H-bonding of an NH₃ gas molecule to H₂O/Pt(111) — A barrier-free path

Graeme Henkelman[1,a)] and Peter J. Feibelman[2,a)]
[1]*Department of Chemistry and the Institute for Computational and Engineering Sciences,*
University of Texas at Austin, Austin, Texas 78712, USA
[2]*1401 Sigma Chi Rd. NE, Albuquerque, New Mexico 87106, USA*

Does an OH-flipping barrier hinder H-bond formation between a gas phase molecule and a water monolayer whose free OH ligands point toward a substrate? According to density functional theory calculations for water on Pt(111) the answer is *yes*, when the molecule is CO or N₂, but *no* when it is NH₃. The difference is the relatively strong attraction of the NH₃ lone pair to free OH ligands. © *2016 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4940921]

A main goal of surface science since its beginnings has been to provide information on important chemical processes in very well controlled and characterized environments. Over the past 15-20 years, the surface science approach has been applied to adsorbed ultra-thin water layers,[1] with considerable success despite water's relatively weak interactions with itself, with other molecules, and with solids. Driving this effort has been water's ubiquity in nature and in technology, and its correspondingly vast importance.

The work reported herein was aimed at understanding recent studies of molecular adsorption on among the best understood of water monolayers, the $\sqrt{37} \times \sqrt{37}$-R25.3° and $\sqrt{39} \times \sqrt{39}$-R16.1° periodic water molecule arrangements on Pt(111).[2] Experiments by Kimmel *et al.*,[3] and by Lechner *et al.*,[4] have shown that CO,[3] N₂,[3] and NH₃[4] molecules stick to these water layers at temperatures as low as 20 K, implying that if there is a barrier to adsorption, it is not large.

With no data suggesting otherwise, it is reasonable to assume that capture into a physisorption well explains the low barriers observed to CO and N₂ adsorption. But, STM images *are* available for NH₃, and they show it adsorbing at specific sites on the water-covered surface.[4] This means NH₃ sticks not as a physisorbed molecule, delocalized over the water layer, but through hydrogen bond formation.

Our question was how H-bond formation is possible when at 0 K the free OH ligands in the $\sqrt{37}$ and $\sqrt{39}$ structures are oriented such that their H atoms lie between the O atom directly above and the Pt surface below.[2] (This is called "pointing down" in the literature.) Typically, one expects H-bonds to form where an OH ligand points "up" (i.e., where an H atom resides on the vacuum side of its neighboring O atom). If there are no upward pointing OH ligands, as in the 0 K, $\sqrt{37}$ and $\sqrt{39}$ structures then H-bonding of an incident NH₃ to one of these structures should require overcoming a barrier to OH "flipping," from down to up orientation.

A 2004 theoretical study of OH flipping, although conducted for an idealized arrangement of water on Pt(111) that does not occur in nature, yielded a barrier estimate of ~0.1 eV.[5] This value is relatively small, but large enough that

site-specific sticking by formation of an H-bond should be rather improbable below 100 K (=8.7 meV).

The progress we report has come by eliminating the assumption that calculations of OH flipping barriers can be reliable when conducted with the incoming molecule absent. Arguing against this assumption is that low barrier reaction paths are generally those along which new bonds form *at the same time* as old ones break.[6] In adsorption onto a water layer, this means the cost of H-bond breaking along an adsorption path should simultaneously be compensated by the gain from new H-bond formation. If the incident molecule is not in the theoretical model, then compensation for H-bond breaking in the water layer is impossible, and the calculated barrier is apt to turn out too large. The calculations reported herein strongly support this argument.

Two OH flipping mechanisms were considered in Ref. 5. One is water molecule rotation about its OH bond in the water monolayer. At first blush, one might imagine that no H-bond breaks in the course of such a rotation; a free, down-pointing OH simply turns and thereby becomes a free, up-pointing OH. In comparison, rotation of a water molecule in its H–O–H plane seems a less obvious candidate for low-barrier flipping, because it directly involves breaking a water-water hydrogen bond.

