

# **Nonadiabatic Excited-State Dynamics of SMe: Analysis of TDDFT Trajectories and Photophysical Behavior**

Nicolás Rojo Esteban

**QH1: How do the torsional angles (e.g., 6-7-9-10) and bond lengths (e.g., 7-9) change? Use the atom order of the figure below.**

Figure 1 shows the optimized  $S_0$  and  $S_1$  geometries obtained with TDDFT. Overall, both structures are extremely similar: the chromophore remains essentially planar and no torsion is observed. The differences between the two states are limited to small changes as shown in the selected bond lengths and in the local dihedral angle.

Table 1: Key structural parameters for the optimized  $S_0$  and  $S_1$  geometries.

State	Dihedral (deg)	d(7-9) (Å)	d(6-7) (Å)
$S_0$	9.70	1.3547	1.4434
$S_1$	9.93	1.3746	1.4420

These numerical values confirm that the excitation does not produce a strong distortion of the ground-state geometry. The dihedral angle changes by less than  $0.3^\circ$ , while the 7–9 and 6–7 bond lengths vary only by  $0.02 \text{ \AA}$  and  $0.001 \text{ \AA}$ , respectively. This indicates that the  $S_1$  minimum lies very close to the  $S_0$  minimum in nuclear configuration space, with only minor  $\pi-\pi^*$  reorganization in the chromophore.

This small structural difference contrasts with the much larger torsional motions observed during the nonadiabatic dynamics (QH11–QH12), where the chromophore twists substantially as the system explores regions of strong  $S_1/S_0$  coupling.

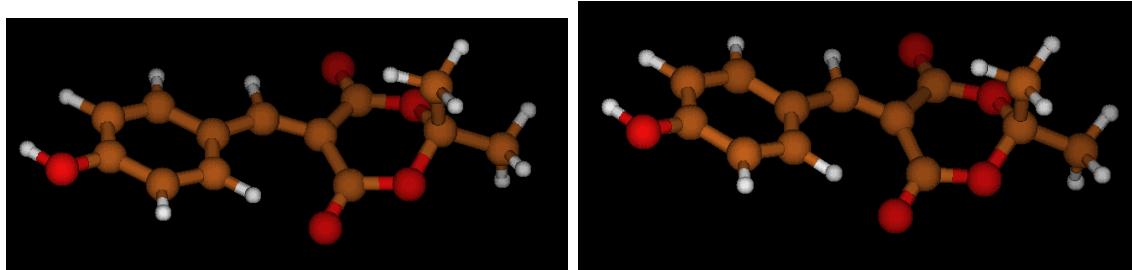


Figure 1: Optimized geometries of  $S_0$  (left) and  $S_1$  (right).

**QH2. What are the absorption and emission energies?**

From the TDDFT calculations, the first excited state ( $S_1$ ) of Sinapoyl Meldrum (SMe) was analyzed at both the ground-state ( $S_0$ ) and excited-state ( $S_1$ ) optimized geometries.

- At the  $S_0$  geometry, the first vertical excitation ( $S_0 \rightarrow S_1$ ) occurs at an energy of **3.832 eV (323.55 nm)** with an oscillator strength of **f = 0.8765**. This value corresponds to the vertical absorption energy, representing the electronic transition from the ground state to the first excited state.
- At the  $S_1$  geometry, the TDDFT calculation gives a vertical energy difference ( $S_1 \rightarrow S_0$ ) of **0.532 eV (2330.59 nm)** with an oscillator strength of **f = 0.0000**. This value corresponds to the vertical emission energy, the energy that would be released if the system relaxed radiatively back to  $S_0$  from the optimized excited-state structure.

Therefore, the computed absorption and emission energies are:

$$E_{\text{abs}} = 3.832 \text{ eV} \quad (323.55 \text{ nm})$$

$$E_{\text{em}} = 0.532 \text{ eV} \quad (2330.59 \text{ nm})$$

The large Stokes shift ( $\Delta E = E_{\text{abs}} - E_{\text{em}} \approx 3.30 \text{ eV}$ ) indicates a significant geometrical relaxation of the molecule in the excited state, leading to a strong stabilization of  $S_1$  before emission. This behavior is consistent with an efficient nonradiative decay pathway, typical for systems that dissipate the absorbed UV energy as heat rather than fluorescence[1].

### **QH3. What are the P and B values in the CASSCF calculation?**

From the CASSCF conical intersection analysis, the following topography parameters were obtained:

$$\text{Pitch } (\delta_{gh}) = 6.92618 \times 10^{-2} \text{ Eh}/a_0, \quad \text{Asymmetry } (\Delta_{gh}) = 4.37169 \times 10^{-1},$$

$$\text{Relative tilt } (\sigma = s/\delta_{gh}) = 2.33080,$$

and the dimensionless parameters that classify the intersection:

$$P = 3.78010, \quad B = 2.17494.$$

### **QH4. How would you characterize this MECP?**

According to the criterion of Ref. [2], the intersection is classified by the magnitudes and signs of  $P$  and  $B$ :

- $P > 1 \Rightarrow$  sloped intersection,
- $B > 1 \Rightarrow$  single-path.

According to the standard CI topography classification,  $P > 1$  identifies a sloped intersection and  $B > 1$  indicates a single-path character. Therefore, the  $S_1/S_0$  MECP is classified as a sloped, single-path conical intersection.

