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Dramatic Changes in Geometry after Ionization: Experimental and Theoretical Studies on the Electronic Properties of Fluorocarbonyl (Mono-, Di-, and Tri-) Sulfur Compounds

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In this work, we present a complete study on He I photoelectron spectroscopy (PES) for the fluorocarbonyl mono-, di-, and trisulfur compounds FC(O)SCl, FC(O)SSCH$_3$, and FC(O)SSSC(O)F. After optimizations of the structure for stable conformers at different levels of theory, a complete theoretical study involving the calculation of the ionization energies using orbital valence Green's functional (OVGF) was performed. Calculations of radical-cationic forms were carried out in order to compare their properties with those of the neutral molecules. The first IP values are 10.7, 9.0, and 10.5 eV for FC(O)SCl, FC(O)SSCH$_3$, and FC(O)SSSC(O)F, respectively. The groups bonded to the S atom mainly influence the ionizations originating from the sulfur lone pairs. A wide electronic delocalization in the FC(O)S moiety can be deduced from experimental and theoretical results, which leads to a strong energetic stabilization of the n''_S (sulfur lone pair π orbital). Other conclusions relate to effects on the substituents attached to the S atom and the importance of the molecular planarity in the orbital stabilization of the FC(O)S moiety for the neutral molecules. It is worthwhile mentioning that FC(O)SCl retains its planar structure after ionization, but drastic changes occur in the geometry of both FC(O)SSCH$_3$ and FC(O)SSSC(O)F. The FC(O)SSCH$_3$ molecule adopts a heavy atom planar structure after ionization. The FC(O)SSS moiety becomes a planar form after the ionization of the FC(O)SSSC(O)F molecule, whereas the second C(O)F group maintains its original conformation with respect to the SSS group.

Introduction

Thioester compounds containing carbonyl groups have been the subject of many theoretical and experimental investigations. Thus, a wide series of these SC(O)-containing molecules was analyzed in order to systematically describe their conformational properties. Fluorocarbonylsulfenyl chloride, FC(O)SCl, was one of the first compounds investigated in this context. Gas electron diffraction,[1] vibrational analysis,[2] and ab initio calculations[3] demonstrate that this molecule exists as a mixture of two planar conformers with the syn form (C═O bond syn with respect to the S─Cl bond) being lower in energy than the anti conformation by 1.2(3) ($\Delta G = G_{\text{anti}} - G_{\text{syn}}$, gas electron diffraction) or 1.4 kcal mol^{-1} (infrared spectroscopy). Other related molecules exhibit the same characteristics with respect to their conformational properties, and they exist either as a mixture of syn and anti forms or only in the syn conformation. In all reported cases, the syn rotamer represents the most stable structure.[4−11] The preference of the syn form was rationalized in terms of a natural bond orbital (NBO) analysis for the series of XC(O)SCl, with X = CF$_3$, OCH$_3$, Cl, F.[11] These

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results show that the stabilization of the syn structure is due to both anomeric and mesomeric effects, through the interaction of the lp(πS) with the π^*(C═O) antibonding orbital (resonance) and that of the lp(σS) with the σ^*(C═O) or σ^*(C−X) antibonding orbitals (anomeric effect) for the syn and anti forms, respectively.

On the other hand, the conformation of disulfides and trisulfides is mainly determined by the geometry of the SS and SSS moieties, respectively. Gas-phase structures of noncyclic disulfides XSSX are characterized by dihedral angles δ(XSSX) close to 90°: for example, H_2S_2 90.6(5)°,[12] S_2F_2 87.7(4)°,[13] Cl_2S_2 85.2(2)°,[14] $(CH_3)_2S_2$ 85.3(37)°,[15] and $(CF_3)_2S_2$ 104.4(40)°.[16] The interpretation of the population analysis[17] is consistent with two qualitative arguments about the ∼90° preference of the XSSX dihedral angle. A plausible interpretation of the population analysis is related to the resulting barrier formed by the repulsion of 3pπ AO lone pairs. The repulsion is minimized, if these AOs are oriented orthogonal to each other. The second argument[18] is based on a hyperconjugative mechanism, whereby the π-character of the S−S bond is enhanced when, for example in HSSH, the S−H bonds are aligned for maximum transfer of electron density through the 3pπ AOs to the hydrogen, like in $H{-}S^+{=}S\ H^-$. This feature is consistent with the anomeric effect, that is, the electron donation from the sulfur lone pair into the empty σ^* orbitals of the opposite S−H bonds.[19] For other alkyl[20] and non-alkyl-substituted[21] species, a similar feature was observed.

Earlier studies show that the most stable conformer of FC(O)SSCH$_3$ possesses C_1 symmetry with the FC(O) group gauche with respect to the CH_3 group, and the C═O bond in syn position to the S−S bond.[22] The microwave spectra for the ground and four excited vibrational states are consistent with the syn form being the most stable structure. Evidence about the stabilization of the C═O bond due to electronic delocalization effects on the FC(O)S moiety was also obtained.[23]

The simplest trisulfide, HSSSH, possesses a trans structure,[24] resulting in a C_2 molecular symmetry. For trisulfides, this type of conformation can be formally considered as being derived from the S_8 ring. Other trisulfides reported in the literature, such as CH_3SSSCH_3[25] and CF_3SSSCF_3,[26] also exhibit trans conformation. Such trans trisulfides will exist in two enantiomorphic forms.

The interpretation of the vibrational data for FC(O)SSSC(O)F leads to a trans arrangement of the FC(O) groups with both C═O bonds syn to the S−S bonds (C_2 symmetry). Complementary measurements of dipole moments of the liquid substance suggest a mixture of two forms, the second with one of the two C═O bonds in anti position to the S−S bond.[27]

In the context of the valence electronic distribution of SC(O) containing molecules, relevant studies were performed using pre-resonant-Raman techniques in combination with UV−vis spectroscopy.[28] Thus, the pre-resonant-Raman behavior of XC(O)SNSO compounds (with X = Cl[9] and F[29]) agrees with a planar structure, where the π(C═O) and the NSO molecular orbitals should be extended over the entire molecule. In the case of CF_3SNSO,[30] the molecular skeleton is planar, whereas in CF_3SSNSO[31] the structure depends on the stereochemistry of the S−S moiety, with only the SSNSO group being planar. The resonant Raman effect is different in both cases. In CF_3SNSO, all vibrational modes are enhanced, whereas in the case of CF_3SSNSO only the modes related to the SNSO group undergo enhancement. Although several cases based on these considerations have been reported, knowledge of this subject is far from complete.