Notwithstanding, calculations of Michaelides *et al.*[5] showed this guesswork to be precisely backwards. Because of H–H repulsion in the transition geometry, in effect the temporary formation of a D-type Bjerrum defect,[7] an H-bond *is* broken in the course of the "obvious" rotation of a water molecule about its OH bond in the water monolayer. By contrast, no such defect impedes rotation in the H–O–H plane, while the cost of breaking an H-bond in the water layer is compensated, to some degree, as the free, down-pointing OH becomes an H-bonding OH. The latter is thus the low-barrier flipping mechanism.

The present density functional theory (DFT) results do not contradict this scenario, but do yield a surprise: once including the adsorbing NH₃ into the calculations, the required OH-flip is predicted to be barrier-free. The reason is incipient formation of an OH···NH₃ hydrogen bond. With rotation occurring in its H–O–H plane, the water molecule that will host the adsorbed

a)Electronic addresses: henkelman@utexas.edu and pjfeibe@msn.com

NH_3 starts with one H-bonding OH and one free, H-down OH. As the NH_3 descends, the host's H-bond to the rest of the water layer is breaking, but new H-bonds are simultaneously forming to the water adlayer and to the adsorbing NH_3. The result, as noted, is barrier-free adsorption.[4]

Aiming at a more complete picture, we also attempted to compute the energetics of adsorption when the required OH flip results from host water molecule rotation about its bonding OH. We anticipated that, as in Ref. 5, transient formation of a Bjerrum D-type defect would now produce a non-zero barrier. The result, though, was another surprise: Avoiding costly defect formation entirely, the incoming NH_3 attached to a neighboring water molecule, which had exposed a dangling OH by rotating in *its* H–O–H plane. The NH_3 adsorption barrier, accordingly, was once again zero. Needless to say, this surprise is beyond the reach of calculations that do not include the descending NH_3.

These results appear to explain the physics behind low-T localized adsorption of NH_3, namely, that simultaneous formation of an $OH\cdots NH_3$ hydrogen bond compensates the loss of H-bonding in the water layer. Still, we undertook to confirm the importance of including the adsorbing molecule in barrier estimates by repeating our calculations for the sticking processes studied in Ref. 3, adsorption of CO and of N_2 on $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O/Pt(111).

The results were telling. Because neither CO nor N_2 binds as strongly as NH_3 to a free OH, incipient bond formation with an N_2 or CO provides less compensation for the simultaneous disruption of the water monolayer's H-bond network, and the H-bonding of either of these species to the water layer is correspondingly impeded by an OH flipping barrier. Moreover, the barrier estimates track the molecular adsorption energy. As summarized in Table I, the highest barrier and weakest binding to the water adlayer is for N_2, followed by CO and NH_3.

A *caveat* regarding the quoted sticking barriers is that, even without using van der Waals interaction corrected DFT, we found shallow physisorption wells of 19 meV for N_2 and 17 meV for CO. The barriers quoted in Table I were computed on the assumption that the molecules first relax into these wells before surmounting the barriers to H-bonded adsorption states. To the extent that localized adsorption

TABLE I. PBE binding energies and H-bond formation barriers for a single N_2, CO, or NH_3 molecule adsorption on $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O/Pt(111). In all three cases, the mechanism of OH flipping from down to up was rotation of the host H_2O in its H–O–H plane. These results were obtained using a gamma-point-only sample of the surface Brillouin zone (SBZ) and a plane-wave cutoff of 400 eV. Refining the calculations by using a 3×3 SBZ sample or a plane-wave cutoff of as much as 756 eV is expected to change these results only slightly, based on test calculations for NH_3.

