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

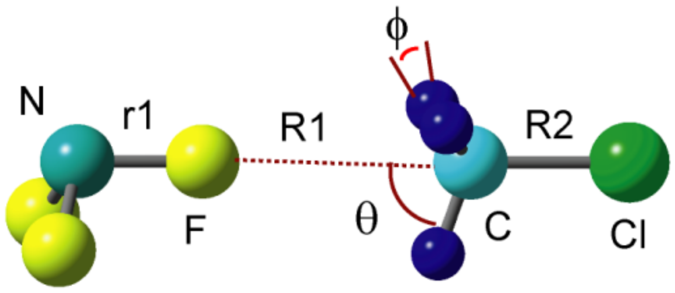
Supporting Information

Reaction Mechanism of an Intracluster S_N2 Reaction Induced by Electron Capture

Hiroto TACHIKAWA*
Division of Applied Chemistry, Faculty of Engineering
Hokkaido University, Sapporo 060-8628, JAPAN

Table S1. Geometrical parameters of NF_3-CH_3Cl calculated at the MP2 and CAM-B3LYP/6-311++G(d,p) levels of theory. Bond lengths and angles are in Å and degrees, respectively.

	MP2	**CAM**
R1	3.064	3.124
R2	1.777	1.791
r1	1.375	1.371
θ	71.2	71.9
ϕ	110.0	110.4



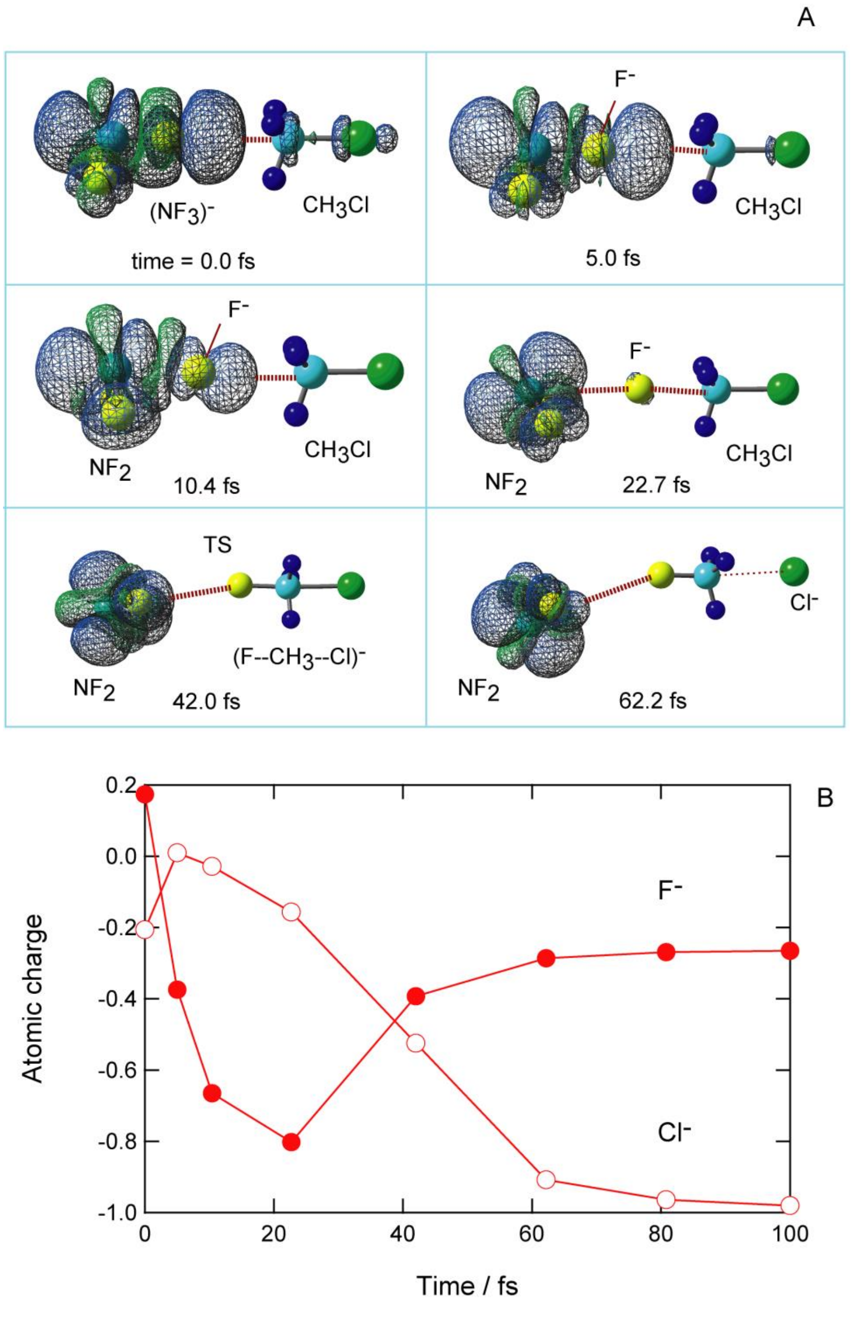


Figure S1. (A) Spatial distributions of spin density of $[NF_3\text{-}CH_3Cl]^-$ superimposed on snapshots and (B) atomic charges of F and Cl plotted as a function of time. The calculation was performed at the MP2/6-311++G(d,p) level.

