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The Influence of the Electronic Structure Method on Intersystem Crossing Dynamics.

The Case of Thioformaldehyde

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Abstract

The ability of different electronic structure methods to describe correctly intersystem crossing dynamics is evaluated, using thioformaldehyde as a test case. Mischievously, all methods considered—ranging from the multi-reference methods MR-CISD, MS-CASPT2, or SA-CASSCF, to the single-reference methods ADC(2), CC2, and TDDFT in different flavours—provide the same state ordering and energies of the low-lying singlet and triplet electronic excited states within an acceptable error of 0.2–0.3 eV. However, the outcome of the non-adiabatic simulations after excitation to the lowest S_1 ($^1n\pi^*$) state are dramatically different. While MS-CASPT2, ADC(2), BP86, and PBE do not transfer population to the triplet states within 500 fs—in consonance with experimental evidence—SA-CASSCF, B3LYP, and BHLYP predict intersystem crossing yields between 3% and 21% within the same time. The different

excited state dynamics can be rationalized by inspecting potential energy profiles along the C–S bond stretch mode and single-triplet energy gaps. It is found that already at a C–S bond length of 1.9Å, all the single-reference methods struggle to describe the correct asymptotic behavior of the potentials. Moreover, some methods, including SA-CASSCF, obtain incorrect $^1n\pi^* - ^3\pi\pi^*$ energy gaps, leading to compensation of errors (ADC(2), BP86, PBE), or wrong dynamics (SA-CASSCF, B3LYP, BHHLYP). Only the accurate MRCISD and MS-CASPT2 methods are able to describe the C–S bond correctly and thus able to deliver the correct potential energy surfaces and dynamics for the right reason. A correlation with the amount of Hartree-Fock exchange in the density functional and the easiness to access the $^3\pi\pi^*$ state from the $^1n\pi^*$ is able to explain the different behavior observed for GGA and hybrid functionals. It is thus illustrated that even in the case of a simple molecule, like CH₂S, the sole assessment of vertical excitation energies as reliability predictors for non-adiabatic is inadequate. The reason is that ISC does not occur at the FC geometry, but rather at distorted geometries where the singlet-triplet gaps become small. Hence, a characterization of the potential energy surfaces beyond the Franck-Condon region is mandatory.

1 Introduction

Intersystem crossing (ISC) is the radiationless transition between electronic states of different spin multiplicities, e.g., from a singlet to a triplet state. Given the involvement of ISC in many applications such as dye-sensitized solar cells,¹ organic light-emitting diodes,^{2,3} or photodynamic therapy,^{4,5} many studies aim at understanding this oftentimes highly complex process.⁶ Only recently it has become possible to carry out nonadiabatic molecular dynamics simulations including ISC and internal conversion on the same footing.^{7–12}

A key ingredient in any nonadiabatic molecular dynamics simulation is the level of theory employed to calculate the electronic potential energy surfaces (PESs), on which the nuclei are moving. The aim of this work is to compare the effect that different electronic structure

methods have on such simulations. An important question is to investigate how reliable it is to validate these methods only at the Franck-Condon (FC) geometry, and assume that beyond that geometry the PESs will be parallel at different levels of theory, an issue that, for singlet PESs, has been the focus of several previous studies, e.g., Refs.^{13–16} With this in mind, here we compare the accuracy of different electronic structure methods to describe the ISC dynamics of thioformaldehyde (CH_2S).

CH_2S has been chosen because it is small enough to enable high-level benchmark calculations, to which cheaper levels of theory can be compared, in terms of total ISC yields, bond length variations, and other parameters. From the experimental side, the low-lying electronic excited states of thioformaldehyde have been studied in detail for several decades.^{17–20} Thioformaldehyde possesses two low-lying $n\pi^*$ states, a singlet (origin at 2.03 eV) and a triplet (at 1.80 eV).¹⁹ The second triplet state, $^3\pi\pi^*$, is located around 2.70 eV.²¹ After excitation to the $^1n\pi^*$ state, fluorescence with a life time of 70–300 μs ^{19,22} is typically reported. The analysis of the rovibrational structure of the absorption spectrum revealed that many lines are perturbed by a number of singlet-triplet interactions. The ISC rate is not reported to our knowledge; based on the high fluorescence emission yields,^{19,22,23} it is likely to be small. For comparison, an ISC time scale of around 400 ps was obtained in surface hopping simulations for formaldehyde,²⁴ so it can be expected that thioformaldehyde exhibits a time constant around a few hundred picoseconds.

2 Computational Details

2.1 Electronic Structure Methods

The state-averaged complete active space self consistent field (SA-CASSCF),^{38,62} multi-state complete active space second order perturbation theory (MS-CASPT2),^{31–34,63} multi-reference configuration interaction including single and double excitations with the Pople size-extensivity correction (MRCISD+P),^{27,28,64} time-dependent density functional theory

Table 1: Electronic structure levels of theory included in the present study. The column “Dynamics” indicates which levels of theory were employed to simulate nonadiabatic dynamics.

