

## Structure and Charge States of the Selected Hydrogenated Silicon Clusters Si<sub>2</sub>-Si<sub>8</sub> by Non-Conventional Tight-Binding Method

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Structures of Si<sub>n</sub>H<sub>m</sub> clusters in neutral, positive and double positive charge states have been calculated by nonconventional tight-binding method and molecular dynamics. An influence of the charge state and the termination by hydrogen of dangling bonds on cluster structures those are obtained as a result of chemical vapor precipitation in silane, is considered for the first time. Fully hydrogenated clusters have tetrahedral branched structures. Other isomers have forms of closed circles.

**Keywords:** Nanosilicon, Tight-binding method, Charged silicon clusters, Hydrogenated nanoparticles.

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### 1. INTRODUCTION

Recently small hydrogenized silicon clusters used to produce thin films in process of the chemical vapor deposition have being interested both practically and theoretically [1-4].

Computer simulation of ground states of small pure [5-9] and hydrogenated [10-12] silicon clusters were studied in many works. Many of these results were confirmed by high-resolution ion mobility measurements [13-14], absorption spectroscopy [15], ion mass spectrometry and light scattering [16]. Several models on charged clusters were supposed recently [17]. Application of genetic algorithms to hydrogenated silicon clusters was performed in [18]. Study of anions and neutrals in low-pressure silane plasmas was carried out in [19]. In [20] supposed three types of stable compact structures of hydrogenated silicon clusters Si<sub>6</sub>H<sub>x</sub> (where  $x = 1, 7, 13$ ) grown from silane gas.

Disilane Si<sub>2</sub>H<sub>6</sub> molecule is most studied intensively [21-24]. Non classical bridged structures of the hydrogen atom bonded with two silicon atoms had been first predicted [22, 23] and have subsequently found out in spectra of high resolution [24]. It has shown [25] by method of the photoelectron spectroscopy and ab-initio calculations of the silicon (Si<sub>n</sub>H)<sup>-</sup> ( $n = 2-4$ ) monohydrids that H atom in Si<sub>4</sub>H and Si<sub>4</sub>H<sup>-</sup> binded with only one silicon atom, while bridged hydrogen structures realize in smaller clusters [26]. Detail understanding of their formation in atomistic level especially from silane is important for producing nanosized silicon structures suitable for creation of the microelectronic devices. This can take place through breaking of the Si-H bond and distribution of the hydrogen on silicon grid with forming different configurations of H. The detail modeling of the hydrogenized silicon nanoparticles is a way to understanding of the fundamental properties of the nanosilicon formation process.

Thermochemical properties (enthalpy, entropy, thermal capacity) of the hydrogenised silicon clusters synthesized in the laboratory of chemical engineering at Buffalo [27] have been calculated using ab-initio methods [28]. These are 135 radicals of the silane homological row formed in the process of the chemical vapor deposition using silane (SiH<sub>4</sub>) gas. We use Non-

conventional Tight-Binding Method (NTBM) combined with molecular dynamics (MD) [29] to study a stability of the silicon clusters in different charge states. Particular attention is paid to low-symmetry particles and irregular forms, which can be observed experimentally.

### 2. COMPUTATIONAL DETAILS

NTBM provides the interatomic potential. The equilibrium geometry of clusters was optimized by MD. A total energy functional expression in NTBM is different in form from commonly used TB energy functional and is written as [30]

$$E_{tot} = \sum_{\mu} \sum_{\nu > \mu} \frac{Z_{\mu}^{scr} Z_{\nu}^{scr}}{R_{\mu\nu}} + \sum_{\mu} \sum_{\nu > \mu} \frac{Q_{\mu} Q_{\nu}}{R_{\mu\nu}} + \sum_{\mu} \sum_{\nu > \mu} \sum_i \sum_j P_{\mu i, \nu j} H_{\mu i, \nu j} + \sum_{\mu} (E_{\mu} - E_{\mu}^0) \quad (1)$$

where

$$Z_{\mu}^{scr} = Z_{\mu}^{scr}(R_{\mu\nu}, \{N_{\mu i}^0\}) = Z_{\mu} - \sum_i N_{\mu i}^0 [1 - \alpha_{\mu i} \exp(-\alpha_{\mu i} R_{\mu\nu} / R_{\mu i}^0)] \quad (2)$$

$$Q_{\mu} = Z_{\mu}^{scr}(R_{\mu\nu}, \{N_{\mu i}^0\}) - Z_{\mu}^{scr}(R_{\mu\nu}, \{N_{\mu i}\}) \quad (3)$$

