Supporting Information
for
Adsorption, Dissociation and Dehydrogenation of Water Monomer and Water Dimer on the Smallest 3D Aluminum Particle. The O-H Dissociation Barrier Disappears for the Dimer

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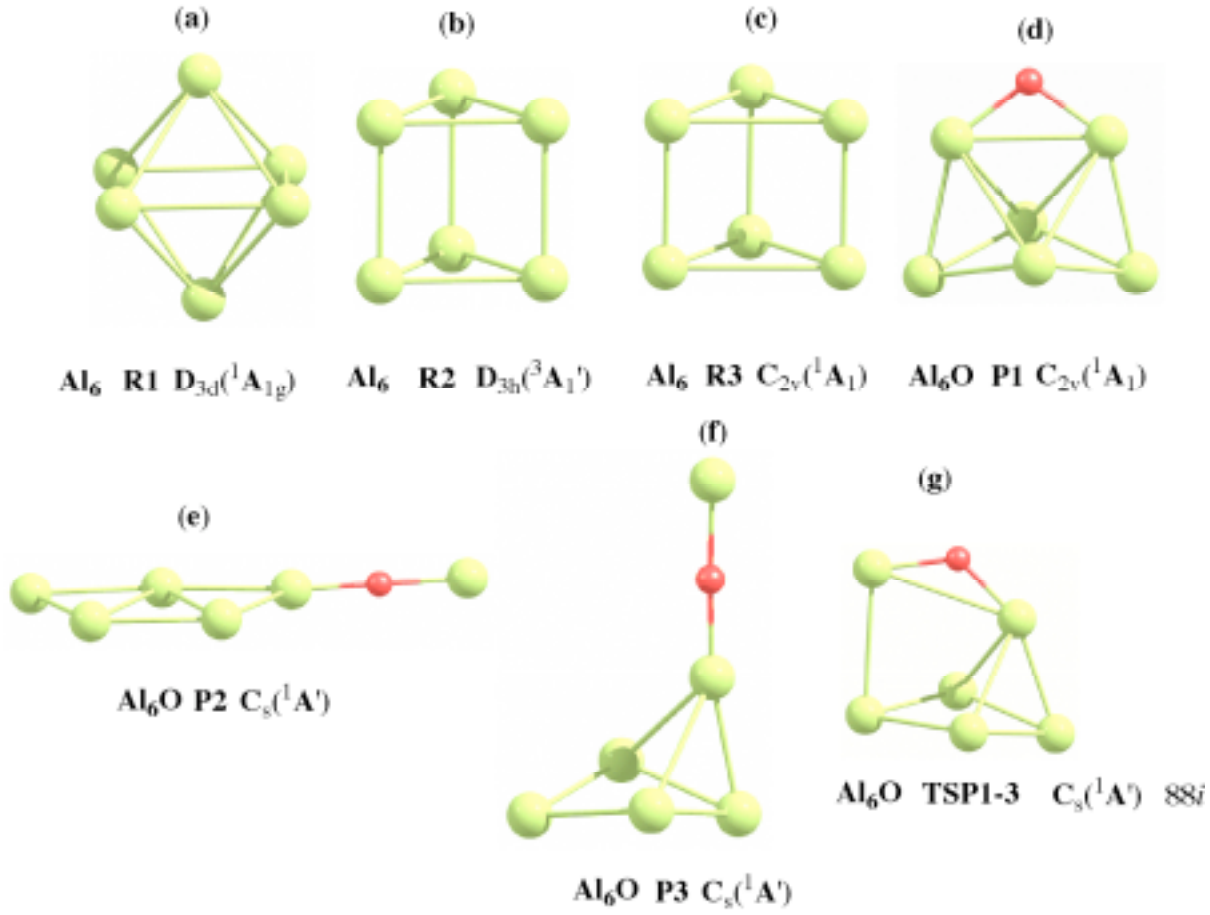


Figure S1.