Program	Method	Basis Set	Dynamics
— Benchmark methods —			
COLUMBUS ^{25,26}	MRCISD+P(12,10) ^{27,28}	ANO-RCC-VQZP ²⁹	
MOLCAS ³⁰	MS-CASPT2(12,10) ^{31–34}	ANO-RCC-VQZP	
— Multi-reference methods —			
MOLCAS	MS-CASPT2(10,6)	cc-PVDZ ^{35–37}	yes
MOLCAS	SA-CASSCF(10,6) ³⁸	cc-PVDZ	yes
— Ab initio single-reference methods —			
TURBOMOLE ³⁹	ADC(2) ^{40,41}	def2-SVP ⁴²	yes
TURBOMOLE	SCS-ADC(2)	def2-SVP	
TURBOMOLE	SOS-ADC(2)	def2-SVP	
TURBOMOLE	CC2 ^{43,44}	def2-SVP	
TURBOMOLE	SCS-CC2 ⁴⁵	def2-SVP	
TURBOMOLE	SOS-CC2 ⁴⁵	def2-SVP	
— TDDFT-based methods —			
ADF ^{46–48}	BP86 ^{49,50}	DZP ⁵¹	yes
ADF	PBE ⁵²	DZP	yes
ADF	B3LYP ^{53–55}	DZP	yes
ADF	mPW1PW ⁵⁶	DZP	
ADF	BHHLYP ^{54,57}	DZP	yes
— For ground state only —			
MOLPRO ^{58,59}	MP2 ^{60,61}	def2-SVP	

(TDDFT)^{65,66} and algebraic diagrammatic construction scheme for the polarization propagator to the second order (ADC(2))^{40,41,67} methods are employed to investigate the photophysics of CH₂S. Table 1 compiles the employed quantum chemistry codes, methods, the basis sets, and relevant references.

For the most accurate multi-reference calculations (MRCISD+P, MS-CASPT2, and SA-CASSCF), the active space orbitals are presented in Figure S1 in the supporting information (SI). The MRCISD+P computations utilized orbitals coming from a CASSCF(12,10) computation with state-averaging including 2 singlet and 2 triplet states (i.e., SA(2S+2T)-CASSCF(12,10)), and were performed within C_{2v} symmetry, with 6 frozen core orbitals, and with the Douglas-Kroll-Hess scalar relativistic Hamiltonian.⁶⁸ The SA-CASSCF and

MS-CASPT2 calculations were also performed using the Douglas-Kroll-Hess Hamiltonian. Following the suggestions in Ref.,⁶⁹ the MS-CASPT2 computations with the large ANO-RCC-VQZP basis set used an IPEA shift⁷⁰ of 0.25 a.u. and an imaginary level shift⁷¹ of 0.2 a.u.; the MS-CASPT2 computations with the cc-pVDZ used an IPEA shift of zero and an imaginary level shift of 0.3 a.u. The ADC(2) and CC2 computations used the resolution-of-the-identity approximation⁷² and a non-relativistic Hamiltonian. All TDDFT calculations utilized the scalar-relativistic zeroth order regular approximation (ZORA),^{73–77} with numerical integration performed with a Becke grid^{78,79} of “good” quality and a Zlm fit⁸⁰ of “normal” quality. All TDDFT calculations used the Tamm-Dancoff approximation (TDA)^{81,82} and the adiabatic local density approximation (ALDA).⁸³ To test the influence of the exchange-correlation functional, we considered two GGA functionals (BP86,⁴⁹ PBE⁵²), two typical hybrid functionals (B3LYP,⁵³ mPW1PW⁵⁶), and one hybrid with a large fraction of Hartree-Fock (HF) exchange (BHHLYP⁵⁷).

The MRCISD+P(12,10) and MS-CASPT2(12,10) computations with the ANO-RCC-VQZP basis set are the most accurate ones. They serve as reference methods here and will be denoted as “benchmark” methods.

The ground state geometry—which is employed for the vertical excitation calculations, the starting point of the PES scans, and the initial condition generation (see below)—was optimized with a smaller set of electronic structure methods. The MRCISD+P, MS-CASPT2, and ADC(2)/CC2 methods all shared the ground state geometry optimized at the MP2/def2-SVP level of theory. For the SA-CASSCF method, the ground state geometry was obtained at the same SA-CASSCF level of theory. All TDDFT methods were used with the same ground state geometry computed at the BP86/DZP level.

Using these geometries, we performed vertical excitation calculations, computing the lowest excited singlet state ($^1n\pi^*$) and the two lowest triplet states ($^3n\pi^*$ and $^3\pi\pi^*$). The same states were included in the PES scan along the C-S bond from the initial, optimized value up to 2.2 Å, with all other internal coordinates left unchanged. Along each of the PES

scans, we also computed the SOC matrix elements, as given in the relevant literature for COLUMBUS,^{84,85} MOLCAS,⁸⁶ TURBOMOLE/ORCA,^{67,87} and ADF.^{88,89}

2.2 Nonadiabatic Dynamics Simulations

For the ab initio excited-state dynamics simulations, we used the Surface Hopping including ARbitrary Couplings (SHARC) program package⁷⁻⁹ in combination with a subset of electronic structure methods—MS-CASPT2(10,6), SA-CASSCF(10,6), ADC(2), and TDDFT with two GGA (BP86, PBE) and two hybrid (B3LYP, BHHLYP) exchange-correlation functionals. The initial conditions for the dynamics were randomly sampled from ground-state harmonic oscillator Wigner distributions,^{90,91} based on frequency calculations for the optimized geometries as specified above. For each electronic structure method, we generated 1000 initial conditions and computed an absorption spectrum with the line-broadening method.⁹²

