Ultrafast photo-induced dynamics of 1,3-cyclohexadiene using XMS-CASPT2 surface hopping: Supporting Information

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1 Cartesian coordinates for important geometries

Table 1: Cartesian coordinates for CHD ground state minimum energy geometry given in Bohr

C	0.599883	1.319040	-2.251994
C	0.094339	2.698095	0.201375
C	-0.077162	1.376330	2.396650
C	0.139605	-1.399504	2.380291
C	-0.089458	-2.699928	0.177574
C	-0.658624	-1.297231	-2.248348
H	2.673176	1.092395	-2.474471
H	0.012806	4.766414	0.209623
H	-0.347821	2.351884	4.201122
H	0.456969	-2.392557	4.167500
H	-0.008281	-4.768263	0.163631
H	-2.736979	-1.068427	-2.414828
H	-0.057408	2.438898	-3.881061
H	-0.043966	-2.401156	-3.904816

Table 2: Cartesian coordinates for the S_1/S_2 MECI geometry given in Bohr

C	0.647291	1.423284	-2.429970
C	0.175665	2.741027	-0.134238
C	0.422852	1.490177	2.247672
C	0.487297	-1.170903	2.417241
C	-0.143295	-2.729725	0.302728
C	-1.471953	-1.712672	-1.801927
H	2.365154	0.276087	-2.576701
H	-0.678299	4.628803	-0.199708
H	0.534769	2.617685	3.979753
H	1.059142	-2.058041	4.197584
H	0.669174	-4.632373	0.172554
H	-3.147656	-0.549419	-1.445013
H	0.055137	2.317102	-4.203556
H	-1.564570	-2.846970	-3.533961

Table 3: Cartesian coordinates for the S_0/S_1 MECI geometry given in Bohr

C	0.719178	1.581350	-2.699836
C	0.180564	2.438460	-0.222517
C	0.743529	1.273354	2.173099
C	0.780083	-1.377121	2.331794
C	-0.377938	-2.763823	0.371845
C	-1.825331	-1.255141	-1.345532
H	2.096901	0.086238	-3.043775
H	-0.815021	4.265048	-0.132726
H	0.893447	2.473047	3.847677
H	1.637300	-2.333289	3.958010
H	0.250727	-4.654966	-0.175133
H	-3.322241	-0.059807	-0.552172
H	0.152876	2.768803	-4.290545
H	-2.214502	-1.927543	-3.264459

