Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Mechanism of Ionic Dissociation of HCl in Smallest Water Clusters

Hiroto TACHIKAWA*

Division of Applied Chemistry, Faculty of Engineering

Hokkaido University, Sapporo 060-8628, JAPAN

Email: hiroto@eng.hokudai.ac.jp

Table S1. Optimized geometrical parameters of $HCl(H_2O)_n$ (*n*=3-5), calculated at all levels of theory.

***n*=3**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(W1)]	2.988	2.915	2.808
r2[O(W1)-O(W2)]	2.727	2.671	2.603
r3[O(W2)-O(W3)]	2.77	2.721	2.681
r4[O(W3)-Cl]	3.308	3.258	3.211

***n*=4**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(W1)]	3.018	2.964	2.881
r2[O(W1)-O(W2)]	2.647	2.598	2.551
r3[O(W2)-O(W3)]	2.816	2.769	2.742
r4[O(W3)-Cl]	3.375	3.327	3.298
r5[O(W1)-O(W4)]	2.925	2.876	2.848

***n*=5**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(W1)]	3.092	3.091	2.972
r2[O(W1)-O(W2)]	2.630	2.631	2.604
r3[O(W2)-O(W3)]	2.656	2.656	2.665
r4[O(W3)-O(W4)]	2.674	2.647	2.914
r5[O(W3)-O(W5)]	2.744	2.647	2.629
r6[O(W5)-Cl]	2.773	2.745	2.62

Table S2. Optimized geometrical parameters of solvent separated ion-pairs (ssIP) and contact ion-pair (cIP) for $H^+Cl^-(H_2O)_n$ (*n*=4 and 5), calculated at all levels of theory.

***n*=4(ssIP)**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(H_3O^+)]	3.497	3.544	3.562
r2[Cl-O(W1)]	3.004	3.020	3.033
r2[Cl-O(W1)]	3.004	3.022	3.031
r1[O(W2)-O(H_3O^+)]	3.005	3.021	3.032

***n*=4(cIP)**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(H_3O^+)]	2.773	2.840	2.871
r2[Cl-O(W1)]	3.112	3.112	3.099
r3[O(W1)-O(W2)]	2.672	2.672	2.608
r1[O(W2)-O(H_3O^+)]	2.551	2.551	2.488

***n*=5(ssIP)**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(H_3O^+)]	3.675	3.783	3.768
r2[Cl-O(W1)]	3.046	3.065	3.071
r3[O(W1)-O(W2)]	2.640	2.617	2.604
r1[O(W2)-O(H_3O^+)]	2.527	2.522	2.505

***n*=5(cIP)**			
	MP2/6-311++G(d,p)	CAM-B3LYP/6-311++G(d,p)	CAM-B3LYP/6-311G(d,p)
r1[Cl-O(H_3O^+)]	2.830	2.886	2.910
r2[Cl-O(W1)]	3.104	3.101	3.108
r3[O(W1)-O(W2)]	2.670	2.642	2.626
r1[O(W2)-O(H_3O^+)]	2.558	2.540	2.516

