

Supporting Information

Size-dependent Acidity of Aqueous Nano-aerosols

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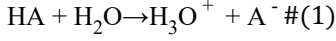
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Table of Contents

Section I: Simulation Methods	2
Section II: Supporting Figures	6
Section III: Supporting Tables	15
Section IV: References	23

Section I: Simulation Methods

Calculation of pK_a. The dissociation of an acid HA in aqueous solution is expressed as follows,



For the dissociation equilibrium of HA, the relationship is as follows,

$$\mu_{\text{aq}}(\text{A}^-) + \mu_{\text{aq}}(\text{H}_3\text{O}^+) - \mu_{\text{aq}}(\text{HA}) - \mu_{\text{aq}}(\text{H}_2\text{O}) = 0 \#(2)$$

where $\mu_{\text{aq}}(\text{X})$ represents the chemical potential of X in the aqueous phase, which can be calculated as follows by Pliego¹,

$$\mu_{\text{aq}}^{\text{M}}(\text{X}) = \mu_{\text{gas}}^{\text{M}}(\text{X}) + \Delta G_{\text{s}}(\text{X}) + RT \ln[\text{X}] \#(3)$$

where “M” represents the standard state of 1 M, and $\mu_{\text{gas}}^{\text{M}}(\text{X})$ represents the chemical potential of X in the gas phase, considered to be the ideal gas at 1 M. The second term $\Delta G_{\text{s}}(\text{X})$ is the solvation free energy leading the solute from a fixed position in gas phase to the fixed position in the solution defined by Ben-Naim². And the last term is in connection with the concentration of X in solution.

The deprotonation free energy of the HA molecule in the aqueous phase could be obtained through Eq. (2-3),

$$\Delta G_{\text{aq}} = -RT \ln \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \#(4)$$

$$\Delta G_{\text{aq}} = \Delta G_{\text{gas}}^{\text{M}} + \Delta \Delta G_{\text{s}} \#(5)$$

$$\Delta \Delta G_{\text{s}} = \Delta G_{\text{s}}(\text{H}_3\text{O}^+) + \Delta G_{\text{s}}(\text{A}^-) - \Delta G_{\text{s}}(\text{HA}) - \Delta G_{\text{s}}(\text{H}_2\text{O}) \#(6)$$

$$\Delta G_{\text{gas}} = \mu_{\text{gas}}^{\text{M}}(\text{H}_3\text{O}^+) + \mu_{\text{gas}}^{\text{M}}(\text{A}^-) - \mu_{\text{gas}}^{\text{M}}(\text{HA}) - \mu_{\text{gas}}^{\text{M}}(\text{H}_2\text{O}) \#(7)$$

where $\Delta \Delta G_{\text{s}}$ is the difference of the solvation free energy between the dissociated state

and the undissociated state, ΔG_s is the solvation free energy of aerosol particle, ΔG_{gas} is the deprotonation free energy of HA in the gas phase, respectively.

For the dissociation of HA, the equilibrium constant K_{eq} is related to the dissociation constant K_a according to following equation,

$$K_{\text{eq,HA}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} = \frac{K_{\text{a,HA}}}{[\text{H}_2\text{O}]} \#(8)$$

Thus, the dissociation constant $\text{p}K_a$ can be calculated by

$$\text{p}K_{\text{a,HA}} = \frac{\Delta G_{\text{aq}}}{2.303RT} - \lg[\text{H}_2\text{O}] \#(9)$$

Aerosol acidity calculation. Without consideration of multiphase distribution, the concentration of hydronium ions in the solution can be calculated by

$$[\text{H}_3\text{O}^+]_{\text{total}} = [\text{H}_3\text{O}^+]_{\text{HA}} + [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} = \frac{[\text{HA}]K_{\text{a,HA}}}{[\text{A}^-]} + \frac{[\text{H}_2\text{O}]K_{\text{a,H}_2\text{O}}}{[\text{OH}^-]} \#(10)$$

When the acidity is derived from the simulated system, the concentration is variable, and the aerosol acidity is the result of the combination of concentration and solvent size.

The solute concentration is calculated by

$$c_{\text{HA}} = 55.5/N \#(11)$$

where N denotes the molecular number of nanodroplet. The corresponding pH value of the system is

$$\text{pH} = -\lg(\sqrt{55.5 \cdot K_{\text{a,HA}}/N} + \sqrt{55.5 \cdot K_{\text{a,H}_2\text{O}}}) \#(12)$$

In the second situation, we considered a statistic system with varying aerosol size and fixed solute concentration (e.g., 0.001M). The pH value is calculated by

$$\text{pH} = -\lg(\sqrt{0.001 \cdot K_{\text{a,HA}}} + \sqrt{55.5 \cdot K_{\text{a,H}_2\text{O}}}) \#(13)$$

In order to understand the size-dependent acidity of nucleation mode aerosols containing buffer pairs, the buffer pairs in nanodroplets under the constant concentration of 0.001 M were also discussed. The corresponding pH value is

$$\text{pH} = -\lg(\sqrt{K_{a,\text{HA}}} + \sqrt{55.5 \cdot K_{a,\text{H}_2\text{O}}}) \quad (14)$$

Considering the distribution of acids between the gas and liquid phases, the pH^* value in above situation is calculated by

$$\text{pH}^* = -\lg(\sqrt{55.5 \cdot K_{a,\text{HA}}^* / N} + \sqrt{55.5 \cdot K_{a,\text{H}_2\text{O}}^*}) \quad (15)$$

$$\text{pH}^* = -\lg(\sqrt{0.001 \cdot K_{a,\text{HA}}^*} + \sqrt{55.5 \cdot K_{a,\text{H}_2\text{O}}^*}) \quad (16)$$

$$\text{pH}^* = -\lg(\sqrt{K_{a,\text{HA}}^*} + \sqrt{55.5 \cdot K_{a,\text{H}_2\text{O}}^*}) \quad (17)$$

Relationship between the number of water molecules ($N^{-\frac{1}{3}}$) and the size of nano-particles. In our studies, $N^{-\frac{1}{3}}$ is corresponding to the particle size of nanoparticle in the simulation. All the simulated geometric structures and its size are shown in Section II (Supporting Figures). Based on our modelling methods, the relationship between $N^{-\frac{1}{3}}$ and the radius of nano-particle (R) is as follows:

$$N^{-\frac{1}{3}} = \left(\frac{N_A \rho \left(\frac{4}{3} \pi R^3 \right)}{M_{\text{water}}} \right)^{-\frac{1}{3}} = \left(\frac{4 \pi N_A \rho}{3 M_{\text{water}}} \right)^{-\frac{1}{3}} \frac{1}{R} \quad (18)$$

where N_A is the Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), ρ is the density of water, R is the radius of nano-particle ($R = 1, 1.5, 2, 2.5, 3, 3.5, 4 \text{ nm}$), and M_{water} is the mole-mass of water.

