



Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2017

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

Melina V. Cozzarín and Rosana M. Romano*

Experimental and Computational Section

Sample preparation. FC(O)SSCI was prepared according to the recently published procedure,^[1] by the ambient-temperature reaction of fresh-prepared ClC(O)SSCI^[2] with dried TIF in vacuum conditions. The purity of FC(O)SSCI was checked by means of its FTIR, Raman and electron-impact mass spectra.^[1]

Matrix photochemistry experiments. A gas mixture of FC(O)SSCI with argon, in an approximately 1:1000 proportion, was prepared by standard manometric methods. The Ar gas (AGA) was passed through a trap cooled to -90°C to retain possible traces of impurities. The mixture was then deposited on a CsI window cooled to ca. 10 K by means of a Displex closed-cycle refrigerator (SHI-APD Cryogenics, model DE-202), using the pulse deposition technique.^[3-5] FTIR spectra of the matrix were recorded at resolutions of 0.5 and 0.125 cm^{-1} , with 256 scans, using a Nexus Nicolet instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000-400 or 600-180 cm^{-1} , respectively). Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV-visible radiation ($200 \leq \lambda \leq 800 \text{ nm}$) from a Spectra-Physics Hg-Xe arc lamp operating at 800 W. The output from this lamp was limited by a water filter to absorb IR radiation and so minimize any heating effects. The FTIR spectra of the matrices were recorded at different irradiation times in order to follow the progress of the photolysis.

Computational calculations. All quantum chemical calculations were performed using the Gaussian 03 program package.^[6] Geometry optimizations were performed using standard gradient techniques by simultaneous relaxation of all geometrical parameters. The vibrational properties were calculated to characterize the structures as true minima, with no imaginary vibrational frequency, and to compare the theoretical wavenumbers of unknown species with the photoproducts obtained during the photolysis of FC(O)SSCI isolated in solid Ar. The interaction energy (ΔE) in the molecular complexes were calculated and corrected for the basis set superposition error (BSSE) using the counterpoise correction procedure proposed by Boys and Bernardi^[7] and the zero-point energy differences. The bonding properties of the complexes were interpreted by natural bond orbital (NBO) analysis in terms of “donor-acceptor” interactions.^[8]

Table S1. Vibrational wavenumbers of the 1:1 OCS:CISF molecular complexes calculated with the B3LYP/6311+G* approximation. Relative IR intensities are given between parentheses.

| (OCS⋯CISF)-I | | (OCS⋯CISF)-II | | (OCS⋯CISF)-III | | (OCS⋯CISF)-IV | | Assignment |
|---------------------------|--|---------------------------|--|---------------------------|--|---------------------------|--|-----------------|
| ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | |
| 2122.8 (100) | +6.5 | 2121.3 (100) | +5.0 | 2114.4 (100) | -1.9 | 2108.9 (100) | -7.4 | ν (C=O) |
| 870.7 (1) | -5.1 | 871.3 (1) | -4.5 | 874.8 (1) | -1.0 | 881.7 (<1) | +5.9 | ν (C=S) |
| 717.1 (12) | -0.1 | 714.7 (18) | -2.5 | 717.6 (12) | +0.4 | 715.2 (10) | -2.1 | ν (SF) |
| 510.4 (<1) | -1.1 | 512.2 (<1) | +0.7 | 511.0 (<1) | -0.5 | 515.1 (<1) | +3.6 | δ (OCS) |
| 508.2 (<1) | -3.3 | 508.0 (<1) | -3.5 | 510.3 (<1) | -1.2 | 513.2 (<1) | +1.7 | δ (OCS) |
| 499.9 (1) | -2.8 | 500.8 (5) | -1.9 | 503.1 (7) | +0.4 | 499.7 (9) | -3.0 | ν (SCI) |
| 255.0 (<1) | +1.8 | 253.1 (<1) | -0.1 | 252.3 (<1) | -0.9 | 256.2 (<1) | +3.0 | δ (SCIF) |

