Supporting information

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Catalytic effect of water, water dimer and water trimer on the $NO_2 + H_2O$ formations from the HNO_2 + HO reaction in tropospheric conditions†

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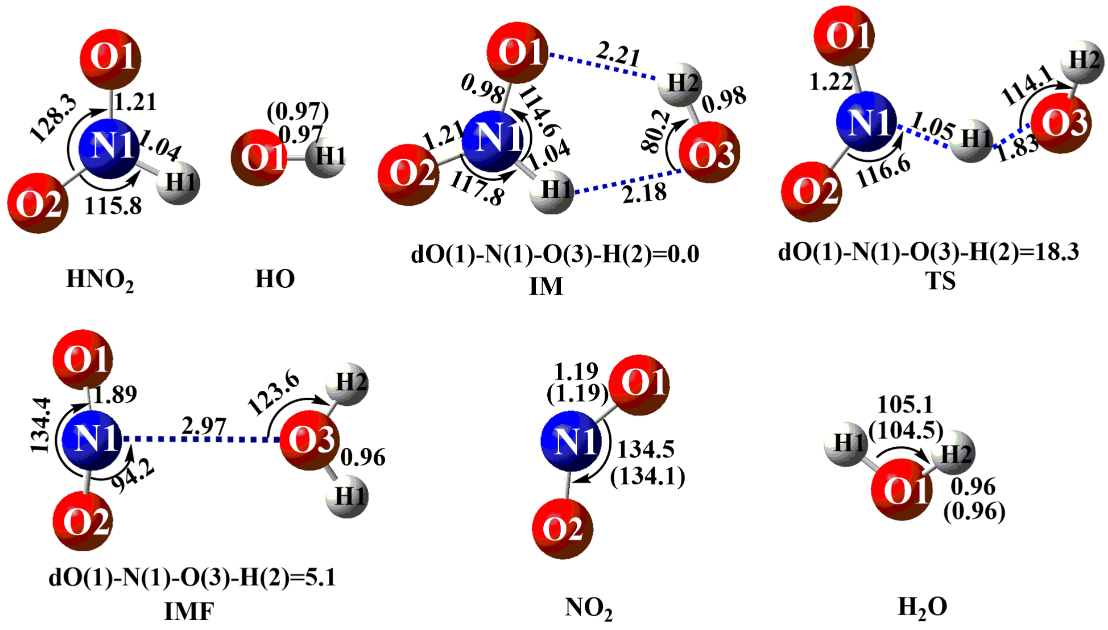

Fig. S1 Geometrical parameters for the naked reaction of HNO_2 + HO optimized at the B3LYP/6-311+G(3*df*,2*pd*) level of theory.

Table S1 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (Δ*E* and Δ(*E* + ZPE)/(kcal·mol^{-1})), enthalpies (Δ*H*(298)/(kcal·mol^{-1})), and free energies (Δ*G*(298)/(kcal·mol^{-1})) for the HNO_2 + HO reaction [a]

Species	ZPE	S	△(*E* + ZPE)	△*E*	△*H*	△*G*
HNO_2 + OH	19.1	99.5	0.0	0.0	0.0	0.0
IM	20.5	76.2	-3.4	-4.9	-3.8	3.2
TS	19.3	76.9	-2.3	-2.6	-2.8	3.9
IMF	19.6	89.5	-48.8	-49.4	-47.9	-45.0
NO_2 + H_2O	18.9	102.4	-47.2	-47.1	-46.9	-47.8

[a] ZPE and S values obtained at B3LYP/6-311+G(3*df*,2*pd*) level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(3*df*,2*pd*) level.

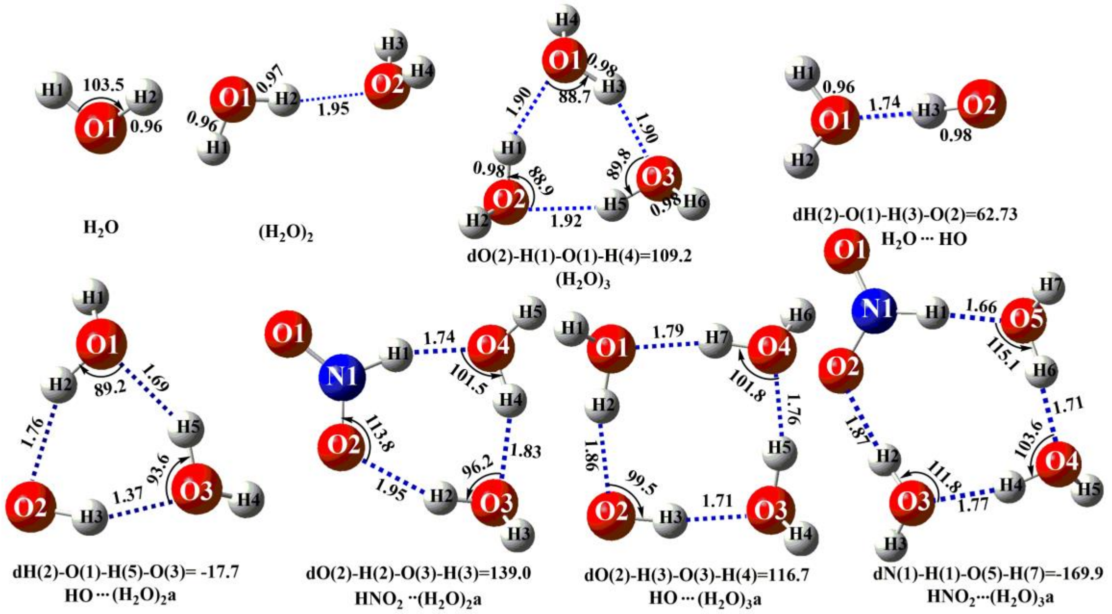

Fig. S2 The geometrical structures for the optimized transitions state, intermediates, and complexes involved in water-assisted Channels occurring through H_2O, $(H_2O)_2$, $(H_2O)_3$, H_2O···HO, HO···$(H_2O)_2$a, HNO_2···$(H_2O)_2$a, HO···$(H_2O)_3$a, HNO_2···$(H_2O)_3$a complexes

Table S2 Zero point energy (ZPE/(kcal·mol^{-1})), entropies (S/ (cal·mol^{-1}·K^{-1})), relative energies (Δ*E* and Δ(*E* + ZPE)/(kcal·mol^{-1})), enthalpies (Δ*H*(298)/(kcal·mol^{-1})), and free energies (Δ*G*(298)/(kcal·mol^{-1})) for the binary complexes (HO⋯H_2O, H_2O⋯HO, H_2O⋯HNO_2 and HNO_2⋯H_2O, the trinary complexes HNO_2⋯$(H_2O)_2$, HNO_2⋯$(H_2O)_2$a, HO⋯$(H_2O)_2$ and HO⋯$(H_2O)_2$a and the quadruple complexes (HNO_2⋯$(H_2O)_3$, HNO_2⋯$(H_2O)_3$a, HO⋯$(H_2O)_3$ HO⋯$(H_2O)_3$a)

