Competing interactions in molecular adsorption: NH$_3$ on Si(001)

TOPICAL REVIEW

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Abstract
Ammonia is a good model system for the study of co-adsorption interactions, including indirect effects such as charge and strain-induced local effects on adsorption sites, and direct interactions such as hydrogen bonding. On the Si(001) surface, it adsorbs molecularly, via a dative bond from the N atom to the down atom of a buckled dimer, and is therefore very sensitive to the local charge conditions. It will then dissociate into –H and –NH$_2$ groups, adsorbed on the dangling bonds of the Si dimers. The NH$_2$ groups do not diffuse, so any correlations deriving from interactions during adsorption are preserved, and can be derived by analysis of the arrangements of the NH$_2$ groups. Hydrogen-bonding interactions are crucial in understanding the behaviour of this system, with significant co-adsorption interactions occurring both along and across rows, outweighing the electrostatic or buckling-related effects. In recent years, there have been several scanning tunnelling microscopy studies and extensive computational modelling of the NH$_3$ on Si(001) system, attempting to determine a dominant mechanism governing co-adsorption effects. In this review, I will discuss both experimental and theoretical results, make a comparison with similar molecules such as phosphine (PH$_3$), and review the different ways in which experimentalists and modellers have approached this complex system.

(Some figures in this article are in colour only in the electronic version)

Contents

1. Introduction

Ammonia has technological applications as a precursor for the growth of silicon nitride and oxynitride thin films in the electronics industry, with applications as gate dielectrics, oxidation masks, and insulators. For these applications, control of the thin film growth processes is critical to achieve atomic-layer control over the thickness, and to achieve atomically-sharp interfaces. While reaction of ammonia with the Si(001) surface to form silicon nitride typically requires temperatures over 1000 K, a greater understanding of the surface reaction processes could lead to techniques for nitride growth at much lower temperatures, for example by using

electronic excitation [1, 2] to form ultrathin Si_3N_4 layers, even at 90 K. Scientifically, the adsorption of ammonia is also an intriguing prototypical case for the study of molecular interaction with the technologically important Si(001) surface, showing strong co-adsorption effects. As a result, it has been the subject of many theoretical studies as well as experiments, and remains an active topic, both from a scientific and a technological point of view. In this review, I shall describe the current understanding of this system, focusing on the balance between various adsorbate–adsorbate and surface–adsorbate interactions, making a comparison to the phosphine (PH_3) system which shows quite different behaviour. I will discuss some of the pitfalls that many of the theoretical studies have strayed into, particularly in respect to the search for a dominant interaction mechanism, and in considering the dynamic nature of the surface at finite temperature. Finally, I will draw conclusions about the current state of knowledge of this system, and how they might provide insight into surface adsorption in general.

The bulk of this review will explore co-adsorption effects. The adsorption of a molecule into one site on this surface can influence the adsorption of molecules onto neighbouring sites because they are only 3.84 Å apart and are connected through the substrate. Substrate-mediated interactions such as strain or an electrostatic influence on local dimer buckling arrangements can control the attractiveness of local adsorption sites, while direct molecule–molecule interactions, such as hydrogen bonding or steric repulsion can control access to particular sites. We will see that the interplay of these different sources of interaction is rather complex. The final pattern of adsorption will be determined by the balance between these different co-adsorption interactions, leading to the possibility that via control of the dominant correlation mechanisms, it would be possible to control the pattern of adsorption, for example forming 1D atomic chains along a dimer row.

Before discussing adsorption, it is necessary to explain some important points about the substrate. In the Si(001) surface reconstruction, the atoms are joined via a strong σ-bond, thus halving the number of dangling bonds compared to the unreconstructed surface, and forming rows of dimers. In a conceptual flat dimer, this would leave a half-filled dangling bond on each Si atom. In practice, these dangling bonds interact to form a weak π-bond. Furthermore, the dimer also undergoes a Jahn–Teller distortion and buckle, so that one atom tends towards a planar sp^2 configuration with an empty lone pair, and the other atom tends towards an sp^3 configuration with a filled lone pair. This lowers the energy of the system by about 0.2 eV/dimer compared to the flat dimer, and opens up a large surface band gap [3]. The sign of the buckling alternates along a dimer row, which minimizes surface strain. In room temperature STM, the dimers have a symmetric appearance, which is a time-average of the two buckled isomers. Surface species, such as defects, or adsorbates, however, can pin neighbouring dimers into one buckling direction. The appearance of a buckled dimer at room temperature is therefore a signature of a strong interaction between a surface feature and its neighbouring dimers. By cooling the substrate down to around 120 K or lower [4],

the motion of the dimers is frozen out, and the dimers will have a buckled appearance across the whole surface. If the buckling direction is in phase between dimer rows, the p(2×2) reconstruction is produced. A weak interaction between rows promotes a phase shift between neighbouring dimer rows, however, giving the c(4×2) reconstruction, with a hexagonal appearance. In practice, both of these are seen in experiment, as in figures 1 and 2.

The two ends of the buckled dimer thereby offer favourable adsorption sites to both electron-donating and electron-accepting species, onto the electron-poor and electron-rich 'down' and 'up' dimer atoms respectively, giving the surface intriguing chemistry [5, 6]. For a complete understanding of experimental results, the dynamics of the buckled dimers, which flip rapidly between two buckling directions above 120 K, with a barrier of ~0.1 eV, must also be taken into account. Furthermore, because we are concerned with adsorption on a surface, the isolated dimer picture is not sufficient, It is also necessary to consider the effects of the proximity of equivalent sites on neighbouring dimers, bearing in mind the possibility of different adsorption arrangements, and of interactions between one site and another.

There have been many studies of various species adsorbed on the Si(001) surface. As a result of the opposite buckling behaviour, many adsorbates, even those which would otherwise be repulsive, are found to form clusters of adsorption [7], so as to minimize any strain effects of the adsorbed species. Monovalent species, of which the simplest is atomic hydrogen (H_2 is unreactive), will generally adsorb onto one end of a Si dimer. This breaks the Si–Si π-bond, leaving a single unpaired electron. However, it is possible for this single electron to delocalize into nearby states in order to reduce its energy away from the Fermi level [8]. Ammonia, and the methylamines, are also examples of monovalent adsorbates, in that they adsorb via their lone pair onto a single dimer atom. Likewise, molecules with empty lone pairs, such as BF_3, will adsorb preferentially onto the up atom. In fact, taking advantage of the site selectivity of these molecules, species of both types can be co-adsorbed onto the same dimer, for example BF_3 and trimethylamine (TMA) [9]. At higher coverages, atomic H forms the monohydride and dihydride structures on Si(001) [10]. With small amounts of atomic hydrogen (4 L), both the dangling bonds on the existing Si dimers are saturated by hydrogen, giving the monohydride structure, with a much lower energy than the singly-occupied dimer. This surface is remarkably inert, surviving exposure to atmosphere for several hours [11]. Much larger doses of atomic H (40 L), are required to attack the dimer σ-bonds, forming the dihydride structure, which leads to etching of Si from the surface.

An alternative adsorption route onto a single dimer for unsaturated hydrocarbon molecules, such as ethylene and acetylene, is across a single Si dimer via a cycloaddition reaction, forming a Si–C–C–Si ring. Adsorption for low coverages occurs preferentially on alternate dimers [12]; steric effects are unlikely for these molecules, and the reason for the preferred alternate adsorption might therefore be charge transfer. Larger aromatic molecules, such as benzene [13],
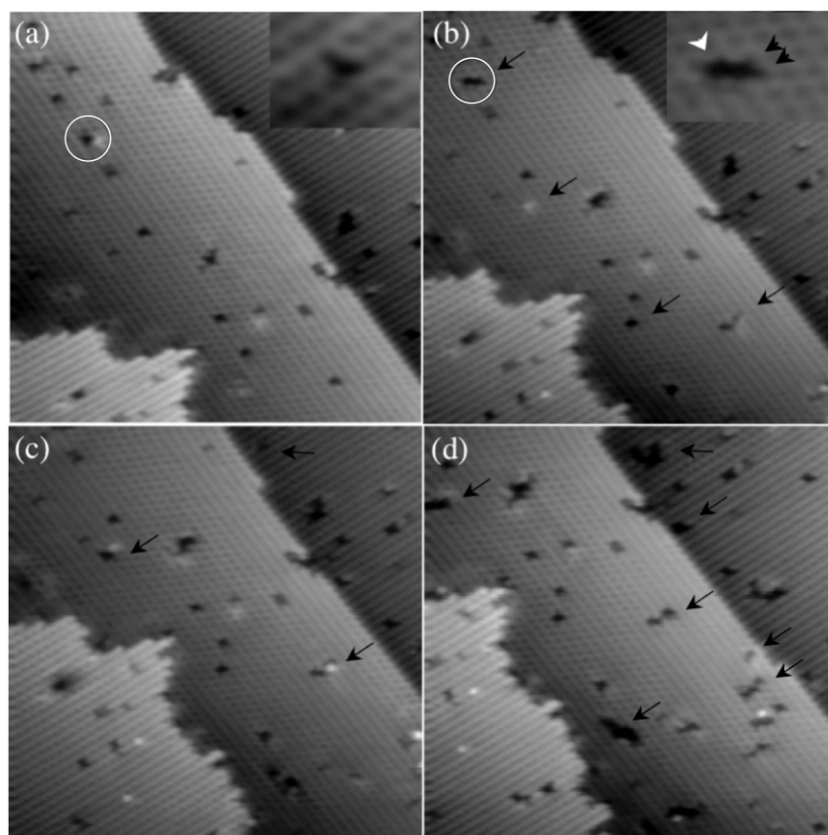
Figure 1. A series of 38 nm × 38 nm STM images of the Si(001) surface exposed to increasing amounts of NH_3 at 65 K. The imaging conditions were −2.0 V sample bias and 0.1 nA. (a)–(d) show the surface after 3, 4, 5 and 7 doses of NH_3 respectively (one dose ≈0.1 L). Arrows in (b)–(d) indicate places where changes have occurred between images. The final coverage in (d) is 0.02 ML. The circle in (a) shows an example of a bright dot adjacent to a dark dimer, which converts to a larger dark patch in (b). Thus both direct dissociation to an NH_2–H dimer and metastable molecular adsorption can occur at this temperature. Reprinted with permission from Hossain *et al* [30]. Copyright (2003) by the American Physical Society.

can adsorb in the same way as ethylene, but can also form a structure bridging across two dimers. A fuller discussion of the various types of interactions of organic molecules with the Si(001) surface can be found elsewhere [5]. Owing to the proximity of the neighbouring adsorption sites, polyvalent species, including Gr. III and Gr. IV atoms as well as species such as PH and SiH_2, can adsorb across the ends of two dimers, as well as adsorbing onto a single dimer. Pairs of polyvalent atoms will form ad-dimers, either on top of a dimer row, or bridging the trench between dimer rows [14, 15]. Such adsorption leaves two single dangling bonds, on the bare ends of the underlying Si dimers. As has been seen in the case of dangling bond wires on H:Si(001) [16], in adsorbed water [17] and SiH_2 [18], the two dangling bonds can interact, undergoing a Peierls distortion, which opens up a surface band gap, and reduces the energy, just as with dimer buckling. Despite this, the bare ends are reactive sites, and long chains of ad-dimers, the 'diluted dimer rows' [19], self-organize. By careful study of the several stages of dissociation, diffusion, and interaction, complete reaction pathways have been determined for a few molecules, such as the route from disilane (Si_2H_6) to an epitaxial layer of Si on Si(001) [20, 21], or the decomposition of PH_3 [22]. In both cases, the complexity of the reactions makes it difficult to isolate the effect of different interactions.

In the context of these many different possible behaviours, ammonia is a good model system to study the interactions between adsorbed and adsorbing species, because its behaviour, at least at room temperature and below, is relatively simple. It adsorbs molecularly in a strongly site-specific way, and then dissociates into NH_2 and H. Further dissociation does not occur at room temperature. Models of all the isolated structures discussed in this work are shown in figure 3. Furthermore, as all of the reaction products are monovalent, many of the adsorption arrangements described above are not available. At the same time, the possible sources of co-adsorption interactions are quite rich. The dative bond formed by the NH_3 molecule and any charge redistribution will have a strong effect on local buckling patterns, while hydrogen-bonding interactions are known to be strong in polar molecules such as ammonia. Finally, the effects of any co-adsorption interactions can be determined from the locations of the NH_2 species, as these remain in the same location as the adsorbed NH_3, in contrast to PH_2, which has been observed to diffuse. For these reasons, the adsorption of ammonia has been the source of many studies both experimental and theoretical, as I will describe in this review.

The review is arranged as follows. In section 2 I will describe the process of ammonia adsorption and dissociation into the on-dimer and inter-dimer structures, discussing the
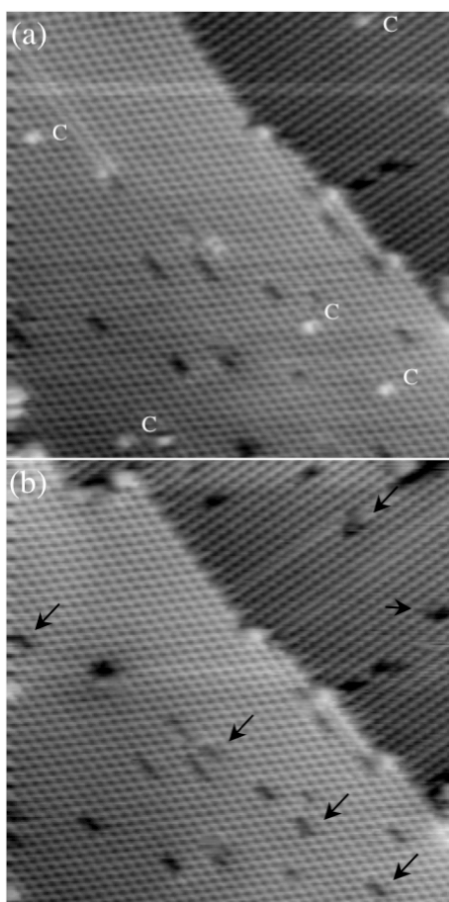
Figure 2. Empty states STM images of the same area (a) before and (b) after a does of ≈0.1 L of NH$_3$ exposure at 65 K. The imaging conditions were +2.0 V sample bias and 0.1 nA. The bright protrusions indicated by C in (a) are identified as C defects on Si(100). However, these may actually be ammonia ID structures. The arrows in (b) indicate the sites where NH$_3$-induced changes were observed. Reprinted with permission from Hossain *et al* [30]. Copyright (2003) by the American Physical Society.

kinetic pathways and the energetics of the final structures. Also I will discuss the appearance of these features in STM. In section 3, I will review the different possible co-adsorption interactions, describing how the adsorption process of ammonia is affected by these interactions. In section 4, I will make a comparison to the adsorption of PH$_3$ and the less-studied AsH$_3$, showing that these behave quite differently to ammonia. I will review the different approaches taken by modellers in studying this system in section 5. Finally, in section 6 I will draw some conclusions.

2. Molecular adsorption and dissociation

2.1. The adsorbed species

Studies of the degree of dissociation of the NH$_3$ molecule on the Si(001) surface at or below room temperature have reached a consensus. An early STM study of the ammonia-saturated Si(001) surface [23] had seen no asymmetry between the two halves of the saturated Si dimers, and concluded

that ammonia dissociated completely, with the N moving subsurface, and the H forming monohydride surface dimers. However, other experimental studies, using photoemission and other spectroscopic techniques [24, 25], showed that ammonia adsorbed molecularly below around 100 K, and that NH$_x$ species were dominant on the surface from 200 K up to 500 K. The sticking probability is around 0.9 at room temperature [26]. A significant amount of Si–N, indicating the movement of the N atoms subsurface and the loss of all the hydrogen, was only seen above about 600 K. These results have been confirmed by a variety of experimental techniques, including LEED/ESDIAD [27], HREELS [28] and UPS [29]. An STM study at a substrate temperature of 65 K [30] found that while most ammonia adsorption resulted in the formation of dark dimers, a small fraction resulted in the formation of bright features centred on one half of a Si dimer. The bright feature, identified as molecularly-adsorbed NH$_3$, is marked with a circle in figure 1(a), which converts into a dark feature in (b).

