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# Matrix Isolation of the Elusive Fluorocarbonylsulfenyl Fluoride Molecule $\text{FC(O)SF}$

Melina V. Cozzarín,<sup>†</sup> Rosana M. Romano,<sup>\*†</sup> Helge Willner,<sup>‡</sup> and Carlos O. Della Védova<sup>‡,§</sup>

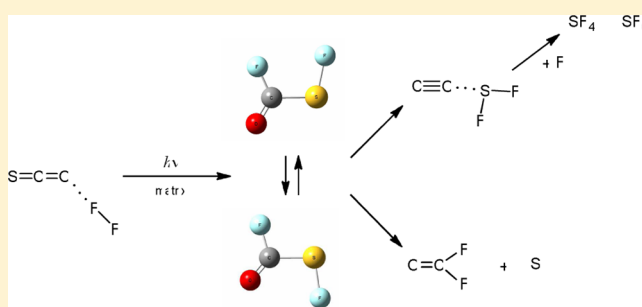
<sup>†</sup>CEQUINOR (UNLP-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, (1900) La Plata, Argentina

<sup>‡</sup>Anorganische Chemie, Bergische Universität Wuppertal, Gaußstraße 20, D-42097 Wuppertal, Germany

<sup>§</sup>Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Camino Centenario e/505 y 508, (1897) Gonnet, Argentina

**S** Supporting Information

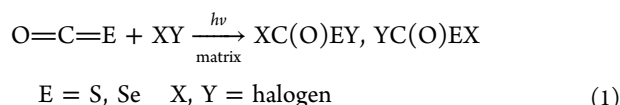
**ABSTRACT:** The *syn* and *anti* conformers of the hitherto unknown fluorocarbonylsulphenyl fluoride FC(O)SF were formed through the photochemical reactions between OCS and F<sub>2</sub>, isolated in solid Ar. The reactions were followed by Fourier transform infrared (FTIR) spectroscopy, and the unknown products were proposed by comparison of the observed IR absorptions with their computed IR spectra. The reactions occur through a 1:1 molecular complex between OCS and F<sub>2</sub>, forming the *anti*-FC(O)SF first, which subsequently transforms into the *syn* form, through a randomization process. At longer times of irradiation, FC(O)SF decomposes by extrusion of a CO molecule with the concomitant formation of SF<sub>2</sub> and the formation of a difluoride in the matrixes is proposed to explain the formation of SF<sub>4</sub> and



## ■ INTRODUCTION

Compounds of the general formula  $\text{XC}(\text{O})\text{SY}$ , with X and Y halogen, were known since the 1960s. Nowadays chlorocarbonylsulphenyl chloride,  $\text{ClC}(\text{O})\text{SCl}$ ,<sup>1</sup> is a commercial reagent, widely used in organic and inorganic synthesis.<sup>2</sup>  $\text{FC}(\text{O})\text{SCl}$ ,<sup>3</sup>  $\text{FC}(\text{O})\text{SBr}$ ,<sup>4</sup> and  $\text{ClC}(\text{O})\text{SBr}$ <sup>5</sup> constitute other examples of this interesting family of compounds. However, fluorocarbonylsulphenyl fluoride,  $\text{FC}(\text{O})\text{SF}$ , has remained unknown, in spite of attempts at its preparation following different chemical strategies. Moreover, to the best of our knowledge, no  $\text{XC}(\text{O})\text{SF}$  molecule, with X = halogen, has been previously reported. Attempts to prepare  $\text{FC}(\text{O})\text{SF}$  by halogen exchange on  $\text{FC}(\text{O})\text{SCl}$  with different fluorination agents such as  $\text{SbF}_3$ ,  $\text{AgF}$ ,  $\text{KF}$ , and so on failed. The thermal reaction of equimolar amounts of  $\text{OCS}$  with  $\text{F}_2$  in the gas phase yielded high partial pressures of  $\text{SF}_2 + \text{CO}$ , which enabled measurements of its high-resolution gas-phase IR<sup>6</sup> and gas-phase NMR<sup>7</sup> spectra.

During the past few years we have prepared novel, unstable compounds, through photochemical reactions in matrix conditions (see, for example, ref 8 and references cited therein). Different penta-atomic molecules were isolated through the general matrix photochemical reaction described by eq 1.



The main characteristics of photochemical reactions performed under matrix conditions are the isolation of the

reactants and the low temperatures. In general, due to the rigidity of solid argon that confines the isolated species in a matrix cage, the photoproducts are formed only from atoms initially present in the matrix cage. Considering the high dilutions of the reactants with respect to the matrix gas, the matrix sites will be most probably occupied by each of the reactants alone, and only a few of them would host the two reactants, unless they form a molecular complex. In this case, the reaction will occur through these “pre-reactive” complexes, which were proposed to play a very important role in the course of photochemical reactions.<sup>9</sup>

In this work we have investigated the products of the photochemical reactions between OCS and F<sub>2</sub>, isolated together in solid argon matrixes, by means of Fourier transform infrared (FTIR) spectroscopy, motivated by the possibility of isolating the hitherto elusive FC(O)SF molecule. To propose a detailed photochemical mechanism, the matrixes were exposed to UV radiation for different periods of time, and IR spectra were taken after each stage of irradiation. The novel species proposed in this contribution were also theoretically investigated, since comparison with the simulated spectra would be a valuable tool for the assignment of the experimental IR absorptions developed on photolysis to the unknown molecules.