Species	ZPE	S	Δ(*E* + ZPE)	Δ*E*	Δ*H*	Δ*G*
H_2O + HO	18.7	87.7	0.0	0.0	0.0	0.0
HO⋯H_2O	20.1	70.1	-2.2	-3.6	-2.6	2.7
H_2O⋯HO	20.8	66.6	-3.8	-5.9	-4.5	1.8
H_2O + HNO_2	27.1	102.0	0.0	0.0	0.0	0.0
H_2O⋯HNO_2	28.5	82.9	-1.1	-2.5	-1.1	4.6
HNO_2⋯H_2O	28.5	83.9	-2.2	-3.5	-2.1	3.3
H_2O + H_2O	26.8	92.9	0.0	0.0	0.0	0.0
$(H_2O)_2$	29.0	69.4	-3.0	-5.2	-3.5	2.7
$(H_2O)_2$ + HNO_2	42.7	126.3	0.0	0.0	0.0	0.0
HNO_2⋯$(H_2O)_2$	45.0	89.1	-12.3	-14.6	-13.0	-2.0
HNO_2⋯$(H_2O)_2$a	45.2	88.1	-12.6	-15.0	-13.4	-2.0
$(H_2O)_2$ + HO	34.3	112.0	0.0	0.0	0.0	0.0
HO⋯$(H_2O)_2$	37.2	79.2	-7.5	-10.3	-8.8	1.0
HO⋯$(H_2O)_2$a	37.0	80.3	-7.2	-9.9	-8.4	1.0
$(H_2O)_2$ + H_2O	42.4	115.8	0.0	0.0	0.0	0.0
$(H_2O)_3$	45.8	79.5	-7.7	-11.1	-9.0	1.4
$(H_2O)_3$ + HNO_2	59.5	136.3	0.0	0.0	0.0	0.0
HNO_2⋯$(H_2O)_3$	60.9	103.2	-12.7	-14.1	-12.9	-3.0
HNO_2⋯$(H_2O)_3$a	60.6	105.4	-12.6	-13.7	-12.6	-3.3
HO + $(H_2O)_3$	51.1	122.0	0.0	0.0	0.0	0.0
HO⋯$(H_2O)_3$	53.4	91.9	-8.4	-10.7	-9.3	-0.4
HO⋯$(H_2O)_3$a	53.2	93.5	-8.2	-10.3	-9.0	-0.5

Table S3 The equilibrium constants of the relevant complexes $HO\cdots H_2O$, $H_2O\cdots HO$, $H_2O\cdots HNO_2$, $HNO_2\cdots H_2O$, $HNO_2\cdots(H_2O)_2$, $HNO_2\cdots(H_2O)_2$a, $HO\cdots(H_2O)_2$, $HO\cdots(H_2O)_2$a, $HNO_2\cdots(H_2O)_3$, $HNO_2\cdots(H_2O)_3$a, $HO\cdots(H_2O)_3$, $HO\cdots(H_2O)_3$a at 240 - 325 K.[a, b]

T/K	$HO\cdots H_2O$	$H_2O\cdots HO$	$H_2O\cdots HNO_2$	$HNO_2\cdots H_2O$	$HNO_2\cdots(H_2O)_2$	$HNO_2\cdots(H_2O)_2$a
240	5.48×10^{-22}	5.06×10^{-21}	2.35×10^{-23}	8.20×10^{-23}	1.09×10^{-16}	6.92×10^{-17}
250	4.56×10^{-22}	3.61×10^{-21}	2.02×10^{-23}	7.06×10^{-23}	3.77×10^{-17}	2.32×10^{-17}
278	2.97×10^{-22}	1.61×10^{-21}	1.43×10^{-23}	5.00×10^{-23}	2.92×10^{-18}	1.68×10^{-18}
288	2.61×10^{-22}	1.26×10^{-21}	1.30×10^{-23}	4.52×10^{-23}	1.32×10^{-18}	7.45×10^{-19}
298	2.32×10^{-22}	1.00×10^{-21}	1.19×10^{-23}	4.13×10^{-23}	6.35×10^{-19}	3.50×10^{-19}
308	2.08×10^{-22}	8.08×10^{-22}	1.09×10^{-23}	3.80×10^{-23}	3.20×10^{-19}	1.73×10^{-19}
325	1.77×10^{-22}	5.83×10^{-22}	9.68×10^{-24}	3.37×10^{-23}	1.10×10^{-19}	5.78×10^{-20}
T/K	$HO\cdots(H_2O)_2$	$HO\cdots(H_2O)_2$a	$HNO_2\cdots(H_2O)_3$	$HNO_2\cdots(H_2O)_3$a	$HO\cdots(H_2O)_3$	$HO\cdots(H_2O)_3$a
240	1.89×10^{-19}	2.03×10^{-19}	9.58×10^{-16}	1.41×10^{-15}	3.81×10^{-18}	4.26×10^{-18}
250	9.53×10^{-20}	1.04×10^{-19}	3.28×10^{-16}	4.96×10^{-16}	1.80×10^{-18}	2.06×10^{-18}
278	1.83×10^{-20}	2.09×10^{-20}	2.50×10^{-17}	4.03×10^{-17}	2.94×10^{-19}	3.58×10^{-19}
288	1.10×10^{-20}	1.28×10^{-20}	1.13×10^{-17}	1.86×10^{-17}	1.68×10^{-19}	2.09×10^{-19}
298	6.80×10^{-21}	8.03×10^{-21}	5.39×10^{-18}	9.08×10^{-18}	9.95×10^{-20}	1.26×10^{-19}
308	4.36×10^{-21}	5.22×10^{-21}	2.71×10^{-18}	4.65×10^{-18}	6.11×10^{-20}	7.87×10^{-20}
325	2.18×10^{-21}	2.67×10^{-21}	9.31×10^{-19}	1.64×10^{-18}	2.86×10^{-20}	3.79×10^{-20}

[a] Equilibrium constants in units of cm^3 $molecule^{-1}$.

[b] All equilibrium constants were calculated by using energies computed at the CCSD(T)/aug-cc-pVTZ level and partition functions obtained at the B3LYP/6-311+G(3*df*,2*dp*) level.

[c] The concentration of the corresponding complexes at 298 K.

