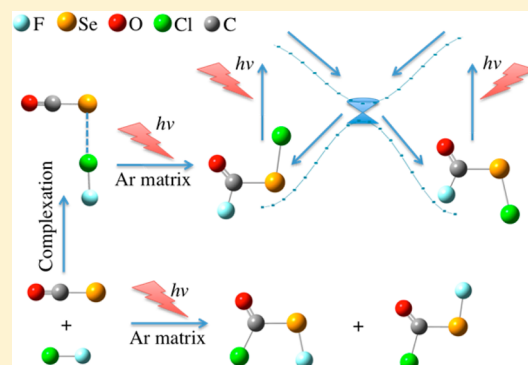


# Photochemical Reaction of OCSe with ClF in Argon Matrix: A Light-Driven Formation of XC(O)SeY (X, Y = F or Cl) Species

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## Supporting Information

**ABSTRACT:** The photochemistry of OCSe with ClF trapped together in argon matrices at cryogenic temperatures has been explored and the first interhalogen representatives of the elusive XC(O)SeY family, namely *syn*-ClC(O)SeF, *anti*-ClC(O)SeF, *syn*-FC(O)SeCl, and *anti*-FC(O)SeCl, as well as the hitherto triatomic species ClSeF complexed by a CO molecule, were obtained. Both ClC(O)SeF conformers appear to be produced independently by photolysis of the respective precursors; while formation of both FC(O)SeCl structures is ruled by the presence of an angular molecular complex OCSe...Cl-F formed prior to photolysis. This latter photochemical pathway seems to favor the formation of the less stable *anti*-FC(O)SeCl structure instead of the more stable *syn*- one. With the aid of quantum chemical calculations, using *ab initio*, DFT, TDDFT, and CASSCF methods, the mechanism for this photochemical reaction is rationalized both in terms of radical processes as well as a photoinduced electron transfer occurring into the OCSe...Cl-F complex. Also a singlet–triplet conical intersection between *anti* and *syn* rotamers of the FC(O)SeCl molecule is theoretically explored.



## INTRODUCTION

While halogenated sulfenylcarbonyl compounds XC(O)SY (X, Y = halogen) have been studied for over 50 years,<sup>1,2</sup> the halogen–selenocarbonyl congeners XC(O)SeY have remained elusive.<sup>3,4</sup> The limited accessibility of the selenium compounds are due to their low thermal stabilities—and thus higher reactivities—and unsuitable synthetic strategies. In order to obtain such unknown unstable and transient species, *matrix-isolation photochemistry* (MIP) has shown to be a valuable technique.

Considering the large excess of matrix gas with respect to the substrate molecules and the low temperature employed in MIP experiments, the photoproducts are formed only from species initially present in the matrix cage. When two (or more) substrate species are premixed, in an adequate ratio with the inert gas, and codeposited on a cold matrix support to form the solid matrix, some cages will be occupied simultaneously by the substrates, so favoring intermolecular interactions and leading to the formation of molecular complexes prior to photolysis. In spite of their low energy contribution, these types of interactions have proved to play a crucial role in the photochemical mechanisms of the species trapped in the solid matrix.<sup>3–8</sup>

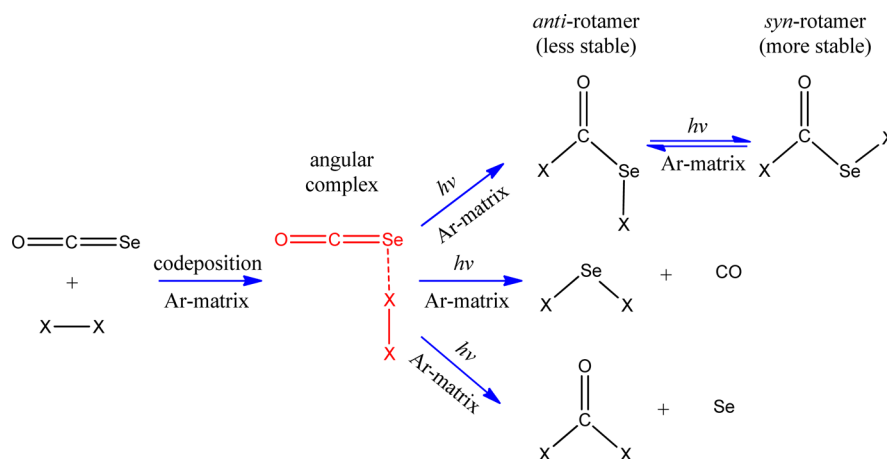
In recent years we have isolated FC(O)SeF, ClC(O)SeCl, and BrC(O)SeBr molecules as first members of the family of the halogen carbonyl–Se halides, by means of broad band UV–vis irradiation ( $200 \leq \lambda \leq 800$  nm) of OCSe/X<sub>2</sub> mixtures (X = F, Cl or Br) trapped in argon matrices at cryogenic temperatures.<sup>3,4</sup> Primarily, the respective less stable *anti*-XC(O)SeX (X = F or Cl) conformer was formed, which then interconverted photochemically to the more stable *syn* structure. Furthermore, in these experiments two additional photochemical channels were observed, one for the formation of phosgene molecules, XC(O)X, and the other for triatomic SeX<sub>2</sub> molecules. Outline of the photochemical reaction of OCSe and X<sub>2</sub> isolated together in solid argon matrices is presented in Scheme 1.

In this work, we report a combined experimental–theoretical study for the photolysis of OCSe with ClF in an argon matrix. This study is presented with the aim of exploring not only the effect caused by the interhalogen substitution (XY) on the reactants in the photochemical reaction used by us to obtain molecules of the new family of the halogen carbonyl–Se halides

Received: December 10, 2016

Revised: March 7, 2017

Published: March 31, 2017

Scheme 1. Argon Matrix Photochemistry of Angular Bonded Complexes of the General Formula OCSe...X<sub>2</sub> (X = F, Cl)

(Scheme 1), but also of scrutinizing the photostereo-specificity exhibited by OCSe...XY molecular complexes to form *anti*-XC(O)SeY structures.

## EXPERIMENTAL AND THEORETICAL METHODS

Chlorine monofluoride, ClF, was prepared by mixing gas streams ( $\sim 9 \text{ L h}^{-1}$ ) of F<sub>2</sub> and Cl<sub>2</sub> in a steel cylinder placed inside an oven heated to 400 °C. The gaseous products passed through a water-cooled condenser and traps cooled at  $-78$  and  $-196$  °C. The ClF collected at  $-196$  °C was further purified by repeated trap-to-trap condensations in vacuum, and then a sample was transferred into a 1 L stainless steel container in a vacuum line and diluted 2:100 with Ar. A separate sample of OCSe, prepared according to literature,<sup>9</sup> was mixed with argon in a 0.5 L glass container in a ratio of 1:100. Both containers were connected via needle valves and stainless steel capillaries to the spray-on nozzle of the matrix device. About 0.5–1 mmol of the gas mixtures were codeposited within 10–20 min on the mirror support of a rhodium plated copper block held at 15 K. For photolysis experiments the radiation from a 150 W mercury high-pressure lamp (TQ150, Heraeus, Hanau, Germany) was used for periods from 1 to 90 min and the progress in time was observed through IR spectroscopy. Details of the matrix apparatus are given elsewhere.<sup>10</sup> Matrix IR spectra were recorded on an IFS 66v/S spectrometer with a resolution of  $1 \text{ cm}^{-1}$ , in absorption/reflection mode as described in ref<sup>10</sup>. The IR intensities were determined by integrating the absorptions using the OPUS software.

