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Electronic Structure of Optimized Si_mH_n Clusters: $MINDO3$ and $AM1$ Calculations

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Abstract

We have investigated the electronic structure of optimized hydrogenated silicon microclusters. Si_mH_n ($m = 2, 3, 5, 6$; $n = 4, 6$) have been investigated. The calculations were performed using both $MINDO3$ and $AM1$ semiempirical molecular orbital methods.

Keywords: Electronic structure, clusters, semiempirical methods.

Silicon hydride species of saturated and unsaturated types have been the subject of a remarkable number of investigations [1–9]. Silanes are widely used in the microelectronics industry for the production of silicon thin films and the mechanics of such deposition process involves silane chemistry. Much effort has been directed towards the understanding of silicon chemical vapor deposition process used in the microelectronics industry to produce hydrogenated amorphous silicon films. In these processes silane is often decomposed by electric discharge, producing to various degrees the species, Si, SiH, SiH_2, SiH_3, Si_mH_n ($m \geq 2$) and some SiH_n^+ type cations as well [1,2,6,7]. Photoionization mass spectrometric and direct current silane glow discharge studies of transient Si_2H_n ($n = 2 - 5$) have been reported [6,7]. On the other hand, thermochemical data on the Si_2H_n species are important for understanding and improving deposition processes [3].

Numerous theoretical studies have been performed on silanes and some other silicon derivatives [3,4,9–13] using different approaches, but unfortunately the results have shown a lack of uniformity [1]. For example, for SiH_3 different vibrational frequencies have been reported [14,15]. The previous studies on Si_mH_n clusters were limited as $m = 2$ and $n = 2$ to 6. In a recent work [9], the same systems, considered in the present work, were investigated through a tight–binding calculation without geometry optimization. In the

present work we performed the semiempirical molecular orbital geometry optimization methods using, namely, $MINDO3$ and $AM1$ methods.

In the present study, various silanes having $2-6$ silicon atoms (we will call these systems as hydrogenated silicon microclusters) have been subject to semiempirical geometry optimization methods. The emphasis has been given to those systems such that each silicon atom in the clusters has fourfold coordination. Thus the silicon atoms have nearly tetrahedral bonding environment. From this point of view the studies on Si_mH_n microclusters having $Si-H$ bonds play important roles in understanding the fundamental properties of the hydrogenated amorphous silicon ($a-Si:H$) films, which are important in thin film devices such as solar cells, photosensors, and FETs for display circuits. The hydrogenated silicon microclusters considered in the present work are Si_2H_6, Si_3H_6, Si_5H_4, Si_5H_6, and Si_6H_6.

In the calculations the geometry of the considered cluster is optimized and various energies are calculated. The calculated optimum geometries of the considered systems are shown in Figure 1. The corresponding electronic energy levels are depicted in Figure 2. The geometrical parameters are given in Tables 1 and 2, whereas the calculated energy values are tabulated in Tables 3 and 4. The calculated net charges on the atoms are given in Table 5.

Table 1. Optimized geometry of the clusters (distances in $\mathring{A}$, angles in degree).

Cluster	Quantity*	$MINDO3$	$AM1$
Si_2H_6	a	2.2935	2.4266
	b	1.4756	1.4663
	θ_1	112.89	109.63
	θ_2	105.84	109.31
	$tr(8-1-2-6)$	-60.0	-60.0
Si_3H_6	a	2.2992	2.4088
	b	1.4719	1.4648
	θ_1	60.0	60.0
	θ_2	120.46	118.97
	θ_3	108.32	111.99
	$tr(8-3-1-4)$	-140.29	-142.73
Si_5H_4	a	2.2503	2.3629
	b	2.5030	2.3948
	c	1.4665	1.4525
	θ_1	90.0	90.0
	θ_2	63.29	60.44
	θ_3	53.42	59.12
	θ_4	134.89	134.89
	θ_5	126.02	137.74
	θ_6	78.96	88.49

(*) a, b's are bond lengths; θ_i's are bond angles; tr's are torsion angles.

