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CEPA Calculations on Open-Shell Molecules. V. The Vibration Frequencies of SF and SCl

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Ab initio calculations for the $^2\Pi$ ground states of SF and SCl have been performed on Hartree–Fock level and with inclusion of valence shell correlation effects by means of the CI and CEPA approaches. The calculated properties are: Equilibrium distances, vibration frequencies, and dipole moment curves in the vicinity of the respective equilibrium geometries. Our best estimates for the $0 \rightarrow 1$ infrared absorption frequencies ν_0 for SF and SCl are 786 cm^{-1} and 520 cm^{-1}, respectively, both with an uncertainty of about 10 cm^{-1}. This confirms a recent experimental value obtained by Willner for SF (791 cm^{-1}), but indicates that for SCl both experimental values reported previously in the literature (617 cm^{-1} and 574 cm^{-1}) are wrong. The S—F and S—Cl bonds in SF and SCl are very similar to the ones in SF_2 and SCl_2, being essentially single *p*-bonds in either case. In the analogous oxygen-halogen molecules the situation is different, the O—F and O—Cl bonds in the diatomic radicals OF and OCl have partial double bond character and are much stronger than those in OF_2 and OCl_2 or in HOF and HOCl.

Kew words: CEPA-calculations – SF and SCl radicals – Molecular properties – Vibration frequencies.

1. Introduction

The sulfur halogen radicals SF and SCl are highly reactive and rather short-lived, therefore the measurement of their molecular properties such as equilibrium distances, vibration frequencies etc. is rather difficult. During the last years, matrix isolation techniques and mass spectroscopic methods have been applied for studying several small sulfur-halogen molecules [1], but most of the properties of the diatomic radicals SF and SCl are still unknown.

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To our knowledge, no experimental value for the vibration frequency of SF has been published so far. Recently, Willner [2] tentatively assigned a peak at 791 cm^{-1} in a matrix isolation IR spectrum of photolyzed mixtures of OCS and F_2 to the $0 \rightarrow 1$ absorption frequency (ν_0) of SF. However, this spectrum is very complex and contains signals from many stable and unstable photolysis products, therefore the assignment of the 791 cm^{-1} peak to SF is not completely unique.

For SCl, the situation is even worse: Two recent experimental studies of matrix-isolated SCl differed considerably as to the reported absorption frequencies: Feuerhahn et al. [3] assigned values of 617 and 612 cm^{-1} to ν_0 of $^{32}S^{35}Cl$ and $^{32}S^{37}Cl$, respectively, while Willner [4] proposed much lower values: $\nu_0 = 574.2$, 566.5, and 565.55 cm^{-1} for $^{32}S^{35}Cl$, $^{32}S^{37}Cl$, and $^{34}S^{35}Cl$, respectively. Since the $^{35}Cl/^{37}Cl$ isotope shift expected for the band at 617 cm^{-1} amounts to 8.0 instead of 5 cm^{-1} it is dubious whether the assignment of Feuerhahn et al. [3] is correct at all.

The oxygen analogues of the above radicals, OF and OCl, are much better known experimentally; ω_e values for them are already quoted in Huber and Herzberg's compilation of diatomic molecules [5]: 1028.7 and 853.8 cm^{-1}, respectively [5]. For more recent values see section 4.

The amount of theoretical work performed on these radicals is equally small and consists entirely of a series of quite early, but excellent Hartree–Fock calculations by O'Hare and Wahl on OF [6], OCl [7], and SF [8, 9]. Harmonic vibration frequencies ω_e were calculated by these authors for OF [6] and SF [9], but the results were much too high: $\omega_e = 1211\ \mathrm{cm}^{-1}$ for OF and 914 cm^{-1} for SF. It is well known that the Hartree–Fock method yields vibration frequencies which are by 5–20% too high, large errors occuring in particular for multiple bonds. O'Hare and Wahl estimate that their Hartree–Fock value of 914 cm^{-1} for ω_e of SF will be reduced by electron correlation to about $830 \pm 20\ \mathrm{cm}^{-1}$ [9]. This estimate is quite close to Willner's much later experiment [2].

