▌ **Inorganic Chemistry**

Unimolecular Photochemical Mechanisms of FC(O)SSCl Isolated in Solid Ar

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The photochemistry of FC(O)SSCl isolated in solid Ar was investigated on the basis of the IR spectra of the matrices before and after different times of broad-band UV-visible irradiation. The first process occurring on broad-band UV-visible irradiation was the transformation of the *syn-gauche* form of FC(O)SSCl into the *anti-gauche* conformer. FC(O)SCl and ClFC=O were produced, involving the loss of one or two sulfur atoms, respectively. Other mechanisms have originated CO···ClSSF, OCS···ClSF, OCS···ClF, CO···ClSF and CS₂···ClF molecular complexes, identified by the comparison of the experimental IR spectra with that simulated with DFT (B3LYP/6-311+G*) calculations, with the exception of OCS···ClF, which was assigned on the basis of the comparison with reported IR absorptions.

Introduction

FC(O)SSCl, a new exponent of the FC(O)S- family and a potentially useful reactant to chemically transfer the FC(O)SS- moiety, was recently reported. According with results of IR and Raman vibrational spectroscopies, analysed with the aid of quantum-chemical calculations, FC(O)SSCl exhibits a conformational equilibrium between *syn-gauche* and *anti-gauche* rotamers (see Figure 1), both in vapour and liquid phases, with an

Figure 1. *Syn-gauche* and *anti-gauche* conformers of FC(O)SSCl (from reference 1).

approximate ratio of 80:20% at ambient temperature. The title molecule was also isolated in solid Ar at low temperature, and its FTIR spectrum was interpreted in terms of the presence of two conformers in equilibrium.[1]

Matrix isolation photochemistry, combined with vibrational spectroscopy, was revealed as a very useful technique for the study of unimolecular photochemical mechanisms, due to the particular conditions of the experiments, i.e. low temperatures, high dilutions and inert environments (see for example references 2–5 and references cited therein). The formation of high-energy conformers, unstable molecules, free radicals, and molecular complexes can be induced by light in matrices and detected by IR spectroscopy, allowing a detailed determination of the photochemical channels.

In this work we present the study of the UV-visible broad band photochemistry of the recently prepared FC(O)SSCl isolated in solid Ar at ~ 10 K in 1:1000 proportion. The high dilution and rigidity of the matrix guarantee the course of the photolysis through exclusively unimolecular photochemical mechanisms. The photolysis of the title molecule was monitored by FTIR spectroscopy, taking spectra at different irradiation times to follow the evolution of the various photoproducts. The observed IR absorptions for the species developed on photolysis were compared with literature values or with the predictions of DFT calculations for the unknown species.
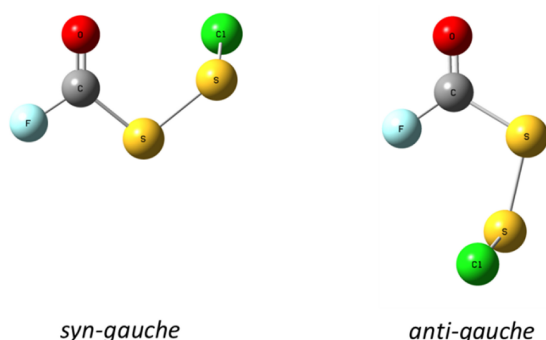
Results and Discussion

Matrix–isolation photochemistry of FC(O)SSCl

A mixture of FC(O)SSCl with Ar in a proportion close to 1:1000 was deposited onto an IR-transparent CsI window cooled to approximately 10 K, forming a solid matrix. The FTIR spectrum of the mixture, taken immediately after deposition, was entirely consistent with that published,[1] with signals arising either from the *syn-gauche* conformer or from the *anti-gauche* form.

The matrix was then irradiated with broad-band UV-visible light for different periods of time, after which FTIR spectra were recorded. Several new IR absorptions were observed to develop

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on photolysis, while the intensities of the bands belonging to FC(O)SSCl also changed during the irradiation. As reported in previous investigations (see for example reference 2) the analysis of the evolution of the developing absorptions against the irradiation time allows for identification of bands that present the same behaviour. This is a very useful criterion for the assignment of the new IR signals to the proposed photoproducts.

The first process that occurs upon irradiation is the light-induced transformation of the *syn-gauche* form into the *anti-gauche* conformer. Figure 2 shows two regions of the IR spectra
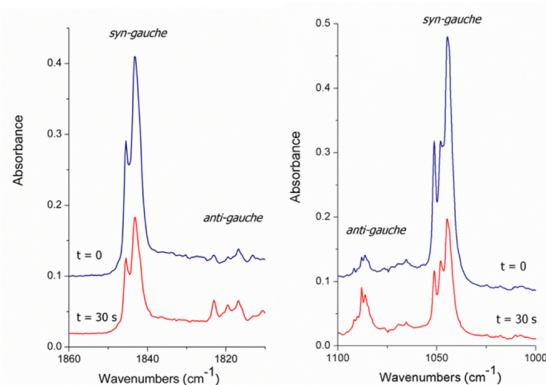
Figure 2. FTIR spectra of an Ar matrix initially containing FC(O)SSCl in 1:1000 proportion (top, blue trace) and after 30 s of broad-band UV-visible photolysis (bottom, red trace) between 1860 and 1810 cm⁻¹ (left) and 1100 and 1000 cm⁻¹ (right). The spectra were taken with 0.125 cm⁻¹ resolution and 256 scans.

