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# Effect of hydrogen on ground state properties of silicon clusters ( $\text{Si}_n\text{H}_m$ ; $n = 11\text{--}15$ , $m = 0\text{--}4$ ): a density functional based tight binding study

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## Abstract

The effect of hydrogen addition to silicon clusters  $\text{Si}_n$  ( $n = 11\text{--}15$ ) is examined in terms of the change in their ground state geometry, bonding characteristics (bond lengths, bond angles and Si coordination numbers), structural stability, vibrational spectra and electronic structure. We found that addition of hydrogen caused a drastic change in the structural geometry of silicon clusters. Upon hydrogenation, some clusters become highly symmetric, while some others are completely distorted. Hydrogenation caused a structural transition in silicon clusters; from spherical to elongated in  $\text{Si}_{11}$  and  $\text{Si}_{12}$ , from one side capped elongated to both side capped elongated in  $\text{Si}_{13}$  and  $\text{Si}_{14}$  and from both side capped elongated to one side capped elongated in  $\text{Si}_{15}$ . Hydrogen preferred to bond with either under-coordinated or over-coordinated Si atoms. Each H atom is bonded to only one Si atom and localized outside the silicon cluster skeleton. Hydrogenation caused a significant change in the vibrational spectra and electronic structures of bare  $\text{Si}_n$  silicon clusters. There exists a band gap near the Fermi level in EDOS in all the bare and hydrogenated silicon clusters. The band gap of a silicon cluster depends on its size and amount of hydrogenation.

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

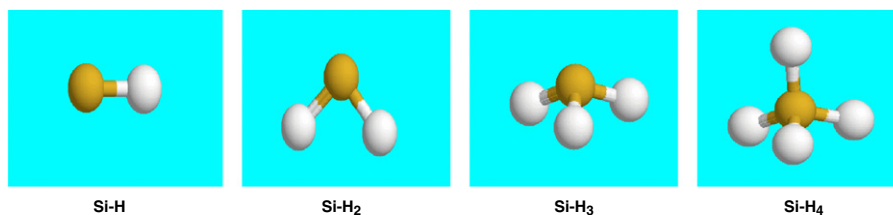
## 1. Introduction

There is an intense interest in the theoretical study of atomic clusters using computer simulation techniques [1–14]. In particular, silicon clusters have attracted considerable attention due to their future technological applications in optoelectronics and nanotechnology [15–19]. The experimental and theoretical investigations on the ground state structures for small silicon clusters have shown that they are not simply small pieces of crystalline silicon. Rather, small silicon clusters are largely unrelated to the bulk silicon in their structures and other properties [20]. These clusters do not have equilibrium symmetric fullerene structures like carbon but rather exhibit more compact structures, which favour fourfold bonding. This has been attributed to the competition between the requirement for appropriate bonding

characteristics (bond angles, bond lengths, coordination number etc) and geometrically symmetric features that distribute strain evenly [21–33]. Theoretical investigations show that the ground state structures of small silicon clusters  $\text{Si}_n$  ( $n = 5\text{--}13$ ) are polyhedrons [4, 20, 34–36]. The direct experimental observations of atomic arrangements in small cluster structures is practically not possible. Therefore, a combination of theoretical calculations and indirect experimental measurements is used to determine the atomic arrangements in small clusters. One such approach is vibrational spectroscopy, where the frequencies observed in infrared (IR) or/and Raman experiments are matched with the frequencies calculated for a given structure. Raman and IR spectroscopy combined with theoretical *ab initio* quantum chemistry has been successfully used to determine the structures of  $\text{Si}_n$  ( $n = 3\text{--}7$ ) clusters [37, 38].

There is a significant interest in hydrogenated silicon clusters because they may be used to model the absorption

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**Figure 1.** The ground state structures of  $\text{Si-H}_n$  ( $n = 1-4$ ) clusters. The structures have been obtained by employing simulated annealing and then CG optimization based upon the DFTB approach within LDA and self-consistent field. The dark balls represent Si atoms and the light balls represent H atoms. The average values of the Si-H bond length, H-Si-H bond angle and vibrational frequencies in these clusters are given in table 1.

and emission of visible light in quantum devices [39, 40]. The study of small hydrogenated silicon clusters is also important because of their role in Si thin film growth by chemical vapour deposition (CVD) [41–43], hydrogenated amorphous silicon (a-Si:H) film growth [44, 45] and Si nanoparticle production [46–48]. Hydrogenated Si cluster formation hinders the deposition of crystalline Si in CVD by contaminating the surface. However, on the other hand, it is believed to enhance the growth of a-Si:H and is the initial step for the gas-phase production of Si nanoparticles [42, 43]. Hydrogenated silicon clusters are also thought to be present in hydrogenated amorphous silicon, porous silicon and silicon surfaces. Hydrogen plays an important role in phenomena like photoluminescence of porous silicon, potential fluctuations and the Staebler–Wronsky effect in a-Si:H [49, 50]. The study of hydrogenated small silicon clusters may throw some light on the complex phenomena occurring in these systems. Several theoretical calculations have been done for small hydrogenated silicon clusters by using various techniques [9, 51–54]. Experimental studies have been carried out for the hydrogenated silicon clusters using a quadrupole ion trap [55], where  $\text{Si}_n\text{H}_m^+$  ( $n = 2-10$ ,  $m = 0-20$ ) were grown from silane gas. Using mass spectra of these clusters, it was shown how the stability of a silicon cluster is affected by hydrogenation. Chambreau *et al* [56] have described the experimental production, isolation and detection of small bare and hydrogenated silicon clusters,  $\text{Si}_n\text{H}_m$  ( $n = 3-10$ ,  $m = 0-3$ ). The most stable structures are found to prefer the H-Si single bonds rather than the bridged Si-H-Si bonds. Although the effect of hydrogen addition on the ground state properties of small silicon clusters,  $\text{Si}_n$  ( $n = 2-10$ ), has been reported by many groups [9, 51, 55–58], the effect of hydrogen addition on the ground state properties of intermediate silicon clusters,  $\text{Si}_n$  ( $n \geq 11$ ), is still lacking. In this paper, we carried out a study of ground state structural, vibrational and electronics properties of hydrogenated silicon clusters ( $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 1-4$ ) using a density functional tight binding (DFTB) approach within the local density approximation (LDA).

## 2. Computational details

We used the DFTB approach of Frauenheim *et al* [59] to generate the structures of silicon clusters and to examine vibrational and electronic properties of the generated structures. For the structural optimization by molecular

dynamics (MD) simulations, we used simulated annealing and adopted the canonical ensemble scheme where the kinetic energy of ionic motions is constantly rescaled to the simulation temperature. The force tolerance threshold in the simulated annealing mode of the MD program is set to 0.000 01 (atomic units), and the probability of velocity rescaling to 0.2. We used s and p orbitals as the basis set for Si atoms and s orbitals as the basis set for H atoms. The range of repulsive potential and cut-off distance (in atomic units) for the next nearest neighbour respectively is 4.8 and 4.8 for Si-Si interactions, 3.2 and 3.2 for Si-H interactions and 2.99 and 2.0 for H-H interactions. The ionic motions are calculated with discrete time steps of about 1 fs. The Brillouin zone of the supercell lattice is sampled at the  $\Gamma$  point alone. To perform simulated annealing the system was taken to high temperatures (1600 K in steps of 200 K with equilibration for 1000 time steps at each temperature), equilibrated for a long time at 1600 K (10 000 time steps) and then slowly cooled down (in steps of 100 K with equilibration for 1000 time steps at each temperature) to 300 K where the structure is allowed to relax for a long time (50 000 time steps). Finally, these optimized structures are further optimized using conjugate gradient (CG) optimization.

