Electronic Supplementary Information

for

Excited State Dynamics of Thiophene and Bithiophene: New Insights into Theoretically Challenging Systems

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Contents

1. Triplet excitation energies of thiophene and bithiophene

Table S1. Triplet excitation energies (in eV) of thiophene and bithiophene at the ADC(2)/def2-SVPD level.

Thiophene	$B_2(\pi_3\pi_4{*})$	$A_1(\pi_2\pi_4{*})$	$B_1(\pi_3\sigma{*})$	$A_1(\pi_3\pi_5{*})$	$A_2(\pi_2\sigma{*})$
ADC(2)	4.09	4.95	6.28	6.34	6.37

Bithiophene	$B(\pi_6\pi_7{*})$	$A(\pi_6\pi_8{*})$	$A(\pi_5\pi_7{*})$	$B(\pi_4\pi_7{*})$	$B(\pi_6\sigma{*})$
ADC(2)	3.19	4.19	4.65	4.72	5.60

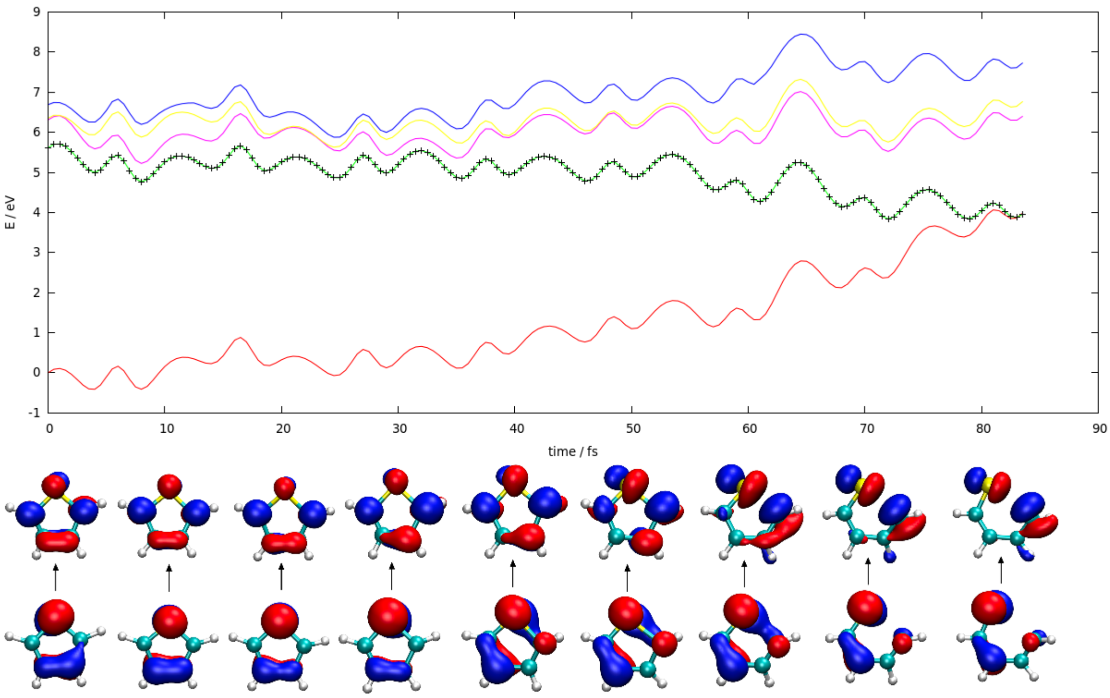
2. Trajectory analysis with natural transition orbitals

The excited states were analyzed by means of natural transition orbitals to gain a better insight into the ring opening and ring puckering mechanisms of thiophene. Figure S1 depicts two of the trajectories shown in Figure 3a (ring opening) and 3c (ring puckering) of the main text, both exhibiting a deactivation by adiabatic change of character. The orbitals are plotted for each 10fs frame, and correspond to the running S_1 state.