are screened nuclear and nonpoint ionic charges, respectively;  $Z_{\mu}$  is the charge of the  $\mu^{\text{th}}$  nucleus plus core electrons;  $R_{\mu\nu}$  is the internuclear distance;  $R_{\mu}^0 = n_{\mu i} / \zeta_{\mu i}^0$  is the most probable distance between the  $i^{\text{th}}$  electron and the corresponding  $\mu^{\text{th}}$  nucleus,  $n_{\mu i}$  and  $\zeta_{\mu i}^0$  are the principal quantum number and Slater exponent of  $i^{\text{th}}$  atomic orbital (AO) centered at the  $\mu^{\text{th}}$  nucleus;  $E_{\mu}^0$  and  $E_{\mu}$  are the total energies of individual atoms in non-interacting and interacting systems characterized by sets of occupancy numbers  $\{N_{\mu i}^0 \equiv P_{\mu i, \mu i}^0\}$  and  $\{N_{\mu i} \equiv P_{\mu i, \mu i}\}$  and energies  $\{E_{\mu i}^0\}$  and  $\{E_{\mu i}\}$  of valence AOs, respectively;  $\alpha$  and  $a$  are fitting param-

ters.  $Q_\mu$ ,  $P_{\mu,vj}$  and  $H_{\mu,vj}$  are the non-point charge of the atoms, bond order matrix, and Hamiltonian matrix, respectively.

A secular equation  $\sum_{vj}(H_{\mu,vj} - \varepsilon\delta_{\mu,vj})C_{vj} = 0$  is solved self-consistently to obtain electronic spectra  $\{\varepsilon_k\}$  and AO expansion coefficients  $\{C_{vj}(k)\}$  of the molecular orbitals (MO) of the system. AOs are defined such that they are orthogonal.

NTB uses a new definition of the repulsive energy term with simple physical content; it is the sum of the repulsion energy between nuclei and half of the attraction energy of electrons to "foreign" nuclei. In NTB, this term (the first term in (1) in the non-self-consistent calculation case), unlike that in traditional TB, does not contain the complex interatomic electron-electron interaction energy even implicitly, and thus can be represented more reliably by short-range pairwise functions of interatomic distances. Moreover, accurate and detailed parameterization of ionization and promotion energies of atoms and ions is one of the principal differences of NTB from traditional TB models, enabling one to account adequately for the majority of correlation effects in multiatomic systems as well. AO energies, depending on the charge and excited states of atoms were parameterized with six parameters fit to the electron transition energies between high-spin states of the silicon atom and ion. Repulsive and ion-ionic parts include 4 parameters. NTBM matrix elements include 16 parameters, 4 parameters for each type of matrix element (ss, sp, pp- $\sigma$ , pp- $\pi$ ). All 20 parameters have been fitted to the following data on small silicon  $\text{Si}_n$  clusters where  $2 \leq n \leq 7$  [31]: 1) experimental bond lengths [32], bond energy, frequency, adiabatic ionization potential (IP) [33] and electron affinity (EA) [34] of  $\text{Si}_2$ , bond lengths of the  $\text{Si}_2^+$  cation and  $\text{Si}_2^-$  anion calculated by the MP2(full)/6-311G(3df, 2p) method (2.258 Å and 2.118 Å respectively); 2) experimental cohesion energies [35] of  $\text{Si}_n$  where  $3 \leq n \leq 7$ , excepting  $\text{Si}_5$  for which the G2 theoretical result was accepted [36]; 3) geometry of  $\text{Si}_n$  where  $3 \leq n \leq 7$ , obtained by the MP2/6-31G\* method [37] and specified with 2 geometrical parameters in each case (Fig. 1): by 2 equal bond lengths and angle between them for  $\text{Si}_3$ , by length of edge and short diagonal of rhombus for  $\text{Si}_4$ , by distance between apex atoms and edge of bases of the equilateral polygon of the trigonal ( $\text{D}_{3h}$ ), tetragonal ( $\text{D}_{4h}$ ) and pentagonal ( $\text{D}_{5h}$ ) bipyramids for  $\text{Si}_5$ ,  $\text{Si}_6$ , and  $\text{Si}_7$  correspondently. For other formulae and details of NTB see Ref. [25].

Molecular Dynamics (MD) was used here for determination of the possible spatial structures. It was based on numerical integration of Newton's equations [38]:

$$m_i \frac{d^2 r_i}{dt^2} = m_i a_i = F_i; \quad F_i = -dU/dr_i, \quad (4)$$

where  $m_i$ ,  $r_i$  and  $a_i$  are mass, position and acceleration of the  $i^{\text{th}}$  particle, respectively;  $F_i$  is the total force exerted on the  $i^{\text{th}}$  particle by all other particles; and  $U$  is the total potential energy of the system, which can be computed by one of the approximation methods.

The MD method employed here actually performs minimization of the many variable function, i.e. it min-

imizes the total energy of the system (locally) by varying the coordinates of atoms following Newton's laws, with occasional damping by removal of kinetic energy from the system. This can also be done by other well-known numerical methods, such as the conjugate gradient method. However the MD approach has several advantages. For example, it is algorithmically simple to realize, and it naturally differentiates light and fast particles from heavy and slow ones which is helpful in avoiding some undesirable and non-physical situations.

