

## Mechanism of Ammonia Molecules Protonation on the Naturally Oxidized Silicon Surface

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The protonation of a single ammonia molecule in the presence of several (1-5) water molecules on the surface of the hydroxylated  $\beta$ -cristobalite surface was studied by means of density functional method with the potential B3LYP using 6-311 ++ g (d, p) basis set in the cluster approximation. The important role of surface OH-groups and H<sub>2</sub>O molecules in this process is shown. The energy required for the ammonia molecule protonation decreases with the number of adsorbed H<sub>2</sub>O molecules in the vicinity of this molecule, and the protonation becomes energetically favorable when the adsorbed water molecules form more than one layer. The phenomenon of Si natural surface charging in wet ammonia vapors can also be explained by protonation of NH<sub>3</sub> molecules.

**Keywords:** Quantum chemical calculations, Adsorption, Protonation, Ammonia, Water, Silicon, Silicon oxide.

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### 1. INTRODUCTION

Adsorption of molecules on the hydroxylated (covered with OH-groups) silicon dioxide surface plays an important role in catalysis, chromatography and work of chemical sensors, biosensors, etc. When developing gas sensors based on mesoporous silicon [1], silicon nanowires [2] and *p-n* junctions [3], authors deal with adsorption processes on the SiO<sub>2</sub> surface which always appear when silicon comes into contact with the ambient air. Adsorption processes are studied with the aid of test objects which are, customarily, NH<sub>3</sub> (donor) and NO<sub>2</sub> (acceptor) molecules. Donor properties of NH<sub>3</sub> molecules on the surface of crystalline Si [3] and mesoporous silicon [4] appear in the presence of water vapor in the ambient atmosphere. The mechanism of simultaneous interaction between NH<sub>3</sub> and H<sub>2</sub>O molecules with the silicon surface coated with a layer of its own oxide has been insufficiently studied. Modelling of H<sub>2</sub>O molecule adsorption on SiO<sub>2</sub> surface carried out in the works [5-12]. Adsorption parameters of NH<sub>3</sub> molecules on SiO<sub>2</sub> surface were computed in the works [5, 10, 12, 13]. Protonation of ammonia (transformation of an NH<sub>3</sub> molecule to NH<sub>4</sub><sup>+</sup> ion by adding a proton) in its water solution was considered in computation papers [14-17]. It is only in paper [17] the ammonia protonation was modelled in the presence of water molecules on SiO<sub>2</sub> surface. In this paper the model surface had just one silanol ( $\equiv$ Si-OH) group, therefore the model adequacy is open to question.

The presented paper deals with modelling the ammonia protonation process on the hydroxylated SiO<sub>2</sub> surface in the presence of water molecules as the first stage of the mechanism for acquiring *n*-type conductivity in silicon structures at adsorption of NH<sub>3</sub> molecules. The main task of modelling was to establish a possibility in principle and the required and sufficient conditions for protonation of the adsorbed ammonia molecule on the hydroxylated SiO<sub>2</sub> surface in the presence of water molecules.

### 2. OBJECTS AND DETAILS OF COMPUTATIONS

Surface properties of all silicon dioxide modifications depend, primarily, on the presence and density of hydroxyl groups. It was shown in [12] that when hydroxyl groups are located very closely (like in  $\alpha$ -quartz), the neighbouring OH-groups may form infinite chain links between them. Such links determine relatively weak adsorption (hydrophilic) properties. Other SiO<sub>2</sub> modifications, such as cristobalite or tridymite, are characteristic of less dense location of the surface OH-groups and weaker hydrogen link between themselves. That is why they exhibit greater adsorption capacity, in particular, more pronounced hydrophilic properties (e.g., a water molecule adsorbed on them may have a tri-coordinated link with OH-groups). It is also known [18, 19] that  $\beta$ -cristobalite presents the most adequate model of mesoporous SiO<sub>2</sub> or of silicon surface after natural oxidizing. They have similar local structure and close values of density and refraction index. It is due to these properties that the completely hydroxylated plane (111) of  $\beta$ -cristobalite was selected as the object of modelling. This plane is ended with silanol groups  $\equiv$ Si-OH, same as the natural oxide layer on silicon surface [20], while the plane (100) is ended with twin groups  $=$ Si(OH)<sub>2</sub>.

