Electronic supplementary information

Facilitated inversion complicates the stereodynamics of a S_N2 reaction at nitrogen center

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1. Absolute energies and Cartesian coordinates of the stationary points

Absolute energies (in hartree) and Cartesian coordinates (in angstrom) of the stationary points of the $F^- + NH_2Cl$ reaction on the newly-developed potential energy surface (PES) corresponding to Figure 1 are provided below. The benchmark energies and geometries can be found in Ref 30.

Reactants:

```
  -615.38395758430761
H      0.46929635   0.81254635  -1.46268832
H      0.46971547  -0.81225892  -1.46201866
N     -0.07638689   0.00011612  -1.18767086
F      0.00045823   0.44037572  30.00553876
Cl     0.00055310   0.00085543   0.55782117
```

Reactants (inversion intermediate):

```
  -615.36882503644199
H     -0.00000000   0.88296427  -1.60043329
H     -0.00000000  -0.88297396  -1.60042533
N     -0.00000000  -0.00000276  -1.13709865
F     -0.00000000   0.00000004  30.00001105
Cl    -0.00000000   0.00000479   0.53720917
```

H premin

-615.43255935063360

H	-1.33134440	0.85840513	-0.02589609
H	-0.31316260	-0.06586242	-1.01658833
N	-0.92240288	-0.07466047	-0.07048130
F	0.30159584	-0.00208390	-2.22493255
Cl	0.25859436	0.00136284	1.24488956

Pre-DI TS:

-615.42154806878375

H	0.00000000	-0.14901254	-1.40356618
H	-0.00000000	-1.71081019	0.23274317
N	0.00000000	-0.76176888	-0.11980249
F	-0.00000000	0.25637012	-2.35149386
Cl	0.00000000	0.21861504	1.33519709

FS premin:

-615.40363186816933

H	-0.80271769	-0.51951318	-2.24237852
H	0.80271089	-0.51951158	-2.24238057
N	-0.00000365	0.05103176	-1.98952648
F	-0.00000001	-0.00471650	2.01876632
Cl	-0.00000164	-0.00654501	-0.15646847

W TS:

-615.40370014438497

H	0.79788718	0.39862867	-0.63269240
H	-0.79788774	0.39862750	-0.63269220
N	0.00000019	-0.22404728	-0.55509007
F	0.00000017	0.06422962	-2.46864492
Cl	0.00000020	0.03099681	1.58126750

PT TS:

-615.39990008234065

H	0.92934576	-1.36388289	1.14345197
H	-0.03123071	-0.04279313	-1.20821238
N	-0.07505551	-1.18869033	1.01932959
F	0.01974041	-0.15339364	-2.14203321
Cl	0.00677932	0.61249880	0.77250725

PT postmin:

-615.40078408563750

H	0.82885953	-1.27192466	1.22976088
H	-0.00198728	-0.08008598	-1.22773357
N	-0.00145180	-0.83739257	1.64909127
F	0.04701737	-0.38028827	-2.12475598
Cl	-0.03050209	0.67155578	0.63327846

FS TS:

-615.32913570760832

H	0.27223571	-0.84055688	-1.73191998
H	0.63854232	-1.28777125	-0.17804126
N	-0.13049449	-1.20092300	-0.84779255
F	-0.04032259	0.69690398	-1.80874625
Cl	0.18959362	0.14788253	1.37333976

H postmin:

-615.43228384274676

H	0.92779718	-0.92457706	-1.28474792
H	-0.22298402	-0.26168845	-0.38495376
N	-0.06472131	-0.69220112	-1.31618192
F	-0.01168521	0.47154991	-2.17694848
Cl	-0.04570877	0.12173466	1.75471909

Post-DI TS:

-615.40443021915848

H	0.00000000	-0.23317910	0.30689297
H	0.00000000	-1.49754299	1.69542904
N	0.00000000	-0.59427039	1.26854253
F	-0.00000000	0.39950014	2.25648882
Cl	0.00000000	0.09306720	-1.77253526

S_N2 products:

