Electronic Supplementary Material (ESI) for Faraday Discussions

Supplementary information for:
Comparing simulated and experimental molecular cluster distributions

Tinja Olenius, Siegfried Schobesberger, Oona Kupiainen-Määttä, Alessandro Franchin, Heikki Junninen, Ismael K. Ortega, Theo Kurtén, Ville Loukonen, Douglas R. Worsnop, Markku Kulmala and Hanna Vehkamäki

Figures S1-S4 show the modeled and experimental concentrations of negatively charged sulfuric acid mono-, di-, tri-, tetra- and pentamers as a function of sulfuric acid concentration in different conditions. Concentrations of *i*-mers containing only sulfuric acid and total concentrations of pure *i*-mers plus *i*-mers containing ammonia molecules are shown as separate lines and markers. Figure S1 shows the concentrations at 278 K and with ionization rate due to GCR (3 ion pairs s^{-1} cm^{-3}), including the experimental error bars calculated from the standard deviation of the conversion function (note that the same data is presented in Fig. 1 of the main article without the error bars). Figure S2 shows the concentrations at 278 K and with beam-augmented ionization rate (40 ion pairs s^{-1} cm^{-3}, corresponding to pion beam intensity of 60 kHz). Figures S3 and S4 show the concentrations at 292 K and 248 K, respectively, with ionization rate due to GCR. Note the different scales in the y-axes and the different ranges of ammonia mixing ratios in the different figures.

The thermochemical parameters in Table S1 and the dipole moments and the polarizabilities of the neutral clusters in Table S2 are for the minimum-free energy structures of the clusters at 298.15 K. In simulations performed at different temperatures, the Gibbs free energies corresponding to the minimum-free energy structures at the temperature in question were used. For almost all the clusters the minimum-energy configurations at the temperatures used in this study are the same as at 298.15 K. For the clusters that have a different minimum-energy structure at some of the different temperatures, the data of these configurations at 298.15 K are given in the footnotes.

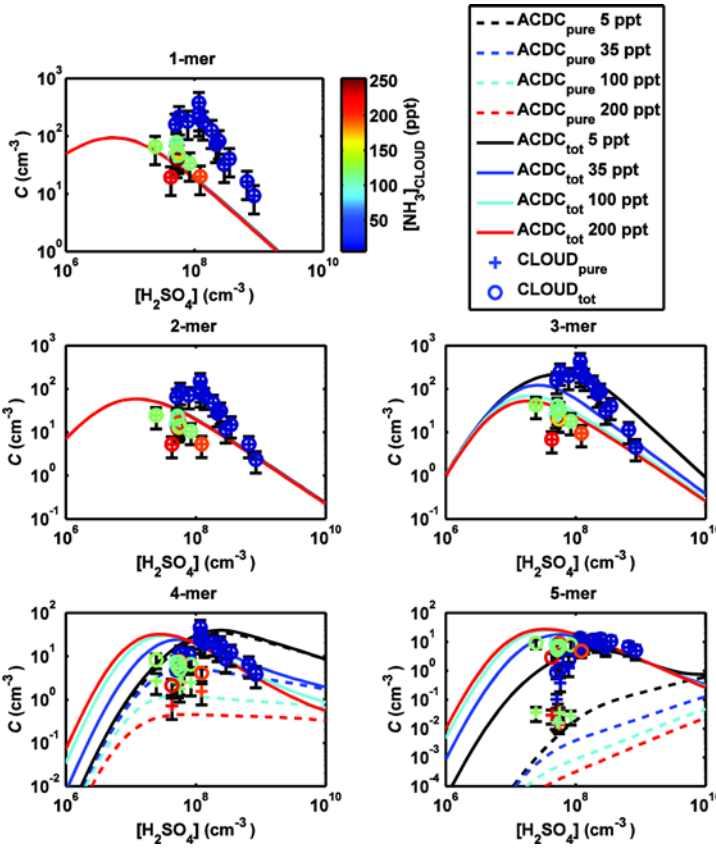

Figure S1: Modeled and experimental concentrations of negatively charged sulfuric acid mono-, di-, tri-, tetra- and pentamers as a function of sulfuric acid concentration at 278 K and with ionization rate due to GCR (3 ion pairs s^{-1} cm^{-3}), including the experimental error bars calculated from the standard deviation of the conversion function.

