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

# Supplementary Information

## *Ab Initio* Metadynamics Calculations of Dimethylamine for Probing p$K_b$ Variations in Bulk *vs.* Surface Environments

Sohag Biswas,[a] Hyuna Kwon,[a] Kelley C. Barsanti,[a] Nanna Myllys,[b] James N. Smith,[b] and Bryan M. Wong[a,c,*]

[a] *Department of Chemical & Environmental Engineering, University of California-Riverside, Riverside, California 92521*

[b] *Department of Chemistry, University of California-Irvine, Irvine, California 92697*

[c] *Materials Science & Engineering Program, Department of Chemistry, and Department of Physics & Astronomy, University of California-Riverside, Riverside, California 92521*

Email: bryan.wong@ucr.edu, Webpage: http://www.bmwong-group.com

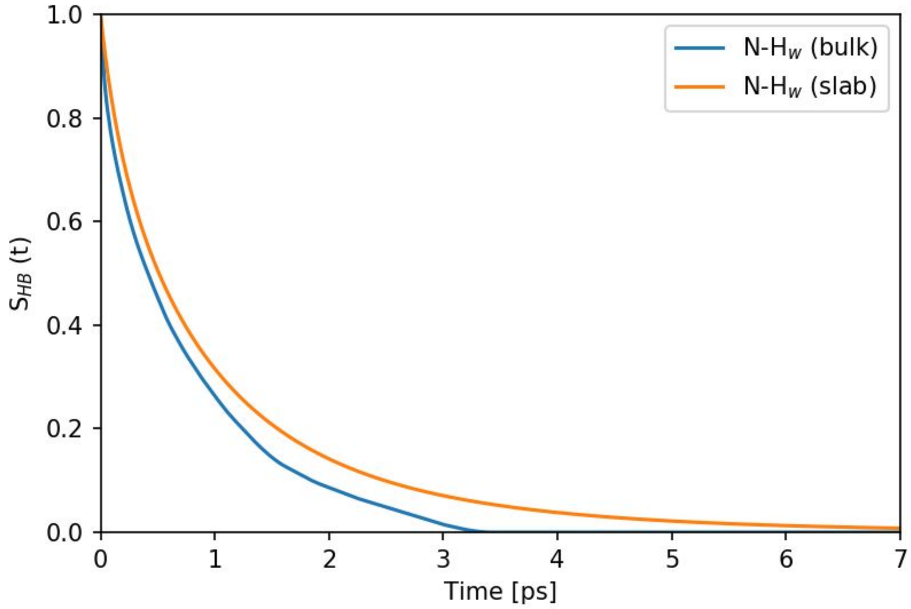

Figure S1. Continuous hydrogen bond auto-correlation functions (calculated using distance and angle-based criteria) for the N-$H_w$ pair. The lifetime for N-$H_w$ (bulk) and N-$H_w$ (slab) is 0.86 and 1.40 ps, respectively.

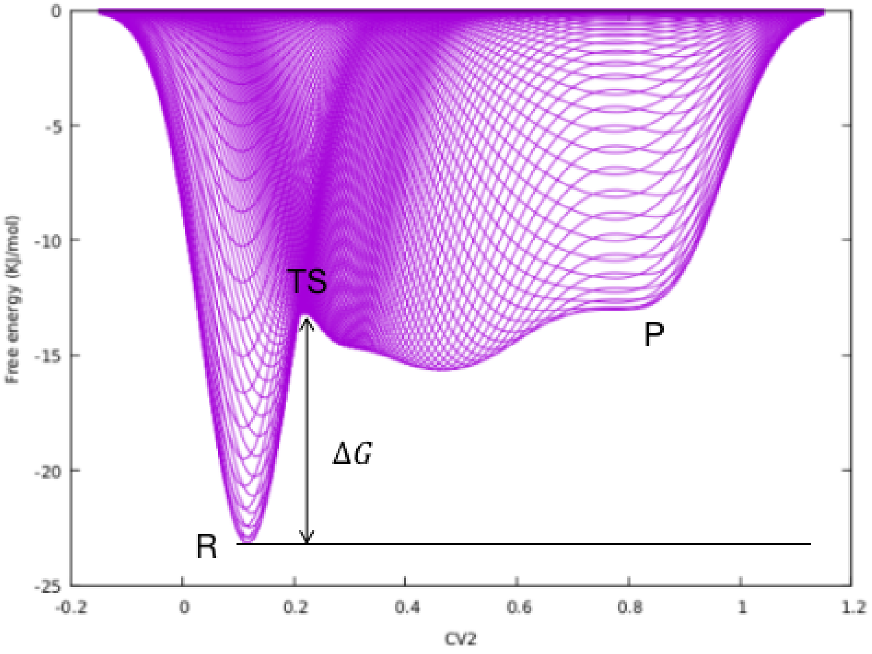

Figure S2. Gradual accumulation of the metadynamics free energy profile along the path variable CV2. In the reactant state (CV2 = 0.12), dimethylamine is hydrogen-bonded to water, and in the product state (CV2 = 0.91), dimethylamine is protonated by water molecules. The initial condition for the metadynamics calculation was taken from trajectory 04.

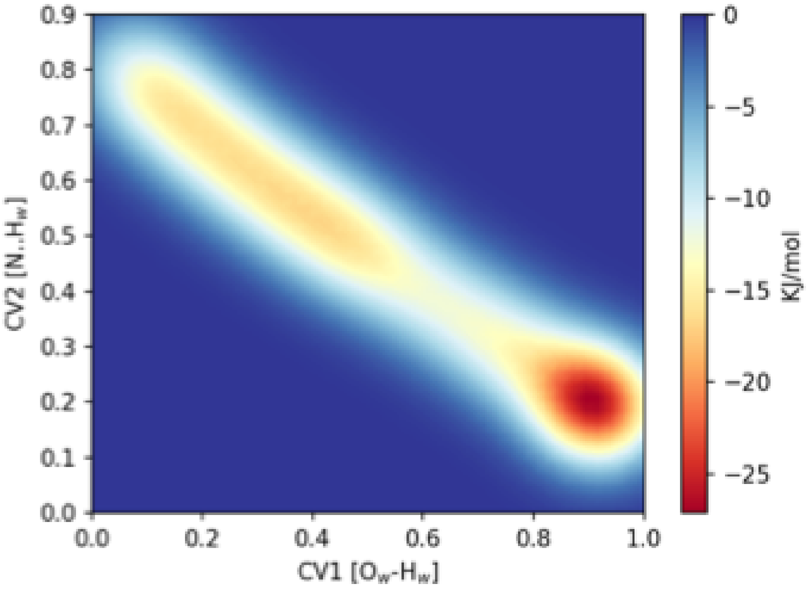

Figure S3. Free energy surface in a bulk aqueous environment from different initial conditions. The initial geometry was taken from trajectory 001. The reactant is located at CV1 = 0.88, CV2 = 0.12, and the product is located at CV1 = 0.1, CV2 = 0.91. The transition state is situated at CV1 = 0.60, CV2 = 0.32. The free energy barrier is ~14.83 kJ/mol, and the free energy difference between the product and reactant is ~11 kJ/mol.

