Supporting Information for

Direct *ab initio* dynamics study of radical C_4H ($\tilde{X}\,^2\Sigma^+$) + CH_4 reaction

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Table S1 Cartesian coordinates for various species on the potential energy surface of the C_4H+ CH_4 reaction optimized at the BB1K/6-311G(d,p) level.

C_4H	C	0.000000000	0.000000000	2.045126000	CH_4	C	0.000000000	0.000000000	0.000000000
	C	0.000000000	0.000000000	0.766964000		H	-0.626163000	0.626163000	0.626163000
	C	0.000000000	0.000000000	-0.562013000		H	0.626163000	-0.626163000	0.626163000
	C	0.000000000	0.000000000	-1.777231000		H	-0.626163000	-0.626163000	-0.626163000
	H	0.000000000	0.000000000	-2.837076000		H	0.626163000	0.626163000	-0.626163000
HC_4H	C	0.000000000	0.000000000	1.880235000	C_4H_2	C	2.878308000	-0.610634000	-0.000070000
	C	0.000000000	0.000000000	0.682790000		C	1.715163000	-0.089511000	-0.000011000
	C	0.000000000	0.000000000	-0.682790000		C	0.543917000	0.435954000	0.000051000
	C	0.000000000	0.000000000	-1.880235000		C	-0.634377000	0.964469000	0.000111000
	H	0.000000000	0.000000000	-2.938705000		H	-0.752768000	2.036921000	-0.000418000
	H	0.000000000	0.000000000	2.938705000		H	-1.513308000	0.338605000	0.000609000
TS1	C	-0.686732000	1.047898000	-0.001935000	TS2	C	2.843006000	-0.686244000	-0.000051000
	C	0.372507000	0.397059000	0.001899000		C	1.711830000	-0.107386000	0.000014000
	C	1.652343000	-0.035938000	0.002643000		C	0.566381000	0.497192000	0.000057000
	C	2.785193000	-0.444150000	-0.001738000		C	-0.600917000	1.001231000	0.000072000
	H	3.782932000	-0.798748000	-0.003670000		H	-0.926330000	2.024214000	-0.000376000
	C	-2.864739000	-0.516580000	-0.000146000		C	-2.686619000	-0.673431000	-0.000026000
	H	-2.704705000	-1.111451000	-0.889397000		H	-2.191685000	-1.631994000	-0.033579000
	H	-2.722768000	-1.093338000	0.904022000		H	-3.160660000	-0.412709000	0.933467000
	H	-2.083080000	0.326387000	-0.000341000		H	-1.527871000	0.198935000	0.000665000
	H	-3.823809000	-0.012581000	-0.014951000		H	-3.195541000	-0.366621000	-0.900574000
CH_3	C	0.000000000	0.000000000	0.000000000					
	H	0.000000000	1.075195000	0.000000000					
	H	0.931146000	-0.537597000	0.000000000					
	H	-0.931146000	-0.537597000	0.000000000					

Table S2 Cartesian coordinates for various species on the potential energy surface of the C_4H + CH_4 reaction optimized at the CCSD/6-31G(d,p) level.

C_4H	C	0.000000000	0.000000000	2.077916000	CH_4	C	0.000000000	0.000000000	0.000000000
	C	0.000000000	0.000000000	0.785299000		H	0.627900000	0.627900000	0.627900000
	C	0.000000000	0.000000000	-0.570888000		H	-0.627900000	-0.627900000	0.627900000
	C	0.000000000	0.000000000	-1.795957000		H	-0.627900000	0.627900000	-0.627900000
	H	0.000000000	0.000000000	-2.860601000		H	0.627900000	-0.627900000	-0.627900000

HC_4H	C	0.000000000	0.000000000	1.908758000	TS1	C	-0.689121000	-0.635694000	0.000391000
	C	0.000000000	0.000000000	0.694004000		C	0.470730000	-0.211091000	-0.000336000
	C	0.000000000	0.000000000	-0.694004000		C	1.834572000	0.031372000	-0.000718000
	C	0.000000000	0.000000000	-1.908758000		C	3.028760000	0.265954000	0.000505000
	H	0.000000000	0.000000000	-2.972497000		H	4.074875000	0.459149000	0.000588000
	H	0.000000000	0.000000000	2.972497000		C	-3.214933000	0.294139000	0.000000000
						H	-3.920404000	-0.531477000	-0.017670000
						H	-3.297635000	0.882940000	0.908506000
						H	-2.153937000	-0.187528000	0.001943000
						H	-3.282944000	0.908837000	-0.892412000
CH_3	C	0.000000000	0.000000000	0.000000000					
	H	0.000000000	1.077471000	0.000000000					
	H	0.933118000	-0.538736000	0.000000000					
	H	-0.933118000	-0.538736000	0.000000000					

Table S3 Harmonic vibrational frequencies (cm^{-1}) for various species calculated at the BB1K/6-311G(d,p) level and available experimental data.

