Supporting information for
Role of hydration in atmospheric salt particle formation

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Thermodynamic data

Binding enthalpies and entropies for acid–base clusters are given in Table S1 and for acid–base–water in Table S2.

Table S1: Calculated binding enthalpies (ΔH in kcal/mol) and entropies (ΔS in cal/(mol·K)) for dry acid–base clusters.

acid	SA		MSA		NA	
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
1acid1GUA	-29.40	-29.04	-26.64	-34.87	-20.48	-32.73
1acid2GUA	-49.52	-69.39	-49.75	-82.27	-38.81	-72.63
1acid3GUA	-71.42	-110.28	-69.77	-115.90	-59.85	-112.66
1acid4GUA	-90.96	-150.95	-91.71	-161.64	-81.18	-160.10
2acid1GUA	-62.19	-79.74	-55.46	-81.60	-37.35	-66.67
2acid2GUA	-100.87	-109.31	-99.16	-119.34	-77.20	-114.54
2acid3GUA	-126.59	-165.05	-116.45	-160.71	-95.75	-146.07
2acid4GUA	-151.05	-205.20	-139.55	-210.30	-119.21	-198.56
3acid1GUA	-86.21	-116.91	-81.01	-126.13	-51.51	-94.67
3acid2GUA	-131.47	-162.07	-124.77	-162.59	-92.68	-148.12
3acid3GUA	-170.35	-196.83	-167.69	-211.77	-132.75	-175.01
3acid4GUA	-203.96	-236.47	-190.57	-253.26	-157.38	-238.29
4acid1GUA	-107.51	-156.25	-100.07	-167.38	-70.75	-143.11
4acid2GUA	-156.94	-204.28	-146.43	-206.54	-105.82	-177.28
4acid3GUA	-202.91	-242.23	-196.21	-261.68	-145.92	-206.30
4acid4GUA	-255.84	-288.12	-255.45	-308.82	-206.46	-285.94
2acid	-17.77	-34.17	-18.88	-39.70	-9.40	-33.34
3acid	-36.72	-76.66	-35.12	-80.41	-14.15	-63.96
4acid	-52.64	-102.62	-54.73	-128.53	-24.87	-101.67
2GUA					-12.42	-34.16
3GUA					-24.89	-73.20
4GUA					-44.93	-115.52

Table S2: Calculated binding enthalpies (ΔH in kcal/mol) and entropies (ΔS in cal/(mol·K)) for acid–base–water clusters.

acid	SA		MSA		NA	
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
1acid1GUA1W	-41.17	-67.23	-39.75	-73.68	-28.46	-60.82
1acid1GUA2W	-57.13	-100.96	-55.49	-107.62	-43.85	-102.09
1acid1GUA3W	-70.81	-135.78	-69.09	-140.22	-59.51	-138.64
1acid1GUA4W	-80.10	-165.32	-80.12	-176.64	-69.79	-167.55
1acid2GUA1W	-65.14	-108.17	-63.76	-111.86	-54.03	-109.56
1acid2GUA2W	-76.70	-137.43	-73.77	-143.04	-64.85	-139.48
1acid2GUA3W	-88.72	-173.22	-85.70	-178.02	-76.51	-174.13
1acid2GUA4W	-104.35	-221.79	-95.87	-210.84	-88.46	-211.69
2acid1GUA1W	-73.59	-108.58	-68.43	-113.90	-49.43	-102.57
2acid1GUA2W	-87.18	-144.17	-82.98	-151.62	-64.68	-141.75
2acid1GUA3W	-98.36	-179.52	-94.56	-186.78	-75.80	-174.90
2acid1GUA4W	-107.91	-204.46	-105.26	-221.76	-85.92	-203.64
2acid2GUA1W	-113.27	-152.33	-109.62	-156.87	-87.99	-142.22
2acid2GUA2W	-127.19	-188.67	-120.31	-186.75	-97.97	-164.88
2acid2GUA3W	-138.87	-223.02	-132.96	-226.69	-111.22	-211.81
2acid2GUA4W	-147.64	-244.43	-144.07	-252.43	-122.57	-248.71
1acid1W	-11.13	-29.45	-10.97	-31.74	-8.71	-28.94
1acid2W	-21.70	-61.35	-21.03	-64.71	-16.89	-57.68
1acid3W	-32.44	-97.39	-32.05	-98.71	-25.22	-89.91
1acid4W	-43.40	-125.52	-42.22	-135.37	-32.92	-121.95
2acid1W	-26.40	-69.46	-28.25	-70.61	-17.35	-62.67
2acid2W	-37.95	-99.82	-41.27	-112.93	-27.34	-93.65
2acid3W	-49.48	-137.31	-52.95	-147.38	-36.73	-127.58
2acid4W	-60.80	-177.98	-68.50	-187.48	-43.80	-161.82
2GUA1W					-20.73	-65.79
2GUA2W					-33.52	-99.10
2GUA3W					-41.65	-135.31
2GUA4W					-48.54	-162.99