Details of MD Simulations. The bulk phase system was simulated in a cubic box of $3.0 \times 3.0 \times 3.0 \text{ nm}^3$, including one solute and 900 SWM4-NDP³ water molecules. The MD simulations were performed in the constant pressure and constant temperature (NPT) ensemble using the periodic boundary conditions,⁴ using the Langevin dynamics to control fluctuations in the barostat. For the droplet system, the nanoaerosol was simulated in a large cubic box, in which the self-interaction between the solute and its replica could

be neglected.⁵ The nanoaerosol systems (containing one solute and 60, 140, 270, 470, 750, and 1120 SWM4-NDP water molecules, respectively) were simulated in the constant volume and constant temperature (NVT) ensemble. In all the MD simulation, the Langevin dynamics with a dual Langevin thermostat was used to keep the temperature of systems at 298.15 K and the Drude oscillators at 1.0 K, with a timestep of 0.5 fs. The coupling parameter for simulation of ions varied linearly from 0 to 1 in increments of 0.1, while the increment was set as 0.05 for the neutral molecules to obtain accurate values. For each window, the forward and backward productions were carried out and the Bennett's acceptance ratio⁶ method was used to calculate the solvation free energy. During the production stage, each window was equilibrated for 50.0 ps, and then the production trajectory was collected for the next 250.0 ps.⁷ Figure S1-S9 list the initial structures of HNO₃, NO₃⁻, NH₄⁺, NH₃, H₃O⁺, OH⁻, H₂O, HSO₄⁻ and SO₄²⁻ in bulk solution and nanodroplets with different diameters, which were constructed using the Packmol package, respectively.⁸

Solvation Free Energy. The solvation free energy was calculated using the FEP method.⁹ The Gibbs free energy change from state A to state B was obtained by

$$\Delta G(A \rightarrow B) = G_B - G_A = -k_B T \ln \left\langle \exp \left[\frac{-(U_B - U_A)}{k_B T} \right] \right\rangle_A \quad (19)$$

where U_A and U_B were the potential energies of states A and B, respectively. The transition between the initial state and the final state was implemented by introducing coupling parameters.¹⁰

Deprotonation Free Energy in Gas Phase. The deprotonation energies of HA in the gas phase were calculated using the density functional theory (DFT) method implemented in Gaussian 09 package.¹¹ All the geometries were optimized at the

B3LYP/6-311++G** level.¹² The single point energy was computed at the CCSD(T)/aug-cc-pVTZ¹³ level, while except the M05-2X/6-31G* level for HSO₄⁻ and SO₄²⁻, since the energy value at M05-2X/6-31G* level for HSO₄⁻ and SO₄²⁻ is the closest to the experimental values.¹⁴ Table S1 compares the single point energy of HSO₄⁻ and SO₄²⁻ and dissociation constants of HSO₄⁻ calculated at different levels.

Section II: Supporting Figures

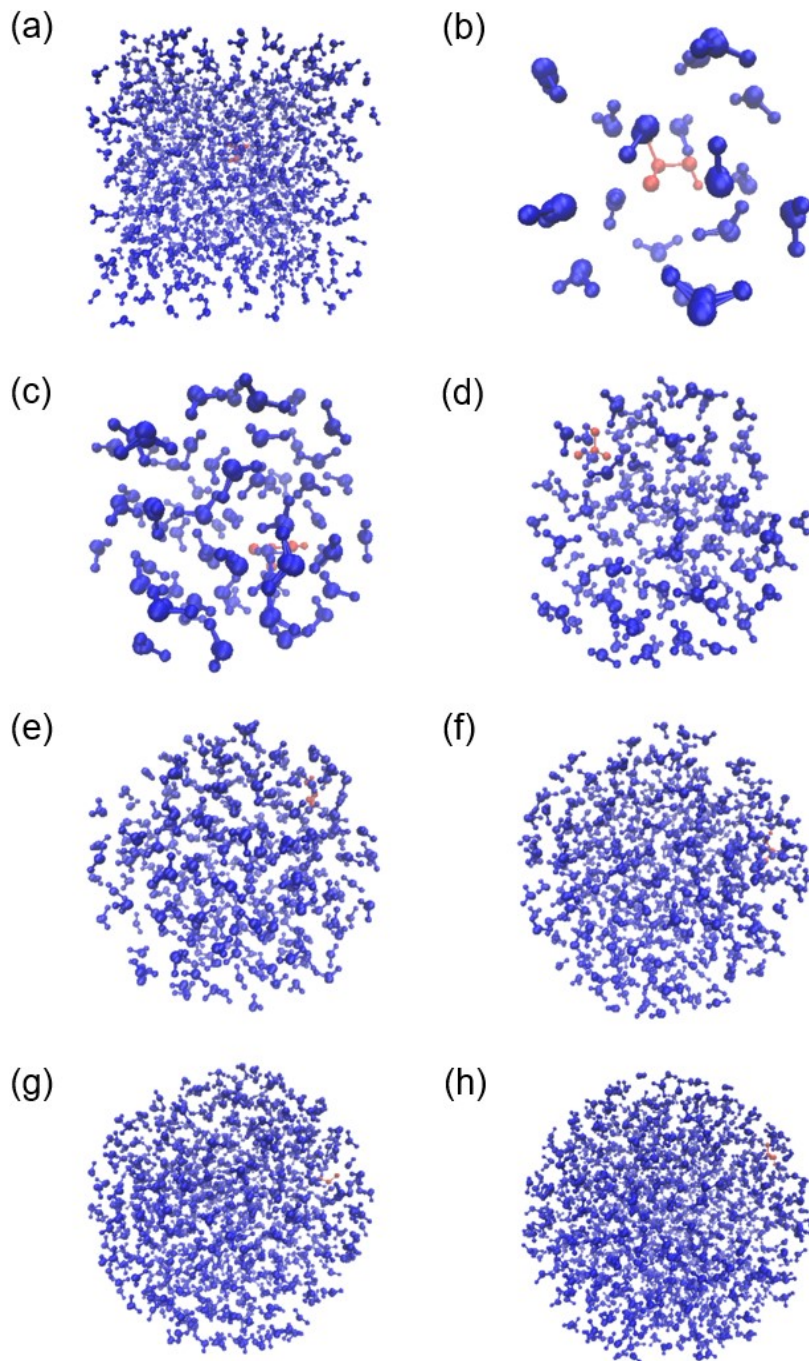


Figure S1. The initial structures constructed by Packmol⁸ package: (a) HNO₃ in the bulk water, HNO₃ in nanodroplets of (b) 1nm, (c) 1.5nm, (d) 2nm, (e) 2.5nm, (f) 3nm, (g) 3.5nm, (h) 4nm. The blue molecules represent SWM4-NDP water molecules and the red ions represent HNO₃.