2 Adiabatic population: Bootstrapping

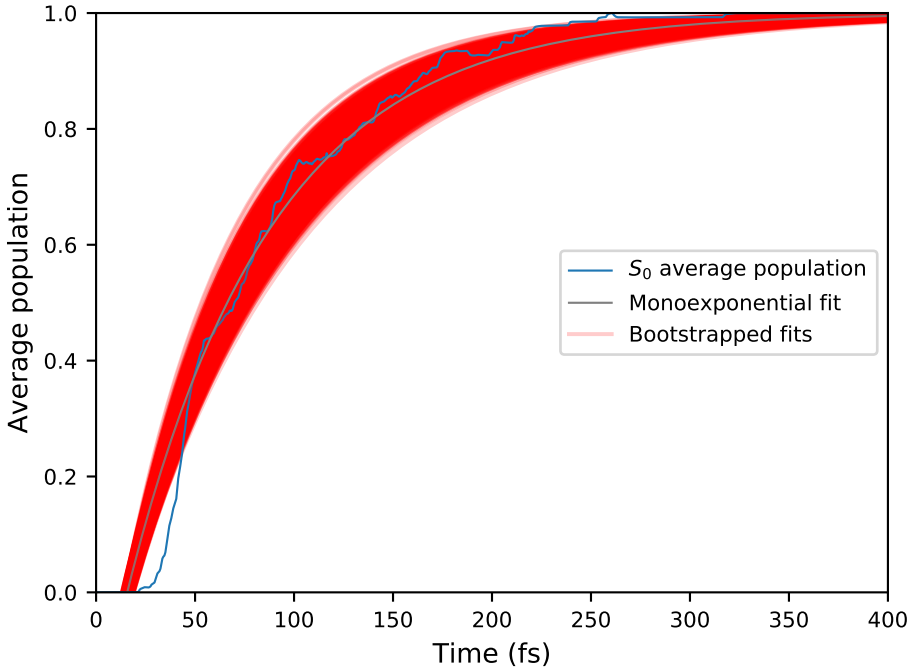

Figure 1: Average adiabatic population for the S_0 state, its monoexponential fit and fits to the 10000 samples drawn at random from the original set of 136 trajectories with replacement. The average decay constant, latency and associated margins of error are then calculated for the obtained distribution of fitted functions.

3 Energy conservation

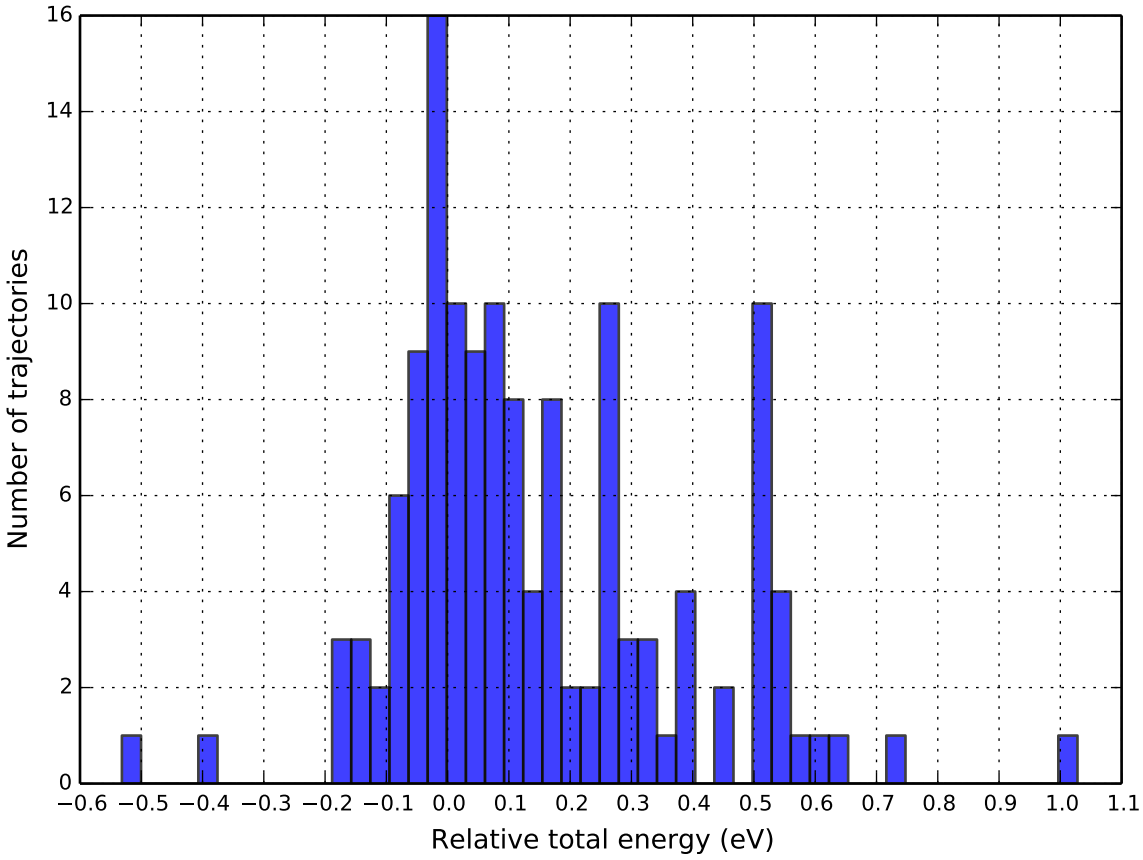

Figure 2: Distribution of final relative total energies, calculated as the difference between the total energy at the final and initial time steps for each trajectory. Trajectories having the relative total energy less than −0.5 eV or more than 0.5 eV have been stopped prematurely.