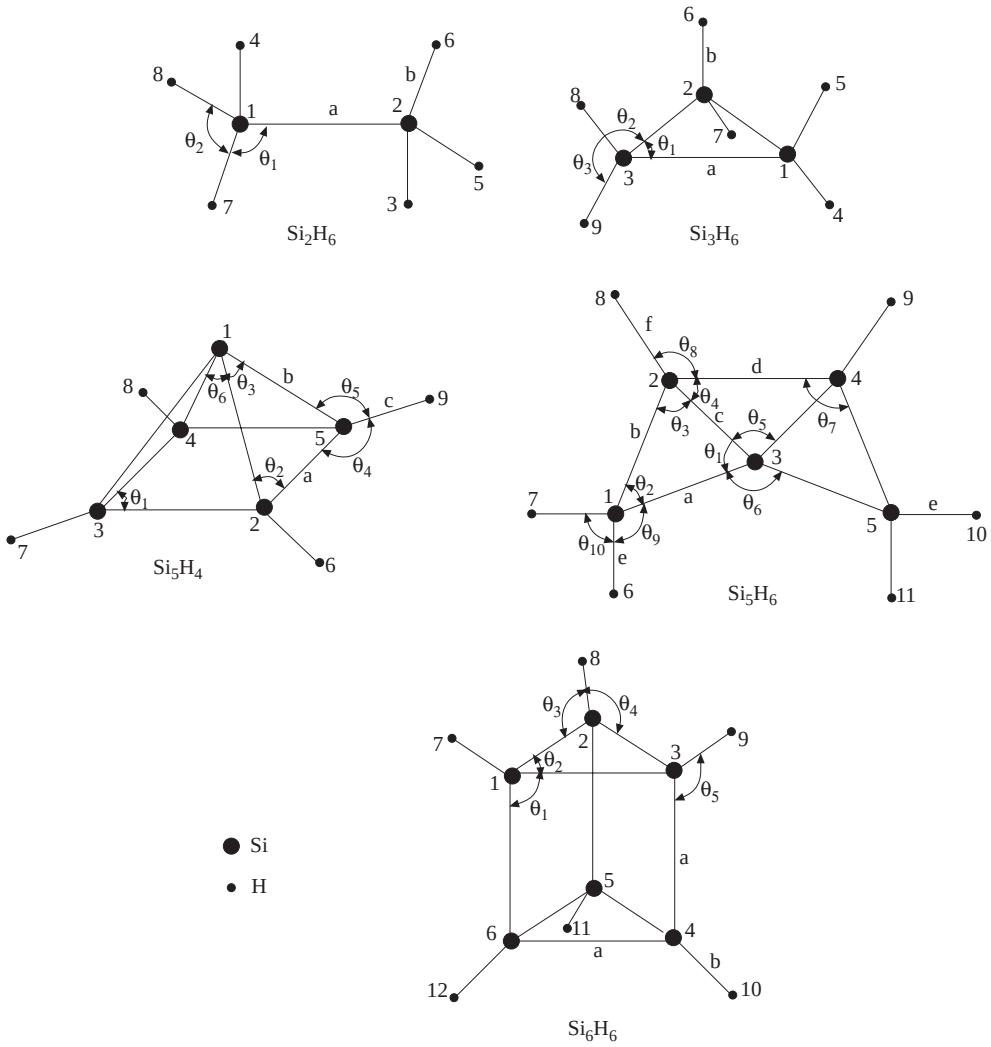

Figure 1. Geometry of the optimized Si_mH_n clusters.

Ho et al. [3] in their Hartree–Fock type electronic structure calculations obtained the value of 19.1 kcal/mol for the heat of formation of a Si_2H_6 cluster. Ruscic and Berkowitz [6] in their photoionization mass spectrometric study reported the value of 22.9 kcal/mol for the heat of formation of Si_2H_6 clusters. The values of the heat of formation for Si_2H_6 in both of the theoretical calculations, the present calculation and other calculation [3], are smaller than that of the experimentally predicted value [6]. Using the Gaussian–2 ab-initio MO calculation Curtiss et al. [11] obtained the optimized parameters for the geometry of Si_2H_6 as $r(Si-Si) = 2.335$ $\mathring{A}$, $r(Si-H) = 1.487$ $\mathring{A}$, and

$\theta(Si-Si-H) = 110.4$ degrees. To the best of our knowledge, no other data is available in the literature for the other hydogenated silicon clusters considered in the present work.

Table 2. Optimized geometry of the clusters (distances in $\mathring{A}$, angles in degree).

Cluster	Quantity*	$MINDO3$	$AM1$
Si_5H_6	a	2.3562	2.3473
	b	2.2931	2.3788
	c	2.7161	2.4448
	d	2.1531	2.2931
	e	1.4806	1.4615
	f	1.4824	1.4569
	θ_1	53.18	59.48
	θ_2	71.48	62.30
	θ_3	55.34	58.21
	θ_4	66.65	62.03
	θ_5	46.70	55.93
	θ_6	106.53	105.15
	θ_7	110.73	107.58
	θ_8	120.62	124.72
	θ_9	126.26	114.91
	θ_{10}	104.49	112.24
	$tr(10-5-4-9)$	-3.49	13.20
	$tr(11-5-4-9)$	-124.33	-127.68
Si_6H_6	a	2.3603	2.4096
	b	1.4793	1.4600
	θ_1	90.0	90.0
	θ_2	60.0	60.0
	θ_3	130.81	132.47
	θ_4	130.81	132.47
	θ_5	131.0	128.76

(*) Same as Table 1.