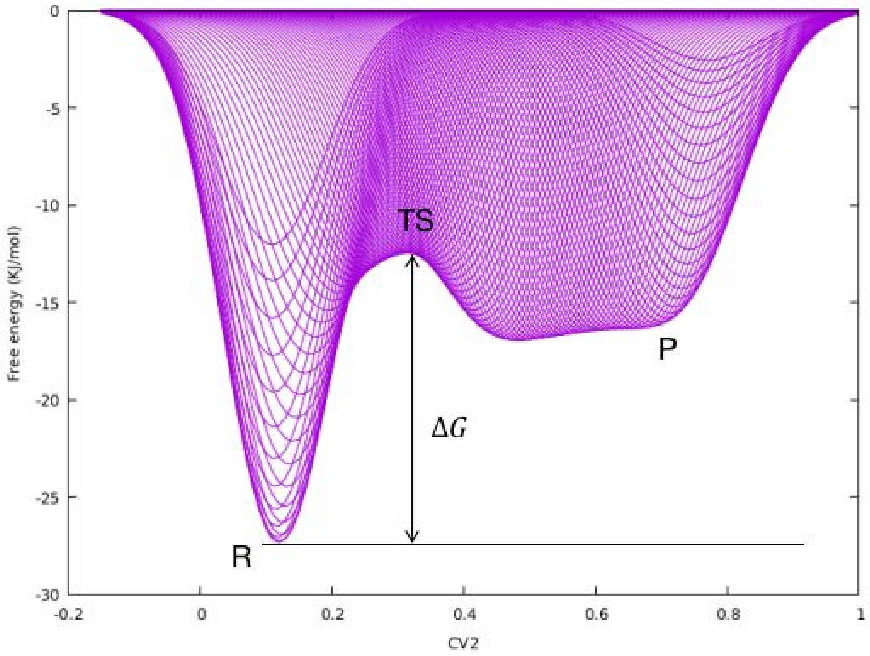

Figure S4. Gradual accumulation of the metadynamics free energy profile along the path variable CV2. In the reactant state (CV2 = 0.12), dimethylamine is hydrogen-bonded to water, and in the product state (CV2 = 0.70), dimethylamine is protonated by water molecules. The initial condition for the metadynamics calculation was taken from trajectory 01.

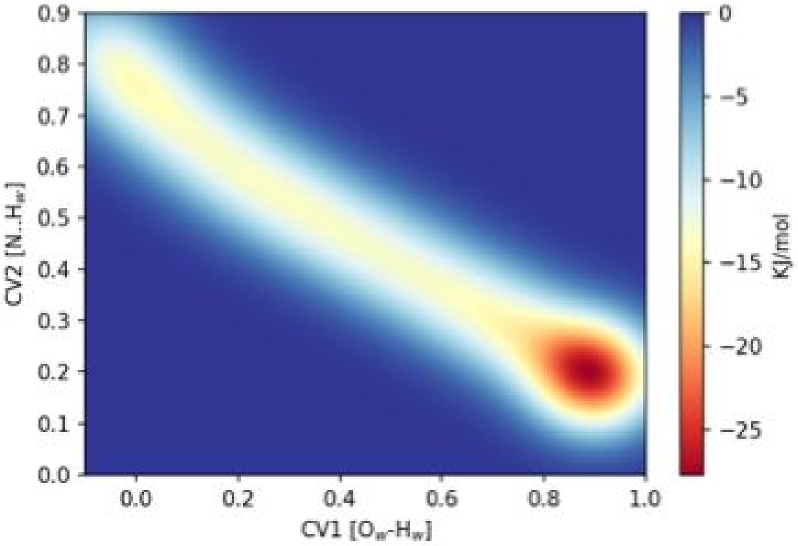

Figure S5. Free energy surface in a bulk aqueous environment from different initial conditions. The initial geometry was taken from trajectory 005. The reactant state is located at CV1 = 0.90, CV2 = 0.12, and the product is located at CV1 = 0.08, CV2 = 0.70. The transition state is situated at CV1 = 0.57, CV2 = 0.30. The free energy barrier is ~14.56 kJ/mol, and the free energy difference between the reactant and product is ~12.20 kJ/mol.

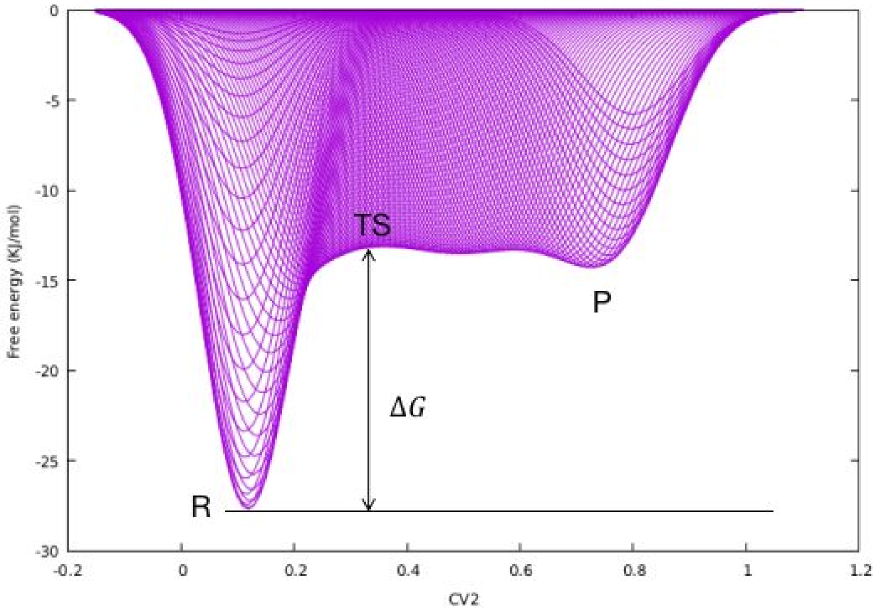

Figure S6. Gradual accumulation of the metadynamics free energy profile along the path variable CV2. In the reactant state (CV2 = 0.11), dimethylamine is hydrogen-bonded to water, and in the product state (CV2 = 0.73), dimethylamine is protonated by water molecules. The initial condition for the metadynamics calculation was taken from trajectory 05.

