Investigation of Some Sulphur Halides – An Application of the Pseudopotential Method

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Semilocal pseudopotentials are used in combination with a density-functional approximation for the correlation energy and special optimized basis sets to investigate the sulphur halides SF, SF_2, SF_3, FSSF, SSF_2, SCl, SCl_2, ClSSCl and $SSCl_2$. It turns out that the inclusion of d-orbitals in the basis set playes a significant role with respect to the quality of the calculated molecular parameters. Properties of SF_3 are calculated for the first time, and the differences between the disulphur difluorides and the disulphur dichlorides are explained.

1. Introduction

Sulphur is one of the most important and versatile elements. Among the immense quantity of sulphur compounds the pure halides form a rather limited area which has an enormous fascination. It is the aim of this paper to point out some of the questions concerning a better understanding of the sulphur halides. Because of the special behaviour of some small sulphur halides, which nevertheless can serve as model compounds for the whole group, and on computational grounds we have considered the molecules SF, SF_2, SF_3, SCl, SCl_2, FSSF, SSF_2, ClSSCl and the unknown $SSCl_2$. For SF_3 we present the first theoretical investigation. In addition to a special analysis of the importance of d-orbitals in sulphur-sulphur- and sulphur-halogen-bonds some calculated properties of the di- and triatomic compounds are compared with experimental values. The condition of the S–F-bonds in SF_3 is examined together with a prediction for the geometry of this molecule. The features of the S–S-bonds in the dihalogen disulfanes and thiothionyl halides are compared, and an explanation is given for the nonexistence of thiothionyl chloride.

To calculate the molecular properties we used the pseudopotential approach, which was employed for the first time by Hellmann [1] and Gombás [2]. The basic idea of this method is to replace the inner electrons of the atoms which build up the molecule by a potential, for these core electrons mostly do not affect the chemical behaviour of the molecule. In this manner the dimension of the Roothaan-Hartree-Fock and the secular problem can be reduced without a significant loss of accuracy of the calculation, if only the pseudopotential is well-chosen.

2. The Method

The first publications with the aim to give a theoretical foundation of the pseudopotential concept came from Phillips and Kleinman [3] and other authors, particularly Austin, Heine and Sham [4], who laid down the first general pseudopotential theory for systems described by an effective one-electron Hamiltonian. Weeks, Hazi and Rice [5] generalized this result for the case of the multi-electron operator. An alternative approach to generate a unified theory of the pseudopotential was proposed by Szasz and Brown [6].

In practice the exact pseudopotential expression is often approximated by a simple analytical term with some free parameters, which are adjusted to the experimental energies of the ground and first excited terms of the one-valence-electron ion of the respective atom. Based on the work of Schwarz [7], Stoll and coworkers [8] have proposed a semilocal potential of the form

$$V_l(r) = -Z^R/r + \sum_l (B_l \exp(-\beta_l r^2) + C_l \exp(-\gamma_l r^2)) \boldsymbol{P}_l ,$$

which is used in the present work. Pseudopotentials are generally nonlocal both in the quantum number

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Table 1. Pseudopotential parameters.

	Sulphur	Fluorine	Chlorine
Z^R	6	7	7
$\beta_{0,1}$	5.33	23.1	6.88
$\gamma_{0,1}$	2.67	11.5	3.44
β_2	4.04	17.5	5.21
γ_2	2.02	8.73	2.61
B_0	54.618	103.926	67.064
C_0	6.2295	20.205	12.499
B_1	26.421	−4.3040	30.412
C_1	7.4331	0.15282	12.457
B_2	−6.0854	−10.380	−7.4066
C_2	−0.18201	1.3593	−0.31531

n and l. The non-locality in n is omitted in the above ansatz, but the l-dependence is taken into account by including the projectors $\boldsymbol{P}_l$, which operate on the l-dependent angular terms of the basis functions. Z^R is the charge of the atomic core. Wedig [9] has generated potentials with only one l-dependent term. He got a linear relation between the optimized exponents and the respective reciprocal square of the approximately calculated atomic radius. So it is possible to choose splitted optimal exponents for the pseudopotentials used in the present work, and one is able to use a linear least-squares-fit to adjust the coefficients B_l and C_l, so that the two lowest energies of the different l excitation spectra are reproduced. In this manner we obtain the pseudopotential parameters shown in Table 1.

The correlation energy is calculated within the framework of the local spin-density approximation according to the method of Stoll [10], which has the provision to exclude the self-correlation of the electrons. We use the formula of Vosko, Wilk and Nusair [11] to calculate the correlation energy per electron.