In the first example (Figure S1a), the system is initially excited into S_1 ($\pi_2\pi_4{*}$ character). By passing the avoided crossing between 30 and 40fs, initial orbital changes its shape, while the overall character looks like a mixture between $\pi_2\pi_4{*}$ and $\pi_3\pi_4{*}$. In terms of Hartee-Fock orbitals, the S_1 state, which is initially dominated by the excitation from the HOMO-1 (30fs) changes to an excitation from the HOMO (40fs). A transition from $\pi\pi{*}$ to $\pi\sigma{*}$ occurs only between 50 and 60fs, which is associated with a rather large avoided crossing with the S_2 state. This is followed by a rapid increase of ground state energy (> 60fs) until the crossing between S_1 and S_0 is encountered (80fs). Weinkaufet al.[1] also found that the system spends most of the time in the$\pi\pi^*$ states, which is followed by a fast ring opening due to the $\pi\sigma^*$ character. As shown in the Figure, the natural transition orbitals change their shape significantly as the geometry gets distorted, and the relation with the orbitals of the optimized geometry is not straightforward. Here we follow the notation as used earlier by Marian et al.[2] and Stenrup,[3] and assign the ring opening to the $\pi_3\sigma^*$ state (see Figure 3 in the main text).

In case of the ring puckering trajectory (Figure S1b), the molecule is excited into S_1 with a $\pi_2\pi_4^*$ character. The transition to $\pi_3\pi_4^*$ occurs between 30 and 40 fs, when the system proceeds to the ring-distorted intersection with the ground state.

a)



b)

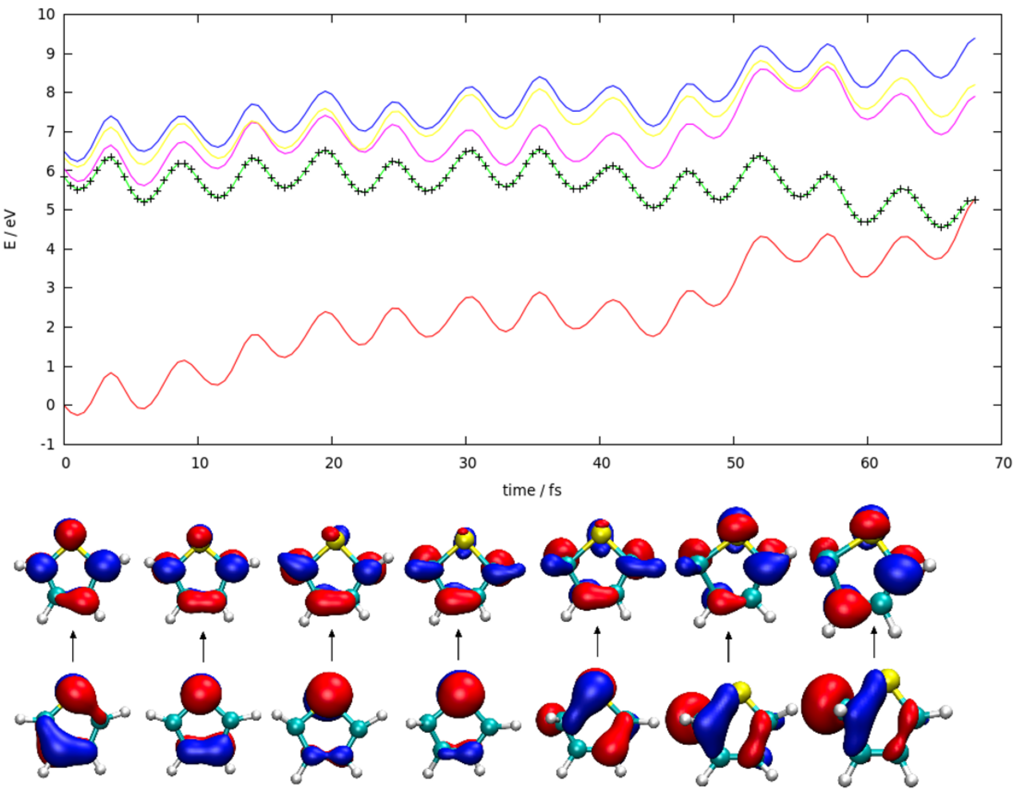


Figure S1. Energy profiles of two trajectories shown in Figure 3a (ring opening) and 3c (ring puckering) of the main text. The time evolution of the ground and four lowest excited adiabatic singlet states are given in color, while the black dots correspond to the running state. The energies are plotted with respect to the initial ground state energy (0fs). Natural transition orbitals with the largest contribution to the S_1 (running) state are displayed for each 10fs frame.

