Supplementary data

Can nitrous acid contribute to atmospheric new particle formation from nitric acid and water?

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Table S1 shows MAE, MES and MaxE of the binding energies calculated through M06-2X method along with three different basis sets (6-311G(d,p), 6-311+G(2d,p) and 6-311++G(3df,3dp)) and the single point energy calculations are treated with MP2/cc-pVTZ level on the basis of the DFT results on five reactions:

$HNO_3 + HONO \Leftrightarrow (HNO_3)(HONO)$

$HONO + H_2O \Leftrightarrow (HONO)(H_2O)$

$HNO_3 + HONO + H_2O \Leftrightarrow (HNO_3)(HONO)(H_2O)$

$HNO_3 + HONO + 2H_2O \Leftrightarrow (HNO_3)(HONO)(H_2O)_2$

$HNO_3 + HONO + 3H_2O \Leftrightarrow (HNO_3)(HONO)(H_2O)_3$

MAE, MES and MaxE of M06-2X are almost smallest except a few values in comparison with the results of the other DFT methods, whereas the PW91PW91 is inapposite. It is easy to find the single point energy performed on MP2/cc-pVTZ is extremely close to ones of CCSD(T)/6-311++G(d,p) observed from Table S1, whose MAE maximum is 0.485 kcal/mol and MaxE maximum is 1.280 kcal/mol. The three error values are diminished obviously by replacing 6-311G (d,p) to 6-311+G(2d,p), nevertheless the reduction appears awfully confined by replacing 6-311+G(2d,p) to 6-

311++G(3df,3dp).

Table S1. MAE, MES and MaxE[a] of the binding energies calculated on three methods and three levels and the binding energies obtained from the single point energy calculations on the MP2/cc-pVTZ on the basis of the DFT results on the five reactions.

Method and basis set	MAE	MES	MaxE
M06-2X/6-311G(d,p)	7.524	-7.524	13.523
MP2/cc-pVTZ//M06-2X/6-311G(d,p)	0.362	-0.362	0.465
PW91PW91/6-311G (d,p)	9.672	-9.672	20.663
MP2/cc-pVTZ//PW91PW91/6-311G(d,p)	0.485	-0.485	0.890
ωB97X-D/6-311G(d,p)	8.642	6.924	10.120
MP2/cc-pVTZ/ωB97X-D/6-311G(d,p)	0.396	-0.396	0.575
M06-2X/6-311+G(2d,p)	0.535	-0.535	1.146
MP2/cc-pVTZ//M06-2X/6-311+G(2d,p)	0.246	-0.136	0.585
PW91PW91/6-311+G(2d,p)	0.902	-0.476	2.372
MP2/cc-pVTZ//PW91PW91/6-311+G(2d,p)	0.336	-0.336	1.280
ωB97X-D/6-311+G(2d,p)	0.851	0.694	1.691
MP2/cc-pVTZ/ωB97X-D/6-311+G(2d,p)	0.266	-0.266	0.643
M06-2X/6-311++G(3df,3dp)	0.462	0.282	1.639
MP2/cc-pVTZ//M06-2X/6-311++G(3df,3dp)	0.246	-0.172	0.581
PW91PW91/6-311++G(3df,3dp)	0.597	0.382	0.980
MP2/cc-pVTZ//PW91PW91/6-311++G(3df,3dp)	0.286	0.196	0.820
ωB97X-D/6-311++G(3df,3dp)	1.439	1.439	2.784
MP2/cc-pVTZ/ωB97X-D/6-311++G(3df,3dp)	0.266	-0.192	0.636

[a] MAE, MES and MaxE donate the mean absolute error, the mean effective error and the maximum error respectively, taking single point energy on CCSD(T)/6-311++G(d,p) as criterion.

Table S2. The binding energies (ΔE), enthalpy energies (ΔH) and Gibbs free energies (ΔG) at 298.15 K, for isomers of $(HNO_3)(HONO)(H_2O)_n$ (n=1,2,3) (in kcal/mol) at MP2/cc-pVTZ//M06-2X/6-311+G(2d,p) level.

Isomers	ΔE	ΔH	ΔG
I-1	-17.18	-17.27	0.19
I-2	-16.96	-17.21	0.76
II-1	-27.41	-28.61	1.25
II-2	-26.56	-27.58	0.97
II-3	-26.31	-27.51	3.02
II-4	-25.97	-26.88	1.49
II-5	-25.96	-26.88	1.54
II-6	-26.88	-28.09	3.49
II-7	-25.95	-25.83	3.26
II-8	-25.83	-25.80	2.86
III-1	-34.76	-36.44	2.46
III-2	-34.64	-36.06	2.15
III-3	-32.56	-34.26	3.06
III-4	-34.16	-35.82	2.76
III-5	-33.90	-33.72	3.15
III-6	-33.76	-35.62	4.82
III-7	-33.18	-34.36	2.72
III-8	-32.96	-34.43	3.96

Table S3. The binding energies (ΔE), enthalpy energies (ΔH) and Gibbs free energies (ΔG) at 298.15 K, for isomers of $(HNO_3)(HONO)(H_2O)_n$ (n=4) (in kcal/mol) at MP2/cc-pVTZ//M06-2X/6-311+G(2d,p) level.

Isomers	ΔE	ΔH	ΔG
IV-1	-45.33	-47.79	1.02
IV-2	-44.94	-41.07	1.52
IV-3	-43.95	-46.56	3.84
IV-4	-43.94	-46.55	3.88
IV-5	-44.45	-47.05	2.96
IV-6	-43.03	-45.27	2.36
IV-7	-43.07	-45.22	2.40
IV-8	-44.67	-47.52	3.15
IV-9	-43.10	-45.44	3.06
IV-10	-42.94	-44.95	0.23
IV-11	-43.11	-45.51	3.96
IV-12	-44.27	-46.53	3.33

Table S4. The binding energies (ΔE), enthalpy energies (ΔH) and Gibbs free energies (ΔG) at 298.15 K, for isomers of $(HNO_3)(HONO)(H_2O)_n$ (n=5) (in kcal/mol) at MP2/cc-pVTZ//M06-2X/6-311+G(2d,p) level.