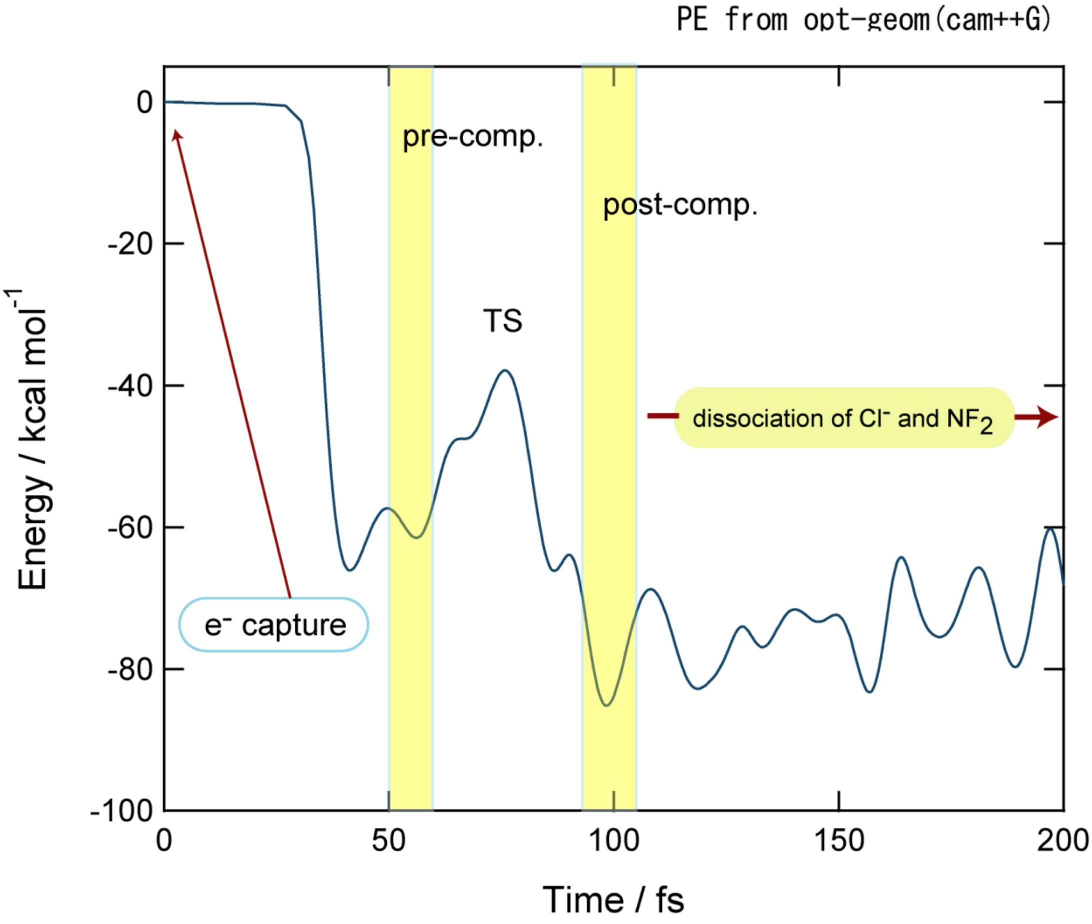


Figure S2. Time evolution of the potential energy of $(NF_3\text{-}CH_3Cl)^-$ following the vertical electron capture of the neutral $NF_3\text{-}CH_3Cl$. The optimized geometry obtained at the CAM-B3LYP/6-311++G(d,p) level was used as initial geometryat time zero. Direct AIMD calculation was performed at the CAM-B3LYP/ 6-311++G(d,p) level.

