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Ab Initio and Density Functional Study of Complexes between the Methylamines and Water

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We present results of ab initio and density functional studies of the interaction between the methylamines (methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA)) and one or two water molecules. The structures and energetics of the hydrogen-bonded complexes of MA and DMA with one and two water molecules and of TMA with one water molecule are reported at three levels of theory: MP2/6-31+G(d,p), B3LYP/6-31+G(d,p), and B3LYP/6-311+G(2d,p). All three levels of theory give ZPE and BSSE corrected binding energies of 20−22 kJ mol^{-1} for the 1:1 complexes and 32−40 kJ mol^{-1} for the 1:2 complexes. The calculated thermodynamics of 1:1 and 1:2 complex formation are used to estimate the adsorption thermochemistry of the amines at the air−water interface. This adsorption is best described by a "critical complex" formed of one amine molecule and two water molecules. The formation of the amine−water complexes in the atmosphere is also briefly discussed. Because of the strong hydrogen bonding possible, such complexes could act as cloud condensation nuclei.

Introduction

The relatively high concentration of water in all its physical phases throughout the atmosphere makes its interactions with trace species important. The potential significance of small water complexes (containing 1−3 water molecules) to solar radiative transfer[1] (and hence climate) and atmospheric chemistry[2,3] has recently been discussed. Trace atmospheric species may also have important interactions with condensed-phase water. Many important environmental reactions are governed by the heterogeneous interaction of gas-phase molecules with liquid-water surfaces. These types of interactions are known to be a key step in processes such as acid rain, the removal of anthropogenic species, ozone depletion, and the creation of cloud condensation nuclei.[4−7]

In this laboratory, we have used both experimental (surface second harmonic generation spectroscopy, equilibrium and nonequilibrium surface tension measurements) and theoretical quantum calculations to study the adsorption of several volatile solutes at the air−water interface, including SO_2,[8,9] NH_3 (hereinafter **I**),[10] several partially oxidized organics (hereinafter **II**),[11,12] and methylamines (hereinafter **III**).[13] The general conclusions from these studies can be summarized as the following: (1) When hydrogen bonding is possible, adsorption at the air−water interface is primarily through hydrogen bonding to the "dangling" water O−H bonds, with the saturated coverage approximately equal to the number of dangling O−H bonds at the water surface; (2) the correlation between the standard enthalpy of adsorption from the gas phase (ΔH_{ads}^o) and the standard enthalpy of solvation (ΔH_{sol}^o) is consistent with the formation of a partially solvated surface species, perhaps a "critical complex", as suggested by Davidovits and co-workers.[14]

In **I**, we proposed a model for gas adsorption to the air−water interface, in which this critical complex is composed of the adsorbate molecule, hydrogen bonded to a few water molecules. We tested this model by explicit high-level ab initio calculation of the hydrogen-bonding energies for NH_3 with one and two water molecules, to compare the predicted adsorption energetics with experimental measurements. The binding enthalpies calculated in this way were assumed to represent the standard enthalpies of binding to the surface, assuming the critical complex to be composed of ammonia with one and two water molecules, respectively. The standard free energy of adsorption was estimated using this value for ΔH_{ads}^o and a value of ΔS_{ads}^o estimated following the procedure outlined in Adamson[15] (vide infra).

When applied to ammonia adsorption in **I**, the calculated ΔG_{ads}^o with one and two water molecules in the critical complex were the same and both very close to experiment. The ΔH_{ads}^o calculated with a single water was much smaller than the measured value; inclusion of a second water molecule, mostly likely in a cyclic hydrogen bonded complex, gave results much closer to experiment. A tilted geometry of NH_3 at the air−water interface, consistent with a cyclic hydrogen bond[10] has been inferred in a surface sum frequency generation study[16] and seems to hold for NH_3 adsorbed on ice as well.[17] In **III** this same approach was taken for the methylamines. At that time, we calculated the binding enthalpies only, at a lower level of theory than the ammonia calculations. Comparison of these with experimental values was not conclusive, but suggested that either one or two waters were involved in the surface complex.

