TABLE 1: Geometry[a] (R (Å), ϕ(degrees)), Net Charges q, and Binding Energies BE(eV) and Corrected Values for BSSE BE_{BSSE}(eV) of the **a**, **b**, **c** and **d** Structures of M-Si(111), M = B, Al, Ga, and In, at the Early Stage of Adsorption, at B3LYP/DGDZVP Level of Theory.

Structures	R_1	R_2	f	q_1	q_2	q_3	**BE(BE$_{BSSE}$)**	**BE(BE$_{BSSE}$)**[b]
Si(111)					+0.22	+0.08		
a-B	1.97	2.07	80	-0.24	+0.27	+0.08	2.89(2.85)	[c]
a-Al	2.52	2.84	58	+0.64	-0.25	+0.06	2.26(2.23)	2.22(2.20)
a-Ga	2.55	2.91	56	+0.59	-0.21	+0.06	2.16(2.13)	2.19(2.14)
a-In	2.75	3.24	50	+0.75	-0.32	+0.06	1.70(1.63)	1.65(1.61)
b-B	1.95	1.99	150	-0.20	+0.17	-0.02	2.85(2.80)	3.08(3.04)
b-Al	2.62	2.71	113	+0.84	-0.23	-0.41	2.24(2.21)	2.18(2.13)
b-Ga[d]	2.93	2.77	102	+0.71	-0.09	-0.43	2.05(1.99)[e]	[f]
b′-Ga[d]	3.07	2.67	102	+0.69	-0.02	-0.49	2.15(2.09)[e]	[f]
b-In	3.01	2.86	99	+0.79	-0.13	-0.49	2.15(2.06)[e]	[f]
c-B		2.10	111	+0.16	+0.22	-0.27	2.33(2.31)	2.36(2.30)
c-Al		2.61	128	+0.68	+0.11	-0.62	2.23(2.20)	2.33(2.26)
c-Ga		2.62	122	+0.63	+0.20	-0.57	2.15(2.10)	2.19(2.09)
c-In		2.88	138	+0.72	-0.04	-0.57	1.99(1.91)	2.15(1.93)
d-B	2.08		138	+0.16	-0.14	+0.08	2.20(2.18)	[c]
d-Al	2.57		141[g]	+0.68	-0.49	+0.06	1.77(1.75)	2.16(2.13)
d-Ga	2.58		141	+0.65	-0.42	+0.06	1.72(1.69)	1.69(1.66)
d-In	2.77		133	+0.71	-0.50	+0.06	1.77(1.71)	1.66(1.64)

[a] The energy optimization was done with respect to coordinates of M, Si-adatom and Si-rest atom.

[b] B3LYP/LANL2DZ.

[c] The structure is not stable and it changes over to e-B-Si(111) cluster.

[d] Equivalent, nearly identical structures.

[e] The $BE(BE_{BSSE})$ = 2.14(2.08) eV for b-Ga; 2.24(2.18) for b′-Ga; 2.24(2.15) for b-In when the energy optimization was done with respect to coordinates of seven atoms of the M-Si(111) structures; i.e., (1,2,3,4,5,9,10), see Figure 1.

[f] The structure is not stable and it changes over to c-M-Si(111) cluster.

[g] The angle ϕ can change from 128 to 141 degrees without significant change in energy.

TABLE 2: Binding Energies BE(eV) and Corrected Values for BSSE BE_{BSSE}(eV) of the **a**, **b**, **e**, **f**, **g** and **h** Structures of M-Si(111), M = B, Al, Ga, and In, for Different Optimization Procedures at B3LYP/ DGDZVP Level of Theory.

