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Hydration of Atmospherically Relevant Molecular Clusters: Computational Chemistry and Classical Thermodynamics

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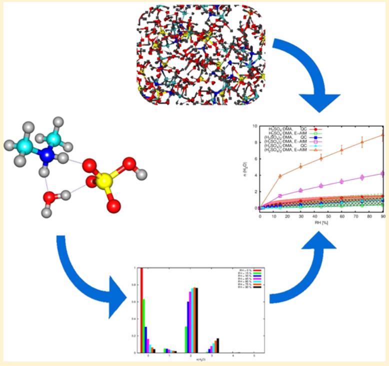
Supporting Information

ABSTRACT: Formation of new particles through clustering of molecules from condensable vapors is a significant source for atmospheric aerosols. The smallest clusters formed in the very first steps of the condensation process are, however, not directly observable by experimental means. We present here a comprehensive series of electronic structure calculations on the hydrates of clusters formed by up to four molecules of sulfuric acid, and up to two molecules of ammonia or dimethylamine. Though clusters containing ammonia, and certainly dimethylamine, generally exhibit lower average hydration than the pure acid clusters, populations of individual hydrates vary widely. Furthermore, we explore the predictions obtained using a thermodynamic model for the description of these hydrates. The similar magnitude and trends of hydrate formation predicted by both methods illustrate the potential of combining them to obtain more comprehensive models. The stabilization of some clusters relative to others due to their hydration is highly likely to have significant effects on the overall processes that lead to formation of new particles in the atmosphere.



INTRODUCTION

Atmospheric aerosols affect our life in a number of ways, both in terms of their effect on health[1] and due to their effect on climate patterns.[2,3] Aerosols arise to a large fraction from particles formed through the condensation of gas phase molecules.[4,5] The process in which new particles are formed is, however, only roughly understood, partly owing to the fact that the very first steps of electrically neutral cluster formation are hardly accessible by experiment. Especially the water content of clusters is currently completely barred from experimental investigation, as water is comparatively weakly bound and thus evaporates in the currently used instruments before any measurement can take place.

Sulfuric acid is generally believed to play a central role in the particle formation process in many conditions, and also water is likely to be involved, as its concentration exceeds that of other condensable gases often by 8−10 orders of magnitude.[6] Observed formation rates are, however, much higher than would result from binary nucleation of sulfuric acid and water. As a likely third component involved in particle formation, ammonia has been widely discussed.[6,7] Although a formation rate-enhancing effect is relatively well-known for ammonia, it is not sufficient to explain observed formation rates in the atmosphere.[8] An alternate group of compounds that can stabilize sulfuric acid clusters are amines.[9] Dimethylamine (DMA) has been of interest, as it could be detected in atmospheric particles[10] and theoretically could be shown to have a much stronger stabilizing effect on sulfuric acid clusters than ammonia.[11] Recently, it was confirmed by experiments that dimethylamine can at least partly explain atmospheric levels of formation rates.[12]

To understand and accurately describe the very first steps of particle formation, i.e., the clustering of the first few molecules from the gas phase, electronic structure calculations can be utilized. Results from these calculations give detailed information about the structures and relative stabilities of the clusters, which can be used in the direct modeling of the particle formation processes.[13,14] Unfortunately, due to the computational requirements rising steeply with the size of the system studied, calculations of good accuracy are to date limited to a few molecules. Relevant growth processes of the newly formed particles, however, extend well beyond this size range. Therefore, other methods reliably describing molecular clusters of larger sizes are needed to enable more comprehensive modeling of the process.

Thermodynamic models created for the study of systems with bulk thermodynamic properties are computationally consid-

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erably less demanding compared to methods based on molecular structure. Additionally, their performance for the bulk systems can be directly evaluated using experimental data. This makes thermodynamic models promising candidates for explaining the growth of clusters into larger sizes. For thermodynamic models to successfully simulate the energetics of nanometer-sized clusters, they must perform well also at the very smallest sizes. By carrying out a systematic comparison of the performance of thermodynamics at the smallest sizes against calculations at a higher level of theory (i.e., electronic structure), we can obtain information on the performance of the state-of-the-art thermodynamic theories for the smallest molecular clusters. Such model comparisons can also serve as a basis for future model development and guidance for where new experimental data is most needed.

One problem for the simulation of atmospheric particle formation processes is the availability of reliable descriptions for the hydration of molecular clusters.[15] Although a series of studies using a number of different methods has been published on the hydration of both the sulfuric acid/water,[16−23] the sulfuric acid/ammonia/water,[24−27] and the sulfuric acid/dimethylamine/water system,[28,29] we now present a comprehensive set of calculations on all these systems. We study the structures and energetics of these clusters, along with the equilibrium cluster distributions as a function of relative humidity. Furthermore, we compare the results to predictions using a classical thermodynamic model currently used in atmospheric studies. Finally, we discuss the potential reasons and implications of the differences between these two methodologies.

THEORETICAL METHODS

Electronic Structure Methods. Electronic structure calculations for systems containing sulfuric acid, water, and ammonia or DMA were performed using a multistep approach recently composed by Ortega et al. (see ref 30, for details). This method was specifically shaped and found to give reliable formation free energies at an affordable computational cost for simulations of sulfuric acid/amine clusters.[30] Though an extensive comparison of the reliability of the used and a series of other methods can be found in ref 31, the error in terms of resulting equilibrium constants can be estimated to be approximately 1 order of magnitude (corresponding to approximately 1 kcal/mol). Trends within the data should, however, be much more accurate, as the underlying chemical phenomena are fully covered by the method. All cluster geometries were optimized using the Becke three-parameter (B3LYP) functional[32] and CBSB7 (6-311G(2d,d,p)) basis set,[33] as implemented in the Gaussian 09 program package.[34] This way, up to 99 conformations for each cluster were optimized. Frequency calculations have been performed on all optimized geometries, confirming them to exhibit no imaginary frequencies. The obtained frequencies were used without scaling for the calculation of Gibbs free energies. On the basis of Gibbs free energy at the B3LYP/CBSB7 level, cluster geometries were chosen for single point calculations covering approximately 3 kcal/mol from the lowest energy. Single point energy calculations were performed using the Turbomole program package[35] for the RICC2 method[36] with a aug-cc-pV(T+d)Z[37,38] basis set for sulfur, and aug-cc-pVTZ[39−41] for all other atoms.

The obtained Gibbs free energies of hydration at standard state ($\Delta_{\text{hydr}}G^0$) were converted into equilibrium constants for formation of the respective hydrate (linked to the evaporation rates or, in bulk thermodynamic terms, the equilibrium vapor pressures of the clusters), using the single lowest energy structure for each system (the effect of Boltzmann averaging over configurations on comparable systems was studied by Temelso et al.[22] and found to be minimal in case of free energies of hydration). From these, relative equilibrium hydrate populations were calculated at several relative humidities, using the formula for the temperature dependency of the water saturation vapor pressure derived by Wexler.[42] This gives the relative population x_n of the hydrate containing n water molecules as

$$x_n = \left(\frac{p(\mathrm{H_2O})}{p^0}\right)^n x_0 \mathrm{e}^{-\Delta_{\text{hydr}}G^0(n)/RT} \tag{1}$$

with the population of the dry cluster x_0 chosen so that $\sum_0^5 x_n = 1$. $p(\mathrm{H_2O})$ is the water partial pressure, p_0 is the reference pressure (1 atm), T is the temperature (in our case 298.15 K), and R is the molar gas constant.

Thermodynamic Calculations with E-AIM. The thermodynamic calculations of the hydrates were performed using the models of Clegg and co-workers,[43−48] which are available online as the extended aerosol inorganic model (E-AIM).[49,50] This model calculates the thermodynamic equilibrium of systems with coexisting gas, aqueous, hydrophobic liquid, and solid phases, from the relative humidity, temperature, pressure, volume, and the total number of moles of each component in the system. In our calculations only the formation of gas and aqueous phases of the binary system H_2SO_4−H_2O, and the ternary systems H_2SO_4−H_2O−NH_3 and H_2SO_4−H_2O−DMA, are allowed.

