Fundamental Role of the H-Bond Interaction in the Dissociation of NH_3 on Si(001)-(2 × 1)

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Further insight into the dissociative adsorption of NH_3 on Si(001) has been obtained using a combined computational and experimental approach. A novel route leading to the dissociation of the chemisorbed NH_3 is proposed, based on H-bonding interactions between the gas phase and the chemisorbed NH_3 molecules. Our model, complemented by synchrotron radiation photoelectron spectroscopy measurements, demonstrates that the low temperature dissociation of molecular chemisorbed NH_3 is driven by the continuous flux of ammonia molecules from the gas phase.

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The most recent advances in the use of Si in microelectronics, energy conversion, and gas sensing concern the preparation of selectively modified surfaces presenting new chemical reactivity compared to bare silicon that are capable of binding specific organic or metal-organic molecules for the fabrication of innovative molecular electronic and sensing devices [1–3]. In this respect, the modification of Si surfaces with N atoms or N-carrying ligands is an effective way to expand the Si chemical functionalities, thus providing the ability to graft specific molecules [3,4] or to obtain passivating barriers against unwanted chemical reactions, spanning from environmental contamination to oxygen diffusion [1].

Ammonia is the most common and most widely investigated donor of N atoms to Si surfaces. The interaction of NH_3 with the Si(001) surfaces has been the subject of numerous and extensive investigations which have elucidated most of the reactions leading to the formation of Si-N bonds [2,5–14]. Concerning the interaction of NH_3 with the bare Si(001)-(2 × 1) surface at around or below room temperature, it is well assessed that the molecule adsorbs by dissociative chemisorption, resulting in the NH_2 and H fragments bonded to two Si atoms belonging to the same or to neighboring dimers. This reaction, which is on the whole exothermic, consists of an initial adsorption of undissociated molecules and is characterized by an internal energy barrier against the dissociation, which might stabilize, to some extent, the chemisorbed NH_3 in a metastable configuration. Theoretical calculations have provided different estimations of this barrier spanning from values as low as 0.6 eV [15–17], which would correspond to a thermal activation in the range 218–252 K [15], to values of the order of 1 eV [14,18].

In order to overcome the barrier for NH_3 dissociation at low temperature, it is required that the internal energy of the ammonia molecule is spent for the dissociation rather than being released to the substrate phonons. Even in the most convenient case of a shallow potential well, at temperature of the order of 150 K it is conceivable that some undissociated NH_3 molecules stay steadily on the Si surface [10]. Indeed, intact NH_3 molecules have been observed at low temperature [9,10], but exclusively on Si surfaces exposed to a very low dose of ammonia. On the contrary, only NH_2 and H fragments are revealed on the Si(001)-(2 × 1) surface dosed at saturation, even at temperatures (≤ 90 K) that reduce the probability of desorption [5–7]. Being the unimolecular fragmentation of the chemisorbed NH_3 inhibited in this thermal regime, different dissociative routes, likely based on intermolecular cooperative effects, must be identified to explain the observed behavior. As matter of fact, whereas theoretical calculations [19] predict a role for the interaction between two adsorbed NH_3 in speeding-up the dissociation process, the importance of the interaction between adsorbed and gas phase NH_3 has never been recognized.

In order to explain the disappearance of the chemisorbed NH_3 molecules for coverages close to saturation, we performed energetics and structural density functional theory (DFT) calculations to study the two-body dissociation triggered by incoming NH_3 molecules from the gas phase. Furthermore, we used fast core-level spectroscopy with synchrotron radiation to identify the differently coordinated N atoms present on the Si surface and to follow their evolution while dosing NH_3. The combined computational and experimental approach allowed us to unambiguously reveal the occurrence of NH_3 molecular adsorption and to emphasize the role of the continuous ammonia flux in promoting the complete dissociation of NH_3 into the NH_2 and H fragments.