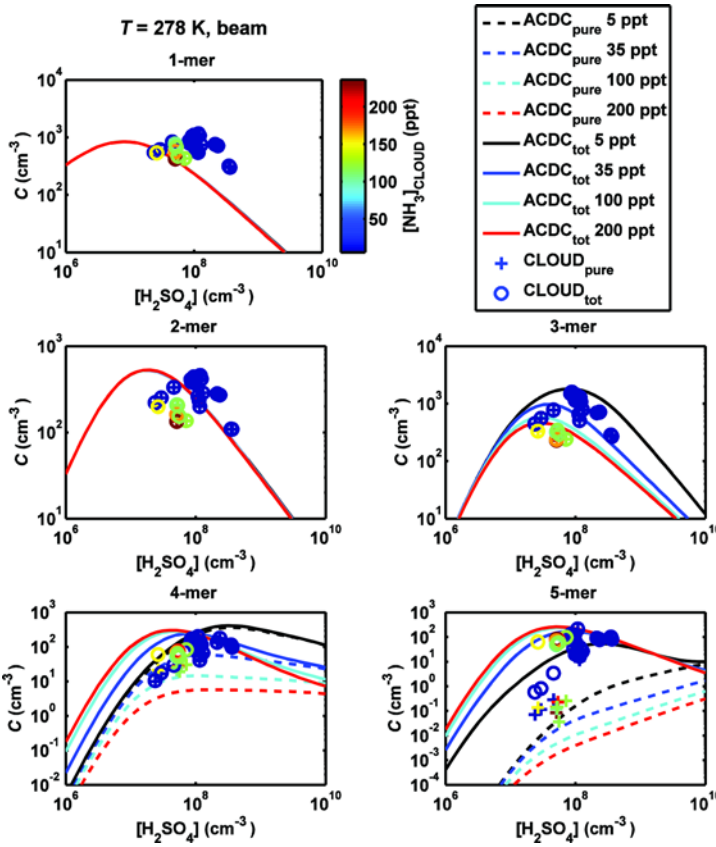

Figure S2: Modeled and experimental concentrations of negatively charged sulfuric acid mono-, di-, tri-, tetra- and pentamers as a function of sulfuric acid concentration at 278 K and with beam-augmented ionization rate (40 ion pairs s^{-1} cm^{-3}).