Received: September 19, 2012

**Revised:** December 24, 2012

**Published:** December 25, 2012

## EXPERIMENTAL SECTION

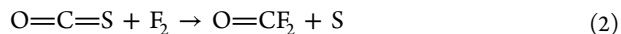
Samples of  $F_2$  (Solvay, Germany) were transferred into a 1 L stainless steel container at a vacuum line and diluted with Ar in two different proportions ( $F_2$ :Ar = 1:100 and 1:600). Separately, samples of OCS (prepared according to ref 10) were mixed with argon in a 0.5 L glass container in two different proportions (OCS:Ar = 1:100 and 1:600). Both containers were connected via needle valves and stainless steel capillaries to the spray-on nozzle of the matrix support. About 0.5–1.0 mmol of the gas mixtures were codeposited within 10–20 min on the mirror support at 15 K (a mirror plane of a rhodium-plated copper block). The full light of a 150 W mercury high-pressure lamp (TQ150, Haereus, Hanau, Germany) was directed through water cooled quartz lenses onto the matrix for 1–120 min. The photolysis process was followed by IR spectroscopy. Details of the matrix apparatus are given elsewhere.<sup>11</sup> For comparison purposes, the experiment was repeated on an Ar-matrix containing only OCS. Matrix IR spectra were recorded on a IFS 66v/S spectrometer with a resolution of  $0.5\text{ cm}^{-1}$ , in absorption/reflection mode, as described in ref 11. The IR intensities were determined integrating the areas of the absorptions using the OPUS Program.

All of the quantum chemical calculations were performed using the Gaussian 03 program suit.<sup>12</sup> MP2 and density functional theory (B3LYP) methods were tried, in combination with different basis sets. Geometry optimizations were sought using standard gradient techniques by simultaneous relaxation of all the geometrical parameters. The calculated vibrational properties correspond in all cases to potential energy minima with no imaginary frequencies.

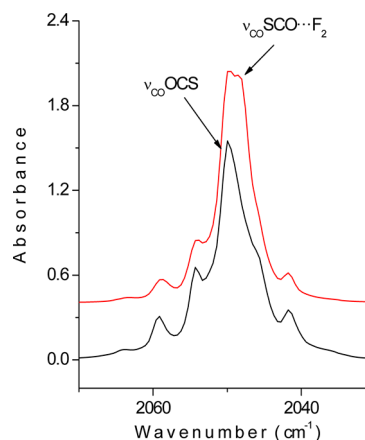
The binding energies of the molecular complexes were calculated using the correction proposed by Nagy et al.<sup>13</sup> The basis set superposition errors have been calculated by applying the counterpoise procedure developed by Boys and Bernardi.<sup>14</sup>

## RESULTS AND DISCUSSION

**Matrix-Isolation Experiments.** Previously we studied several photochemically induced reactions in matrices of reactants that were diluted together in inert gases before deposition.<sup>15–17</sup> However, the highly reactive  $F_2$ –OCS mixtures, even diluted in Ar, did not survive mixing. Instead, the matrices were formed by codeposition of OCS and  $F_2$ , both diluted in Ar, on the matrix support at 15 K. The FTIR spectra of the matrices were compared with the IR spectrum of OCS isolated under the same conditions. Besides the characteristic absorptions of OCS,<sup>18</sup> low intensity signals at 1940.3, 1912.3, and 1243.7/1240.4/1237.9  $\text{cm}^{-1}$  attributable to fluorophosgene,  $O=CF_2$ ,<sup>19</sup> were detected in the spectra, denoting a fast chemical reaction during codeposition (eq 2).

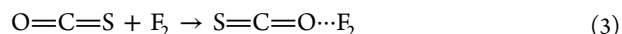


The IR spectra taken immediately after deposition of the mixtures in the spectral region corresponding to the  $C=O$  stretching fundamental of the OCS molecule, together with the spectrum of an OCS sample isolated in the same conditions, is depicted in Figure 1. A close inspection reveals the presence of an additional absorption in the mixture, red-shifted approximately  $2\text{ cm}^{-1}$  with respect to the free OCS band. The relative intensity of this band with respect to the one assigned to free OCS decreases in the more diluted matrix. This new feature may be assigned to OCS perturbed by the presence of a fluorine molecule in the same matrix site. The formation of a

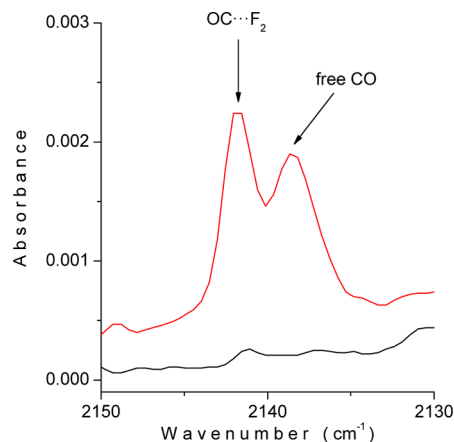


**Figure 1.** FTIR spectra of Ar matrices containing OCS in the proportion 200:1 (bottom) and OCS and  $F_2$  in the proportion 200:1:2 (top) in the 2030 to 2070  $\text{cm}^{-1}$  region after deposition.

molecular complex between these two species was investigated by ab initio and density functional theory (DFT) methods. As presented below, an angular structure in which the oxygen atom of the OCS unit interacts with the fluorine molecule constitutes the form that best reproduces the observed experimental shift of the  $\nu(C=O)$  fundamental of OCS ( $\Delta\tilde{\nu}_{\text{exp}} = -2.0\text{ cm}^{-1}$ ,  $\Delta\tilde{\nu}_{\text{calc}} = -1.8\text{ cm}^{-1}$ ). Thus monomeric OCS and  $F_2$  form a 1:1  $SCO:F_2$  molecular complex during deposition (eq 3).



Two very weak features were observed in the region of the absorption of the CO molecule (see Figure 2): a band at



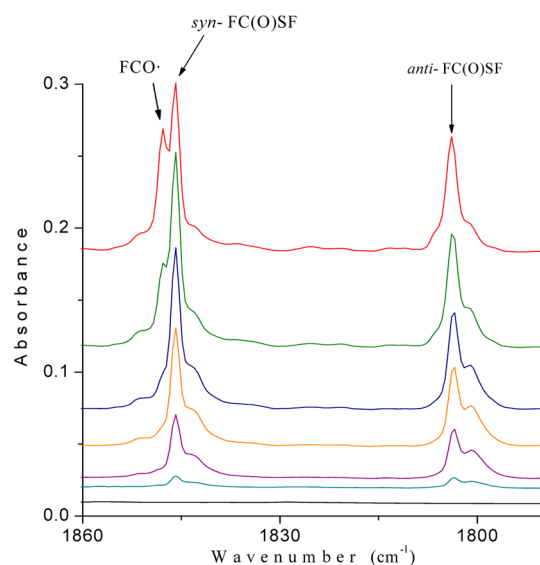
**Figure 2.** FTIR spectra of Ar matrices containing OCS in the proportion 200:1 (bottom) and OCS and  $F_2$  in the proportion 200:1:2 (top) in the 2130 to 2150  $\text{cm}^{-1}$  region after deposition.