To define the cluster configurations that are local and global minima, one must construct an initial geometry from which to start the MD. While it is possible that the intuitively chosen initial geometry could be close to a local (or the global) minimum, this is unlikely. Thus, atoms will exert forces on each other and will move from their initial positions towards new ones which correspond to a lower potential energy. Then kinetic energy of the system will increase as the potential decreases. The kinetic energy is tracked, and when there is a time-step during which it decreases (indicating that the potential energy has increased), kinetic energy is removed from the system, quenching it near a local minimum. This dissipation is repeated as the system oscillates around the local minimum, being forced closer to it each time that the kinetic energy is removed. The simulation is ended when the kinetic energy of the system remains sufficiently small. Note that the same dissipation occurs in real clusters as they cool, exchanging energy with the surrounding gas or, via radiation, with solid surfaces. The calculation is repeated for different initial configurations of the clusters and the stable and metastable structures are determined by comparing total energies of the cluster geometries obtained with the given number of atoms.

### 3. RESULTS AND DISCUSSIONS










We have calculated atomization energies of the full and partial hydrogenised  $\text{Si}_2\text{-Si}_8$  clusters in neutral, positive and double positive charge states. The clusters consist of the different isomers of the silane homological row. Both tetrahedron structures and closed ones with 3-, 4-, 5- and 6-angle are on base of it, have been considered. In this article only results on most stable  $\text{Si}_n\text{H}_m$  isomers, where  $n = 2-8$ ,  $m = 2-16$  choosed by comparing their atomization energies are given.

#### 3.1 $\text{Si}_2\text{H}_m$ Clusters

Most energetically favorable among particles with structural formulae of  $\text{Si}_2\text{H}_m$  in neutral state is disilane  $\text{Si}_2\text{H}_6$ , where all valence orbitals of silicon atoms are completely saturated by hydrogen atoms (Table 1).  $\text{Si}_2\text{H}_2$  radicals have symmetric structure where each silicon atom has hydrogen atom and here the atoms are not polarized. Electron orbitals of the silicon atoms are  $\text{sp}^2$ -hybridized. However, the hydrogen atoms are slightly shifted and the angles between H-Si-Si bonds are more than  $120^\circ$ . Non-symmetrical structure with both hydrogen atoms bonded to one of the Si atoms (which charge is equal to  $+0.56e$ ) in positive charged state is stable and the angle is  $153.9^\circ$ . Electron deficiency in the cluster is mostly compensated by the sili-

con atom non-bonded to hydrogen atoms which charge is  $+0.44e$ . But a symmetrical structure once again becomes the most stable in the case of bication what can be probably explained by missing non-hybrid p-orbitals of the silicon atoms.

**Table 1** – Stable configurations and total bond energies (in eV) of the  $\text{Si}_2\text{H}_m$  isomers in different charge states\*

$m$	Neutral $\text{Si}_2\text{H}_m$		Cations $(\text{Si}_2\text{H}_m)^+$		Bications $(\text{Si}_2\text{H}_m)^{2+}$	
2		9.87		1.60		13.31
4		16.74		7.94		6.69
6		23.03		13.3		2.51

\* Silicon atom marked as big circle and hydrogen is small one in the picture. Free bonds of silicon have not shown.

In  $\text{Si}_2\text{H}_4$  and  $\text{Si}_2\text{H}_6$  clusters, configuration of atoms does not depend on charge of cluster and missing electron which compensated by charge redistribution between the atoms. Bond distances increase due to a rise in the contribution of ion-ion repulsion between the atoms of the same charges as well as decrease the overlap of electronic orbitals and the weakening of bonds. (Fig. 1).

Thus, the influence of the cluster charge state on its geometric configuration depends on saturation degree of the bonds by hydrogen atoms. For clusters  $\text{Si}_2\text{H}_m$  with a large number of unpaired electrons the stable state configuration changes in the case of electron removing.

### 3.2 $\text{Si}_3\text{H}_m$ Clusters

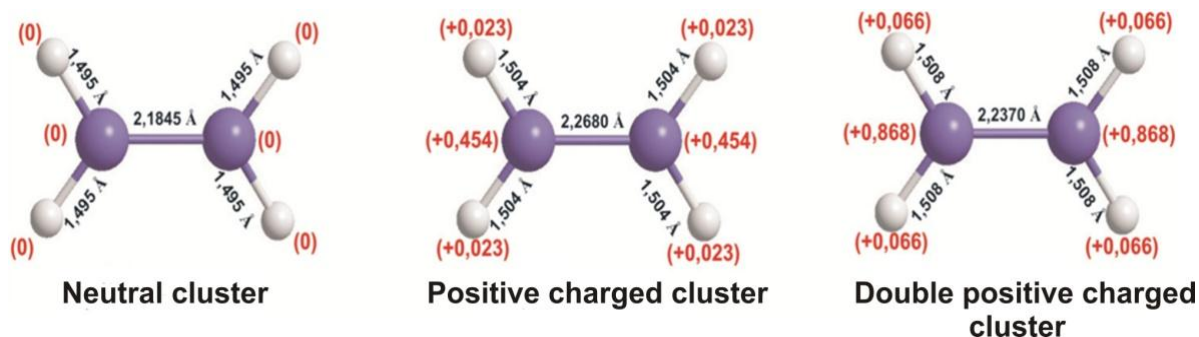
Full saturated  $\text{Si}_3\text{H}_8$  cluster with tetrahedron  $sp^3$ -configuration of silicon atoms is the most stable among isomers of this row and has the highest atomization energy in all three charge states (Table 2). In  $(\text{Si}_3\text{H}_8)^{2+}$  cluster extreme silicon atoms form a bond between each other, circling chain into triangle. Two hydrogen atoms move to bridged positions, which away from the line linking centers of neighboring silicon atoms (Fig. 2).