Caption to Figure S1. (a) Singlet octahedral **R1** (D_{3d},$^1A_{1g}$), (b) Triplet prism **R2** (D_{3h},$^3A_1'$), (c) Singlet prism **R3** (C_{2v},$^1A_1$) structures of Al_6, and singlet (d) **P1** (C_{2v},$^1A_1$), (e) **P2** (C_s,$^1A'$), (f) **P3** (C_s,$^1A'$) structures of Al_6O, and (g) Transition state **TSP1-3** (C_s,$^1A'$) for interconversion between the **P1** and **P3** isomers of Al_6O (with the corresponding imaginary frequency) (Figure S1). All structures are optimized at the B3LYP/aug-cc-pVTZ level.

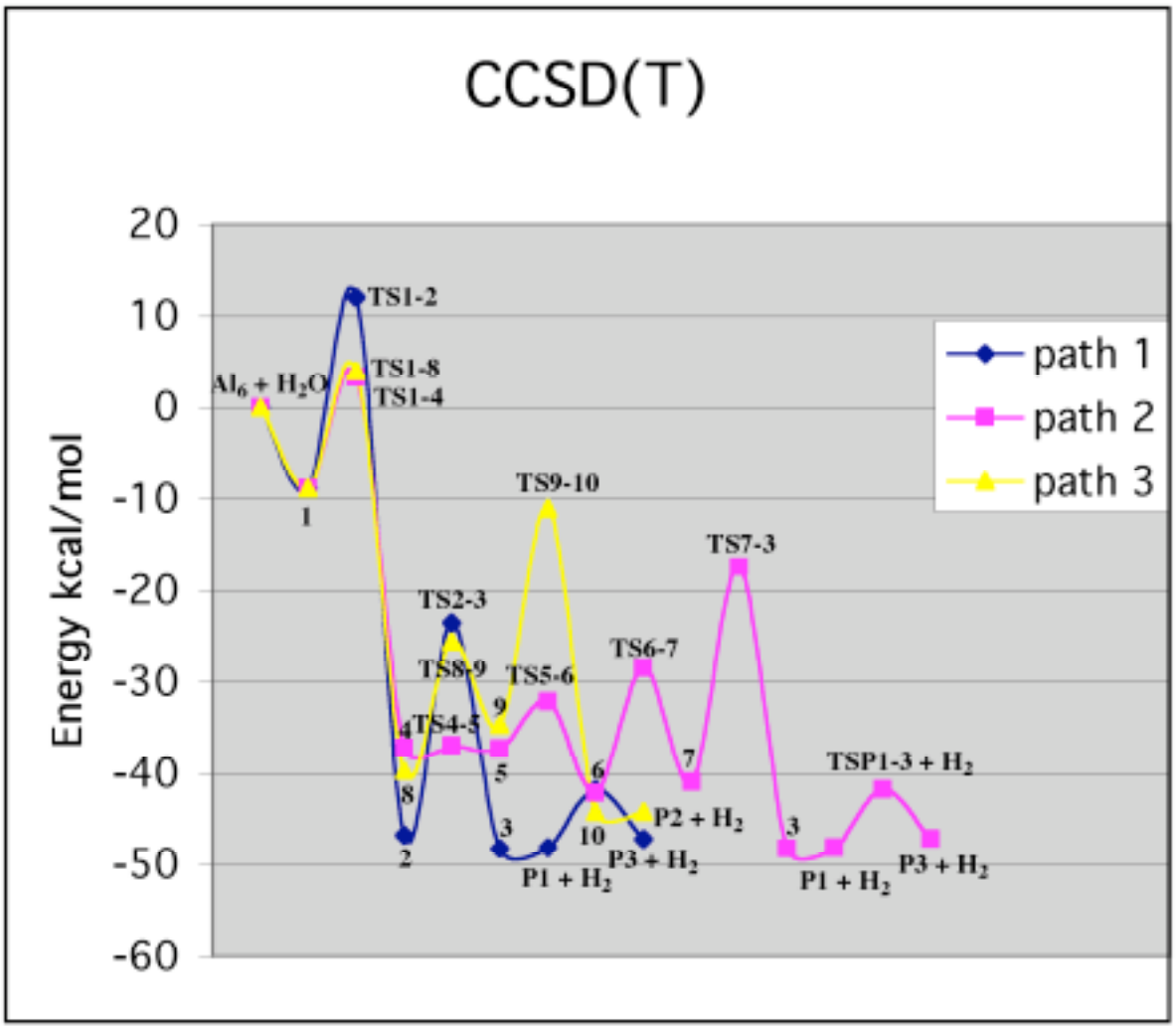


Figure S2.