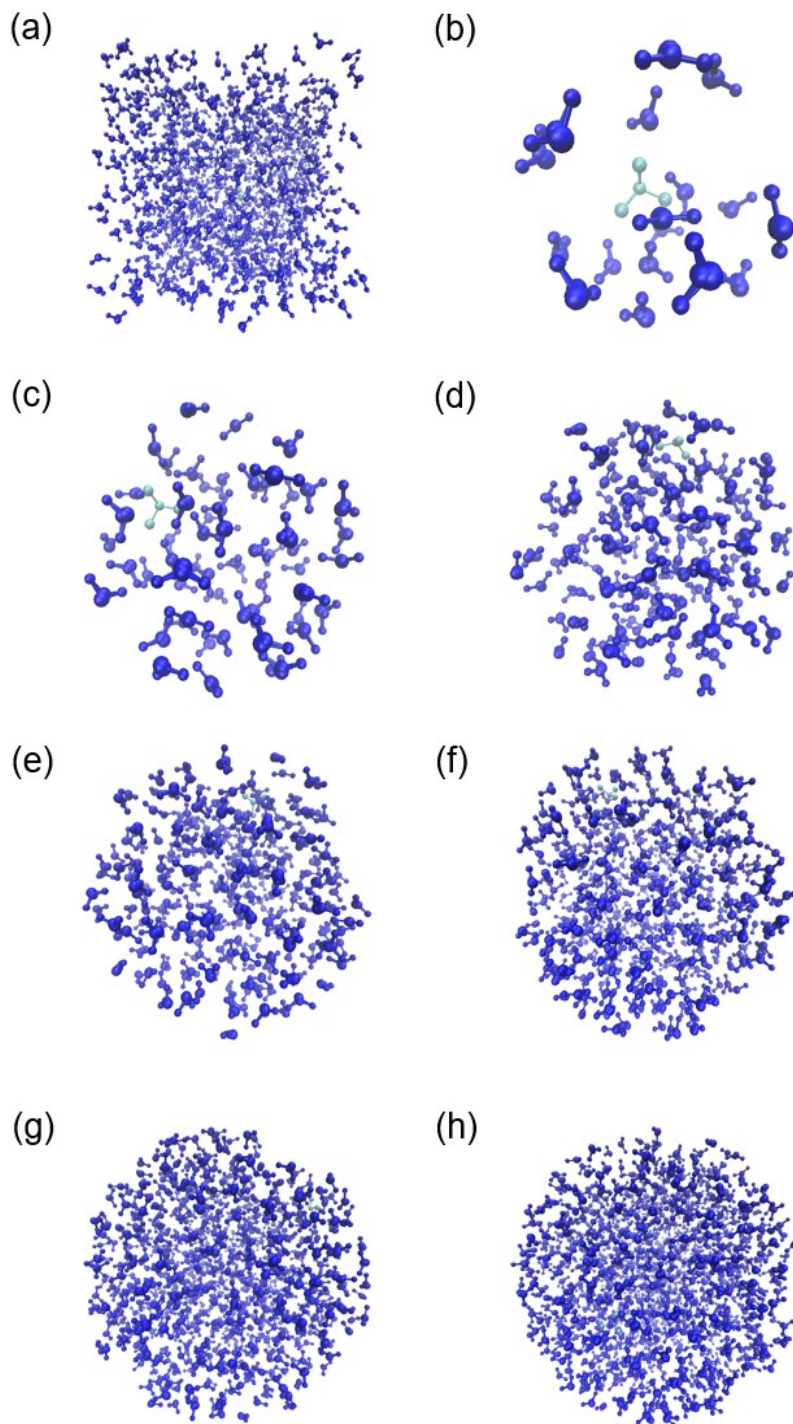


Figure S2. The initial structures constructed by Packmol package: (a) NO_3^- in the bulk water, NO_3^- in nanodroplets of (b) 1 nm, (c) 1.5nm, (d) 2nm, (e) 2.5nm, (f) 3nm, (g) 3.5nm, (h) 4nm. Blue molecules represent SWM4-NDP water molecules and cyan ions represent NO_3^- .

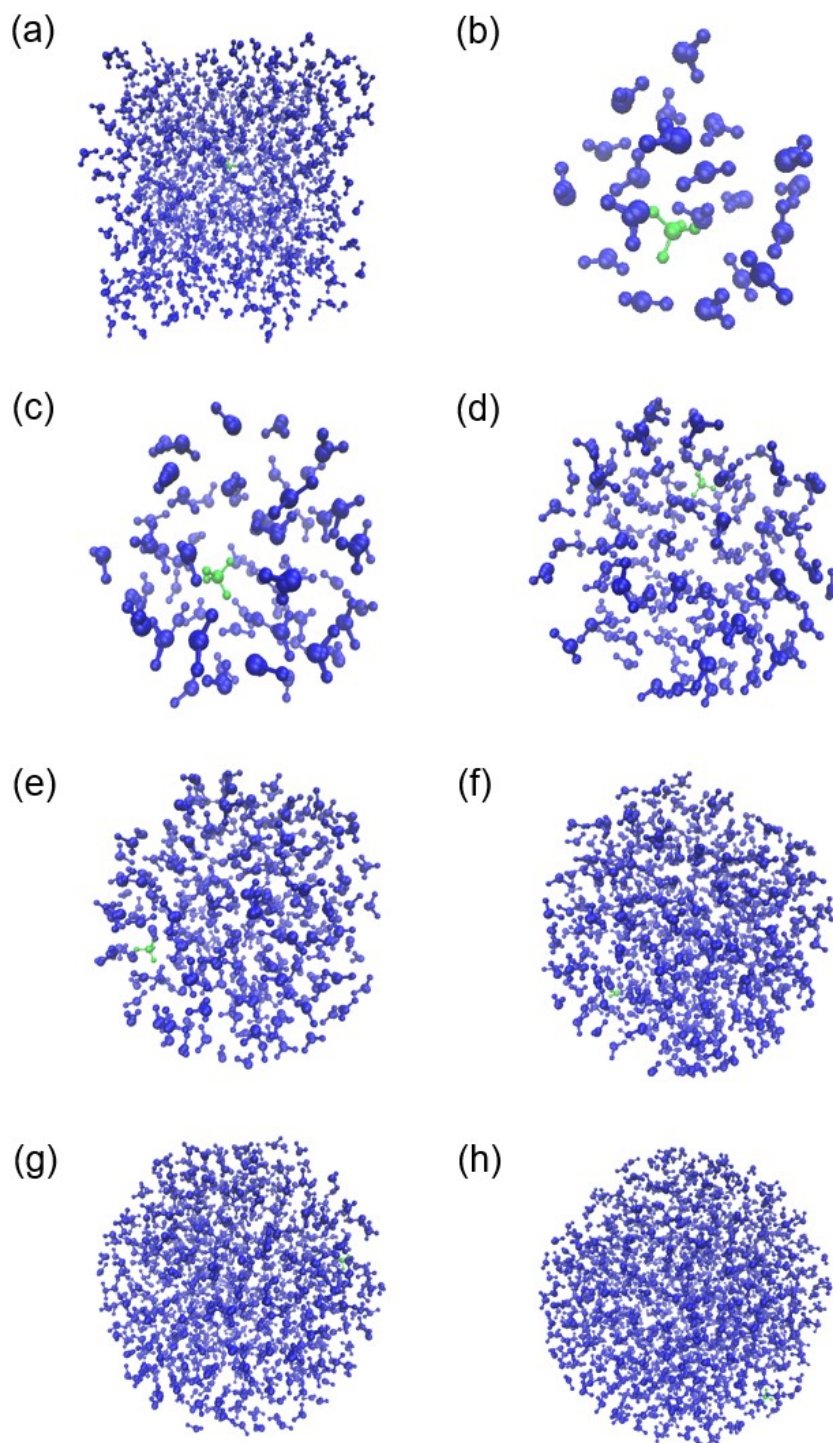


Figure S3. The initial structures constructed by Packmol package: (a) NH_4^+ in the bulk water, NH_4^+ in nanodroplets of (b) 1 nm, (c) 1.5nm, (d) 2nm, (e) 2.5nm, (f) 3nm, (g) 3.5nm, (h) 4nm. Blue molecules represent SWM4-NDP water molecules and green ions represent NH_4^+ .