A closed triangular configuration of the  $\text{Si}_3\text{H}_2$  cluster was found to be stable as more as 1.11 eV than linear structure. Valence orbitals of the silicon atoms in neutral charge state are  $sp^2$ -hybridized, hydrogen atoms lie in the plane of Si-Si-Si bonds. In charged  $(\text{Si}_3\text{H}_2)^+$  and  $(\text{Si}_3\text{H}_2)^{2+}$  clusters the moving an electron away is proceeded by the destruction of the  $\sigma$ -bond between hydrogen-kept silicon atoms. As a result the triangle is opened and  $sp$ -hybridization of the silicon atoms orbitals with the angles between the bonds to be set to  $180^\circ$  is observed (Fig. 3). Balamurugan, Chakraborti, and Prasad found by Car-Parrinello molecular dynamics with simulated annealing [39] and using a non-orthogonal tight-binding [40] that  $\text{Si}_3\text{H}_2$  and  $\text{Si}_3\text{H}_4$  have bridge bonded hydrogen atoms apart from our results.

Neutral  $\text{Si}_3\text{H}_4$  cluster has the form of isosceles triangle where the top angle is equal to  $56^\circ$  and vertex silicon atom bonded to two hydrogen atoms ( $sp^3$ -hybridization). In electron losing the top angle increases up to  $69^\circ$  and hydrogen atoms arrange symmetrically on the peripheral silicon atoms. In losing the second electron the cluster configuration becomes strictly linear where the silicon atoms are  $sp^2$ -hybridized.

$\text{Si}_3\text{H}_6$  cluster has the form of an equilateral triangle with Si-Si bond length being equal to  $2.36 \text{ \AA}$  and atomization energy of 26.13 eV. Each silicon atom bonds with two hydrogen atoms. A disclosed structure with lower symmetry, where the central silicon atom forms an angle equal to  $122^\circ$  with two other Si atoms, is observed in the loss of electron. H atom keeps on the central Si atom, the second H moves to the one of the Si atoms.  $(\text{Si}_3\text{H}_6)^{2+}$  cluster has a linear configuration and two hydrogen atoms placed on diametrically opposed bridged positions around the Si-Si bonds.

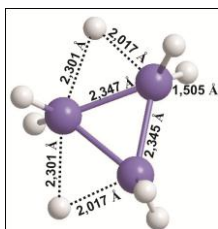
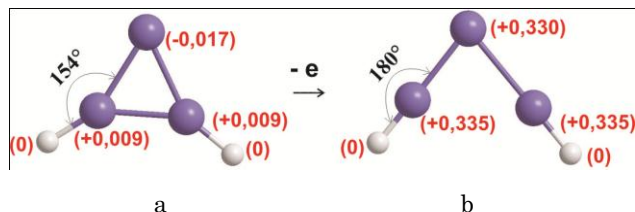
Thus, all neutral clusters of the  $\text{Si}_3\text{H}_m$  row, except  $\text{Si}_3\text{H}_8$ , have a closed triangular shape, the removal of electron in all the cases considered leads to the destruction of one of the Si-Si bonds and an opening of the triangle, even to the reformation into linear structure in some cases which can easily be explained by removing strong angular stress in the triangular structures. The transformation of the cluster form mostly occurs simultaneously with the localization of hydrogen atoms on the peripheral atoms of silicon.



**Fig. 1** – Charge distribution and bond length in  $\text{Si}_2\text{H}_4$  clusters

**Table 2** – Stable configurations and total bond energies (in eV) of  $\text{Si}_3\text{H}_m$  isomers in different charge states

$m$	Neutral $\text{Si}_3\text{H}_m$		Cations $(\text{Si}_3\text{H}_m)^+$		Bications $(\text{Si}_3\text{H}_m)^{2+}$	
2		13.84		5.62		8.33
4		19.35		11.28		2.00
6		26.13		17.49		4.18
8		32.01		23.00		10.07

**Fig. 2** –  $\text{Si}_3\text{H}_8$  cluster structure**Fig. 3** – The stable structures of the  $\text{Si}_3\text{H}_2$  (a) and  $(\text{Si}_3\text{H}_2)^+$  (b) clusters

### 3.3 $\text{Si}_4\text{H}_m$ Clusters

Among the neutral  $\text{Si}_4\text{H}_m$  clusters fully hydrogen-saturated branched  $\text{Si}_4\text{H}_{10}$  structure with atomization energy of 41.22 eV is most favorable. (Table 3). Cations and bications favor linear structures. To transit from cation structure to bication one is required energy of 12.46 eV corrected for relaxation as the neutral cluster transition to the positively charged one requires 8.72 eV.