Caption to Figure S2. CCSD(T)/aug-cc-pVTZ energy profile for the $Al_6 + H_2O \rightarrow Al_6O + H_2$ reaction calculated at the B3LYP/aug-cc-pVTZ geometries, with (zero-point energy) ZPE (B3LYP) corrections.

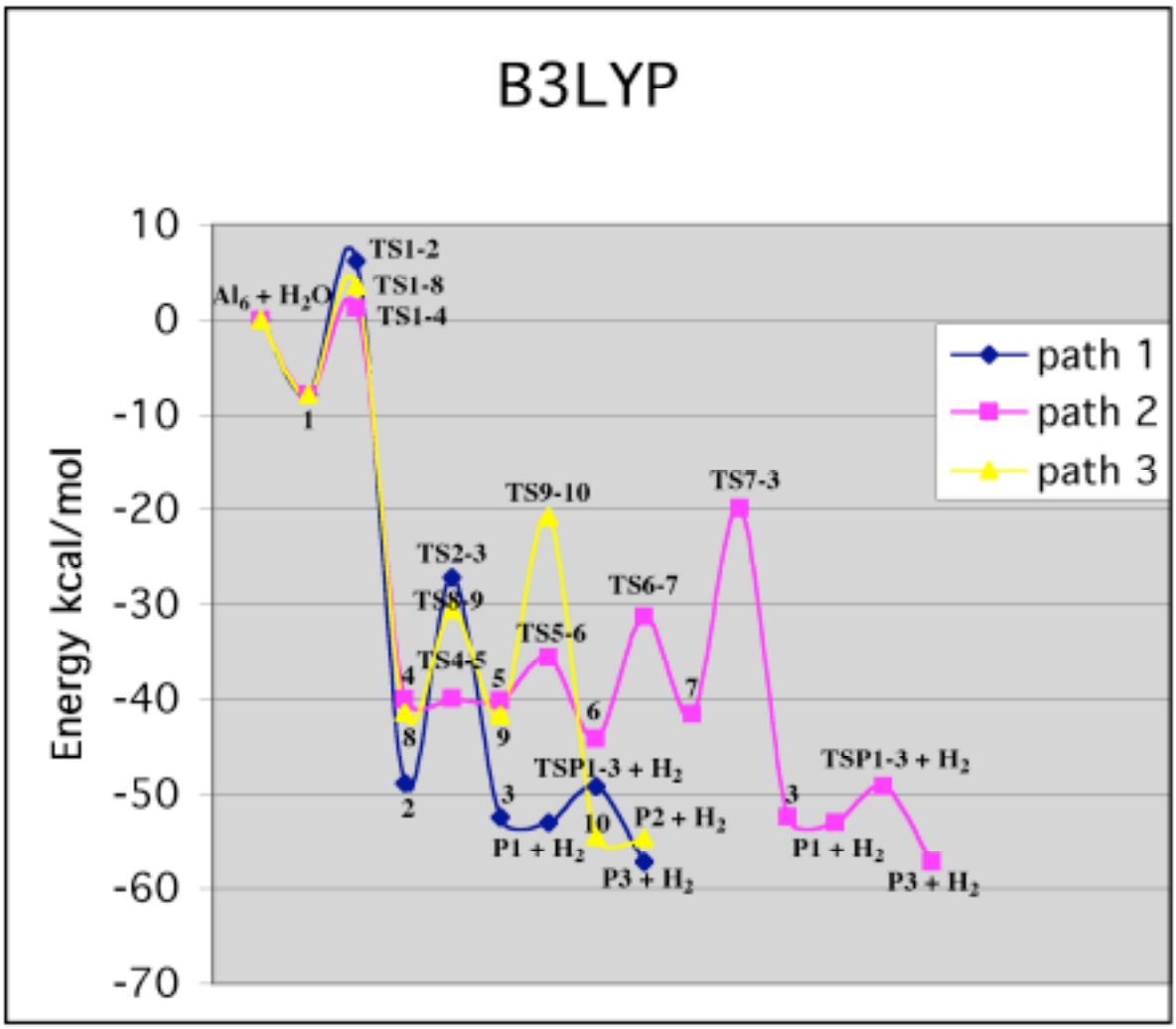
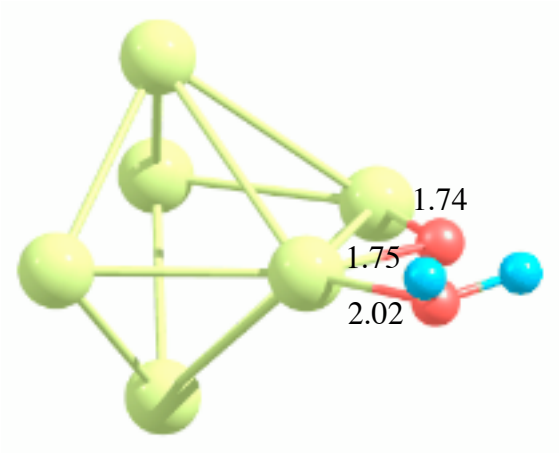
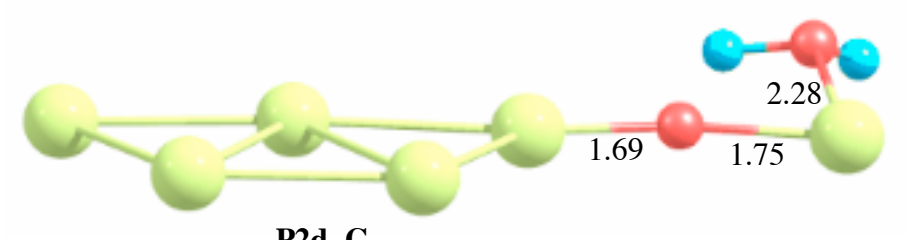