Considering the information available for these compounds, we became interested in the study of some selected, hitherto unknown photoelectron spectra. The relation between structure and valence electron distribution for a series of S-containing compounds is a relevant task, and it constitutes the aim of the present article. Furthermore, among the various results that could be obtained by means of photoelectron spectra, the study of the substituent effects on the molecular structure is one of the main targets of the present study.

Another aspect of interest in relation to property differences between the neutral molecule and the corresponding ion is the geometry of the most stable structure. Dimethyl

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disulfide, CH_3SSCH_3,[15,32] possesses a CSSC dihedral angle of 83.7°, while the lowest energy structure of the radical ion, $CH_3SSCH_3^{\bullet +}$, exhibits a planar CSSC chain with a dihedral angle of 180°, which is explained by the formation of a three-electron π-bond.[33] Experimental and theoretical studies on substituted disulfide ions are of great importance, because results from these studies can provide a sound basis for understanding the complexity of sulfur−sulfur bonding interactions.[34] Disulfide bonds also play important roles in maintaining protein structure.[17] Conformational properties of diallyl sulfides and diallyl disulfides have been examined as models for allylic sulfide linkages in biologically active compounds.[35]

In this work, we present the results of a photoelectron spectroscopy study of fluorocarbonyl sulfenyl chloride, FC(O)SCl, methylfluorocarbonyl disulfide, $FC(O)SSCH_3$, and bis(fluorocarbonyl) trisulfide, FC(O)SSSC(O)F. For comparison of the experimental ionization values, a complete theoretical study involving structure calculations of stable conformers at different levels of theory was performed. MO analysis and ionization energy calculations were also carried out.

Experimental Section

Fluorocarbonylsulfenyl chloride, FC(O)SCl, was prepared by the reaction between ClC(O)SCl and SbF_3.[36] The liquid product was purified by fractional distillation and subsequently purified several times by fractional condensation at reduced pressure in order to eliminate volatile compounds. The purity of the compound was checked by IR (vapor), Raman (liquid), and ^{19}F and ^{13}C NMR spectroscopy.

Methylfluorocarbonyl disulfide, $FC(O)SSCH_3$, was prepared by the reaction of FC(O)SCl with CH_3SH at room temperature and subsequently distilled trap-to-trap several times.[37]

Bis(fluorocarbonyl) trisulfide, FC(O)SSSC(O)F, was prepared by the reaction of FC(O)SCl with H_2S and, alternatively, by UV irradiation of FC(O)SSC(O)F.[38]

The He PES was recorded at the Institut für Anorganische Chemie der Universität, Frankfurt, Germany, using a Perkin-Elmer PS 16 spectrometer. The $2p_{3/2}$ and $2p_{1/2}$ peaks of argon and xenon were used for calibration.

Because the values and the order of the MO energies depend on the molecular geometry, the search for the optimum conformations was performed applying ab initio (HF and MP2) and density functional theory (DFT) calculations using the Gaussian 98 suite of programs.[39] To find the most suitable computational procedure, a preliminary study focusing on *syn*-FC(O)SCl was done for two reasons: (1) the structural and conformational properties are known from experimental data; (2) FC(O)SCl is the simplest molecule studied in this work, and computational methods at high levels of theory can be performed using our parallel computer system. Geometric parameters[40] as obtained by HF/6-31+G* and B3LYP/6-31+G* are in good agreement with the experimental values, while the more complete 6-311++G** basis set does not result in better accuracy. Energy values for the MOs according to the Koopmans' theorem ($-\epsilon_j$), calculated for syn FC(O)SCl, and the ionization energies and pole strengths from the Green's function calculations (OVGF method), show that the HF method with both basis sets overestimates the ionization potentials. The MP2 perturbative method does not result in an improvement for the values of ionization potentials. However, the OVGF formalism gives ionization energies in very good agreement with experimental results. From these comments, and considering the economy in the computational cost, HF, B3LYP, and MP2 methods with the 6-31+G* basis set for geometry optimizations and the outer valence Green function (OVGF) method with the 6-31G basis set for the ionization energies were selected for the structures with the exception of FC(O)SSSC(O)F, for which the less expensive MP2/3-21+G* was used. The Mulliken population analysis was applied for assigning charges for both neutral and radical cationic forms.

Scheme 1. Syn (I) and Anti (II) Stable Planar Forms of Thioester Compounds

Results and Discussion

Structures and Conformations. The sulfenylcarbonyl-containing molecules always prefer the syn conformation as the most stable form. The general observation is that most of the compounds of the type FC(O)SX exhibit an appreciable amount of the anti form in equilibrium with the syn one. As described previously, the conformers are planar with two potential energy minima (Scheme 1), corresponding to the syn (I) and anti (II) forms.

In the case of FC(O)SCl, gas electron diffraction (GED) results in a mixture of both forms, the syn structure being the most stable one, with a syn/anti ratio of 88/12.[1] Thus, a small contribution of the anti form can be expected in the PE spectrum. However, theoretical calculations (ROVGF/6-311++G**) for this form predict that the difference in

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(40) These results can be obtained from the authors upon request. The total energies and geometric parameters for FC(O)SCl were obtained from the HF, B3LYP, and MP2 methods with 6-31+G* and 6-311++G** basis sets. The ionization energies were obtained from the OVGF method using the 6-31G, 6-31+G*, and 6-311++G** basis sets. Geometric parameters and vibrational frequencies for the $FC(O)SCl^{\bullet +}$ were obtained from UMP2/6-31+G* calculations.