The present work expands upon the theoretical work reported in **III**. We have recalculated the structures, vibrational frequencies, and energies of the 1:1 and 1:2 complexes of methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA) with water at a higher level of theory than in **III**, using density functional theory and a larger basis set. We use the results to further test the model for trace gas adsorption on water and to estimate the ability of amino compounds to act as cloud condensation nuclei (CCN) in the atmosphere.

Computational Details

Ab initio calculations for both the monomers and complexes were carried out at the MP2 level using the Gaussian 98[18] suite

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TABLE 1: Selected Structural Parameters of All 1:1 Complexes (X−H2O)[a]

			B3LYP	
X	parameter	MP2/6-31+G(d,p)	6-31+G(d,p)	6-311+G(2d,p)
MA	r(N−O)	2.884	2.872	2.897
	r(N−H)	1.923	1.899	1.927
	∠NHO	166.2	169.2	159.2
DMA	r(N−O)	2.870	2.861	2.885
	r(N−H)	1.905	1.887	1.914
	∠NHO	174	172	160.5
TMA	r(N−O)	2.849	2.861	2.884
	r(N−H)	1.868	1.882	1.908
	∠NHO	169.9	171.2	171.3
H_2O	r(O−O)	2.915	2.887	2.899
	r(O−H)	1.947	1.919	1.940
	∠HOH	175.7	173.5	173.5

[a] Bond lengths in Å; angles in degrees.

TABLE 2: Structural Parameters for 1:2 Complexes X−$(H_2O)_2$[a]

			B3LYP	
X	parameter	MP2/6-31+G(d,p)	6-31+G(d,p)	6-311+G(2d,p)
MA	r(N−HO)	1.843	1.818	1.845
	r(NH−O)	2.210	2.232	2.257
	r(OH−O)	1.897	1.859	1.876
DMA	r(N−HO)	1.816	1.806	1.832
	r(NH−O)	2.180	2.233	2.255
	r(OH−O)	1.893	1.859	1.877

[a] Bond lengths in Å.

TABLE 3: Energetics Calculated at MP2/6-31+G(d,p)[a]

reaction	ΔE	ΔZPE	BSSE	$\Delta E_o{}^o$
MA + H_2O → MA−H_2O	−39.6	+8.6	+10.2	−20.8
MA + $(H_2O)_2$ → MA−$(H_2O)_2$	−57.3	+9.9	+9.7	−37.7
MA−H_2O + H_2O → MA−$(H_2O)_2$	−44.4	+10.1	+8.8	−25.5
DMA + H_2O → DMA−H_2O	−41.9	+8.1	+12.9	−20.9
DMA + $(H_2O)_2$ → DMA−$(H_2O)_2$	−61.8	+9.0	+12.7	−40.1
DMA−H_2O + H_2O → DMA−$(H_2O)_2$	−46.6	+10.5	+9.6	−26.5
TMA + H_2O → TMA−H_2O	−38.1	+8.2	+8.5	−21.4
H_2O + H_2O → $(H_2O)_2$	−26.7	+9.9	+6.6	−10.2
H_2O + $(H_2O)_2$ → $(H_2O)_3$	−51.4	+14.1	+8.1	−29.2

[a] Energies in kJ mol^{-1}.

TABLE 4: Energetics Calculated at B3LYP/6-31+G(d,p)[a]

reaction	ΔE	ΔZPE	BSSE	$\Delta E_o{}^o$
MA + H_2O → MA−H_2O	−33.7	+9.7	+2.3	−21.7
MA + $(H_2O)_2$ → MA−$(H_2O)_2$	−49.9	+11.0	+3.7	−35.2
MA−H_2O + H_2O → MA−$(H_2O)_2$	−41.5	+11.3	+3.0	−27.2
DMA + H_2O → DMA−H_2O	−33.0	+9.1	+2.0	−21.9
DMA + $(H_2O)_2$ → DMA−$(H_2O)_2$	−49.2	+10.0	+2.9	−36.3
DMA−H_2O + H_2O → DMA−$(H_2O)_2$	−41.4	+10.8	+3.3	−27.3
TMA + H_2O → TMA−H_2O	−31.8	+8.7	+2.1	−21.0
H_2O + H_2O → $(H_2O)_2$	−25.3	+9.9	+3.4	−12.0
H_2O + $(H_2O)_2$ → $(H_2O)_3$	−49.9	+14.7	+5.4	−29.8