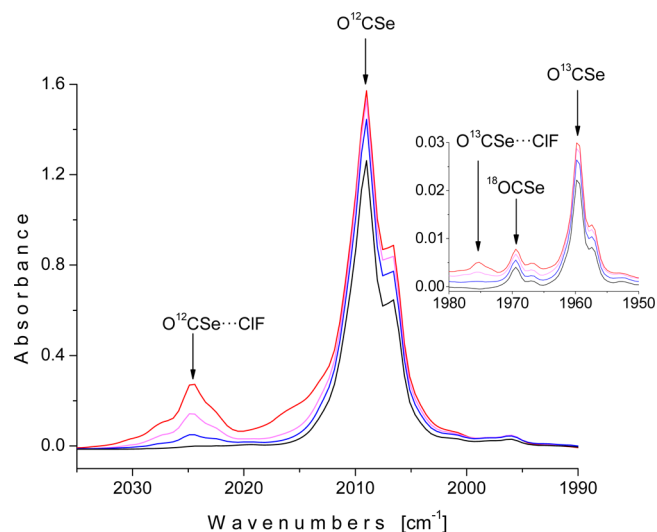
Quantum chemical calculations were performed with the Linux/UNIX version of Gaussian 09 (Rev. C.01) software,<sup>11</sup> under the TCP Linda parallel execution environment, running on our scalable computational cluster named “Atomic” (“a team of multiprocessors in support of chemical calculations”). Initial explorations of the potential energy surfaces (PES) were carried out using relaxed two-dimensional scans, constructed by varying simultaneously two dihedral angles using the B3LYP/6-31+G(d) approximation. Geometry optimizations and frequencies were computed using DFT and post-Hartree–Fock methods in combination with 6-311+G(d) or aug-cc-pVDZ basis sets. time-dependent DFT (TDDFT) methods using B3LYP and CAM-B3LYP functionals were used to predict vertical excitations and optimized excited structures of the OCSe...ClF complex and XC(O)SeY (X,Y = Cl or F) molecules. Conical intersections were located using the complete active space self consistent field method (CASSCF).

The binding energies of the molecular complexes were calculated using the correction proposed by Nagy et al.<sup>12</sup> The basis set superposition errors were calculated by applying the counterpoise procedure developed by Boys and Bernardi.<sup>13</sup>

## RESULTS AND DISCUSSION

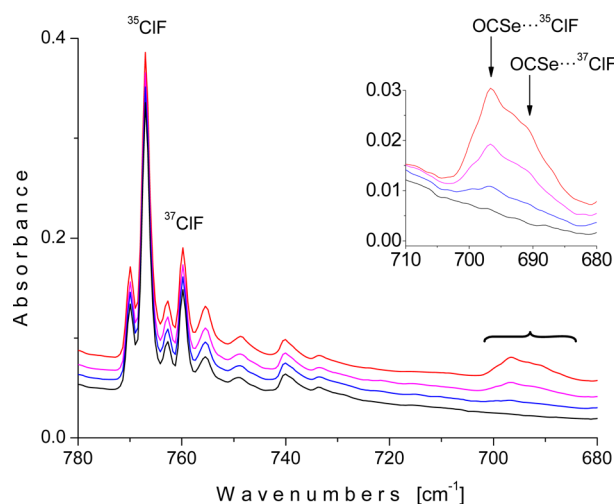
**Ar-Matrix Isolation and Computational Study of the OCSe...ClF Complex.** First of all, ClF and OCSe were isolated in solid argon and their FTIR spectra recorded. The spectra obtained in these blank experiments were in good agreement with previous argon matrix studies. In particular, the spectrum of ClF showed two intense sharp bands at 767.0 and 759.8  $\text{cm}^{-1}$ , due to <sup>35</sup>ClF and <sup>37</sup>ClF in natural abundance,<sup>14</sup> as well as other features of lower intensity at 769.9 and 762.7  $\text{cm}^{-1}$ , attributed to matrix effects, and also at 755.5, 748.7, and 740.0  $\text{cm}^{-1}$  due to molecular aggregation.<sup>7,14</sup> In the case of OCSe, it was as published.<sup>9</sup> Subsequently, OCSe/Ar and ClF/Ar mixtures were codeposited on the matrix support at 15 K.

The FTIR spectrum recorded after codeposition showed as a main feature the strong CO stretching band of OCSe in solid argon at 2099.0  $\text{cm}^{-1}$ .<sup>9</sup> However, as shown in Figure 1 (see red



**Figure 1.** C=O stretching region of OCSe in the initial FTIR spectrum of the OCSe/ClF/Ar matrix (red), and after 1 (magenta), 3 (blue), and 8 (black) min of UV-vis irradiation.

line) there was an additional blue-shifted band at 2024.6  $\text{cm}^{-1}$ . It was assigned to the OCSe/CIF complex as found for OCSe/ $\text{F}_2$ , OCSe/ $\text{Cl}_2$ , OCSe/ $\text{Br}_2$ , OCS/ $\text{F}_2$ , and OCS/CIF mixtures in solid argon.<sup>3–7</sup> This observation was also supported by the appearance of a new set of absorptions in the FTIR spectrum at 696.4 and 691.7  $\text{cm}^{-1}$ , red-shifted to the stretching mode (767.0  $\text{cm}^{-1}$ ), of free CIF (see red line in Figure 2), and another at 627.7  $\text{cm}^{-1}$ , red-shifted in respect to the C=Se stretching mode (643.9  $\text{cm}^{-1}$ ), of free OCSe.



**Figure 2.** Stretching region of CIF in the initial FTIR spectrum of the OCSe/CIF/Ar matrix (red) and after 1 (magenta), 3 (blue), and 8 (black) min of UV-vis irradiation.

Other weak features were due to matrix-isolated CO,<sup>15</sup>  $\text{F}_2\text{CO}$ ,<sup>16</sup>  $\text{FCOCl}$ ,<sup>17</sup> and  $\text{Cl}_2\text{CO}$ <sup>18</sup> molecules, and to the OC...CIF complex<sup>19</sup> also detectable in the initial FTIR spectrum of the OCSe/CIF/Ar matrix. These carbonyl-containing molecules can be formed in trace amount during the codeposition by thermal reaction between halogens and the CO liberated from OCSe.<sup>9</sup> Se-containing molecules like  $\text{SeX}_2$  and  $\text{YSeX}$  ( $\text{X}, \text{Y} = \text{Cl}$  or  $\text{F}$ ) may also have formed during codeposition, but their presence in the initial FTIR matrix spectrum could not be confirmed; probably because of the high noise appeared in baseline in the characteristic Se–Cl vibration region ( $\sim 400 \text{ cm}^{-1}$ ),<sup>4</sup> as well as the interference generated by some impurity of  $\text{CO}_2$  in the Se–F stretching region ( $\sim 660 \text{ cm}^{-1}$ ).<sup>20</sup> Another reason for nondetection of selenium-containing molecules other than OCSe could be attributed to the formation of amorphous selenium during codeposition.<sup>9</sup> A complete list of absorptions appearing immediately after codeposition, with their corresponding assignments, is presented in Table 1.