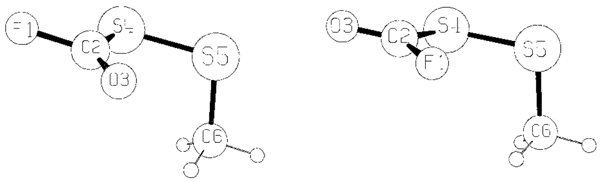

Figure 1. Schematic representation of the syn (I) and anti (II) conformers of $FC(O)SSCH_3$.

Table 1. Calculated Relative Energies [kcal/mol] for the Syn and Anti Conformers of $FC(O)SSCH_3$

	HF		B3LYP		MP2	
	6-31G*	6-31+G*	6-31G*	6-31+G*	6-31G*	6-31+G*
syn	0	0	0	0	0	0
anti	1.78	1.88	1.41	1.09	1.84	2.08

Table 2. Experimental and Calculated Geometric Parameters for the Syn Conformer of $FC(O)SSCH_3$ and for the Radical-Cation Form, $FC(O)SSCH_3^{\bullet+}$, Using Different Theoretical Approaches with the 6-31+G* Basis Set[a]

	$FC(O)SSCH_3$				$FC(O)SSCH_3^{\bullet+}$	
	HF	MP2	B3LYP	exptl[b]	HF	MP2
r_{C2F1}	1.3197	1.3728	1.3644	1.346	1.2866	1.3256
r_{C2O3}	1.1641	1.1973	1.1872	1.180	1.1547	1.1859
r_{S4C2}	1.7707	1.7673	1.7884	1.767	1.8178	1.8507
r_{S4S5}	2.0485	2.0541	2.0783	2.035	2.0042	1.9836
r_{C6S5}	1.8146	1.8115	1.8334	1.810	1.8226	1.8107
r_{C6H} (av)[c]	1.0812	1.0921	1.0932	1.035	1.0833	1.0925
α_{F1C2O3}	122.26	122.26	122.25	124.0 ± 5.0	127.63	128.61
α_{O3C2S4}	129.88	130.54	130.90	130.5 ± 1.0	125.20	125.86
α_{C2S4S5}	102.77	100.84	102.60	97.6 ± 1.5	97.37	96.31
α_{C6S5S4}	102.62	101.31	102.56	108.2 ± 1.0	100.62	100.36
α_{S5C6H} (av)[c]	109.15	109.34	109.09	109.5	108.01	110.25
$\delta_{C2S4S5C6}$	80.25	76.05	81.33	83.5 ± 1.5	−179.99	−179.99
$\delta_{HC6S5S4}$	−66.98	−66.83	−67.30		−61.08	−61.67
$\delta_{S5S4C3O2}$	−5.83	−5.95	−4.77		0.01	0.00

[a] Distances in angstroms, angles in degrees. For atom numbering, see Figure 1. [b] Plausible structure of $FC(O)SSCH_3$ from ref 23. [c] Av: average.

the values of the ionization energies between the two conformers is negligible with respect to the experimental resolution.

For $FC(O)SSCH_3$, results of microwave spectroscopy studies reveal the expected behavior of a C_1 symmetry conformer. The vibrational analysis confirms this result and evidences the existence of a conformational equilibrium for this species.[22] Because no theoretical calculations were carried out so far, a complete search for local minima was performed at the HF/6-31+G* level of approximation. Only two forms are found to be stable (Figure 1). Relative energies of the two conformers as obtained by several quantum chemical calculations are listed in Table 1. In accordance with both experimental and theoretical results, only the syn form presents an appreciable concentration at ambient temperature. The geometric parameters for this conformer, as predicted by the HF, B3LYP, and MP2 methods applying the 6-31+G* basis set, are listed in Table 2.

In the case of $FC(O)SSSC(O)F$, quantum chemical calculations lead to the existence of six minima, which can be divided into two groups, cis (C) and trans (T), depending on the mutual orientation of the C(O)F groups (see Figure 2). Relative energies of these conformers are collected in Table 3. Very strong dependence on both the theoretical approximation and quality of the basis set was found for the $FC(O)SSSC(O)F$ molecule. Thus, energy difference values for both HF and B3LYP methods with the 6-31G basis set are smaller than the values obtained with the more extended 6-31+G* basis set for all conformers. As has been well established, the presence of sulfur atoms requires the use of polarization functions in order to obtain reliable results. Even if energy differences between the conformers were quantitatively unsounded, theoretical energy values obtained with HF/6-31+G* and B3LYP/6-31+G* methods are in agreement with the trend $T_{s-s} < T_{s-a} < C_{s-s} < C_{s-a} < T_{a-a} < C_{a-a}$. Results using the MP2/3-21+G* approximation differ only in the relative order between the T_{s-a} and C_{s-s} conformers. However, all methods coincide such that the more stable form corresponds to the T_{s-s} conformer. Therefore, taking into consideration results from the B3LYP/6-31+G*, HF/6-31+G*, and MP2/3-21+G* approximations, the T_{s-s} form can be expected to be the most abundant under normal working conditions.

Table 3. Calculated Relative Energies [kcal/mol] of Different Conformers of $FC(O)SSSC(O)F$

	T_{s-s}	T_{s-a}	T_{a-a}	C_{s-s}	C_{s-a}	C_{a-a}
HF/6-31G	0	1.52	3.02	1.50	1.94	3.51
HF/6-31+G*	0	1.95	3.87	2.36	2.88	4.72
B3LYP/6-31G	0	0.85	1.70	1.17	1.43	2.08
B3LYP/6-31+G*	0	1.38	2.73	1.71	2.34	3.36
MP2/3-21+G*	0	2.32	4.66	1.27	3.30	5.02
MP2/6-31G	0	1.51	3.02	0.58	1.86	3.15

Table 4. Calculated Geometric Parameters for the T_{s-s} Conformer of $FC(O)SSSC(O)F$ and for the Radical-Cationic Form $(FC(O)SSSC(O)F)^{\bullet+a}$

