

On the Uptake of Ammonia by the Water/Vapor Interface

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The passage of a single ammonia molecule from an infinitely dilute gas through the water/vapor interface is studied by constrained molecular dynamics simulations. The free energy of the system as a function of the distance between the ammonia and the interface has a minimum in the interfacial region. It is found that the preference of the ammonia for the interface is mainly due the disruption of the solvent structure caused by the ammonia in the bulk region, which results in an increase of the solvent internal energy.

Introduction

The general problem of the uptake of small molecules by water has been the subject of several recent theoretical and experimental works.^{1–6} The importance of this subject stems mainly from the role that the water/vapor interface plays in atmospheric chemistry.⁷

Ammonia is one of the most important trace gases found in the atmosphere. Since it is released by natural and anthropogenic sources, it is considered a primary pollutant and is certainly not innocuous.^{8,9} Particularly, ammonia is a reactive and variable gas, and its atmospheric cycle is linked to liquid water. Because it is basic and also highly soluble in water, ammonia compounds play a key role in the acid–base exchange processes in clouds. The concentration of NH_3 in the atmosphere varies between 0.1 and 10 ppbv;⁷ it can be higher over polluted cities or agricultural fields and much lower over remote oceans. Absorption of ammonia by water spray is also an important cleaning strategy in some technological processes, especially in the semiconductor industry.¹⁰

The interfacial properties of ammonia–water mixtures have been recently studied by Paul and Chandra¹¹ using molecular dynamics simulations. They have considered several (finite) ammonia concentrations and studied the surface tension, density profiles, molecular orientation, and diffusion behavior in the bulk and the surface region among other properties. It was found that the ammonia molecules have a higher preference to occupy the interfacial region than the water molecules. The dependency of the surface tension with the ammonia concentration was found to be in qualitative agreement with the equilibrium surface tension measurement performed by Donaldson² and also with the older results of O. K. Rice.^{12,13} This surface tension behavior is consistent with an accumulation of ammonia molecules at the surface and led to the idea of surface-bound states.^{1,14} This idea was further developed by Donaldson,² who also provides a discussion of the thermodynamic and kinetic theory used to analyze the adsorption process and applies it to the ammonia case. By using Henry's law and extrapolating the results to zero vapor pressure, the standard free energy for ammonia adsorption

from the gas phase was determined to be -19.1 kJ/mol at 298 K and -20.6 kJ/mol at 278 K. Supported by the experimental results and ab initio calculation of the $\text{NH}_3\text{--H}_2\text{O}$ and $\text{NH}_3\text{--}(\text{H}_2\text{O})_2$ complexes, Donaldson concludes that ammonia is bound to a small number (two or three) of water molecules forming a surface-bound state. Moreover, this state is stabilized by a more favorable ammonia–water interaction at the surface than that in the bulk region. Sum frequency generation experiments performed by Shultz et al.¹⁵ have provided the first experimental picture of NH_3 at the water/vapor interface. Their findings indicate that the ammonia docks to the dangling OH bonds in such a way that the C_3 molecular axis forms an average angle of $25\text{--}38^\circ$ with the normal to the interfacial plane.

Besides the formation of the surface-bound states stabilized by a low enthalpy of adsorption, another possible origin of the lower free energy of the adsorbed state with respect to the fully solvated one is the energetic cost to rearrange the solvent molecules around the solute. To the best of our knowledge, this possibility has not been explored with molecular simulations yet, and as it will be shown below, this is the main reason for the occurrence of the surface minimum in the free-energy profile.

From the atomistic simulation point of view, a practical methodology to study the passage of small molecules through the water/vapor interface is constrained molecular dynamics. This method has been well described by Somasundaram et al.,³ and a recent review⁵ summarizes the findings of several groups. Dang and Garrett⁴ have applied this technique to the particular case of the ammonia/water. In their study, they have used polarizable model potentials to describe the water–water and water–ammonia interactions. The free energy of the system as a function of the position of the solute molecule is calculated. The results of Dang and Garrett⁴ show no minimum at the water/vapor interface; instead, the free energy decreases monotonically as the ammonia enters the water phase.

In this paper, we use constrained molecular dynamics simulations to determine the free-energy profile for ammonia uptake. We use the same pairwise additive model potentials used by Paul and Chandra¹¹ and employ a similar methodology to the one used by Dang and Garrett.⁴ The simulations were run

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over a sufficiently long time to be able to estimate the change in the solvent internal energy as the ammonia enters the bulk phase. We find that the free energy has a minimum when the ammonia molecule is at the water/vapor interface. This minimum is mainly the result of the increase of the solvent internal energy due to the disruption of the liquid structure caused by the solute.