Subsequently, for each method we excited 200 initial conditions to the S_1 state, and propagated 200 trajectories for 1000 fs using a time step of 0.5 fs. The electronic wave functions were propagated with a 0.02 fs time step with the local diabaticization method.⁹³ The required (approximate) wave function overlaps were computed for all methods with the WFOverlap code;⁹⁴ to this end, for SA-CASSCF we used the actual wave function, for MS-CASPT2 the perturbatively-modified³³ CASSCF wave function, and approximate configuration interaction singles (CIS)-like wave functions for ADC(2)⁹⁵ and TDDFT.^{96,97} An energy-based decoherence correction⁹⁸ was applied to the electronic wave function coefficients in the eigenfunction basis.⁹ SOC's were computed on-the-fly at the same level of theory as energies and gradients. In all cases, the trajectories considered the S_0 , S_1 , T_1 , and T_2 , giving a total of 8 spin-coupled states, as the triplet components are treated separately.⁸

Figure 1: Vertical excitation energies at the Franck-Condon geometry obtained with the different electronic structure methods as indicated. The dashed lines show the average between the results of MRCISD+P and MS-CASPT2(12,10).

3 Results

3.1 Vertical Excitation Energies

The most straightforward way of comparing the performance of the electronic structure methods is to inspect the vertical excitation energies at the FC geometry. These energies are sketched in Figure 1 and listed in Table 2. All electronic structure methods agree on the state characters, with S_1 and T_1 being $n\pi^*$ and T_2 being $\pi\pi^*$ (see Figure S2 in the SI).

Figure 1 also shows experimental¹⁹ $0-0$ transition energies for the two lowest states. These serve as a reference but as they are not directly comparable to the computed vertical energies, the two benchmark calculations (MRCISD+P and MS-CASPT2(12,10)) will be used to compare with the rest of the methods. In any case, these two calculations provide results in remarkably good agreement with the experiment. Thus, the average of the MRCISD+P and MS-CASPT2(12,10) excitation energies, which are indicated in the figure as dashed lines, will be used for further comparisons.

The differences between the results are typical for such a diverse set of electronic structure methods, in the sense that the excitation energies agree within 0.2–0.3 eV.⁹⁹ Compared

Table 2: Vertical excitation energies for the different electronic structure methods, for the S_1 , T_1 , and T_2 excited states. The two last columns give the RMSD of the excitation energies (E) and the $S_1 - T_1$, $S_1 - T_2$, and $T_1 - T_2$ energy differences (ΔE), relative to the average of the two reference methods.

Method	S_1 ($^1n\pi^*$)	T_1 ($^3n\pi^*$)	T_2 ($^3\pi\pi^*$)	RMSD (E)	RMSD (ΔE)
Exp ¹⁹	2.03	1.80			
MRCISD+P(12,10)	2.19	1.91	3.42		
MS-CASPT2(12,10)	2.25	2.00	3.45		
MS-CASPT2(10,6)	2.14	1.84	3.31	0.11	0.04
SA-CASSCF(10,6)	2.31	2.03	3.09	0.21	0.35
ADC(2)	2.32	1.88	3.45	0.07	0.13
SCS-ADC(2)	2.36	1.98	3.40	0.09	0.13
SOS-ADC(2)	2.38	2.04	3.38	0.11	0.16
CC2	2.43	1.97	3.49	0.13	0.15
SCS-CC2	2.47	2.07	3.44	0.16	0.18
SOS-CC2	2.49	2.12	3.41	0.18	0.21
BP86	2.19	1.66	3.70	0.23	0.40
PBE	2.18	1.65	3.71	0.24	0.41
B3LYP	2.26	1.69	3.38	0.16	0.22
mPW1PW	2.28	1.70	3.34	0.16	0.22
BHHLYP	2.37	1.75	2.99	0.30	0.43

to the two reference methods, the best result is obtained with the smaller MS-CASPT2 computation, whose energies are shifted by about 0.1 eV from the reference, whereas the energy gaps are accurate to 0.04 eV, as measured by the root-mean-square deviation (RMSD). SA-CASSCF delivers accurate results only for the $n\pi^*$ states (S_1 and T_1), whereas the $^3\pi\pi^*$ state is significantly underestimated. The different flavors of ADC(2) and CC2 all provide very good triplet energies, but systematically overestimate the S_1 . Still, these methods provide RMSDs of 0.07–0.18 eV and can be regarded as accurate. Within the TDDFT methods, the hybrid functionals (B3LYP and mPW1PW) appear to perform best, although all TDDFT methods generally underestimate the T_1 energy. Furthermore, the energy of the T_2 state depends strongly on the amount of Hartree-Fock exchange, which leads to large RMSDs for the GGA functionals and BHHLYP. We also note that the two GGAs provide virtually identical results; the same holds for B3LYP and mPW1PW. We note here that all TDDFT methods employed the TDA^{81,82} and ALDA.⁸³ As shown in Table S1 in the

SI, usage of the TDA is imperative for a reasonable description of the T_2 state, because that state suffers from triplet instability problems¹⁰⁰ otherwise. Table S1 also shows that not employing the ALDA tends to produce slightly better results, but unfortunately in ADF gradient calculations cannot be performed without the ALDA, making dynamics simulations not possible.