2138.5  $\text{cm}^{-1}$  is attributed to free CO isolated in the Ar matrix,<sup>20</sup> and a second absorption at 2141.8  $\text{cm}^{-1}$  is attributed to a complexed CO.<sup>21</sup> The small amount of CO was generated during deposition as a consequence of the fast reaction of OCS with  $F_2$ .<sup>6,7</sup>

After codeposition of the gas mixtures, the resulting matrices were irradiated for different times, and the changes were followed by FTIR spectroscopy. Several new absorptions, with distinct photolysis behaviors developed, while the IR band of the  $SCO\cdots F_2$  molecular complex decayed during the first irradiation. The features corresponding to free OCS decreased

only 20% from their original value after 2 h of photolysis, giving clear indications that most of the photoproducts were produced from the complex. As useful criteria for the assignment of the IR bands to the photoproducts, the absorptions were grouped together according to their behaviors against the irradiation time.

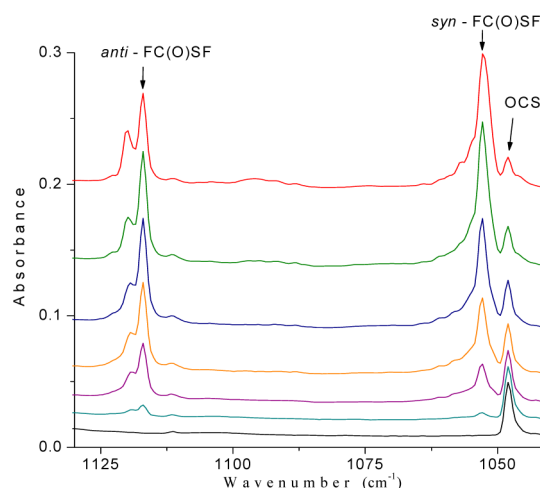
On the basis of the quantum chemical calculations, presented below, and the comparison with related molecules, particularly  $\text{FC(O)SCl}^{22}$  and  $\text{FC(O)SBr}^4$ , we expect for the target species,  $\text{FC(O)SF}$ , intense IR absorptions in the spectral region corresponding to the  $\text{C=O}$  and  $\text{C-F}$  stretching fundamentals. Figure 3 shows the IR spectra between  $1790$  and  $1860\text{ cm}^{-1}$  of



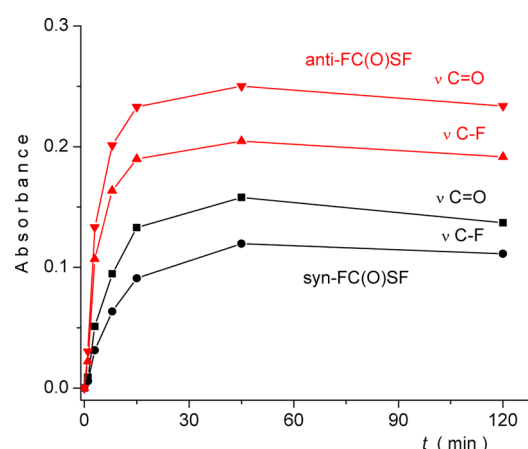
**Figure 3.** FTIR spectra of an Ar matrix containing OCS and  $\text{F}_2$  ( $\text{OCS:F}_2\text{:Ar} = 1:2:200$ ) in the  $1790\text{--}1860\text{ cm}^{-1}$  region immediately after deposition (bottom) and after 1, 2, 8, 15, 45, and 120 min photolysis (from bottom to top).

a matrix containing  $\text{OCS:F}_2\text{:Ar}$  in a  $1:2:200$  proportion at different irradiation times. While there are no absorptions in this spectral region in the initial spectrum, two features clearly developed on photolysis. Two other bands are also formed on photolysis in the spectral region corresponding to the  $\nu(\text{C-F})$  fundamental, as depicted in Figure 4.

Figure 5 shows a plot of the intensities of these four absorptions, at  $1845.5$ ,  $1803.6$ ,  $1116.6$ , and  $1052.5\text{ cm}^{-1}$ , against the irradiation time. Although the four bands present a similar behavior with the irradiation time, from the relative intensities of these absorptions plotted against time, depicted in Figure 6, the presence of two different photoproducts becomes clear. The  $1803.6$  and  $1116.6\text{ cm}^{-1}$  bands belong to one species, while the other two features, at  $1845.5$  and  $1052.5\text{ cm}^{-1}$ , correspond to a second one. Considering this behavior, the prediction of theoretical calculations, and also the comparison with related molecules, we propose the formation of the *anti* (the  $\text{S-F}$  single bond *anti* with respect to the  $\text{C=O}$  double bond) and *syn* (the  $\text{S-F}$  single bond *syn* with respect to the  $\text{C=O}$  double bond) conformers of  $\text{FC(O)SF}$  as responsible for the  $1803.6/1116.6$  and  $1845.5/1052.5\text{ cm}^{-1}$  bands, respectively. As can be seen in Table 1, the agreement between the wavenumbers attributed to the *syn* and *anti* forms of different  $\text{FC(O)SX}$  molecules is excellent, reinforcing the proposed assignment.

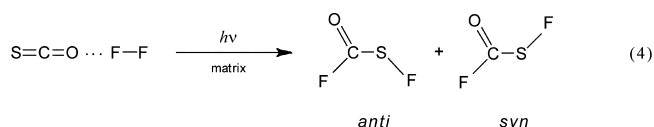


**Figure 4.** FTIR spectra of an Ar matrix containing OCS and  $\text{F}_2$  ( $\text{OCS:F}_2\text{:Ar} = 1:2:200$ ) in the  $1040\text{--}1130\text{ cm}^{-1}$  region immediately after deposition (bottom) and after 1, 2, 8, 15, 45, and 120 min photolysis (from bottom to top).