In this paper we report on a series of *ab initio* calculations on SF and SCl, on Hartree–Fock level and with electron correlation included. (Since confusion with the chemical symbols SF and SCl is possible we will mostly use the term "Hartree–Fock" instead of the synonymous, but more common name "self consistent field", abbreviated by "SCF").

The main difficulty in *ab initio* calculations on molecules containing halogen atoms, in particular F atoms, is that correlation effects are very important (for instance dispersion-type interactions between lone pairs), and it needs extended CI calculations and quite large basis sets to properly account for these effects. This has been outlined in some detail in recent calculations on F_2 [10] and F_2, F_2O, O_2F_2 [11].

The main aim of this study is to check whether or not Willner's tentative assignment of $\nu_0(SF) = 791\ \mathrm{cm}^{-1}$ is correct and whether one of the two reported values of 617 and 572.4 cm^{-1} can be $\nu_0(SCl)$ at all. Beyond this we try to compare the properties of oxygen–halogen bonds with those of sulfur–halogen bonds. To this purpose we have also performed Hartree–Fock calculations for the vibration frequency of OCl, for OF we refer to the corresponding Hartree–Fock results of O'Hare and Wahl [6].

2. Method of Calculation and Basis Sets

For all Hartree–Fock (SCF) calculations we used our open-shell program which is based on McWeeny's proposal [12] of constructing a single Fock operator by properly projecting onto the subspaces of fully occupied, partly occupied, and virtual orbitals. For the radicals treated here which have a $^2\Pi$ ground state with an electronic configuration such as π^3 our wavefunctions are spin-restricted, i.e. pure doublets, but spatially unrestricted, since the doubly occupied orbital, π_x say, is not required to have the same form as the singly occupied π_y-orbital.

Electron correlation effects are treated with our open-shell CEPA–PNO program (coupled electron pair approximation using pair natural orbitals). This has been described in detail in part I of this series [13], the method is an extension of our closed-shell CEPA scheme [14] and very similar to Meyer's CEPA approach [15, 16]. Most of the calculations have been performed on CEPA and CI levels including all singly and doubly substituted configurations (denoted by CEPA(SD) and CI(SD), respectively); in some cases only the doubles were taken (CEPA(D) or CI(D)). We have used the CEPA-2 variant [16, 17] in most calculations, but sometimes also a variant which is close to CEPA-3 [17]. The differences are so small (e.g. for SF, where we have used both variants, values for ω_e differed by about 3 cm^{-1}) that we will not discuss this point in more detail.

As usual in the calculations in this series, we used an energy threshold of 10^{-6} a.u. for the truncation of the PNO expansion; for the large basis of SCl an additional limit of 31 was set to the size of the CI expansion of one individual pair. In all calculations canonical occupied Hartree–Fock orbitals were used. After some experimentation it became apparent that it is necessary to correlate the whole valence shell (including the 2*s* and 3*s* orbitals) in order to obtain the correct correlation contribution to the molecular properties. The *K*-shells as well as the *L*-shells of the second row atoms could be left uncorrelated.

Basis sets of contracted gaussian lobe functions were used throughout, exponents and contraction coefficients were taken from Huzinaga's tables [18] as far as *s*- and *p*-AO's are concerned. These *s*, *p* basis sets had to be augmented by (a) *d*-AO's with exponents as optimized in previous calculations [19, 20] and (b) additional diffuse *s*- and *p*-AO's with exponents chosen as to yield a smoothly decreasing set together with the Huzinaga exponents. The full information about the basis sets used here is given in Table 1.

For SF, we started from a basis of $DZ+d$ type (double zeta plus one set of *d*-AO's) for *S* and a more flexible $TZ+d$-type (triple zeta$+d$) set for F in order to account for the higher electronegativity of the F-atom (basis I). It turned out that this basis is not well balanced, e.g. the dipole moment is too large. Therefore, we increased the flexibility in the valence region of S by adding one more *d*-set