In  $\text{Si}_4\text{H}_m$  ( $m = 2, 4$  and  $8$ ) clusters with fewer hydrogen the most stable structures are that had a square base. And in these structures the angle between the Si-Si-Si bonds takes values from  $80^\circ$  to  $88^\circ$ , Si-Si-Si-Si dihedral angle is from  $148^\circ$  to  $160^\circ$  depending on the cluster charge state and the degree of saturation by hydrogen atoms. The silicon atoms are saturated uniformly with hydrogen in  $\text{Si}_4\text{H}_8$  clusters for all charge states considered. Bication takes the form of the rhombus and the Si atoms are placed on the same plane.

In the case of  $m = 6$ , neutral  $\text{Si}_4\text{H}_6$  cluster has a square configuration. The structure of cation retains a square shape, but atomization energy (21.20 eV) is re-

duced. For  $(\text{Si}_4\text{H}_6)^{2+}$  bication is typical an opened unclosed structure. Stronger angle stress appears to be affected in contrast to other clusters of this type.

**Table 3** – Stable configurations and total bond energies (in eV) of the  $\text{Si}_4\text{H}_m$  isomers in different charge states

$m$	Neutral $\text{Si}_4\text{H}_m$		Cations $(\text{Si}_4\text{H}_m)^+$		Bications $(\text{Si}_4\text{H}_m)^{2+}$	
4		23.53		15.39		2.16
6		29.74		21.20		8.37
8		35.90		27.01		14.67
10		41.22		32.50		20.04

A quadrangular configuration of the  $\text{Si}_4\text{H}_4$  cluster does not change with its charge state. Dihedral angle between the opposing silicon atoms is  $150^\circ$ , angle between the neighboring Si atoms are  $80^\circ$ . Hydrogen atoms located asymmetrically and as a result one of the silicon atoms has two broken bonds, on the other Si bonded two hydrogen atom.

### 3.4 $\text{Si}_5\text{H}_m$ Clusters

The most stable  $\text{Si}_5\text{H}_{12}$  cluster of this series has the diamondlike structure symmetrically full saturated with hydrogen with bond energy per atom of 2.99 eV (Table 4). The structure becomes linearlike in once charged state, but branched form again becomes the most stable one for bication  $(\text{Si}_5\text{H}_{12})^{2+}$ .

**Table 4** – Structure and atomization energy (in eV) of the  $\text{Si}_5\text{H}_m$  clusters in different charge states

$m$	Neutral $\text{Si}_5\text{H}_m$		Cations $(\text{Si}_5\text{H}_m)^+$		Dications $(\text{Si}_5\text{H}_m)^{2+}$	
6		33.01		25.18		12.96
8		39.08		30.79		18.47
10		45.21		36.46		24.57
12		50.87		41.87		29.75

All partially saturated  $\text{Si}_5\text{H}_m$  clusters are closed structures on the base of three-, four- and pentagons. Neutral  $\text{Si}_5\text{H}_m$  ( $m = 6-10$ ) clusters have mostly cyclical form and clusters take the form of pentagon-cyclopentasilane in reducing quantity of the electron orbitals unbonded.

Configuration of the  $\text{Si}_5\text{H}_6$  cluster bases on the square kept unchanged in all charge states, but atomization energy greatly reduces with the loss of electrons. Neutral  $\text{Si}_5\text{H}_6$  cluster with atomization energy of 33.01 eV is the most stable one. Hydrogen atoms redistribution is observed for +2 charge state.

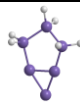
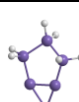
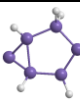
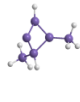
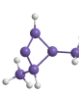
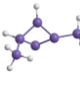
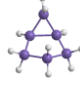
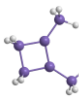
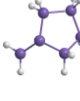
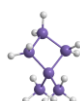
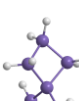
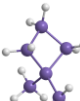
The most stable pentagonal  $\text{Si}_5\text{H}_8$  cluster has atomization energy is equal to 39.08 eV. Note that competed with it square structure with hydrogen atoms placed asymmetrically has close atomization energy (39.07 eV). In removing an electron quadrangular structure becomes stable, but the loss of two electrons leads to pentagonal one to be stable again.

$\text{Si}_5\text{H}_{10}$  cluster structure changes strong depend on its charge state. Neutral cluster is a closed pentagon with hydrogen atoms arranged symmetrically. Cation is a complex triangular structure where the atoms arranged so that no broken bonds. Stable quadrangular form with a extra silicon atom with atomization energy of 24.57 eV for bication.

### 3.5 $\text{Si}_6\text{H}_m$ Clusters

$\text{Si}_6\text{H}_m$  ( $m = 6-12$ ) clusters consist of closed rings of various sizes both individually and in attached form (Table 5). But none of these clusters form a hexagon rings, the most frequent energetically stable structure of hydrocarbons. The severing of the electron does not lead to large changes in their geometry, except for the case  $m = 10$ .