3. CS bond stretch

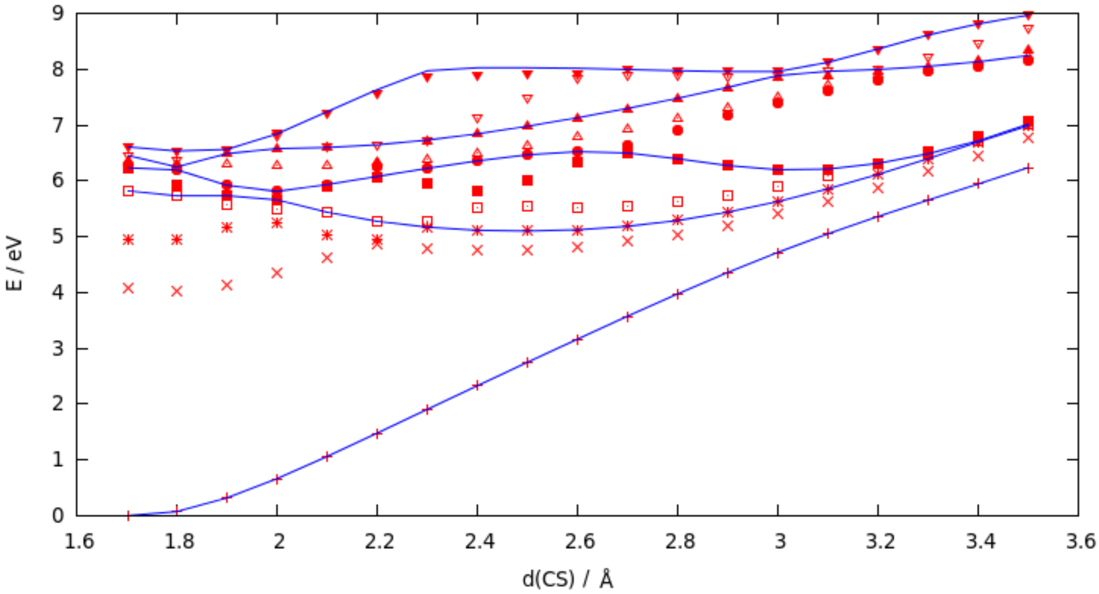


Figure S2. Evolution of the potential energies of the ground and excited states with respect to the rigid stretch of the CS bond distance. The ground and nine excited states (singlets and triplets) computed with unrestricted MP2+ADC(2)/def2-SVPD are depicted in red, and compared to the results obtained with restricted formalism (the ground and four lowest singlet states are depicted in blue).

4. Additional trajectories

In addition to the 200 thiophene trajectories presented in the main text, we computed additional ones, especially for the initial conditions of the S_1 state occurring below the selected S_1 window (< 5.70 eV; see Figure 2a in the main text) and for the initial S_2 conditions falling within the 5.70 ± 0.15 eV range (S_1 window). In both cases, the 10 test trajectories lead to an ultrafast relaxation via ring opening and ring puckering. In the first set of trajectories started at S_1, seven of them terminated with a ring opening and three with a ring puckering. For those initiated at S_2 with an excitation energy entering the 5.70 ± 0.15 eV window, five trajectories underwent a ring opening and five a ring puckering mechanism. Interestingly, in one of the trajectory the ring puckering proceeded through a pyramidalization at the β-carbon (with respect to sulphur, see Figure S3), a mechanism that was unidentified in the original computations.

