Supplemental Information

Effect of hydration and base contaminants on sulfuric acid diffusion measurement: a computational study

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This supplemental information contains the following:

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Including larger hydrates in the fit applied to the experimental data

Different boundary conditions tested in the kinetic simulations

Determining the measurable k_{wall} from the simulated cluster concentrations

Supplemental tables:

Table S2: Electronic energies and thermochemical data for clusters not previously published at the B3LYP/CBSB7//RICC2/aug-cc-pV(T+d)Z level of theory, corresponding to the most stable structure at 298.15 K.

Tables S3–S5: Gibbs free energies of formation from monomers and equilibrium constants for sulfuric acid hydrates $\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_n$ calculated with different quantum chemical methods by Kurtén *et al.* (2007), Temelso *et al.* (2012) and Nadykto and Yu (2007).

Table S6: Diffusion coefficients of the molecules and clusters included in the dynamic simulations, calculated according to the Enskog–Chapman theory at 298.15 K.

Table S7: Cartesian coordinates for clusters not previously published at the B3LYP/CBSB7//RICC2/aug-cc-pV(T+d)Z level of theory, corresponding to the most stable structure at 298.15 K.

Details concerning the fitting procedure

The fits to the theoretical diffusion coefficient as a function of relative humidity in Figures 2–5 of the article represent the best goodness of fit achieved with the non-linear least squares procedure in terms of the sum of squares due to error (SSE) and the coefficient of multiple determination (R^2). SSE is the sum of the squares of the differences between the values predicted by the fit f_i and the original data values y_i

$$SSE = \sum_{i=1}^n (y_i - f_i)^2, \quad (S1)$$

and R^2 is expressed as

$$R^2 = 1 - \frac{SSE}{SST}, \quad (S2)$$

where SST is the sum of squares about the mean

$$SST = \sum_{i=1}^n (y_i - \bar{y})^2. \quad (S3)$$

However, in some cases the fitted function (Eq. (2) of the article), even if it yields the best achieved values for the goodness-of-fit statistics, does not reproduce the shape of the original data curve, as a function of the form of Eq. (2) is simply not suited for the data. For instance, in the case of the MP2/aug-cc-pV(D+d)Z// $\Delta E_{0,3}$ -step data with hydration by more than two water molecules enabled (Figure 2), the function could not be perfectly fitted to the data.

Including larger hydrates in the fit applied to the experimental data

According to the quantum chemical data used in this work, hydrates containing up to four water molecules affect the effective diffusion coefficient of the H_2SO_4 molecule at the studied temperature and RH range (Section 3.1). Therefore we extended Eq. (2) to include hydrates with up to four waters, and applied the extended fit on the original experimental data (Hanson and Eisele 2000) to study if including the larger hydrates in the fit affects the fitted K_1 and K_2 values. Figure S1 shows the fits on the experimental data including hydrates containing up to 1) $n_{\max} = 2$, and 2) $n_{\max} = 4$ water molecules. The K_n values obtained from fits 1 and 2 are presented in Table S1. For both fits two sets of parameters, obtained with slightly different initial guesses for the parameter values, are presented with their goodness-of-fit statistics, that are the sum of squares due to error (SSE) and the coefficient of multiple determination (R^2). Different initial guesses were tested because the K_n are not known *a priori*, and the parameter values obtained from the fit may depend on the guesses. Fit 2a was obtained by setting the initial value for K_3 to be higher than that for K_2 , whereas for fit 2b, the initial value for K_3 was set to be lower than that for K_2 . As can be seen from Table S1, these different guesses lead to different K_n values with essentially the same goodness of fit. Based on fits 2a and 2b, the experimental data can be explained by hydrates with up to only two water molecules in the case that the larger hydrates have relatively lower K values. On the other hand, the presence of larger hydrates cannot be ruled out, and omitting them in the fit may skew the values obtained for K_1 and K_2 in the case that the K values of the larger hydrates are relatively higher or comparable to those of the smaller hydrates.