[a] Energies in kJ mol^{-1}.

of programs; the Gaussian 94[19] package was used for DFT calculations which employed the B3LYP functionals and the 6-31+G(d,p) basis set. Density functional calculations were also carried out using the Gaussian 94 package and the 6-311+G(2d,p) basis set. The B3LYP functional has proven highly effective at predicting properties for hydrogen-bonded complexes, at least for basis set as large as 6-31+G(d,p).[20−22] Density functional theory offers an electron correlation effect frequently comparable to MP2 but at a considerably lower computational cost.[23] Geometry optimizations were carried out at all levels of theory without constraints, except for species with symmetry known from experiment; for example, methylamine[24] and dimethylamine[25] are known to have C_s symmetry from microwave spectroscopy. At each stationary point found, a vibrational analysis was performed to characterize it as a minimum on the potential-energy surface.

Empirical scaling factors appropriate for B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2d,p) were obtained by scaling the harmonic frequencies of the optimized monomers; scaling of the B3LYP/6-31+G(d,p) frequencies by a factor 0.9692 and the B3LYP/6-311+G(2d,p) frequencies by 0.9729 agreed with experiment.[26] A similar scaling has been reported by Jorgensen and co-workers.[27] Agreement between MP2/6-31+G(d,p) frequencies scaled by 0.9427[26b] and experiment is also good.

The interaction energy between the partners in each complex at the energetic minimum was calculated using the supermolecule method,[28] which defines it as the difference between the electronic energy of the complex and the combined energies of the isolated molecules,

$$\Delta E_{i,j,...} = E_{i,j,...}(I,J,..) - \Sigma E_i(I)$$

where the terms in brackets denote the basis set used. The relevant energies were corrected for zero-point differences using harmonic frequencies calculated as outlined above. Since we use an incomplete basis set, the results are contaminated with basis set superposition error (BSSE):[29] each molecule in the complex may use the basis set of the other, resulting in an overestimation of the interaction energy. The interaction energy was corrected for BSSE using the counterpoise method of Boys and Bernardi.[30] In this approach, for example, the water nuclei and electrons are removed in the CH_3NH_2–H_2O complex and the energy is calculated; the result gives the lowering of the methylamine energy by the presence of basis functions on water. This energy, labeled $E(CH_3NH_2-(H_2O)^{gh})$, is subtracted from $E(CH_3NH_2)$ to give the BSSE estimate for methylamine in the complex, $BSSE_{CH_3NH_2}$. The interaction energy is then calculated to be $\Delta E = E(CH_3NH_2\text{–}H_2O) - E(CH_3NH_2) - E(H_2O) + BSSE_{CH_3NH_2} + BSSE_{H_2O} + \Delta ZPE$.

Structures and Energetics of Amine−Water Complexes

All of the 1:1 amine−water complexes exhibit strong hydrogen bonding, with the water acting as the donor and the amine as the acceptor through the lone pair of electrons on the nitrogen atom. The hydrogen bond length in the 1:1 complexes decreases somewhat with increasing methylation. The 1:2 complexes have the additional water molecule acting as both a hydrogen donor, with a strong hydrogen bond to the first water molecule, and a hydrogen acceptor, forming a weaker hydrogen bond with the amine. The important structural parameters of the optimized geometries of the 1:1 and 1:2 complexes at each level of theory are given in Tables 1 and 2, respectively. The energetics of the complex-forming reactions are presented in Tables 3−5 for MP2/6-31+G(d,p), B3LYP/ 6-31+G(d,p), and B3LYP/6-311+G(2d,p) levels of calculation, respectively. The full geometries and energies for all the complexes studied here are available from the authors upon request.

1:1 Complexes. To the best of our knowledge, the CH_3NH_2−H_2O complex has not been studied experimentally but has been the subject of theoretical study. Our calculated structure of the complex is illustrated in Figure 1a, and the corresponding structural parameters are given in Table 1. Molecular dynamics simulations[31] give an N−O separation of 2.85 Å in aqueous methylamine solution and a hydrogen bond length, r(N−H),

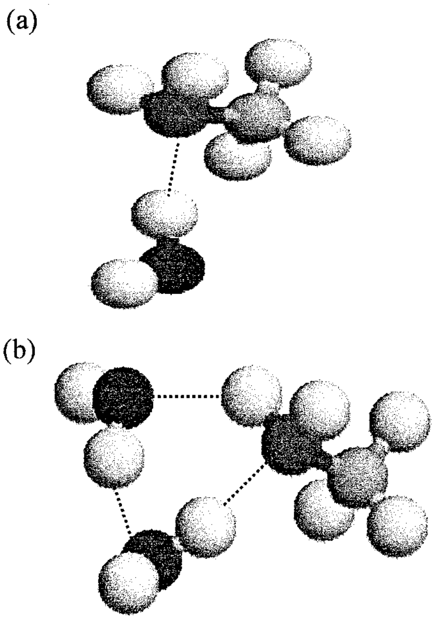

Figure 1. Calculated minimum energy structure (a) of the 1:1 methylamine−water complex and (b) the 1:2 methylamine−water complex. A cyclic structure is observed for the 1:2 complex with the amine acting as both a hydrogen donor and acceptor.

TABLE 5: Energetics Calculated at B3LYP/6-311+G(2d,p)[a]

reaction	ΔE	ΔZPE	BSSE	ΔE_o^o
MA + H_2O → MA−H_2O	−29.8	+9.0	+1.0	−19.8
MA + $(H_2O)_2$ → MA−$(H_2O)_2$	−44.9	+11.0	+2.3	−31.6
MA−H_2O + H_2O → MA−$(H_2O)_2$	−38.0	+11.2	+2.7	−24.1
DMA + H_2O → DMA−H_2O	−29.4	+8.7	+0.8	−19.9
DMA + $(H_2O)_2$ → DMA−$(H_2O)_2$	−44.7	+10.1	+2.3	−32.3
DMA−H_2O + H_2O → DMA−$(H_2O)_2$	−38.0	+10.7	+2.7	−24.6
TMA + H_2O → TMA−H_2O	−28.6	+8.5	+1.2	−18.9
H_2O + H_2O → $(H_2O)_2$	−22.8	+9.2	+2.6	−11.0
H_2O + $(H_2O)_2$ → $(H_2O)_3$	−46.1	+14.5	+4.5	−27.1

[a] Energies in kJ mol^{-1}.

between the H atom in water and the N atom of methylamine of 1.9 Å. Recent DFT calculations by Jorgensen and co-workers,[27] similar to those presented here, yield a hydrogen bond length of 1.92 Å, essentially identical to the present result.

The energetics of formation of the CH_3NH_2–H_2O complex at the different levels of theory are shown in Tables 3−5. Density functional theory gives a very small BSSE correction compared to that for MP2 calculations. The calculated binding energy for the complex (not BSSE-corrected) is larger at the MP2 level than using DFT but becomes a bit smaller after the BSSE correction. The larger basis set gives a somewhat smaller ΔE_o^o; all three results yield zero point and BSSE-corrected binding energies of 20−22 kJ mol^{-1}. These energies are also in excellent agreement with those reported by Jorgensen and co-workers.[27]

Calculations performed at the B3LYP/6-31+G(d,p) level give a better BSSE and ZPE corrected binding energy of the water dimer, $\Delta E_o^o = -12.0$ kJ mol^{-1}, than the other two methods when compared to previous calculations and experimental estimates.[32a] The water dimer has been studied extensively; the most commonly structural parameter used for comparisons is the O−O distance. The experimental O−O distance is 2.976 Å,[32b] but large anharmonic vibrational corrections are present. These effects have been estimated by Odutola and Dyke, yielding an O−O distance of 2.946 Å.[32c] The best available theoretical value of 2.912 Å for the O−O distance was recently calculated by Klopper and co-workers at the CCSD(T) level of theory.[32d] Our calculated distances are all near 2.91 Å, in good agreement with experiment.

