Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intersystem Crossing in Tunneling Regime: $T_1 \rightarrow S_0$ Relaxation in Thiophosgene

Supplementary Information

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Atomic Cartesian coordinates (Å) of Cl_2CS

CCSD(T)/def2-TZVP			
T_1 minimum			
Cl	-3.8012293973	-0.0455054886	0.0144637643
Cl	-0.9162445295	-0.6784030290	0.0412832788
C	-2.1864736428	0.4048649614	-0.4068518399
S	-1.8174591807	2.0920066556	-0.2879497149
S_0 minimum			
Cl	-3.7686624483	-0.1084395202	-0.0178740818
Cl	-0.9715867393	-0.7220599879	0.0081257822
C	-2.1607276437	0.5340527391	-0.1274785093
S	-1.8172554026	2.0911862610	-0.3285863091
T_1/S_0 Minimum energy crossing point			
Cl	-3.58768637	0.12135658	0.16390042
Cl	-0.77373328	-0.82847591	0.08800210
C	-1.97706669	0.22227906	-0.58311239
S	-1.94406978	1.98219359	-0.27434766
T_1/S_0 Transition state crossing point			
Cl	-3.58173655	0.17367164	0.17390345
Cl	-0.69993083	-0.60389958	0.08933721
C	-2.04423284	0.22999499	-0.66929995
S	-1.55974415	1.98341938	-0.27992964

CCSD(T)/def2-QZVP			
T_1 minimum			
Cl	-3.7950574757	-0.0440990161	0.0137484140
Cl	-0.9212472832	-0.6745453156	0.0404640522
C	-2.1863587190	0.4054429309	-0.4055646823
S	-1.8187432723	2.0861645002	-0.2877022955
T_1/S_0 Minimum energy crossing point			
Cl	-3.57983618	0.12374893	0.16242339
Cl	-0.77891856	-0.82480449	0.08735520
C	-1.97728172	0.22282909	-0.58177272
S	-1.94651966	1.97557978	-0.27356340
S_0 minimum			
Cl	-3.7640050528	-0.1065627556	-0.0181934713
Cl	-0.9750244547	-0.7184073512	0.0077311491
C	-2.1609659495	0.5329723081	-0.1273391507
S	-1.8182367769	2.0867372906	-0.3280116451
T_1/S_0 Transition state crossing point			
Cl	-3.57448941	0.17588922	0.17290974
Cl	-0.70511825	-0.59839825	0.08870749
C	-2.04442026	0.22919310	-0.66925172
S	-1.56161646	1.97650237	-0.27835444

CASPT2(10,9)/def2-TZVP			
T_1 minimum			
Cl	-3.7987709732	-0.0430227353	0.0137354069
Cl	-0.9174246522	-0.6751223687	0.0405211051
C	-2.1862423979	0.4059678380	-0.4056862796
S	-1.8189687269	2.0851403653	-0.2876247441
S_0 minimum			
Cl	-3.7670547666	-0.1104608643	-0.0176502781
Cl	-0.9738965866	-0.7232219172	0.0083131723
C	-2.1602462433	0.5362351322	-0.1277604782
S	-1.8170346374	2.0921871412	-0.3287155340
T_1/S_0 Minimum energy crossing point			
Cl	-3.59135619	0.12134677	0.16001840
Cl	-0.77363359	-0.83160906	0.08019643
C	-1.97083145	0.23822666	-0.56297992
S	-1.94673488	1.96938894	-0.28279244
T_1/S_0 Transition state crossing point			
Cl	-3.6038513	0.2009073	0.1697909
Cl	-0.6673794	-0.5916077	0.0836280
C	-2.0389692	0.2483995	-0.6622357
S	-1.5754443	1.9254873	-0.2771722