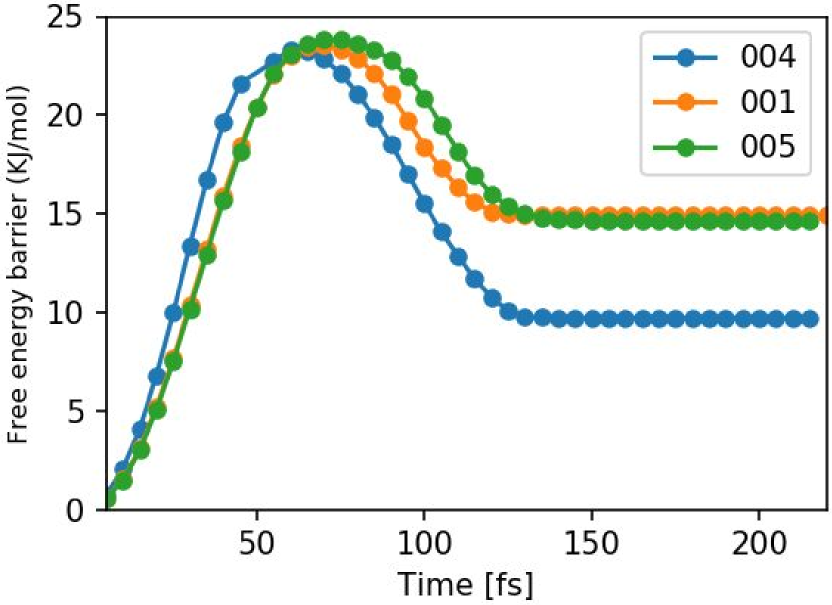

Figure S7. The free energy difference between the transition state and reactant as a function of time. The free energy did not converge initially but converged after ~145 fs. It is worth noting that due to its high reactivity, the Gaussian hills were approximately deposited at every 10 MD steps (5 fs).

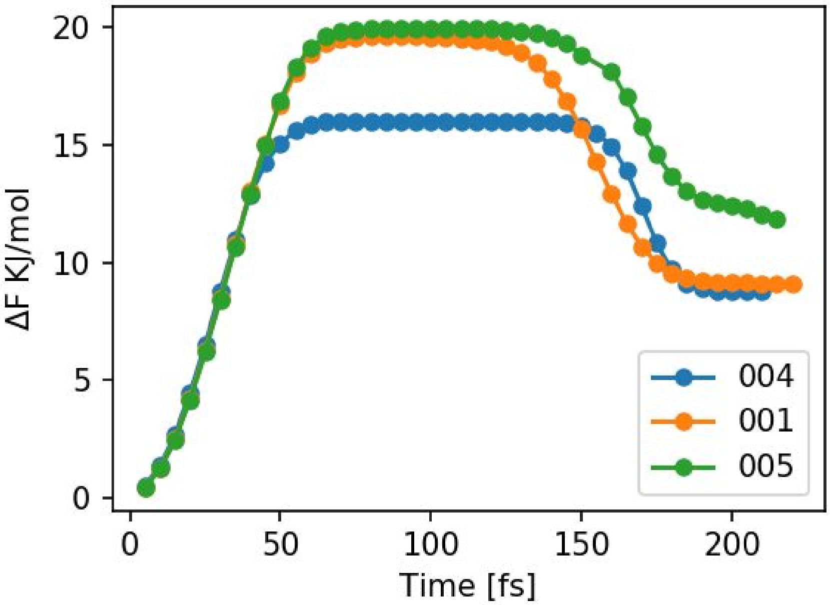

Figure S8. The free energy difference between the product and reactant as a function of time. The free energy did not converge initially but converged after ~175 fs. It is worth noting that due to its high reactivity, the Gaussian hills were approximately deposited at every 10 MD steps (5 fs).

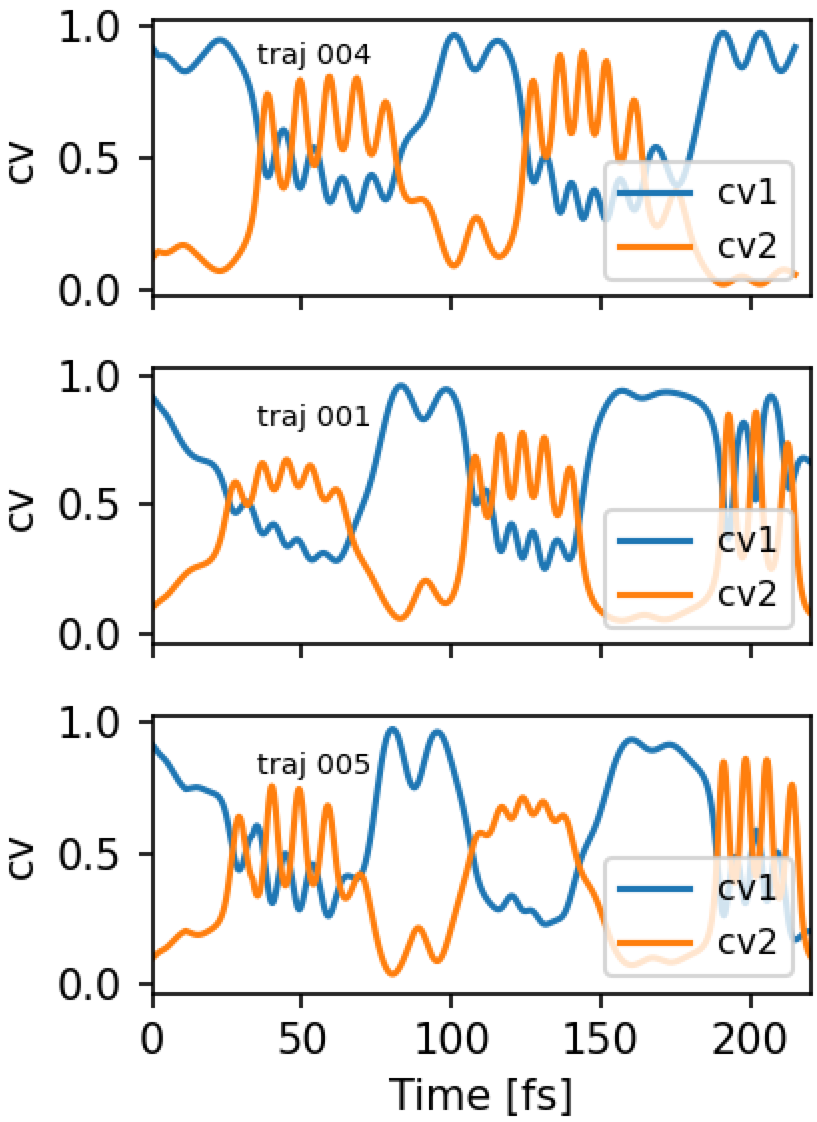

Figure S9. Fluctuation of CV values as a function of time in the bulk aqueous environment. Several forward and backward transitions can be observed in the simulations.