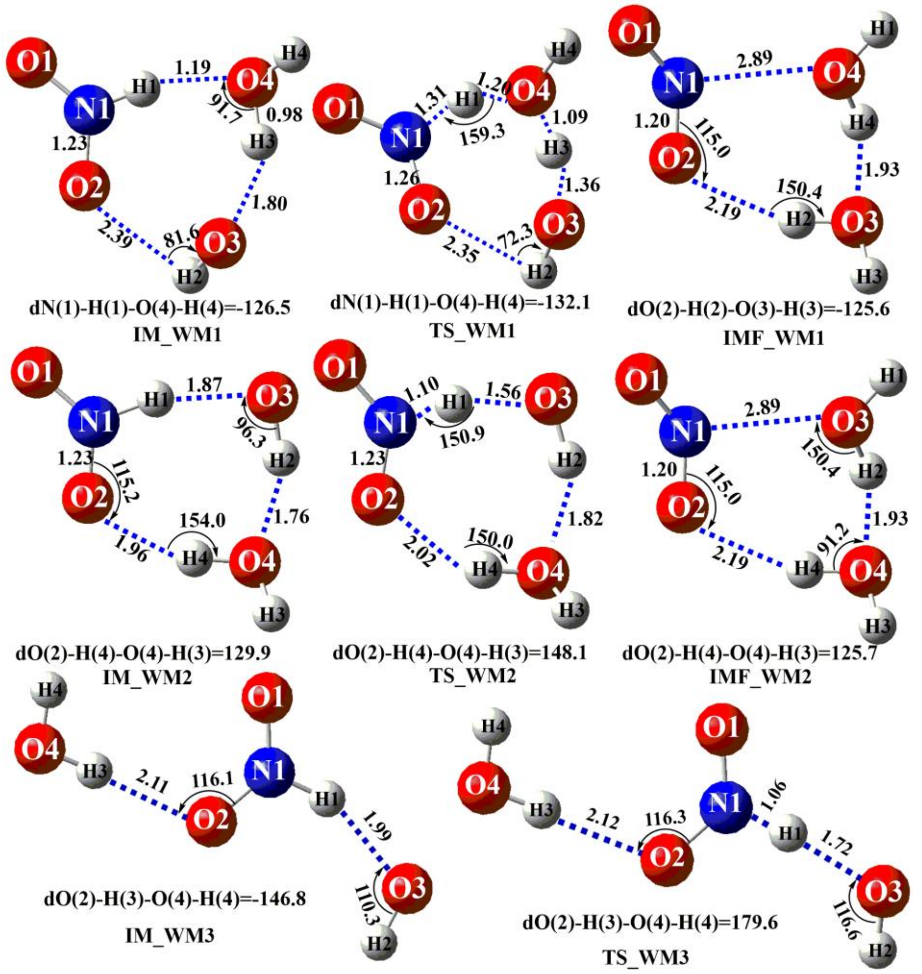

Fig. S3 The geometrical structures of the optimized transitions state, intermediates, and complexes involved in water-assisted channels occurring through $HO\cdots H_2O$ + HNO_2, $H_2O\cdots HO$ + HNO_2, $H_2O\cdots HNO_2$ + HO and $HNO_2\cdots H_2O$ + HO reactions

Table S4 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (Δ*E* and Δ(*E*+ZPE)/(kcal·mol^{-1})), enthalpies (Δ*H*(298)/(kcal·mol^{-1})), and free energies (Δ*G*(298)/(kcal·mol^{-1})) for water-assisted the formation of NO_2 + H_2O from the HNO_2 + HO reaction [a]

Species	ZPE	S	△(*E* + ZPE)	△*E*	△*H*	△*G*
HO•••H_2O + HNO_2	33.9	127.0	0.0	0.0	0.0	0.0
H_2O•••HNO_2 + HO	33.8	125.4	1.1	0.1	1.5	1.9
IM_WM1	36.3	89.5	-9.0	-11.5	-9.7	1.4
TS_WM1	33.4	79.4	2.5	3.0	0.5	14.7
IMF_WM1	35.8	98.5	-51.0	-52.9	-50.8	-42.3
H_2O•••H_2O + NO_2	34.5	126.7	-48.0	-48.6	-47.9	-47.8
H_2O•••HO + HNO_2	34.6	123.5	0.0	0.0	0.0	0.0
H_2O•••HNO_2 + HO	33.8	125.4	2.6	2.3	3.4	2.8
IM_WM2	36.6	88.8	-5.5	-7.5	-6.0	4.3
TS_WM2	35.1	85.1	-5.6	-6.2	-6.7	4.8
IMF_WM2	35.9	98.5	-49.4	-50.7	-48.9	-41.4
H_2O•••H_2O + NO_2	34.5	126.7	-46.4	-46.4	-46.0	-46.9
HNO_2•••H_2O + HO	33.8	126.5	0.0	0.0	0.0	0.0
IM_WM3	34.8	107.7	-2.3	-3.3	-2.3	6.7
TS_WM3	34.1	100.2	-2.2	-2.5	-2.8	7.5
NO_2•••H_2O + H_2O	33.3	135.2	-45.6	-45.0	-45.0	-2.2

[a] ZPE values obtained at B3LYP/6-311+G(3*df*,2*pd*) level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(3*df*,2*pd*) level.

