# Nonradiative relaxation mechanisms of the elusive silole molecule: Supporting Information

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## Orbitals, Basis Set, Shift Parameter and Triplet Vertical Excitations



**Figure S1.** Relevant orbitals for calculations presented in Tables 3 and 4. Hartree-Fock (HF) def2-SVPD orbitals for ADC(2) are shown on the left. A 0.04 cutoff was used for the valence orbitals, while cutoffs of 0.025, 0.02 and 0.02 were used for Ryd3s, Ryd3p<sub>x</sub> and Ryd3p<sub>y</sub> orbitals, respectively. def2-TZVPD and aug-cc-pVTZ relevant HF orbitals that differed significantly from def2-SVPD ones are shown with 0.025 and 0.01 cutoffs, respectively. Lastly, only the 4-XMS-CASPT2(8,8)/def2-TZVP(-f\*)  $\sigma_2^*$  optimized orbital is shown (0.04 cutoff), as others are similar to the valence orbitals in Figure 1.



**Figure S2.** 4-XMS-CASPT2(8,8)/def2-TZVP(- $f^*$ ) active orbital with the smallest occupation number (left) in the  $S_0$  minimum geometry, and active orbital (right) that replaced the former for some intermediary geometries in potential energy curve calculations (Figure 10 in main text).

**Table S1.** Test of the shift value (4-XMS-CASPT2(8,8)/SVP) on distorted geometries generated by the initial conditions tool in SHARC (Figure S3). "w" and EE stand for, respectively, weight of the reference CASSCF function and excitation energy (eV). Convergence was not obtained for omitted shift values (0.0 and 0.1).

Geometry		1				2				3					
Shift value		0	.1	0	.2	0	.3	0	.2	0	.3	0	.2	0	.3
		EE	W	EE	W	EE	W	EE	W	EE	W	EE	W	EE	w
	$S_0$	-	0.8 4	-	0.8 5	-	0.8 6	-	0.8 5	-	0.8 6	-	0.85	-	0.86
State	$S_{I}$	4.5 2	0.8 1	4.5 4	0.8 3	4.5 7	0.8 4	4.9 3	0.8 3	4.9 6	0.8 4	4.87	0.83	4.91	0.84
	$S_2$	5.4 4	0.8 1	5.5 9	0.8 3	5.6 2	0.8 4	5.6 2	0.8 3	5.6 6	0.8 4	5.94	0.83	6.05	0.84
	$S_3$	5.72	0.76	5.88	0.84	5.92	0.85	6.27	0.83	6.37	0.85	6.13	0.82	6.22	0.85
	C-C-C- C		3.1 -3.7					3.6				-11.3			
Dihedral (°)	C4-C5- C2-Si							-6.5				7.2			
	C5-C4- C3-Si			-0	).7			2.3		9.1					



**Figure S3.** Distorted geometries used for Table S1. From left to right, geometries: 1, 2 and 3. Numbering scheme of atoms is shown in the first (left).

**Table S2.** Excitation energy (EE, eV), oscillator strength (OS) and symmetry (sy) of excited states of silole, at MP2/def2-TZVP minimum geometry. A real level shift of 0.3 was used, and the active spaces are shown in Figures 1 and S1.

	11-2	XMS-C	ASPT2(12,8)				4-	XMS-C	ASPT2(8,8)			
State		jun-cc	-pVDZ		def2-S	SVP	d	ef2-TZV	/P(-f*)		def2-TZ	ZVP
	EE	OS	sy	EE	OS	sy	EE	OS	sy	EE	OS	sy
$S_I$	4.71	0.05 7	B2 $\pi_2 - \pi_1^*$	4.95	0.08 4	B2 $\pi_2 - \pi_1^*$	4.65	0.08 1	$\begin{array}{c} \text{B2} \\ \pi_2 \text{-} \pi^*_1 \end{array}$	4.63	0.08 2	B2 $\pi_2 - \pi_1^*$
$S_2$	5.85	0.00 0	$A2 \\ \sigma^2 - \pi^*_1 \\ + \pi_2 - Ryd3p_x \\ (a)$	6.15	$\begin{array}{c} 0.00\\ 0 \end{array}$	A2 $\sigma_2 - \pi^*_1$	5.91	0.00 0	A2 $\sigma_2 - \pi_1^*(b)$	5.85	$\begin{array}{c} 0.00\\ 0 \end{array}$	$\begin{array}{c} A2\\ \sigma_2\text{-}\pi^*{}_1\end{array}$
$S_3$	6.11	0.01 0	A1 $(\pi_2)^2 - (\pi_1^*)^2$	6.26	0.00 6	A1 $(\pi_2)^2$ - $(\pi^*_1)^2$	6.12	0.00 6	A1 $(\pi_2)^2$ - $(\pi^*_1)^2$	6.14	0.00 6	A1 $(\pi_2)^2$ - $(\pi^*_1)^2$