Isomers	ΔE	ΔH	ΔG
V-1	-54.48	-58.16	4.12
V-2	-54.30	-57.81	4.31
V-3	-54.12	-57.53	3.79
V-4	-53.84	-57.26	4.12
V-5	-52.92	-56.37	4.65
V-6	-54.11	-57.67	4.29
V-7	-53.67	-57.17	4.02
V-8	-53.31	-56.67	4.75
V-9	-52.24	-55.37	2.82
V-10	-52.65	-55.80	3.95
V-11	-53.17	-56.77	5.61
V-12	-52.72	-56.12	4.92

Table S5. The binding energies (ΔE), enthalpy energies (ΔH) and Gibbs free energies (ΔG) at 298.15 K, for isomers of $(HNO_3)(HONO)(H_2O)_n$ (n=6) (in kcal/mol) at MP2/cc-pVTZ//M06-2X/6-311+G(2d,p) level.

Isomers	ΔE	ΔH	ΔG
VI-1	-66.74	-70.13	2.23
VI-2	-66.61	-65.09	4.12
VI-3	-64.41	-65.10	4.60
VI-4	-64.52	-69.06	3.96
VI-5	-65.56	-70.18	3.32
VI-6	-64.59	-69.61	3.41
VI-7	-64.42	-69.60	4.36
VI-8	-64.42	-69.67	3.22
VI-9	-65.06	-69.86	4.93
VI-10	-65.03	-69.93	4.78
VI-11	-65.07	-69.98	4.83
VI-12	-65.07	-69.98	4.80

Table S6. The Gibbs free energies 298.15 K, for isomers of $(HNO_3)(H_2O)_n$ (n=1—6) (in kcal/mol) at MP2/cc-pVTZ//M06-2X/6-311+G(2d,p) level.

cluster	ΔG
HNO_3-W	-0.43
HNO_3-2W	-1.05
HNO_3-3W	-1.23
HNO_3-4W	0.70
HNO_3-5W	1.13
HNO_3-6W	0.71

Table S7. The binding energies (ΔE), enthalpy energies (ΔH) and Gibbs free energies (ΔG) at 298.15 K, for isomers of $(HNO_3)(HONO)(H_2O)_n$ (n=7－10, 15, 20) (in kcal/mol) at M06-2X/6-311+G(2d,p) level.

	Clusters	ΔE	ΔH	ΔG
7	$(HNO_3)(HONO)(H_2O)$	-71.94	-77.23	1.53
8	$(HNO_3)(HONO)(H_2O)$	-80.61	-87.03	2.66
9	$(HNO_3)(HONO)(H_2O)$	-87.36	-93.73	4.16
10	$(HNO_3)(HONO)(H_2O)$	-94.06	-101.36	5.64
$)_{15}$	(HNO3)(HONO)(H2O	-151.95	-164.42	2.38
20	$(HNO_3)(HONO)(H_2O)$	-192.94	-209.15	1.35

Table S8. The AIM parameters including Density of all electrons $\rho(r)$, Laplacian density $\nabla^2\rho(r)$, Lagrangian kinetic energy $G(r)$, Potential energy density $V(r)$ and Energy density $H(r)$ for the clusters at M06-2X/6-311+G(2d,p) level (in a.u.).

Conformer	BCP Number	I-1	II-1	III-1	IV-1	V-1	VI-1
ρ(r)	1	0.013	0.020	**0.037**	*0.067*	*0.040*	*0.038*
	2	*0.045*	*0.048*	*0.070*	0.020	*0.058*	0.025
	3	0.035	0.024	*0.044*	0.032	0.033	0.025
	4		*0.069*	0.033	*0.044*	*0.050*	*0.072*
	5			0.020	*0.054*	0.011	0.036
	6				0.028	0.029	0.031
	7				0.016	0.030	*0.050*
	8				0.012*	0.034	0.029
	9						0.013*
	10						0.029
	11						0.022
∇²ρ(r)	1	0.060	0.091	0.130	0.144	0.130	0.130
	2	0.143	0.146	0.148	0.081	0.146	0.108
	3	0.125	0.097	0.143	0.124	0.126	0.100
	4		0.146	0.131	0.142	0.143	0.145
	5			0.091	0.148	0.039	0.129
	6				0.113	0.115	0.120
	7				0.073	0.116	0.144
	8				0.039*	0.122	0.115
	9						0.048*
	10						0.114
	11						0.092
$G(r)$	1	0.013	0.019	0.033	0.054	0.035	0.033

	2	0.040	0.042	0.057	0.017	0.049	0.024
	3	0.031	0.022	0.039	0.029	0.030	0.022
	4		0.056	0.031	0.039	0.043	0.058
	5			0.019	0.046	0.009	0.032
	6				0.026	0.027	0.028
	7				0.015	0.027	0.043
	8				0.008*	0.030	0.026
	9						0.010*
	10						0.026
	11						0.020
$V(r)$	1	-0.010	-0.016	-0.033	-0.073	-0.037	-0.034
	2	-0.044	-0.047	-0.076	-0.014	-0.061	-0.020
	3	-0.030	-0.019	-0.043	-0.028	-0.029	-0.020
	4		-0.076	-0.030	-0.042	-0.050	-0.080
	5			-0.015	-0.056	-0.008	-0.032
	6				-0.024	-0.025	-0.027
	7				-0.012	-0.025	-0.050
	8				-0.007*	-0.029	-0.024
	9						-0.008*
	10						-0.024
	11						-0.017
$H(r)$	1	0.003	0.003	**0.000**	*-0.018*	*-0.002*	*-0.001*
	2	*-0.004*	*-0.005*	*-0.020*	0.003	*-0.012*	0.003
	3	0.000	0.003	*-0.003*	0.001	0.001	0.003
	4		*-0.020*	0.001	*-0.003*	*-0.007*	*-0.022*
	5			0.004	*-0.009*	0.001	0.000
	6				0.002	0.002	0.001
	7				0.003	0.002	*-0.007*
	8				0.002*	0.001	0.002
	9						0.002*
	10						0.002

	11	0.003

* N-H···O is expressed by "*", and the others are O-H···O.