Alongside the experimental studies, a variety of modelling studies, using both small finite clusters and larger periodically-repeating calculation slabs, have been performed. These studies have reached a similar consensus that the NH$_3$ molecule is able to adsorb intact in a metastable molecular state; there is a barrier to dissociation, although it is smaller than the adsorption energy, as can be seen from table 1. As expected from a simple Lewis base picture, the NH$_3$ molecule forms a dative bond with the empty dangling bond of a down atom of a dimer, while being repelled by the filled lone pair on the up atom. A ball-and-stick model of the molecularly-adsorbed state is shown in figure 3. The dative Si–N bond formed is strong: cluster calculations have found values for the adsorption energy ranging between 0.94 and 1.56 eV [32]. Periodic DFT slab calculations give values between 1.27 and 1.36 eV [33–35]. These are all considerably larger than the value of 0.62 eV found for PH$_3$ [36]. The Si–N dative bond length is likewise shorter than that of Si–P. The chemisorption weakens the Si–Si dimer bond, which lengthens. Calculated lengths of Si–Si, Si–N and N–H-bonds from different sources [35] are given in table 1. In the simple Lewis base picture, the reason for this weakening is that the Si–Si π-bond electrons are now localized onto the dangling bond on the up atom of the dimer. However, the actual behaviour is not that simple; importantly for the future discussion of co-adsorption effects, several authors [37, 38] have found that the donated electrons from the NH$_3$ molecule are delocalized across more than one dimer. There is a significant enhancement of electron density on the two up dimer atoms neighbouring the NH$_3$ molecule, as shown in figure 4. This demonstrates the difference between intermolecular reaction and adsorption onto a surface; the surface provides not only a large density of adjacent adsorption sites, but also a medium for interaction between them.

Since the adsorption is so site-specific, it is important to introduce the two different surface regimes. The Si dimers can flip between two oppositely-buckled states, with a barrier of about 0.1 eV. The dimers are therefore frozen in place below about 120 K, and the surface is effectively static.
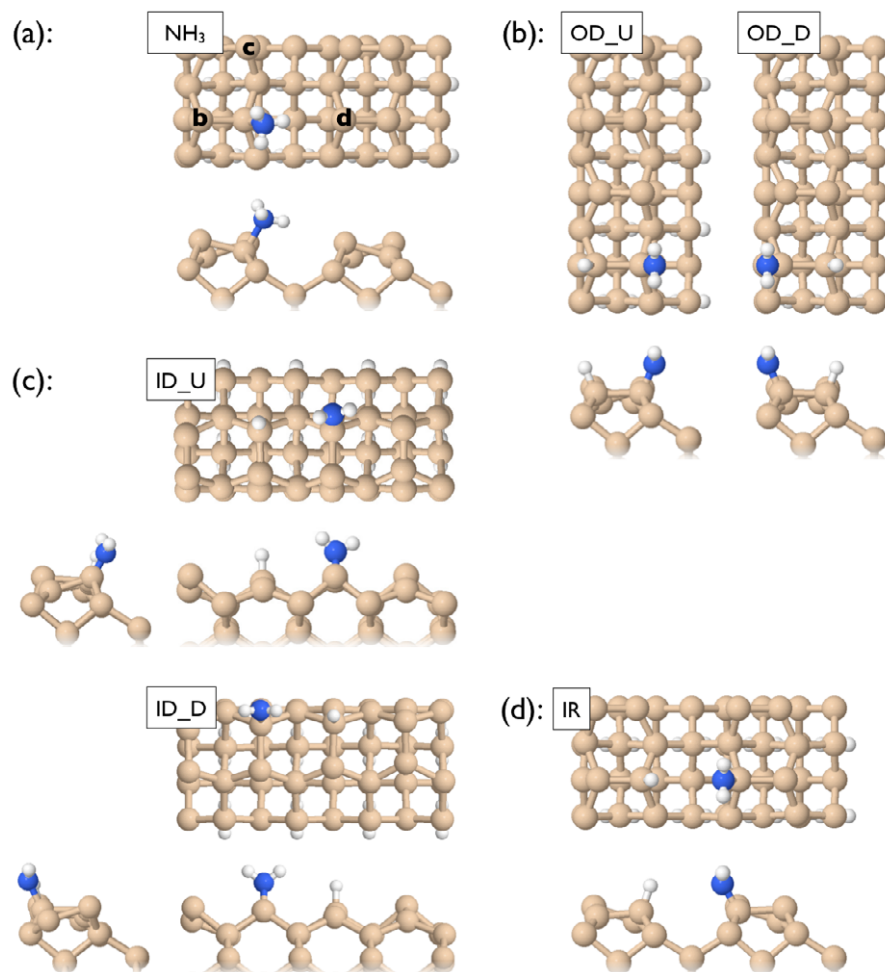
Figure 3. Ball-and-stick models of the adsorption configurations of an isolated ammonia molecule. (a) The metastable molecularly-adsorbed NH$_3$ state. Loss of an H atom to the nearby Si atoms as labelled in the plan view leads to the respective NH$_2$–H structures, shown in (b)–(d). (b) The on-dimer (OD) NH$_2$–H configuration. Both UU and DD isomers are shown. (c) The inter-dimer (ID) NH$_2$–H configuration. Both U and D isomers are shown, and (d) the inter-row (IR) NH$_2$–H configuration. The energies of these different states from DFT are given in table 1.

Table 1. Adsorption energies, dissociation barriers and bond lengths for NH$_3$ and the NH$_2$, H structures on Si(001). Ranges of energies calculated in various modelling studies are given for NH$_3$ and the OD and ID structures. Equivalent numbers for PH$_3$ and AsH$_3$ are given for comparison where available.

Fragment	Energy (eV)	Barrier (eV)	Si–Si (Å)	Si–Si (θ)	Si–X (Å)	Si–H (Å)	X–H (Å)
Si dimer, NH$_3$ (g)	0.00	—	2.35	17–19	—	—	1.05
NH$_3$ (ads)	−0.94–1.48	0	2.35–2.43	11.9–13	1.98	—	1.03
NH$_2$/H (OD, DD)	−2.00	1.03	2.42	−1.7	1.73	—	—
NH$_2$/H (OD, UU)	−1.96–2.45	0.6–0.99	2.36–2.50	−1 to +2.7	1.71–2.04	1.38–1.52	1.02–1.14
NH$_2$ + H (ID, U)	−1.69–1.94	0.74–0.77	2.47	4.3	1.73		
NH$_2$ + H (ID, D)	−1.59	0.87	2.43	−0.2	1.73		
NH$_2$ + H (IR)	−1.56–1.60	1.12	2.44–2.47	−4 to −6	1.73		
PH$_3$ (ads)	−0.62–0.90	0.05	2.38	12	2.23–2.37	—	1.45
PH$_2$/H (OD, UU)	−1.92–2.04	0.3–0.76	2.39	1.4	2.27	1.51–1.64	1.46
PH$_2$/H (ID, U)	−1.71	0.54	—	—	—	—	—
AsH$_3$ (ads)	−0.71	0.45	2.36	13	2.48	—	1.54
AsH$_2$/H (OD, UU)	−1.97–2.15	0.45	2.39	1.07	2.33	1.51	1.55
AsH$_2$/H (ID, U)	−1.83	—	—	—	—	—	—

Above this temperature, the dimers are able to flip between two oppositely-buckled states (at a rate of about 10^{11} s^{-1} at 300 K), thus the local adsorption probability on a particular site depends strongly on the local dynamics of the buckling. On the frozen surface, the molecule has a 50% chance of landing at the correct site, but then a 100% of adsorbing there,
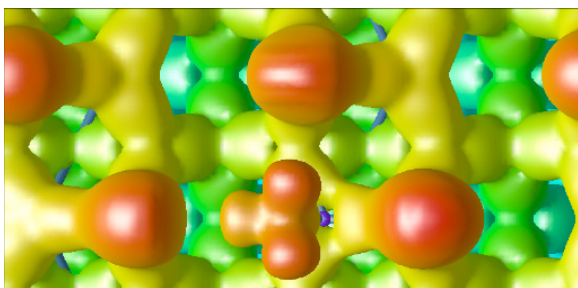
Figure 4. An electron localization function [31] isosurface plot at a value of 0.6 showing the dangling bonds adjacent to an adsorbed NH_3 molecule. The electron clouds of the dimer up atoms either side of the NH_3 molecule and the atom at the opposite end of the same dimer as the NH_3 molecule are larger than normal, as a result of charge transfer out of the adsorbed molecule. Moreover, they are distorted from a spherical shape by electron repulsion with the lone pair on the NH_3, as is the lone pair of the up atom on the neighbouring row. Image courtesy of David Bowler.

while on a dynamic surface these probabilities are reversed; on 100% of sites, there is a 50% chance of being in the correct state for adsorption. On the dynamic surface, furthermore, the 50% chance of meeting a down atom can be modified by local distortions of the buckling, for example via charge transfer as a result of previous adsorption as explained above, and can rule it out completely. Significant pinning, required to block adsorption on a particular site, will require a difference in energy of the two buckled isomers which is large in relation to the buckling barrier (ca. 0.1 eV). As will become clear in later discussion, it is important that this concept of a dynamic, probabilistic adsorption process should replace a conceptual static surface, which is only relevant below about 100 K.

The first stage of decomposition of the adsorbed NH_3 molecule involves the loss of one hydrogen to nearby Si atoms. There are three possible structures which can arise, assuming that the H atom and NH_2 must bond to a neighbouring Si atom, and cannot diffuse. These are shown as sites b, c, d in figure 3. While diffusion of PH_2 groups has been identified [39], there is no evidence for similar motion of NH_3 or NH_2 groups in low-coverage STM [30, 34, 40]. Likewise, the barriers to diffusion for H atoms to sites b,c, and d are 1.4 eV [41], 1.7 eV [42] and 2.1 eV respectively, so these are also not expected to diffuse at 300 K.

The resulting structures, shown in figure 3 are: NH_2 and H on the same dimer (known as the 'NH_2–H dimer' [43] or 'on-dimer (OD)' structure [34]); NH_2 and H on adjacent dimers in the same dimer row (the inter-dimer (ID) structure); and NH_2 and H on adjacent dimers in different dimer rows (the inter-row (IR) configuration). Hereafter these will be referred to as the OD, ID and IR structures. Most early modelling studies considered only the OD structure [44–46, 32]. While the possibility of forming the ID structure was known in the case of water [47, 48], spectroscopic studies were unable to distinguish it from the OD structure in the ammonia case, and it has only been identified in recent low-coverage STM experiments [34, 40]. The energies and some important bond lengths for these structures from experiment and from modelling studies [32, 49, 34], are given in table 1.

The appearance of the OD structure is a single dark dimer, similar to a missing dimer defect, but with one end brighter than the other [30, 50, 34], while the ID structure appears as a pair of dimers with one bright end and one dark end [34]. Examples of these are marked in figures 5(a)–(c), by triangles and arrows respectively. As shown in figure 5(d), the OD structure appears to be more prevalent [34]. The ID structure was not identified in the 65 K [30] experiments, with any such features being attributed to C-type defects, which has the appearance of a pair of asymmetric dimers, with one half bright and the other half black. First identified in the early study of the Si(001) surface [51], these have been identified as ID structures resulting from water adsorption [47, 48]. Owing to the similarity in appearance, it is quite possible that some of the C-type defects seen in the 65 K experiments, and shown in figure 2(a) as bright patches marked 'C', are in fact ID structures resulting from ammonia adsorption. With further adsorption, the ammonia fragments form patches [30, 34], rather than spreading randomly across the surface. This indicates either that there is an attractive interaction between adsorbed species and incoming gas-phase species, or that the neighbouring Si dimers are a strongly preferential adsorption site. In all cases, the NH_2 species remains on the same Si atom as the adsorbed NH_3 molecule, enabling the analysis of adsorption patterns from the locations of the NH_2 groups. At saturation coverage, as shown in figure 6, these patches merge, and the surface becomes covered with dimers with an asymmetric appearance, arranged in both linear and zigzag patterns.

DFT calculations have found that the OD dimer, with an NH_2 group at one end and a H at the other end, is essentially flat [44–46, 52, 49, 34]. Two isomers can be obtained, depending upon the sign of buckling of the neighbouring clean dimers. Initially, the NH_2 group will be between two 'up' dimer atoms (UU), as it has adsorbed onto a 'down' atom. However, as its neighbours flip, the NH_2 will be between two down atoms. It is energetically better to have the NH_2 group next to the 'up' atoms of the neighbouring dimers (UU) by about 0.04 eV [35]. This is a little larger than the PH_3 case (0.01 eV) [36]. The same effect is also seen for the ID case, where the configuration with an 'up' atom next to the NH_2 group (U) is 0.1 eV more stable than that with a 'down' atom next to it (D) [35]. Models of both isomers for the OD and ID structures are shown in figure 3. Note that the buckling angles for the 'D' isomers are slightly negative, indicating that the Si atom with the NH_2 is slightly up. Since the Si dimer in the OD structure is flat, it is unlikely that the energy difference between the UU and DD isomers is caused by any physical strain effect. It is more likely that there is a small charge redistribution between the neighbouring lone pairs and the slightly electropositive NH_2 group [53], which would not be possible in the case of the DD isomer, resulting in a slightly higher energy compared to the UU isomer. This will be discussed more fully in section 3. However, the difference in energy, although larger than kT at room temperature, is smaller than the buckling barrier, and in room temperature STM [34], there is no evidence of pinned dimers on either side of either the OD or ID structures.
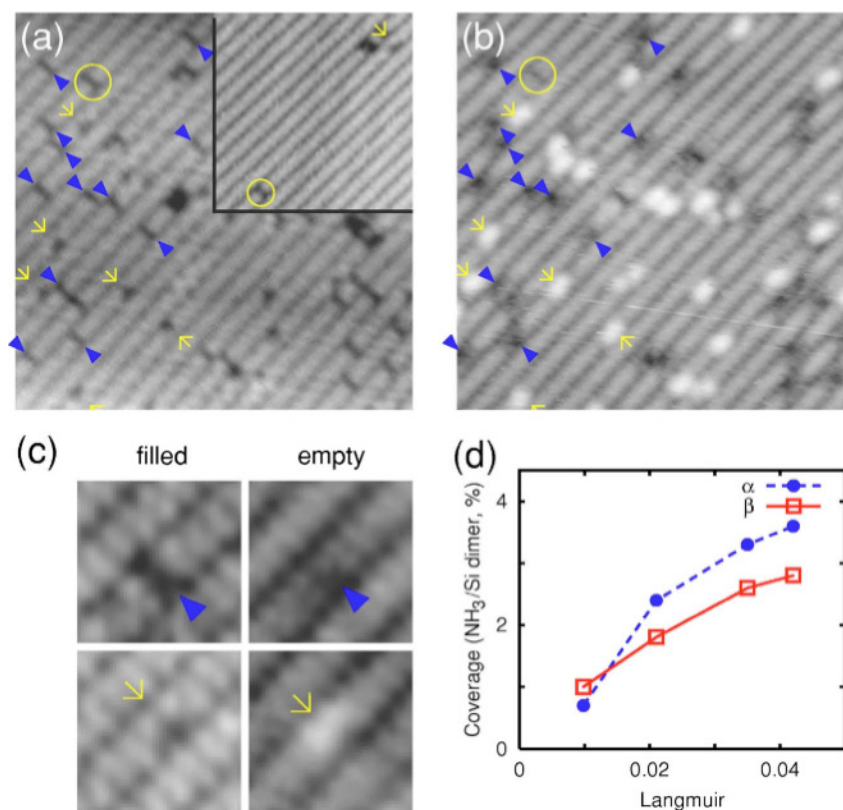
Figure 5. STM images of the Si(001) surface after exposure to 0.04 L of NH$_3$ at 300 K. (a) Filled states (-2.0 V), (b) empty states ($+0.7$ V). The OD (α) and ID (β) structures are marked by triangles (blue in online version), and arrows (yellow in online version) respectively. (c) Enlarged images of an OD and ID feature. (d) The coverages of OD(α) and ID(β) features as a function of NH$_3$ exposure. Reprinted with permission from Chung *et al* [34]. Copyright (2006) by the American Physical Society.

A general feature of molecular adsorption on the Si(001) surface is that it is energetically favourable to place adsorbates on both ends of a single dimer, where this is sterically possible. Adsorption on one end of a dimer breaks the π-bond of the dimer, leaving an unpaired electron, which can then be passivated by adding an adsorbate at the other end. This explains the low energy of the on-dimer configuration relative to other configurations. However, due to the proximity of neighbouring dimers along a row, it is also possible for the dangling bonds to interact with each other along a dimer row, as we have noted earlier. Here, the breaking of 2 π-bonds is compensated by interaction between the two dangling bonds. In this context, note that the adsorption energies of the inter-dimer and inter-row structures differ by $\sim$0.1 eV.