To test the DFTB approach within the LDA for the Si-H interactions, we generated the structures of  $\text{Si-H}_n$  ( $n = 1-4$ ) using simulated annealing and then the CG optimization method. The optimized low energy structures are given in figure 1. We calculated the Si-H bond length, H-Si-H bond angle and vibrational frequencies of various vibrational modes in the  $\text{Si-H}_n$  ( $n = 1-4$ ) clusters. The results are given in table 1. It is found that our calculated values for  $\text{Si-H}_n$  ( $n = 1-4$ ) ground state structures are in quite good agreement with available theoretical [60, 61] and experimental results [62, 63] reported in the literature. This DFTB approach has also already been used to study pure silicon clusters [21] and hydrogenated amorphous silicon [64]. This shows that our calculational procedure is able to give the correct structures for hydrogenated silicon clusters.

Some silicon clusters are heated to 1800 and 2000 K but it was found that the resulting ground state structures are the same. In the case of  $\text{Si}_n\text{H}_4$  ( $n = 11-15$ ) clusters, however, if heated above 1600 K, some of the H atoms lost the bonding to the Si cluster. We also optimized clusters at 0 K and then raised the temperature to 300 K but we found no significant difference to those optimized at 300 K. The vibrational density of states (VDOS) and the IR intensities of the various vibrational

**Table 1.** Comparison of calculated and experimental values of bond lengths, bond angles and vibrational frequencies of Si–H<sub>*n*</sub> (*n* = 1–4) clusters. The theoretical values in parentheses are from [60]; those in square brackets are from [61] and experimental values are computed from [62] and [63]. The experimental values from [63] are given in curly brackets.

	Bond length (Si–H) (Å)		Bond angle (H–Si–H) (deg)		Vibrational frequencies (cm <sup>-1</sup> )	
	Theory	Exp.	Theory	Exp.	Theory	Exp.
SiH (C <sub>∞v</sub> )	1.547 (1.560)	1.520			1982 (1942) [2013]	2042
SiH <sub>2</sub> (C <sub>2v</sub> )	1.539 (1.550)	1.514	93.73 (90.60)	92.00	983, 2008, 2036 (954, 1977, 1986) [1024, 2036, 2038]	999, 1993, 1996
SiH <sub>3</sub> (C <sub>3v</sub> )	1.502	1.468	108.68	110.50	738, 860, 2116, 2173 [760, 936, 2192, 2233]	728, 922, 2136, 2185
SiH <sub>4</sub> (T <sub>d</sub> )	1.491 (1.500)	1.480	109.48	109.47	804, 924, 2206, 2237, 2238 (829–848, 2190, 2200) [922, 980, 2235, 2243, 2244]	914, 975, 2187, 2191 {914, 953, 2189, 2267}

modes of optimized structures are calculated using a Gaussian broadening function with broadening width of 20 cm<sup>-1</sup>. The details of calculation of IR intensities of various vibrational modes can be found in the literature [21]. The electronic density of states (EDOS) of the optimized structures has been calculated at the  $\Gamma$ -point alone using a Fermi broadening function with a Fermi temperature of 300 K.

### 3. Results and discussion

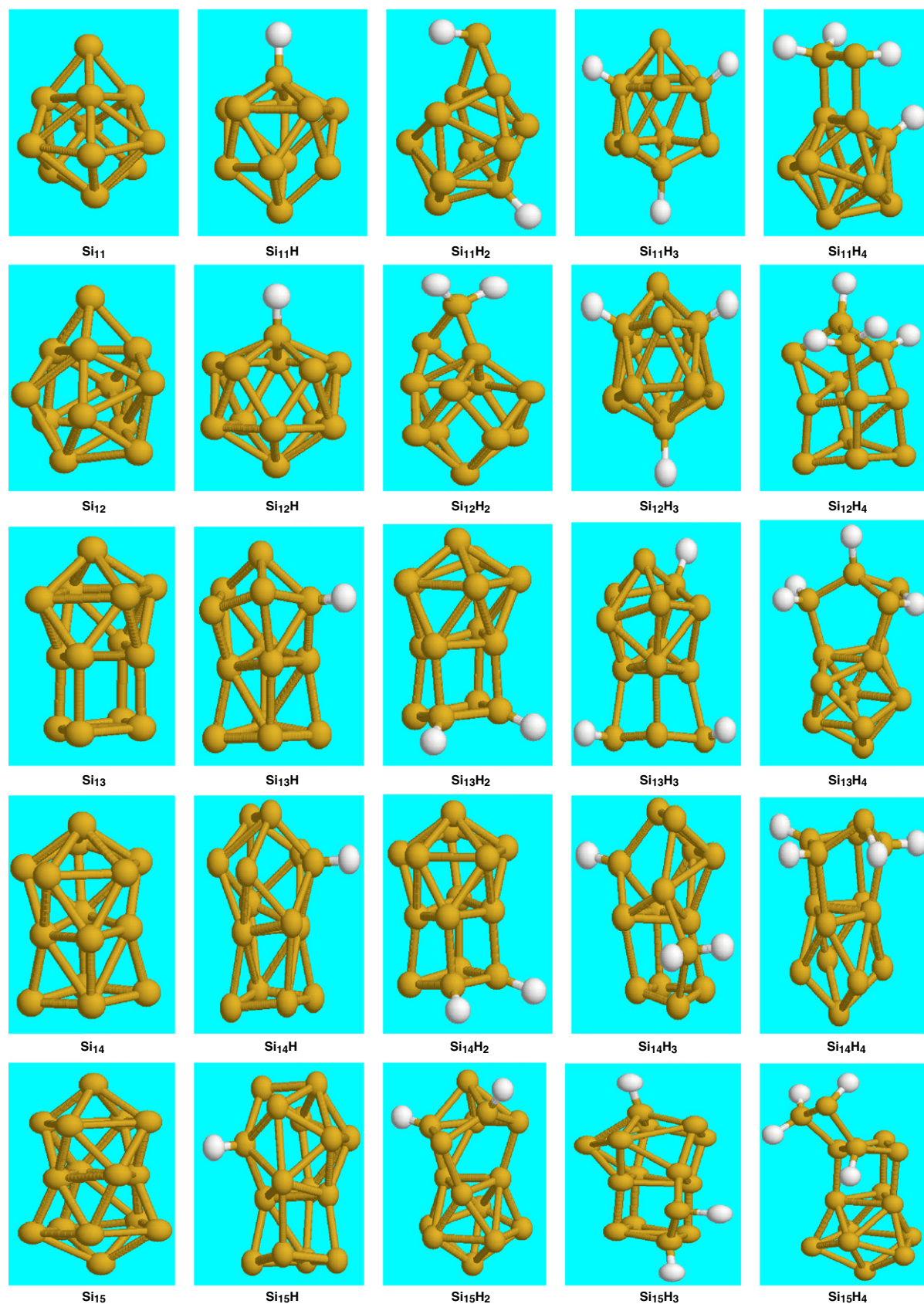
#### 3.1. Structural properties

In this section we discuss the structural properties of bare and hydrogenated silicon clusters (Si<sub>*n*</sub>H<sub>*m*</sub>; *n* = 11–15, *m* = 0–4) obtained by using simulated annealing and CG optimization based upon DFTB within the LDA and self-consistent field. The optimized structures are given in figure 2. The Si–Si and Si–H bondings are defined with cut-off distances of 2.70 and 1.80 Å, respectively. From figure 2 it can be noticed that, while Si<sub>11</sub> and Si<sub>12</sub> clusters have near-spherical geometry, Si<sub>13</sub>, Si<sub>14</sub> and Si<sub>15</sub> have capped elongated geometry. Zhu *et al* [65, 66] have also reported similar isomers of silicon clusters. They found that small silicon clusters prefer spherical-like structure, while Si<sub>*n*</sub> (*n* ≥ 13) prefer elongated structures. Small clusters prefer spherical-like structure because spherical-like shape minimizes the surface area and dangling bonds [35]. We started with different isomers but the final structure is always the same. The most important part is the effect of hydrogen addition on the structure and energy of silicon clusters. The addition of hydrogen caused a drastic change in the structural geometry of host silicon clusters. Upon hydrogenation some clusters become highly symmetric, while others are completely distorted. In all silicon clusters, except for Si<sub>13</sub>Hi<sub>4</sub>, each H atom is bonded to one Si atom from outside the silicon skeleton. This is consistent with the results reported earlier in the literature [9, 53]. The structural properties of the clusters are examined by calculating the bonding characteristics (bond lengths, bond angles and average coordination number of Si atoms). The results are given in table 2. The bonding