**Table 5** – Structure and atomization energy (in eV) of  $\text{Si}_6\text{H}_m$  clusters in different charge states

$m$	Neutral $\text{Si}_6\text{H}_m$		Cations ( $\text{Si}_6\text{H}_m$ ) <sup>+</sup>		Bications ( $\text{Si}_6\text{H}_m$ ) <sup>2+</sup>	
6		36.75		28.99		17.29
8		42.37		34.51		22.81
10		48.54		40.35		28.52
12		54.32		45.80		34.34

The stable neutral cluster consists of two closed structures as triangle and pentagon. Hydrogen atoms arranged in one part of the molecule where angle stress is weaker between bonds. This cluster configuration

keeps in all charge states, but hydrogen atoms slightly shifts in +2 state.  $\text{Si}_6\text{H}_8$  cluster has quadrangular structure in all three charge states. Two silicon atoms are  $sp^2$ -hybridized as other has  $sp^3$ -hybridization.

Neutral  $\text{Si}_6\text{H}_{10}$  cluster consists of triangle and pentagon adjoined each to other and has not broken bonds. This cluster structure gets a cardinal change in changing of the charge state. ( $\text{Si}_6\text{H}_{10}$ )<sup>+</sup> cation consists of square and two of the silicon atoms are  $sp^2$ -hybridized, then pentagonal structure becomes favoritely again in double charge state.

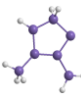
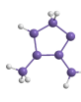
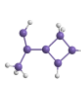
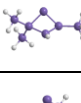
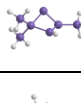
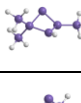
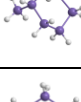
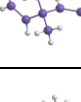
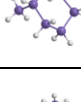
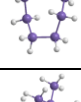
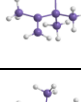
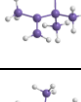
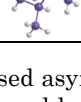
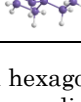
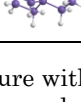
For full saturated  $\text{Si}_6\text{H}_{12}$  cluster the closed triangular structure with two silicon branch where hydrogen atoms arranged symmetrically is stable in all three charge states.

### 3.6 $\text{Si}_7\text{H}_m$ Clusters

Among quadrangular and pentagonal configurations the hexagonal and heptagonal structures get to formation for the first time in neutral clusters of this row (Table 6). And large-size rings are stabilized with growing of the hydrogen atoms quantity, except full saturated cluster which has no cyclic form. As expected,  $\text{Si}_7\text{H}_{16}$  cluster with branched diamondlike structure and fully saturated by hydrogen is most stable in all three charge states of the system.

For  $\text{Si}_7\text{H}_{14}$  clusters the ring with total atomization energy of 63.16 eV included seven Si atoms and hydrogen atoms distributed uniformly is the most stable structure in neutral state. Branched unclosed structure contained broken bonds is typical for the charged states.

**Table 6** – Structure and atomization energy (in eV) of  $\text{Si}_7\text{H}_m$  clusters in different charge states

$m$	Neutral $\text{Si}_7\text{H}_m$		Cations ( $\text{Si}_7\text{H}_m$ ) <sup>+</sup>		Bications ( $\text{Si}_7\text{H}_m$ ) <sup>2+</sup>	
8		45.49		37.96		26.20
10		51.81		43.97		32.57
12		56.56		48.87		37.92
14		63.16		55.07		42.97
16		68.97		60.65		49.04

Closed asymmetrical hexagonal structure with  $\text{SiH}_3$  branch and hydrogen atoms distributed around cluster non-uniformly prevailed energetically in  $\text{Si}_7\text{H}_{12}$  and ( $\text{Si}_7\text{H}_m$ )<sup>2+</sup> clusters. All silicon atoms are  $sp^3$ -hybridized except a vertex silicon atom with a two unpaired electrons. Unclosed branched tetrahedron structure is stable in +1 charge state.

$\text{Si}_7\text{H}_{10}$  cluster configuration keeps the form of closed and branched quadrangle as stable in all charge states. One of the Si atoms parting quadrangle has  $sp^2$ -hybridized valence orbitals, as other Si atoms external electrons are  $sp^3$ -hybridized.

In the case of  $\text{Si}_7\text{H}_8$  cluster the most quantity of the unpaired electrons is typical for the stable state. Its pentagonal structure with two silil branch is not changed by removing an electron. Two silicon atoms, vertex atom of the pentagon and  $\text{SiH}_3$  silil radical have  $sp^3$ -hybridized orbitals, other silicon atoms are  $sp^2$ -hybridized. The structure gets the form of the quadrangular ring in removing the second electron.

### 3.7 $\text{Si}_8\text{H}_m$ Clusters

From cluster size with the eight silicon atoms a compact spatial structures are starting to form. The most favorable configuration for the  $\text{Si}_8$  cluster was found to be a pentagonal bipyramid with non-regular basis and a silicon atom placed on bipyramid out. Moreover, the configuration where the both of hydrogen atoms binding with this silicon atom in neutral  $\text{Si}_8\text{H}_2$  cluster found to have the most atomization energy. In positive charged state the geometry of the cluster does not change but atom-atomic distances lengthen. Dication formation leads to breaking certain bonds of apex atoms.