Table 1. Basis sets used for SF, SCl, and OCl

Number	Type	Atom	Huzinaga's *sp*-part[a]	Additional functions	Total number of contracted functions
I	$TZ+d$	O, F	9, 5 → 5, 3	$d_O(1.25)$; $d_F(1.6)$	19
	$DZ+d$	S, Cl	11, 7 → 7, 4	$d_S(0.55)$; $d_{Cl}(0.6)$	24
II	$TZ+d$	F		as basis I	
	$TZ+2d$	S	11, 7 → 7, 4[b]	$s_S(0.10)$; $p_S(0.10)$; $d_S(0.95, 0.32)$	33
III	$TZ+2d$	S, Cl	12, 8 → 8, 5	$d_S(0.95, 0.32)$; $d_{Cl}(1.05, 0.35)$	33
IV	extended	O, F	10, 6 → 7, 5	O: $s(0.083)$; $p(0.055)$; $d(2.0, 0.5)$ F: $s(0.11)$; $p(0.07)$; $d(3.4, 0.85)$	36(32)[c]
		S, Cl	12, 8 → 9, 6	S: $s(0.06)$; $p(0.05)$; $d(0.95, 0.32)$ Cl: $s(0.07)$; $p(0.06)$; $d(1.05, 0.35)$	41(37)[c]

[a] The notation 9, 5 → 5, 3 means: 9*s* and 5*p* contracted to 5*s* and 3*p* groups, where always the steepest functions are contracted into one group

[b] In order to bridge the gap between the *L* and *M* shell AOs the two smallest exponents of the Huzinaga *s* and *p* basis set have been slightly increased

[c] In parentheses the number of σ and π functions which are only necessary in the Hartree–Fock calculation

and diffuse *s*- and *p*-AO's at the S atom (basis II). However, there is still an unbalance between the *L*- and *M*-shells of the S-atom in basis II. Therefore, for SCl, we used an increased set of the original Huzinaga *s*- and *p*-exponents instead, yielding a description which is nearly of the same flexibility for the *L* and *M*-shells (basis III). Finally for some Hartree–Fock calculations we used an extended set (basis IV), the results of which are, at least for SF where a comparison with the work of O'Hare [9] is possible, rather close to the Hartree–Fock limit. Unfortunately, the use of this basis for the calculation of correlation effects is beyond our computer capacities.

3. Molecular Properties of SF and SCl

The results of our calculations are given in Table 2 for SF and Table 3 for SCl. Dipole moment curves in the vicinity of the respective equilibrium distances for SF and SCl as calculated with the different methods and basis sets are plotted on Figs. 1 and 2. Some comments to the two tables seem to be appropriate:

1. In all cases between 5 and 7 points around the respective minima have been calculated, the spacing between the points being mostly $0.05\,a_0 = 0.02646$ Å. From polynomial fits to these points values for R_e and ω_e have been obtained which are stable within 0.002 Å and 2 cm^{-1}, respectively.

Table 2. Calculated properties of SF

Property	Method[a]	Basis set I	II	IV	Other work
R_e(Å)	SCF	1.6009	1.5878	1.5798	1.58 [9]
	CI	1.6236	1.6107		
	CEPA	1.6410	1.6306	(1.61)[b]	
	exp (R_0)				1.599 [21]
$E(R_e)$[c] (a.u.)	SCF	−0.89283	−0.90397	−0.95321	−0.96729 [9]
	CI	−1.20462	−1.22681		
	CEPA	−1.23470	−1.26115		
ω_e (cm^{-1})[d]	SCF	898	874	915	914 [9]
	CI	851	825		
	CEPA	804	771	(810)[b]	
ν_0 (cm^{-1})[d]	SCF	890	857	897	898 [22][e]
	CI	841	807		
	CEPA	792	747	(786)[b]	
	exp				791 [2]
μ(D)[f]	SCF	−1.563	−1.401	−1.229	−1.395 [9][g]
	CI	−1.302	−1.106		
	CEPA	−1.174	−0.968	(−0.80)[b]	
	exp				−0.794 [23]
D_e (eV)	SCF	1.178	1.245	1.486	1.45±0.14 [8]
	CI	2.145	2.098		
	CEPA	2.713	2.731		
	exp[h]				3.56 [24] 3.52 [25]

[a] Hartree–Fock abbreviated by SCF; CI(SD) and CEPA-3(SD) throughout.

[b] The values in parentheses are extrapolated and should be considered as our prediction for the respective properties.