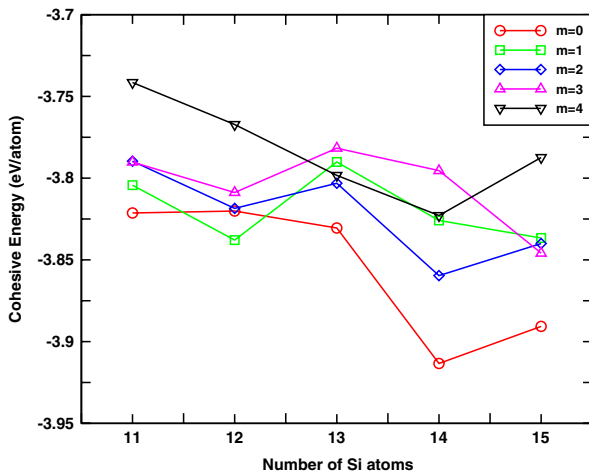
**Table 2.** The bonding characteristics (average coordination number of the Si atoms, Si–Si bond length, Si–H bond length, Si–Si–Si bond angle and Si–Si–H bond angle) of low energy structures of Si<sub>*n*</sub>H<sub>*m*</sub>, *n* = 11–15, *m* = 0–4, obtained by employing simulated annealing and then conjugate gradient (CG) optimization.

		<i>m</i>				
		0	1	2	3	4
Average	Si <sub>11</sub> H <sub><i>m</i></sub>	4.91	4.91	4.36	4.55	4.36
coordination	Si <sub>12</sub> H <sub><i>m</i></sub>	4.83	5.00	4.17	4.83	3.50
number of Si	Si <sub>13</sub> H <sub><i>m</i></sub>	4.31	4.15	4.15	4.15	4.00
atom	Si <sub>14</sub> H <sub><i>m</i></sub>	4.57	4.29	4.00	3.57	4.00
	Si <sub>15</sub> H <sub><i>m</i></sub>	4.80	4.40	4.67	4.13	4.27
Si–Si bond	Si <sub>11</sub> H <sub><i>m</i></sub>	2.559	2.567	2.534	2.543	2.536
length (Å)	Si <sub>12</sub> H <sub><i>m</i></sub>	2.562	2.578	2.517	2.567	2.444
	Si <sub>13</sub> H <sub><i>m</i></sub>	2.524	2.511	2.525	2.520	2.506
	Si <sub>14</sub> H <sub><i>m</i></sub>	2.542	2.531	2.498	2.456	2.500
	Si <sub>15</sub> H <sub><i>m</i></sub>	2.559	2.537	2.548	2.503	2.517
Si–H bond	Si <sub>11</sub> H <sub><i>m</i></sub>	—	1.505	1.520	1.503	1.510
length (Å)	Si <sub>12</sub> H <sub><i>m</i></sub>	—	1.502	1.500	1.501	1.501
	Si <sub>13</sub> H <sub><i>m</i></sub>	—	1.505	1.502	1.520	1.499
	Si <sub>14</sub> H <sub><i>m</i></sub>	—	1.505	1.511	1.502	1.514
	Si <sub>15</sub> H <sub><i>m</i></sub>	—	1.503	1.507	1.512	1.513
Si–Si–Si bond	Si <sub>11</sub> H <sub><i>m</i></sub>	82.49	82.64	83.97	83.52	83.59
angle (deg)	Si <sub>12</sub> H <sub><i>m</i></sub>	84.16	83.96	85.45	84.42	90.35
	Si <sub>13</sub> H <sub><i>m</i></sub>	86.05	88.15	87.81	87.56	87.04
	Si <sub>14</sub> H <sub><i>m</i></sub>	86.43	88.06	89.58	91.27	88.25
	Si <sub>15</sub> H <sub><i>m</i></sub>	85.72	87.77	85.86	88.81	86.22
Si–Si–H bond	Si <sub>11</sub> H <sub><i>m</i></sub>	—	116.52	110.85	112.03	112.72
angle (deg)	Si <sub>12</sub> H <sub><i>m</i></sub>	—	113.50	115.67	111.79	116.42
	Si <sub>13</sub> H <sub><i>m</i></sub>	—	114.39	120.19	105.76	113.01
	Si <sub>14</sub> H <sub><i>m</i></sub>	—	118.27	124.06	114.11	110.80
	Si <sub>15</sub> H <sub><i>m</i></sub>	—	113.84	116.06	110.48	108.52

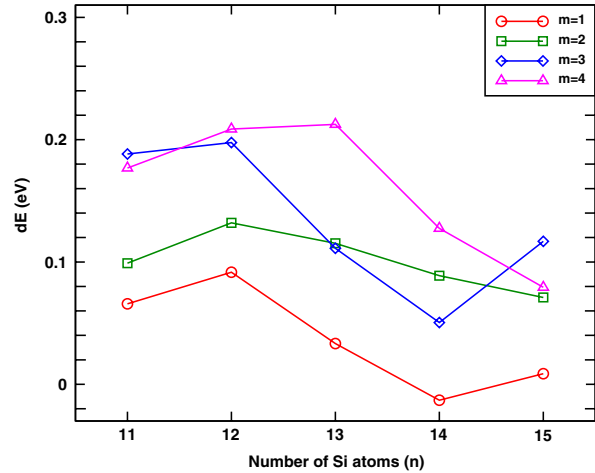
characteristics of bare silicon clusters are influenced quite significantly upon hydrogenation. The average values of the silicon coordination number, Si–Si bond length, Si–H bond length, Si–Si–Si bond angles and Si–Si–H bond angles in the optimized bare and hydrogenated silicon clusters lie, respectively, in the ranges 4.00–5.00, 2.51–2.56, 1.50–1.52 Å,



**Figure 2.** The ground state structures of hydrogenated silicon clusters ( $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 0-4$ ). The structures have been obtained by employing simulated annealing and then CG optimization based upon the DFTB approach within the LDA and self-consistent field. The dark balls represent Si atoms and the light balls represent H atoms.



**Figure 3.** The cohesive energy per atom for various optimized low energy structures,  $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 0-4$ .



**Figure 4.** The total energy difference ( $dE$ ) defined by equation (1) for various optimized low energy structures of hydrogenated silicon clusters ( $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 1-4$ ).