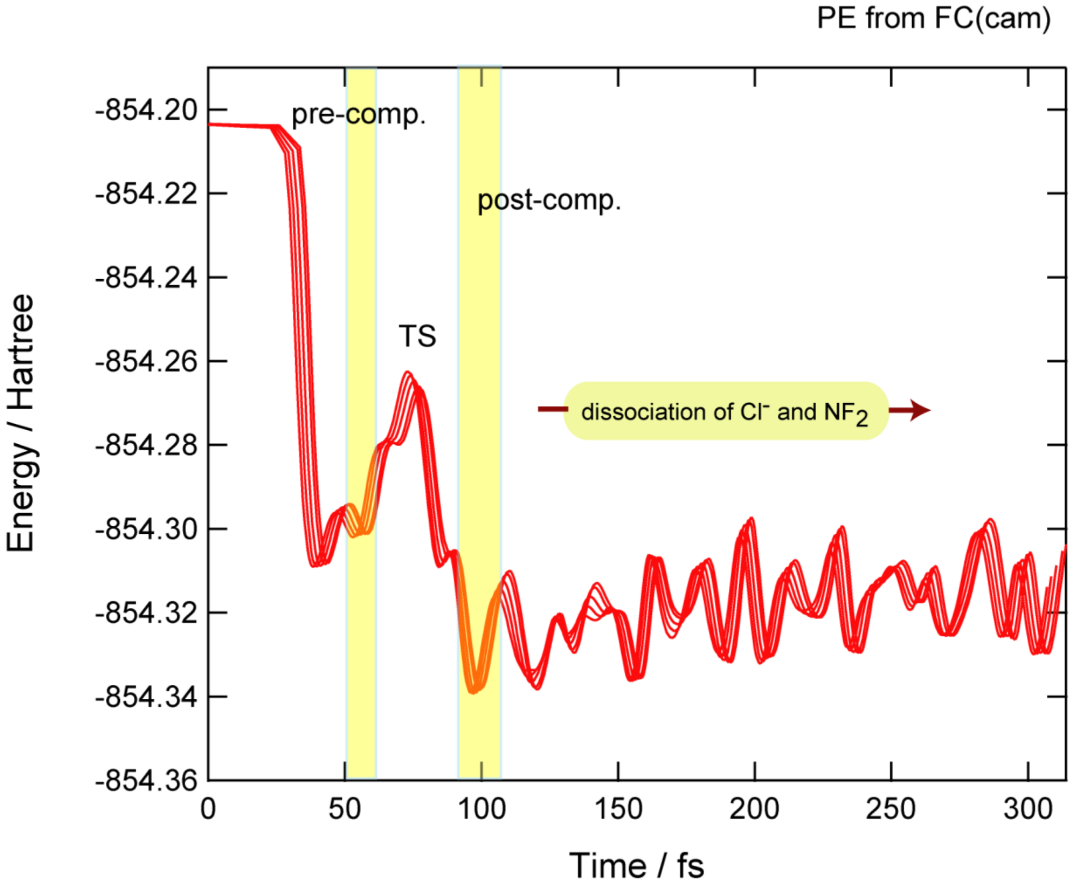


Figure S3. Time evolution of the potential energies of $(NF_3\text{-}CH_3Cl)^-$ following the vertical electron capture of the neutral $NF_3\text{-}CH_3Cl$. Initial geometries were selected randomly from Franck-Condon (RC) region. AIMD calculations were performed at the CAM-B3LYP/ 6-311++G(d,p) level.

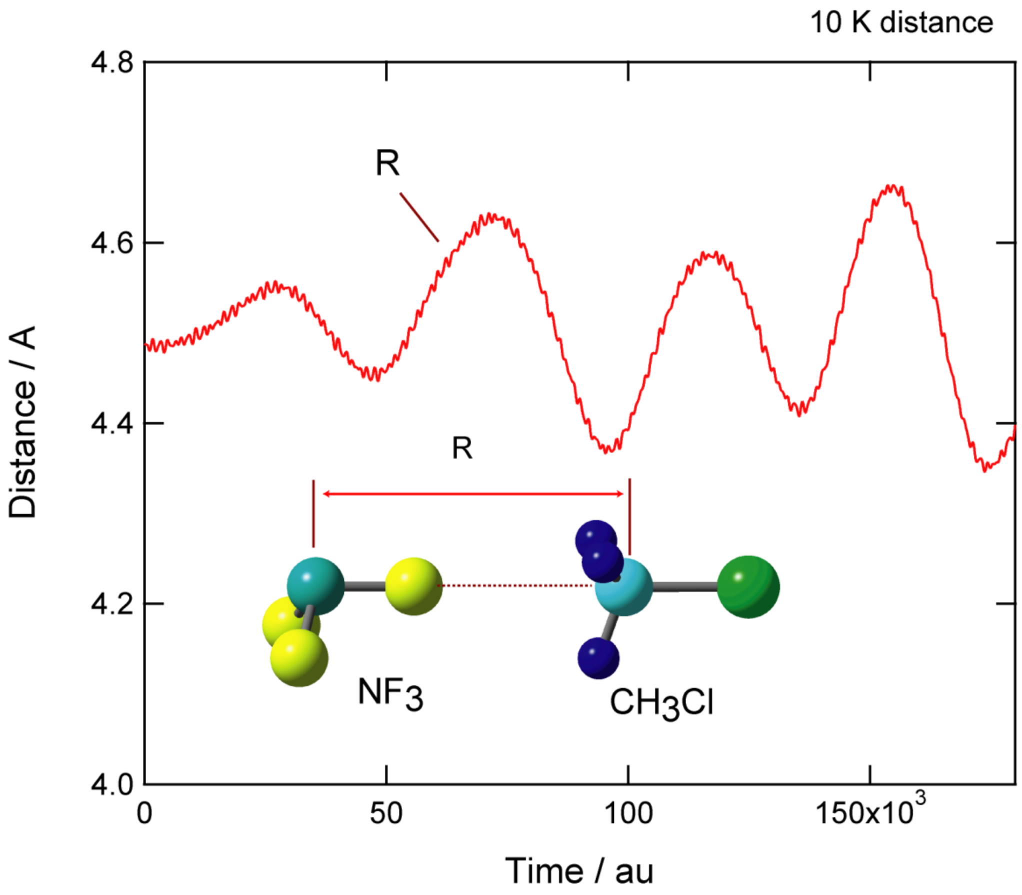


Figure S4. Time evolution of intermolecular distance of neutral state of NF_3-CH_3Cl calculated at 10 K. AIMD calculation was performed at the CAM-B3LYP/ 6-311++G(d,p) level. The CAM-B3LYP/6-311++G(d,p) optimized geometry was used as the initial geometry at time zero.