of the matrix, corresponding to the most intense absorptions assigned to the C=O and C-F stretching modes, taken after deposition and following 30 s of irradiation. The group of bands at 1822.9/1819.4/1816.7 cm⁻¹, assigned to the ν(C=O) of the *anti-gauche* form, is observed to grow at the expense of the 1845.3/1842.9 cm⁻¹ absorptions of the same vibrational mode of the *syn-gauche* form. The bands assigned to the ν(C-F) fundamental modes, occurring at 1087.8/1086.2 and 1051.2/1048.0/1044.7 cm⁻¹ for the *anti-gauche* and *syn-gauche* conformers, respectively, also present the same behaviour upon irradiation (see Figure 2). The plots of the relative intensities of these two fundamentals in each of the forms ($I\nu(C=O)_{a-g}/I\nu(C=O)_{s-g}$ and $I\nu(C-F)_{a-g}/I\nu(C-F)_{s-g}$) against the irradiation time are presented as supporting information (Figure S1). The rest of the absorptions of the *anti-gauche* conformer (a complete list was published in reference [1]), although with much lower intensity, also increase their relative intensities with respect to the *syn-gauche* form. These results constitute a very important tool for the assignment of the IR absorptions of each of the conformers.

The new IR absorptions appearing after photolysis, excluding those previously described for the *anti-gauche* conformer that are already present in the unirradiated matrix, are listed in Table 1. As discussed in the introduction, the high dilution of

Table 1. Wavenumbers (in cm⁻¹) and proposed assignment for the IR absorptions developed after broad-band UV-visible photolysis of FC(O)SSCl isolated in an Ar matrix in 1:1000 proportion

ν (cm⁻¹)	Proposed Assignment Molecule	Vibrational Mode	Reported Wavenumber
2154.3	(OC⋯ClSF)-I	νC=O	This work
2151.8	(OC⋯ClSF)-II	νC=O	This work
2141.0 \ 2140.4	OC⋯ClSSF	νC=O	This work
2138.2	CO	νC=O	2138.2 [a]
2136.9	OC⋯ClSSF	νC=O	This work
2058.7	OCS⋯ClF	νC=O	2058.7 [b]
2054.0	(OCS⋯ClSF)-I	νC=O	This work
2050.5	(OCS⋯ClSF)-II	νC=O	This work
2049.6	OCS	νC=O	2049.6 [b]
2046.9	OCS⋯FCl	νC=O	2046.8 [b]
2042.0	(OCS⋯ClSF)-IV	νC=O	This work
2039.4	SCO⋯ClF	νC=O	2039.9 [b]
2022.6	¹⁸OCS⋯ClF	νC=O	2022.0 [b]
2005.9	O¹³CS⋯ClF	νC=O	2006.2 [b]
1862.9	FClC=O	νC=O	1865.2 [c]
1841.9 \ 1840.7 \ 1836.5 \ 1833.2	syn-FC(O)SCl	νC=O	1843 [d]
1803.5 \ 1800.7	anti-FC(O)SCl	νC=O	1803 [d]
1526.3	CS²⋯ClF	$\nu^{as}CS^2$	This work
1128.0 \ 1127.0	FC(O)SCl	2ν(S-Cl)	1133 \ 1127 \ 1121
1102.6	anti-FC(O)SCl	ν(C-F)	1109 \ 1104 \ 1099
1082.9 \ 1081.9	FClC=O	ν(C-F)	1083.2 \ 1082.7
1044.9	syn-FC(O)SCl	ν(C-F)	1059 \ 1054 \ 1049
857.0	SCO⋯ClF	ν(C=S)	865.7 [b]
778.5 \ 776.4	(OCS⋯ClSF)-IV	ν(S-F)	This work
774.5	(OC⋯ClSF)-II	ν(S-F)	This work
771.5 \ 770.1	(OCS⋯ClSF)-II	ν(S-F)	This work
769.2	(OCS⋯ClSF)-I	ν(S-F)	This work
761.1 \ 760.3 \ 758.3	CS²⋯ClF	ν(Cl-F)	This work
752.3	FC(O)SCl	νC-S	753 \ 748 \ 742
720.5	OCS⋯ClF	ν (Cl-F)	730.6 \ 724.0
628.5	FC(O)SCl	δoop(C=O)	634 \ 628 \ 620
623	OC⋯ClSSF	ν(S-F)	This work
567.5 \ 562.0	FC(O)SCl	ν (S-Cl)	565 \ 560

[a] Ref. 18 [b] Ref. 14 [c] Ref. 6 [d] Ref. 7

FC(O)SSCl in the noble gas prevents any photochemical transformation other than unimolecular mechanisms. Then, only the possible photoproducts formed from just one molecule of FC(O)SSCl were considered. Some of the products were readily identified by comparison of the IR bands with literature values.