The presented investigation was carried out with the aid of a modified version of the program Gaussian 76 [12], which uses cartesian gaussian type functions to generate the Slater-determinant. Since the purpose of pseudopotentials is to remove the core electrons from further consideration, it is no longer necessary to assemble basis functions for describing the high electron density in the range of the atomic nuclei. There are two possibilities to construct basis sets which are appropriate for pseudopotential calculations. On the one hand one can cancel the functions with high exponent values in the basis sets for common Hartree-Fock calculations, and on the other hand it is possible to produce special pseudopotential-adapted basis sets. To do this we calculated the atoms sulphur, fluorine and chlorine by use of pseudopotentials and extended basis sets, chose a suitable orbital for each quantum number l and reduced the description of the orbital, given by the exponents and the vector of the coefficients, by help of a non-linear optimization method to a description in less dimensions, i.e. the number of basis functions necessary to describe the orbital is reduced. One has to look for the minimum of

$$\int \left\{ \sum_{j=1}^{J} c_{ij} \chi_j(r) - \sum_{k=1}^{K} c_{ik} \chi_k(r) \right\}^2 \mathrm{d}r$$

with respect to the coefficients c_{ik} and the exponents α_k by use of the gradient method of Murtagh and Sargent [9, 13]. J is larger than K and the functions χ_k constitute the small basis. In this work we made use of both possibilities to generate basis sets of triple-zeta quality. Set I was extracted out of the basis recently given by Tavouktsoglou and Huzinaga [14], set II was adapted to our pseudopotentials in the above manner. The exponents of the extended and the reduced basis are shown in Table 2 together with the characteristics of the non-linear regression. Test calculations for the ionization energies yielded in both cases very similar and mostly satisfactory results.

It is also the purpose of this paper to answer the question, whether the application of basis sets augmented by d-functions is important only to describe polarization effects or has a comprehensive influence on the description of the bonds. So it became necessary to find exponents for d-functions of sulphur, fluorine and chlorine. To achieve this we provided the basis sets I and II with d-functions and optimized the exponents with respect to the total energy of some test molecules (SF_2, SCl_2 and FSSF) using their experimental geometry. The values are contained in Table 3.

3. The Role of d-Orbitals

Since the fifties, when the valence-bond theory of Pauling began to celebrate great success among the practical chemists, contradicting views exist regarding the role d-orbitals really play in sulphur-sulphur- and sulphur-halogen-bonds. However, most

Table 2. Basis sets II.

Type of function	Sulphur		Fluorine		Chlorine	
	large basis	small basis	large basis	small basis	large basis	small basis
s	5.0	1.83487	12.5935	8.57270	89.0063	2.17123
	2.52106	0.44965	5.15966	1.23620	31.2371	0.77248
	1.46236	0.15596	1.44274	0.37125	7.76951	0.23310
	0.403651		0.8		3.07933	
	0.147347		0.446441		0.651038	
	0.049116		0.2		0.240798	
					0.089063	
p	1.95919	3.51385	10.2971	6.57191	10.4071	3.64526
	0.753257	0.48100	4.86553	1.39819	3.37330	0.71274
	0.289607	0.13716	2.14974	0.32702	0.748495	0.19368
	0.110548		1.03153		0.207855	
	0.042198		0.472432		0.057721	
			0.2			

Type of function		Sulphur	Fluorine	Chlorine
s	square error integral	1.56-4	3.93-5	2.65-4
	gradient	3.37-8	3.62-8	4.79-8
p	square error integral	4.68-4	9.80-4	1.48-4
	gradient	3.14-8	3.87-8	1.07-7

of the corresponding statements stand on a wabbly ground, for terms like "hybridization" and "molecular orbital" are describing conditions and things which in a strict quantum chemical sense are not at all existing. Simply and solely the total density of an atomic or molecular electron system has physically reality. The orbital of an electron is only a useful artefact, which arises from the model of independent particles. Too frequently the orbital concept is used as if orbitals were seizable and unchangeable things, and people forget that one set of orbitals can easily be converted by a linear transformation to another set of extremely different shape without changing the total density, i.e. the physical reality. Based on this reasoning the whole question of the importance of d-orbitals has to be reformulated: If we divide the total density or the total wavefuntion of a molecule into the different symmetry types characterized by the quantum number 1, we will get in most cases a non-vanishing, but sometimes very small, contribution of d-symmetry. Now the problem is only to find out whether this contribution is already generated by s- and p-type basis functions or not. The simplest way to ascertain this is to calculate molecular properties which are not very sensitive to changes in the basis quality, both with and without d-functions. If the results calculated by use of the d-containing basis are much better in comparison with the experimental values than those obtained without the aid of d-type functions, it is justified to state that density and wavefunction have a distinct share from d-symmetry, i.e. – in a simple diction – d-orbitals are important.

Table 3. d-Exponents.