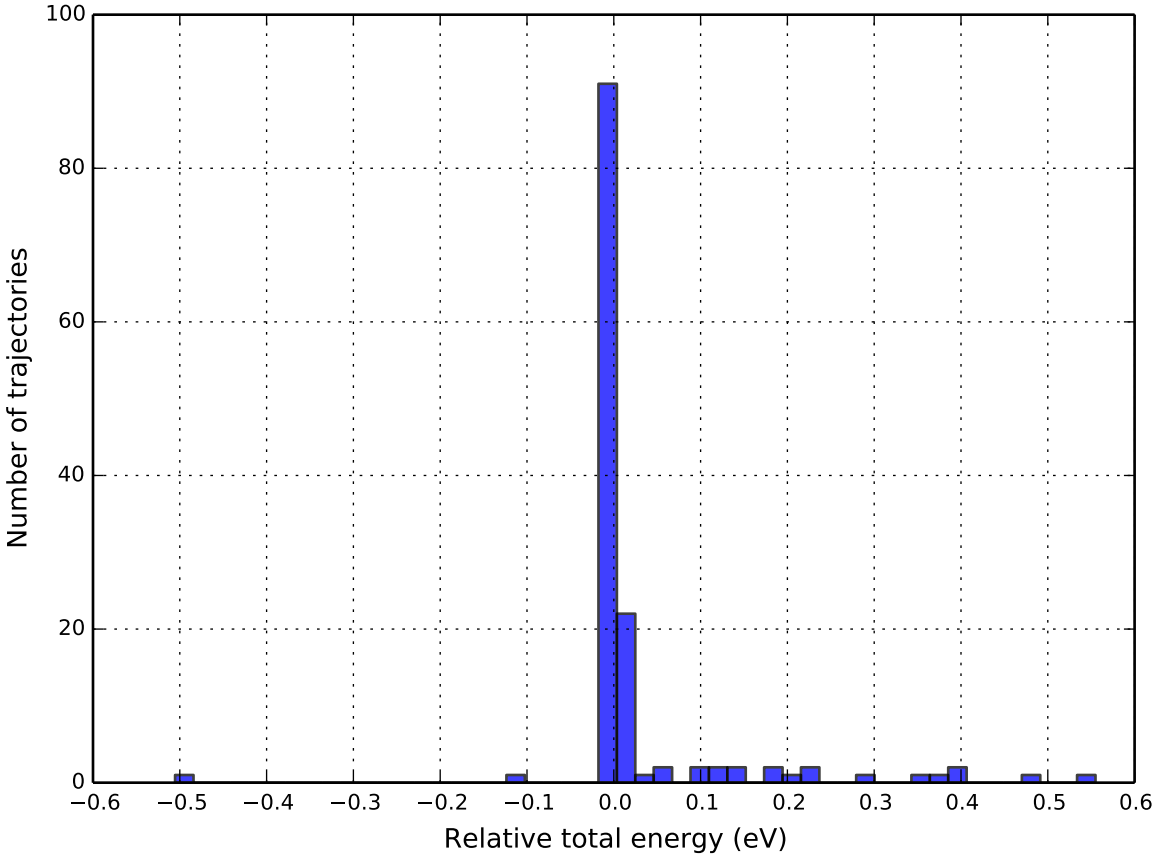

Figure 3: Distribution of final relative total energies, calculated as the difference between the total energy at the final and the last but one time steps for each trajectory. Trajectories having the relative total energy less than -0.5 eV or more than 0.5 eV have been stopped prematurely.