A very important ingredient for ISC dynamics is the energy difference between the singlet and triplet states, according to the energy-gap law.¹⁰¹ Experimentally, the $S_1 - T_1$ energy gap ($0 - 0$) was estimated to be 0.23 eV.¹⁰² This value is closely reproduced by the benchmark methods (0.28 for MRCISD+P, 0.24 for MS-CASPT2(12,10)) and the other multi-reference methods, but overestimated by all other calculations. However, the SOC matrix elements between S_1 ($^1n\pi^*$) and T_1 ($^3n\pi^*$) are symmetry forbidden within the C_{2v} point group. Consequently, ISC might preferably take place between S_1 ($^1n\pi^*$) and T_2 ($^3\pi\pi^*$), which makes the $S_1 - T_2$ gap more important to assess. For this gap, the benchmark computations give a value of around 1.2 eV. SA-CASSCF, CC2, and BHHLYP significantly underestimate this value, while BP86 and PBE give a too large gap.

In summary, all electronic structure methods provide excitation energies within less than ± 0.3 eV from the benchmark calculations and give qualitatively the same state ordering. It could then be expected that MS-CASPT2(10,6), ADC(2)/CC2, and B3LYP/mPW1PW will provide a dynamics closest to that of the benchmark methods, while SA-CASSCF, BP86/PBE, and BHHLYP might not be completely accurate due to their error in the singlet-triplet gaps. Nevertheless, based only on these vertical energy results it is difficult to predict the outcome of the dynamics.

3.2 Nonadiabatic Dynamics Simulations

Excited-state dynamics simulations were performed for seven of the 15 electronic structure methods considered so far. We did not perform dynamics with the two benchmark methods (MRCISD+P(12,10) and MS-CASPT2(12,10)), due to their computational expense. How-

Figure 2: Populations of 200 trajectories for a duration of 500 fs of the T_1 (red) and T_2 (orange) states in CH_2S using different levels of theory. The populations shown here are the sum of the squared coefficients for each state of the wave function set rather than the ‘classical’ populations.

ever, as MS-CASPT2(10,6) delivers very similar stationary results (see also later) as the benchmark methods, we will employ the latter method as the reference for comparison.

Besides MS-CASPT2(10,6), the nonadiabatic dynamics simulations were carried out with SA-CASSCF(10,6), ADC(2), and TDDFT with the four functionals BP86, PBE, B3LYP, and BHHLYP (as indicated in Table 1). The aim of the dynamics simulations is to find whether the vertical excitation energies allow estimating the suitability of the different electronic structure methods.

For all 7 methods considered, Figure 2 shows the time evolution of the populations, based on 200 trajectories and 500 fs simulation time. The populations shown are the sums of the squared state coefficients in the MCH basis.⁹

We first analyze the dynamics employing MS-CASPT2(10,6) potentials. As can be seen in Figure 2, at this level of theory no persistent triplet population is building up within

500 fs. Consequently, no trajectory performed any hop out of the dominantly singlet state into a dominantly triplet state. The same behavior was found when the simulation time was extended to 1000 fs (not shown). The population plot only shows small, damped oscillations of the T_2 population between zero and 0.002. These oscillations stem from the fact that with SHARC the trajectories are propagated on spin-mixed potential energy surfaces (the so-called “diagonal” representation⁹), and the composition of the spin-mixed active potential changes between 100% and 99.8% singlet character. The reason for this variation in spin mixing lies in the variation of the C-S bond length over time, which is shown in Figure 3 for all electronic structure methods. As can be seen, the variation of the bond length matches accurately with the apparent T_2 population. The variation in the C-S bond length modulates the $S_1 - T_2$ energy gap (see below), which in turn has a direct effect on the amount of spin mixing. The oscillations in the T_2 population can be regarded as the SHARC equivalent of perturbation of the vibrational levels by the singlet-triplet interaction, as singlet-triplet mixing in SHARC also has an effect on the gradients and thus the mixing can affect the vibrational motion.

Another observation in Figure 3 is the coherence of the C-S bond stretch motion over all 200 trajectories. The oscillations are visibly coherent for the full 500 fs time window, although coherence slowly degrades over time due to coupling to the other vibrational degrees of freedom. The oscillation period is approximately 43 fs for the MS-CASPT2 trajectories, corresponding to 775 cm^{-1} and in good agreement with the experimental findings (41 fs or 820 cm^{-1}).¹⁹

Based on the MS-CASPT2 results, we conclude that CH_2S does not undergo ISC on a sub-ps time scale after vertical excitation from the ground state minimum. This is fully consistent with experimental findings on the molecule,^{19,22,23} and with 300 ps surface hopping simulations on the related formaldehyde molecule.²⁴ In the following, we will discuss which electronic structure methods are able to reproduce these findings.