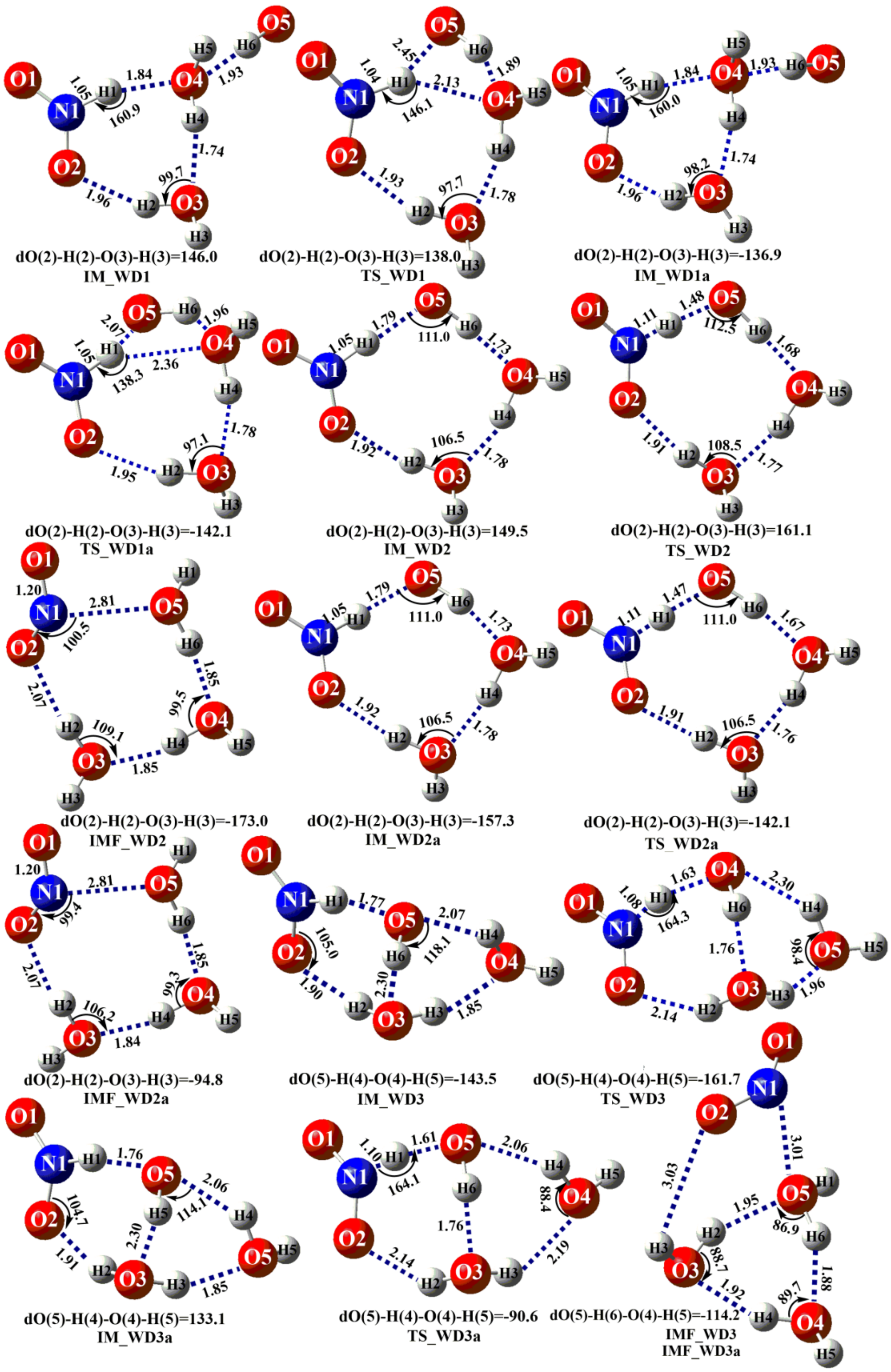

Fig. S4 The geometrical structures of the optimized transitions state, intermediates, and complexes involved in water-assisted channels occurring through $HNO_2\cdots(H_2O)_2$ + HO, $HNO_2\cdots(H_2O)_2$a + HO, $HO\cdots(H_2O)_2$ + HNO_2 and $HO\cdots(H_2O)_2$a + HNO_2 reactions

Table S5 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (ΔE and$\Delta(E$ + ZPE)/(kcal·mol^{-1})), enthalpies (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the HNO_2 + HO with two water molecule reaction

Species	ZPE	S	$\Delta(E$ + ZPE)	ΔE	ΔH	ΔG
$HNO_2 \cdots (H_2O)_2$ + HO	50.3	131.7	0.0	0.0	0.0	0.0
IM_WD1	52.1	108.5	-0.8	-2.6	-1.2	5.7
TS_WD1	51.7	104.7	-1.5	-2.3	-2.2	5.9
IM_WD2	52.2	105.8	-1.2	-3.0	-1.8	6.0
TS_WD2	50.1	102.8	-1.6	-1.4	-2.6	6.0
IMF_WD2	51.4	118.4	-43.8	-44.9	-43.1	-39.2
NO_2 + $(H_2O)_3$	51.3	136.7	-42.8	-43.7	-43.1	-44.6
$HNO_2 \cdots (H_2O)_2$a + HO	50.5	130.7	0.0	0.0	0.0	0.0
IM_WD1a	52.4	107.2	-2.9	-4.8	-3.3	3.7
TS_WD1a	51.8	106.6	-1.0	-2.3	-1.4	5.8
IM_WD2a	52.4	103.7	-1.3	-3.3	-2.0	6.1
TS_WD2a	50.4	100.7	-1.6	-1.4	-2.6	6.3
IMF_WD2a	51.6	115.3	-43.9	-45.1	-43.3	-38.8
NO_2 + $(H_2O)_3$	51.3	136.7	-42.3	-43.1	-42.5	-44.3
$HO \cdots (H_2O)_2$ + HNO_2	50.9	136.0	0.0	0.0	0.0	0.0
IM_WD3	53.0	100.8	-3.5	-5.6	-3.8	6.7
TS_WD3	50.8	104.0	-1.6	-1.4	-1.7	7.8
IMF_WD3	51.8	117.6	-49.9	-50.8	-48.9	-43.4
NO_2 + $(H_2O)_3$	51.3	136.7	-47.5	-47.9	-47.2	-47.4
$HO \cdots (H_2O)_2$a + HNO_2	50.7	137.2	0.0	0.0	0.0	0.0
IM_WD3a	53.0	100.6	-3.6	-5.9	-4.0	6.9
TS_WD3a	50.3	104.5	0.9	1.2	0.6	10.4
IMF_WD3a	51.8	117.6	-50.0	-51.1	-49.2	-43.3
NO_2 + $(H_2O)_3$	51.3	136.7	-47.8	-48.4	-47.6	-47.5

[a] ZPE and S values obtained at B3LYP/6-311+G(3*df*,2*pd*) level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(3*df*,2*pd*) level.

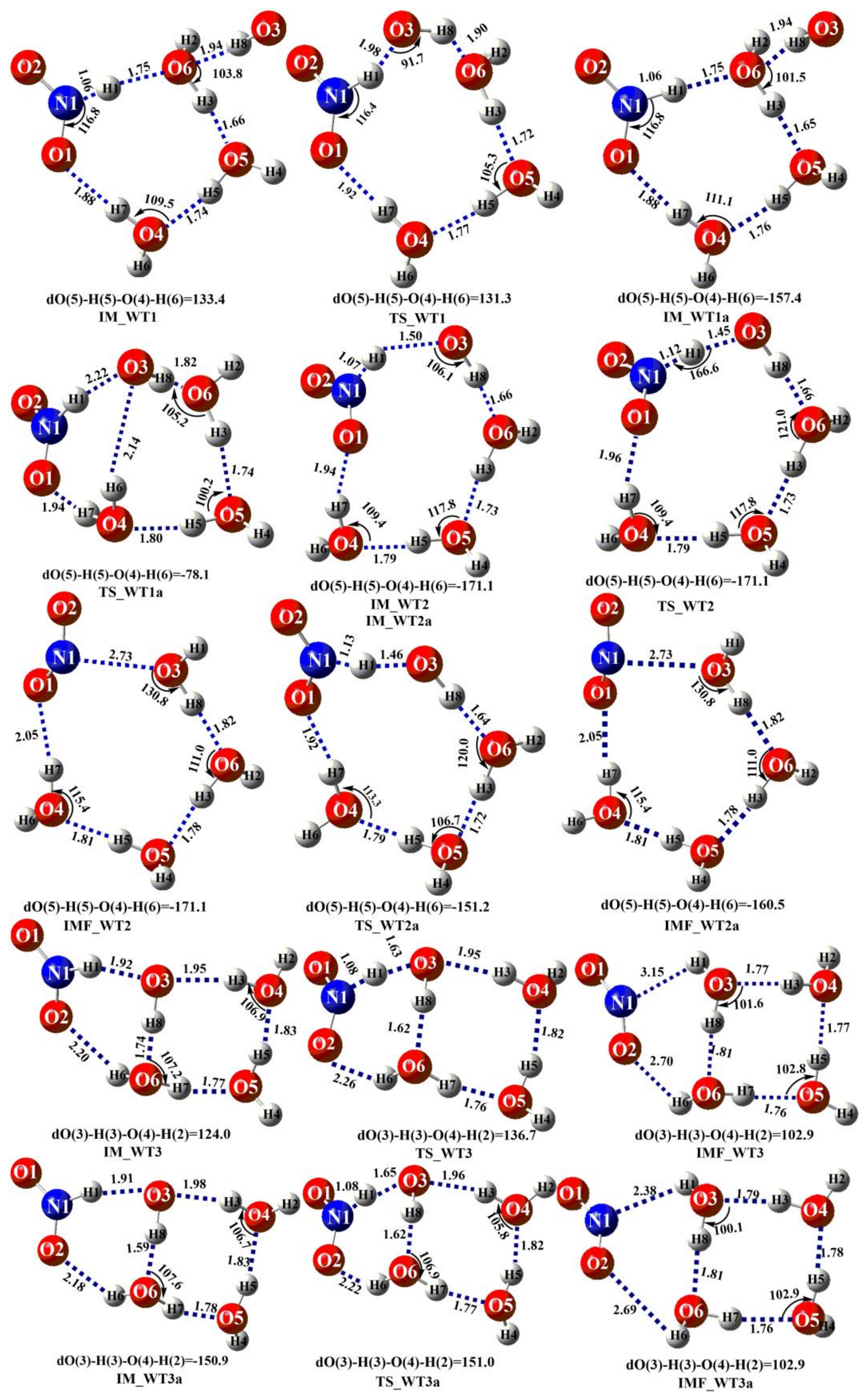

Fig. S5 The geometrical structures of the optimized transitions state, intermediates involved in water-assisted channels occurring through $HNO_2\cdots(H_2O)_3$ + HO, $HNO_2\cdots(H_2O)_3$a + HO, and $HO\cdots(H_2O)_3$ + HNO_2, $HO\cdots(H_2O)_3$a + HNO_2 reactions