From a physical point of view, a sloped, single-path MECP implies that the branching plane is inclined in such a way that the nuclear wavepacket is driven downhill along a preferred direction toward the ground state, favouring efficient nonradiative relaxation from  $S_1$  to  $S_0$  through this unique decay channel.

### **QH5: What is the energy difference ( $\Delta E$ ) between the ground and $S_1$ states at this geometry? What are the implications of such gap in the choice of electronic structure method?**

At the TDDFT MECP geometry, the total electronic energies of the two states are:

$$E_{S_0}^{\text{MECP}} = -878.443233128 \text{ Ha}, \quad E_{S_1}^{\text{MECP}} = -878.442262112 \text{ Ha}.$$

The energy gap at this geometry is therefore

$$\Delta E = E_{S_1}^{\text{MECP}} - E_{S_0}^{\text{MECP}} = 9.71 \times 10^{-4} \text{ Ha} \approx 0.0264 \text{ eV}.$$

This very small gap ( $\sim 0.03$  eV) shows that the two potential energy surfaces are nearly degenerate at this geometry, as expected for a minimum energy crossing point (MECP). Consequently, this region provides an efficient funnel for nonradiative decay from  $S_1$  to  $S_0$ .

Although TDDFT (TD-KS) can qualitatively identify regions of near-degeneracy, it is a single-reference method and does not correctly describe the configuration mixing and nonadiabatic couplings that of a conical intersection. For a quantitatively description of the crossing topology and associated dynamics, a multireference method such as CASSCF or CASPT2 would be more appropriate.

**QH6. What is the energy difference between the  $S_1$  minimum and the MECP?**

From the TDDFT calculations, the total energy of  $S_1$  at its minimum (file `S1.log`) and at the MECP geometry (file `MECP.log`) are:

$$E_{S_1}^{\min} = -878.450178124 \text{ Ha}, \quad E_{S_1}^{\text{MECP}} = -878.442262112 \text{ Ha}.$$

The corresponding energy difference is

$$\Delta E = E_{S_1}^{\text{MECP}} - E_{S_1}^{\min} = 7.92 \times 10^{-3} \text{ Ha} \approx 0.215 \text{ eV}.$$

**QH7. Is the MECP energetically accessible from the  $S_1$  minimum?**

The  $S_1/S_0$  MECP lies only above the optimized minimum of the  $S_1$  potential energy surface.

After absorbing a photon of  $\sim 3.83$  eV, the system is promoted vertically to a highly vibrationally excited region of the  $S_1$  surface. A barrier of only  $\sim 0.2$  eV is therefore small compared to the vibrational energy available after excitation.

The wavepacket on  $S_1$  can access the MECP region without difficulty. The  $S_1/S_0$  crossing is therefore energetically accessible, providing an efficient funnel for nonradiative decay via internal conversion.

**QH8. How many peaks do you identify in each spectrum?**

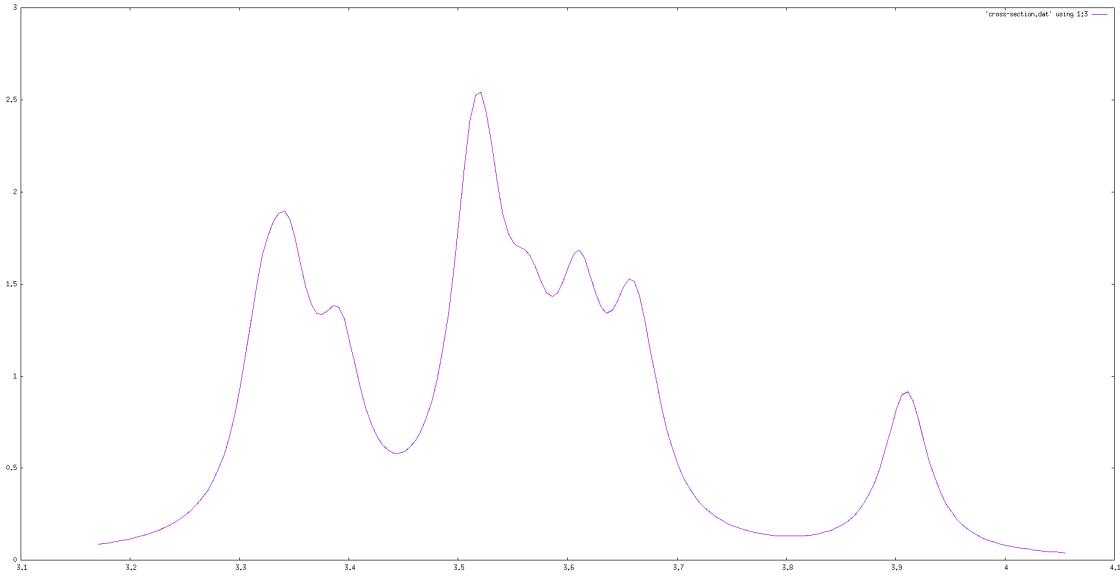


Figure 2: Vibronic absorption spectrum obtained using 10 sampled geometries.

In the spectrum computed with only 10 points, six distinct peaks are visible.