Computational Details

In the present study, we use the intermolecular potential function for ammonia proposed by Gao et al.¹⁶ In this model, the ammonia molecule is represented by a rigid structure with four interacting sites located on the atoms' centers. The length of the NH bond is 0.10124 nm, and the HNH angle is 106.67°. A Lennard-Jones interacting site is on the nitrogen atom, with $\sigma_a = 0.336$ nm and $\epsilon_a = 0.87864$ kJ/mol. The nitrogen atom carries a negative charge of $-1.026 e$, which is neutralized by three positive charges of $0.342 e$ located on each hydrogen atom. The water molecule is modeled by the SPCE potential.¹⁷ This model is also based on a rigid molecule with a Lennard-Jones site on the oxygen atom with $\sigma_w = 0.3166$ nm and $\epsilon_w = 0.65$. The oxygen carries a negative charge of $-0.8476 e$, neutralized by positive charges on the hydrogen atoms. The OH distance is 0.1 nm, and the HOH angle is 104.5°. The ammonia-water interaction is constructed by using the Lorentz-Berthelot combination rules, that is, $\sigma_{aw} = (\sigma_a + \sigma_w)/2$ and $\epsilon_{aw} = \sqrt{\epsilon_a \epsilon_w}$, where the σ_a , ϵ_a and σ_w , ϵ_w are the Lennard-Jones parameters for ammonia and water, respectively. The total intermolecular interaction is completed by adding the Coulombic intermolecular interactions using the corresponding partial charges. A spherical cutoff was imposed at 0.9 nm, and Ewald summation was used to treat the long-range electrostatic interactions. The time step for the integrations was set to 1 fs, and all simulations were done at constant volume and coupled to a Nose-Hoover thermostat at 277 K. This is the same model and the same temperature as those used by Paul and Chandra,¹¹ and our work extends and complements their study.

The molecular dynamics simulations were performed using GROMACS v3.3.1.¹⁸ The simulated system consisted of 864 water molecules and 1 ammonia molecule. The system size and geometry were chosen so that the water formed a liquid slab in the center of the simulation box. This water slab was prepared following these steps: (i) An isotropic, cubic system with 864 water molecules was simulated for 1 ns at constant temperature (277 K) and constant pressure (1 atm). (ii) The final configuration of the system after step (i) was used to prepare the initial conformation of the pure water in slab geometry that was then simulated at constant volume. The size of the simulation box is $L_x = L_y = 2.95913$ nm and $L_z = 9.00$ nm. (iii) The water slab prepared in step (ii) was equilibrated for 1 ns.

Once the water slab was equilibrated, we added one ammonia molecule and performed constrained molecular dynamics (see below) for 11 ns. The first nanosecond of simulation was ignored in the calculation of the reported results.

Let us define a coordinate system with the z axis normal to water/vapor interface with its origin in the center of mass of the water slab. The position of the ammonia molecule is described by the z coordinate of its nitrogen atom, z_N . Constrained molecular dynamics simulations are performed at fixed z_N . In order to keep the ammonia molecule at z_N , an external force is applied, and its value $F(z)$ is monitored throughout the simulation. The Helmholtz free-energy difference between a reference state and a state characterized z_N can be expressed as^{3,4}

$$A(z_N) - A_0 = - \int_{z_0}^{z_N} \langle F(z) \rangle dz \quad (1)$$

where $\langle F(z) \rangle$ is the time average of the z component of the external force acting on the solute.

As a reference state, we have chosen any point sufficiently far from the interface, that is, in the gas phase, so that $\langle F(z_0) \rangle = 0$. Therefore, for z_N corresponding to the interior of the water slab, the result of eq 1 should be negative for solvable molecules. Integration of eq 1 across the complete water layer should result in no change of the free energy. The free-energy profile is also related to the concentration (or density) profile of the solute in the water slab

$$A(z) - A_0 = -RT \ln[c(z)/c_0] \quad (2)$$

where R is the gas constant and c_0 the concentration in the gas phase.