^a $\Delta\nu = \nu_{\text{complex}} - \nu_{\text{monomer}}$

Table S2. Geometrical parameters (distances in Å, angles in degrees) of the 1:1 OCS:CISF molecular complexes calculated with the B3LYP/6311+G* approximation.

| Molecular complex | α_1^a | α_2^b | r_{eq} | r_{vdw}^c | d_p^d |
|-------------------|--------------|--------------|----------|-------------|---------|
| (OCS⋯CISF)-I | 100.8 | 75.0 | 3.53 | 3.17 | -0.36 |
| (OCS⋯CISF)-II | 100.8 | 88.8 | 3.80 | 3.60 | -0.20 |
| (OCS⋯CISF)-III | 101.0 | 104.3 | 4.13 | 3.60 | -0.53 |
| (OCS⋯CISF)-IV | 99.1 | 79.6 | 3.13 | 3.32 | 0.19 |

^a $\alpha_1 = \alpha_{CISF}$

^b $\alpha_2 = \alpha_{SSF}$ for complex I, α_{SSCI} for complexes II and III, α_{OSF} for complex IV.

^c Sum of van der Waals radii.^[9]

^d van der Waals penetretation distance, $d_p = r_{vdw} - r_{eq}$.

Table S3. $\Delta E^{(SCF)}$, ΔE^{CP} , ΔE , BSSE and GEOM corrections (in kcal.mol⁻¹), transferred charge (q) and orbital stabilization energy ($\Delta E^{(2)}$ in kcal.mol⁻¹) for the 1:1 OCS:CISF molecular complexes calculated using the B3LYP/ 6-311+ G* approximation.

| Molecular complex | ΔE^{SCF} | ΔE^{CP} | ΔE | BSSE | GEOM | q (e) | $\Delta E_{i \rightarrow j}^{(2)}$ | Orbital interaction |
|-------------------|------------------|-----------------|------------|-------|-------|--------|------------------------------------|---|
| (OCS...CISF)-I | -0.45 | -0.03 | -0.02 | -0.43 | +0.01 | 0.0034 | -0.62 -0.11 | $n_p(S) \rightarrow \sigma^*(S-Cl)$ $\pi^*(C=O) \rightarrow \sigma^*(S-F)$ |
| (OCS...CISF)-II | -0.33 | +0.05 | +0.06 | -0.38 | +0.01 | 0.0036 | -0.90 -0.07 | $n_p(S) \rightarrow \sigma^*(S-F)$ $n_p(Cl) \rightarrow \pi^*(C=O)$ |
| (OCS...CISF)-III | -0.31 | +0.10 | +0.10 | -0.41 | 0.00 | 0.0044 | -0.21 | $n_p(S) \rightarrow \sigma^*(C=S)$ |
| (OCS...CISF)-IV | -1.31 | -0.68 | -0.67 | -0.64 | +0.02 | 0.0092 | -1.41 -0.98 -0.35 | $n_p(O) \rightarrow \sigma^*(S-Cl)$ $n_s(O) \rightarrow \sigma^*(S-Cl)$ $n_p(F) \rightarrow \pi^*(C=S)$ |

Table S4. Vibrational wavenumbers of the 1:1 CO:CISF molecular complexes calculated with the B3LYP/6311+G* approximation. IR intensities are given between parentheses.

| (CO...CISF)-I | | (CO...CISF)-II | | (OC...CISF)-I | | (OC...CISF)-II | | Assignment |
|---------------------------|--|---------------------------|--|---------------------------|--|---------------------------|--|-----------------|
| ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | |
| 2205.8 (100) | -5.9 | 2205.4 (98) | -6.3 | 2223.0 (75) | +11.3 | 2220.3 (100) | +8.6 | ν (C=O) |
| 718.6 (86) | +1.4 | 716.6 (100) | -0.6 | 710.3 (100) | -6.9 | 713.3 (93) | -3.9 | ν (S-F) |
| 498.5 (55) | -4.2 | 501.4 (45) | -1.3 | 497.4 (38) | -5.3 | 496.5 (73) | -6.2 | ν (S-Cl) |
| 251.8 (3) | -1.4 | 252.0 (2) | -1.2 | 251.5 (2) | +1.5 | 254.7 (4) | +1.5 | δ (SCIF) |

