Supplementary material for "The effect of H_2SO_4 – amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid" by Theo Kurtén, Tuukka Petäjä, James Smith, Ismael Kenneth Ortega, Mikko Sipilä, Heikki Junninen, Mikael Ehn, Hanna Vehkamäki, Lee Mauldin, Douglas R. Worsnop and Markku Kulmala.

Thermodynamic parameters for all studied species at the PW91/6-311++G(3df,3pd) level are given in Table S1. G3 and G3MP2 data are given in Tables S2 and S3, respectively.

species	E_{elec}	H	G
NO_3^-	-280.420276	-280.402790	-280.430767
HNO_3	-280.947455	-280.917532	-280.947884
$NO_3^-(HNO_3)$	-561.417333	-561.371343	-561.416255
$(HNO_3)_2$	-561.910671	-561.848793	-561.893823
$NO_3^-(HNO_3)_2$	-842.397501	-842.318061	-842.379618
$(HNO_3)_3$	-842.865390	-842.771590	-842.832897
HSO_4^-	-699.831804	-699.799930	-699.834776
H_2SO_4	-700.338253	-700.294267	-700.328228
$(HSO_4^-)(HNO_3)$	-980.830960	-980.768576	-980.815010
$(HSO_4^-)(HNO_3)_2$	-1261.804765	-1261.711921	-1261.775388
H_2O	-76.436455	-76.411861	-76.433304
$H_2SO_4(H_2O)$	-776.795786	-776.724888	-776.765904
$H_2SO_4(H_2O)_2$	-853.254271	-853.156860	-853.203983
$H_2SO_4(H_2O)_3$	-929.711331	-929.586781	-929.640283
$(HSO_4^-)(HNO_3)(H_2O)$	-1057.283241	-1057.194325	-1057.250199
$(HSO_4^-)(HNO_3)(H_2O)_2$	-1133.737286	-1133.621237	-1133.684731
$(HSO_4^-)(HNO_3)(H_2O)_3$	-1210.203388	-1210.059382	-1210.120702
$(HSO_4^-)(HNO_3)_2(H_2O)$	-1338.262855	-1338.142919	-1338.212507
$(HSO_4^-)(HNO_3)_2(H_2O)_2$	-1414.722814	-1414.576196	-1414.649874
$(HSO_4^-)(HNO_3)_2(H_2O)_3$	-1491.176766	-1491.003270	-1491.084545
NH_3	-56.558822	-56.521537	-56.543402
$(CH_3)_2NH$	-135.148750	-135.053548	-135.084498
$(HSO_4^-)(NH_3)$	-756.405597	-756.333888	-756.376106
$(H_2SO_4)(NH_3)$	-756.925278	-756.842536	-756.884778
$(HSO_4^-)(NH_3)(HNO_3)$	-1037.405892	-1037.302665	-1037.355868
$(HSO_4^-)(NH_3)(HNO_3)_2$	-1318.390912	-1318.257872	-1318.323259
$(HSO_4^-)(CH_3)_2NH$	-834.999365	-834.870131	-834.918231
$(H_2SO_4)[(CH_3)_2NH]$	-835.524550	-835.381956	-835.431597

$(HSO_4^-)[(CH_3)_2NH](HNO_3)$	-1116.000751	-1115.838908	-1115.900139
$(HSO_4^-)[(CH_3)_2NH](HNO_3)_2$	-1396.985572	-1396.79309	-1396.866042
$(HSO_4^-)(H_2SO_4)$	-1400.244186	-1400.168086	-1400.215030
$(H_2SO_4)_2$	-1400.704959	-1400.615703	-1400.667238
$(HSO_4^-)(H_2SO_4)[(CH_3)_2NH]$	-1535.421066	-1535.245225	-1535.305992
$(H_2SO_4)_2[(CH_3)_2NH]$	-1535.909977	-1535.720845	-1535.784036
$(HSO_4^-)(H_2SO_4)[(CH_3)_2NH]_2$	-1670.585350	-1670.313928	-1670.387476
$(H_2SO_4)_2[(CH_3)_2NH]_2$	-1671.095858	-1670.806839	-1670.883484

Table S1. Electronic energies (E_{elec}), enthalpies (H) and Gibbs free energies (G) of all studied species, at the PW91/6-311++G(3df,3pd) level. For clusters with multiple structural isomers, only data for the isomer with the lowest Gibbs free energy is shown. Enthalpies and Gibbs free energies have been computed at T = 298.15 K and 1 atm reference pressure. All values in Hartrees (the atomic unit for energy; 1 Hartree = 627.509 kcal/mol). Electronic energies do not contain zero-point energy contributions.

