

SUPPORTING INFORMATION FOR:

**Nonadiabatic Molecular Dynamics  
by Multiconfiguration Pair-Density Functional Theory**

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# Section S1. Optimized structures and their energies

Table S1. Coordinates (in Å) of optimized thioformaldehyde ground-state structures

SA-CASSCF(10,6)				MC-PDFT(10,6)			
S	0.00000004	-0.00000000	0.59577926	S	-0.00000002	0.00000000	0.60125191
C	-0.00000016	0.00000000	-1.02982499	C	0.00000007	-0.00000000	-1.01943135
H	0.00000006	0.92316560	-1.60177713	H	-0.00000003	0.93561423	-1.60971028
H	0.00000006	-0.92316560	-1.60177713	H	-0.00000003	-0.93561423	-1.60971028
SA-CASSCF(12,10)				MC-PDFT(12,10)			
S	-0.00001935	-0.00000000	0.61994676	S	0.00000001	0.00000000	0.60475156
C	0.00007317	0.00000000	-1.02391928	C	-0.00000003	-0.00000000	-1.02387855
H	-0.00002691	0.94165948	-1.61681374	H	0.00000001	0.93951028	-1.60923651
H	-0.00002691	-0.94165948	-1.61681373	H	0.00000001	-0.93951028	-1.60923651

Table S2. The C–S bond distances (in Å) in the optimized structures

SA-CASSCF(10,6)	1.626
MC-PDFT(10,6)	1.621
SA-CASSCF(12,10)	1.644
MC-PDFT(12,10)	1.629

Table S3. Electronic energies (in  $E_h$ ) of optimized thioformaldehyde structure

	$S_0$	$S_1$	$T_1$	$T_2$
SA-CASSCF(10,6)	-437.50	-437.42	-437.43	-437.39
MC-PDFT(10,6)	-438.16	-438.08	-438.09	-438.03
SA-CASSCF(12,10)	-437.58	-437.49	-437.50	-437.45
MC-PDFT(12,10)	-438.16	-438.07	-438.09	-438.03

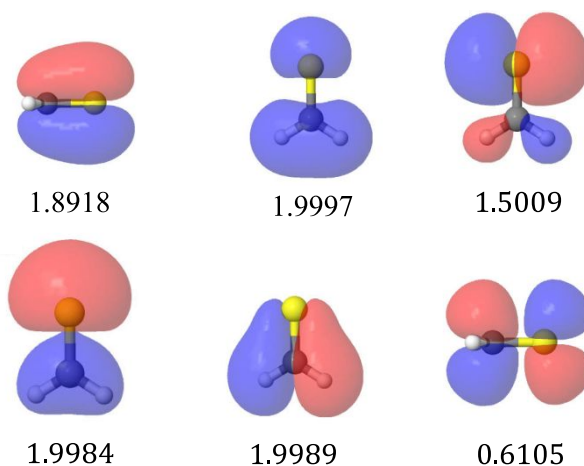
## Section S2. Relativistic Basis Set Dependence on the Excitation Energies

We evaluate the accuracy of the cc-pVDZ basis set with the Douglas-Kroll-Hess Hamiltonian by calculating the SA-CASSCF(10,6) vertical excitation energy using the cc-pVDZ-DK basis set with the Douglas-Kroll-Hess Hamiltonian. Calculations were performed using OpenMolcas v21.10. We also examine the vertical excitation energies for cc-pVDZ-DK optimized structure of thioformaldehyde. Energies in the manuscript use the nonrelativistic energies, but here we present the nonrelativistic and relativistic energies under the Energy column to show their dependence on the basis sets. We note that the vertical excitation are nearly identical when using the cc-pVDZ and the cc-pVDZ-DK basis set.

Table S4: SA-CASSCF(10,6) Vertical Excitation Energy

Basis Set	Energy	S <sub>1</sub>	T <sub>1</sub>	T <sub>2</sub>
<b>Previous Work<sup>1</sup></b>				
cc-pVDZ	Not Provided	2.31	2.03	3.09
<b>Present Work: cc-pVDZ Optimized Structure</b>				
cc-pVDZ (In paper)	nonrelative	2.31	2.02	3.08
cc-pVDZ	relative	2.31	2.03	3.07
cc-pVDZ-DK	nonrelative	2.31	2.03	3.08
cc-pVDZ-DK	relative	2.31	2.02	3.07
<b>Present Work: cc-pVDZ-DK Optimized Structure</b>				
cc-pVDZ	nonrelative	2.30	2.02	3.07
cc-pVDZ	relative	2.31	2.02	3.07
cc-pVDZ-DK	nonrelative	2.30	2.02	3.07
cc-pVDZ-DK	relative	2.31	2.02	3.07

### Section S3. Molecular Orbitals for the (10,6) Active Space



**Figure S1.** Molecular orbitals for the (10,6) active space. The orbitals were plotted using a cutoff of 0.025 a.u.

### Section S4. Wigner Distribution Frequencies ( $\text{cm}^{-1}$ )

The Wigner Distribution was used to generate 10,000 initial conditions using the normal mode frequencies in Table S4. The excitation energies and transition dipole moment of all configurations are presented in the attached folder in the directory “1\_Wigner\_Distribution”. The files in this directory follow the format of initconds.excited in the *SHARC* package. The initial conditions for the simulations are selected using the procedure of Barbatti et al.<sup>2</sup> using *SHARC*’s excite.py script.