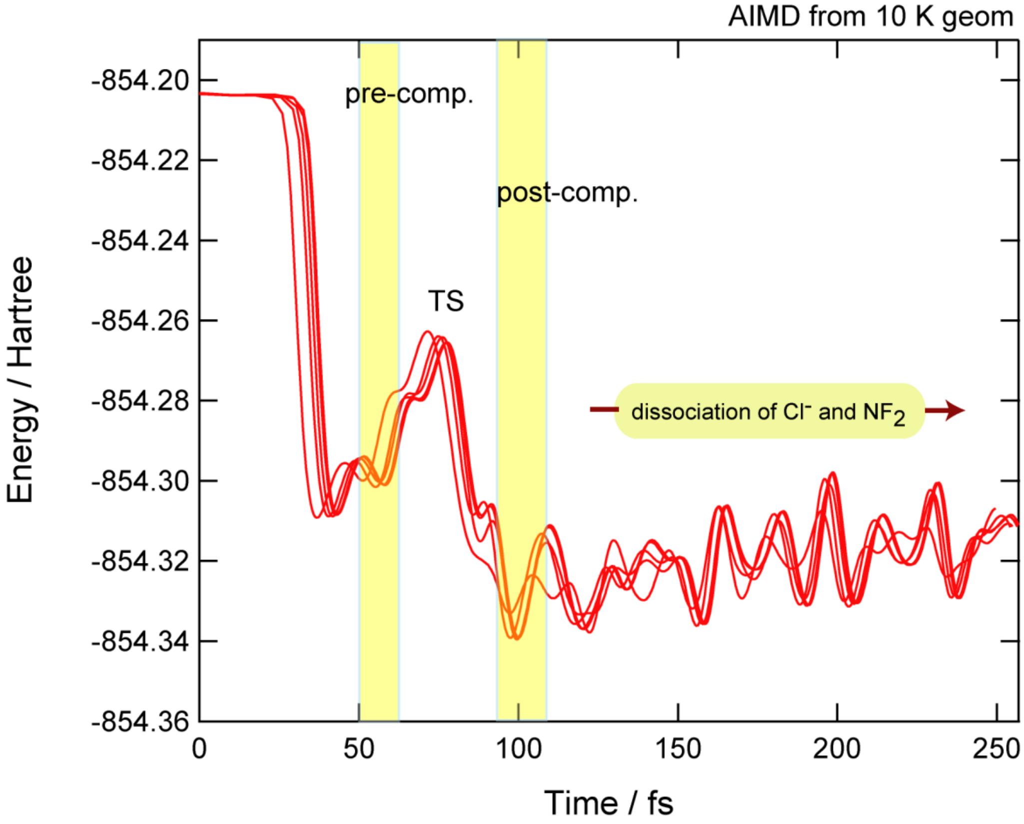


Figure S5. Time evolution of the potential energies of $(NF_3\text{-}CH_3Cl)^-$ after vertical electron capture of the neutral $NF_3\text{-}CH_3Cl$. Initial geometries were generated at thermal activation at 10 K. AIMD calculations were performed at the CAM-B3LYP/ 6-311++G(d,p) level.

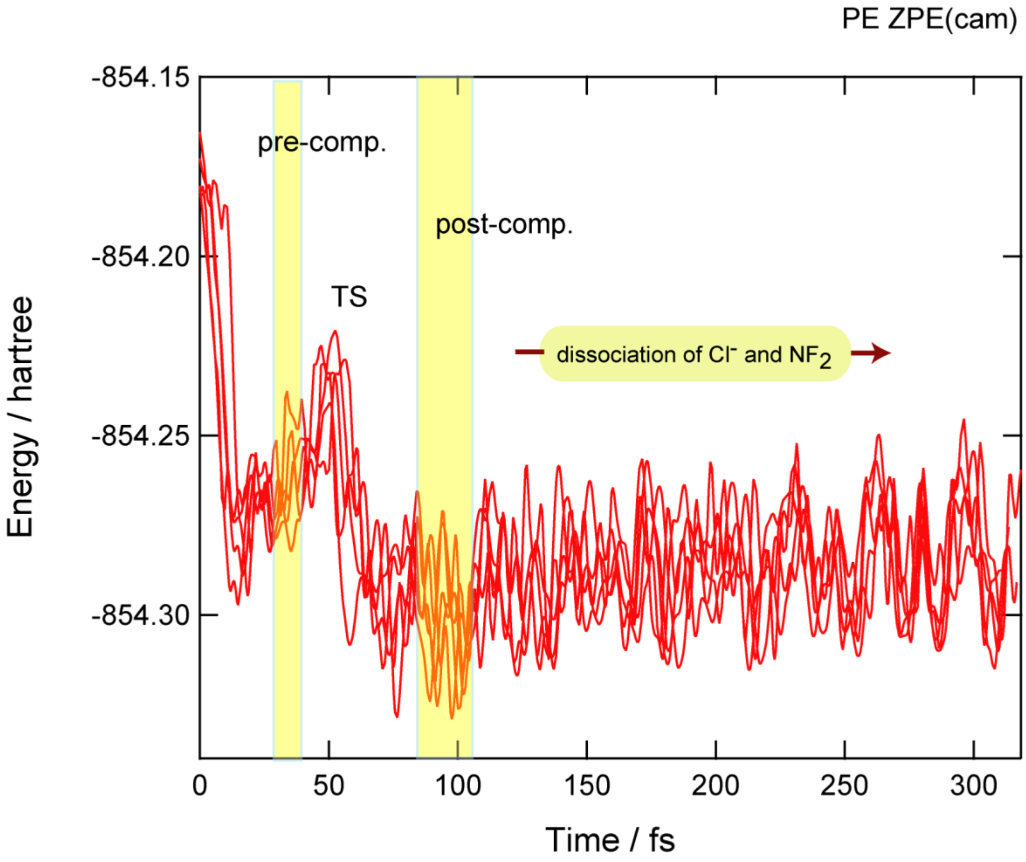


Figure S6. Effects of zero point energy (ZPE) on reaction mechanism. Time evolution of the potential energies of $(NF_3\text{-}CH_3Cl)^-$ after vertical electron capture of the neutral $NF_3\text{-}CH_3Cl$. Initial geometries were generated at thermal activation at 10 K. AIMD calculations were performed with ZPE at the CAM-B3LYP/ 6-311++G(d,p) level.