Species	Frequencies(cm^{-1})	Expt.
C_4H	3519, 2180, 1915, 941, 739, 583, 494, 374, 214, 47	3307[1], 2084[1], 2064[2-4], 2061[1,3,5], 960[6]
CH_4	3217, 3217, 3217, 3091, 1585, 1585, 1356, 1356, 1356	3019, 2917, 1534, 1306[7]
TS1	3532, 3263, 3253, 3132, 2181, 2044, 1773, 1505, 1488, 1315, 1290, 1221, 941, 727, 659, 511, 509, 356, 291, 211, 205, 65, 39, -342	
TS2	3323, 3316, 3313, 3144, 2212, 1840, 1443, 1442, 1373, 1194, 1019, 996, 940, 676, 591, 555, 534, 437, 308, 206, 193, 76, 24, -1160	
HC_4H	3583, 3583, 2409, 2218, 948, 810, 810, 706, 706, 635, 635	3329, 3293, 2184, 2020, 874, 630, 627, 482, 231[7]
C_4H_2	3335, 3242, 2264, 1833, 1401, 968, 965, 825, 538, 423, 187, 144	
CH_3	3357, 3357, 3166, 1426, 1426, 479	3087[8], 2931[9], 1428[9], 1323[8]

Table S4 Harmonic vibrational frequencies (cm^{-1}) for various species calculated at the CCSD/6-31G(d,p) level .

Species	Frequencies(cm^{-1})
C_4H	3515, 2177, 1911, 1013, 903, 615, 554, 384, 300, 201
CH_4	3235, 3235, 3235, 3106, 1615, 1615, 1404, 1404, 1404
TS1	3525, 3271, 3269, 3144, 2361, 2059, 1542, 1527, 1522, 1326, 1317, 1208, 881, 587, 573, 452, 448, 376, 310, 210, 199, 61, 16, -502
HC_4H	3526, 2315, 2119, 901, 616, 616, 581, 581, 511, 511, 249, 249
CH_3	382, 3382, 3196, 1475, 1475, 422

Table S5 Sum of electronic and zero-point energies(E(elec)+ZPE), sum of electronic and thermal energies(E(elec)+Ecorr), sum of electronic and thermal Enthalpies(E(elec)+Hcorr), sum of electronic and thermal free energies(E(elec)+Gcorr) for various species on the PES at the BB1K/6-311G(d,p) level, respectively. (Unit. Hartree)

Species	*E(elec)+ZPE*	*E(elec)+Ecorr*	*E(elec)+Hcorr*	*E(elec)+Gcorr*
C_4H	-152.695	-152.690	-152.689	-152.720
CH_4	-40.449	-40.446	-40.445	-40.466
TS1	-193.140	-193.133	-193.132	-193.172
TS2	-193.106	-193.099	-193.098	-193.138
HC_4H	-153.368	-153.363	-153.363	-153.390

C_4H_2	-153.304	-153.299	-153.298	-153.330
CH_3	-39.787	-39.784	-39.783	-39.805

Table S6 Sum of electronic and zero-point energies(E(elec)+ZPE), sum of electronic and thermal energies(E(elec)+Ecorr), sum of electronic and thermal Enthalpies(E(elec)+Hcorr), sum of electronic and thermal free energies(E(elec)+Gcorr) for various species on the PES at the CCSD/6-31G(d,p) level, respectively. (Unit. Hartree)

Species	***E(elec)+ZPE***	***E(elec)+Ecorr***	***E(elec)+Hcorr***	***E(elec)+Gcorr***
C_4H	-152.28328	-152.279191	-152.278246	-152.307246
CH_4	-40.339798	-40.336938	-40.335993	-40.357106
TS1	-192.621955	-192.614583	-192.613639	-192.654604
HC_4H	-152.98703	-152.982570	-152.981625	-153.009844
CH_3	-39.68325	-39.680119	-39.679175	-39.701391