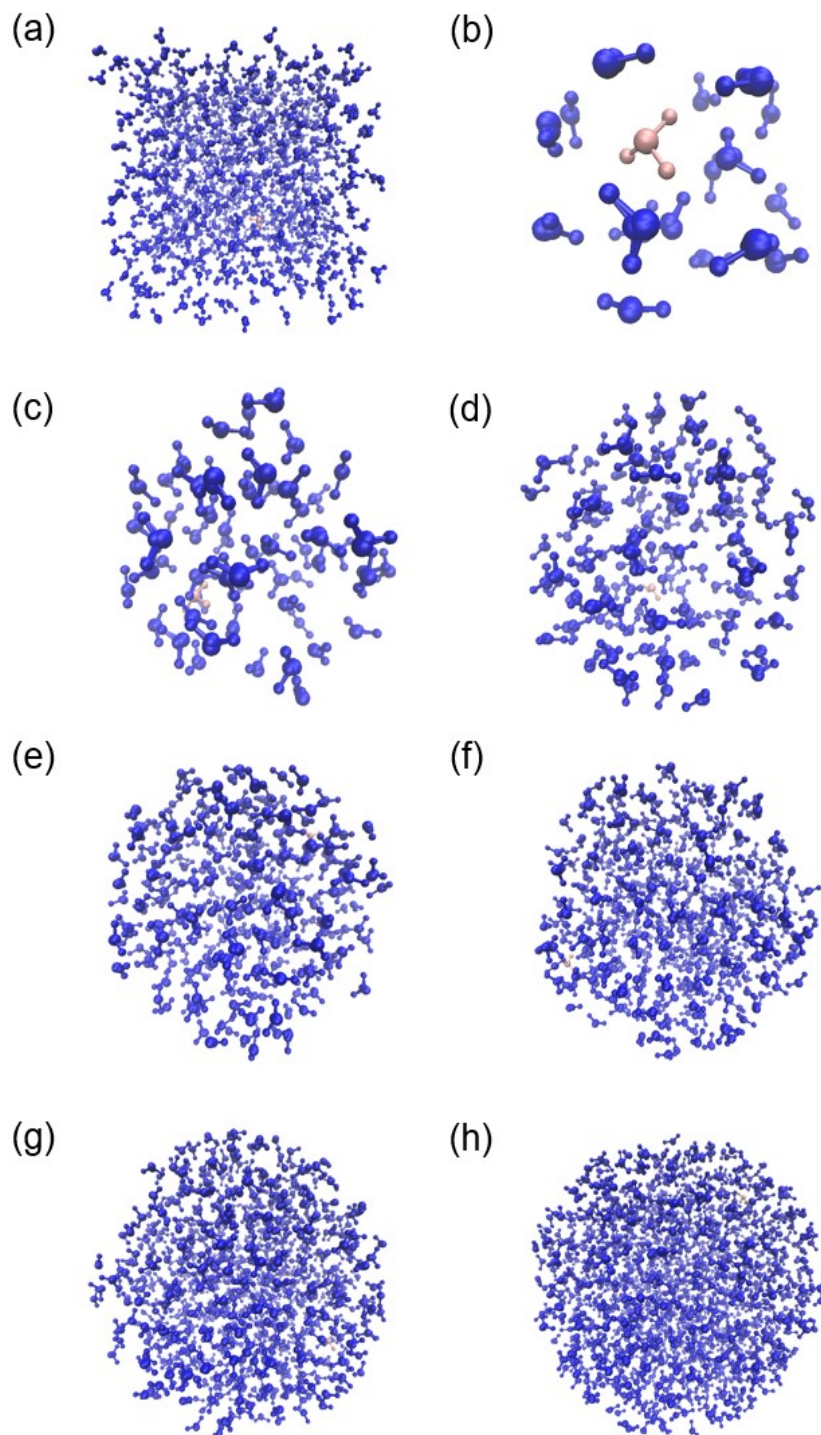


Figure S4. The initial structures constructed by Packmol package: (a) NH_3 in the bulk water, NH_3 in nanodroplets of (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, (f) 3 nm, (g) 3.5 nm, and (h) 4 nm. Blue molecules represent SWM4-NDP water molecules and pink molecules represent NH_3 .