Test molecule	Basis set	Atom	Exponent
SF_2	I	S	0.62782
FSSF	I	S	0.62951
FSSF	I + S − d	F	0.68635
SCl_2	II + S − d	Cl	0.54536

Because of their rather different geometries, compositions and electronic structures the molecules SF, SF_2, SCl_2 and FSSF form an appropriate test set for the d-participation. Among all molecular properties interatomic distances are least affected by changes in the basis quality. So we further considered the S–F-distance in SF and SF_2 and the S–S-distance in FSSF with basis I. Table 4 shows the results both with and without sulphur-d-functions. Indeed, the s-p-basis is able to reproduce the trend with respect to SF and SF_2, but the absolute errors are considerably large, especially in the case of FSSF. In contrast the results become partly excellent if we use the d-augmented basis. One could object that the number of s- and p-functions in the non-d-basis might have been too small to produce good results at all. The inclusion of d-functions might have in-

Table 4. Bond lengths with and without S – d-functions.

Bond	S-F	SF-F	FS-SF
r (calc.) without S-d	3.160	3.147	3.910
r (calc.) with S-d	3.039	3.024	3.724
r (exp.)	3.022	3.004	3.568

References for all experimental values are contained in [34]. Bond lengths are given in atomic units.

creased the poor quality of the s- and p-functions only. We could refute this supposition, for the calculation of the SF molecule with the rather bigger 6/5-basis, which we took from Dunning and Hay and prepared as mentioned above, yielded an S–F-distance of 3.164 au, which is nearly the same as obtained by use of the normal 3/3-basis. Thus to get good results it is more important to include d-functions into the basis set than to increase the number of s- and p-functions. The behaviour of the dissociation energy points in the same direction. The use of the d-augmented basis leads to an increase of about 20 kcal/mole to a value roughly double that of the original one. Nevertheless the absolute value is not very comparable to the experimental value, probably due to the slightly inadequate correlation functional.

Not only the geometry and coupled properties are of interest in the investigation of a molecule, but also properties which are much more sensitive to errors in the approximation of the wavefunction, especially the dipole moment. Indeed, a first order error in this approximation only brings about a second order error in the energy and the directly related properties, but an error of first order in all those properties whose operators do not commute with the Hamiltonian. Therefore one has to assume that the emplyoment of sulphur-d-functions alone will not have such a positive effect on the dipole moments as on the distances. Table 5 confirms this statement. A simple basis extension (8/6/2 for sulphur, 7/5 for fluorine) is not able to improve the dipole moment of the sulphur monofluoride significantly. An improvement could only be achieved by the use of a 3/3/1-basis for both atoms. The same holds for SCl_2 too.

Table 5. Dipole moments with and without Hal-d-functions.

Molecule	SF	SCl_2
μ (calc.) with S-d only	1.55	1.35
μ (calc.) with S-d and Hal-d	1.20	0.75
μ (exp.)	0.82	0.36

All values are given in Debye. Basis set II was used. [The correlation is not included in the wavefunction used to calculate the molecular properties, but is taken into account as an energy correction after the last iteration step.]

To summarize the results one can say that the densities and wavefunctions of all the systems considered have a significant d-character, so that S–d-functions must be included into the basis set in order to get a reasonable description of the bonds. Functions of d-symmetry, which are located at the halogen atoms, are extremely important to get acceptable dipole moments, which nevertheless are confronted with distinct but systematic errors.

All further calculations were carried out with d-augmented basis sets of type II for all atoms.

4. Sulphur monofluoride and Sulphur monochloride

Up to date two theoretical investigations of the SF molecule have been done by O'Hare [15] on Hartree-Fock level and by Staemmler [16], who applied the CEPA-PNO method. O'Hare used Slater-type functions including S–d and F–d while Staemmler used a very extended gaussian type basis, contracted to 7/4/1 for sulphur for example. Since his basis set is larger than ours and the CEPA calculations are expected to be more accurate, the too large S–F-distance Staemmler obtained is astonishing and leads to doubts regarding the accuracy of the corresponding value for SCl.

The results of the calculations are listed in Table 6 together with the experimental values.

The spin-density of an atom, which can be calculated from the population analysis, is a measure for the localization of the free electron of a radical on the respective atom. For S we obtained 0.967, i.e. we have the typical case of a localized radical electron and can write the formula as $\cdot\overline{\underline{S}}-\overline{\underline{F}}|$.

The population analysis leads to a charge of + 0.41 at the sulphur atom and an S–F-overlap population of only 0.074. Hence the molecule has a rather ionic character.

Sulphur monochloride is scarcely investigated experimentally. In Table 6 the calculated properties are compared with the values of Staemmler. By reason of the high sulphur spin-density of 0.956 and of the same ground state symmetry of SCl and SF one can expect that the general bond type is the

Table 6. Sulphur monofluoride ($^2\pi$) and sulphur monochloride ($^2\pi$).