For example, the features at 1862.9 and 1082.9/1081.9 cm⁻¹, which grow until 30 min of irradiation and then slightly decrease under further photolysis, were associated with the formation of FClC=O, according with its Ar-matrix published spectrum.[6] From the very beginning FC(O)SCl was developed, in both its *syn-* and *anti-*conformational forms, as recognized by comparison of several of the new absorptions with the IR spectrum of this compound isolated in Ar matrix (see Table 1).[7] The loss of sulfur atoms from photolysis of a sulfur-containing molecules was previously reported (see for examples references 8–12).

Figure 3 depicts the IR spectral region between 2080 and 2020 cm⁻¹, characteristic of the carbonyl stretching mode of
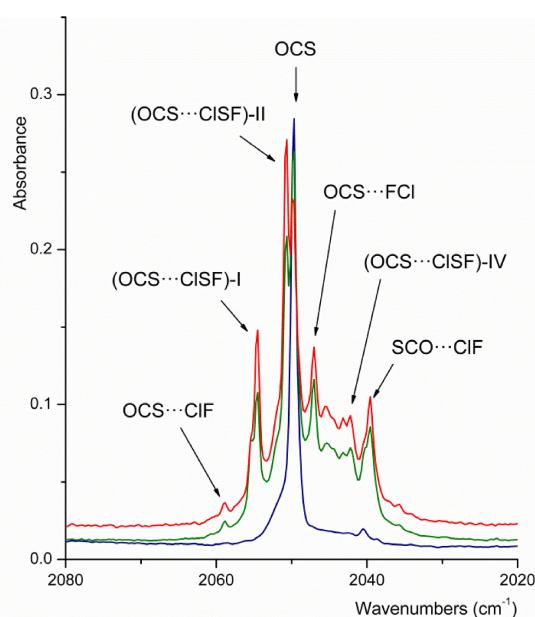
Figure 3. FTIR spectra of an Ar matrix initially containing FC(O)SSCl in 1:1000 proportion (bottom, blue trace) and after (from bottom to top) 900 (green trace) and 1800 s (red trace) of broad-band UV-visible photolysis between 2080 and 2020 cm⁻¹. The spectra were taken with 0.125 cm⁻¹ resolution and 256 scans.

the OCS molecule. In the spectrum of the matrix recorded before irradiation, an absorption at 2049.6 cm⁻¹ typical of free OCS is observed.[13] The presence of OCS in this spectrum may be due to thermal decomposition of the sample. Taking into account the high dilution of the compound with the matrix gas, and also that the IR signal corresponds to unperturbed OCS, the isolation of this contaminant in different matrix sites than FC(O)SSCl can be considered. After irradiation, several new bands appear in this spectral region, following distinct kinetics and consequently assignable to different photoproducts. OCS is known to form molecular complexes with halogen or interhalogen molecules.[14] The production of molecular complexes between OCS and the species that can be generated together from the unimolecular evolution of FC(O)SSCl, i.e. either ClF or ClSF, were investigated. For this purpose the

observed IR absorptions were compared with reported complexes, and also integrated intensities of the absorptions were plotted against the irradiation time and compared with the behaviour of other bands developed in the spectra. Theoretical calculations were also performed, for the cases in which no reports were found in the literature.

The bands observed at 2058.7, 2046.9, and 2039.4 cm⁻¹ are coincident with the values previously reported by our group for the OCS···ClF, OCS···FCl, and SCO···ClF molecular complexes.[14] In a previous work, these species were isolated through two different experiments. In the former case, FC(O)SCl isolated in Ar or N₂ matrices was irradiated using broad-band UV-visible light. Alternatively, gaseous mixtures of OCS, ClF, and Ar in different proportions were deposited on a cooled CsI window. In the latter experiment, only the complexes bounded by the chlorine atom of the interhalogen molecule, OCS···ClF and SCO···ClF, were detected.

For the remaining bands appearing in the 2080–2020 cm⁻¹ region, molecular complexes between OCS and the rest of the molecule, i.e. ClSF, were considered. To the best of our knowledge, these complexes were not previously described. Moreover, the only way to obtain the triatomic molecule ClSF was the photolysis of FC(O)SCl isolated in matrix conditions.[15] Possible complexes between OCS and ClSF were calculated to help in the interpretation of the experimental findings. The results are presented later in this paper. As depicted in Figure 4, the bands at 2050.5 and 2042.0 cm⁻¹ exhibit a temporal evolution coincident with the 771.5/770.1 and 778.5/776.4 cm⁻¹ absorptions, respectively. A third IR feature, occurring at 2054.0 cm⁻¹, presents a different behaviour and may probably be assigned to a different species. Table 2 presents a tentative

Table 2. Comparison of the experimental wavenumbers of the IR absorptions assigned to 1:1 OCS:ClSF molecular complexes obtained from the photolysis of FC(O)SSCl isolated in solid Ar with that calculated with the B3LYP/6-311 + G* theoretical approximation