In order to support our FTIR assignments for the molecular OCSe...CIF complex, a series of DFT calculations were performed. The OCSe unit can interact with either its oxygen or selenium atom with one of the two atoms of the CIF unit. A total of four 2D relaxed scans, resulting from varying simultaneously the distance  $\text{E}\cdots\text{X}$  and the angle  $\text{C} = \text{E}\cdots\text{X}$  ( $\text{E} = \text{O}$  or  $\text{Se}$ ,  $\text{X} = \text{Cl}$  or  $\text{F}$ ), were employed to search for planar equilibrium structures of the OCSe...CIF complex. Equilibrium structures different from planar were excluded from this PES exploration, in line with our previous argon-matrix results obtained on other very similar complexes.<sup>3–7</sup> Figure S1 (in the Supporting Information) displays the six minima ( $\text{M}_1$  to  $\text{M}_6$ ) found, at first glance, from the four 2D scans performed on the

**Table 1.** Frequencies and assignment for the IR absorptions of the initial OCSe/CIF/Ar matrix

Ar-matrix $\nu$ [ $\text{cm}^{-1}$ ]	assignment		wavenumber reported previously
	species	vibrational mode	
2157.6	OC...CIF	$\nu(\text{CO})$	2158.4 <sup>a</sup>
2138.3	CO	$\nu(\text{CO})$	2138.0 <sup>b</sup>
2024.6	OCSe...CIF	$\nu(\text{CO})$	this work
1975.4	OCSe...CIF	$\nu(^{13}\text{CO})$	this work
1941.4	$\text{F}_2\text{C}=\text{O}$	$\nu(\text{CO})$	1941.4 <sup>c</sup>
1913.2	$\text{F}_2\text{C}=\text{O}$	$2\nu_2$	1913.5 <sup>c</sup>
1863.3	$\text{FClC}=\text{O}$	$\nu(\text{CO})$	1863.3 <sup>d</sup>
1817.4	$\text{Cl}_2\text{C}=\text{O}$	$\nu(\text{CO})$	1815.58/1814.78/1814.26 <sup>e</sup>
1237.8	$\text{F}_2\text{C}=\text{O}$		1239.0 <sup>c</sup>
739.9	OC...CIF	$\nu(^{35}\text{CIF})$	739.6 <sup>a</sup>
733.5	OC...CIF	$\nu(^{35}\text{CIF})$	732.9 <sup>a</sup>
696.4	OCSe... <sup>35</sup> CIF	$\nu(^{35}\text{CIF})$	this work
691.7	OCSe... <sup>37</sup> CIF	$\nu(^{37}\text{CIF})$	this work
627.7	OCSe...CIF	$\nu(\text{CSe})$	this work

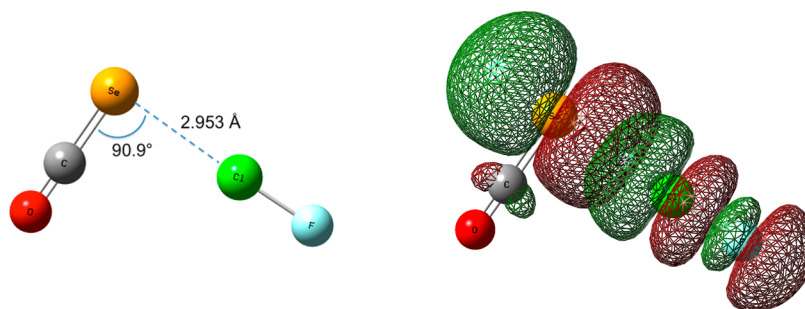
<sup>a</sup>Reference 19. <sup>b</sup>Reference 15. <sup>c</sup>Reference 16. <sup>d</sup>Reference 17. <sup>e</sup>Reference 18.

molecular complex system OCSe:CIF using the B3LYP/6-31+G\* approximation, and Table S1 (in the Supporting Information) compares their corresponding  $\text{E}\cdots\text{X}$  distances,  $\text{C} = \text{E}\cdots\text{X}$  angles, and relative energies.

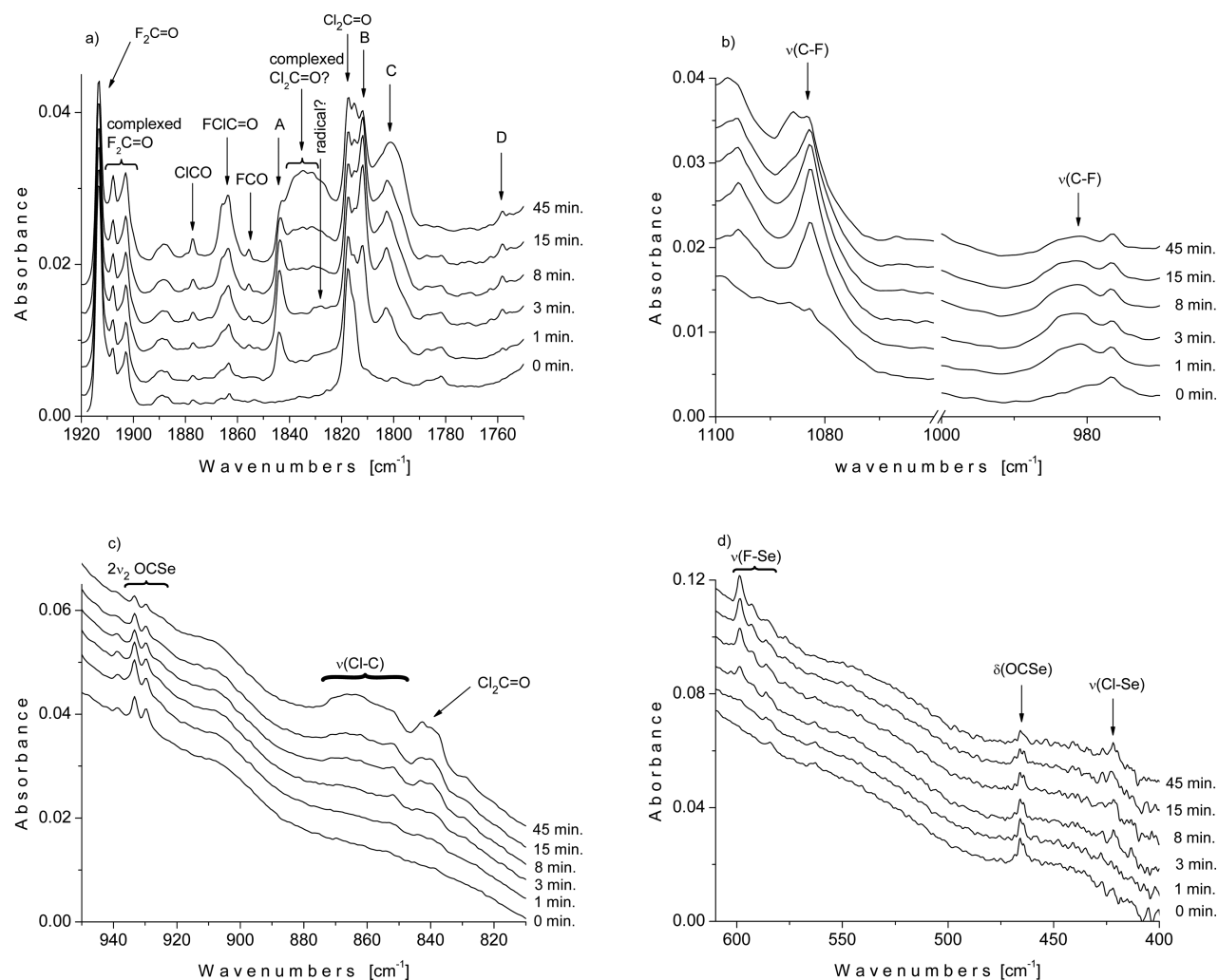
All six minima were subsequently used as starting structures for geometry optimizations and frequency calculations using the B3LYP/6-311+G\* level of theory. These calculations revealed that structures  $\text{M}_2$ ,  $\text{M}_3$ , and  $\text{M}_5$  were actually saddle points, since each of them presented one imaginary frequency. From the remaining three minima ( $\text{M}_1$ ,  $\text{M}_4$ , and  $\text{M}_6$ ), only the angular structure  $\text{M}_1$  (Figure 3) was considered as possible equilibrium geometry for OCSe...CIF complex, since  $\text{M}_1$  is 2 kcal/mol lower in energy than  $\text{M}_4$  and  $\text{M}_6$ . This correlation was also reinforced by the good match obtained by comparing the vibrational shifts (with respect to the free OCSe molecule) associated with the complex OCSe...CIF in argon matrix with those calculated for the angular  $\text{M}_1$  structure (see Table S2 in the Supporting Information).