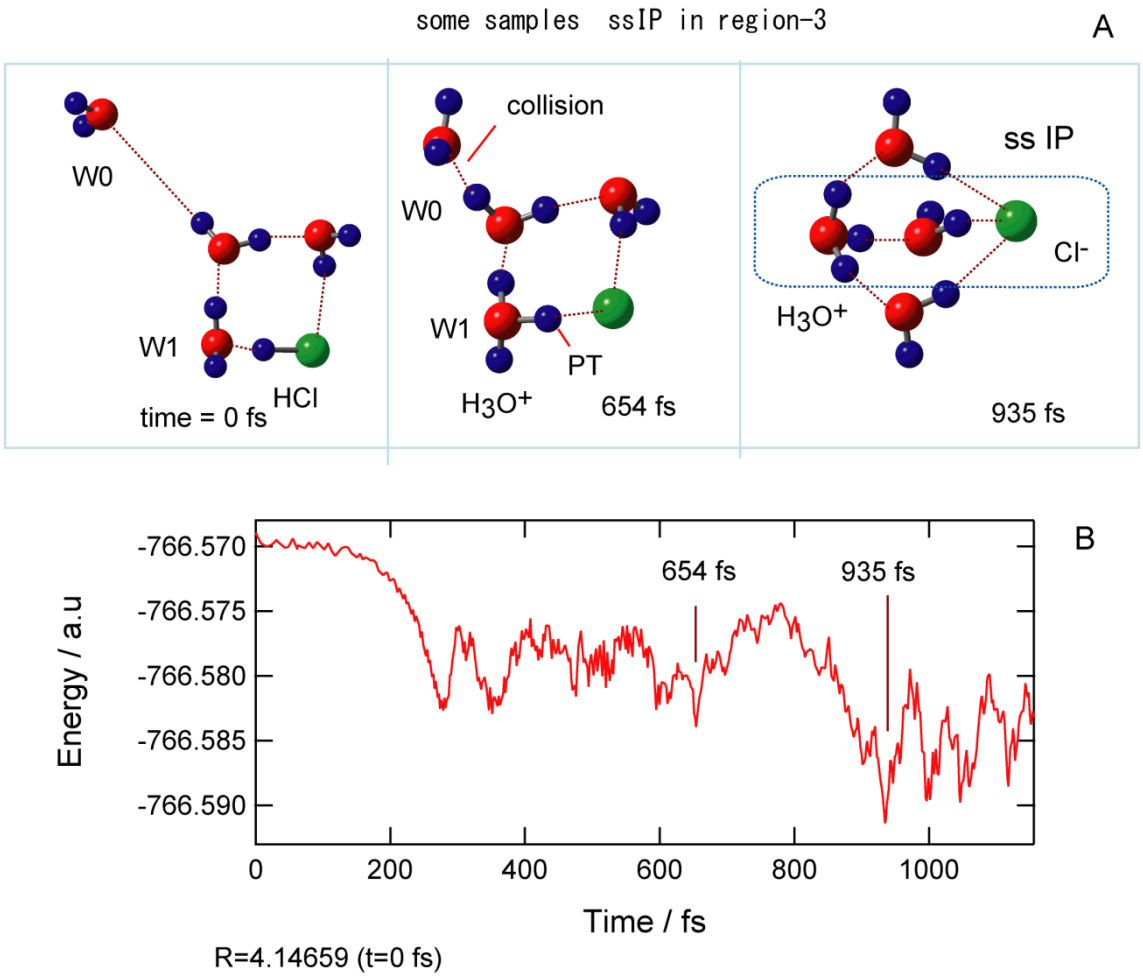

Figure S1. Sample trajectory for ssIP channel (sample-1): (A) Snapshots of $HCl(H_2O)_n$ + H_2O (n = 3+1) reaction system given as a function of time, and (B) time evolutions of potential energy. H_2O(W0) approaches to HCl from region-III.

