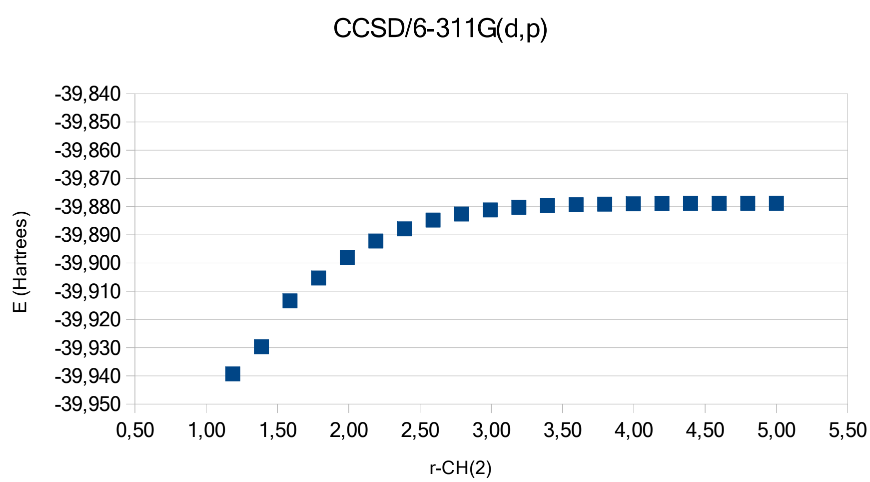
Supplementary Information

Table 1 Vibrational frequencies of methane cation grouped by symmetry. Values are given in cm^{-1}

Level	A1	A1	A1	A1	A2	B1	B1	B2	B2
CAS(5,6)/6-31G**	1191.48	1614.61	2538.14	3168.63	763.34	899.74	2279.44	1354.91	3433.96
CAS(5,6)/6-311G**	1189.63	1606.71	2503.32	3133.69	750.54	877.15	2232.40	1338.37	3402.15
NEVPT2(5,6)/6-31G**	1254.75	1654.48	2637.73	3234.51	653.53	931.85	2374.07	1392.52	3388.33
NEVPT2(5,6)/6-311G**	1223.35	1626.80	2577.35	3183.91	641.37	913.36	2301.69	1357.01	3350.05
CAS(7,8)/6-31G**	1167.95	1572.84	2531.52	3120.59	665.60	874.35	2264.62	1331.73	3268.87
CAS(7,8)/6-311G**	1168.03	1565.70	2497.49	3083.87	645.21	851.19	2219.34	1310.97	3235.64
NEVPT2(7,8)/6-31G**	1220.89	1616.94	2630.87	3205.37	557.70	934.98	2367.84	1457.98	3360.88
NEVPT2(7,8)/6-311G**	1184.00	1576.71	2572.65	3142.46	568.72	890.37	2309.18	1315.50	3317.74
CAS(7,8)/6-311G(2df,2pd)	1180.39	1573.38	2488.08	3083.49	642.67	841.17	2216.43	1306.13	3231.80
NEVPT2(7,8)/6-311G(2df,2pd)	1149.31	1749.98	2826.96	3147.74	866.60	1008.24	2561.88	1487.67	3372.07
CAS(7,8)/cc-pvqz	1182.58	1576.09	2478.94	3080.19	651.60	837.35	2216.15	1307.75	3230.50
NEVPT2(7,8)/cc-pvQZ	1174.13	1598.50	2580.78	3168.09	713.51	1005.25	2412.19	1519.10	3300.49

Figure 1 Stretching of rC-H(2) bond distance using coupled cluster methods. Both methods predicts the formation of planar CH_3^+ and H . The dissociation energy without ZPE correction is 38.0 and 22.2 kcal mol^{-1} at CCSD/6-311G(d,p) and CCSD(T)/6-311G(d,p), respectively.