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

Table S5. Geometrical parameters (distances in Å, angles in degrees) of the 1:1 CO:CISF molecular complexes calculated with the B3LYP/6311+G* approximation.

| Molecular complex | α_1^a | α_2^b | r_{eq} | r_{vdw}^c | d_p^d |
|-------------------|--------------|--------------|----------|-------------|---------|
| (CO···CISF)-I | 100.7 | 78.8 | 3.32 | 3.32 | 0.00 |
| (CO···CISF)-II | 100.9 | 89.4 | 3.33 | 3.32 | -0.01 |
| (OC···CISF)-I | 100.4 | 88.9 | 3.25 | 3.50 | 0.25 |
| (OC···CISF)-II | 100.4 | 75.5 | 3.34 | 3.50 | 0.16 |

^a $\alpha_1 = \alpha_{CISF}$

^b $\alpha_2 = \alpha_{OSF}$ for CO···CISF complexes, α_{CSF} for OC···CISF complexes.

^c Sum of van der Waals radii.^[9]

^d van der Waals penetretation distance, $d_p = r_{vdw} - r_{eq}$.

Table S6. $\Delta E^{(\text{SCF})}$, ΔE^{CP} , ΔE , BSSE and GEOM corrections (in kcal.mol⁻¹), transferred charge (q) and orbital stabilization energy ($\Delta E^{(2)}$ in kcal.mol⁻¹) for the 1:1 CO:CISF molecular complexes calculated using the B3LYP/ 6-311+ G* approximation.

| Molecular complex | ΔE^{SCF} | ΔE^{CP} | ΔE | BSSE | GEOM | q (e) | $\Delta E_{i \rightarrow j}^{(2)}$ | Orbital interaction |
|-------------------|-------------------------|------------------------|------------|-------|------|--------|------------------------------------|--|
| (CO···CISF)-I | -0.55 | -0.18 | -0.18 | -0.37 | 0.00 | 0.0014 | -0.16 | $n_s(\text{O}) \rightarrow \sigma^*(\text{S}-\text{Cl})$ |
| (CO···CISF)-II | -0.57 | -0.26 | -0.26 | -0.31 | 0.00 | 0.0016 | -0.29 | $n_s(\text{O}) \rightarrow \sigma^*(\text{S}-\text{F})$ |
| (OC···CISF)-I | -1.03 | -0.60 | -0.58 | -0.45 | 0.02 | 0.0051 | -1.04 | $n_s(\text{C}) \rightarrow \sigma^*(\text{S}-\text{Cl})$ |
| (OC···CISF)-II | -1.09 | -0.75 | -0.73 | -0.36 | 0.02 | 0.0081 | -1.84 | $n_s(\text{C}) \rightarrow \sigma^*(\text{S}-\text{F})$ |

Table S7. Vibrational wavenumbers of the 1:1 CS₂:CIF molecular complex calculated with the B3LYP/6311+G* approximation. IR intensities are given between parentheses.

| ν (cm ⁻¹) | $\Delta\nu$ (cm ⁻¹) ^a | Assignment |
|---------------------------|--|-------------------------------|
| 1547.0 (100) | -6.0 | ν_{as} (CS ₂) |
| 671.8 (<<1) | -1.7 | ν_s (CS ₂) |
| 646.3 (32) | -93.4 | ν (CIF) |
| 403.3 (<1) | +5.4 | δ (CS ₂) |
| 393.3 (<1) | -4.6 | δ (CS ₂) |