	$FC(O)SSSC(O)F$			$(FC(O)SSS-C(O)F)^{\bullet+}$
	HF/6-31+G*	B3LYP/6-31+G*	MP2/3-21+G*	HF/6-31+G*
r_{C3F4}	1.3157	1.3582	1.4408	1.2878
r_{C3O5}	1.1621	1.1850	1.2193	1.1579
r_{S1C3}	1.7763	1.7962	1.7711	1.8074
r_{S1S2}	2.0518	2.0870	2.0538	2.0756
r_{S2S6}	2.0519	2.0873	2.0538	1.9889
r_{S6C7}	1.7763	1.7961	1.7711	1.8317
r_{F8C7}	1.3156	1.3582	1.4407	1.2831
r_{O9C7}	1.1621	1.1850	1.2193	1.1529
α_{S1C3O5}	129.59	130.61	132.45	125.84
α_{C7S6S2}	101.81	101.64	100.07	97.12
α_{S1C3F4}	107.44	106.40	105.71	107.19
α_{C3S1S2}	101.82	101.64	100.07	97.41
α_{S1S2S6}	105.83	107.08	105.28	102.41
α_{F8C7S6}	107.45	106.40	105.71	107.11
α_{O9C7S6}	129.59	130.61	132.45	124.44
α_{O9C7F8}	122.96	122.98	121.82	128.45
$\delta_{O5C3S1S2}$	5.13	4.89	5.88	6.67
$\delta_{S6S2S1C3}$	−82.94	−84.90	−80.18	−82.78
$\delta_{C7S6S2S1}$	−82.92	−84.90	−80.18	179.95
$\delta_{F8C7S6S2}$	−175.65	−175.80	−175.46	179.93

[a] Distances in angstroms, angles in degrees. For atom numbering, see Figure 2.

Geometric parameters as obtained by the HF, B3LYP (6-31+G*), and MP2 approaches (3-21+G*) for the most stable form (C_2 symmetry) with both CO bonds in syn position to the SS bonds are given in Table 4.

Photoelectron Spectra. The assignment of PES bands to photoionization processes from specific molecular orbitals is straightforward for small species such as fluorocarbonyl-

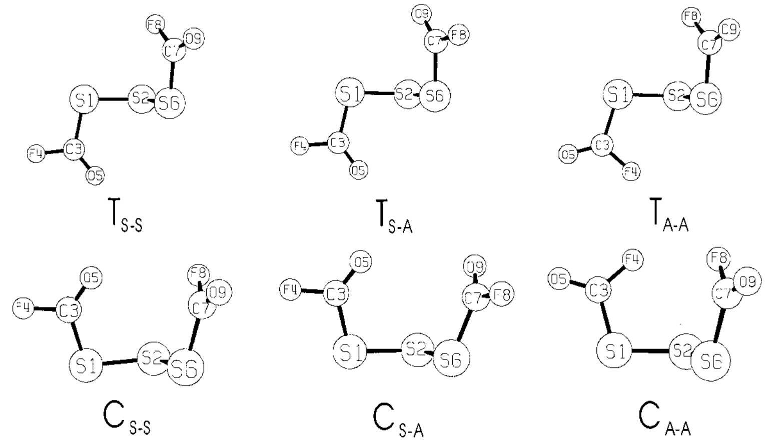

Figure 2. Schematic representation of six conformers of FC(O)SSSC(O)F.

sulfenyl chloride by comparison with similar data reported in the literature. PE spectra of sulfur containing molecules such as alkyl substituted sulfides and disulfides,[41] CF_3 and Cl substituted sulfides and disulfides,[42] as well as fluorocarbonyl derivatives, such as cyanoformyl fluoride, FC(O)CN,[43] are of particular interest in connection with our present study. Also, the predicted vertical ionization energies derived from the orbital eigenvalues, $IE_j = -\epsilon_j$ of the HF calculation (6-31+G*), and the ionization energies and pole strengths as obtained from the Green's function calculations were calculated for FC(O)SCl, $FC(O)SSCH_3$, and FC(O)SSSC(O)F. The pole strengths are, in the sudden limit, a measure of the relative intensities for the electron ejection out of a given orbital.

Because of the very poor Franck−Condon factors for the ionization transition near the threshold displayed by several sulfur-containing molecules, the true adiabatic ionization energies might not be observable for the photoelectron spectroscopy technique.

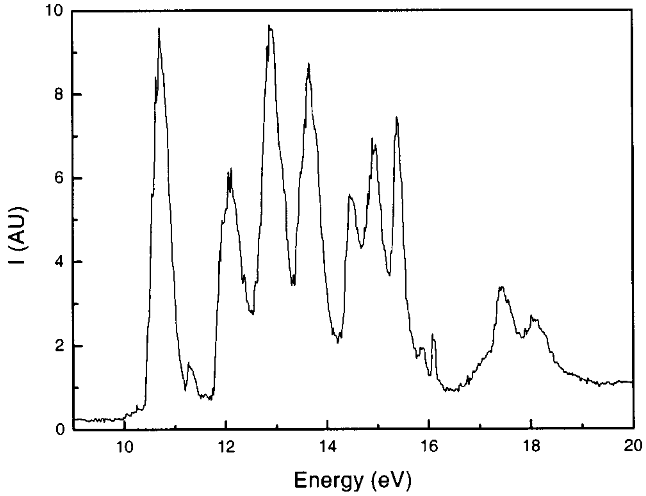

Figure 3. He I photoelectron spectrum of FC(O)SCl.