$82.5^\circ-91.3^\circ$  and  $110.5^\circ-124.1^\circ$ . However, in a-Si:H the average values of silicon coordination number, Si-Si bond length, Si-H bond length, Si-Si-Si bond angles and Si-Si-H bond angles calculated using the same DFTB approach are found, respectively, to be in the ranges 3.89–3.92, 2.36–2.39, 1.53–1.56 Å,  $108.0^\circ-109.0^\circ$  and  $103.0^\circ-105.0^\circ$  [64]. Thus, in  $\text{Si}_n\text{H}_m$  ( $n = 11-15$ ,  $m = 0-4$ ) clusters the Si-Si bond length is longer, the Si-H bond length and Si-Si-Si bond angle are shorter and the Si-Si-H bond angle is broader as compared to those in a-Si:H. It is also noticed that Si-Si bond length, Si-H bond length, Si-Si-Si bond angles and Si-Si-H bond angles in these clusters are not simply related to the cluster size. Onida and Andreoni [54] have also reported similar results for selected hydrogenated crystalline silicon fragments. Hydrogen preferred to bond with either an over-coordinated Si atom or an under-coordinated Si atom. H atom bonding to an under-coordinated Si atom is due to the presence of a dangling bond in an under-coordinated Si atom. However, H bonding to an over-coordinated Si atom may be attributed to the higher electronegativity of H atom compared to Si atom and consequently a H atom bonds to a Si atom having a higher number of electrons (over-coordinated). From tables 1 and 2 it is noticed that the Si-H bond length in these clusters is smaller than that in the Si-H dimer and the Si-H<sub>2</sub> cluster but approximately equal to that in Si-H<sub>3</sub> and Si-H<sub>4</sub> clusters. The addition of H atoms to silicon clusters decreases the number of unsaturated bonds on the cluster surface, which changes the structure and energy of cluster. The effect of hydrogen addition on the ground state geometry of silicon clusters is discussed in brief in the following.

The addition of one H atom made  $\text{Si}_{11}$  and  $\text{Si}_{12}$  clusters more symmetric with fullerene-like structures. The structural symmetry is changed from  $C_8$  to icosahedral. Hydrogenated  $\text{Si}_{11}\text{H}$  and  $\text{Si}_{12}\text{H}$  clusters are more compact than bare  $\text{Si}_{11}$  and  $\text{Si}_{12}$  clusters. The H atom is bonded from outside the silicon cluster skeleton to an over-coordinated Si atom. The addition of an H atom to  $\text{Si}_{11}$  and  $\text{Si}_{12}$  clusters decreases the number of dangling bonds and hence makes them more

spherical-like. But the addition of one more H atom distorts the silicon skeleton in both  $\text{Si}_{11}\text{H}_2$  and  $\text{Si}_{12}\text{H}_2$  clusters. The high symmetry structures with incomplete electronic shells become more stabilized through geometry deformation [67]. The distortion is mainly due to the configuration of Si atoms bonded to H atoms. Ten Si atoms formed a compact cluster in both  $\text{Si}_{11}\text{H}_2$  and  $\text{Si}_{12}\text{H}_2$ . Addition of three H atoms to  $\text{Si}_{11}$  and  $\text{Si}_{12}$  silicon clusters made them again symmetric. The H atoms are bonded symmetrically to silicon atoms from outside the silicon skeleton, making an angle of approximately  $120^\circ$  to each other. Each H atom is bonded to an over-coordinated Si atom. But addition of four H atoms distorts the silicon skeleton of  $\text{Si}_{11}$  and  $\text{Si}_{12}$  clusters completely and the distortion is again due to the configuration of Si atoms bonded to H atoms. Here, it is quite interesting to note that there is a complete structural transition from spherical to elongated clusters upon hydrogenation of  $\text{Si}_{11}$  and  $\text{Si}_{12}$  clusters.

The ground state structures of  $\text{Si}_{13}$  and  $\text{Si}_{14}$  clusters are elongated—capped on one side and a base of four Si atoms on other side. The  $\text{Si}_{13}$  cluster has the lowest value of average Si coordination and Si-Si bond length as compared to other bare silicon clusters considered in this computational work. The addition of one H atom to  $\text{Si}_{13}$  and  $\text{Si}_{14}$  clusters changed their geometrical structure and decreased the average silicon coordination and Si-Si bond length. The Si atom bonded to H has fivefold coordination. The addition of one more H atom made the clusters again have the same geometrical structure as the corresponding bare  $\text{Si}_{13}$  and  $\text{Si}_{14}$  clusters. Addition of three and four H atoms to the  $\text{Si}_{13}$  and  $\text{Si}_{14}$  clusters distorted their geometrical symmetry completely. Here, one can notice that there is a structural transition from one side capped elongated structures to both side capped elongated structures upon hydrogenation.

The ground state structure of  $\text{Si}_{15}$  is elongated—capped on both sides. The addition of one H atom to the  $\text{Si}_{15}$  cluster changed its geometrical symmetry and decreased the average Si coordination and Si-Si bond length.  $\text{Si}_{15}\text{H}$  has a similar geometrical structure as  $\text{Si}_{14}\text{H}$  with a base of four atoms on

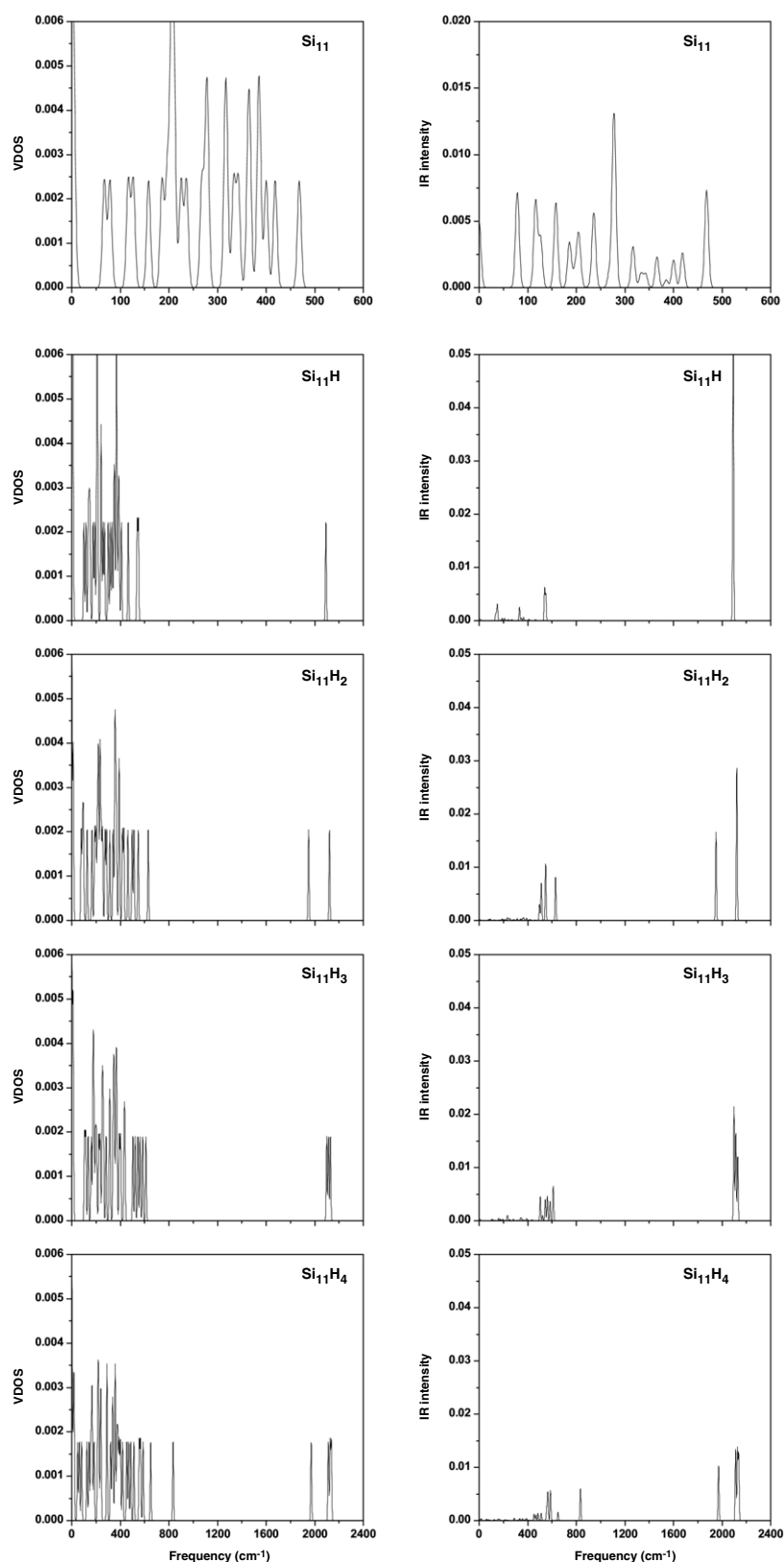


Figure 5. The VDOS and IR intensities of various vibrational modes in the clusters,  $\text{Si}_{11}\text{H}_m$  ( $m = 0-4$ ).