CASPT2(24,16)/def2-TZVP			
T_1 minimum			
Cl	-3.8007856898	-0.0418471139	0.0150787791
Cl	-0.9151270598	-0.6748915999	0.0419045417
C	-2.1864581234	0.4048045142	-0.4099927775
S	-1.8190358772	2.0848972990	-0.2860450550
T_1/S_0 Minimum energy crossing point			
Cl	-3.59796920	0.12388670	0.16809065
Cl	-0.77441502	-0.83264390	0.08595042
C	-1.97071062	0.23349616	-0.56355930
S	-1.93946126	1.97261424	-0.29603937
S_0 minimum			
Cl	-3.7671576398	-0.1116597031	-0.0174984417
Cl	-0.9743076531	-0.7243535293	0.0084621926
C	-2.1600684706	0.5370403125	-0.1278642716
S	-1.8166984710	2.0937124115	-0.3289125969
T_1/S_0 Transition state crossing point			
17	0.695669765	0.003886463	-1.520612070
17	0.695669760	0.003886453	1.520612067
6	0.031808484	0.623709335	0.000000022
16	-1.533690023	-0.242596812	0.000000001

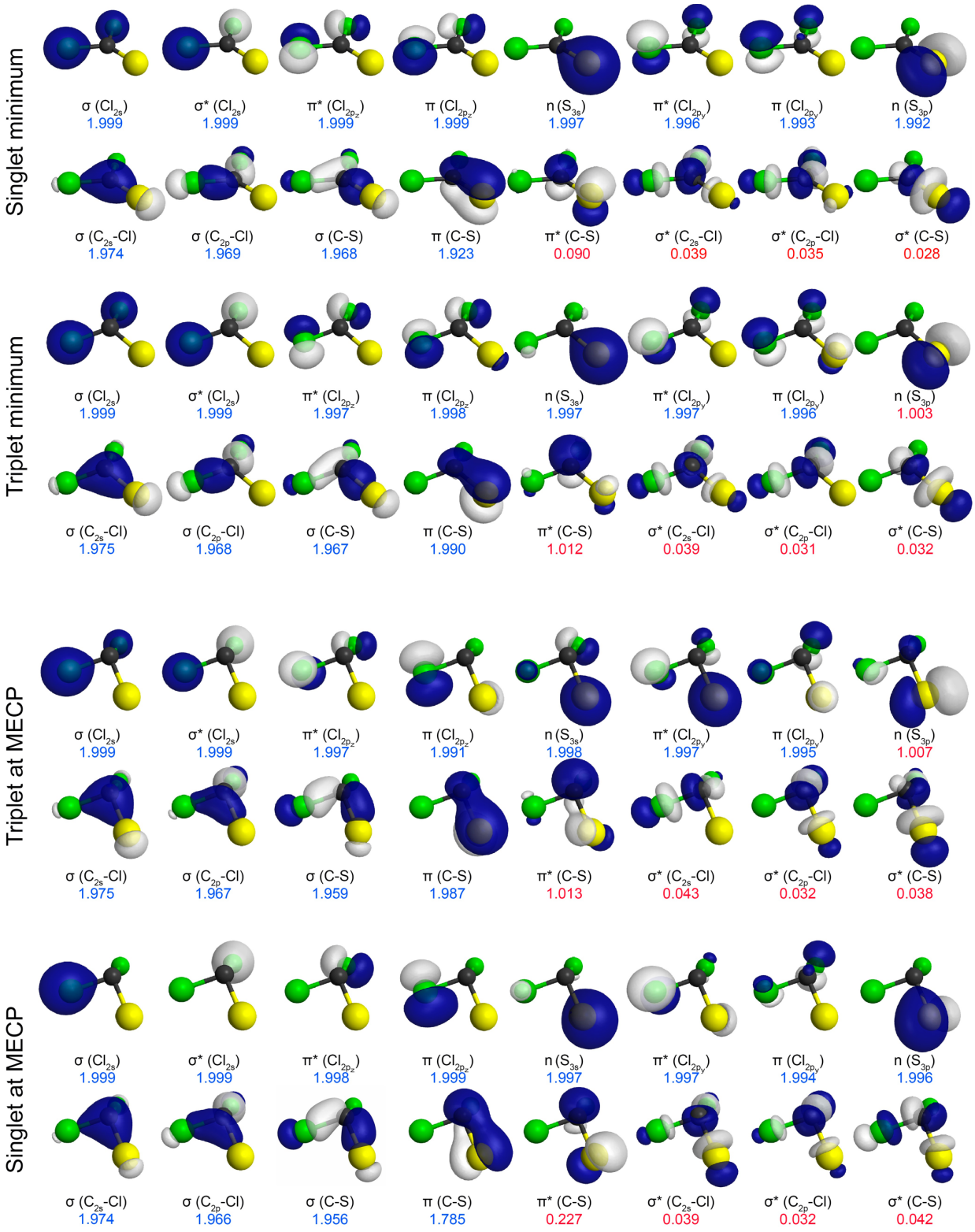

Figure S1. Natural bonding orbitals of (24,16) active space. The occupation numbers of molecular orbitals are given in blue and red.

Internal coordinates of S_0, T_1, MECP, and TSCP in Cl_2CS

Table S1. The T_1 (C_s) excited state.

Parameter	CASPT2(24,16)/ def2-TZVP	CASPT2(10,9)/ def2-TZVP	CCSD(T)/ def2-TZVP	CCSD(T)/ def2-QZVP
r(C-Cl_2), Å	1.728	1.726	1.729	1.722
r(C-S), Å	1.724	1.723	1.731	1.724
α(Cl_1-C-S), deg.	115.7	115.9	115.9	115.9
β(Cl_2-C-Cl_1), deg.	117.5	117.4	117.4	117.4
θ(Cl_1-S-Cl_2-C), deg.	21.5	21.2	21.3	21.3

Table S2. The S_0 (C_{2v}) ground state.