In the aqueous phase, acid dissociation and base protonation are taken into account. Sulfuric acid is assumed to always at least singly deprotonate when present in aqueous solutions at the concentrations of interest here. Mole fractions of the deprotonated acids and protonated bases were determined using the acid dissociation constants of the compounds. For the DMA containing systems, the activities of the dimethylammonium ions were calculated using the same model parameters as for ammonium ions due to the lack of experimental data for interactions between SO_4^{2-} and HSO_4^- anions and the dimethylammonium cation. This has, however, been shown to be a reasonable assumption for the water uptake of larger aerosol particles.[48]

The difference between the acidified DMA and ammonia containing systems in the thermodynamic calculations is thus determined mainly by the differences in their densities and surface tensions. The online E-AIM model calculates equilibrium vapor pressures, mole fractions, and aqueous phase activities of all dissolved species but does not take into account the surface curvature of particles. To add the effects of surface curvature, the results from E-AIM were adjusted to estimate the true equilibrium water activities of the nanometer sized clusters by multiplying the calculated bulk solution water activity by the following Kelvin effect term, $K_{\mathrm{e,H_2O}}$:[51,52]

$$K_{\mathrm{e,H_2O}} = \mathrm{e}^{2\sigma V_{\mathrm{H_2O}}/rRT} \tag{2}$$

where σ is the surface tension of the mixture, r is the radius of the cluster, and $V_{\mathrm{H_2O}}$ is the partial molar volume of the liquid water estimated from the solution density. The surface tension of the H_2SO_4−H_2O−NH_3 and H_2SO_4−H_2O−DMA systems were estimated following refs 53 and 54, respectively. The densities of H_2SO_4−H_2O and H_2SO_4−H_2O−NH_3, and the corresponding partial molar volumes of water (based upon the study of Clegg and Wexler[46]), were obtained from E-AIM. In the second case

Table 1. Quantum Chemically Derived Free Energies of Hydration at $T = 298.15$ K and $p^0 = 1$ atm ($\Delta_{hydr}G^0$) in kcal mol^{-1}

	$n(H_2O)$				
cluster	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
H_2SO_4	−2.60	−4.40	−5.83	−7.05	−6.81
$(H_2SO_4)_2$	−3.36	−6.38	−8.61	−10.97	−12.75
$(H_2SO_4)_3$	−5.17	−8.22	−12.75	−16.16	−17.78
$(H_2SO_4)_4$	−2.67	−7.80	−13.96	−13.49	−15.78
$H_2SO_4{\cdot}NH_3$	−1.67	−5.93	−7.16	−7.09	−8.23
$(H_2SO_4)_2{\cdot}NH_3$	−2.68	−4.00	−6.67	−7.33	−8.48
$(H_2SO_4)_3{\cdot}NH_3$	−3.26	−6.70	−9.08	−9.48	−10.92
$(H_2SO_4)_2{\cdot}(NH_3)_2$	−4.14	−7.56	−7.75	−8.18	−9.58
$(H_2SO_4)_3{\cdot}(NH_3)_2$	−3.30	−3.40	−7.16	−7.76	−9.46
$H_2SO_4{\cdot}DMA$	−2.89	−5.26	−5.02	−5.81	−5.73
$(H_2SO_4)_2{\cdot}DMA$	−2.47	−2.86	−5.69	−6.26	−6.02
$(H_2SO_4)_3{\cdot}DMA$	0.06	−4.16	−4.89	−6.06	−6.58
$(H_2SO_4)_2{\cdot}(DMA)_2$	1.35	−0.51	0.62	−1.34	−1.77
$(H_2SO_4)_3{\cdot}(DMA)_3$	−1.84	−3.97	−3.31	−8.19	−9.83

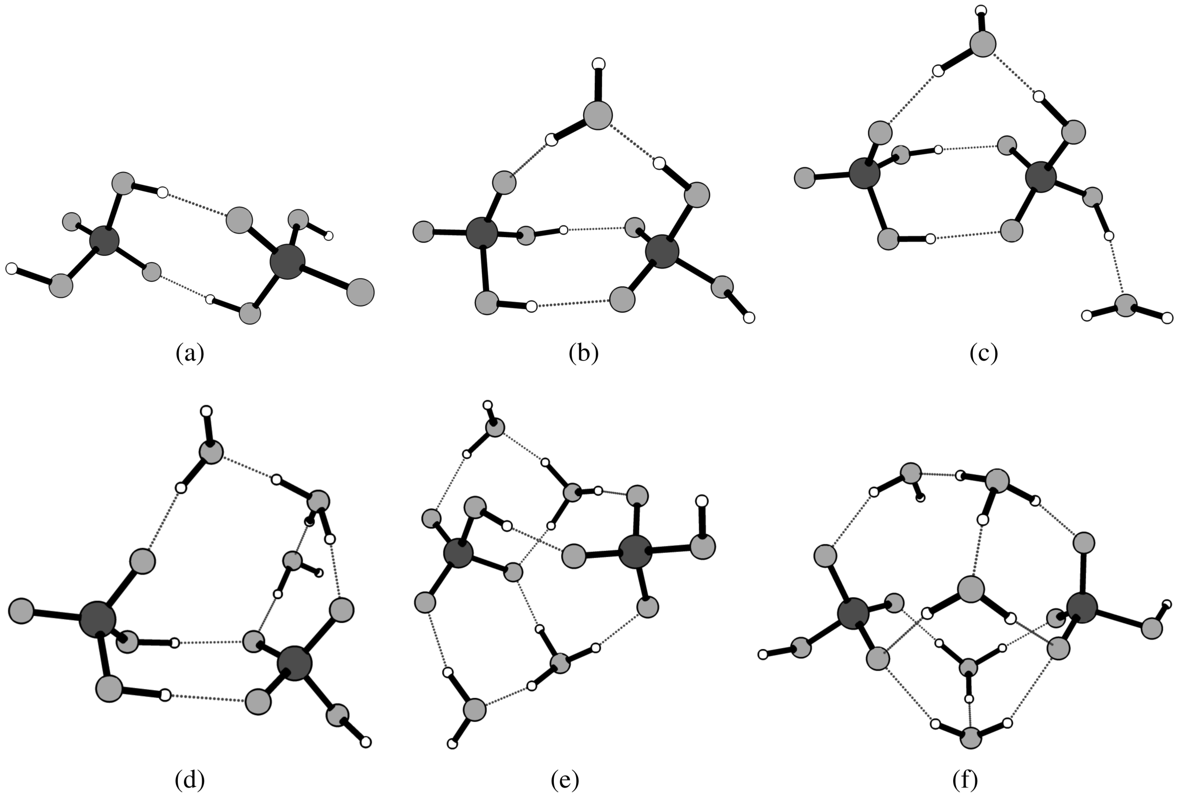

(a) (b) (c) (d) (e) (f)

Figure 1. Structures of $(H_2SO_4)_2$ hydrates.

the densities of the mixture, in which H_2SO_4 is always in excess, were estimated from those of H_2SO_4–H_2O and $(NH_4)_2SO_4$–H_2O using eq 11 of Semmler et al.[55] Densities of the H_2SO_4–H_2O–DMA systems were estimated in a similar way, using data from Clegg et al.,[48] and then calculating the partial molar volume of water by numerical differentiation of the total solution volume. Finally, we calculated the average numbers of water molecules in the clusters by assuming spherical clusters with the given numbers of sulfuric acid and base molecules, using the water mole fractions calculated by E-AIM (for each RH), and the partial molar volumes of water in these mixtures.

The equilibrium partial pressure of water ($P_{eq,H_2O}(T)$) is then calculated as

$$P_{eq,H_2O} = P_{sat,H_2O}(T)a_{H_2O}K_{e,H_2O} \tag{3}$$

where $P_{sat,H_2O}(T)$ is the pure water saturation vapor pressure over a flat surface and a_{H_2O} is the bulk water activity.

RESULTS AND DISCUSSION

Structures and Energetics. The calculated Gibbs free energies of hydration (defined so that $\Delta_{hydr}G^0 = 0$ for the dry clusters), are summarized in Table 1. A table containing the Gibbs free energies of addition of single molecules of water $\Delta_1\Delta_{hydr}G^0$ is to be found in the Supporting Information.

Hydrates of Base-Free Systems. For the systems containing only sulfuric acid and water, the free energies for addition of one water molecule at standard state are negative for all except two steps. The first of these cases is the fifth hydration of a single sulfuric acid molecule. This behavior in terms of Gibbs free energy (both qualitatively and quantitatively) has also been reported by Temelso et al. using RI-MP2/CBS//aug-cc-pVDZ with scaled harmonic frequencies,[22] who also included a sixth hydrate of a single sulfuric acid molecule in their study and reported an even larger endergonic step for this. Thus, this can be attributed to the acid molecule being saturated with water molecules in the fourth hydrate. The other case, in which the addition of a water molecule leads to a rise in molar Gibbs free energy is the fourth hydration of the cluster containing four sulfuric acid molecules. This case can be attributed to the extraordinary stability of the third hydrate. Compared to the energy of the second hydrate, the energy of the fourth hydrate ($\Delta_2\Delta_{\mathrm{hydr}}G^0 = 5.69$ kcal mol^{-1}) is similar to energies observed for the addition of two water molecules to other systems containing only sulfuric acid and water. In general, the energies obtained for the one-sulfuric-acid cluster are in qualitative agreement with previous studies by our group (using an energy corrected MP2/aug-cc-pV(D+d)Z with anharmonically corrected frequencies,[21] and a RI-MP2/aug-cc-pV(D+d)Z with scaled frequencies,[28] respectively) and recent results by others.[22] Quantitatively, the deviations between this study and previous studies are in all cases below 1 kcal mol^{-1}.