Next we consider the SA-CASSCF dynamics, which was approximately 10 times cheaper

Figure 3: C–S bond length variation over the first 500 fs for all 200 trajectories calculated using the indicated method. For BHHLYP, color indicates the state in which the trajectory is currently moving (S_1 blue, T_1 red, T_2 yellow).

than the MS-CASPT2 dynamics. However, SA-CASSCF does not produce the correct ISC dynamics. As can be seen in Figure 2, for this method a non-negligible fraction of the trajectories has the propensity to undergo ultrafast ISC to the T_2 ($^3\pi\pi^*$) state. Already after half of a C–S oscillation period (i.e., at around 25 fs) the T_2 population reaches almost 2%, and each further oscillation increases the T_2 population further. Within 500 fs, the T_2 population reaches 5%. This is consistent with the results of a related generalized *ab initio* multiple spawning (GAIMS) study.¹⁰³ GAIMS is a nonadiabatic dynamics method that solves the time-dependent Schrödinger equation in a basis of classically moving, frozen Gaussians, effectively adding some quantum-mechanical effects to surface hopping simulations. Using SA-CASSCF(4,3)/6-31G*, the GAIMS method predicted a T_2 population of 5% after already 200 fs (present work: 3% after 200 fs). This shows that the too large ISC rate is not due to the SHARC formalism, but is directly related to the SA-CASSCF PESs.

Next we shall consider the GGA exchange-correlation functionals BP86 and PBE, which

give virtually identical results, as seen in Figures 2 and 3. With either functional, no population transfer to the T_2 occurs in the first 500 fs. However, as discussed for the MS-CASPT2 trajectories, there are weak oscillations of the T_2 population due to the modulation of the C-S bond length and consequently of the $S_1 - T_2$ energy gap and the singlet-triplet mixing. These oscillations are smaller by a factor of three, compared to the MS-CASPT2 results. This decreased T_2 contribution might be related to the very large $S_1 - T_2$ energy gap predicted by the GGA functionals, as shown in Figure 1.

The situation is quite different in the case of the hybrid functional B3LYP. Similar to SA-CASSCF, B3LYP predicts a non-zero ISC yield in the simulations, reaching a T_2 population of 3% after 500 fs. The evolution of the T_2 population still shows an oscillatory pattern due to the influence of the C-S stretch mode.

The BHHLYP functional performs even worse in the ISC dynamics, as can be easily spotted in Figure 2. With BHHLYP, one observes a rapid population transfer from the S_1 to the triplet states (even requiring a different y axis scale). Unlike in the other simulations, both T_2 and T_1 are populated here, indicating that at this level of theory the two states have an easily accessible crossing. Note that the figure shows *adiabatic* populations, i.e., where T_1 is the lower-energy state no matter the state character—hence, in the presence of a crossing the T_1 population is not equivalent to the $^3n\pi^*$ population. The fast oscillations between T_1 and T_2 are then only related to surface switching at the T_1/T_2 crossing, but are not related to population transfer between $^3n\pi^*$ and $^3\pi\pi^*$. We estimated the $^3n\pi^*$ population to be approximately half of the T_1 population shown in Figure 2, i.e., around 3% after 500 fs. The total triplet population after 500 fs is 21% after 500 fs, seven times higher than with B3LYP even though the initial conditions were identical.

The final electronic structure method considered for the dynamics is ADC(2). The populations in Figure 2 show that no ISC occurs in this case, with the weak oscillations of T_2 having an amplitude about half as large as for MS-CASPT2. This is due to the overestimated $S_1 - T_2$ energy gap that ADC(2) produces. The C-S stretch motion in Figure 3 is

quite similar to the MS-CASPT2 results, indicating that the shape of the S_1 potential is well-described with ADC(2).

3.3 Potential Energy Surfaces

The widely varying results shown in the previous section—with ISC yields ranging from 0% to 20%—can hardly be explained from predictions based on the vertical excitation data in Table 2. The reason is that ISC does not occur at the FC geometry, but rather at distorted geometries where the singlet-triplet gaps become small. Hence, electronic structure methods for dynamics simulations should not only be validated from vertical excitation energies. Instead, it is essential that the electronic structure methods are scrutinized based on all relevant parts of the PESs,^{13–16} even though this makes comparison to experimental data more difficult.

For CH_2S , the principal degree of freedom involved in the excited-state dynamics is the C-S bond stretch,¹⁰³ which controls the energy difference between singlet and triplet states. At large bond lengths S_1 , T_1 , and T_2 approach each other as the π bond becomes weaker; the three states correspond to degenerate states of the dissociated system (CH_2+S). Furthermore, the increased bond length increases the magnitude of SOCs between the states. Thus, in Figure 4 we show PES scans along the C-S bond stretch coordinate for all 15 electronic structure methods considered here, together with the positions of the excited-state minima. The numeric data for the minima is given in Table S2 in the SI.

As in the case of the vertical excitation calculations, the two benchmark methods agree very well with each other, both qualitatively and quantitatively. After downshifting the MS-CASPT2(12,10) PESs by 0.06 eV, the remaining RMSD (over all four states and across the full scan range) between MRCISD+P and MS-CASPT2 is only 0.05 eV. In general, the two scans show that upon elongation of the C-S bond the three excited states go through a minimum before increasing in energy at long bond lengths. The $^1n\pi^*$ and $^3n\pi^*$ approach each other quickly—with their gap falling below 0.1 eV at 1.9 Å—reflecting a decay of the

Figure 4: Potential energy scans for CH_2S along the C–S bond length internal coordinate for different method and functional choices. The dots mark the FC point and excited-state minima. A shaded background indicates that the method was used in the nonadiabatic dynamics simulations. All coordinate systems use the same axis ranges.

exchange interaction of the involved electrons. The $^3n\pi^* - ^3\pi\pi^*$ and $^1n\pi^* - ^3\pi\pi^*$ gaps are larger, and fall below 0.2 eV only above 2.1 Å; these gaps are related to the strength of the π bond.

