

Supporting Information

for

Guanidine: A Highly Efficient Stabilizer in Atmospheric New-Particle Formation

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Benchmark Results

In order to ensure sufficient accuracy of the chosen level of theory, we have benchmarked the DLPNO-CCSD(T) method against an explicitly correlated RI-CCSD(T)-F12 method (as implemented in Orca). Figure S1 shows the binding energies of sulfuric acid and guanidine, dimethylamine, ammonia, or water complexes. We have utilized the aug-cc-pV x Z, cc-pV x Z (where $x=2-5$) and def2- x ZVPP (where $x=3-4$) basis sets with DLPNO-CCSD(T), and the cc-pV x Z-F12 (where $x=2-4$) basis sets with RI-CCSD(T)-F12 (referred to as F12/V x Z). In the DLPNO calculations we used the corresponding auxiliary basis sets and in explicitly correlated calculations we utilized the corresponding CABS and one cardinal number higher for the auxiliary basis sets.

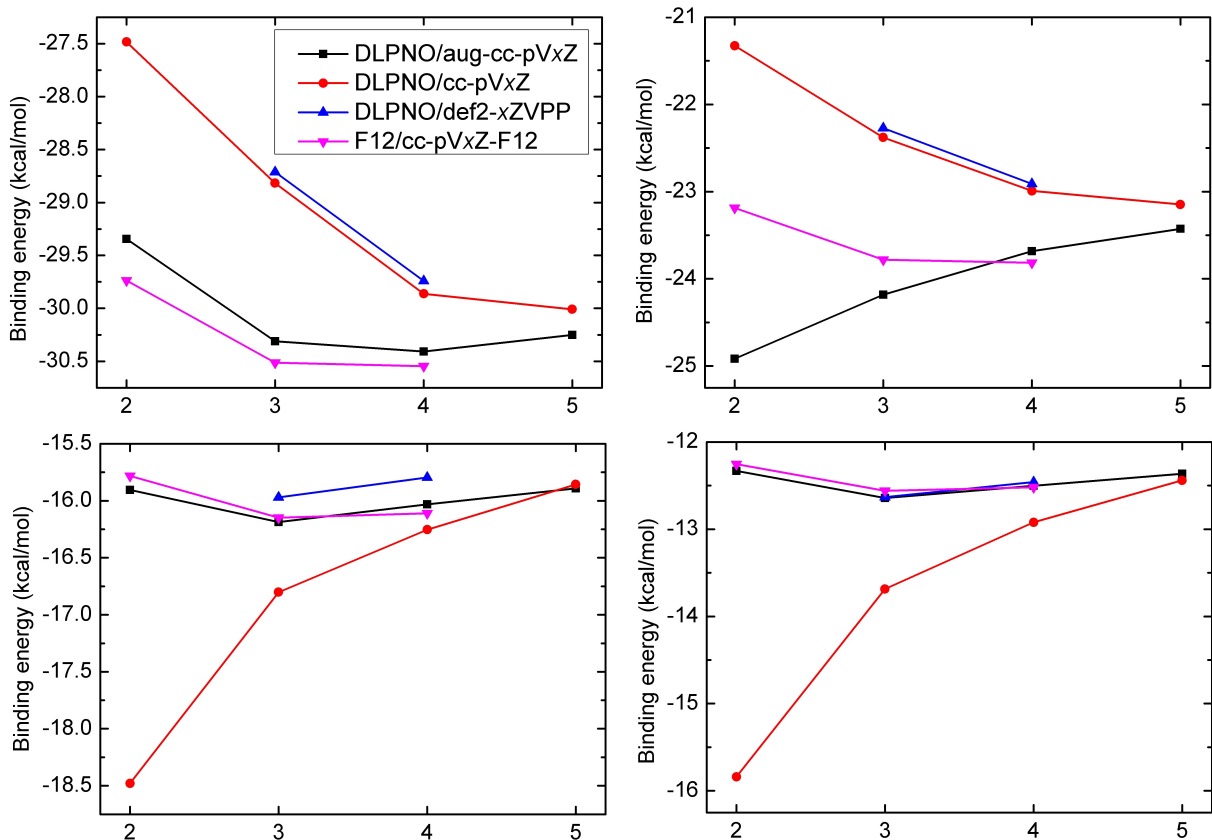


Figure S1: Binding energies (kcal/mol) as a function of basis set cardinal number ($x=2-5$) for guanidine-sulfuric acid (top, left), dimethylamine-sulfuric acid (top, right), ammonia-sulfuric acid (down, left), and water-sulfuric acid (down, right) clusters. Calculations are performed using DLPNO-CCSD(T) and RI-CCSD(T)-F12 methods with different basis sets.