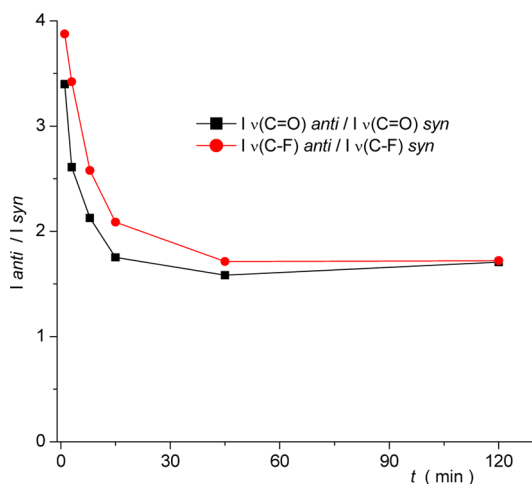
**Figure 5.** Plots as a function of irradiation time of the intensities of the bands assigned to *syn* (black) and *anti* (red)  $\text{FC(O)SF}$  in the IR spectrum of an Ar matrix initially containing OCS,  $\text{F}_2$ , and Ar in the proportions  $1:2:200$ .

The formation of the *syn* and *anti* conformers of  $\text{FC(O)SF}$  appears as the main channel in the photochemical reaction of OCS and  $\text{F}_2$  isolated together in an Ar matrix (eq 4). According to Figure 6, the proportion of the *anti* form with respect to the *syn* conformer is higher at the first irradiation, and then decays up to an approximately constant value. This finding may be interpreted either as the formation of the *anti* form first, presumably favored by the geometry of the  $\text{OCS}\cdots\text{F}_2$  molecular complex, and then the production of the *syn* form by a randomization process, or by different formation kinetics for each of the conformers.



As predicted by the calculations, three further IR absorptions between  $600$  and  $800\text{ cm}^{-1}$  are expected for each conformer, with medium or weak intensities, assigned to the  $\nu(\text{S-F})$ ,  $\nu(\text{C-S})$ , and  $\delta(\text{C=O})_{\text{oop}}$ . The IR spectra taken after irradiation are very congested in this spectral region, due to





**Figure 6.** Plots as a function of irradiation time of the relative intensities of the bands assigned to *anti* form of FC(O)SF with respect to the absorptions of the *syn* form in the IR spectrum of an Ar matrix initially containing OCS, F<sub>2</sub>, and Ar in the proportions 1:2:200.

**Table 1. Comparison of the Wavenumbers of the Most Intense IR Absorptions of the *syn* and *anti* Forms of FC(O)SX Compounds (with X = Cl, Br) Isolated in Solid Ar with the Proposed *syn* and *anti* FC(O)SF**

FC(O)SF		FC(O)SCL <sup>a</sup>		FC(O)SBr <sup>b</sup>		assignment
<i>syn</i>	<i>anti</i>	<i>syn</i>	<i>anti</i>	<i>syn</i>	<i>anti</i>	
1845.5	1803.6 1800.8	1843	1803	1838	1800	ν (C=O)
1052.5	1119.6 1116.6	1044	1102	1043	1106	ν (CF)

<sup>a</sup>Reference 22. <sup>b</sup>Reference 4.

the photochemical formation of several products, particularly molecules containing S–F bonds, which prevent the observation of the bands belonging to both forms of FC(O)SF. However, two bands discernible at 477.8 and 509.9 cm<sup>−1</sup>, are attributed to the δ(O=C–S) of the *anti* and *syn* conformers of FC(O)SF respectively, based on their behaviors against the irradiation time, and also exhibit very good agreement with the theoretically predicted values.

Besides the absorptions assigned to FC(O)SF, several new bands were observed in the IR spectra of the irradiated matrices, particularly important at longer irradiation times. A complete list of the wavenumbers, together with a proposed assignment and a comparison with reported values, is presented in Table 2.

Figure 7 depicts the IR spectra of the matrix containing OCS:F<sub>2</sub>:Ar in a 1:2:200 proportion at different irradiation times, in the absorption spectral region of the CO molecule. A group of absorptions, at 2152.3/2150.1/2146.6 cm<sup>−1</sup>, blue-shifted with respect to the free CO molecule, suggests a CO complexed with other photoproduct. Two other signals, close to 822 and 795 cm<sup>−1</sup> and readily assigned to SF<sub>2</sub> by comparison with reported values,<sup>23</sup> accompany the time behavior of the complexed CO, as shown in Figure 8. The formation of a 1:1 CO:SF<sub>2</sub> loose complex is proposed, presumably from a decomposition of the FC(O)SF conformers described in eq 5.



The proposed mechanism was also found as the main photochemical pathway for several XC(O)SY compounds isolated in inert solid matrixes. Some unstable triatomic sulphides, such as ClSF,<sup>24</sup> BrSF,<sup>25</sup> and BrSCL,<sup>26</sup> were isolated from FC(O)SCL, FC(O)SBr, and ClC(O)SBr, respectively, using this strategy. The photolysis of ClC(O)SCL isolated in Ar and N<sub>2</sub> matrixes follows also the same channel, giving the well-known SCL<sub>2</sub> molecule.<sup>27</sup> The experimental wavenumbers of the absorptions assigned to the CO:SF<sub>2</sub> molecular complex are in very good agreement with the simulated spectrum of this species, presented below.

Another absorption observed in Figure 7, at 2140.7 cm<sup>−1</sup>, coincides with the band formed after irradiation of an Ar matrix containing only OCS, and was then assigned to a CO molecule interacting with a S atom in the same matrix cage.



