Supporting Information

Ar-matrix studies of the photochemical reaction between CS_2 and ClF: pre-reactive complexes and bond isomerism of the photoproducts

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Table S1. Geometric parameters for the different complexes formed between CS_2 and ClF (distances in Å, angles in degrees) calculated using the B3LYP/6-311+G(d,p) approximation

Molecular complex	r(C=S1)	Δr(C=S1)[a]	r(C=S2)	Δr(C=S2)[b]	r(Cl–F)	Δr(Cl–F)[c]	r(S2···X)[d]	α(C=S2···X)[d]	d_p [35]
S=C=S···Cl–F	1.5525	-8.0×10^{-3}	1.5690	8.6×10^{-3}	1.7104	0.0316	2.9411	97.9	0.62
S=C=S··· F–Cl	1.5618	1.3×10^{-3}	1.5598	-6×10^{-4}	1.6795	6×10^{-4}	3.2531	180.0	0.05

[a] $\Delta r(\text{C=S1}) = r(\text{C=S1})_{\text{complex}} - r(\text{C=S1})_{\text{free}}$. S1 corresponds to the interacting sulfur atom.
[b] $\Delta r(\text{C=S2}) = r(\text{C=S2})_{\text{complex}} - r(\text{C=S2})_{\text{free}}$. S2 corresponds to the non-interacting sulfur atom.
[c] $\Delta r(\text{Cl–F}) = r(\text{Cl–F})_{\text{complex}} - r(\text{Cl–F})_{\text{free}}$.
[d] X = Cl or F.

Table S2. $\Delta E^{(SCF)}$, ΔE^{CP}, BSSE and GEOM corrections (in kcal.mol^{-1}), transferred charge (q), orbital stabilization energy ($\Delta E^{(2)}$ in kcal.mol^{-1}) for the different complexes formed between CS_2 and ClF computed using the B3LYP/6-311+G(d,p) approximation

Molecular complex	ΔE^{SCF} (kcal/mol)[a]	ΔE^{CP} (kcal/mol)[b]	BSSE (kcal/mol)[c]	GEOM (kcal/mol)[d]	q (e)	$\Delta E^{(2)}$[e] (kcal/mol)	Orbital interaction
S=C=S···Cl–F	−3.48	−1.89	−0.33	−1.26	−0.0894	−9.79	$lp_S \rightarrow \sigma^*_{ClF}$
S=C=S··· F–Cl	−1.84	−0.06	−0.48	−1.30	−0.0013	−0.71	$\sigma_{ClF} \rightarrow Ry_S$
						−0.29	$lp_F \rightarrow \sigma^*_{C=S}$

[a] Uncorrected binding energy, $\Delta E^{(SCF)} = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B)$, where the subscripts refer to the geometry and the superscript refer to the bases set used to calculate the energy at the geometry defined by the subscript.

[b] Counterpoise corrected binding energy, $\Delta E^{CP} = E_{AB}^{AB}(AB) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B)$.

[c] Basis set superposition error correction, $BSSE = E_{AB}^{AB}(A) - E_{AB}^{A}(A) + E_{AB}^{AB}(B) - E_{AB}^{B}(B)$

[d] Geometry correction, $GEOM = E_{AB}^{A}(A) - E_A^A(A) + E_{AB}^{B}(B) - E_B^B(B)$

[e] Orbital stabilization energy

Table S3. Wavenumbers for the different complexes formed between CS_2 and ClF computed with the B3LYP/6-311+G(d,p) approximation (wavenumbers are in cm^{-1} and relative IR intensities are given between parentheses) and comparison with the experimental values

Ar-matrix		B3LYP/6-311+G(d,p)				Tentative Asignment
		S=C=S···Cl–F		S=C=S··· F–Cl		
ν (cm^{-1})	Δν (cm^{-1}) [a]	ν (cm^{-1})	Δν (cm^{-1}) [a]	ν (cm^{-1})	Δν (cm^{-1}) [a]	
2169.5	–8.3					ν_{as}(SCS) + ν_{s}(SCS)
1522.2	–5.7	1547.1 (100)	–6.2	1552.2 (100)	–1.9	ν_{as}(SCS)
		671.8 (<1)	–2.1	673.3 (<1)	–0.6	ν_{s}(SCS)
718.5	–48.6	646.5 (31.8)	–93.3	740.3 (3.8)	+0.7	ν(^{35}Cl–F)
712.2	–47.7	640.8 (31.8)	–92.2	733.2 (3.7)	+0.5	ν(^{37}Cl–F)
		403.3 (<1)	+5.7	398.7 (2.6)	+1.1	$\delta_{i.p.}$(SCS)
		393.3 (<1)	–4.2	398.7 (2.6)	+1.1	$\delta_{o.o.p.}$(SCS)
		137.2 (<1)		71.0 (<1)		
		107.6 (<1)		71.0 (<1)		
		92.6 (2.2)		21.7 (<1)		
		34.4 (<1)		17.5 (<1)		
				17.5 (<1)		