In the case of sulfuric acid and guanidine or dimethylamine, in which a proton has been transferred from sulfuric acid to the base, the cc-pV x Z basis sets approach the largest aug-cc-pV5Z basis set from above, whereas in the case of sulfuric acid and ammonia or water clusters, in which proton transfer has not occurred, the cc-pV x Z basis sets approach aug-cc-pV5Z from below. Figure S1 shows the importance of using diffuse functions for the description of ionic clusters. When the cluster is not ionic in nature, the cc-pV x Z basis sets with small cardinal numbers tend to overbind due to basis set superposition error (BSSE) and the basis set incompleteness error (BSIE). The errors in the aug-cc-pV x Z basis sets are more or less the combination of the error of the method as well as BSIE. When using sufficiently large basis sets (aug-cc-pVQZ, aug-cc-pV5Z, cc-pV5Z, and def2-QZVPP), DLPNO systematically underbinds compared to the F12/VQZ level. That is because the difference compared to explicitly correlated CCSD(T) is mainly caused by the error associated with the method. In the case of the aug-cc-pVTZ basis set, the BSIE and error of the method seem to be same size but opposite sign, implying a systematic cancellation of errors.

We have calculated the mean absolute errors (MAEs) for sulfuric acid and guanidine, dimethylamine, ammonia, or water clusters compared to the highest F12/VQZ level. Relative computational times are calculated for sulfuric acid–guanidine complex relative to the computationally cheapest DLPNO–CCSD(T)/cc-pVDZ level of theory. Figure S2 shows that all other level of theories except DLPNO with double or triple basis sets without diffuse functions yield results close to the F12/VQZ level of theory. DLPNO/aug-cc-pVTZ performs well, with a MAE of 0.2 kcal/mol, MSE of -0.08 kcal/mol, and a maximum error of 0.4 kcal/mol, with only four times higher computational time than DLPNO/cc-pVDZ. This justifies the further usage of DLPNO–CCSD(T)/aug-cc-pVTZ level of theory in studies of sulfuric acid–guanidine clusters.

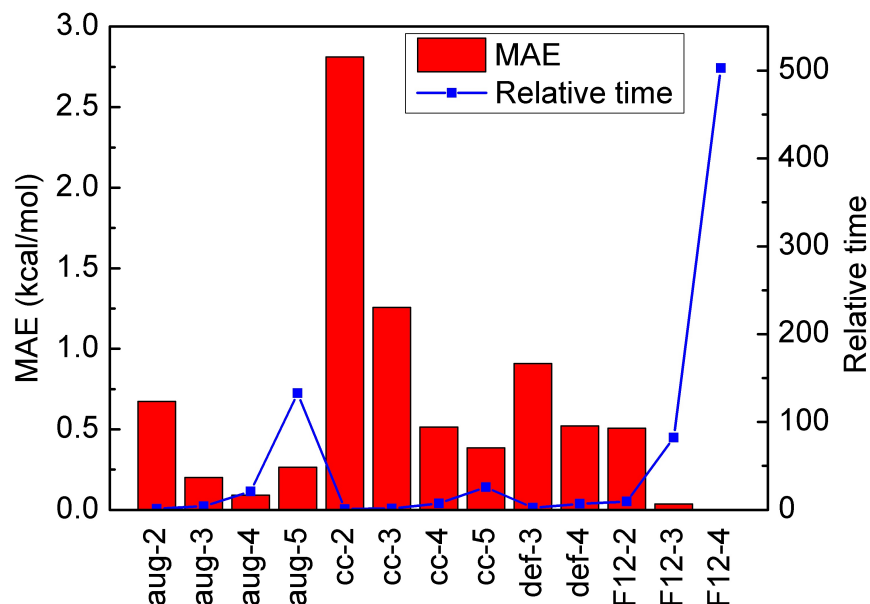


Figure S2: Mean absolute errors (red bars) calculated relative to RI-CCSD(T)-F12/cc-pVQZ-F12 and computational times (blue squares) relative to DLPNO/cc-pVDZ. Calculations are performed using DLPNO-CCSD(T) (aug, cc, and def basis sets) and RI-CCSD(T)-F12 (F12 basis sets).

Guanidine-Sulfuric Acid Clusters

Table S1 shows the thermal contributions to the Gibbs free energy calculated at three density functionals and electronic energy corrections (which are calculated on top of the DFT structures using DLPNO) for all studied structures. Gibbs free energies are calculated as an average and the lowest values are used to calculate Gibbs free binding energies. All the structures with DFT electronic energies are in the zip folder.

Table S1: Thermal contributions to the Gibbs free energies (G_{Therm}) at 298.15 K using DFT/6-31++G**, single point energies (E_{SPE}) on top of the DFT structures using DLPNO-CCSD(T)/aug-cc-pVTZ, and the average Gibbs free energies (G_{ave}) at 298.15 K using DLPNO//DFT, where DFT corresponds to M06-2X, PW91, and ω B97X-D density functionals. Values are tabled for all studied structures and the lowest G_{ave} are bolded.