	SF				SCl		
	(15)	(16)	this work	exp.	(16)	this work	exp.
$r_{\text{S-Hal}}$	2.986	3.081	2.989	3.022	3.836	3.699	unknown
E_{diss}	34	63	44	82	49	39	60
μ	1.26	0.97	1.20	0.82	0.24	0.63	unknown

Distances are given in atomic units, dissociation energies in kcal/mole and dipole moments in Debye. This holds for all following tables too.

same both for SF and SCl. But the polarity of the latter molecule is smaller, as one can presume on account of the decreased electronegativity of chlorine compared with that of fluorine. Since the sulphur charge merely amounts to + 0.20 charge units and the overlap population increases to 0.103, the covalent character of the bond must be more pronounced in SCl than in SF.

5. Sulphur difluoride and Sulphur dichloride

In contrast to the molecules treated in the last paragraph, SF_2 has received great attention. The first Hartree-Fock calculation was published by Radom and Schaefer III [17], who used a 4−31 G basis set without great success. Further work in the *ab initio* frame was done by Thomson [18] and Hay [19]. Hay applied the GVB method but did not optimize the geometry parameters. Besides various calculations on CNDO level [20], Carlsen [21] published some papers in which he used the Hartree-Fock method and employed floating s- and p-functions to substitute the expensive d-functions. The results of Schaefer III, Thomson and Hay and those calculated by use of our pseudopotential approach are given in Table 7.

Sulphur dichloride has received much less attention during the last years. Apart from the EHT and CNDO calculations of Colton and Rabalais [22], there is only one Hartree-Fock investigation done by Solouki, Rosmus and Bock [23] by use of a gaussian basis set contracted to 7/4/1 for each atom. Unfortunately the authors have not optimized the geometry. The other results are shown together with our values in Table 7.

The population analysis yields the following values for SF_2:

sulphur charge	+0.83
S−F-overlap population	0.103
F−F-overlap population	−0.016

So we have a system with a pronounced positive pole. A distinct antibonding interaction exists among the two fluorine atoms. The above mentioned properties take the following values, if SCl_2 is considered:

sulphur charge	+0.41
S−Cl-overlap population	0.131
Cl−Cl-overlap population	−0.037

It is easy to note that the trend already pointed out in the case of the monohalides is continued. Sulphur dichloride is much less polar than its fluorine analogue and the bond has a large covalent share. This difference shows up in the dimerization reactions of SF_2 and SCl_2:

$$2\,SF_2 \rightarrow F_3S{-}SF$$
$$2\,SCl_2 \rightarrow ClSSCl + Cl_2$$

The first reaction could proceed by an ionic mechanism, but for the second one a radical pathway is

Table 7. Sulphur difluoride and sulphur dichloride.

	SF_2					SCl_2		
	(17)	(18)	(19)	this work	exp.	(23)	this work	exp.
$r_{\text{S-Hal}}$	3.177	3.090	–	2.975	3.004	–	3.781	3.808
angle	97.1	98.5	–	98.0	98.1	–	102.6	102.8
E_{diss}	–	–	–	46	93	45	30	61
μ	–	1.68	1.78	1.42	1.05	0.61	0.75	0.36

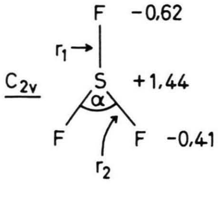
The Hal-S-Hal angle is given in decimal degrees. Dissociation products are SHal and Hal.

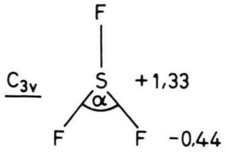
probable. In conformity with this behaviour, SF_2 is calculated to be of chiefly ionic character, whereas the chlorine analogue is more covalent and so enabled to dissociate homolytically.

6. Sulphur trifluoride

The sulphur halide radicals are all together substances of an enormous instability and are therefore difficult to produce and to investigate. Except the already considered monohalides only SF_3 and SF_5 are known. The electronic structure of sulphur pentafluoride was calculated by use of the INDO method some years ago [24], but up to now no theoretical investigation of the SF_3 molecule does exist. Morton, Preston and Strach [25] observed the anisotrope ESR spectrum of sulphur trifluoride in a γ-radiated single crystal of $SF_3^+BF_4^-$. The analysis of the g^2 tensor as well as the main values of the hyperfine coupling tensors and their direction cosines shows that the molecule has two somewhat different sets of magnetic axes in one plane. If one bears in mind on the one hand the fundamental difference between magnetic and molecular axes and on the other hand the fact that measurements in a crystal lattice do not yield the same values as gas-phase investigations, one is able to say that the radical SF_3 has either a planar or a slightly spatial distorted geometry and belongs to the point group C_{2v} or C_{3v} [26]. The positions of the maxima of the hyperfine coupling tensors allow to predict a $^2A_1$ ground state.