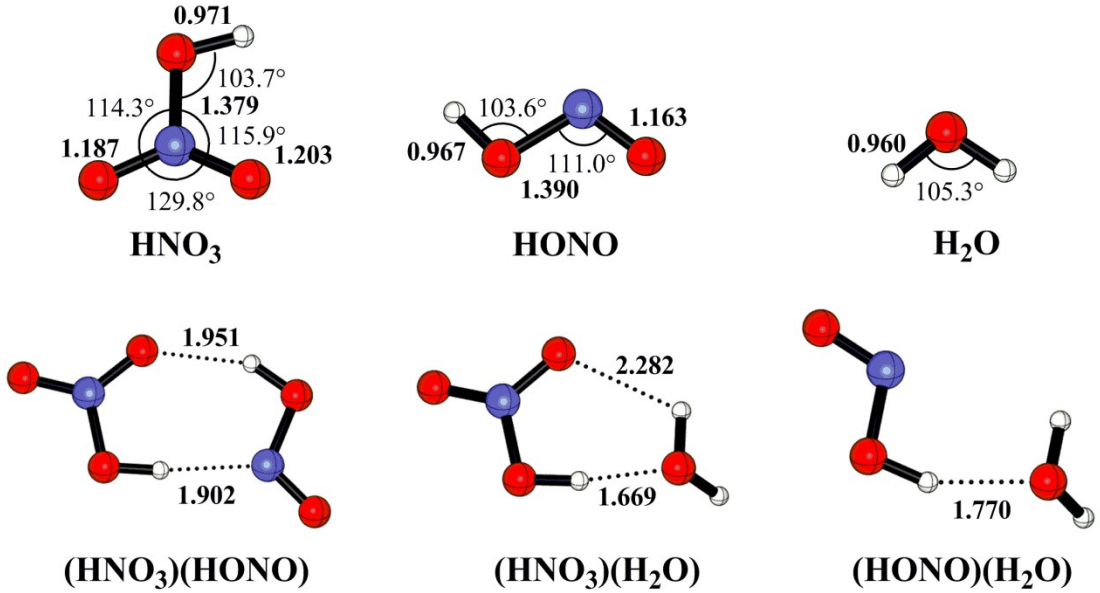
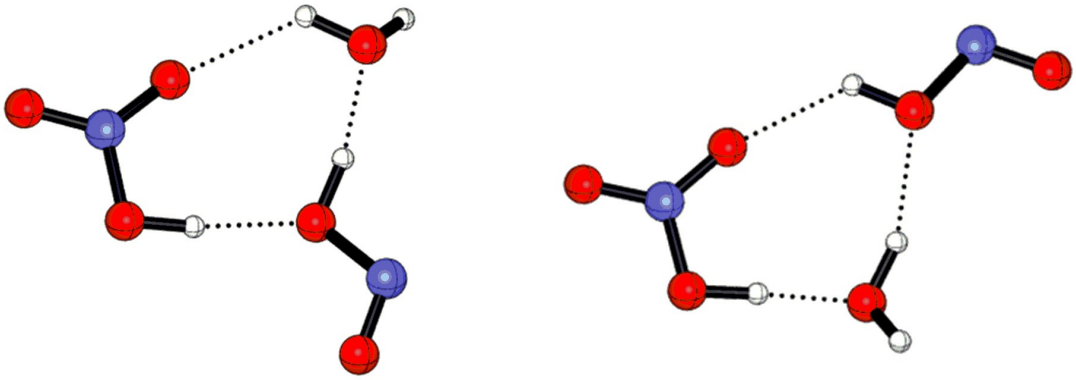


Figure S1. The geometrical configurations of monomers HNO_3, HONO and H_2O and dimers optimized at M06-2X/6-311+G(2d,p) level.



I-1
0.00

I-2
0.22

Figure S2. The geometrical configurations of $(HNO_3)(HONO)(H_2O)$ optimized at the M06-2X/6-311+G(2d,p) level. The underlying figures are relative binding energies compared with the I-1 (in kcal/mol).