Parameter	CASPT2(24,16)/ def2-TZVP	CASPT2(10,9)/ def2-TZVP	CCSD(T)/ def2-TZVP	CCSD(T)/ def2-QZVP	Exp.[1*]	Exp.[2*]
r(C-Cl_2), Å	1.737	1.736	1.735	1.729	1.729±0.003	1.728±0.003
r(C-S), Å	1.607	1.606	1.607	1.604	1.601±0.003	1.602±0.005
α(Cl_1-C-S), deg.	124.6	124.5	124.4	124.4	124.41±0.16	124.41±0.16
β(Cl_2-C-Cl_1), deg.	110.8	110.9	111.2	111.3	111.19±0.16	111.2±0.3
θ(Cl_1-S-Cl_2-C), deg.	0	0	0	0	0	0

[*] uncertainties are given as standard deviations for observable values of $^{35}Cl_2CS$

Table S3. The T_1/S_0 (C_1) minimum energy crossing point (MECP).

Parameter	CASPT2(24,16)/ def2-TZVP	CASPT2(10,9)/ def2-TZVP	CCSD(T)/ def2-TZVP	CCSD(T)/ def2-QZVP
r(C-Cl_1), Å	1.788	1.778	1.778	1.770
r(C-Cl_2), Å	1.729	1.730	1.733	1.727
r(C-S), Å	1.760	1.754	1.787	1.780
α(Cl_1-C-S), deg.	90.9	90.7	90.0	89.9
β(Cl_2-C-Cl_1), deg.	116.0	116.0	121.2	121.2
θ(Cl_1-S-Cl_2-C), deg.	42.0	42.0	42.9	43.0

Table S4. The T_1/S_0 transition state crossing point (TSCP).

Parameter	CASPT2(26,14)/ def2-TZVP	CASPT2(10,9)/ def2-TZVP	CCSD(T)/ def2-TZVP	CCSD(T)/ def2-QZVP
r(C-Cl_1), Å	1.771	1.773	1.754	1.747
r(C-Cl_2), Å	1.771	1.773	1.754	1.747
r(C-S), Å	1.789	1.782	1.860	1.854
α(Cl_1-C-S), deg.	99.1	98.8	99.1	98.9
β(Cl_2-C-Cl_1), deg.	118.3	118.2	116.6	116.6
θ(Cl_1-S-Cl_2-C), deg.	36.6	36.9	37.1	37.2

Table S5. Fitting parameters for S_0 and T_1 PESs along the ISC reaction path approximated by quartic functions ($ax^4+bx^3+cx^2+dx+e$).

