Supporting Information for:

Photochemical dynamics of ethylene cation $C_2H_4^+$

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This document contains a comparative table of oscillator strengths and excitation energies at the different levels of theory used in the accompanying paper, and geometries in Cartesian coordinates and energies (in Angstrom and Hartree) for all points of interest described in Fig. 2. All calculations were done with the 6-311G** basis set. For the dynamical trajectories, two active spaces have been used. For excitations to D_1 and D_2, an active space averaging over the three lowest double states was used, with eleven electrons in eight orbitals (SA3-CASSCF(11/8)). For excitations to D_3, an active space averaging over the four lowest doublet states was used, with eleven electrons in seven orbitals (SA4-CASSCF(11/7)). Besides the three highest σ orbitals involved in the excitations, the π and the π^* orbitals, these two active spaces contain two additional low-lying σ orbitals for increased flexibility of the electronic wavefunction during the on-the-fly calculations. Dynamical trajectories initiated on D_1 and D_2 states also allowed the possibility to add one σ^* in the active space, while it was not possible for trajectories on D_3 due to the presence of a $\pi\pi^*$ intruder state. Results at the CASSCF level with multi-state perturbation theory corrections (XMS-CASPT2) are used to provide accurate thermochemical data on the ground-state as well as to validate the on-the-fly CASSCF calculations by comparing the optimized MECIs (SA4-CASPT2(11/7)). All optimizations were performed with the MOLPRO 2012 package and the FMS-MOLPRO program was used for dynamics calculations. A level shift of 0.2 Ha was achieved for all the MECI optimizations. For the ground state minima and transition states at the CASPT2 level, a level shift of 0.4 Ha was necessary in order to optimize the TS2 structure. Therefore we report here the energies and cartesian coordinates of the global minima optimized at the CASPT2 level with both level shifts.

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Table S1: Transition dipole moment *d* (D), oscillator strength *f*, and excitation energy *hv* (eV). Values are calculated for the neutral (regular) and cation (bold) geometries, with the singlet neutral system optimized using the different methods without state averaging. Experimental values are derived from Holland, D. M. P.; Shaw, D. A.; Hayes, M. A.; Shpinkova, L. G.; Rennie, E. E.; Karlsson, L.; Baltzer, P.; Wannberg, B. *Chem. Phys.* **1997,** *219,* 91.

Transitions		SA3-CASSCF(11/8)		SA4-CASSCF(11/7)		SA4-CASPT2(11/7)		**Exp.**
	d	0.0112	**0.0055**	0	**0.0067**	0	**0.0056**	-
D_1-D_0	*f*	1.27e^{-6}	**4 .06e^{-7}**	0	**6.13e^{-7}**	0	**3.78e^{-7}**	-
	hv	2.68	**3.59**	2.89	**3.78**	2.39	**3.41**	1.93
	d	0.2081	**0.0841**	0.2070	**0.0847**	0.2070	**0.0784**	-
D_2-D_1	*f*	7.38e^{-4}	**1.19e^{-4}**	7.16e^{-4}	**1.17e^{-4}**	6.71e^{-4}	**9.66e^{-5}**	-
	hv	4.50	**4.44**	4.41	**4.51**	4.13	**4.36**	3.93
	d	-	-	0	**1.9017**	0	**1.8595**	-
D_3-D_2	*f*	-	-	0	**8.24e^{-2}**	0	**7.32e^{-2}**	-
	hv	-	-	5.90	**5.88**	5.47	**4.78**	5.24

Table S2: $C_2H_4^+$ D_0 global minimum, SA4-CASPT2(11/7)//6-311G**

$E(D_0)$ = -77.97414815; $E(D_1)$ = -77.84839527

$E(D_2)$ = -77.81338000; $E(D_3)$ = -77.79588869

C	0.061937	-0.149560	0.002758
C	0.043240	1.255894	0.034095
H	0.061643	-0.684263	-0.945936
H	0.076752	-0.725779	0.926709
H	0.422940	1.797509	0.899202
H	-0.351507	1.825192	-0.806148

Table S3: $C_2H_4^+$ D_0 bridged minimum, SA4-CASPT2(11/7)//6-311G**

$E(D_0)$ = -77.93330856; $E(D_1)$ = -77.80894808

$E(D_2)$ = -77.69151814; $E(D_3)$ = -77.64323173

C	0.077474	-0.016339	-0.698090
C	-0.007873	0.066388	0.661009
H	-0.607934	0.080558	-1.539068
H	0.879883	-0.096152	1.276628
H	-0.308777	-1.044629	0.222993
H	-0.906983	0.476560	1.137215