2.2. Kinetic pathways to decomposition

In the determination of the expected surface structures, it is necessary also to consider the kinetics of the dissociation process. The formation of the OD structure has been modelled extensively, giving a range of values for the barrier from 0.6 eV to 1.04 eV [44, 54, 46, 49, 55, 56, 37, 48, 35, 57]. Formation of the ID structure, which was detected experimentally only quite recently, has been less modelled; barriers of 0.88 eV [49], 0.77 eV [35], 0.74 eV [48] and 0.7 eV [57] have been calculated (an earlier paper [46] states that the barrier is $\sim$0.2 eV higher than that for on-dimer formation, which is
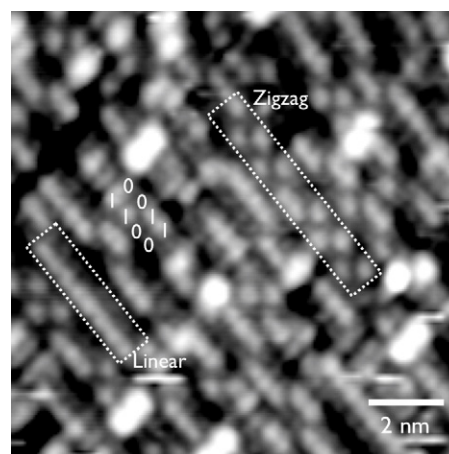

Figure 6. 12×12 nm STM image of the Si(001) surface saturated with ammonia at 300 K. The surface is covered in dimers with an asymmetric appearance; the labels '1' and '0' refer to bright and dark ends respectively. Examples of strings of dimers in the linear and zigzag configurations are marked. The tunnelling conditions were -2 V sample bias, tunnelling current of 0.3 nA. Reprinted with permission from Bowler *et al* [35]. Copyright (2007) by the American Physical Society.

opposite to the given calculations). Decomposition into the inter-row (IR) configuration is slightly higher than that for the OD structure, 1.12 eV [35] due to its larger diffusion

distance. Values for these barriers from various papers have
been collected in table 1. All these barriers are smaller
than the chemisorption energy of the NH_3 onto Si (1.37 eV),
so that the overall reaction can be considered barrierless.
The barrier for decomposition into the ID structure is lower
than that for the OD structure, despite the larger diffusion
distance. One likely reason for this is the flexible S–N dative
bond, which allows the H to move about 0.5 Å sideways
without a large increase in energy [35], as can be seen in
figure 7. There is almost no energy rise for a displacement
of 0.6 Å for the ID feature, while for the same displacement
along the OD pathway, the energy rise is over 0.1 eV. Despite
the lower barrier in the calculations, in experiment the ID
structure has lower frequency than the OD structure in room
temperature STM data [34], and is not observed at all in the
65 K experiment [30] (although in fact, some of the C-type
defects observed may be ID structures). There are a number
of possible reasons for this. The calculations do not identify
the preferred modes of vibration of the Si dimers; the flip-
flopping dimer motion may induce movement of the NH_3
molecule in the plane of the dimer bond, in preference to the
sideways motions required for formation of the ID structure,
thus altering the overall rate of dissociation. An autocatalytic
effect has been proposed [58], in that the change in buckling
angle caused by adsorption of an NH_3 molecule decreases
the barrier for H atom motion, and hence for dissociation. It
is suggested that this would lead to a dominance of zigzag
pairs, which is in accordance with the results of low-coverage
STM [40]. Furthermore, the adsorbed NH_3 molecule arrives
with an adsorption energy larger than any of these barriers.
Since decomposition into the OD structure has been observed
at 65 K, as in figure 1, it must be the case that the adsorbing
NH_3 does not lose its energy to the substrate immediately. For
such an excited molecule, the energy landscape may look quite
different, and it may be able to dissociate before dissipating its
energy to the substrate. Since dissociation occurs by diffusion
of an H atom, the possibility of proton tunnelling through the
potential barrier should not be overlooked. Tunnelling has
been proposed as an alternative dissociation route [49, 58].
They have calculated that there should be a preference of
about 4:1 in favour of the OD structure at low temperature,
while at room temperature, the balance is about 20:1 in favour
of the ID structure. Since they also suggest that tunnelling
should dominate over thermally activated decomposition at
room temperature, these simulations are in conflict with the
observed experimental data [34].

2.3. The appearance in STM

In order to study adsorption patterns and co-adsorption effects
in real space using STM, it is necessary to have a good
knowledge of the appearance of various configurations on the
surface. Early STM data [23] found that the appearance of
the ammonia-saturated surface was very similar to that of
the H-terminated monohydride surface, with little asymmetry
between the two ends of the dimers. However, it was
quickly determined that the dominant surface structure would
be NH_2–H dimers, in which the NH_2 group is physically higher
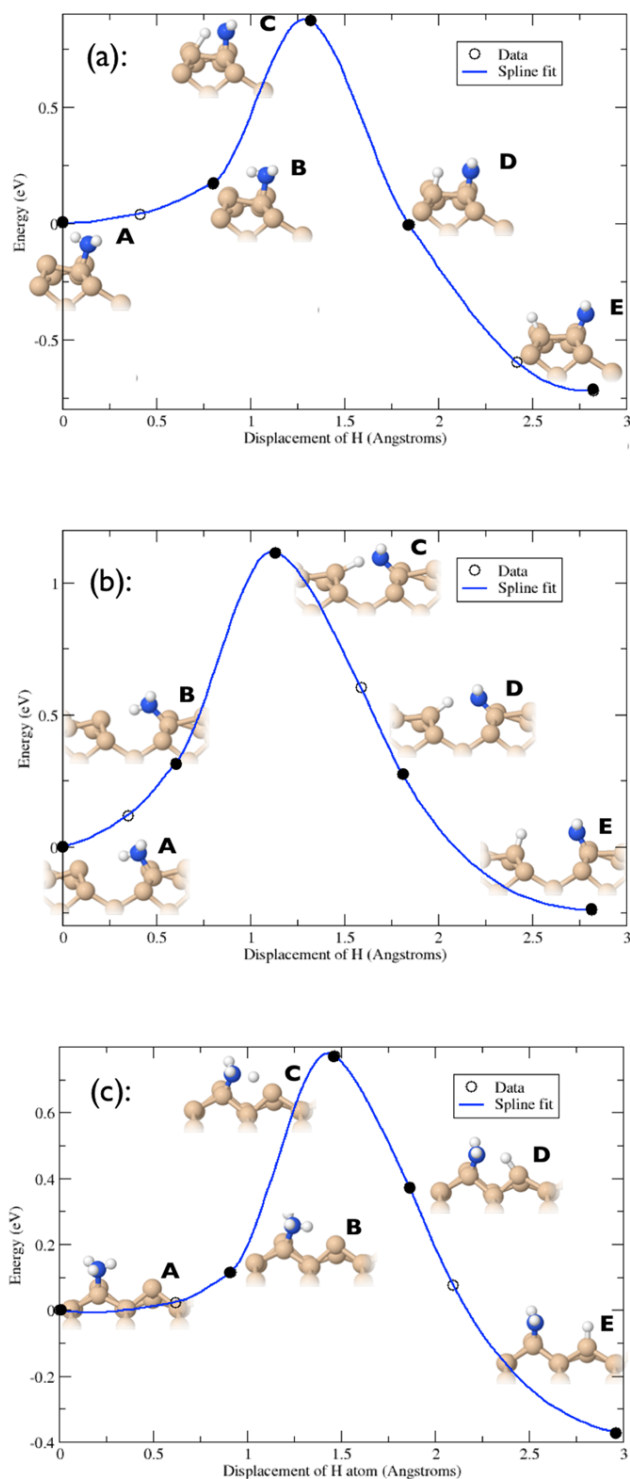

Figure 7. Graphs showing the barriers to dissociation of the NH_3
molecule into NH_2 and H. for: (a) the on-dimer (OD) configuration,
(b) the inter-dimer (ID) configuration, and (c) the inter-row (IR)
configuration. The reaction coordinate is the displacement of the H
atom from its starting position towards its destination. The barrier for
on-dimer dissociation is approximately 1.0 eV, while the barrier for
inter-dimer dissociation is only 0.8 eV. The circles mark the energies
of relaxed structures; the spline fit is a guide to the eye. The models
shown correspond to the filled circles. In each case, models A & E
represent the beginning and end points, while model C represents the
intermediate structure at the peak of the barrier. Reprinted with
permission from Bowler *et al* [35]. Copyright (2007) by the
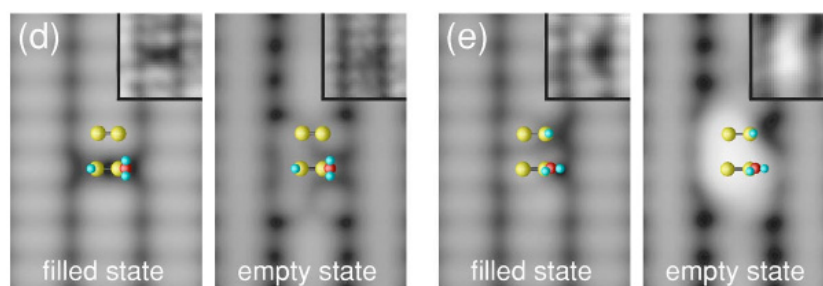American Physical Society.

Figure 8. Simulated STM images of the OD (d) and ID (e) structures at low coverages. Filled and empty states images, at −0.7 V and +0.6 V respectively, were obtained from the averaged tunnelling current of the two oppositely-buckled configurations to simulate the room temperature fluctuation of the Si dimers. Insets are corresponding experimental images (taken at −2.0 V and +0.7 V). Reprinted with permission from Chung *et al* [34]. Copyright (2006) by the American Physical Society.

than the H atom, and with a much larger electron density, and thus would be expected to show quite different contrast. Surprisingly, the ammonia/Si(001) system was not revisited by an STM study until quite recently, and thus the question of the appearance of the OD structure remained unresolved.

In all the STM studies, relatively large bias voltages were used, around ±2.0 V. This is likely to be due for practical reasons. In the high-coverage study, for example, we found it difficult to obtain a stable image at lower voltages, below −1.5 V, or above −2.5 V. The STM adsorption study performed at 65 K [30] attributed a bright spot at one end of a dimer to an adsorbed NH_3 group, which over time were observed to change into dark dimers, which were attributed to OD structures. Similar dark dimers were seen at room temperature [34], as shown above in figure 5. These images were taken at bias voltages of around −2 V. However, the contrast between the clean Si dimers and these dark dimers makes it difficult to determine the relative contrast between the two ends. More detailed low-coverage images taken at room temperature found that one end of the dark dimer was brighter than the other [34, 59], as had been expected from basic physics. Room temperature images also found a second feature, similar in appearance to the C-type feature (which results from water adsorption in an inter-dimer structure) [47]. This feature occupied two dimers, with one half brighter than the background Si, and the other half dark. This feature has been identified as the ID structure [34].

As can be seen in figure 6, the majority feature on the saturated surface is an asymmetric dimer, with one end about 0.8 Å higher than the other. We described this as a '10' or '01' configuration [35] where the '1' refers to the bright end, and the '0' to the dark end. Other features, such as a '11' or '00' dimer, with two bright or dark ends respectively, were also seen. Using this notation, the patterns of dimers for a whole STM image could be written down and analysed, without prejudging the origin of any feature. For example, a zigzag pair of the NH_2–H dimers can arise either from dissociation of ammonia into two OD dimers, or by the formation of one ID, which then attracts another ammonia molecule, as appears to be the case in the 65 K STM data. Thus the observed dominance of the NH_2–H dimer does not necessarily imply a dominance of decomposition into the OD structure. For this reason, when referring to patterns of NH_2 and H groups on the surface, I

will always use the notation (10) introduced here, while when referring to the structures formed by decomposition of NH_3, they will be identified as OD and ID structures.

While the patterns of bright and dark dots in STM can be analysed without knowledge of their identity, in order to understand the surface reactions, they must be interpreted and assigned to particular adsorbed species. The basic physics would suggest that the NH_2 group would be higher than the H group; the physical height difference in an atomic model matched the measured height difference in STM at −2 V sample bias, and the lone pair on the N atom would appear bright relative to the H atom. However, this interpretation has been disputed [59–61].

Two sets of STM simulations have been performed to test the identification of these features. The authors of the low-coverage study [34] used a Tersoff–Hamann-based STM simulation for both filled states and empty states images, with sample bias voltages in the simulation of −0.7 V, and +2 V respectively. The results are shown in figure 8. For the high-coverage study, STM simulations at −1 and −2 V were performed, using both Tersoff–Hamann and Bardeen tunnelling formalisms [35]. The results are shown in figure 9.

The simulated appearance of the molecularly-adsorbed NH_3 molecule, shown in figure 9(a), is in good agreement with experimental images [30]. The filled dangling bond at the opposite end of the dimer from the NH_3 molecule is *brighter* than the other up atoms on the clean surface; this indicates that the bright dot seen in STM images of early-stage NH_3 adsorption [30] is not the NH_3 itself, but the effect of its adsorption on the dimer. (this is similar to the situation of a Si dimer with a single H atom adsorbed at one end [42].) A similar appearance is found for the PH_3 case, shown as structure A1 in figure 10(a). For the NH_2–H dimer, the appearance changes with bias voltage. At low bias voltages, as used by Chung *et al* and shown in figure 8, the H appears brighter than the NH_2 group. At higher bias voltages, used in the high-coverage study [35], the NH_2 group appears higher than the H atom. This reversal in contrast indicates that simulation of the appearance of the ammonia fragments must be undertaken with care. The simulations at −2 V match the bias voltage used in STM for both low- and high-coverage studies, and would therefore appear to be favoured. However, the authors of the low-coverage STM work have
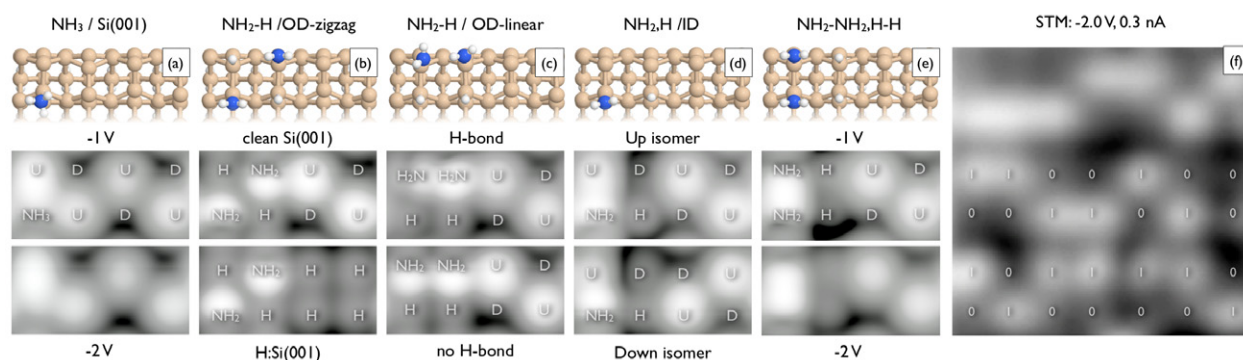
Figure 9. Simulated STM images showing surfaces of constant current for adsorbed NH_3 and NH_2, H configurations. The simulated voltage was -2 V for all structures, except for (a) and (e) as marked. For NH_3, (a), the up atom opposite the adsorbate appears brighter than the other up atoms, while the NH_3 itself appears dark. For NH_2–H dimers in the linear (b) and zigzag (c) configurations, the NH_2 group is brighter than the H atom at bias voltages between -1 and -2 V and is darker than the up atoms of the clean dimers. When a H-bond forms between two NH_2 groups in the linear configuration, one NH_2 lone pair turns sideways, and hence is less bright in the simulated STM. These data is in good agreement with the assignments given to species on the basis of STM data [30, 50]. For the ID structure, the pair of clean ends buckle, and hence are not as bright as the unpaired clean end in (a). Both cases, with the 'up' and 'down' atoms opposite the NH_2 species, have been considered, and are shown in (d). The dimer with the NH_2 adsorbed is brighter than the dimer with the H adsorbed in both cases, and the appearance is similar to that of the (NH_2–NH_2, H–H) structure, shown in (e). Note that the height ranges (which determine the greyscale) in all figures are different. A section of an STM image of the saturated surface taken at -2.0 V, 0.3 nA is shown to the same scale for comparison in (f). Reprinted with permission from Bowler *et al* [35]. Copyright (2007) by the American Physical Society.

argued [60] that their use of modelling voltages enables the overall contrast between NH_3 fragments and the clean Si to be made correct and that in the -2 V simulations the NH_2 is relatively too bright compared to the Si up atoms. Further, that their assignment of H and NH_2 matches the empty states simulation as well as the filled states.