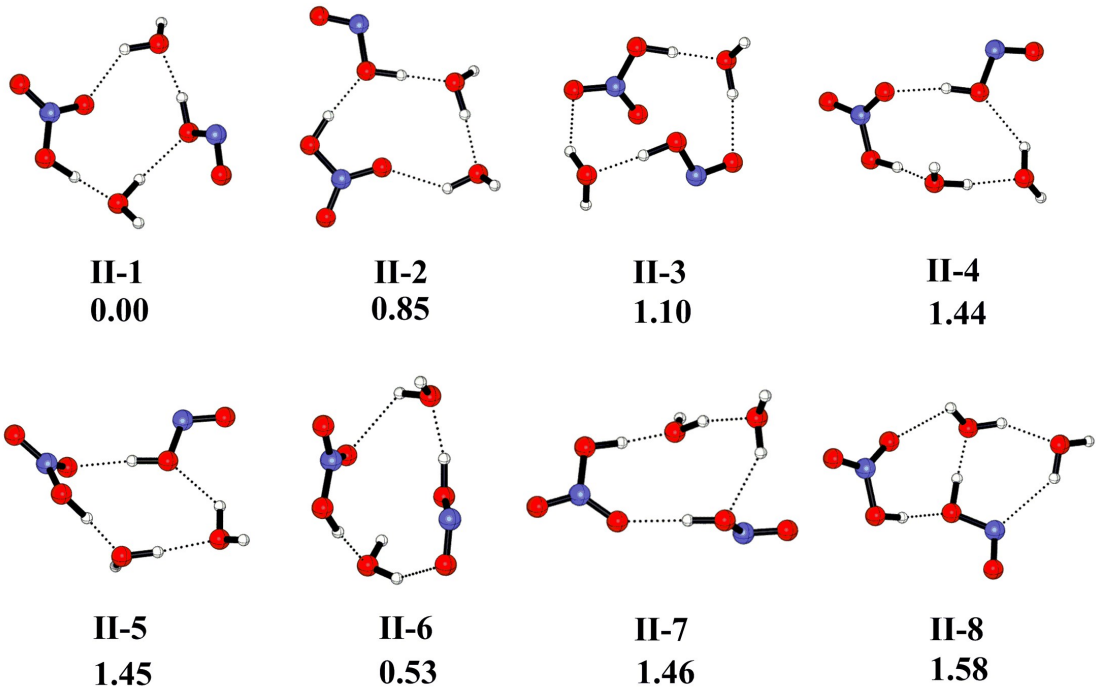


Figure S3. The geometrical configurations of $(HNO_3)(HONO)(H_2O)_2$ optimized at the M06-2X/6-311+G(2d,p) level. The underlying figures are relative binding energies compared with the II-1 (in kcal/mol).

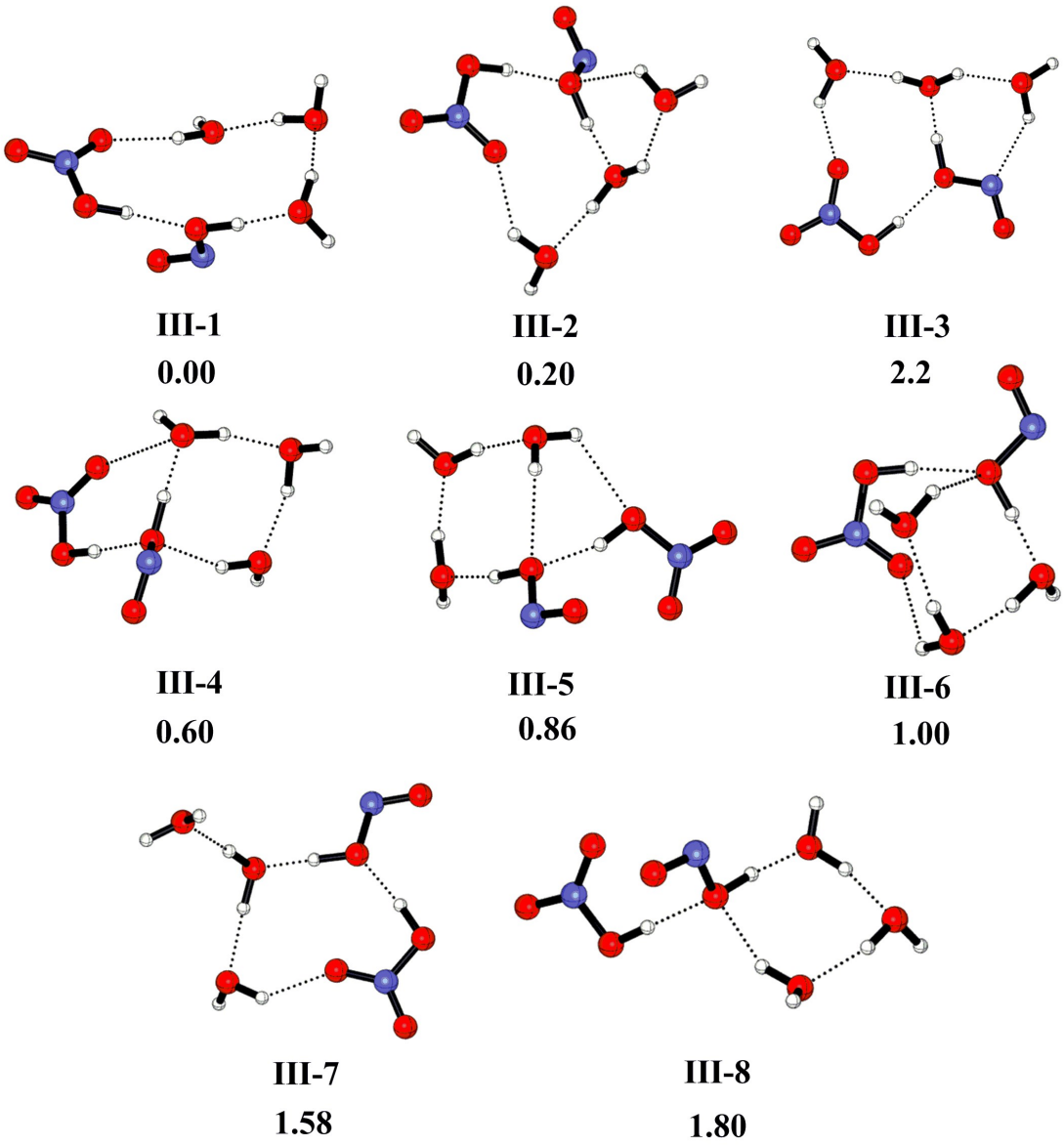


Figure S4. The geometrical configurations of $(HNO_3)(HONO)(H_2O)_3$ optimized at the M06-2X/6-311+G(2d,p) level. The underlying figures are relative binding energies compared with the III-1 (in kcal/mol).