Due to the high dilution of the reactants in the matrix, and also considering the equilibrium described by eq 3, it is plausible to think that some matrix cages were occupied by the OCS⋯F<sub>2</sub> complex, while other hosted OCS or F<sub>2</sub> molecules. The resultant IR spectra should then be interpreted as the sum of the photoproducts formed in each matrix site. Similar results were found in the photolysis of OCSe isolated in solid Ar, being the proposed CO⋯Se complex observed at 2140.1 cm<sup>−1</sup>.<sup>8,28</sup>

Difluorophosgene, O=CF<sub>2</sub>, is another photoproduct of the studied matrix reactions. Besides the IR absorptions already present in the spectrum taken before irradiation, several new features, slightly shifted to lower wavenumbers with respect to the free O=CF<sub>2</sub>, were observed to appear (see Table 2), denoting some kind of complexation, presumably with F<sub>2</sub>. By comparison with previous studies of the photochemical matrix reactions of CO and halogen and interhalogen molecules,<sup>29</sup> the formation of difluorophosgene may be attributed to the reaction between CO and F<sub>2</sub> assisted by light, as described by eq 7.



The feature at 1847.5 cm<sup>−1</sup>, discernible in the spectra after 45 min of photolysis, was assigned to the FCO· radical, according to the reported value.<sup>30</sup> This radical may be attributed either to migrating F atoms and their reaction with CO, or to the photodecomposition of FC(O)SF or O=CF<sub>2</sub> molecules.

Several absorptions appear below the 950 cm<sup>−1</sup> spectral region (see Figure 9). As presented in Table 2, the comparison with Ar-matrix reported values of SF<sub>x</sub> compounds, with x = 2, 4, 6, allow us to propose the photochemical formation of these molecules in the matrix. As already mentioned above, the SF<sub>2</sub> species is apparently complexed with a CO molecule, while the other SF<sub>x</sub> compounds, SF<sub>4</sub><sup>31</sup> and SF<sub>6</sub>,<sup>32,33</sup> seemed to be isolated, at least on the evidence of their IR spectra. The formation of SF<sub>5</sub> radical may be proposed, but the evidence is not conclusive, since the two reported absorptions for this species, near 812 and 552 cm<sup>−1</sup>,<sup>34</sup> are close to the bands assigned to OC⋯<sup>34</sup>SF<sub>2</sub> and SF<sub>4</sub>, respectively. The comparison of their behavior against the irradiation time, depicted in Figure 10, shows that the formation of the species containing the largest number of fluorine atoms, SF<sub>6</sub>, is favored at longer irradiation times.

**Quantum Chemical Calculations.** *Fluorocarbonylsulphenyl Fluoride*, FC(O)SF. Two planar structures, the *syn* (with the C=O double bond *syn* with respect to the S–F single bond) and the *anti* forms depicted in Figure 11, were found as energy minima in the theoretical study of FC(O)SF using different

**Table 2.** Wavenumbers and Assignments of the IR Absorptions Appearing after Broad-Band UV–Visible Photolysis of an Ar Matrix Containing a Mixture of OCS and F<sub>2</sub> at ca. 15 K

Ar matrix	assignment		wavenumbers reported previously	Ar matrix	assignment		wavenumbers reported previously
$\tilde{\nu}$ [cm <sup>-1</sup> ]	molecule	vibrational mode	$\tilde{\nu}$ [cm <sup>-1</sup> ]	$\tilde{\nu}$ [cm <sup>-1</sup> ]	molecule	vibrational mode	$\tilde{\nu}$ [cm <sup>-1</sup> ]
2152.3 } 2150.1 } 2146.6 }	OC...SF <sub>2</sub>	$\nu$ (C=O)	this work	937.9	SF <sub>6</sub>	$\nu_{as}$ (SF <sub>6</sub> ) ( $\nu_3$ )	938.6 } 937.9 } 937.6 } <sup>c</sup>
2140.7 } 1946.7 } 1938.2 } 1935.9 }	OC...S O=CF <sub>2</sub>	$\nu$ (C=O) $\nu$ (C=O) ( $\nu_1$ )	this work 1941.4 <sup>a</sup>	920.6	<sup>34</sup> SF <sub>6</sub>	$\nu_{as}$ ( <sup>34</sup> SF <sub>6</sub> ) ( $\nu_3$ )	921.4 } 920.8 } 920.3 } <sup>d</sup>
1913.9 } 1911.0 } 1907.6 } 1905.8 } 1899.9 }	O=CF <sub>2</sub>	$2\nu_2$	1913.5 <sup>a</sup>	884.0	SF <sub>4</sub>	$\nu_{as}$ (SF <sub>4</sub> ) ( $\nu_1$ )	884.0 <sup>e</sup>
1847.5 } 1845.5 } 1803.6 } 1800.8 }	FCO• <i>syn</i> -FC(O)SF <i>anti</i> -FC(O)SF	$\nu$ (C=O) $\nu$ (C=O) $\nu$ (C=O)	1855.0 <sup>b</sup> this work this work	856.7	SF <sub>4</sub>	$\nu_{as}$ (SF <sub>4</sub> ) ( $\nu_6$ )	{ 859.7 856.4 <sup>e</sup>
1257.6 } 1251.4 } 1246.3 }	O=CF <sub>2</sub>	$\nu_{as}$ (CF <sub>2</sub> ) ( $\nu_4$ )	1237.8 <sup>a</sup>	825.4 } 822.9 } 821.0 }	OC...SF <sub>2</sub>	$\nu_{as}$ (SF <sub>2</sub> )	this work
1119.6 } 1116.6 }	<i>anti</i> -FC(O)SF	$\nu$ (CF)	this work	813.9 } 805.0 } 795.0 } 793.1 }	OC... <sup>34</sup> SF <sub>2</sub> OC...SF <sub>2</sub>	$\nu_{as}$ ( <sup>34</sup> SF <sub>2</sub> ) $\nu_s$ (SF <sub>2</sub> )	this work this work
1052.5 } 972.8 } 968.1 } 965.7 } 962.0 }	<i>syn</i> -FC(O)SF O=CF <sub>2</sub>	$\nu$ (CF) $\nu_s$ (CF <sub>2</sub> ) ( $\nu_2$ )	this work 965.5 <sup>a</sup>	771.6 } 767.0 }	O=CF <sub>2</sub>	$\gamma$ (CO) $\nu_4$	768.9 <sup>a</sup>
				705.0 } 701.9 } 699.1 }	SF <sub>4</sub>	$\nu_{as}$ (SF <sub>4</sub> ) ( $\nu_8$ )	709 } 706 } 704.5 } <sup>e</sup>
				552.5 } 528.2 }	SF <sub>4</sub> SF <sub>4</sub>	$\delta$ (SF <sub>2</sub> ) ( $\nu_3$ ) wag (SF <sub>2</sub> ) ( $\nu_7$ )	552 <sup>e</sup> 529 <sup>e</sup>
				509.9 } 477.8 }	<i>syn</i> -FC(O)SF <i>anti</i> -FC(O)SF	$\delta$ (O=C–S) $\delta$ (O=C–S)	this work this work