Among the other methods, only the MS-CASPT2 results with small basis set are fully consistent with the benchmark PES scans, with an $\text{RMSD}\Delta$ (RMSD of the $^1n\pi^* - ^3n\pi^*$, $^1n\pi^* - ^3\pi\pi^*$, and $^3n\pi^* - ^3\pi\pi^*$ energy differences between 1.6 and 2.2 Å) of 0.02 eV. The relevant part of this PES scan is given by the C–S bond length evolution shown in Figure 3— for MS-CASPT2, the maximum C–S bond length is about 2.1 Å. According to the potentials shown in Figure 4, at this bond length the $S_1 - T_2$ energy gap is about 0.25 eV, whilst the SOC is only 170 cm^{-1} (0.021 eV), as given in Figure S3 in the SI. Thus, in this case the gap

is still too large for ISC to occur in an efficient manner, and only the weak singlet-triplet mixing discussed above is observed.

According to the PES scan, ISC should only occur if the molecule is excited to at least 2.7 eV, which is the minimum energy of the $^3\pi\pi^*$ state. At lower energies, only the $^1n\pi^*$ state (minimum energy of 2.1 eV) can be populated, as ISC to the lower-energy $^3n\pi^*$ state will not play a significant role due to the vanishing coupling between $^1n\pi^*$ and $^3n\pi^*$.

The SA-CASSCF method provides good qualitative shapes for the PESs, with smooth convergence of the energies of $^1n\pi^*$, $^3n\pi^*$, and $^3\pi\pi^*$ at long bond lengths. However, SA-CASSCF noticeably underestimates the energy of the $^3\pi\pi^*$ and therefore obtains an RMSD Δ of 0.19 eV. The underestimated $^1n\pi^* - ^3\pi\pi^*$ gap is also the reason why SA-CASSCF overestimates the ISC rate.

According to Figure 3, there is a significant number of the SA-CASSCF trajectories whose maximum bond length exceeds 2.1 Å (10% of all trajectories), and some even go to 2.3 Å. Upon close inspection, these trajectories with long C-S bonds tend to undergo ISC more readily, although not all of them do so within the simulation time. This is consistent with the computed PESs, which show that at 2.1 Å separation the $S_1 - T_2$ energy gap is only 0.1 eV, with the SOCs being around 170 cm⁻¹ (0.021 eV; see Figure S3 in the SI). The reduced gap compared to MS-CASPT2(10,6)—which had the same SOC value—provides a much higher probability for ISC at the SA-CASSCF(10,6) level.

Regarding the computed PESs, the performance of the ADC(2) methods is no better than SA-CASSCF. These methods give comparable RMSD Δ s: 0.20 eV, 0.17 eV, and 0.19 eV for regular, SCS-, and SOS-ADC(2). Furthermore, these methods show qualitative inaccuracies in the PESs. All ADC(2) variants predict a too steep S_0 PES (at MP2 level) at long bond lengths, which leads to the formation of a S_1/S_0 crossing at around 2.2 Å. The upshift of S_0 also increases the energy of $^3\pi\pi^*$ and thus leads to large $^1n\pi^* - ^3\pi\pi^*$ gaps, which never drop below 0.5 eV. This very large gap is the reason why ADC(2) predicts no ISC in the dynamics simulations, accidentally giving the correct qualitative result. The bad quality of

the ADC(2) surfaces at long bond lengths can be linked to the very large values of the D₁ and D2 diagnostics^{104,105} for the MP2 ground state, as presented in Figure S4 in the SI.

All CC2 methods provide similar RMSDΔs of 0.18 eV (regular CC2), 0.23 eV (SCS-CC2), and 0.30 eV (SOS-CC2). CC2 describes the ground state better than ADC(2), as CC2 obeys the non-crossing rule for S_0/S_1 while ADC(2) does not.¹⁰⁶ This is unexpected, because at long bond distances the D₁ and D2 diagnostics^{104,105} for the CC2 ground state (Figure S4 in the SI) reaches very high values. The energy gaps between the excited states are too large with CC2, whereas both SCS-CC2 and SOS-CC2 show too small $^1n\pi^* - ^3\pi\pi^*$ gaps, apparently overcompensating from CC2. Judging from the PES scans, we expect that regular CC2 would give the same result as ADC(2), due to the large $^1n\pi^* - ^3\pi\pi^*$ gap, whereas the SCS-CC2 and SOS-CC2 curves somewhat resemble the SA-CASSCF potentials and might give too large ISC rates.

As can be seen in Figure 4, all TDDFT methods fail at properly describing the PESs at stretched bond lengths, i.e., when the π bond component of the C-S bond starts breaking. In particular, the S_0 , $^1n\pi^*$, and $^3n\pi^*$ PESs are too steep (the steeper the more HF exchange is employed, see below), and are nearly parallel in all cases, instead of converging towards each other. Due to this steepness, the $^1n\pi^*$ and $^3n\pi^*$ states also show minima at too short bond lengths. Conversely, the $^3\pi\pi^*$ PES is actually rather good, especially with B3LYP and mPW1PW. However, this imbalance in the description of the states leads to wrong energy gaps. While the $^1n\pi^* - ^3\pi\pi^*$ gaps are reasonably described by the GGA functionals—except for slightly too small gaps at large bond lengths—the functionals with HF exchange fail completely for the $^1n\pi^* - ^3\pi\pi^*$ gap. Actually, for the three hybrid functionals (B3LYP with 20% HF exchange, mPW1PW with 42.8%, and BHHLYP with 50%) at large bond lengths $^3\pi\pi^*$ crosses with $^3n\pi^*$, such that $^3\pi\pi^*$ becomes the lowest triplet. This also means that the $^3\pi\pi^*$ crosses with the $^1n\pi^*$ state at very small bond lengths and at low energies. These inaccuracies will likely affect the ISC dynamics to a very large extent.