Modelling was based on cluster approximation because the cluster model quite well describes crystalline compound with a high degree of ionic bond, which is SiO<sub>2</sub>. Other quantum-chemical methods, for instance, those that use periodic boundary conditions or plane waves are unsuitable for computing charged structures. The basis of the model is a double-layered cluster Si<sub>74</sub>O<sub>133</sub>H<sub>66</sub> of twelve hexagonal cells in each layer, see Fig. 1. The broken Si atomic bonds on the upper plane of the cluster were saturated with OH-groups while on the lower and side planes – with H atoms. When modelling, first the cluster geometry with hydrogen atoms on all planes was optimized. Then the H atoms on the upper plane were substituted with OH-groups and their

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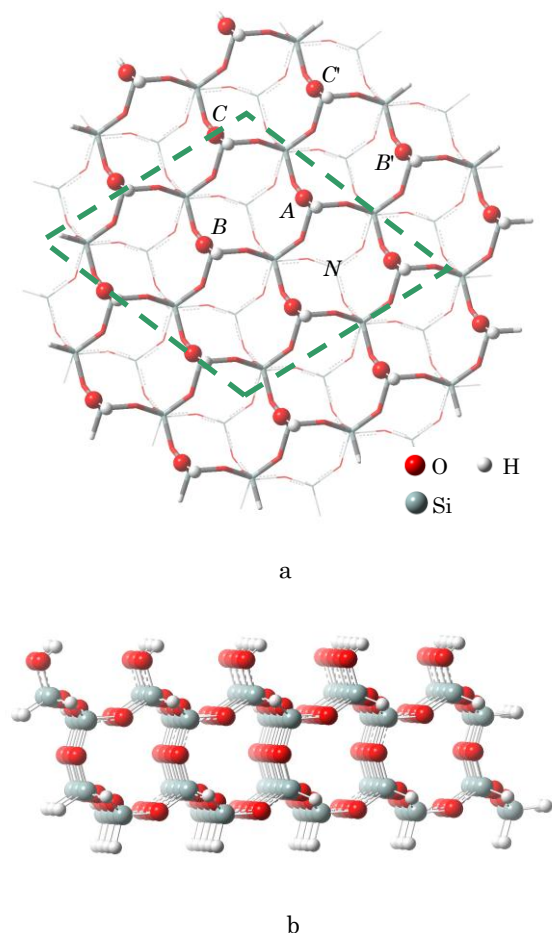


Fig. 1 – Model cluster: top view (a), side view (b)

positions on the position in the other faces were frozen. Without such fixation of H atom positions the cluster bent because of attraction between OH groups. Said fixation of H atoms did not, practically, influenced the computed results as the modelled adsorbed molecules of ammonia and water were located far from the frozen H atoms. When modelling, the structures with one adsorbed  $\text{NH}_3$  molecule and several (1-5) water molecules in various positions were analyzed. This made it possible to determine the most energetically favorable way sequential adsorption of molecules of water and ammonia. Also, the appropriate configurations with an ion pair of protonated ammonia  $\text{NH}_4^+$  and the group  $\equiv\text{Si}-\text{O}^-$  as well as the corresponding transition states were modelled. This allowed us to find the energy of the ion pair formation and the corresponding height of the barrier in the presence of different number of water molecules, and establish the configuration of the minimum energy model cluster and the minimum protonation energy.