Table 5. Experimental Ionization Values (eV), Calculated $-\epsilon_j$ Values via Koopman's Theorem at the HF/6-31+G* Level, and IP Values as Obtained by ROVGF/6-31G Calculations for the Syn FC(O)SCl Molecule

exptl IE (eV)	HF/6-31+G* $(-\epsilon_j)^c$(eV)	ROVGF/6-31G^{a,b} IE (eV)^c	assignment
18.1	21.04		π^+_{FCO} (n''$_F$)
17.5	20.40		σ_{CF}
15.4	17.59	15.60 (0.90)	n'$_F$
14.9	16.29	14.89 (0.89)	π^-_{FCO} ($\pi''_{C=O}$)
14.5	15.17	14.51 (0.92)	n'$_S$
13.7	14.36	13.56 (0.91)	n''$_{Cl}$
12.9	14.05	12.83 (0.91)	n'$_{Cl}$
12.1	13.22	11.83 (0.92)	n'$_O$
10.7	11.69	10.28 (0.93)	n''$_S$

^{a} Pole strength between parentheses. ^{b} Geometry optimized at the HF/6-31+G* level of approximation. ^{c} Abbreviations: IE = ionization energy, ϵ = ab initio SCF energy of MOs.

FC(O)SCl. The PE spectrum of FC(O)SCl is presented in Figure 3. The experimentally determined and theoretical ionization energies are listed in Table 5. The planar structure of fluorocarbonylsulfenyl chloride allows the MOs to be labeled as in-plane (a′) and out-of plane (a″). The following analysis uses a localized orbital approach by means of SCF population analysis. The first band at 10.7 eV can be assigned to an ionization process from an orbital nominally labeled as n″(S), an out-of-plane lone pair corresponding to a sulfur atom. The first IP of hydrogen sulfide appears at 10.43 eV.[44] Formal substitution of the hydrogen atom by more electronegative groups leads to larger IP values. For example, the first IP values of some related molecules obtained from electron measurements[45] show that a chlorine atom is not as effective as a CF_3 group in increasing the IP value. On the other hand, substitution of hydrogen by electron-releasing alkyl groups results in a decrease of the IP value. Thus, CH_3SCl and CF_3SCl possess IPs of 9.2 ± 0.1 and 10.7 ± 0.1 eV, respectively. The IP value of CF_3SH[45] is 11.35 ± 0.1

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(42) (a) Cullen, W. R.; Frost, D. C.; Vroom, D. A. *J. Am. Chem. Soc.* **1969**, *8*, 1803. (b) Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D., Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17,* Supplement No. 1. Controversies about the adiabatic IE for CH_3SSCH_3 still exist. Li et al. have reported a value of 8.18 ± 0.03 obtained by the pulsed molecular beam photoionization mass spectroscopy method. (c) Li, W.-K.; Chiu, S.-W.; Ma, Y.-X.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1993**, *99* (11), 8440.

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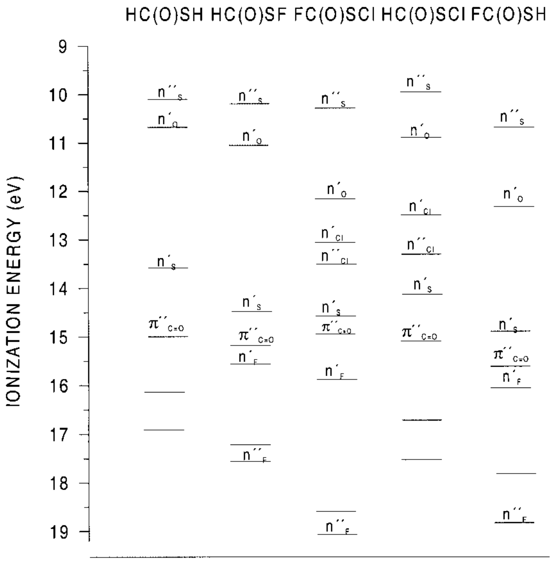


Figure 4. Schematic representation of ionization energy values for model molecules (FC(O)SH, HC(O)SCl, and HC(O)SF) and HC(O)SH as compared to FC(O)SCl, from HF/6-31+G*//OVGF/6-31+G* calculations.

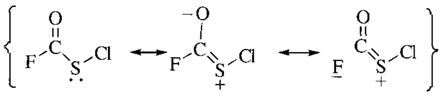
Table 6. Atomic Charge for the Molecular and Cation-Fadical Form of FC(O)SCl, Calculated with the UMP2/6-31+G* Approximation

	atoms					
	F	C	S	O	Cl	TAC[a]
FC(O)SCl	−0.33	0.49	0.28	−0.38	−0.06	0
$FC(O)SCl^{\bullet+}$	−0.22	0.51	0.74	−0.22	0.19	+1
Δq[b]	0.11	0.02	0.46	0.16	0.25	+1

[a] Total atomic charge. [b] $\Delta q = q_{(FC(O)SCl^{\bullet+})} - q_{(FC(O)SCl)}$.

eV, and the value for $S(CH_3)_2$ amounts to 8.67 eV.[41] The stabilization of the HOMO n″(S) orbital in FC(O)SCl is similar to that in CF_3SCl. However, this effect must be interpreted in terms of delocalization effects of the out-of-plane orbitals, rather than as inductive effects of the substituents. This feature is in agreement with the population analysis, which shows a remarkable interaction of the chlorine and the oxygen out-of-plane orbitals with the parent n″(S) orbital. This stabilization seems to be caused by the planar XC(O)S moiety around the C(sp^2) and is independent of the nature of X. The first IP values calculated (ROVGF/6-31+G*) for three model compounds HC(O)SCl, HC(O)SF, and FC(O)SH, as well as for HC(O)SH, are 9.8, 10.3, 10.7, and 10.2 eV, respectively. A diagrammatic feature of the relative energy levels of the orbitals is shown in Figure 4. These results are in agreement with the reported IP value for $CH_3C(O)SH$, which amounts to 10.00 ± 0.02 eV.[46] Further calculations (UMP2/6-31+G*) were performed in order to analyze the nature of the cation formed in the first ionization process. The results demonstrate that the atomic charges are delocalized all over the molecule, with an appreciable fraction localized at the S atom, as is evident from Table 6. In a similar way, the SC bond length and the OCF and OCS angles are the geometric parameters most influenced by ionization. The planar form, with syn orientation of the C═O and S—Cl bonds, is retained after ionization, in accordance with previous calculations.[47] The values of the adiabatic IPs derived from these calculations are 10.3 and 9.3 eV in the UMP2/6-31+G* and UHF/6-31+G* approximations, respectively. Further vibrational calculations performed for the cationic form result in shifts (567 and 102 cm^{-1}) of the wavenumbers for $\nu_{C=O}$ and ν_{C-F} toward higher values, as compared to the neutral form, while the ν_{C-S} wavenumber exhibits a shift of 439 cm^{-1} in the opposite direction. These results agree with the picture of an electron ionization mainly localized at the S atom, with the concomitant interruption of the mesomeric effect and with a reinforced bond character in the C═O and C—F bonds and the decrease in the corresponding S—C bond. Thus, the left form of the three resonant structures in Scheme 2 becomes more effective.

