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Supplementary Information for: A Molecular Perspective on Tully Models for Nonadiabatic Dynamics

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Abstract

The following document contains additional information on the dynamics of DMABN and fulvene (as mentioned in the main text), as well as a comment on the computational cost of the fulvene dynamics with dTSH and AIMS.

The initial conditions for all the nonadiabatic dynamics presented in the main text are provided as an external zip file ('molecular_tully_models.zip', see webpage of the Journal, in the supporting information section).

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I. ADDITIONAL INFORMATION ON THE DYNAMICS OF DMABN AND FULVENE

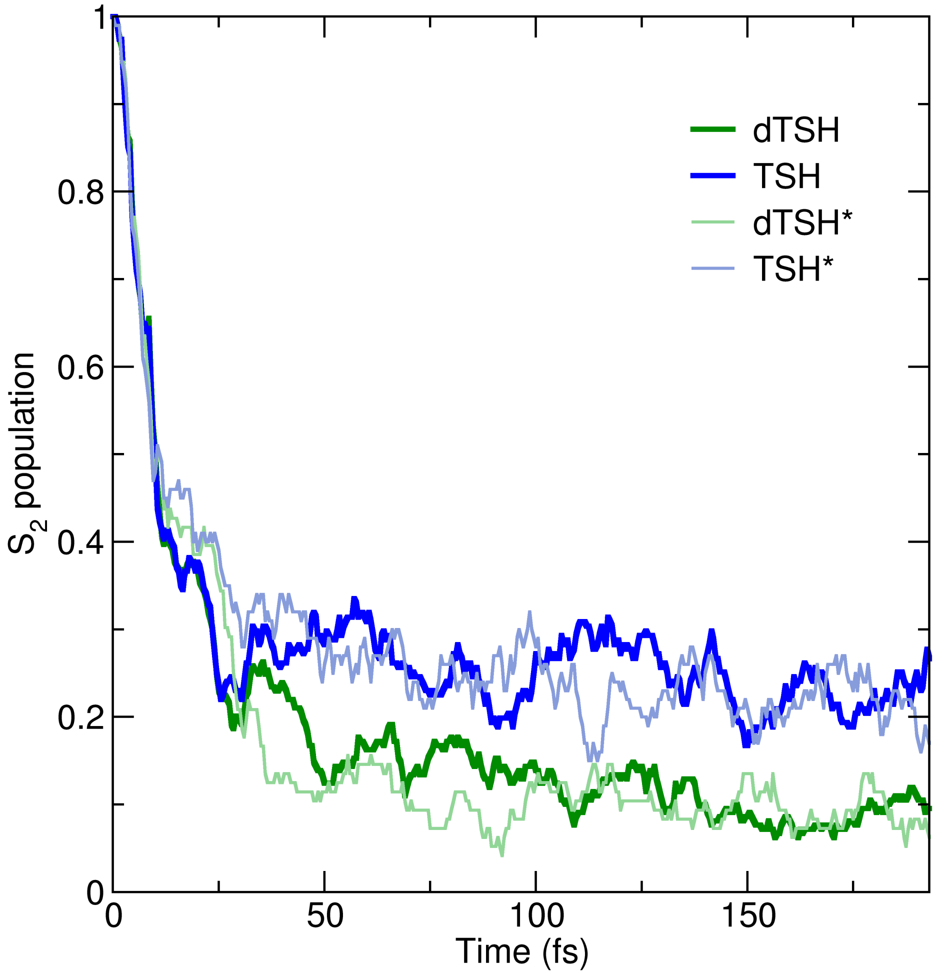

FIG. S1: Photodynamics of DMABN as a molecular Tully model II. TSH (blue) and decoherence-corrected TSH ('dTSH', green) are the population traces depicted in the main text and obtained with 21 initial conditions each repeated 10 times. TSH* (light blue) and dTSH* (light green) show the population trace for a different set of 100 initial conditions, each ran only once. The difference observed between the original trajectory surface hopping dynamics and the one using the EDC correction is evident from both set of initial conditions.