Figure S3.

Caption to Figure S3. B3LYP/aug-cc-pVTZ energy profile for the $Al_6 + H_2O \rightarrow Al_6O + H_2$ reaction calculated at the B3LYP/aug-cc-pVTZ geometries, with (zero-point energy) ZPE (B3LYP) corrections.



P1d C_1



P2d C_1

Figure S4.

Caption to Figure S4. **P1d** and **P2d** structures of the H_2O-Al_6O product of the reaction of the water dimer with Al_6 optimized at the B3LYP/aug-cc-pVTZ level.

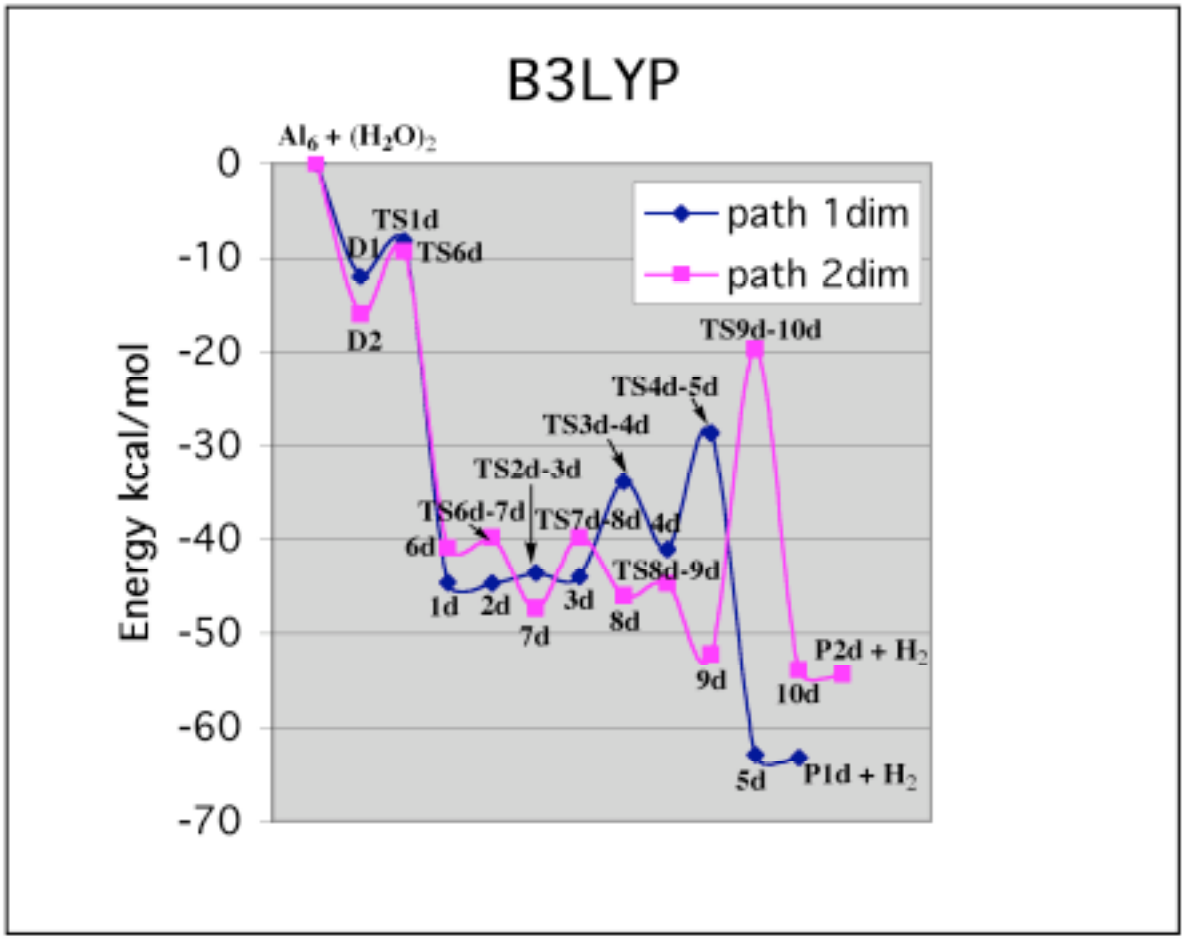


Figure S5.

Caption to Figure S5. B3LYP/aug-cc-pVTZ energy profile for the $Al_6 + (H_2O)_2 \rightarrow H_2O\text{-}Al_6O + H_2$ reaction calculated at the B3LYP/aug-cc-pVTZ geometries, with (zero-point energy) ZPE (B3LYP) corrections.