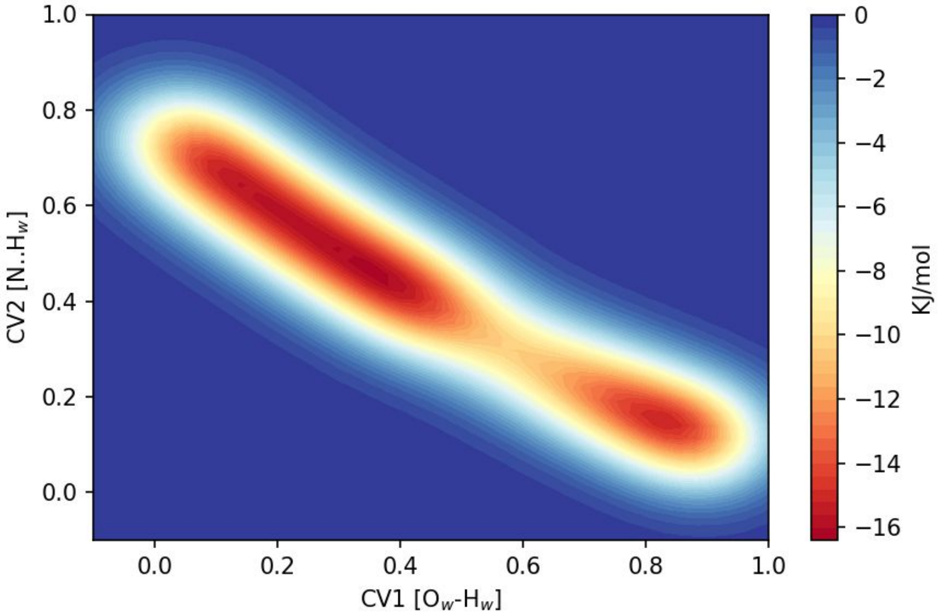

Figure S10. Free energy profile for the pronation of dimethylamine in the bulk aqueous environment with a 10-fs Gaussian hill deposition rate. The free energy barrier is 4.84 kJ/mol.

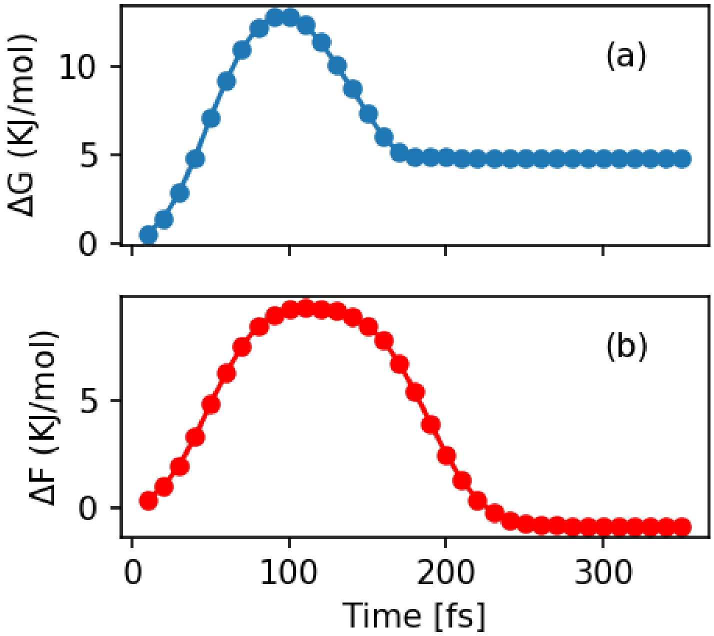

Figure S11. Panel (a): Free energy difference between the transition state and reactant as a function of time obtained from a 10-fs Gaussian hill deposition rate for the bulk aqueous environment. After roughly 180 fs, the free barrier is stabilized at around 4.86 kJ/mol. Panel (b): Free energy difference between the product and reactant as a function of time. After roughly 200 fs, the ΔF value is converged.

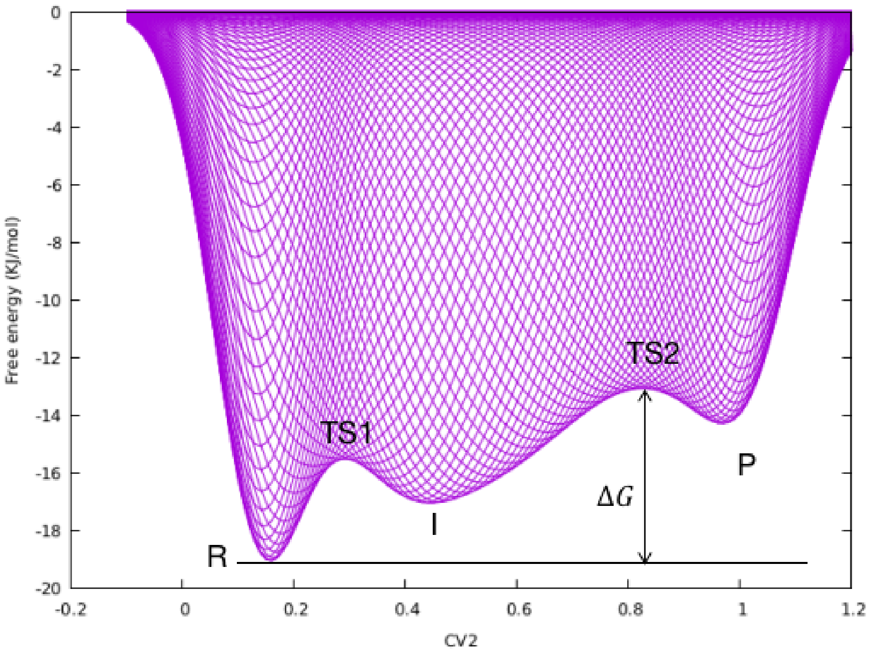

Figure S12. Gradual accumulation of the metadynamics free energy profile projected along the path variable CV2 for the proton transfer from water to dimethylamine at the air-water interface. The initial condition was taken from trajectory 02. The 3D free energy surface is shown in the main text.