Parameters	CASSPT2(10,9)/def2-TZVP		CASSPT2(24,16)/def2-TZVP	
	Singlet	Triplet	Singlet	Triplet
a	-4.847727	2.5062140×10^{-2}	-1.0873181	1.9255065×10^{-2}
b	1.4218237×10^{1}	-2.5452152×10^{-2}	2.9084331	-1.7934022×10^{-2}
c	-1.5528009×10^{1}	2.8364697×10^{-2}	-2.8377169	2.1629875×10^{-2}
d	7.6198993	-1.5135414×10^{-3}	1.3121716	-1.2585686×10^{-3}
e	-1.4383768	1.6287824×10^{-5}	-2.6934314×10^{-1}	2.1580948×10^{-5}

Table S6. CCSD(T) diagnostic parameters for def2-TZVP and def2-QZVP basis sets.

Basis set	Property	S_0 minimum	T_1 minimum	^{1}MECP (singlet)	^{3}MECP (triplet)
def2-TZVP	$\|\mathbf{t}_1\|$	0.101	0.159	0.272	0.197
	$\|\mathbf{t}_2\|$	0.564	0.546	0.609	0.555
	T_1 diagnostic	0.015	0.020	0.039	0.026
	D_1 diagnostic	0.049	0.076	0.181	0.100
def2-QZVP	$\|\mathbf{t}_1\|$	0.101	0.160	0.265	0.195
	$\|\mathbf{t}_2\|$	0.568	0.551	0.610	0.559
	T_1 diagnostic	0.015	0.020	0.038	0.026
	D_1 diagnostic	0.048	0.075	0.176	0.099

Table S7. Leading determinants with reference coefficients greater than 0.05.

Structure	Determinant	Coefficient
^{1}MECP (singlet)	2222222222220000	0.9163104
	2222222222202000	-0.2457760
	2222222222/\2000	-0.0758129
	222222/2222\2000	-0.0695163
	2222222/222\2000	-0.0689836
	22222222222/\000	-0.0583794
^{3}MECP (triplet)	22222222222//000	0.9592358
S_0 minimum	2222222222220000	0.9514682
	2222222222022000	-0.1364950
	222222/222\22000	0.0766083
	222/\22222220/\0	0.0600286
	2222022222220020	-0.0514540
T_1 minimum	22222222222//000	0.9644293
	222222/2222/2000	-0.0611195
	22220222222//020	-0.0542657

Zhu-Nakamura formulas

The spin-orbit coupling constant, H_{SOC}, is expressed as

$$H_{SOC} = \sqrt{\sum_{M_S=-S}^{S}\sum_{M'_S=-S'}^{S'}\left|\left\langle SM_S\left|\hat{H}_{SO}\right|S'M'_S\right\rangle\right|^2}, \quad \text{(S1)}$$

where M_S and M_S' are the magnetic quantum numbers, and the sum runs over spins S and S'. To calculate the probability of transition using the Zhu-Nakamura formula for a sloped intersection, one should determine a single passage probability p_{ZN} and the total phase ψ. In the case of energies equal and higher than the critical point ($b \geq 0$), ψ can be found from the following equation:

$$\psi = \sigma + \phi_S. \quad \text{(S2)}$$

The phase σ varies with respect to $\varepsilon_\perp$ as

$\varepsilon_\perp \le E_1(r_0)$

$$\sigma = \sigma_0, \tag{S3}$$

$$\delta = -\int_{r_0}^{t_1} \left|K_1(r)\right| dr + \int_{r_0}^{t_2} \left|K_2(r)\right| dr + \delta_0 \tag{S4}$$