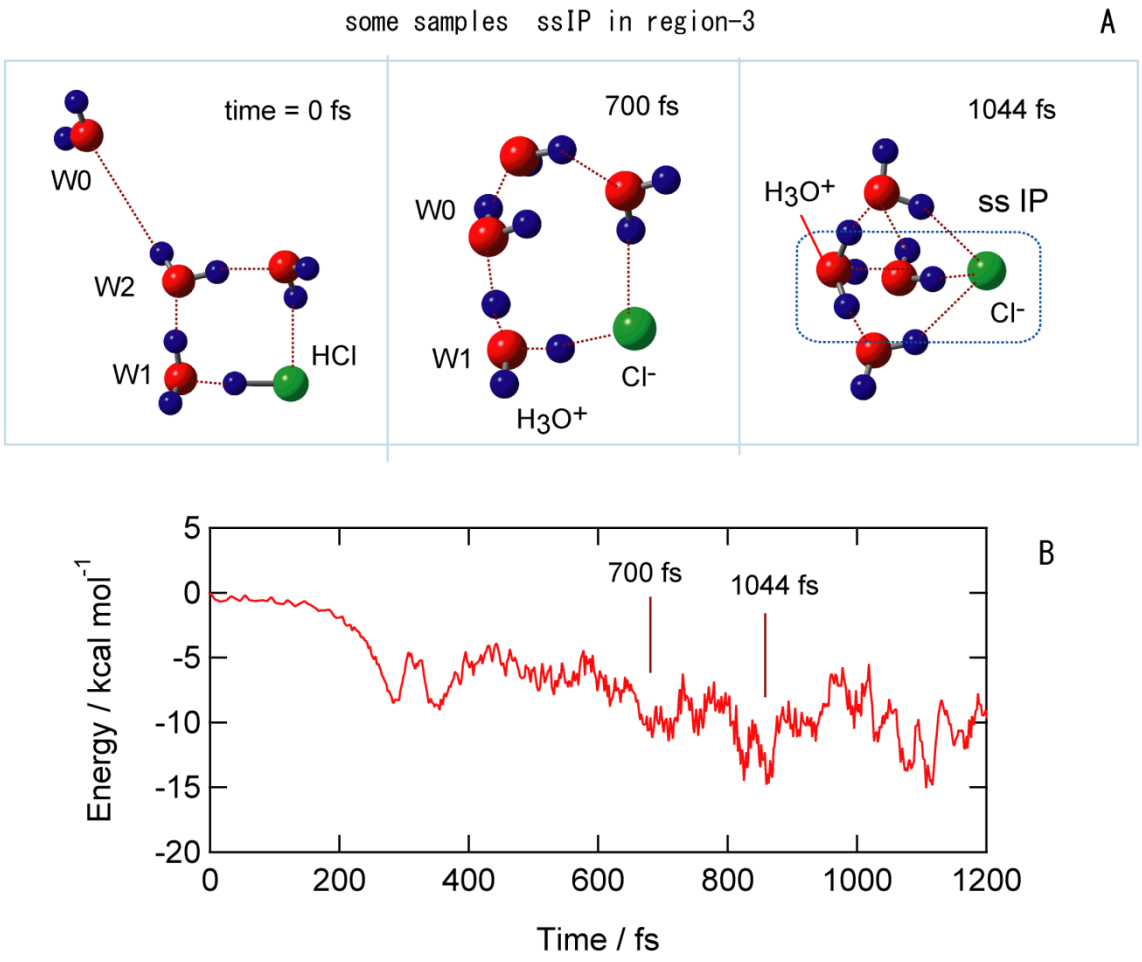

Figure S2. Sample trajectory for ssIP channel (sample-2): (A) Snapshots of $HCl(H_2O)_n$ + H_2O (n = 3+1) reaction system given as a function of time, and (B) time evolutions of potential energy. H_2O(W0) approaches to HCl from region-III.