Table S4: $C_2H_4^+$ D_0 transition state 1, SA4-CASPT2(11/7)//6-311G**

$E(D_0)$ = -77.93100786; $E(D_1)$ = -77.79260335

$E(D_2)$ = -77.69146159; $E(D_3)$ = -77.63823771

C	-0.064576	0.094721	0.002632
C	-0.503909	1.381546	0.082491
H	0.475926	-0.546201	-0.701781
H	-1.038282	1.637256	1.006624
H	0.739472	1.007041	0.479911
H	-0.345358	2.076932	-0.747529

Table S5: $C_2H_4^+$ D_0 transition state 2, SA4-CASPT2(11/7)//6-311G**

E(D0) = -77.93020486; E(D1) = -77.87928280

E(D2) = -77.67221671; E(D3) = -77.65973602

C	0.038225	0.074517	-0.726607
C	-0.003607	-0.082070	0.640614
H	-0.578915	0.026777	-1.592103
H	0.914383	0.020191	1.207854
H	-0.676445	-0.896308	0.971238
H	-0.622166	0.856894	0.774082

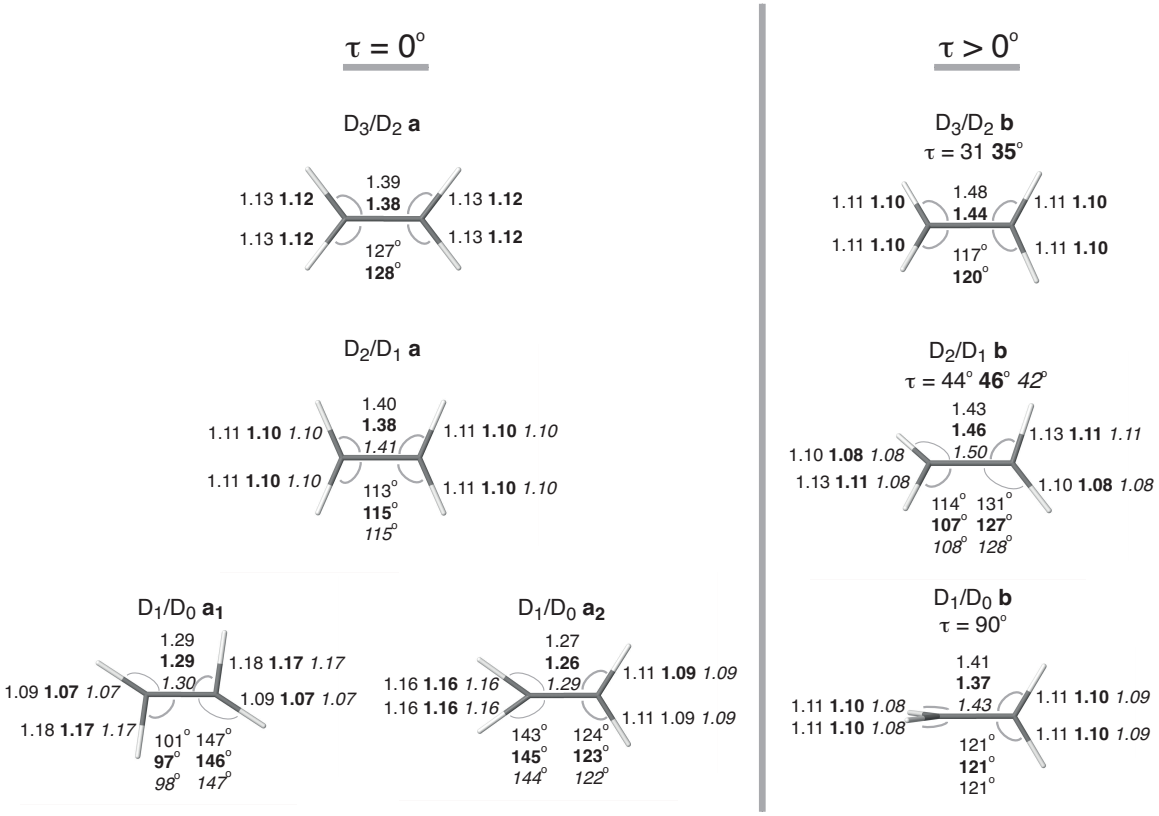

Figure S1: Structures of the D_1/D_0, D_2/D_1, D_3/D_2 MECIs optimized at the SA3-CASSCF(11/8) (italic), SA4-CASSCF(11/7) (bold), SA4-CASPT2(11/7) (regular) levels of theory.