In addition, binding energies ( $\Delta E$ ), energy corrections, net charge  $q$  transferred and orbital stabilization energies for the angular complex  $\text{M}_1$  were calculated using both B3LYP/6-311+G\* and B3LYP/aug-cc-pVDZ approximations (see Table S3 in Supporting Information). All binding energies of  $\text{M}_1$  were between  $-3.0$  and  $-3.7$  kcal/mol (Table S3), indicating a high electronic stabilization for this molecular arrangement. The origin of such a strong stabilization can be justified theoretically by the high orbital stabilization energy of  $-15.3$  kcal/mol (B3LYP/6-311+G\*), resulting for a charge transfer from the  $n_{\text{Se}}$  orbital to the  $\sigma_{\text{Cl-F}}^*$  orbital (see Figure 3), as predicted by our NBO calculations.

**Ar-Matrix Photochemistry of OCSe with CIF.** The OCSe–CIF–Ar matrix was photolyzed with broadband UV-visible light for different times, and the changes monitored by FTIR spectroscopy. Upon photolysis, new absorptions due to different photoproducts appeared, while the bands assigned to the angular OCSe...CIF molecular complex vanished completely after 8 min irradiation (see Figures 1 and 2). After the same period of irradiation the features corresponding to free OCSe and CIF molecules decreased by only 35% and 5% respectively. This is a clear indication that many of the new



**Figure 3.** Molecular representations for the optimized geometry (left) and main delocalization overlap (right) of the angular OCSe...ClF complex calculated at the B3LYP/6-311+G\* level of theory.



**Figure 4.** (a) CO, (b) CF, (c) CCl, and (d) XSe stretching regions in the FTIR spectra of argon matrix isolated OCSe/ClF before and after 1, 3, 8, 15, and 45 min of photolysis.

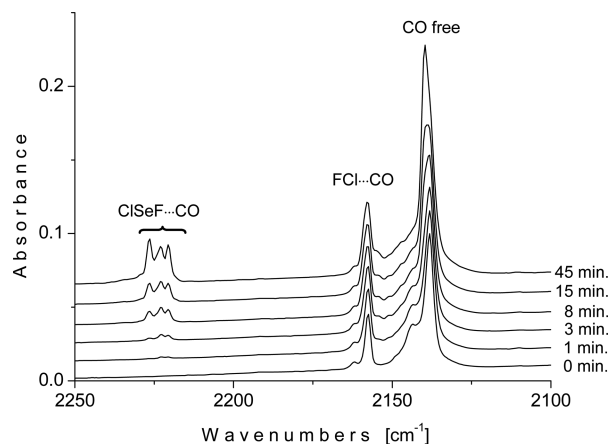
absorptions were produced by the complex. As useful criteria for the assignment of the IR bands to the photoproducts, the absorptions were grouped together according to their behaviors against the irradiation time.

Several of the absorptions that appeared after photolysis were located in the characteristic region of the carbonyl stretching mode,  $\nu(\text{C}=\text{O})$ , at 1877.3, 1855.5, 1843.4, 1811.8, 1802.3, and 1758.2  $\text{cm}^{-1}$  (see Figure 4a). Tiny bands at 1877.3 and 1855.5  $\text{cm}^{-1}$  were identified as the CO vibration of the ClCO and FCO radicals, as reported previously.<sup>21,22</sup> In contrast, four new CO absorptions, marked as A (1843.4  $\text{cm}^{-1}$ ), B (1811.8  $\text{cm}^{-1}$ ),

C (1802.3  $\text{cm}^{-1}$ ), and D (1758.2  $\text{cm}^{-1}$ ) in the spectra of Figure 4a, did not match any known species considered to arise from OCSe and ClF units. However, two different behaviors distinguished bands A–D. On the one hand, bands A and B both showed a rapid increase in their intensity up to 8 min of irradiation followed by a slow decrease with longer radiation time. On the other hand, bands C and D each showed an asymptotic increase behavior as a function of irradiation time.

Additional new absorptions were detected in other regions of the FTIR spectra after irradiation, at 2226.5/2223.0/2220.6, 1082.8, 981.7, 871.6/866.5/861.3/851.7, 598.6/593.0/586.1,

and 421.9/419.9  $\text{cm}^{-1}$  (see Figures 4b–d and Figure 5). As can be observed in Figure 6a, bands at 1082.8 and 981.7  $\text{cm}^{-1}$