Figure S1: Different fits of the effective diffusion coefficient pD_{eff} (Eq. (2)) to the experimental data, with the number of water molecules in the largest hydrate included in the fit being $n_{\text{max}} = 2$ (top panel), and $n_{\text{max}} = 4$ (bottom panel). Note that in the top panel, the lines of the two fits 1a and 1b fall on top of each other, although their parameter values are slightly different.

Table S1: Equilibrium constants K_n obtained from the fits to the experimental data (Figure S1), including hydrates containing up to $n_{\max}$ water molecules. 95% confidence bounds are stated in the parenthesis.

$n_{\max}$	Fit	Goodness of fit (SSE, R^2)	K_1	K_2	K_3	K_4
2	1a	1.2986×10^{-4} , 0.9414	0.1296 (0.06131, 0.1980)	0.02821 (0.01753, 0.03888)	—	—
	1b	1.2986×10^{-4} , 0.9414	0.1305 (0.06175, 0.1992)	0.02822 (0.01753, 0.0389)	—	—
4	2a	1.4736×10^{-4} , 0.9336	0.1998 (0.01743, 0.3821)	0.005313 (0.0, 0.04199)	0.03662 (0.0, 0.4389)	0.0003469 (0.0, 0.03753)
	2b	1.2999×10^{-4} , 0.9414	0.1352 (0.005395, 0.2651)	0.02649 (0.0, 0.08487)	0.0006322 (0.0, 0.04506)	3.149×10^{-5} (0.0, 0.5320)

Different boundary conditions tested in the kinetic simulations

As explained in Sect. 2.4 in the article, clusters were not allowed to grow out of the simulated system by disabling collisions leading to clusters outside the system. This is justifiable if the clusters that form in the collisions leading out can be assumed to instantaneously evaporate back to their initial parts. However, in the case of a H_2SO_4 -base system, the evaporation pathways may be different. For example, when two $\text{H}_2\text{SO}_4 \cdot \text{DMA}$ clusters collide, the resulting $(\text{H}_2\text{SO}_4)_2 \cdot (\text{DMA})_2$ cluster is more likely to decay by evaporating successively an acid and a base molecule, instead of fragmenting back into two $\text{H}_2\text{SO}_4 \cdot \text{DMA}$ pairs (Ortega *et al.* 2012). Therefore we performed additional ACDC simulations to ensure that the results are not significantly altered by the choice of boundary conditions.

For the systems containing clusters with up to one acid and one base molecule, the outgrowing clusters were brought back to the simulation system by evaporating monomers out of them, as explained in the example above. For the system containing clusters with up to two H_2SO_4 and two DMA molecules, we used a different approach: the outgrowing clusters may be stable enough to not evaporate back into the system at all, as their evaporation rates are very low (Ortega *et al.* 2012). Thus the test simulations were performed by letting clusters with a favorable composition, in other words, a favorable acid:base ratio, grow out of the system. Based on our previous studies, the main growth pathway out of the simulation system containing clusters with up to two H_2SO_4 and two DMA molecules is via the $(\text{H}_2\text{SO}_4)_3 \cdot (\text{DMA})_3$ cluster (Olenius *et al.* (2013) and Kupiainen-Määttä *et al.* (2013)). Therefore clusters containing at least three H_2SO_4 and three DMA molecules were allowed to grow out. Outgrowing clusters that did not satisfy this boundary condition were brought back into the system by evaporating monomers out of them (this procedure has been previously described by Olenius *et al.* (2013) and Kupiainen-Määttä *et al.* (2013)). The results of these additional test simulations did not in practice differ

from those presented in the article, indicating that in the studied conditions, the cluster distributions are not significantly affected by the choice of boundary conditions. The shapes of the (RH, pD_{eff}) -curves did not change, and the absolute pD_{eff} values obtained from the test simulations differed at maximum by approximately $0.001 \text{ atm cm}^{-2} \text{ s}^{-1}$ from those presented in the article.