Table S6 Zero-point energy (ZPE/(kcal·mol^{-1})), relative energies (Δ*E* and Δ(*E*+ZPE)/(kcal·mol^{-1})), enthalpies (Δ*H*(298)/(kcal·mol^{-1})), and free energies (Δ*G*(298)/(kcal·mol^{-1})) for the HNO_2 + HO with water trimer [a]

Species	ZPE	S	Δ(*E* + ZPE)	Δ*E*	Δ*H*	Δ*G*
HNO_2···$(H_2O)_3$ + HO	66.2	145.8	0.0	0.0	0.0	0.0
IM_WT1	68.1	121.9	-3.0	-4.8	-3.4	3.7
TS_WT1	67.2	122.0	-0.9	-1.9	-1.2	5.9
IM_WT2	67.7	118.5	-0.5	-2.1	-1.1	7.0
TS_WT2	65.4	120.7	0.1	1.0	-0.6	6.9
IMF_WT2	67.3	131.9	-41.9	-43.0	-41.2	-37.1
NO_2+ $(H_2O)_4$	67.5	149.3	-43.6	-45.0	-44.1	-45.2
HNO_2···$(H_2O)_3$a+ HO	66.0	148.0	0.0	0.0	0.0	0.0
IM_WT1a	67.8	124.9	-3.4	-5.3	-3.9	3.0
TS_WT1a	67.6	116.8	-1.0	-2.6	-1.8	7.5
IM_WT2a	67.7	118.5	-0.7	-2.4	-1.4	7.3
TS_WT2a	66.3	108.1	0.4	0.1	-1.6	10.3
IMF_WT2a	67.2	133.7	-41.5	-42.8	-40.9	-36.6
NO_2 + $(H_2O)_4$	67.2	152.0	-43.0	-44.2	-43.4	-44.6
HO···$(H_2O)_3$ + HNO_2	67.1	148.8	0.0	0.0	0.0	0.0
IM_WT3	68.1	118.9	-6.2	-7.2	-6.0	2.9
TS_WT3	67.1	114.8	-3.4	-3.3	-3.6	6.5
IMF_WT3	68.1	128.3	-50.4	-51.4	-49.5	-43.4
NO_2 + $(H_2O)_4$	67.5	149.3	-47.9	-48.4	-47.7	-47.8
HO···$(H_2O)_3$a + HNO_2	66.9	150.3	0.0	0.0	0.0	0.0
IM_WT3a	68.0	119.4	-5.6	-6.7	-5.5	3.8
TS_WT3a	67.1	114.7	-4.7	-4.9	-5.1	5.6
IMF_WT3a	67.8	130.6	-51.1	-52.0	-50.1	-44.2
NO_2 + $(H_2O)_4$	67.2	152.0	-47.6	-47.9	-47.2	-47.7

[a] ZPE values obtained at B3LYP/6-311+G(3*df*,2*pd*) level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(3*df*,2*pd*) level.

Table S7 Effective Rate constants (cm^3·$molecules^{-1}$·s^{-1}) for the HNO_2 + HO → NO_2 + H_2O reaction with and without $(H_2O)_n$ (n = 1-3) within the temperature range of 240 – 325 K.

T/K	K_{eq}(IM)	k_{TS}	k_{R1}	K_{eq} (IM_WM1)	*k*(TS_WM1)
240	1.59×10^{-24}	1.71×10^{12}	2.72×10^{-12}	8.90×10^{-20}	5.74×10^{2}
250	1.49×10^{-24}	1.90×10^{12}	2.83×10^{-12}	4.06×10^{-20}	9.49×10^{2}
278	1.29×10^{-24}	2.44×10^{12}	3.15×10^{-12}	6.14×10^{-21}	3.69×10^{3}
288	1.24×10^{-24}	2.63×10^{12}	3.27×10^{-12}	3.43×10^{-21}	5.85×10^{3}
298	1.20×10^{-24}	2.83×10^{12}	3.40×10^{-12}	2.00×10^{-21}	9.12×10^{3}
308	1.16×10^{-24}	3.04×10^{12}	3.53×10^{-12}	1.21×10^{-21}	1.40×10^{4}
325	1.11×10^{-24}	3.38×10^{12}	3.77×10^{-12}	5.53×10^{-22}	2.79×10^{4}

T/K	*k*(WM1)	*k*'(WM1)	K_{eq} (IM_WM1a)	*k*(TS_WM1a)	*k*(WM1a)
240	5.11×10^{-17}	2.90×10^{-21}	2.35×10^{-23}	5.74×10^{2}	1.35×10^{-20}
250	3.85×10^{-17}	4.57×10^{-21}	2.02×10^{-23}	9.49×10^{2}	1.92×10^{-20}
278	2.27×10^{-17}	3.23×10^{-21}	1.43×10^{-23}	3.69×10^{3}	5.28×10^{-20}
288	2.01×10^{-17}	4.03×10^{-21}	1.30×10^{-23}	5.85×10^{3}	7.61×10^{-20}
298	1.82×10^{-17}	3.64×10^{-21}	1.19×10^{-23}	9.12×10^{3}	1.09×10^{-19}
308	1.69×10^{-17}	5.29×10^{-21}	1.09×10^{-23}	1.40×10^{4}	1.53×10^{-19}
325	1.54×10^{-17}	6.28×10^{-21}	9.68×10^{-24}	2.79×10^{4}	2.70×10^{-19}

T/K	*k*'(WM1a)	K_{eq} (IM_WM2)	*k*(TS_WM2)	*k*(WM2)	*k*'(WM2)
240	3.29×10^{-26}	1.64×10^{-20}	2.09×10^{12}	3.42×10^{-8}	1.79×10^{-11}
250	1.01×10^{-25}	8.44×10^{-21}	2.11×10^{12}	1.78×10^{-8}	1.67×10^{-11}
278	3.62×10^{-25}	1.70×10^{-21}	2.16×10^{12}	3.67×10^{-9}	2.84×10^{-12}
288	7.61×10^{-25}	1.04×10^{-21}	2.17×10^{12}	2.25×10^{-9}	2.18×10^{-12}
298	1.11×10^{-24}	6.54×10^{-22}	2.18×10^{12}	1.43×10^{-9}	1.23×10^{-12}
308	2.50×10^{-24}	4.25×10^{-22}	2.20×10^{12}	9.33×10^{-10}	1.13×10^{-12}
325	6.01×10^{-24}	2.17×10^{-22}	2.21×10^{12}	4.81×10^{-10}	6.45×10^{-13}