^a $\Delta\nu = \nu_{\text{complex}} - \nu_{\text{monomer}}$

Table S8. Geometrical parameters (distances in Å, angles in degrees) of the 1:1 CS₂:CIF molecular complex calculated with the B3LYP/6311+G* approximation.

| α (SCIF) | r_{eq} | r_{vdw}^a | d_p^b |
|-----------------|-----------------|--------------------|---------|
| 102.7 | 3.10 | 3.55 | 0.45 |

^a Sum of van der Waals radii.^[9]

^b van der Waals penetretation distance. $d_p = r_{\text{vdw}} - r_{\text{eq}}$.

Table S9. $\Delta E^{(\text{SCF})}$, ΔE^{CP} , ΔE , BSSE and GEOM corrections (in kcal.mol⁻¹), transferred charge (q) and orbital stabilization energy ($\Delta E_{i \rightarrow j}^{(2)}$ in kcal.mol⁻¹) for the 1:1 CS₂:ClF molecular complex calculated using the B3LYP/ 6-311+ G* approximation.

| ΔE^{SCF} | ΔE^{CP} | ΔE | BSSE | GEOM | q (e) | $\Delta E_{i \rightarrow j}^{(2)}$ | Orbital interaction |
|-------------------------|------------------------|------------|-------|------|--------|------------------------------------|--------------------------------|
| -2.18 | -2.21 | -1.86 | -0.31 | 0.35 | 0.0896 | -9.81 | n _p (S) → σ* (Cl-F) |

Table S10. Geometrical parameters (distances in Å, angles in degrees) of CISSF calculated with the B3LYP/6311+G* approximation.

| Geometrical parameter | B3LYP/6311+G* |
|-----------------------|---------------|
| r (Cl-S) | 2.149 |
| r (S-S) | 1.954 |
| r (S-F) | 1.689 |
| α(CISS) | 109.96 |
| α(SSF) | 106.78 |
| τ(CISSF) | 87.98 |

Table S11. Vibrational wavenumbers of CISSF calculated with the B3LYP/6311+G* approximation. IR intensities are given between parentheses

| ν (cm ⁻¹) | Assignment |
|---------------------------|-----------------|
| 633.6 (100) | ν (S–F) |
| 542.8 (6) | ν (S–S) |
| 400.1 (55) | ν (S–Cl) |
| 275.4 (7) | δ (SSF) |
| 221.0 (3) | δ (CISS) |
| 128.8 (<19) | τ (CISSF) |

Table S12. Cartesian coordinates (in Å) of (OCS⋯CISF)-I molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| O | 3.0221 | 1.5525 | -0.2766 |
| C | 2.8044 | 0.4279 | -0.1262 |
| S1 | 2.51893 | -1.1038 | 0.0760 |
| F | -0.6161 | 0.9454 | 0.5665 |
| S2 | -1.2703 | -0.4407 | -0.0633 |
| Cl | -3.2610 | 0.0715 | -0.1371 |

Table S13. Cartesian coordinates (in Å) of (OCS...CISF)-II molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| O | -3.0707 | 1.3140 | 0.2896 |
| C | -2.6848 | 0.2418 | 0.0974 |
| S1 | -2.1647 | -1.2168 | -0.1658 |
| F | 3.2315 | -0.6606 | 0.1497 |
| S2 | 1.5750 | -0.6270 | 0.1033 |
| Cl | 1.2368 | 1.3814 | -0.1911 |

Table S14. Cartesian coordinates (in Å) of (OCS...CISF)-III molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| O | -4.7969 | 0.3348 | 0.0105 |
| C | -3.6516 | -0.1682 | -0.0046 |
| S1 | -2.0995 | 0.0570 | -0.0250 |
| F | 1.6726 | 1.4689 | -0.7089 |
| S2 | 1.9472 | 0.5428 | 0.6364 |
| Cl | 2.8040 | -1.1253 | -0.2034 |