Table S6: $C_2H_4^+$ D_0 global minimum, SA4-CASPT2(11/7)//6-311G**, lshift = 0.2 Ha
$E(D_0)$ = -77.97689776; $E(D_1)$ = -77.85174808
$E(D_2)$ = -77.81673238; $E(D_3)$ = -77.80130543

C	0.061980	-0.149955	0.002730
C	0.043279	1.256290	0.034104
H	0.064140	-0.684933	-0.946595
H	0.074229	-0.726515	0.927331
H	0.425457	1.798269	0.898756
H	-0.354082	1.825836	-0.805647

Table S7: D_1/D_0 MECI a1, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.90186279 ; $E(D_1)$ = -77.90181213
$E(D_2)$ = -77.73154902 ; $E(D_3)$ = -77.72246438

C	-0.332435	-0.039728	0.250713
C	0.178776	1.092986	-0.083643
H	-0.841148	-0.364297	-0.763947
H	-0.474308	-0.772892	1.041651
H	0.688434	1.416986	0.930729
H	0.322254	1.825303	-0.875075

Table S8: D_1/D_0 MECI a2, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.89694548 ; $E(D_1)$ = -77.89693938
$E(D_2)$ = -77.74351969 ; $E(D_3)$ = -77.71207998

C	-0.191981	0.060780	0.096976
C	0.122958	1.284635	0.034817
H	-0.701050	-0.794753	-0.507227
H	-0.142898	-0.872484	0.791745
H	0.639841	1.830697	0.850432
H	-0.087118	1.931937	-0.841211

Table S9: D_1/D_0 MECI b, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.93312429 ; $E(D_1)$ = -77.93311423
$E(D_2)$ = -77.72307707 ; $E(D_3)$ = -77.69143341

C	0.033464	-0.121732	-0.117170
C	-0.002473	1.270889	0.124301
H	0.552519	-0.534579	-0.991684
H	-0.456551	-0.830149	0.563031
H	0.774116	1.765088	0.722383
H	-0.808108	1.897948	-0.279150

Table S10: D_2/D_1 MECI a, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.96160259 ; $E(D_1)$ = -77.84759053
$E(D_2)$ = -77.84758082 ; $E(D_3)$ = -77.73701536

C	-0.004039	-0.151122	0.078359
C	-0.070918	1.250888	0.116989
H	-0.199043	-0.560175	-0.930376
H	0.231390	-0.594600	1.063649
H	0.123998	1.659936	1.125743
H	-0.306472	1.694359	-0.868275

Table S11: D_2/D_1 MECI b, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.96291981 ; $E(D_1)$ = -77.83408777
$E(D_2)$ = -77.83408336 ; $E(D_3)$ = -77.77150420

C	0.170033	-0.165412	0.047822
C	0.145125	1.266875	0.050794
H	0.131740	-0.630007	-0.985454
H	0.018107	-0.883931	0.864307
H	0.669121	1.740215	0.937549
H	-0.456548	1.971778	-0.538355

Table S12: D_3/D_2 MECI a, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.96298156 ; $E(D_1)$ = -77.88666538
$E(D_2)$ = -77.79148199 ; $E(D_3)$ = -77.79148065

C	0.119661	-0.141801	-0.009486
C	0.039999	1.246549	0.065268
H	-0.118155	-0.791095	-0.903322
H	0.435398	-0.851647	0.811192
H	0.277791	1.895840	0.959113
H	-0.275755	1.956396	-0.755402

Table S13: D_3/D_2 MECI b, SA4-CASPT2(11/7)//6-311G**
$E(D_0)$ = -77.97079439 ; $E(D_1)$ = -77.82297320
$E(D_2)$ = -77.82296455 ; $E(D_3)$ = -77.82292326

C	0.055600	-0.223149	0.014977
C	0.044138	1.252150	0.054114
H	0.093835	-0.706272	-0.980113
H	0.027340	-0.759190	0.982896
H	0.509629	1.741753	0.930643
H	-0.430453	1.780278	-0.794696

Table S14: D_1/D_0 MECI a1, SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.64309171 ; $E(D_1)$ = -77.64308719
$E(D_2)$ = -77.44903573 ; $E(D_3)$ = -77.44148254

C	0.145221	-0.062526	-0.101031
C	-0.062614	1.177005	0.177943
H	0.874437	-0.819959	-0.316547
H	-0.975959	-0.391024	-0.084176
H	1.058560	1.505516	0.161187
H	-0.791839	1.934372	0.393670

Table S15: D_1/D_0 MECI a2, SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.63517126 ; $E(D_1)$ = -77.63515843
$E(D_2)$ = -77.46535834 ; $E(D_3)$ = -77.42996009

C	0.015745	0.017066	0.181748
C	0.057382	1.277829	0.099831
H	-0.588112	-0.896241	0.574257
H	0.556662	-0.976944	-0.087015
H	-0.717047	1.921078	0.520246
H	0.870492	1.809139	-0.396963

Table S16: D_1/D_0 MECI b, SA2-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.67489649 ; $E(D_0)$ = -77.67488994
Single-point energies at the SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.67515697 ; $E(D_1)$ = -77.66637811
$E(D_2)$ = -77.45369823 ; $E(D_3)$ = -77.42531282