Assignment	Experimental ν (cm⁻¹)	Δν (cm⁻¹)[a]	B3LYP/6-311 + G* ν (cm⁻¹)	Δν (cm⁻¹)[a]
(OCS···ClSF)-I				
ν (C=O)	2054.0	+4.5	2122.8	+6.5
ν (S-F)	769.2	-	717.1	-0.1
(OCS···ClSF)-II				
ν (C=O)	2050.5	+1.0	2121.3	+5.0
ν (S-F)	771.5/770.1	-	714.7	-2.5
(OCS···ClSF)-IV				
ν (C=O)	2042.0	-7.5	2108.9	-7.4
ν (S-F)	778.5/776.4	-	715.2	-2.0
[a] $\Delta \nu = \nu_{complex} - \nu_{monomer}$				

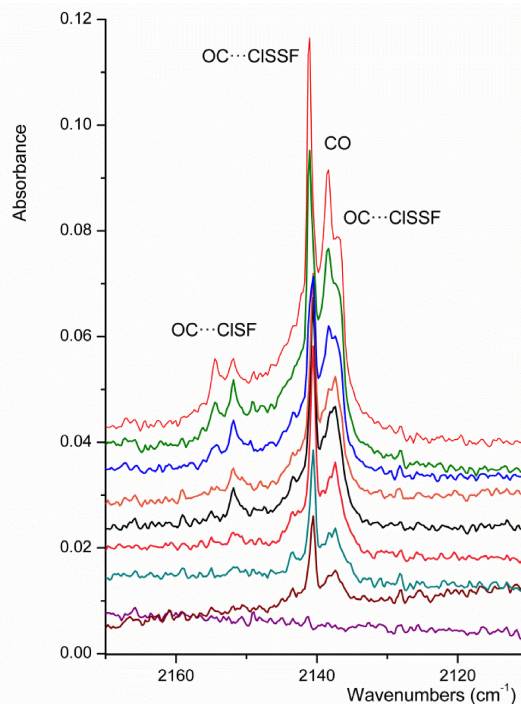assignment of the IR signals attributable to the 1:1 OCS:ClSF complexes, based on the comparison with results of DFT calculations.

Figure 5 shows the absorptions developed upon photolysis of FC(O)SSCl in the spectral region characteristic of the CO molecule. The most intense signals, occurring near 2141 and 2137 cm⁻¹, are tentatively assigned to CO interacting with the
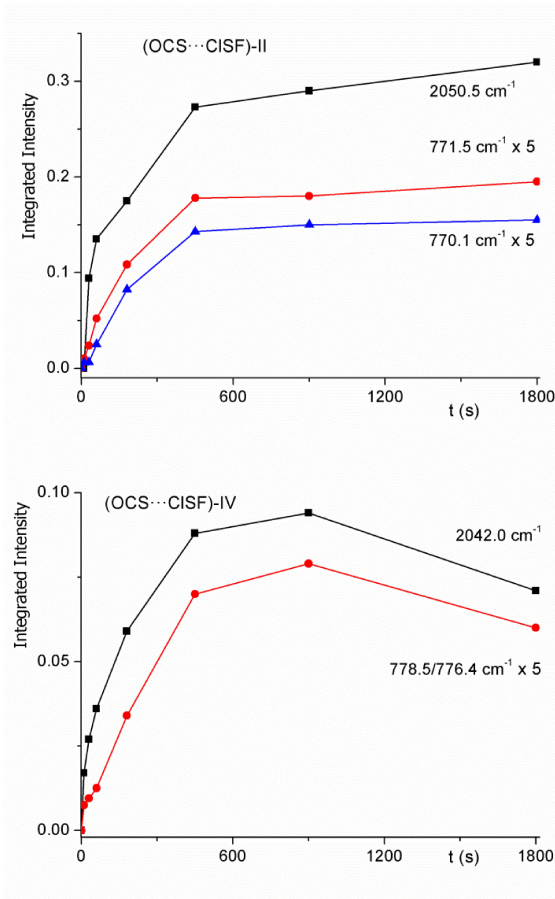
Figure 4. Plots of the integrated intensities of the IR absorptions assigned to 1:1 OCS:ClSF molecular complexes developed after UV-visible photolysis of a matrix originally containing FC(O)SSCl and Ar in 1:1000 proportion.

Figure 5. FTIR spectra of an Ar matrix initially containing FC(O)SSCl in 1:1000 proportion (bottom) and after (from bottom to top) 10, 30, 60, 180, 480, 900, 1800 and 3600 s of broad-band UV-visible photolysis between 2170 and 2130 cm^{-1}. The spectra were taken with 0.125 cm^{-1} resolution and 256 scans.

ClSSF molecule, formed in a same matrix cage. Although ClSSF was previously reported,[16] to the best of our knowledge, its IR spectrum has yet to be published. A B3LYP/6-311+G* calculation predicts an IR spectrum composed mainly of two signals, at 634 and 400 cm^{-1}. In our experiments, a very low-intensity band at 623 cm^{-1} can be tentatively assigned to this species. The photochemical extrusion of the CO molecule reported for several -C(O)S- compounds isolated in solid matrices supports the hypothesis of the proposed photochemical mechanisms.[1,3–5,17] The non-planar structure of the ClSSF molecule, and the various possibilities for its interaction with the CO molecule, turns the theoretical study of the 1:1 CO:ClSSF molecular complexes into a very complex task, with several structures that can explain the experimental results. Moreover, the calculated relative stabilities of the different complexes do not constitute a useful criterion for the assignment of the absorptions to a particular complex, since high-energy species can be photochemically formed in matrix conditions.