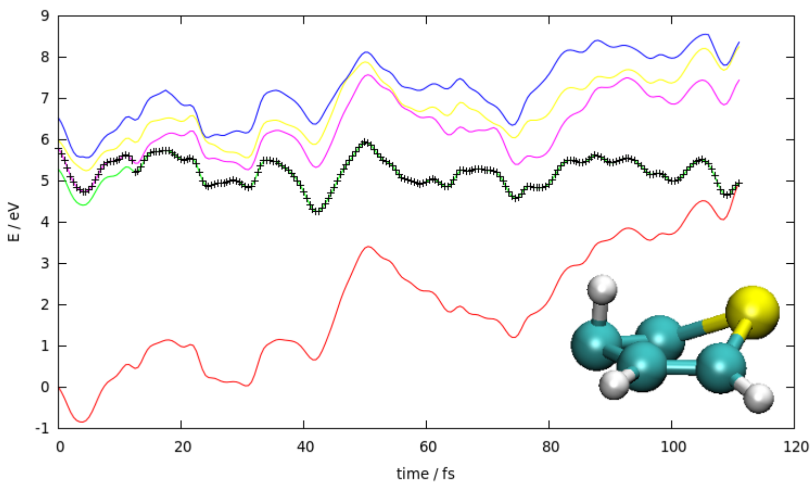


Figure S3. Energy profiles of the trajectory undergoing the ring puckering mechanism. The time evolution of the ground and four lowest excited adiabatic singlet states are given in color, while the running state is indicated by the black dots. The energies are plotted with respect to the initial ground state energy (0fs). The displayed molecular geometry is taken at the final step of the dynamics.

5. Analysis of the D_1 parameter

The D_1 diagnostics of ADC(2) measures the quality of the ground state wavefunction. Values around 0.04 (and smaller) indicate that problems with the multireference character should not be expected. However, values as high as 0.10 and 0.15 may eventually be acceptable.[4] In Figure S4, we show two thiophene trajectories with ring opening (upper left panel) and and ring puckering mechanism (upper right panel). As shown in the Figure, the D_1 values increase significantly only before the intersection with the ground state, a region where single reference method is not appropriate. However, most of the excited state dynamics (which will finally bring the system close to this crossing region) is considered as reliable. This is further illustated by the histogram in Figure S5 which shows the D_1 values are in the acceptable range formost of the time. Similar conclusion holds for bithiophene dynamics (Figure S6).

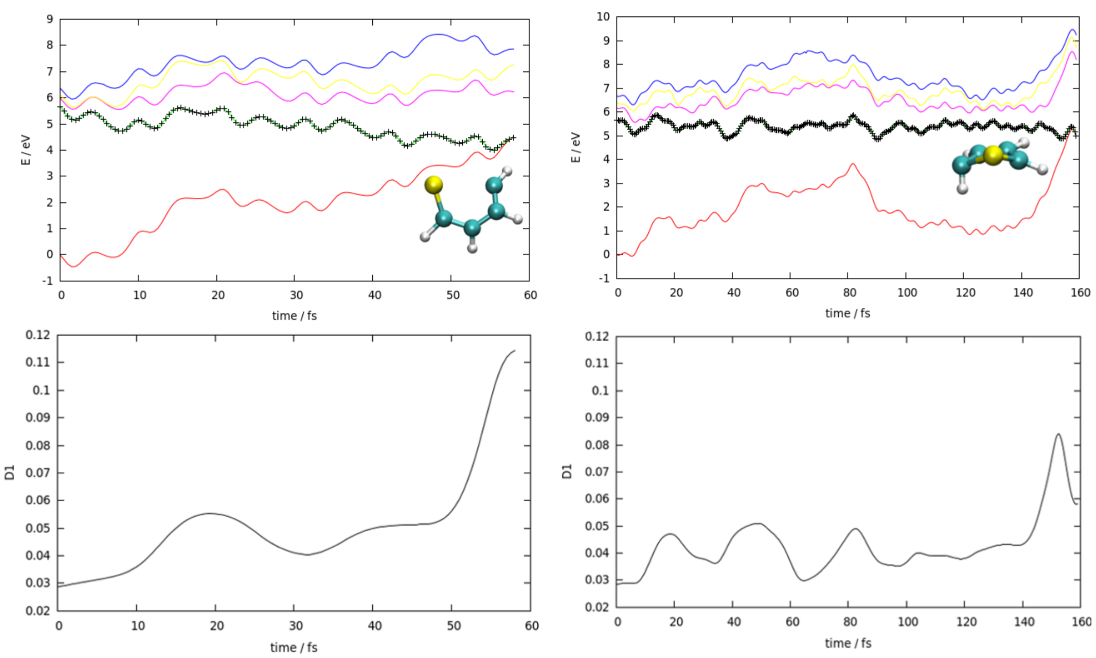


Figure S4. Energy profiles for two thiophene trajectories corresponding to the ring opening (upper left panel) and ring puckering mechanism (upper right panel). The time evolution of the ground and the four lowest excited adiabatic singlet states are shown, while the running state is indicated in black. Energies are plotted relative to the initial ground state energy (0fs). The molecular geometry at the final step of the dynamic is shown.The lower panels display the time evolution of the D_1 parameter.