For the cluster containing two sulfuric acid molecules (depicted in Figure 1) we obtained hydration energies that are in the same range as those reported in earlier studies on PW91/DNP,[19] and RI-MP2/CBS//6-31+G* level of theory with scaled frequencies,[23] and the above-mentioned study by Loukonen et al.[28] Energies for each hydration step for this cluster are invariably negative. Our energy results tend, however, to be somewhat lower than those obtained earlier (more negative energies are only reported by Loukonen et al. for the first two,[28] and Ding et al. for the third and following hydrates[19]). Only in the early study by Ianni and Bandy (using B3LYP/6-311++G(2d,2p) level of theory under exclusion of proton transfers) are much higher values (weaker hydration) reported.[18]

The number of proton transfers in each structure (compared to its neutral constituents), as obtained from electronic structure calculations, is summarized in Table 2. Proton transfer within a structure can generally lead to additional stabilization of hydrates. However, as can be seen by comparing Tables 1 and 2, the change in Gibbs free energy upon addition of the water molecule facilitating the proton transfer is in many cases comparatively small; in some cases (addition of fifth water molecule to H_2SO_4, and first water molecule to $(H_2SO_4)_3{\cdot}\mathrm{DMA}$) even above zero. This can be explained by the additional energy cost for the entailed separation of charges, whereas structures without the proton transfer are even less stable. Still the proton transfer might help stabilize higher hydrates of the cluster, leading to a higher average hydration of the corresponding cluster. The results presented here for the clusters containing one or two sulfuric acid molecules are commensurate with those of Anderson et al.[56] who found in a first principle molecular dynamics study using BLYP/TZV2P that these clusters have, when hydrated by six water molecules, a number of proton transfers equal to the number of sulfuric acid molecules (also when base molecules were included in the study). In our calculations we observe the same for the clusters containing five water molecules. For the case of the single sulfuric acid molecule, some previous studies reported that proton transfer occurs already in the presence of either three (on PW91/TZP and B3LYP/6-31G** level of theory)[20,57] or four (using B3LYP/D95++(d,p))[17] water molecules. In terms of the Gibbs free energy we found the nonprotolyzed cluster presented here to be more stable than the reported ion pair structures. Temelso et al. have found the proton transfer not to occur until the addition of the sixth water molecule.[22] In a different study[23] these authors also found the second proton transfer in a system with two sulfuric acids require one more water molecule (5) than what was found by us (4). However, the structure we found to have the lowest energy for the combination of two sulfuric acid and four water molecules (Figure 1e) seems not to have been included in that study. Similarly, Ding et al.[19] report the first proton transfer for the two sulfuric acid cluster already with the second hydration, but our lowest energy structure for that system has not been discussed in the study.

Table 2. Number of Proton Transfers within Clusters Predominant at $T = 298.15$ K

cluster	$n(H_2O)$ $n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
H_2SO_4	0	0	0	0	0	1
$(H_2SO_4)_2$	0	0	0	1	2	2
$(H_2SO_4)_3$	0	1	2	2	2	2
$(H_2SO_4)_4$	0	0	2	1	3	2
$H_2SO_4{\cdot}NH_3$	0	1	1	1	1	1
$(H_2SO_4)_2{\cdot}NH_3$	1	1	2	2	2	2
$(H_2SO_4)_3{\cdot}NH_3$	1	2	2	2	3	3
$(H_2SO_4)_2{\cdot}(NH_3)_2$	2	2	2	2	2	2
$(H_2SO_4)_3{\cdot}(NH_3)_2$	2	2	2	2	3	3
$H_2SO_4{\cdot}\mathrm{DMA}$	1	1	1	1	1	1
$(H_2SO_4)_2{\cdot}\mathrm{DMA}$	1	1	2	2	2	2
$(H_2SO_4)_3{\cdot}\mathrm{DMA}$	1	2	3	3	3	3
$(H_2SO_4)_2{\cdot}(\mathrm{DMA})_2$	2	2	2	2	2	2
$(H_2SO_4)_3{\cdot}(\mathrm{DMA})_2$	2	2	2	2	3	3

Hydration energies for the cluster consisting of three sulfuric acid molecules are also found to be negative for each step. The differences between the hydration energies for this cluster and the cluster with two sulfuric acid molecules are similar in magnitude to those between the two- and the one-sulfuric-acid-cluster.

The system containing four sulfuric acid molecules (depicted in Figure 2) shows some unusual aspects in its sequence of hydration energies. With the dry structure resembling a dimer of the dry $(H_2SO_4)_2$ cluster, the first water molecule is only weakly bound to one end of the cluster, giving a hydration energy similar to that of the single sulfuric acid molecule. For the second, fourth, and fifth hydrate the hydration energies are of magnitudes similar to those for two and three sulfuric acid clusters. The third hydrate of the $(H_2SO_4)_4$ cluster, however, is an exception with its hydration free energy being more than 6 kcal mol^{-1} lower than the structure with one less water molecule. Also, it has an even slightly lower energy than the following, fourth, hydrate, which matches the trend of the other hydration energies for the cluster. Structure-wise the $(H_2SO_4)_4{\cdot}(H_2O)_3$ cluster resembles two sulfuric acid dimers (one similar to the lowest energy structure, the other connected via three hydrogen bonds), held together by the three water molecules (cf. Figure 2d). Also in terms of proton transfer, the cluster consisting of four molecules of sulfuric acid exhibits a rather uncommon behavior. In the $(H_2SO_4)_4$ cluster, two proton transfers occur simultaneously upon binding of an additional water molecule both in the case of the second and fourth water molecule. Furthermore, upon addition of the third

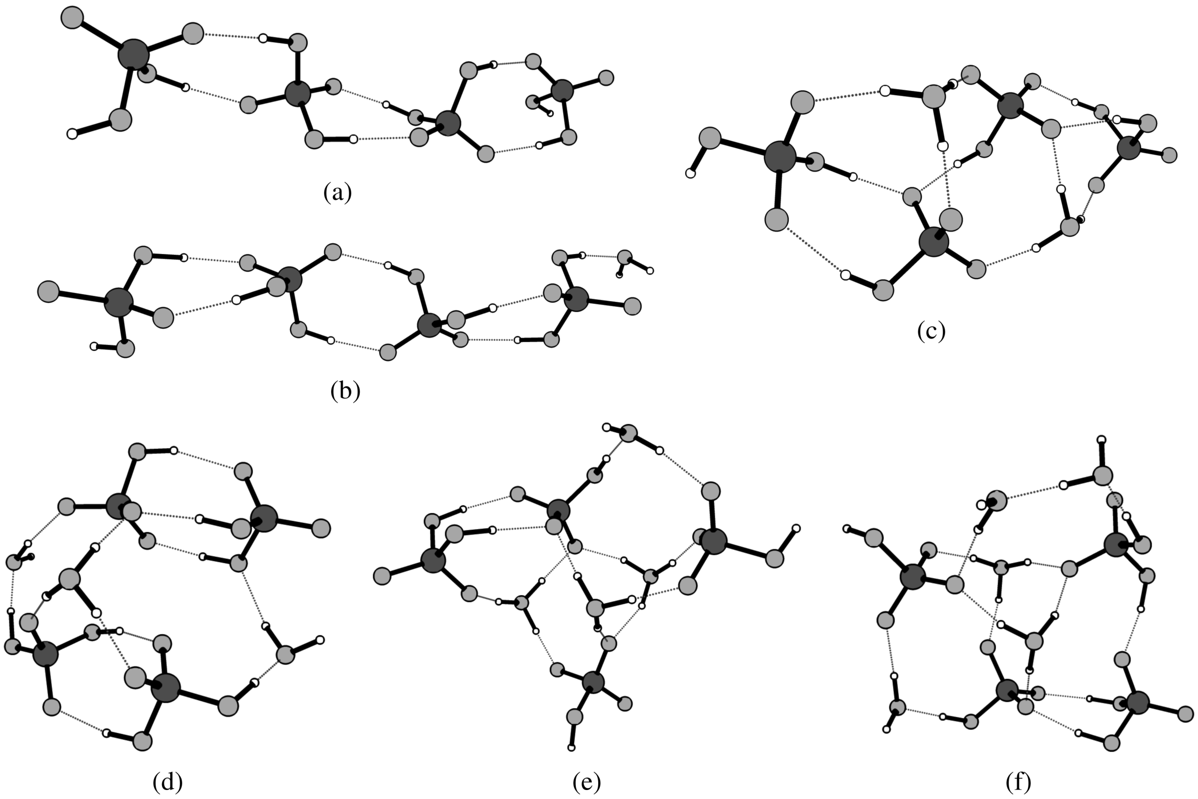


Figure 2. Structures of $(H_2SO_4)_4$ hydrates.