The results of the dynamics simulations for the TDDFT methods can fully be explained

Figure 5: Potential energy scans for CH_2S along the C-S bond length internal coordinate for different HF exchange % in the B3LYP exchange-correlation functional.

by the shapes of the PESs. The GGA functionals show a maximum C-S bond length of about 2.0 Å (in Figure 3), where the $S_1 - T_2$ energy gap is still more than 0.3 eV. Consequently, no ISC was observed for these functionals. For B3LYP, the maximum C-S bond length is even smaller—only 1.95 Å—but due to the $S_1 - T_2$ crossing at around 1.95 Å, these short bond lengths are still sufficient to induce ISC. Finally, the BHHLYP functional shows the most complex C-S bond length evolution. For trajectories moving in the S_1 state (blue lines), the C-S bond length stays below 1.85 Å due to the steep gradient of the PES. Nevertheless, the $S_1 - T_2$ crossing is located at 1.75 Å, allowing for efficient ISC. In Figure 3, the $T_1 - T_2$ intersection seam (transition from gold to red) is also nicely visible at 1.9 Å. Compared to the other electronic structure methods, with BHHLYP the trajectories lose coherent C-S stretching much faster as the ensemble distributes over the three excited states.

3.4 Influence of HF exchange

As can be seen from Figure 4, the percentage of HF exchange has a strong influence on the shape of the PESs. In order to understand better this HF exchange dependence, we performed potential energy scans along the C-S bond with the B3LYP functional, but varying the amount of HF exchange from zero to 100%. The results are shown in Figure 5.

The variation of the amount of HF exchange leads to two clearly identifiable effects. First, at long bonds the ground state energy is increased, i.e., the ground state becomes steeper.

The $^1n\pi^*$ and $^3n\pi^*$ states are similarly affected, although they are destabilized even more than the ground state. Hence, for larger HF exchange the states show even less convergent behavior than is already the case for GGA functionals (0% HF exchange). The increase of steepness also move the $^1n\pi^*$ and $^3n\pi^*$ minima to higher energies and shorter bond lengths.

Second, the $^3\pi\pi^*$ state is stabilized the more HF exchange is included, such that its minimum downshifts from 3 eV to 2 eV; only at long bond lengths, its energy increases. The most dramatic effect of this downshift is the displacement of the $^1n\pi^* - ^3\pi\pi^*$ crossing point, which is located around 2.2 Å for 0% HF exchange, but at 1.7 Å for 50% and below 1.6 Å for more than 80%. This is in stark contrast to the benchmark methods, where the two states never actually touch, but approach each other slowly (0.2 eV gap at around 2.1 Å). Another effect of the downshift of the states is the formation of an accidental symmetry-allowed¹⁰⁷ conical intersection between the $^3\pi\pi^*$ state and the $^3n\pi^*$ state which moves to smaller bond lengths and lower energies for larger HF exchange. While these two states do not touch for any of the wave function methods, with more than about 20% HF exchange in TDDFT they form an intersection which is located between 2.2 Å (for 20% HF exchange) and 1.7 Å (at 100%).

In summary, Figure 5 shows that the amount of HF exchange is the underlying reason for the strong shifts in the PESs among the different DFT functionals. It can be expected that these shifts will markedly affect the ISC rate, as accessing the $^3\pi\pi^*$ state from the $^1n\pi^*$ state becomes increasingly easier due to the displacement of their crossing point. Similarly, these shifts will also enable faster internal conversion from the $^3\pi\pi^*$ state to the $^3n\pi^*$ state, due to the displacement of the corresponding conical intersection. This acceleration might be strongest for 50–70% HF exchange, because in this case the two crossings are very close to the state minima, such that only small C-S bond stretches are required. Hence, for systems with strongly stretched (double) bonds—like CH_2S —it appears that hybrid functionals should be avoided. Conversely, the GGA functionals with 0% HF exchange seem to give reasonable PESs.

3.5 General Discussion

Clearly, the inspection of the PESs along the most important vibrational mode provides significantly more insight into the performance of the electronic structure methods than the vertical excitation energies alone. Especially at stretched bond lengths, large differences between the electronic structure methods are found. It can be argued that a proper description of static correlation is required to correctly describe the stretching/breaking of the π bond. Therefore, the single-reference/TDDFT methods struggle at long bond lengths, whereas they provide reasonable results at the FC geometry where static correlation is less important.

On the contrary, the SA-CASSCF potentials show that dynamic correlation is also required to obtain quantitatively correct results. Therefore, only the MS-CASPT2(10,6) level of theory fully agrees with the much more expensive benchmark computations and can be expected to deliver the right ISC dynamics for the right reasons.