Results

The average force experienced by the ammonia molecule is displayed in Figure 1. This force is calculated as the negative of the average external force imposed on the nitrogen in order to maintain the ammonia molecule at fixed z . A positive force on the left side of the water slab or a negative force on the right side, means that the water layer is attracting the ammonia molecule and vice versa. The integration of $\langle F(z) \rangle$ with respect to z leads to the Helmholtz free-energy profile of the system as a function of the position of the ammonia molecule, eq 1. The curve displayed in Figure 2 was obtained applying a simple trapezoidal rule to integrate the results displayed in Figure 1. Several important conclusions are drawn from Figure 2. First, let us note that the numerical integration of the force profile, performed from left to right, introduces errors at each integration step. Yet, at the end of the integration, which correspond to the right boundary of the system, the free energy obtained is very close to zero. Therefore, the total accumulation of errors is negligible. This could be due to a fortuitous cancellation of errors or to a high accuracy in the determination of the force profile. However, the symmetry observed in Figure 1 strongly suggests that the determination of the force profile is very accurate, thus implying that our calculated results are an excellent estimation of the prediction of the model system. Second, the ammonia molecule has a higher affinity for the water/vapor interface than for the bulk water. The decrease in free energy with respect to the reference state is 15 kJ/mol for the ammonia in the interfacial region. The corresponding value for the fully solvated ammonia is 12 kJ/mol. These values are only in qualitative agreement with the experimental results of Donaldson, who reported 19.1 and 10.2 kJ/mol, respectively. In contrast with similar calculations for the uptake of other substances, for example, ethanol,^{5,19} no free-energy barrier is observed between the surface and the solution.

At this point, before analyzing the origin of the minimum in the free energy, it is convenient to see the density profile for the unperturbed water slab as well as the predicted relative concentration profile of ammonia, Figure 3. The relative concentration of ammonia is calculated using eq 2. Note that the water reaches the bulk density in the region of $-1.2 \leq z \leq 1.2$ nm. The ammonia accumulates at the interfacial region, having a peak at $z = \pm 1.55$ nm. This relative concentration profile is valid only for a very dilute solution. At higher ammonia concentrations, Paul and Chandra have also observed this effect; they actually saw that the ammonia molecules have a higher preference to stay in the interfacial region than the

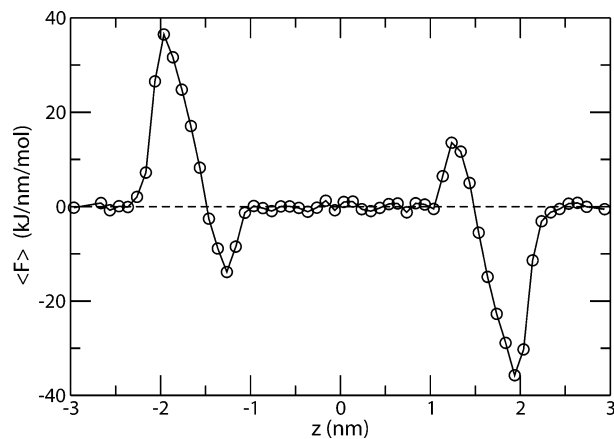


Figure 1. Average force on the ammonia's nitrogen as a function of the distance between the center of the water slab and the nitrogen atom. The circles represent the average external force calculated over 10 ns of simulation. The error in the calculated forces is ~ 0.2 kJ/mol/nm.

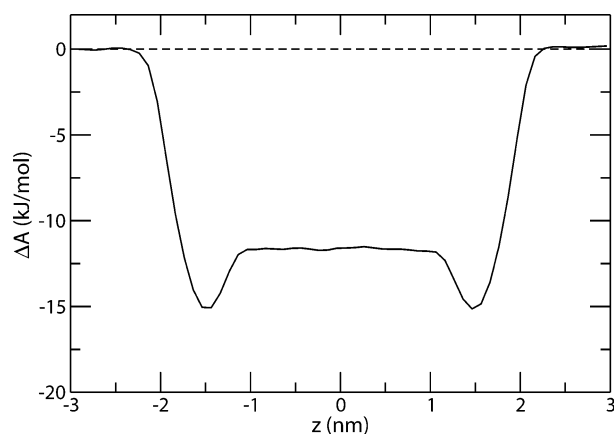


Figure 2. Variation of the Helmholtz free energy of the system with the position of the ammonia molecule. This curve is the result of the numerical integration of the force displayed in Figure 1. The dashed horizontal line represents $\Delta A = 0$.

