Supplementary Information

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Table S1. Relative energies(kcal/mol) of the stationary points at the DFT/M06-2X/aug-cc-pVDZ(LANL2DZ-ECP) and CCSD(T)/aug-cc-pVTZ(PP) levels of theory.

	DFT/M06-2X/aug-cc-pVDZ (LANL2DZ-ECP)	CCSD(T)/aug-cc-pVTZ(PP)
RS ($F^- + NH_2I$)	0.0	0.0
MIN-HBC (MIN-I-HBC)	-32.3	-31.4
MIN-FSC	-33.4	-35.3
MIN-PAC	-11.1	-12.4
MIN-PC	-36.2	-30.0
TS-PAII	-26.6	-26.4
TS-PA	-10.2	-11.6
TS-WI	-14.7	-14.0
TS-FS	-2.9	-5.3
PS ($FNH_2 + I^-$))	-18.7	-17.2
$HF + NHI^-$	5.3	2.0

Table S2. Cartesian coordinates(Å) of the stationary points at the CCSD(T)/aug -cc-pVTZ(PP) level of theory.

RS (NH_2I)

N	-0.150	-1.774	0.000
H	0.404	-2.056	0.808
H	0.404	-2.056	-0.808
I	0.005	0.312	0.000

MIN-HBC

N	-0.784	0.098	-1.354
H	-1.389	-0.713	-1.198
H	-0.098	-0.233	-2.229
I	0.422	0.017	0.354
F	0.559	-0.622	-3.278

MIN-FSC

N	0.588	1.662	1.471
H	0.268	2.508	0.999
H	1.605	1.718	1.398
I	0.047	0.038	0.071
F	-0.516	-1.608	-1.297

MIN-PAC

N	-1.973	-0.318	0.108
H	0.709	-0.050	-2.384
H	-2.291	0.642	-0.096
I	0.102	0.017	-0.033
F	1.011	-0.055	-3.282

MIN-PC

N	0.634	-0.480	-2.427
H	0.303	0.353	-1.935
H	0.353	-1.206	-1.763
I	0.181	-0.111	1.037
F	-0.375	-0.627	-3.463

TS-PAII

N	-0.770	0.148	-1.049
H	-1.658	0.614	-0.881
H	-0.129	-0.379	-2.247
I	0.084	0.057	0.830
F	0.292	-0.736	-3.101

TS-FS

N	1.490	1.300	-0.928
H	0.667	1.753	-1.431
H	1.642	0.568	-1.685
I	-0.421	0.304	0.479
F	-0.566	-2.417	-1.249

TS-PA

N	-1.799	-0.300	-0.153
H	0.344	-0.054	-2.133
H	-2.091	0.689	-0.159
I	0.228	-0.009	0.382
F	0.536	-0.033	-3.053

TS-WI

N	0.011	-0.172	-1.591
H	-1.005	-0.096	-1.607
H	0.164	-1.177	-1.519
I	0.032	0.050	0.859
F	-0.301	-0.660	-3.440

PS (NH_2F)

N	-0.174	-0.676	0.000
H	0.379	-0.962	0.809
H	0.379	-0.962	-0.809
F	0.051	0.739	0.000

NHI^-

N	-1.539	0.063	1.068
H	-1.499	-0.903	1.426
I	0.201	-0.002	-0.142

HF

F	-0.088	0.818	0.238
H	0.007	-0.062	-0.018

Table S3. Harmonic vibrational frequencies (cm^{-1}) for the stationary points at the DFT/M06-2X/aug-cc-pVDZ (LANL2DZ-ECP) level of theory.

	MIN-HBC	MIN-PAC	MIN-FSC	MIN-PC	TS-PAII	TS-PA
ZPE(cm^{-1})	5214	5168	5710	6368	5053	5112
1	104.9	57.6	186.9	103.1	87.2	149.5
2	478.0	152.0	189.5	155.0	363.4	210.2
3	502.1	245.0	317.7	256.0	618.7	464.5
4	618.7	468.2	459.5	957.5	1061.2	495.1
5	1068.4	634.2	805.5	1335.1	1139.3	625.6
6	1199.5	679.0	902.6	1348.7	1364.1	1140.8
7	1420.6	1145.7	1552.3	1599.7	1898.8	3383.9
8	1587.7	3375.0	3462.8	3468.2	3577.7	3759.4
9	3452.8	3583.1	3549.1	3518.3	442.5*i*	89.5*i*

	TS-FS	TS-WI	NH_2I	FNH_2	NHI^-	HF
ZPE(cm^{-1})	5746	5761	5594	6119	2485	2090
1	92.1	222.6	548.6	1020.5	459.4	4182.5
2	166.2	241.3	973.9	1261.4	1126.2	
3	548.6	248.5	1072.7	1381.0	3386.1	
4	1009.6	1000.7	1563.1	1615.8		
5	1067.6	1084.4	3473.4	3440.4		

6	1570.6	1519.3	3560.5	3523.9		
7	3489.9	3558.0				
8	3553.0	3653.4				
9	110.5*i*	410.0*i*				

Table S4. Harmonic vibrational frequencies (cm^{-1}) for the stationary points at the CCSD(T)/aug-cc-pVTZ(pp) level of theory.