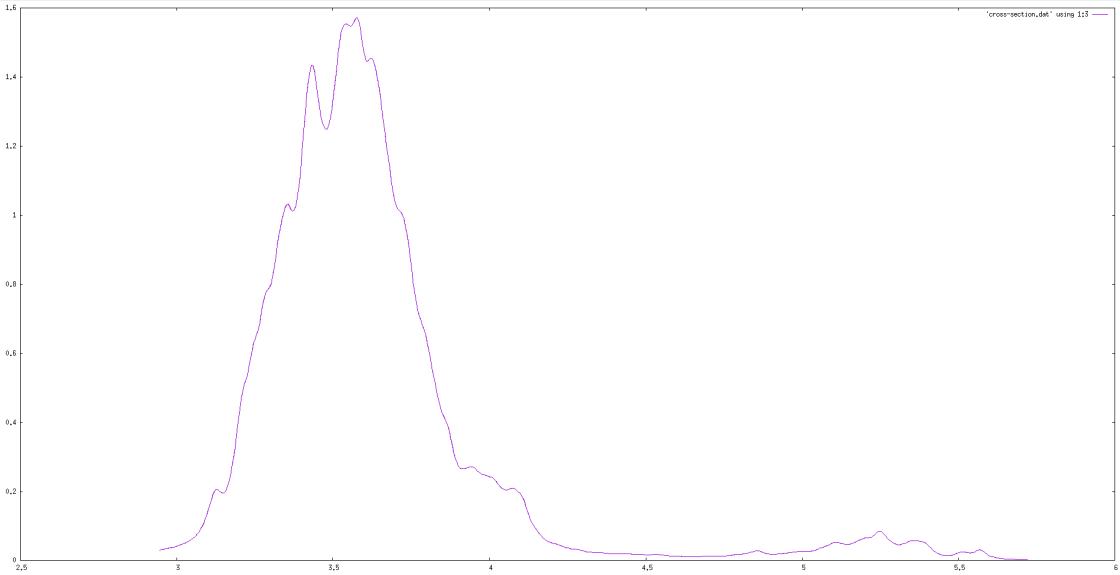


Figure 3: Vibronic absorption spectrum obtained using 300 sampled geometries.

The spectrum computed with 300 points is very different. Here, the line shape becomes smoother and only one broad peak is observed.

**QH9. What region of the spectrum should be the most relevant when running excited-state dynamics on SMe?**

The most relevant region is the energy range corresponding to the dominant absorption band of the vibronic spectrum. In the 300-point spectrum, only one broad peak is observed,

centred approximately between 3.4 and 3.7 eV. This region represents the highest probability of photon absorption and therefore the most likely initial conditions for excitation to the S<sub>1</sub> state.

Excited-state dynamics should therefore be initiated around the maximum of this absorption band. This ensures that the trajectories start from physically meaningful geometries and energies for the excitation of SMe.

**QH10. How many states would you include in your dynamics according to each spectrum?**

If one looked only at the 10-point spectrum, the presence of several apparent peaks could misleadingly suggest that more than one electronic state contributes to the absorption in this energy window. On the basis of that poorly converged spectrum, one might be tempted to include several excited states (S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>...) in the dynamics in order to account for the apparent multi-peak structure.

However, in the 300-point spectrum we can clearly see a single broad absorption band rather than multiple peaks. This indicates that the optical response is dominated by only one bright state which is S<sub>1</sub>, with no clear evidence of additional electronic states contributing as separate bands.

Therefore:

- based on the 10-point spectrum, one could incorrectly think that there we need to include multiple excited states;
- based on the 300-point spectrum, it is sufficient to include only the lowest bright excited state (S<sub>1</sub>) in the excited-state dynamics.

This illustrates how an under-sampled vibronic spectrum may lead to an overestimation of the number of states required for a nonadiabatic dynamics setup.

**QH11: Plot the energy of all states involved with NX/plot. What is happening with the energy gap between S1 and S0 in each trajectory? Open dyn.xyz with VMD and visualize the geometries of SMe during the dynamics (VMD can take a while to load on CINECA, an option is to download dyn.xyz file to your local computer and use molden/vmd locally). What is the main geometrical feature driving the dynamics?**

**True Random Number Generator**

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Max:	67
<b>Generate</b>	
<b>Result:</b>	
<b>16</b>	
Min: 1, Max: 67	
2025-11-24 13:38:50 UTC	

Powered by [RANDOM.ORG](https://www.random.org)

Figure 4: Random number generated to define the initial conditions for trajectory 16.