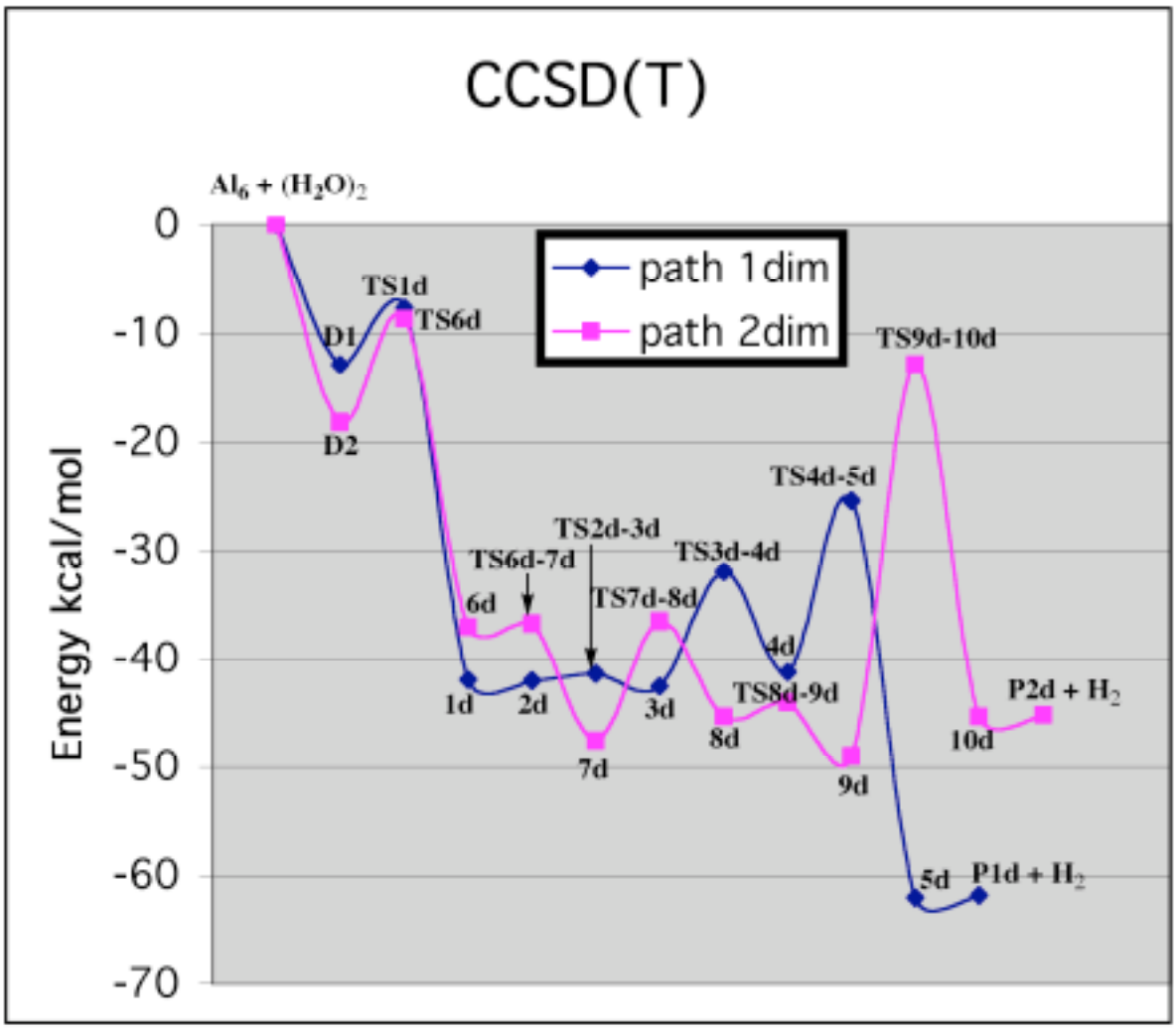


Figure S6.

Caption to Figure S6. CCSD(T)/aug-cc-pVTZ energy profile for the $Al_6 + (H_2O)_2 \rightarrow H_2O\text{-}Al_6O + H_2$ reaction calculated at the B3LYP/aug-cc-pVTZ geometries, with (zero-point energy) ZPE (B3LYP) corrections.

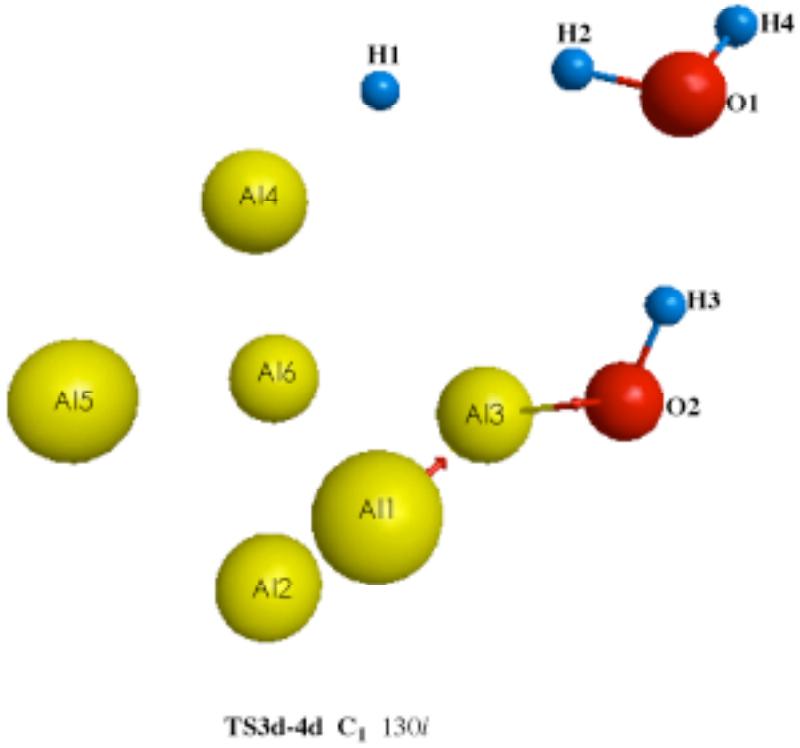


Figure S7.

Caption to Figure S7. Imaginary mode of the transition state **TS3d-4d** of the path 1dim.