The silicon surface was simulated with a Si_9H_{12} cluster [18], where the silicon atoms were saturated by hydrogens in order to force them to have a tetrahedral coordination. Full geometrical optimizations were employed except for the Si-H distances kept at their equilibrium value of 1.49 Å. All the energy barriers were calculated as full geometry relaxed energy potential of the reaction coordinate. The NWCHEM [20] program was employed to simulate the structures and energetics of the molecular systems we have considered here. The DFT functional was built half Hartree-Fock and half Becke, three-parameter, Lee-Yang-Parr (B3LYP) [21] in order to better reproduce the core ionization of the N 1*s* core level; the core-hole chemical shifts were calculated in the framework of the equivalent core model [22]. The Pople 6-31+G* basis set was used for all calculations. The values of the barriers at the 6-31+G* geometries have been calculated also by using triple-zeta, correlation-consistent basis sets of Dunning and their augmented versions with added diffuse functions (cc-pvtz and aug-cc-pvtz), obtaining very similar results.

The experiment was performed in the ultrahigh vacuum experimental chamber of the SuperESCA beam line of Elettra (Trieste, Italy). The Si surface kept at 150 K was repeatedly flashed up to 1170 K until a clear (2 × 1) reconstruction was obtained. NH_3 was dosed by background exposure on the cold surface. The N 1*s* core-level spectra were acquired at photon energy of 450 eV, with an overall energy resolution of 100 meV.

Figure 1 shows the first step of the interaction of NH_3 with the Si(100)-(2 × 1) surface, i.e., the molecular chemisorption with the nitrogen atom bonded to the down atom of the silicon dimer. In this configuration, the N atom is tetra-coordinated, the Si-N bond is dative, and the charge of the lone pair electrons is polarized from the molecule to the substrate. The potential energy curve (PEC) relative to the migration of one hydrogen atom from the chemisorbed NH_3 molecule to the neighboring dangling bond (DB) is plotted as a function of the distance *R* between the N and the migrating H atom. We found that the dissociation is characterized by a barrier of 1.02 eV, in agreement with other calculations based on full treatments of electrons [14,18]. The lower values of about 0.6 eV reported in Refs. [15,17] can be ascribed to the use of pseudopotentials which are known to underestimate the activation energies [23]. Our results show that the final dissociative state is more stable than the chemisorbed state by about 1.0 eV. As mentioned before, the NH_3 molecules can use their internal energy to overcome the barrier. Conversely, if the energy is released to the substrate, at about 150 K, the chemisorbed molecule could only dissociate via a reaction process involving a lower energy barrier.

We have identified a possible route by investigating the stability of an isolated NH_3^c molecule chemisorbed on Si(001)-(2 × 1) that is reached by a second molecule coming from the gas phase NH_3^g. We have considered the formation of a H-bond between NH_3^c and the N atom of the incoming molecule, which produces the reaction intermediate (*B*) shown in the left panel of Fig. 2, whose dissociation energy is 0.43 eV. The NH_3^g molecule, while interacting with the silicon DB nearby, behaves as a hydrogen acceptor and draws the H atom from NH_3^c. The resulting ammonium ion NH_4^+ is bonded abridge between the amino group and the silicon DB and has a Mulliken total charge of +0.86.

The right panel of Fig. 2 shows that the system stabilizes by transferring the H atom from the NH_4^+ ion to the Si DB nearby. Indeed, the PEC as a function of the distance R_2 between the ammonium ion and the migrating H indicates