Low-intensity signals that blue-shifted with respect to free CO, at 2154.3/2151.8 cm^{-1}, were associated with 1:1 CO:ClSF molecular complexes, on the basis of the comparison with the results obtained in the photolysis of Ar-isolated FC(O)SCl.[15] A

theoretical study of these complexes is presented in the Computational Chemistry section. The feature characteristic of the free CO isolated in solid Ar, at 2138.2, was also present in the spectra.[18,19]

From the first 15 min of photolysis, a band at 1526.3 cm^{-1}, characteristic of the antisymmetric stretching of CS_2 isolated in solid Ar, starts to develop, as depicted in Figure 6. The observed shift with respect to the reported value of 1527.5 cm^{-1}[20,21] may be due to molecular complexation. According to the species that could be formed together with CS_2 in the same matrix cage, four different 1:1 complexes were considered: CS_2:OF•, CS_2:FClO, CS_2:ClO•, and CS_2:ClF. The OF• radical has been previously identified by its 1028 cm^{-1} Raman band after photolysis of OF_2 in solid Ar.[22,23] No signals of this radical were found in the present studies. On the other hand, the IR spectra of FClO either isolated in Ar matrix[24] or in gas phase[25] were reported. FClO presents an angular structure and is characterized by its 1038–1036 and 597–588 cm^{-1} IR absorptions, for the ν(Cl-O) and ν(Cl-F), respectively. None of these bands were detected in our experiments, although their presence cannot be totally discarded due to possible overlap with other absorptions in the spectra. ClO• has been identified as a result of the photolysis of Ar-isolated Cl_2O by an IR absorption at 850 cm^{-1}.[26] In our experiments, very weak IR signals at 853.6/851.5 cm^{-1} may be assigned to this radical, but their behaviour over the irradiation time do not follow the same pattern as the $ν_{as}(CS_2)$ band, discarding the possibility of a CS_2:ClO• complex.
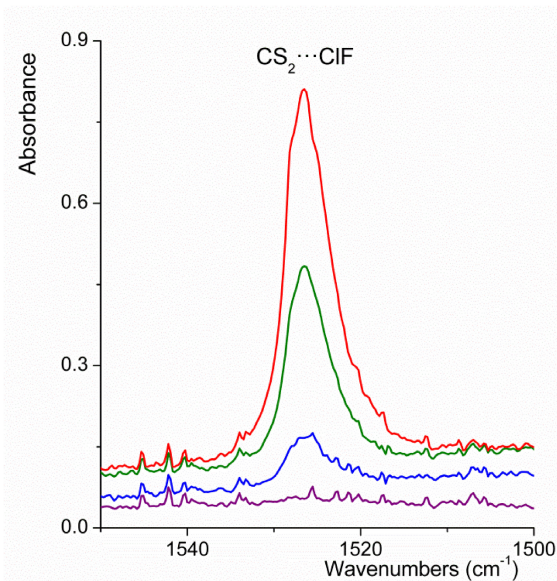
Figure 6. FTIR spectra of an Ar matrix initially containing FC(O)SSCl in 1:1000 proportion after (from bottom to top) 480, 900, 1800 and 3600 s of broadband UV-visible photolysis between 1550 and 1500 cm^{-1}. The spectra were taken with 0.125 cm^{-1} resolution and 256 scans.

Finally, and after the deconvolution and integration of the bands appearing at the 778–758 cm^{-1} region of the irradiated IR spectra, we observed that the absorptions centred at 763.1 and 758.3 cm^{-1}, characteristic of the ClF molecule, following the same behaviour upon photolysis as the band assigned to CS$_2$ (see Figure 7). The formation of a 1:1 CS$_2$:ClF molecular
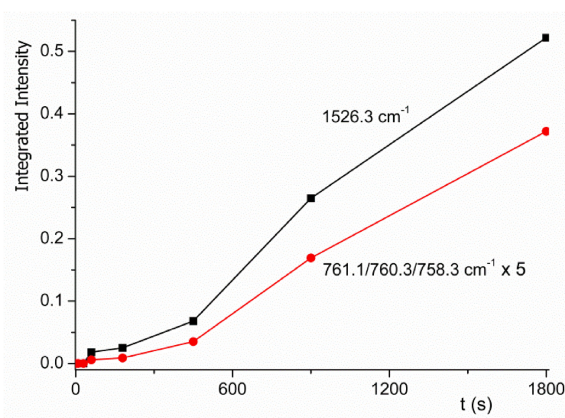
Figure 7. Plot of the integrated intensities of the IR absorption assigned to a 1:1 CS$_2$:ClF molecular complex developed after UV-visible photolysis of a matrix originally containing FC(O)SSCl and Ar in 1:1000 proportion.

complex was proposed to explain the experimental findings. A DFT calculation for the possible structures of this type of complexes, presented below in this paper, predicts only one stable form, with wavenumber shifts with respect to the

monomers that agree, at least in the direction of the shifts, with the experimental observations.