Table S15. Cartesian coordinates (in Å) of (OCS...CISF)-IV molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| O | -1.5692 | -0.8354 | 0.0499 |
| C | -2.6301 | -0.3704 | 0.0109 |
| S1 | -4.0643 | 0.2551 | -0.0414 |
| F | 0.9679 | 1.2146 | 0.0634 |
| S2 | 1.5180 | -0.3494 | 0.0347 |
| Cl | 3.5508 | -0.0305 | -0.0545 |

Table S16. Cartesian coordinates (in Å) of (CO...CISF)-I molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| C | 4.060 | -0.1668 | 0.0037 |
| O | 2.9407 | -0.3064 | -0.0021 |
| F | -0.0436 | 1.3412 | -0.0003 |
| S | -0.3788 | -0.2796 | -0.0015 |
| Cl | -2.4373 | -0.2438 | 0.0012 |

Table S17. Cartesian coordinates (in Å) of (CO⋯CISF)-II molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| C | -3.8048 | -0.1589 | 0.0090 |
| O | -2.6807 | -0.2558 | -0.0063 |
| F | 2.2091 | -1.1390 | -0.0049 |
| S | 0.6250 | -0.6519 | -0.0035 |
| Cl | 0.8467 | 1.3930 | 0.0004 |

Table S18. Cartesian coordinates (in Å) of (OC⋯CISF)-I molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| O | 3.7022 | -0.1721 | -0.0068 |
| C | 2.5800 | -0.2676 | 0.0084 |
| F | -2.2409 | -1.1242 | -0.0050 |
| S | -0.6476 | -0.6592 | 0.0035 |
| Cl | -0.8569 | 1.3910 | -0.0004 |

Table S19. Cartesian coordinates (in Å) of (OC⋯ClSF)-II molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| O | 4.0038 | -0.1068 | -0.0008 |
| C | 2.9056 | -0.3559 | 0.0001 |
| F | -0.0113 | 1.2653 | 0.0002 |
| S | -0.4378 | -0.3372 | 0.0010 |
| Cl | -2.4916 | -1.1757 | -0.0007 |

Table S20. Cartesian coordinates (in Å) of the 1:1 CS₂:ClF molecular complex calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|--------|
| C | 1.3969 | 0.8781 | 0.0000 |
| S1 | 0.000 | 1.5927 | 0.0000 |
| Cl | -1.6850 | -0.8169 | 0.0000 |
| F | -2.6981 | -2.1952 | 0.0000 |
| S2 | 2.7841 | 0.1809 | 0.0000 |

Table S21. Cartesian coordinates (in Å) of CISSF calculated with the B3LYP/6311+G* approximation.

| Atom | x | y | z |
|------|---------|---------|---------|
| Cl | -1.9710 | -0.4915 | 0.1166 |
| S1 | -0.3369 | 0.8150 | -0.3745 |
| S2 | 1.2897 | 0.2169 | 0.5281 |
| F | 2.0291 | -0.9062 | -0.4934 |