[c] Total energy at the respective minima, relative to −496.0 a.u.

[d] For $^{32}S^{19}F$.

[e] The value of 898 cm^{-1} given in the publication cited in [22] is very much at odds to the value of 904 cm^{-1} calculated from $\omega_e = 914$ cm^{-1}, $\omega_e x_e = 5.12$ cm^{-1} [9], but fits much better to our results with basis IV.

[f] At $R = 3.02\ a_0 = 1.5981$ Å; negative sign indicates S^+F^-.

[g] At $R = 3.0217\ a_0$.

[h] D_0 values.

2. We have calculated the $\nu = 0 \rightarrow \nu = 1$ absorption frequency ν_0 by solving the Schrödinger equation for the nuclear motion for a given potential curve, thus obtaining the vibrational levels $G(0)$ and $G(1)$ directly. The connection between ν_0 and the spectroscopic constants ω_e and $\omega_e x_e$ is given by

$$\nu_0 = G(1) - G(0) = \omega_e - 2\omega_e x_e$$

if higher order terms are neglected. From this relation, values for $\omega_e x_e$ may be extracted from the Tables 2 and 3. But owing to the rather small number of points the accuracy for the $\omega_e x_e$ values is hardly better than 1 cm^{-1}.

Table 3. Calculated properties of SCl

Property	Method[a]	Basis set			Other work
		I	III	IV	
R_e(Å)	SCF	2.0149	2.0091	2.0077	
	CI	2.0175	2.0149		
	CEPA	2.0326	2.0298	(2.02)[b]	
$E(R_e)$ (a.u.)[c]	SCF	−0.91310	−0.99597	−1.00118	
	CI	−1.16963	−1.27641		
	CEPA	−1.19957	−1.31363		
ω_e (cm^{-1})[d]	SCF	584	573	573	
	CI	572	560		
	CEPA	542	533	(530)[b]	
ν_0 (cm^{-1})[d]	SCF	580	564	565	
	CI	567	555		
	CEPA	538	522	(520)[b]	
	exp				617 [3]; 574 [4]
μ(D)[e]	SCF	−0.709	−0.604	−0.592	
	CI	−0.482	−0.415		
	CEPA	−0.326	−0.236	(−0.23)[b]	
D_e (eV)	SCF	1.062	1.185	1.167	
	CI	1.579	1.543[f]		
	CEPA	2.109	2.137[f]		
	exp[g]				2.83 [26]

[a] CI(SD) and CEPA-3 (SD) for basis I, CI(D) and CEPA-2(D) for basis III.

[b] The values in parentheses are extrapolated and should be considered as our prediction for the respective properties.

[c] Total energy at the respective minima, relative to −856.0 a.u.

[d] For $^{32}S^{35}Cl$.

[e] At $R = 3.80\ a_0 = 2.0109$ Å, negative sign indicates S^+Cl^-.

[f] CI(SD): 1.571 eV; CEPA-2(SD): 2.220 eV.

[g] D_0.

3. The total energies obtained with the different basis sets are also included in the Tables 2 and 3. On Hartree–Fock level, basis II (for SF) yields only a slight improvement over basis I, contrary to basis III (for SCl). Our extended basis sets IV are quite close to the Hartree–Fock limit, see Ref. [9] for SF. The valence shell correlation energies increase by about 5% for SF and 10% for SCl going from basis I to II and III, respectively. When comparing our results for the isolated atoms with previous calculations [27] we conclude that we have obtained about 65% of the total valence shell correlation energy with basis I and 70–75% with basis II and III.

4. The importance of the CEPA correction is quite different in the two radicals. While in SF the CI results are mostly halfway between Hartree–Fock and CEPA or even closer to the CEPA results, they are much closer to the Hartree–Fock results in SCl. (This holds for CEPA-2, CEPA-3, with and without inclusion of singles). In particular, the CI-correlation energy for SCl is nearly independent of R in the vicinity of R_e, while the CEPA correlation energy increases (in absolute value) with increasing R.