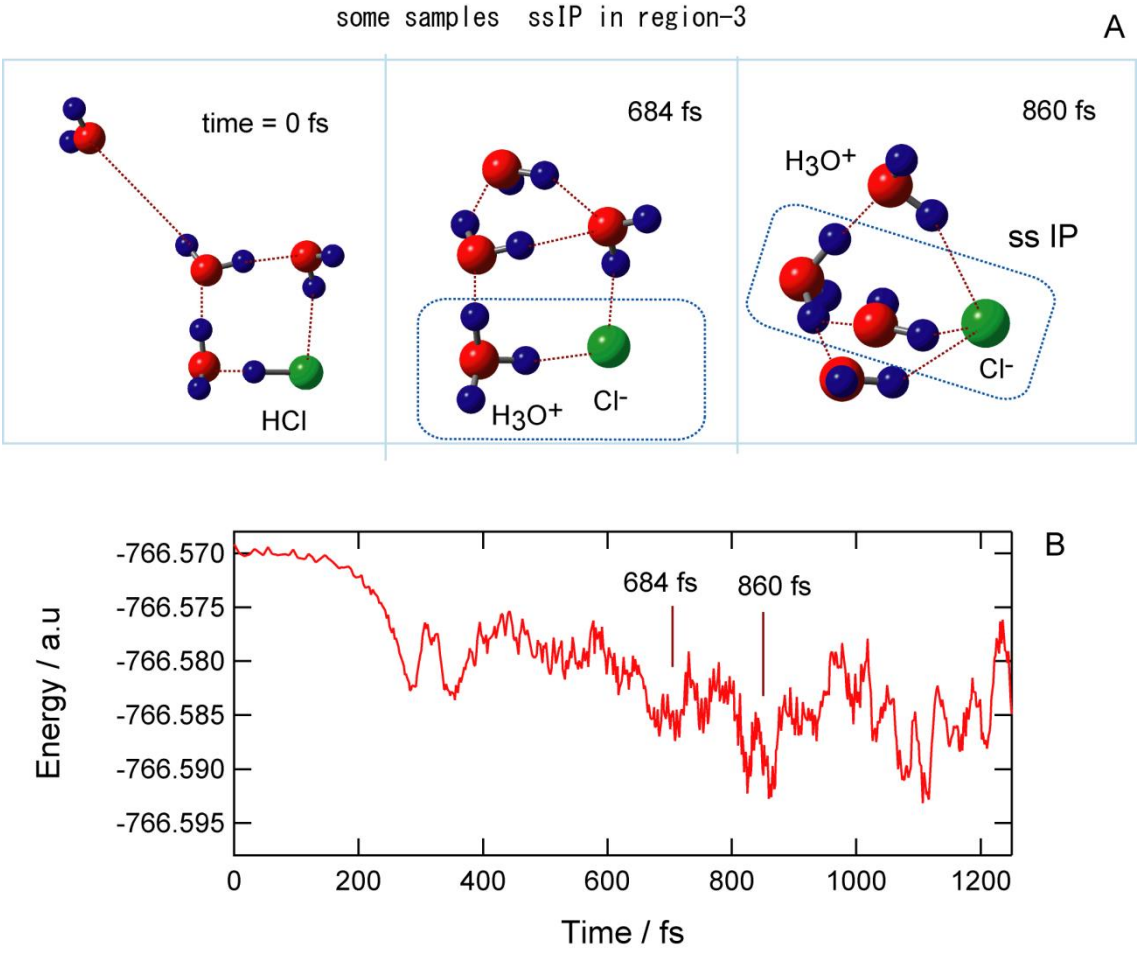

Figure S3. Sample trajectory for ssIP channel (sample-3): (A) Snapshots of $HCl(H_2O)_n$ + H_2O (n = 3+1) reaction system given as a function of time, and (B) time evolutions of potential energy. H_2O(W0) approaches to HCl from region-III.