In this work we investigated two different molecular geometries, namely a planar arrangement with C_{2v} symmetry and a spatial one belonging to the point group C_{3v}. For the second case the geometry optimization yielded a very flat pyramid with the inclination angle φ. The results are summarized in Table 8. The comparison of the total energies shows at once that the pyramid is considerably more stable. The population analysis exhibits the following charge distributions:





The S−F-overlap populations are always negative, i.e. there exist antibonding covalent interactions, which might be overcome by the strong ionic attraction. Since SF_3 and the system $PF_2{-}Ne$ are isoelectronic and the latter can be visualized as resulting from the former by increase of the charge separation and according to the fact that the cores of sulphur and phosphorus as well as those of fluorine and neon are similar, we reservedly can presume that the instability of sulphur trifluoride is related to the instability of the $PF_2{-}Ne$ system, which is evident already by use of simple valence-bond considerations.

Table 8. Sulphur trifluoride.

	Neutral molecule ($^2A_1$)		Cation
Geometry	planar, C_{2v} r_1 3.430 r_2 2.993 α 96.4	spatial, C_{3v} r 3.093 φ 11.0 α 116.5	spatial, C_{3v} r 2.827 (2.829) α 99.6 (97.5)
E_{total} (au)	−82.41160	−82.44153	−82.17563
μ	2.22	0.50	−
Sulphur spin-density	0.898	0.641	−
	sulphur charge		+ 1.78
	S−F-overlap population		0.253

Experimental values are given in brackets.

In addition we investigated the ion SF_3^+, known from various salts as $SF_3^+BF_4^-$ for example. Indeed, the calculated distances and angles of an isolated system have in principle only a limited comparability with values got, as in this case, from X-ray diffraction at a crystal lattice, but the deviations should be rather small for positive ions. It is known that SF_3^+ has a pyramidal shape and belongs to the point group C_{3v}. These facts were used to optimize the molecular geometry, which yielded an almost perfect agreement with the experiment (Table 8). The positive S−F-overlap population in connection with the strong ionic intramolecular attraction may lead to the expected stability of SF_3^+. We also can conclude from the result of this calculation that the description of the neutral molecule is reasonable.

7. The Disulphur difluorides

Since the discovery of the two isomeric disulphur difluorides about twenty years ago experimentalists were engaged in the investigation of their interconversion and relative stabilities. Not until the early seventies theoreticians attempted to calculate properties of these molecules. Chiefly difluoro disulfane was investigated, which is similar in structure to hydrogen peroxide. Most authors used the CNDO method [27–30], but the results are not satisfying and in addition incomplete because of different topics the investigators wanted to treat. In contrast the CNDO results, those of Solouki and Bock [31] are of amazing quality obviously by reason of an appropriate parametrization. This procedure is always justified if one designs to construct an isomerization hypersurface, as the authors did, for such a calculation needs a high quality wavefunction. The only Hartree-Fock calculation was done by Hinchliffe [32], who employed a gaussian basis set with sulphur-d-functions. Drawbacks in his work become obvious if one considers the S–S-distance and the dipole moment of FSSF. The calculated distance lies 0.130 au above the experimental value, and the dipole moment is too large by 0.6 Debye. In Table 9 our calculated molecular properties are compared with the experiment. We have not optimized the angles of difluoro disulfane but used the experimentally known values. Indeed, the results obtained are of better quality than those of all previous investigators, but they are not satisfactory from all respects. The dipole moment of thiothionyl fluoride is determined distinctly too big, and the S–S-distance of the isomer compound also is afflicted with a non-negligible error. To achieve an improvement we tried to enlarge the number of basis functions. It was not possible due to technical reasons to use a second set of d-functions for the bond description, therefore we approximated their effect by employing two diffuse s- and one set of p-functions with exponents 0.1, 0.01 and 0.05, respectively, which were placed in the midst of the symmetric S–S-bond of difluoro disulfane. Since there is no significant change in the results, no further efforts were made to improve the dipole moment of SSF_2.

Wagner and coworkers [28] attempted to give some information about the relationship between FSSF and the isomer compound SSF_2. From the facts that the highest S–S-bonding orbital is equivalent in energy in the two molecules and that both the force constants f_{SS} and the corresponding interatomic distances are similar, they concluded that the two S–S-bonds should have the same character. But a force constant difference of 1.59 mdyn/Å hardly points at a similarity of the bonds and an equivalence of orbital energies is no indication for it too. Therefore this assertion seems to be dubious.

Table 9. Difluoro disulfane and thiothionyl fluoride.

	FSSF		SSF_2	
	calc.	exp.	calc.	exp.
r_{S-S}	3.644	3.568	3.478	3.515
r_{S-F}	3.035	3.090	2.974	3.020
$\sphericalangle$ SSF	–	108.3	107.9	107.5
dihedral angle	–	87.9	–	–
$\sphericalangle$ FSF	–	–	92.2	92.5
μ	1.78	1.45	1.64	1.03

Table 10. Comparison of the S–S-bonds.