5. The dissociation energies of SF and SCl are to a rather large extent due to electron correlation. Our calculations on SF in Table 2 show that it is not difficult to come close to the Hartree–Fock limit of about 1.45 eV [8], which is by almost 2.1 eV smaller than the experimental dissociation energy. Since our basis sets I and II cover only 67% and 72% of the atomic valence shell correlation energies of S+F, we can only expect to obtain about 70% of the correlation contribution to the binding energy. This would be approximately 1.5 eV, and this is exactly what we get on CEPA level while CI yields much less. For SCl, the situation is quite similar. We have performed some additional calculations on SF in order to check whether changes in the *L-M* intershell correlation energy contribute to the binding energy. The effects are very small and are estimated to increase the binding energy by not more than 0.03–0.04 eV. This can be safely neglected in comparison with the defects of the valence shell basis sets.

6. The calculated equilibrium distances both for SF and SCl seem to be slightly too large. The main reason is the use of too small basis sets. This is obviously the case on Hartree–Fock level as the results in the Tables 2 and 3 show. The Hartree–Fock value for R_e of SF decreases by 0.021 Å on proceeding from basis I to IV, and has arrived at the probable Hartree–Fock limit [9] with basis IV. Similarly, we expect our Hartree–Fock result for SCl with basis IV to be close to the Hartree–Fock limit. Inclusion of electron correlation leads to an increase

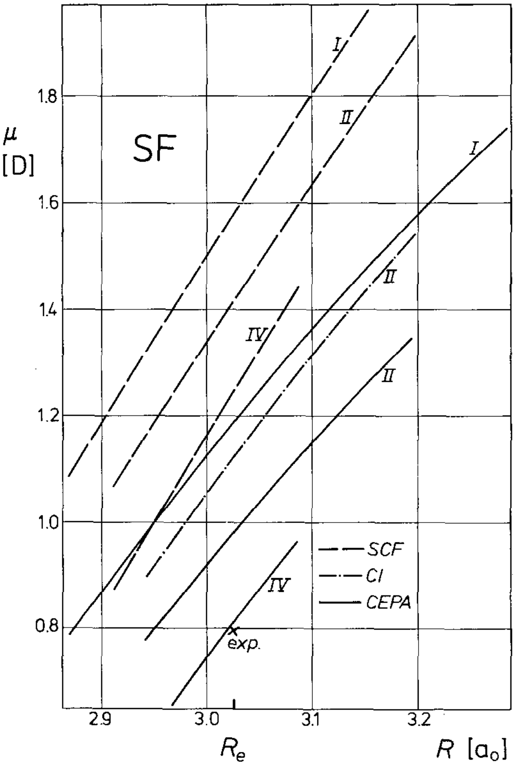

Fig. 1. Dipole moment curves for SF in the vicinity of R_e. The Roman figures (I, II, IV) refer to the basis sets of Table 1. The CEPA-curve with basis IV is extrapolated from SCF IV and CEPA II (see text)

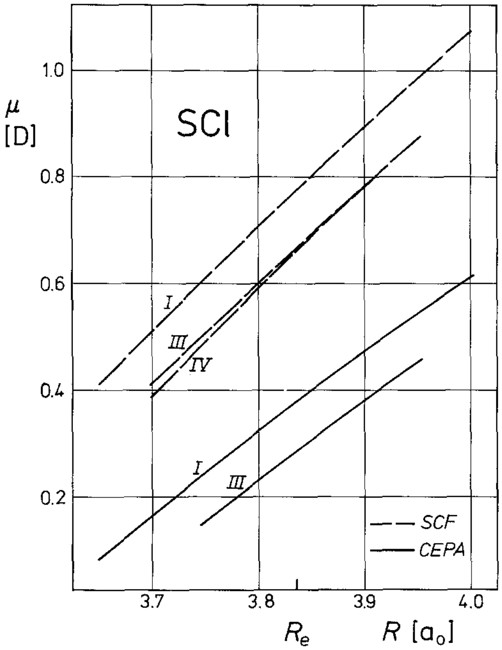

Fig. 2. Dipole moment curves for SCl in the vicinity of R_e. Explanation as in Fig. 1

of R_e, but this increase is too large unless sufficiently large basis sets are used. Comparison with similar calculations on F_2 [10] and F_2, F_2O, F_2O_2 [11] shows, that in particular the addition of f-type basis functions results in a decrease of R_e on CI or CEPA-level. Taking this decrease which is in the order of 0.01 to 0.02 Å for F—F and O—F bonds into account we can extrapolate the following basis IV CEPA results for R_e : SF: 1.61 Å; SCl: 2.02 Å. These values have also been included in the Tables 2 and 3. For SF, this result agrees fairly well with the experimental value for R_0 (1.599 Å) [21], for SCl R_0 has not been observed so far.