	M06-2X	DLPNO	PW91	DLPNO	ω B97X-D	DLPNO	DLPNO//DFT
	G_{Therm}	E_{SPE}	G_{Therm}	E_{SPE}	G_{Therm}	E_{SPE}	G_{ave}
1A	0.0112	-699.4628	0.0082	-699.4577	0.0111	-699.4628	-699.4509
1G	0.0503	-205.0712	0.0477	-205.0706	0.0507	-205.0711	-205.0214
2A	0.0432	-1398.9563	0.0378	-1398.9474	0.0439	-1398.9567	-1398.9118
3A	0.0739	-2098.4475	0.0652	-2098.4340	0.0745	-2098.4485	-2098.3722
4A	0.1007	-2797.9394	0.0903	-2797.9217	0.1017	-2797.9408	-2797.8364
1G1A-1	0.0767	-904.5823	0.0727	-904.5766	0.0781	-904.5823	-904.5046
1G1A-2	0.0770	-904.5823	0.0729	-904.5766	0.0784	-904.5823	-904.5043
1G1A-3	0.0830	-904.5762	0.0740	-904.5702	0.0822	-904.5766	-904.4946
1G1A-4	0.0824	-904.5618	0.0715	-904.5691	0.0838	-904.5622	-904.4851
1G2A-1	0.1164	-1604.1008	0.1078	-1604.0909	0.1176	-1604.1012	-1603.9837
1G2A-2	0.1160	-1604.1002	0.1075	-1604.0903	0.1178	-1604.1007	-1603.9833
1G2A-3	0.1147	-1604.0968	0.1078	-1604.0909	0.1176	-1604.1012	-1603.9830
1G3A-1	0.1485	-2303.6041	0.1368	-2303.5894	0.1496	-2303.6048	-2303.4545
1G3A-2	0.1478	-2303.5986	0.1369	-2303.5860	0.1488	-2303.5994	-2303.4502
1G3A-3	0.1483	-2303.5994	0.1371	-2303.5858	0.1501	-2303.6011	-2303.4502
1G3A-4	0.1480	-2303.5973	0.1342	-2303.5823	0.1481	-2303.5984	-2303.4492
1G4A-1	0.1831	-3003.1000	0.1667	-3003.0799	0.1835	-3003.1021	-3002.9162
1G4A-2	0.1822	-3003.1007	0.1668	-3003.0809	0.1829	-3003.1029	-3002.9176
1G4A-3	0.1814	-3003.0983	0.1648	-3003.0801	0.1831	-3003.1012	-3002.9168
2G-1	0.1182	-410.1640	0.1133	-410.1621	0.1194	-410.1639	-410.0464
2G-2	0.1195	-410.1618	0.1140	-410.1603	0.1205	-410.1618	-410.0433
2G-3	0.1195	-410.1606	0.1132	-410.1592	0.1196	-410.1606	-410.0427
2G1A-1	0.1535	-1109.6916	0.1436	-1109.6844	0.1544	-1109.6917	-1109.5388
2G1A-2	0.1535	-1109.6911	0.1435	-1109.6843	0.1553	-1109.6909	-1109.5380
2G1A-3	0.1517	-1109.6889	0.1423	-1109.6824	0.1513	-1109.6891	-1109.5384
2G1A-4	0.1544	-1109.6917	0.1446	-1109.6844	0.1554	-1109.6917	-1109.5378
2G2A-1	0.1920	-1809.2346	0.1803	-1809.2230	0.1949	-1809.2354	-1809.0419
2G2A-2	0.1915	-1809.2341	0.1804	-1809.2237	0.1931	-1809.2354	-1809.0427
2G2A-3	0.1823	-1809.2368	0.1735	-1809.2264	0.1853	-1809.2370	-1809.0530
2G2A-4	0.1843	-1809.2353	0.1745	-1809.2242	0.1859	-1809.2356	-1809.0501
2G3A-1	0.2233	-2508.7492	0.2076	-2508.7345	0.2245	-2508.7507	-2508.5263
2G3A-2	0.2234	-2508.7496	0.2076	-2508.7346	0.2246	-2508.7508	-2508.5265
2G3A-3	0.2275	-2508.7512	0.2097	-2508.7359	0.2269	-2508.7522	-2508.5251
2G3A-4	0.2261	-2508.7451	0.2094	-2508.7304	0.2270	-2508.7467	-2508.5199
2G4A-1	0.2600	-3208.2501	0.2386	-3208.2287	0.2597	-3208.2532	-3207.9912
2G4A-2	0.2573	-3208.2472	0.2363	-3208.2284	0.2561	-3208.2506	-3207.9922
2G4A-3	0.2578	-3208.2517	0.2390	-3208.2312	0.2597	-3208.2534	-3207.9933