(a) With weights of 0.51 and 0.31, respectively.

(b) With weight of 0.86.

**Table S3.** Excitation energy (EE, eV) and symmetry (sy) of triplet states of silole, at MP2/def2-TZVP minimum geometry. For the XMS-CASPT2 calculation, a real level shift of 0.3 was used and the active space is shown in Figures 1 and S1.

State	4-XMS-0 def2-7	CASPT2(8,8) TZVP(-f*)	ADC(2) def2-SVPD		
State	EE	sy	EE	sy	
$T_{I}$	2.78	B2 $\pi_2 - \pi_1^*$	2.94	B2 $\pi_2 - \pi_1^*$	
$T_2$	4.81	A1 $\pi_1 - \pi^*_1 + \pi_2 - \pi^*_2$	5.72	$\begin{array}{c} A2\\ \sigma_2\text{-}\pi^*{}_1\end{array}$	
$T_3$	5.47	A2 $\sigma_2 - \pi_1^*$	6.12	B1 $\sigma_1$ - $\pi_1^*$	
$T_4$	7.81	B2 $\pi_1\pi_2 - (\pi^*_1)^2 + (\pi_2)^2 - \pi^*_1\pi^*_2$	6.54	Α2 π <sub>2</sub> - Ryd3s	

## **ADC(2)** Absorption Spectrum



**Figure S4.** ADC(2)/def2-SVPD normalized absorption spectrum for silole, by varying the number of distorted geometries used in the nuclear ensemble calculation.



**Figure S5.** ADC(2) normalized absorption spectrum for silole with the def2-SVPD and def2-TZVPD basis sets, using the nuclear ensemble method. 500 distorted geometries were used in each case.



**Figure S6.** Normalized simulated absorption spectrum of silole. Same as Figure 3 in the main text, but in units of energy (eV) instead of wavelength (nm).

## **ADC(2)** Nonadiabatic Surface Hopping Dynamics

Concerning the figures in Section 3.4 in the main text, the ADC(2) trajectories were grouped in four subsets: 89 without issues (group A); 3 discarded due to errors (B); 1 that reached 400.00fs without crossing to  $S_0$  (C); and 7 that reached planar (or quasi) crossing points (D). There was no crossing geometry in C, and puckering parameters were not relevant for crossing geometries of D. To be specific:

1. Figure 5, puckering parameters, used only group A.

- 2. Figures 4 and 7, crossing times histogram and representative crossing points, used groups A and
- D.
- 3. Figure 8, populations, used A, C and D.
- 4. Figure S7, bond distortion analysis, used all trajectories.



**Figure S7.** Maximum bond distortion for each ADC(2) trajectory. Horizontal dashed lines correspond to MP2/def2-TZVP minimum geometry values.

#### **XMS-CASPT2** Nonadiabatic Surface Hopping Dynamics

Trajectories with the following problems were kept:

- 1. Intruder state problem: a total of 46 trajectories had intruder state problems. In the large majority (37) it was restricted to a single point in the trajectory. In 5 and 2 of these trajectories, respectively, intruder state problems were restricted to 2 and 3 nonconsecutive points. On all the 46 cases, the problem was restricted to the  $S_3$  state. Hence, due to the latter fact, the eventual nature of this problem and the fact that these problems are expected in multireference dynamics, this was not considered a factor to discard trajectories.
- 2. Large variations of total energy (0.3 eV) occurred after the final  $S_1 \rightarrow S_0$  transition. See Figure S8. 3 trajectories were kept.
- 3. Large hops (> 1 eV) to state B followed by another hop to the original state A after only a couple of steps (maximum of 3). See Figure S9. Although being an artifact, the molecule was subject to forces of state B for too short a time to expect significant changes relative to the hypothetical "correct" trajectory without the artificial hop. Hence, this does not seem to be a factor which should invalidate a trajectory. Two trajectories were kept.