In the case of addition of two more hydrogen atoms to the cluster considered, neutral and charged states have different most stable structures (Table 7). The configuration where each of hydrogen atoms bonded to the different silicon atoms corresponds to the neutral cluster, whereas in positive and double positive states, H joined by two to silicon atoms. Destruction of the cluster structure in double positively charged state is also observed here.

























The basis of the  $\text{Si}_8\text{H}_6$  cluster becomes 6-atomic ring and planar in all charged states, besides double positively one where it is not planar. Pairs of hydrogen atoms bonded to one silicon atom are distributed on opposite side atoms of the basis to place farthest from each other. One of hydrogen bonded to an apex atom and next to the one of basis Si atoms. On dication, hydrogen atoms bonded to silicon atoms by two.

The  $\text{Si}_8\text{H}_8$  cluster does not almost differ from  $\text{Si}_8\text{H}_6$  by configuration. The only difference is in basis form in double positively state where a chair-like form is acquired.

By increasing of a number of hydrogen atoms the cluster bipyramidal configuration with a 6-ring planar or chair-form basis essentially does not change further. But bipyramid structure conforms to diamond-like ones in  $\text{Si}_8\text{H}_{12}$  and  $\text{Si}_8\text{H}_{14}$ .

As mentioned above, here are atomisation energies of the some partially and completely hydrogenated silicon clusters  $\text{Si}_n\text{H}_m$ ,  $n = 2-8$ ,  $m = 2-16$  in neutral, positive and double positive charged states have been calculated by us. These clusters consist of the homologous series radicals of the silane both classical and imagined bonds between atoms. As seen from the table, the received calculation results of atomization energy of clusters in a neutral charged state coincide with results of non-empirical calculations G3/B3LYP of a various level of complexity and with a various basis set, including empirical correction.

**Table 7** – Structure and atomization energy (in eV) of  $\text{Si}_8\text{H}_m$  clusters in different charge states

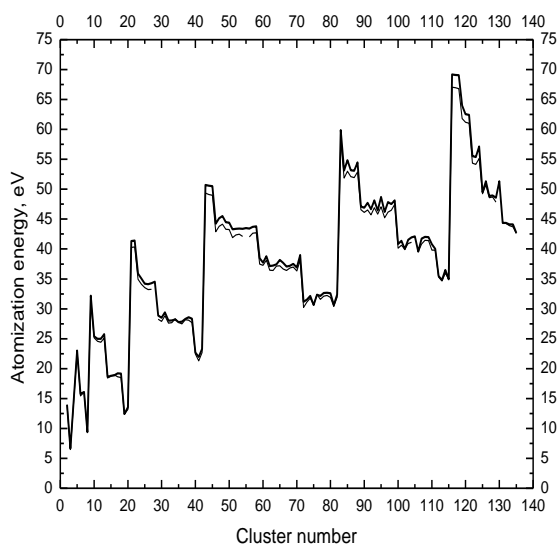
$m$	Neutral $\text{Si}_8\text{H}_m$		Cations ( $\text{Si}_8\text{H}_m$ ) <sup>+</sup>		Bications ( $\text{Si}_8\text{H}_m$ ) <sup>2+</sup>	
2		34.71		27.14		15.08
4		39.73		32.26		20.95
6		44.19		36.47		25.35
8		48.83		41.03		31.06
10		54.85		47.63		37.09
12		60.99		53.38		42.10
14		67.03		59.15		48.05
16		70.82		63.08		52.33

Charged cluster configurations discussed here have not previously been calculated altogether by any of the known ab initio methods. Despite the small size of the clusters, an accurate ab initio calculation of all cluster configurations by CCSD(T) or MP4(SDQ) methods need much more time. The results obtained are the approbation of the DTBM method on hydrogenated small silicon clusters.

Fig. 4 depicts atomization energies of a variety of  $\text{Si}_n\text{H}_m$  clusters ( $n = 1-7$ ;  $m = 2-16$ ), the total number of which was 133, calculated [5] by G3/B3LYP theory and NTB. Except for a few cluster types, all others involved from 2 to 13 isomers, including ones exhibiting non-classical bonding patterns. NTB reproduces both quantitatively and qualitatively the results of the complex and computationally expensive G3/B3LYP theory that involves multiple ab initio calculations at different levels of theory and with different basis sets, as well as empirical corrections.