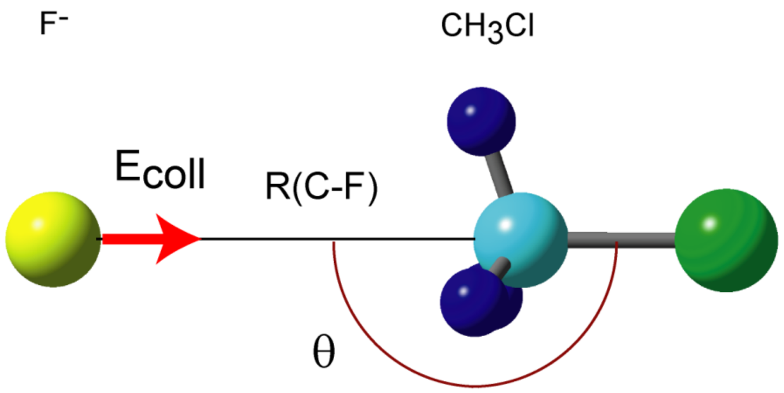


Figure S7. Schematic illustration of initial geometrical configuration in bimolecular S_N2 reaction: $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$. Collision energy was fixed to zero (E_{coll}=0.0 kcal/mol) in the present calculation.

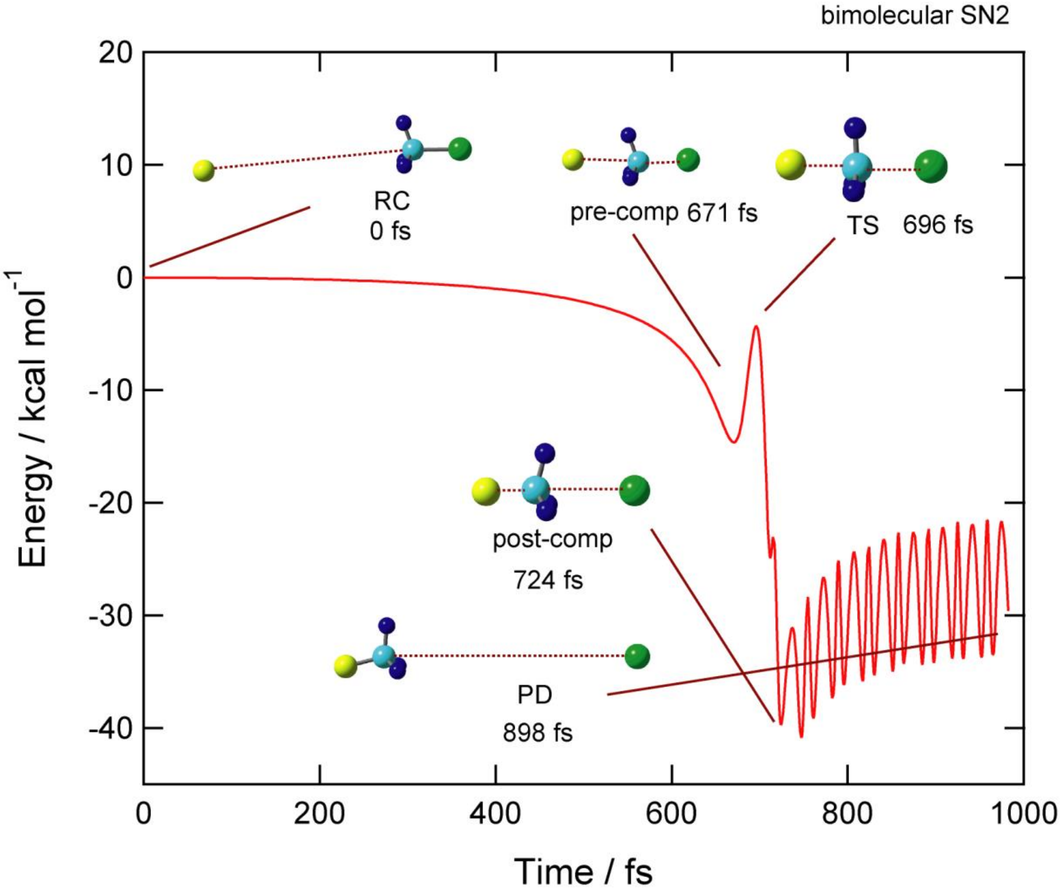


Figure S8. Time evolution of the potential energies of bimolecular S_N2 reaction: $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$. Direct AIMD calculation was performed at the CAM-B3LYP/ 6-311++G(d,p) level.