While the experimental bias voltage and the modelled energy should not in general be expected to match exactly, there are a number of reasons why the use of a small voltage such as -0.7 V in the simulation is suspect. For such low voltages, close to the band edge of silicon, only a few states contribute to the image. For example, strong contrast effects around defects are seen in clean silicon [62, 63] in this voltage range. For any structure, therefore, such a low voltage is inappropriate for the simulation of experimental images taken at bias voltages, such as -2 V, which are far from the band edge [61]. Secondly, DFT is a ground state theory, and notably does not calculate the width of the band gap correctly; calculations of filled states are therefore more reliable than those of empty states, and simulations of filled states images are in general much more reliable than those of empty states images. Moreover, other experimental and theoretical evidence suggests that the NH_2 group should be brighter than the H atom in STM.

- Simulations of the appearance of PH_2 groups on Si(001) [64], shown as structure B1 in figure 10 (b), found that the PH_2 group is brighter than the H. More tellingly, the PH_2 groups stand out against the H-terminated background in STM [22].
- The assignment of the bright end to NH_2 is also consistent with earlier, low temperature data [30]: the brighter end lies between the two up ends of neighbouring clean dimers. At the temperature used in that work, the dimers are pinned and do not flip spontaneously, so the space

between two ends would be a down atom, the natural place for an NH_3 molecule to adsorb. Dissociation into an OD structure would lead to the NH_2 group adsorbed on this same atom; the brighter end must therefore be the NH_2 group.
- Analysis of correlations between dimer rows shows a positive correlation of the bright ends of the dimers [59, 61, 65], and shown below in figure 17. This can be explained naturally by a H-bonding interaction between NH_2 groups, if the bright end of the dimer is the NH_2. On the other hand, if the bright end is an H atom, some unknown mechanism of positive interaction between the H atoms, or a repulsive interaction between NH_2 groups must be invoked.

To summarize, the assignment of the bright and dark ends of the (10) asymmetric dimer to the NH_2 and H groups has been disputed, but the basic physics and the weight of experimental evidence, are in favour of the assumption that the bright end is the NH_2 group, while the H atom is dark. It may well be that the high bias simulations [35] overestimate the relative height of the NH_2 group against the up atoms of the clean Si dimers. One possible reason for this might be the polarizability of the N orbitals compared to those of Si, under the electric field of the STM tip. Such an effect was invoked to explain the contrast reversal found in STM, compared to a standard STM simulation, in the case of C_2H_4 on Si(001) [66]. This overestimate should be borne in mind when considering the appearance of the ID structure.

For the ID structure, there is again a discrepancy between different modelling studies. Here the basic physics, and comparison with the similar case of water, would suggest that the clean ends of the dimers would be bright, while both the NH_2 and H species would be relatively dark. Thus an appearance similar to the well-known C-type defect is
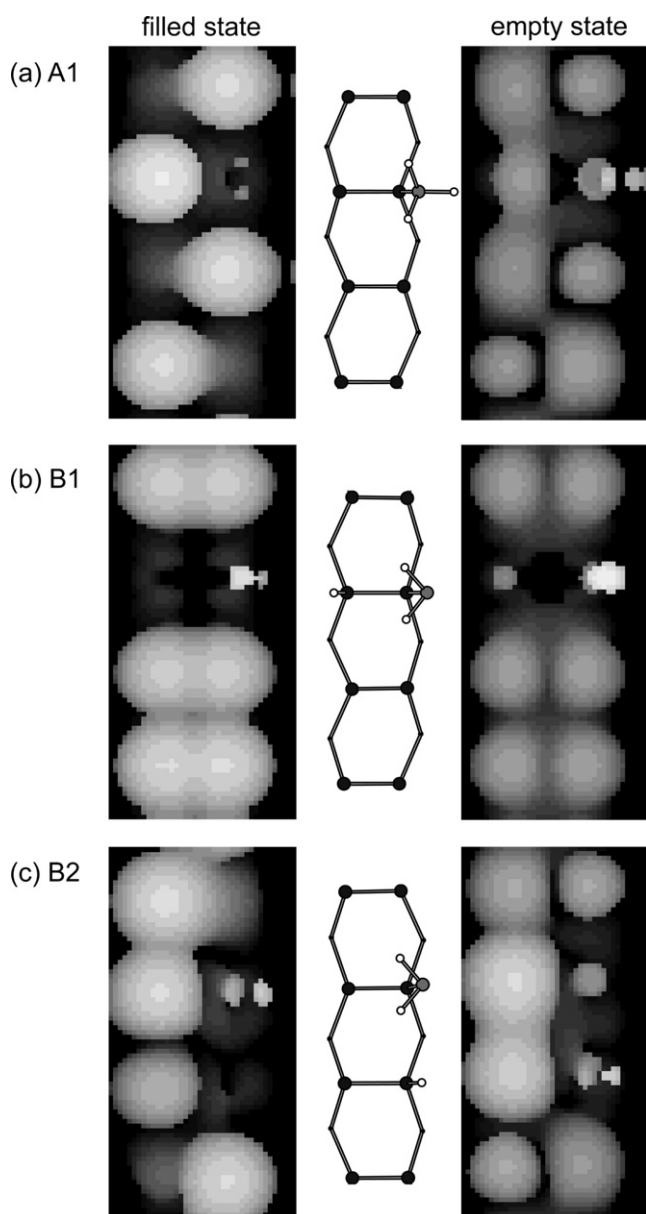
Figure 10. Simulated STM images for structures for molecularly-adsorbed PH_3, and the PH_2–H OD and ID structures. Because the OD structure does not pin adjacent free dimers, unlike PH_3 and the ID structures, simulated images of the OD structure are averaged over the two-dimer buckling configurations. Reprinted with permission from Warschkow *et al* [36]. Copyright (2005) by the American Physical Society.

expected. Indeed, STM simulations of the ID [34] structure have found that the clean ends of the dimers are much brighter than the NH_2 or H species, and brighter than the up atoms of the clean dimers (figure 8). In contrast to the OD case, this study finds that the NH_2 is now brighter than the H atom.

Alternative simulations [35] found that the feature should appear as a pair of bright and dark dimers (notated (11), (00), with '1' indicating a bright spot and '0' a dark spot), as shown in figure 9, with the NH_2 nearly as bright as the clean end of the dimer. Overall, this study found that the ID would therefore have a similar appearance to the NH_2–NH_2, H–H

structure shown in figure 9(e). One possible reason for the difference between these two simulations may be that in the simulation by Chung *et al* [40] the NH_2 lone pair is rotated to point towards the H atom on the neighbouring dimer. The simulated appearance of the PH_3 ID structure [36], shown in figure 10 has an overall appearance that more closely matches that found by Chung *et al* [34]. However, if it is assumed that the apparent height of the NH_2 group is overestimated as in the OD case in the simulations at -2 V, the discrepancy between the modelling results and the experiments might be resolved.

Stemming from the proposed appearance of the ID structure, the authors of the low-coverage study suggested that the linear OD feature, identified in the high-coverage STM data, and shown in figure 6, should be reinterpreted as ID features [40]. As we have argued previously [61], this suggestion leads to a logical contradiction and can be dismissed. If we imagine a group of three (10) dimers, arranged (10), (10), (01). Following this suggestion, the first two dimers would make a linear ID pair, with the bright end bare Si, and the dark ends NH_2 and H. The second two make a zigzag pair, with the bright end NH_2 and the dark end H. Thus, if we are to follow this suggestion, both the bright end and the dark end of the middle dimer would be NH_2 groups, with different contrasts: an obvious contradiction. It is far simpler to interpret these as three OD dimers, with the central dimer having one neighbour with NH_2 on the same side of the row, and the other neighbour with an NH_2 on the opposite side of the row.

In summary, comparison of the simulated appearance of the NH_2–H dimer (figure 9(c)) with the experimentally observed (10) dimer (figure 9(f)) gives good agreement. Thus the dominant feature on the saturated surface is indeed the NH_2–H dimer. While there remains some dispute on this point, it seems reasonable to assume that the bright end seen in STM data at -2 V is NH_2 (arising primarily from the lone pair); moreover, that the (00) dimers should be identified as monohydride dimers, and the (11) dimers as NH_2–NH_2 dimers.

3. Co-adsorption interactions

Having set out the background of the adsorption of ammonia, we now arrive at the main area of interest in the ammonia/Si(001) system: the rich array of co-adsorption behaviour exhibited by this relatively simple molecule, which thus serves as a prototypical adsorbate. As a polar molecule interacting with a surface that can show both Lewis acid and base behaviour [6], with the possibility of charge donation to, and withdrawal from, surface dangling bonds, there are many possible mechanisms for interaction, both between the molecule and the surface, and between molecules. There are various different patterns which can result. Along a dimer row, neighbouring dimers can have the NH_2 groups next to each other, forming linear features, notated (10), (10), or they can have the NH_2 groups at opposite ends of the Si dimers, forming zigzag patterns, notated (10), (01). Examples of these patterns are seen in figure 6. Two NH_2 groups, resulting from the formation of ID structures, can also be adsorbed on the same dimer, forming the (11) dimer. Experimental examples

of these patterns are shown in figure 6. Similar correlations are possible for dimers between rows, forming the (0110) (1010) and (1001) patterns. These have been studied extensively by different modelling groups, with very different conclusions drawn about the likely co-adsorption patterns which would result in experiment.

Several different combinations of species and interactions have been considered:

(i) NH_3 adsorption on dimers neighbouring a pre-adsorbed NH_3 molecule [56, 37, 38],

(ii) a precursor state with a gas-phase NH_3 molecule H-bonding to an adsorbed NH_2 species (or to an adsorbed H atom) [53, 50, 35, 67, 57],

(iii) NH_3 adsorption on dimers neighbouring a pre-adsorbed NH_2 species [68, 37, 50, 38, 35],

(iv) interactions between adsorbed NH_2 species [52,50,35,69].

In situations where the molecularly-adsorbed NH_3 group has a significant lifetime compared to the flux of ammonia, i.e. below about 120 K, co-adsorption effects between gas-phase NH_3 and adsorbed NH_3 may be strong. However, the pattern of adsorption is likely in practice to be determined by the frozen dimers in this temperature range, leading to a dominance of the zigzag pattern along the row. Likewise, apparent correlations between rows will be controlled by the local buckling patterns, either $p(2 \times 2)$ or $c(4 \times 2)$. Above this temperature range, adsorbing NH_3 molecules are likely to encounter mostly dissociated species, i.e. NH_2 and H, and NH_3–NH_3 interactions are less relevant. The interactions between NH_3 and NH_2 then become most relevant. Since the adsorbed fragments are unable to move, interactions between NH_2 groups are in general not relevant when determining patterns of adsorption, but will play a role in the stability of final structures, and will affect the spectra measured by techniques such as NEXAFS [69]. In the PH_3 case, where diffusion of PH_2 species has been observed, they would be relevant. However, the temperature range required for diffusion to occur is also the temperature range where dissociation of PH_2 occurs, and thus surface motion may not be significant in practice. Moreover, since the NH_2 species are immobile, we can backtrack from the final adsorption patterns to the original patterns of NH_3–NH_2 co-adsorption, and understand the underlying interaction mechanisms.

Thus co-adsorption effects, other than the clustering of adsorbates, are likely to be seen only in experiment in the higher temperature dynamic surface regime where the dimers can flip. This ability to flip is crucial to the dominant co-adsorption mechanism, hydrogen bonding, as in nearly all cases, the strongly H-bonded structures, such as the linear NH_2 chains along dimer rows, stem from the less stable buckling isomer. Without the ability to flip, these structures would not be able to form.

3.1. Interactions between NH_3 molecules

For the molecular NH_3 adsorption state, several studies have identified significant charge redistribution between the N lone pair, and the Si surface. Most of this charge is transferred

to the dangling bond at the other end of the Si dimer, and the lone pair is seen as a bright spot in STM [30] and STM simulations by DFT [35]. Some charge, however, is distributed to the neighbouring up atoms to either side of the adsorbed NH_3 [37, 38]. This charge redistribution blocks adsorption of a second NH_3 molecule onto the same dimer. However, no charge redistribution occurs between dimer rows [56]. Adsorption of two NH_3 molecules in a linear pattern along a dimer row is also significantly disfavoured, owing to this charge distribution; the buckling configuration necessary to form it is 0.3 eV worse than that for the zigzag pattern [38] and the adsorption energy for the second NH_3 molecule is about half that of an isolated NH_3 molecule [37], −0.62 eV rather than −1.27 eV. This is comparable in size to the case for PH_3 adsorption, where the calculated energy difference is 0.22 eV [36]. A second effect related to the neighbouring lone pairs is electron-cloud repulsion between the adsorbed NH_3 and the lone pairs. An electron localization function [31] of the lone pairs along and across the dimer rows, shown in figure 4, shows distortion of the shape of the lone pairs near the NH_3 group. This repulsion is even visible between dimer rows, which may have some effect on the relative stability of an up atom at this site, and encourage correlated adsorption between dimer rows. In fact, this is the only case, where the preferred buckling direction is not opposite to that required for a H-bonded precursor. The possibility of NH_3 physisorbed to a surface NH_3 molecule via a hydrogen-bonding interaction has not been addressed by modelling. However, the STM experiments at 65 K found examples of a bright dot converting into a pair of dark dimers, which they interpreted as a surface NH_3 being triggered to dissociate by interaction with an adsorbing NH_3 molecule, to form a pair of NH_2–H dimers. Such an autocatalytic effect has been proposed [58], in that the change in buckling angle caused by adsorption of an NH_3 molecule decreases the barrier for H atom motion, and thus for dissociation.

3.2. Physisorption of gas-phase NH_3 molecules on surface NH_2 species

Several studies which have modelled NH_3–NH_2 precursor states [53, 35, 67, 57], have concluded that H-bonds could form in either direction, but that an H-bond formed between the lone pair of the NH_3 and an H from the NH_2 would be stronger than one formed between the lone pair of the NH_2 and an H on the NH_3. The reason for this is that the NH_2 species has donated charge to the Si surface, and hence has a small positive charge. Recent detailed modelling studies [35, 67, 57] of H-bonded states have confirmed that the H-bond is very strong, around 0.2–0.3 eV. Weaker interactions are also possible between the lone pair of an NH_3 molecule and surface H atoms [57]. The possibility of a H-bonded precursor state may lead to the steering of incoming molecules towards a pre-adsorbed species [67, 57], within a certain capture radius, estimated at 10 Å [67, 65], giving rise to the clustering seen in STM [30]. Various adsorption configurations around the OD and ID structures are shown in figure 13 parts I and II respectively, demonstrating the range of the physisorbed
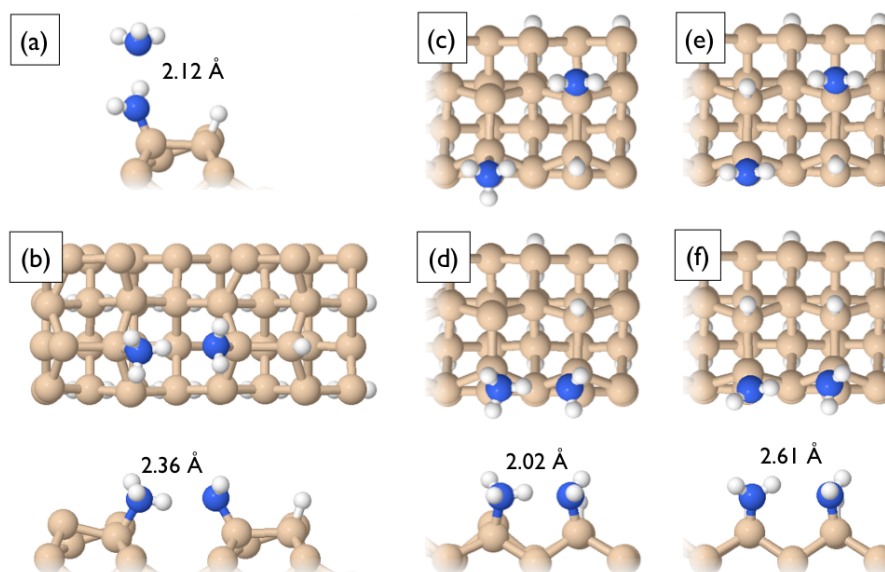
Figure 11. Ball-and-stick models of the adsorption configurations of an NH_3 molecule adjacent to an NH_2–H dimer. There are three unique locations for an NH_3 molecule to adsorb, as shown in (b)–(d). (a) The gas-phase physisorbed state. (b) The inter-row configuration. (c), (d) The zigzag and linear configurations for NH_3, NH_2. (e), (f) The zigzag and linear configurations for NH_2, NH_2. (b), (d) and (f) include side views below the respective plan views. The energies of these different states from DFT are given in table 2. H-bond distances are marked. Reprinted with permission from Bowler *et al* [35]. Copyright (2007) by the American Physical Society.

precursor. Maps of the potential energy surface around the OD and ID structures for an adsorbing NH_3 molecule [67, 57] are shown in figure 14. They show deep potential wells on either side of the NH_2 group, close to the neighbouring dimer atoms. Adsorption into these sites will be highly probable, and will lead to formation of the linear NH_2 chains seen in STM [50], and would also account for the observed correlated adsorption across dimer rows [65]. Additionally, for the ID structure, the potential well wraps around the NH_2 species, so that there is a pathway towards adsorption at the far end of the same Si dimer, forming the (11) feature seen in STM [35, 65].