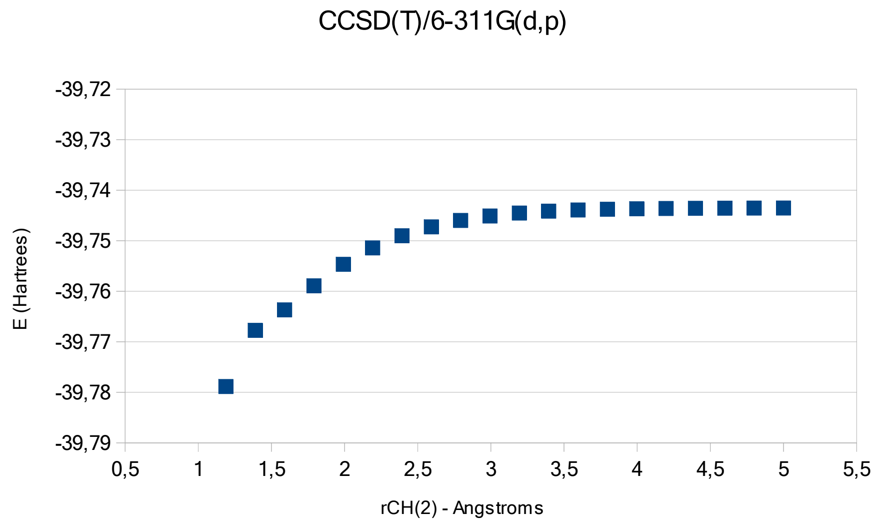
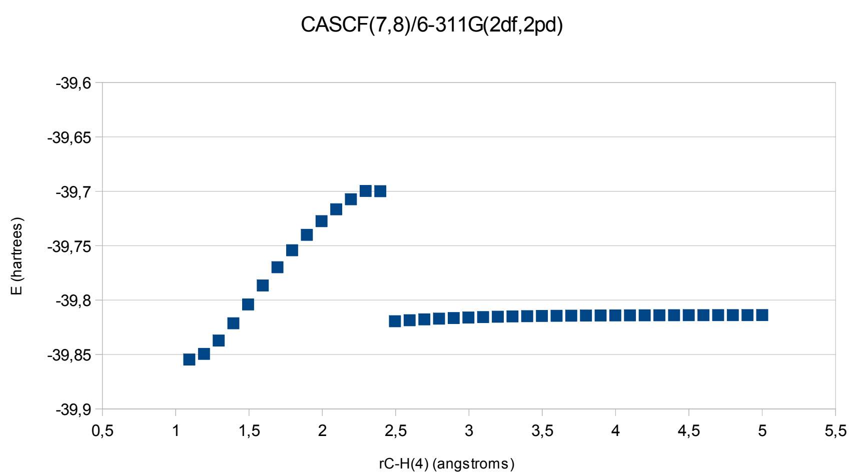
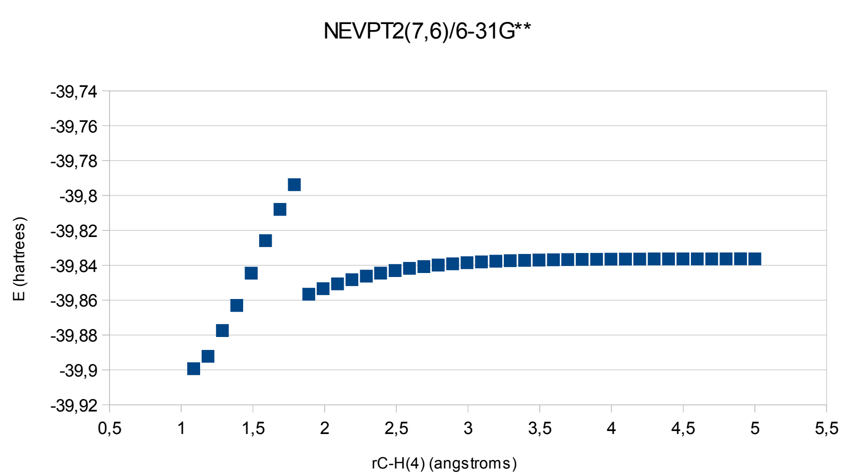


Figure 2 Stretching of rC-H(4) bond in different levels of theory. In each potential energy curve is possible to see the jump discontinuity. Coupled clusters methods doe not present the discontinuity, however, these methods leads to high energy dissociation products.