In the present calculations the total energy, isolated atomic energy, electronic energy, and core–core interaction energy values calculated by $MINDO3$, for all the models considered, are relatively lower than that of the values calculated by $AM1$. However, binding energy and heat of formation values do not show such a trend, their relative magnitudes vary from cluster to cluster. On the other hand, the net charge on the atoms, calculated by $AM1$ method, are larger in magnitude than that of the values calculated by $MINDO3$.

The results of the present study may be usefull in the thermochemical analysis of larger Si_mH_n clusters.

Table 3. Calculated energies (in kcal/mol).

Cluster	Quantity*	$MINDO3$	$AM1$
Si_2H_6	(I)	-6433.448	-5733.872
	(II)	-507.001	-513.323
	(III)	-5926.446	-5220.549
	(IV)	-16242.204	-15758.692
	(V)	9808.757	10024.819
	(VI)	17.611	16.069
Si_3H_6	(I)	-8599.982	-7632.250
	(II)	-575.446	-589.836
	(III)	-8024.536	-7042.414
	(IV)	-24046.811	-23409.288
	(V)	15446.829	15777.038
	(VI)	55.166	47.946
Si_5H_4	(I)	-12245.417	-10754.063
	(II)	-601.457	-593.525
	(III)	-11643.960	-10160.538
	(IV)	-38068.859	-37688.735
	(V)	25823.442	26934.672
	(VI)	136.951	156.833

(*) (I): Total energy, (II): Binding energy, (III): Isolated atomic energy, (IV): Electronic energy, (V): Core–core interaction, (VI): Heat of formation.

Table 4. Calculated energies (in kcal/mol).

Cluster	Quantity*	$MINDO3$	$AM1$
Si_5H_6	(I)	-12955.623	-11406.301
	(II)	-734.907	-720.156
	(III)	-12220.716	-10686.145
	(IV)	-42401.163	-42269.445
	(V)	29445.540	30863.144
	(VI)	107.705	134.406
Si_6H_6	(I)	-15111.667	-13357.296
	(II)	-792.862	-849.287
	(III)	-14318.806	-12508.010
	(IV)	-54406.560	-54018.876
	(V)	39294.893	40661.579
	(VI)	155.750	113.665

(*) Same as Table 3.

Table 5. Calculated net charges on atoms (in units of electron charge e).

Cluster	Atom	$MINDO3$	$AM1$
Si_2H_6	Si	0.0783	0.3498
	H	-0.0261	-0.1166
Si_3H_6	Si	0.0114	0.1558
	H	-0.0057	-0.0779
Si_5H_4	$Si(1)$	-0.0135	-0.8919
	$Si(2) - Si(5)$	-0.0123	0.2937
	H	0.0157	-0.0707
Si_5H_6	$Si(1), Si(5)$	0.0108	0.5466
	$Si(2), Si(4)$	0.0460	0.2428
	$Si(3)$	0.0343	-0.9713
	$H(6), H(11)$	-0.0265	-0.1077
	$H(7), H(10)$	-0.0217	-0.1133
	$H(8), H(9)$	-0.0257	-0.0828
Si_6H_6	Si	0.0240	0.0433
	H	-0.0240	-0.0433

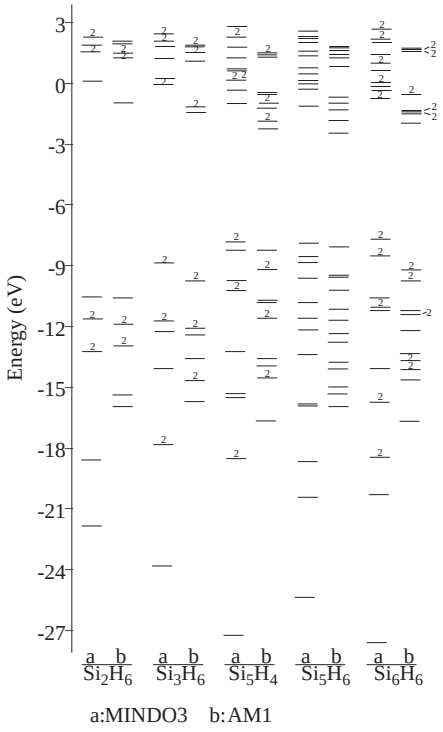

Figure 2. Relative electronic energy levels of the optimized Si_mH_n clusters. Numbers on some of the levels show the degeneracy of the corresponding level.

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