Ad-molecule	Binding energy (meV)	H-bond formation barrier (meV)
N_2	38	84
CO	64	22
NH_3	421	0

of these molecules occurs directly from the gas phase, the relevant transition state energies should be smaller, 65 meV for N_2 and 5 meV for CO. The barrier ordering, and our overall conclusions remain the same, however.

The results reported herein were generated using the projector augmented wave (PAW) version[8] of the VASP, plane-wave DFT code.[9] Electron exchange-correlation effects were treated in the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation.[10]

We modeled the Pt(111) substrate as a 3-layer slab whose lowest layer atoms were fixed at theoretical bulk Pt positions (PBE lattice constant = 3.97 Å, compared to experiment = 3.92 Å). A $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O layer was initially adsorbed on the uppermost Pt layer. In the calculations for NH_3, the molecule was started with its symmetry axis normal to the Pt slab, and its H atoms higher than its N atom, which was some 5.6 Å directly above the O atom of a high-lying, H-down water molecule, as in the left panel of Fig. 1. For N_2 and for CO adsorption, the starting geometries were similar. Each molecule was initially oriented with its axis along the surface normal and its lower atom at the same height as the N of the NH_3 had been. The CO molecule was started with the C atom closer to the substrate.[11]

In the final state of the NH_3 calculation (see Fig. 1, right panel), the ammonia has accepted an H bond from the underlying host H_2O molecule, whose free OH has flipped up to provide it. Now, the N is 2.77 Å from the O atom below

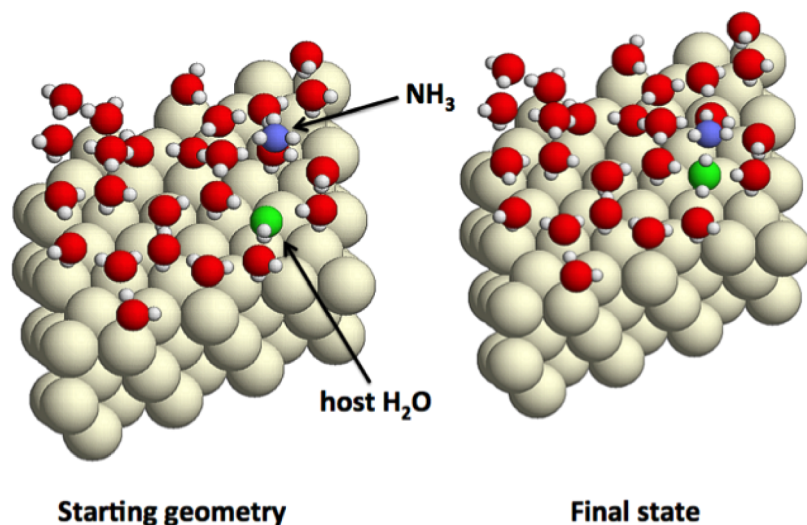FIG. 1. Starting and final geometries for calculations of NH_3 binding to a $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O layer on Pt(111), computed with plane-wave cutoff = 400 eV and a 3×3 SBZ sample. In the initial state, the N atom (colored purple) of the NH_3 lies about 5.6 Å above the (green) O atom of the H_2O, which will "host" the ammonia when it sticks. In the final state, the N atom is 2.77 Å from the host O. O atoms other than the host's are colored red in the figures, H atoms are white, and Pt atoms light yellow.

Starting geometry   **Final state**

it, and the system has gained an adsorption binding energy of about 0.42 eV.[12]

In all atomic arrangements studied relative to NH_3 adsorption, we began by obtaining rough estimates of barrier and binding energies using a gamma-point-only sample of the surface Brillouin zone (SBZ) and a plane-wave-basis cutoff of 29.4 Ry. Subsequently, we compared to calculations wherein the SBZ sample was increased to 3×3, or the energy cutoff was raised to 55.6 Ry. These improvements gave rise to order 10-20 meV changes in barrier height, which justified not making the SBZ sample finer and the cutoff larger at the same time.[13]

Because H_2O, CO, and NH_3 molecules have permanent dipole moments, we took pains to eliminate unphysical electric fields associated with adsorption on the upper Pt surface only.[14] The accuracy of the cancellation requires a sufficiently wide vacuum region between each slab with its upper-layer adsorbates, and the bottom of its periodic neighbor slab. Accordingly, we set the distance between the NH_3 molecule and the bottom of the periodic image slab above it to be about 13.6 Å. We used the same vacuum width for calculations of N_2 and of CO adsorption.

