

Supporting Information

Atomistic Insights into Methane-Derived Molecular Evolution:

Mechanisms of $\text{CH}_4^+/\text{CH}_4$ Ion-Molecule Reactions

Hiroto TACHIKAWA*

*Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060-8628, Japan*

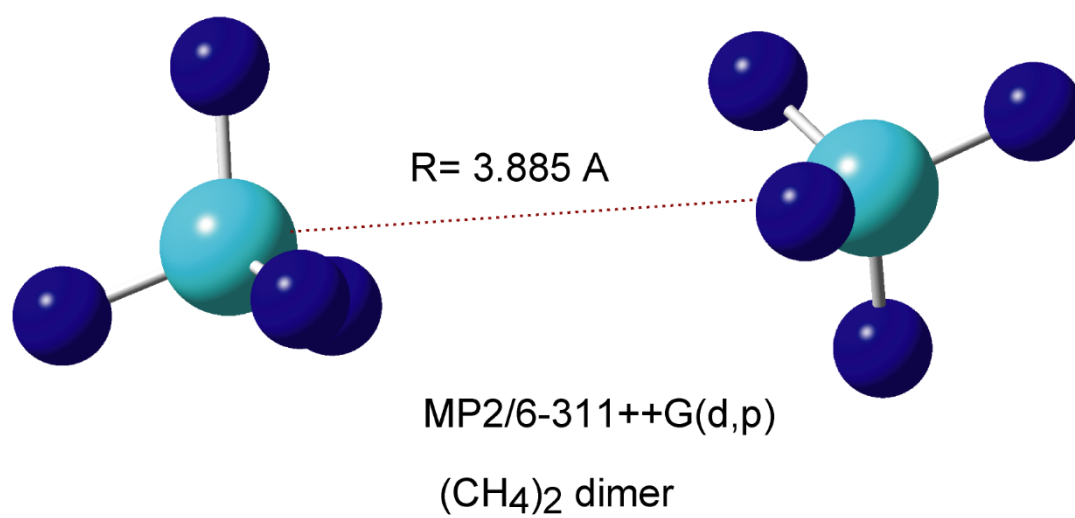


Figure S1. Optimized structures of methane dimer. The calculations were performed at the MP2/6-311++G(d,p) level. Bond lengths are in Å.

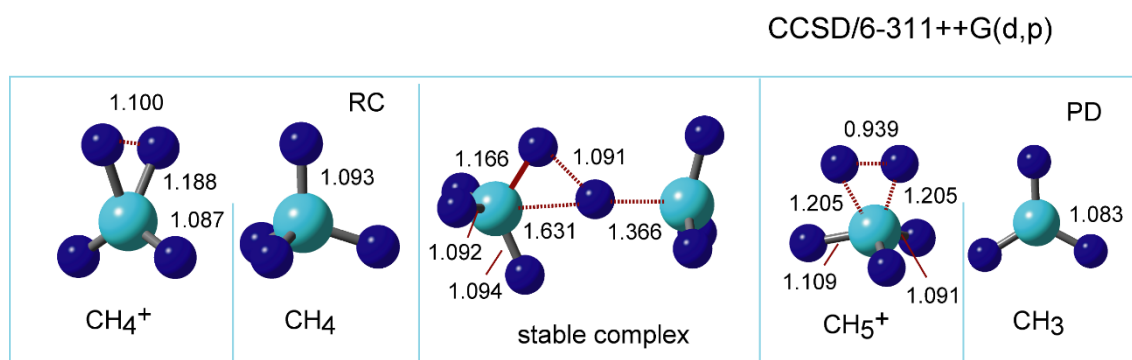


Figure S2. Optimized structures of the reaction system. The geometry optimizations were performed at the CCSD/6-311++G(d,p) level. Bond lengths are in Å.

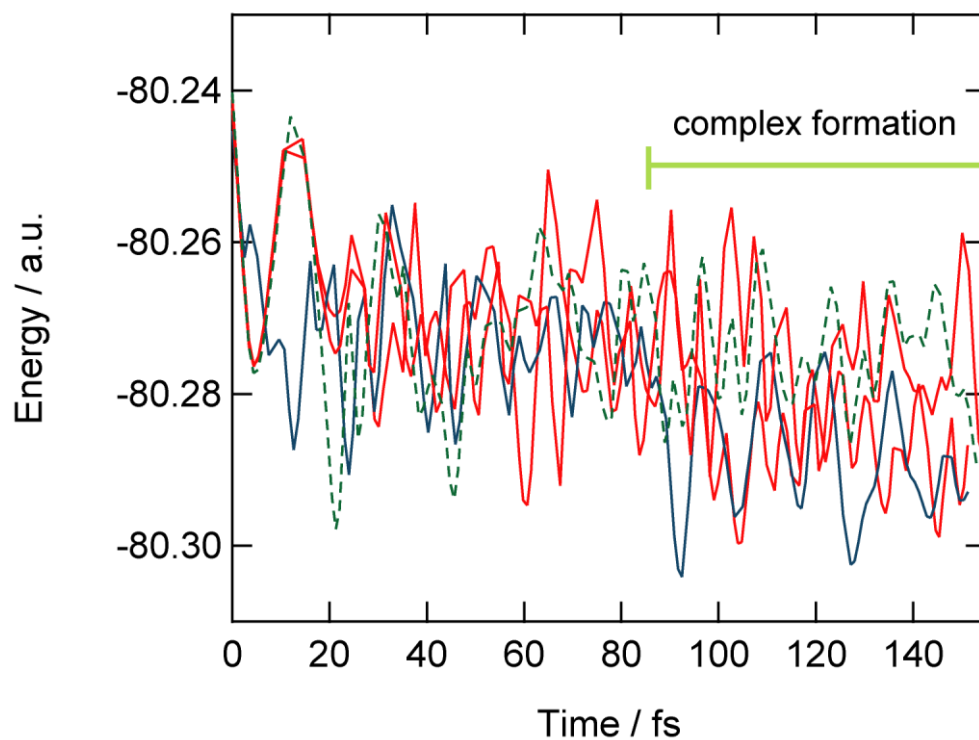


Figure S3. Time evolution of potential energies of methane dimer cation $(\text{CH}_4)_2^+$ following the ionization of $(\text{CH}_4)_2$. Initial geometries of $(\text{CH}_4)_2$ were generated around the equilibrium structure of $(\text{CH}_4)_2$ by thermal activation at 10 K. Four trajectories are given in figure. The calculations were carried out at the MP2/6-311++G(d,p) level.

Table S1. Relative energies (in kcal/mol) calculated by several methods.

	method	RC	complex	PD
1	MP2/6-311++G(d,p)//MP2/6-311++G(d,p)	0.0	-17.8	-1.8
2	CCSD/6-311++G(d,p)//CCSD/6-311++G(d,p)	0.0	-17.1	-1.4
3	MP2/aug-cc-pVTZ//MP2/aug-cc-pVTZ	0.0	-18.9	-1.9
4	CCSD(T)/6-311++G(d,p)//CCSD/6-311++G(d,p)	0.0	-17.1	-1.4
5	CCSD/aug-cc-pVTZ//CCSD/aug-cc-pVTZ	0.0	-17.9	-1.7
6	CCSD(T)/aug-cc-pVDZ//CCSD/aug-cc-pVDZ	0.0	-18.1	-1.3
7	QCISD/6-311++G(d,p)//QCISD/6-311++G(d,p)	0.0	-17.2	-1.4