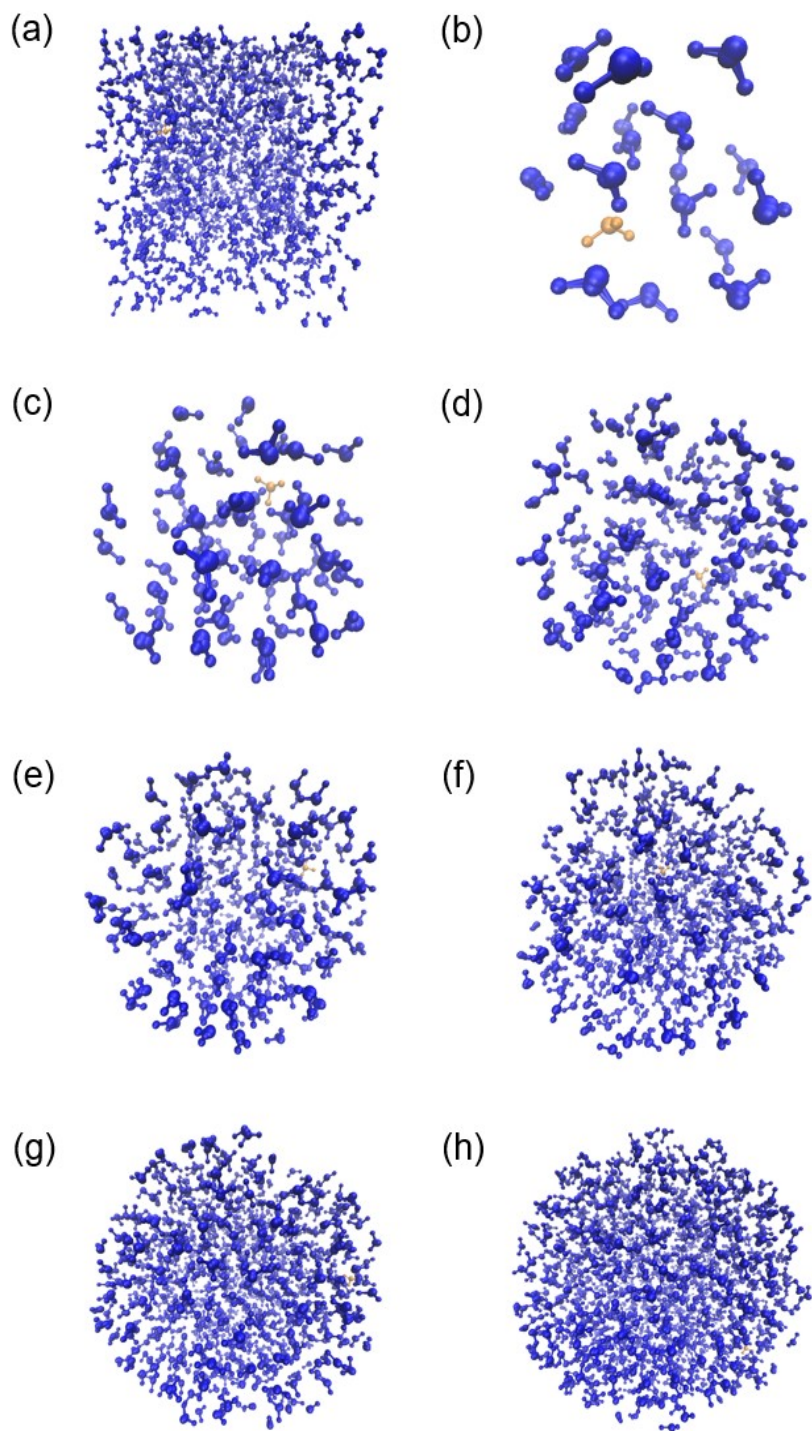


Figure S5. The initial structures constructed by Packmol package: (a) H_3O^+ in the bulk water, H_3O^+ in nanodroplets of (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, (f) 3 nm, (g) 3.5 nm, and (h) 4 nm. Blue molecules represent SWM4-NDP water molecules and orange ions represent H_3O^+ .

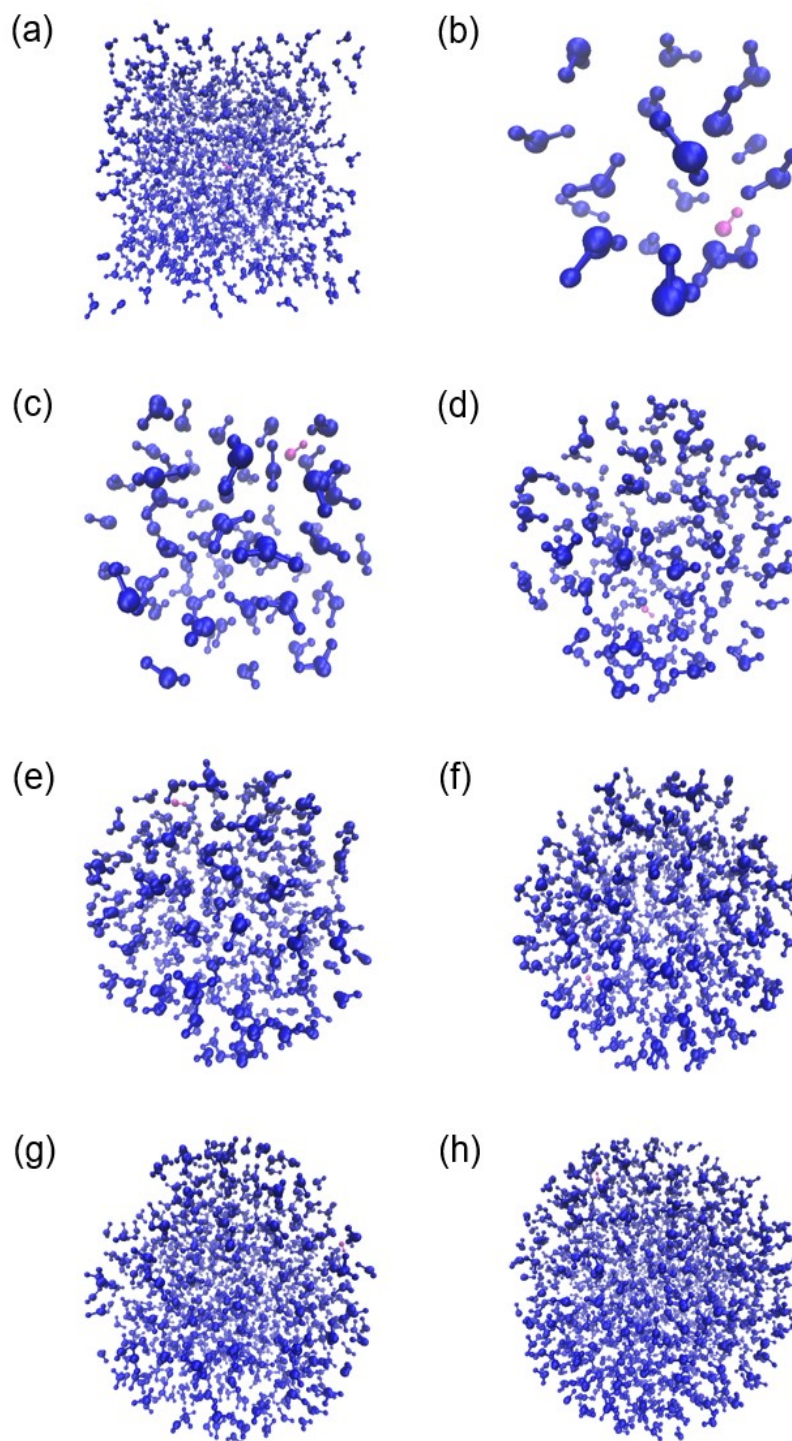


Figure S6. The initial structures constructed by Packmol package: (a) OH^- in the bulk water, OH^- in nanodroplets of (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, (f) 3 nm, (g) 3.5 nm, (h) and 4 nm. Blue molecules represent SWM4-NDP water molecules and magenta ions represent OH^- .