3G-1	0.1901	-615.2578	0.1818	-615.2550	0.1914	-615.2577	-615.0690
3G-2	0.1883	-615.2544	0.1815	-615.2522	0.1905	-615.2548	-615.0670
3G-3	0.1906	-615.2550	0.1806	-615.2522	0.1909	-615.2553	-615.0668
3G-4	0.1907	-615.2561	0.1815	-615.2535	0.1921	-615.2561	-615.0672
3G1A-1	0.2256	-1314.7988	0.2126	-1314.7900	0.2257	-1314.7993	-1314.5747
3G1A-2	0.2234	-1314.7983	0.2118	-1314.7907	0.2246	-1314.7984	-1314.5758
3G1A-3	0.2239	-1314.7982	0.2118	-1314.7906	0.2245	-1314.7982	-1314.5756
3G1A-4	0.2228	-1314.7967	0.2116	-1314.7896	0.2240	-1314.7969	-1314.5749
3G2A-1	0.2614	-2014.3428	0.2463	-2014.3327	0.2638	-2014.3448	-2014.0829
3G2A-2	0.2616	-2014.3416	0.2467	-2014.3298	0.2628	-2014.3428	-2014.0810
3G2A-3	0.2608	-2014.3418	0.2449	-2014.3298	0.2629	-2014.3427	-2014.0819
3G2A-4	0.2616	-2014.3409	0.2468	-2014.3292	0.2627	-2014.3422	-2014.0804
3G3A-1	0.2932	-2713.8857	0.2750	-2713.8674	0.2949	-2713.8864	-2713.5921
3G3A-2	0.2932	-2713.8855	0.2765	-2713.8692	0.2952	-2713.8869	-2713.5922
3G3A-3	0.2928	-2713.8840	0.2749	-2713.8667	0.2940	-2713.8850	-2713.5913
3G3A-4	0.2940	-2713.8870	0.2783	-2713.8712	0.2974	-2713.8884	-2713.5923
3G4A-1	0.3344	-3413.3966	0.3101	-3413.3764	0.3364	-3413.3993	-3413.0638
3G4A-2	0.3298	-3413.4021	0.3079	-3413.3810	0.3309	-3413.4045	-3413.0730
3G4A-3	0.3312	-3413.3983	0.3092	-3413.3786	0.3336	-3413.4012	-3413.0680
4G-1	0.2634	-820.3629	0.2516	-820.3596	0.2647	-820.3630	-820.1019
4G-2	0.2642	-820.3620	0.2507	-820.3591	0.2642	-820.3625	-820.1015
4G-3	0.2642	-820.3603	0.2500	-820.3563	0.2645	-820.3604	-820.0994
4G1A-1	0.2983	-1519.9016	0.2818	-1519.8931	0.3012	-1519.9031	-1519.6055
4G1A-2	0.2956	-1519.9028	0.2807	-1519.8946	0.2970	-1519.9030	-1519.6090
4G1A-3	0.2982	-1519.9004	0.2828	-1519.8917	0.3004	-1519.9004	-1519.6037
4G1A-4	0.2993	-1519.9026	0.2818	-1519.8931	0.3012	-1519.9031	-1519.6055
4G2A-1	0.3291	-2219.4489	0.3130	-2219.4357	0.3317	-2219.4492	-2219.1200
4G2A-2	0.3396	-2219.4551	0.3205	-2219.4411	0.3409	-2219.4557	-2219.1170
4G2A-3	0.3315	-2219.4498	0.3102	-2219.4326	0.3365	-2219.4505	-2219.1182
4G2A-4	0.3312	-2219.4473	0.3150	-2219.4339	0.3334	-2219.4480	-2219.1166
4G3A-1	0.3669	-2919.0147	0.3469	-2918.9949	0.3687	-2919.0156	-2918.6476
4G3A-2	0.3670	-2919.0145	0.3464	-2918.9946	0.3706	-2919.0153	-2918.6468
4G3A-3	0.3680	-2919.0133	0.3464	-2918.9946	0.3677	-2919.0152	-2918.6470
4G4A-1	0.3989	-3618.5566	0.3811	-3618.5566	0.4052	-3618.5574	-3618.1618
4G4A-2	0.4107	-3618.5562	0.3848	-3618.5562	0.4132	-3618.5580	-3618.1539
4G4A-3	0.4001	-3618.5560	0.3816	-3618.5560	0.4059	-3618.5571	-3618.1605

Figure S3 shows the Gibbs free binding energies for the studied clusters at 298.15 K using DLPNO-CCSD(T)/aug-cc-pVTZ//DFT/6-31++G** level of theory, where DFT refers three density functionals (M06-2X, PW91, and ω B97X-D).