	MIN-HBC	MIN-PAC	MIN-FSC	MIN-PC	TS-PAII	TS-PA
ZPE(cm^{-1})	5219	5085	5623	6101	5065	4991
1	100.1	54.6	164.3	79.6	79.2	126.1
2	393.0	123.6	168.8	117.2	313.2	138.0
3	505.1	152.8	330.7	875.5	590.6	442.1
4	528.4	478.8	437.3	1309.0	1025.0	484.5
5	1074.1	659.0	798.3	1333.4	1101.6	610.0
6	1309.9	700.6	878.2	1591.3	1276.6	1109.8
7	1447.9	1118.1	1554.4	3418.1	2243.8	3323.5
8	1648.3	3325.9	3413.3	3478.1	3500.1	3748.5
9	3431.6	3555.9	3501.6	34.8*i*	413.1*i*	118.6*i*

	TS-FS	TS-WI	NH_2I	FNH_2	NHI^-	HF
ZPE(cm^{-1})	5079	5590	5538	6040	2446	2062

1	42.4	204.1	529.6	926.7	469.9	4123.5
2	71.4	218.3	956.0	1269.6	1102.6	
3	520.7	245.1	1037.2	1341.1	3319.2	
4	855.8	925.2	1571.2	1623.2		
5	1039.6	999.9	3443.4	3411.1		
6	1611.2	1528.8	3537.7	3508.3		
7	3017.1	3480.6				
8	3042.9	3578.6				
9	126.2i	355.4i				

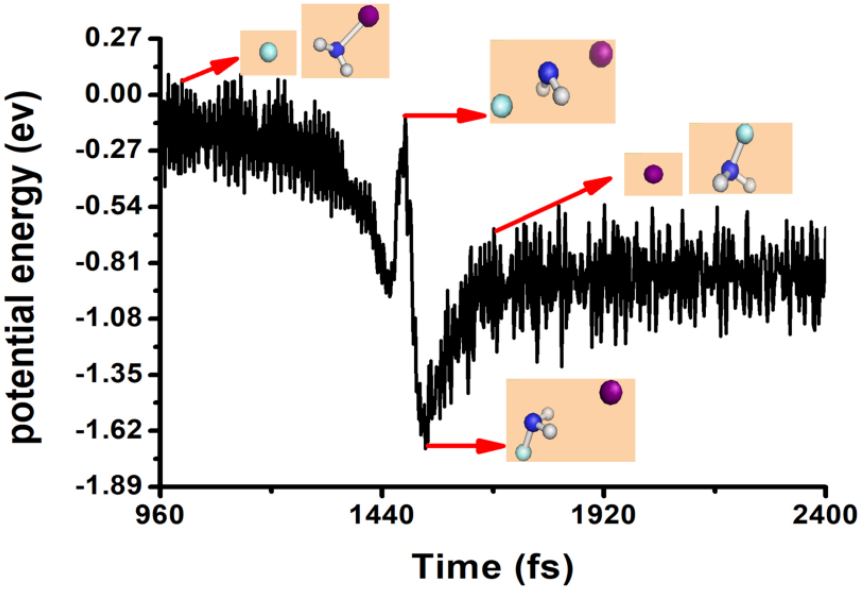

Figure S1. Potential energy versus time from a direct rebound reactive trajectory. The labelled points along this reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, TS-WI, MIN-PC and PS, respectively.