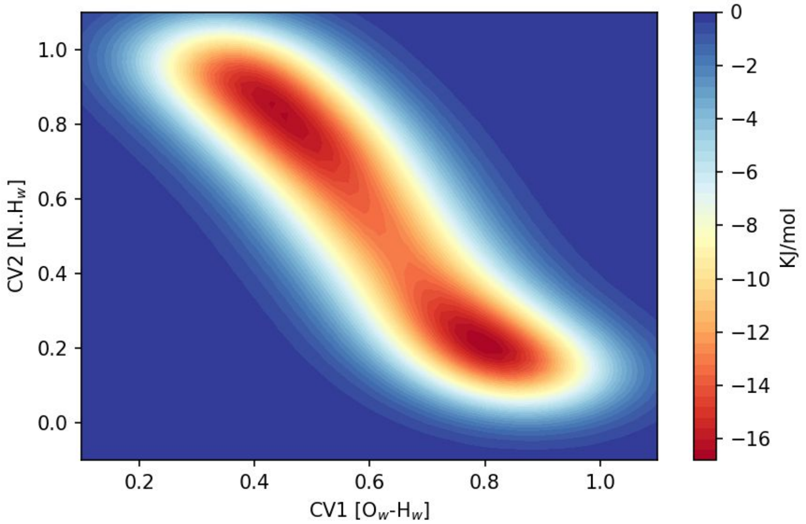

Figure S13. Free energy surface at the air-water interface from different initial conditions. The initial geometry was taken from trajectory 005. The reactant is located at CV1 = 0.80, CV2 = 0.20, and the transition state is located at CV1 = 0.64, CV2 = 0.45. The product is situated at CV1 = 0.40, CV2 = 0.85. The free energy difference between the reactant and transition state is ~3.70 kJ/mol, and the free energy difference between the product and reactant is 0.4 kJ/mol.

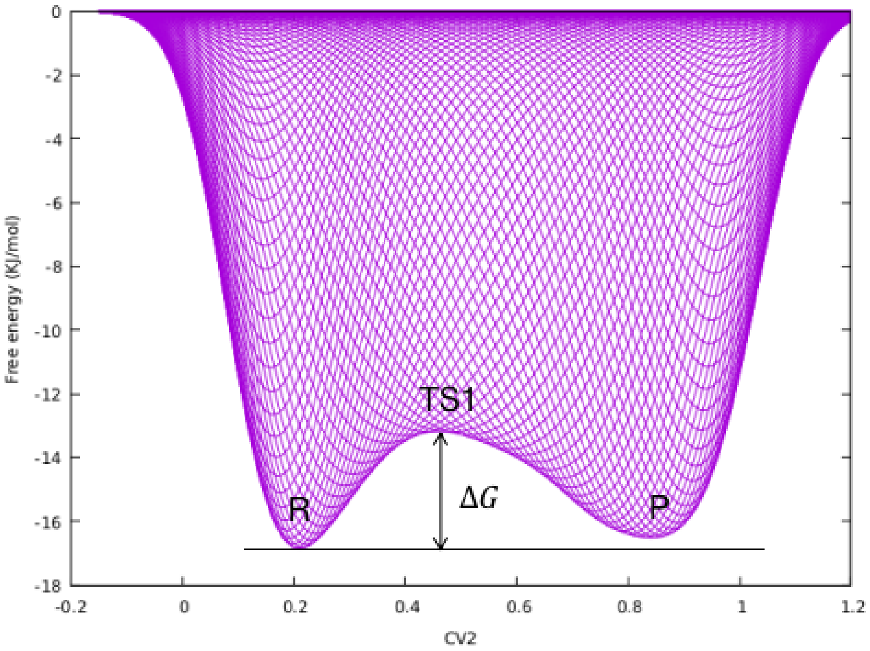

Figure S14. Gradual accumulation of the metadynamics free energy profile projected along the path variable CV2 for the proton transfer from water to dimethylamine at the air-water interface. The initial condition was taken from trajectory 05.

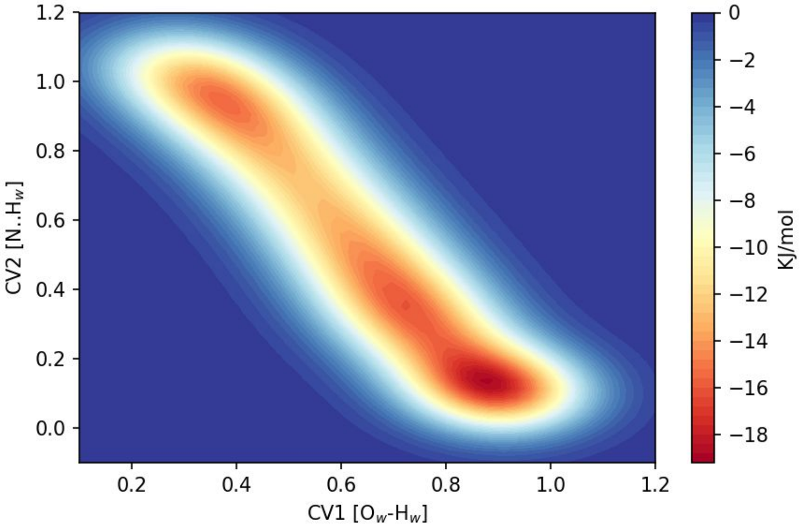

Figure S15. Free energy surface at the air-water interface from different initial conditions. The initial geometry was taken from trajectory 04. The reactant is located at CV1 = 0.87, CV2 = 0.13, and transition state one (TS1) is located at CV1 = 0.78, CV2 = 0.26. Transition state 2 (TS2) is located at CV1 = 0.52, CV2 = 0.70, and the product is situated at CV1 = 0.36, CV2 = 0.87. The free energy difference between the reactant and transition state 1 is ~6.30 kJ/mol, and the free energy difference between the product and reactant is ~3.00 kJ/mol.