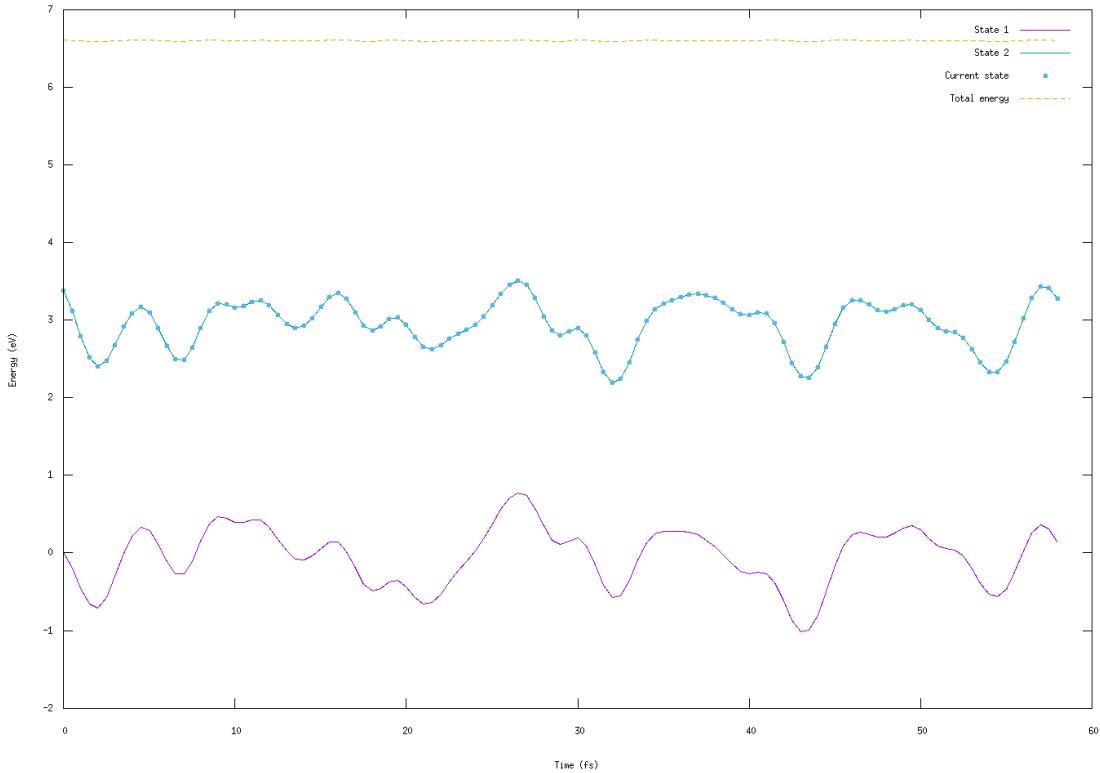


Figure 5: Short-time (0–60 fs) excited-state dynamics for trajectory 16.

In the short 60 fs trajectory, the energies of  $S_0$  and  $S_1$  evolve almost in parallel. The  $S_1-S_0$  energy gap shows only small oscillations, but no significant approach between the states is observed. This is expected because the simulation time is too short to explore the regions of nonadiabatic coupling.

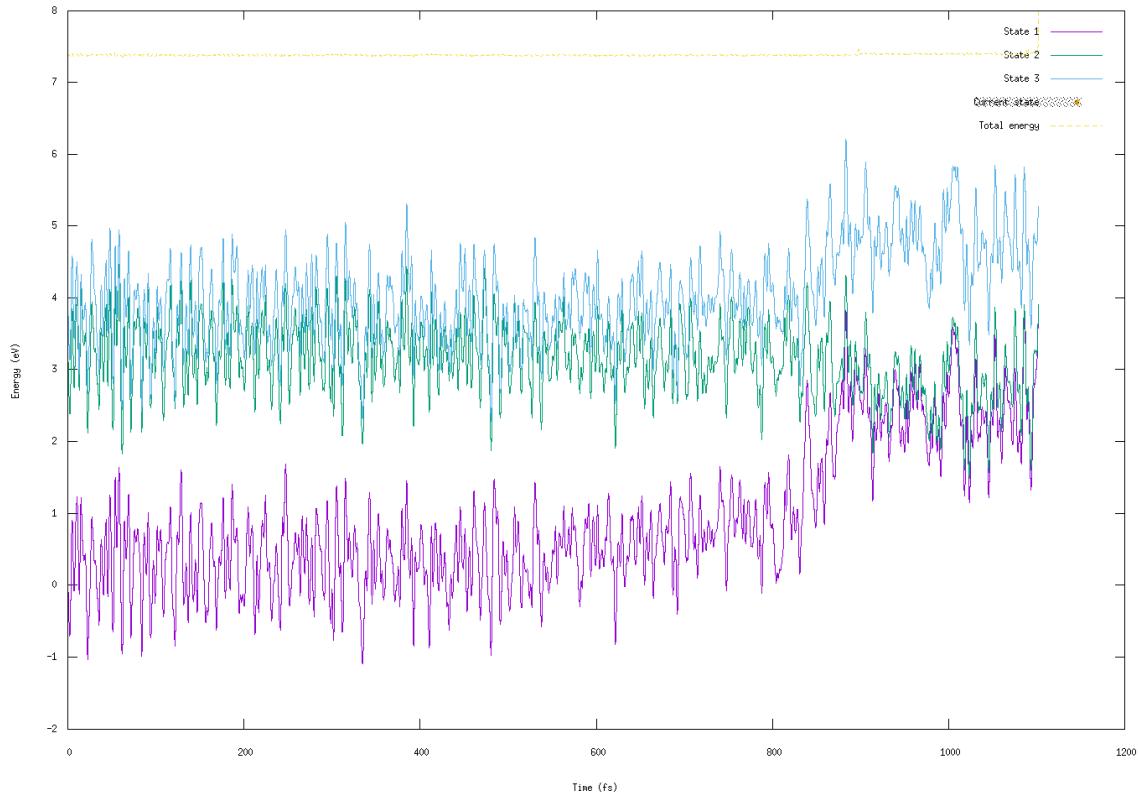


Figure 6: Long-time (0–1000 fs) dynamics including three electronic states for trajectory 16.

In contrast, the long-time trajectory exhibits a bigger change of the excited-state energies. At early times,  $S_1$  and  $S_2$  are nearly degenerate while  $S_0$  remains significantly lower in energy. As the dynamics progresses, the molecular geometry evolves and the relative ordering of the states changes:  $S_0$  increases in energy and approaches  $S_1$ , while  $S_2$  becomes consistently higher than the other two states.

**True Random Number Generator**

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Max:

**Generate**

Result:

**33**

Min: 1, Max: 67  
2025-11-24 13:39:07 UTC

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Figure 7: Random number generated to define the initial conditions for trajectory 33.