Computational Chemistry

As was discussed in the previous section, several IR absorptions appearing after photolysis of FC(O)SSCl isolated in solid Ar could not be interpreted as arising from any reported species, and the formation of different molecular complexes was proposed. The structures were optimized at the B3LYP level of theory with the 6-311+G* basis set, and the vibrational spectra were simulated, first to characterize each structure as a true energy minimum, and secondly to compare the predicted vibrational wavenumbers with the experimental findings. The stabilization energies were also calculated, taking into account the corrections for the superposition base error and the changes in the geometry of the monomers in the complex. NBO calculations were also performed to interpret the nature of the interactions in terms of the "donor-acceptor" model, together with the evaluation of the interaction energies, the charges transferred, and the van der Waals penetration distances.

1:1 OCS:ClSF molecular complexes. Different potential energy scans for the distances between the oxygen atom of the OCS molecule and the sulfur atom of ClSF, and also between the S of OCS and the S of ClSF, together with the scans of the angles αOSCl, αOSF, αSSCl, and αSSF were performed with the B3LYP/6-311+G* model. Four different structures, depicted in Figure 8, were obtained as true energy minima.
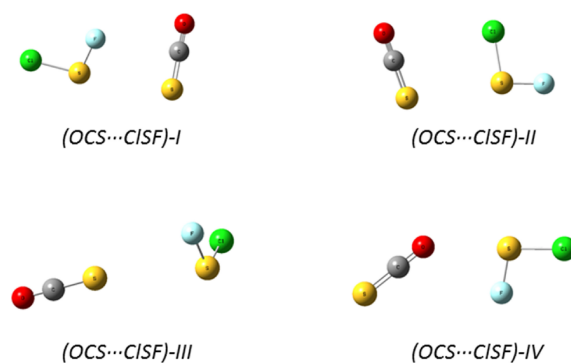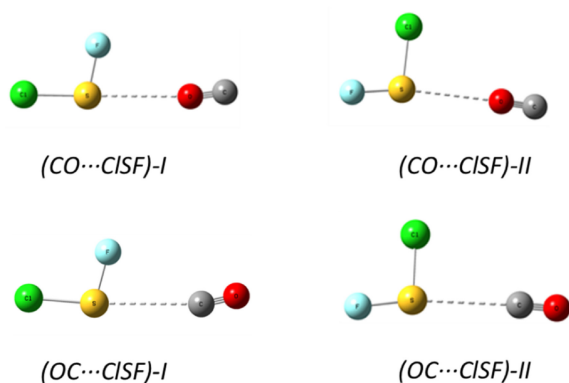

Figure 8. Molecular models of the 1:1 OCS:ClSF molecular complexes calculated with the B3LYP/6-311+G* theoretical approximation.

As was explained previously in this paper, three of these structures, complexes I, II and IV, were proposed to have formed upon photolysis of FC(O)SSCl, according with the comparison of the simulated IR spectra with the experimental ones (see Table 2). The presence of (OCS⋯ClSF)-III could not be confirmed, since the expected wavenumber shift of the carbonyl stretching of OCS is ~ -2 cm^{-1}, very close to the absorption assigned to OCS⋯FCl. A complete list of the calculated vibrational wavenumbers of the four structures depicted in Figure 8 is presented as supplementary material in

Table S1. The calculated geometrical parameters including the penetration distances (Table S2), the energies, charge transferred and orbital stabilization energies (Table S3), and the schematic representation of the orbital interactions (Figure S2), are also presented as supplementary material.

In (OCS···ClSF)-I and (OCS···ClSF)-II the interaction of the two subunits can be explained through a charge transfer from the lone pair orbital of the S atom of the OCS molecule to the antibonding σ orbital of S-Cl or S-F, respectively (Figure S2). This interaction weakens the C=S bond of OCS, and therefore reinforces the C=O bond, which explains the predicted blue-shifts of $+6.5$ and $+5.0$ cm^{-1} of the ν(C=O) vibrational mode in complexes I and II, respectively, with respect to free OCS. There are also other contributions to the orbital stabilization, π(C=O) → σ* (S–F) (complex I) and n_p(Cl) → π*(C=O) (complex II), that favour the planar structure of these species. (OCS···ClSF)-IV also presents a planar structure, stabilized by three different orbital interactions, n_p(O) → σ* (S–Cl), n_s(O) → σ* (S-Cl), and n_p(F) → π*(C=S), which can be responsible for the -7,4 cm^{-1} wavenumber shift of ν(C=O) of the OCS molecule.