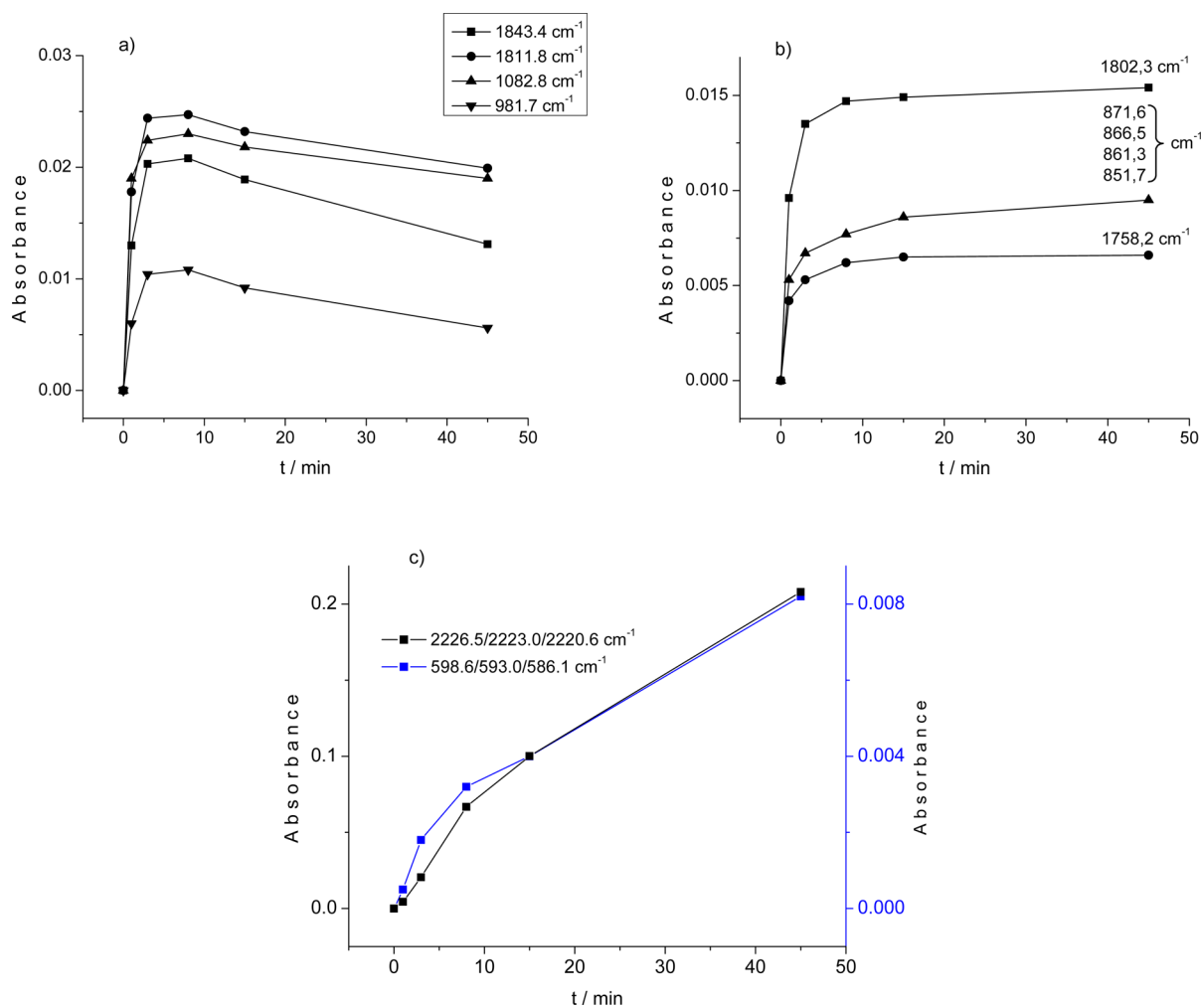


**Figure 5.** Stretching region of the CO molecule in the FTIR spectra of argon matrix isolated OCS<sub>e</sub>/ClF before and after 1, 3, 8, 15, and 45 min of photolysis.

showed the same behavior against irradiation time as did bands A and B, while the photochemical comportment of the

multiplet at 871.6/866.5/861.3/851.7  $\text{cm}^{-1}$  was related much closer to that of bands C and D; see Figure 6b. However, the absorptions at 2226.5/2223.0/2220.6, 598.6/593.0/586.1, and 421.9/419.9  $\text{cm}^{-1}$  presented a unique behavior against photolysis time, suggesting a different photoproduct from those related to bands A, B, C, and D; see Figure 6c.

Given that carbon monoxide was photoliberated from OCS<sub>e</sub>, thus releasing a selenium atom to react with halogens, formation of the triatomic molecule ClSeF was considered as a possible source of the absorptions at 598.6/593.0/586.1 and 421.9/419.9  $\text{cm}^{-1}$ , i.e., the Se–F and Se–Cl stretching modes, respectively. To help on this assumption, a quick couple of opt + freq calculations were performed for the ClSeF molecule at the level of B3LYP/6-311+G\*, obtaining excellent agreement between experimental (421.9/419.9  $\text{cm}^{-1}$ ) and theoretical (423,8/422,0  $\text{cm}^{-1}$ ) frequencies for <sup>35</sup>Cl–Se/<sup>37</sup>Cl–Se vibrations. Conversely, the predicted frequency of F–Se vibration, calculated at 666.0  $\text{cm}^{-1}$ , falls more than 60  $\text{cm}^{-1}$  apart from the experimental one. Such a vibrational shift suggests perturbation of the F–Se bond in ClSeF by another molecule in the same matrix cage. As shown in Figures 5 and 6c, the bands appearing at 2226.5/2223.0/2220.6  $\text{cm}^{-1}$ , ascribed to a perturbed carbon monoxide molecule, exhibited the same photochemical behavior as the bands at 598.6/593.0/586.1



**Figure 6.** Intensities of new absorptions that appeared after irradiation of an argon matrix containing OCS<sub>e</sub> and ClF plotted as a function of photolysis time.

$\text{cm}^{-1}$ , which is clear evidence of the formation of the molecular complex  $\text{ClSeF}\cdots\text{CO}$ . As shown in Scheme 1, similar reactions were observed previously during the irradiation of  $\text{OCSe}$  and  $\text{X}_2$  ( $\text{X} = \text{F}$  or  $\text{Cl}$ ) in an argon matrix, where the species  $\text{SeX}_2$  were photoproducted along with  $\text{CO}$ .<sup>3,4</sup>

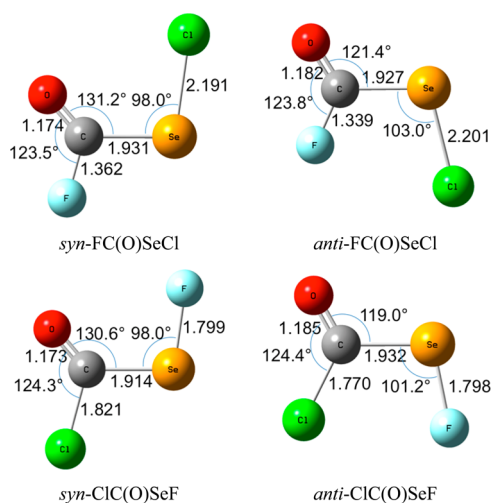
As noted in Figure 4, bands of  $\text{FCICO}$ , detected in the parent matrix FTIR spectrum, increased during the irradiation, indicating that this molecule is also formed by photolysis of  $\text{OCSe}/\text{ClF}$ .

#### Identification of $\text{XC(O)SeY}$ Molecules ( $\text{X}, \text{Y} = \text{Cl}$ or $\text{F}$ ).

The fact observed in Figure 6a that absorptions reach the maxima at the same time that the complex disappears is clear evidence of their precursor-product relationship. These four photogenerated bands, however, were associated with two different molecular structures instead of one by the arguments that follow. First, it is quite improbable that a single structure containing either two carbonyls (bands at 1843.4 and 1811.9  $\text{cm}^{-1}$ ) and two C–F moieties (bands at 1082.8 and 981.7  $\text{cm}^{-1}$ ) could be formed as the only product by direct photolysis of the  $\text{OCSe}\cdots\text{ClF}$  complex in solid argon. Second, the vibrational shifts ( $\Delta\nu$ ) between bands following photolysis either in the carbonyl region ( $\Delta\nu > 30 \text{ cm}^{-1}$ ) or the C–F region ( $\Delta\nu > 40 \text{ cm}^{-1}$ ) surpass the traditional shifts ( $\Delta\nu < 10 \text{ cm}^{-1}$ ) related to matrix effects for a single absorption,<sup>5</sup> suggesting more than one structure. Third, the absorptions at 1843.4 and 1811.9  $\text{cm}^{-1}$  are quite close to those previously reported at 1845.7 and 1808.0  $\text{cm}^{-1}$  for the *syn* and *anti* conformers, respectively, of the  $\text{FC(O)SeF}$  compound, produced during the analogous photochemical reaction between  $\text{OCSe}$  and  $\text{F}_2$ .<sup>3</sup> Consequently, the two more plausible structures formed by photolysis of  $\text{OCSe}\cdots\text{ClF}$  complex in the present experiment correspond to *syn* and *anti* conformers of the hitherto unknown compound  $\text{FC(O)SeCl}$ .

