Near-Barrierless Ammonium Bisulfate Formation via a Loop-Structure Promoted Proton Transfer Mechanism on the Surface of Water

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Part I: Supporting Figures

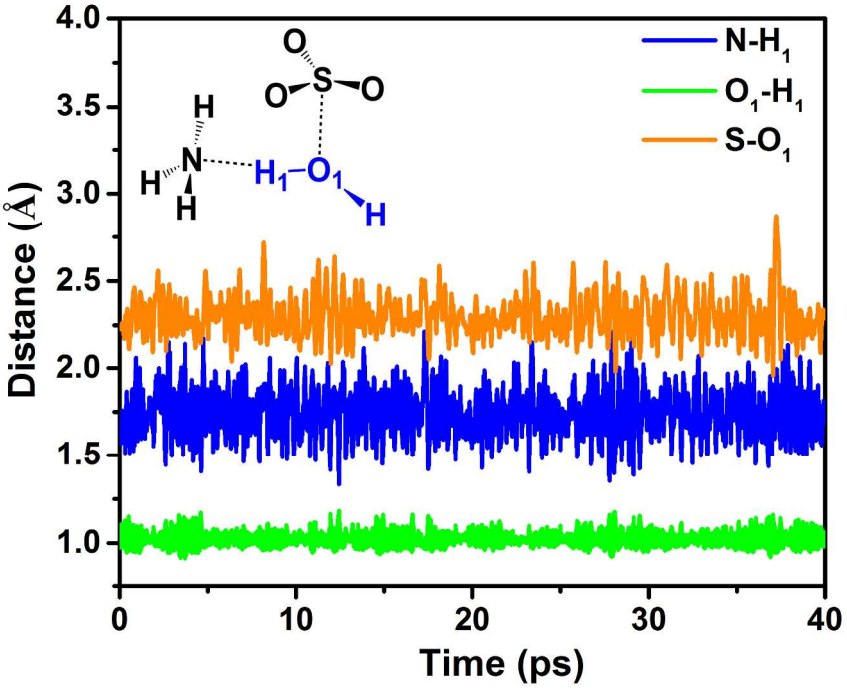

Figure S1. Time evolution of the N-H_1, O_1-H_1 and S-O_1 lengths in the AIMD simulation of the water monomer system. The inset illustrates the structure of the water monomer system.

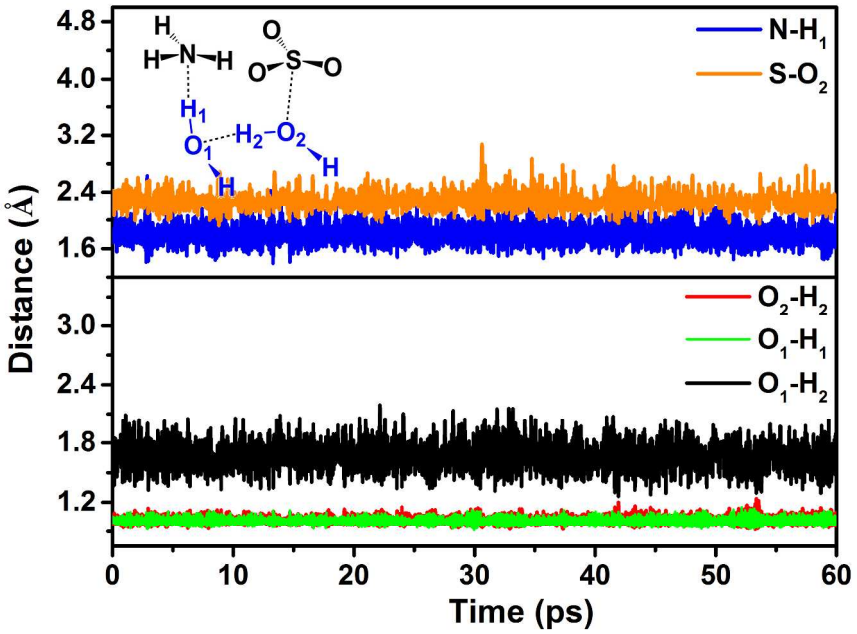

Figure S2. Time evolution of the N-H_1, S-O_2, O_1-H_1, O_1-H_2 and O_2-H_2 lengths in the AIMD simulation of the water dimer system. The inset illustrates the structure of the water dimer system.