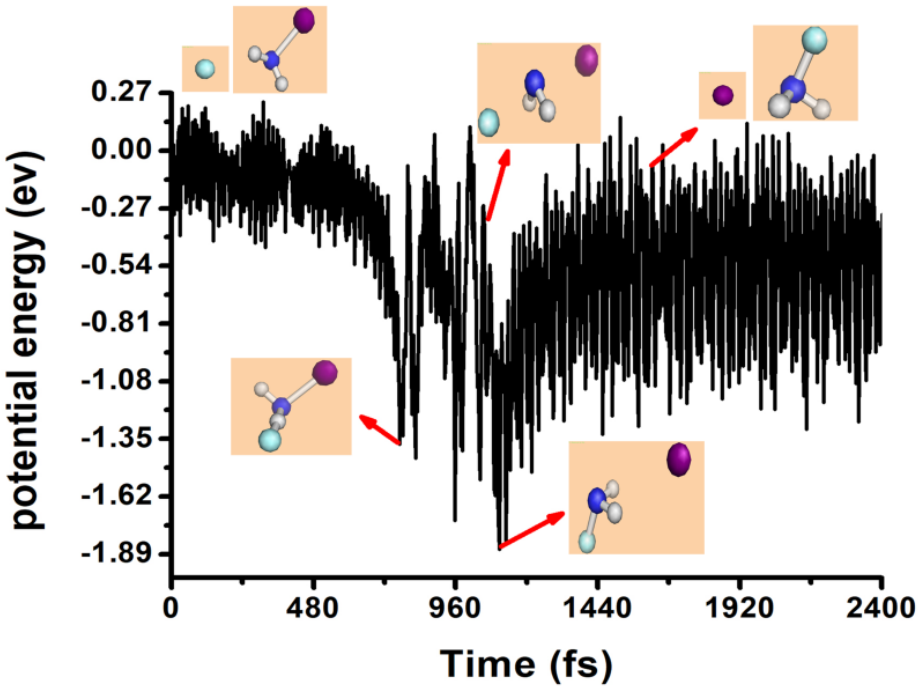

Figure S2. Potential energy versus time from a hydrogen-bond mechanism reactive trajectory. The labelled points along the reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, MIN-HBC, TS-WI, MIN-PC and PS, respectively.

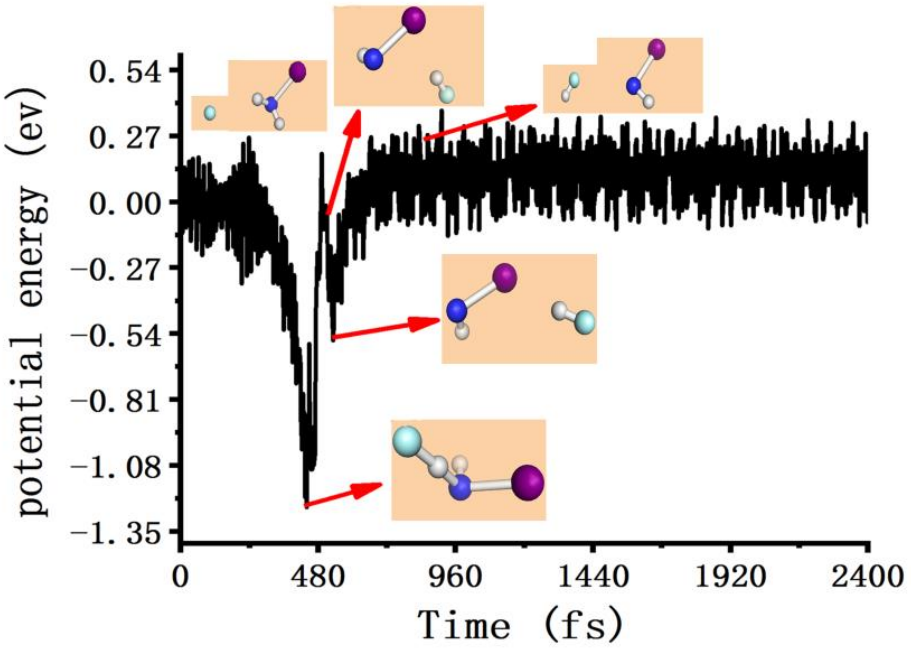

Figure S3. Potential energy versus time from a proton abstraction reactive trajectory. The labelled points along this reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, MIN-HBC, TS-PA, MIN-PAC and HF + NHI^-, respectively.