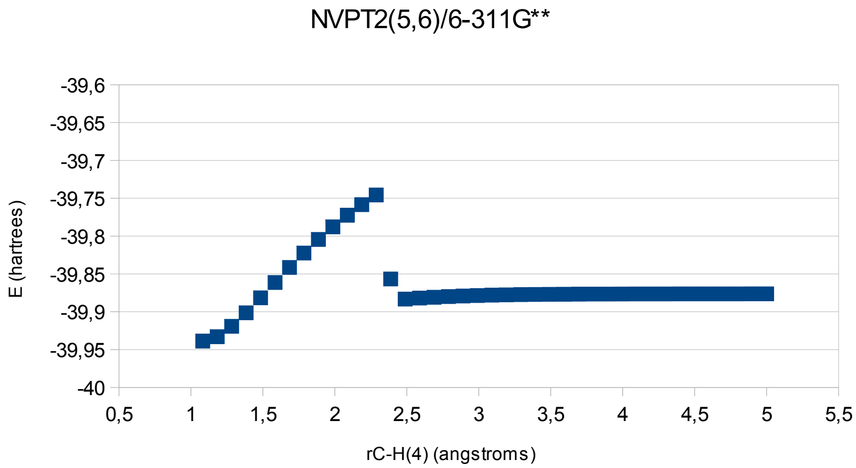


Figure 3 Frequency of collisions (Z) in function of pressure at different temperatures. It was considered a Lennard-Jones collision and the parameters of neutral methane in argon bath.

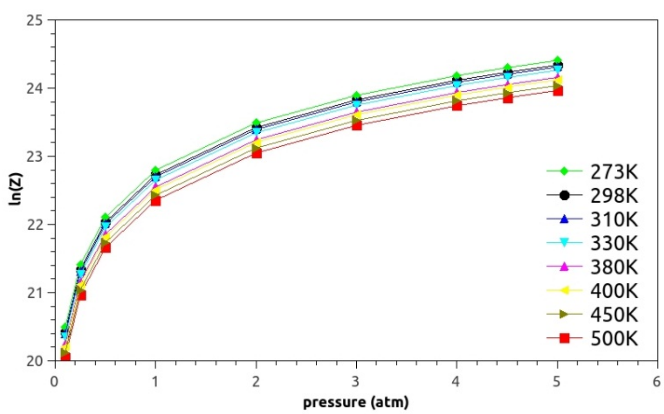


Table 2 Free energy of reaction and equilibrium constant for reaction 3, considering a reference concentration of molecule cm^{-3}.

Temperature (K)	ΔG_r (kcal mol^{-1})	Equilibrium constant
273	33.40	3.89×10^{-08}
298.15	33.03	1.24×10^{-05}
310	32.86	1.33×10^{-04}
330	32.56	5.08×10^{-03}
380	31.83	$8.13\times10^{+00}$
400	31.53	$9.46\times10^{+01}$
450	30.77	$1.64\times10^{+04}$
500	30.01	$1.00\times10^{+06}$
1000	22.49	$8.54\times10^{+13}$
1500	15.36	$2.77\times10^{+16}$

Figure 4 Microcanonical rate coefficients evaluated considering the molecular configuration in the reaction path that minimizes the sum of states. The frequencies and moments of inertia of species were evaluated at NEVPT2(7,8)/6-311G(2df,2pd) level.

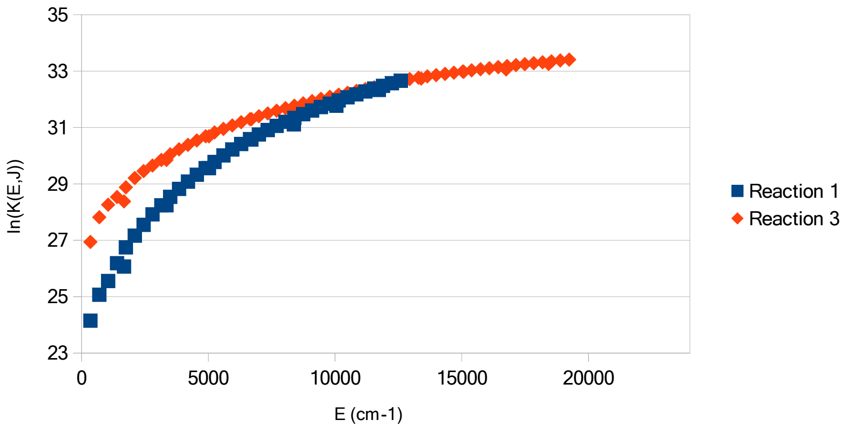


Table 3 Microcanonical rate coefficients, for the Reaction 1, evaluated considering the molecular configuration in the reaction path that minimizes the sum of states. The frequencies and moments of inertia of species were evaluated at NEVPT2(7,8)/6-311G(2df,2pd) level.