[a] $\Delta\nu = \nu_{complex} - \nu_{monomer}$

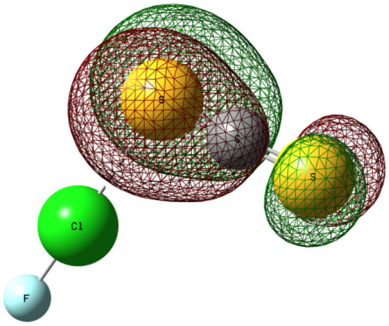
Table S4. Geometrical parameters of anti-ClC(S)SF, syn-ClC(S)SF, anti-FC(S)SCl and syn-FC(S)SCl calculated with the B3LYP/6-311+G(d,p) approximation (distances in Å and angles in degrees)

Geometrical Parameters	anti-ClC(S)SF	syn-ClC(S)SF	anti-FC(S)SCl	syn-FC(S)SCl
r (X–C)	1.7414	1.7916	1.3304	1.3567
r (C=S)	1.6267	1.6042	1.6172	1.6014
r (C–S)	1.7220	1.7376	1.7360	1.7679
r (S–Y)	1.6713	1.6480	2.1006	2.0574
α (X–C=S)	126.6	125.7	124.8	123.6
α (X–C–S)	118.5	104.0	116.3	103.2
α (C–S–Y)	105.3	101.1	106.4	102.9
τ (X–C–S–Y)	0.0	180.0	0.0	180.0
E (Hartree)	−1394.59816341	−1394.59694854	−1394.61707083	−1394.61363235
ΔE (Kcal/mol)	0.00	0.76	0.00	2.16

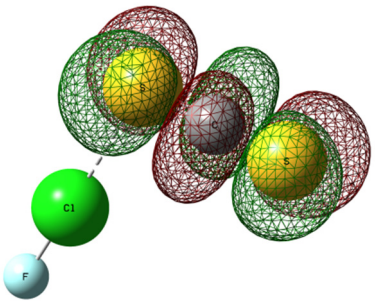
Tabla S5 FTIR wavenumber and proposed assignment of the photoproducts formed by UV-visible irradiation of CS_2 and ClF co-deposited in an Ar matrix (CS_2:ClF:Ar 1:2:200) at cryogenic temperatures

Wavenumber ν (cm^{-1})	Proposed Assignment		Reported Wavenumber ν (cm^{-1})
	Species	Description	
1481.9	Cl•···SCS	ν_{as} S=C=S	1481.5 [5]
1353.6 1346.0	SCF_2	ν C=S	1354.0 [25]
1287.5 1284.0 1281.3	complexed-CS	ν CS	1276 [29]
1228.9 1226.0	syn-FC(S)SCl	ν C=S	This work
1213.5 1208.2	anti-FC(S)SCl	ν C=S	This work
1185.3 1182.2 1179.3	SCF_2	ν_{as} F–C–F	1180 [25]
1160.9	syn-ClC(S)SF	ν C=S	This work
1061.8	anti-ClC(S)SF	ν C=S	This work
997.5	anti-FC(S)SCl	ν C–F	This work
976.3	syn-FC(S)SCl	ν C–F	This work
802.7	anti-ClC(S)SF	ν C–Cl	This work
782.2 779.2	syn-ClC(S)SF	ν S–F	This work
668.8	anti-ClC(S)SF	ν S–F	This work
598.8 595.7	•SCl	ν S–^{35}Cl ν S–^{37}Cl	574.4 566.9 [30]

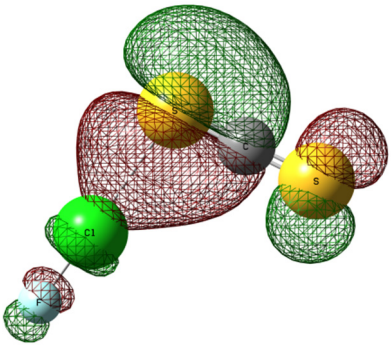
Figure S1. Schematic representations of the main contributions to the orbital interactions in the $CS_2\cdots ClF$ (left) and $CS_2\cdots FCl$ (right) complexes.