Scheme 2. Mesomeric Forms of FC(O)SCl



The band at 12.1 eV can be assigned to an ionization process involving an orbital nominally labeled as n′(O) in-plane orbital at the carbonyl oxygen atom, with a large contribution from the 3p in-plane orbital of sulfur. In the case of acetyl and formyl fluoride, the corresponding bands are found at 11.3 and 12.6 eV, respectively. For cyanoformyl fluoride, this value appears at 13.2 eV, because of the strong inductive effect of the cyano group.[43] Figure 4 demonstrates that this band depends on the atoms bonded to both the carbon and the sulfur atoms in contrast to the behavior earlier described for the n″(S) orbital.

The next two bands (Figure 3), at 12.9 and 13.6 eV, are originated by the presence of a Cl atom and can be assigned to ionization processes arising from the n′(Cl) in-plane and n″(Cl) out-of-plane orbitals, respectively, the latter being delocalized both over the sulfur and the oxygen atoms, in accordance with the calculations. The band at 14.5 eV can be assigned to an ionization process involving the n′(S) in-plane orbital.

The bands in the higher IE region of the spectrum between 15 and 19 eV arise from ionizations related to the C(O)F moiety. The planar geometry of the group allows interactions between the π″(CO) and n″(F) localized orbitals to become effective. Such an interaction is not possible for the in-plane n′(F). Thus, bands at 14.9 eV and at 18.1 eV may involve π″(CO) and n″(F), respectively. The structureless band at 15.4 eV can be related to the n′(F) orbital. The corresponding bands of formyl fluoride[43,48] and propynoyl fluoride,[49] which exhibit remarkably similar shapes, are found at 15.5 and 15.4 eV, respectively. In the case of cyanoformyl fluoride, the value for the band involving n′(F) amounts to 16.6 eV, because of the strong inductive influence of the cyano group. The large energetic splitting of 2.7 eV between n′(F) and

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(46) Watanabe, K.; Nakayama, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369. Referenced in *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991−1992; Chapter 10, p 216.

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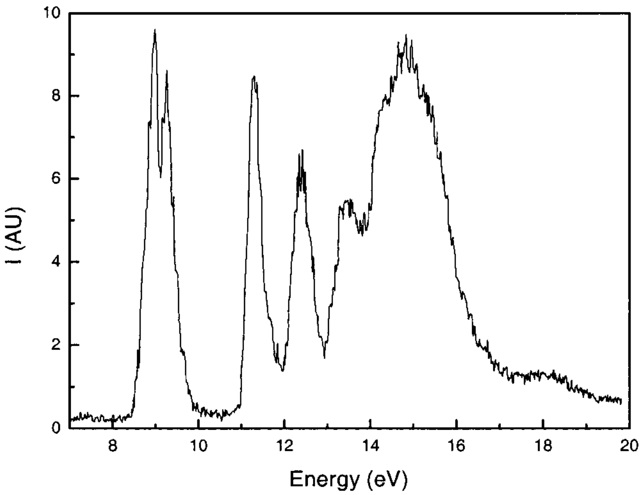

Figure 5. He I photoelectron spectrum of $FC(O)SSCH_3$.

Table 7. Experimental Ionization Values (eV), Calculated -ϵ_j Values via Koopman's Theorem at the 6-31+G* Level, and IP Values as Obtained by ROVGF/6-31G Calculations for the Syn Fc(o)ssch$_3$ Molecule

exptl IE (eV)	HF/6-31+G* $(-\epsilon_j)^c$(eV)	ROVGF/6-31G^{a,b} IE (eV)^c	assignment
	19.82	17.53 (0.87)	
	17.32	15.43 (0.90)	
	16.92	15.61 (0.91)	
	16.57	14.99 (0.91)	
	15.83	14.35 (0.89)	
	14.94	13.70 (0.91)	
12.4	13.63	12.08 (0.91)	n’$_S$
11.3	12.96	11.70 (0.92)	n’$_O$
9.3	11.24	10.13 (0.92)	n’’$_{S-C(O)F}$
9.0	10.47	9.49 (0.92)	n’’$_{S-CH3}$

[a] Pole strength between parentheses. [b] Geometry optimized at the HF/6-31+G* level of approximation. [c] Abbreviations: IE = ionization energy, ϵ = ab initio SCF energy of MOs.

n″(F) suggests a substantial interaction between the π''(CO) and n″(F) orbitals. More realistic labels are π^-(COF) (antisymmetric combination) for the 14.9 eV band and π^+(COF) (symmetric combination) for the 18.1 eV band. A similarly strong interaction was observed in formyl fluoride, propynoyl fluoride, propenoyl fluoride, and cyanoformyl fluoride, with ΔIE values (n″(F) − n′(F)) = 2.3, 1.8, 2.0, and 1.8 eV, respectively.[43] The last band in FC(O)SCl at 17.5 eV can be assigned to an ionization involving the σ(CF) in-plane bonding orbital.

