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

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-O}, R_{N-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.

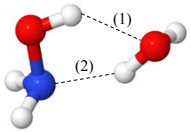
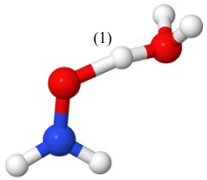
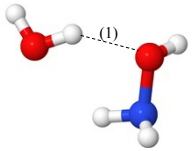
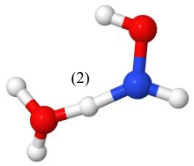
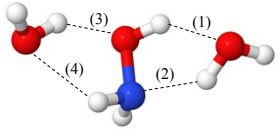
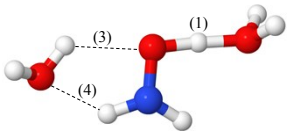
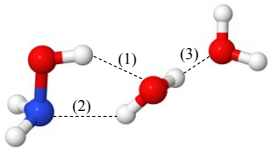
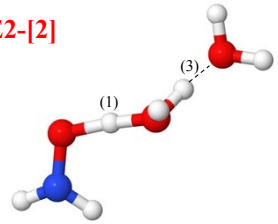
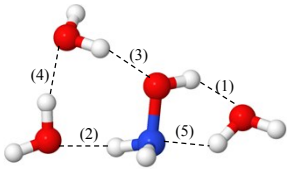
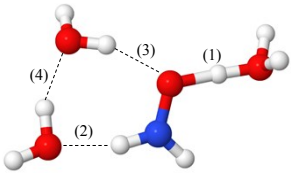
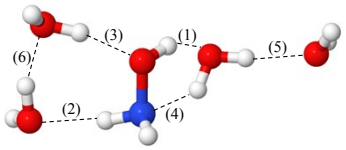
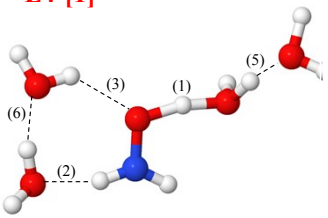
Ground state	Excited state	E^{Tot}	$E^{Ex,[A]}$	$E^{Ex,[B]}$	H-bond	R_{X-O}	Δd_{DA}	ν^{X-H}
G1-[1] 	E1-[1] 	-208.097229 (-207.989814)	(1.87)	(0.22)	(1) (2)	2.87 (2.40) 2.79 (-)	1.12 (-0.15) 0.99 (-)	3535 (-) 3718 (-)
G1-[2] 	E1-[2] 	-208.093684 (-207.969018)	(1.69)	(0.03)	(1) (2)	2.81 (-) - (2.46)	0.98 (-) - (-0.17)	3732 (-)
G2-[1] 	E2-[1] 	-284.513796 (-284.069232)	(1.39)	(0.26)	(1) (2) (3) (4)	2.81 (2.43) 2.78 (-) 2.81 (2.90) 3.04 (2.77)	1.02 (-0.03) 1.00 (-) 1.00 (-1.24) 1.28 (-0.89)	3522 (-) 3719 (-) 3729 (-) 3376 (-)
G2-[2] 	E2-[2] 	-284.511974 (-284.411815)	(1.04) (0.68)	(0.07)	(1) (2) (3)	2.79 (2.36) 2.85 (-) 2.91 (2.49)	0.96 (-0.07) 1.15 (-) 0.97 (0.49)	3449 (-) 3582 (-) 3582 (-)

Table S1 (cont.)

Ground state	Excited state	E^{Tot}	$E^{Ex,[A]}$	$E^{Ex,[B]}$	H-bond	$R_{X\text{-}O}$	Δd_{DA}	$\nu^{X\text{-}H}$
G3-[1]	**E3-[1]**							
		-360.935738 (-360.821527)	(1.62)	(0.15)	(1) (2) (3) (4) (5)	2.78 (2.44) 3.04 (2.84) 2.81 (2.82) 2.77 (2.75) 2.77 (-)	1.00 (-0.24) 1.00 (-0.82) 0.86 (-0.94) 0.85 (-0.86) 0.99 (-)	3485 (-) 3362 (-) 3717 (-) 3721 (-) 3720 (-)
G4-[1]	**E4-[1]**							
		-437.351475 (-437.244843)	(1.22)	(0.19)	(1) (2) (3) (4) (5) (6)	2.73 (2.52) 3.07 (2.80) 2.76 (2.97) 2.84 (-) 2.89 (2.62) 2.77 (2.74)	0.88 (-0.06) 1.03 (-0.83) 0.82 (-1.30) 1.17 (-) 0.95 (-0.45) 0.85 (-0.83)	3506 (-) 3365 (-) 3719 (-) 3576 (-) 3576 (-) 3720 (-)

(…) = values for the dynamic equilibrium structures in the S_1 state.

* = H-bond susceptible to proton dissociation.

X = O or N atom.