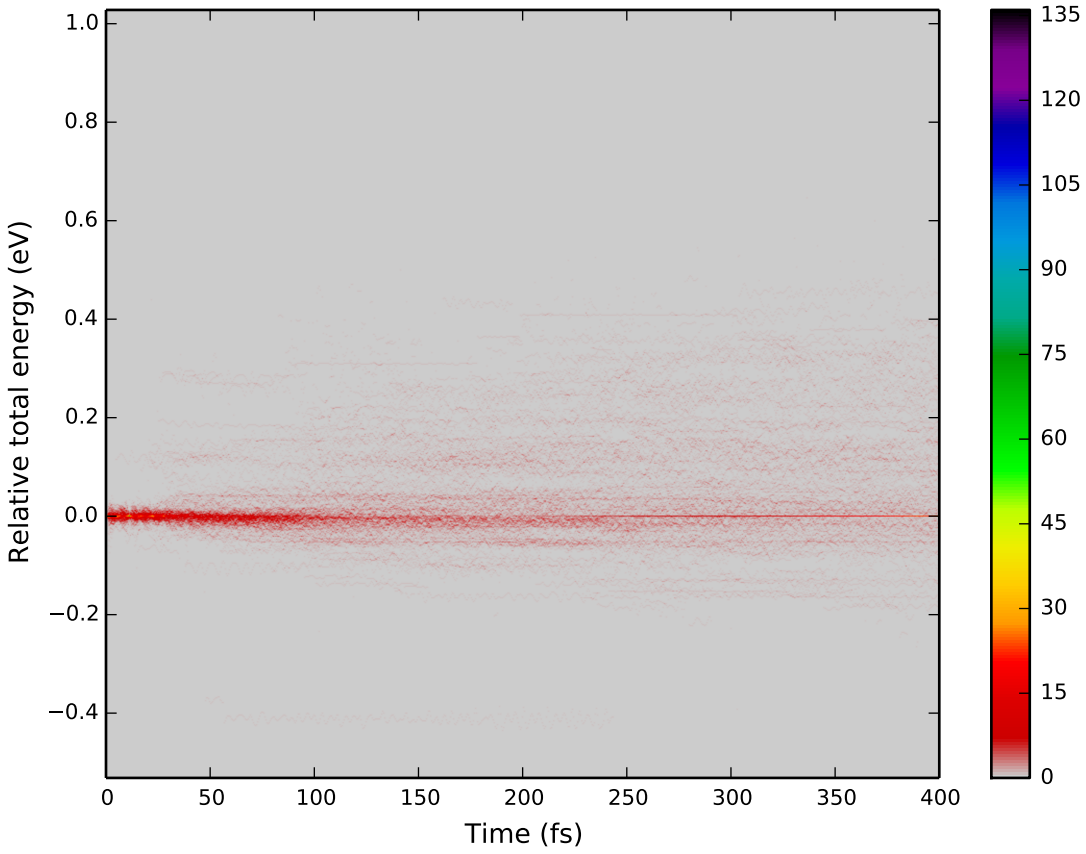

Figure 4: Relative total energy evolution heatmap, calculated for an ensemble of 136 trajectories. Trajectories that have reached the total energy drift of more than 0.5 eV have been stopped prematurely.

4 Computational costs

All calculations have been performed on the two-socket Intel Xeon Gold 6148 CPU @ 2.40GHz with 20 cores per socket. A single step (including calculation of XMS-CASPT2 energy, gradients and NAC) took approximately 2.5 min on average, using shared-memory OpenMP parallelisation over 20 cores per trajectory (resulting in one successful trajectory with 1600 0.25 fs-steps taking $\sim$ 66.5 hrs). We note that shared-memory parallel scaling of XMS-CASPT2 was not very good in our build of BAGEL, so it would take only slightly longer to run the same calculations with only 4 cores per trajectory.