E (cm^{-1})	k(E.J)
0	1.000E-20
349.8	3.079E+07
699.6	7.708E+07
1049.4	1.255E+08
1399.2	2.360E+08
1749	4.134E+08
2098.8	6.277E+08
2448.6	9.206E+08
2798.4	1.333E+09
3148.2	1.843E+09
3498	2.486E+09
3847.8	3.297E+09
4197.6	4.277E+09
4547.4	5.454E+09
4897.2	6.878E+09
5247	8.555E+09
5596.8	1.081E+10
5946.6	1.335E+10
6296.4	1.618E+10
6646.2	1.925E+10
6996	2.270E+10
7345.8	2.654E+10
7695.6	3.079E+10
8045.4	3.559E+10
8395.2	4.092E+10
8745	4.674E+10
9094.8	5.307E+10
9444.6	5.992E+10

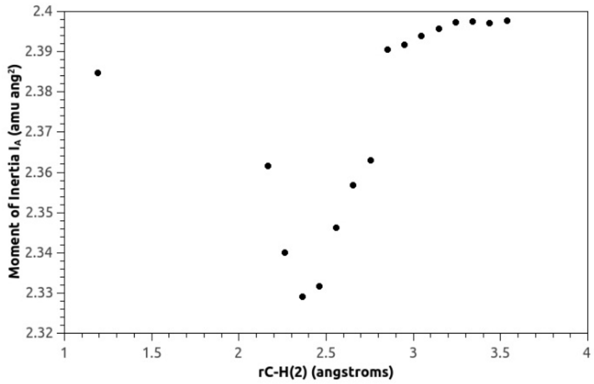
9794.4	6.757E+10
10144.2	7.583E+10
10494	8.469E+10
10843.8	9.415E+10
11193.6	1.043E+11
11543.4	1.154E+11
11893.2	1.272E+11
12243	1.397E+11
12592.8	1.529E+11
1675.2	2.099E+08
3350.3	1.843E+09
5025.5	6.878E+09
6700.6	1.895E+10
8375.8	3.245E+10
10050.9	6.311E+10
11726.1	1.102E+11

Table 3 Microcanonical rate coefficients, for the Reaction 3, evaluated considering the molecular configuration in the reaction path that minimizes the sum of states. The frequencies and moments of inertia of species were evaluated at NEVPT2(7,8)/6-311G(2df,2pd) level.

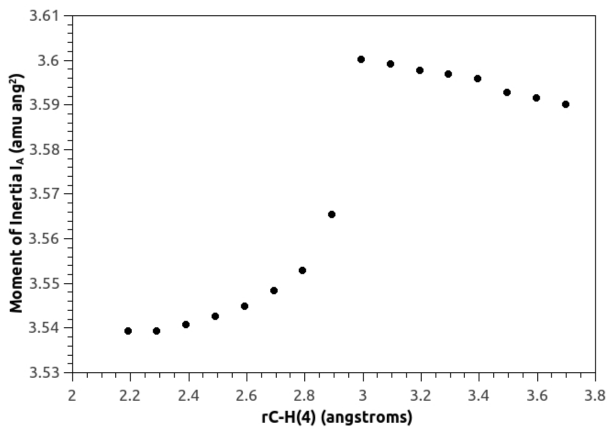
E (cm^{-1})	k(E.J)
0	1.000E-20
349.8	5.015E+08
699.6	1.204E+09
1049.4	1.882E+09
1399.2	2.474E+09
1749	3.488E+09
2098.8	4.850E+09
2448.6	6.202E+09
2798.4	7.554E+09
3148.2	9.208E+09
3498	1.122E+10
3847.8	1.341E+10
4197.6	1.573E+10
4547.4	1.837E+10
4897.2	2.128E+10
5247	2.439E+10
5596.8	2.768E+10
5946.6	3.127E+10
6296.4	3.510E+10
6646.2	3.912E+10
6996	4.339E+10
7345.8	4.794E+10
7695.6	5.273E+10
8045.4	5.773E+10
8395.2	6.299E+10
8745	6.852E+10
9094.8	7.426E+10