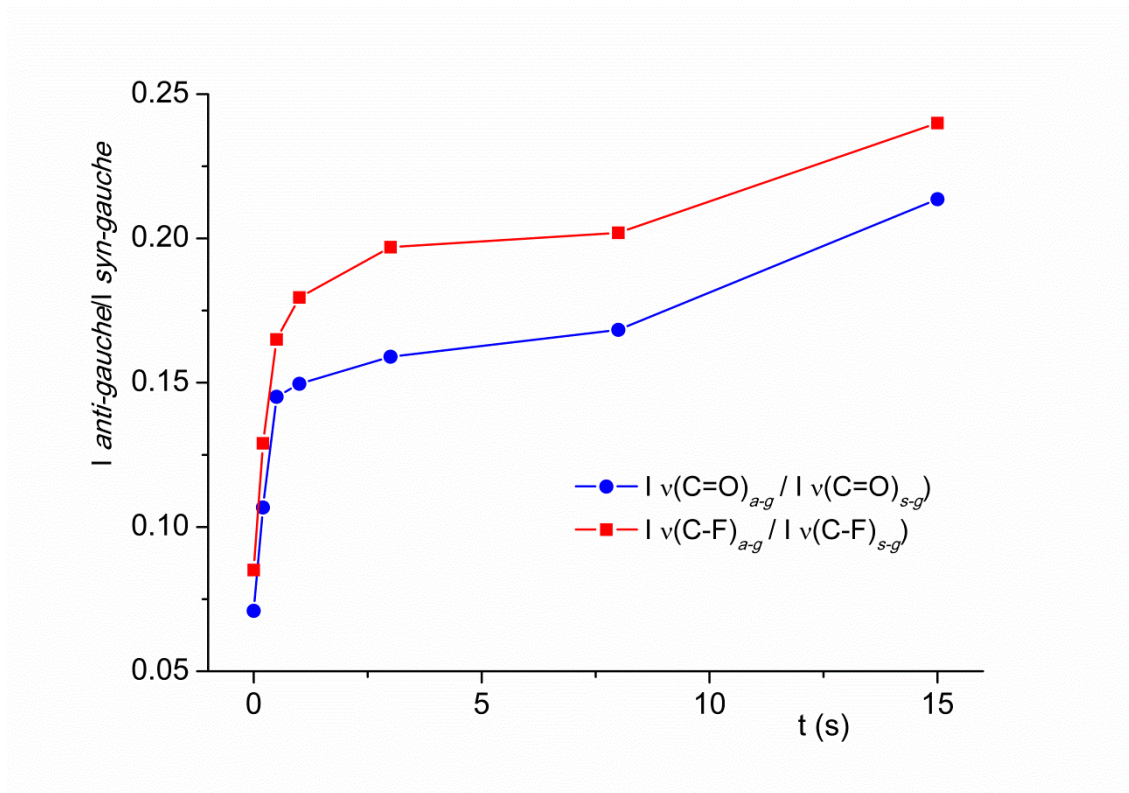


Figure S1. Plots as a function of irradiation time of the relative intensities of the bands assigned to *anti-gauche* form of FC(O)SSCI with respect to the absorptions of the *syn-gauche* conformer in the IR spectrum of an Ar matrix initially containing FC(O)SSCI and Ar in the proportions 1:1000.