one side. The H atom is bonded to a fivefold coordinated Si atom. The Si-H bond length is equal to that in the  $\text{Si-H}_3$  cluster. The addition of one more H atom made the  $\text{Si}_{15}$  cluster

again capped on both sides. Addition of three H atoms to the host  $\text{Si}_{15}$  silicon cluster changed its geometrical structure completely.  $\text{Si}_{15}\text{H}_3$  is an elongated cluster capped only on one

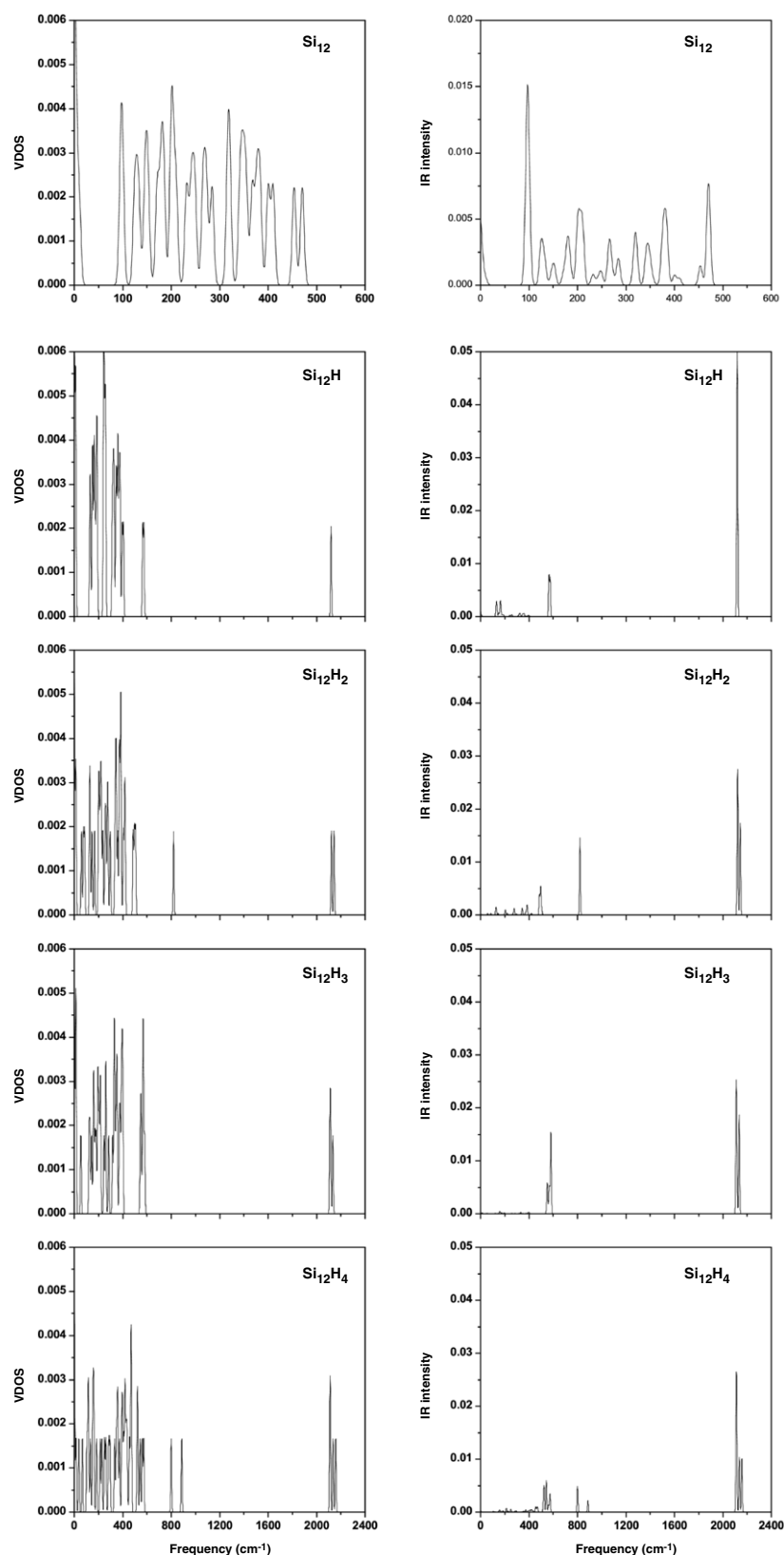


Figure 6. The VDOS and IR intensities of various vibrational modes in the clusters,  $Si_{12}H_m$  ( $m = 0-4$ ).

side and has a four atom base on the other side. The addition of four H atoms distorted the cluster completely and the distortion is mainly due to the configuration of Si atoms bonded to H

atoms. In this case, there is a structural transition from the both side capped elongated cluster to a one side capped elongated cluster upon hydrogenation.