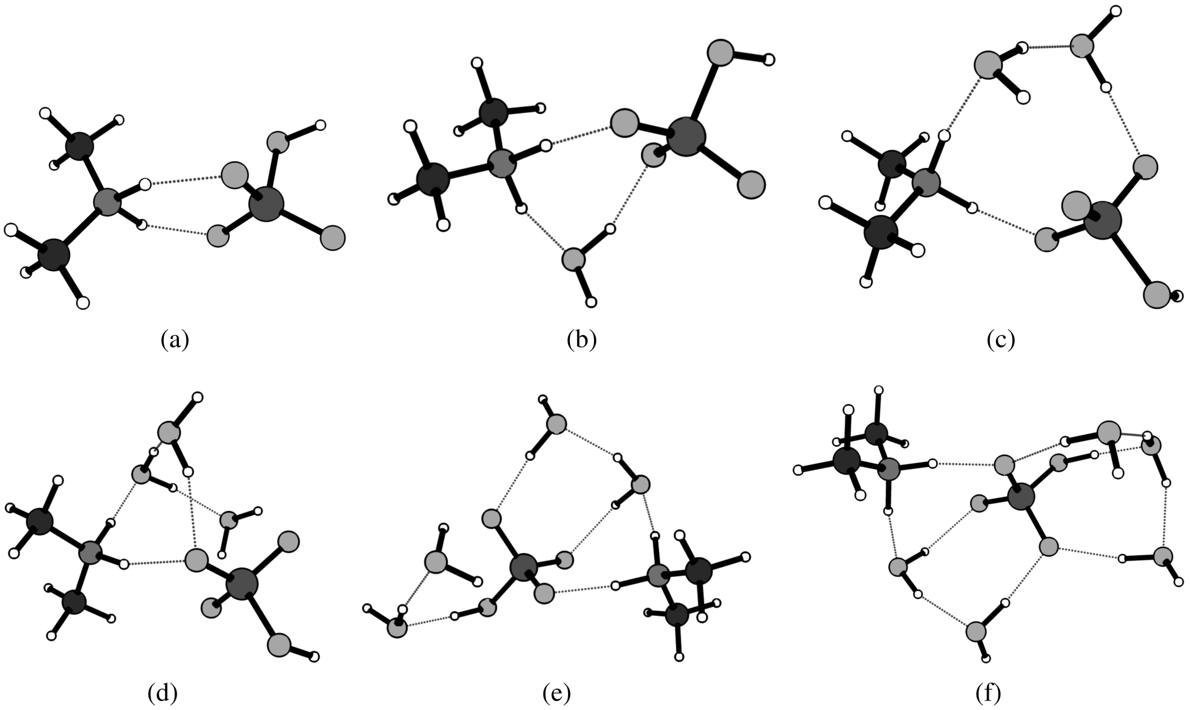


Figure 3. Structures of H_2SO_4·DMA hydrates.

water molecule, the number of internal proton transfers decreases by one. This is accompanied by a considerable drop in free energy, leading to this single hydrate also largely dominating the hydrate distribution of this cluster (as discussed in greater detail below). For all other systems studied, a proton transfer is irreversible in the sense that it is not reversed in the lowest energy structure of higher hydrates, and no more than one additional proton transfer happens for each added water molecule (Table 2).

Hydrates of Sulfuric Acid/Ammonia Clusters. Systems containing a base molecule exhibit proton transfer in almost all cases (Table 2). The only exception is the dry cluster containing

Table 3. Average Number of Water Molecules Per Cluster at T = 298.15 K and Different Relative Humidities Derived from Electronic Structure Calculations (QC) and Thermodynamic Model (E-AIM)[a]

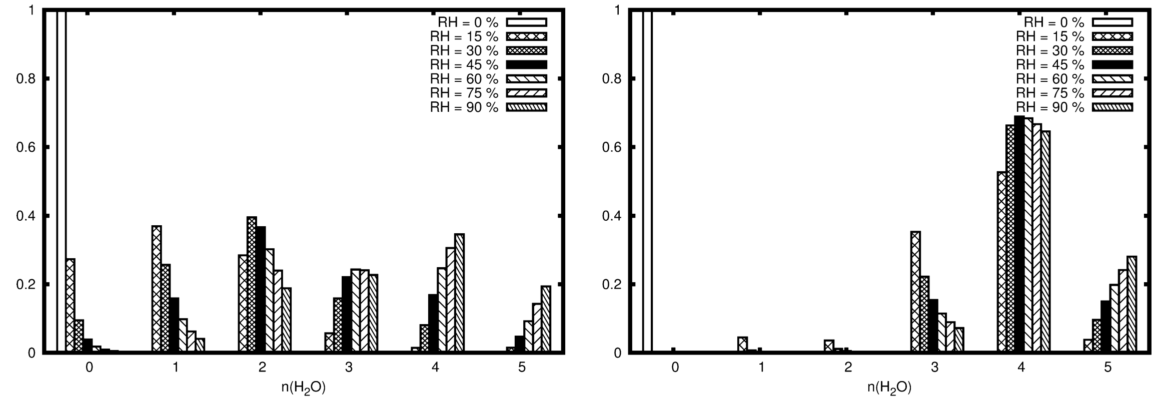
cluster		RH [%]					
		15	30	45	60	75	90
H_2SO_4	QC	**0.32 (0.53)**	**0.57 (0.67)**	**0.78 (0.77)**	**0.97 (0.83)**	**1.13 (0.89)**	**1.28 (0.93)**
	E-AIM	**1.43**	**1.55**	**1.68**	**1.80**	**1.93**	**2.05**
$(H_2SO_4)_2$	QC	**1.18 (0.95)**	**1.92 (1.12)**	**2.46 (1.19)**	**2.88 (1.21)**	**3.20 (1.19)**	**3.45 (1.15)**
	E-AIM	**3.11**	**3.62**	**4.12**	**4.47**	**4.80**	**5.13**
$(H_2SO_4)_3$	QC	**3.47 (0.83)**	**3.83 (0.63)**	**3.98 (0.59)**	**4.08 (0.57)**	**4.15 (0.57)**	**4.21 (0.56)**
	E-AIM	**5.03**	**6.05**	**6.81**	**7.51**	**8.12**	**8.71**
$(H_2SO_4)_4$	QC	**2.99 (0.13)**	**3.00 (0.12)**	**3.01 (0.16)**	**3.02 (0.20)**	**3.03 (0.24)**	**3.04 (0.28)**
	E-AIM	**7.10**	**8.60**	**9.75**	**10.78**	**11.73**	**12.64**
$H_2SO_4 \cdot NH_3$	QC	**0.70 (0.95)**	**1.39 (0.97)**	**1.72 (0.83)**	**1.89 (0.73)**	**2.00 (0.66)**	**2.07 (0.62)**
	E-AIM	*0.02*	*0.02*	*0.03*	*0.03*	*0.04*	*0.05*
$(H_2SO_4)_2 \cdot NH_3$	QC	**0.34 (0.53)**	**0.61 (0.72)**	**0.86 (0.88)**	**1.12 (1.01)**	**1.37 (1.10)**	**1.60 (1.15)**
	E-AIM	*0.46*	*0.72*	*0.99*	*1.24*	*1.49*	*1.73*
$(H_2SO_4)_3 \cdot NH_3$	QC	**1.39 (0.95)**	**1.97 (0.85)**	**2.24 (0.77)**	**2.40 (0.73)**	**2.51 (0.70)**	**2.60 (0.69)**
	E-AIM	*2.31*	*3.02*	*3.64*	**4.24**	**4.80**	**5.30**
$(H_2SO_4)_2 \cdot (NH_3)_2$	QC	**1.49 (0.63)**	**1.72 (0.52)**	**1.82 (0.46)**	**1.87 (0.42)**	**1.91 (0.40)**	**1.94 (0.39)**
	E-AIM	*0.00*	*0.01*	*0.01*	*0.02*	*0.02*	*0.03*
$(H_2SO_4)_3 \cdot (NH_3)_2$	QC	**0.57 (0.55)**	**0.82 (0.65)**	**1.02 (0.79)**	**1.23 (0.93)**	**1.45 (1.04)**	**1.66 (1.12)**
	E-AIM	*0.05*	*0.18*	*0.31*	*0.45*	*0.59*	*0.73*
$H_2SO_4 \cdot DMA$	QC	**0.52 (0.65)**	**0.87 (0.75)**	**1.10 (0.75)**	**1.26 (0.74)**	**1.38 (0.71)**	**1.47 (0.68)**
	E-AIM	*0.04*	*0.10*	*0.16*	*0.23*	*0.30*	*0.37*
$(H_2SO_4)_2 \cdot DMA$	QC	**0.24 (0.44)**	**0.41 (0.55)**	**0.55 (0.64)**	**0.68 (0.72)**	**0.82 (0.81)**	**0.95 (0.90)**
	E-AIM	*1.49*	*2.12*	*2.67*	**3.21**	**3.73**	**4.20**
$(H_2SO_4)_3 \cdot DMA$	QC	**0.05 (0.32)**	**0.20 (0.60)**	**0.40 (0.81)**	**0.63 (0.96)**	**0.85 (1.05)**	**1.06 (1.09)**
	E-AIM	*3.89*	**5.03**	**6.05**	**7.05**	**8.01**	**8.90**
$(H_2SO_4)_2 \cdot (DMA)_2$	QC	**$7 \cdot 10^{-4}$ (0.03)**	**$1.4 \cdot 10^{-3}$ (0.04)**	**$2.4 \cdot 10^{-3}$ (0.06)**	**$3.5 \cdot 10^{-3}$ (0.07)**	**$5 \cdot 10^{-3}$ (0.09)**	**$6.7 \cdot 10^{-3}$ (0.10)**
	E-AI	*0.02*	*0.03*	*0.05*	*0.07*	*0.08*	*0.10*
$(H_2SO_4)_3 \cdot (DMA)_2$	QC	**0.13 (0.38)**	**0.30 (0.64)**	**0.55 (0.94)**	**0.90 (1.27)**	**1.34 (1.55)**	**1.84 (1.74)**
	E-AIM	*0.18*	*0.33*	*0.47*	*0.61*	*0.75*	*0.88*

