

# DFT study of $\text{NH}_3$ dissociation on $\text{Si}(111)\text{-}7 \times 7$ . The role of intermolecular interactions

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Received 23 November 2006; accepted for publication 13 February 2007

Available online 20 February 2007

## Abstract

The adsorption of  $\text{NH}_3$  molecule on the  $\text{Si}(111)\text{-}7 \times 7$  surface modelled with a cluster has been studied using density functional theory (DFT). The results indicate the existence of a precursor state for the non-dissociative chemisorption. The active site for the molecular chemisorption is the adatom; while the  $\text{NH}_3$  molecule adsorbs on the Si restatom via this preadsorbed state, the adsorption on the Si adatom is produced practically without an energy barrier. The ammonia adsorption on the adatom induces an electron transfer from the dangling bond of this atom to the dangling bond of the adjacent Si restatom, hindering this site for the adsorption of a second  $\text{NH}_3$  incoming molecule. However, this second molecule links strongly by means of two H-bonds. The dissociative chemisorption process was studied considering one and two ammonia molecules. For the dissociation of a lonely  $\text{NH}_3$  molecule an energy barrier of  $\sim 0.3$  eV was calculated, yielding  $\text{NH}_2$  on the adatom and H on the restatom. When two molecules are adsorbed, the  $\text{NH}_3\text{-NH}_3$  interaction yields the weakening of a N–H bond of the ammonia molecule adsorbed closer the Si surface. As a consequence, the dissociation barrier practically disappears. Thus, the presence of a second  $\text{NH}_3$  molecule at the adatom–restatom pair of the  $\text{Si}(111)\text{-}7 \times 7$  surface makes the dissociative reaction self-assisted, the total adsorption process elapsing with a negligible activation barrier (less than 0.01 eV).

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**Keywords:**  $\text{NH}_3$ ;  $\text{Si}(111)\text{-}7 \times 7$ ; Silicon surface; DFT; Cluster model

## 1. Introduction

The study of  $\text{NH}_3$  interaction with Si surfaces is of technological interest for the development of silicon nitride films. Both the  $\text{Si}(001)$  and reconstructed  $\text{Si}(111)\text{-}7 \times 7$  surfaces have been considered [1–8]. The latter is particularly interesting because the silicon adatoms ( $\text{Si}_A$ ) and restatoms ( $\text{Si}_R$ ) presumably present different chemical reactivity due to their different local electronic structure [4,5].

Despite the large number of experimental studies devoted to the  $\text{NH}_3$  dissociation on  $\text{Si}(111)\text{-}7 \times 7$ , several issues remain controversial. While it was well established that  $\text{NH}_3$  adsorbs dissociatively on  $\text{Si}(111)\text{-}7 \times 7$  yielding  $\text{NH}_2$  and H even at 80 K [6,7], there is not consensus at the present about the role played by silicon  $\text{Si}_A$  and  $\text{Si}_R$  sites on ammonia dissociation.

In scanning tunneling microscopy studies it was observed that an earlier extinction of restatom dangling bonds (DB's) is produced upon  $\text{NH}_3$  adsorption, suggesting that the Si restatoms are more reactive than Si adatoms [4]. Recently,  $\text{NH}_2$  species was detected on Si restatoms by using N 1s scanned-energy mode photoelectron diffraction [8]. On the other hand, a synchrotron photoelectron spectroscopy study advocates adatoms as preferred active sites [5]. The amino  $\text{NH}_2$  group undergoes a further dissociation into NH and H. This process takes place at temperatures as

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low as 70 K. Moreover, an extra channel for  $\text{NH}_3$  dissociation was observed at low temperatures and high coverages, involving a  $\text{NH}_3$  precursor [7].

From the theoretical point of view, the  $\text{NH}_3$  chemisorption on  $\text{Si}(111)\text{-}7\times 7$  was investigated by means of a cluster model and a density functional theory (DFT) molecular orbital method [9]. In this approach it was shown that the dissociation of  $\text{NH}_3$  occurs readily on either  $\text{Si}_R$  or  $\text{Si}_A$ . Besides, these calculations reveal a significant charge transfer between the DB's of the  $\text{Si}_R\text{-Si}_A$  pair. Later, Kang [10] analyzed the same process in the framework of DFT representing the  $\text{Si}(111)\text{-}7\times 7$  surface by a periodic slab geometry with a  $\text{Si}(4\times 2)$  surface unit cell. This author found that the active sites for molecular adsorption are the adatoms. The restatoms appear to be repulsive towards  $\text{NH}_3$  molecule. From these results, the following picture can be deduced: an incoming  $\text{NH}_3$  molecule first adsorbs on  $\text{Si}_A$  and next dissociates into  $\text{NH}_2 + \text{H}$  through the interaction with an adjacent  $\text{Si}_R$ , thereby saturating the DB's of the  $\text{Si}_A\text{-Si}_R$  pair. This mechanism in conjunction with the 2-to-1 adatom–restatom population ratio of  $\text{Si}(111)\text{-}7\times 7$  surface leads to the early saturation of restatoms and the incomplete saturation of adatoms. In this way a plausible explanation is given to the experimental reaction behaviour of an earlier saturation of the Si restatom features upon  $\text{NH}_3$  adsorption [4].