species	H	G
H_2O	-76.378259	-76.399635
H_2SO_4	-699.988961	-700.022776
NH_3	-56.503213	-56.526055
$(CH_3)_2NH$	-135.015696	-135.046643
$(H_2SO_4)(H_2O)$	-776.385280	-776.427458
$(H_2SO_4)(H_2O)_2$	-852.780433	-852.830029
$(H_2SO_4)(H_2O)_3$	-929.176102	-929.233203
$(H_2SO_4)(NH_3)$	-756.516468	-756.559844
$(H_2SO_4)(NH_3)(H_2O)$	-832.910546	-832.959547
$(H_2SO_4)(NH_3)(H_2O)_2$	-909.311883	-909.367567
$(H_2SO_4)[(CH_3)_2NH]$	-835.041622	-835.093012
$(H_2SO_4)[(CH_3)_2NH](H_2O)$	-911.441107	-911.498582
$(H_2SO_4)[(CH_3)_2NH](H_2O)_2$	-987.837274	-987.900836

Table S2. Enthalpies (H) and Gibbs free energies (G) of $(H_2SO_4)(H_2O)_{0...2}(X)$ and $(H_2SO_4)(H_2O)_3$ clusters, with X = NH_3, $(CH_3)_2NH$, at the G3 level. Enthalpies and Gibbs free energies have been computed at T = 298.15 K and 1 atm reference pressure. All values in Hartrees (the atomic unit for energy; 1 Hartree = 627.509 kcal/mol). Note that free energies at slightly different temperatures can be estimated by calculating S = (H - G)/298.15 K, and then recomputing G = H – T*S at a new T. This approximation is valid provided that T is not too far from 298.15 K.

species	H	G
NO_3^-	-280.063754	-280.091562
HNO_3	-280.579201	-280.609230
(H_2SO_4)	-699.524406	-699.558221
(HSO_4^-)	-699.029526	-699.064038
$NO_3^-(HNO_3)$	-560.687769	-560.734305

$(HSO_4^-)(HNO_3)$	-979.653806	-979.700977
$(HSO_4^-)(HNO_3)_2$	-1260.262689	-1260.327346
NH_3	-56.466333	-56.488137
$(H_2SO_4)(NH_3)$	-756.013775	-756.057151
$(HSO_4^-)(NH_3)$	-755.509557	-755.551131
$(HSO_4^-)(NH_3)(HNO_3)$	-1036.135861	-1036.189577
$(HSO_4^-)(NH_3)(HNO_3)_2$	-1316.752239	-1316.819676
$(CH_3)_2NH$	-134.904739	-134.935686
$(H_2SO_4)[(CH_3)_2NH]$	-834.464087	-834.515475
$(HSO_4^-)(CH_3)_2NH$	-833.952423	-834.001544
$(HSO_4^-)[(CH_3)_2NH](HNO_3)$	-1114.585752	-1114.648007
$(HSO_4^-)[(CH_3)_2NH](HNO_3)_2$	-1395.202982	-1395.278896
$(HSO_4^-)(H_2SO_4)$	-1398.628016	-1398.675796
$(H_2SO_4)_2$	-1399.076068	-1399.128228
$(HSO_4^-)(H_2SO_4)[(CH_3)_2NH]$	-1533.563251	-1533.625343
$(H_2SO_4)_2[(CH_3)_2NH]$	-1534.039427	-1534.104712
$(HSO_4^-)(H_2SO_4)[(CH_3)_2NH]_2$	-1668.488777	-1668.563146
$(H_2SO_4)_2[(CH_3)_2NH]_2$	-1668.990724	-1669.070569

Table S3. Enthalpies (H) and Gibbs free energies (G) of selected clusters, at the G3MP2 level. Enthalpies and Gibbs free energies have been computed at T = 298.15 K and 1 atm reference pressure. All values in Hartrees (the atomic unit for energy; 1 Hartree = 627.509 kcal/mol).

Neutral nitric acid clusters (Hart and Thakkar, 2005; Dimitrova, 2005), neutral and charged sulfuric acid – water (Nadykto et al., 2007, 2008), sulfuric acid - ammonia (Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2007, 2008) and sulfuric acid – dimethylamine (Kurtén et al., 2008; Loukonen et al., 2010) clusters have been studied extensively, and the minimum free-energy structures found in this study are qualitatively identical to those presented previously. To our knowledge, no previous studies of charged or neutral sulfuric acid – nitric acid – water, sulfuric acid – nitric acid – ammonia or sulfuric acid – nitric acid – dimethylamine clusters have been published. The structures of the lowest free – energy isomers of the clusters in this study that have not (to our knowledge) been presented before are given in Figures S1 and S2. (Figure created using Molden; Schaftenaar and Noordik, 2000).