Experimental evidence for a physisorbed precursor state comes from studies of correlations between NH_2 groups [59, 61, 65] between dimer rows, where there are only weak buckling interactions, although a weak repulsion between the NH_2 lone pair and an up atom is possible; in any case, they would not give any net correlations. The adsorption sites on dimers adjacent to the NH_2 groups, which are relevant to a physisorbed precursor state, are shown in figure 15. Sites L and Z on the same dimer row will lead to formation of linear and zigzag patterns along a dimer row respectively. Sites A, B, C & D on the dimer rows either side of the NH_2 are those orthogonal to the dimer rows, and within range of the proposed physisorbed precursor state [67]. Analysis of patterns of co-adsorption across dimer rows at low-coverage by STM [40] found that three patterns of paired features were common after room temperature adsorption; OD–OD pairs, an L-shaped OD–ID pair, and an ID–ID pair. These patterns are shown in figure 16. No statistics of the ID–ID or ID–OD pairs are given, but data for OD–OD pairing shows that there are three possible configurations, as shown in figure 17. Adsorption into sites A or C gives (1010) or (0101), site B—(0110) and site D—(1001) with the 1 representing the bright end of the dimer. This study found a deficit of the (1001) type, with an approximate 2:1 ratio

between the frequencies of other two types. A similar analysis of cross-row correlations on the saturated surface, which also took into account the (11) features which result from ID adsorption [65], found a similar pattern, with a significant deficit of the features resulting from adsorption into site D, equivalent to the (1001) type. The measured data including both OD and OD–ID pairs from the high-coverage analysis, and data for OD–OD only pairing from both studies is given in table 3. While a strictly nearest-neighbour interaction model would suggest that there would be a preference for adsorption only into site B, both sets of data show instead a deficit for adsorption into site D, and an enhancement for adsorption into sites A and C. This distribution of data therefore provides evidence for a physisorbed precursor which captures any NH_3 molecules within range, and then allows for adsorption into any site within range. Meanwhile, analysis of data at 450 K showed no evidence of correlated adsorption, either along or across dimer rows [65], indicating that any physisorbed precursor is unstable at this temperature.

3.3. Interactions between NH_3 molecules and NH_2 groups on the surface

STM observations of the saturated surface [50] indicate that the dominant feature is the NH_2–H dimer, arranged in either zigzag or linear configurations. Other features, such as the (11) dimer, form a small minority. Note that the zigzag configuration could have arisen either from a pair of OD or a pair of ID structures (although the majority will have come from a pair of OD structures), while the linear configurations will all have arisen from OD structures, and all the (11) dimers, arise from ID structures. Models of the structures formed by adsorbing NH_3 near on-dimer and inter-dimer structures are shown in figures 11 and 12 respectively.
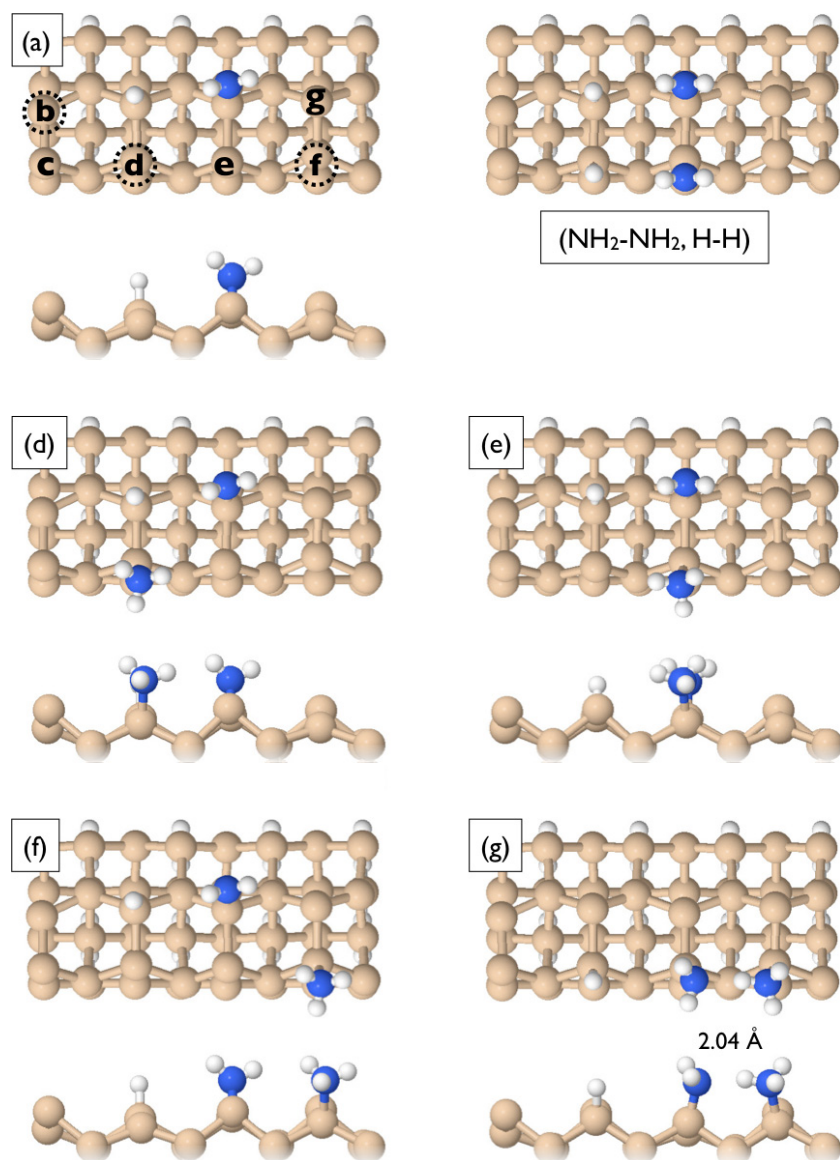
Figure 12. Ball-and-stick models of some of the adsorption configurations of an NH_3 molecule adjacent to an NH_2, H inter-dimer structure. There are six unique adsorption sites, labelled (b)–(g) in (a). (b), (d), (f), circled, are 'down' atoms, and thus would be expected to be preferential adsorption sites. Adsorption in site (d) is likely to lead to the zigzag structure, as in figure 11(e), while adsorption in site (e) will decompose to a pair of NH_2–NH_2, H–H dimers, the (NH_2–NH_2, H–H) pattern shown top right. Adsorption in site (g) leads to strong H-bonding (marked), which will produce a short linear chain of NH_2 groups. Side views show the buckling more clearly. The energies of these different states from DFT are given in table 2. Reprinted with permission from Bowler *et al* [35]. Copyright (2007) by the American Physical Society.

For the on-dimer structure, there are three distinct locations for NH_3 adsorption, as shown in figures 11(b)–(d). Although it is more favourable for the down atom to be away from the NH_2 group, from table 2, i.e. the UU isomer, we see that adsorption on the next dimer in the same row, to form the zigzag structure, produces a structure which is slightly *disfavoured* compared to adsorption of the NH_3 at a random position distant from the NH_2–H dimer. On the other hand, after adsorption onto the down atom in the less favoured buckling configuration, the DD isomer, a H-bond can be formed to the NH_2.

For the inter-dimer structure, six distinct sites are available on the same dimer row: the four adjacent dimer atoms and the clean ends of the dimers with the H and NH_2 groups, as shown in figure 12(a). As with adsorption around the OD, of the sites available, adsorption on a clean dimer next to the NH_2 fragment, figure 12(g), is the most favoured (as it allows a strong hydrogen bond to form), followed by the clean end of the dimer with NH_2 on it, figure 12 (e), which would lead to formation of the (11) dimer. The other sites, i.e. the nominal 'down' atoms in the lowest-energy U isomer, sites figures 12(b), (d), (f), have similar adsorption energies, and are in fact disfavoured compared to adsorption on clean dimers far from the inter-dimer configuration by ∼0.1 eV [35, 57]. In both cases, therefore, the modelling finds that the most stable structure for the NH_2–NH_3 interaction is arrived at via
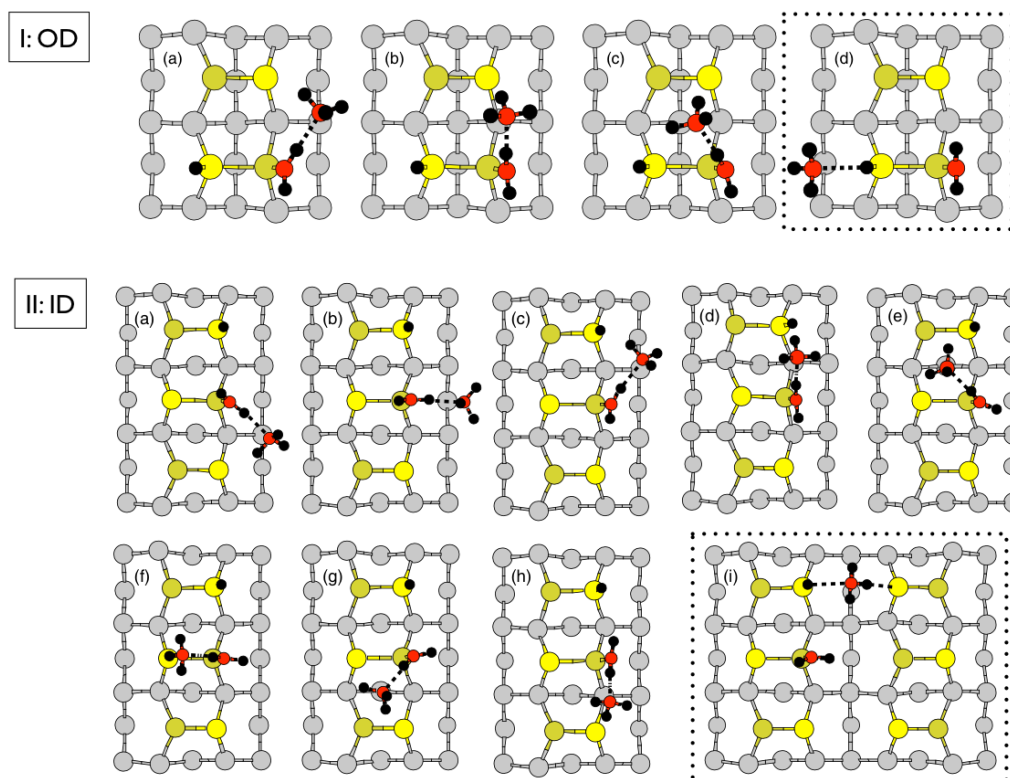
Figure 13. Atomic structures of the physisorption states of an NH_3 molecule near the OD (I) and ID(II) NH_2, H structures. The dark and bright yellow (medium and bright grey) balls are the buckled-down and -up Si atoms on the Si(001) surface, respectively. The red (small dark grey) and black balls are the N and H atoms, respectively. The grey balls below the dimers are the subsurface Si atoms. The H-bonds, indicated by the dashed lines are between the lone pair of the NH_3, and surface H, either of the NH_2, or the adsorbed H (marked with the dotted boxes). Reprinted with permission from Kim *et al* [57]. Copyright (2009) by IOP Publishing.
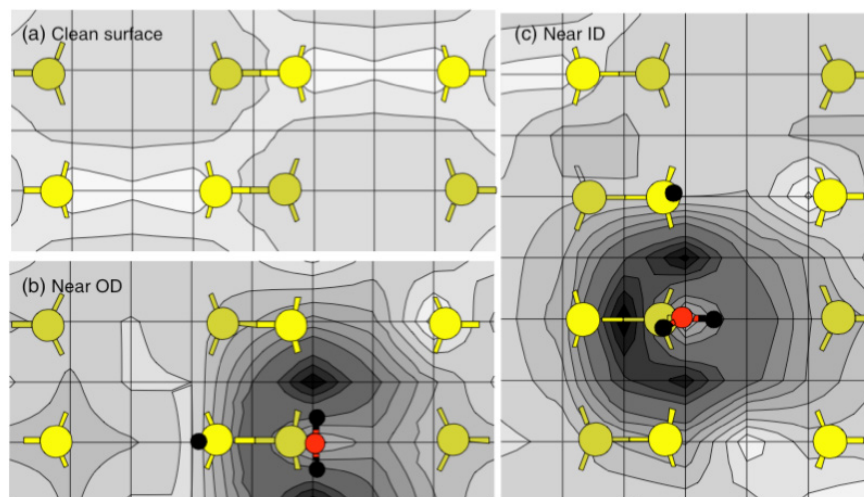

Figure 14. Calculated potential energy surfaces (PES) for NH_3 adsorption at a height of 4 Å above the surface in the vicinity of the clean surface (a), OD (b) and ID (c) structures. The spacing of the mesh is $2a_0/4$, here 1.92 Å, where a_0 is the Si lattice constant. The contour spacing is 0.02 eV from -0.04 to -0.24 eV. Overlaid on the weak potential surface of the buckled dimers, deep wells are seen close to the NH_2 species. Reprinted with permission from Kim *et al* [57]. Copyright (2009) by IOP Publishing.

the less favourable isomer. As for cross-row adsorption, the adjacent down atom on the neighbouring row, shown as site B in figure 15, is again a favourable site, with an interaction energy of 0.24 eV [57], similar to that found for the OD case.

These results demonstrate that the strong H-bonding seen for the physisorbed precursor is maintained as the NH_3 adsorbs onto the surface, but the direction of the bond changes, with the bond now formed between the lone pair on the NH_2 and a H on the adsorbed NH_3. This bond is again surprisingly strong, around 0.2 eV [37]. By removing the Si surface, and calculating the strength of the H-bond for the same atomic positions, a bond strength of about 0.04 eV was found. Thus

Table 2. Adsorption energies and bond lengths for NH_3 adsorption near existing NH_2, H configurations on Si(001) and for pairs of NH_2, H groups. Models of some of these structures may be seen in other figures as indicated. Where two numbers are given for a bond length, this indicates different bonds in different groups.