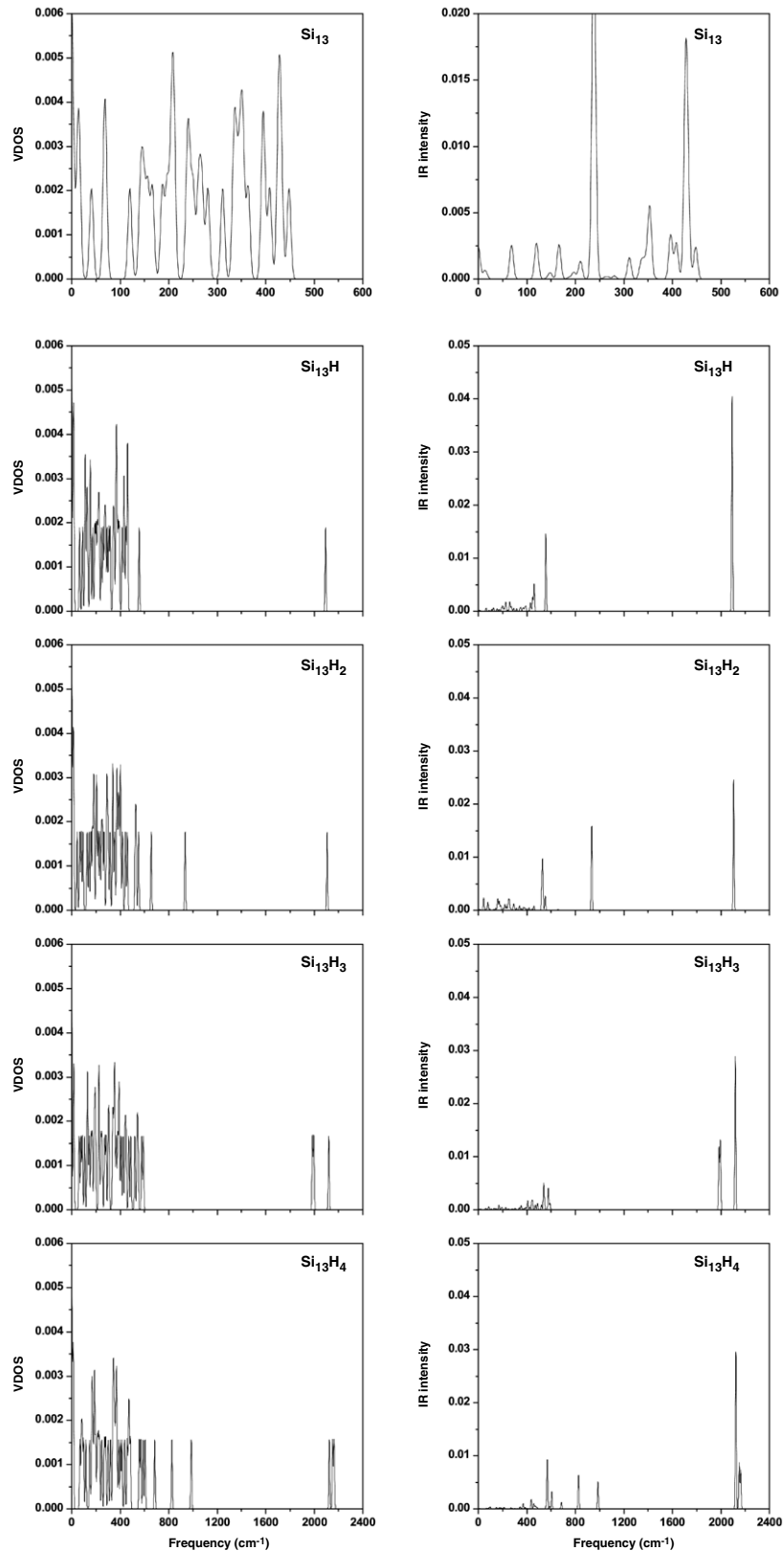
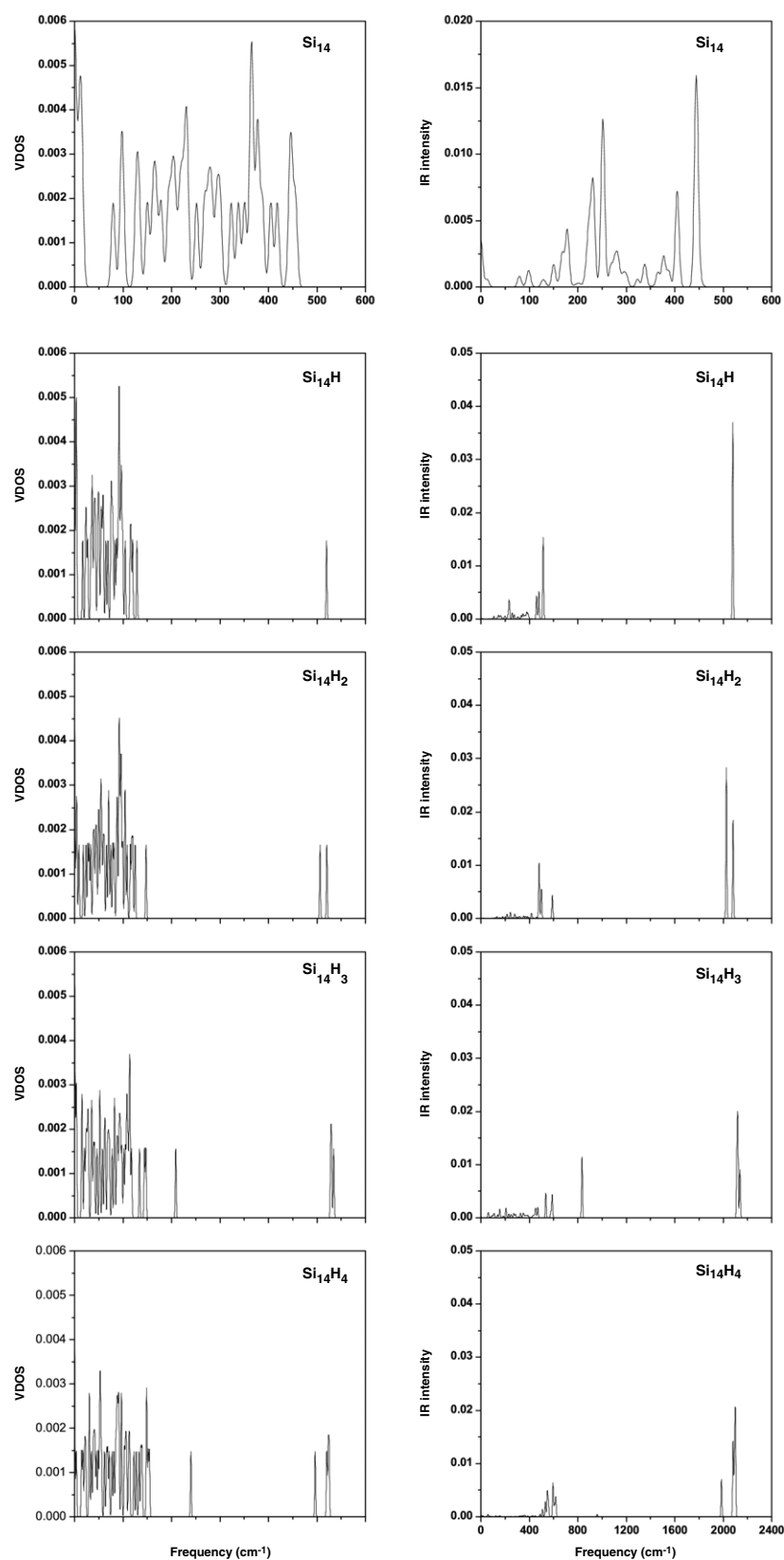


Figure 7. The VDOS and IR intensities of various vibrational modes in the clusters,  $Si_{13}H_m$  ( $m = 0-4$ ).

Finally we report on the effect of hydrogen addition on the stability of bare silicon clusters. It is found that addition of hydrogen reduced the total energy of  $Si_n$  clusters by a

considerable amount. The cohesive energy per atom as given in figure 3 is total cohesive energy divided by total number of atoms (H plus Si atoms). Figure 3 shows that the cohesive



**Figure 8.** The VDOS and IR intensities of various vibrational modes in the clusters,  $\text{Si}_{14}\text{H}_m$  ( $m = 0-4$ ).

energy per atom is not simply related to the number of Si atoms and H atoms in the cluster. The effect of hydrogen addition on the structural stability of  $\text{Si}_n$  clusters is determined

by calculating the energy difference ( $dE$ ) of the modified hydrogenated  $\text{Si}_n\text{H}_m$  cluster and the bare  $\text{Si}_n$  cluster, which is defined as