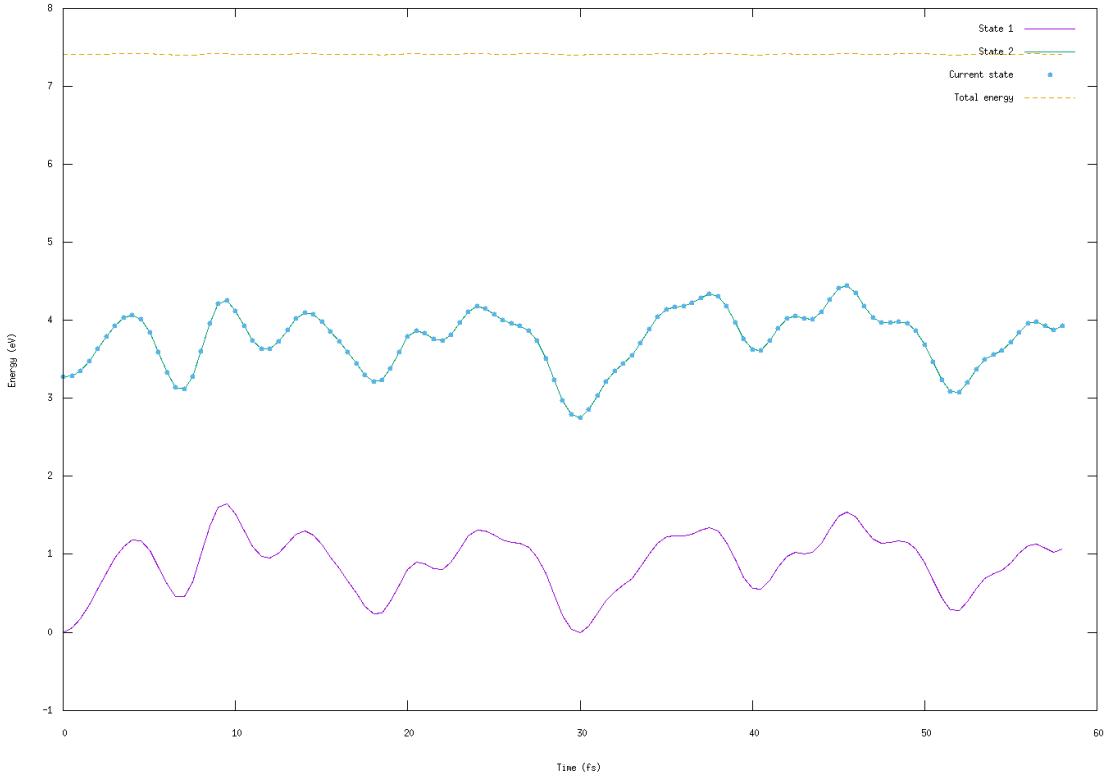


Figure 8: Short-time (0–60 fs) excited-state dynamics for trajectory 33.

In the short-time simulation, the energies of  $S_0$  and  $S_1$  evolve almost in parallel, with only small oscillations caused by the initial nuclear motion. No substantial change in the  $S_1-S_0$  energy gap is observed, which is expected because 60 fs is not long enough for the system to reach geometries where nonadiabatic effects become significant.