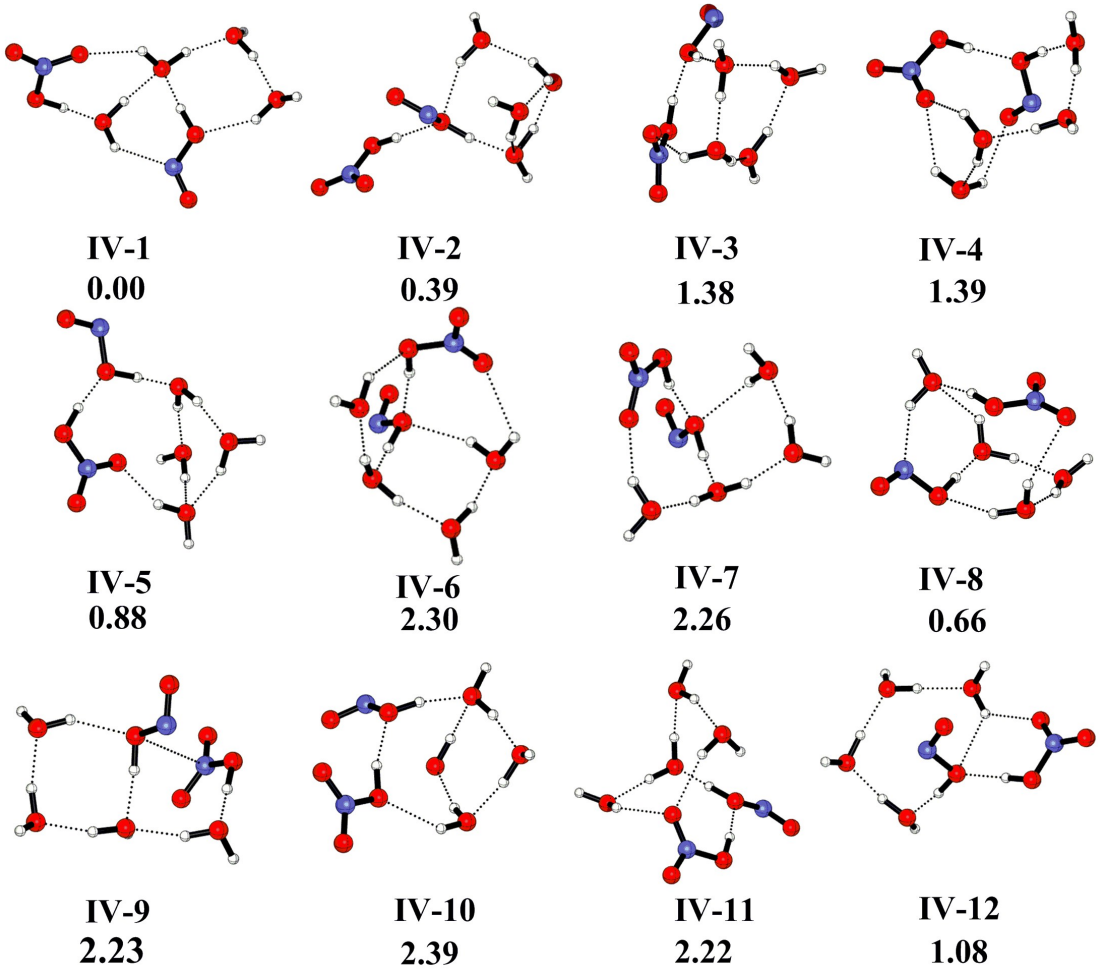


Figure S5. The geometrical configurations of $(HNO_3)(HONO)(H_2O)_4$ optimized at the M06-2X/6-311+G(2d,p) level. The underlying figures are relative binding energies compared with the IV-1 (in kcal/mol).

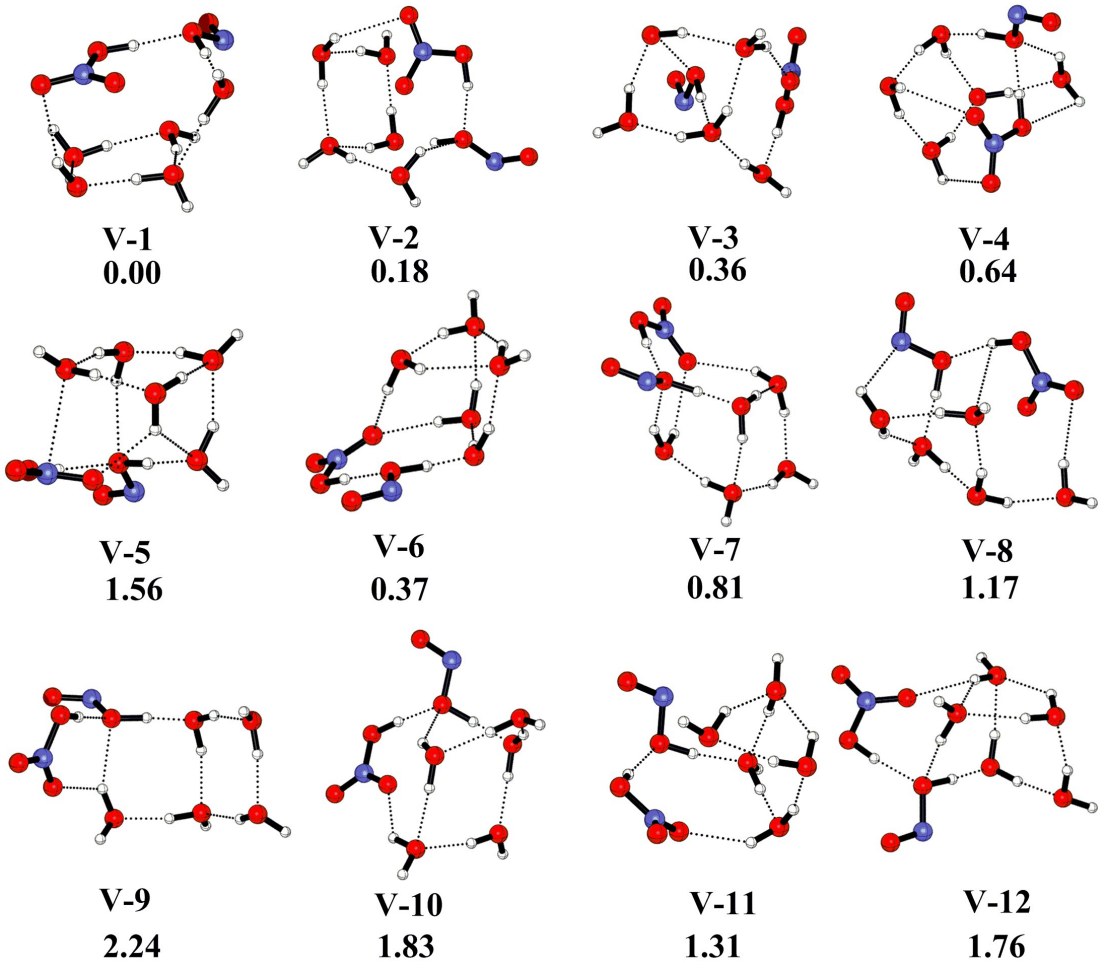


Figure S6. The geometrical configurations of $(HNO_3)(HONO)(H_2O)_5$ optimized at the M06-2X/6-311+G(2d,p) level. The underlying figures are relative binding energies compared with the V-1 (in kcal/mol).