Besides the shape of the PESs and in particular the $S_1 - T_2$ gap, the ISC rate is also determined by the magnitude of the SOC between these two states. A scan of the SOC norms for all methods is plotted in Figure S3 in the SI. This plot shows the SOC between $^1n\pi^*$ and $^3\pi\pi^*$ for all methods, except for SCS/SOS-ADC(2) and the three CC2 variants, for which SOC are currently not available in TURBOMOLE. The other methods all yield qualitatively similar results for the SOC, which was expected as SOC do not strongly depend on electron correlation and the state characters are correct for all methods.¹⁰⁸ Quantitatively, all multi-reference methods agree within $\pm 10 \text{ cm}^{-1}$ with each other. ADC(2) underestimates the SOC elements by about 25 cm^{-1} (i.e., 127 cm^{-1} instead of $150\text{--}160 \text{ cm}^{-1}$ at the FC geometry). The TDDFT methods underestimate the SOC elements by $10\text{--}15 \text{ cm}^{-1}$. These results again show that the most difficult task for the electronic structure method is to produce accurate PESs.

From the above discussion of the PESs, it seems that the ISC propensity in the simulations is related to the difference between the $^1n\pi^*$ vertical excitation energy and the $^3\pi\pi^*$ minimum energy, as this difference controls how easy it is to reach the $^3\pi\pi^*$ state. For the benchmark

methods, this energy difference amounts to 0.61 eV. The differences for the well-performing methods are: 0.54 eV for MS-CASPT2, 0.48 eV for ADC(2), 0.83 eV for BP86, and 0.86 eV for PBE. The three failing methods have values of 0.47 eV for B3LYP, 0.16 eV for SA-CASSCF, and 0.07 eV for BHHLYP. Clearly, a large energy difference leads to less ISC in the simulations. However, the fact that ADC(2) and B3LYP have almost the same value but still give very different ISC yields shows that this energy difference alone is not sufficient to predict the ISC dynamics. Instead, it is necessary to consider the actual shape of the PESs.

4 Summary and Conclusions

The vertical excitation energies and potential energy surfaces of the S_0 , S_1 , T_1 , and T_2 states of CH_2S were investigated using 15 electronic structure methods to determine which of them are appropriate to describe the nonadiabatic dynamics within these states. Seven of these methods were selected to perform nonadiabatic dynamics simulations including intersystem crossing, employing the SHARC surface hopping method. The reference methods for the stationary calculations were the MRCISD+P(12,10) and MS-CASPT2(12,10) levels of theory, both using the ANO-RCC-VQZP basis set. The other considered methods were MS-CASPT2(10,6), SA-CASSCF(10,6), ADC(2) and CC2 (each with different flavors of spin-component scaling), and TDDFT with five different exchange-correlation functionals; these calculations employed double- ζ basis sets. In all cases, it was found that the vertical excitation energies at the Franck-Condon geometry for S_1 , T_1 , and T_2 are in reasonable agreement with the references and with available experimental values, suggesting at first glance that all methods should be able to properly describe the excited-state dynamics.

However, out of the seven methods employed in the dynamics simulations, only MS-CASPT2(10,6), the GGA functionals BP86 and PBE as well as ADC(2) showed that no intersystem crossing should occur in this molecule on a sub-picosecond time scale. Important to note is that only MS-CASPT2(10,6) gave potentials virtually identical to the reference

methods and thus provided the correct dynamics for the right reasons, whereas the latter three methods significantly overestimate the singlet-triplet gap. The remaining methods—SA-CASSCF(10,6), B3LYP, and BHHLYP—predicted a triplet yield between 3 and 21% within 500 fs, clearly wrong in light of the MS-CASPT2 results and experimental evidence.

Inspection of the excited-state potential energy surfaces showed that the good agreement at the Franck-Condon geometry is only deceptive, and that many of the electronic structure methods yield qualitatively wrong surfaces beyond the equilibrium geometry. Most prominently, the hybrid DFT functionals predicted unphysical state crossings at very low energies, whereas ADC(2) and GGA functionals overestimate the relevant singlet-triplet gaps. Thus, using the computed potential energy surfaces one can fully explain the variations in the results obtained in the dynamics simulations.

Overall, the present study illustrates how the results of nonadiabatic dynamics simulations are highly dependent on the choice of electronic structure method. Hence, for every such simulation it is crucial to validate the electronic structure method prior to the dynamics simulations. We caution that such a validation should not solely be carried out in the Franck-Condon region—as it is sometimes seen—because the fate of nonadiabatic dynamics is often decided far away from this region, where many electronic structure methods are less accurate. This was most visible in the case of B3LYP, which gives vertical excitation energies in close agreement with the references, but fails completely in the nonadiabatic dynamics predictions. The results also showcase that already errors of around 0.1–0.2 eV in critical parts of the potential energy surfaces can lead to significant deviations in the results of the dynamics simulations. Certainly, the best option for any excited-state dynamics studies are correlated multi-reference methods, such as MRCI or MS-CASPT2, because only these methods can provide a truly balanced description of all parts of the potential energy surfaces, which is critical even in the seemingly simple molecule thioformaldehyde. However, as such methods are challenging or even unfeasible to employ on large molecules, a careful calibration of the electronic structure level of theory is decisive to obtain meaningful results.

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Supporting Information Available

Active space orbitals, information on state characters at the Franck-Condon geometry, Spin-orbit coupling surfaces, and results of excited-state optimizations.

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