-615.40613977474572

H	0.48807528	0.80762707	-0.99541521
H	0.48816863	-0.80774376	-0.99526716
N	-0.08507653	-0.00006989	-0.75997182
F	0.01023047	0.00006598	0.66230175
Cl	-0.00030416	-0.00001904	30.00022694

SN2 products (inversion intermediate):

-615.38119611353625

H	-0.00000000	0.90955966	-1.12678970
H	-0.00000000	-0.90957697	-1.12678328
N	-0.00000000	-0.00000724	-0.72644965
F	0.00000000	-0.00000238	0.65030361
Cl	-0.00000000	-0.00000018	29.99998200

PT products:

-615.37253424193455

H	0.00381472	0.93897166	-1.45762873
H	29.98934604	-0.00151361	0.87134766
N	0.00423874	-0.07022734	-1.27088383
F	29.98993086	-0.00131981	-0.04460791
Cl	0.00576241	-0.00925471	0.54917109

2. Frequencies of the stationary points

Table S1. Harmonic frequencies (in cm^{-1}) of the stationary points of the $F^- + NH_2Cl$ reaction determined on the newly-developed PES.

No.	React.	React. Inv.	H premin	pre-DI TS	FS premin	W TS	PT TS	PT postmin	FS TS	H postmin	post-DI TS	S_N2 prod.	S_N2 Prod. Inv.	PT prod.
1	690	905i	130	504i	202	427i	146i	70	887i	80	1098i	931	1125i	553
2	1105	868	381	121	208	245	87	141	181i	194	111	1299	1080	1243
3	1211	1117	496	327	252	265	199	216	79	276	214	1432	1200	3327
4	1646	1614	655	703	559	316	538	545	295	897	458	1697	1622	4177
5	3466	3683	1246	1065	1007	1040	568	796	477	1398	1021	3394	3708	
6	3553	3834	1440	1256	1072	1061	759	835	770	1461	1217	3510	3898	
7			1627	1378	1588	1577	1247	1284	1502	1638	1523			
8			1872	1967	3419	3509	3329	3335	3112	3171	3234			
9			3451	3534	3535	3620	3612	3475	3438	3420	3854			