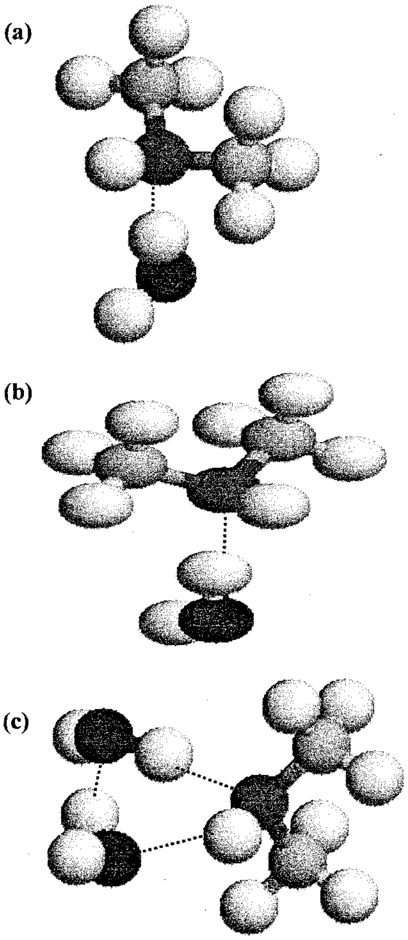

Figure 2. Calculated minimum energy structure of (a) the 1:1 dimethylamine−water complex with the free water hydrogen aligned on the same side as the amino hydrogen and (b) with the free water hydrogen aligned on opposite side to the amino hydrogen and (c) the 1:2 dimethylamine−water complex. A cyclic structure is observed for the 1:2 complex with the amine acting as a hydrogen donor and acceptor.

Figure 2a shows the structure of the $(CH_3)_2NH$−H_2O complex optimized at the MP2/6-31+G(d,p) level. The “free” water hydrogen is aligned on the opposite side to the free amino hydrogen. When this geometry was used as input for B3LYP/6-31+G(d,p), it gave an imaginary frequency of −16 cm^{-1}. Optimization with the free water hydrogen on the same side as the free amino hydrogen, as shown in Figure 2b, did not give an imaginary frequency at any of the levels of theory considered here. The structure displayed in Figure 2b is more stable than the structure shown in Figure 2a by 0.31 kJ mol^{-1} at the B3LYP/6-31+G(d,p) level. The energies reported here all correspond to the structure illustrated in Figure 2b.

The $(CH_3)_2NH$−H_2O complex has been studied experimentally by microwave spectroscopy.[33] The complex has a nonlinear hydrogen bond angle NHO of 169° with a heavy atom separation (R_{NO}) of 2.82 Å and hydrogen bond length of 1.85 Å. There is generally good agreement between our calculated values and experiment. The energetics for the formation of the $(CH_3)_2NH$−H_2O complex are listed in Tables 3−5 for the three levels of theory. The ZPE and BSSE corrected binding energies, 20−22 kJ mol^{-1}, are slightly higher than those for the CH_3NH_2–H_2O complex for all the three levels of theory. This implies slightly

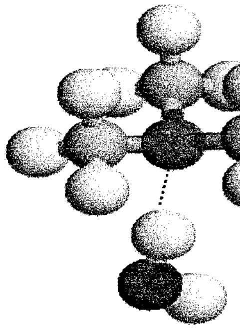

Figure 3. Calculated minimum energy structure of the 1:1 trimethylamine−water complex.

stronger binding on moving from methylamine to dimethylamine; the same trend is inferred from the decreasing hydrogen bond lengths.