A total of 11 trajectories were discarded due to the following conditions:

- Large hops (> 1eV) to state B and the molecule remained in this state for more than 3 steps. See Figure S9. Two trajectories were discarded.
- Variation in total energy larger than 0.3 eV before the final S<sub>1</sub> → S<sub>0</sub> hop. These variations were found through diagnostic.py tool within SHARC2.1 package; largest deviation in norm for each time step relative to the total energy at time step 0; and the difference between the maximum (positive in all cases) and minimum (negative in all cases) deviations relative to reference value. 6 trajectories were discarded (see Figure S8).
- 3. Convergence problems or other software related issue. Three trajectories were discarded.

Regarding the figures in Section 3.4 in the main text, the 113 accepted trajectories were used for Figures 4, 5, 7 and 8. However, 123 trajectories were used for the bond distortion analysis in Figure 6.



**Figure S8.** Examples of trajectories kept despite total energy variation greater than 0.3 eV (left) and discarded due to it (right). KE, ET and OS stand for kinetic energy, total energy and occupied state, respectively.



**Figure S9.** Examples of trajectories discarded due to a large hop (left) and kept despite it (right). KE, ET and OS stand for kinetic energy, total energy and occupied state, respectively.

Crossing points among states of accepted trajectories are represented in Figure S10 through CPRP coordinates, respectively. There were no crossings involving the  $S_3$  state.



**Figure S10.** CPRP coordinates of crossing point geometries between  $S_0$ ,  $S_1$  and  $S_2$  states, calculated at the XMS-CASPT2 dynamics simulation. The color represents the time required to reach each CP. Seven  $S_1 \rightarrow S_2$  and two  $S_2 \rightarrow S_1$  CPs were not included as their geometries were planar.

#### **ADC(2)** Potential Energy Curves



**Figure S11.** ADC(2)/def2-SVPD PECs connecting  $S_0$  minimum to  $S_1 \rightarrow S_0$  CPs of PuckCb, PuckSi and PuckCn conformation types. Both singlet and triplet states are shown, starting at  $S_0$  and  $T_1$  states. CPs used are labeled by squares in Figure 5.

#### **XMS-CASPT2** Potential Energy Curves



**Figure S12.** 4-XMS-CASPT2(8,8)/def2-TZVP(- $f^*$ ) in-plane ring-opening PEC, relaxed at MP2/def2-TZVP level. Singlet and triplet states are shown, starting at  $S_0$  and  $T_1$ , respectively.

#### **Cartesian Coordinates for Relevant Geometries**

#### MP2/def2-TZVP optimized geometry

```
11

Hartree-Fock Energy = -443.92439221436; MP2 Energy = -444.6579767047

Si
0.000000
0.0000000
-1.3737128

C
-0.0000000
-1.3518195
-0.0848740

C
-0.0000000
1.3518195
-0.0848740

C
-0.0000000
0.7398133
1.1218802

C
0.0000000
-0.7398133
1.1218802

H
0.0000000
2.4301454
-0.1785384

H
0.0000000
1.2783224
2.0658525
```

- Н -0.0000000 -1.2783224 2.0658525
- Н 0.0000000 -2.4301454 -0.1785384
- Н -1.2033814 0.0000000 -2.2364237
- Н 1.2033814 0.0000000 -2.2364237

#### ADC(2)/def2-SVPD $S_l$ optimized geometry

```
11
```

HF Energy = -443.5986974697; MP2 Energy= -444.2567027342; ADC(2) Energy = -444.1510722088

- Si 0.7292451 -0.1175714 -1.2790011
- C 0.0976856 -1.3525232 -0.0212710
- C 0.0912265 1.2061604 -0.1189138
- $C \quad 0.0757823 \quad 0.6778572 \quad 1.2117285$
- C 0.0796135 -0.7244281 1.2651909
- Н -0.3302724 2.1854966 -0.3662780
- Н 0.0367666 1.3091529 2.1044909
- Н 0.0449326 -1.2861665 2.2034104
- Н -0.3179606 -2.3504022 -0.1929826
- Н 0.1807519 -0.1705532 -2.6581065
- Н 2.2255988 -0.1196026 -1.3886077