For both host water molecule rotation modes, we used the Climbing Image Nudged Elastic Band (CINEB) method[15] with 5 images along the hypothetical minimum energy path (MEP) for a first estimate of the NH_3 adsorption barrier. This proved adequate for host water molecule rotation in its H–O–H plane, yielding the barrier-free path shown in Fig. 2, which was computed using a gamma-point SBZ sample and a plane wave cutoff of 400 eV.
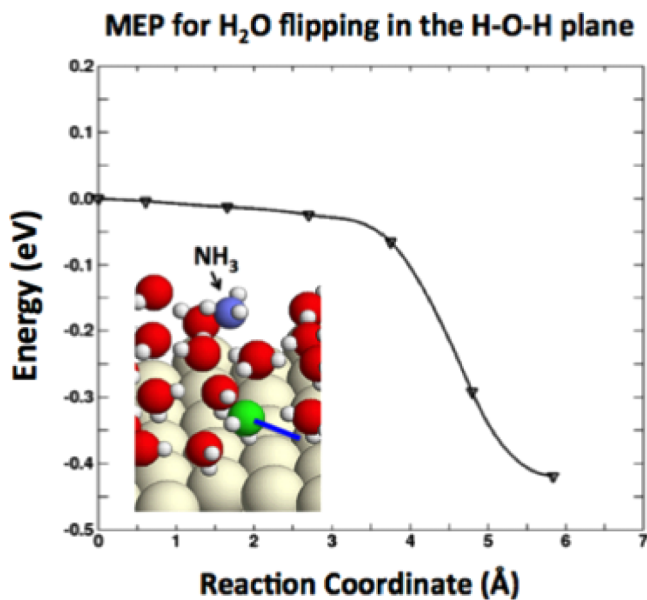
A five-image CINEB calculation proved to be too crude to assess the energetics of adsorption driven by host water molecule rotation about its H-bonding OH bond. Upon close examination, the apparent saddle point we found in such a preliminary calculation proved not to be a saddle at all, but a shoulder on the potential energy surface, where the residual forces on the NEB images were low (<0.05 eV/Å).

To understand what is at stake, recall that in a CINEB calculation of a transition barrier, the user specifies the final state, not physics. In the present study, we chose the final state shown in Fig. 1, with the NH_3 H-bonded to the "green" water molecule. In a more careful calculation, with eight images used to resolve the path (and a tighter force convergence criterion of 0.001 eV/Å), we effectively allowed the NH_3 to follow its own preference, first descending with zero barrier onto a neighboring water molecule (see Fig. 3), which exposed an up-pointing OH by rotating in its H–O–H plane. Only thereafter did the NH_3 obey our requirement that it ultimately bind to the specified host of Fig. 1. But that happened at the cost of surmounting a hopping barrier. Accordingly, we concluded that water molecule rotation about an H-bonding OH bond does *not* yield a secondary adsorption mechanism. The transient formation of a Bjerrum defect in such an OH flipping mode repels the descending NH_3 to a neighboring potential host, which flips without incurring a defect-formation cost.