	FSSF	SSF_2
S–S-overlap population	0.256	0.392
force constant (exp.)	3.66	5.25
sulphur charge (central)	+0.43	+1.07
sulphur charge (end-positioned)	–	−0.28
fluorine charge	−0.43	−0.39

The values of the force constant are given in mdyn/Å. This holds for all following tables too.

Three information sources permit us to investigate the strength – however spongy this term may be – and structure of a chemical bond. The first one, the force constant, is a measure for a certain toughness and firmness of the atomic cohesion, but not for inert reaction behaviour or thermodynamic stability. Secondly the overlap population gives us an idea about the amount of covalent bond forces, and thirdly the analysis of the atomic charges yields the extent of ionic attractions and repulsions existing in the considered system. Table 10 contains the values of these features for the S–S-bonds in difluoro disulfane and thiothionyl fluoride. Overlap population and force constant, which show a striking correspondence, suggest that an obvious stronger bond exists in SSF_2 than in FSSF. Already a simple valence-bond consideration shows that one of the two molecules should have a multiple bond:

The force constants of single-, double- and triple-bonds in organic molecules behave as per the ratio 1:2:3. Transfering this with all caution to the investigated molecules, one can see that the force constant ratio of about 1.5 is also in favour of a multiple bond share in thiothionyl fluoride. Visualizing the molecule SSF_2 as a combination of sulphur difluoride and sulphur and applying this idea to the atomic charges, around 0.8 charge units at the central atom arise from the formation of two S−F-bonds. The charge located at the central sulphur atom should be decreased below the value of SF_2 by the pushing effect of the exposed sulphur, if only a normal single-bond would exist between the two sulphur atoms. But in reality the opposite effect is found. So the unexpected distinct increase of the charge of the central sulphur atom points at another bond type. Comparing the localized sulphur charges for both molecules, an electrostatic repulsion results for FSSF, whereas the atoms of the isomer compound attract each other. So one can write the following resonance structures for thiothionyl fluoride:

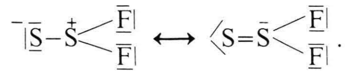


Table 11. Planar (C_{2v}) and pyramidal (C_s) thiothionyl fluoride.

	C_{2v}	C_s
r_{S-S}	3.976	3.478
r_{S-F}	2.947	2.974
∢ SSF	104.5	107.9
E_{total} (au)	−68.51345	−68.64793
sulphur charge (central)	+ 0.83	+ 1.07
sulphur charge (end-positioned)	− 0.16	− 0.28
S−S-overlap population	0.056	0.392
S−F-overlap population	0.135	0.066

The following fact can be concluded from the statements given above: The S−S-bond behaviour of the two compounds is fundamentally different, for in the case of SSF_2 we have a distinct multiple bond character, which is not existing in the case of FSSF (One could object, that the great similarity in the photoelectron spectra of both molecules, as found by Wagner and coworkers [28], does not favour a distinct difference with respect to the bond type. But our calculations too yield a good harmony in the orbital energies of both compounds without contradicting our arguments). But this is only valid with respect to two conditions: Replacing the fluorine atoms by chlorine, the multiple bond character of the S−S-cohesion will significantly decrease as will be established in the next paragraph, and the same also holds when the pyramidal structure (point group C_s) is altered to a planar one (point group C_{2v}). This can be achieved by opening the SSF angle to 180 degrees. Our calculation of the planar SSF_2 molecule contained in Table 11 shows the breakdown of the S−S-bond resulting in a remarkable increase in the total energy. Postulating a harmonic potential curve, which mostly is acceptable within small regions around the minimum, the force constant is calculated to be the second derivative of the curve at the point of minimal energy. The following table represents a comparison between calculated and experimental values. The investigated potential curves make no difficulties with respect to early appearing anharmonicities, so that the bond collapse during the change in symmetry is best demonstrated by use of the force constant, which sinks down from 5.23 to 0.42 mdyn/Å:

	FSSF	$SSF_2(C_s)$	$SSF_2(C_{2v})$
exp.	3.66	5.25	–
calc.	3.84	5.23	0.42
(all values in mdyn/Å)			

8. The Disulphur dichlorides

The small sulphur chlorides and fluorides show great similarity in a wide range, and one should expect thereof that this holds for S_2F_2 and S_2Cl_2 too. But this is not the case, for a fluorine analogous thiothionyl chloride is obviously non-existing, so that only the isomer dichloro disulfane, structural related to FSSF, is known. Although various calculations for the ClSSCl molecule have been published [33], only Solouki and Bock [31] occupied themselves with the question mentioned. They construct an isomerization hypersurface as in the case of S_2F_2 and so could prove that not only $SSCl_2$ is substantially less stable than its isomer, but also that the activation threshold of the isomerization $SSCl_2 \rightarrow ClSSCl$ is very low.