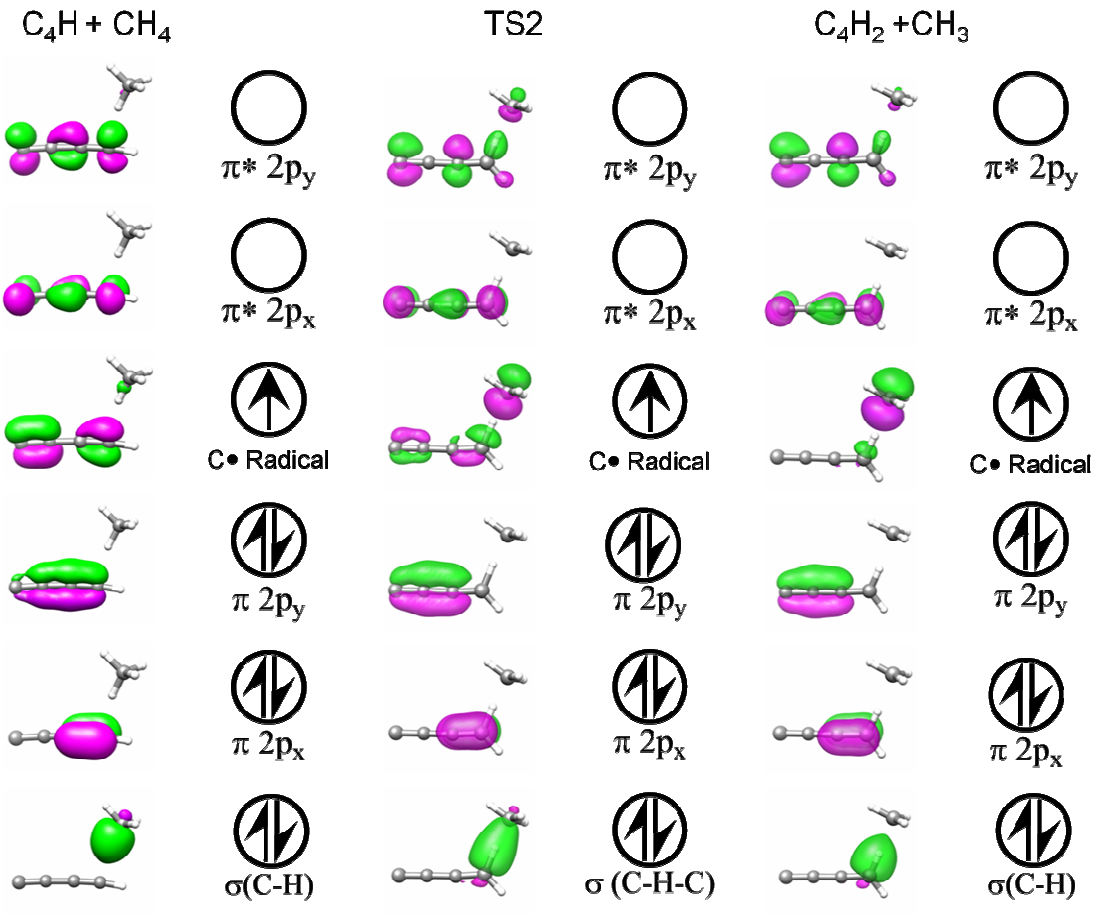
Table S7 The relative electron energies at the BB1K/6-311G(d,p) level (BB1K/B1), UCCSD(T)/6-311+G(2df,p)//BB1K/6-311G(d,p) level (CCSD(T)/B2//BB1K), at the UCCSD(T)/6-311++G(3df,2pd)//BB1K/6-311G(d,p) level (CCSD(T)/B3//BB1K), and at the UCCSD(T)/aug-cc-pVTZ//BB1K/6-311G(d,p) level (CCSD(T)/B4//BB1K), respectively. (Unit. kcal/mol)

Species	**BB1K/B1**	**CCSD(T)/B2//BB1K**	**CCSD(T)/B3//BB1K**	**CCSD(T)/B4//BB1K**
R (C_4H+CH_4)	0.0	0.0	0.0	0.0
TS1	3.31	1.98	2.01	1.63
P (HC_4H+CH_3)	-6.07	-28.93	-27.81	-27.75

Table S8 The Relative free energy BB1K/6-311G(d,p) level (BB1K/B1), UCCSD(T)/6-311+G(2df,p)//BB1K/6-311G(d,p) level (CCSD(T)/B2//BB1K), at the UCCSD(T)/6-311++G(3df,2pd)//BB1K/6-311G(d,p) level (CCSD(T)/B3//BB1K), and at the UCCSD(T)/aug-cc-pVTZ//BB1K/6-311G(d,p) level (CCSD(T)/B4//BB1K), respectively. (Unit. kcal/mol)

Species	**BB1K/B1**			**CCSD(T)/B2**			**CCSD(T)/B3**			**CCSD(T)/B4**		
	ΔE	***ΔH***	***ΔG***	***ΔE***	***ΔH***	***ΔG***	***ΔE***	***ΔH***	***ΔG***	***ΔE***	***ΔH***	***ΔG***
R(C_4H+CH_4)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TS1	2.63	1.83	9.24	1.31	0.49	7.91	1.33	0.52	7.94	0.96	0.15	7.56
P(HC_4H+CH_3)	-6.48	-6.66	-5.40	-28.75	-28.93	-27.67	-28.23	-28.41	-27.15	-28.16	-28.34	-27.08

Fig. S1. The electronic transfer behavior of ***channel 2*** in the title reaction



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