Determining the measurable k_{wall} from the simulated cluster concentrations

The procedure of obtaining the measurable wall loss coefficient k_{wall} , and consequently the effective diffusion coefficient pD_{eff} from the kinetic simulations is explained in Section 2.4.2. Figure S2 presents the simulated time development of the molecule and cluster concentrations in representative conditions, demonstrating in more detail how k_{wall} is obtained. The H_2SO_4 concentration detected by SCIMS, defined as the sum of the H_2SO_4 and $\text{H}_2\text{SO}_4 \cdot \text{base}$ concentrations (including both dry and hydrated clusters; turquoise line in Figure S2), is recorded at four different residence times (dashed vertical lines in Figure S2) as was done in the experiment by Hanson and Eisele (2000). k_{wall} is deduced from the recorded concentrations using the method of the experimental study: the concentration detected by SCIMS is assumed to decay exponentially, and thus k_{wall} is obtained as the slope of a linear fit to the natural logarithm of the detected concentration $\ln([\text{H}_2\text{SO}_4] + [\text{H}_2\text{SO}_4 \cdot \text{base}])$ as a function of time.

Figure S2: Simulated time development of the molecule and cluster concentrations (including both dry and hydrated clusters) in the H_2SO_4 -DMA system in representative conditions. The times at which the H_2SO_4 concentration detected by SCIMS, that is the sum of the H_2SO_4 and $\text{H}_2\text{SO}_4 \cdot \text{DMA}$ concentrations (turquoise line), is recorded are shown as dashed vertical lines.

To provide more insights into the dynamics of the simulated system, the loss rates $k_{\text{wall},i}$ for each molecule or cluster, calculated as the weighted average over the hydrate distribution of the species, and the loss rate of the sum of molecules and clusters that are detected by SCIMS $k_{\text{wall,SCIMS}}$, are presented in Figure S3. $k_{\text{wall,SCIMS}}$ is calculated as the weighted average of the loss rates $k_{\text{wall},i}$ of the species contributing to the SCIMS signal, and thus depends on the relative concentrations of the H_2SO_4 and $\text{H}_2\text{SO}_4\cdot\text{base}$ molecules and clusters. We emphasize that $k_{\text{wall,SCIMS}}$ is presented here only to demonstrate the behavior of the “actual” effective loss rate. The “measurable” effective wall loss coefficient k_{wall} is still determined as explained above in order to obtain more realistic results by treating the simulation data in the same way as the experimental data was treated. Equilibrium hydrate distributions of the H_2SO_4 and DMA molecules and the $\text{H}_2\text{SO}_4\cdot\text{DMA}$ dimer corresponding to the conditions of Figures S2 and S3 are shown in Figure S4.

Figure S3: Wall loss rates for individual molecules and clusters (including both dry and hydrated clusters) in the H_2SO_4 -DMA system and wall loss rate of the sum of molecules and clusters detected by SCIMS as a function of time in representative conditions. Dashed vertical lines correspond to the times at which the H_2SO_4 concentration detected by SCIMS is recorded.

Figure S4: Equilibrium hydrate distributions of the H_2SO_4 and DMA molecules and the $\text{H}_2\text{SO}_4 \cdot \text{DMA}$ dimer corresponding to the conditions of Figures S2 and S3.

Supplemental tables

Table S2: Electronic energies (ΔE_{elec}), enthalpies ($\Delta H_{298.15\text{K}}$), Gibbs free energies ($\Delta G_{298.15\text{K}}$) and entropies ($\Delta S_{298.15\text{K}}$) of formation from monomers and equilibrium constants of hydration ($K_{n,298.15\text{K}}$, related to $\Delta G_{298.15\text{K}}$ according to Eq. (4)) for clusters not previously published at the B3LYP/CBSB7//RICC2/aug-cc-pV(T+d)Z level of theory, corresponding to the most stable structure at 298.15 K. All values are at 298.15 K and 1 atm reference pressure.