7. The dipole moment curves for SF and SCl are given in Fig. 1 and 2 in the vicinity of R_e. In the Hartree–Fock approximation, the dipole moments are much too large, in particular for small basis sets. They decrease gradually when the basis set is improved and correlation is taken care of. For SCl, basis III is expected to yield a reliable dipole moment curve, for SF one has to add the CEPA correction calculated with basis II to the best Hartree–Fock curve as obtained with basis IV. This yields the extrapolated dipole moment curve in Fig. 1 which is rather close to the experimental dipole moment of $-0.794\,D$ [23] at $R = R_e$.

4. Vibration Frequencies of SF and SCl

The Hartree–Fock results for the vibration frequencies of SF and SCl are quite unreliable and depend in a rather unsystematic way on the basis size: Taking the results of the extended basis IV as reference basis I yields either too large

(SCl) or too small (SF) frequencies. Improvement of the basis in an improper way (as with basis II for SF) does not even improve the vibration frequency.

The correlation contributions, on the other hand, are remarkably independent of the basis set, the decrease of ω_e being 94 cm^{-1} (basis I) and 103 cm^{-1} (basis II) for SF, 42 cm^{-1} (basis I) and 40 cm^{-1} (basis III) for SCl, on CEPA level. The choice of the CEPA variant and inclusion of singles are of minor importance and not worth being documented here, but the discrepancy between CI and CEPA calculations is very large.

Anharmonicities are obviously strongly underestimated with the small basis. They are not much affected by correlation which is already a well documented observation [28].

Adding the (nearly basis set independent) CEPA corrections to the best Hartree–Fock vibration frequencies we obtain as estimates for ω_e and $\omega_e x_e$

$$\text{SF: } \omega_e = 810 \pm 10\ \mathrm{cm}^{-1}, \qquad \omega_e x_e = 12 \pm 1\ \mathrm{cm}^{-1}$$

$$\text{SCl: } \omega_e = 530 \pm 10\ \mathrm{cm}^{-1}, \qquad \omega_e x_e = 5 \pm 1\ \mathrm{cm}^{-1}$$

from which $\nu_0 = 786\ \mathrm{cm}^{-1}$ for SF and $\nu_0 = 520\ \mathrm{cm}^{-1}$ for SCl may be derived. This estimate agrees very well with Willner's measurement for SF [2], but for SCl it contradicts both the results of Feuerhahn et al. [3] and Willner [4]. Though our error bars in both cases are only guessed, the experimental ν_0 values for SCl are so far off our result that they are certainly wrong assignments.

How do these results fit into what is known about oxygen and sulfur halogen molecules?

One would first try to estimate correlation corrections to the Hartree–Fock (SCF) vibration frequencies of SF and SCl from those of the molecules OF and OCl for which they are well known. Let

$$\gamma = \frac{\nu_0(\mathrm{exp})}{\nu_0(\mathrm{SCF})} \approx \frac{\omega_e(\mathrm{exp})}{\omega_e(\mathrm{SCF})}$$

be the ratio between the experimental and the best SCF vibration frequencies. This ratio is given in Table 4 for OF, OCl and SF where we used Willner's [2] experimental value for SF. Obviously, there is close similarity between OF and

Table 4. Comparison of Hartree–Fock and experimental vibration frequencies

Molecule	Freqn.	Hartree–Fock	exp	γ
^{16}OF	ν_0	1201 [6]	1033 [29]	0.86
^{32}SF	ν_0	898 [22]	(791 [2])	0.88
^{16}O^{35}Cl	ν_0	867[a]	843 [30]	0.97
^{32}S^{35}Cl	ν_0	565[a]		

[a] This work.