Computation was made in Firefly software environment (version 8.0.1) [21, 22] using the density func-

tional method with B3LYP exchange-correlation functional. For hydroxyl groups of the upper surface and the adsorbed molecules was selected the basis 6-311++g(d, p) with diffuse functions, which are important when modelling weak bonds that are formed at adsorption. To save machine time, other atoms were modelled in 6-31g(d, p) basis. The computation proved that the cluster volume geometry does not, practically, changes when modelling with using the two basis sets. In the cyclic process of the self-consistent field method the iteration procedure was stopped when the energy difference between two sequential cycles was smaller than  $10^{-8}$  Hartree. Convergence of geometry optimization was tested at root-mean-square (rms) and maximum values of the energy gradient (force) and estimated nuclear displacement. Selected convergence criteria were stiffer than the default values and equalled 0.000015 and 0.000003 Hartree/Bohr for the rms and maximum force accordingly, as well as for the rms and maximum displacements of 0.0001 and 0.0018 Bohr accordingly. Such an approach enabled to determine the potential energy minimum more accurately: the difference between the energy values at two last step of optimizations was less than  $10^{-6}$  Hartree.

### 3. RESULTS AND DISCUSSION

At the first stage of work the geometrical parameters of the optimized cluster and the heat adsorption values of water and ammonia molecules were computed in order to test the model adequacy. Table 1 presents the basic computed geometric parameters of the  $\beta$ -cristobalite model cluster compared with appropriate parameters obtained by other authors of the computing and experimental studies. This shows that the selected model cluster and the basis set yield the values of bond lengths and appropriate angles that are very close to the experimental and computing results achieved in works [11, 12, 23].

The computed values of the heat of water molecule adsorption for the sequential adsorption of three molecules located in three neighbouring cells were practically identical and are, respectively, 74.0, 73.0 and 72.7 kJ/mole. This data practically converge with the value of 73 kJ/mole that was computed for the same coating in [12]: one molecule per a cell of  $\beta$ -cristobalite ( $2.2 \text{ molecule/nm}^2$ ). The heat of adsorption of 39 kJ/mole corresponds to the molecules located in the other coating layer that have double bonds. The obtained results qualitatively conform with the experimental data [24]: the measured water molecule heat of adsorption values were decreasing from 90 to 40 kJ/mole with the increase of the coating ratio from 0.5 to 3 molecule/ $\text{nm}^2$ . The computed heat of adsorption of one ammonia molecule equalling 68.5 kJ/mole is even in better agreement with the experimental value of 65 kJ/mole [12] than the result obtained by authors of [11] – 75 kJ/mole.

Table 1 – Main structural parameters of  $\beta$ -cristobalite

Parameters	Experiment [23]	Computation [11]	Computation [12]	This paper
Distance Si-O, Å	1.611	1.612	1.64	1.62
Angle O-Si-O, deg.	107.8-112.8	109.4-110.2	108.7-111.2	108.5-109.2
Angle Si-O-Si, deg.	146.6	150.9-178.5	152.3-154.7	146.4-147.5

The next stage was to find such a configuration of the adsorbed water and ammonia molecules that the energy of the system with  $\text{NH}_4^+$  ion was less than the energy of the corresponding system with non-protonated ammonia. In doing so, the number of adsorbed water molecules should be minimal, and they should form the minimum number of adsorbed layers. When searching for the described configuration, we took guidance of the following considerations that have been confirmed by intermediate computations:

1. Stable conditions where positive ion  $\text{NH}_4^+$  and negative ion  $\text{OH}^-$  formed out of the water molecule exist are impossible. Weak hydrogen bonds of  $\text{OH}^-$  ion with its environment may not prevent its movement towards  $\text{NH}_4^+$  and formation of neutral  $\text{H}_2\text{O}$  i  $\text{NH}_3$  molecules (at modelling no such stable states were detected).