Cluster	ΔE_{elec} (kcal mol ⁻¹)	$\Delta H_{298.15\text{K}}$ (kcal mol ⁻¹)	$\Delta G_{298.15\text{K}}$ (kcal mol ⁻¹)	$\Delta S_{298.15\text{K}}$ (cal K ⁻¹ mol ⁻¹)	$K_{n,298.15\text{K}}$
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}^a$	-13.13	-11.45	-2.60	-29.69	80.13
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_2^a$	-25.78	-22.49	-4.40	-60.69	20.82
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_3^a$	-38.70	-33.49	-5.83	-92.76	11.33
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_4^a$	-51.66	-44.78	-7.05	-126.55	7.79
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_5^a$	-63.03	-54.56	-6.81	-160.16	0.66
$(\text{H}_2\text{SO}_4)_2 \cdot \text{H}_2\text{O}^a$	-34.04	-31.59	-11.24	-68.26	288.67
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_2^a$	-48.02	-43.87	-14.26	-99.30	164.36
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_3^a$	-63.47	-57.24	-16.49	-136.68	42.88
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_4^a$	-79.13	-71.58	-18.86	-176.84	54.18
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_5^a$	-92.61	-82.78	-20.63	-208.44	19.94

$(\text{CH}_3)_2\text{NH}\cdot\text{H}_2\text{O}^b$	-8.18	-6.20	1.92	-27.26	0.039
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_2\text{NH}\cdot\text{H}_2\text{O}^a$	-42.47	-37.89	-18.29	-65.76	130.40
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_2^a$	-56.79	-50.11	-20.66	-98.78	54.75
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_3^a$	-69.20	-60.40	-20.42	-134.12	0.67
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_4^a$	-81.25	-70.78	-21.21	-166.24	3.83
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_5^a$	-92.69	-80.62	-21.13	-199.52	0.87
$(\text{H}_2\text{SO}_4)_2\cdot(\text{CH}_3)_2\text{NH}\cdot\text{H}_2\text{O}^a$	-74.86	-68.96	-37.35	-106.03	65.08
$(\text{H}_2\text{SO}_4)_2\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_2^a$	-86.20	-78.63	-37.74	-137.15	1.92
$(\text{H}_2\text{SO}_4)_2\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_3^a$	-102.59	-93.14	-40.57	-176.35	118.59
$(\text{H}_2\text{SO}_4)_2\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_4^a$	-115.55	-104.35	-41.13	-212.03	2.62
$(\text{H}_2\text{SO}_4)_2\cdot(\text{CH}_3)_2\text{NH}\cdot(\text{H}_2\text{O})_5^a$	-125.72	-112.83	-40.90	-241.28	0.67
$(\text{H}_2\text{SO}_4)_2\cdot((\text{CH}_3)_2\text{NH})_2\cdot\text{H}_2\text{O}^a$	-106.10	-96.66	-52.90	-146.76	0.10
$(\text{H}_2\text{SO}_4)_2\cdot((\text{CH}_3)_2\text{NH})_2\cdot(\text{H}_2\text{O})_2^a$	-118.30	-107.12	-54.76	-175.59	23.11
$(\text{H}_2\text{SO}_4)_2\cdot((\text{CH}_3)_2\text{NH})_2\cdot(\text{H}_2\text{O})_3^a$	-130.03	-116.60	-53.63	-211.20	0.15
$(\text{H}_2\text{SO}_4)_2\cdot((\text{CH}_3)_2\text{NH})_2\cdot(\text{H}_2\text{O})_4^a$	-145.52	-130.05	-55.59	-249.73	27.33
$(\text{H}_2\text{SO}_4)_2\cdot((\text{CH}_3)_2\text{NH})_2\cdot(\text{H}_2\text{O})_5^a$	-154.96	-138.03	-56.03	-275.03	2.10
$\text{NH}_3\cdot\text{H}_2\text{O}$	-6.74	-4.94	0.35	-17.73	0.56
$\text{NH}_3\cdot(\text{H}_2\text{O})_2$	-16.01	-12.08	4.80	-56.63	0.00054
$\text{NH}_3\cdot(\text{H}_2\text{O})_3$	-27.22	-21.45	4.83	-88.16	0.96
$\text{NH}_3\cdot(\text{H}_2\text{O})_4$	-36.42	-28.93	5.80	-116.49	0.19
$\text{H}_2\text{SO}_4\cdot\text{NH}_3\cdot\text{H}_2\text{O}^a$	-30.63	-27.41	-9.28	-60.83	16.69
$\text{H}_2\text{SO}_4\cdot\text{NH}_3\cdot(\text{H}_2\text{O})_2^a$	-47.53	-41.65	-13.54	-94.26	1341.55
$\text{H}_2\text{SO}_4\cdot\text{NH}_3\cdot(\text{H}_2\text{O})_3^a$	-59.40	-51.67	-14.77	-123.76	7.89
$\text{H}_2\text{SO}_4\cdot\text{NH}_3\cdot(\text{H}_2\text{O})_4^a$	-71.09	-61.32	-14.70	-156.39	0.89