Position	Energy (eV)	Si–Si (Å)	Si–N (Å)	N–H (Å)	H-bond (Å)
Distant NH_3 (g)	0	—	—	1.02	—
Distant NH_3 (ads)	−1.28 to −1.48	2.43	1.98	1.03	—
NH_3 near NH_3					
Same row, zigzag	−0.99	2.44/2.42	1.73/1.99	1.03	—
Same row, linear	−0.52	2.41/2.42	1.79/1.96	1.06	2.02
NH_3 near OD, figures 11 and 13					
Above NH_2, figure 11(a)	−0.25 −0.32	2.41	1.72	1.03	1.99–2.12
Above H, figure 13	−0.093	—	—	—	2.77
Next row, NH_2, figure 11(b)	−1.44 to −1.53	2.43/2.44	1.78/1.98	1.04	2.36
Same row, H, figure 11 (c)	−1.09 to −1.29	2.44/2.42	1.73/1.99	1.03	—
Same row, NH_2, figure 11(d)	−0.91, −1.50	2.41/2.42	1.79/1.96	1.06	2.02
NH_3 near ID, figures 12 and 13					
Above NH_2, figure 13	−0.26 −0.32	—	—	—	1.98–2.06
Above H, figure 13	−0.093	—	—	—	2.85
Next to H, figure 12(b)	−1.24–1.25	2.41	2.00	1.03	—
Clean end, H, figure 12(d)	−1.26 −1.27	2.41	1.97	1.03	—
Clean end, NH_2, figure 12(e)	−1.41	2.49	1.77/1.97	1.04/2.37	—
Next to clean end, figure 12 (f)	−1.21–1.25	2.42	1.98	1.02	—
Next to NH_2, figure 12(g)	−1.50	2.42	1.96	1.03	2.04
Next row, NH_2, [57]	−1.56	—	—	—	—
Pairs of NH_2,H					
Zigzag ODs, figure 11(e)	−2.00 −2.10	2.42	1.73	1.02	—
Linear ODs, figure 11(f)	−2.02 −2.10	2.41/2.43	1.72/1.75	1.02	2.61
Linear ODs (no H-bond), figure 9(c)	−1.94 −2.02 −2.04	2.43	1.74	1.02	—
NH_2–NH_2, H–H dimers, figure 12	−2.02	2.41/2.44	1.73	1.02	—

the unusual strength of this H-bond results from interactions between the adsorbed species and the surface. In fact, it is thought to be partly due to a restoration of the electron density in the NH_2 lone pair, as a result of charge transfer from the adsorbed NH_3 through the Si substrate. This accounts for the reversal in the sign of the H-bond (i.e. that the lone pair is now provided by the NH_2, rather than the NH_3, as in the physisorbed precursor). With the dissociation of the second NH_3 molecule, this source of enhancement is lost, and the strength of the H-bond in the case of NH_2–NH_2 bonding declines to around 0.09 eV [52].

Buckling effects for the NH_2–H structures are much smaller than for the molecularly-adsorbed state, with the UU isomer about 0.03 eV lower in energy than the DD isomer for both OD and ID structures. The effect of this asymmetry in the absence of any other interactions is that it is more probable for an incoming NH_3 to encounter a down atom at the opposite end of the dimer to the pre-adsorbed NH_2, which by itself would favour a zigzag pattern of adsorption. The fraction can be related to the energy difference using Boltzmann statistics. The UU OD isomer would be expected around 55% of the time at 450 K [50] for example. As a result of these competing effects, any net effect will be weak, and experimental evidence for correlations along the dimer rows will be much less dramatic than for inter-row correlations.

The results of analysis of correlation along the dimer rows are presented in table 4, showing the number of different types of OD and ID pairs measured. Analysis of the patterns of co-adsorption along the dimer row at low coverages have

Table 3. NH_2 distribution data between dimer rows for NH_3 adsorption. (a) Pairing data on the saturated surface at 300 and 450 K from a high-coverage analysis [65], including both OD and ID pairs. (b) OD–OD pairing data across dimer rows for NH_3 adsorption at 300 K, as exemplified in figure 17. For the high-coverage data [65], the total number of pairs of each type is given, along with a percentage. For the low-coverage data [59], the data is presented as coverages, as the raw pairing data is not given. At 300 K, the number of pairs resulting from adsorption in site D is significantly reduced relative to the expected values, in both the high and low-coverage data, with the remainder of the pairs distributed evenly between sites A, B, C. At 450 K, there are no statistically significant correlations.

OD & ID data	300 K: 2567 pairs		450 K: 921 pairs	
Sites A & C	1346	52.4%	486	52.8%
Site B	716	27.9%	217	23.6%
Site D	494	19.2%	210	22.8%

OD-only data	High coverage: 4 L		Low coverage: 0.12 L	
(1010), (0101)	1249	53.3%	1.9×10^{-3}	58.4%
(0110)	628	26.8%	1.1×10^{-3}	33.8%
(1001)	467	19.9%	2.5×10^{-4}	7.7%

found a predominance of zigzag OD pairs, as well as a OD–ID pair [40]. Very few linear OD pairs were seen. However, analysis of the patterns of co-adsorption at saturation coverage [50], found only a small shift away from purely random adsorption along a dimer row. At 300 K, this was found to be in the direction of linear features (52%:48%), while at 450 K, this was found to be in the direction of zigzag pairs (46%:54%).
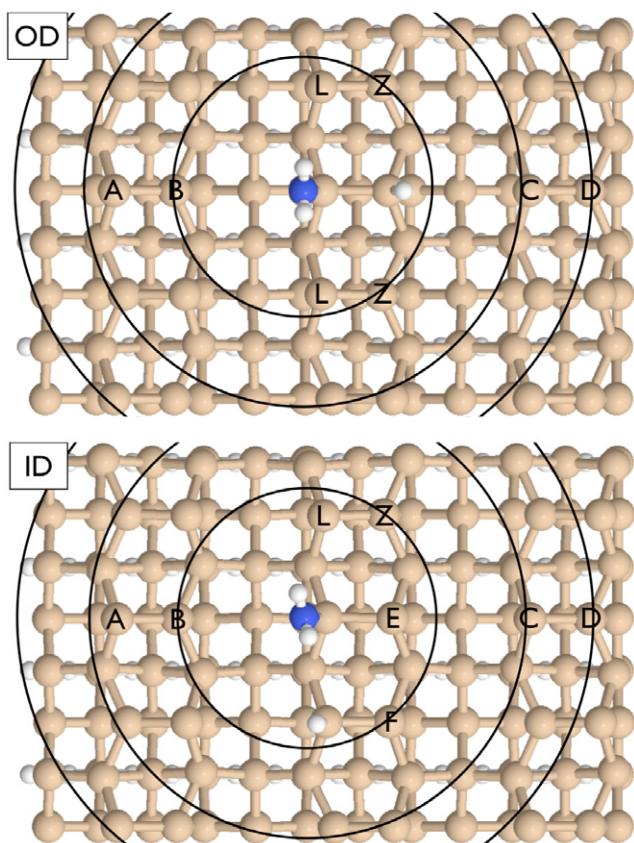
Figure 15. The adsorption sites around the NH_2 group in the OD and ID structures considered for correlation along and across dimer rows. Sites on neighbouring dimer rows are marked A, B, C and D. Of these, B is closest (4.7 Å), A and C are approximately the same distance away (8 Å), and D is furthest (10.5 Å). For the ID structure, the clean ends of the dimers with NH_2 and H adsorbed are additional sites, marked E and F. Sites on the same dimer row which lead to the linear and zigzag features are shown by L and Z respectively. E and L are the closest, while Z is about the same distance as B.

Figure 16. Filled state STM images of $NH_3/Si(001)$, taken at -2 V and 0.5 nA, after dosing with (a) 0.03 L, (b) 0.06 L and (c) 0.10 L of NH_3 respectively. Examples of paired NH_2–H structures are marked in (b) and (c). The three common types of pair are marked as α (OD–OD pair), β (OD–ID) and γ (ID–ID) in (c). Reprinted with permission from Chung *et al* [59]. Copyright (2009) by Elsevier.

Table 4. Top: NH_2 distribution data for ammonia adsorption at 300 K and 450 K for high-coverage analysis [50]. The numbers of correlated strings (either linear or zigzag) of length two. There is a significant excess population of linear chains at 300 K, while the trend reverses for 450 K, with a significant excess population of zigzags. Bottom: OD and ID pairing data for ammonia adsorption at 300 K for low coverages [40]. The coverages of different types of pair are given as percentages for an exposure of 0.10 L NH_3.

High coverage: 4 L	300 K		450 K	
Linear	1764	52.1%	1123	46.1%
Zigzag	1622	47.9%	1312	53.9%
Low coverage: 0.10 L	300 K			
Zigzag OD–OD	0.35 ± 0.03%	44%		
OD–ID (1)	0.20 ± 0.06%	25%		
Linear ID–ID	0.16 ± 0.05%	20%		
OD–ID (2)	0.06 ± 0.03%	7.6%		
Linear OD–OD	0.02 ± 0.01%	2.5%		

Apart from STM, two groups have analysed spectroscopic data to determine the dominant pattern of adsorption. A sample deposited at 200 K [68] found that the peaks corresponding to the zigzag con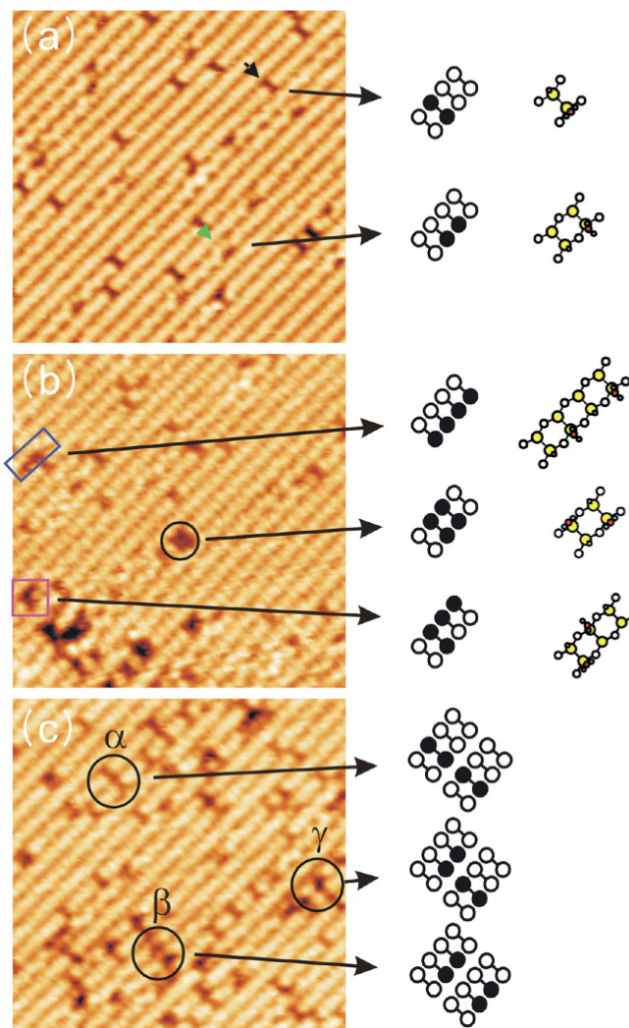figurations were predominant on their sample, while a study of a sample deposited at 300 K found a mixture of linear and zigzag features. This study showed that broadening and shifting of the peaks seen in spectroscopy, as seen in figure 18, results from H-bonding interactions between NH_2 groups on the surface, and thus the earlier 200 K analysis may have drawn an incorrect conclusion [70]. Instead, the recent study has found that the data is best explained by a surface with a majority of linear features, forming H-bonded structures both along and between dimer rows. At room temperature, they have concluded that a ratio of linear:zigzag of 2:1 is likely, although this is a much greater deviation from random adsorption than found from the STM data. NEXAFS and XPS spectroscopy of this system draws a similar conclusion, that an isolated NH_2 group should result in a sharp N 1s XPS peak, and that the experimentally observed broadening is likely to be due to interactions, probably H-bonding, between NH_2 groups on the surface, particularly between dimer rows. Thus this data supports the mixture of linear and zigzag features seen in the high-coverage STM study.
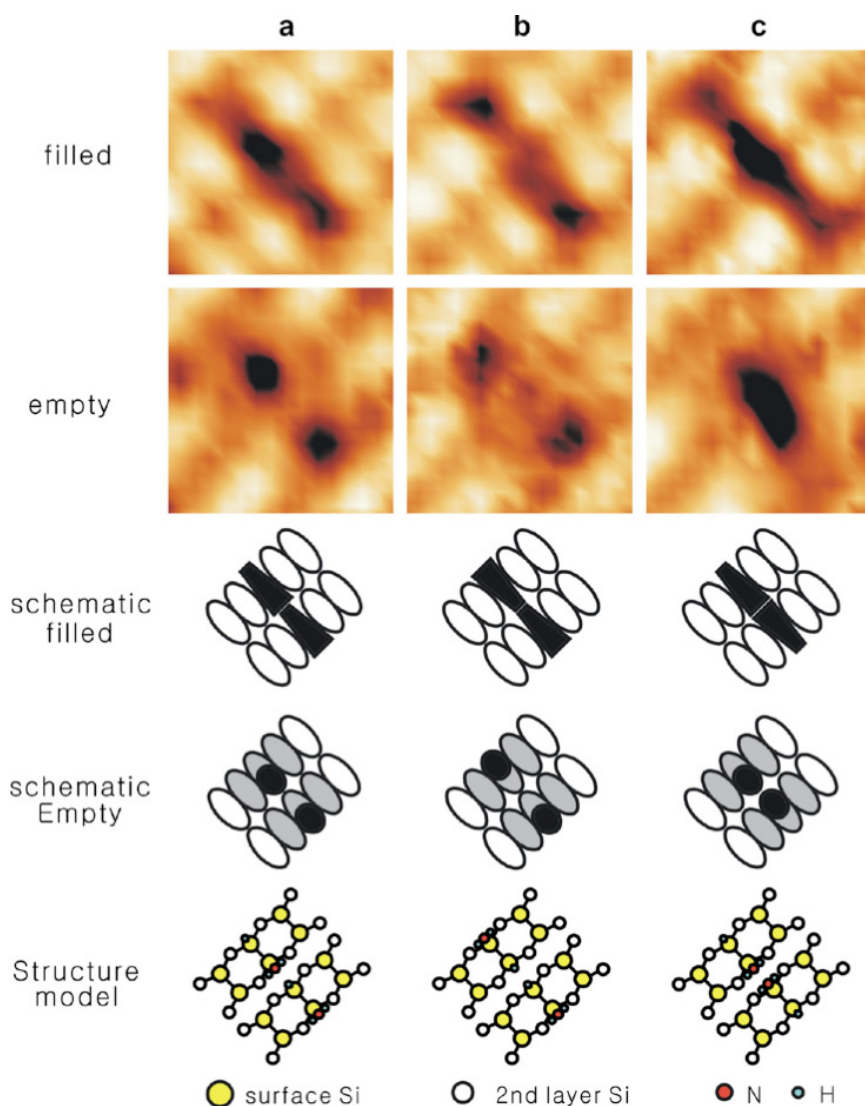
Figure 17. Filled and empty states STM images, schematic images, and structure models of the three arrangements of OD–OD inter-row pairs. (a) The (1010) or (0101) pair. (b) The (0110) pair. (c) The (1001) pair. The appearance of the dimers is clearly asymmetric, in filled and empty states images. (The H atom is identified as the bright end of the dimer in the structural model here, but this is unlikely to be correct. See section 2.3 for details.) Statistics for the different types are given in table 3. Reprinted with permission from Chung *et al* [59]. Copyright (2009) by Elsevier.

While there is agreement between the high-coverage STM study and the spectroscopy studies, the discrepancy between low- and high-coverage STM studies, evident from table 4, should be addressed. First, it is possible that the ammonia flux used could affect the outcome; the flux used in the saturation experiments [50] was much higher than for the low-coverage experiments [34, 40]. The results of adsorption of PH_3 is sensitive to the flux used, for example [22]. Unfortunately, the raw data behind the low-coverage results, such as the number of dimer pairs analysed, have not been presented, so that the statistical value of the results cannot be judged. A second issue is a disagreement over interpretation over the identification of linear features (01),(01) as OD or ID structures, as we have discussed above in section 2.3. On the contrary, if in fact, as a result of this misidentification, the low-coverage STM study has counted some linear OD pairs as ID structures,

they will have overcounted the number of ID–ID pairs, and undercounted the number of linear OD pairs, which might resolve the discrepancy between the two sets of data.

