in km mol^{-1} (given in parentheses). Calculated wavenumbers were scaled by 1.05. Notation used: *e* equatorial, *a* axial, *t* terminal, ν stretching (ν_a asymmetric and ν_s symmetric), δ bending, ρ rocking, ω wagging, and τ for torsion

	F_tSSF_3 (C_1)		SSF_4 (C_{2v})	
experiment	calculated	assignment	calculated	assignment
825 vs	829 (198)	$\nu(SF_t)$	a_1: 918 (476)	$\nu(SS)$
805 vs	805 (219)	$\nu(SF_e)$	b_1: 856 (175)	$\nu_a(SF_a)$
675 vs	681 (265)	$\nu(SF_a)$	b_2: 773 (383)	$\nu_a(SF_e)$
620 s	635 (604)	$\nu(SS)$	a_1: 674 (0.6)	$\nu_s(SF_a) + \nu_s(SF_e) + \nu(SS)$
524 m	531 (27)	$\nu(SF_a)$	a_1: 598 (11)	$\nu_s(SF_e) + \nu_s(SF_a) + \nu(SS)$
462 vw	458 (6)	$\delta(F_eSF_a)$	b_2: 547 (18)	$\omega(F_aSF_a)$
412 w	412 (15)	$\delta(F_aSF_e)$	a_2: 536 (0)	$\delta(F_aSF_a) + \delta(F_eSF_e)$
350 w	344 (12)	$\delta(F_aSS)$	a_1: 502 (25)	$\delta(F_eSF_e) + \delta(F_aSF_a)$
	273 (3)	$\delta(F_tSS)$	b_1: 494 (5)	$\omega(F_eSF_e)$
	224 (4)	$\delta(F_aSS)$	b_2: 376 (0.6)	$\rho(F_eSF_e)$
	211 (6)	$\tau(F_tSSF_e)$	b_1: 220 (0)	$\rho(F_aSF_a)$
	136 (0.1)	$\tau(F_tSSF_a)$	a_1: 193 (0.5)	$\delta(F_aSF_a) + \delta(F_eSFF_e)$

The wavenumbers were scaled by a factor of 1.05, which was obtained by a linear least square fit to the experimental wavenumbers listed in the Table 4. There is a very good agreement between observed and calculated wavenumbers and infrared intensities of **2a**. The assignments of several normal modes are only approximate since there is a strong coupling between some fundamentals due to the low symmetry of the molecule. The same holds for the SS stretching mode and the symmetric stretching vibration of the equatorial SF_2 group in SSF_4 (**3**); these two fundamentals belong to the same symmetry class A_1.

Summary

We have shown that the molecular structure of $FSSF_3$ derived from microwave spectroscopy, electron diffraction data, and HF calculations[9] is essentially correct. For the first time, the energy differences between several S_2F_4 isomers were calculated at a high level of theory. The dimerization of SF_2, producing $FSSF_3$, proceeds via a triangular transition state that corresponds to a combination of a new SS bond formation and a 1,2-fluorine shift. The isomerization of $FSSF_3$ to SSF_4 proceeds via a 1,2-fluorine shift. Both reactions are calculated to have rather high activation barriers. With such a high barrier, the hypothetical SSF_4 molecule, which is metastable towards unimolecular rearrangement to the more stable $FSSF_3$, should be an observable species in the gas phase.

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