Electronic Supplementary Information for

Photoisomerization of matrix isolated F$_2$CS into *cis* and *trans* FCSF

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Sample preparations:

A few mg of F$_2$CS used in this study were taken out of sealed glass ampoules which were stored at liquid nitrogen temperature in a long term Dewar vessel. The sample of F$_2$CS was used before for vibrational studies.[1] The ampoules were opened at a vacuum line by using a special device.[2] A 30% ^{34}S-enriched F$_2$CS sample was prepared in a flame-sealed glass tube (o.d. 6 mm, vol. 3 ml) by pyrolyzing small pieces of Teflon (10 mg) with a torch and then by reacting the gaseous products with 30% ^{34}S-enriched sulfur (5 mg) at 400 °C for a few minutes. About 0.07 mmol of ^{34}S-enriched F$_2$CS was obtained by repeated fractional condensation in vacuum. The purity of all samples was checked by FT-IR in the gas phase.

Spectroscopic investigations:

Infrared spectra of the matrix-isolated species were recorded on a FTIR spectrometer (IFS 66v/S Brucker) in reflectance mode using a transfer optic. A KBr beam splitter and a MCT detector was used in the region of 5000 – 530 cm^{-1} and a Ge-coated 6-μ mylar beam splitter with He(l) cooled Si bolometer in the region of 700 – 150 cm^{-1}. For each spectrum 64 scans at resolution of 0.25 cm^{-1} were coadded.

Preparation of the matrices: The stable gaseous precursor F$_2$CS was mixed with argon (1:500) in a 1-L stainless-steel storage container and then small amounts (2 mmol) of the mixtures were deposited within 20 minutes onto the cold matrix support (16 K, Rh plated Cu block) in high vacuum. Photolysis experiments were carried out with ArF excimer laser (Lambda-Physik, 2mJ, 1 hour). Details of the matrix apparatus have been described elsewhere.[3]

Theoretical Calculations: Quantum chemical calculations were carried out using the Gaussian03 software package, and the 6-311+G(3df) basis set was used for all calculations.[4] The geometries of all stationary points were fully optimized with MP2,[5] MPW1PW96,[6] B3LYP,[7] BP86,[8] and CBS-QB3[9] methods. Local minima were confirmed by vibrational frequency analysis, and transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations.[10] Spin-unrestricted methods were utilized for the calculations of the triplet species. Natural bond order (NBO) analysis was performed using NBO 3.1 implemented in Gaussian 03 with the B3LYP method.[11]
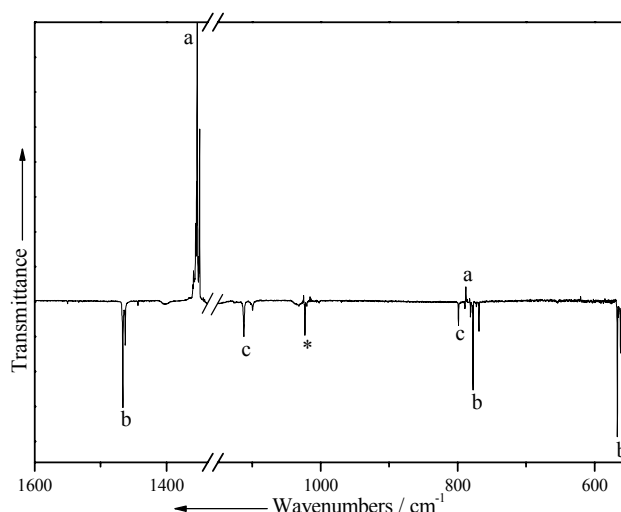
Figure S1. Difference IR spectrum (in transmittance) by subtracting the IR spectrum of Ar matrix isolated 30% ^{34}S-enriched F_2CS recorded before and after ArF excimer laser irradiation (λ = 193 nm). Bands associated with F_2CS, *cis* FCSF, and *trans* FCSF are denoted by a, b, and c, respectively. The band marked with * is due to the incompensation of a strong SiF_4 band.

Computational results:

Table S1. Calculated total energies (a.u.) and relative energies (kJ mol^{-1}) of F_2CS isomers and transition states for the 1,2-fluorine shift (TS1), the *trans-cis* isomerization transition states of the carbon-inversion (TS2) and the rotation around the C-S bond (TS2') using the 6-311+G(3df) basis set.

	F_2CS	FCSF (^3A)	TS1	*trans* FCSF	TS2	TS2'	*cis* FCSF
B3LYP	-636.064267	-635.933109	-635.888187	-635.967478	-635.958190	-635.919361	-635.986688
BP86	-636.095079			-636.000250			-636.025592
MPW1PW91	-636.005693			-635.904176			-635.923152
MP2	-635.152541	-634.998399	-634.952525	-635.039634	-635.030854	-634.990493	-635.065745
CBS-QB3	-635.288695			-635.187335			-635.206680
E_{Rel}(B3LYP)	0.0	344.5	462.5	254.2	278.6	380.6	203.8
E_{Rel}(BP86)	0.0			249.1			182.5
E_{Rel}(MPW1PW91)	0.0			266.6			216.8
E_{Rel}(MP2)	0.0	404.9	525.4	296.6	319.6	425.6	228.0
E_{Rel}(CBS-QB3)	0.0			266.2			215.4

Table S2. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) in parenthesis for F_2CS with different methods using the 6-311+G(3df) basis set.