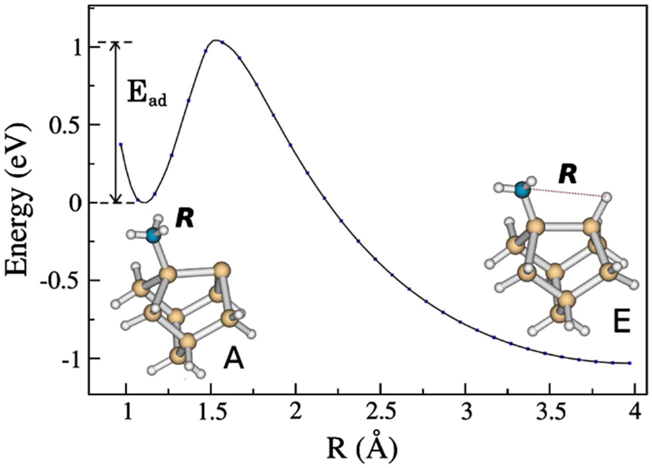

FIG. 1 (color online). Dissociative adsorption of the NH_3 on Si(001)-(2 × 1): H (white), Si (yellow/gray), and N (blue/dark gray). Potential energy curve along the reaction coordinate *R*, i.e., the distance between the nitrogen and the migrating hydrogen atom. E_{ad} indicates the adsorption energy.

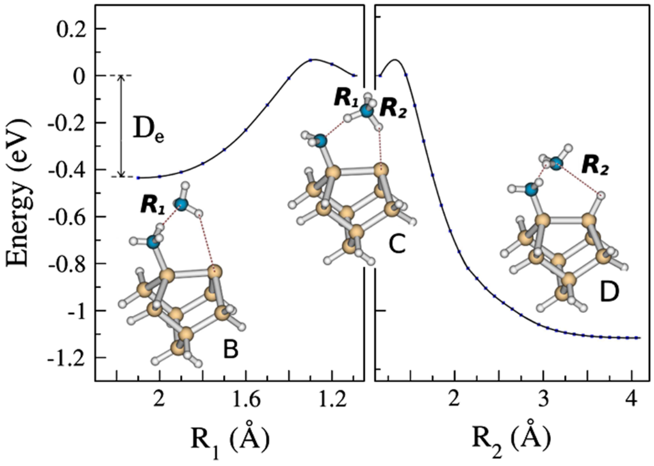

FIG. 2 (color online). Potential energy curves relative to the "H-bonding mediated" reaction, along the reaction coordinates R_1 and R_2, corresponding to the distances between the hydrogen of the chemisorbed NH_3^c and the nitrogen of the incoming NH_3^g molecule, and between the nitrogen of the ammonium ion and migrating hydrogen, respectively. D_e represents the energy required to dissociate the H-bond between NH_3^c and NH_3^g.

that the NH_4^+ dissociation turns out to be almost barrierless (0.016 eV), producing a very stable structure more than 1 eV below the intermediate energy state *C*. In this configuration, the initially chemisorbed NH_3^c molecule is dissociated into NH_2 and H while the NH_3^g molecule remains physisorbed being H-bonded both to the amino group and to the H atom. This H-bond mediated reaction path has an overall barrier of 0.50 eV, about half the activation energy calculated for the unimolecular dissociation. The whole energy balance including the energy of NH_3^g makes this process active even at temperatures as low as 150 K. The interaction with the gas phase molecules acts as a catalytic route for the dissociation of NH_3 and promotes even at low temperature the complete functionalization of the Si surface with NH_2 and H fragments.

For each configuration of the N atom in Figs. 1 and 2, we have calculated the binding energy (BE) shift of the N 1*s* core level, relative to the N 1*s* energy position of the chemisorbed NH_2 (see Fig. 3). The results show that BE shifts of +3.2 eV were found for the two configurations where the N atom is tetra-coordinated, that is in the chemisorbed NH_3^c (*A*) and in the NH_4^+ intermediate (*C*). The BE shift vanishes for the amino group (*C*, *D*), independently on the presence of the H-bonded NH_3^g or NH_4^+ species. On the contrary, the physisorbed NH_3^p in the configurations *B* and *D* correspond to significantly different BE values depending on the relocalization of the hydrogen atoms. Note that, since the migration of the H atoms can be estimated to occur within few tens of femtosecond [24], the configurations *B*, *C*, and *D* represent short living states that do not survive on the surface long enough to be recorded in x-ray photoelectron spectroscopy spectra.