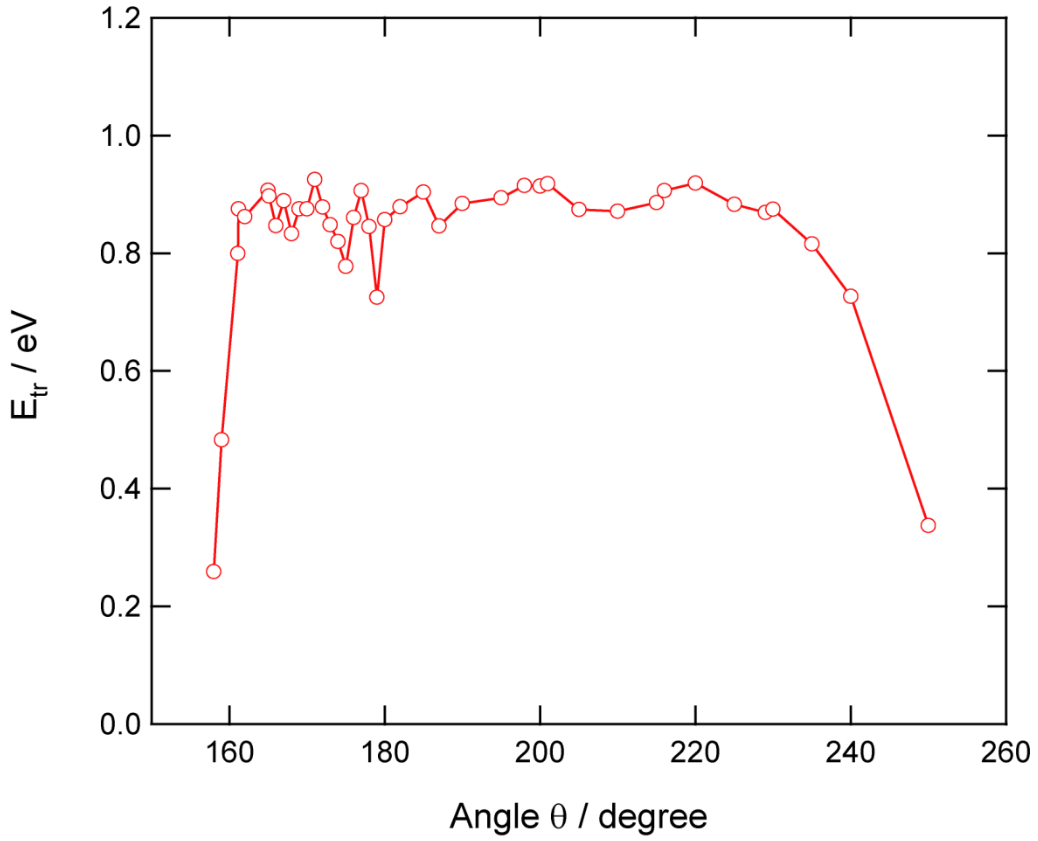


Figure S9. Angle dependency of relative translational energies of dissociating Cl- ion after bimolecular S_N2 reaction: $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$. Direct AIMD calculation was performed at the CAM-B3LYP/6-311++G(d,p) level. The CAM-B3LYP/ 6-311++G(d,p) optimized geometry was used as the initial geometry of CH_3Cl at time zero, and collision energy was zero.

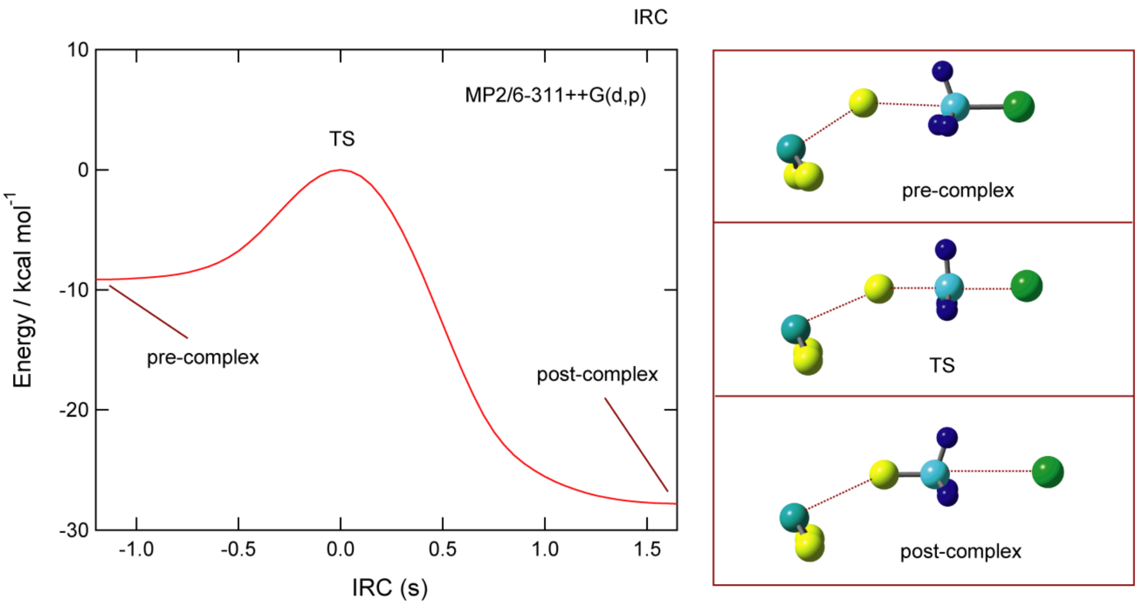


Figure S10. Intrinsic reaction coordinate (IRC) of intracluster S_N2 reaction: $(NF_3\text{-}CH_3Cl)^- \rightarrow NF_2 + CH_3F + Cl^-$, calculated at the MP2/6-311++G(d,p) level.