B3LYP	BP86	MPW1PW96	MP2	CBS-QB3
1356.8 (642)	1312.4 (579)	1399.3 (659)	1408.3 (608)	1356.5 (658)
1185.6 (247)	1121.4 (240)	1238.2 (250)	1213.0 (247)	1203.5 (269)
799.2 (7)	769.1 (9)	821.3 (6)	807.7 (14)	793.7 (7)
633.7 (1)	607.2 (1)	649.6 (1)	644.6 (1)	628.3 (3)
527.5 (7)	508.7 (7)	537.5 (7)	535.7 (10)	524.9 (7)

419.9 (0)	404.7 (0)	425.9 (0)	427.0 (0)	418.4 (< 1)

Table S3. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) in parenthesis for *cis* FCSF with different methods using the 6-311+G(3df) basis set.

B3LYP	BP86	MPW1PW96	MP2	CBS-QB3
1502.2 (232)	1481.2 (224)	1549.9 (232)	1689.9 (216)	1495.3 (228)
801.8 (90)	779.1 (106)	822.5 (94)	857.1 (159)	797.6 (95)
567.2 (216)	540.9 (178)	600.7 (234)	524.1 (2)	565.5 (170)
493.2 (2)	483.0 (2)	503.1 (2)	514.5 (181)	487.6 (1)
475.9 (48)	464.8 (40)	482.6 (37)	453.4 (103)	480.4 (27)
135.1 (22)	139.4 (16)	141.9 (22)	134.3 (24)	136.0 (18)

Table S4. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) in parenthesis for *trans* FCSF with different methods using the 6-311+G(3df) basis set.

B3LYP	BP86	MPW1PW96	MP2	CBS-QB3
1144.7 (256)	1126.5 (250)	1190.9 (260)	1143.9 (257)	1126.8 (252)
791.6 (105)	744.7 (84)	826.6 (107)	847.2 (68)	733.8 (80)
721.8 (7)	667.0 (16)	748.6 (7)	789.4 (59)	701.3 (9)
438.6 (< 1)	406.2 (< 1)	446.0 (< 1)	451.6 (< 1)	428.9 (1)
282.3 (< 1)	280.2 (< 1)	290.0 (< 1)	293.0 (< 1)	275.8 (< 1)
236.4 (9)	221.7 (11)	240.4 (8)	235.3 (7)	227.0 (8)

Table S5. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) in parenthesis for triplet FCSF with different methods using the 6-311+G(3df) basis set.

B3LYP	MP2
1254.5 (288)	1292.4 (274)
812.4 (10)	821.0 (11)
606.6 (139)	721.3 (149)
430.6 (2)	452.5 (7)
393.7 (< 1)	402.5 (< 1)
151.0 (2)	162.9 (2)

Table 6. Experimental and calculated geometries for F_2CS obtained with different methods at the 6-311+G(3df) basis set. Distances in (Å) and bond angles in (º).

parameters	Exptl[12]	B3LYP	BP86	MPW1PW96	MP2	CBS-QB3
C-F	1.315 (1)	1.313	1.327	1.303	1.311	1.316
C-S	1.589 (1)	1.594	1.603	1.589	1.590	1.598
∠(FCF)	107.1 (1)	107.2	107.2	107.4	107.1	107.4

Table S7. Calculated geometries for *cis* FCSF obtained with different methods using the 6-311+G(3df) basis set. Distances in (Å) and bond angles in (º).

parameters	B3LYP	BP86	MPW1PW96	MP2	CBS-QB3
C-F	1.285	1.292	1.277	1.274	1.289
C-S	1.549	1.560	1.542	1.518	1.553
S-F'	1.717	1.752	1.691	1.766	1.752
$\angle$(FCS)	140.0	142.2	140.4	151.2	140.0
$\angle$(CSF')	124.8	128.6	124.7	131.85	126.1

Table S8. Calculated geometries for *trans* FCSF obtained with different methods using the 6-311+G(3df) basis set. Distances in (Å) and bond angles in (º).

parameters	B3LYP	BP86	MPW1PW96	MP2	CBS-QB3
C-F	1.327	1.336	1.317	1.329	1.335
C-S	1.680	1.679	1.670	1.670	1.689
S-F'	1.610	1.634	1.595	1.596	1.643
$\angle$(FCS)	110.1	112.8	110.6	108.3	108.9
$\angle$(CSF')	97.7	96.5	97.7	98.5	97.2

Table S9. Calculated geometries for triplet FCSF obtained at the B3LYP and MP2 levels of theory using the 6-311+G(3df) basis set. Distances in (Å) and bond angles in (º).

| parameters	B3LYP	MP2
C-F	1.309	1.306
C-S	1.657	1.657
S-F'	1.676	1.643
$\angle$(FCS)	128.4	128.5
$\angle$(CSF')	104.5	103.5
φ(FCSF')	90.6	88.1

Table S10. Experimental and calculated IR vibrations for the F_2CS.