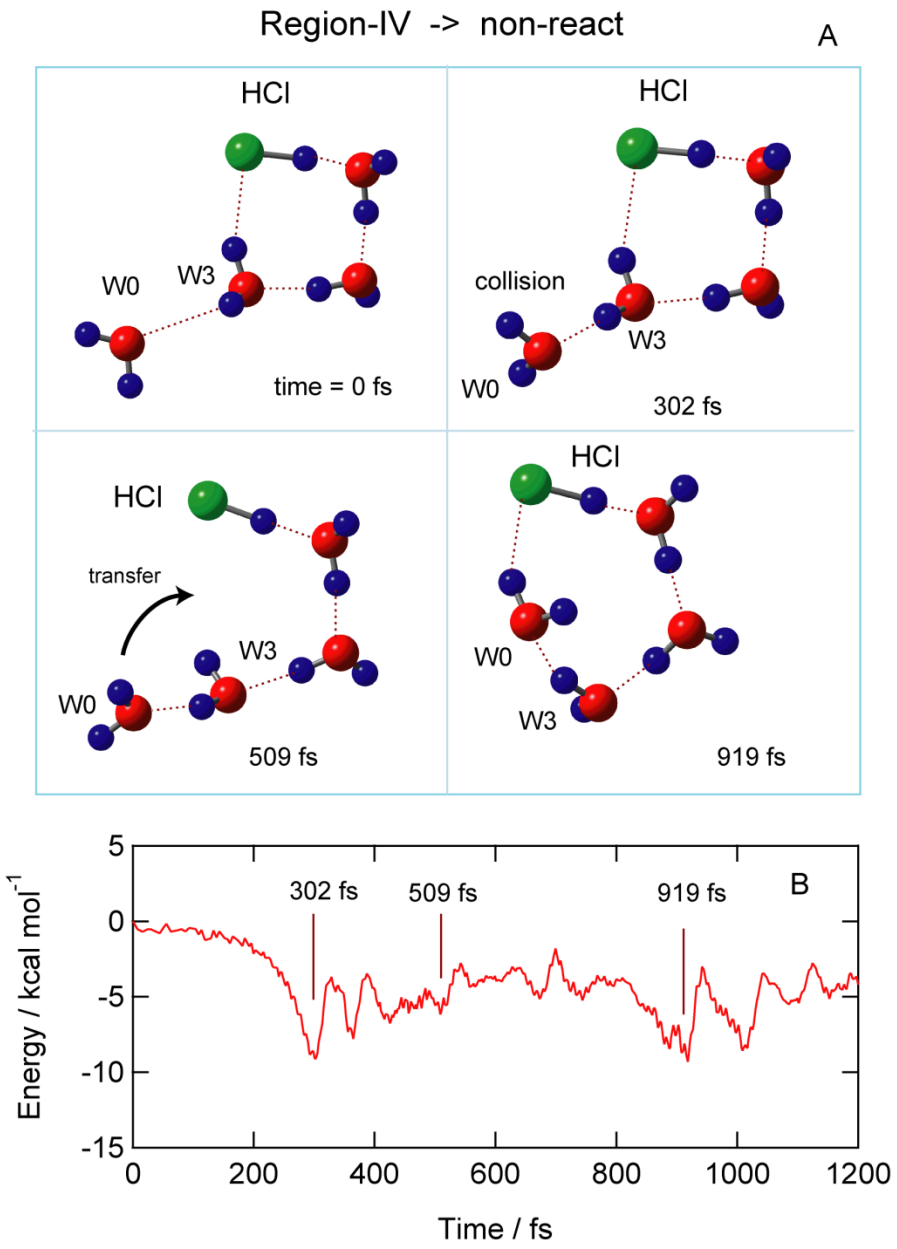

Figure S4. Sample of non-reactive trajectory: (A) Snapshots of $HCl(H_2O)_n + H_2O$ (n = 3+1) reaction system given as a function of time, and (B) time evolutions of potential energy. H_2O(W0) approaches to HCl from region-IV.