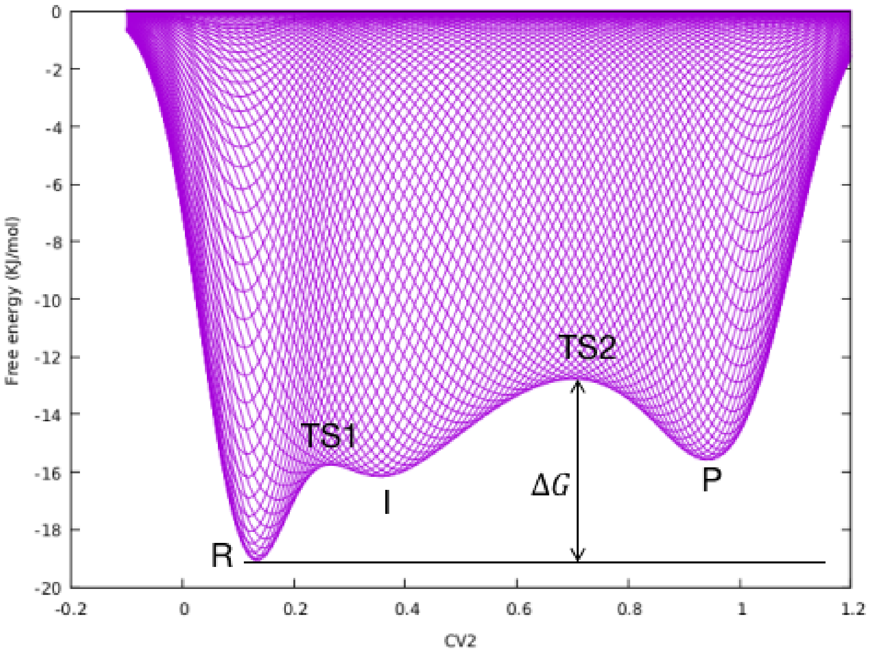

Figure S16. Gradual accumulation of the metadynamics free energy profile projected along the path variable CV2 (N-$H_w$) for the proton transfer from water to dimethylamine at the air-water interface. The initial condition was taken from trajectory 04.

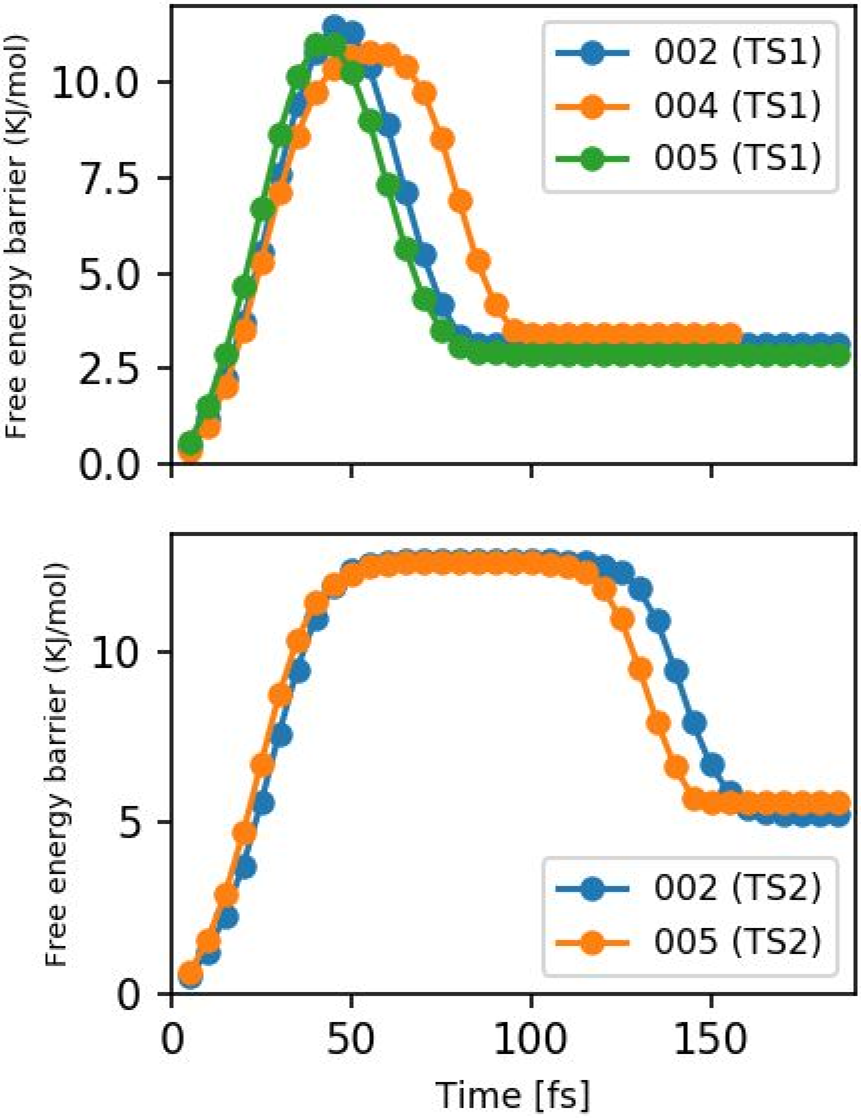

Figure S17. Upper panel: Free energy difference between transition state 1 (TS1) and the reactant as a function of time. The free energy did not converge initially but converged after ~110 fs. Lower panel: Free energy difference between transition state 2 (TS2) and the reactant (TS2 is absent for trajectory 005). Due to its high reactivity, the Gaussian hills were approximately deposited at every 10 MD steps (5 fs).