Assignment	Calcd[a]	Exptl (in Ar matrix)[b]	Exptl (in gas phase)[b]
v_1 (a_1)	1356.8 (642)	1353.6 vs	1366.712
$v_2 + v_5$ (b_1)		1212.5 s	1209.1
v_4 (b_1)	1185.6 (247)	1180.0 s	1190.084
v_2 (a_1)	799.2 (7)	787.9 m	789.535
v_6 (b_2)	633.7 (1)	620.5 w	623.187
v_3 (a_1)	527.5 (7)	527.7 m	526.697
v_5 (b_1)	419.9 (0.1)	419.0 wv	419.546

[a] At DFT B3LYP/6-311+G(3df) level of theory with absolute intensities (km mol^{-1}) in parenthesis, frequencies in (cm^{-1}). [b] Relative intensities are given in vs very strong, s strong, m medium, w weak. [c] See ref[13].

Table S11. Natural bond orbital (NBO**)** analysis results for F_2CS isomers at the B3LYP/6-311+G(3df) level of theory.

	NBO natural charges			
	F	C	S	F'
F_2CS	-0.31	0.62	0.01	
trans FCSF	-0.33	0.07	0.72	-0.45
cis FCSF	-0.28	0.07	0.76	-0.54
	NBO Wiberg bond index (WBI)			
	F-C	C-S	S-F'	
F_2CS	0.92	1.94		
trans FCSF	0.97	1.66	0.76	
cis FCSF	1.01	2.26	0.53	
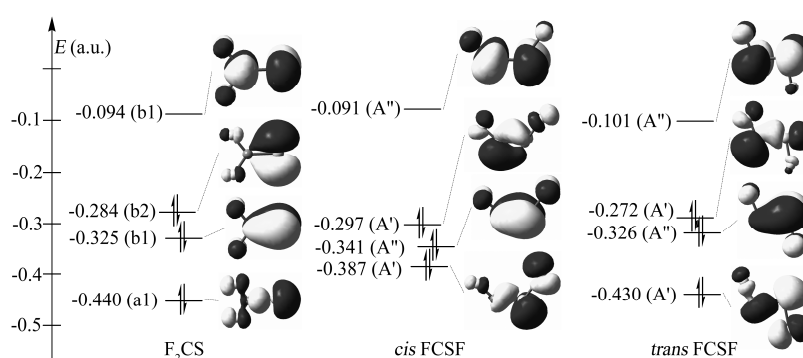
Figure S2. Calculated frontier molecular orbitals (isovalue = 0.05) and orbital energies (a.u.) of F_2CS and *cis/trans* FCSF at the B3LYP/6-311+G(3df) level of theory. Molecular orbitals (MOs) were generated using the program of Gauss View.[14]

Optimized Z-matrix coordinates (angstroms) of all species optimized at the B3LYP/6-311+G(3df) level of theory.

F_2CS (C_{2v})

Atoms	X	Y	Z
F	0.000000	1.057510	-1.066455
F	0.000000	-1.057510	-1.066455
C	0.000000	0.000000	-0.287141
S	0.000000	0.000000	1.307439

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trans FCSF (C_s, $^1A'$)

Atoms	X	Y	Z
F	1.610141	0.722336	0.000000
F	-1.482287	-1.292469	0.000000
C	-0.191782	-0.981018	0.000000
S	0.000000	0.688582	0.000000

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cis FCSF (C_s, $^1A'$)

Atoms	X	Y	Z
F	1.707616	0.589605	0.000000
F	-1.032422	-1.688202	0.000000
C	-1.012791	-0.403153	0.000000
S	0.000000	0.769143	0.000000

TS1 C_1, ($F_2CS \rightarrow$ *trans* FCSF)

Atoms		X	Y	Z
F	0	0.000000	0.000000	0.000000
F	0	0.000000	0.000000	2.215782
C	0	0.447360	0.710863	1.224117
S	0	1.969514	0.000000	0.300966

TS2 (C_s, *trans* FCSF $\rightarrow$ *cis* FCSF)

Atoms	X	Y	Z
F	0.000000	0.000000	0.000000
F	0.000000	0.000000	3.857969
C	0.079087	0.000000	1.286477
S	1.027999	0.000000	2.480551

TS2' (C_1, *trans* FCSF $\rightarrow$ *cis* FCSF)

Atoms	X	Y	Z
F	1.233389	0.000000	-0.345988
F	0.077174	1.646281	1.858954
C	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.935200

FCSF (C_1, ^3A)

Atoms	X	Y	Z
F	-1.515013	0.791073	0.018291
F	1.928609	0.349347	-0.184898
C	0.911419	-0.131602	0.484581
S	-0.574430	-0.592136	-0.088002

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