The $(CH_3)_3N-H_2O$ complex has also been studied previously by microwave spectroscopy[34] and theoretically by Jorgensen and co-workers.[27] The experimental value of R_{NO} is reported as either 2.849 or 2.881 Å, depending on the method of analysis; the corresponding hydrogen bond lengths are 1.818 and 1.853 Å, respectively. Our calculated structure is illustrated in Figure 3, with important geometrical parameters shown in Table 1. The heavy atom separation we calculate is well within the range of the experimental values, but the calculated hydrogen bond length is somewhat greater than experiment at all levels of theory. Reference 27 lists a hydrogen bond length of 2.102 Å, longer than experiment or any of our results.

The energetics of the reaction forming the $(CH_3)_3N-H_2O$ complex, $(CH_3)_3N + H_2O \rightarrow (CH_3)_3N-H_2O$, are given in Tables 3−5. Again, the calculated binding energies all lie within in the 19−22 kJ mol^{-1} range. Interestingly, the binding energy reported by Rablen et al.,[27] 18.7 kJ mol^{-1} when corrected for zero-point energies, is very similar to those we find, even though their reported hydrogen bond length is significantly longer.

1:2 Complexes. The $CH_3NH_2-(H_2O)_2$ complex has not previously been reported either from experiment or from theoretical calculations. The optimized geometry at the MP2/6-31+G(d,p) level is illustrated in Figure 1b. Important structural parameters are listed in Table 2. This geometry was used as the input for B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2d,p) calculations; no imaginary frequencies were found at any level, suggesting that this is indeed a minimum in the potential-energy surface.

Addition of a second water molecule allows the formation of a cyclic hydrogen-bonded complex, as we reported[10] for $NH_3-(H_2O)_2$. The "old" hydrogen bond becomes significantly shorter in the 1:2 complex, decreasing in length by about 0.1 Å. The "new" water−amine hydrogen bond is quite a bit longer, by about 0.3 Å. It is similar in length to that reported by Marten et al.[35] for the 1:1 complex with MA acting as the hydrogen donor. The third hydrogen bond, formed between the two water molecules, is also significantly shorter than that in the water dimer.

Energetics for the formation of the $CH_3NH_2-(H_2O)_2$ complex from CH_3NH_2 interacting with $(H_2O)_2$ as well as for the addition of a water molecule to the 1:1 complex are given in Tables 3−5. As seen for 1:1 complex formation, the larger basis set gives a somewhat smaller binding energy. For the addition of MA to the water dimer, the three levels of theory give ZPE and BSSE corrected binding energies of 32−38 kJ mol^{-1}. This energy can be considered as the sum of the two MA−water hydrogen bonds. Assuming the bond with water acting as the hydrogen donor maintains the same strength as in the 1:1 complex, the new hydrogen bond, with water as acceptor, contributes about 10−15 kJ mol^{-1} to the total binding energy. This compares well with the energies reported by Marten et al.[35] and Rizzo and Jorgensen[36] for the hydrogen-bonding energy in the 1:1 complex with water acting as the hydrogen acceptor.

The $(CH_3)_2NH-(H_2O)_2$ complex has also not, to the best of our knowledge, been reported before, either experimentally or theoretically. The geometry of the complex is illustrated in Figure 2c. No imaginary frequencies are calculated at any level of theory suggesting that the displayed complex represents a true minimum in the potential-energy surface. The energetics of the reaction forming $(CH_3)_2NH-(H_2O)_2$ from DMA and the water dimer, as well as forming the 1:2 complex from the 1:1 complex and water are both given in Tables 3−5. As for the $MA-(H_2O)_2$ complex, the calculated zero point and basis set corrected binding energies are roughly equivalent to the addition of "water donor" and "water acceptor" hydrogen-bond energies. For the $(CH_3)_2NH-(H_2O)_2$ complex, they are 32−40 kJ mol^{-1}, depending on the level of theory, slightly higher than those for the corresponding MA system.