First of all let us have a look on the results of our pseudopotential calculations contained in Table 12. No experimental counterparts of the $SSCl_2$ properties doing exist, we estimated the geometry parameters according to the following formula with the aid of known data of the other molecules:

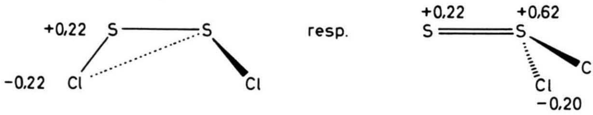
$$x_{SSCl_2} = x_{SSF_2}\ (x_{ClSSCl}/x_{FSSF})\,.$$

The enormous deviation of the calculated ClSSCl dihedral angle is unexplainable, but the correspond-

Table 12. Dichloro disulfane and thiothionyl chloride.

	ClSSCl		$SSCl_2$	
	calc.	exp.	calc.	est.
r_{S-S}	3.741	3.670	3.544	3.616
r_{S-Cl}	3.823	3.886	3.851	3.798
∢ SSCl	106.3	107.9	110.3	107.1
dihedral angle	66.5	85.0	–	–
∢ ClSCl	–	–	96.7	–
E_{total}	−50.61281	–	−50.57436	–
μ	1.28	1.60	1.46	–

ing potential curve is rather flat, so that the total energy would increase only by 2.5 kcal/mole for the case of the experimental angle. This cannot much afflict the distinct energy difference between the two molecules. It turns out that ClSSCl is about 24 kcal/mole more stable than its isomer. Additionally, considering the charge distribution in both molecules, it is to realize that the electrostatic attraction, which is important for the isomerization according to the mechanism proposed by Solouki and Bock, of the dichloro disulfane atoms connected with the dotted line drops to about half the value of the corresponding fluorine compound. Indeed, the considered chlorine atom is a little bit more extended and polarizable than the fluorine atoms in FSSF, but the distance between the interacting atoms is larger in the chloro compound too, so that finally no steric effect will increase the lowered attraction. We summarize: A tendency towards isomerization of ClSSCl to $SSCl_2$ hardly exists, and consequently it is clear that disulphur dichloride is present only as the thermodynamically more stable dichloro disulfane in contrast to the S_2F_2 case.



To explain this surprisingly different behaviour of S_2F_2 and S_2Cl_2, we first make a comparison between the S–S-bonds in SSF_2 and in $SSCl_2$, which is given in Table 13. According to the general trend force constant, polarity and overlap population decrease with the change from F to Cl, i.e. the bond of the sulphur atoms is becoming weaker. In contrast to this the little increase of the interatomic distance is remarkable. Comparing the corresponding properties of the disulfanes it is easy to see that the alterations evoked by the fluorine-chlorine exchange have the same trend but are distinctly smaller. Thus alterations among the elements of the seventh main group of the period system have a larger effect on the thiothionyl halides than on their isomeres. Comparing the differences between HalSSHal and $SSHal_2$ for Hal=F and Cl with respect to some special properties, one can ascertain that the sulphur-sulphur-bond in $SSCl_2$ is more similar to the corresponding bond of the ClSSCl molecule than it is the case for the analogous fluorine compounds. Obviously the multiple bond character is decreasing from SSF_2 to $SSCl_2$, accompanied by a strong increase of the relative total energy.

The formation of two S–Cl-bonds yields a positive charge of about 0.4 at the sulphur atom of SCl_2. Considering $SSCl_2$, this amount does not lower at all but is growing at about the same measure as in SSF_2, and in both cases weak antibonding interactions exist between the halogen atoms and the end-positioned sulphur. So we have the same bond type in both molecules, and the weakness of thiothionyl chloride has its reason in a gradual, not in a fundamental difference of the molecules.

Obviously the thiothionyl type arrangement of halogen atoms around a S_2 unit is stable only if a bond with distinct multiple character can come into existence between the sulphur atoms. The fact that this is much less possible with chlorine than it is with fluorine can be attributed to the enlarged

Table 13. Comparison of the S–S-bonds.

	SSF_2	$SSCl_2$	Δ	FSSF	ClSSCl	Δ
Force constant (calc.)	5.23	4.11	1.12	3.84	3.58	0.32
Charge diff. of the S-atoms	1.36	0.84	0.52	–	–	–
r_{S-S} (calc.)	3.478	3.544	0.066	3.644	3.741	0.097
S–S-overlap population	0.392	0.296	0.096	0.256	0.183	0.073

Difference of S–S-	F	Cl
Force constants (calc.)	1.59	0.53
Overlap populations	0.136	0.113

interaction of chlorine orbitals with the central sulphur, i.e. to a better overlap of the bond-forming orbitals of S and Cl, which mainly are expected to have p-symmetry. Comparing the total values of the overlap integrals calculated with respect to the various distances for all orbital pairs S_p-Cl_p and S_p-F_p, the S−Cl-overlap is about 1.2 times bigger. If we also take into consideration the S−Hal-overlap populations, we get the same factor of 1.2.