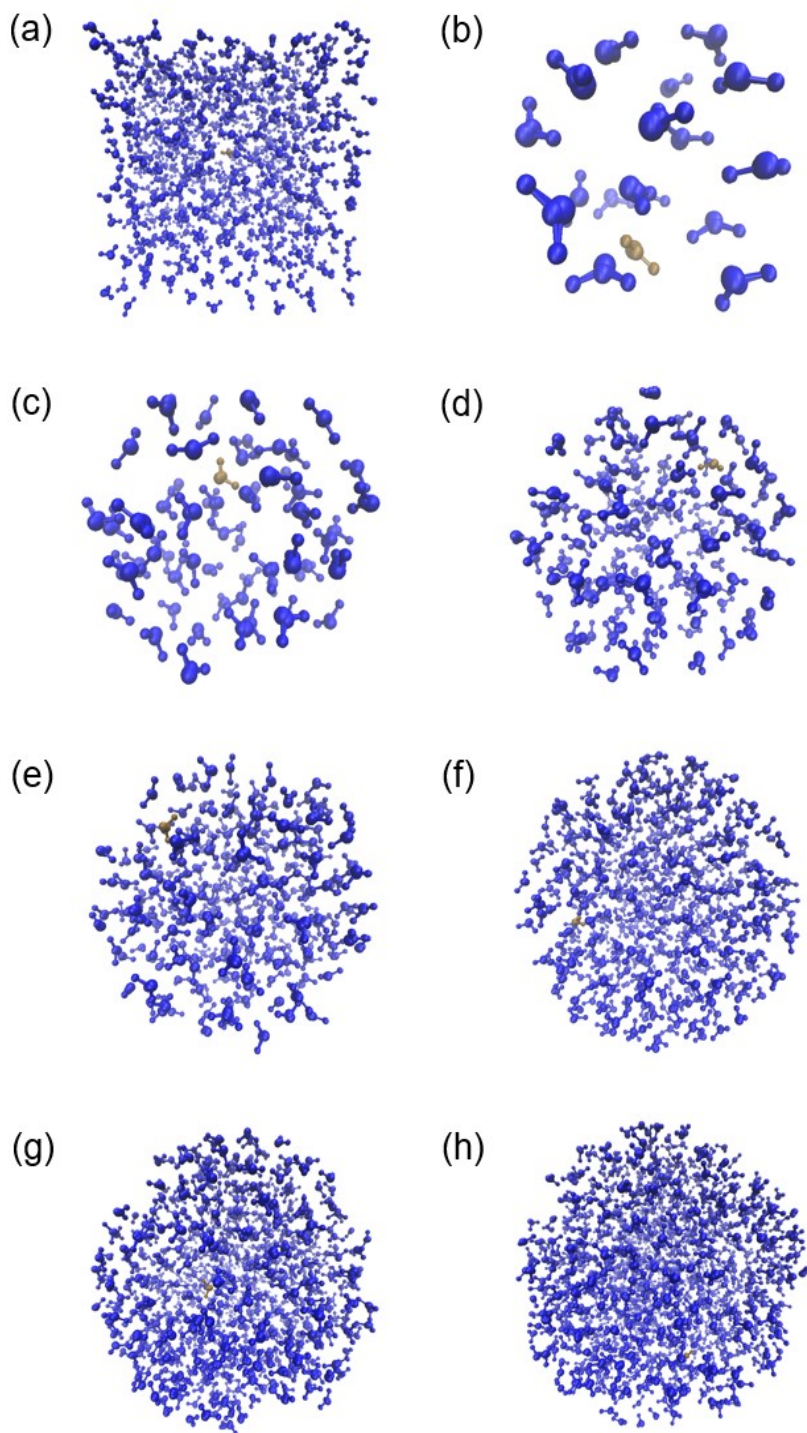


Figure S7. The initial structures constructed by Packmol package: (a) H₂O in the bulk water, H₂O in nanodroplets of (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, (f) 3 nm, (g) 3.5 nm, and (h) 4 nm. Blue molecules represent SWM4-NDP water molecules and brown molecules represent H₂O adopted SWM4-NDP model.

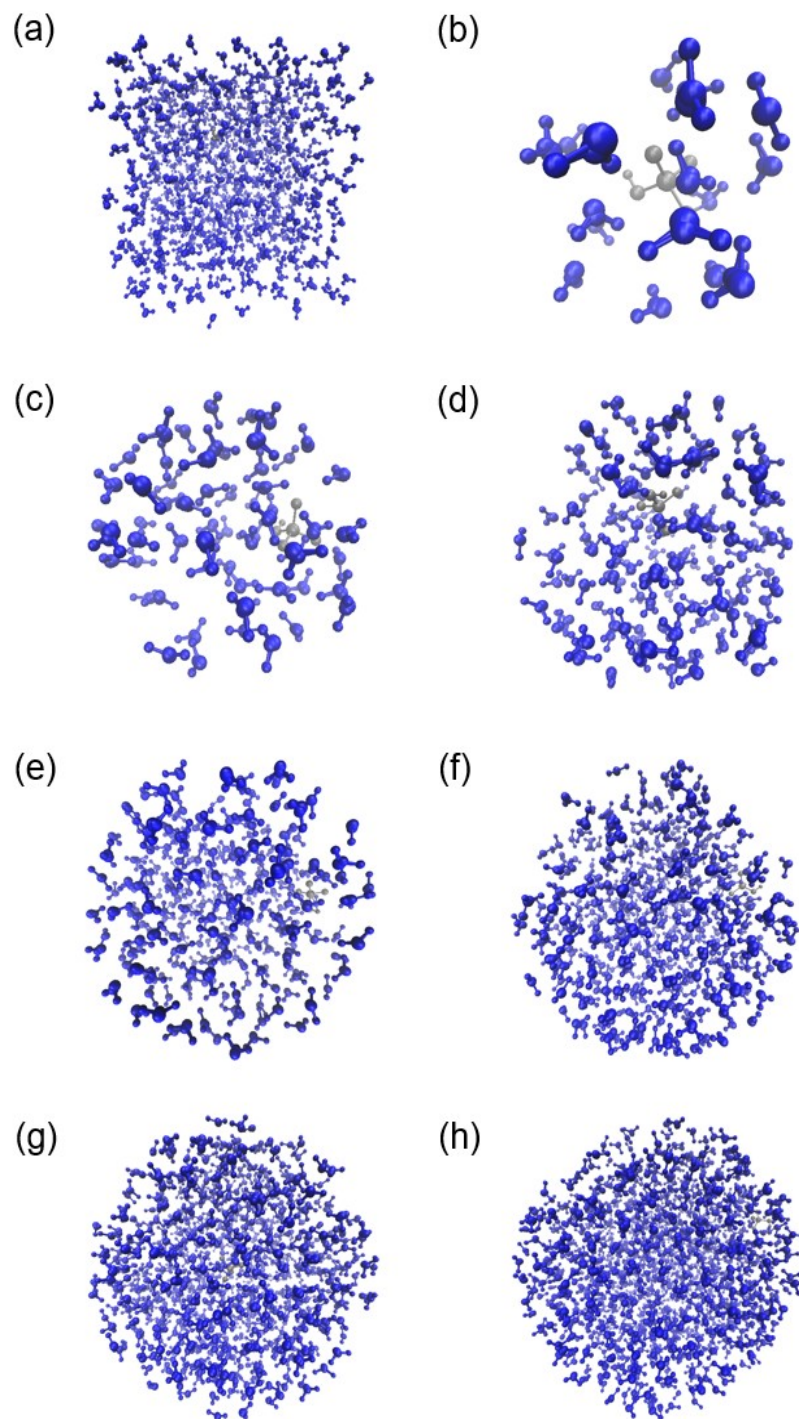


Figure S8. The initial structures constructed by Packmol package: (a) HSO_4^- in the bulk water, HSO_4^- in nanodroplets of (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, (f) 3 nm, (g) 3.5 nm, (h) 4 nm. Blue molecules represent SWM4-NDP water molecules and gray ions represent HSO_4^- .