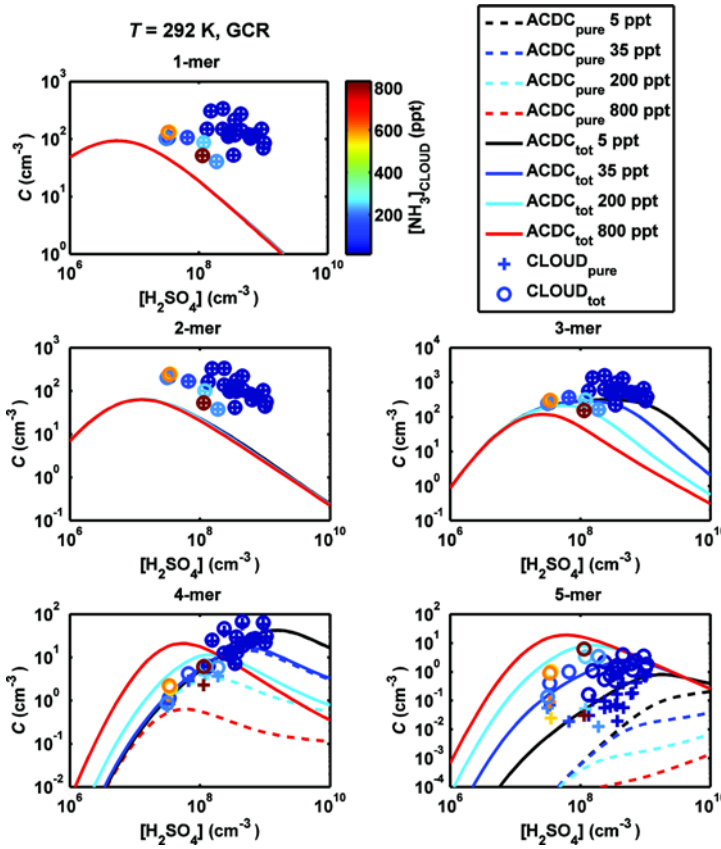

Figure S3: Modeled and experimental concentrations of negatively charged sulfuric acid mono-, di-, tri-, tetra- and pentamers as a function of sulfuric acid concentration at 292 K and with ionization rate due to GCR (3 ion pairs s^{-1} cm^{-3}).

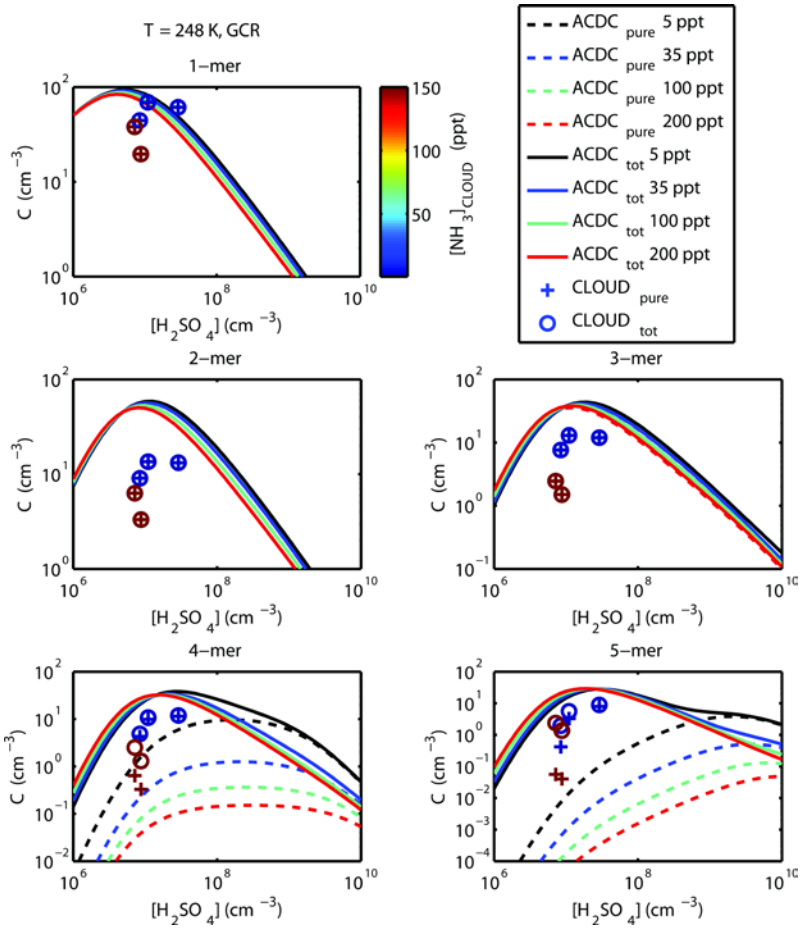

Figure S4: Modeled and experimental concentrations of negatively charged sulfuric acid mono-, di-, tri-, tetra- and pentamers as a function of sulfuric acid concentration at 248 K and with ionization rate due to GCR (3 ion pairs s^{-1} cm^{-3}).

Table S1: Electronic energies (ΔE_{elec}), enthalpies ($\Delta H_{298.15K}$), Gibbs free energies ($\Delta G_{298.15K}$) and entropies ($\Delta S_{298.15K}$) of formation from monomers for all clusters not previously published at this level of theory. All values are in kcal mol^{-1}, at 298.15 K and 1 atm reference pressure.