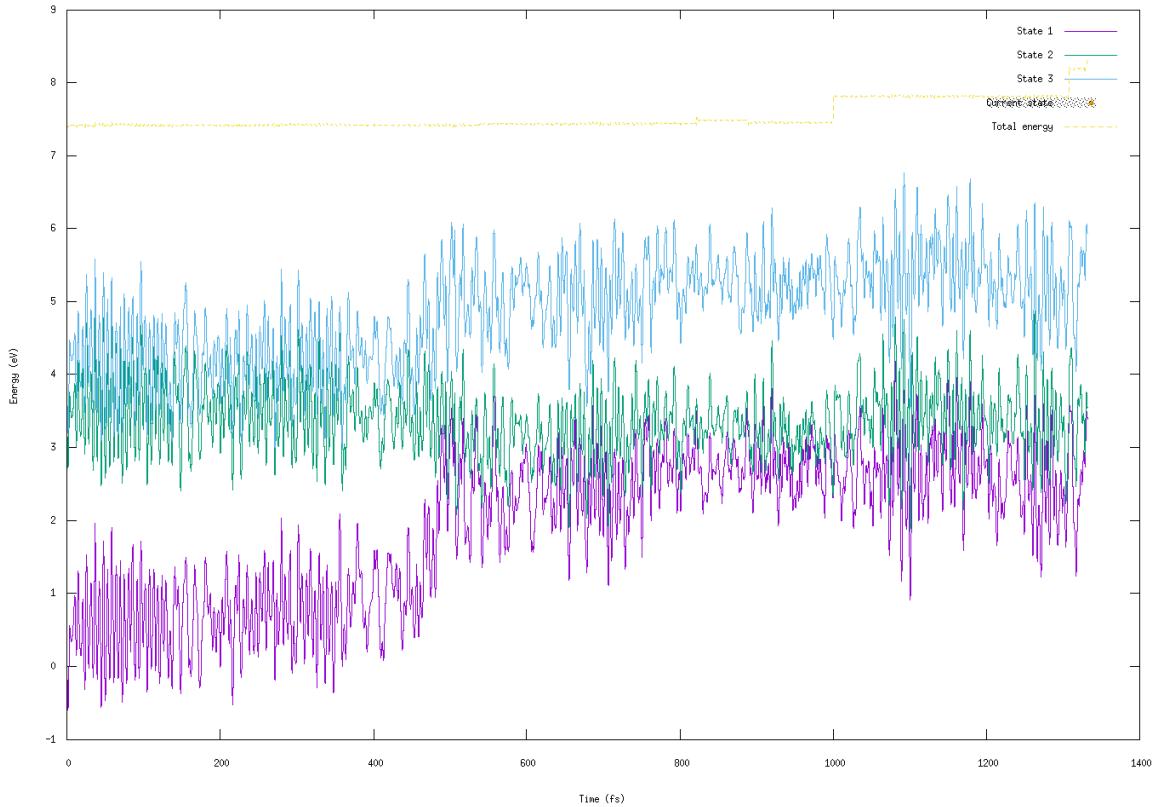


Figure 9: Long-time (0–1300 fs) dynamics including three electronic states for trajectory 33.

At early stages,  $S_1$  and  $S_2$  remain relatively close in energy while  $S_0$  lies considerably lower. As the geometry evolves, the energy of  $S_0$  increases and approaches that of  $S_1$ , while  $S_2$  fluctuates above them. This indicates that the system is exploring regions of strong coupling between the ground state and the  $S_1$  excited state.

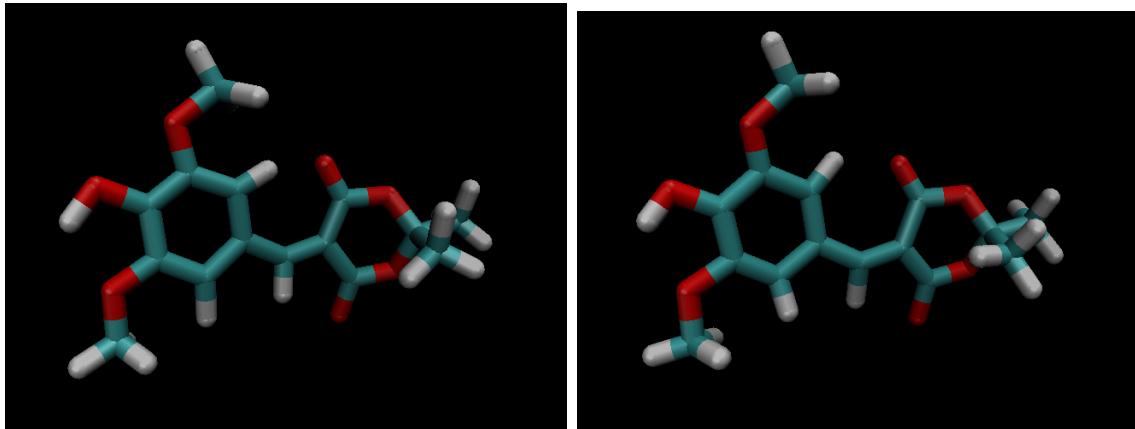


Figure 10: Initial (left) and final (right) geometries of the short 60 fs trajectory for trajectory 16.

A comparison between the initial and final geometries shows that the nuclei have barely

moved over the 60 fs simulation. Because nuclear motion is limited in this short time window, the electronic energies of  $S_0$  and  $S_1$  evolve almost in parallel and the energy gap of  $S_1 - S_0$  remains nearly constant.

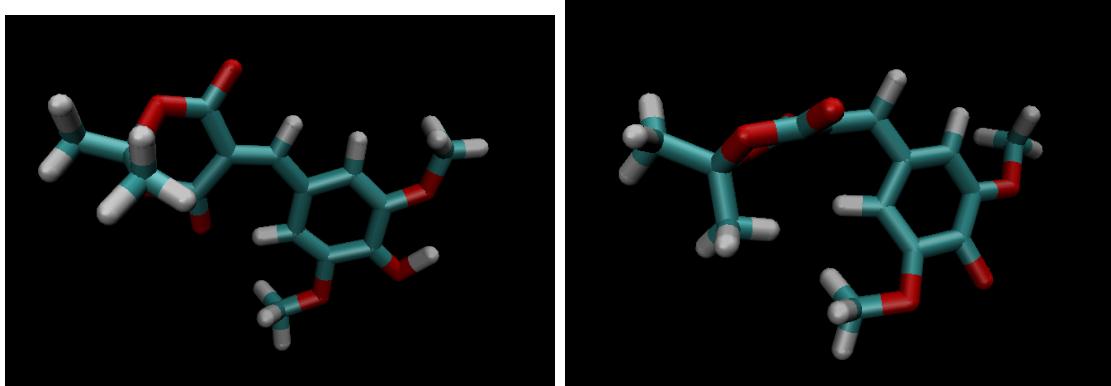


Figure 11: Initial (left) and final (right) geometries of the full excited-state trajectory for trajectory 16.

The full trajectory shows a much more substantial structural change than the short 60 fs run.

The chromophore of SMe corresponds to the extended  $\pi$ -system formed by the two aromatic rings and the conjugated bridge connecting them. This region hosts the electronic density involved in the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  excitations determining the character and energy of the excited states.

During this trajectory, the greatest structural change is the torsion between the two aromatic rings. The initial geometry shows the rings arranged in an almost parallel orientation, while the final geometry shows them in a nearly perpendicular configuration. This torsional motion modifies the electronic coupling within the chromophore. When the rings rotate, the overlap between their  $\pi$ -systems changes substantially, altering the strength of the  $\pi - \pi^*$  interactions that define the potential energy surfaces of  $S_0$ ,  $S_1$  and  $S_2$ .

