

Electronic Supporting Information

Ultrafast Dynamics and Excited-State Trapping in [3.3]Paracyclophane

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SI-1. IR Spectrum of [3.3]PCP at the S_0 minimum

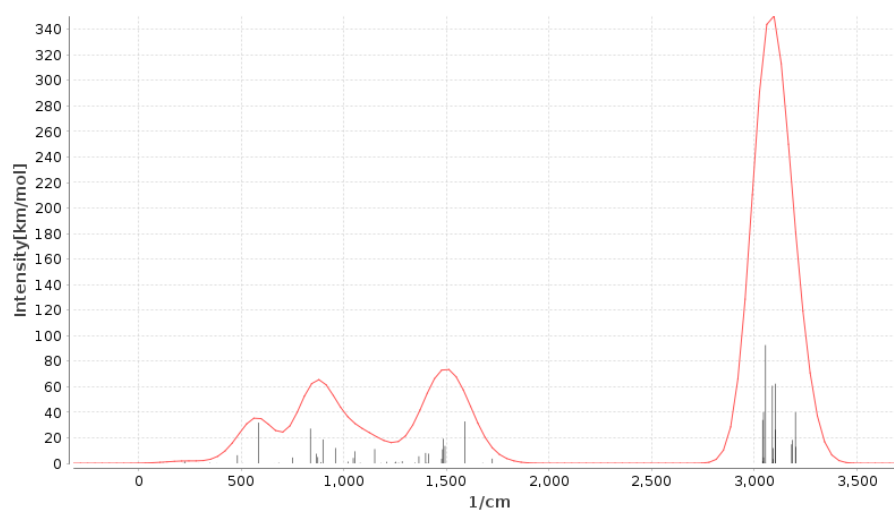


Figure SI 1. Simulated IR spectrum of [3.3] PCP computed with DFT at the CAM-B3LYP/def2-SV(P)+D4 level.

SI-2. Surface hopping results with other velocity rescaling algorithms

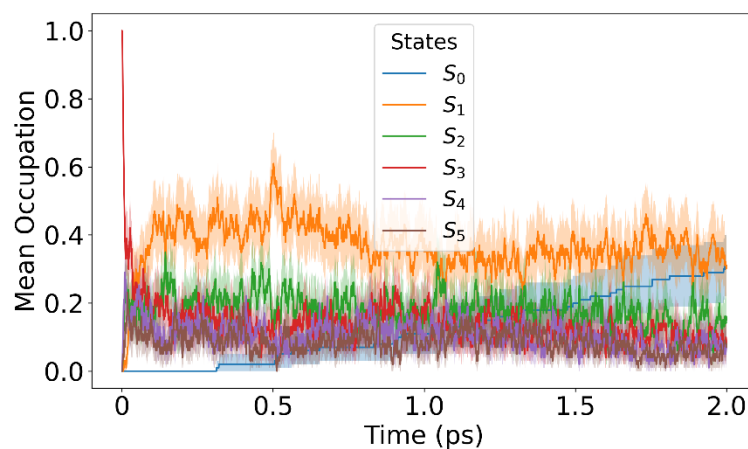


Figure SI 2. Mean state occupation over time from surface hopping dynamics using momentum rescaling along the momentum direction with full kinetic energy reservoir (**p**).