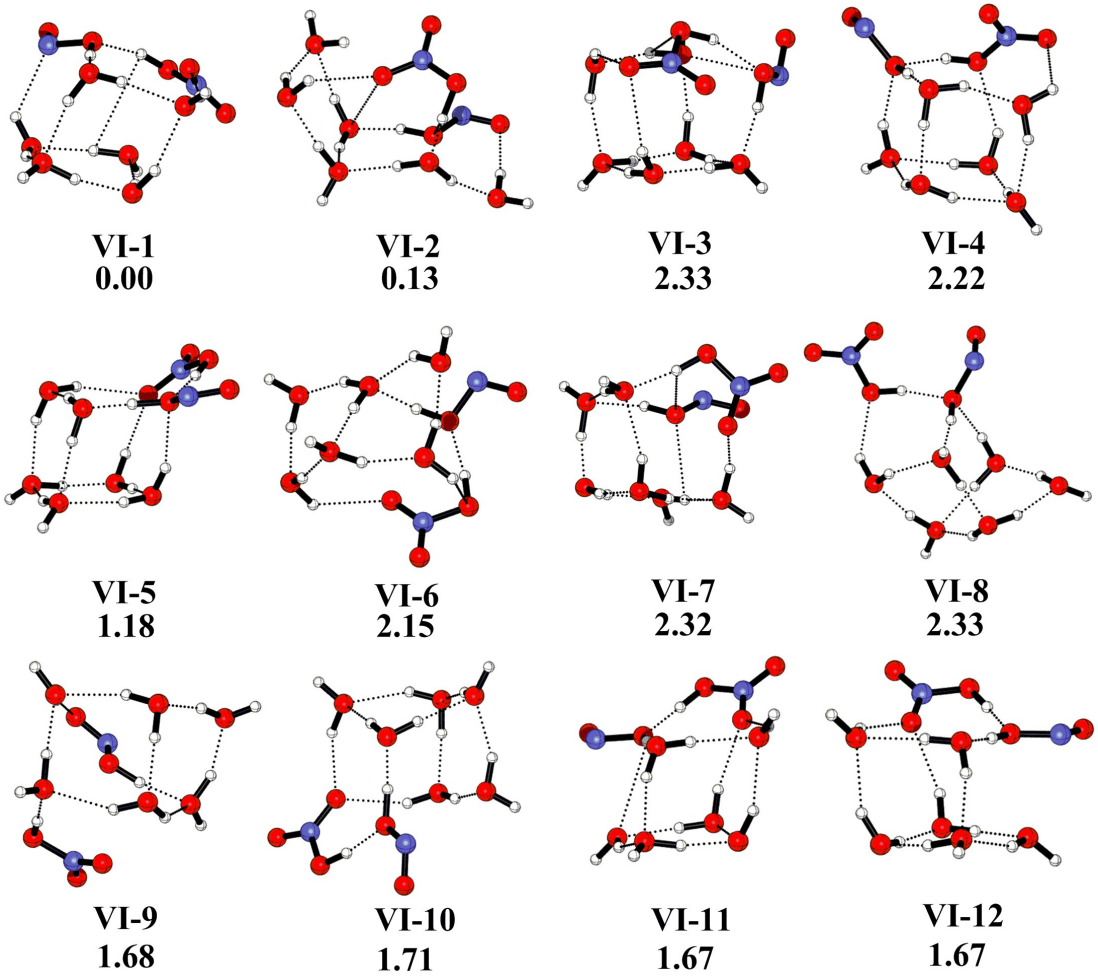
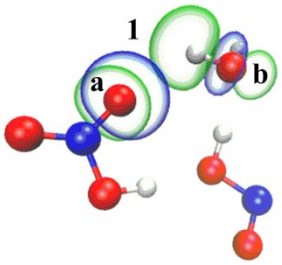
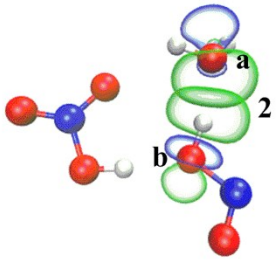


Figure S7. The geometrical configurations of $(HNO_3)(HONO)(H_2O)_6$ optimized at the M06-2X/6-311+G(2d,p) level. The underlying figures are relative binding energies compared with the VI-1 (in kcal/mol).



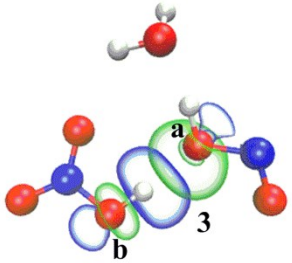
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

I-1 (0.84 kcal/mol)



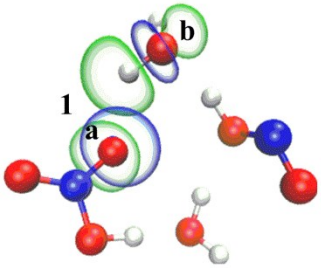
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

I-1 (27.26 kcal/mol)



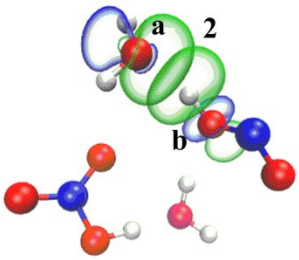
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

I-1 (15.10 kcal/mol)



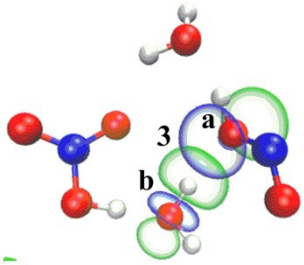
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