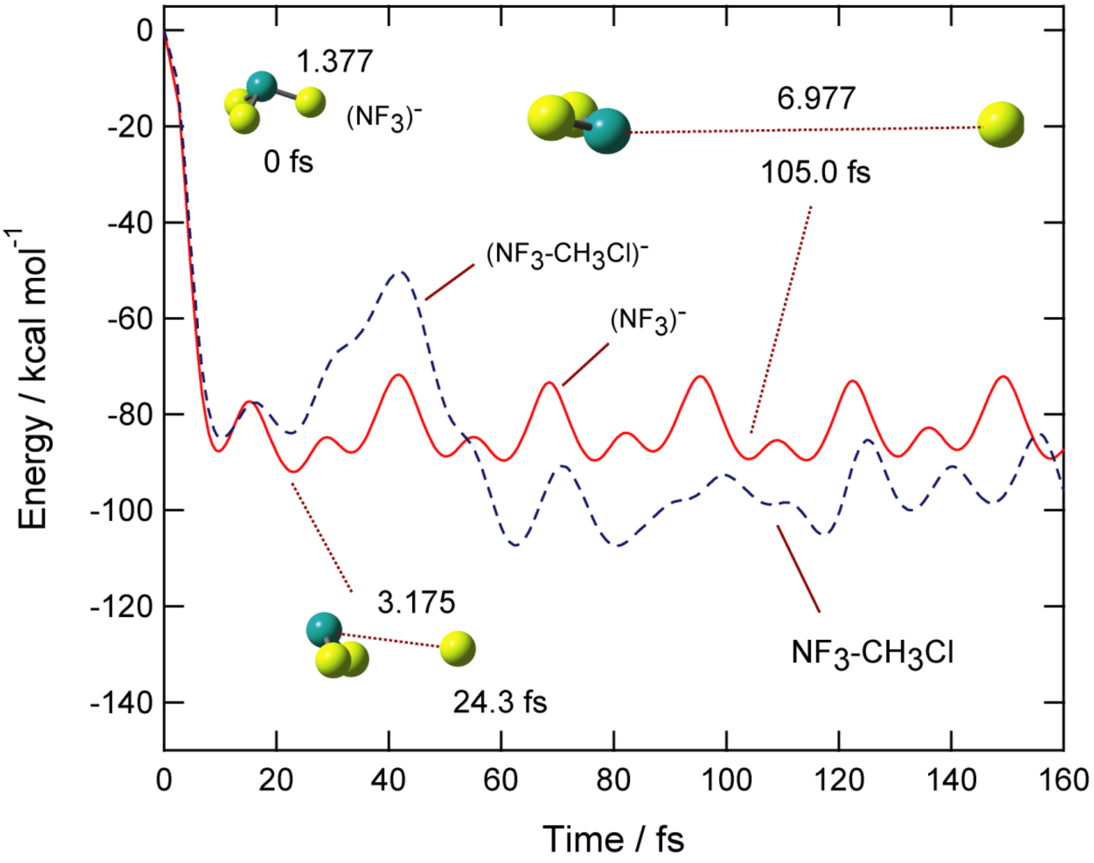


Figure S11. Comparison of time evolution of the potential energies of $(NF_3)^-$ (solid red line) and $(NF_3\text{-}CH_3Cl)^-$ (dashed blue line) after vertical electron capture of the neutral states. Direct AIMD calculation was performed at the MP2/6-311++G(d,p) level. The MP2/6-311++G(d,p) optimized geometry was used as the initial geometry at time zero.

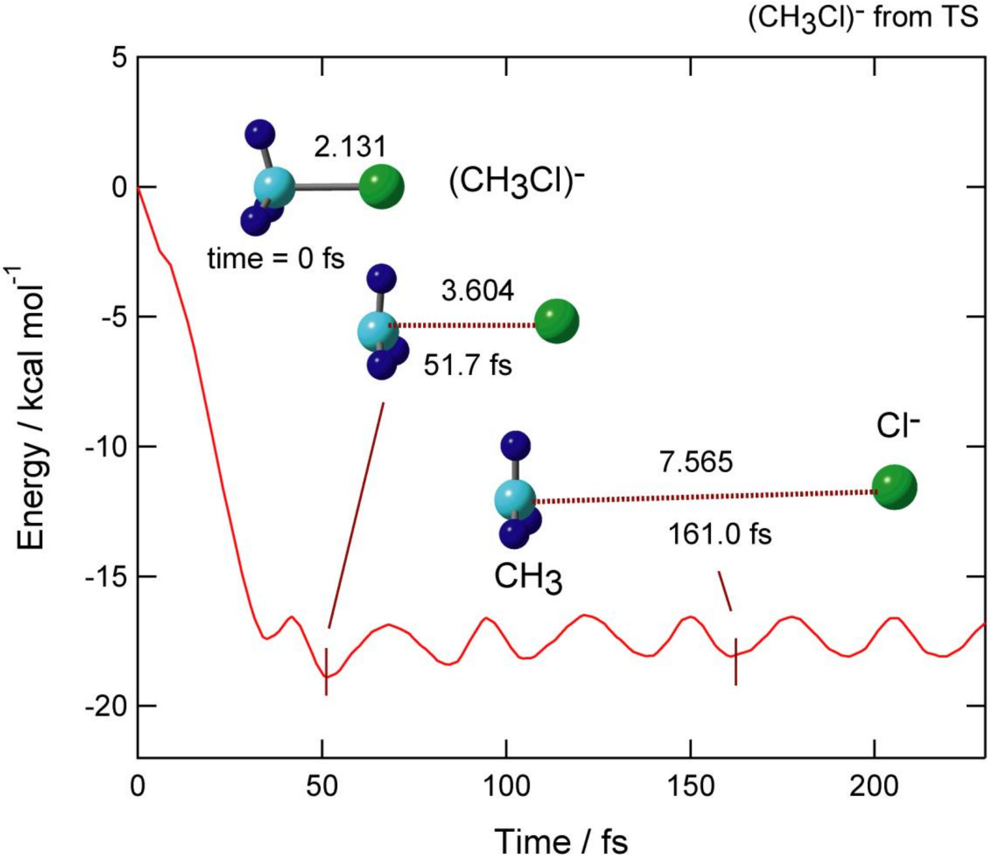


Figure S12. Time evolution of the potential energy of $(CH_3Cl)^-$ started from TS. Snapshots of $(CH_3Cl)^-$ are given as insert figures. Direct AIMD calculation was performed at the MP2/6-311++G(d,p) level. The MP2/6-311++G(d,p) optimized geometry was used as the initial geometry of TS at time zero.