$\text{H}_2\text{SO}_4\cdot\text{NH}_3\cdot(\text{H}_2\text{O})_5^a$	−84.03	−72.31	−15.83	−189.42	6.82
$\text{CH}_3\text{NH}_2\cdot\text{H}_2\text{O}$	−7.34	−5.40	2.55	−26.66	0.014
$\text{CH}_3\text{NH}_2\cdot(\text{H}_2\text{O})_2$	−17.03	−13.15	4.19	−58.15	0.063
$\text{H}_2\text{SO}_4\cdot\text{CH}_3\text{NH}_2$	−22.83	−20.82	−11.46	−31.36	−
$\text{H}_2\text{SO}_4\cdot\text{CH}_3\text{NH}_2\cdot\text{H}_2\text{O}$	−38.41	−34.10	−13.74	−68.29	46.49
$\text{H}_2\text{SO}_4\cdot\text{CH}_3\text{NH}_2\cdot(\text{H}_2\text{O})_2$	−53.04	−46.85	−18.13	−96.32	1662.37
$\text{H}_2\text{SO}_4\cdot\text{CH}_3\text{NH}_2\cdot(\text{H}_2\text{O})_3$	−67.21	−58.48	−17.91	−136.09	0.68
$(\text{CH}_3)_3\text{N}\cdot\text{H}_2\text{O}$	−8.19	−6.27	1.81	−27.11	0.047
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_3\text{N}^c$	−28.49	−26.04	−15.74	−34.54	−
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_3\text{N}\cdot\text{H}_2\text{O}^c$	−40.49	−35.52	−15.71	−66.44	0.94
$\text{H}_2\text{SO}_4\cdot(\text{CH}_3)_3\text{N}\cdot(\text{H}_2\text{O})_2^c$	−51.96	−45.19	−16.80	−95.23	6.31

^aThermochemistry and coordinates for the hydrated H_2SO_4 , $\text{H}_2\text{SO}_4\text{-(CH}_3)_2\text{NH}$ and $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters previously published by Henschel *et al.* (2014).

^bDifferent values and structure than those published by Paasonen *et al.* (2012), which were incorrect.

^cCorrected values for the structures published by Paasonen *et al.* (2012); the values in the paper by Paasonen *et al.* (2012) were obtained with a less accurate energy conversion.

Table S3: Gibbs free energies of formation from monomers and equilibrium constants for sulfuric acid hydrates $\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_n$ calculated with the MP2/aug-cc-pV(D+d)Z// ΔE_0 ,3-step method by Kurtén *et al.* (2007). All values are at 298.15 K and 1 atm reference pressure.

Cluster	$\Delta G_{298.15\text{K}}$ (kcal mol ⁻¹)	$K_{n,298.15\text{K}}$
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-3.44	332.30
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_2$	-5.74	48.52
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_3$	-8.49	103.70
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_4$	-9.75	8.39

Table S4: Gibbs free energies of formation from monomers and equilibrium constants for sulfuric acid hydrates $\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_n$ calculated with the RI-MP2/aug-cc-pVDZ//RI-MP2/CBS method by Temelso *et al.* (2012). All values are at 298.15 K and 1 atm reference pressure.