1:1 CO:ClSF molecular complexes. The theoretical investigation of the possible molecular complexes that can be formed between CO and ClSF were performed taking into consideration the geometries previously found for the related 1:1 CO:SF$_2$[12] and CO:SeX$_2$ (con X=Cl, F)[27] species, and also that CO can interact either through the C or O atoms.[19] After relaxed potential energy scans of the C···S and O···S interaction distances, four different structures were found and subsequently optimized with the B3LYP/6-311+G* approximation (Figure 9). The calculated vibrational wavenumbers (Table S4),
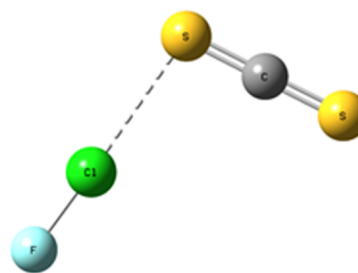

Figure 9. Molecular models of the 1:1 CO:ClSF molecular complexes calculated with the B3LYP/6-311+G* theoretical approximation.

the geometrical parameters including the penetration distances (Table S5), the energies, charge transferred and orbital stabilization energies (Table S6), and the schematic representation of the orbital interactions (Figure S3) were included as supplementary material. In the complexes coordinated by the O atom of the CO molecule, stabilized by n(O) → σ* (S–X) orbital interactions, with X=Cl or F, red shifts of the ν(CO) vibrational mode are predicted. On the other hand, the theoretical 11.3

and 8.6 cm^{-1} blue-shifted CO stretching vibrational modes for complexes (OC···ClSF)-I and (OC···ClSF)-II, respectively, are in very good agreement with the $+15.8$ and $+13.3$ cm^{-1} experimental shifts. For these two complexes the orbital overlap between the n(C) and σ* (S–X) orbitals is more effective than in the other two species, which leads to higher stabilization energies (see Table S6).

1:1 CS$_2$:ClF molecular complexes. The calculation of the possible structures formed by the interaction of the triatomic CS$_2$ molecule with ClF was performed starting from the reported geometries for the 1:1 molecular complexes of carbon disulphide and halogen or interhalogen molecules (Cl$_2$, Br$_2$, BrCl, ICl, and IBr).[28] Only one form was found as a stable structure with the B3LYP/6-311+G* approximation, depicted in Figure 10. This complex presents an unusually high stabilization

Figure 10. Molecular model of the 1:1 CS$_2$:ClF molecular complex calculated with the B3LYP/6-311+G* theoretical approximation.

energy, mainly due to an n_p(S) → σ* (Cl-F) orbital interaction. The predicted red shift of either ν_{as}(S=C=S) and ν(Cl-F) is in agreement with the experimental observations. Tables S7, S8 and S9 of the supplementary material contain the calculated vibrational wavenumbers, the geometrical parameters, the energy, charge transferred, and orbital stabilization energies of the complex, while Figure S4 depicts the schematic representation of the main orbital interaction.

The structure of ClSSF was optimized with the B3LYP/6-311+G* approximation and the vibrational IR spectrum was simulated with the same theoretical model. The geometrical parameter (Table S10), the vibrational wavenumbers including the IR intensities (Table S11), and the calculated molecular structure (Figure S5) are presented as supplementary material.

Conclusions

The UV-visible broad-band photochemistry of FC(O)SSCl in matrix conditions was investigated by means of IR spectroscopy as a function of irradiation time. The high dilution of the compound together with the rigidity of the matrix prevents any other than unimolecular mechanisms. The different photoproducts, produced by alternative channels, are schematically depicted in Scheme 1.

A light-induced transformation of the *syn-gauche* conformer into the *anti-gauche* form of FC(O)SSCl was observed. The growth of the intensities of the IR absorbances of the *anti-*
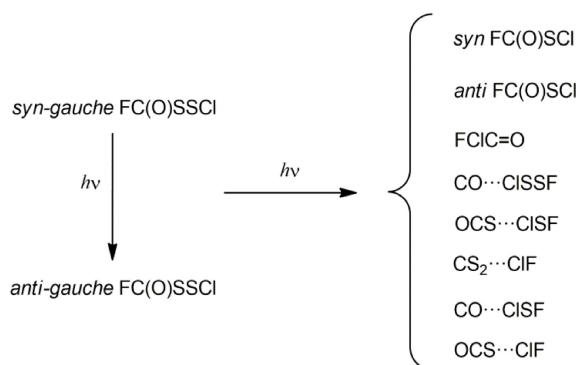
Scheme 1. Proposed photoproducts in the photolysis of FC(O)SSCl isolated in solid Ar in 1:1000 proportion.

gauche rotamer at the expense of the intensities of the bands corresponding to the *syn-gauche form* at the beginning of the irradiation constitutes an additional tool for the correct assignment of the IR bands of each conformer. The loss of one or two sulfur atoms, to yield either FC(O)SCl or ClFC=O, respectively, was also detected. The rest of the photochemical mechanisms lead to molecular complexes, whose formation is favoured by the rigidity of the Ar matrix. Two of these proposed species, CO⋯ClSSF and OCS⋯ClSF, correspond to the extrusion of CO and OCS, respectively, interacting with the rest of the molecule, i.e. ClSSF and ClSF. In the other three loose complexes, CS_2⋯ClF, CO⋯ClSF and OCS⋯ClF, oxygen or sulfur atoms were also released. CO⋯ClSF and OCS⋯ClF can also be formed from the photoevolution of *syn-* and *anti-*FC(O)SCl, as previously reported.[15,14]