3.4. Interactions between NH_2 groups on the surface

Since the arrangements of the NH_2 groups are determined by interactions between NH_3 and NH_2 groups, the interactions between surface NH_2 groups are not important in co-adsorption studies. However, the interactions between NH_2 groups are discussed here for completeness, and because these interactions have been held responsible for the broadening of peaks in IR studies [70]. First, the strength of the NH_3–NH_2 H-bonded structures discussed above is not carried over into the NH_2–NH_2 situation. The two configurations of adjacent NH_2–H dimer adsorption, i.e. the linear and zigzag features shown in tables 2(e) and (f), have very
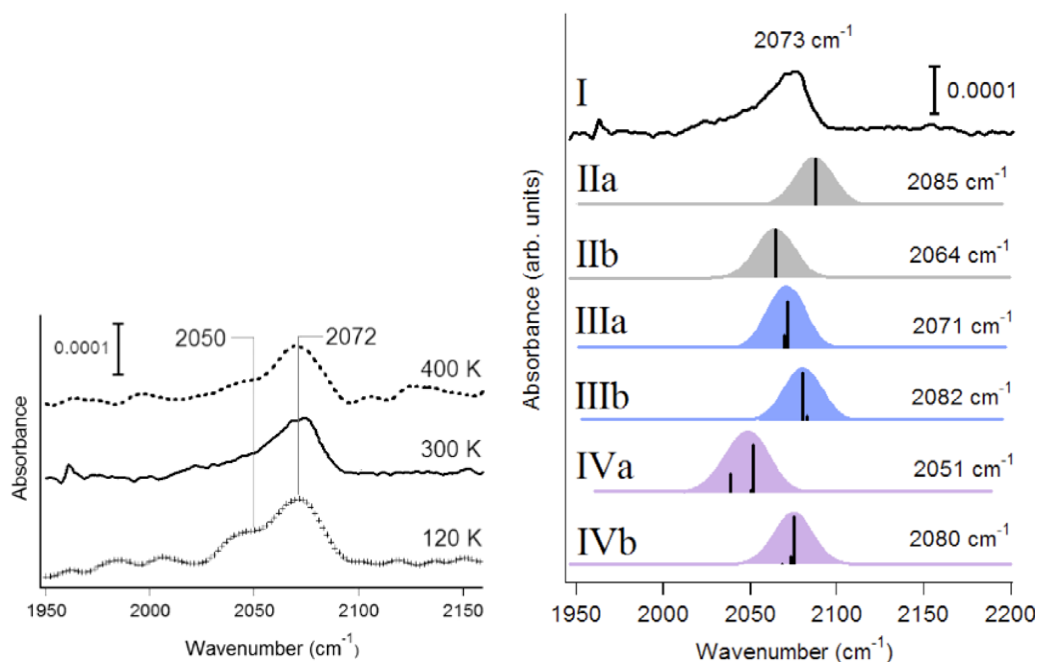
Figure 18. (a) Infrared peaks of the Si(001) surface after exposure of 10 L NH$_3$ at 120, 300 and 400 K, showing major peaks at 2050 and 2072 cm^{-1}. (b) Experimental 300 K spectrum together with simulated spectra from various arrangements of dissociated NH$_3$. IIA is from an OD structure, IIB is from an ID structure. IIIA and IIIB are from the zigzag and linear structures respectively, using a two-dimer cluster, while IVa and IVb are the spectra resulting from the zigzag and linear structures, using a three-dimer cluster. Reprinted with permission from 2007 [70]. Copyright (2007) from the American Physical Society.

similar energies in DFT simulations [52, 38, 50]. A linear feature without the hydrogen bond is only 0.08 eV worse in energy [52, 35] than with one, while the difference between linear and zigzag is around 0.06 eV [69]. Apart from H-bonding interactions, it has been suggested that neighbouring NH$_2$ groups repel each other, either via steric repulsion, or electrostatic interactions between the lone pair electrons on neighbouring groups [38, 59, 60]. However, the calculated strengths of these repulsive interactions are probably misleading; the identical positions of the neighbouring NH$_2$ groups suggests that independent rotation of the two species to a lower-energy structure was not permitted in these calculations. Where rotation to maximize H-bonding and minimize steric repulsion has been allowed, the two-NH$_2$ linear structure, shown in figures 11(b)–(d) [37, 50] or even a triple-NH$_2$ linear structure [70], have lower energies than zigzag arrangements.

The overall strength of the H-bonding is reflected in the bond lengths in the various cases; lengths are marked in figure 11. For the gas-phase ammonia, the H-bond length is 2.12 Å, and for adsorption adjacent to the OD and ID on the same dimer row, it is slightly shorter, around 2.0 Å. Across the dimer row, the H-bond length is longer; 2.36 Å. However, for the NH$_2$ H-bonded to NH$_2$ along the dimer row, the H-bond length is 2.6–2.7 Å, and is thus much weaker than for any of the NH$_3$–NH$_2$ cases. One reason for the difference in bond lengths is likely to be the much stiffer Si–N bond of Si–NH$_2$ compared to Si–NH$_3$ [35]. From the shape of the ID dissociation barrier shown in figure 7(b), it can be seen that the H atom on the NH$_3$ group can move sideways between 0.5 and 1 Å before there is any large increase in energy, demonstrating

the flexibility of the adsorbed NH$_3$. This allows the N–N bond length to be 0.38 Å smaller in the NH$_3$–NH$_2$ case compared to the NH$_2$–NH$_2$ case. Notably, the NH$_2$–NH$_2$ inter-row H-bond length, at 2.27 Å, is much shorter than the intra-row bond length [69], probably due to the possibility of a favourable orientation of the H atom on one NH$_2$ group. Thus inter-row H-bonding is found to be much stronger than intra-row H-bonds in this case.

3.5. Summary of Co-adsorption effects

To summarize, I have considered several types of interactions between ammonia fragments. Molecular adsorption of NH$_3$ pins the dimers to alternate sides, promoting a zigzag arrangement of adsorption. However, molecular adsorption is not stable above around 100 K. Much more significant with respect to patterns of correlated adsorption, are strong correlations between NH$_3$ and adsorbed NH$_2$ groups, both along and across dimer rows. While there are buckling effects present, caused by charge transfer out of the NH$_2$ group, these are outweighed by H-bonding interactions. Moreover, the H-bonds formed are surprisingly strong, as much as 0.2–0.3 eV, even between dimer rows. They promote adsorption of NH$_3$ to sites adjacent to NH$_2$, either via direct adsorption, or via an H-bonded precursor state, which counteracts any buckling effects. The long chains of NH$_2$ groups seen in STM demonstrate the existence of short-range H-bonding interactions, likely trapping of molecules in the deep potential wells adjacent to adsorbed NH$_2$ groups shown in figure 14. However, other evidence, such as the clustering of adsorbates, and the cross-row correlated adsorption into sites A and C as well as B, points
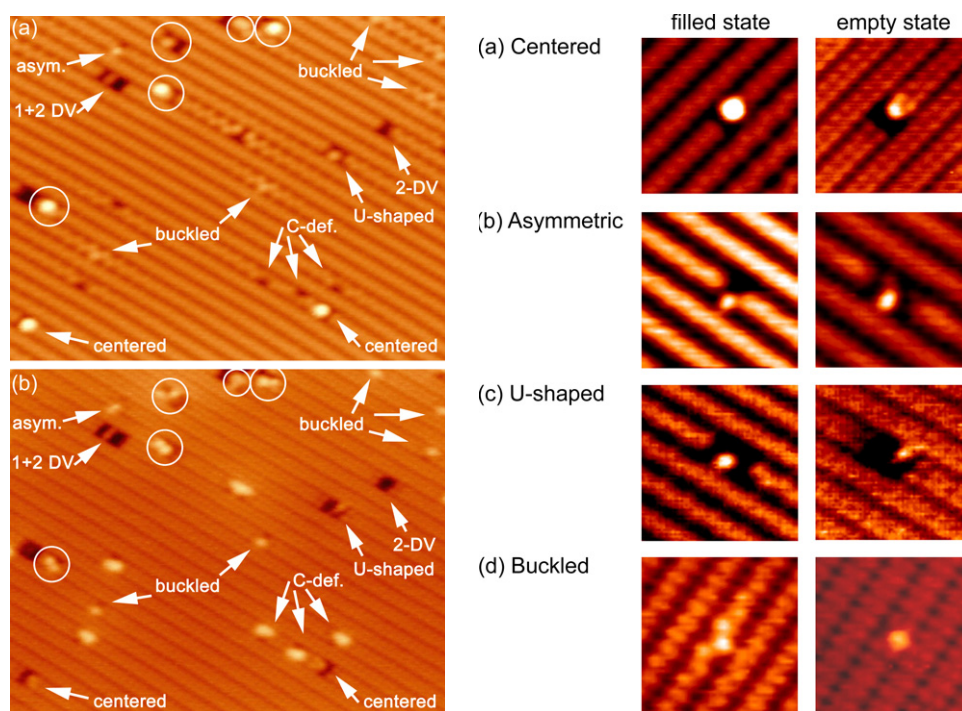
Figure 19. Filled states (a) and empty states (b) STM images of the Si(001) surface taken after low dose (0.001 L) PH3 exposure at room temperature. Four prominently observed STM features associated with PH3 dosing are labelled as the asymmetric feature (OD), centred feature, U-shaped feature, and the buckled feature. Other less common PH3 related STM features are marked by circles. High-resolution images of these features are shown at right. Filled state images acquired with -1.6 V, 0.1 nA. Empty state images acquired with $+1.2$ V, 0.1 nA. Reprinted with permission from Warschkow *et al* [36]. Copyright (2005) by the American Physical Society.

to the existence of a physisorbed precursor [67, 57, 65], with a range of around 9–10 Å.

The buckling configurations required to adsorb at these sites are generally less favourable, but only by a small margin, so that these pathways are accessible at room temperature, but will become inaccessible at lower temperatures, as the dimers become pinned. Meanwhile, adsorption of NH_3 onto the down atoms found in the lowest-energy buckling configurations, is generally disfavoured compared to random adsorption elsewhere on the surface, and further disfavoured compared to the H-bonded configurations. The majority configuration will therefore depend upon the lifetime of any precursor state, and its ability to select the lowest-energy adsorption configurations. Above room temperature where the lifetime of the precursor state is short, a majority of the zigzag configuration is likely [50]. H-bonding correlations will be more significant at temperatures where the lifetime of the precursor state is long. Indeed, spectroscopy data suggests that the linear pattern should be even more favoured below room temperature than it is at room temperature. Nevertheless, where the buckling distortions are strong enough to pin dimers adjacent to an adsorbed NH_2, which will also occur at lower temperatures, zigzag configurations will become more prevalent. The effect of substrate temperature on the patterns of adsorption is therefore not easily predicted. It is likely that STM studies of different coverages at different temperatures below 300 K would be needed to answer this question. Moreover, studies of the effects of different fluxes have also not been carried out, although they make a significant

difference to the resulting structures for PH_3 case, as we will see below.

4. Comparison to PH3

Phosphine is the phosphorus analogue of ammonia, and so the chemistry might be expected to be similar. It is not the purpose of this review to give a detailed account of the decomposition of PH_3. Recently, a detailed STM and DFT investigation of the PH_3 has been conducted, with the aim of placing P dopant atoms into a Si(001) surface with atomic precision. More details can be found elsewhere [64, 36, 71, 39, 22, 72]. Readers are directed, not only to the original papers, but also to an upcoming review in this subject in this journal. Here I will give a brief overview of the differences between ammonia and phosphine behaviour, and try to draw some conclusions about the reasons for the differences.

A filled and empty state pair of STM images of a small dose of PH_3 on the Si(001) surface, along with detailed images of some important structures, is shown in figure 19. The initial stages of adsorption of PH_3 on the Si(001) surface are the same as NH_3; adsorption as an intact molecule, followed by dissociation to PH_2 and H, the asymmetric structure in figure 19, which is equivalent to the OD structure of ammonia. However, as can be seen in figure 19, there are many more, different, structures seen in the PH_3 case. These include the Centred structure, comprising a PH group inserted into a Si dimer, with the neighbouring Si dimer saturated with 2 H atoms, and the U-shaped features, comprising a P atom
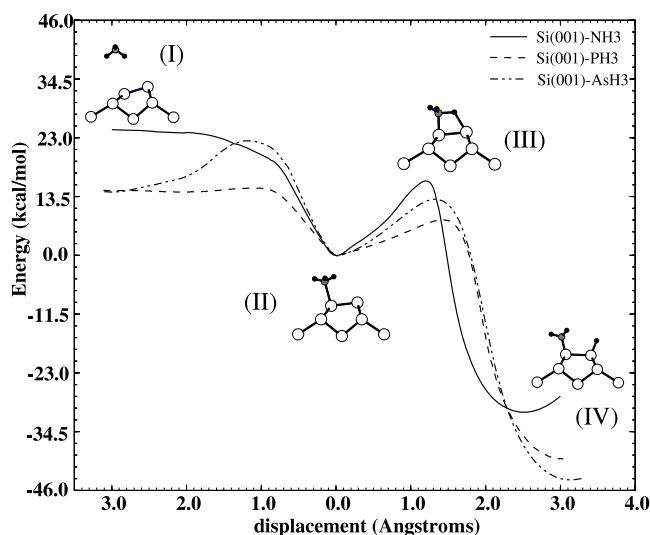
Figure 20. Comparative graph of adsorption and dissociation energies of PH$_3$, NH$_3$ and AsH$_3$. Energies are given in kcal mol^{-1}; the major points on the scale correspond to 0.5 eV steps. Reprinted with permission from Miotto *et al* [54], Copyright (2001), American Institute of Physics.

bridging two dimers, with 3 H atoms adsorbed close by. No such features are seen on the ammonia-exposed surface.

The barriers for the first dissociation step, shown above in table 1, are much smaller than for NH$_3$, at 0.54 eV and 0.76 eV for formation of the ID and OD structures respectively, (compared to 0.7–0.88 eV for ID and 0.76–1.04 eV for OD for NH$_3$), and thus dissociation will occur at correspondingly lower temperatures. Further decomposition to PH + 2H, forming the Centred feature, also occurs at temperatures as low as 200 K [22]. These figures [36] are in good qualitative agreement with an earlier comparison of the three Gr. V hydrides [54], as shown in figure 20, which has the NH$_3$ decomposition with the highest barrier of the three species (although the modelled barriers in that work are all much lower).

The major difference lies in the processes leading to complete dissociation of the molecules. For PH$_3$, the barrier to formation of PH + 2H, forming the Centred structure in figure 19 has been calculated to be around 1.23 eV, which appears too high to occur at room temperature, but from experiment, this barrier is not insuperable. Decomposition has been observed *in situ* [36], with an asymmetric structure (the OD structure) changing over a timescale of a few minutes into the PH + 2H centred structure. As can be seen from the range of values given for OD formation for NH$_3$, calculation of a barrier is very path-dependent and can give variable results, and in fact a more recent calculation by the same authors suggests that a better estimate of the barrier is approximately 0.99 eV [73]. The pathway from the OD to the PH + 2H structure involves the diffusion of the PH$_2$ from one dimer to the next. This is possible for PH$_2$; diffusion has been observed in STM. However, no evidence of diffusion of NH$_2$ groups has been found in low-coverage STM [34] at room temperature. Thus this pathway appears not to be available to NH$_3$ at room temperature. Secondly, the energy gain from

this process is much larger for PH$_3$ compared to NH$_3$ [71]. The likely underlying difference has been exposed as the Si–X bond length. Calculation of the Si–N, Si–P and Si–As bond lengths [71] has found bond lengths of 1.70, 2.36 and 2.38 Å. The dramatically shorter Si–N bond length will result in a much higher barrier for diffusion of NH$_2$ than for PH$_2$, and higher barriers for any process which involves stretching this bond. It will also affect the relative stability of the different XH$_x$ structures. The adsorption energy of NH$_3$ is much larger for example, 1.48 eV compared to 0.90 eV for PH$_3$, and the energy gain from OD to the PH + 2H Centred structure is only 0.27 eV for ammonia, compared to 0.9 eV for phosphine. Thus, PH$_3$ and AsH$_3$ may behave in a similar fashion, but will be different from NH$_3$. For studies of adsorption patterns, the relative simplicity of the ammonia system is a benefit, as it is possible to isolate the effect of different mechanisms, such as H-bonding, without the complication of multiple structures. Such studies are next to impossible to perform with PH$_3$, owing to the complexity of the surface processes. No studies of co-adsorption effects of PH$_3$ have been made, for example, so that the strength, or otherwise, of interactions such as H-bonding in this system is unknown.

5. Modelling: assumptions and limitations

Many of the modelling studies have been undertaken in an attempt to determine the dominant mechanism controlling adsorption patterns of ammonia. It is interesting therefore to look at some of the assumptions, implicit or otherwise, made by the modelling groups in their studies, which have in some cases led them to erroneous conclusions. The major assumption may in fact be that there *is* a dominant mechanism, as high-coverage STM data shows that the adsorption is close to random between 300 and 450 K.

The first assumption is to treat the surface as a molecule, and model the surface using a single Si dimer, and a few subsurface atoms. Such severe approximation of the surface is partly driven by the limitations on cluster sizes with some chemistry-orientated simulation codes, in which the computational time required scales prohibitively with the number of atoms. Owing to the longer-range effects such as charge transfer and dimer buckling, a minimum cluster size of at least 2–3 dimers would be required to model adsorption properly, and those calculations based upon 1-dimer clusters [44] are unlikely to have captured the chemistry of this system correctly. Indeed, the adsorption energy difference between a 1-dimer and a 3-dimer cluster is found to be around 0.3 eV [55, 37] for example. Similarly for periodic slab calculations, a 4-dimer cell would be preferable to a 2-dimer cell. A detailed comparison of different cluster and slab calculations has been made elsewhere [74], which suggests that neither slab nor cluster calculation is inherently better, and that corrections can be made to account for some of the differences between cell sizes.