9444.6	8.022E+10
9794.4	8.641E+10
10144.2	9.286E+10
10494	9.950E+10
10843.8	1.064E+11
11193.6	1.135E+11
11543.4	1.208E+11
11893.2	1.283E+11
12243	1.413E+11
12592.8	1.519E+11
12942.6	1.618E+11
13292.4	1.700E+11
13642.2	1.783E+11
13992	1.865E+11
14341.8	1.945E+11
14691.6	2.031E+11
15041.4	2.120E+11
15391.2	2.208E+11
15741	2.295E+11
16090.8	2.381E+11
16440.6	2.474E+11
16790.4	2.568E+11
17140.2	2.660E+11
17490	2.751E+11
17839.8	2.841E+11
18189.6	2.940E+11
18539.4	3.038E+11
18889.2	3.134E+11
19239	3.228E+11
1675.2	2.117E+09
3350.3	9.208E+09
5025.5	2.128E+10
6700.6	3.912E+10
8375.8	5.134E+10
10050.9	8.641E+10
11726.1	1.208E+11
13401.2	1.647E+11
15076.4	2.099E+11
16751.5	2.277E+11
18426.7	2.769E+11

Figure 5 Moments of inertia calculated along the reaction path at NEVPT2(7,8)/6-311G(2df,2pd) level. a) Reaction 1; b) Reaction 3.



(a)



(b)

Vibrational Frequencies and moments of inertia for CH_4^+ evaluated at at NEVPT2(7,8)/6-311G(2df,2pd) level.

1 Vibrator Freq(har)= 866.60 (cm-1)

2 Vibrator Freq(har)= 1008.24 (cm-1)

3 Vibrator Freq(har)= 1149.31 (cm-1)

4 Vibrator Freq(har)= 1487.67 (cm-1)

5 Vibrator Freq(har)= 1749.98 (cm-1)

6 Vibrator Freq(har)= 2561.88 (cm-1)

7 Vibrator Freq(har)= 2826.96 (cm-1)

8 Vibrator Freq(har)= 3147.74 (cm-1)

9 Vibrator Freq(har)= 3372.07 (cm-1)

10 Clas.Rot Amu Ang^2 = 3.89 Symm = 2

11 Clas.Rot Amu Ang^2 = 3.89 Symm = 2

12 Clas.Rot Amu Ang^2 = 2.48 Symm = 2

Vibrational Frequencies and moments of inertia for the configuration that minimizes the sum of states along the reaction path $CH_4^+ \rightarrow CH_2^+ + H_2$. NEVPT2(7,8)/6-311G(2df,2pd).

1 Vibrator Freq(har)= 920.80 (cm-1)

2 Vibrator Freq(har)= 1069.44 (cm-1)

3 Vibrator Freq(har)= 1095.11 (cm-1)

4 Vibrator Freq(har)= 1319.69 (cm-1)

5 Vibrator Freq(har)= 1487.28 (cm-1)

6 Vibrator Freq(har)= 2524.98 (cm-1)

7 Vibrator Freq(har)= 3141.38 (cm-1)

8 Vibrator Freq(har)= 3361.76 (cm-1)

9 Clas.Rot Amu Ang^2 = 8.44 Symm = 2

10 Clas.Rot Amu Ang^2 = 8.44 Symm = 2

11 Clas.Rot Amu Ang^2 = 2.33 Symm = 2

Vibrational Frequencies and moments of inertia for the configuration that minimizes the sum of states along the reaction path $CH_4^+ \rightarrow CH_3^+ + H$. NEVPT2(7,8)/6-311G(2df,2pd).

1 Vibrator Freq(har)= 1237.39 (cm-1)

2 Vibrator Freq(har)= 1384.69 (cm-1)

3 Vibrator Freq(har)= 1692.04 (cm-1)

4 Vibrator Freq(har)= 2792.45 (cm-1)

5 Vibrator Freq(har)= 3069.92 (cm-1)

6 Vibrator Freq(har)= 3455.03 (cm-1)

7 Vibrator Freq(har)= 3801.52 (cm-1)

8 Vibrator Freq(har)= 4043.87 (cm-1)

9 Clas.Rot Amu Ang^2 = 10.86 Symm = 2

10 Clas.Rot Amu Ang^2 = 10.86 Symm = 2

11 Clas.Rot Amu Ang^2 =   3.55 Symm = 2