[a] For the numbers derived from electronic structure calculations, standard deviations are given in parentheses. These values should not be interpreted as measure of precision, but rather as an indication of the underlying diversity of hydrate structures. Italicized nonbold values represent a ratio $n_{H_2O}/n_{H_2SO_4} \leq 1.39$ from thermodynamic theory that are less reliable.

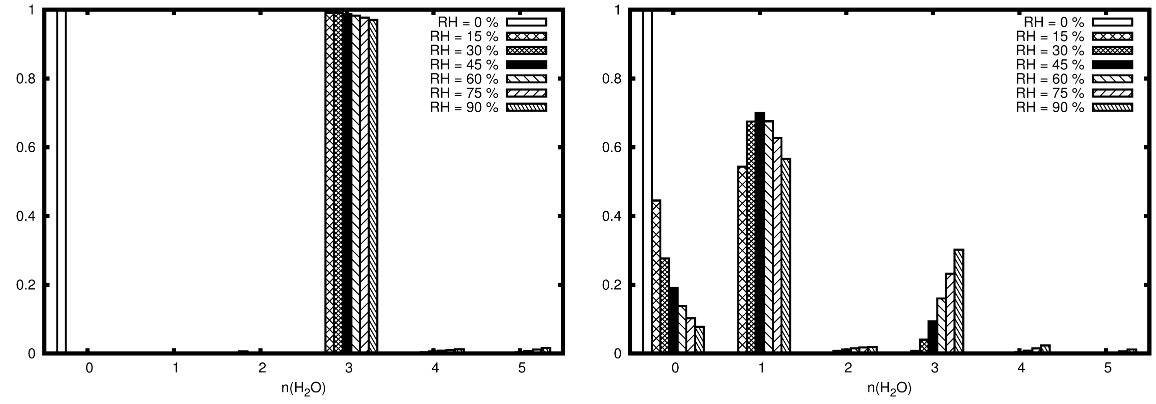
one sulfuric acid and one ammonia molecule. In a study using B3LYP/6-311++G(2d,2p) it has been suggested that for this cluster the proton transfer does not take place until the addition of the fourth water molecule,[24] we find, however, that one molecule of water is sufficient, which corresponds to earlier results for this system, which were obtained using B3LYP/6-311++G(d,p) and MP2/6-31++G(d,p).[25] The first hydration free energy of this cluster is small, whereas the second and subsequent hydration free energies are of magnitudes similar to that for the base free system. This is in contrast to the other systems containing a single ammonia molecule, whose energies resemble those of the ammonia free cluster with one less sulfuric acid molecule. For these clusters the ammonia "neutralizes" the effect of one sulfuric acid molecule. The cluster consisting of two sulfuric acid and ammonia molecules exhibits comparatively large first and second hydration free energies, whereas the energies for the third and following hydrations are similar to those of the one-acid—one-ammonia and two-acid—one-ammonia clusters. Interestingly, the cluster containing one sulfuric acid molecule more, that is, the three-acid—two-ammonia system, has invariably lower hydration free energies. Still, with exception of the second hydration free energy, which is much smaller, they are close to those of the cluster with two acid and two ammonia molecules. This matches the description that for systems containing more sulfuric acid than ammonia molecules, the ammonia molecules cancel the hygroscopy of one sulfuric acid molecules each.

Hydrates of Sulfuric Acid/Dimethylamine Clusters. The effect of dimethylamine is predicted to be quite different from that of ammonia. Although the first two hydration steps for the one-sulfuric-acid—one-dimethylamine cluster are slightly more exergonic than those of an isolated sulfuric acid molecule, further hydration gives only minute changes in energy. As can be seen from Figure 3, this can be ascribed to the dry cluster having a rather strained geometry with both protons of the dimethylammonium forming hydrogen bonds with different oxygen atoms of the sulfuric acid. After this strain is removed, no energy is gained by further hydration.

The cluster consisting of one dimethylamine and two sulfuric acid molecules exhibits roughly two discernible energy levels for its hydrates. The first two and the following three hydrates have similar free energies. These energies are similar to those of the first and third hydrate of the single sulfuric acid molecule, respectively. Thus, even in this system the base compensates the hygroscopic effect of one acid molecule. Some hydration steps (namely the second, fourth, and fifth), however, are hindered even more strongly. Also, the addition of another sulfuric acid molecule to this system, resulting in a cluster containing three sulfuric acid and one dimethylamine molecules, does not generally lead to an enhanced hydration. Only the second (by 2.30 kcal mol^{-1}) and fifth (by 0.56 kcal mol^{-1}) hydrates of this larger cluster are more favorable. Especially, the first hydration step for this system has been found to be slightly endergonic. The



(a) $(H_2SO_4)_2$ (b) $(H_2SO_4)_3$



(c) $(H_2SO_4)_4$ (d) $(H_2SO_4)_3 \cdot (NH_3)_2$

Figure 4. Relative hydrate populations at T = 298.15 K from computational chemistry calculations of the clusters containing two to four sulfuric acid, three sulfuric acid, and two ammonia molecules, respectively.

free energy gain upon going from the first to second hydrate, however, is relatively large, which can be rationalized in terms of the proton transfer connected with it. In total, a single dimethylamine molecule has a much stronger effect on the hydrophilicity of the cluster than ammonia. Also, its effect exceeds solely compensating the effect of one sulfuric acid molecule.

The presence of a second dimethylamine molecule in the cluster renders it much less hydrophilic. Especially the cluster consisting of two sulfuric acid and two dimethylamine molecules has very unfavorable hydration energies. The first hydration step is relatively strongly endergonic, but although the following steps tend toward becoming more feasible, the hydrate formed with three water molecules lies again energetically higher than the dry cluster. The cluster with a third sulfuric acid exhibits negative hydration free energies throughout. The hydrates of this cluster are all more stable than the corresponding structures containing ammonia as a base (i.e., containing three molecules of sulfuric acid and two of ammonia). Compared with the corresponding cluster with one less dimethylamine molecule, the second and third hydrates of this cluster have fewer proton transfers and are also less stable. Identical numbers of proton transfers as found within the other hydrate structures entail larger stability of the cluster containing more base molecules. The reason for this is not obvious, though it could be related to a greater possibility of structural relaxation due to the additional molecule.

Hydration Profiles. The equilibrium distributions of the hydrates for a series of different relative humidities were calculated according to eq 1 using the computed energies of the hydrates. From these the average number of water molecules bound to each cluster was determined. These values are listed together with the corresponding values derived from the thermodynamic model in Table 3. For the data derived from electronic structure calculations, also the standard deviation of the number of water molecules is given as an approximate measure of width and regularity of the distribution of populated hydrates. This standard deviation should not be understood as a measure of the precision of the value presented. Although the conversion of calculated energies into average numbers of water molecules is exact, a discussion of the expected margin of error of the used electronic structure methods can be found in ref 30. The thermodynamic model used is only intended for calculations with hydration ratios $n_{H_2O}/n_{H_2SO_4} > 1.39$; lower hydration numbers are less reliable and are italicized in the table.