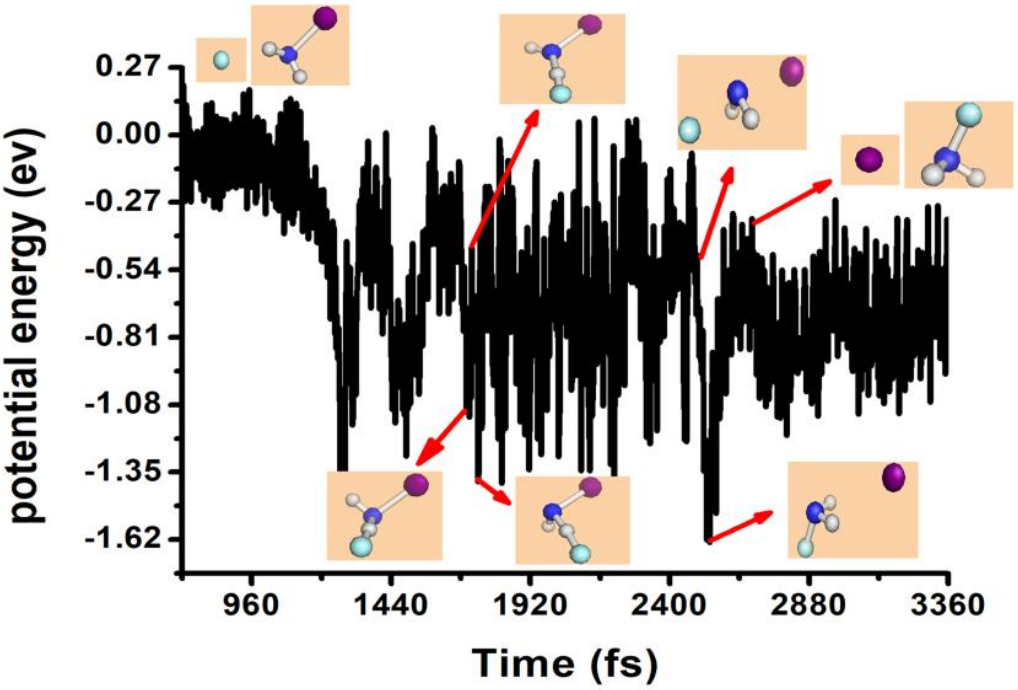

Figure S4. Potential energy versus time from a PAII&WI reactive trajectory. The labelled points along the reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, MIN-HBC, TS-PAII, MIN-I-HBC, TS-WI, MIN-PC and PS, respectively.

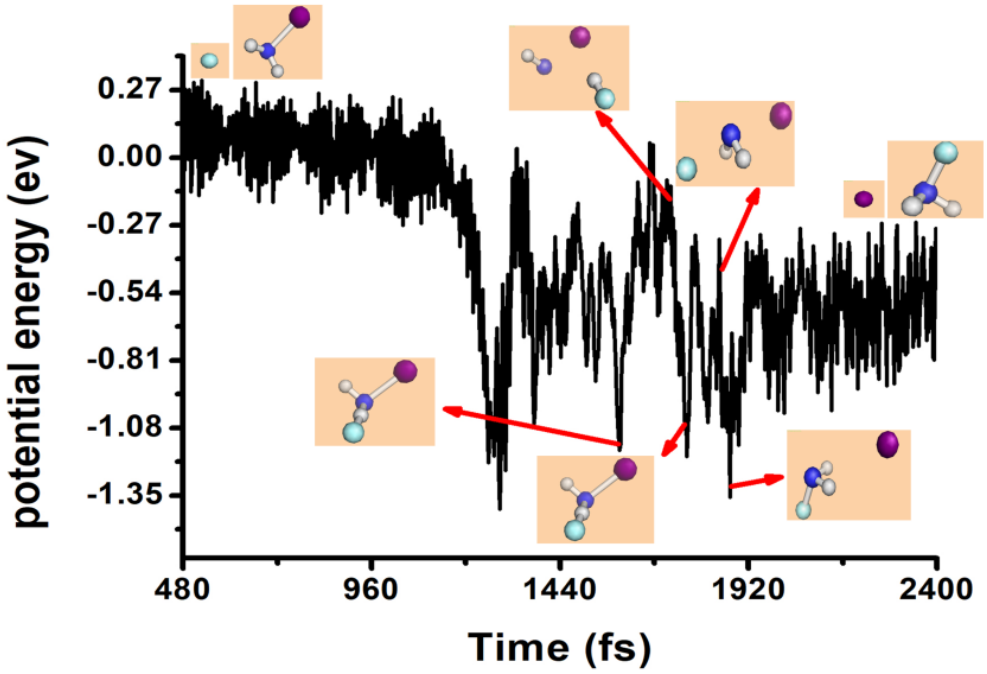

Figure S5. Potential energy versus time from another PAR&BAR reactive trajectory. The labelled points along the reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, MIN-HBC, TS-PA, MIN-HBC, TS-WI, MIN-PC and PS, respectively.