The largest deviation in absolute total energy was 2.25 eV or 0.11 eV per atom with an average deviation of 0.05 eV per atom. For cluster types with several isomers, the global minimum predicted by NTB was the same as that predicted by G3/B3LYP in 15 of 20 cases. In 4 of the remaining cases the first and second lowest energy minima were exchanged, and in one case the first and third lowest energy minima were exchanged. For cluster types with up to four isomers, the energetic

ordering of all lowest energy minima was predicted consistently with G3/B3LYP theory. The few deviations in energy ordering of isomers are not only due to small deficiencies of the present parameterization of NTB, but also result from the very small differences ( $< 0.1$  eV) in energy between minima, which are comparable uncertainties in both the NTB and G3/B3LYP calculations. The G3/B3LYP method also includes empirical corrections that are different for isolated atoms and atoms in molecules. The net empirical corrections (correction in molecule minus correction for isolated atom) are  $-0.0574$  eV per H atom and  $-0.0957$  eV per Si atom in a given molecule. So, the maximum effect on the binding energy is about 1.5 eV for the largest clusters. Note that NTB results do not involve any additional corrections like this. Nevertheless, NTB atomization energies for the 133 clusters considered are, on average, only 0.216 eV lower than the corresponding G3 results. This suggests that NTB can account for a significant part of the correlation energies in molecular species that is still absent in the sequence of ab initio calculation procedures of G3 theory. This is, in particular, because of the accurate parameterization for atomic species involved, as well as the quite accurate NTB total energy functional that avoids any explicit treatment of the complex electron-electron interaction energy, in particular, exactly removing its interatomic part.



**Fig. 4** – Atomization energies of  $\text{Si}_m\text{H}_n$  ( $m = 1-7$ ;  $n = 2-16$ ) clusters calculated by G3/B3LYP theory (solid line) [5] and NTB (thin line)

Results obtained by us show that clusters full saturated with hydrogen have opened and branched structures. Reduction of the hydrogen atoms leads to cyclic form becomes most stable for all clusters because of the valence electrons of silicon atoms are saturated with hydrogen atoms in closed structure. Further decreasing of the hydrogen atoms stabilizes cyclic configurations, and as much possibility of the small-size ring formation as more unbounded electrons in the cluster. Despite of there is a large angle stress between Si-Si bonds, triangular structures show high stability. The angle stress appeared in less degree in quadrangular structures.  $\text{Si}_7\text{H}_m$  clusters generates in form of the double ring

structures.  $\text{Si}_8\text{H}_m$  clusters contrasted from smaller ones by spatial configuration which is compacted and diamond-like structure is forming therein.

Comparative study of the dependency of cluster geometry on charge revealed that the positive charge influences to cluster construction on different ways and depends on both amount of the silicon atoms in cluster and the saturation degree of the cluster by hydrogen atoms and positive charge value. So, if triangular ring is broken easily in clusters  $\text{Si}_3\text{H}_m$  belong to strong angle stress, quadrangular structure in  $\text{Si}_4\text{H}_m$  clusters is not broken in the case of removing an electron and weakened bonds between atoms. Electron revealing leads to stabilization of small-size rings in larger clusters. For cyclic structures, there is often taken place a breaking of the Si-Si bond and unclosed structures formed as result. Neutral and double positive charged structures have the same geometry for most clusters.

Note that ideal classic structures with maximal saturation of the silicon free bonds where silicon atoms base cluster core, has a highest energy among different isomers of the clusters with equal number of silicon and hydrogen atoms as a rule. However the charged clusters for which classic structure is not have to be most favorable, can participate in real growth process of the hydrogenated clusters from silane gas [9]. In particular, the destabilization of the monohydric bond and formation of the bridged hydrogen atom for positive charged cluster is possible. Such states of hydrogen could be also impregnated with growing cluster inside while cluster growth and a large hydrogenated silicon clusters could be non-ideal both by stoichiometry and structure too as a result.

#### 4. CONCLUSION

The atomization energies of the some partially and completely hydrogenated silicon clusters  $\text{Si}_m\text{H}_n$ ,  $n = 2-8$ ,  $m = 2-16$  in neutral, positive and double positive charged states have been calculated.

For cluster types with several isomers, the global minimum predicted by NTB was the same as that predicted by G3/B3LYP in 15 of 20 cases. The few deviations in energy ordering of isomers are not only due to small deficiencies of the present parameterization of NTB, but also result from the very small differences ( $< 0.1$  eV) in energy between minima, which are comparable uncertainties in both the NTB and G3/B3LYP calculations. The G3/B3LYP method also includes empirical corrections that are different for isolated atoms and atoms in molecules. The net empirical corrections (correction in molecule minus correction for isolated atom) are  $-0.0574$  eV per H atom and  $-0.0957$  eV per Si atom in a given molecule. So, the maximum effect on the binding energy is about 1.5 eV for the largest clusters. Note that NTB results do not involve any additional corrections like this. Nevertheless, NTB atomization energies for the 133 clusters considered are, on average, only 0.216 eV lower than the corresponding G3 results. This suggests that NTB can account for a significant part of the correlation energies in molecular species that is still absent in the sequence of ab initio calculation procedures of G3 theory. This is, in particular, because of the accurate parameterization for atom-

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Comparative study of the dependency of cluster geometry on charge revealed that the positive charge influences to cluster construction on different ways and depends on both amount of the silicon atoms in cluster and the saturation degree of the cluster by hydrogen atoms and positive charge value. So, if triangular ring is broken easily in clusters  $\text{Si}_3\text{H}_m$  belong to strong angle stress, quadrangular structure in  $\text{Si}_4\text{H}_m$  clusters is not

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## 5. ACKNOWLEDGEMENTS

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