Cluster	$\Delta G_{298.15\text{K}}$ (kcal mol ⁻¹)	$K_{n,298.15\text{K}}$
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-2.87	126.98
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_2$	-4.11	8.11
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_3$	-6.71	80.50
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_4$	-7.84	6.73
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_5$	-7.62	0.69
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_6$	-6.70	0.21

Table S5: Gibbs free energies of formation from monomers and equilibrium constants for sulfuric acid hydrates $\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_n$ calculated with the PW91PW91/6-311++G(3df,3pd) method by Nadykto and Yu (2007). All values are at 298.15 K and 1 atm reference pressure.

Cluster	$\Delta G_{298.15\text{K}}$ (kcal mol ⁻¹)	$K_{n,298.15\text{K}}$
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-2.28	46.91
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_2$	-5.28	158.13
$\text{H}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_3$	-7.17	24.29

Table S6: Pressure-independent diffusion coefficients in nitrogen gas for the molecules and clusters included in the dynamic simulations, calculated according to the Enskog–Chapman theory (Eq. (5)) at 298.15 K.

Cluster	pD ($\times 10^{-2}$ atm cm ² s ⁻¹)
H ₂ SO ₄	9.61
H ₂ SO ₄ •H ₂ O	8.39
H ₂ SO ₄ •(H ₂ O) ₂	7.53
H ₂ SO ₄ •(H ₂ O) ₃	6.88
H ₂ SO ₄ •(H ₂ O) ₄	6.38
H ₂ SO ₄ •(H ₂ O) ₅	5.96
(H ₂ SO ₄) ₂	6.78
(H ₂ SO ₄) ₂ •H ₂ O	6.30
(H ₂ SO ₄) ₂ •(H ₂ O) ₂	5.90
(H ₂ SO ₄) ₂ •(H ₂ O) ₃	5.57
(H ₂ SO ₄) ₂ •(H ₂ O) ₄	5.29
(H ₂ SO ₄) ₂ •(H ₂ O) ₅	5.04
(CH ₃) ₂ NH	9.90
(CH ₃) ₂ NH•H ₂ O	8.45
H ₂ SO ₄ •(CH ₃) ₂ NH	6.60
H ₂ SO ₄ •(CH ₃) ₂ NH•H ₂ O	6.15
H ₂ SO ₄ •(CH ₃) ₂ NH•(H ₂ O) ₂	5.77
H ₂ SO ₄ •(CH ₃) ₂ NH•(H ₂ O) ₃	5.45
H ₂ SO ₄ •(CH ₃) ₂ NH•(H ₂ O) ₄	5.18
H ₂ SO ₄ •(CH ₃) ₂ NH•(H ₂ O) ₅	4.95
(H ₂ SO ₄) ₂ •(CH ₃) ₂ NH	5.40

$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot \text{H}_2\text{O}$	5.14
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_2$	4.91
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_3$	4.71
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_4$	4.53
$(\text{H}_2\text{SO}_4)_2 \cdot (\text{CH}_3)_2\text{NH} \cdot (\text{H}_2\text{O})_5$	4.37
$((\text{CH}_3)_2\text{NH})_2$	6.61
$\text{H}_2\text{SO}_4 \cdot ((\text{CH}_3)_2\text{NH})_2$	5.30
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2$	4.61
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot \text{H}_2\text{O}$	4.44
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_2$	4.29
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_3$	4.15
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_4$	4.02
$(\text{H}_2\text{SO}_4)_2 \cdot ((\text{CH}_3)_2\text{NH})_2 \cdot (\text{H}_2\text{O})_5$	3.91
$(\text{CH}_3)_3\text{N}$	8.14
$(\text{CH}_3)_3\text{N} \cdot \text{H}_2\text{O}$	7.25
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_3\text{N}$	5.97
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_3\text{N} \cdot \text{H}_2\text{O}$	5.62
$\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_3\text{N} \cdot (\text{H}_2\text{O})_2$	5.32

Table S7: Cartesian coordinates for clusters not previously published at the B3LYP/CBSB7//RICC2/aug-cc-pV(T+d)Z level of theory, corresponding to the most stable structure at 298.15 K optimized at the B3LYP/CBSB7 level.