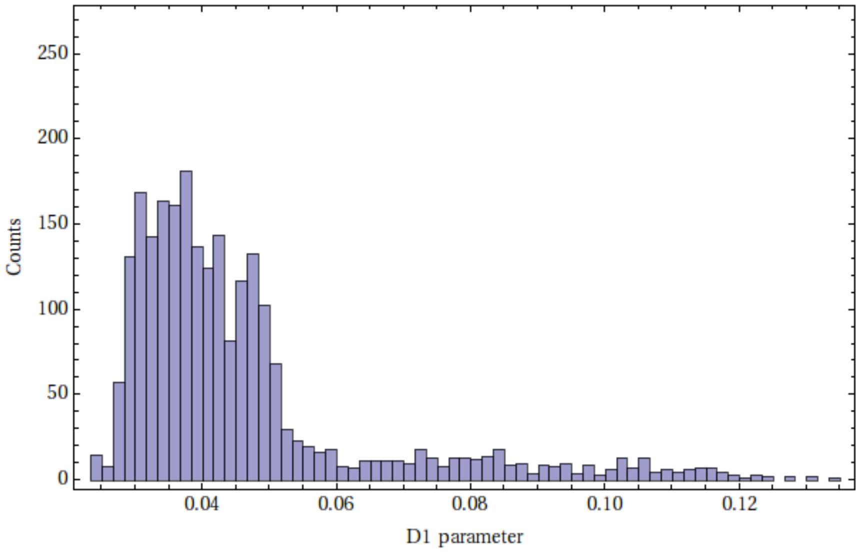


Figure S5. Histogram of the D_1 values based on 10 randomly chosen thiophene trajectories including both ring opening and ring puckering. All the nuclear time steps are considered in analysis.

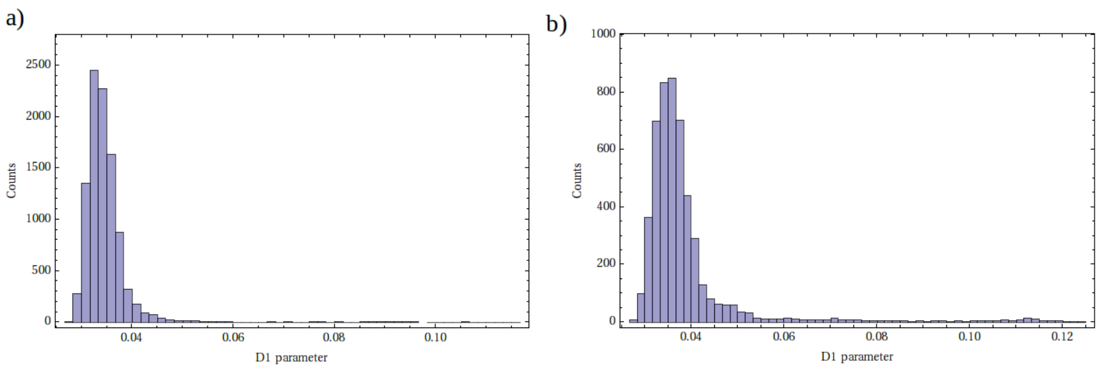


Figure S6. Histograms of the D_1 values based on 10 randomly chosen bithiophene trajectories from: a) lower and b) higher energy window. All the nuclear time steps are considered in analysis.

6. References

(1) R. Weinkauf, L. Lehr, E. W. Schleg, S. Salzmann and C. M. Marian, *Phys. Chem. Chem. Phys.*, 2008, **10**, 393.

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(3) M. Stenrup, *Chem. Phys.*, 2012, **397**, 18.

(4) A. Köhn and C. Hättig, *J. Chem. Phys.*, 2003, **119**, 5021.