T/K	K_{eq} (IM_WM2a)	*k*(TS_WM2a)	*k*(WM2a)	*k*'(WM2a)	K_{eq} (IM_WM3)
240	1.52×10^{-22}	2.09×10^{12}	3.18×10^{-10}	2.70×10^{-15}	3.35×10^{-22}
250	9.45×10^{-23}	2.11×10^{12}	1.99×10^{-10}	3.65×10^{-15}	2.86×10^{-22}
278	3.03×10^{-23}	2.16×10^{12}	6.54×10^{-11}	1.57×10^{-15}	1.97×10^{-22}
288	2.14×10^{-23}	2.17×10^{12}	4.65×10^{-11}	1.62×10^{-15}	1.76×10^{-22}
298	1.55×10^{-23}	2.18×10^{12}	3.38×10^{-11}	1.20×10^{-15}	1.60×10^{-22}
308	1.15×10^{-23}	2.20×10^{12}	2.52×10^{-11}	1.44×10^{-15}	1.46×10^{-22}
325	7.23×10^{-24}	2.21×10^{12}	1.60×10^{-11}	1.24×10^{-15}	1.27×10^{-22}

T/K	*k*(TS_WM3)	*k*(WM3)	*k*'(WM3)	K_{eq} (IM_WD2)	*k*(TS_WD2)
240	3.28×10^{11}	1.10×10^{-10}	7.48×10^{-17}	3.97×10^{-24}	8.51×10^{11}
250	3.30×10^{11}	9.43×10^{-11}	1.47×10^{-16}	3.71×10^{-24}	8.70×10^{11}
278	3.34×10^{11}	6.58×10^{-11}	7.41×10^{-16}	3.18×10^{-24}	9.19×10^{11}
288	3.35×10^{11}	5.91×10^{-11}	1.14×10^{-15}	3.04×10^{-24}	9.35×10^{11}
298	3.36×10^{11}	5.37×10^{-11}	1.69×10^{-15}	2.92×10^{-24}	9.50×10^{11}
308	3.37×10^{11}	4.91×10^{-11}	2.45×10^{-15}	2.82×10^{-24}	9.66×10^{11}
325	3.39×10^{11}	4.30×10^{-11}	4.40×10^{-15}	2.68×10^{-24}	9.90×10^{11}

T/K	*k*(WD1)	*k*'(WD1)	K_{eq} (IM_WD2a)	*k*(TS_WD2a)	*k*(WD1a)

240	1.70×10^{-11}	1.29×10^{-17}	2.66×10^{-22}	6.39×10^{10}	3.38×10^{-12}
250	5.46×10^{-10}	7.83×10^{-16}	2.09×10^{-22}	7.82×10^{10}	3.23×10^{-12}
278	3.18×10^{-10}	1.96×10^{-15}	1.17×10^{-22}	1.27×10^{11}	2.92×10^{-12}
288	2.70×10^{-10}	2.22×10^{-15}	9.80×10^{-23}	1.48×10^{11}	2.84×10^{-12}
298	2.32×10^{-10}	2.49×10^{-15}	8.33×10^{-23}	1.71×10^{11}	2.78×10^{-12}
308	2.01×10^{-10}	2.73×10^{-15}	7.16×10^{-23}	1.95×10^{11}	2.72×10^{-12}
325	1.62×10^{-10}	3.19×10^{-15}	5.68×10^{-23}	2.38×10^{11}	2.65×10^{-12}

T/K	*k'*(WD1a)	K_{eq} (IM_WD3)	*k*(TS_WD3)	*k*(WD2)	*k'*(WD2)
240	1.63×10^{-18}	1.33×10^{-24}	2.96×10^{11}	3.93×10^{-13}	5.18×10^{-22}
250	2.85×10^{-18}	9.86×10^{-25}	3.69×10^{11}	3.64×10^{-13}	1.32×10^{-21}
278	1.03×10^{-17}	4.86×10^{-25}	6.32×10^{11}	3.07×10^{-13}	1.18×10^{-20}
288	1.32×10^{-17}	3.92×10^{-25}	7.48×10^{11}	2.93×10^{-13}	2.00×10^{-20}
298	1.64×10^{-17}	3.21×10^{-25}	8.76×10^{11}	2.81×10^{-13}	3.24×10^{-20}
308	1.99×10^{-17}	2.68×10^{-25}	1.02×10^{12}	2.72×10^{-13}	5.02×10^{-20}
325	2.74×10^{-17}	2.02×10^{-25}	1.28×10^{12}	2.59×10^{-13}	1.01×10^{-19}

T/K	K_{eq} (IM_WD3a)	*k*(TS_WD3a)	*k*(WD2a)	*k'*(WD2a)	K_{eq} (IM_WT2)
240	1.07×10^{-24}	1.70×10^{11}	1.81×10^{-13}	2.57×10^{-22}	2.58×10^{-22}
250	7.80×10^{-25}	2.19×10^{11}	1.71×10^{-13}	6.77×10^{-22}	2.01×10^{-22}
278	3.68×10^{-25}	4.09×10^{11}	1.50×10^{-13}	6.64×10^{-21}	1.11×10^{-22}
288	2.92×10^{-25}	4.97×10^{11}	1.45×10^{-13}	1.15×10^{-20}	9.28×10^{-23}
298	2.37×10^{-25}	5.98×10^{11}	1.41×10^{-13}	1.92×10^{-20}	7.85×10^{-23}
308	1.94×10^{-25}	7.10×10^{11}	1.38×10^{-13}	3.05×10^{-20}	6.73×10^{-23}
325	1.44×10^{-25}	9.31×10^{11}	1.34×10^{-13}	6.38×10^{-20}	5.31×10^{-23}

T/K	*k*(TS_WT2)	*k*(WT1)	*k'*(WT1)	K_{eq} (IM_WT2a)	*k*(TS_WT2a)
240	9.81×10^{9}	2.53×10^{-12}	4.11×10^{-21}	4.11×10^{-21}	2.59×10^{8}
250	1.31×10^{10}	2.63×10^{-12}	1.05×10^{-20}	1.05×10^{-20}	3.41×10^{8}
278	2.64×10^{10}	2.93×10^{-12}	9.01×10^{-20}	9.01×10^{-20}	6.66×10^{8}
288	3.28×10^{10}	3.04×10^{-12}	1.39×10^{-19}	1.39×10^{-19}	8.19×10^{8}
298	4.01×10^{10}	3.15×10^{-12}	2.04×10^{-19}	2.04×10^{-19}	9.94×10^{8}
308	4.84×10^{10}	3.26×10^{-12}	2.87×10^{-19}	2.87×10^{-19}	1.19×10^{9}
325	6.47×10^{10}	3.44×10^{-12}	4.97×10^{-19}	4.97×10^{-19}	1.57×10^{9}