On the other hand, the bands that appeared in the C=O stretching region at 1802.3 and 1758.2 (Figure 4a) and in the C–Cl stretching region at 871.6/866.5/861.3/851.7  $\text{cm}^{-1}$  (Figure 4c) were tentatively attributed to two extra conformers, also *syn* and *anti*, of the new carbonylselenyl halide  $\text{ClC(O)SeF}$ , because of their close similarity to the absorptions previously assigned to the *syn* (1801.3 and 856.8/850.9/848.4  $\text{cm}^{-1}$ ) and *anti* (1755.4 and 766.6  $\text{cm}^{-1}$ ) conformers of the  $\text{ClC(O)SeCl}$  compound formed during the photolysis of  $\text{OCSe}$  and  $\text{Cl}_2$  in argon matrix.<sup>4</sup>

To support such vibrational assignments, and to establish specific assignments of absorptions in the F–C and Cl–C infrared regions after photolysis, a computational study, using B3LYP and MP2 methods and the 6-311+G\* basis set, was performed on the *syn* and *anti* conformers of both  $\text{FC(O)SeCl}$  and  $\text{ClC(O)SeF}$  molecules. Accordingly, Figure S2 (in the Supporting Information) shows the potential energy curves (at B3LYP/6-311+G\* level) obtained for  $\text{FC(O)SeCl}$  and  $\text{ClC(O)SeF}$  by rotation of the corresponding Se–X moiety around the Se–C bond using relaxed scans. In both instances, conformer *syn* ( $\tau_{\text{XSeCO}} = 0^\circ$ ) presented a lower energy compared to conformer *anti* ( $\tau_{\text{XSeCO}} = 180^\circ$ ). All four conformers were subject to opt + freq calculations at both B3LYP/6-311+G\* and MP2/6-311+G\* approximations, and no imaginary frequencies were found in any case, confirming their identity as equilibrium structures. Figure 7 presents optimized structures and geometric parameters for *syn* and *anti* conformers of  $\text{FC(O)SeCl}$  and  $\text{ClC(O)SeF}$  molecules, calculated using the B3LYP/6-311+G\* level of theory. Likewise, Table S4 (in Supporting Information) presents the



**Figure 7.** Optimized molecular models for conformers *syn* and *anti* of  $\text{ClC(O)SeF}$  and  $\text{FC(O)SeCl}$  molecules calculated using the B3LYP/6-311+G(d) approximation. Distances in Ångströms and angles in degrees.

relative population distribution calculated for  $\text{FC(O)SeCl}$  and  $\text{ClC(O)SeF}$  structures. In addition, Figure S3 shows an energy comparison of the four conformers, including ZPE correction, calculated with both levels of theory.

Also, frequency calculations (MP2/6-311+G\*) showed a sequence of IR absorptions at 1887.1  $\text{cm}^{-1}$  (*syn-FC(O)SeCl*), 1847.8  $\text{cm}^{-1}$  (*anti-FC(O)SeCl*), 1827.3  $\text{cm}^{-1}$  (*syn-ClC(O)SeF*), and 1768.1  $\text{cm}^{-1}$  (*anti-ClC(O)SeF*) for the C=O stretching mode that nearly coincides with the pattern of assignment that emerged from this photochemical experiment at 1843.4, 1811.8, 1802.3, and 1758.2  $\text{cm}^{-1}$ . In the case of C–F vibrations, both B3LYP/6-311+G\* and MP2/6-311+G\* approximations predicted higher frequencies, at 1068.2 and 1089.3  $\text{cm}^{-1}$  respectively, for *anti-FC(O)SeCl* than those calculated at 989.8 and 1031.1  $\text{cm}^{-1}$  for the *syn* conformer; therefore, the band photoproducted at 1082.8  $\text{cm}^{-1}$  was related to *anti-FC(O)SeCl*, the band generated at 981.7  $\text{cm}^{-1}$  to the *syn-FC(O)SeCl* conformer. Concerning the set of absorptions appearing in the C–Cl region at 871.6/866.5/861.3/851.7  $\text{cm}^{-1}$ , the three lower in frequency were assigned to the conformer *syn-ClC(O)SeF* while the band at 871.6 to the *anti-ClC(O)SeF* structure; this by association with the absorptions calculated at 807.3 (*syn*) and 875.4  $\text{cm}^{-1}$  (*anti*) for  $\text{ClC(O)SeF}$  using the approximation MP2/6-311+G\*. The complete set of absorptions appearing after photolysis of  $\text{OCSe}$  with  $\text{ClF}$  in argon matrix, along with the corresponding assignment, is presented in Table 2.

**Photochemical Mechanism Analysis.** According to the behavior exhibited during the irradiation (Figure 6b), the proposed *syn* and *anti* conformers of  $\text{ClC(O)SeF}$  seem to be formed by photolysis of uncomplexed  $\text{OCSe}$  and  $\text{ClF}$  molecules. Given the broad band light employed in this experience ( $200 \leq \lambda \leq 800 \text{ nm}$ ), formation of Cl and F radicals are expected from  $\text{ClF}$  (electronic transition:  $\lambda = 537 \text{ nm}$ ),<sup>23</sup> and thus a halogen addition reaction to  $\text{OCSe}$  should be considered for explaining this photochemical path. Other related experiences, like the photochemistry of small olefin molecules with dihalogens in solid argon, have been explained also by means of radical addition reactions. For instance, the both stable conformers (*trans* and *gauche*) of  $\text{XCH}_2\text{—CH}_2\text{X}$  molecules ( $\text{X} = \text{Br}$  or  $\text{I}$ ) were formed by irradiation of matrix-

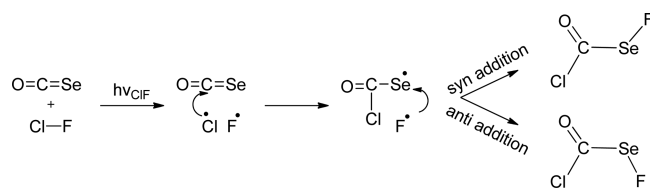
**Table 2.** Band Positions (in  $\text{cm}^{-1}$ ) and Assignments of the IR Absorptions That Appeared after Photolysis of a Mixture of OCSe with ClF Molecules Trapped in an Argon Matrix at 15 K

IR frequencies in $\text{cm}^{-1}$		assignment			IR frequencies reported previously
Ar-matrix	MP2/6-311+G*	species	mode		
2226.5/2223.0/2220.6	—	ClSeF...CO	$\nu(\text{CO})$	this work	
2157.6	—	OC...ClF	$\nu(\text{CO})$	2158.4 <sup>a</sup>	
2138.3	—	CO	$\nu(\text{CO})$	2138.0 <sup>b</sup>	
1941.4	—	F <sub>2</sub> C=O	$\nu(\text{CO})$	1941.4 <sup>c</sup>	
1913.2	—	F <sub>2</sub> C=O	$2\nu_2$	1913.5 <sup>c</sup>	
1877.3	—	ClCO	$\nu(\text{CO})$	1876.7 <sup>f</sup>	
1863.3	—	FCIC=O	$\nu(\text{CO})$	1863.3 <sup>d</sup>	
1855.5	—	FCO	$\nu(\text{CO})$	1855.0 <sup>g</sup>	
1843.4	1887.1	<i>syn</i> -FC(O)SeCl	$\nu(\text{CO})$	this work	
1817.4	—	Cl <sub>2</sub> C=O	$\nu(\text{CO})$	1815.58/1814.78/1814.26/1813.56/1810.12 <sup>e</sup>	
1811.8	1847.8	<i>anti</i> -FC(O)SeCl	$\nu(\text{CO})$	this work	
1802.3	1827.3	<i>syn</i> -ClC(O)SeF	$\nu(\text{CO})$	this work	
1758.2	1768.1	<i>anti</i> -ClC(O)SeF	$\nu(\text{CO})$	this work	
1237.8	—	F <sub>2</sub> C=O	$\nu(\text{CF})$	1239.0 <sup>c</sup>	
1082.8	1089.3	<i>anti</i> -FC(O)SeCl	$\nu(\text{CF})$	this work	
981.7	1031.1	<i>syn</i> -FC(O)SeCl	$\nu(\text{CF})$	this work	
871.6	875.4	<i>anti</i> -ClC(O)SeF	$\nu(\text{CCl})$	this work	
866.5/861.3/851.7	807.3	<i>syn</i> -ClC(O)SeF	$\nu(\text{CCl})$	this work	
842.4/839.7/837.6	—	Cl <sub>2</sub> C=O	$\nu_{\text{as}}(\text{CCl}_2)$	837.36/837.20/836.38/836.22/835.37/835.23 <sup>e</sup>	
739.9	—	OC...ClF	$\nu(^{35}\text{ClF})$	739.6 <sup>a</sup>	
733.5	—	OC...ClF	$\nu(^{37}\text{ClF})$	732.9 <sup>a</sup>	
598.6/593.0/586.1	—	ClSeF...CO	$\nu(\text{SeF})$	this work	
421.9/419.9	423.8	ClSeF...CO	$\nu(\text{SeCl})$	this work	