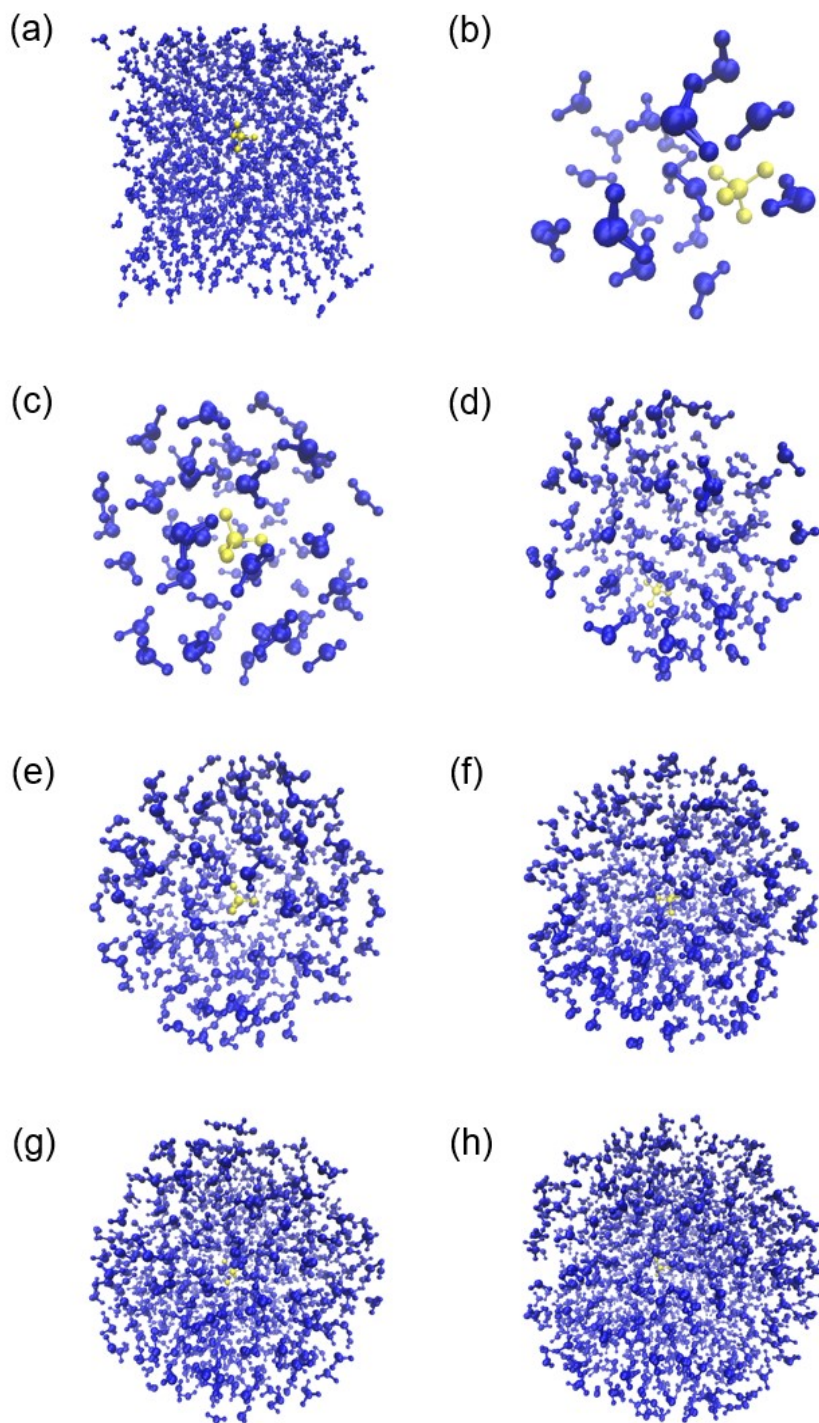


Figure S9. The initial structures constructed by Packmol package: (a) SO_4^{2-} in the bulk water, SO_4^{2-} in nanodroplets of (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, (f) 3 nm, (g) 3.5 nm, and (h) 4 nm. Blue molecules represent SWM4-NDP water molecules and yellow ions represent SO_4^{2-} .

Section III: Supporting Tables

Table S1. The charge, polarizability and LJ parameters of each atom in molecules.

Molecular type	Atom type	q	ϵ	$R_{\min}/2$	α
SWM4 -NDP ³	O	1.71640	0.2109	1.7869	-0.9783
	DO	-1.71640	0.0000	0.0000	
	M	-1.11466	0.0000	0.0000	
H ₃ O ⁺¹⁸	H	0.55733	0.0000	0.0000	
	O	1.3013	0.1496	1.7117	-0.98
	DO	-1.7179	0.0000	0.0000	
OH ⁻¹⁹	H	0.472	0.0000	0.0000	
	O	1.315	0.1825	1.9755	-2.1
	DO	-2.515	0.0000	0.0000	
NH ₃	H	0.2	0.0000	0.0000	
	N	1.260	0.1043	2.078	-1.69
	DN	-2.256	0.0000	0.0000	
NH ₄ ⁺	H	0.332	0.0699	0.5558	
	N	1.36132	0.0250	1.5500	-1.4
	DN	-2.05332	0.0000	0.0000	
	H	0.423	0.0100	0.7500	

Continued Table S1. The charge, polarizability and LJ parameters of each atom in the molecules.

Molecular type	Atom type	q	ϵ	$R_{\min}/2$	α
HNO ₃ ²⁰	N	0.857	0.0858	2.1199	
	O	1.633	0.1463	1.9202	-1.3
	DO	-1.979	0.0000	0.0000	
	OH	1.137	0.093	2.0439	-0.9
	DOH	-1.646	0.0000	0.0000	
NO ₃ ⁻	N	0.95	0.2	2.1888	
	O	1.32863	0.1550	1.7701	-1.3
NO ₃ ⁻	DO	-1.97863	0.0000	0.0000	
HSO ₄ ⁻	S	3.00353	0.27	1.90	-0.93
	DS	-1.67353	0.0000	0.0000	
	O	1.02067	0.07	1.865	-0.99
	DO	-1.72667	0.0000	0.0000	
	OH	0.86046	0.17	1.77	-0.67
SO ₄ ²⁻	DOH	-1.42046	0.0000	0.0000	
	H	0.348	0.01	0.4	
	S	3.67353	0.27	1.90	-0.93
	DS	-1.67353	0.0000	0.0000	
	O	0.72667	0.15	1.95	-0.99
	DO	-1.72667	0.0000	0.0000	

In this table, the element symbol represents the corresponding atom in the molecules, XH represents the atom connected to the hydrogen atom in the molecule, and DX represents the Drude oscillator connected to the X.

Table S2. The single point energy (a.u.) of HSO₄⁻ and SO₄²⁻, the deprotonation energy (kcal/mol) in the gas phase and dissociation constants of HSO₄⁻ calculated on different levels.

	CCSD(T)/ aug-cc-pVTZ	M05-2X/ 6-31G*	M06-2X/ 6-311++G**	M06-2X/ aug-cc- pVTZ	M06-2X/ 6-31G*
HSO ₄ ⁻	-698.95602	-699.62820	-699.69100	-699.77614	-699.03236
SO ₄ ²⁻	-698.23111	-698.88238	-698.97011	-699.05368	-698.30514
ΔG_{gas}	285.84	298.90	283.22	305.21	281.16
pK _a	-5.62	0.90	-7.54	8.57	-9.05
pK _{a,exp}			2		

Table S3. Fitted parameters in the function of $\Delta G_s(X,N) = \Delta G_s(X,\infty) + a \cdot N^{-1/3}$ (all in kcal/mol).