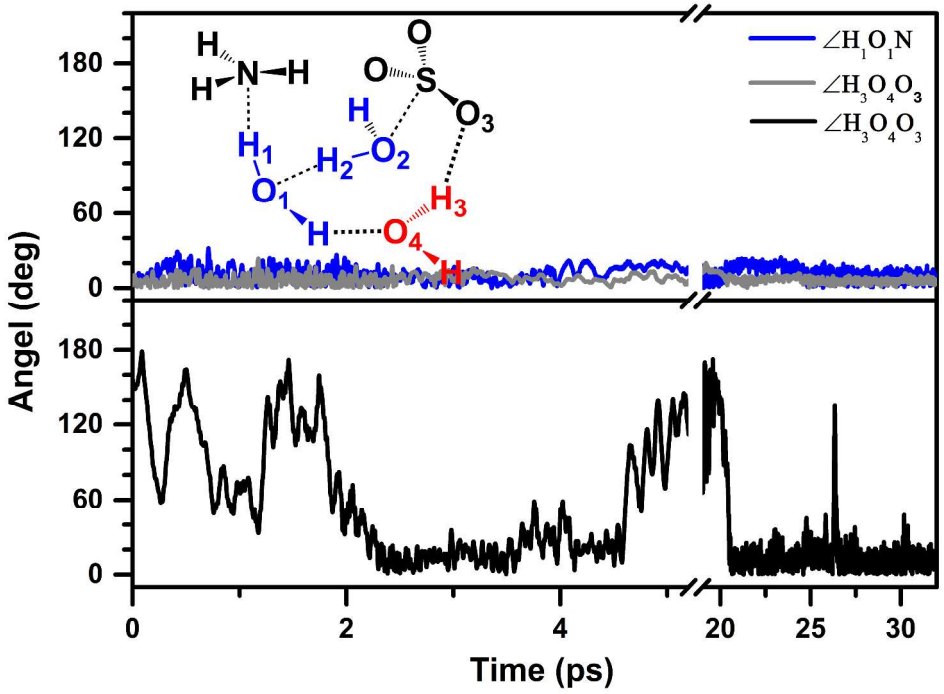

Figure S3. Angular variations *versus* the AIMD simulation time for the water trimer system. The inset illustrates the structure of the water trimer system.