In this paper, the reaction of  $\text{NH}_3$  with  $\text{Si}(111)\text{-}7\times 7$  surface is examined using DFT calculations and the cluster approach. The results are compared with previous DFT studies. Besides, the role played by a second  $\text{NH}_3$  molecule is also considered. Some aspects of the dissociation mechanism at low temperatures are re-interpreted in light of these new results.

## 2. Computational details

The molecular orbital calculations have been performed within the density functional theory (DFT) using the hybrid B3LYP exchange–correlation functional [11] as implemented in the software package Gaussian03 [12].

The  $\text{Si}(111)\text{-}7\times 7$  surfaces was represented using a  $\text{Si}_{22}\text{H}_{22}$  cluster (Fig. 1a). The terminal silicon atoms were saturated with hydrogens in order to eliminate spurious effects due to the dangling bonds. It corresponds to a silicon aggregate extracted from the real unit cell [13], in the faulted region nearby the hole. The adsorbed  $\text{NH}_3$  molecule was fully optimized. At the surface the coordinates of Si adatom and restatom on which adsorption takes place were relaxed, while the rest of the geometric structure was kept fixed following the coordinates reported by Tong et al. [13]. The N and H atomic orbitals were described with the all-electron 6–31 G\*\* basis set. For Si, the 6–31 G basis was used and polarization functions were added to Si rest- and adatoms.

The adsorption energies ( $E_{\text{ads}}$ ) were calculated as the difference between the energy for the  $\text{NH}_3/\text{Si}_{22}\text{H}_{22}$  system and the sum of energies for the separated fragments ( $\text{NH}_3 + \text{Si}_{22}\text{H}_{22}$ ), being the isolated Si cluster and the ammonia molecule at the electronic configuration of lowest energy. The evolution of  $E_{\text{ads}}$  was followed as a function of specific defined reaction coordinates. The character of  $E_{\text{ads}}$  maxima was analyzed by looking at the number of imaginary frequencies.

## 3. Results and discussion

First, the electronic configuration of clean  $\text{Si}(111)\text{-}7\times 7$  surface was investigated. For that, the singlet and triplet states were considered. The triplet state turns out to be more stable in 0.55 eV than the singlet. In the former case, the spin population employing the Mülliken population analysis gives  $\sim 0.54$  spin and  $\sim 0.89$  spin for silicon  $\text{Si}_A$  and  $\text{Si}_R$  atoms, respectively. Thus, these results favor the picture that the adatom–restatom pair could be best regarded as a di-radical pair where the two unpaired electrons are localized on  $\text{Si}_A$  (mainly) and  $\text{Si}_R$  dangling bonds [14,15]. The HOMO localizes mainly on silicon  $\text{Si}_A$  while the HOMO-1, which is 0.49 eV lower in energy, does on silicon  $\text{Si}_R$ . All these observations are in agreement with experiments. Indeed, it is known that adatom and restatom

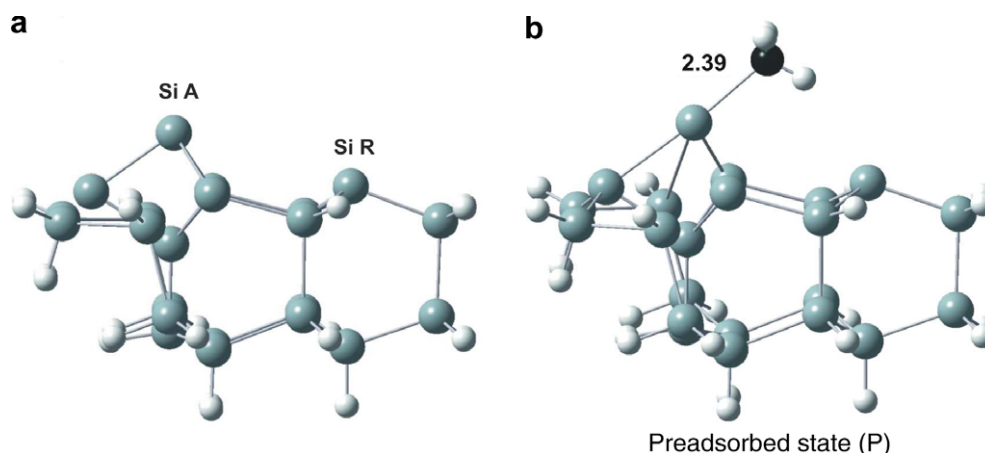


Fig. 1. (a) Side view of the  $\text{Si}_{22}\text{H}_{22}$  cluster model.  $\text{Si}_A$  is the adatom, and  $\text{Si}_R$  is the restatom. (b) Optimized geometry for the “preadsorbed state” of  $\text{NH}_3$ .

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