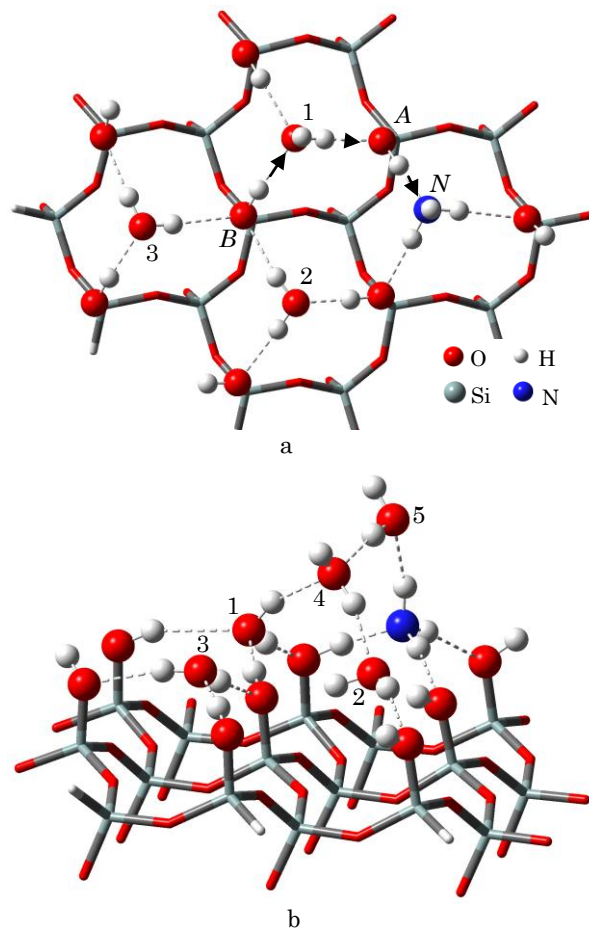
2. Steady states with ion pairs are possible only in case when the negative ion  $\equiv\text{Si}-\text{O}^-$  is formed from a rigidly fixed silanol group which proton separation energy is less than the water molecule separation energy.

3. Stable ion pair  $(\text{NH}_4^+) + (\equiv\text{Si}-\text{O}^-)$  may be formed only with a participation of the silanol group that is located in the hexagonal cell of  $\beta$ -cristobalite which is adjacent to the cell whereon the ammonia molecule was adsorbed (but not in the same cell).

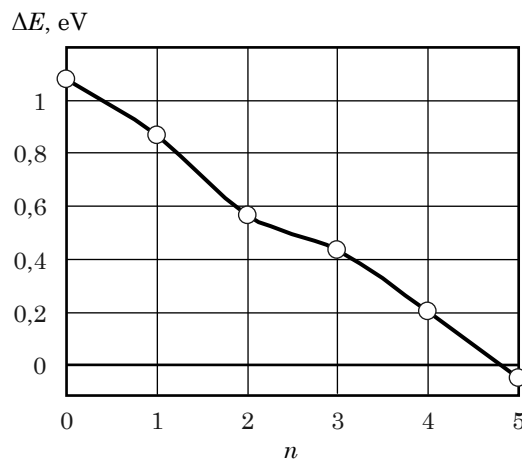
4. Most of the adsorbed water molecules should be located between ions  $\text{NH}_4^+$  and  $\equiv\text{Si}-\text{O}^-$ . These molecules reduce the electrical field between ions, and one of them participates in protonation.