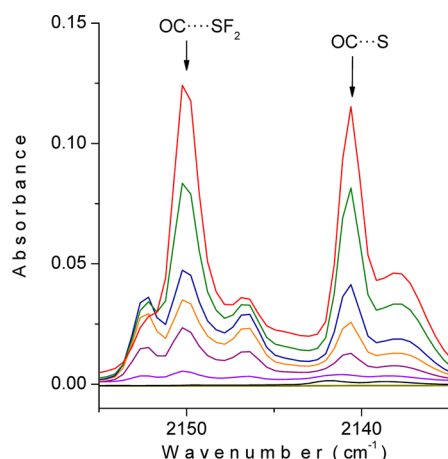
<sup>a</sup>Reference 19. <sup>b</sup>Reference 30. <sup>c</sup>Reference 32. <sup>d</sup>Reference 33. <sup>e</sup>Reference 31

approximations. The calculated geometrical parameters of the conformers using the B3LYP and MP2 theoretical approximations in combination with the 6-311+G\* basis set are presented as Supporting Information (Table S1 and S2). The *syn* conformer was predicted as the most stable one, in agreement with previous reports, based both in experimental and theoretical results, for other XC(O)SY molecules. The energy difference between the *anti* and *syn* forms of FC(O)SF, corrected by zero point energy, is predicted to be 2.5 and 4.2 kJ·mol<sup>-1</sup> according to the B3LYP and MP2 approximation, respectively. The calculated energy barrier for the *syn*–*anti* isomerization, occurring through a *gauche* form, was 31.0 (B3LYP) and 25.9 (MP2) kJ·mol<sup>-1</sup>.

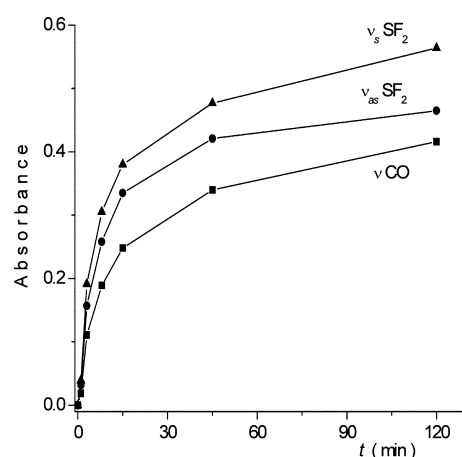
The vibrational frequencies were calculated to characterize the structures as energy minima, and also to compare the experimental wavenumbers assigned to these species with the theoretical predictions. Table 3 compiles the wavenumbers of the *syn* and *anti* conformers of FC(O)SF, together with the experimental absorptions. The predicted IR intensities of the fundamental modes, also included in the table, are in agreement with the experimental findings. The  $\nu$ (C=O) and  $\nu$ (C–F) modes, observed in the spectra as a consequence of the photochemical reaction between OCS and F<sub>2</sub>, are the most intense ones in the calculated spectra. The rest of the fundamentals are predicted with low relative intensity, as presented in Table 3. Only the vibrational absorptions assigned to the  $\delta$ (O=C–S) of each conformer are discernible in the spectral

region below 800 cm<sup>-1</sup>. The other three vibrational modes expected in this region are presumably overlapped by the intense features belonging to the SF<sub>x</sub> species. The anharmonic wavenumbers were also computed with the B3LYP/6-311+G\* level of approximation: the  $\nu$ (C=O) fundamental is predicted at 1850.0 and 1829.3 cm<sup>-1</sup> for the *syn* and *anti* conformers, respectively, while the theoretical values for the  $\nu$ (C–F) mode are 984.4 (*syn*) and 1079.3 (*anti*) cm<sup>-1</sup>.

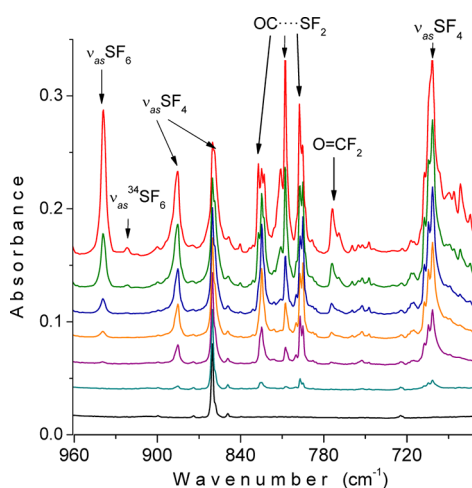
**Molecular Complexes between OCS and F<sub>2</sub>.** To help in the interpretation of the IR matrix spectra of the OCS and F<sub>2</sub> mixtures taken after deposition, 1:1 molecular complexes between these species were theoretically investigated. As a starting point in the search of structures that may correspond to energy minima, previous studies on van der Waals complexes between OCS and Cl<sub>2</sub> or Br<sub>2</sub> were considered. For these systems, three different structures were predicted by the calculations, in agreement with the observed in matrix experiences.<sup>9</sup> In the most stable structure, the sulfur atom of the OCS coordinates with one of the halogen atoms of the dihalogen molecule in an angular structure. In the other two, the OCS interacts through the oxygen atom, forming either an angular or linear structure. For the OCS:F<sub>2</sub> system, only two structures were found to correspond to energy minima when B3LYP and MP2 methods were employed. Both complexes present angular geometries, as depicted in Figure S1 of the Supporting Information: one interacting through the oxygen atom of the OCS moiety, while in



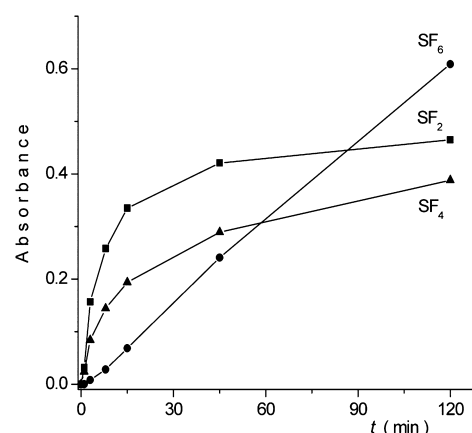
**Figure 7.** FTIR spectra of an Ar matrix containing OCS and  $F_2$  ( $OCS:F_2:Ar = 1:2:200$ ) in the  $2135\text{--}2155\text{ cm}^{-1}$  region immediately after deposition (bottom) and after 1, 2, 8, 15, 45, and 120 min photolysis (from bottom to top).