$(\text{CH}_3)_2\text{NH}\cdot\text{H}_2\text{O}$

O	-1.053919	-1.559849	-1.879323
H	-1.725254	-0.901738	-2.079257
H	-1.311181	-1.905894	-1.001872
N	-1.159229	-2.170409	0.901808
H	-1.821389	-2.683840	1.473205
C	-1.113203	-0.772246	1.331181
H	-2.126829	-0.365215	1.356444
H	-0.653723	-0.628579	2.321702
H	-0.540446	-0.199532	0.597692
C	0.149011	-2.826734	0.950247
H	0.642749	-2.747293	1.931616
H	0.036263	-3.883372	0.699249
H	0.799352	-2.373676	0.198028

$\text{NH}_3\cdot\text{H}_2\text{O}$

O	-1.210404	-1.726333	-2.178200
H	-2.089046	-1.377661	-2.352375
H	-1.185319	-1.818211	-1.207728
N	-1.104929	-2.012752	0.734582
H	-1.033069	-1.126927	1.225463
H	-0.254744	-2.533191	0.929169
H	-1.873694	-2.529590	1.150220

N	-1.592484	-0.506376	-0.005061
O	0.303016	1.552905	-0.107426
O	1.371588	-1.018653	0.111306
H	-0.748580	-1.082871	0.028711
H	-2.142892	-0.795234	-0.807363
H	-2.139621	-0.707248	0.825910
H	1.827000	-1.209239	-0.714109
H	1.217703	-0.053103	0.082190
H	0.272911	2.083703	0.694186
H	-0.535973	1.034602	-0.105132

N	1.601954	-1.186363	-0.085393
H	1.990452	-1.555098	-0.948279
H	0.618891	-1.481207	-0.037240
H	2.098661	-1.635316	0.678177
O	-1.510217	1.208330	-0.004286
H	-1.799446	1.600186	-0.833639
H	-0.550767	1.429521	0.054735
O	1.182052	1.554282	0.013540
H	1.578852	1.888603	0.823121
H	1.453042	0.598085	-0.039826
O	-1.340287	-1.534105	0.004982
H	-1.756949	-1.803264	0.828718
H	-1.498796	-0.565023	-0.041904

N	-1.737537	1.619663	0.113538
H	-2.090088	1.956379	1.004981
H	-2.177926	2.186406	-0.605634
H	-0.729400	1.822424	0.080274
O	2.303816	-0.387334	-0.067145
H	1.609874	-1.075513	0.070462
H	2.742314	-0.644788	-0.883188
O	0.367661	-2.254696	0.158163
H	0.297262	-2.707869	1.003089
H	-0.524064	-1.853595	0.009710
O	-2.049748	-1.115177	-0.139107
H	-2.453274	-1.261733	-0.999431
H	-1.975992	-0.124038	-0.045375
O	1.163069	2.088166	-0.073861
H	1.588119	1.201860	-0.124040
H	1.597541	2.515159	0.669988

N	0.767766	0.741256	0.047564
C	1.250913	-0.646054	-0.025968
H	1.292579	1.273922	0.733298
H	0.593861	-1.207109	-0.692296
H	2.287527	-0.753115	-0.371113
H	1.172819	-1.100763	0.964250
H	0.891130	1.208223	-0.845481
O	-1.979605	-0.071556	-0.095170
H	-2.146455	-0.549790	0.721971
H	-1.134454	0.388606	0.073592

N	1.014600	-0.030348	0.583018
C	2.109501	-0.133163	-0.390411
H	0.352814	-0.798658	0.458437
H	2.789292	0.714513	-0.273694
H	2.697773	-1.056954	-0.311841
H	1.692706	-0.087330	-1.398968
H	1.373298	-0.083371	1.530890
O	-1.287562	1.450705	0.004160
H	-0.379371	1.164370	0.268341
H	-1.168754	1.957499	-0.804567
O	-1.611060	-1.310921	-0.189223
H	-2.218528	-1.578146	0.506872
H	-1.709459	-0.338779	-0.233622