C	0.182610	-0.218964	0.015837
C	0.136567	1.173469	-0.034335
H	0.581410	-0.813462	-0.803468
H	-0.176712	-0.781638	0.873489
H	1.020627	1.757662	0.204360
H	-0.672050	1.673837	-0.559317

Table S17: D_2/D_1 MECI a, SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.72335531 ; $E(D_1)$ = -77.59460408
$E(D_2)$ = -77.59460270 ; $E(D_3)$ = -77.48451294

C	0.017294	-0.164401	0.008114
C	0.011032	1.219573	0.054656
H	-0.215181	-0.590236	-0.978950
H	0.253847	-0.653471	0.964424
H	0.243072	1.645393	1.041828
H	-0.225169	1.708639	-0.901740

Table S18: D_2/D_1 MECI b, SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.70693432 ; $E(D_1)$ = -77.56895460
$E(D_2)$ = -77.56894602 ; $E(D_3)$ = -77.49211296

C	0.022946	-0.181122	-0.098027
C	0.096205	1.268674	0.091264
H	0.419190	-0.746374	-0.924583
H	-0.262560	-0.626989	0.881657
H	0.579117	1.791883	0.899200
H	-0.186459	1.741677	-0.876441

Table S19: D_3/D_2 MECI a, SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.71854737 ; $E(D_1)$ = -77.62863646
$E(D_2)$ = -77.53362633 ; $E(D_3)$ = -77.53362596

C	0.051692	-0.112858	0.010940
C	0.047238	1.262628	0.099470
H	-0.133132	-0.738424	-0.901664
H	0.240929	-0.849048	0.835898
H	0.232115	1.888197	1.012064
H	-0.142058	1.998816	-0.725475

Table S20: D_3/D_2 MECI b, SA4-CASSCF(11/7)//6-311G**
$E(D_0)$ = -77.72872913 ; $E(D_1)$ = -77.55807833
$E(D_2)$ = -77.55806089 ; $E(D_3)$ = -77.55804642

C	0.054380	-0.206272	0.015640
C	0.044363	1.234745	0.053677
H	0.128149	-0.721722	-0.952624
H	-0.008263	-0.773381	0.955298
H	0.529931	1.757782	0.889915
H	-0.448470	1.794419	-0.754086

Table S21: D_1/D_0 MECI a1, SA3-CASSCF(11/8)//6-311G**
$E(D_0)$ = -77.66487622 ; $E(D_1)$ = -77.66487225 ; $E(D_2)$ = -77.48392402

C	0.033069	-0.012984	-0.133409
C	0.054819	1.246608	0.083685
H	0.015193	-0.794199	-0.868507
H	0.034094	-0.463483	1.010491
H	0.072605	2.044752	0.802333
H	0.051924	1.578250	-1.039218

Table S22: D_1/D_0 MECI a2, SA3-CASSCF(11/8)//6-311G**

$E(D_0)$ = -77.66940040 ; $E(D_1)$ = -77.66938362 ; $E(D_2)$ = -77.50112999

C	0.213102	-0.035864	-0.072855
C	0.197147	1.250180	-0.075156
H	0.042019	-0.979922	-0.718197
H	0.407555	-0.972554	0.576802
H	0.440659	1.834996	0.812650
H	-0.060911	1.825672	-0.964940

Table S23: D_1/D_0 MECI b, SA3-CASSCF(11/8)//6-311G**

$E(D_0)$ = -77.70617885 ; $E(D_1)$ = -77.70613343 ; $E(D_2)$ = -77.49028337

C	0.040955	-0.161015	-0.037815
C	0.018314	1.265928	-0.128484
H	0.391026	-0.765125	-0.867712
H	-0.291573	-0.666000	0.862543
H	0.873966	1.859803	0.175084
H	-0.855092	1.789213	-0.503061

Table S24: D_2/D_1 MECI a, SA3-CASSCF(11/8)//6-311G**

$E(D_0)$ = -77.75122209 ; $E(D_1)$ = -77.62150226 ; $E(D_2)$ = -77.62150175

C	0.102797	-0.132184	0.013336
C	0.096273	1.277955	0.036501
H	-0.106219	-0.560507	-0.975615
H	0.315082	-0.590812	0.987897
H	0.304831	1.706258	1.025557
H	-0.116543	1.736563	-0.937951

Table S25: D_2/D_1 MECI b, SA3-CASSCF(11/8)//6-311G**

$E(D_0)$ = -77.73913714 ; $E(D_1)$ = -77.60014187 ; $E(D_2)$ = -77.60014106

C	-0.052707	-0.201800	-0.067002
C	0.014858	1.287368	0.086933
H	0.123578	-0.782089	-0.955648
H	-0.115958	-0.644685	0.952237
H	0.581758	1.851395	0.806657
H	-0.464043	1.742113	-0.809090