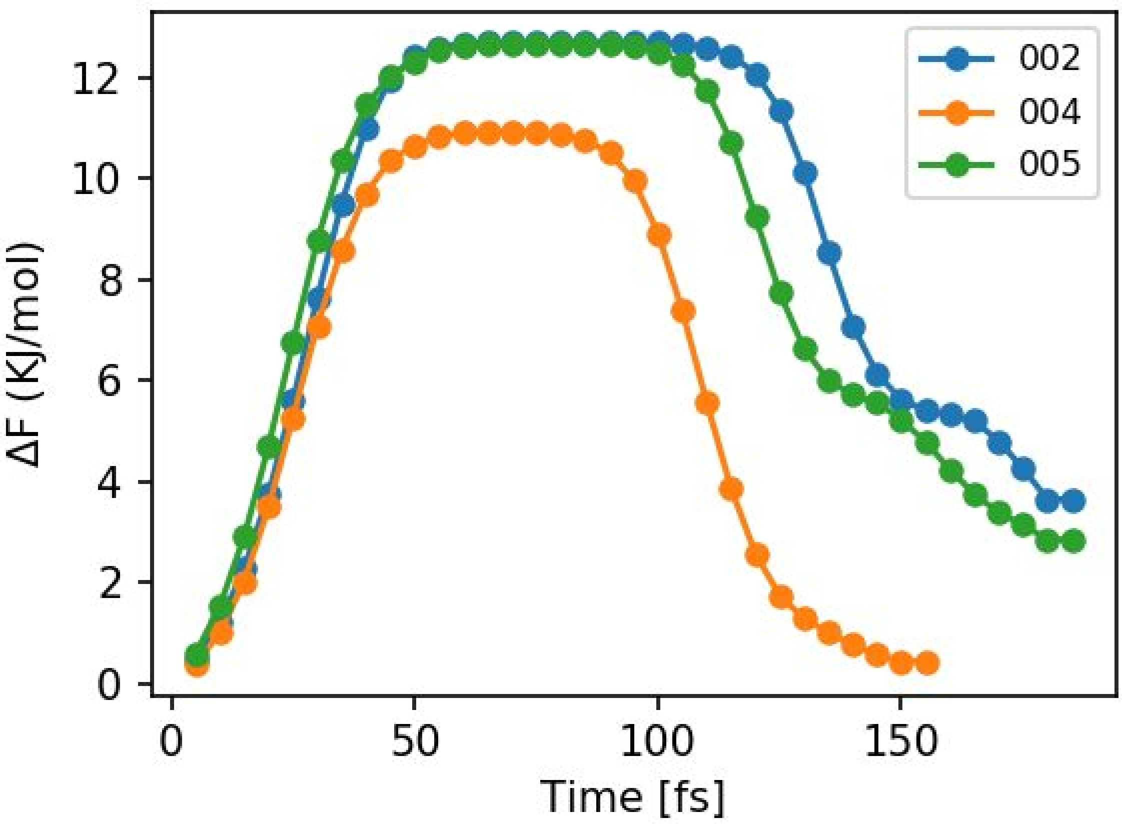

Figure S18. Free energy difference between the product and reactant as a function of time. The free energy did not converge initially but converged after ~125 fs. It is worth noting that due to its high reactivity, the Gaussian hills were deposited at every 10 MD steps (5 fs).

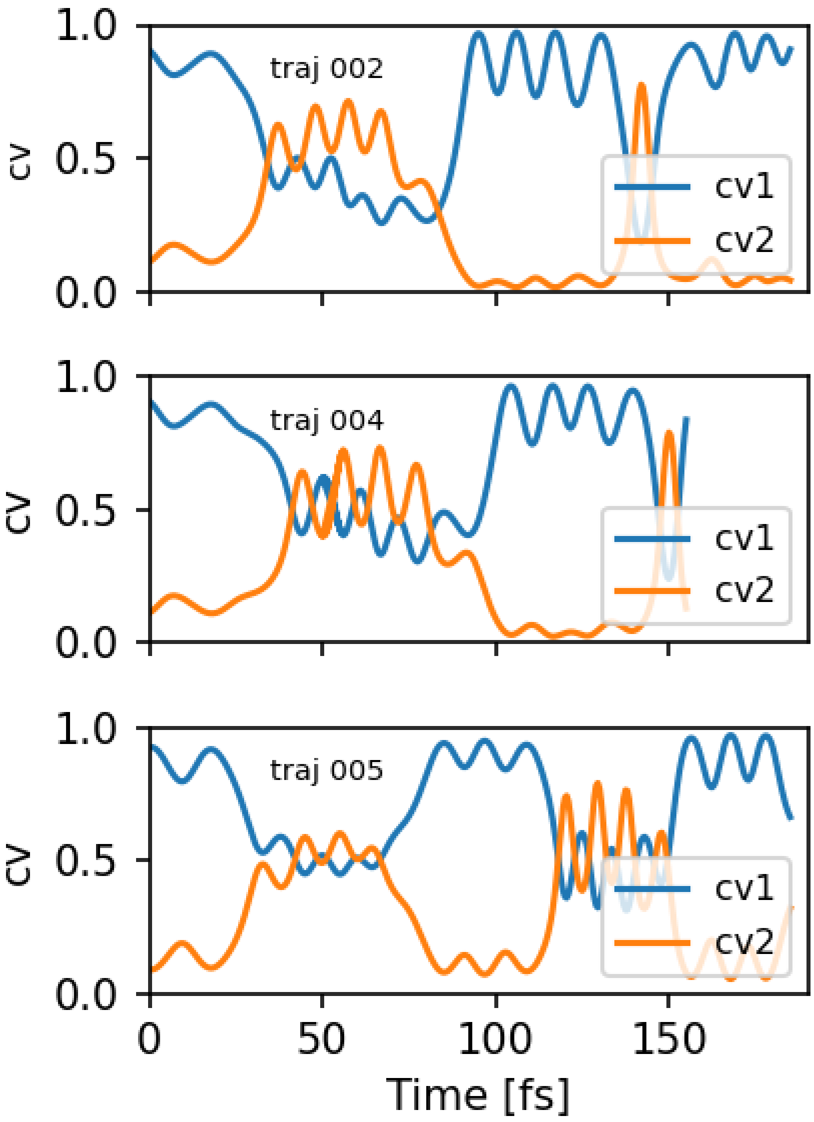

Figure S19. Fluctuation of CV values as a function of time at the air-water interface. Several forward and backward transitions can be observed in the simulations.

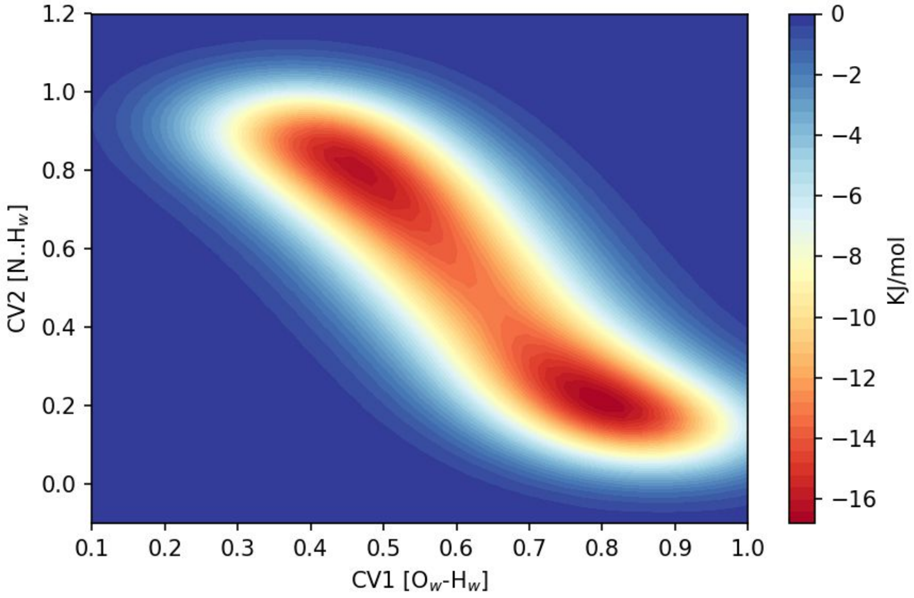

Figure S20. Free energy profile for the protonation of dimethylamine at the aqueous interface obtained with a 10-fs Gaussian hill deposition rate. The free energy barrier is 3.60 KJ/mol.