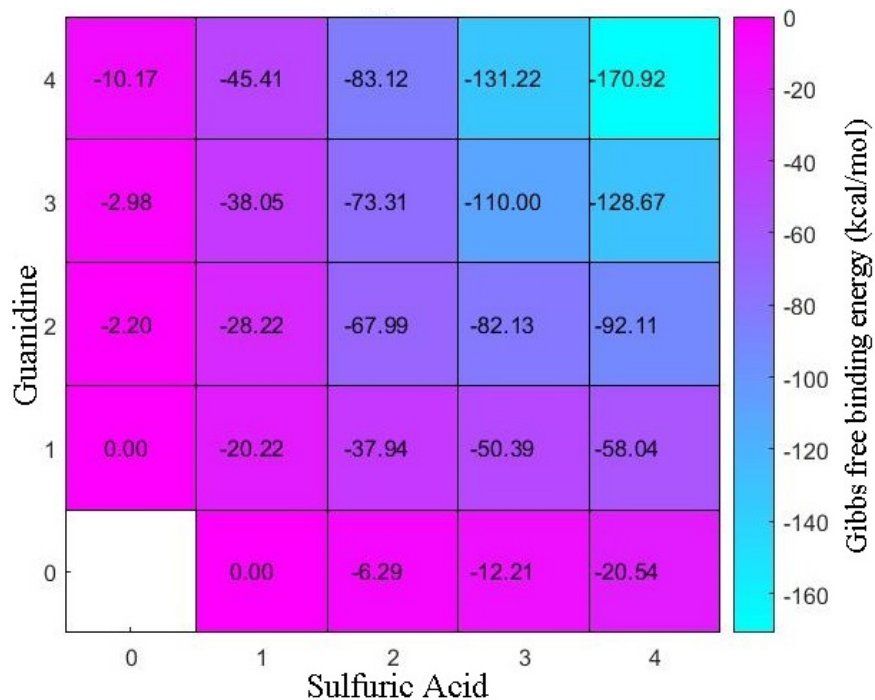


Figure S3: Gibbs free binding energies for guanidine-sulfuric acid clusters at 298.15 K. Number of sulfuric acid molecules is in x -axis and number of guanidine molecules is in y -axis.

Figures S4 and S5 show the actual Gibbs free energies and the main cluster growth pathways for guanidine-sulfuric acid clusters at 298.15 K, when sulfuric acid monomer concentration is 10^6 cm^{-3} , and the concentration of guanidine is 10^{-3} and 10^{-6} ppt_V .

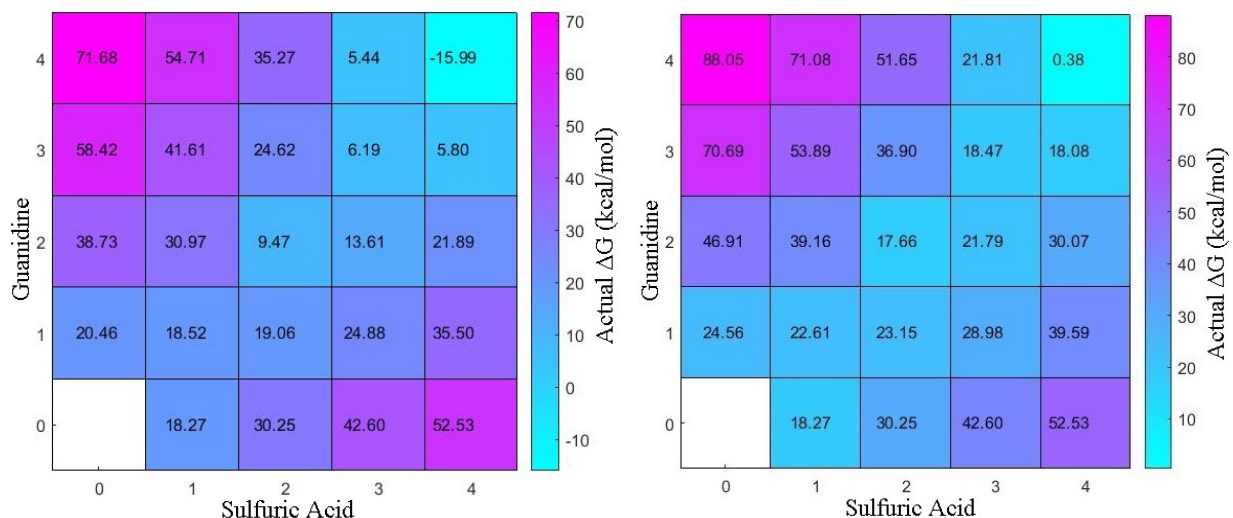


Figure S4: Actual Gibbs free energies for guanidine-sulfuric acid clusters at concentrations of $[A]=10^6$ cm⁻³, and $[G]=1$ ppqV (left) and $[A]=10^6$ cm⁻³ and $[G]=0.001$ ppqV (right) at 298.15 K. Note the different scale of axes.