EOM-CCSD S<sub>1</sub> optimized geometry

HF Energy = -443.60711687020859 ; CCSD Energy = -444.333970093114544 ; EOM-CCSD Energy = -444.214059232781

- Si 0.4023008309 -0.0440063955 -1.1798391459
- C -0.2181132786 -1.2775398895 0.0829046434
- C -0.2244065660 1.2790520210 -0.0146032270
- C -0.2473781453 0.7549500664 1.3026218926
- C -0.2439297124 -0.6547466661 1.3563861669
- Н -0.6140633868 2.2701373807 -0.2614955464
- $H \quad -0.2942853515 \quad 1.3797343401 \quad 2.1978707812$
- Н -0.2879418556 -1.2097493026 2.2966313001
- Н -0.6028520027 -2.2864525760 -0.0877111704
- Н -0.1487129728 -0.0979216464 -2.5580851679
- Н 1.8990292739 -0.0452530084 -1.3088291441

ADC(2)/def2-SVPD  $S_1 \rightarrow S_0$  crossing point used as endpoint of PuckSi PEC

11

```
HF Energy = -443.4603658905; MP2 Energy= -444.1267995792
```

Si	0.251306	-0.098316	-1.378504
С	-0.328355	-1.339919	-0.153490
С	-0.420785	1.259490	-0.146511
С	0.128797	0.744495	1.150508
С	0.170712	-0.652889	1.066596
Η	-0.999321	2.290054	0.089101
Н	0.747969	1.201606	1.977749
Η	0.571354	-1.296589	1.903247
Η	-1.318306	-1.875061	0.022966
Н	-0.107684	-0.170642	-2.778388
Η	1.807965	0.088179	-1.247758

ADC(2)/def2-SVPD  $S_1 \rightarrow S_0$  crossing point used as endpoint of PuckCb PEC

11

HF Energy = -443.4642359567 ; MP2 Energy= -444.1239970187

Si	0.135382	-0.094109	-1.564095
С	-0.046792	-1.283028	-0.182062
С	-0.178940	1.232333	-0.103807
С	0.242548	0.762995	1.329894

С	-0.037131	-0.568588	1.268121
Η	-0.915270	1.952413	-0.116626
Η	0.019074	1.331780	2.282464
Н	-0.274673	-1.360484	2.012953
Η	-0.494481	-2.259026	-0.208471
Η	-1.069502	-0.016685	-2.675028
Н	1.525429	-0.048128	-2.307780

ADC(2)/def2-SVPD  $S_1 \rightarrow S_0$  crossing point used as endpoint of PuckCn PEC

```
11
```

```
HF Energy = -443.4246974698 ; MP2 Energy= -444.0887816038
```

Si	0.047809	-0.133826	-1.490119
С	-0.154288	-1.321994	-0.173904
С	0.035787	1.292162	-0.185859
С	-0.176088	0.654254	1.396488
С	0.113797	-0.625739	1.240193
Н	0.413102	2.464942	-0.377236
Н	0.309893	1.297330	2.360658
Н	0.363177	-1.330146	2.095977
Н	0.219558	-2.362805	-0.169078
Н	-1.147696	0.203042	-2.448287
Н	1.254520	0.358361	-2.500519

ADC(2)/def2-SVPD  $S_1 \rightarrow S_0$  planar crossing point (an example)

```
11
```

MP2 Energy= -444.104084

- SI -0.00297852 -0.08455155 -1.52980069
- C -0.02061509 -1.30260780 -0.26652465
- C 0.04421680 1.21806908 -0.03042277
- C -0.02252451 0.75208176 1.40268587
- C -0.06936091 -0.55015788 1.31248044
- H 0.28068218 2.27438091 -0.10792300
- H 0.23741108 1.41038755 2.19656886
- H 0.25170983 -1.13434580 2.31884381
- Н 0.35690080 -2.42443440 -0.10163540
- H -1.26382788 0.25063680 -2.40797487
- Н 1.03959966 0.57799617 -2.35627814

4-XMS-CASPT2(8,8)/def2-TZVP(-f\*) (real shift = 0.3)  $S_1 \rightarrow S_0$  crossing point used as endpoint of PuckCn PEC 11