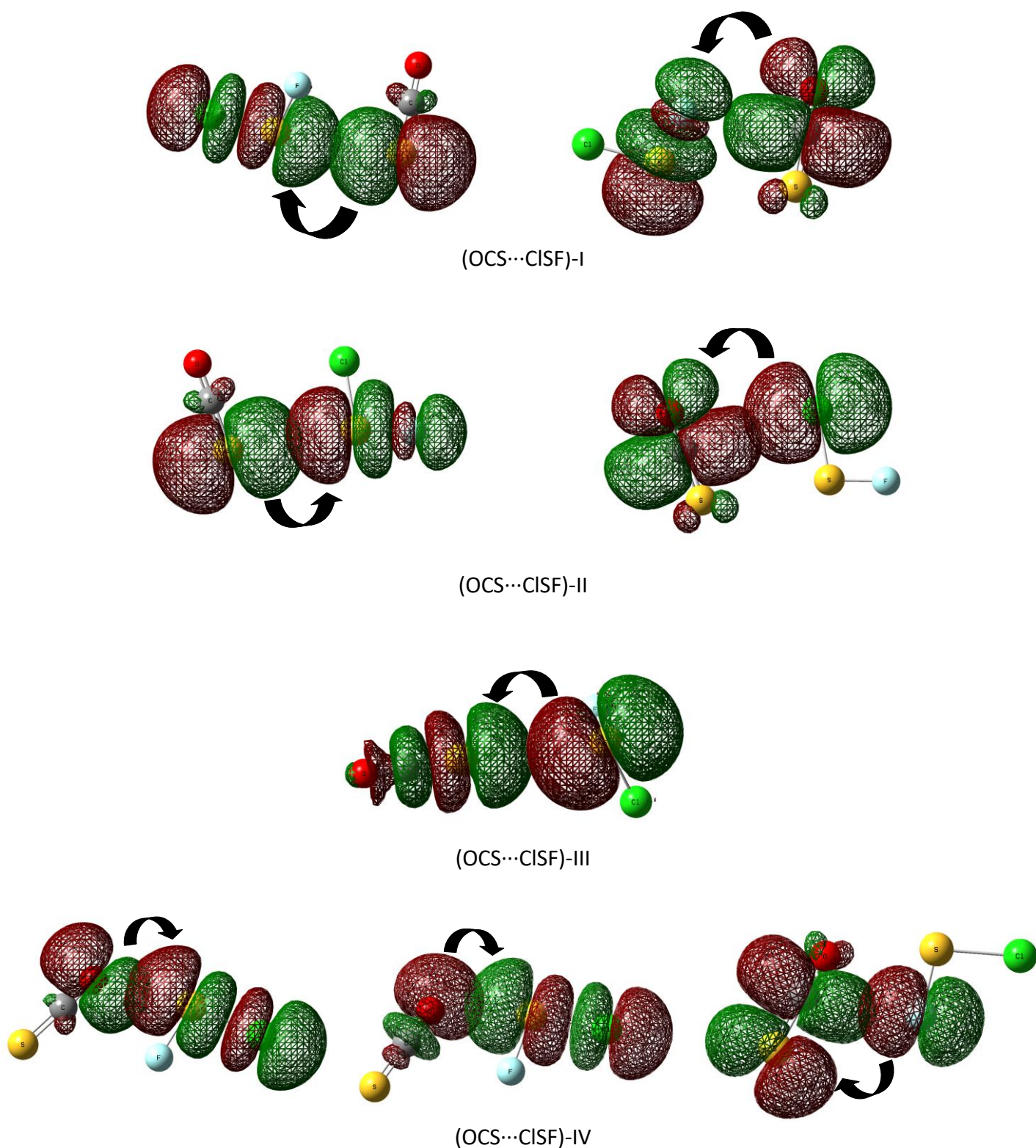


Figure S2. Schematic representation of the most relevant orbital interactions for the 1:1 molecular complexes between OCS and CISF calculated with the B3LYP/6-311+G* approximation.