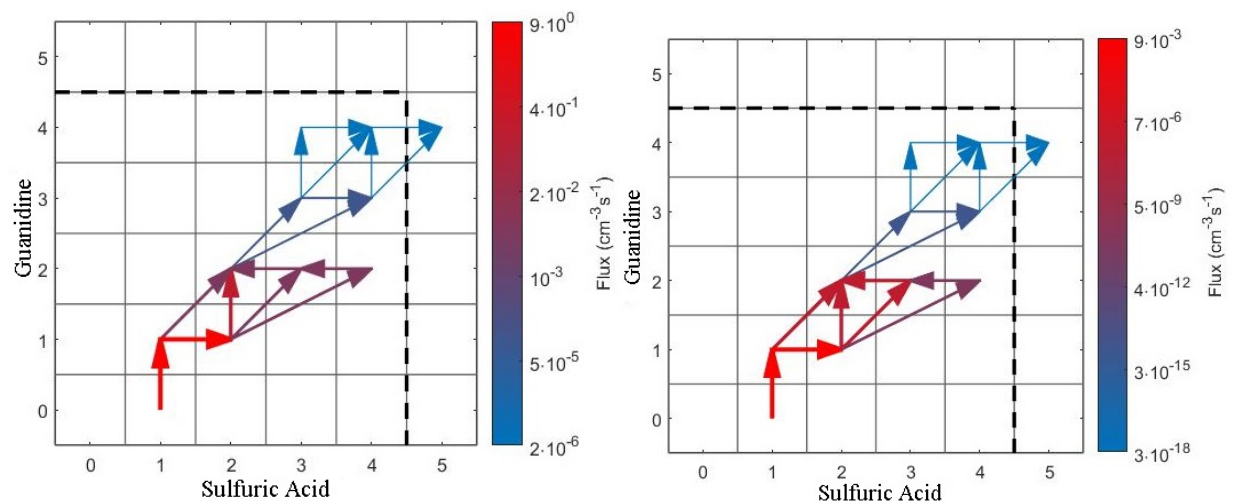


Figure S5: Main growth pathways for sulfuric acid-guanidine clusters at 298.15 K, $[A]=10^6$ cm⁻³, when $[G]=1$ ppqV (left) and $[G]=0.001$ ppqV (right). Note the different scale of axes.

Figure S6 presents the monomer collision-evaporation frequency relation at 298.15 K, $[A]=10^6$ cm⁻³, and $[G]=1$ ppqV.

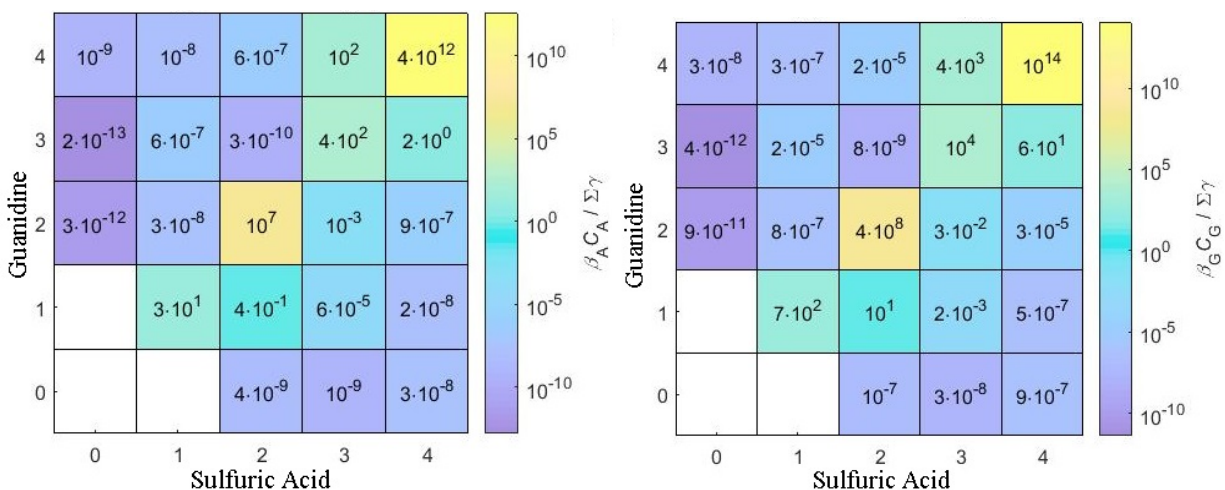


Figure S6: Sulfuric acid (left) and guanidine (right) monomer collision and evaporation frequencies ratios for sulfuric acid–guanidine clusters at concentrations of $[A]=10^6 \text{ cm}^{-3}$, and $[G]=1 \text{ ppqv}$ at 298.15 K.

Figure S7 shows guanidine–ammonia–sulfuric acid clusters detected using an APi-TOF mass spectrometer operating in negative mode.

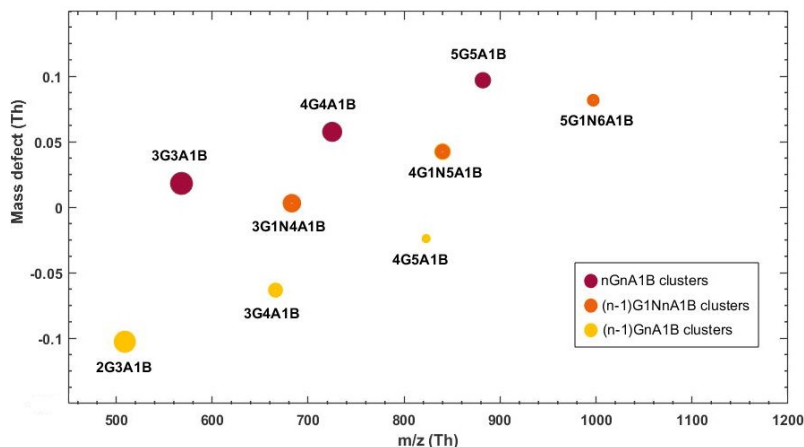


Figure S7: Mass defect plot of large negative clusters, including ammonia-containing clusters. The size of the symbols is proportional to the logarithm of the count rate.