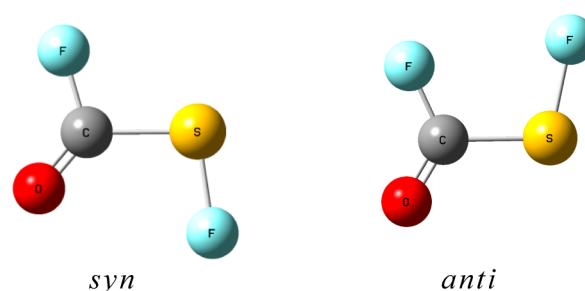
**Figure 8.** Plots as a function of irradiation time of the intensities of the bands assigned to the  $OC\cdots SF_2$  molecular complex in the IR spectrum of an Ar matrix initially containing OCS,  $F_2$ , and Ar in the proportions 1:2:200.



**Figure 9.** FTIR spectra of an Ar matrix containing OCS and  $F_2$  ( $OCS:F_2:Ar = 1:2:200$ ) in the  $670\text{--}960\text{ cm}^{-1}$  region after deposition (bottom) and after 1, 2, 8, 15, 45, and 120 min photolysis (from bottom to top).



**Figure 10.** Plots of the intensities of bands assigned to  $SF_2$ ,  $SF_4$ , and  $SF_6$  in the IR spectrum of an Ar matrix initially containing OCS,  $F_2$ , and Ar in the proportion 1:2:200 versus irradiation times.



**Figure 11.** Molecular models of the *syn*- and *anti*- $FC(O)SF$  calculated with the B3LYP/6-311+ $G^*$  approximation.

the other the interaction occurs through the sulfur atom. The third structure, with linear geometry, does not correspond to an energy minimum, since its theoretical vibrational spectrum presents imaginary frequencies, and will then not be further considered. The binding energies  $\Delta E$ , energy corrections, net charge  $q$  transferred, orbital stabilization, and geometrical parameters for the two complexes between OCS and  $F_2$ , calculated with the B3LYP/6-311+ $G^*$  approximation, are compiled in Table S2. The comparison of the experimental evidence with the quantum chemically predicted IR spectra for both complexes (see Table S3 of the Supporting Information) allows us to conclude that an adduct in which the oxygen atom of the OCS unit interacts with the fluorine molecule with an angular structure is the one that reproduces the  $-2.0\text{ cm}^{-1}$  observed experimental shift of the  $\nu(C=O)$  vibration. In addition, the activation of the F–F stretching vibration is predicted to have very low intensity, in coincidence with the lack of its appearance in the IR spectra of a matrix containing the complex, and in contrast with the predictions for the complex binding through the S atom. The activation of the  $\nu(F-F)$  mode was previously reported for the  $OCSe\cdots F_2$  molecular complex.<sup>8</sup> Figure S2 of the Supporting Information depicts a schematic representation of the orbital interaction between the lone pair of an O atom of OCS and the unfilled antibonding  $\sigma^*$  orbital of the  $F_2$  molecule in the  $SCO\cdots F_2$  complex.

**Molecular Complexes of CO with  $F_2$  and  $SF_2$ .** 1:1 molecular complexes between CO and  $F_2$  or  $SF_2$  were theoretically investigated. The results are presented as Supporting Information in Tables S4 and S5 and Figure S3 for the CO/ $F_2$  system, and in Tables S6 and S7 and Figures S4 and S5 for the complexes formed between CO and  $SF_2$ . The main

**Table 3.** Experimental and Calculated Wavenumbers (in  $\text{cm}^{-1}$ ) of *syn* and *anti*-FC(O)SF (Relative IR Intensities Given in Parentheses)

<i>syn</i> -FC(O)SF			<i>anti</i> -FC(O)SF			assignment
Ar matrix	theoretical calculations		Ar matrix	theoretical calculations		
$\tilde{\nu}$ [cm <sup>-1</sup> ]	B3LYP/6-311+G*	MP2/6-311+G*	$\tilde{\nu}$ [cm <sup>-1</sup> ]	B3LYP/6-311+G*	MP2/6-311+G*	
1845.5 (100)	1910.9 (100)	1895.6 (83)	1803.6 } 1800.8 } (100)	1857.4 (100)	1851.3 (92)	$\nu(\text{C}=\text{O})$
1052.5 (70)	1025.0 (98)	1055.5 (100)		1109.0 (93)	1137.5 (100)	$\nu(\text{C}-\text{F})$
	766.3 (17)	782.1 (18)	1119.6 } 1116.6 } (82)	739.5 (25)	754.6 (29)	$\nu(\text{S}-\text{F})$
	737.4 (8)	749.4 (8)		749.0 (3)	766.5 (<1)	$\nu(\text{C}-\text{S})$
	620.3 (3)	627.5 (2)		628.7 (3)	634.8 (3)	$\delta(\text{C}=\text{O})_{\text{oop}}$
509.9 (4)	501.1 (1)	517.4 (2)	477.8 (4)	471.9 (3)	487.0 (4)	$\delta(\text{O}=\text{C}-\text{S})$
	371.3 (<1)	385.0 (<1)		396.2 (<1)	410.3 (<1)	$\delta(\text{F}-\text{C}-\text{S})$
	200.4 (<1)	211.2 (1)		199.7 (1)	215.7 (2)	$\delta(\text{F}-\text{S}-\text{C})$
	139.8 (<1)	137.7 (<1)		123.9 (<1)	113.2 (1)	$\tau$

motivation of these calculations was the assignment of the experimental wavenumbers by the comparison with the calculated spectra for the different molecular complexes.