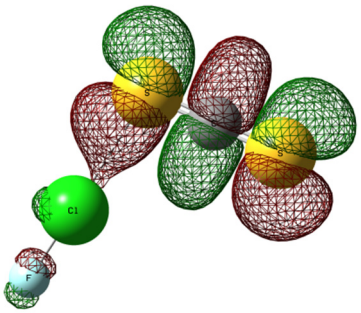
HOMO (π_z (C=S1))



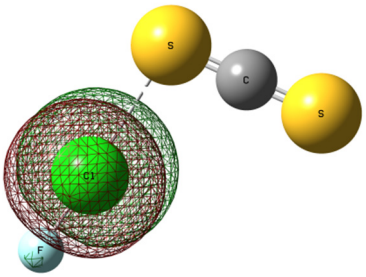
LUMO (π_z* (S=C=S))



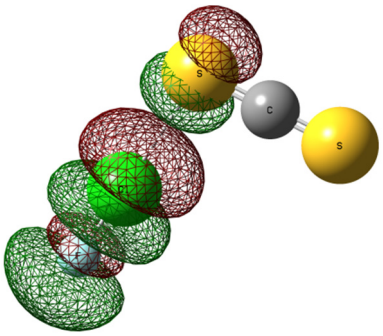
HOMO–1 ($\pi_{i.p.}$ (C=S1))



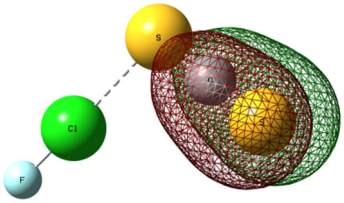
LUMO+1 ($\pi_{i.p.}$* (S=C=S))



HOMO–2 (lp_z Cl)



LUMO+2 (σ* (Cl–F))



HOMO–3 (π_z (C=S2))

Figure S2. Schematic representation and approximate assignment of the molecular orbitals of the $CS_2\cdots ClF$ complex involved in the electronic transitions with $\lambda > 200$ nm and $f \geq 0.002$, calculated with the B3LYP/6-311+G(d,p) approximation.

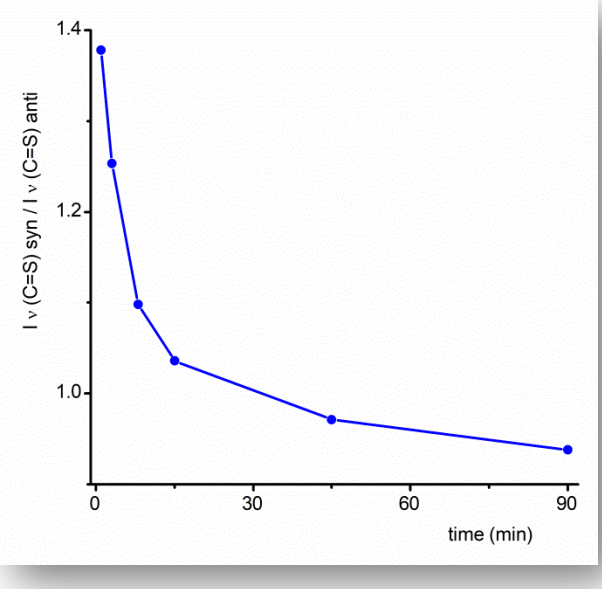


Figure S3. Plot of the relative intensities of the ν(C=S) absorptions of *syn*- and *anti*-ClC(S)SF as a function of the broad-band UV-visible irradiation time.

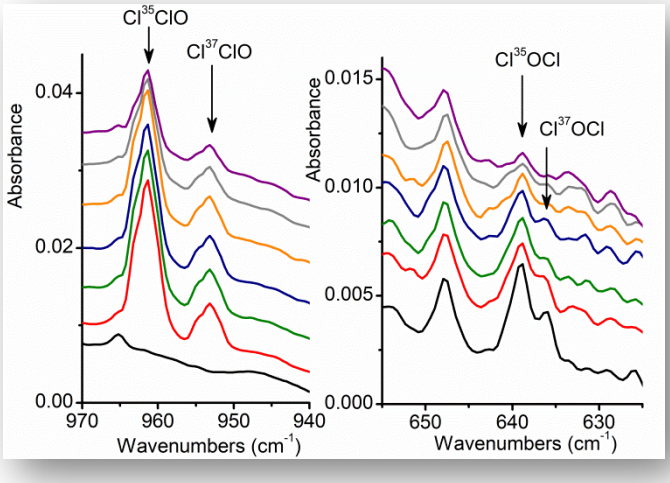


Figure S4. FTIR spectra of the CS_2/ClF/Ar matrix (CS_2:ClF:Ar = 1:2:200) at about 15 K after deposition (bottom, black-trace) and (from bottom to top) 1 (red-trace), 3 (green-trace), 8 minutes (blue-trace), 15 minutes (orange-trace), 45 minutes (grey-trace) and 90 minutes (purple-trace) of irradiation with broad-band UV-visible light (225 ≤ λ ≤ 800 nm) in the 970–940 and 655–635 cm^{-1} regions.

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