Comparison with Dimethylamine Clusters

Figure S8 presents the Gibbs free binding energies for guanidine–sulfuric acid and dimethylamine–sulfuric acid clusters at 298.15 K using DLPNO–CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G** level of theory.

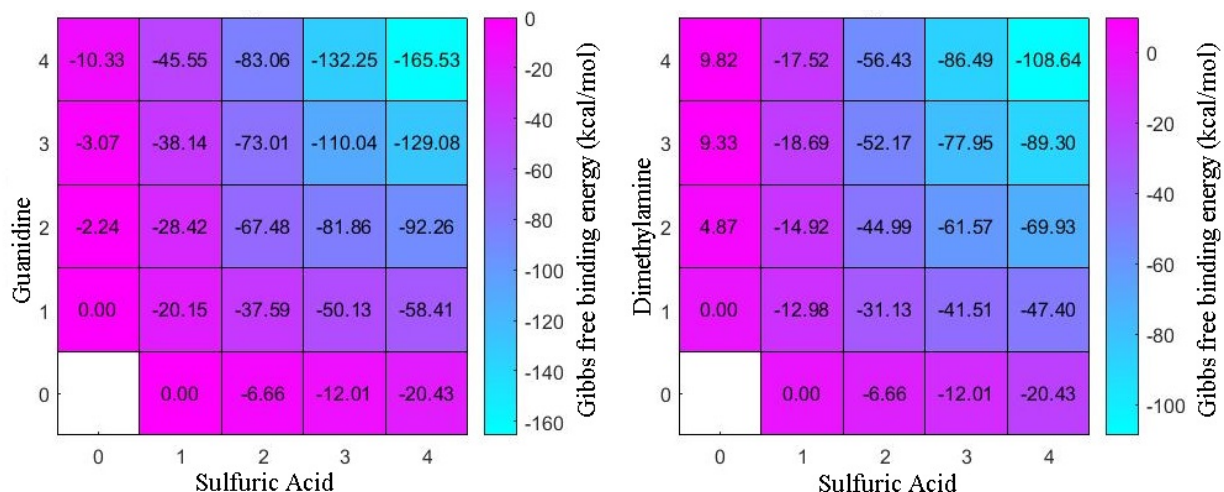


Figure S8: Gibbs free binding energies for guanidine–sulfuric acid (left) and dimethylamine–sulfuric acid (right) clusters at 298.15 K. Number of sulfuric acid molecules is in x -axis and number of base molecules is in y -axis.

Figure S9 shows the vapor-concentration dependent Gibbs free energies at 298.15 K, $[A]=10^6 \text{ cm}^{-3}$, and $[Base]=1 \text{ ppt}_V$ for guanidine–sulfuric acid and dimethylamine–sulfuric acid clusters.

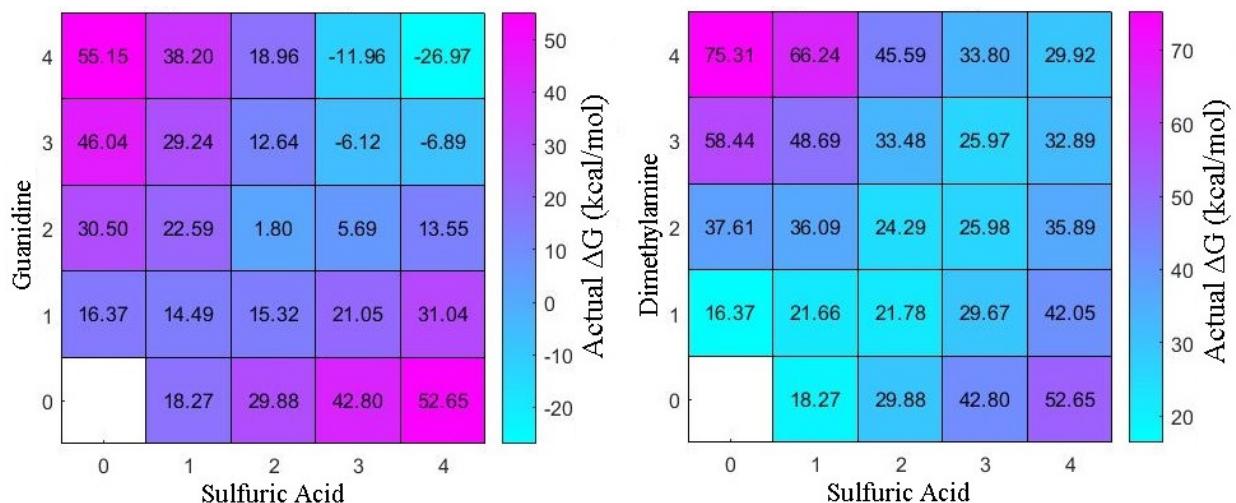


Figure S9: Actual Gibbs free energies for guanidine–sulfuric acid (left) and dimethylamine–sulfuric acid (right) clusters at 298.15 K, $[A]=10^6 \text{ cm}^{-3}$, and $[Base]=1 \text{ ppt}_V$. Number of sulfuric acid molecules is in x -axis and number of base molecules is in y -axis.