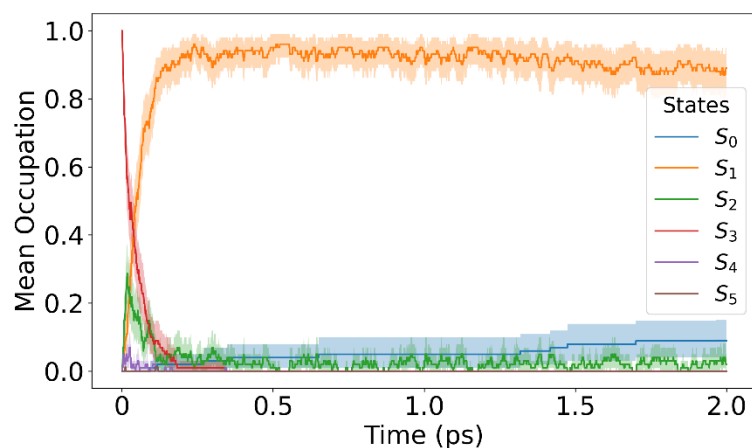


Figure SI 3. Mean state occupation over time from surface hopping dynamics using momentum rescaling along the momentum direction with reduced kinetic energy reservoir (**p-redKE**).

SI-3. Internal conversion pathway

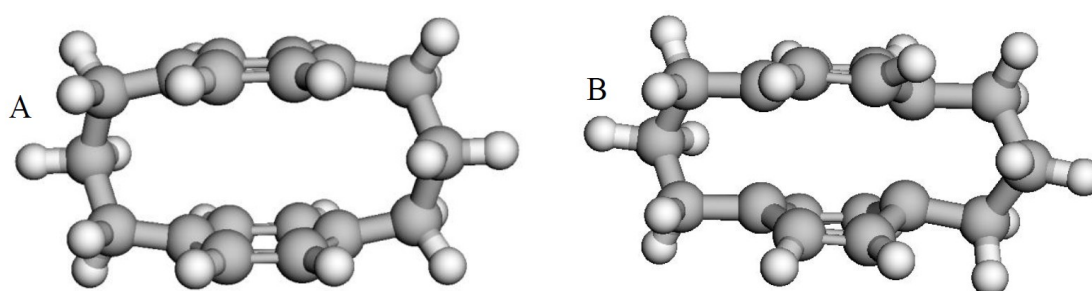


Figure SI 4. A) Ground state minimum and B) the S_1/S_0 intersection geometry.

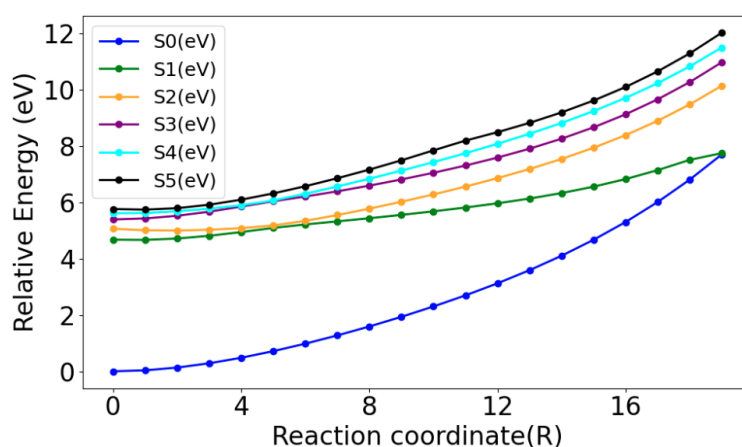


Figure SI 5. Plot of linear interpolation of internal coordinates between the ground state minimum and the S_1/S_0 intersection geometry.