II-1 (4.84 kcal/mol)



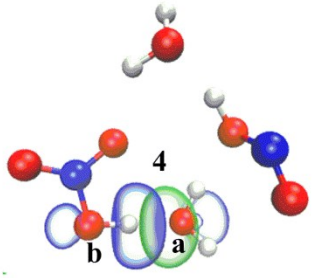
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

II-1 (29.34 kcal/mol)



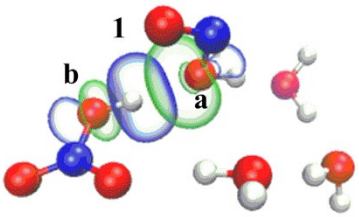
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

II-1 (7.97 kcal/mol)



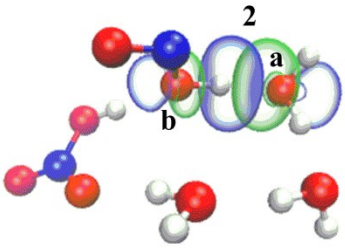
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

II-1 (53.02 kcal/mol)



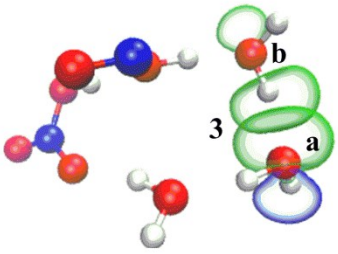
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

III-1 (19.66 kcal/mol)



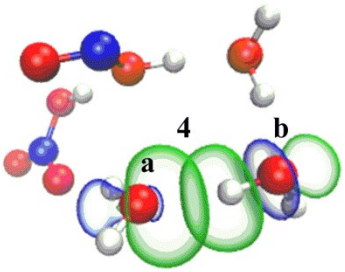
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

III-1 (52.50 kcal/mol)



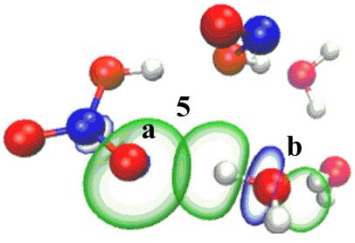
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

III-1 (23.53 kcal/mol)



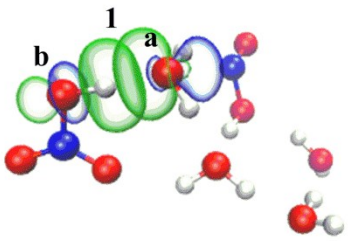
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

III-1 (13.90 kcal/mol)



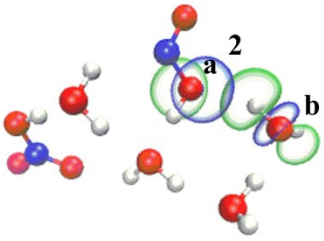
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

III-1 (5.52 kcal/mol)



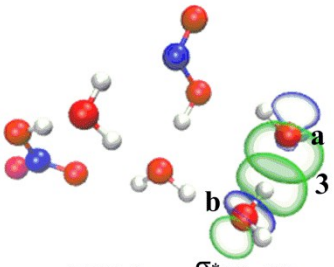
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (51.00 kcal/mol)



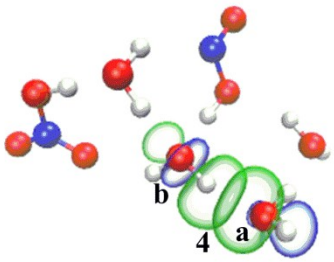
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (4.46 kcal/mol)



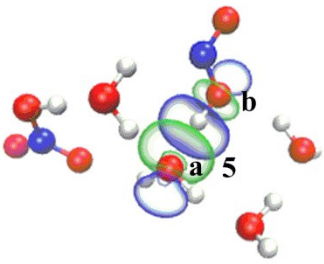
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (13.84 kcal/mol)



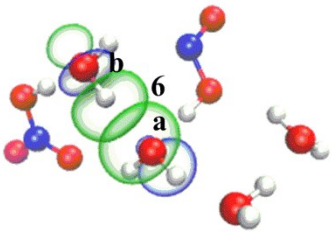
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (23.10 kcal/mol)



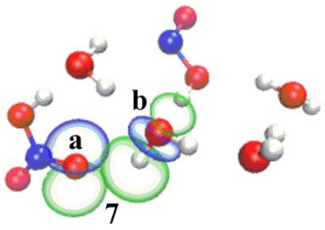
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (35.48 kcal/mol)



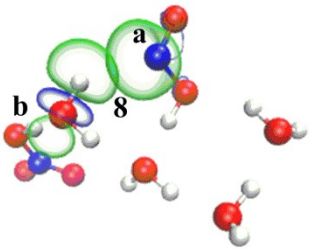
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (11.31 kcal/mol)



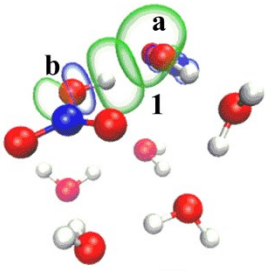
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (1.72 kcal/mol)



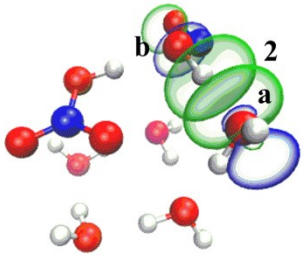
$LP(N_a) \rightarrow \sigma^*(O_b\text{-}H)$

IV-1 (1.19 kcal/mol)



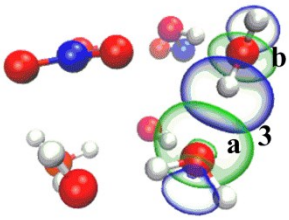
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

V-1 (24.39 kcal/mol)



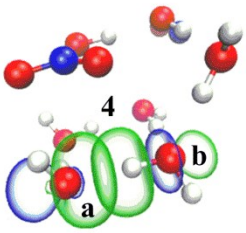
$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