The presence of chemisorbed NH_3^c molecules on the Si surface in the early adsorption stage and the occurrence of complete dissociation at increasing coverage were investigated by following the NH_3 adsorption on Si(001)-(2×1) at 150 K by fast N 1*s* core-level spectroscopy.

The whole sequence of spectra measured while exposing the Si surface to NH_3 up to a dose of 1.8 L ($1\ \mathrm{L} = 10^{-6}$ Torrs) is shown as a two-dimensional intensity plot in Fig. 4(a). Selected spectra together with their components are shown in Fig. 4(b). All the spectra were best fitted with Voigt functions to derive the component intensities reported in Fig. 4(c). The spectra acquired for a NH_3 dose up to 0.3 L show the presence of two components at 399.0 and 402.0 eV, respectively. The first one (N_d), whose BE is taken as a reference, is attributed to the chemisorbed amino group NH_2 [25]. The second component (N_c), that to our best knowledge has never been reported, shows a BE shift of +3.0 eV, close to the value of +3.2 eV calculated for the tetra-coordinated N atom and is assigned to NH_3^c molecules. As predicted by the theory, the Si-N bond is dative, the charge transfer occurs from the nitrogen to the silicon atoms: the higher the electronic charge depletion, the higher the BE. The component N_p at 400.6 eV appearing at NH_3 doses higher than 0.3 L is due to condensed NH_3 molecules. The N_d and N_c components have a similar intensity at about 0.2 L. With increasing coverage, N_d continues to rise reaching a saturation value at about 0.4 L, while the intensity of the N_c starts to decrease and the peak disappears completely above 0.4 L. Since at saturation, the NH_2 coverage is 0.5 monolayer (ML) [7], the maximal coverage of N_c can be estimated to be about 0.12 ML. Condensed NH_3 molecules start to pile up at the interface in concert with the saturation of N_d when all surface sites are occupied. The constant intensity of N_p above 0.5 L indicates an equilibrium coverage equivalent to 0.15 ML. These molecules can be easily desorbed by annealing above 200 K [26].

Our results show that below 0.15 L the number of dissociated ammonia molecules (N_d) is negligible. As discussed above, this is due to the low dissociation yield determined by the energetics of the system. In principle, even for gas phase molecules approaching the Si surface

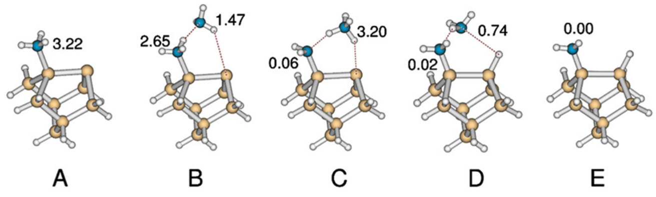

FIG. 3 (color online). H-bonding mediated dissociation process. The migration of the hydrogen atom from the chemisorbed ammonia molecule to the dangling bond of the same dimer, is favored by the presence of a H-bonded ammonia molecule. Each nitrogen atom is labeled with its N 1*s* binding energy shift (eV) relative to the structure E.