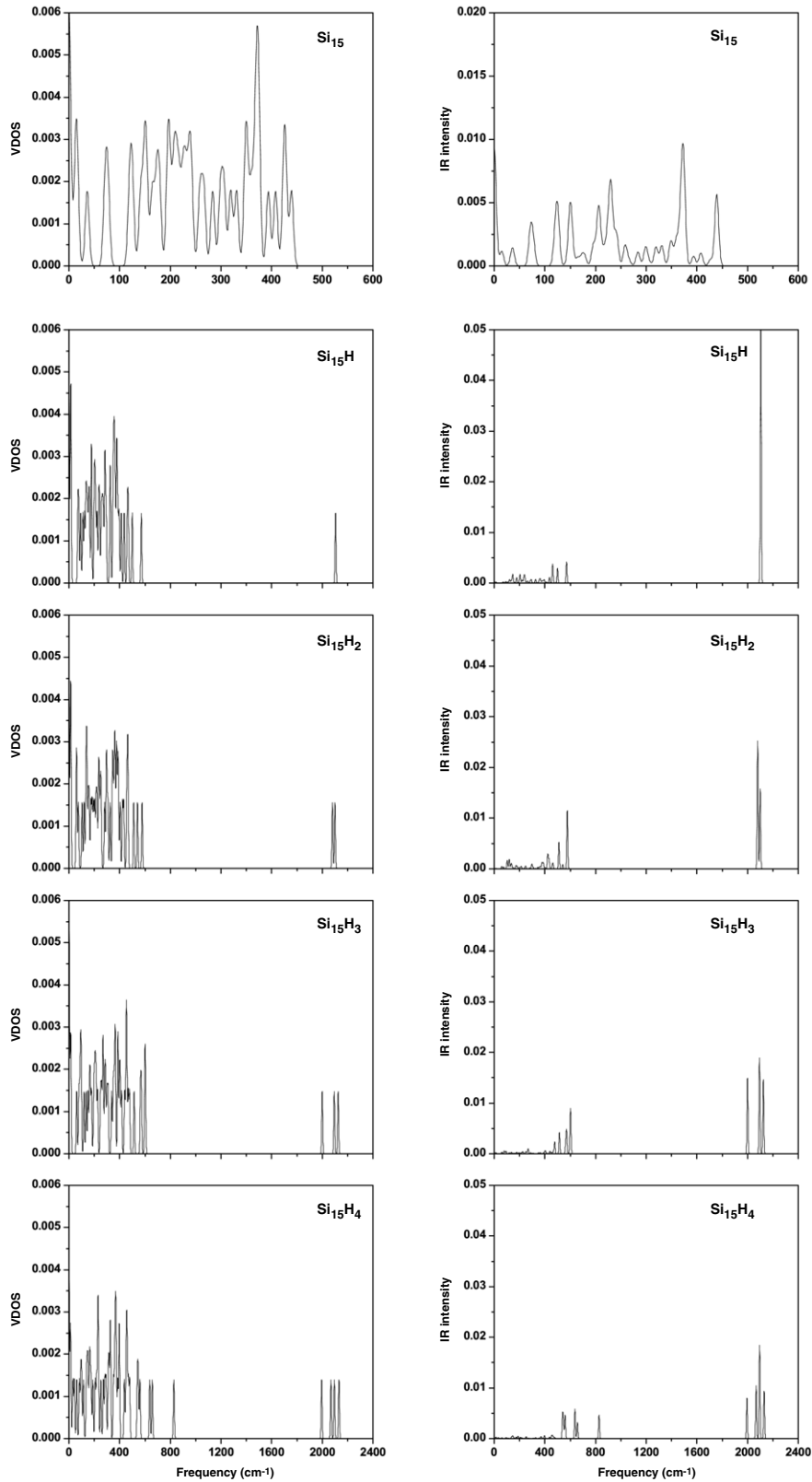
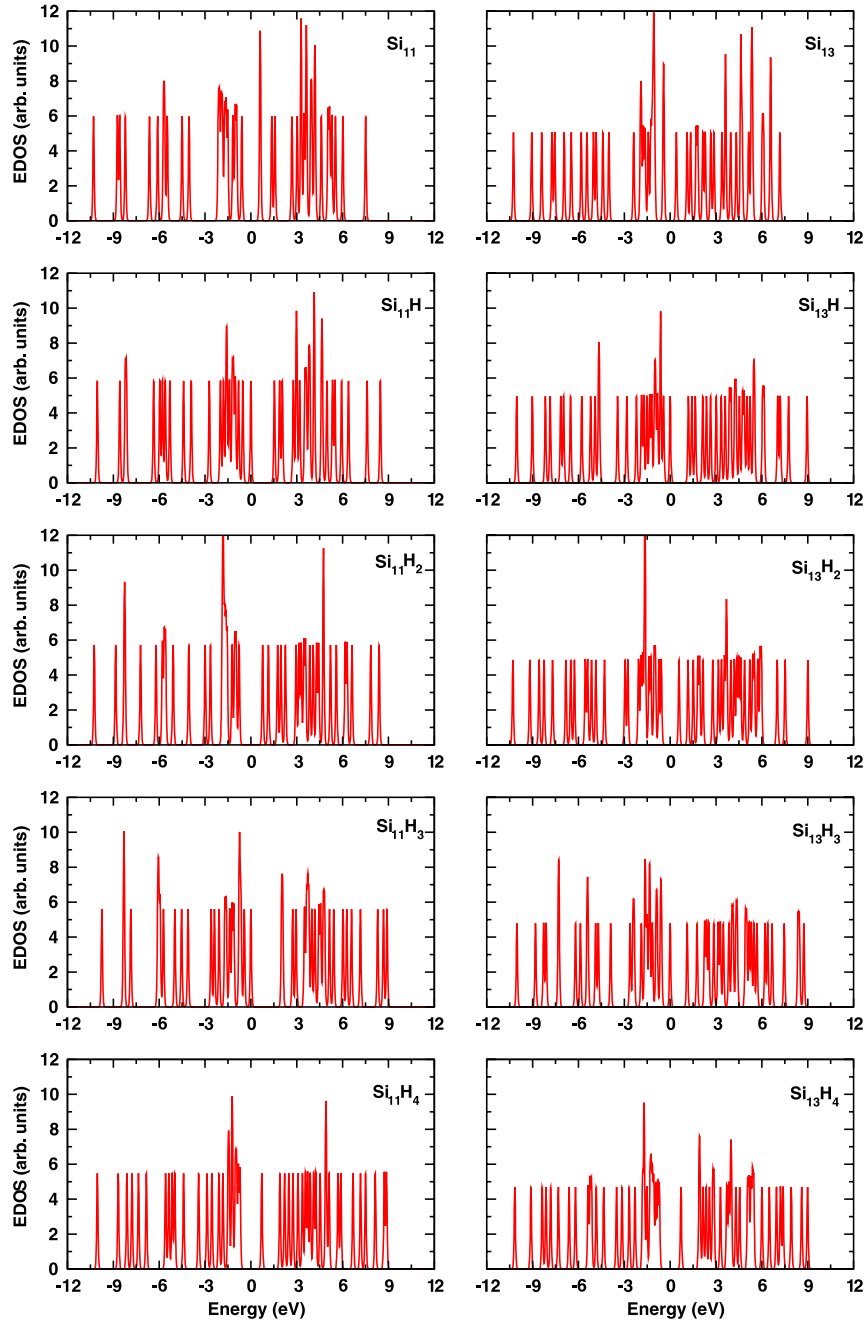


Figure 9. The VDOS and IR intensities of various vibrational modes in the clusters,  $\text{Si}_{15}\text{H}_m$  ( $m = 0-4$ ).

$$dE = E(\text{Si}_n\text{H}_m) - E(\text{Si}_n) - mE(\text{H}), \quad (1)$$

where  $E(\text{Si}_n)$  and  $E(\text{Si}_n\text{H}_m)$  are the total energies of the  $\text{Si}_n$  and  $\text{Si}_n\text{H}_m$  clusters, respectively, and  $mE(\text{H})$  is the total

energy of H atoms in the  $\text{Si}_n\text{H}_m$  cluster. The value of  $dE$  of each cluster is given in figure 4. The  $dE$  is a measure of distortion of the host  $\text{Si}_n$  silicon cluster from its ground state due to hydrogenation. The positive value of  $dE$  means that



**Figure 10.** The EDOS of  $\text{Si}_{11}\text{H}_m$  ( $m = 0-4$ ) and  $\text{Si}_{13}\text{H}_m$  ( $m = 0-4$ ).  $E = 0$  eV corresponds to the Fermi level.

the hydrogenated silicon cluster  $\text{Si}_n\text{H}_m$  is more stable than the bare  $\text{Si}_n$  cluster. The larger the value of  $dE$ , the more stable the corresponding hydrogenated silicon cluster. The negative value of  $dE$  for the  $\text{Si}_{14}\text{H}$  cluster means that  $\text{Si}_{14}\text{H}$  is less stable than the bare  $\text{Si}_{14}$  cluster. Figure 4 shows that the value of  $dE$  decreases non-monotonically with increasing number of Si atoms. However, for a given silicon cluster it increases non-monotonically with increasing amount of hydrogenation. Because of the large surface/volume ratio and unsaturated bonds on the cluster surface non-monotonic behaviour of  $dE$  is expected in small silicon clusters. Luo *et al* [68] pointed out that the electronic configuration of an atom and the number of atoms in the cluster can play a major role in its stability.