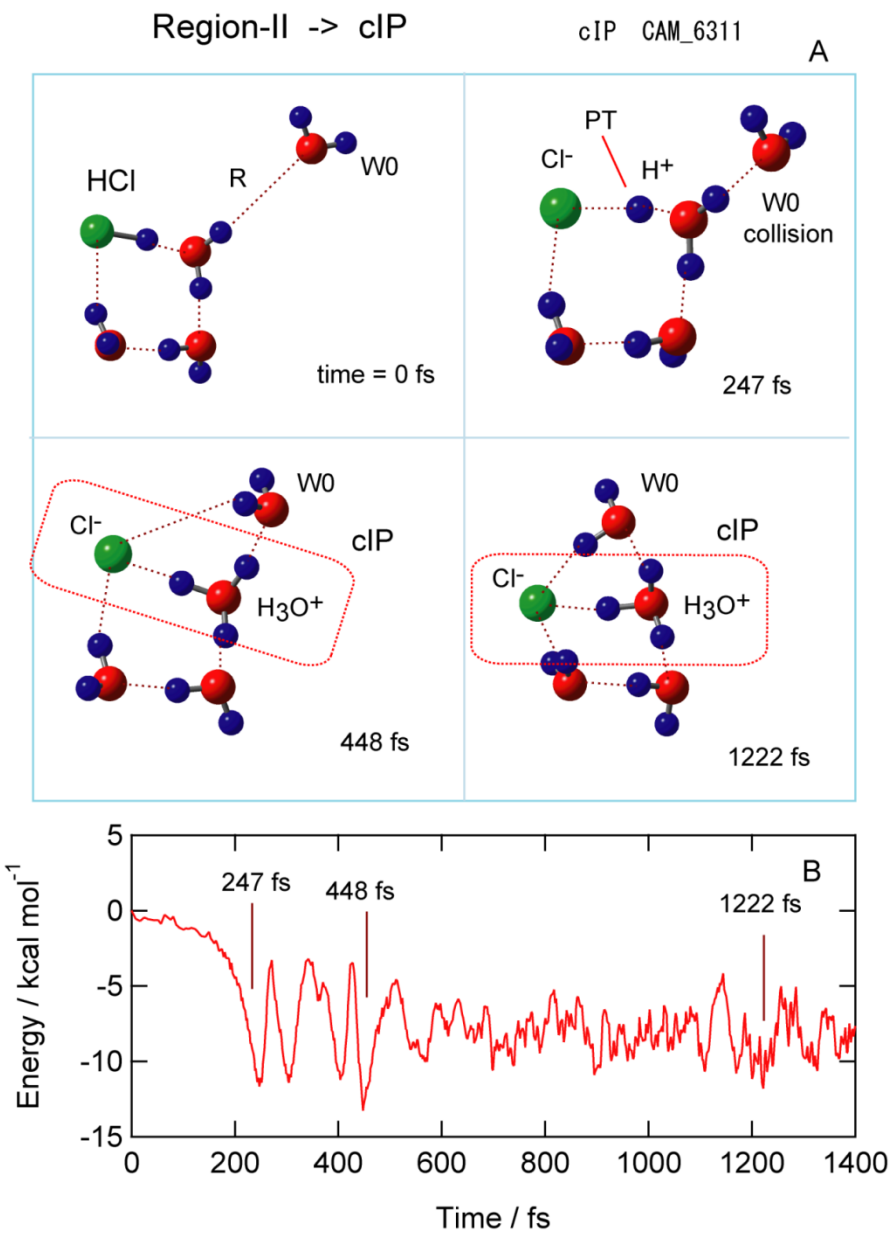

Figure S5. Sample trajectory of cIP (contact ion-pair) channel: (A) Snapshots of $HCl(H_2O)_n + H_2O$ (n = 3+1) reaction system given as a function of time, and (B) time evolutions of potential energy. H_2O(W0) approaches to HCl from region-II.