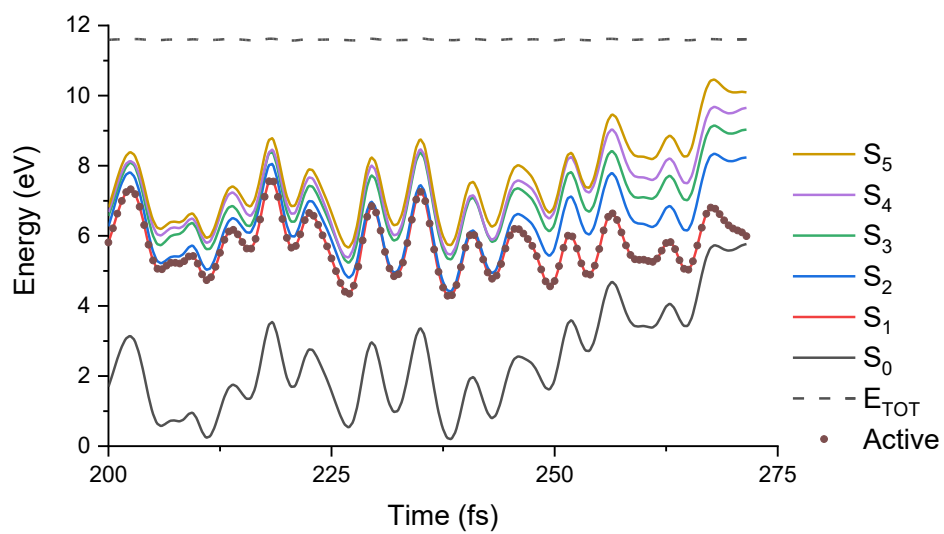


Figure SI 6. Potential energies as a function of time for a single trajectory reaching the crossing region between S_1 and S_0 .

SI-4. [3.3]PCP Cartesian coordinates

All geometries optimized with (TD)DFT at the CAM-B3LYP/def2-SV(P)+D4 level. Values in Angstrom.

S₀ minimum

C	0.5819403	-1.6710825	1.2402921
C	1.4065548	-1.5127761	0.1252463
C	0.7963351	-1.5069848	-1.1297086
C	-0.5876805	-1.5034397	-1.2534817
C	-1.4131562	-1.5211999	-0.1294325
C	-0.8028668	-1.6834538	1.1155798
H	1.0318323	-1.7193195	2.2364552
H	1.4100509	-1.4275799	-2.0318236
H	-1.0372592	-1.4157905	-2.2470391
H	-1.4197348	-1.7451813	2.0175212
C	0.6272446	1.6263567	1.2896780
C	1.4538428	1.6426553	0.1664694
C	0.8448298	1.8037938	-1.0793434
C	-0.5398047	1.7914189	-1.2054320
C	-1.3655807	1.6342681	-0.0910371
C	-0.7566878	1.6301640	1.1645180
H	1.0757692	1.5395256	2.2837814
H	1.4626408	1.8641236	-1.9807245
H	-0.9887435	1.8385585	-2.2020785
H	-1.3711638	1.5523905	2.0662433
C	-2.8506222	1.3825155	-0.2356550
H	-3.4135854	2.2113576	0.2302497
H	-3.1171224	1.3951983	-1.3065399
C	-3.3565244	0.0720374	0.3969064
H	-3.0914423	0.0621972	1.4686699
H	-4.4598874	0.0908980	0.3629931
C	-2.8958269	-1.2521676	-0.2426899
H	-3.4621057	-2.0672287	0.2419643
H	-3.1880175	-1.2607245	-1.3068929
C	2.9363058	1.3730555	0.2814714
H	3.2266824	1.3790062	1.3461859
H	3.5036183	2.1892432	-0.2001189
C	3.3976222	0.0504521	-0.3607806
H	3.1331198	0.0626512	-1.4326700
H	4.5009608	0.0312283	-0.3262783
C	2.8918407	-1.2618003	0.2684404
H	3.4538899	-2.0892274	-0.2010365
H	3.1600047	-1.2778474	1.3388636