In Figure 4 the population profiles of the hydrates of the clusters consisting of two, three, and four sulfuric acid molecules, as well as three sulfuric acid and two ammonia molecules, are shown as representative examples. Population profiles of all other clusters included in this study are presented in the Supporting Information. The cluster consisting of two sulfuric acid molecules exemplifies the case of a system with relatively evenly spaced hydrate energies, resulting in a relatively continuous shift toward higher hydrates with rising relative humidity (Figure 4a). However, even for this system the shift of the distribution is not entirely continuous. The maximum of the distribution changes from two water molecules at relative humidities up to 60% (apart from being one at 15% RH) to four at higher humidities. The hydrate containing three water molecules never marks the

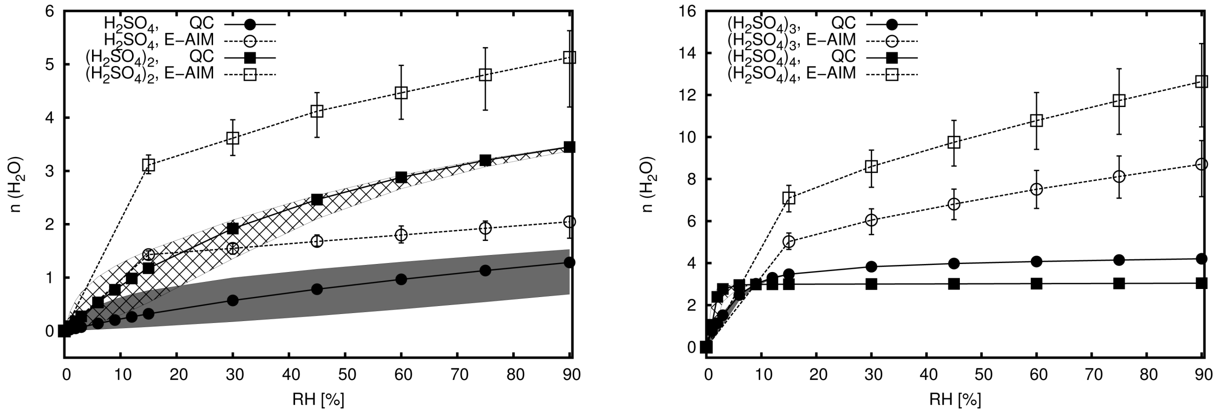


Figure 5. Average hydration numbers of base-free clusters at T = 298.15 K. Shaded areas (partly too small to be visible) represent uncertainties in the hydration from electronic structure calculations assuming a deviation of 1 kcal/mol. The vertical bars represent the sensitivity of the thermodynamic calculations to 20% variations in surface tension and density (see the text for details).

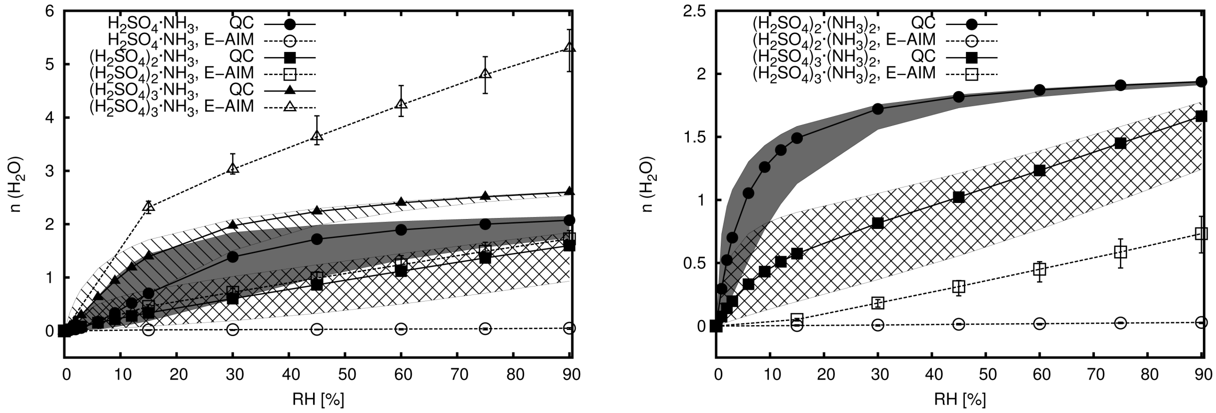


Figure 6. Average hydration numbers of clusters containing ammonia at T = 298.15 K. Shaded areas represent uncertainties in the hydration from electronic structure calculations assuming a deviation of 1 kcal/mol. The vertical bars represent the sensitivity of the thermodynamic calculations to 20% variations in surface tension and density (see the text for details).

maximum of the distribution; the fourth hydrate is, due to its high stability, already more highly populated at 60% RH. This even but rather broad distribution is characterized by comparatively large values for the standard deviation of the average number of water molecules, ranging from 0.95 to 1.21. Also, this system exhibits a non-negligible population of the hydrate containing five water molecules at higher humidities, suggesting that inclusion of even larger hydrates into the calculations might give a significant contribution to the average hydration.

The hydrate distribution for the system containing three sulfuric acid molecules (Figure 4b) is more narrow than that for the system with two sulfuric acid molecules but exhibits a similar continuous shift toward higher hydrates with higher relative humidity. However, the distribution has a maximum at four water molecules for all relative humidities. This more narrow distribution is represented by a correspondingly lower standard deviation of the average hydration, being approximately 0.6 for all relative humidities above 15%, at which also the first and second hydrate are significantly populated and the standard deviation is 0.83. Even for this system higher hydrates could contribute to the average hydration in a significant way at high relative humidities, as the population of the highest hydrate included in this study reaches values above 20%. An extreme case of a narrow distribution is represented by the system containing four sulfuric acid molecules (Figure 4c). In this case, essentially only the hydrate with three water molecules is populated at all relative humidities. Consequently, the standard deviation of the hydration numbers is also comparatively low, being below 0.3 for all relative humidities.

A different type of distribution leading to a relatively large values for the standard deviation is shown in Figure 4d. In this case, though otherwise giving a relatively narrow distribution that continuously shifts toward larger hydrates, the second hydrate has so low stability that it is not significantly populated at any relative humidity, leaving a gap in the distribution. For high relative humidities, this system has a standard deviation of hydration numbers similar to that for the system containing two sulfuric acid molecules, despite only three hydrates being significantly populated.

Comparison with Results from the Classical Thermodynamic Model. *Hydrates of Base-Free Clusters.* The average hydration numbers for the base-free sulfuric acid systems obtained through both methods are depicted in Figure 5. For the data from electronic structure calculations, additional points at relative humidities below 15% are shown to illustrate the smooth behavior of chemical equilibrium curves at low water vapor concentrations.

Generally, the trends and magnitude of hydration predicted by both methods agree reasonably well, particularly taking into account the model uncertainties and the fact that the thermodynamic model is based solely upon the properties of bulk solutions and mixtures instead of small molecular clusters.

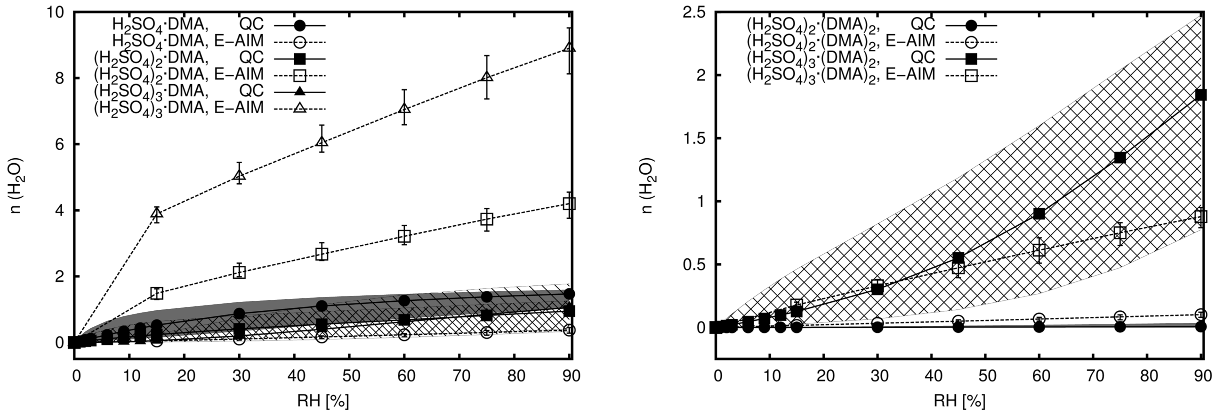
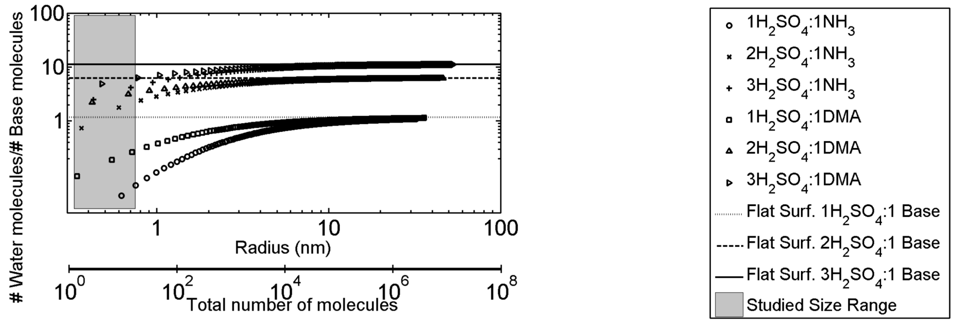