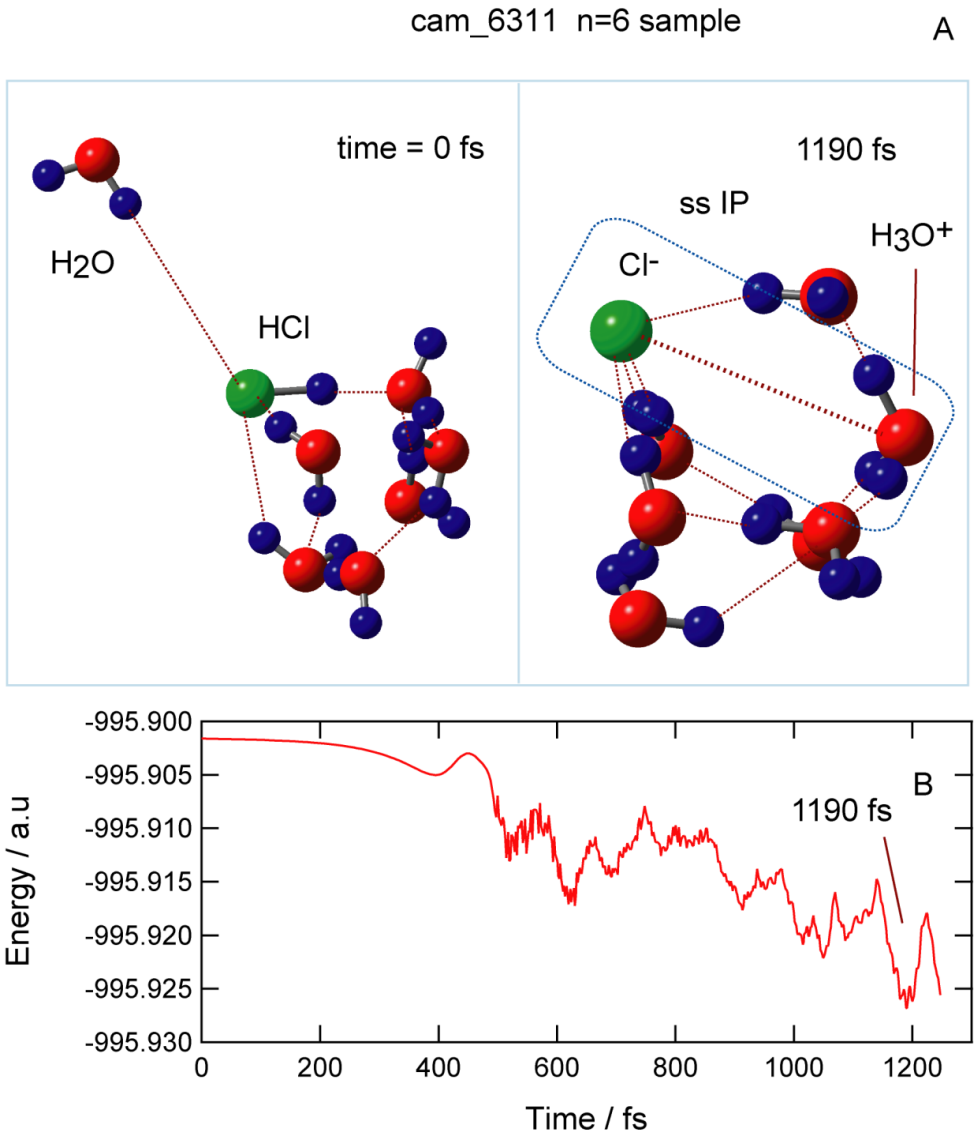

Figure S6. Sample trajectory for ssIP channel: (A) Snapshots of $HCl(H_2O)_n + H_2O$ (n = 6+1) reaction system given as a function of time, and (B) time evolutions of potential energy.