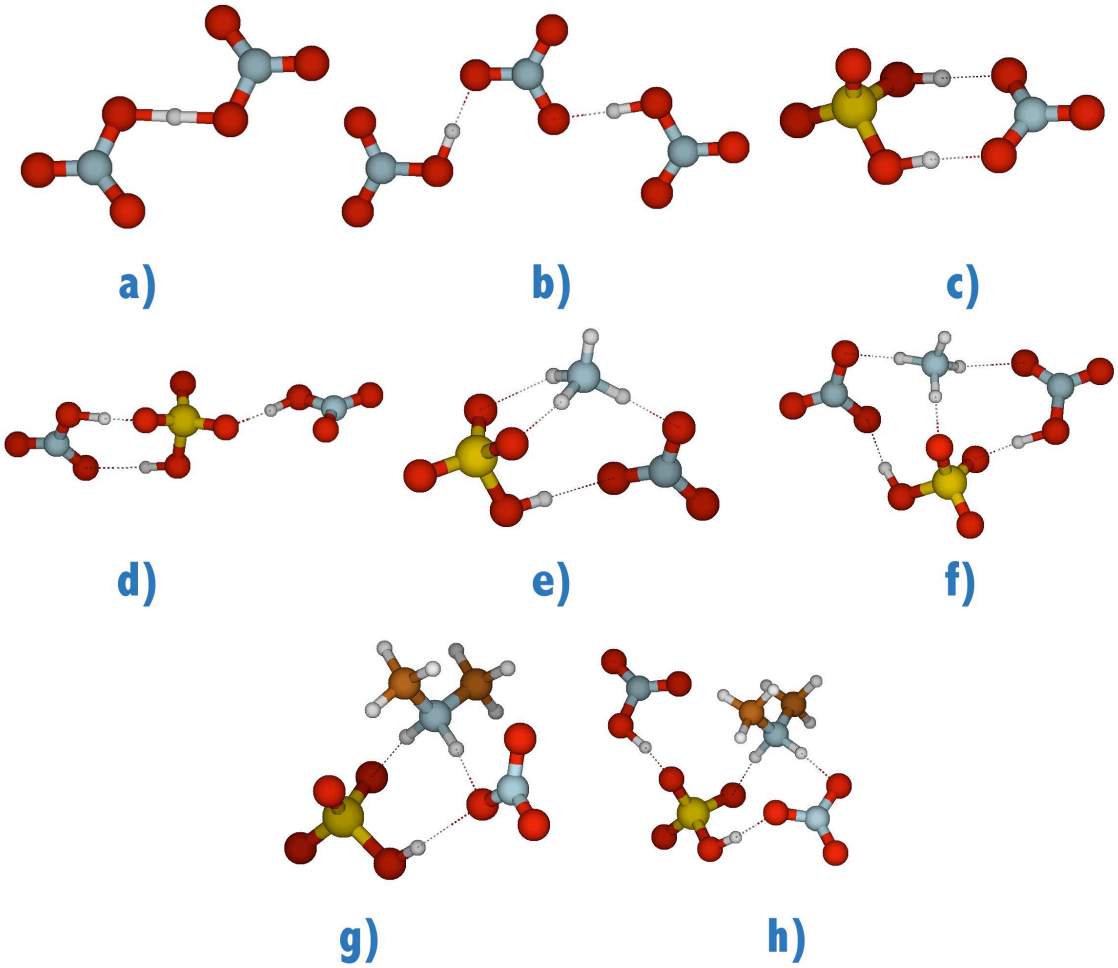

Figure S1: Minimum – free energy (at 298.15 K) structures, at the PW91/6-311++G(3df,3pd) level, for: a)(NO_3^-)(HNO_3), b)(NO_3^-)(HNO_3)$_2$, c)(HSO_4^-)(HNO_3), d)(HSO_4^-)(HNO_3)$_2$, e)(HSO_4^-)(NH_3)(HNO_3), f)(HSO_4^-)(NH_3)(HNO_3)$_2$, g)(HSO_4^-)(HNO_3)(CH_3)$_2$NH, h)(HSO_4^-)(HNO_3)$_2$(CH_3)$_2$NH. Color coding: yellow = sulfur, red = oxygen, blue = nitrogen, brown = carbon and white = hydrogen. Hydrogen bonds are indicated with dashed lines.