T/K	*k*(WT1a)	*k'*(WT1a)	K_{eq} (IM_WT3)	*k*(TS_WT3)	*k*(WT2)
240	2.39×10^{-13}	6.09×10^{-22}	1.31×10^{-22}	1.49×10^{11}	7.21×10^{-11}
250	2.38×10^{-13}	1.52×10^{-21}	8.96×10^{-23}	1.66×10^{11}	5.05×10^{-11}
278	2.36×10^{-13}	1.24×10^{-20}	3.64×10^{-23}	2.14×10^{11}	2.17×10^{-11}
288	2.37×10^{-13}	1.87×10^{-20}	2.77×10^{-23}	2.32×10^{11}	1.68×10^{-11}
298	2.37×10^{-13}	2.72×10^{-20}	2.16×10^{-23}	2.49×10^{11}	1.33×10^{-11}
308	2.38×10^{-13}	3.77×10^{-20}	1.71×10^{-23}	2.67×10^{11}	1.07×10^{-11}
325	2.40×10^{-13}	6.41×10^{-20}	1.20×10^{-23}	2.98×10^{11}	7.63×10^{-12}

T/K	*k'*(WT2)	K_{eq} (IM_WT3a)	*k*(TS_WT3a)	*k*(WT2a)	*k'*(WT2a)
240	4.97×10^{-22}	1.68×10^{-22}	4.30×10^{11}	1.95×10^{-11}	1.41×10^{-22}
250	1.17×10^{-21}	1.11×10^{-22}	4.53×10^{11}	1.48×10^{-11}	3.71×10^{-22}
278	8.28×10^{-21}	4.22×10^{-23}	5.14×10^{11}	7.80×10^{-12}	3.43×10^{-21}

288	1.20×10^{-20}	3.15×10^{-23}	5.34×10^{11}	6.42×10^{-12}	5.40×10^{-21}
298	1.67×10^{-20}	2.39×10^{-23}	5.54×10^{11}	5.38×10^{-12}	8.14×10^{-21}
308	2.23×10^{-20}	1.86×10^{-23}	5.73×10^{11}	4.57×10^{-12}	1.17×10^{-20}
325	3.55×10^{-20}	1.26×10^{-23}	6.05×10^{11}	3.56×10^{-12}	2.10×10^{-20}

k_R is the rate constant of Channel R; k_{eq}(IM) is the rate constant of the process of HNO_2 + HO → IM. k_{TS} is the rate constant of the process of IM → TS→ NO_2 + H_2O. k_R is the rate constant of the process of HNO_2 + HO → IM → TS → NO_2 + H_2O. $k_R = k_{eq}(IM) \cdot k_{TS}$.

K_{eq}(IM_WM1) is the equilibrium constant for the process of HO···H_2O + HNO_2 → IM_WM1; K_{eq}(IM_WM1a) is the equilibrium constant for the process of H_2O···HNO_2 + OH → IM_WM1a; K_{eq}(IM_WM2) is the equilibrium constant for the process of H_2O···HO + HNO_2 → IM_WM2; K_{eq}(IM_WM2a) is the equilibrium constant for the process of HNO_2···H_2O + OH → IM_WM2a; K_{eq}(IM_WM3) is the equilibrium constant for the process of HNO_2···H_2O + HO → IM_WM3. $k_{(TS\_WM1)}$ is the rate constant for the process of IM_WM1 → TS_WM1 → IMF_WM1 → $(H_2O)_2$ + NO_2, $k_{(TS\_WM1a)}$ is the rate constant for the process of IM_WM1a → TS_WM1a → IMF_WM1a → $(H_2O)_2$ + NO_2, $k_{(TS\_WM2)}$ is the rate constant for the process of IM_WM2 → TS_WM2 → IMF_WM2 → $(H_2O)_2$ + NO_2, $k_{(TS\_WM2a)}$ is the rate constant for the process of IM_WM2a → TS_WM2a → IMF_WM2a → $(H_2O)_2$ + NO_2, $k_{(TS\_WM3)}$ is the rate constant for the process of IM_WM3 → TS_WM3 → IMF_WM3 → NO_2···H_2O + H_2O, respectively. k(WM1), k(WM1a), k(WM2), k(WM2a) and k(WM3) is the rate constant of water-assisted Channels WM1, WM1a, WM2, WM2a, and WM3. k'(WM1), k'(WM1a), k'(WM2) k'(WM2a) and k'(WM3) is the effective rate constant of water-assisted Channels WM1, WM1a, WM2, WM2a and WM3. $k(WM1) = K_{eq}(IM\_WM1)\cdot k_{(TS\_WM1)}$, $k(WM1a) = K_{eq}(IM\_WM1a)\cdot k_{(TS\_WM1a)}$, $k(WM2) = K_{eq}(IM\_WM2)\cdot k_{(TS\_WM2)}$, $k(WM2a) = K_{eq}(IM\_WM2a)\cdot k_{(TS\_WM2a)}$, $k(WM3) = K_{eq}(IM\_WM3)\cdot k_{(TS\_WM3)}$, respectively; $k'(WM1) = k(WM1)\cdot K_{eq}(HO\cdots H_2O)\cdot[H_2O]$, $k'(WM1) = k(WM1a)\cdot K_{eq}(H_2O\cdots HNO_2)\cdot[H_2O]$, $k'(WM2) = k_{(WM2)}\cdot K_{eq}(H_2O\cdots HO)\cdot[H_2O]$, $k'(WM2a) = k_{(WM2a)}\cdot K_{eq}(HNO_2\cdots H_2O)\cdot[H_2O]$, $k'(WM3) = k(WM3)\cdot K_{eq}(HNO_2\cdots H_2O)\cdot[H_2O]$, respectively.

K_{eq}(IM_WD2) is the equilibrium constant for the process of HNO_2···$(H_2O)_2$ + HO → IM_WD2, K_{eq}(IM_WD2a) is the equilibrium constant for the process of HNO_2···$(H_2O)_2$a + HO → IM_WD2a, K_{eq}(IM_WD3) is the equilibrium constant for the process of HO···$(H_2O)_2$ + HNO_2 → IM_WD3, K_{eq}(IM_WD3a) is the equilibrium constant for the process of HO···$(H_2O)_2$a + HNO_2 → IM_WD3a, respectively. $k_{(TS\_WD2)}$ is the rate constant for the process of IM_WD2 → TS_WD2 → IMF_WD2 → $(H_2O)_3$ + NO_2, $k_{(TS\_WD2a)}$ is the rate constant for the process of IM_WD2a; $k_{(TS\_WD3)}$ is the rate constant for the process of IM_WD3 → TS_WD3 → IMF_WD3 → $(H_2O)_3$ + NO_2, $k_{(TS\_WD3a)}$ is the rate constant for the process of IM_WD3a→ TS_WD3a → IMF_WD3a → $(H_2O)_3$ + NO_2, respectively. k(WD2) is the rate constant for the process of HNO_2···$(H_2O)_2$ + HO → IM_WD1 → TS_WD1 → IM_WD2 → TS_WD2 → IMF_WD2 → $(H_2O)_3$ + NO_2, k(WD2a) is the rate constant for the process of HO + HNO_2···$(H_2O)_2$a → IM_WD1a → TS_WD1a → IM_WD2a → TS_WD2a → IMF_WD2a → $(H_2O)_3$ + NO_2, respectively. k(WD3) is the rate constant for the process of HO···$(H_2O)_2$ + HNO_2 → IM_WD3 → TS_WD3 → IMF_WD3 → $(H_2O)_3$ + NO_2, k(WD3a) is the rate constant for the process of HNO_2 + HO···$(H_2O)_2$a → IM_WD3a → TS_WD3a → IMF_WD3a → $(H_2O)_3$ + NO_2, respectively. k'(WD2) is the effective rate constant for the process of HO + HNO_2···$(H_2O)_2$ → IM_WD1 → TS_WD1 → IM_WD2 → TS_WD2 → IMF_WD2 → $(H_2O)_3$ + NO_2, k'(WD2a) is the effective rate constant for the process of HO + HNO_2···$(H_2O)_2$a → IM_WD1a → TS_WD1a → IM_WD2a → TS_WD2a → IMF_WD2a → $(H_2O)_3$ + NO_2, respectively. k'(WD3) is the effective rate constant for the process of HNO_2 + HO···$(H_2O)_2$ → IM_WD3 → TS_WD3 → IMF_WD3 → $(H_2O)_3$ + NO_2, k'(WD3a) is the effective rate constant for the process of HNO_2 + HO···$(H_2O)_2$ → IM_WD3a → TS_WD3a → IMF_WD3a → $(H_2O)_3$ + NO_2, respectively. k(WD1), k(WD2) is the rate constant of water dimer-assisted Channels WD1, WD2, respectively. k'(WD1), k'(WD2) is the effective rate constant of water dimer-assisted Channels WD1, WD2, respectively. $k_{(WD1)} =$