Figure 7. Average hydration numbers of clusters containing dimethylamine at $T = 298.15$ K. Shaded areas represent uncertainties in the hydration from electronic structure calculations assuming a deviation of 1 kcal/mol. The vertical bars represent the sensitivity of the thermodynamic calculations to 20% variations in surface tension and density (see the text for details).

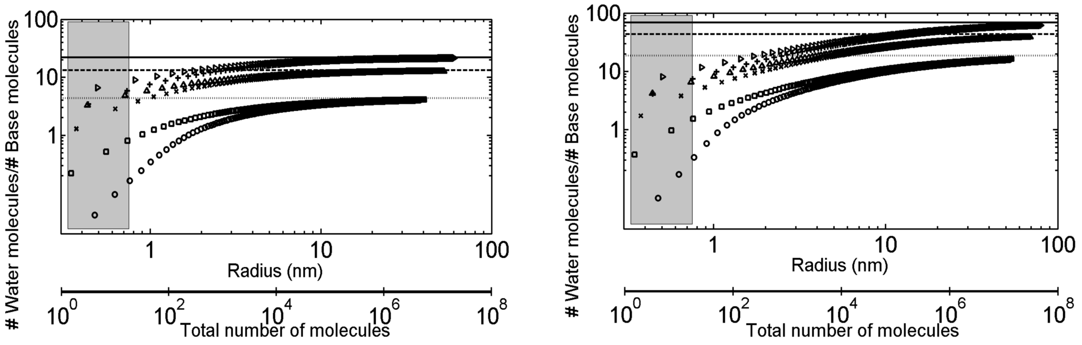
For the systems containing one or two sulfuric acid molecules and no base, the predicted hydration trends with increasing RH are found to be similar for both models. However, E-AIM predicts somewhat higher numbers of water molecules in the equilibrium clusters, as compared with the electronic structure calculations. The hydrates of the three- and four-sulfuric-acid clusters are, on the basis of the electronic structure calculations, dominated by a single hydrate structure (Figure 4b,c). This leads to hydration profiles in which the average hydration initially rises sharply with relative humidity but remains nearly constant with higher humidities. Also, this prevents the emergence of any clear trends in the hydration within the series of base free clusters as derived from electronic structure calculations. The equilibrium thermodynamic calculations, on the other hand, yield a behavior similar to that of the clusters consisting of one and two sulfuric acid molecules, although with considerably larger hydration numbers and steeper slope than the electronic structure calculations. In general, the equilibrium thermodynamic calculations seem to overestimate the hygroscopic effect of sulfuric acid at these very small sizes compared to the electronic structure calculations. This might be partly explained by the fact that the thermodynamic model assumes at least single deprotonation of all sulfuric acid molecules, as would be the case for bulk solutions of sulfuric acid in water up to about 40 mol kg^{-1} molality (a detailed overview over the protonation states assumed by the E-AIM is included in the Supporting Information).

Hydrates of Sulfuric Acid/Ammonia Clusters. The hydration of the clusters including ammonia are depicted in Figure 6. Hydration numbers derived from electronic structure calculation range in all cases between those derived for the base-free systems containing one or two molecules of sulfuric acid (cf. Figure 5 and Table 3). Interestingly, the electronic structure calculations suggest that the clusters with equal numbers of sulfuric acid and ammonia acquire more water than those with one excess molecule of sulfuric acid. This is true for systems with both one and two molecules of ammonia. A reason for this phenomenon might be that the relatively strong separation of charges, which can occur in these systems, can be partially balanced by the additional sulfuric acid molecules. Unsurprisingly, the same effect cannot be seen in the data from the thermodynamic model. Here, the clusters with equal numbers of sulfuric acid and ammonia molecules show over all relative humidities close to no hydration. In systems with larger numbers of molecules of sulfuric acid than ammonia, the influence of the additional acid molecule is predicted to be somewhat stronger than in the electronic structure calculations. For the cluster containing two acid and one base molecule, the E-AIM predicts hydration numbers very close to those from the electronic structure calculations. Upon addition of another molecule of sulfuric acid, on the other hand, the hydration numbers become higher. This is similar to the base-free systems: the absolute hydration numbers are comparable to those of the corresponding base-free cluster with one less molecule of sulfuric acid, though the increase with humidity is generally larger. Meanwhile, in the system containing two molecules of ammonia, the excess sulfuric acid molecule is not sufficient to fully compensate for the loss in hydrophilicity caused by the presence of the base. In summary, the thermodynamic model seems to overestimate the opposing effects of both sulfuric acid and ammonia, as compared with the electronic structure calculations. For systems with identical numbers of both types of molecules, according to the thermodynamic model the ammonia cancels nearly completely the hygroscopic effect of sulfuric acid, whereas in systems with an excess of sulfuric acid molecules the total water uptake is overestimated as in the base-free systems.

Hydrates of Sulfuric Acid/Dimethylamine Clusters. As shown in Figure 7, the hydration numbers of systems containing one molecule of dimethylamine derived from electronic structure calculations follow the same pattern as those for the ammonia-containing clusters, although with even lower hydration numbers. In this case, the cluster with both one sulfuric acid molecule and one base molecule is slightly more strongly hydrated than both clusters with one base molecule and excess sulfuric acid. The hydration profile of the cluster containing three sulfuric acid molecules differs slightly from the other profiles, as the slope at low relative humidities is very low, and then nearly constant for higher relative humidities. The other profiles show a trend toward saturation at higher relative humidities. The cluster containing three sulfuric acid and two dimethylamine molecules exhibits an even stronger deviation from the typical profile. In this case the slope is continuously rising with larger relative humidity. The cluster containing two sulfuric acid and two dimethylamine molecules represents an extreme case, even among the generally lowly hydrated dimethylamine-containing clusters, as it practically does not take up any water at all under the modeled conditions. This is of particular importance as this cluster has been suggested to be central for sulfuric acid/dimethylamine nucleation.[12] The hydration profiles of the



(a) RH = 30 %



(b) RH = 60 %

(c) RH = 90 %

Figure 8. Level of hydration from the E-AIM model for systems containing ammonia vs DMA as a function of the number of molecules in the system at T = 298.15 K. The corresponding geometric diameter (assuming bulk density) is also shown.

dimethylamine-containing clusters given by the thermodynamic model are also similar to the corresponding profiles obtained for the ammonia-containing systems. However, the thermodynamic model predicts invariably stronger hydration for dimethylamine-containing than ammonia-containing clusters, whereas the used electronic structure methods predict with only one exception (three sulfuric acid, two dimethylamine at 90% RH) considerably lower hydration for the dimethylamine case. The reasons for these differences and the applicability of the thermodynamic model for the clusters studied here are discussed in more detail in the following section.