Cluster	ΔE_{elec} (kcal mol^{-1})	$\Delta H_{298.15K}$ (kcal mol^{-1})	$\Delta G_{298.15K}$ (kcal mol^{-1})	$\Delta S_{298.15K}$ (cal K^{-1}mol^{-1})
a) Electrically neutral clusters				
$(H_2SO_4)_5$	−74.69	−70.10	−29.91	−134.79
$(H_2SO_4)_5 \cdot NH_3$	−114.22	−106.17	−49.19	−191.10
$(H_2SO_4)_5 \cdot (NH_3)_2$	−145.32	−134.98	−67.96	−224.81
$(H_2SO_4)_5 \cdot (NH_3)_3$	−182.09	−168.79	−91.11	−260.55
$(H_2SO_4)_5 \cdot (NH_3)_4$	−207.77	−191.86	−105.08	−291.05
$(H_2SO_4)_4 \cdot (NH_3)_5$	−202.46	−186.47	−98.07	−296.51
$(H_2SO_4)_5 \cdot (NH_3)_5$	−240.28	−221.65	−122.52	−332.49
b) Negatively charged clusters				
$H_2SO_4 \cdot HSO_4^-$	−49.08	−48.32	−34.51	−46.32
$(H_2SO_4)_2 \cdot HSO_4^-$	−78.95	−76.45	−52.13	−81.57
$(H_2SO_4)_3 \cdot HSO_4^-$	−103.92	−100.02	−64.76	−118.26
$(H_2SO_4)_4 \cdot HSO_4^-$	−125.62	−120.92	−74.55	−155.53
$NH_3 \cdot HSO_4^-$	−10.94	−9.10	1.23	−34.67
$H_2SO_4 \cdot NH_3 \cdot HSO_4^-$	−61.93	−58.81	−35.06	−79.64
$(H_2SO_4)_2 \cdot NH_3 \cdot HSO_4^-$	−99.92	−96.71	−59.64	−124.32
$(H_2SO_4)_3 \cdot NH_3 \cdot HSO_4^-$	−129.49	−123.14	−77.39	−153.45
$(H_2SO_4)_4 \cdot NH_3 \cdot HSO_4^-$	−157.25	−149.99	−91.50	−196.17
$(H_2SO_4)_2 \cdot (NH_3)_2 \cdot HSO_4^-$	−119.15	−111.62	−67.32	−148.59
$(H_2SO_4)_3 \cdot (NH_3)_2 \cdot HSO_4^-$	−157.37	−149.17	−90.57	−196.55
$(H_2SO_4)_4 \cdot (NH_3)_2 \cdot HSO_4^-$	−186.48	−177.10	−106.72	−236.06
$(H_2SO_4)_3 \cdot (NH_3)_3 \cdot HSO_4^-$	−180.90	−168.72	−100.60	−228.46
$(H_2SO_4)_4 \cdot (NH_3)_3 \cdot HSO_4^-$	−218.45	−205.58	−124.07	−273.39
$(H_2SO_4)_4 \cdot (NH_3)_4 \cdot HSO_4^-$	−230.51	−216.66	−125.70	−305.06
c) Positively charged clusters				
$(H_2SO_4)_3 \cdot NH_3 \cdot NH_4^+$	−109.29	−103.67	−62.97	−136.50
$(NH_3)_2 \cdot NH_4^+$	−46.54	−43.94	−29.38	−48.81
$H_2SO_4 \cdot (NH_3)_2 \cdot NH_4^+$	−77.48	−73.76	−48.07	−86.14
$(H_2SO_4)_3 \cdot (NH_3)_2 \cdot NH_4^{+\dagger}$	−141.94	−133.67	−84.26	−165.72
$(H_2SO_4)_4 \cdot (NH_3)_2 \cdot NH_4^+$	−166.03	−156.00	−93.64	−209.15
$(H_2SO_4)_2 \cdot (NH_3)_3 \cdot NH_4^+$	−138.34	−130.13	−81.77	−162.20
$(H_2SO_4)_3 \cdot (NH_3)_3 \cdot NH_4^+$	−175.50	−164.31	−103.27	−204.72
$(H_2SO_4)_4 \cdot (NH_3)_3 \cdot NH_4^+$	−199.17	−186.85	−114.94	−241.17
$(H_2SO_4)_3 \cdot (NH_3)_4 \cdot NH_4^+$	−195.05	−182.42	−111.92	−236.46
$(H_2SO_4)_4 \cdot (NH_3)_4 \cdot NH_4^+$	−228.03	−213.20	−129.76	−279.86
$(H_2SO_4)_5 \cdot (NH_3)_4 \cdot NH_4^+$	−255.15	−239.03	−144.13	−318.29

†Different minimum-energy structure at 248 and 278 K, for which ΔE_{elec} = −144.11 kcal mol^{-1}, $\Delta H_{298.15K}$ = −135.73 kcal mol^{-1}, $\Delta G_{298.15K}$ = −84.15 kcal mol^{-1} and $\Delta S_{298.15K}$ = −172.98 cal K^{-1}mol^{-1}.

