

Supporting Information for “A real-time time-dependent density functional tight-binding implementation for semiclassical excited state electron-nuclear dynamics and pump-probe spectroscopy simulations”

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1 Additional data for section 4

1.1 Molecular dynamics

In order to study the influence of the temperature in the charge transfer process we sample the complex configuration space using a Born-Oppenheimer molecular dynamics scheme. We have simulated 25 ps with a time step of 0.25 fs at 300 K (linearly increasing the temperature in the first 1000 steps) for the system described in the present work ($C_{190}H_{110}+PDI$), within a NVT ensemble using an Andersen Thermostat. The figure 1 shows the total energy and the temperature throughout the simulated time.

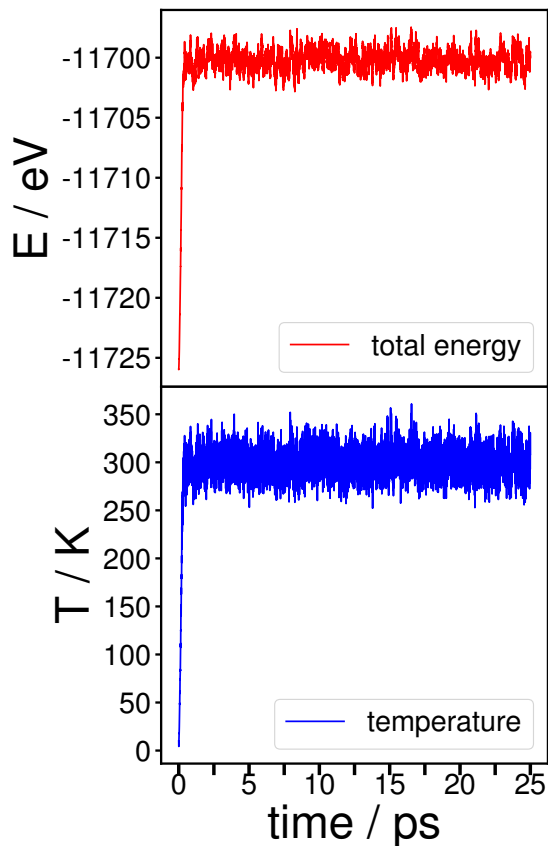


Figure 1: (up) Total energy of the system as a function of time.(bottom) Temperature of the system as a function of time.

1.2 Velocity autocorrelation function

The velocity autocorrelation function (VAF) was calculated by averaging over the entire 25 ps MD trajectory with a correlation time window of 5 fs, following previous strategies and methods.¹ In the figure 2 the correlation function as a function of time and the exponential fitting can be seen, showing the decay of the autocorrelation.

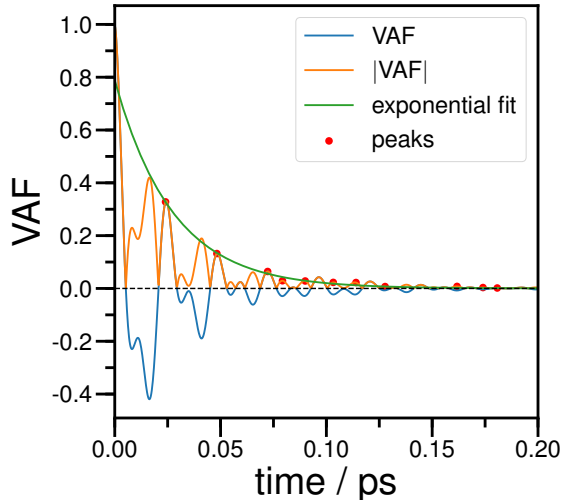


Figure 2: Velocity autocorrelation function as a function of time (blue), absolute value of the function (orange), peaks of the oscillations (red) and exponential decay fit (green).

1.3 Relevant details of the selection of frames and Ehrenfest dynamics

To study the influence of the temperature in the charge transfer process we took 15 configurations after 6.25 ps, in intervals of 1.25 ps between them to ensure decorrelation. Note that this separation time is roughly 10 times bigger than the decorrelation time calculated (See figure 2). Then, we ran Ehrenfest dynamics for each configuration and initial velocities sampled from the molecular dynamics. The pulse perturbation was in tune with the acceptor excitation energy calculated for the optimized geometry in all cases.

References

- (1) *Journal of Chemical Theory and Computation* **2015**, *11*, 3357–3363.