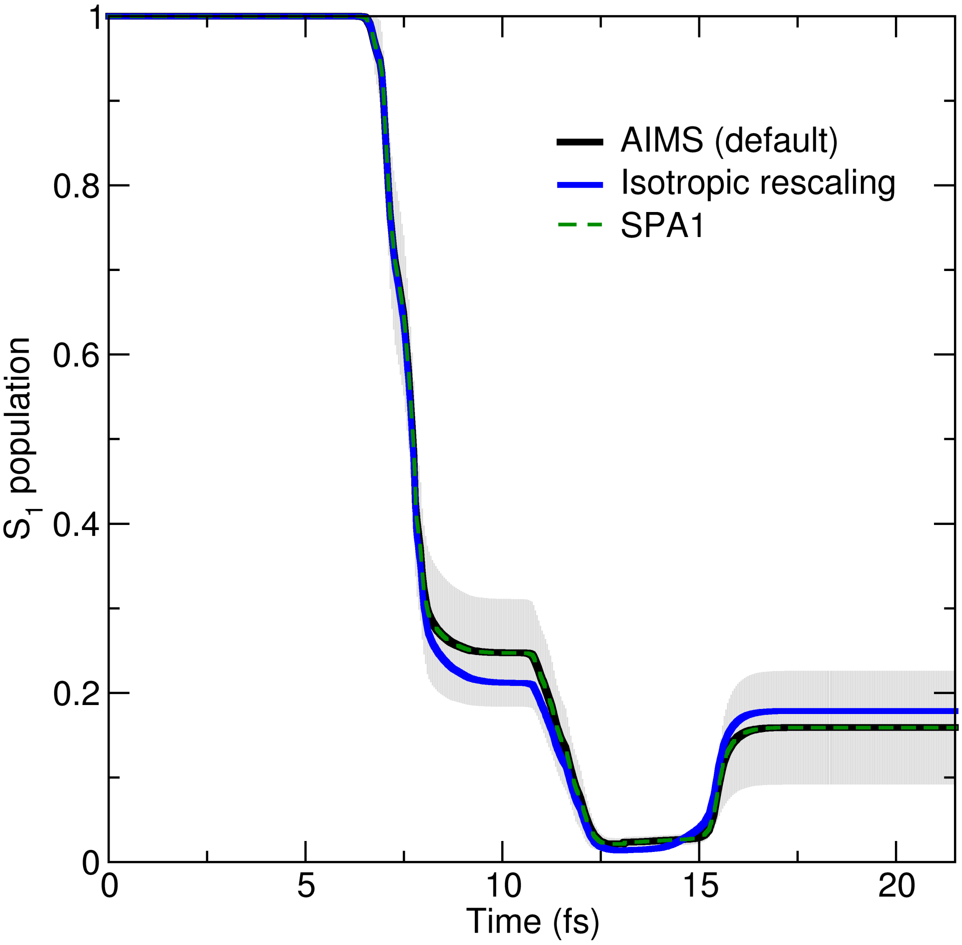

FIG. S2: Photodynamics of fulvene as a molecular Tully model III. Comparison between the AIMS population trace using a rescaling along the nonadiabatic coupling vectors (black, as presented in the main text) and AIMS using an isotropic rescaling of the child TBFs velocities following spawning (blue). Both AIMS dynamics are in close agreement. We also tested the influence of the SPA on the AIMS dynamics by employing the higher level SPA1 for all intrastate couplings (dashed green curve). The result of AIMS-SPA1 is in line with AIMS-SPA0.

	AIMS			dTSH		
	Number of child TBFs	Number of time steps	time (s)	Number of hops	Number of time steps	time (s)
IC A	1	131	$7.63\cdot10^3$	25	100	$2.48\cdot10^4$
IC B	8	284	$5.96\cdot10^4$	14	100	$2.56\cdot10^4$
IC C	15	339	$1.27\cdot10^5$	27	100	$2.52\cdot10^4$

TABLE S1: Number of spawns or hops, timings, and total number of time steps for the full dynamics (50 fs) of three initial conditions performed with AIMS (one run per initial condition) and dTSH (ten repetitions with different random seeds for each initial condition). Each timing given here is an average over three successive (independent) repetitions conducted on the same machine (one core on an Intel Xeon 6152, 2.1 GHz), where the AIMS and dTSH dynamics of the same initial condition were run simultaneously.

II. COMMENT ON THE COMPUTATIONAL COST OF DTSH AND AIMS FOR THE FULVENE PHOTODYNAMICS

A simple one-to-one comparison of the computational cost of the AIMS method as compared to TSH is not straightforward due to the difference in their respective implementation. The FMS90 code, as implemented in MOLPRO [1], employs two different nuclear integration time steps – one for the adiabatic propagation of the TBFs and one when TBFs evolve in a nonadiabatic coupling region. In addition, a variable time step procedure is used to ensure a proper total (classical) energy and norm conservation, as well as to make sure that a TBF does not jump over a nonadiabatic region over an integration time step. As a result, the number of time steps (and hence electronic structure calls) is significantly different from the ones of TSH (see Table S1). To provide an idea of the computational cost of an AIMS or a TSH run, we present the overall timings for an entire AIMS or dTSH dynamics (50 fs) starting from three different initial conditions of fulvene (Table S1). These three initial conditions were selected as they trigger a very different number of spawns in the AIMS dynamics. The dTSH dynamics starting from each initial condition was run ten times with different random seeds (as done for all (d)TSH dynamics in this work) and the timings of all the runs were added up. The computational effort for the different AIMS runs differs significantly, as a run with more spawns also implies a more frequent use of a reduced time step, resulting in a significantly larger number of electronic structure calculations to compute the couplings between all TBFs. We note that, formally, the number of electronic structure calculation per time step in an AIMS run with N_{TBFs} TBFs is proportional to $\frac{N_{\text{TBFs}}\times(N_{\text{TBFs}}+1)}{2}$. The number of time steps in the dTSH runs is constant at 100 for each of the 10 runs, as the size of the time step is fixed in the implementation employed. The number of hops, however, differs largely between the different repetitions, as the usage of different random seeds allows for a broader sampling of different nonadiabatic transitions (Table S1 gives the total number of hops in all 10 runs). The overall run time is, however, only marginally affected by this variation.

References

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[1] B. G. Levine, J. D. Coe, A. M. Virshup and T. J. Martinez, *Chemical Physics*, 2008, **347**, 3–16.