$E_1(r_0) \le \varepsilon_\perp \le E_2(r_0)$

$$\sigma = \int_{t_1}^{r_0} K_1(r)\, dr + \sigma_0, \tag{S5}$$

$$\delta = \int_{r_0}^{t_2} \left|K_2(r)\right| dr + \delta_0 \tag{S6}$$

$\varepsilon_\perp > E_2(r_0)$

$$\sigma = \int_{t_1}^{r_0} K_1(r) dr - \int_{t_2}^{r_0} K_2(r) dr + \sigma_0, \tag{S7}$$

$$\delta = \delta_0 \tag{S8}$$

where

$$K_i(r) = \sqrt{\frac{2\mu}{\hbar^2}\left(\varepsilon_\perp - E_i(r)\right)}, \tag{S9}$$

$$\sigma_0 + i\delta_0 = \frac{\pi}{a\sqrt{8}} \frac{C_- + iC_+}{F_-^2 + F_+^2}, \tag{S10}$$

$$F_\pm = \sqrt{\sqrt{\left(b^2+\gamma_1\right)^2 + \gamma_2} \pm \left(b^2+\gamma_1\right)} + \sqrt{\sqrt{\left(b^2-\gamma_1\right)^2 + \gamma_2} \pm \left(b^2-\gamma_1\right)}, \tag{S11}$$

$$C_+ = F_+\left(b^2 \to \left[b^2 - \frac{0.16 b_x}{\sqrt{b^4+1}}\right]\right), \tag{S12}$$

$$C_- = F_-\left(\gamma_2 \to \left[\frac{0.45d}{1+1.5\exp(2.2 b_x \left|b_x\right|^{0.57})}\right]\right), \tag{S13}$$

$$b_x = b^2 - 0.9553,\ \gamma_1 = 0.9\sqrt{d^2-1},\ \gamma_2 = \frac{7}{16}d\,. \tag{S14}$$

Finally, the dynamical phase ϕ_S is given as

$$\phi_S = -\frac{\delta_\psi}{\pi} + \frac{\delta_\psi}{\pi}\ln\left(\frac{\delta_\psi}{\pi}\right) - \arg\Gamma\left(i\frac{\delta_\psi}{\pi}\right) - \frac{\pi}{4}, \tag{S15}$$

with δ_ψ being simply a correction for δ

$$\delta_\psi = \delta\left(1 + \frac{5a^{1/2}}{a^{1/2}+0.8} 10^{-\sigma}\right). \tag{S16}$$

In case of energies lower than the critical point (b<0), ψ appears as an argument of the Stokes constant U_1,

$$\psi = \arg(U_1), \tag{S17}$$

$$\mathrm{Re}(U_1) = \cos(\sigma)\left[e^{\delta}\sqrt{B(\sigma/\pi)} - g_1 \sin^2(\sigma)\frac{e^{-\delta}}{\sqrt{B(\sigma/\pi)}} \right], \tag{S18}$$

$$\mathrm{Im}(U_1) = \sin(\sigma)\left[B(\sigma/\pi)e^{2\delta} - g_1^2 \cos^2(\sigma)\sin^2(\sigma)\frac{e^{-2\delta}}{B(\sigma/\pi)} + 2g_1\cos^2(\sigma) - g_2 \right]. \tag{S19}$$

The parameters g_1, g_2 and function $B(x)$ are given as

$$g_1 = 1.8\left(a^2\right)^{0.23} e^{-\delta}, \tag{S20}$$

$$g_2 = \frac{3\sigma}{\pi\delta}\ln(1.2 + a^2) - \frac{1}{a^2}, \tag{S21}$$

$$B(x) = \frac{2\pi x^{2x}\exp(-2x)}{x\Gamma^2(x)}. \tag{S22}$$

References

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(4) Clouthier, D. J.; Moule, D. C. In *Relationships and Mechanisms in the Periodic Table*; Springer Berlin Heidelberg: Berlin, Heidelberg, 1989; Vol. 150, pp 167–247.