Solute X	$\Delta G_s(X, \infty)$	a	R ²	$\Delta G_{s,\text{exp}}$
H ₃ O ⁺	-109.35	82.93	0.990	-110.40
OH ⁻	-107.72	85.75	0.990	-105
NH ₄ ⁺	-83.46	62.53	0.992	-84.90
NO ₃ ⁻	-75.05	83.77	0.980	-76
HSO ₄ ⁻	-72.78	87.54	0.991	-70
SO ₄ ²⁻	-262.63	255.45	0.995	-258.13
H ₂ O	-5.96	12.61	0.944	-6.32
NH ₃	-3.68	7.65	0.969	-4.31
HNO ₃	-8.88	10.76	0.944	-9.05

Table S4. Parameters of the function $\text{p}K_a = \text{p}K_\infty + A_1 N^{-1/3}$, expect $\text{p}K_b$ for NH₃.

X	$\text{p}K_{a,\infty}$ ($\text{p}K_{b,\infty}$)	A_1	$\text{p}K_{a,\text{exp}}^{15}$ ($\text{p}K_{b,\text{exp}}$)
H ₂ O	13.11	111.22	15.74
HNO ₃	-1.89	111.12	-1.3
HSO ₄ ⁻	0.69	180.67	2
NH ₃	1.74	99.90	4.74

Table S5. Calculated pH values of H₂O, HNO₃, HSO₄⁻ and NH₃ of simulated concentrations in nanodroplets with different diameters.

<i>R/nm</i>	<i>N</i> ^{-1/3}	pH			
		H ₂ O	HNO ₃	HSO ₄ ⁻	NH ₃
1.0	0.389	27.24	20.34	27.24	34.51
1.5	0.255	19.96	13.33	19.96	26.21
2.0	0.193	16.47	10.03	16.46	22.18
2.5	0.155	14.33	8.03	14.18	19.68
3.0	0.129	12.84	6.67	12.29	17.93
3.5	0.110	11.76	5.69	10.77	16.64
4.0	0.096	10.95	4.97	9.59	15.67

Table S6. Calculated pH values of HNO₃, HSO₄⁻ and NH₃ in nanodroplets with different diameters (*c*_{HA} = 0.001 M).

<i>R/nm</i>	<i>N</i> ^{-1/3}	pH		
		HNO ₃	HSO ₄ ⁻	NH ₃
1.0	0.389	22.09	27.24	32.76
1.5	0.255	14.82	19.96	24.72
2.0	0.193	11.33	16.47	20.88
2.5	0.155	9.19	14.31	18.52
3.0	0.129	7.71	12.75	16.89
3.5	0.110	6.63	11.45	15.71
4.0	0.096	5.82	10.34	14.82

Table S7. Calculated pH values $\text{HSO}_4^-/\text{SO}_4^{2-}$, $\text{HNO}_3/\text{NO}_3^-$ as well as $\text{NH}_3/\text{NH}_4^+$ ion pairs in nanodroplets with different diameters ($c_{\text{HA}} = c_{\text{A}^-} = 0.001 \text{ M}$).

R/nm	$N^{-1/3}$	pH		
		$\text{HNO}_3/\text{NO}_3^-$	$\text{HSO}_4^-/\text{SO}_4^{2-}$	$\text{NH}_3/\text{NH}_4^+$
1.0	0.389	27.24	27.24	27.24
1.5	0.255	19.96	19.96	19.96
2.0	0.193	16.47	16.47	16.47
2.5	0.155	14.29	14.33	14.33
3.0	0.129	12.28	12.84	12.86
3.5	0.110	10.24	11.76	11.82
4.0	0.096	8.64	10.95	11.16

Table S8. Calculated pOH values of NH_3 in nanodroplets of different diameters.

R/nm	$N^{-1/3}$	pOH		
		$c_{\text{NH}_3}=55/\text{N}$	$c_{\text{NH}_3}=0.001 \text{ M}$	$c_{\text{NH}_3} = c_{\text{NH}_4^+} = 0.001 \text{ M}$
1.0	0.389	19.97	21.72	27.24
1.5	0.255	13.72	15.20	19.96
2.0	0.193	10.76	12.06	16.47
2.5	0.155	8.98	10.14	14.33
3.0	0.129	7.77	8.80	12.84
3.5	0.110	6.89	7.83	11.71
4.0	0.096	6.25	7.09	10.76

Table S9. Fitting parameters of the function $\ln H = \ln H_\infty + b \cdot N^{-1/3}$ in the unit of mol/(m³ · Pa).

X	$\ln H_\infty$	b	R ²	$\ln H_{\text{exp}}^{16}$
NH ₃	-1.13	-15.57	0.902	-0.53
H ₂ O	2.76	-23.62	0.938	2.85
HNO ₃	7.5	-19.95	0.946	7.65

Table S10. Parameters of the function $\text{p}K_a^* = \text{p}K_{a,\infty}^* + A_2 N^{-1/3}$.

X	$\text{p}K_{a,\infty}^*$	A_2	$\text{p}K_a^{*17}$
H ₂ O	18.52	121.47	-
HNO ₃	1.46	119.78	2.1
HSO ₄ ⁻	0.69	180.67	2
NH ₄ ⁺	2.53	6.91	2.4

Table S11. Calculated pH* values of H₂O, HNO₃, HSO₄⁻ and NH₄⁺ of simulated concentrations in nanodroplets with different diameters.

R/nm	$N^{-1/3}$	pH*			
		H ₂ O	HNO ₃	HSO ₄ ⁻	NH ₄ ⁺
1.0	0.389	31.94	23.76	32.01	2.35
1.5	0.255	23.97	16.05	23.31	2.16
2.0	0.193	20.16	12.46	17.94	2.13
2.5	0.155	17.82	10.34	14.66	2.14
3.0	0.129	16.21	8.90	12.43	2.17
3.5	0.110	15.03	7.89	10.85	2.21
4.0	0.096	14.15	7.15	9.70	2.25

Table S12. Calculated pH* values of HNO₃, HSO₄⁻ and NH₄⁺ in nanodroplets with different diameters ($c_{\text{HA}} = 0.001 \text{ M}$).

R/nm	$N^{-1/3}$	pH*		
		HNO ₃	HSO ₄ ⁻	NH ₄ ⁺
1.0	0.389	25.52	31.94	4.11
1.5	0.255	17.53	23.93	3.65
2.0	0.193	13.76	19.26	3.43
2.5	0.155	11.50	15.86	3.30
3.0	0.129	9.93	13.47	3.21
3.5	0.110	8.82	11.75	3.15
4.0	0.096	8.00	10.46	3.10

Table S13. Calculated pH* values of HSO₄⁻/SO₄²⁻, HNO₃/NO₃⁻ and NH₄⁺/NH₃ ion pairs in nanodroplets with different diameters ($c_{\text{HA}} = c_{\text{A}^-} = 0.001 \text{ M}$).

R/nm	$N^{-1/3}$	pH*		
		HNO ₃ /NO ₃ ⁻	HSO ₄ ⁻ /SO ₄ ²⁻	NH ₄ ⁺ /NH ₃
1.0	0.389	31.94	31.94	5.22
1.5	0.255	23.97	23.97	4.30
2.0	0.193	20.16	20.16	3.86
2.5	0.155	17.82	17.82	3.60
3.0	0.129	16.12	16.21	3.42
3.5	0.110	14.49	15.03	3.29
4.0	0.096	12.96	14.15	3.20

Section IV: References

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