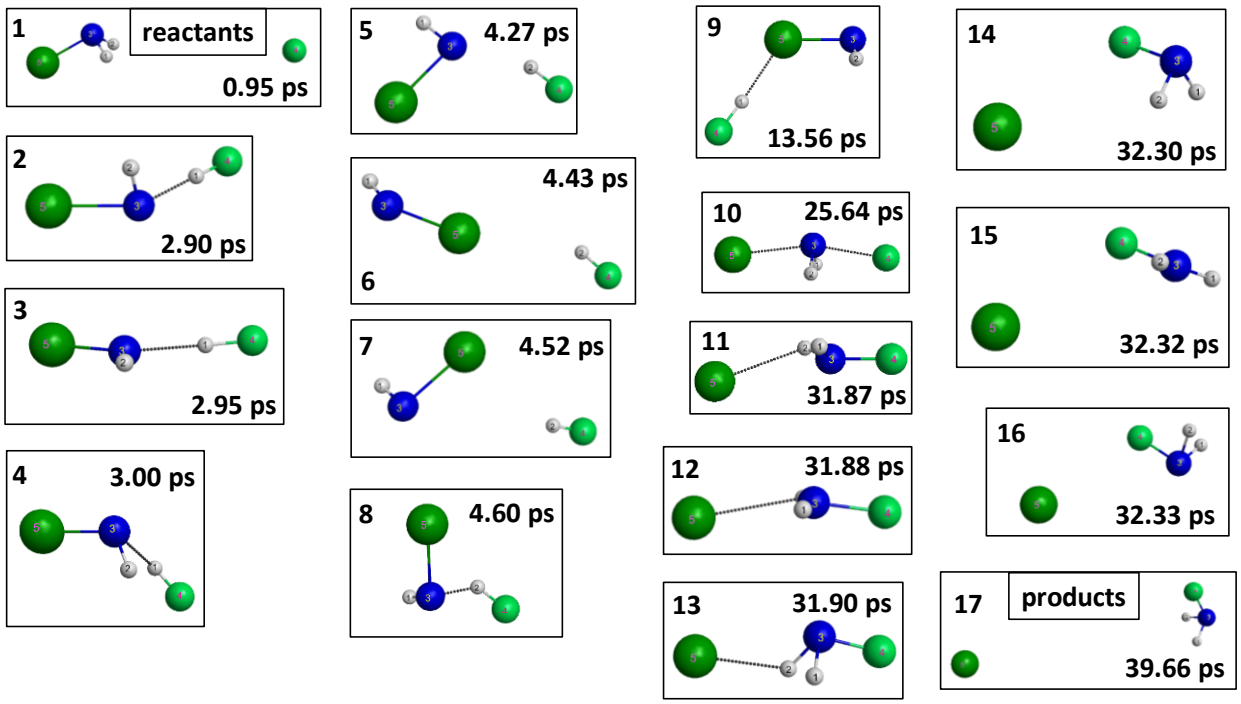

Figure S1. Snapshots along a representative indirect S_N2 ($F^- + NH_2Cl \rightarrow Cl^- + NH_2F$) trajectory from QCT simulations at 0.9 kcal/mol collision energy and zero impact parameter. Trajectory length is 40.07 ps, and the following mechanisms can be observed in the figure: 2−4: inversion through pre-DI TS, 5−8: roundabout/roaming, 9: spending time near PT TS/postmin (reflecting the indirect nature of the trajectory), 10: Walden-inversion, 11−13: inversion through post-DI TS, 14−16: self-inversion of the NH_2F product. Note, that most of the above actions occur multiple times along this trajectory (except Walden-inversion).

3. T_1 diagnostics in the stationary points

Table S2. T_1 diagnostic values obtained at the CCSD-F12b/aug-cc-pV5Z level of theory at the CCSD(T)-F12b/aug-cc-pVTZ optimized geometries of the stationary points of the F^- + NH_2Cl reaction shown in Figure 1.

Stationary point	T_1 diagnostic value
NH_2Cl	0.0100
NH_2Cl inv. TS	0.0089
F^-	0.0189
H premin	0.0131
pre-DI TS	0.0124
FS premin	0.0167
W TS	0.0244
PT TS	0.0144
PT postmin	0.0143
FS TS	0.0461
H postmin	0.0104
post-DI TS	0.0096
NH_2F	0.0117
NH_2F inv. TS	0.0100
Cl^-	0.0044
$NHCl^-$	0.0171
HF	0.0087

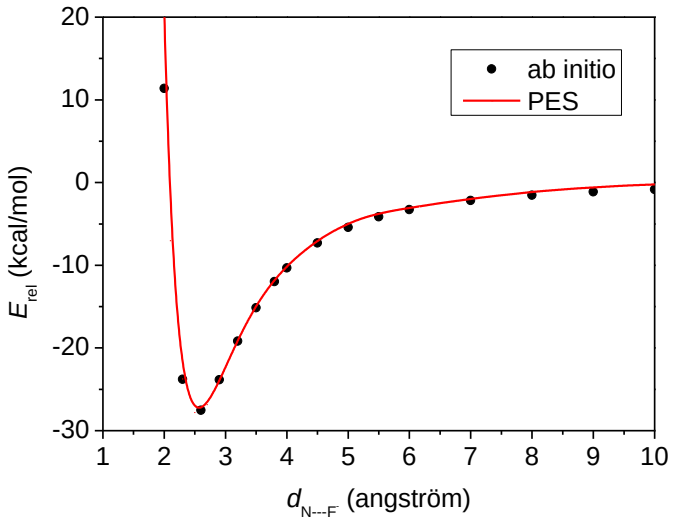

Figure S2. One-dimensional cut of the newly-developed PES along the N−H−F axis in the entrance channel of the F^- + NH_2Cl reaction compared to CCSD(T)-F12b/aug-cc-pVTZ *ab initio* data.