Sensitivity of Equilibrium Thermodynamic Predictions to Uncertainties in Bulk Thermodynamic Properties. Densities of aqueous sulfuric acid are taken from ref 58, where the mean reported deviation between measured and parametrized values is about 0.02%. The same deviation for surface tension is 1−2%.[45] The model of Clegg and Brimblecombe[59] represented measured water activities for the 0−40 mol kg^{-1} acid at 298.15 K to within ±0.003 in the stoichiometric osmotic coefficient (see their Figure 2). At a water activity of 0.50 (i.e., a relative humidity of 50%) this is equivalent to ±0.001 uncertainty. Hyvärinen et al.[53] estimated a deviation of parametrized and measured values for the system DMA−H_2SO_4−H_2O of maximum 18% and 2% for surface tension and density, respectively. The same deviations in the system NH_3−H_2SO_4−H_2O are 3% and 2% for surface tension and density, respectively.[54] Note, however, that the data from Hyvärinen et al.[53,54] are restricted to relatively narrow concentration ranges (for the DMA-containing system mole fractions of 0−0.48 for H_2SO_4 and 0−0.21 for DMA and for the NH_3-containing system mole fractions of 0−0.45 for H_2SO_4 and 0−0.26 for NH_3). In the cases where hydration is relatively low, we had to extrapolate the parametrizations beyond these limits (see Supporting Information, Figure S29−S30). The corresponding uncertainty in the water activity is expected to be small in the case of NH_3−H_2SO_4−H_2O, for example, about ±0.015 in the water activity for equimolar NH_3, H_2SO_4, and water (and better than this at lower concentrations),[43] whereas water activities in the DMA containing systems have not been reported to date, so the uncertainty related to these values is difficult to quantify but is certainly much larger.

We investigated the sensitivity of the thermodynamic calculations to uncertainties in the bulk thermodynamic properties by varying the density by ±20% around the base value, and the surface tension by varying the difference between the base value and the surface tension of water at the same temperature by ±20%, and selecting the two combinations that resulted in the largest positive and largest negative deviation for the hydration value. The results of these sensitivity studies are shown as vertical bars in Figures 5−7 (see also and Table S3 in the Supporting Information). As the model uncertainties in the activity predictions are generally much smaller than those related to surface tensions, the water activities were not varied. The bounds used in the sensitivity analysis were chosen as a conservative measure to estimate the maximum likely variability in the thermodynamic calculations as a result of the uncertainty estimates discussed in the previous paragraph. It should, however, be noted that these boundaries do not include the experimental uncertainty related to the measurement of the thermodynamic properties themselves. Specifically it should be noted that the ammonia-containing systems are experimentally much better constrained than the corresponding values for the DMA-containing systems, which is not reflected in the error bars. The maximum sensitivity of the hydration occurs for the largest clusters at high relative humidities (Figures 5−7). These conservative uncertainty estimates widen the possible range for hydration of each cluster, but it is clear that the model sensitivity to surface tension and density values does not explain the main findings of the quantum chemical calculations including the discrete cluster configuration. Equations 2 and 3 suggest that the surface tension is the dominant variable causing the uncertainty in the thermodynamic calculations.

The equilibrium thermodynamic calculations cannot be expected to be accurate for clusters containing small numbers of molecules, but it is unclear where the transition to bulk behavior occurs. It is not yet possible to carry out quantum chemical calculations for very large numbers of molecules, but we have examined the dependence of the thermodynamic model predictions of hydration on the numbers of molecules present, as governed by the Kelvin effect. Figure 8 shows examples of E-AIM predictions of the hydration of ammonia- and DMA-containing systems, for clusters and particles containing up to 10^8 molecules. First of all, it can be seen that due to the similar activity treatment of the ammonium and the dimethylammonium salts (see the methods section), the predictions of hydration at the limit of bulk solutions are the same in both systems. For bulk solutions, current experimental data suggest this is reasonable.[48] Second, the figures illustrate the importance of the Kelvin effect (eq 2) below 10 nm (of the order of 10 000 molecules): the hydration numbers predicted for the clusters investigated are generally about 1−2 orders of magnitude lower than the corresponding bulk solution predictions. This strong sensitivity to the system size is largely caused by the sensitivity of the Kelvin equation to the surface tension of the investigated solution (eqs 2 and 3), which is assumed to be independent of particle size (capillarity assumption).

The validity of the capillarity assumption has been explored extensively in the context of nucleation predictions (see, e.g., refs 60 and 61 and references therein), and the general trends for the size dependence of surface tension have been established for simple fluids. The surface tension of symmetric Lennard-Jones fluids typically decreases with decreasing particle size.[62−64] For our predictions this would mean even larger hydration numbers than currently predicted with equilibrium thermodynamics and is thus an unlikely explanation of the differences between the quantum chemical and bulk thermodynamic calculations. For more complex molecules, theoretical predictions suggest that the surface tensions of small clusters can be either smaller or larger than the bulk values, depending on the cluster size and the molecules in question. The largest increases reported by Napari and Laaksonen[64] for (still relatively simple) asymmetric model dimers and trimers, however, are typically less than 10%, and thus within the envelope of our conservative sensitivity estimates given above. Unfortunately, there are no experimental measurements of the surface tensions of sulfuric acid clusters as small as investigated in this study. Given the known limitations of the applicability of bulk thermodynamics to systems containing only a few molecules, the large sensitivity of the treatment to the Kelvin effect and the uncertainties in the surface tensions and densities of the mixed systems, the overall agreement between the thermodynamic and the electronic structure approaches in terms of the magnitude of hydration is encouraging. However, resolving the discrepancy between the relative effects of ammonia and DMA in hydration deserves further work, potentially in the form of size-dependent correction factors for the activities of the ammonium vs dimethylammonium salts, along with the further experimental constraints for the bulk thermodynamic properties of these systems.

■ CONCLUSIONS

We have conducted calculations on a comprehensive set of hydrates of atmospherically relevant molecular clusters. For pure acid clusters containing three or four molecules, a much stronger trend toward hydration numbers already leveling off at intermediate relative humidities was found than for the clusters containing only one or two sulfuric acid molecules. Clusters containing ammonia were found to be considerably less hydrated than the corresponding base-free clusters, as expected. In general, the effect of a molecule of ammonia can be approximated as canceling the effect of one molecule of sulfuric acid. However, clusters with identical numbers of acid and ammonia were found to be hydrated more strongly than would be expected from this trend, and even more strongly than the corresponding clusters with one more molecule of sulfuric acid. The effect of inclusion of dimethylamine molecules into the clusters was similar to that of ammonia, though more pronounced. Clusters containing dimethylamine were found to be in general only very weakly hydrated, binding not much more than one water molecule in average, even at elevated relative humidities. The cluster consisting of two sulfuric acid and two dimethylamine molecules marks an extreme point of this behavior, practically not binding any water at all.

In comparison with the results obtained from electronic structure calculations, the calculations based upon bulk thermodynamic properties predict similar trends with relative humidity for hydration numbers of pure sulfuric acid clusters. However, though of the same order of magnitude, hydration numbers are consistently overestimated. Thermodynamic calculations cannot reproduce the relatively strong trends toward saturation for the clusters with three and four molecules of sulfuric acids, as the specific features of the energy profiles of their hydrates cannot sufficiently be modeled without taking into account the molecular structure of clusters. For systems also containing base molecules, the thermodynamic calculations correctly predicted significantly lower hydration numbers than for base-free clusters. However, in contrast to the electronic structure calculations, the effect of ammonia on the hydration is predicted to be larger than that of dimethylamine. Furthermore, for clusters with equal numbers of acid and base, the thermodynamic model predicts (with the exception of the two sulfuric acid−two DMA cluster) the clusters to be generally less hydrated than do the electronic structure calculations. Clusters with more acid than base molecules are again more strongly hydrated in the thermodynamic model than predicted by the electronic structure calculations. Thus, for small clusters the thermodynamic model seems to overpredict both the hygroscopic effect of sulfuric acid, as well as the reduction caused by the base molecules that were included in this study. As the deviation is for all substances toward a stronger effect, this might be adjustable in future model development.

The qualitative agreement of the results from the two methods used suggests that the equilibrium thermodynamic calculations might, in principle, be extended to model the hydration behavior of small molecular clusters by adjusting for the differences between the calculated hydration levels and those determined from electronic structure calculations. The thermodynamic model could itself be improved by further measurements of densities and surface tensions for both ternary mixtures, and of water activities for DMA−H_2SO_4−H_2O. The effect of temperature on the thermodynamic properties of DMA−H_2SO_4−H_2O (important for atmospheric calculations) has not yet been investigated. To obtain more detailed information like the population of distinct hydrate structures and correct behavior for individual clusters, electronic structure calculations will remain indispensable. Some effects of the hydration of clusters on the pathways of cluster growth, potentially leading eventually to particle formation, can be estimated from the average hydration numbers, with highly hydrated clusters being stabilized by the hydration and therefore becoming more important in cluster growth pathways. This can easily be predicted for the base-free sulfuric acid trimer and tetramer, which both form very stable hydrates. For a correct description of the effects on the kinetics of collision and especially evaporation processes, however, the complex network of possible routes between the individual hydrates will need to be taken into account.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates, energies of hydration steps, structure depictions, and hydration profiles of all optimized structures. Protonation numbers and variability from thermodynamic theory. Parametrization of surface tension. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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