$FC(O)SSCH_3$. The PE spectrum of $FC(O)SSCH_3$ is presented in Figure 5, and the experimental ionization energies are collected in Table 7. The photoelectron spectrum shows a splitting of the first PE band at 9.0 and 9.3 eV. A similar behavior was observed in the case of HSSH as well as for the symmetrically substituted disulfides CH_3SSCH_3 and $(CH_3)_3CSSC(CH_3)_3$.[41] This splitting is originated by the interaction of the two lone pairs at the adjacent S atoms showing a clear dependence on the dihedral angle. However, in the case of $FC(O)SSCH_3$, the reason for this splitting seems to be different. The molecule is not symmetrical, possessing substituents of different nature in their electronic properties (donor/acceptor). Thus, the CH_3 group is an electron ejector, while the effect of the FC(O) moiety on the S lone pair ionization potential is similar to the very electronegative CF_3 group. Thus, the first band at 9.0 eV can be attributed to the S lone pair at the sulfur atom bonded to the CH_3 group, and the second band, at 9.3 eV, to the S lone pair of the sulfur atom bonded to the FC(O) group. These assignments are in agreement with both the ROVGF/6-31G calculations and with the results obtained by a charge analysis (UMP2/6-31+G*) for the cation-radical $FC(O)SSCH_3^{\bullet+}$, which shows that the positive charge is mainly localized at the $S-CH_3$ sulfur atom (see Table 8). A value of $IP^{ad} = 9.0$ eV is derived from this approximation.

Table 8. Atomic Charge for the Molecular and Cation-Radical Form of $FC(O)SSCH_3$ Calculated with the UMP2/6-31+G* Approximation^a

	atoms							
	F_1	C_2	O_3	S_4	S_5	C_6	H(av)	TAC^b
$FC(O)SSCH_3$	−0.34	0.45	−0.41	0.21	0.12	−0.76	0.24	0
$FC(O)SSCH_3^{\bullet+}$	−0.25	0.50	−0.30	0.35	0.61	−0.84	0.31	+1
Δq^c	0.09	0.05	0.11	0.14	0.49	−0.08	0.07	+1

[a] For atom numbering, see Figure 1. [b] Total atomic charge. [c] $\Delta q = q_{(FC(O)SSCH3^{\bullet+})} - q_{(FC(O)SSCH3)}$.

The IE values obtained for related disulfides support these assumptions. For example, the IPs for $(CH_3)_2S_2$ and $(CF_3)_2S_2$ amount to 8.7 and 10.6 eV, respectively, demonstrating a strong influence of the substituents on the ionization values of the S lone pair.[42]

Another aspect of interest related to the charged form is the change in the geometry after ionization. As can be seen from Table 2, this structure possesses a planar skeleton, with a CSSC dihedral angle of 180°. This finding is in agreement with previous results obtained by semiempirical calculations for CH_3SSCH_3[50] and by the comparison of the experimental rates of dissociation with statistically expected rates for the CH_3SSCH_3 ion.[33] This change in the geometry may be the reason for the structureless broad band observed when the first ionization process occurs. A similar behavior was also observed recently for the ionization of the CH_3SSCH_2 radical.[51] After the original study performed by Walsh,[52] many workers[50,53] have published qualitative and quantitative MO studies using Walsh diagrams. Thus, they have been able to predict geometry differences between the ground and ionized state. This qualitative picture agrees with the results of our full ab initio calculations for the radical-cation geometry.

The bonds most affected by ionization are those related to the FC(O)S moiety. This fact gives additional evidence with respect to the importance of the anomeric effect via the interaction of the S lone pair in the conformation of the ground state, that is, the CSSC dihedral angle with values close to 90°.

The bands at higher energies between 13 and 16 eV show a broad signal that is characteristic of the CH_3 moiety. This unresolved signal makes a further assignment difficult.

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(50) Gillbro, T. *Phosphorus Sulfur Relat. Elem.* **1978**, *4*, 133.
(51) Backer, J.; Dyke, J. M. *J. Phys. Chem.* **1994**, *98*, 757.
(52) Walsh, A. D. *J. Chem. Soc.* **1953**, 2260.
(53) For instance: (a) Kimura, K.; Osafune, K. *Bull. Chem. Soc. Jpn* **1975**, *48* (9), 2421. (b) Gimarc, B. M. *J. Am. Chem. Soc.* **1970**, *92*, 266.

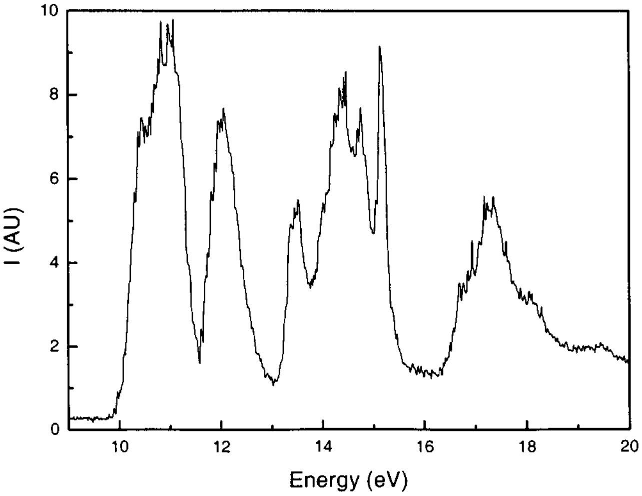

Figure 6. He I photoelectron spectrum of FC(O)SSSC(O)F.

Table 9. Experimental Ionization Values (eV), Calculated $-\epsilon_j$ Values via Koopman's Theorem at the HF/6-31+G* Level, and IP Values as Obtained by ROVGF/6-31G Calculations for the T_{s-s} Conformer of FC(O)SSSC(O)F

exptl IE (eV)	HF/6-31+G* $(-\epsilon_j)^c$(eV)	ROVGF/6-31G^{a,b} IE (eV)^c	assignment
17.3			
16.9	18.04	15.61 (0.89)	
15.1	17.53	15.14 (0.89)	n^A_F
14.8	16.63	14.83 (0.88)	$\pi_{C=O}$
14.8	16.51	14.79 (0.88)	$\pi_{C=O}$
14.4	15.73	14.32 (0.90)	n^A_S
13.5	15.02	13.51 (0.90)	n^A_S
12.1	14.19	12.29 (0.90)	n^B_O
12.1	13.88	12.09 (0.90)	n^A_O
11.0	12.04	10.68 (0.92)	n^A_S
10.8	12.13	10.57 (0.92)	n^B_S
10.5	12.07	10.48 (0.92)	n^B_S

[a] Pole strength between parentheses. [b] Geometry optimized at the HF/6-31+G* level of approximation. [c] Abbreviations: IE = ionization energy, ϵ = ab initio SCF energy of MOs.