$k_{(WD1)} + k_{(WD1a)}$, $k'_{(WD1)} = k'_{(WD1)} + k'_{(WD1a)}$, $k_{(WD2)} = k_{(WD2)} + k_{(WD2a)}$, $k'_{(WD2)} = k'_{(WD2)} + k'_{(WD2a)}$, $1/k_{(WD1)} = 1/k_{(TS\_WD1)} + 1/k_{(TS\_WD2)}$, $1/k_{(WD1a)} = 1/_{(TS\_WD1a)} + 1/_{(TS\_WD2a)}$, $k'_{(WD1)} = K_{eq}(HNO_2\cdots(H_2O)_2)\bullet[(H_2O)_2]\bullet k_{(WD1)}$, $k'_{(WD1a)} = K_{eq}(HNO_2\cdots(H_2O)_2a)\bullet[(H_2O)_2]\bullet k_{(WD1a)}$, $k'_{(WD2)} = K_{eq}(HO\cdots(H_2O)_2)\bullet[(H_2O)_2]\bullet k_{(WD2)}$, $k'_{(WD2a)} = K_{eq}(HO\cdots(H_2O)_2a)\bullet[(H_2O)_2]\bullet k_{(WD2a)}$, respectively.

K_{eq}(IM_WT2) is the equilibrium constant for the process of $HNO_2\cdots(H_2O)_3$ + HO → IM_WT2, K_{eq}(IM_WT2a) is the equilibrium constant for the process of $HNO_2\cdots(H_2O)_3$a + HO → IM_WT2a, K_{eq}(IM_WT3) is the equilibrium constant for the process of $HO\cdots(H_2O)_3$ + HNO_2 → IM_WT3, K_{eq}(IM_WT3a) is the equilibrium constant for the process of $HO\cdots(H_2O)_3$a + HNO_2 → IM_WT3a, respectively. $k_{(TS\_WT2)}$ is the rate constant for the process of IM_WT2 → TS_WT2 → IMF_WT2 → $(H_2O)_4$ + NO_2, $k_{(TS\_WT2a)}$ is the rate constant for the process of IM_WT2a; $k_{(TS\_WT3)}$ is the rate constant for the process of IM_WT3 → TS_WT3 → IMF_WT3 → $(H_2O)_4$ + NO_2, $k_{(TS\_WT3a)}$ is the rate constant for the process of IM_WT3a→ TS_WT3a → IMF_WT3a → $(H_2O)_4$ + NO_2, respectively. *k*(WT2) is the rate constant for the process of $HNO_2\cdots(H_2O)_3$ + HO → IM_WT1 → TS_WT1 → IM_WT2 → TS_WT2 → IMF_WT2 → $(H_2O)_4$ + NO_2, *k*(WT2a) is the rate constant for the process of HO + $HNO_2\cdots(H_2O)_3$a → IM_WT1a → TS_WT1a → IM_WT2a → TS_WT2a → IMF_WT2a → $(H_2O)_4$ + NO_2, respectively. *k*(WT3) is the rate constant for the process of $HO\cdots(H_2O)_3$ + HNO_2 → IM_WT3 → TS_WT3 → IMF_WT3 → $(H_2O)_4$ + NO_2, *k*(WT3a) is the rate constant for the process of HNO_2 + $HO\cdots(H_2O)_3$a → IM_WT3a → TS_WT3a → IMF_WT3a → $(H_2O)_4$ + NO_2, respectively. *k*'(WT2) is the effective rate constant for the process of HO + $HNO_2\cdots(H_2O)_3$ → IM_WT1 → TS_WT1 → IM_WT2 → TS_WT2 → IMF_WT2 → $(H_2O)_4$ + NO_2, *k*'(WT2a) is the effective rate constant for the process of HO + $HNO_2\cdots(H_2O)_3$a → IM_WT1a → TS_WT1a → IM_WT2a → TS_WT2a → IMF_WT2a → $(H_2O)_4$ + NO_2, respectively. *k*'(WT3) is the effective rate constant for the process of HNO_2 + $HO\cdots(H_2O)_3$ → IM_WT3 → TS_WT3 → IMF_WT3 → $(H_2O)_4$ + NO_2, *k*'(WT3a) is the effective rate constant for the process of HNO_2 + $HO\cdots(H_2O)_3$ → IM_WT3a → TS_WT3a → IMF_WT3a → $(H_2O)_4$ + NO_2, respectively. *k*(WT1), *k*(WT2) is the rate constant of water dimer-assisted Channels WT1, WT2, respectively. *k*'(WT1), *k*'(WT2) is the effective rate constant of water dimer-assisted Channels WT1, WT2, respectively. $k_{(WT1)} = k_{(WT1)} + k_{(WT1a)}$, $k'_{(WT1)} = k'_{(WT1)} + k'_{(WT1a)}$, $k_{(WT2)} = k_{(WT2)} + k_{(WT2a)}$, $k'_{(WT2)} = k'_{(WT2)} + k'_{(WT2a)}$, $1/k_{(WT1)} = 1/k_{(TS\_WT1)} + 1/k_{(TS\_WT2)}$, $1/k_{(WT1a)} = 1/_{(TS\_WT1a)} + 1/_{(TS\_WT2a)}$, $k'_{(WT1)} = K_{eq}(HNO_2\cdots(H_2O)_3)\bullet[(H_2O)_3]\bullet k_{(WT1)}$, $k'_{(WT1a)} = K_{eq}(HNO_2\cdots(H_2O)_3a)\bullet[(H_2O)_3]\bullet k_{(WT1a)}$, $k'_{(WT2)} = K_{eq}(HO\cdots(H_2O)_3)\bullet[(H_2O)_3]\bullet k_{(WT2)}$, $k'_{(WT2a)} = K_{eq}(HO\cdots(H_2O)_3a)\bullet[(H_2O)_3]\bullet k_{(WT3a)}$, respectively.