As a result, the energies of the excited states vary significantly along the trajectory. The approach or separation of the states observed in the energy plots reflects how the chromophore responds to this torsional motion. The reorientation of the aromatic rings is the key nuclear motion driving the excited-state dynamics in SMe.

**QH12: Compare the results of this trajectory with the one you ran yourself. Are the results similar? Do you expect them to be similar? Explain.**

**True Random Number  
Generator**

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Max:	67
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Powered by <a href="https://www.random.org">RANDOM.ORG</a>	

Figure 12: Random number used to generate the initial conditions for trajectory 41.

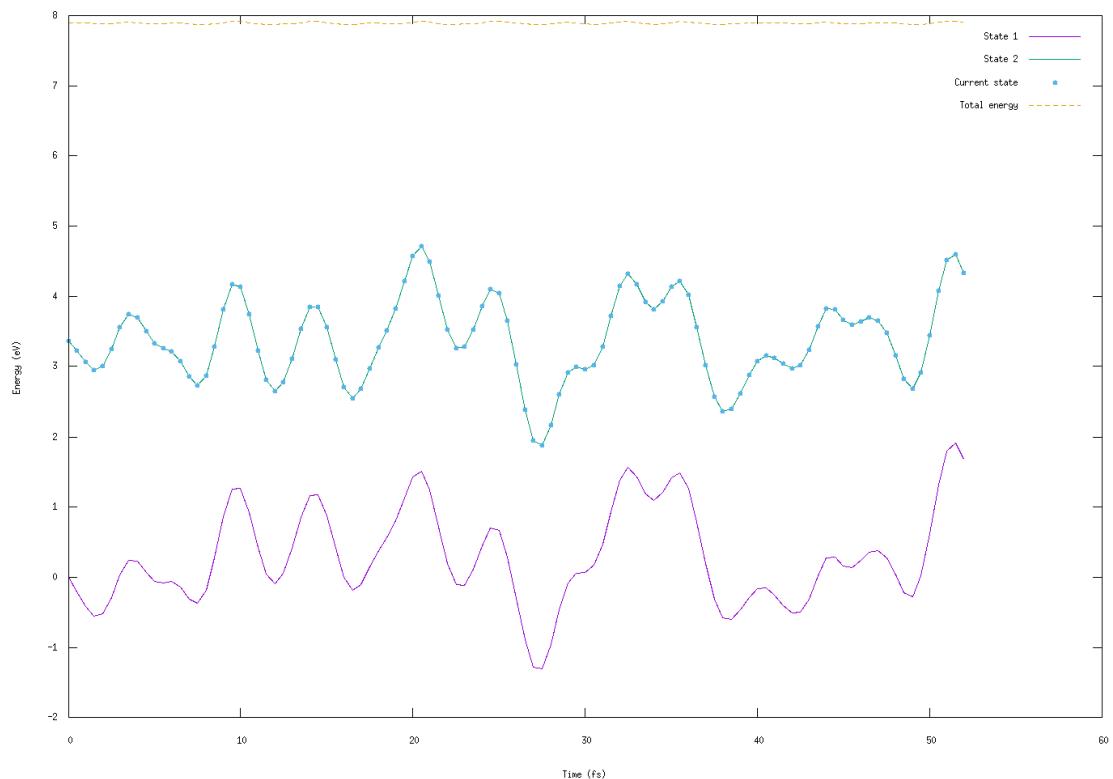


Figure 13: Short-time (0–60 fs) excited-state dynamics for trajectory 41.