Hydration of 2acid2guanidine clusters

Molecular structures of hydrated 2acid2guanidine clusters are shown in Figure S1.

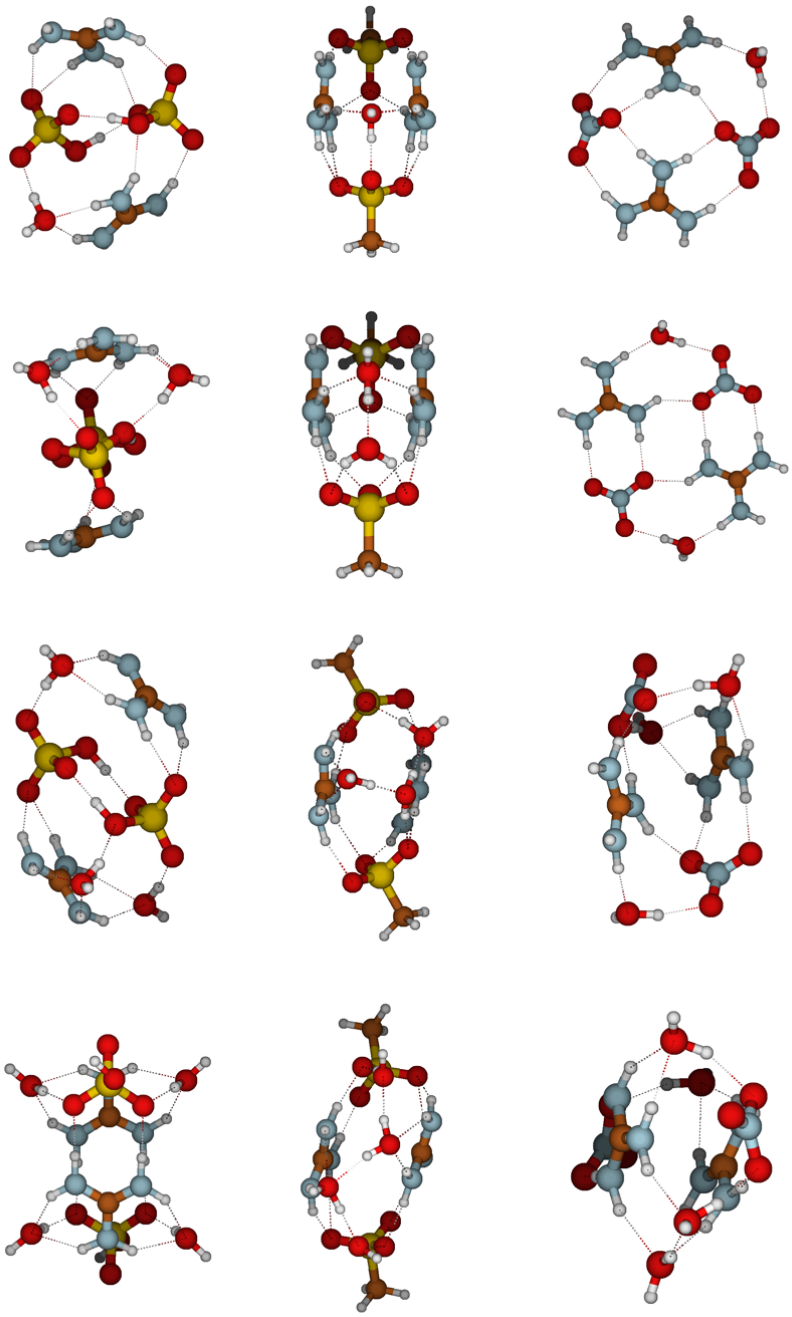

Figure S1: Molecular structures of 2SA2GUA (left), 2MSA2GUA (middle), and 2NA2GUA clusters with one to four water molecules.