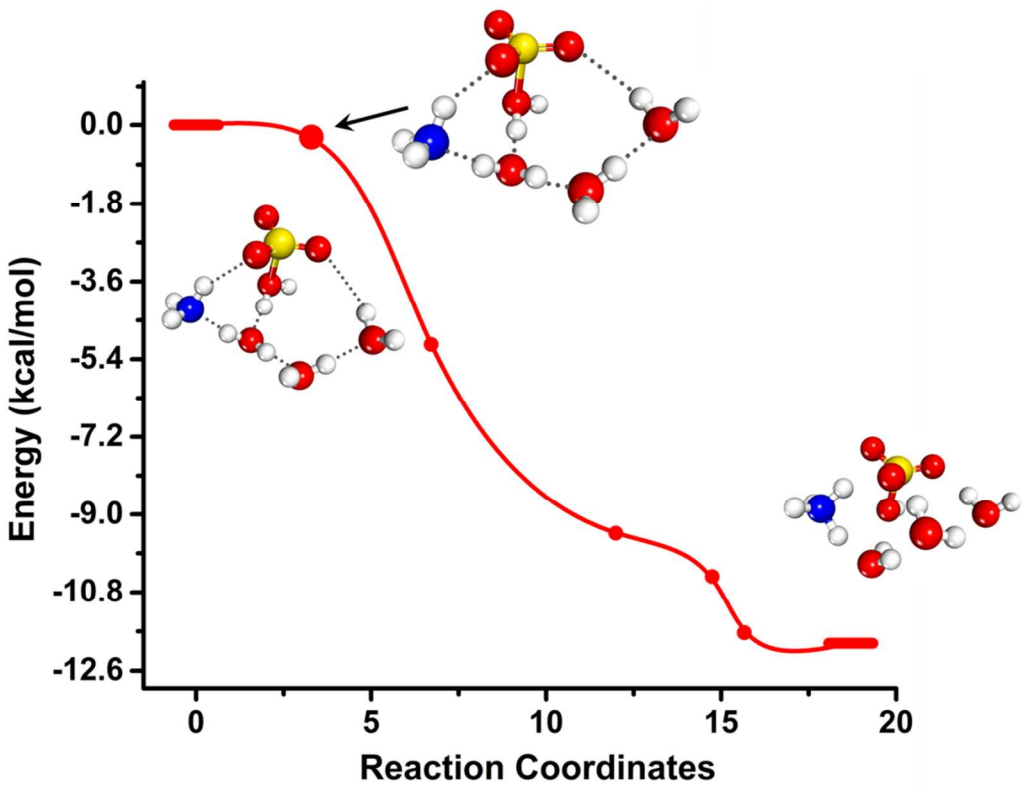

Figure S4. A schematic illustration of the energy profiles of the reaction among NH_3 and SO_3 molecules with a water tetramer (in red). The horizontal bar denotes either the reactant or the product state. The larger solid circle represents the transition state, and the smaller solid circles correspond to the replicas in the CI-NEB computation. The white, blue, red and yellow spheres represent H, N, O and S atoms, respectively.

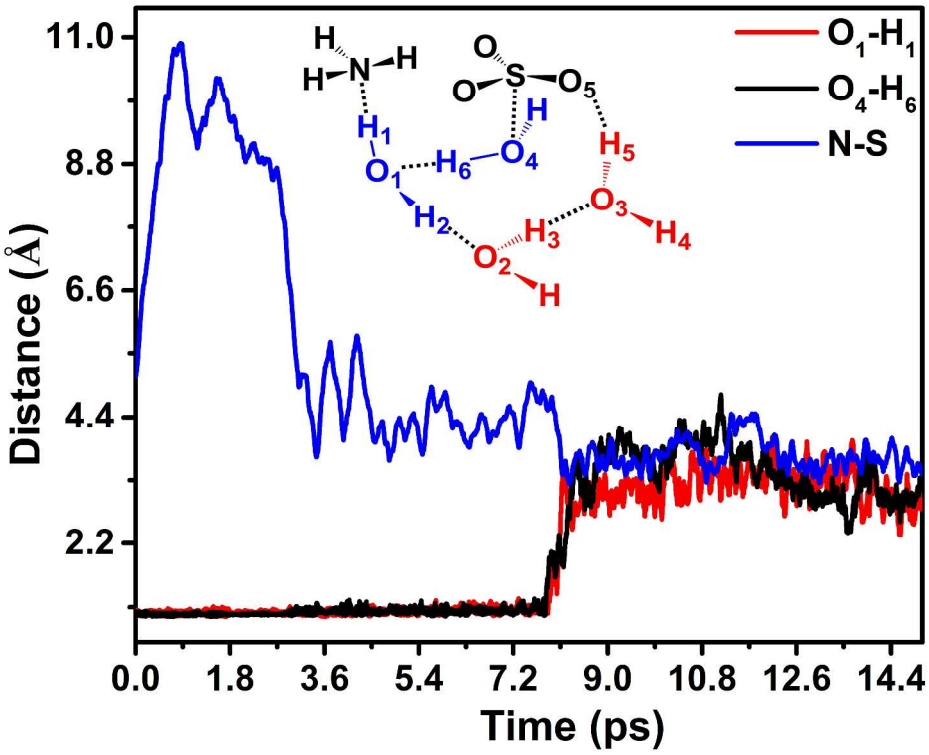

Figure S5. Time evolution of the N-S, O_1-H_1 and O_2-H_2 lengths in the AIMD simulation of the water-droplet system. The inset illustrates the structure of the loop structure formed prior to the formation of the NH_4^+/HSO_4^- ion pair.