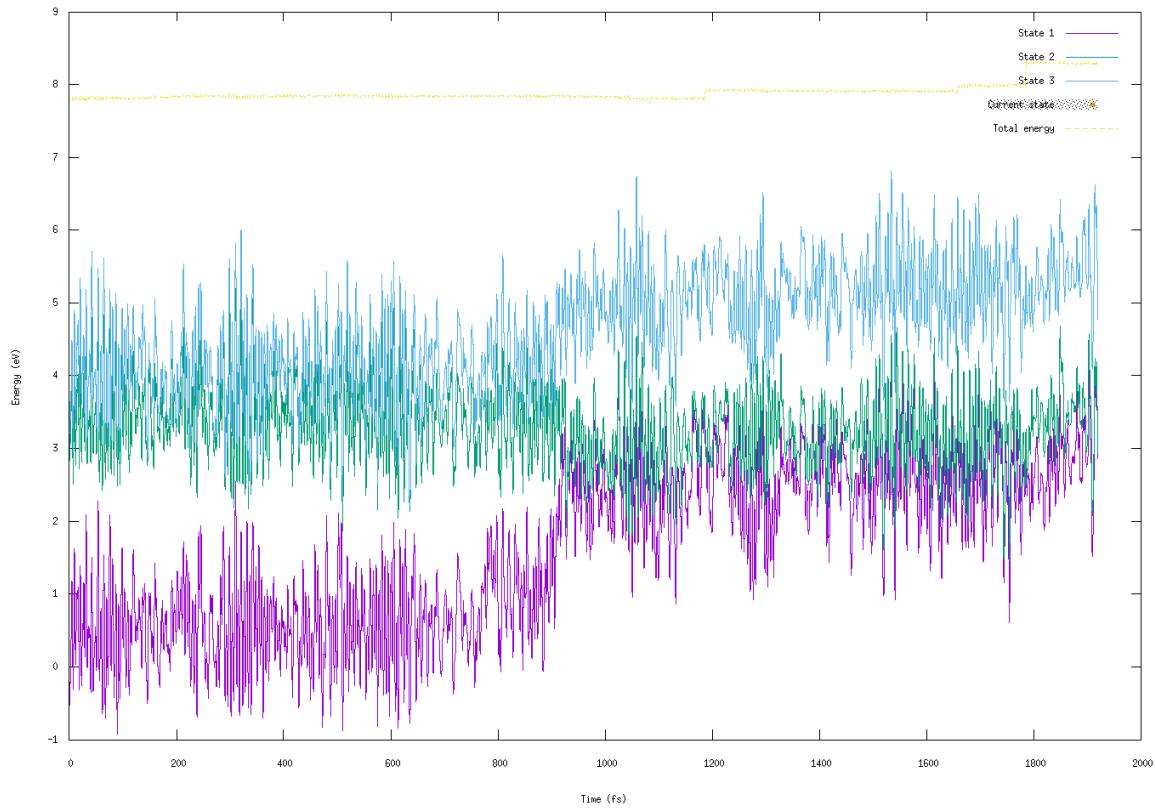


Figure 14: Long-time excited-state dynamics including three electronic states for trajectory 41.

All three trajectories (16, 33, and 41) behave in a similar way during the first 60 fs.  $S_0$  and  $S_1$  stay almost parallel and the energy gap hardly changes. This is normal, because such a short simulation does not give the nuclei enough time to move.

In the long-time runs, the trajectories are not identical, but they show the same general pattern. In all cases, the molecule undergoes a large torsion of the chromophore, and this motion produces oscillations in the energies of  $S_0$ ,  $S_1$ , and  $S_2$ . The differences between trajectories are simply due to the different random initial conditions, so we do not expect them to be exactly the same. However, they are qualitatively similar, as observed.

**QH13: Based on the diagnostic analysis you did in Section 6.C, notice that all trajectories finished with an error, which is expected for TDDFT. Can you rationalize why this is the case (Tip: check Q11 of the hands-on session)?**

The diagnostic “energy conservation failed” appears because TDDFT does not provide a variational description of excited states. In TDDFT, the excited-state energy and the excited-state gradient do not originate from a common energy functional. As a result, the forces are not fully consistent with the electronic energy, and the total energy of the molecule cannot remain constant during long dynamics. This is visible in the energy plots. The total energy is constant at the beginning of the trajectory but it starts to increase after several hundred femtoseconds, which is when the code stops the simulation.

This behaviour becomes critical when the molecule explores geometries where the elec-

tronic states change character or become nearly degenerate. In the twisted chromophore,  $S_1$  and  $S_2$ , and  $S_0$  and  $S_1$  mix strongly, and the excited states acquire multireference character. Standard adiabatic TDDFT cannot describe such situations, leading to inconsistent energies and gradients and to the breakdown of the dynamics.

A multireference method such as CASSCF would be more appropriate for excited-state dynamics in this system, because these methods treat several states consistently and maintain energy conservation even in regions of strong state mixing.

**QH14: Given the answer to QH13, what are the implications for the internal conversion rate constant obtained with TDDFT? How does it compare to the rate constants obtained with multireference methods? Discuss.**

Since all TDDFT trajectories fail precisely when the system reaches the region where  $S_1$  and  $S_0$  become strongly coupled, any internal conversion (IC) rate constant derived from these simulations would be unreliable. TDDFT is not able to describe the multireference character of the  $S_1/S_0$  crossing region.

In contrast, multireference methods such as CASSCF or CASPT2 correctly describe the topology of the  $S_1/S_0$  crossing and maintain stable dynamics. These methods produce smooth and physically meaningful population curves from which reliable internal conversion rate constants can be obtained. Therefore, TDDFT fails for the excited-state dynamics in this system, and its predicted internal conversion rates cannot be compared quantitatively to those obtained with multireference approaches.

**QH15: Based on the statistical analysis you did in Section 6.C, plot the fraction of trajectories in each state as a function of time and fit an exponential function to the  $S_1$  state. What is the  $S_1$  lifetime?**



Figure 15: Fraction of trajectories in  $S_0$ ,  $S_1$  and  $S_2$  as a function of time, together with the exponential fit of the  $S_1$  decay.

Figure 15 shows the fraction of trajectories in  $S_0$ ,  $S_1$  and  $S_2$  as a function of time, obtained from the statistical analysis of the TDDFT trajectories. The  $S_1$  population remains close to 1 during the first  $\sim 800$  fs, after which it begins to decay as more trajectories transition to  $S_0$ .

To estimate the  $S_1$  lifetime, the decay portion of the  $S_1$  population was fitted in the 800–2000 fs window using a single-exponential expression:

$$P_{S1}(t) = A e^{-t/\tau} + C.$$

The fitted parameters were:

$$P_{S1}(t) = 2.6387 e^{-t/1043.1} - 0.3104.$$

From this fit, the  $S_1$  lifetime is therefore

$$\tau_{S1} \approx 1.043 \times 10^3 \text{ fs} (\sim 1.0 \text{ ps}).$$

This value characterizes the overall timescale of internal conversion from  $S_1$  to  $S_0$  in the TDDFT dynamics.

## References

- [1] J. M. Toldo, M. T. do Casal, and M. Barbatti, *J. Phys. Chem. A* **125** (2021) 5499–5508.
- [2] Y. Y. *et al.*, *J. Chem. Theory Comput.* **12** (2016) 3636–3653.