S₁ minimum

C	0.5928995	-1.4839698	1.2624652
C	1.4081456	-1.4254714	0.1192966
C	0.7997748	-1.4846520	-1.1610978
C	-0.5923418	-1.4853242	-1.2611273
C	-1.4076087	-1.4260257	-0.1180143
C	-0.7992197	-1.4838195	1.1624361
H	1.0683491	-1.4873875	2.2468046
H	1.4181724	-1.5217418	-2.0596830
H	-1.0677902	-1.4897851	-2.2454623
H	-1.4176012	-1.5202558	2.0610583
C	0.5922957	1.4854403	1.2611439
C	1.4076175	1.4260665	0.1180728
C	0.7992725	1.4839063	-1.1624022
C	-0.5928412	1.4840243	-1.2624875
C	-1.4081433	1.4254575	-0.1193608
C	-0.7998182	1.4847267	1.1610587
H	1.0676980	1.4899753	2.2455018
H	1.4176849	1.5203998	-2.0610016
H	-1.0682470	1.4874583	-2.2468493
H	-1.4182470	1.5218644	2.0596199
C	-2.8965904	1.2858934	-0.2402199
H	-3.3858336	2.1430072	0.2608625
H	-3.1887171	1.3244472	-1.3027793
C	-3.4495242	-0.0004491	0.3956183
H	-3.2264082	0.0001257	1.4754566
H	-4.5493321	-0.0007023	0.3044619
C	-2.8961143	-1.2872192	-0.2389332
H	-3.3849525	-2.1440236	0.2630714
H	-3.1882936	-1.3270092	-1.3014325
C	2.8961125	1.2871235	0.2390624
H	3.1882180	1.3267176	1.3015897
H	3.3850606	2.1439676	-0.2627699
C	3.4495058	0.0004160	-0.3956394
H	3.2263647	-0.0000587	-1.4754725
H	4.5493154	0.0006585	-0.3045113
C	2.8966010	-1.2860025	0.2400732
H	3.3857639	-2.1430677	-0.2611721
H	3.1888126	-1.3247211	1.3026026

S_1/S_0 crossing

C	0.5983155238	-1.5066099104	1.2545843787
C	1.4369247379	-1.1322825238	0.1025621553
C	0.7687909059	-1.4072543835	-1.1872922478
C	-0.5896294283	-1.4559991663	-1.3015262983
C	-1.4603525312	-1.1429126606	-0.1576262001
C	-0.7326384941	-1.4164986634	1.1350961983
H	1.1119446803	-1.9348518874	2.1701903598
H	1.5556478516	-1.7787411370	-1.9451515691
H	-0.9502424750	-1.2982378855	-2.3180293402
H	-1.2477513084	-1.6832266977	2.1073138136
C	0.5693382148	1.4682620517	1.3361076894
C	1.4165842627	1.0566891340	0.1445869374
C	0.8161253284	1.6222518534	-1.0996493741
C	-0.5091286872	1.5965932210	-1.2155344515
C	-1.4025453304	1.2523650656	-0.0670205314
C	-0.7721408977	1.5479913234	1.2576187853
H	0.9763352431	1.6599947631	2.3851323611
H	1.3873928699	1.8698908793	-2.0500138044
H	-0.7591424478	2.1161136763	-2.1484764740
H	-1.4094299573	1.4904217091	2.1977480153
C	-2.9759912742	1.3146266214	-0.2085079422
H	-3.4401348743	2.1774564492	0.2481868125
H	-3.1298210963	1.3855028469	-1.2923733355
C	-3.5754077837	0.1043197681	0.4693491592
H	-3.0818030216	0.0699272753	1.4620133982
H	-4.7300591191	0.0153149189	0.3853732741
C	-2.9847669739	-1.0914794394	-0.1808201868
H	-3.4485070555	-2.0532444173	0.1958376589
H	-3.3057330634	-0.9646160013	-1.2120616805
C	2.9791685945	1.2743097615	0.2489770948
H	3.3450900912	1.3705125288	1.3250906416
H	3.1513505126	2.2989347950	-0.3225635474
C	3.7253083910	0.0942454229	-0.3803822643
H	3.4675626283	-0.0562996305	-1.4211162213
H	4.8139290640	0.0488896171	-0.1875237703
C	3.0435375232	-1.1722948852	0.1776594999
H	3.4519362538	-2.0984908353	-0.3577321594
H	3.3697735220	-1.1433108994	1.2254301052