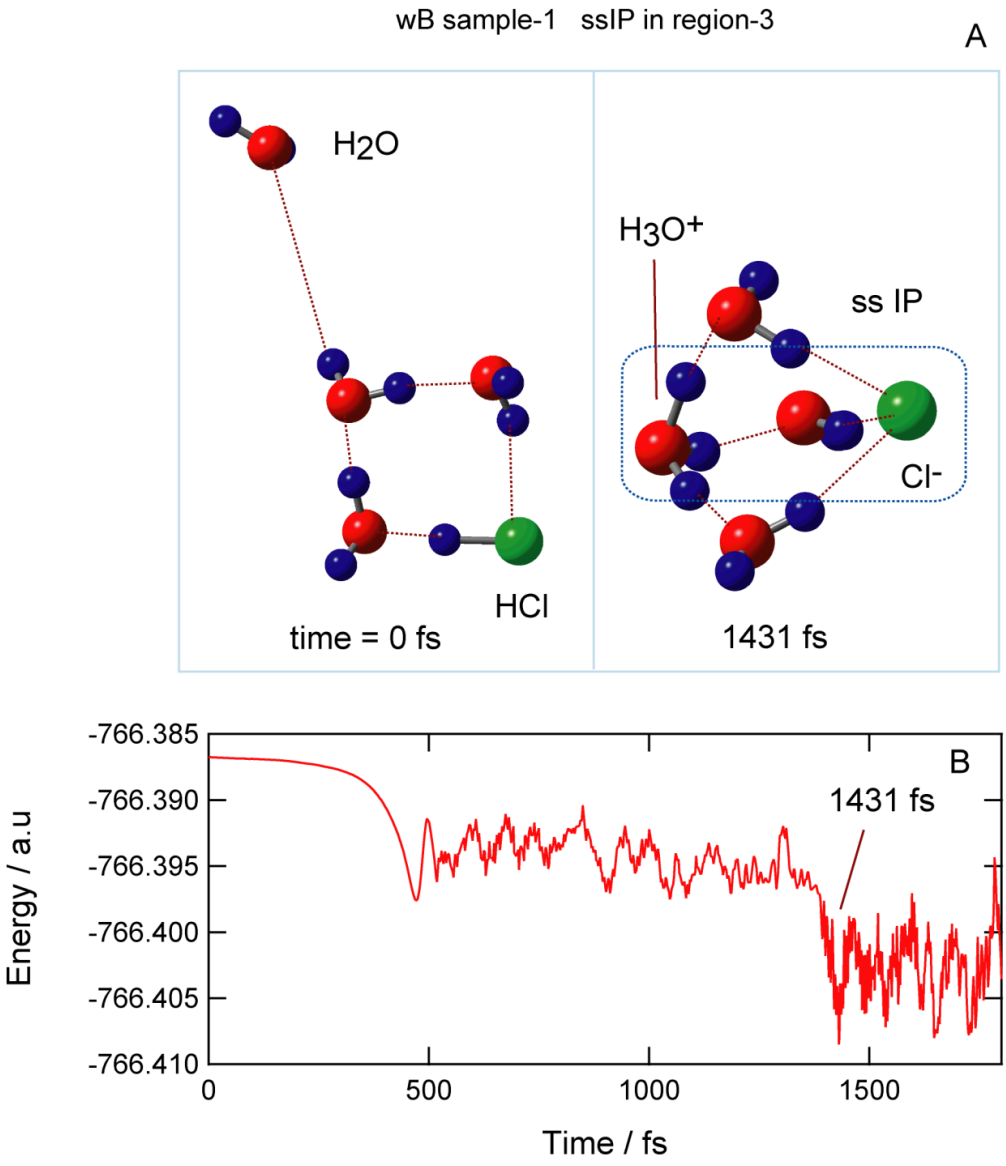

Figure S7. Effect of functional on reaction mechanism. Calculation was carried out at the wB97XD/6-31G(d) level. Sample trajectory of ssIP (solvent-separated ion-pair) channel: (A) Snapshots of $HCl(H_2O)_n$ + H_2O (n = 3+1) reaction system given as a function of time, and (B) time evolutions of potential energy. H_2O(W0) approaches to HCl from region-III.

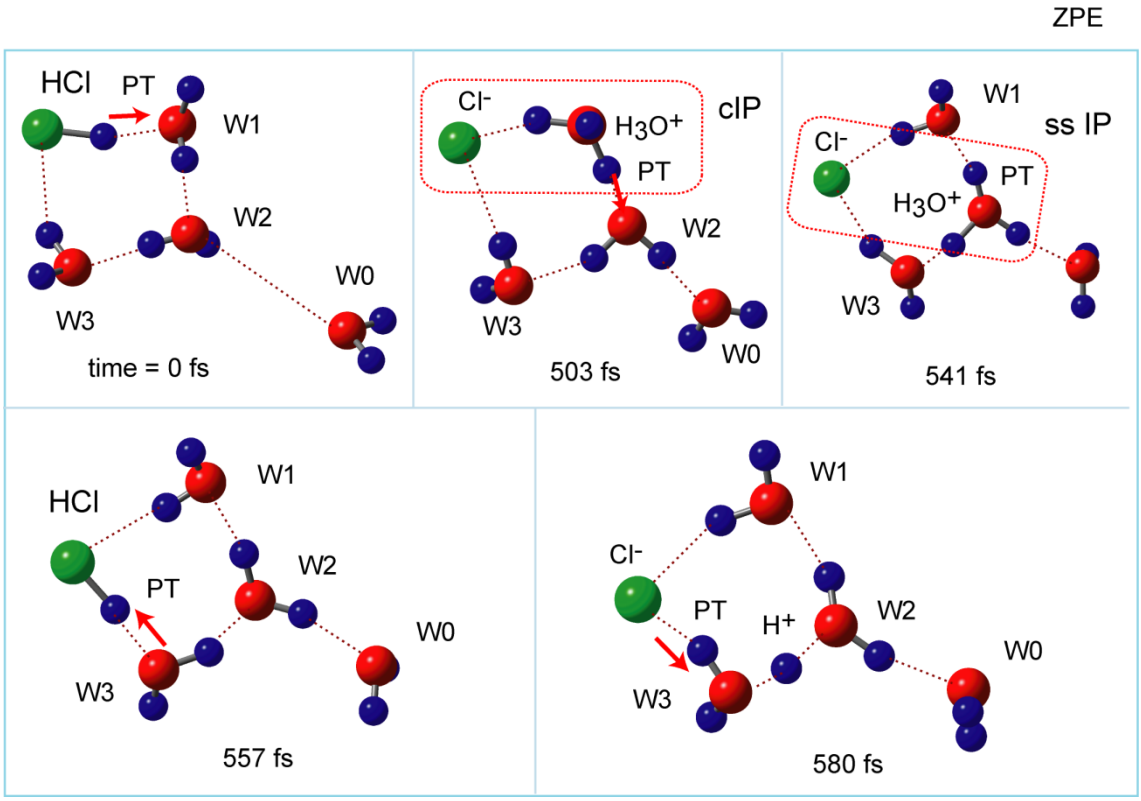

Figure S8. Effects of ZPE on reaction mechanism: snapshots of $HCl(H_2O)_n + H_2O$ (n = 3+1) reaction system given as a function of time. H_2O(W0) approaches to HCl from region-III.