Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA21126

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Details of the STSM

Title: Pathways of naphthalene stabilization after UV light excitation

Start and end date: 05/02/2024 to 16/02/2024

Description of the work carried out during the STSM

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

(max. 500 words)

First task during the STSM was to simulate electronic absorption spectrum for the naphthalene molecule using Wigner distribution at ACD(2)/cc-pVDZ level of theory. We observed two naphthalene characteristic and distinctive peaks as showed in Figure 1. Afterwards, we performed nonadiabatic dynamics using CASPT2(10,10) method for selected geometries in the appropriate energy window. Orbitals considered in the active space are presented in Figure 2. Relative energies for the ground and the excited states along trajectories for the two selected nonadiabatic (NAD) simulations are compiled in the Figure 3.

Two distinctive behaviours during nonadiabatic simulations are observed. As showed in Figure 3., for representative NAD trajectories, both starting adopted geometries are excited to the bright S_2 state. Upper panel show trajectory with the transition to the S_1 state quickly after the excitation in which system stayed until the end of the dynamics. I took only ≈ 60 fs for the system to reach S_2/S_1 conical intersection. For the NAD presented in the lower panel, system also exhibit quick transition to the S_1 state (≈ 120 fs). The plan was to identify and extract vibrational motions that couple the two lowest excited states.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

However, for the presented trajectory, around 650 fs active state becomes highly excited S_5 electronic state.

Description of the STSM main achievements and planned follow-up activities

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

(max. 500 words)

Primary goal of the STSM was to investigate whether vibrational motion can establish a coupling between the two lowest electronic states and influence the diabatic exchange of populations. However, we found that the hopping criteria used in Tully's surface hopping algorithm was not adequate since we used a condition that total kinetic energy is greater than potential energy separation between two adjacent electronic states. In this STSM we addressed this issue, i.e. implemented a new hopping condition which considers only the kinetic energy component directed towards gradient of the potential. Extended testing are being conducted.

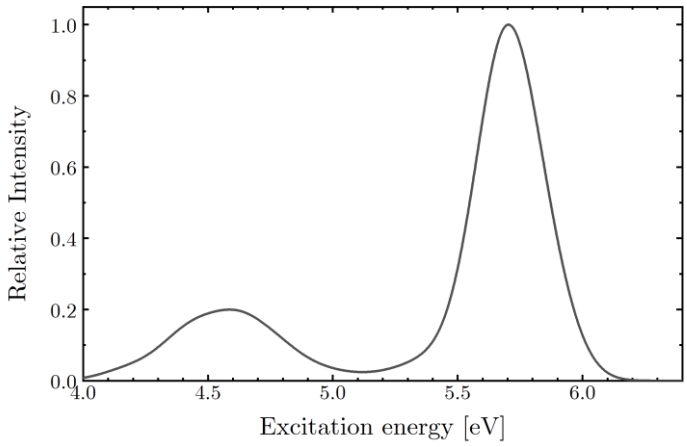


Figure 1. Simulated absorption spectra using Wigner distribution at ACD(2)/cc-pVDZ level of theory.

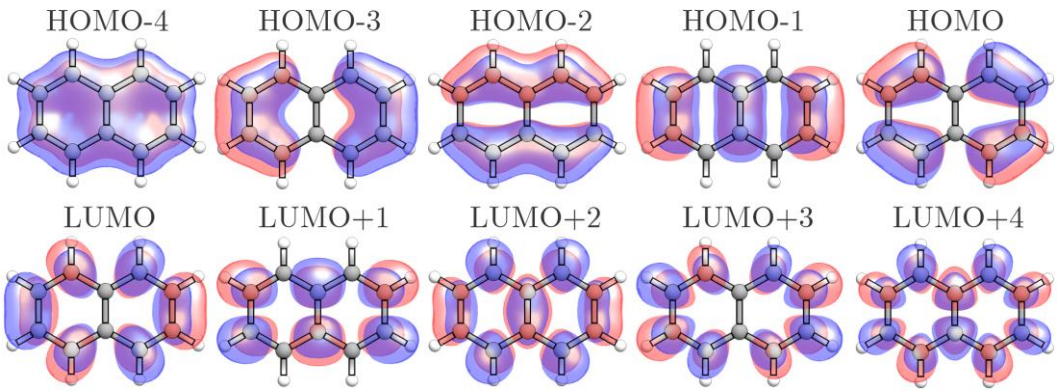


Figure 2. Molecular orbitals considered in the active space.

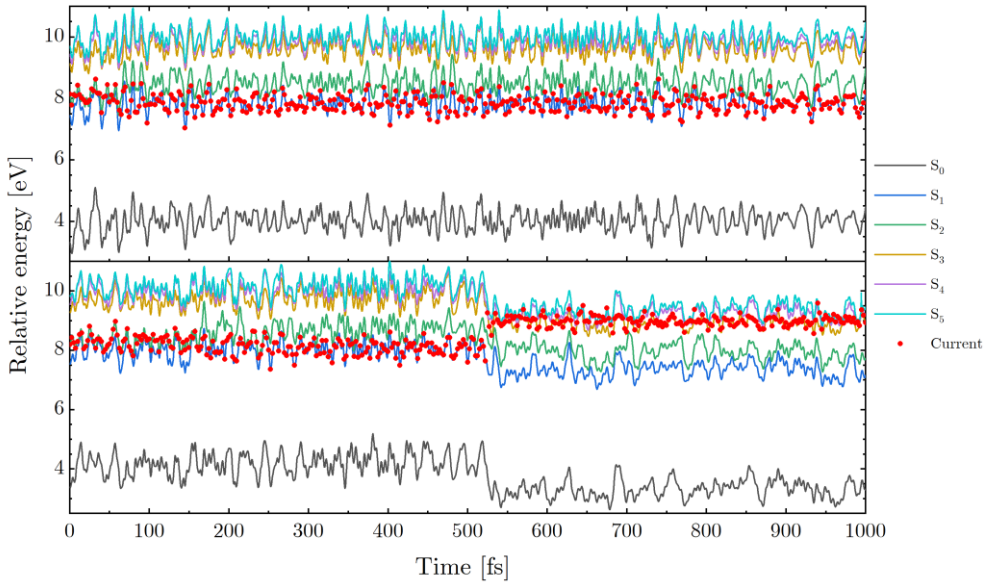


Figure 3. Selected nonadiabatic trajectories.