Finally, as a systematic test of the notion that the relatively strong attraction between the host water molecule
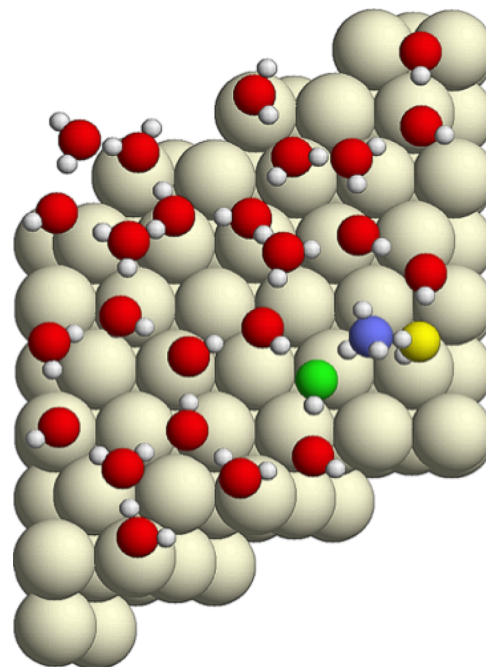

FIG. 2. Energetics of NH_3 binding to a $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O layer on Pt(111), computed assuming rotation of the host H_2O in the H–O–H plane. These results were obtained using a plane-wave cutoff = 400 eV and a gamma-point SBZ sample. Atom position data for a brief movie of the process are provided in the supplementary material.[16] Inset: the N atom of the NH_3 is purple and the O of the host H_2O is green. Remaining O atoms are red, H atoms white, and Pt atoms light yellow. The rotation axis of the host H_2O is indicated as a blue bar.

FIG. 3. From our attempt to find a barrier to NH_3 binding by means of water molecule rotation about an OH ligand in the water adlayer on a $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O layer on Pt(111), the fifth image along an 8-image CINEB calculation. The plane-wave cutoff = 400 eV and a 3×3 SBZ sample. The N atom of the NH_3 is colored purple. The O atom of the intended host H_2O, which does not appear to have rotated at all, is 3.14 Å away and colored green. The O atom of the neighboring H_2O, to which the NH_3 can stick with no barrier is colored yellow and lies only 2.73 Å from the N. It has exposed a dangling OH by rotating in its H–O–H plane. Other O atoms in the figure are colored red, H atoms are white, and Pt atoms light yellow.

and the incident NH_3 reduces the energy needed to flip the host's dangling OH, we conducted CINEB calculations of the barriers to N_2 and to CO attachment to the same host molecule of the same water monolayer, in both cases confining the test to host H_2O rotation in its H–O–H plane. PBE optimizations of the final states yielded binding energies of 38 meV (N_2) and 64 meV (CO), compared to 421 meV for NH_3 (cf., Table I). This suggests that compensation for breaking an H-bond as the host molecule rotates is weakest if the incident molecule is N_2, somewhat weaker if it is CO, and strongest for NH_3. Thus, we can understand the PBE results that there are 84 and 22 meV barriers to N_2 and CO attachment by H-bond formation, in contrast to the zero barrier we found for NH_3.

Inclusion of van der Waals corrections to PBE would doubtless affect these results quantitatively, particularly for N_2, whose PBE binding to the water layer is only 38 meV. The focus of this article is, however, the systematics behind zero-barrier NH_3 sticking. Accordingly, we have put off the study of van der Waals interactions in sticking for future work.

To recapitulate, DFT/PBE calculations point to the relatively strong attraction between OH ligands and the ammonia molecule's N atom as the reason an NH_3 molecule can H-bond to $\sqrt{37} \times \sqrt{37}$-R25.3° H_2O/Pt(111) and to $\sqrt{39} \times \sqrt{39}$-R16.1° H_2O/Pt(111) without having to overcome an energy barrier.[4] For CO and N_2, because their attraction to dangling OH ligands is weaker, flipping barriers must be overcome. Thus, the probabilities for localized adsorption of these species can be expected to be much smaller than for NH_3, at low temperatures.

Looking to the future, our discovery that an NH_3 molecule can H-bond to a water monolayer through barrier-free OH flipping strongly suggests that second-layer *water* molecules will also easily disrupt and reorganize what seem to be hydrophobic regions of a water first layer. Accordingly, empirical-potential-based molecular dynamics simulations of multilayer adsorbed water, such as those of Limmer *et al.*,[17] should be revisited.