Supporting Information Summary

Experimental and computational details, vibrational wavenumbers, $\Delta E^{(SCF)}$, ΔE^{CP}, ΔE, BSSE and GEOM corrections, transferred charge, orbital stabilization energies, geometrical parameters and Cartesian coordinates of the 1:1 OCS:ClSF, CO:ClSF and CS_2:ClF molecular complexes calculated with the B3LYP/6311+G* approximation, vibrational wavenumbers, geometrical parameters and Cartesian coordinates of ClSSF calculated with the B3LYP/6311+G* approximation, plots as a function of irradiation time of the relative intensities of the bands assigned to *anti-gauche* form of FC(O)SSCl with respect to the absorptions of the *syn-gauche* conformer in the IR spectrum of an Ar matrix initially containing FC(O)SSCl and Ar in the proportions 1:1000, schematic representation of the most relevant orbital interactions for the 1:1 molecular complexes OCS:ClSF, CO:ClSF, and CS_2:ClF, and molecular model of ClSSF calculated with the B3LYP/6-311+G* approximation can be found in the supporting information.

[1] M. V. Cozzarín, S. Tong, M. F. Ge. C. O. Della Védova, R. M. Romano, *Eur. J. Inorg. Chem.* **2016**, 5568–5574.
[2] R. M. Romano, C. O. Della Védova, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2001**, *123*, 5794–5801.
[3] R. M. Romano, C. O. Della Védova, A. J. Downs, *Chem. – E.J.* **2007**, *13*, 8185–8192.
[4] R. M. Romano, C. O. Della Védova, A. J. Downs, *J. Phys. Chem. A* **2004**, *108*, 7179–7187.
[5] J. A. Gómez Castaño, R. M. Romano, H. Beckers, H. Willner, C. O. Della Védova, *E. J. Inorg. Chem.* **2013**, 4585–4594.
[6] L. Schriver, O. Abdelaoui, A. Schriver, *J. Phys. Chem.* **1992**, *96*, 8069–8073.
[7] C. O. Della Vedova, E. H. Cutin, E. L. Varetti, A. H. Jubert, P. J. Aymonino, *Can. J. Anal. Sci. Spectr.* **1984**, *29*, 130–133.
[8] M. Hawkins, A. J. Downs, *J. Phys. Chem.* **1984**, *88*, 1527–1533, 3042–3047.
[9] M. Hawkins, M. J. Almond, A. J. Downs, *J. Phys. Chem.* **1985**, *89*, 3326–3334.
[10] L. Khriachtchev, M. Pettersson, E. Isoniemi, .M. Räsänen, *J. Chem. Phys.* **1998**, *108*, 5747–5754.
[11] Y. A. Tobón, R. M. Romano, C. O. Della Védova, A. J. Downs, *Inorg. Chem.*, **2007**, *46*, 4692–4703.
[12] M. V. Cozzarín, R. M. Romano, H. Willner, C. O. Della Védova, *J. Phys. Chem. A* **2013** *117*, 855–862.
[13] F. D. Verderame, E. R. Nixon, *J. Chem. Phys.* **1966**, *44*, 43–49.
[14] A. L. Picone, C. O. Della Védova, H. Willner, A. J. Downs, R. M. Romano, *Phys. Chem. Chem. Phys.* **2010**, *12*, 563–571.
[15] H. Willner, *Z. Naturforsch.* **1984**, *39b*, 314–316.
[16] F. Seel, R. Budenz, W. Gomhler, *Chem. Ber.* **1970**, *103*, 1701–1708.
[17] C. O. Della Védova, H.-G. Mack, *Inorg. Chem.* **1993**, *32*, 948–950.
[18] H. Dubost, *Chem. Phys.* **1976**, *12*, 139–151.
[19] R. M. Romano, A. J. Downs, *J. Phys. Chem. A*, **2003**, *107*, 5298–5305.
[20] A. Givan, A. Loewenschuss, K. D. Bier, H. J. Jodl, *Chem. Phys.* **1986**, *106*, 151–159.
[21] M. Bahou, Y. C. Lee, Y. P. Lee, *J. Am. Chem. Soc.* **2000**, *122*, 661–667.
[22] L. Andrews, *J. Chem. Phys.* **1972**, *57*, 51–55.
[23] A. Arkell, R. R. Reinhard, L. P. Larson, *J. Am. Chem. Soc.* **1965**, *87*, 1016–1020.
[24] L. Andrews, F. K. Chi, A. Arkell, *J. Am. Chem. Soc.* **1974**, *96*, 1997–2000.
[25] H. S. P. Müller, *Chem. Phys. Lett.* **1999**, *314*, 396–402.
[26] F. K. Chi, L. Andrews, *J. Phys. Chem.* **1973**, *77*, 3062–3067.
[27] A. L. Picone, PhD Thesis, Universidad Nacional de La Plata, **2008**.
[28] R. M. Romano, A. L. Picone, A. J. Downs, *J. Phys. Chem. A* **2006**, *110*, 12129–12135.