S	-0.941483	0.151545	0.023285
O	-1.830320	1.283843	0.031600
O	-1.887263	-1.188280	-0.018881
O	-0.087339	0.054781	-1.193608
O	-0.136268	-0.080917	1.233447
N	2.121642	-0.619084	-0.030441
C	3.146915	0.452737	0.006323
H	-2.662051	-0.962098	-0.550711
H	1.364204	-0.427245	-0.770290
H	1.481951	-0.581174	0.800295
H	3.705209	0.458914	-0.928682
H	3.824531	0.295812	0.844574
H	2.629712	1.402575	0.126756
H	2.516716	-1.549750	-0.139818

H	-1.115195	-0.709320	-0.886637
S	1.151149	-0.284767	0.092046
O	1.407310	1.177062	-0.672523
O	0.271670	0.118121	1.193956
O	2.456626	-0.790745	0.420736
O	0.411600	-1.087629	-0.913244
H	2.280923	1.121472	-1.080953
N	-2.106919	-0.342740	-0.690881
H	-2.676115	-0.414015	-1.531339
C	-2.695654	-1.091389	0.454260
H	-2.006062	-0.993076	1.289744
H	-2.795518	-2.141608	0.184479
H	-3.668433	-0.674738	0.712122
H	-1.966964	0.669295	-0.443562
O	-1.314706	2.139265	0.217261
H	-0.690437	2.555622	-0.389567
H	-0.718227	1.641577	0.814107

H	1.232230	-0.000016	0.934175
S	-1.379461	-0.000008	0.156298
O	-1.327923	1.223944	-0.650855
O	-1.327755	-1.223749	-0.651165
O	-2.830366	-0.000181	0.891289
O	-0.460698	-0.000101	1.296951
N	2.096286	0.000036	0.345453
H	1.984644	0.843613	-0.261532
C	3.349264	0.000095	1.134167
H	3.381856	-0.889245	1.761876
H	3.381739	0.889398	1.761934
H	4.206864	0.000174	0.462128
H	1.984734	-0.843546	-0.261538
O	1.201070	-2.172146	-1.093834
H	1.243610	-2.300780	-2.045869
H	0.252262	-1.987020	-0.906879
O	1.200910	2.172118	-1.093915
H	1.243341	2.300498	-2.045978
H	0.252116	1.987069	-0.906821
H	-3.503503	0.000076	0.196789

H	1.073106	-1.412926	-0.197157
S	-1.461669	-0.395666	-0.032211
O	-1.472181	-0.144949	1.406603
O	-1.130382	0.784147	-0.846039
O	-3.000389	-0.685939	-0.466993
O	-0.694404	-1.589554	-0.413782
N	1.974332	-0.913900	-0.047926
H	1.830243	-0.362864	0.838092
C	3.151297	-1.810814	-0.003138
H	3.235929	-2.350809	-0.945322
H	3.035990	-2.522095	0.813635
H	4.052286	-1.220177	0.157590
H	2.016002	-0.204082	-0.816505
O	1.543857	1.107389	-1.903800
H	1.477481	1.893992	-1.335460
H	0.608560	0.875138	-2.026005
O	1.185706	0.676199	2.055484
H	1.072670	1.538644	1.614588
H	0.268841	0.356016	2.141277
H	-3.327181	-1.401687	0.095757
O	0.494798	2.686116	0.202201
H	0.180146	3.584836	0.336970
H	-0.281506	2.151579	-0.077175

N	-0.391563	0.005136	0.076984
C	-0.333717	1.122717	-0.863102
C	-1.491922	0.149650	1.024951
C	-0.446612	-1.275804	-0.627076
H	0.445252	-1.385634	-1.246708
H	-0.456587	-2.092309	0.098235
H	-1.466364	-0.670027	1.746335
H	-0.265970	2.062949	-0.309990
H	-1.387495	1.089337	1.572473
H	0.561100	1.025908	-1.480644
H	-1.218264	1.171818	-1.521288
H	-2.480425	0.145848	0.532495
H	-1.340758	-1.366987	-1.267726
O	2.462328	-0.093005	0.376026
H	1.500595	-0.041089	0.539769
H	2.784732	0.788891	0.581312