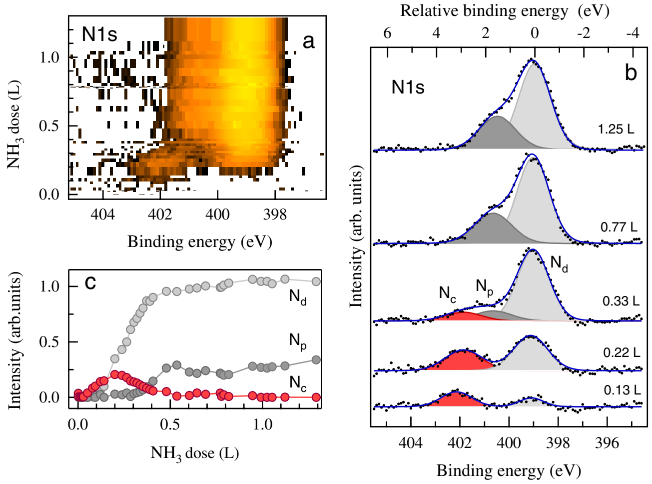

FIG. 4 (color online). NH_3 adsorption on the Si(100)-(2×1) surface. (a) Two-dimensional plot of the N 1*s* core-level spectra as a function of the NH_3 dose. (b) Selected N 1*s* spectra measured at different NH_3 doses. N_d, N_c, and N_p represent the chemisorbed NH_2 amino groups, the chemisorbed, and the physisorbed NH_3 molecules, respectively. (c) Intensity of the N_d, N_c, and N_p components as a function of the NH_3 dose.

($T = 300$ K) with a small kinetic energy (~ 27 meV), the direct dissociation should be possible because of the internal energy acquired during the adsorption ($E_{ad} = 1.05$ eV) to overcome the dissociation barrier (1.02 eV) (see Fig. 1). This process, however, can only occur if the internal energy is totally localized in a single internal degree of freedom of the molecule, possibly in one of the three N-H bonds. This is an unlikely event with respect to the more probable energy redistribution into the vibrational levels of the NH_3 and to the energy dissipation to the Si substrate. At 0.15 L the yield of the H-bonding mediated dissociation process is low because of the short time exposure to the ammonia flux and, due to this, the dissociated NH_2 fragments are less numerous than the intact NH_3 molecules on the Si surface. By increasing the NH_3 dose, the intensity of the N_d component equals and then overcomes that of N_c. On the other hand, Fig. 4(c) shows that at 150 K such undissociated NH_3 molecules are observed exclusively for ammonia doses lower than 0.4 L and cannot be observed on the surface dosed at saturation. This behavior can be rationalized considering the interaction mechanism between chemisorbed and gas phase molecules identified above. The evolution of the N_c peak with NH_3 dose results from the balance between the chemisorption rate and the two-body dissociation rate. With increasing coverage, the number of sites available for further NH_3^c molecules drops, while the interaction with gas phase NH_3^g dissociates those present on the surface. At late adsorption stage the rate of dissociation prevails and the surface is covered only by NH_2 and H fragments.

The attractive forces exerted in the formation of H-bonds between adsorbates and gas phase molecules have been ascertained in the case of NH_2 fragments and found responsible to drive the NH_3 physisorption, inducing clustering and zigzag features on the Si surface [12]. Similarly, in our case, the H-bond that forms between the lone pair of NH_3^g and the electron deficient H atom of the NH_3^c molecule forces the impinging molecule to have the optimal orientation to bind also with the close-by Si DB and transfer the H atom. It is worth considering that this reaction requires the DB close to NH_3^c be available for the H transfer, and in principle the lack of this site could stabilize the undissociated molecule even in the presence of a high flux of NH_3^g. Recent calculations have shown that NH_3 tends to chemisorb close to NH_2 moieties occupying the down atom of a neighboring free dimer [13]. This turns out to be true also for NH_2-H pairs in the interdimer or interrow configurations when they sit on two different dimers and leave two DBs available. Because NH_2 and H diffusion is inhibited at 150 K [14,27], this predicted scenario would imply that the DB next to the chemisorbed NH_3 is unoccupied and available to accept the migrating H atom.

In conclusion, we have unambiguously identified undissociated NH_3 molecules on the Si(001)-(2×1) surface at 150 K and have demonstrated that their number drops as the coverage increases. We propose the interaction with gas phase ammonia molecules to be responsible for the low temperature dissociation of NH_3 chemisorbed on Si. This route consists of a two-body H-bond mediated reaction which favors the migration of a H atom from the chemisorbed NH_3 to the neighboring Si DB. The reaction which is characterized by an energy barrier half that of unimolecular dissociative chemisorption, turns out to be a catalytic route for the complete ammonia dissociation at low temperature. By facing adsorbate-gas phase interactions, which are usually left out in the modeling of the ammonia dissociation on Si surface, we elucidate the microscopic aspect of the initial silicon nitridation.

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