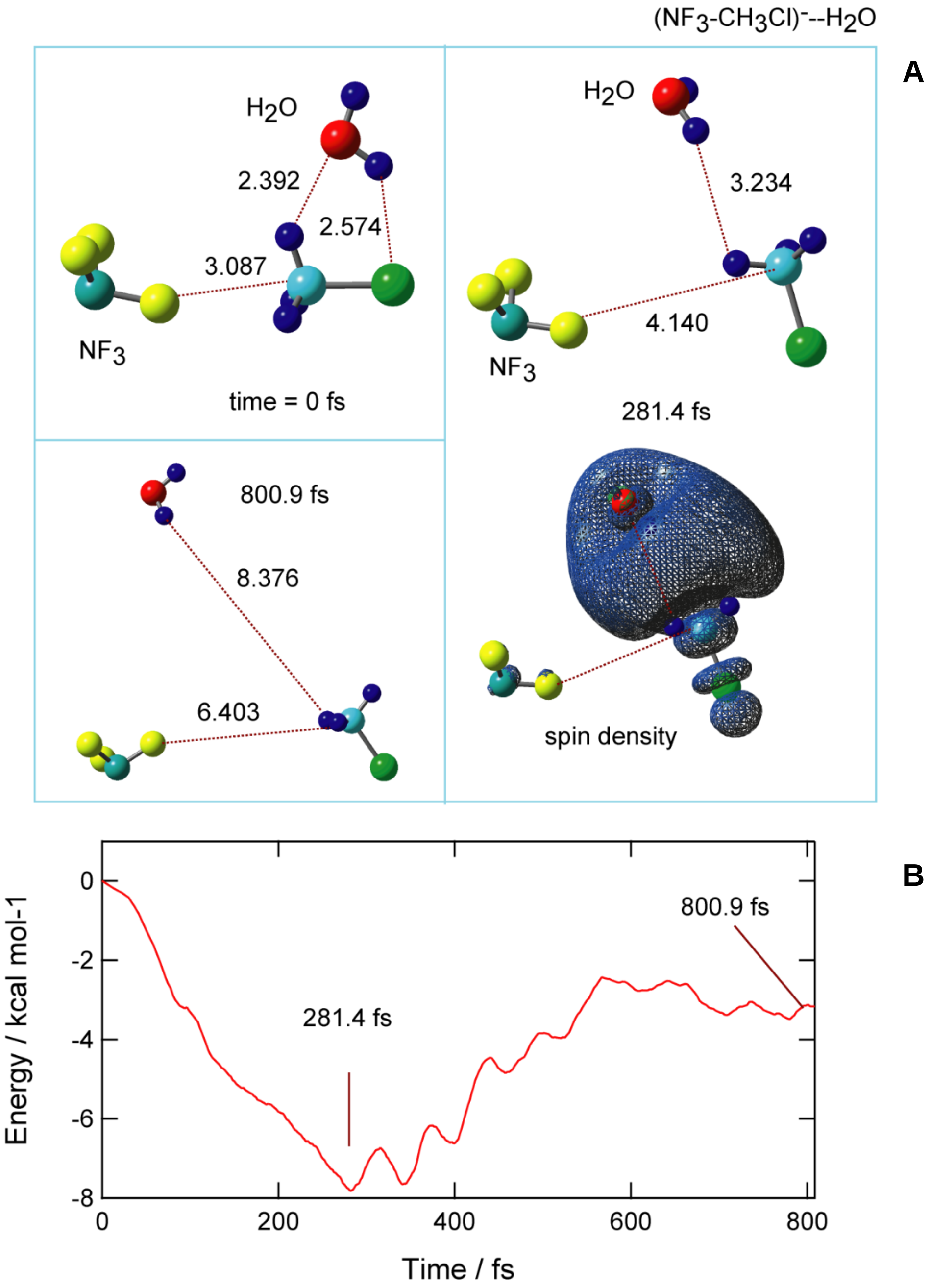


Figure S13. (A) Snapshots and (B) time evolution of the potential energy of $(NF_3\text{-}CH_3Cl\text{-}H_2O)^-$ after vertical electron capture of the neutral cluster of $NF_3\text{-}CH_3Cl\text{-}H_2O$. Direct AIMD calculation was performed at the CAM-B3LYP/6-311++G(d,p) level. The CAM-B3LYP/6-311++G(d,p) optimized geometry was used as the initial geometry at time zero.

Table S2. Relative translational energies (E_{tr} / eV) of Cl^- generated from intracluster S_N2 reaction of $(NF_3\text{-}CH_3Cl)^-$ in Franck-Condon region. Direct AIMD calculations were carried out at the MP2/6-311++G(d,p) and CAM-B3LYP/6-311++G(d,p) levels of theory. Ten trajectories were run in each level. SD means standard deviation (σ_n).

RUN	**MP2**	**CAM-B3LYP**
1	2.22	1.61
2	2.17	1.62
3	2.12	1.64
4	2.08	1.68
5	2.32	1.69
6	2.39	1.71
7	2.16	1.73
8	2.16	1.75
9	2.23	1.79
10	2.22	1.77
average	2.21	1.70
SD (σ_n)	0.09	0.06