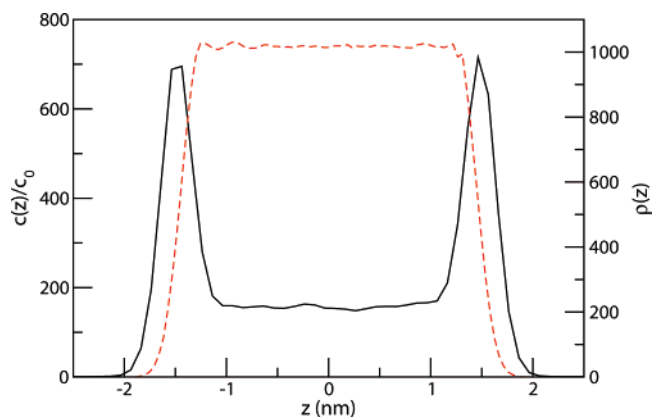


Figure 3. Relative density profile of adsorbed ammonia (solid black line, left scale) and the water density profile of the unperturbed water slab (dashed red line, right scale).

water molecules.¹¹ The accumulation of ammonia at the interface is also in agreement with the experimental findings of Shultz et al.¹⁵

As we stated above, the present study shares the methodology with the work of Dang and Garrett.⁴ In contrast with their results, obtained with polarizable potential models, the simpler pairwise additive potential models used here show the proper qualitative behavior. Another important difference between the two works is the simulation time used to calculate the average external

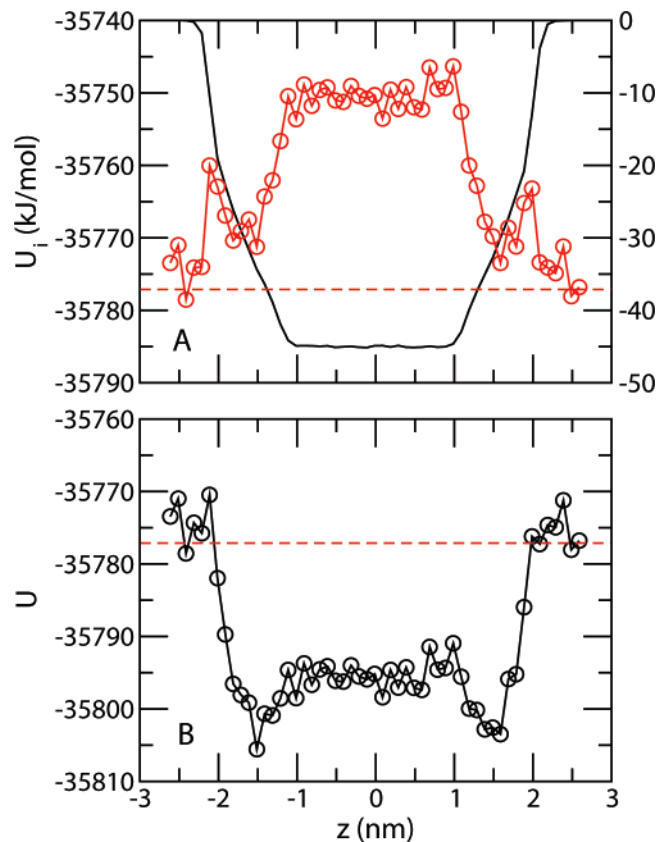


Figure 4. (A) Individual contributions to the total potential energy of the system as a function of the ammonia position. $U_{NH_3-sol}(z)$ (black line) decreases monotonically from 0 to -45 kJ/mol as the NH_3 enters the solvent. The relative changes in U_{sol} (red line with symbols) are only 0.1%, and therefore, its determination by a simulation has a much larger uncertainty. (B) Total potential energy of the system as a function of the ammonia position. In both panels, the horizontal dashed line represents the total potential energy of the unperturbed water slab.

force in the constrained molecular dynamics. It has been shown by Ismail et al.²⁰ that long simulation times (at least 1 ns) are needed in order to accurately compute the surface tension of water. This conclusion was obtained by performing simulations in a slab geometry and for several (nonpolarizable) model potentials. In their simulations, Dang and Garrett equilibrated the system over 0.1 ns, and they calculated the force over a total time of 0.3 ns. These times are much shorter than our simulation times and the minimum 1 ns suggested in ref 20. Therefore, it is possible that the results of Dang and Garrett⁴ are not fully equilibrated averages, and therefore, their results may change if longer simulation times are used.