Root 1 ( $S_0$ ) Energy = -444.4393990424 ; Root 2 ( $S_1$ ) Energy = -444.4340488650

Si	0.139532	-0.058696	-1.341911
С	-0.047236	-1.610828	-0.009457
С	-0.003739	1.373514	-0.001777
С	-0.146894	0.681222	1.121947
С	0.115308	-0.726434	1.160983
Н	0.336686	2.425044	-0.205011
Н	-0.280305	1.243682	2.003093
Н	1.005704	-0.875563	1.663711
Н	-1.042435	-1.598507	-0.377960
Н	-1.065051	0.150456	-2.269945
Н	1.176061	-0.110871	-2.288470

4-XMS-CASPT2(8,8)/def2-TZVP(-f\*) (real shift = 0.3)  $S_1 \rightarrow S_0$  crossing point used as endpoint of PuckSi PEC 11

```
Root 1 (S_0) Energy = -444.3989083548 ; Root 2 (S_1) Energy = -444.3954742746
```

Si	0.400097	-0.022362	-1.486687
С	-0.550533	-1.205885	0.004674
С	-0.430752	1.066203	-0.147165
С	0.244338	0.799518	1.129753
С	0.144999	-0.622815	1.140213
Н	-1.251035	1.664950	0.073807
Η	0.635706	1.330450	2.100682
Η	0.508599	-1.179490	2.196358
Η	-0.449535	-2.234074	-0.516291
Η	-0.370293	0.492205	-2.613117
Η	1.818938	-0.002798	-1.698241

4-XMS-CASPT2(8,8)/def2-TZVP(-f\*) (real shift = 0.3)  $S_1 \rightarrow S_0$  MECI used as endpoint of PuckCb PEC

11

Root 1 ( $S_0$ ) Energy = -444.4764059396 ; Root 2 ( $S_1$ ) Energy = -444.4763854467

Si	0.249655	-0.001056	-1.463648
С	-0.200470	-1.208575	-0.146649
С	-0.358097	1.069137	-0.063902

С	0.365667	0.765002	1.181925
С	0.015571	-0.597634	1.145773
Η	-1.341382	1.537778	-0.004590
Η	0.241506	1.339838	2.089670
Η	-0.210770	-1.146868	2.057819
Η	-0.819153	-2.093759	-0.222550
Η	-0.608946	-0.006170	-2.662391
Н	1.674577	0.181780	-1.812854

2-XMS-CASPT2(4,4)/SVP (level shift not used)  $S_1 \rightarrow S_0$  MECI PuckSi

11

```
Root 1 (S_0) Energy = -444.3360362616; Root 2 (S_1) Energy = -444.3360114826
```

С	0.62250	0.12450	-1.30877
С	-0.75429	0.27257	-1.38607
С	-1.22046	-0.10358	-0.03694
Si	0.01723	0.65029	1.07712
С	0.96843	-0.64799	-0.11972
Η	0.08565	0.23161	2.50605
Η	0.23220	2.11133	0.89999
Η	1.35388	0.50225	-2.03952
Η	1.97357	-0.61659	0.35903
Η	-1.38429	0.55486	-2.23176
Н	-2.05221	-0.79460	0.16583

MP2/def2-TZVP geometry used as endpoint for the ring-opening PEC (Figure 12)

11

HF Energy = -443.7082157673 ; MP2 Energy= -444.4925744066

```
H \quad -0.0001031 \quad -2.0871334 \quad -2.5264892
```

```
Н 0.0001017 0.5731767 -2.8846039
```

```
C -0.0001051 -1.2193432 -1.8872766
```

 $C \quad 0.0000044 \quad 0.0981869 \ \text{-}1.8960072$ 

Н 1.2152724 -0.4759414 2.5800663

Si 0.0000420 -0.4754533 1.7306154

Н -1.2152019 -0.4760728 2.5800478

 $C \quad -0.0000124 \quad 1.0928542 \quad -0.8037323$ 

 $C \quad \text{-}0.0000286 \quad 0.9683145 \quad 0.5486155$ 

H = 0.0000089 = 2.1095889 - 1.1899079

#### Н -0.0001001 1.9418209 1.0446979