Structures	**BE(BE_{BSSE})**	**BE(BE_{BSSE})**	**BE(BE_{BSSE})**	**BE(BE_{BSSE})**
	1,2,3[a]	1,2,4[a]	1,2,4,5,6[a]	1,2,4,5,6,7[a]
a-B	2.89(2.85)	2.96(2.92)	3.05(3.01)	3.24(3.21)
a-Al	2.26(2.23)	2.31(2.28)	2.33(2.31)	2.53(2.51)
a-Ga	2.16(2.13)	2.21(2.17)	2.28(2.24)	2.40(2.36)
a-In	1.70(1.63)	2.04(1.96)	2.11(2.02)	2.26(2.19)
	1,2,3[a]			1,2,3,4,5,9,10[a]
b-Ga[b]	2.05(1.99)			2.14(2.08)
b-Ga[b]	2.15(2.09)			2.24(2.18)
b-In	2.15(2.06)			2.24(2.15)
	1,2,3[a]		1,2,4,5,6[a]	1,2,4,5,6,7[a]
e-B	4.34(4.27)		4.37(4.30)	4.48(4.40)
e-Al	2.05(2.01)		2.19(2.15)	2.48(2.40)
e-Ga	1.60(1.51)		1.71(1.65)	1.99(1.91)
e-In	1.09(1.06)		1.25(1.24)	1.63(1.62)
	1,3[a]		1,4,5,6,7[a]	1,3,4,5,6,7[a]
f-B(T_4)	4.88(4.83)		5.14(5.12)	5.14(5.12)
f-Al	3.08(3.04)		3.47(3.43)	3.47(3.43)
f-Ga	2.54(2.53)		2.91(2.90)	2.91(2.90)
f-In	2.05(2.00)		2.58(2.51)	2.61(2.54)
			1,3,4,5[a]	1,3,4,5,6,7[a]
g-B(H_3)			c	c
g-Al			2.15(2.09)	2.67(2.61)
g-Ga			1.73(1.70)	2.24(2.21)
g-In			1.64(1.51)	2.20(2.05)
			1,2,4,5,6[a]	1,2,4,5,6,8[a]
h-B(S_5)			5.76(5.64)	6.37(6.26)
h-Al			2.39(2.29)	2.39(2.30)
h-Ga			2.02(1.83)	2.03(1.83)
h-In			0.36(0.03)	0.52(0.19)

[a] The atoms whose the coordinates were energetically optimized, see Fig. 1.

[b] Equivalent, nearly identical structures.

[c] The g-B(H_3) is not stable and its optimization leads to f-B(T_4).

TABLE 3: Geometry[a] (R (Å), ϕ(degrees)), and Net Charges q of M or Si Atoms of the **a**, **e**, **f**, **g**, and **h** Structures of M-Si(111), M = B, Al, Ga, and In at B3LYP/DGDZVP Level of Theory.

	Si(111)	B-Si(111)	Al-Si(111)	Ga-Si(111)	In-Si(111)
			a		
R(1-2)		1.95	2.54	2.57	2.76
R(1-4)		2.02	2.79	2.85	3.05
R(2-4)	2.44	2.87	2.67	2.68	2.70
R(2-5)	2.44	2.39	2.48	2.49	2.48
R(9-4)	2.39	2.39	2.43	2.43	2.43
R(4-7)	2.39	2.40	2.38	2.38	2.37
R(5-7)	2.39	2.38	2.34	2.34	2.34
R(2-6)	2.47	2.45	2.47	2.48	2.49
R(7-6)	2.38	2.37	2.34	2.34	2.34
R(2-7)	2.70	2.63	2.70	2.71	2.73
R(7-8)	2.18	2.36	2.32	2.33	2.33
f **(4-1-2)**		93	60	59	55
f **(4-2-5)**	90	91	90	90	89
f **(4-7-5)**	93	104	101	101	101
f **(7-2-6)**	55	55	54	53	53
f **(8-7-6)**	122	115	118	118	118
q_1		-0.24	+0.62	+0.57	+0.69
q_2	+0.22	+0.27	-0.19	-0.16	-0.23
q_3	+0.08	+0.08	+0.06	+0.06	+0.06
q_4	-0.09	+0.03	-0.35	-0.33	-0.37
q_5	-0.09	-0.05	-0.06	-0.08	-0.08
q_6	-0.09	-0.07	-0.10	-0.10	-0.10
q_7	-0.17	-0.19	-0.15	-0.16	-0.15
			e		
R(1-4)	2.44	2.16	2.53	2.55	2.74
R(10-4)	2.39	2.43	2.40	2.40	2.40
R(1-2)		1.94	2.44	2.41	2.63
R(2-6)		2.44	2.41	2.41	2.40
R(7-6)	2.38	2.38	2.42	2.41	2.42
R(4-7)	2.39	2.33	2.36	2.35	2.36
R(7-8)	2.18	2.28	2.38	2.38	2.41
R(1-7)	2.70	2.29	2.73	2.78	3.00
f **(4-1-5)**	90	109	94	92	86
f **(4-7-5)**	93	98	104	103	105
f **(1-2-6)**		70	72	74	75
f **(8-7-6)**	122	119	115	115	114
f **(7-1-2)**		123	105	103	96
q_1		-0.96	+0.62	+0.37	+0.67
q_2	+0.22	+0.58	+0.15	+0.21	+0.12
q_3	+0.08	+0.07	+0.07	+0.08	+0.07
$q_{4,5}$	-0.09	+0.16	-0.26	-0.19	-0.28