Table S5. Normal mode frequencies ( $\text{cm}^{-1}$ )

	SA-CASSCF(10,6)	SA-CASSCF(12,10)
1	3364.0	3067.1
2	3261.2	2977.3
3	1582.6	1469.4
4	1101.3	1034.8
5	1058.0	994.5
6	962.7	965.6

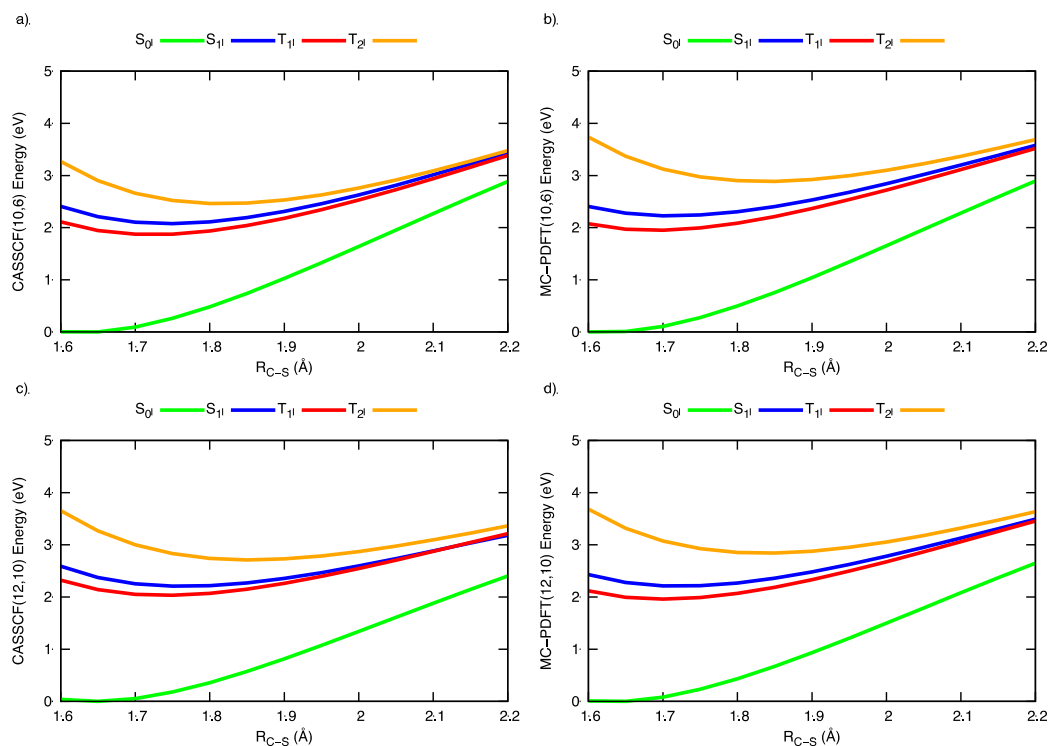
## Section S5. *SHARC* Input files

All *SHARC* input and output files follow the format documented in the *SHARC* manual, with the exception of the MOLCAS.template file. Here we present the input file that was representative for all simulations. The files of the various methods differ by the following: 1) ezero values, 2) rngseed, and 3) tmax value. All SA-CASSCF simulations were ran for a tmax value of 1,000, while MC-PDFT simulations were ran for 500 fs. Example simulations for SA-CASSCF and MC-PDFT can be found in the attached folder.

To run *SHARC* simulations with MC-PDFT, one simply needs to replace the SHARC\_MOLCAS.py script in the \$SHARC directory (sharc/bin directory) with the SHARC\_MOLCAS.py script in the attached folder. One then needs to set the method in the MOLCAS.template file to MCPDFT and add the line “functional” with the corresponding MC-PDFT functional one would like to use. The script is set up to use tPBE, tBLYP, tLSDA, trevPBE, ftPBE, ftBLYP, ftLSDA, and ftrevPBE. The SHARC\_MOLCAS.py has only been verified to work for tPBE.

<u>File Name: input</u>	<u>File Name: MOLCAS.template</u>
printlevel 2	basis cc-pVDZ
geomfile "geom"	ras2 6
veloc external	nactel 10
velocfile "veloc"	inactive 7
	roots 2 0 2
nstates 2 0 2	method MCPDFT
actstates 2 0 2	functional TPBE
state 2 mch	
coeff auto	
rngseed -22004	
ezero -438.1634787000	
tmax 500.000	
stepsize 0.500000	
nsubsteps 25	
surf diagonal	
coupling overlap	
gradcorrect	
ekincorrect parallel_vel	
reflect_frustrated none	
decoherence_scheme edc	
decoherence_param 0.1	
hopping_procedure sharc	
grad_all	
nac_all	
select_directly	
write_overlap	
output_format ascii	
output_dat_steps 1	

## Section S6. Potential energies as functions of C–S internuclear distance



**Figure S2.** Potential energy scans along the C–S bond distance for (a) SA-CASSCF(10,6), (b) MC-PDFT(10,6), (c) SA-CASSCF(12,10), and (d) MC-PDFT(12,10). The C–S bond was stretched while keeping all other internal coordinates fixed at their values in the  $S_0$  optimized structure.

## References

1. Mai, S.; Atkins, A. J.; Plasser, F.; González, L. The Influence of the Electronic Structure Method on Intersystem Crossing Dynamics. The Case of Thioformaldehyde. *J. Chem. Theory Comput.* **2019**, *15*, 3470-3480.
2. Barbatti, M.; Granucci, G.; Persico, M.; Ruckebauer, M.; Vazdar, M.; Eckert-Maksić, M.; Lischka, H. The On-The-Fly Surface-Hopping Program System Newton-X: Application to Ab Initio Simulation of the Nonadiabatic Photodynamics of Benchmark Systems. *J. Photochem. Photobiol., A* **2007**, *190*, 228-240.