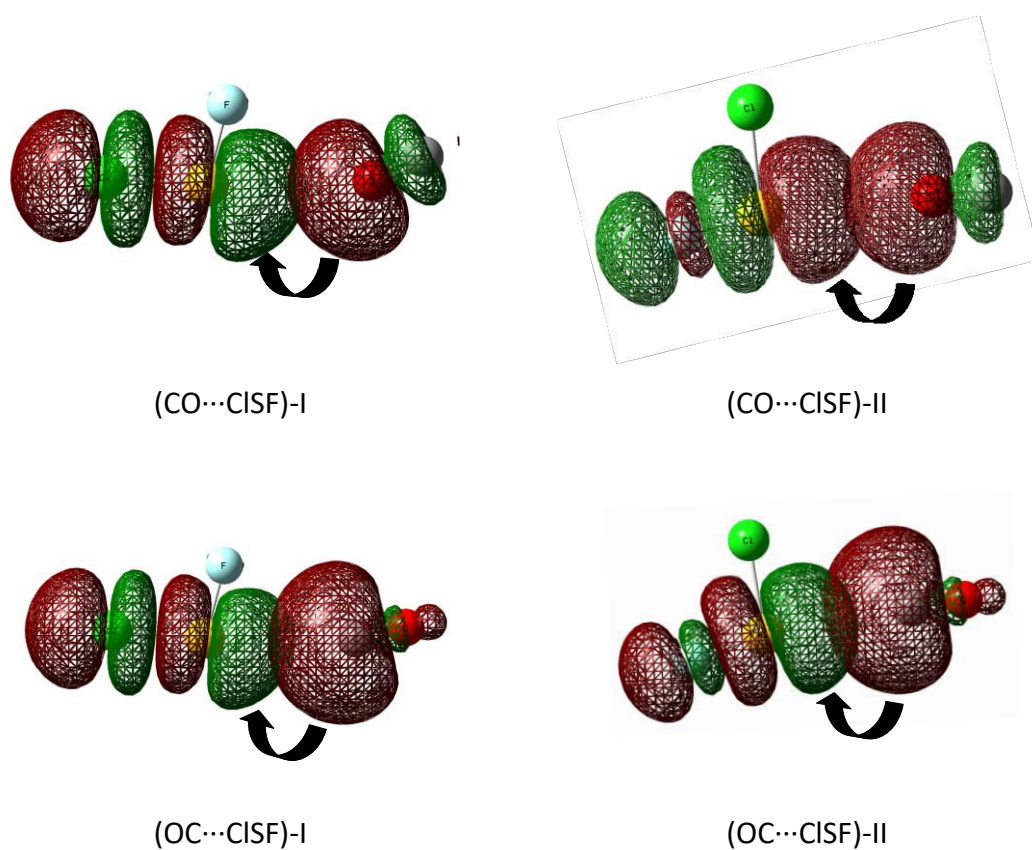


Figure S3. Schematic representation of the most relevant orbital interactions for the 1:1 molecular complexes between CO and CISF calculated with the B3LYP/6-311+G* approximation.

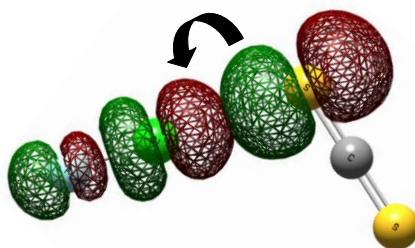


Figure S4. Schematic representation of the most relevant orbital interaction for the 1:1 molecular complex between CS₂ and ClF calculated with the B3LYP/6-311+G* approximation.

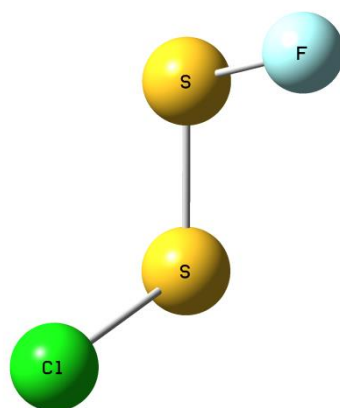


Figure S5. Molecular model of CISSF calculated with the B3LYP/6-311+G* approximation.

References

- [1] M. V. Cozzarín, S. Tong, M. F. Ge, C. O. Della Védova, R. M. Romano, *Eur. J. Inorg. Chem.* **2016**, 5568-5574.
- [2] Y. A. Tobón, M. V. Cozzarín, W. G. Wang, M. F. Ge, C. O. Della Védova, R. M. Romano, *J. Phys. Chem. A* **2011**, *115*, 10203-10210.
- [3] I. R. Dunkin in *Matrix-Isolation Techniques: A Practical Approach*, Oxford University Press, New York, **1998**.
- [4] M. J. Almond, A. J. Downs in *Spectroscopy of Matrix Isolated Specie Adv. in Spectroscopy*, Volume 17, Chichester, **1989**.
- [5] R. N. Perutz, J. J. J. Turner, *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 452-461.
- [6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, revision B.05; Gaussian, Inc.: Pittsburgh, PA, **2003**.
- [7] S. F. Boys, F. Bernardi, **1970**, *19*, 553-566.
- [8] A. E. Reed, L. A. Curtiss, *Chem. Rev.* **1988**, *88*, 899-926.
- [9] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441-451.