[1] For reviews, see P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7**, 211 (1987); M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002); A. Hodgson and S. Haq, *ibid.* **64**, 381 (2009); P. J. Feibelman, Phys. Today **63**(2), 34 (2010); J. Carrasco, A. Hodgson, and A. Michaelides, Nat. Mater. **11**, 667–674 (2012).

[2] S. Nie, P. J. Feibelman, N. C. Bartelt, and K. Thürmer, Phys. Rev. Lett. **105**, 026102 (2010).

[3] G. A. Kimmel, T. Zubkov, R. S. Smith, N. G. Petrik, and B. D. Kay, J. Chem. Phys. **141**, 18C515 (2014).

[4] B. A. J. Lechner, Y. Kim, P. J. Feibelman, G. Henkelman, H. Kang, and M. Salmeron, J. Phys. Chem. C **119**, 23052 (2015).

[5] S. Meng, E. G. Wang, and S. Gao, Phys. Rev. B **69**, 195404 (2004); An earlier study, for water on Ru(0001), by A. Michaelides, A. Alavi, and D. A. King, J. Am. Chem. Soc. **125**, 2746 (2003), yielded an OH flipping barrier of roughly 0.3 eV.

[6] P. J. Feibelman, Phys. Rev. Lett. **67**, 461 (1991).

[7] N. Bjerrum, Kong. Dansk. Vid. Sels. Mat.-fys. Medd **27**, 1 (1951); V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford University Press, Oxford, 1999), Sections 4.4 and 6.5.

[8] (a) P. Blöchl, Phys. Rev. B **50**, 17953 (1994); (b) G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).

[9] (a) G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); (b) G. Kresse and J. Hafner, *ibid.* **49**, 14251 (1994).

[10] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[11] For completeness, we tested the possibility that CO might prefer to bind with its O atom down. According to DFT, however, this orientation is unfavorable relative to C-down by 74 meV. We also looked into the possibility tacitly implied by the inset in Fig. 2 of Ref. 3, that N_2 might prefer to adsorb "side-on," i.e., with its molecular axis parallel to the Pt surface. This orientation, however, is disfavored by 83 meV, according to our DFT optimization.

[12] As noted, when we attempted to predict an adsorption barrier corresponding to rotation of the intended host water molecule (with the green O atom in Fig. 1) about its OH bond in the water adlayer, the NH_3 found a zero energy path instead, leading to attachment to a neighboring water molecule. The figure corresponding to that endpoint, accordingly, would look similar to Fig. 1, but with the NH_3 bonded to a upward pointing OH on, e.g., the water molecule immediately to the right of the "green" one.

[13] Having found small barriers to CO and to N_2 adsorption, as compared to NH_3, we deemed it important to check for a proportionately smaller effect on those barriers of increasing the plane-wave cutoff to 700 eV. Satisfyingly, that improvement did not affect the qualitative picture. It produced binding and barrier energies changes smaller than 1 meV, for CO adsorption. For N_2, the changes were more noticeable though still small. The physisorption well deepened by 10 meV. The barrier to direct adsorption from the gas phase increased from 65 to 67 meV, and to adsorption from the physisorption well from 84 to 95 meV.

[14] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992), as corrected by L. Bengtsson, Phys. Rev. B **59**, 12301 (1999).

[15] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000).

[16] See supplementary material at http://dx.doi.org/10.1063/1.4940921 for file "barrierless_NH3_adsorption" and atom position data corresponding to NH_3 attachment to an OH ligand exposed by water molecule flipping in its H–O–H plane.

[17] D. T. Limmer, A. P. Willard, P. Madden, and D. Chandler, Proc. Natl. Acad. Sci. U. S. A. **110**, 4200 (2013).