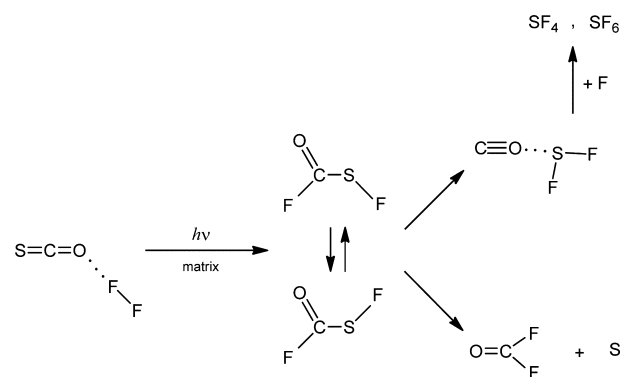
As previously reported for complexes between CO and halogen or interhalogen molecules,<sup>35</sup> different linear structures are plausible for the complexes, arising from the donor possibilities of either the C or the O atoms of the CO molecule. In the present case, the experimental blue-shift wavenumber of the CO vibration is consistent with the predictions for the  $\text{OC}\cdots\text{F}_2$  structure. In addition, the calculated stabilization energy of this form with respect to the monomers is predicted to be higher than in the  $\text{CO}\cdots\text{F}_2$  form.

Two different structures were also predicted for the 1:1 complexes between CO and  $\text{SF}_2$ , as depicted in Figure S4. In the most stable one, the two units are held together through the orbital interaction of the electron lone pair localized at the C atom of CO with one of the unfilled antibonding  $\sigma_{\text{SF}}^*$  orbital of the  $\text{SF}_2$  molecule (see Figure S5), while in the second structure, the O of the CO acts as an electron donor. Based mainly on the comparison between the experimental shift of the  $\nu(\text{C}=\text{O})$  fundamental of  $+11.6\text{ cm}^{-1}$  with respect to free CO isolated in solid Ar, and the calculated shifts of  $+14.7$  and  $-7.9\text{ cm}^{-1}$  for  $\text{OC}\cdots\text{SF}_2$  and  $\text{CO}\cdots\text{SF}_2$ , respectively, we propose that the former structure was formed in the matrix.

## CONCLUSIONS

The photochemical reactions between Ar-matrix-isolated OCS and  $\text{F}_2$  by broad-band UV–visible radiation were investigated. The photoproducts were proposed by comparison of the bands developed in the spectra with reported values for known compounds, and with the prediction of theoretical calculation and the comparison with related molecules for novel species. A proposed general mechanism is depicted in Scheme 1.

Before irradiation, the matrix is composed by different cages containing free OCS, the  $\text{SCO}\cdots\text{F}_2$  complex, and small amounts of  $\text{O}=\text{CF}_2$  formed during deposition. Taking into consideration the high dilution of the reactants in the Ar matrix, and also the rigidity of the solid environment, we can in principle consider that the photochemical products would be originated inside each of the matrix sites. In the sites containing the  $\text{SCO}\cdots\text{F}_2$  complex, the most efficient process, starting from the first irradiation period, was the formation of the *anti* and *syn* conformers of the hitherto unknown fluorocarbonylsulphenyl fluoride, FC(O)SF. The formation of the *anti* conformer is favored

**Scheme 1.** Schematic Representation of the Photochemical Reactions Occurring in Matrix Sites Originally Containing the  $\text{SCO}\cdots\text{F}_2$  Molecular Complex

at the beginning of the irradiation, and then slowly transformed into the *syn* form, in a general process observed for sulphenylcarbonyl compounds known as photochemical randomization.

These penta-atomic molecules photoevolved at longer irradiation times following two different channels, in agreement with previous studies on similar compounds. In one channel, the extrusion of a CO molecule with the concomitant formation of  $\text{SF}_2$  was observed. The matrix cage effect prevents these two molecules from escaping from the site, favoring the formation of a van der Waals complex. In an alternative channel, difluorophosgene was produced.

A very unusual and interesting process is the photochemical formation of  $\text{SF}_x$  molecules, with  $x = 4, 6$ . The isolation of four molecules in the same matrix site ( $3\text{ F}_2 + \text{OCS}$ ), necessary for the photoproduction of  $\text{SF}_6$ , is highly improbable at the proportions used in the experiments. If this hypothesis is discarded, these observed photoproducts may be explained through a very efficient migration of F atoms in the matrix. Long-range atomic migration of F atoms upon photodissociation in solid Ar were predicted from molecular dynamics simulations<sup>36</sup> and also verified by experimental studies.<sup>37</sup>

## ASSOCIATED CONTENT

### Supporting Information

Calculated geometrical parameters (B3LYP/6-311+G\*) for the *syn*- and *anti*-FC(O)SF (Table S1). Uncorrected and corrected binding energies  $\Delta E$ , BSSE and GEOM corrections, net charge  $q$  transferred, orbital stabilization, and geometrical parameters



for the different complexes between OCS and F<sub>2</sub> (Table S2), CO and F<sub>2</sub> (Table S4), and CO and SF<sub>2</sub> (Table S6), calculated with the B3LYP/6-311+G\* approximation. Computed vibrational IR spectra (B3LYP/6-311+G\* and MP2/6-311+G\*) for the different complexes between OCS and F<sub>2</sub> (Table S3), CO and F<sub>2</sub> (Table S5), and CO and SF<sub>2</sub> (Table S7). Models for the different complexes between OCS and F<sub>2</sub> (Figure S1), CO and F<sub>2</sub> (Figure S3), and CO and SF<sub>2</sub> (Figure S4). Schematic representation of the orbital interaction for the SCO...F<sub>2</sub> (Figure S2) and OC...SF<sub>2</sub> (Figure S5) molecular complexes. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

C.O.D.V. and R.M.R. thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 0352), the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, PICT 33878 and 322), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), and the Facultad de Ciencias Exactas, UNLP for financial support.

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