Another assumption, which may also be related to computational limits, has been to block some degrees of freedom of relaxation of the structures. Many studies failed to find the best atomic positions to maximize H-bonding

interactions, leading them to conclude that they are not significant. For example, H-bonding between NH_3 and NH_2 was dismissed by Wang *et al* [38], but in their simulations neither the NH_3 nor NH_2 groups were allowed to rotate around their Si–N-bonds to maximize the attractive interaction. Also these authors, along with Cho *et al* [52] while looking at NH_2–NH_2 H-bonding, allowed the molecules to rotate, but did not allow each molecule to rotate independently, and therefore did not calculate their full strength. Only in very recent studies [35, 70, 69] have the independent rotation of each species been performed (this is a very soft mode, and relaxes slowly, so is expensive in computer time), leading to the conclusion that H-bonding is in fact remarkably strong, and outweighs other effects.

Finally, the major assumption made by some modellers is that of considering only the buckling isomer giving the lower energy (e.g. the UU OD configuration). As a result, only half the available Si atoms, i.e. those orientated down in the lowest-energy relaxed DFT structures (e.g. figures 11(b), (c) and 12(b), (d), (f)), can be adsorption sites. This is equivalent to considering adsorption of ammonia only below about 100 K, where the dimers do not flip. Examples of the results of this assumption can be found in figure 5 of Chung *et al* (2006) [40] and figure 4 of Kim *et al* (2009) [57], where none of the intermediate structures which could lead to the linear arrangement are shown. The justification given is that the low-coverage STM data [40, 67, 57] favours the zigzag arrangement, but this is not supported by other evidence, i.e. the saturation-coverage experimental data and other modelling [50, 35, 70, 69], and thus as a general rule, a modelling study should consider the precursors to the linear arrangement, if only to dismiss them. Furthermore, in any system on Si(001), consideration of both buckling isomers, even though they may have a slightly higher energy, is crucial in order to provide a complete picture of adsorption on a surface above 100 K, where the dimers are flipping, and all Si atoms will be available for adsorption at least some of the time. Moreover, in the particular case of the NH_3/Si(001) system, all of the favoured NH_3–NH_2 intermediate states shown in figures 11 and 12 occur with the NH_3 adsorbed on the nominal up atom in the lowest-energy isomer. The implicit assumption of a static surface in these papers misses much of the interesting surface chemistry by ignoring these important surface configurations, preventing a complete comparison to experimental studies at or around room temperature.

6. Conclusions

We have seen that the process of dissociation of ammonia has reached some consensus. There is a large barrier to the further decomposition of NH_2, which means that NH_2–H dimers are the dominant species on the surface below about 600 K. There is good agreement between experiments and modelling on the structures formed by dissociation of ammonia, i.e. the OD and ID structures. Despite its higher barrier to formation, and other kinetic data, which appears to favour ID formation, the OD is the majority structure in experiment. The reason for this remains unknown, but may lie in the preferred vibrational

modes of the Si(001) surface. On other points, however, there remains substantial disagreement. The appearance of these structures in STM has been disputed, but the weight of evidence from experiment and theory indicates that the NH_2 group should appear higher than the H atom in the OD structure. Similarly, there remains disagreement as to the dominant arrangement of NH_2 species on the surface. High-coverage STM shows an almost random distribution of NH_2 groups, and room temperature spectroscopy data indicate that the linear outweighs the zigzag arrangement by 2:1. However, low-coverage STM has concluded that the zigzag pattern is more common in the initial stages of deposition below about 0.1 ML. This discrepancy remains unresolved.

Modelling of possible interactions has found that there are charge-transfer effects on the buckling patterns of the dimers, which would favour the zigzag pattern, but overall the dominant process affecting the patterns of adsorption is hydrogen bonding, of which there are two types. There is good evidence for the existence of a physisorbed H-bonded precursor state with a range of about 10 Å, explaining the observed clustering of adsorbates. Furthermore, surface H-bonding between adsorbed NH_3 and NH_2 is very strong, probably due to cooperative charge transfer from the NH_3 to the NH_2 via the surface. Thus this 'direct' intermolecular interaction is in fact substrate-mediated (this point underlines the necessity for calculations to treat the surface properly as a semi-infinite block). These strong H-bonding effects are responsible for the observed linear adsorption patterns along the dimer rows and the strongly correlated adsorption between dimer rows observed experimentally.

It may be possible to influence the adsorption arrangements by varying either the substrate temperature or the flux. By finding conditions which maximize the effect of the H-bonding interactions, such as a lower substrate temperature, and a smaller flux of ammonia to discourage random adsorption, long linear chains of NH_2 groups (the longest seen thus far is 8 dimers) could be formed, and act as templates for the adsorption of molecules to form 1D atomic scale structures. Alternatively, by deposition at lower temperatures where the buckling distortions will pin the neighbouring dimers and block the formation of the linear features, a majority zigzag surface could be achieved. The effect of varying the flux has not been studied, but the differing conclusions of the low- and high-coverage STM data, where the fluxes used were quite different, and the flux-dependent behaviour of PH_3 suggests that more study is required in this area.

The dominant interaction may also be affected by modification of the molecule. The replacement of H atoms with methyl groups, forming the methylamines, changes the balance of charge transfer. In the CH_3NH–H dimer, the H atom is slightly buckled down, and the DD configuration is lower in energy than the UU configuration by 0.5 eV [75], promoting the growth of the linear arrangement. Dimethylamine may behave in a similar fashion, but the possibility of H-bonding will be removed, and steric effects may be significant. For trimethylamine, decomposition of the molecule is kinetically blocked, as the barrier for breaking the N–CH_3 bond is too high. This is then trapped in the molecular state, and a

zigzag pattern is enforced by steric repulsion, as well as by buckling effects. Taking advantage of this state, BF_3 has been adsorbed onto the up atom of trimethylamine-adsorbed dimers, an intriguing demonstration of control of the surface chemistry [9].

Comparison of the behaviour of NH_3 to PH_3 (and AsH_3), which might be expected to have similar behaviour, shows that NH_3 is unusual in having a much shorter Si–N than either Si–P or Si–As. As a result, diffusion of NH_2 groups has not been observed, contrary to observations of PH_2, which can diffuse along and sometimes across dimer rows. This difference is also likely to be the cause of the differing dissociation behaviour, as the pathway traced for PH_2 dissociation involves diffusion of the PH_2 to the neighbouring dimer. The adsorption of AsH_3 has been little studied, but it can be expected that it would behave in a similar way to PH_3.

In conclusion, I have surveyed the available literature on the ammonia/Si(001) system, and have found that hydrogen-bonding interactions play a dominant role in the co-adsorption processes, outweighing other effects. Moreover, owing to the selective adsorption on the down atom of the Si dimers, the possibility of forming the hydrogen-bonded intermediates is dependent upon dimer flipping, so that the appropriate bonding sites are available. As a result, those modelling studies which have not taken all the possible buckling arrangements into account have drawn the wrong conclusions about the dominant mechanism. Thus it is crucial to consider the dynamics of the Si(001) surface in studies of adsorption processes.

Acknowledgments

References

[1] Bozso F and Avouris P 1986 *Phys. Rev. Lett.* **57** 1185
[2] Avouris P, Bozso F and Hamers R J 1987 *J. Vac. Sci. Technol.* B **5** 1387
[3] Chadi D J 1979 *Phys. Rev. Lett.* **43** 43
[4] Wolkow R A 1992 *Phys. Rev. Lett.* **68** 2636
[5] Filler M A and Bent S F 2003 *Prog. Surf. Sci.* **73** 1
[6] Yoshinobu J 2004 *Prog. Surf. Sci.* **77** 37
[7] Chen D and Boland J J 2004 *Phys. Rev. Lett.* **92** 096103
[8] Radny M W, Smith P V, Reusch T C G, Warschkow O, Marks N A, Wilson H F, Schofield S R, Curson N J, McKenzie D R and Simmons M Y 2007 *Phys. Rev.* B **76** 155302
[9] Cao X and Hamers R J 2002 *J. Phys. Chem.* B **106** 1840
[10] Boland J J 1990 *Phys. Rev. Lett.* **65** 3325
[11] Hersam M C, Guisinger N P, Lyding J W, Thompson D S and Moore J S 2001 *Appl. Phys. Lett.* **78** 886
[12] Mayne A J, Avery A R, Knall J, Jones T S, Briggs G A D and Weinberg W H 1993 *Surf. Sci.* **284** 247
[13] Self K W, Pelzel R I, Owen J H G, Yan C and Weinberg W H 1998 *J. Vac. Sci. Technol.* A **16** 1031
[14] Nogami J 2000 *Surf. Rev. Lett.* **7** 555
[15] Takeuchi N 2001 *Phys. Rev.* B **63** 035311
[16] Bird C F, Fisher A J and Bowler D R 2003 *Phys. Rev.* B **68** 115318
[17] Okano S and Oshiyama A 2004 *Surf. Sci.* **554** 272
[18] Bowler D R and Goringe C M 1996 *Surf. Sci. Lett.* **360** L489
[19] Mo Y W, Kariotis, Swartzenruber B S, Webb M B and Lagally M G 1990 *J. Vac. Sci. Technol.* A **8** 201
[20] Wang J, Li M and Altman E I 2004 *Phys. Rev.* B **70** 233312
[21] Owen J H G, Miki K, Bowler D R, Goringe C M, Goldfarb I and Briggs G A D 1997 *Surf. Sci.* **394** 79
[22] Schofield S R, Curson N J, Warschkow O, Marks N A, Wilson H F, Simmons M Y, Smith P V, Radny M W, McKenzie D R and Clark R G 2006 *J. Phys. Chem.* B **110** 3173
[23] Hamers R J, Avouris P and Bozso F 1987 *Phys. Rev. Lett.* **59** 2071
[24] Hlil E K, Kubler L, Bischoff J L and Bolmont D 1987 *Phys. Rev.* B **35** 5913
[25] Bozso F and Avouris P 1988 *Phys. Rev.* B **38** 3937
[26] Takaoka T and Kusunoki I 1998 *Surf. Sci.* **412/413** 30
[27] Dresser M, Taylor P, Wallace R, Choyke W and Yates J T Jr 1989 *Surf. Sci.* **218** 75
[28] Fujisawa M, Taguchi Y, Kuwahara Y, Onchi M and Nishijima M 1989 *Phys. Rev.* B **39** 12918
[29] Bischoff J, Lutz F, Bolmont D and Kubler L 1991 *Surf. Sci.* **248** L240
[30] Hossain M Z, Yamashita Y, Mukai K and Yoshinobu J 2003 *Phys. Rev.* B **68** 235322
[31] Becke A D and Edgecombe K E 1990 *J. Chem. Phys.* **92** 5397
[32] Miotto R, Ferraz A C and Srivastava G P 1998 *Phys. Rev.* B **58** 7944
[33] Kim H J and Cho J H 2004 *Phys. Rev.* B **69** 233402
[34] Chung O N, Kim H, Chung S and Koo J Y 2006 *Phys. Rev.* B **73** 033303
[35] Bowler D R and Owen J H G 2007 *Phys. Rev.* B **75** 155310
[36] Warschkow O, Wilson H F, Marks N A, Schofield S R, Curson N J, Smith P V, Radny M W, McKenzie D R and Simmons M Y 2005 *Phys. Rev.* B **72** 125328
[37] Widjaja Y and Musgrave C B 2004 *J. Chem. Phys.* **120** 1555
[38] Wang Y and Hwang G S 2005 *J. Chem. Phys.* **122** 164706
[39] Schofield S R, Curson N J, Simmons M Y, Warschkow O, Marks N A, Wilson H F, McKenzie D R, Smith P V and Radny M W 2006 *e-J. Surf. Sci. Nanotechnol.* **4** 609
[40] Chung O N, Kim H, Koo J Y and Chung S 2006 *Phys. Rev.* B **74** 193312
[41] Bowler D R, Owen J H G, Goringe C M, Miki K and Briggs G A D 2000 *J. Phys.: Condens. Matter* **12** 7655
[42] Owen J H G, Bowler D R, Goringe C M, Miki K and Briggs G A D 1996 *Phys. Rev.* B **54** 14153
[43] Rignanese G M and Pasquarello A 2000 *Appl. Phys. Lett.* **76** 553
[44] Fattal E, Radeke M R, Reynold G and Carter E A 1997 *J. Phys. Chem.* B **101** 8658
[45] Franco N, Avila J, Davila M E, Asensio M C, Woodruff D P, Schaff O, Fernandez V, Schindler K-M, Fritzsche V and Bradshaw A M 1997 *Phys. Rev. Lett.* **79** 673
[46] Lee S H and Kang M H 1998 *Phys. Rev.* B **58** 4903
[47] Hossain M Z, Yamashita Y, Mukai K and Yoshinobu J 2003 *Phys. Rev.* B **67** 153307
[48] Lee J Y and Cho J H 2006 *J. Phys. Chem.* B **110** 18455
[49] Smedarchina Z K and Zgierski M Z 2003 *Int. J. Mol. Sci.* **4** 445
[50] Owen J H G, Bowler D R, Kusano S and Miki K 2005 *Phys. Rev.* B **72** 113304
[51] Hamers R J and Kohler U K 1990 *J. Vac. Sci. Technol.* A **7** 2854
[52] Cho J H and Kim K S 2000 *Phys. Rev.* B **62** 1607
[53] Loh Z H and Kang H C 2000 *J. Chem. Phys.* **112** 2444
[54] Miotto R, Srivastava G P, Miwa R H and Ferraz A C 2001 *J. Chem. Phys.* **114** 9549

[55] Widjaja Y, Mysinger M and Musgrave C B 2000 *J. Phys. Chem.* B **104** 2527

[56] Widjaja Y and Musgrave C B 2000 *Surf. Sci.* **469** 9

[57] Kim Y S, Koo J Y and Kim H 2009 *J. Phys.: Condens. Matter* **21** 064237

[58] Zgierski M Z and Smedarchina Z K 2003 *Europhys. Lett.* **63** 556

[59] Chung O N, Kim H, Koo J Y and Chung S 2008 *Surf. Sci. Lett.* **602** L69

[60] Koo J Y, Kim H, Chung O N and Chung S 2008 *Surf. Sci.* **602** 3763

[61] Owen J H G and Bowler D R 2008 *Surf. Sci.* **602** 3760

[62] Owen J H G, Bowler D R, Goringe C M, Miki K and Briggs G A D 1995 *Surf. Sci. Lett.* **341** L1042

[63] Schofield S R, Curson N J, O'Brien J L, Simmons M Y, Clark R G, Marks N A, Wilson H F, Brown G W and Hawley M E 2004 *Phys. Rev.* B **69** 085312

[64] Wilson H F, Warschkow O, Marks N A, Schofield S R, Curson N J, Smith P V, Radny M W, McKenzie D R and Simmons M Y 2004 *Phys. Rev. Lett.* **93** 226102

[65] Owen J H G and Bowler D R 2009 *Surf. Sci.* **603** 2902

[66] Ness H and Fisher A J 1997 *Phys. Rev.* B **55** 10081

[67] Kim Y S, Koo J Y and Kim H 2008 *Phys. Rev. Lett.* **100** 256105

[68] Queeney K T, Chabal Y J and Raghavachari K 2001 *Phys. Rev. Lett.* **86** 1046

[69] Mathieu C, Bai X, Bournel F, Gallet J J, Carniato S, Rochet F, Sirotti F, Silly M G, Chauvet C, Krizmancic D and Hennies F 2009 *Phys. Rev.* B **79** 205317

[70] Rodríguez-Reyes J C F and Teplyakov A V 2007 *Phys. Rev.* B **76** 075348

[71] McDonell T L, Marks N A, Warschkow O, Wilson H F, Smith P V and Radny M W 2005 *Phys. Rev.* B **72** 193307

[72] Wilson H F, Warschkow O, Marks N A, Curson N J, Schofield S R, Reusch T C G, Radny M W, Smith P V, McKenzie D R and Simmons M Y 2006 *Phys. Rev.* B **74** 195310

[73] Warschkow O 2009 private communication

[74] Warschkow O, McDonell T and Marks N 2007 *Surf. Sci.* **601** 3020

[75] Cho J H and Kleinman L 2003 *Phys. Rev.* B **67** R201301