V-1 (41.44 kcal/mol)



$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

V-1 (14.71 kcal/mol)



$LP(O_a) \rightarrow \sigma^*(O_b\text{-}H)$

V-1 (30.13 kcal/mol)

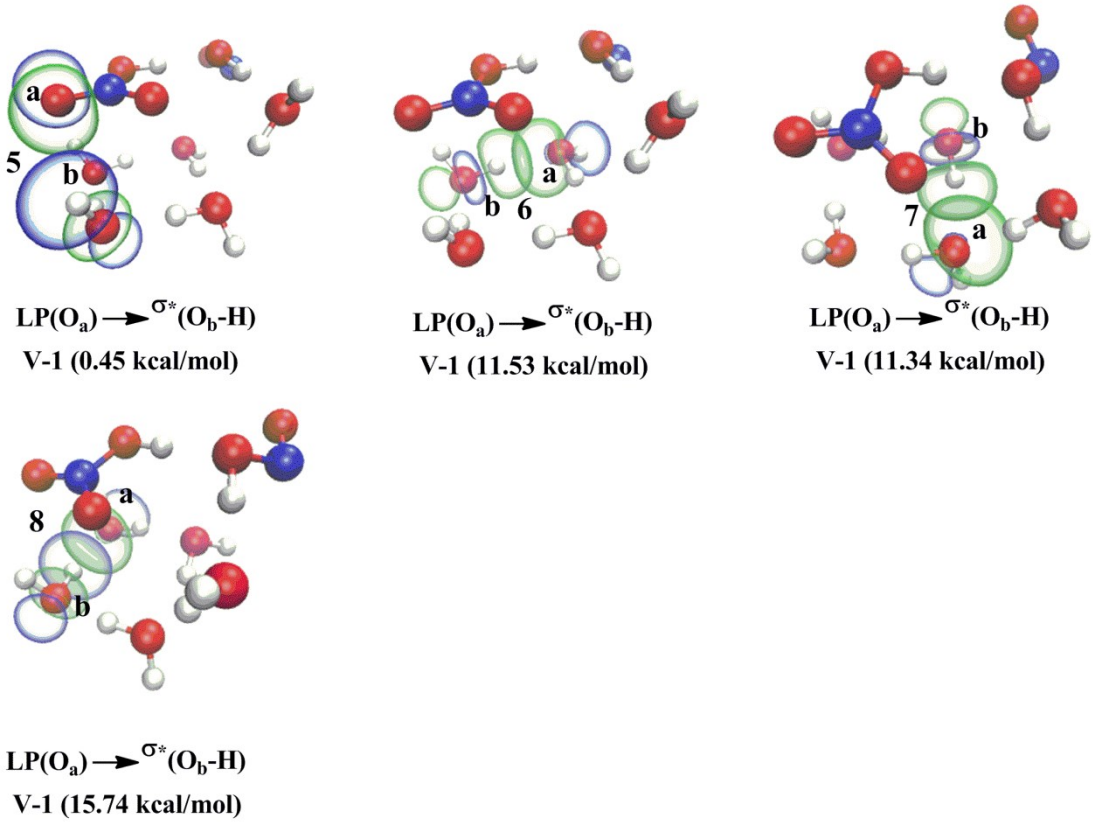


Figure S8. Natural bond orbital (NBO) analysis of donor–acceptor orbital interactions in I-1, II-1, III-1, IV-1 and V-1 (0.05 e $Å^{-3}$ isosurface from M06-2X/6-311+G(2d,p) model chemistry). The second-order stabilisation energies are given in parentheses.

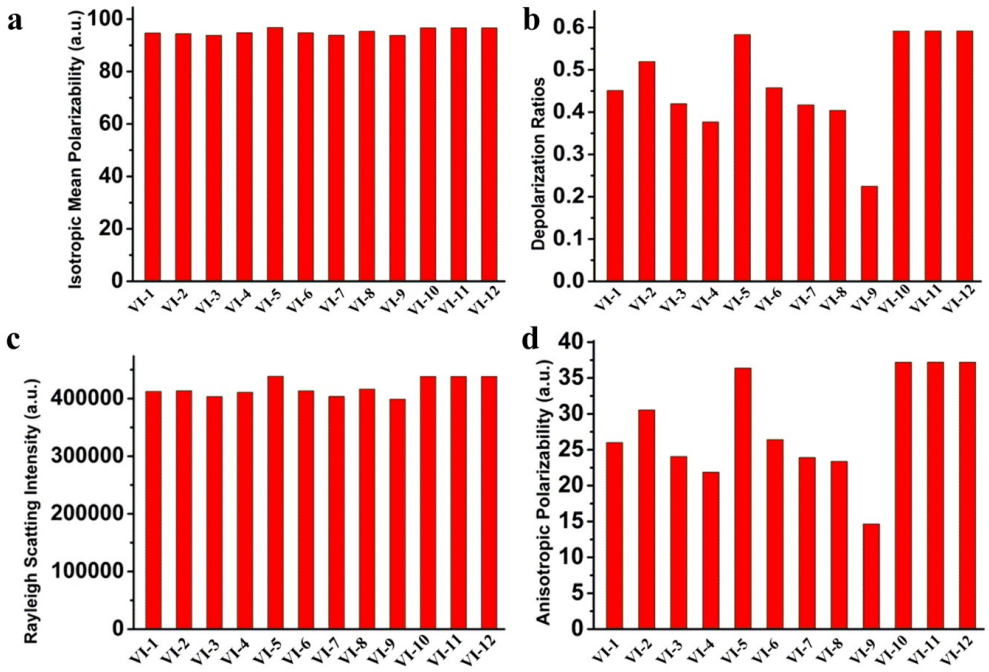


Figure S9. The Rayleigh light scattering and cluster polarizability properties of different isomers of $(HNO_3)(HONO)(H_2O)_6$: (a) isotropic mean polarizabilities; (b) depolarization ratios; (c) Rayleigh light scattering intensities; (d) anisotropic polarizabilities.