Now, we go back to the free-energy profile and the origin of the minima when the ammonia molecule lies on the surface. To elucidate this, we study the individual contributions to the average potential energy of the system. There are two contributions, one due to the solvent–solvent (U_{sol}) interaction and the other due to the ammonia–solvent (U_{NH_3-sol}) interaction, and they are displayed in Figure 4A. U_{NH_3-sol} is equal to zero when the NH_3 molecule is sufficiently far from the interface and decreases monotonically as it enters the bulk of the water. The variation of U_{NH_3-sol} is easily calculated, and short simulations are enough to calculate accurate averages. This is not true for the other component of the potential energy. The magnitude of the total potential energy (for the system size used in this research) is around 36000 kJ/mol; therefore, the variation of the free energy represents only 0.1% of this magnitude. Therefore, in order to obtain a meaningful result from the

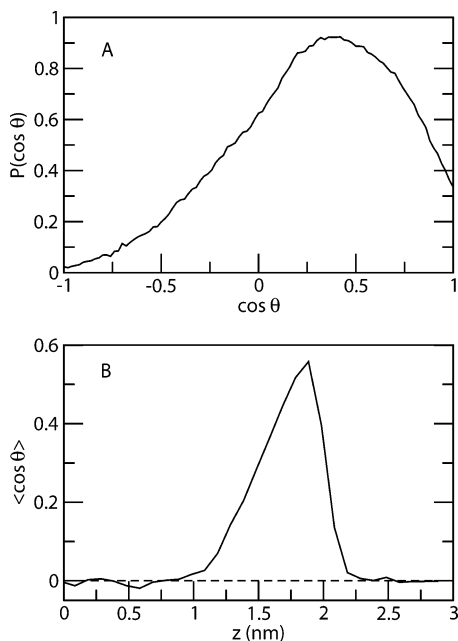


Figure 5. Orientation of the ammonia molecule. (A) Probability distribution function for the orientation of the ammonia at $z = 1.5$ nm, which corresponds to the maximum in the ammonia density profile. (B) Average value of the cosine of the angle formed by the ammonia C_3 axis and the z axis as a function of the position of the ammonia molecule.

simulations, these have to be long enough so that the error in the determination of $\langle U_{\text{sol}} \rangle$ is significantly smaller than 0.1%. The 10 ns simulations that we have performed are sufficient to show the general behavior of the system, as displayed also in Figure 4. $\langle U_{\text{sol}} \rangle$ has a sharp increase exactly at $z = \pm 1.2$, where the water has already reached its average bulk density. The increase in $\langle U_{\text{sol}} \rangle$ is approximately 25 kJ/mol. The other contribution, $U_{\text{NH}_3\text{-sol}}$, decreases smoothly in the interfacial region by 45 kJ/mol. The combination of the two components, displayed in the bottom panel of Figure 4 has the same features as the free-energy profile. Namely, the internal energy of the system varies, with respect to the position of the ammonia, qualitatively in the same way as the free energy does. The picture that emerges is that the leading reason behind the affinity of the ammonia for the surface is the increase in the solvent enthalpy due to the disruption created by the solute in the fully solvated state. Therefore, our results suggest that the entropic terms are only a minor contribution to the free-energy change as a function of the position of the ammonia molecule.

Figure 5 shows the probability distribution function, $P(\cos \theta)$, for the cosine of the angle between the ammonia dipole moment and the normal to the interface, from the constrained simulations with $z_N = 1.5$ nm. The results show that most of the time, the ammonia has the nitrogen atom toward the liquid, in agreement with experimental findings.²¹ The mean value of the distribution $P(\cos \theta)$ is displayed in the lower panel of Figure 5 as a function of the z coordinate of the ammonia's nitrogen. The orientation effect is only present when the NH_3 molecule is at the interfacial region and disappears for $z < 1$ nm.

Discussion

We have performed a constrained molecular dynamics simulation study to determine the free-energy profile for the intake of an ammonia molecule by the water/vapor interface.

Using a simple pairwise additive intermolecular potential, the main experimental results have been qualitatively reproduced. These main effects are (a) the formation of a surface layer of adsorbed ammonia, consistent with a minimum in the free-energy profile at the interfacial region and (b) the adsorbed molecules being oriented with the nitrogen atom toward the liquid. It has been shown by Paul and Chandra that the same model provides a good qualitative description of ammonia/water solutions.

The high surface affinity of the ammonia molecules is mainly due to energetic cost to reaccommodate the water molecules to solvate the ammonia. This conclusion results from the observation that the solvent internal energy has the same qualitative features as the calculated free-energy profile. This result contradicts previous arguments attributing the surface affinity of the ammonia to a lower enthalpic contribution of the ammonia solvent interaction at the surface than that in the bulk region.²

The qualitative agreement between experimental results and the simulations presented here suggests that the model captures the essential features of the system. The free-energy profile derived from this work is, so far, the most realistic molecular-level description of the uptake of ammonia and may be used as an input for the modeling of the kinetics of ammonia uptake by water droplets at atmospheric conditions.^{5,6} More accurate potential energy surfaces, valid for a wide temperature range, are necessary in order to have complete and quantitative molecular-level description of ammonia at the water/vapor interface. The present study represents a step toward that goal.

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