The Potential Role of Amine−Water Clusters in the Atmosphere. In recent publications, we[2] and others[1,3] have discussed the formation and properties of complexes of atmospheric gases with water. Aloisio et al.[37] have very recently presented structures and energies of formation of several water−formic acid complexes containing up to four water molecules, calculated at a similar level of theory to the present work. One aim of that study was to compare the "water condensing" ability of formic acid−water complexes to that of pure water complexes of the same size. It was found that formic acid-containing complexes display a larger binding energy for the addition of further water molecules than do pure water complexes. The authors conclude that organic acids may thus act as effective cloud condensation nuclei (CCN).[37]

The present calculations are not as extensive as those of Aloisio et al.,[37] since we concentrate only on the lowest energy complex in each case. Since we ignore all higher-energy complexes, which might also contribute to water condensation, true thermodynamic parameters for establishing relative CCN abilities cannot be calculated. However, we can compare the binding energies of water to the amino complexes to the binding energy of water to same-sized water complexes, all in their most stable configurations. The results shown in Tables 3−5 give the requisite data for the comparison. By this measure, the unclustered amines are more effective than water at forming the initial water-bound species and slightly less effective at binding a second water molecule. We are currently extending the study to include an additional water molecule and are exploring the role of less stable complexes in the CCN ability of amines.

Modeling Adsorption at the Air−Water Surface. In **I,** we presented a model for adsorption of volatile solutes at the air−water interface which, although simple, seemed to capture the important physics of the process. Analogous to the "critical cluster" model of Davidovits and co-workers,[14] it proposes that specific interactions between the adsorbate and a few surface water molecules (which together comprise the critical cluster) are responsible for the observed adsorption behavior. For the classes of compounds we have investigated to date,[8−13] the specific interactions primarily involve the formation of hydrogen bonds between the adsorbate and water molecules. We modeled the adsorption thermochemistry by taking the standard enthalpy of adsorption ΔH_{ads}^{o} to be due to hydrogen bonds to a few water

TABLE 6: Adsorption Thermochemistry at 298 K (B3LYP/6-311+G(2d,p) Results)[a]

	1:1 complex			1:2 complex			experiment[b]		
amine	ΔG_{ads}^0	ΔH_{ads}^0	ΔS_{ads}^0	ΔG_{ads}^0	ΔH_{ads}^0	ΔS_{ads}^0	ΔG_{ads}^0	ΔH_{ads}^0	ΔS_{ads}^0
MA	−13.2	−17.6	−14.8	−23.1	−30.9	−26.1	−22 ± 1	−28 ± 3	−19 ± 10
DMA	−16.4	−17.7	−4.4	−25.5	−31.1	−18.8	−24 ± 1	−37 ± 3	−45 ± 10
TMA	−16.8	−16.6	0.7				−23.2 ± 1	−34 ± 3	−36 ± 10

[a] Energies in kJ mol^{-1}; entropies in J K^{-1} mol^{-1}. [b] From ref 13.

molecules only. The standard free energy of adsorption, ΔG_{ads}^o, is given (at a particular temperature) by $\Delta G_{ads}^o = \Delta H_{ads}^o - T \Delta S_{ads}^o$.

The standard entropy of adsorption is estimated as described in Adamson[15] to be $\Delta S_{ads}^o = (S^{o,\sigma}_{config} + S^{o,\sigma}_{trans-2D} + S^{o,\sigma}_{internal}) - S^{o,g}$, where the terms in brackets represent the configurational, translational, and internal contributions to the entropy of the adsorbed species, respectively, and the standard entropy of gas-phase species is denoted $S^{o,g}$. The standard configurational entropy is given by $S^{0,\sigma}_{config} = -R \ln(\Theta^0/(1 - \Theta^0))$, where Θ^0 represents the relative surface coverage in the standard state, and the standard translational entropy is that of a particle in a 2-D box having the same area as that occupied by the adsorbed species in its standard state. In **I,** we argued that the surface standard state occupies an area per molecule of 22.53 T Å^2. Values of Θ^0 for each of the methylamines are estimated from the experimental results reported in **III**. The standard internal entropy of the adsorbed species is estimated to be the difference between the vibrational entropy of the complex and the vibrational entropy of water. The vibrational entropies and the entropy of the gas-phase amine are calculated from the GAUSSIAN output, using standard statistical mechanical methods.