Cluster Population Dynamics Simulations

The time evolution and behavior of a population of clusters of different sizes and compositions is obtained by integrating the time derivatives of the cluster concentrations using the Atmospheric Cluster Dynamics Code.[1,2] These birth–death equations include all possible processes where the clusters can be formed or destroyed. For cluster i of a given composition, the time derivative is

$$\begin{aligned}\frac{dC_i}{dt} =& \frac{1}{2}\sum_{j<i}\beta_{j,(i-j)}C_jC_{(i-j)} + \sum_j \gamma_{(i+j)\rightarrow i,j}C_{(i+j)} - \sum_j \beta_{i,j}C_iC_j - \\ & \frac{1}{2}\sum_{j<i}\gamma_{i\rightarrow j,i-j}C_i + S_i - L_iC_i,\end{aligned} \tag{1}$$

where C_i is the concentration of cluster i, $\beta_{i,j}$ is the collision rate coefficient between i and j, $\gamma_{(i+j)\rightarrow i,j}$ is the evaporation rate coefficient of cluster $(i+j)$, S_i is an external source term, and L_i is an external loss term corresponding to coagulation onto pre-existing surfaces. The loss rate L_i was assumed to depend on cluster size according to the parametrization by Lehtinen *et al.*.[3] The reference loss rate, corresponding to a sulfuric acid molecule, was set to 10^{-3} s^{-1}, and the scavenging coefficient m to -1.6 corresponding to typical atmospheric conditions.

The evaporation rates of the clusters are obtained from the Gibbs free binding energies ΔG of the evaporating cluster and its products as

$$\gamma_{(i+j)\rightarrow i,j} = \beta_{i,j}\frac{p_{\mathrm{ref}}}{k_{\mathrm{B}}T}\exp\left(\frac{\Delta G_{i+j} - \Delta G_i - \Delta G_j}{k_{\mathrm{B}}T}\right). \tag{2}$$

The collision coefficients are computed from kinetic gas theory as

$$\beta_{i,j} = \left(\frac{3}{4\pi}\right)^{1/6}\left[6k_{\mathrm{B}}T\left(\frac{1}{m_i}+\frac{1}{m_j}\right)\right]^{1/2}\left(V_i^{1/3}+V_j^{1/3}\right)^2, \tag{3}$$

where m_i and V_i are the mass and volume of cluster i, respectively. The volumes are calculated using bulk liquid densities (1830, 1480, 1510, and 1300 $\frac{kg}{m^3}$ for sulfuric acid, methanesulfonic acid, nitric acid and guanidine, respectively) assuming spherical clusters and ideal mixing.

Boundary conditions in particle formation simulations

In ACDC simulations, clusters are allowed to grow out of the 2acid2base simulation system as "stable" particles. In these simulations, clusters containing at least three acid and two base molecules were selected as outgrowing particles. It should be noted that to obtain accurate absolute NPF rates, larger simulation size is needed (at least four acid and four base). Therefore, the formed particle outside of a simulation box might not truly be stable (especially in the case of nitric acid clusters), which leads artificially too high NPF rates. Thus, reader should be careful with absolute J values and focus on computed humidity factors.

References

[1] M. J. McGrath, T. Olenius, I. K. Ortega, V. Loukonen, P. Paasonen, T. Kurtén, M. Kulmala and H. Vehkamäki, Atmospheric Cluster Dynamics Code: a Flexible Method for Solution of the Birth–Death Equations, *Atmos. Chem. Phys.*, 2012, **12**, 2345–2355.

[2] T. Olenius, O. Kupiainen-Määttä, I. K. Ortega, T. Kurtén and H. Vehkamäki, Free Energy Barrier in the Growth of Sulfuric Acid–Ammonia and Sulfuric Acid–Dimethylamine Clusters, *J. Chem. Phys.*, 2013, **139**, 084312.

[3] K. E. Lehtinen, M. D. Maso, M. Kulmala and V.-M. Kerminen, Estimating Nucleation Rates from Apparent Particle Formation Rates and vice versa: Revised Formulation of the Kerminen–Kulmala Equation, *J. Aerosol Sci.*, 2007, **38**, 988–994.