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

Supplementary Section

for

Mechanism of excited state proton dissociation in microhydrated hydroxylamine clusters

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Table S1 Equilibrium structures of the intermediate complexes for proton dissociation and transfer in $NH_2OH(H_2O)_n$(n = 1-4) in the S_0 and S_1 states. The S_0 state structures were obtained from DFT/B3LYP/aug-cc-pVDZ geometry optimizations and those in the S_1 state were representative dynamic equilibrium structures sampled from NVT-BOMD simulations at the TD-DFT/B3LYP/aug-cc-pVDZ level. The total energies (E^{Tot}) and H-bond distances ($R_{O\text{-}O}$, $R_{N\text{-}O}$ and Δd_{DA}) are in au and Å, respectively. The excitation energies ($E^{Ex,[A]}$ and $E^{Ex,[B]}$) and vibrational frequencies are in eV and cm^{-1}, respectively.

Table S2 Selected Z-matrices of the static and dynamic equilibrium structures of the intermediate complexes in the S_0 and S_1 states obtained from DFT/B3LYP/aug-cc-pVDZ geometry optimizations and sampled from NVT-BOMD simulations at the TD-DFT/B3LYP/aug-cc-pVDZ level, respectively.

Table S3 Drifts in the energies, temperature and velocity of proton in structure **E1-[1]** in the S_1 state obtained from NVT-BOMD simulations at 250 K. Energies and velocity are in atomic unit (au) and temperature is in K.

Table S4 Drifts in the energies, temperature and velocity of proton in structure **E1-[1]** in the S_1 state obtained from NVT-BOMD simulations at 350 K. Energies and velocity are in atomic unit (au) and temperature is in K.

Table S5 Averages of properties (<A>) and the corresponding standard deviations (σ_A) obtained from NVT-BOMD simulations on structure **E1-[1]** in the S_1 state at 298 K. **P1** and **P2** are for the large- and small-amplitude O-O vibrations, respectively.

Table S6 Averages of properties (<A>) and the corresponding standard deviations (σ_A) obtained from NVT-BOMD simulations on structure **E1-[1]** in the S_1 state at 500 K. **P1** and **P2** are for the large- and small-amplitude O-O vibrations, respectively.

Table S7 Average lowest singlet-excitation ($<E^{Ex}>$) and kinetic ($<E^{Kin}>$) energies and the corresponding standard deviations ($\sigma_E{}^{Ex}$ and $\sigma_E{}^{Kin}$, respectively) of structure **E1-[1]** obtained from NVT-BOMD simulations over the temperature range of 250-500 K.

Table S8 Kinetics of proton dissociation in the smallest intermediate complex (structure **E1-[1]**) in the S_1 state obtained from NVT-BOMD simulations over the temperature range of 250-400 K. Lifetimes (τ) and first order-rate constants (k) are in fs and ps^{-1}, respectively.

Table S9 Kinetics of proton dissociation in the smallest intermediate complex (structure **E1-[1]**) in the S_1 state obtained from BOMD simulations over the temperature range of 250-500 K. **P1** and **P2** are the dynamics for the large- and small-amplitude O-O vibrations, respectively. Lifetimes (τ) and first order-rate constants (k) are in fs and ps^{-1}, respectively.

Figure S1 Spatial distributions of the HOMO and LUMO wavefunctions of the isolated NH_2OH and the intermediate complexes in Fig. 1. The values of the HOMO and LUMO isosurfaces are 0.10 and 0.04, respectively. a) Isolated NH_2OH in $\varepsilon = 1$ and $\varepsilon = 78$. b) – c) The intermediate complexes in $\varepsilon = 1$ and 78, respectively.

Figure S2 Energy profile of the potential energy surface for proton displacement in structure **E1-[1]** in the S_1 states ($\varepsilon = 1$) computed with and without non-adiabatic effects. Δd_{DA} = asymmetric stretching coordinate (Å); $R_{O\text{-}O}$ = H-bond distance (Å); $[B]^*$ = minimum on the S_1 state surface.

Figure S3 Variations of temperature (T), potential energy (E^{Pot}), vertical excitation energy (E^{Ex}), and the H-bond distances ($R_{O\text{-}O}$ and $R_{O\text{-}H}$) as a function of the simulation time, obtained from NVT-BOMD simulations on structure **E1-[1]** at 298 and 500 K. **P1** and **P2** are examples of the large- (L) and small-(S) amplitude O-O vibrations, respectively. Distances and energies are in Å and atomic unit (au), respectively. a) 298 K (400-700 fs), b) 500 K (250-1200 fs).