Figure S10 shows the total evaporation rates for guanidine–sulfuric acid and dimethylamine–sulfuric acid clusters at 298.15 K.

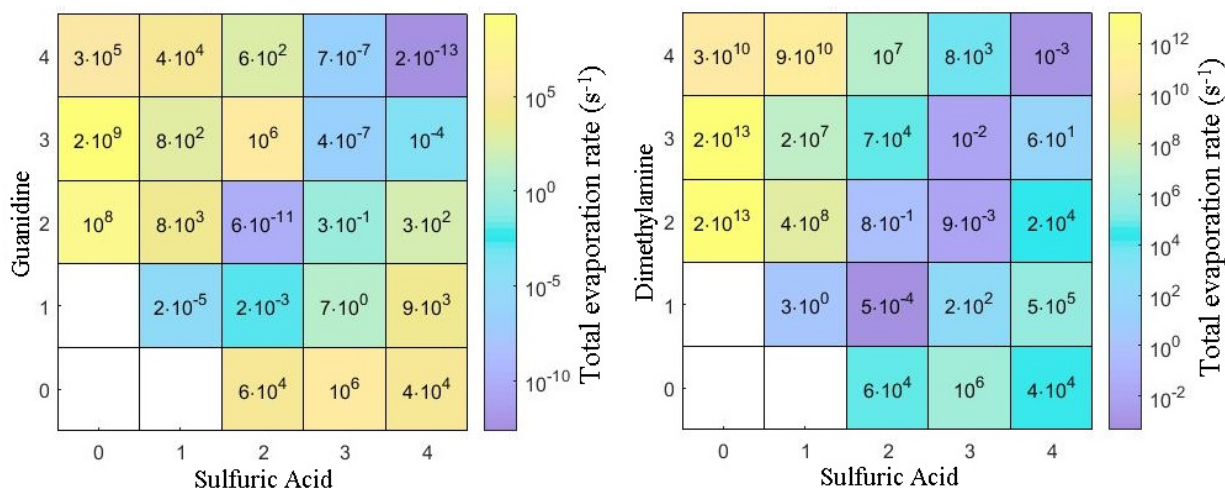


Figure S10: Overall evaporation rates for guanidine–sulfuric acid (left) and dimethylamine–sulfuric acid (right) clusters at 298.15 K. Number of sulfuric acid molecules is in x -axis and number of base molecules is in y -axis.

Figure S11 shows that the steady-state dimethylamine–sulfuric acid cluster distribution at 298.15, when sulfuric acid monomer concentration is 10^6 cm^{-3} , and $[D]=2200 \text{ ppt}_V$. Using as high dimethylamine concentration, heterodimer concentration (1D1A) is equal to the heterodimer concentration (1G1A) at $[G]=1 \text{ ppt}_V$.

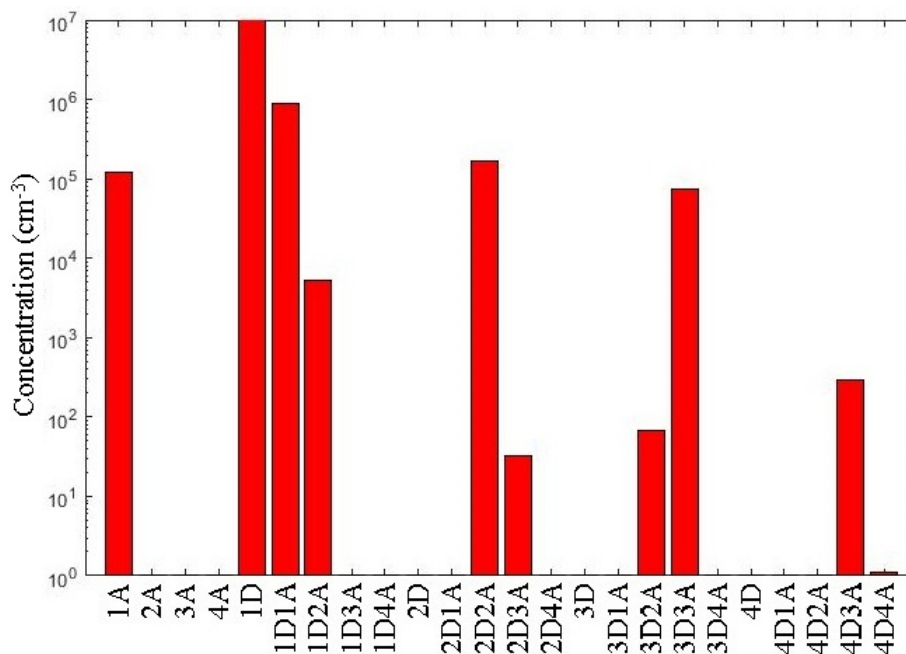


Figure S11: Steady-state distribution of sulfuric acid–dimethylamine clusters at 298.15 K and $[A]=10^6 \text{ cm}^{-3}$, when $[D]=2200 \text{ ppt}_V$.