<sup>a</sup>Reference 19. <sup>b</sup>Reference 15. <sup>c</sup>Reference 16. <sup>d</sup>Reference 17. <sup>e</sup>Reference 18. <sup>f</sup>Reference 21. <sup>g</sup>Reference 22.

isolated complexes  $\text{C}_2\text{H}_2\cdots\text{X}_2$  with visible light ( $\lambda > 300$  nm).<sup>8,24</sup> These results were explained by means of a radical mechanism, in which a haloalkyl radical intermediate,  $\text{XC}_2\text{H}_2$ , was formed after cleavage of the dihalogen bond. Likewise, a radical addition reaction explains formation of the *syn* and *anti* forms of ClC(O)SeF as represented in Scheme 2. Such a

### Scheme 2. Proposed Radical Mechanisms for the Photochemical Formation of *syn* and *anti* Forms of ClC(O)SeF from Uncomplexed OCSe and ClF in Argon Matrix



photochemical path is also in agreement with the theoretical stability estimated, using the UB3LYP/6-311+G\* approximation, for a triangular bridge radical intermediate, ClC(O)Se; for which no imaginary frequency was found. Moreover, carbonyl stretching of radical ClC(O)Se, calculated at  $1823.9\text{ cm}^{-1}$ , was found close to the intermediate tiny bands observed around  $1830\text{ cm}^{-1}$  (see Figure 4a) in our argon-matrix experiences.

Formation of the bridge radical intermediate FCOSe was also theoretically tested using the UB3LYP/6-311+G\* approximation, finding a planar triangular stable structure as well. In theory, this radical would also be contributing to the formation of the *syn* and *anti* forms of FC(O)SeCl through a photochemical pathway analogous to Scheme 2; however, the higher production of these rotamers was better associated with

the photolysis of the complex OCSe...ClF, as explained below. In addition, no experimental evidence was obtained in our argon-matrix spectra supporting formation of the radical FCOSe.

Comparing the infrared C=O stretching mode intensities of both conformers of FC(O)SeCl in argon matrix, normalized according to our B3LYP/6-311+g(d) frequency calculations, a ratio of 2:1 *anti* to *syn* conformer was indicated for the first minutes after irradiation of the initial matrix. Preferential formation of the less stable *anti* conformer of FC(O)SeCl should thus be related to a light-driven path controlled in some way by the corresponding precursor species, in this case the angular complex OCSe...Cl-F.

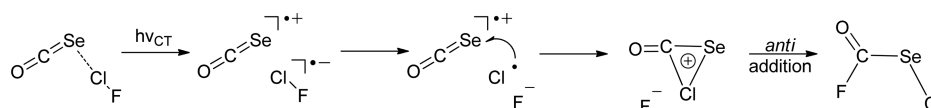
To gain deeper insight into the apparent stereofavored formation of the *anti*-FC(O)SeCl structure by photolysis of the OCSe...Cl-F complex a time-dependent DFT (TDDFT) study was performed on this molecular system. TDDFT calculations of the vertical excitations on the OCSe...Cl-F complex were computed using the B3LYP functional, the 6-31+g(d), 6-311+g(d) and aug-cc-pVDZ basis set, and also the CAM-B3LYP/aug-cc-pVDZ approximation. As can be seen in Table 3, all these four TDDFT approximations predicted an intense band ( $f = 0.1\text{--}0.3$ ), ranging at  $\lambda_{\text{max}} = 245\text{--}259$  nm, for the OCSe...Cl-F molecular complex, related to the fourth excited state ( $S_4$ ) and originating from a charge transference (CT) from the lone pair on selenium atom (HOMO-1) to the antibonding Cl-F orbital (LUMO).

According to the Mulliken theory of the charge transfer complex,<sup>25</sup> a photoinduced electron transfer in a D...A dimer (where D = donor unit and A = acceptor unit) generates an ion radical pair ( $\text{D}^+\cdots\text{A}^-$ ), which brings about a bridge-radical species that can present conformational selectivity. For example, George et al., in a recent MIP experiment,<sup>8</sup> have

**Table 3.** TDDFT Vertical Excitations [in nanometers] for the OCSe...ClF Complex and for the *anti* and *syn* Conformers of FC(O)SeCl, Calculated with Different Levels of Approximation and with Oscillator Strengths in Parentheses

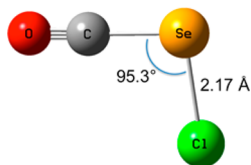
excited state	transition	type	B3LYP/6-31+g(d)	B3LYP/6-311+g(d)	B3LYP/aug-cc-pVDZ	cam-B3LYP/aug-cc-pVDZ
OCSe...ClF complex						
1: <sup>1</sup> A''	HOMO–LUMO	$\pi$ – $\sigma^*$	340.1(0.0)	353.1(0.0)	345.1(0.0)	315.3(0.0)
2: <sup>1</sup> A'	HOMO–2–LUMO	$\pi$ – $\sigma^*$	324.9(0.0)	334.8(0.0)	326.4(0.0)	308.7(0.0)
3: <sup>1</sup> A''	HOMO–3–LUMO	$\pi$ – $\sigma^*$	296.9(0.0)	305.9(0.0)	298.3(0.0)	264.4(0.0)
4: <sup>1</sup> A'	HOMO–1–LUMO	donor–acceptor CT	256.1(0.3)	259.4(0.3)	258.4(0.2)	244.6(0.1)
<i>anti</i> -FC(O)SeCl						
1: <sup>1</sup> A''	HOMO–LUMO	$n$ – $\pi^*$	395.8(0.0)	398.4(0.0)	398.5(0.0)	391.6(0.0)
2: <sup>1</sup> A'	HOMO–1–LUMO	$n$ – $\pi^*$	268.5(0.0)	269.5(0.0)	270.2(0.0)	253.1(0.0)
3: <sup>1</sup> A'	HOMO–LUMO+1	$n$ – $\sigma^*$	226.4(0.1)	228.2(0.1)	228.4(0.1)	210.8(0.1) <sup>a</sup>
4: <sup>1</sup> A''	HOMO–1–LUMO+2	$n$ – $\sigma^*$	224.4(0.0)	226.4(0.0)	226.7(0.0)	221.8(0.0) <sup>b</sup>
5: <sup>1</sup> A''	HOMO–3–LUMO	$n$ – $\pi^*$	217.2(0.0)	218.0(0.0)	218.1(0.0)	207.5(0.0)
<i>syn</i> -FC(O)SeCl						
1: <sup>1</sup> A''	HOMO–LUMO	$n$ – $\pi^*$	387.1(0.0)	389.9(0.0)	389.5(0.0)	382.4(0.0)
2: <sup>1</sup> A'	HOMO–1–LUMO	$n$ – $\pi^*$	259.7(0.0)	260.6(0.0)	261.3(0.0)	246.4(0.0)
3: <sup>1</sup> A'	HOMO–2–LUMO	$n$ – $\pi^*$	233.2(0.0)	234.2(0.0)	234.8(0.0)	212.1(0.0) <sup>a</sup>
4: <sup>1</sup> A''	HOMO–LUMO+2	$n$ – $\sigma^*$	222.3(0.0)	224.2(0.0)	224.3(0.0)	219.6(0.0) <sup>b</sup>
5: <sup>1</sup> A'	HOMO–LUMO+1	$n$ – $\sigma^*$	220.1(0.1)	221.7(0.1)	222.0(0.1)	203.6(0.1) <sup>c</sup>