In **I,** this procedure gave predicted adsorption thermodynamic parameters in excellent agreement with experimental results when a critical complex involving two or three water molecules was assumed. In **III**, we estimated the standard adsorption enthalpies only, at the MP2/6-31+G(d,p) level, for critical complexes of the methylamines with one and two water molecules. It remained uncertain in that work whether one or two waters are involved in amino binding to the water surface, though it seemed that the number should be less than three. Here, we estimate the ΔG_{ads}^o, ΔH_{ads}^o, and ΔS_{ads}^o for the three methylamines binding to a water surface through either a 1:1 or a 1:2 critical complex, using the results of our higher level calculations, reported above.

The standard configurational entropy for methylamine is estimated to be 34.79 J K^{-1} mol^{-1} from data reported in **III**. The standard translational entropy is 105.75 J K^{-1} mol^{-1} and the standard internal entropy of the adsorbed species is estimated to be 69−72 J K^{-1} mol^{-1} for the 1:1 complex and 60−70 J K^{-1} mol^{-1} for the 1:2 complex, depending on the level of theory. To compare with experiment, we choose the B3LYP/6-311+G(2d,p) results, since they give binding energies for the 1:1 complex in best agreement with higher level calculations.[27] This set yields a value of $S_{internal}^0$ of 70.9 J K^{-1} mol^{-1} for the 1:1 complex and 59.6 J K^{-1} mol^{-1} for the 1:2 complex. $S^{o,g}$ for methylamine is calculated to be about 226 J K^{-1} mol^{-1}, yielding an adsorption entropy $\Delta S_{ads}^o = -14.8$ J K^{-1} mol^{-1} for the 1:1 complex and −26.1 J K^{-1} mol^{-1} for the 1:2 complex. ΔG_{ads}^o then becomes −13.2 kJ mol^{-1}, assuming a 1:1 interaction between MA and a single surface water molecule, or −26.1 kJ mol^{-1}, assuming the interaction is with two surface waters. The experimental value of ΔG_{ads}^o is -22.3 ± 0.5 kJ mol^{-1}; the experimental value of ΔH_{ads}^o is -28 ± 3 kJ mol^{-1}. These results, and those for the other methylamines, are summarized in Table 6.

The experimental adsorption thermochemistry of both methylamine and dimethylamine at the air−water interface is remarkably well captured by a model in which the amine molecule interacts simultaneously with two mutually hydrogen-bonded water molecules. Experimental results for the adsorption thermochemistry of trimethylamine are poorly reproduced assuming that a single amine−water hydrogen-bonding interaction is responsible for the adsorption. Although we did not calculate the structure or energy of a 1:2 TMA−water complex, our results strongly suggest that two water molecules are involved in binding TMA to the water surface.

Conclusions

The primary aim of this study was to test more completely the surface adsorption model presented in **I**. To accomplish this, we have calculated the thermochemical parameters relating to the formation of methylamine−water complexes containing one and two water molecules at a moderate level of theory. Binding of the amines with two water molecules involves a cyclic structure, in which the amines act both as hydrogen donor (to one water) and acceptor (to the other), while the two water molecules also share a hydrogen bond. The binding energy of the amine to a water dimer is roughly equal to the sum of the two hydrogen-bond energies involving the amine. The model given in **I** works remarkably well, given its simplicity, and suggests that the amines are associated with two water molecules at the air−water interface. The present results further suggest that amines may act as cloud condensation nuclei, with efficiencies comparable to that of water.

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