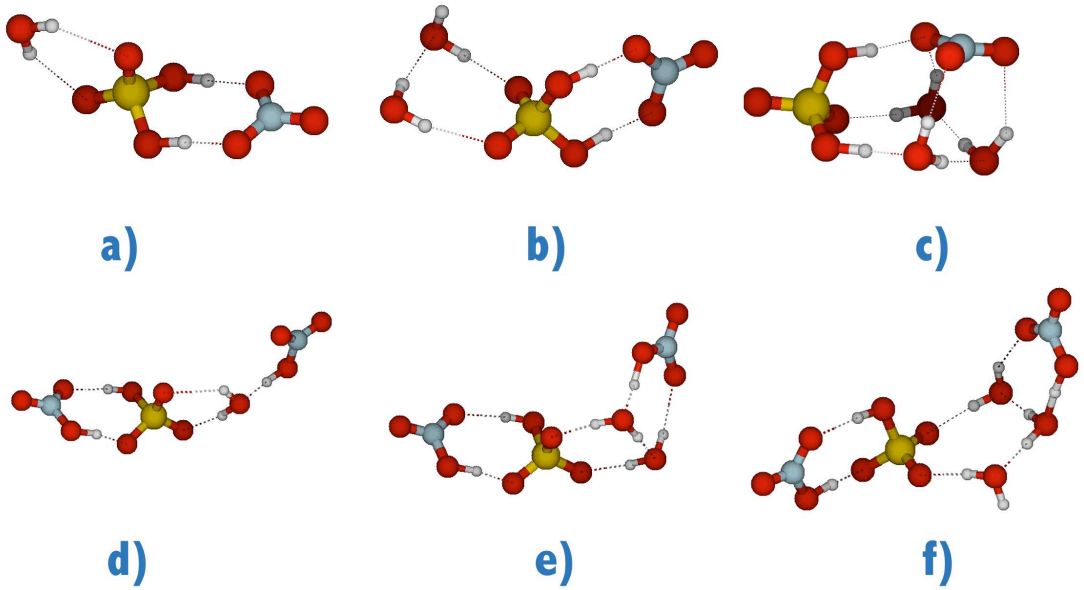

Figure S2: Minimum – free energy (at 298.15 K) structures, at the PW91/6-311++G(3df,3pd) level, for: a) $(HSO_4^-)(HNO_3)(H_2O)$, b) $(HSO_4^-)(HNO_3)(H_2O)_2$, c) $(HSO_4^-)(HNO_3)(H_2O)_3$, d) $(HSO_4^-)(HNO_3)_2(H_2O)$, e) $(HSO_4^-)(HNO_3)_2(H_2O)_2$, f) $(HSO_4^-)(HNO_3)_2(H_2O)_3$. Color coding: yellow = sulfur, red = oxygen, blue = nitrogen, brown = carbon and white = hydrogen. Hydrogen bonds are indicated with dashed lines.

Curiously, the lowest free-energy isomer for the $(HSO_4^-)(HNO_3)$ cluster, with or without hydration, is actually predicted to have the structure $(H_2SO_4)(NO_3^-)$, i.e. the proton prefers to stay with the sulfuric acid molecule. To test whether this was an artefact of the PW91 method, we reoptimized the structure at the RI-MP2/aug-cc-pV(T+d)Z level using the Turbomole 6.0 program (Ahlrichs et al., 1989), but the same pattern persisted. Addition of one nitric acid molecule (as shown in Figure S1) leads to the pattern expected from vacuum proton affinity or bulk pKa values; the proton jumps to the weaker acid HNO_3. The clusters containing base molecules all have one proton transferred to the base, yielding a ion triplet of HSO_4^-, NO_3^- and the ammonium / dimethylammonium cation. (Multiple input guesses without this proton transfer were constructed, but all either reverted to the structures displayed here, or led to local minima several kcal/mol above them.)

References given in the supplementary material:

Ahlrichs, R., Bär, M., Häser, M., Horn, H. and Kölmel, C.: Electronic structure calculations on workstation computers: The program system Turbomole, Chem. Phys. Lett., 162, 165-169, 1989.

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Schaftenaar, G., and Noordik, J. J.: Molden: a pre- and post-processing program for molecular and electronic structures, J. Comput.-Aided Mol. Design, 14, 123-134, 2000.