We summarize: The alteration of intraatomic characteristics obeying the rules of the period system is disturbing and weakening the sulphur-sulphur interaction and so destabilizing the system $SSCl_2$ in contrast to SSF_2 relative to the respective disulfane.

[1] H. Hellmann, J. Chem. Phys. **3,** 61 (1935).
[2] P. Gombás, Z. Physik **94,** 473 (1935) and **118,** 164 (1941).
[3] J. C. Phillips and L. Kleinman, Phys. Rev. **116,** 287 (1959).
[4] B. J. Austin, V. Heine, and L. J. Sham, Phys. **127,** 276 (1961).
[5] J. D. Weeks, A. Hazi, and S. A. Rice, Adv. Chem. Phys. **16,** 283 (1969).
[6] L. Szasz and L. Brown, J. Chem. Phys. **65,** 1393 (1976).
[7] T.-C. Chang, P. Habitz, and W. H. E. Schwarz, Theor. Chim. Acta **44,** 61 (1976).
[8] H. Stoll, J. Flad, E. Golka, and Th. Krüger, Surf. Sci. **106,** 251 (1981).
[9] U. Wedig, Master's Thesis, Institut für Theoretische Chemie der Universität Stuttgart, 1982.
[10] H. Stoll, C. M. E. Pavlidou, and H. Preuß, Theor. Chim. Acta **49,** 143 (1978); H. Stoll, E. Golka, and H. Preuß, Theor. Chim. Acta **55,** 29 (1980).
[11] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58,** 1200 (1980); and S. H. Vosko and L. Wilk, Phys. Rev. **B 22,** 3812 (1980).
[12] J. S. Binkley et al., Program Gaussian (1978), **A 76.**
[13] B. A. Murtagh and R. W. H. Sargent, Comp. J. **13,** 185 (1970).
[14] A. N. Tavouktsoglou and S. Huzinaga, J. Chem. Phys. **72,** 1385 (1980).
[15] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **53,** 2834 (1970); P. A. G. O'Hare, J. Chem. Phys. **59,** 3842 (1973).
[16] V. Staemmler, Theor. Chim. Acta **62,** 69 (1982).
[17] L. Radom and H. F. Schaefer III, Austr. J. Chem. **28,** 2069 (1975).
[18] C. Thomson, Chem. Phys. Letters **44,** 475 (1976).
[19] P. J. Hay, J. Amer. Chem. Soc. **99,** 1003 (1977).
[20] V. Bonačić-Koutecký and J. I. Musher, Theor. Chim. Acta **33,** 227 (1974); R. D. Brown and J. D. Peel, Austr. J. Chem. **21,** 2605 (1968); R. G. Hyde, J. B. Peel, and K. Terauds, J. Chem. Soc. Faraday Trans. II **69,** 1563 (1973); D. Gonbeau and G. Pfister-Guillouzo, J. Chim. Phys. **73,** 787 (1976).
[21] P. G. Burton, N. R. Carlsen, and E. A. Magnusson, Mol. Phys. **32,** 1687 (1976); P. G. Burton and N. R. Carlsen, Chem. Phys. Letters **46,** 48 (1977); N. R. Carlsen, Chem. Phys. Letters **47,** 203 (1977).
[22] R. J. Colton and J. W. Rabalais, J. Electron Spectros. Rel. Phen. **3,** 345 (1974).
[23] B. Solouki, P. Rosmus, and H. Bock, Chem. Phys. Letters **26,** 20 (1974).
[24] A. R. Gregory, Chem. Phys. Letters **28,** 552 (1974).
[25] J. R. Morton, K. F. Preston, and S. J. Strach, J. Chem. Phys. **69,** 1392 (1978).
[26] G. Kothe, private communication.
[27] C. Leibovici, J. Molec. Struct. **16,** 158 (1973).
[28] G. Wagner et al., Chem. Ber. **106,** 1285 (1973).
[29] L. J. Saethre, Acta Chem. Scand. **A 29,** 558 (1975).
[30] D. Gonbeau and G. Pfister-Guillouzo, J. Chem. Phys. **73,** 787 (1976).
[31] B. Solouki and H. Bock, Inorg. Chem. **16,** 665 (1977).
[32] A. Hinchliffe, J. Molec. Struct. **55,** 127 (1979).
[33] See Ref. [29], [30] and [31].
[34] Th. Krüger, Master's Thesis, Institut für Theoretische Chemie der Universität Stuttgart, 1982.