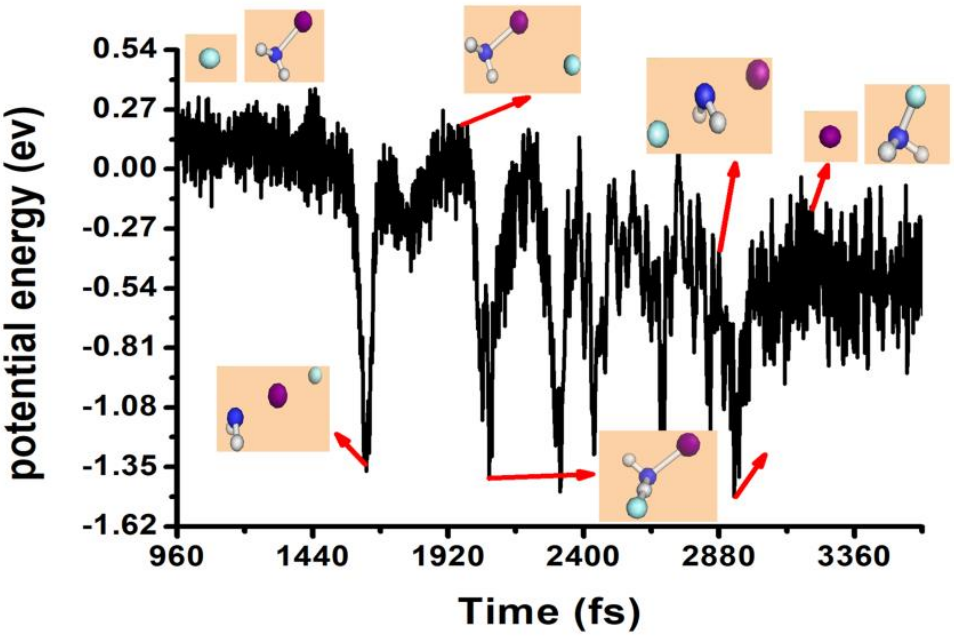

Figure S6. Potential energy versus time from a FSA&BAR reactive trajectory. The labelled points along the reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, MIN-HBC, TS-PA, MIN-HBC, TS-WI, MIN-PC and PS, respectively.

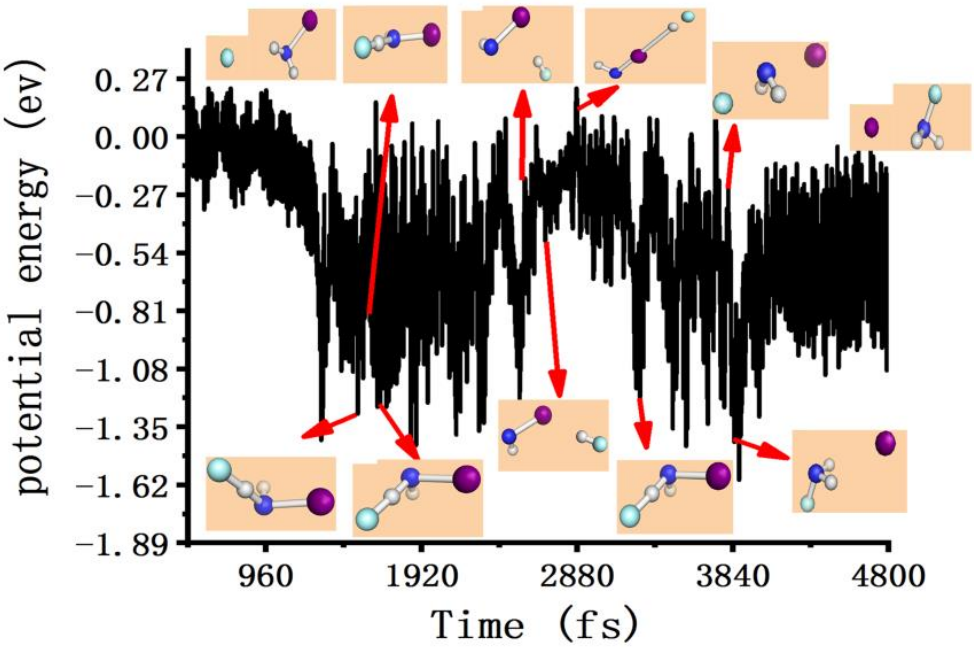

Figure S7. Potential energy versus time from a PAII&PAR&BAR reactive trajectory. The labelled points along the reactive trajectory are used to obtain the stationary points in Figure 2 and 7, leading to the stationary points: RS, MIN-HBC, TS-PAII, MIN-I-HBC, TS-PA, MIN-HBC, TS-WI, MIN-PC and PS, respectively.