<sup>a</sup>Excitation for state 4. <sup>b</sup>Excitation for state 3. <sup>c</sup>Excitation for state 6.

**Scheme 3.** Proposed Charge Transfer Mechanism for Photolysis of Angular OCSe...ClF Complex in Solid Argon

proved that *trans*-1,2-dibromoethane can be obtained exclusively from the donor–acceptor complex  $C_2H_4 \cdots Br_2$  by a photoinduced electron transfer using UV light ( $\lambda = 220$  nm). In our case, a Mulliken donor–acceptor complex mechanism would also be completely consistent with the stereopreference observed in the production of *anti*-FC(O)SeCl by photolysis in argon matrix of the OCSe...ClF complex, which can be represented according to Scheme 3.

To test this proposal theoretically, an opt + freq calculation was performed on the chloronium ion intermediate (OCSeCl)<sup>+</sup>, starting from a triangular planar structure similar to that in Scheme 3, using the UB3LYP/6-311+G(d) approximation. Optimization resulted in an angular O=C=Se–Cl geometry (see Figure 8), for which no imaginary

**Figure 8.** Optimized molecular model of the OCSe–Cl intermediate ion using the UB3LYP/6-311+G(d) approximation.

frequencies were found. This spatial arrangement clearly favors a nucleophilic *anti* addition to carbon—rather than *syn*—for a fluoride anion located near the immediacy of the chlorine atom; this is in agreement with our experimental evidence in argon matrix.

Unlike the FC(O)SeF and ClC(O)SeCl molecules formed by photolysis of OCSe...X<sub>2</sub> complexes (see Scheme 1), the photoinduced interconversion between the *syn* and *anti* forms of FC(O)SeCl (produced by photolysis of OCSe...ClF

complex) was not observable. Nevertheless, this phenomenon was theoretically evaluated given the possibility of a reaction rate high enough to be monitored with FTIR spectroscopy. For this, the vertical excitations of both *syn* and *anti* rotamers of FC(O)SeCl were initially calculated, using the same TDDFT levels of approximation that were used for the OCSe...ClF complex (see Table 3). In both instances, the only absorption with  $f \geq 0.1$  always corresponded to the HOMO – LUMO+1 transition (Table 3), ranging at  $\lambda_{max} = 211$ –228 nm (*anti*) and 204–222 nm (*syn*), which is associated with an electron displacement from the lone pair on selenium ( $n_{Se}$ ) to the antibonding Se–Cl orbital ( $\sigma_{SeCl}^*$ ). Given that this type of photoinduced electron transference can cause the electron configuration of the system FC(O)SeCl to be switched from a singlet excited state ( $S_4$ ) to a fundamental triplet state ( $T_1$ ), the next calculations we executed were aimed at exploring the potential energy surface (PES) for the state  $T_1$ . Consequently, *syn* and *anti* forms of FC(O)SeCl were both confirmed as transition structures (saddle points) on the triplet PES, this according to our opt = (ts) + freq calculations employing the UB3LYP/6-311+G(d) approximation. Further geometrical relaxation (using opt keyword) on each of these planar transition structures gives rise to one of the two equivalent *gauche*-FC(O)SeCl triplet global minima (confirmed by freq calculations), depending on direction of rotation of the ClSeCO dihedral angle.

Considering that triplet ( $T_1$ ) *gauche*-FC(O)SeCl minimum coincides geometrically with the singlet ( $S_1$ ) *gauche*-FC(O)SeCl transition structure, a  $T_1/S_1$  conical intersection/avoided crossing emerged as an evident option. To explore this, a complete active space study using six electrons and four orbitals, CAS(6,4), was defined for the triplet state. The molecular orbitals (MOs) included in the CAS were those for



MOs = 38, 37, 36 and 34, which are related to electrons on chlorine and lone pairs on selenium; see Figure S4. Switching between MOs 34 and 35 was requested using the guess = alter option. Basis set projection was performed in the sequence  $3g \rightarrow 3-21g \rightarrow 6-31g \rightarrow 6-31g(d)$ , and in all instances the selected orbitals were checked to ensure that they were the correct ones to be included in the active space. Optimization on triplet *gauche*-FC(O)SeCl minima structure using CAS(6,4)/6-31g(d) ended normally. The final CAS(6,4)/6-31g(d) calculation using opt = conical option converged correctly, predicting an energy difference of only 1.4 kcal mol<sup>-1</sup> between T<sub>1</sub> and S<sub>1</sub> PESs, thus confirming the singlet–triplet conical intersection.

## CONCLUSION

Using an argon matrix experiment combined with a series of quantum *ab-initio*, DFT, TDDFT, and CASSCF calculations we explored the photochemical reaction between OCSe and ClF molecules. Photochemical products were assigned as the novel *syn* and *anti* forms of both ClC(O)SeF and FC(O)SeCl species—which correspond to the first interhalogen members of the halogen-selenocarbonyl family, XC(O)SeY—as well as ClFCO and CO and the hitherto unknown complex ClSeF...CO. Preferential formation of the *anti*-FC(O)SeCl conformer in this reaction was explained by considering a charge transference (CT) photoinduced transition occurring between the HOMO–1 ( $n_{Se}$ ) and LUMO ( $\sigma^*_{Cl-F}$ ) (predicted at  $\lambda_{max} \sim 245$ – $259$  nm, according to our TDDFT calculations) in the angular OCSe...ClF complex, formed chemically between precursors prior to photolysis. Photoinduced rotational interconversion between the *syn* and the *anti* forms of FC(O)SeCl is theoretically feasible by means of a triplet–singlet conical intersection as indicated by our CASSCF calculations. In contrast, *syn* and *anti* conformers of ClC(O)SeF are formed directly from uncomplexed OCSe and ClF molecules, presumably by a photochemical channel involving an halogen radical addition to OCSe ( $\lambda_{max} > 300$  nm, according to our TDDFT calculations).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b12448.

Additional quantum-chemical calculation data, 2D potential energy surfaces for complexes OCSe:ClF, potential energy curves for ClC(O)SeF and FC(O)SeCl molecules, and selected active space orbitals for CASSCF study (PDF)

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### Author Contributions

The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

J.A.G.C. thanks the Universidad Pedagógica y Tecnológica de Colombia (UPTC) for financial support for Project SGI 1535 of Dirección de Investigaciones (DIN) and the Deutscher Akademischer Austausch Dienst (DAAD) for the Ph.D. award during his studies in La Plata. C.O.D.V and R.M.R. acknowledge financial support from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, and ANPCyT.

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