FC(O)SSSC(O)F. The PE spectrum of FC(O)SSSC(O)F is presented in Figure 6. The experimental ionization energies are given in Table 9.

The C_2 symmetry of the most stable conformer enables the classification of the molecular orbitals as symmetric (A) and antisymmetric (B) orbitals with respect to the C_2 symmetry axis. The following analysis uses a localized orbital approach by means of the SCF population analysis.

The first broad band in the spectrum can be deconvoluted into three bands at 10.4, 10.8, and 11.1 eV. According to the orbital population analysis, the first two bands are related to B symmetry orbitals, while the third one is assigned to an A symmetry orbital, all of them being localized mainly at the sulfur atoms. The ROVGF/6-31G calculations result in three IP values very close together at 10.5, 10.6, and 10.7 eV. In addition, calculations for the radical-cation form using the UHF/6-31+G* approximation agree with this feature, as can be derived from the charge analysis and the changes in the molecular geometry after ionization. As is evident from Table 10, the change in charge after ionization is mainly induced at the S2 atom. The C2SSS dihedral angle results in a value of ≈ −180° for the charged form (Table 4), so an antiplanar structure is deduced for the FC(O)SSS moiety in the cation-radical form. From this calculation, an IP_{ad} value of 9.4 eV is obtained.

The first adiabatic ionization potentials for CH_3SSSCH_3 measured by photoelectron spectroscopy are 8.7, 9.1, and 11.1 eV, respectively, and the corresponding values of CF_3SSSCF_3 were observed at 10.2, 12.8, and 13.5 eV.[42,54] The effect of the FC(O) group on the ionization of the S lone pair is similar to that of CF_3, as already discussed in the comparison between FC(O)SCl and CF_3SCl.

As can be seen from Table 4, one of the SSSC dihedral angles in the charged form is close to 180°, while the other one retains the gauche conformation. The bond length most influenced by ionization is in the SC bond, in accordance with $FC(O)SSCH_3$.

The general features of the PE spectrum of FC(O)SSSC(O)F are very similar to the ones observed in the case of FC(O)SCl. This is due to the similarity in the substituents bonded to the S atom. The assignments of the bands in the FC(O)SSSC(O)F spectrum are quite similar to the FC(O)SCl ones, except those corresponding to the chlorine atom.

Thus, the band at 12.1 eV can be assigned to an ionization process arising from an orbital located on the carbonyl oxygen atoms, with an important contribution from the 3p in-plane orbital of the sulfur atoms. The ROVGF/6-31G calculation results in two bands with A and B symmetries at 12.1 and 12.3 eV, respectively.

The band at 13.5 eV can be assigned to an ionization arising from an A orbital, which has a prominent contribution from the equivalent sulfur atoms. The ROVGF/6-31G approximation predicts a value of 13.5 eV, in agreement with the experiment. The next band at 14.4 eV can be attributed to the corresponding ionization of an antisymmetric orbital located on the S2 atom.

The band at 14.8 eV originates from the C=O groups. The ROVGF/6-31G calculation results in two bands at 14.79 and 14.83 eV, with B and A symmetry, respectively. The narrow and structureless band at 15.1 eV is characteristic of an ionization produced in the fluorine atoms and presents A symmetry. The bands in the higher IE region of the spectrum over 16.0 eV show a broad feature making it difficult for further assignments.

Conclusion

The first IP values for FC(O)SCl, $FC(O)SSCH_3$, and FC(O)SSSC(O)F originate from the sulfur lone pairs and are mainly influenced by the groups bonded to the S atom. The first band in the He I photoelectron spectra of the three sulfur containing molecules shows a clear dependence on the substituents attached to the sulfur atom. Thus, in the spectra of $FC(O)SSCH_3$ and FC(O)SSSC(O)F, this band is split into two and three components, respectively, corresponding to the ionization of different sulfur atoms. The first IP values are 10.7, 9.0, and 10.5 eV for the mono-, di-, and trisulfur

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(54) The first adiabatic ionization potential measured by electron impact for CH_3SSSCH_3 is 8.80 ± 0.15 eV. Hobrock, B. G.; Kiser, R. W. *J. Phys. Chem.* **1963**, *67*, 1283.

Table 10. Atomic Charge for the Molecular and Cation-Radical Form of FC(O)SSSC(O)F as Obtained by the UHF/6-31+G* Approximation[a]

	atoms									
	F_4	C_3	O_5	S_1	S_2	S_6	F_8	C_7	O_9	TAC[b]
FC(O)SSSC(O)F	−0.30	0.43	−0.37	0.23	0.02	0.23	−0.30	0.43	−0.37	0
FC(O)SSSC(O)$F^{\bullet +}$	−0.25	0.48	−0.33	0.35	0.38	0.39	−0.25	0.49	−0.26	+1
Δq[c]	0.05	0.05	0.04	0.12	0.36	0.16	0.05	0.06	0.11	+1

[a] For atom numbering, see Figure 2. [b] Total atomic charge. [c] $\Delta q = q_{(FC(O)SSSC(O)F^{\bullet +})} - q_{(FC(O)SSSC(O)F)}$.

compounds discussed in this work, respectively. The rather high ionization potential values obtained for the sulfur atom bonded to the C(O)F moiety are a consequence of the mesomeric effect, which can be explained as the result of wide electronic delocalization in the planar FC(O)S moiety.

The calculations performed in the FC(O)SSCH$_3$ and FC(O)SSSC(O)F molecules show a typical structure observed in other disulfides and trisulfides reproducing also the syn conformation of the C═O double bond with respect to the S─S single bond.

After ionization, the heavy atom nonplanar di- and trisulfide structures, FC(O)SSCH$_3$ and FC(O)SSSC(O)F, become totally planar and planar for the FC(O)SSS moiety, respectively.

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