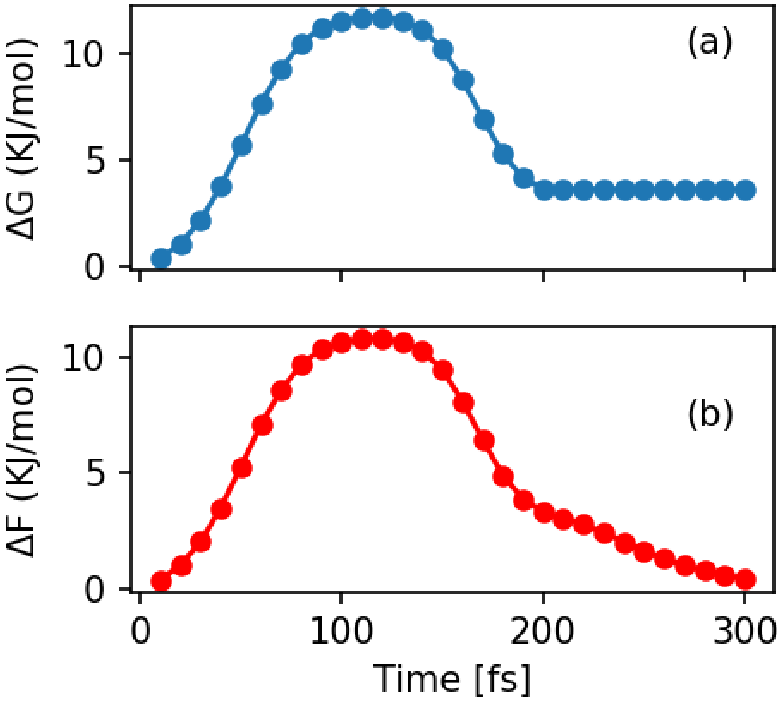

Figure S21. Panel (a): Free energy difference between the transition state and reactant as a function of time obtained from a 10-fs Gaussian hill deposition rate for the air-water interface configuration. After roughly 200 fs, the free energy barrier is stabilized at around 3.60 kJ/mol. Panel (b): Free energy difference between the product and reactant as a function of time. After roughly 200 fs, the ΔF value is converged.

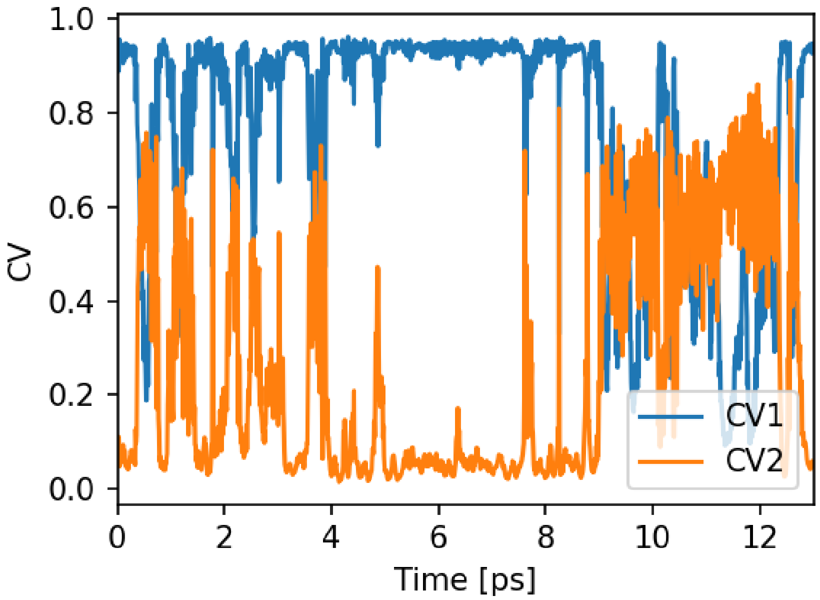

Figure S22. Fluctuations of CV values as a function of time obtained from the well-tempered metadynamics simulations in the bulk aqueous environment.

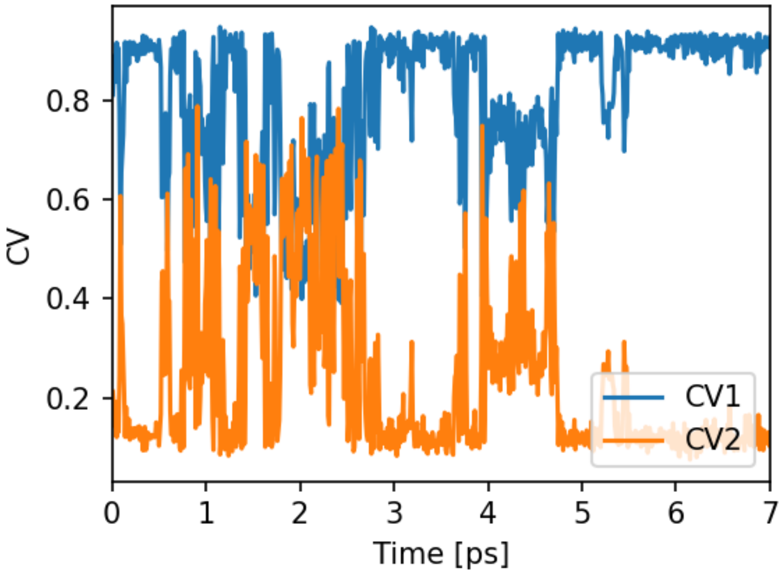

Figure S23. Fluctuations of CV values as a function of time obtained from the well-tempered metadynamics simulations for the air-water interface configuration.