SF while correlation effects in OCl seem to be quite different. No conclusion can be drawn for SCl: if the correlation effects change ν_0 in a way similar to that in OCl the high value of Willner (574 cm^{-1}) would be correct, if they are closer to those in SF a low value would be preferred. Our estimate of 520 cm^{-1} corresponds to $\gamma = 0.92$ which is just in between SF and OCl. Only Feuerhahn's result (617 cm^{-1}) seems quite improbable.

A better understanding is achieved if one compares the properties of chalkogen–halogen bonds in different di- and triatomic molecules as it is done in Table 5. There seems to be a dramatic difference between oxygen and sulfur halogens: The O—F bond is much stronger in OF than in HOF, OF_2 and larger molecules containing OF bonds. This is apparent from a much shorter OF distance, a larger OF stretching frequency and a larger OF bond energy. The same holds for OCl. For the sulfur halogens, on the other hand, the S—X bond seems to have the same strength in the diatomic and larger molecules. The S—X bond distances are even slightly longer and the bond energies slightly smaller in the diatomics. Therefore, the conclusion seems to be justified that S—X vibration frequencies should be slightly smaller in SF and SCl than in SF_2 and SCl_2. This is in line with our calculations. Unfortunately, nothing is known so far about HSF and HSCl.

The main reason for the large difference in the properties of the oxygen and sulfur halogen radicals has to be attributed to the small overlap of the p-AO's

Table 5. Comparison of equilibrium distances, vibration fundamentals and bond energies in some oxygen and sulfur halogen molecules[a]

Molecule	OF	OCl	SF	SCl
R_e (Å)	1.358 [29]	1.570 [30]	1.601 [5]	(2.03)
ν_0 (cm^{-1})	1033 [29]	842.6 [30]	(786)	(520)
D_0 (eV)	2.23 [5]	2.75 [5]	3.52 [25]	2.83 [26]
Molecule	**HOF**	**HOCl**	**HSF**	**HSCl**
R_e $(E-X)$[b]	1.442	1.72		
ν_0 $(E-X)$	889.0	739		
D_0 $(HE-X)$	2.19	2.56		
Molecule	**OF_2**	**OCl_2**	**SF_2**	**SCl_2**
R_e $(E-X)$[b]	1.412	1.701	1.588 [32]	2.014 [35, 36]
ν_1	928	686	838.5 [33,34][c]	527 [37]
ν_2	461	300	357	214
ν_3	831	640	813	525
D_0 $(XE-X)$	1.65	1.36	3.98 [25]	2.89 [26]

[a] If no reference is given the data are from Ref. [31]; values in parentheses are results of this work.

[b] $E = O, S$; $X = F, Cl$.

[c] Harmonic frequencies 840 ± 20, 357 ± 2, 809 ± 10 cm^{-1} [31].

between second-row atoms as compared to that of first-row atoms [38, 39]. Therefore the π-MO's loose their bonding and antibonding character in the sequence OF; OCl, SF; SCl. The electronic configuration

$$\cdots \sigma^2 \pi^4 \pi^{*3}$$

of the valence electrons then corresponds to a bond order of only 1.0 in SCl instead of 1.5 in OF. Since in the triatomic molecules contained in Table 5 all bonds are genuine single bonds, this explains why the O–F bond in OF is stronger than in OF_2 while the S—Cl bonds in SCl and SCl_2 have the same strengths. OCl and SF are expected to behave in a way intermediate between OF and SCl, but Table 5 shows that there are some irregularities. Overall, OCl is closer to OF and SF closer to SCl. Finally, due to the larger overlap of the p-AO's of first-row atoms, the repulsion of doubly occupied cores (or lone pairs) is larger in first-row systems such that the OF binding energy is smaller than the SCl binding energy (compare F_2 and Cl_2 [39]).

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Note added in proof

In a recent analysis of the microwave spectrum of SF (Y. Endo, S. Saito, E. Hirota, J. Mol. Spectrosc. **92**, 443 (1982)) a value of 833 cm^{-1} was estimated for the vibrational frequency of SF, by using the observed value of the centrifugal distortion constant D_0. While this value is much higher than our result, the value reported for R_0 (1.5946 Å) is in satisfactory agreement with earlier experimental values and with the present theoretical result.

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