Table S2: Dipole moments and polarizabilities of all studied clusters at 298.15 K. For molecules we used experimental values, except for the sulfuric acid polarizability, for which only a theoretical value is available, and for clusters we used values calculated for the minimum-free energy clusters (at the corresponding temperature) at the B3LYP/CBSB7 level of theory.

Cluster	Dipole moment (D)	Polarizability (Å^3)
H_2SO_4	2.96[a]	6.2[b]
$(H_2SO_4)_2$	0.002	9.061
$(H_2SO_4)_3$	3.692	13.710
$(H_2SO_4)_4$	3.252	18.759
$(H_2SO_4)_5$	3.358	23.653
NH_3	1.47[c]	2.81[c]
$H_2SO_4 \cdot NH_3$	5.259	6.073
$(H_2SO_4)_2 \cdot NH_3$	9.309	10.733
$(H_2SO_4)_3 \cdot NH_3$	4.580	15.482
$(H_2SO_4)_4 \cdot NH_3$	8.006	20.171
$(H_2SO_4)_5 \cdot NH_3$	4.103	24.822
$(NH_3)_2$	0.000	3.106
$H_2SO_4 \cdot (NH_3)_2$	3.990	7.826
$(H_2SO_4)_2 \cdot (NH_3)_2$	6.762	12.455
$(H_2SO_4)_3 \cdot (NH_3)_2$	10.065	17.121
$(H_2SO_4)_4 \cdot (NH_3)_2$ [†]	9.769	21.828
$(H_2SO_4)_5 \cdot (NH_3)_2$	8.476	26.755
$(NH_3)_3$	0.000	4.964
$H_2SO_4 \cdot (NH_3)_3$	7.430	9.633
$(H_2SO_4)_2 \cdot (NH_3)_3$	4.006	14.184
$(H_2SO_4)_3 \cdot (NH_3)_3$	7.700	18.719
$(H_2SO_4)_4 \cdot (NH_3)_3$	7.163	23.637
$(H_2SO_4)_5 \cdot (NH_3)_3$	5.099	28.112
$(NH_3)_4$	0.000	6.797
$H_2SO_4 \cdot (NH_3)_4$	5.798	11.458
$(H_2SO_4)_2 \cdot (NH_3)_4$	4.208	15.980
$(H_2SO_4)_3 \cdot (NH_3)_4$	2.150	20.630
$(H_2SO_4)_4 \cdot (NH_3)_4$	4.011	25.383
$(H_2SO_4)_5 \cdot (NH_3)_4$	8.192	30.007
$(H_2SO_4)_4 \cdot (NH_3)_5$	1.863	27.075
$(H_2SO_4)_5 \cdot (NH_3)_5$	3.209	31.636

[a]Sedo et al. (ref. 35)
[b]Nadykto and Yu (ref. 36)
[c]CRC Handbook of Chemistry and Physics (ref. 37)
[†]Different minimum-energy structure at 248 K, for which the dipole moment and the polarizability at 298.15 K are 0.749 D and 22.053 Å^3, and $\Delta E_{elec} = -125.08$ kcal mol^{-1}, $\Delta H_{298.15K} = -116.68$ kcal mol^{-1}, $\Delta G_{298.15K} = -60.34$ kcal mol^{-1} and $\Delta S_{298.15K} = -188.95$ cal K^{-1}mol^{-1}.

References

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37 D. Lide, ed., CRC Handbook of Chemistry and Physics, 91th Edition, CRC Press/Taylor and Francis, Boca Raton, FL, 2010.