At modelling an ammonia molecule was placed in cell  $N$  (Fig. 1). This molecule has hydrogen bonds with three OH-groups of cell  $N$ . The nitrogen atom of this molecule participates in the hydrogen bond with  $A$  OH-group only. Therefore, the only possible first step protonation of  $\text{NH}_3$  molecules have proton transition from that group. The computation showed that the so formed ion pair  $(\text{NH}_4^+) + (\equiv\text{Si}-\text{O}^-)$  is unstable. Stable pairs can form only with a participation of one of the OH-groups  $B$  and  $C$  (or  $B'$  and  $C'$  that are symmetrical to them). The difference between the energy of stable ion pairs with a participation of  $B$  and  $C$  groups and the energy of the neutral configuration (protonation energy)  $\Delta E = E_i - E_0$  amounts to 1.08 and 1.33 eV, accordingly. That is why in further computations we considered protonation with the participation of OH-group  $B$  only. Distance between H atom of group  $B$  and O atom of group  $A$  is  $\sim 4 \text{ \AA}$ , therefore a possibility of the direct transition of a proton between these groups is small. Water molecule 1 shown in Fig. 2 may serve as an intermediate link in this transition. Proton transition is accomplished as it is shown by arrows: an ammonia molecule (with  $N$  atom) attracts a proton of the closest OH-group  $A$  accompanied with a formation of ion  $\text{NH}_4^+$ ; this group is added with a proton of water molecule 1 which, in its turn, is receives a proton from OH-group  $B$  of the adjacent cell and ion  $\equiv\text{Si}-\text{O}^-$  is formed. In this case the protonation energy is 0.87 eV. When adding water molecules 2 and 3 near the OH- group  $B$ , the protonation energy decreases as shown in Fig. 3. The reason for this is that the electrical field between ions

is reduced due to polarization of these molecules. Addition of molecules 4 and 5 in the second adsorption layer, as shown in Fig. 2b, leads to a further reduction of  $\Delta E$  value until it reaches -0.05 eV when protonation becomes energetically favorable. At this condition the barrier of protonation is 0.35 eV.  $\text{H}_2\text{O}$  molecules added to other cells that are adjacent to the adsorbed molecule  $\text{NH}_3$  reduce  $\Delta E$  insignificantly (by hundredths of eV).



**Fig. 2** – A model cluster fragment shown with dotted line in Fig. 1: with three adsorbed water and ammonia molecules (a), and with five adsorbed water and ammonia molecules (b)



**Рис. 3** – Залежність енергії протонування аміаку  $\Delta E$  від кількості адсорбованих молекул води  $n$

We point out that water molecule 5 that is adsorbed above the ammonia molecule reduces  $\Delta E$  significantly (by  $\sim 0.25$  eV). This effect was observed for other test configurations as well: presence of H<sub>2</sub>O molecule above NH<sub>3</sub> was the decisive factor. Hence, for the protonation to be effective, it is necessary that water molecules are located in the other adsorbed layer as well, i.e., the coating density should be greater than 1 molecule per a cell of  $\beta$ -cristobalite or 2.2 molecules/nm<sup>2</sup>, which correlates with the water vapour pressure of  $\sim 60$  Pa [24].

#### 4. CONCLUSIONS

Protonation of ammonia may occur on the surface of the hydroxylated  $\beta$ -cristobalite (or on the surface of the naturally oxidized silicon) in the presence of water molecules. The role of surface OH-groups and water molecules in the ammonia protonation process may be explained as follows: surface hydroxyl groups are, firstly, peculiar “hooks” which effectively fix positive ions NH<sub>4</sub><sup>+</sup> (by triple hydrogen bonds), and, secondly, they may give out the proton more effectively than water molecules. Water molecules serve, firstly, as a “transfer link” in the transfer of protons from silanol groups to an ammonia molecule, and, secondly, they screen the

electrical field between the ion pair and reduce the energy of the pair. Protonation of ammonia becomes energetically favorable when water molecules form more than one surface layer – one H<sub>2</sub>O molecule should necessarily be located above the ammonia molecule.

The above described mechanism of protonation of ammonia on the hydroxylated surface of  $\beta$ -cristobalite may play an important role in other physical processes which are a subject for interpretation in academic literature. They are, for instance, protonation of organic molecules that have amino end-groups on the surface of the naturally oxidized silicon, and the process of laser desorption-ionization of N-terminal amino acids that was described in [25]. The authors indicate that this process may take place in the presence of water molecules only.

Model computations also explain the process of charging the naturally oxidized silicon surface and formation of the near surface area which has the  $n$ -type conductivity when wet ammonia is adsorbed. The formed ion pairs with their local electric field increases energy levels closest to the surface defects. This defect may give the electron in the conduction band, and positively charged. The next paper will be devoted to a detailed analysis of this process.

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