### 3.2. Vibrational properties

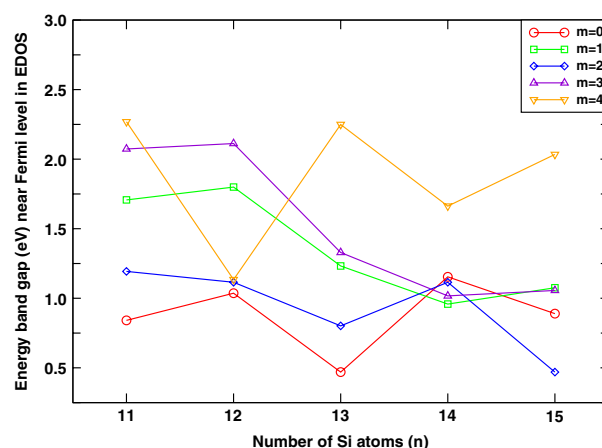
The calculation of vibrational spectra of small atomic clusters including VDOS, Raman and IR intensities provides unique spectral information on the chemical bonding, which can be used to determine the structures of these atomic clusters and to identify them in experiments. This approach has been successfully applied to determine the structures of silicon clusters up to seven atoms [37]. However, to our knowledge, no work has been reported on the vibrational spectra of hydrogenated silicon clusters with more than 10 atoms. Our calculated vibrational frequencies for  $\text{Si}-\text{H}_n$  ( $n = 1-4$ ) clusters, as given in table 1, are in quite good agreement

with the available theoretical [60, 61] and experimental results [62, 63] reported in the literature. We examined the vibrational properties of bare and hydrogenated silicon clusters ( $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 0-4$ ) by calculating VDOS and IR intensities of various vibrational modes of each cluster. The VDOS and IR spectra of various silicon clusters are shown in figures 5–9. Vibrational spectra of host silicon clusters are affected significantly by the addition of hydrogen. In bare silicon clusters, the Si–Si vibrational modes exist below  $500\text{ cm}^{-1}$ . The vibrational frequencies are quite comparable to those reported by Zhu *et al* [65, 66]. Hydrogen addition extends these modes above  $500\text{ cm}^{-1}$ . In a-Si:H the Si–Si bond vibrations are extended up to  $600\text{ cm}^{-1}$  [64]. The vibrational modes due to Si–H vibrations lie in the frequency range of  $600-900$  and  $1900-2200\text{ cm}^{-1}$ . There are mainly three types of Si–H vibrational mode: (i) wagging modes ( $600-700\text{ cm}^{-1}$ ), (ii) bending modes ( $800-900\text{ cm}^{-1}$ ) and (iii) stretching modes ( $2000-2200\text{ cm}^{-1}$ ) [69]. IR activity of Si–H bond vibrations is more pronounced compared to those of Si–Si bond vibrations. The IR spectra given in figures 5–9 are the predicted IR signatures for these clusters, which could be used to identify them in experiments.

### 3.3. Electronic properties

The optimized clusters of pure and hydrogenated silicon clusters with two and four hydrogen atoms are in the singlet state, while hydrogenated silicon clusters with one and three hydrogen atoms are in the doublet state. We investigated the electronic structure of the bare and hydrogenated silicon clusters by calculating the EDOS and energy band gap near the Fermi level in the EDOS for each silicon cluster. In figure 10 we display the EDOS of  $\text{Si}_{11}\text{H}_m$  and  $\text{Si}_{13}\text{H}_m$  ( $m = 0-4$ ) clusters. The energy  $E = 0.0\text{ eV}$  in these plots corresponds to the Fermi level energy of the corresponding clusters. Figure 10 shows that the EDOS in bare  $\text{Si}_n$  silicon clusters are extended up to  $-10.5\text{ eV}$  below the Fermi level and up to  $7.5\text{ eV}$  above the Fermi level. Addition of H atoms to  $\text{Si}_n$  silicon clusters extends the EDOS up to  $9.0\text{ eV}$  above the Fermi level, whereas it remained the same below the Fermi level. However, hydrogenation changed the shape of the EDOS significantly both below and above the Fermi level.

There exists a band gap near the Fermi level in the EDOS in all bare and hydrogenated silicon clusters. However, there are energy states at the Fermi level and in the gap in some clusters. The values of band gap for all clusters are given in figure 11. It is clear from figure 11 that the energy band gap is not simply related to the number of Si atoms and H atoms in a given cluster. Overall, the band gap of a silicon cluster depends on its size and amount of hydrogenation. Previous experimental [70] and theoretical [71, 72] calculations have also reported size dependent optical spectra of nanostructured silicon. This is an important electronic property of silicon clusters, which can be used to develop new Si devices having better optical properties by controlling the size and hydrogenation of silicon clusters.



**Figure 11.** The energy gap (eV) near the Fermi level in the EDOS in the optimized low energy structures,  $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 0-4$ . Energy states exist in the gap in some clusters.

## 4. Conclusions

The low energy structures of bare and hydrogenated silicon clusters ( $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 0-4$ ) are generated using simulated annealing and then the conjugate gradient optimization method based upon the DFTB approach within the LDA and self-consistent field. Hydrogen addition to a bare silicon cluster caused a drastic change in its structural geometry. While some clusters become highly symmetric, some others are completely distorted upon hydrogenation. Each H atom is bonded to only one Si atom and localized outside the silicon cluster skeleton. Hydrogen preferred to bond with either over-coordinated Si atoms or under-coordinated Si atoms. H atom bonding to an under-coordinated Si atom is due to the presence of a dangling bond in the under-coordinated Si atom. However, H bonding to an over-coordinated Si atom may be attributed to the higher electronegativity of a H atom compared to a Si atom. Hydrogenation caused a structural transition in silicon clusters: from a spherical to an elongated in  $\text{Si}_{11}$  and  $\text{Si}_{12}$ , from a one side capped elongated to a both side capped elongated in  $\text{Si}_{13}$  and  $\text{Si}_{14}$  and from a both side capped elongated to a one side capped elongated in  $\text{Si}_{15}$ .

We also examined vibrational spectra by calculating VDOS and IR intensities for the various vibrational modes and the electronic structure by calculating the EDOS of the optimized low energy structures. Hydrogenation caused a significant change in the vibrational spectra and in the electronic structure of bare silicon clusters  $\text{Si}_n$  ( $n = 11-15$ ). There exists a band gap near the Fermi level in the EDOS in all the bare and hydrogenated silicon clusters ( $\text{Si}_n\text{H}_m$ ;  $n = 11-15$ ,  $m = 0-4$ ). The band gap of a silicon cluster depends on its size and amount of hydrogenation.

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