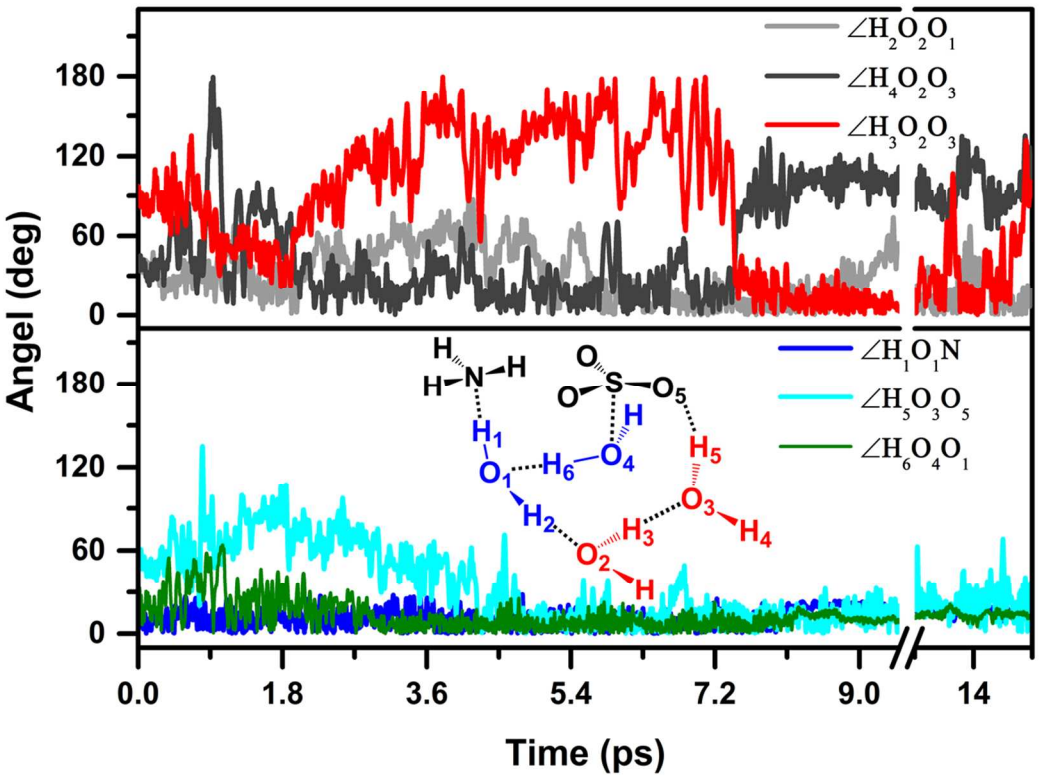

Figure S6. Angular variations *versus* the AIMD simulation time for the water-droplet system. The inset illustrates the structure of the loop structure formed prior to the formation of the NH_4^+/HSO_4^- ion pair.

Part II: Coordinates of the transition states for the water monomer, dimer and trimer systems.

(1). Transition state for the water monomer system

O	0.502908	1.273176	-0.222654
H	0.269827	1.987549	0.385571
H	1.619268	0.718386	-0.039306
S	-0.725051	-0.164110	0.015966
O	0.011234	-1.115118	-0.814653
O	-0.600454	-0.347749	1.455857
O	-1.946640	0.401472	-0.505184
N	2.532657	-0.097843	0.009070
H	2.063642	-0.936599	-0.346898
H	2.854944	-0.280234	0.955744
H	3.328163	0.127312	-0.580975

(2). Transition state for the water dimer system

O	0.187380	0.952473	1.123392
H	-0.838905	1.320113	0.524702
H	0.841598	1.666172	1.233482
O	-1.813425	1.454136	-0.133954
H	-1.414711	1.459336	-1.025075
H	-2.232527	0.489217	-0.062539
S	1.008048	-0.229618	-0.141411
O	0.390729	-1.502597	0.321295
O	0.449747	0.340670	-1.405845
O	2.431791	0.024785	0.163820
N	-2.558973	-1.029053	0.092461
H	-3.033837	-1.464141	-0.698543
H	-3.079710	-1.289497	0.929949
H	-1.627636	-1.459672	0.163708

(3). Transition state for the water trimer system

O	-0.261537	-0.908865	1.339970
H	0.715612	-0.445942	1.392133
H	-0.754554	-0.691769	2.155162
O	2.049182	0.102834	1.252217
H	2.442914	-0.591180	0.674654
H	1.972682	0.921775	0.642654
S	-1.291879	0.060038	-0.194888
O	-2.465196	-0.792746	-0.132375
O	-1.349531	1.407958	0.371443
O	-0.307482	-0.149342	-1.268770
N	1.600312	2.136218	-0.502853
H	1.420193	1.623015	-1.368104
H	2.242738	2.902622	-0.706230
H	0.700077	2.525923	-0.213981
O	1.984209	-1.939584	-0.734854
H	1.156029	-1.527557	-1.060202
H	2.375028	-2.393064	-1.498963