q_6	-0.09	-0.08	-0.29	-0.24	-0.29
q_7	-0.17	-0.08	-0.20	-0.23	-0.23
			f(T_4)		
R(1-4)	2.44	2.10	2.50	2.52	2.71
R(4-9)	2.39	2.48	2.42	2.42	2.40
R(4-7)	2.39	2.35	2.38	2.37	2.38
R(1-7)	2.70	2.05	2.54	2.57	2.81
R(1-6)	2.47	2.05	2.47	2.48	2.69
R(7-6)	2.38	2.42	2.41	2.40	2.40
R(7-8)	2.18	2.23	2.35	2.35	2.40
R(3-10)	2.38	2.38	2.38	2.38	2.38
f **(4-1-5)**	90	113	96	95	88
f **(4-7-5)**	93	97	102	102	104
f **(8-7-6)**	122	119	117	117	115
f **(7-1-6)**	55	72	57	57	52
f **(10-3-9)**	110	110	110	110	110
q_1	+0.22	-0.76	+0.78	+0.55	+0.83
q_3	+0.08	+0.08	+0.08	+0.08	+0.08
$q_{4,5}$	-0.09	+0.18	-0.26	-0.18	-0.27
q_6	-0.09	+0.21	-0.28	-0.20	-0.29
q_7	-0.17	-0.06	-0.27	-0.26	-0.29
				g(H_3)	
R(1-3)			2.70	2.80	2.91
R(1-4)			2.53	2.58	2.75
R(4-7)	2.39		2.36	2.35	2.36
R(6-7)	2.38		2.35	2.35	2.35
R(3-11)	2.37		2.51	2.50	2.47
R(3-9)	2.38		2.39	2.38	2.40
R(7-8)	2.18		2.47	2.47	2.49
R(4-9)	2.39		2.38	2.37	2.38
f **(3-1-5)**			94	91	87
f **(4-1-5)**			97	94	88
f **(4-7-5)**	93		106	107	108
f **(9-3-10)**	110		110	110	109
f **(8-7-6)**	122		111	111	111
q_1			+0.88	+0.69	+0.91
q_3	+0.08		-0.33	-0.25	-0.31
$q_{4,5}$	-0.09		-0.35	-0.27	-0.33
q_6	-0.09		+0.09	+0.09	+0.09
q_7	-0.17		-0.23	-0.24	-0.25
			h(S_5)		
R(2-4)	2.44	2.37	2.43	2.44	2.44
R(1-2)	2.70	2.22	2.41	2.41	2.57
R(1-4)	2.39	2.09	2.44	2.42	2.62
R(1-8)	2.18	2.04	2.32	2.28	2.46
R(1-6)	2.38	2.13	2.51	2.52	2.68
R(9-4)	2.39	2.43	2.41	2.41	2.42
R(2-6)	2.47	2.34	2.39	2.39	2.45
f **(4-2-5)**	90	93	102	101	104

f **(4-1-5)**	93	110	101	103	94
f **(8-1-6)**	122	110	119	115	127
f **(1-2-6)**	55	56	63	63	65
$\mathbf{q_1}$	-0.17	-1.46	+0.84	+0.44	+0.94
$\mathbf{q_2}$	+0.22	+0.30	+0.09	+0.11	+0.04
$\mathbf{q_3}$	+0.08	+0.08	+0.09	+0.08	+0.09
$\mathbf{q_{4,5}}$	-0.09	+0.21	-0.32	-0.24	-0.32
$\mathbf{q_6}$	-0.09	+0.18	-0.25	-0.21	-0.31
$\mathbf{q_8}$	-0.20	+0.18	-0.49	-0.35	-0.36

[a] The energy optimization was done with respect to coordinates of six atoms of the M-Si(111) structures; i.e., **a** and **e** (1,2,4,5,6,7); **f** and **g** (1,3,4,5,6,7); **h** (1,2,4,5,6,8).

TABLE 4: Energy Barriers EB(eV) and Corrected Values for BSSE EB_{BSSE}(eV) for the Transitions **a** → **e** and **g**(H_3) → **f**(T_4) of M-Si(111), M = B, Al, Ga, and In at B3LYP/ DGDZVP Level of Theory.

Structure	**Energy Barrier EB(EB_{BSSE})[a]**	**Energy Barrier EB(EB_{BSSE})[a]**
	a → **i**	**i** ← **e**
B-Si(111)	0.49(0.49)	1.71(1.67)
Al-Si(111)	1.63(1.63)	1.58(1.53)
Ga-Si(111)	1.69(1.75)	1.28(1.30)
In-Si(111)	1.85(1.87)	1.21(1.30)
	f(T_4) → **j**	**j** ← **g**(H_3)
B-Si(111)[b]		
Al-Si(111)	1.21(1.25)	0.41(0.44)
Ga-Si(111)	1.06(1.10)	0.39(0.40)
In-Si(111)	0.66(0.67)	0.25(0.20)

[a] The energy optimization was done with respect to the coordinates of six atoms of the M-Si(111) structures; i.e., **a** and **e** (1,2,4,5,6,7); **f** and **g** (1,3,4,5,6,7).

[b] Optimization of the g-B (H_3) leads to f-B (T_4).