

Structure and Binding of Neutral and Charged  $\text{Si}_n\text{H}_2\text{O}$  ( $n = 1, 2, 7$ ) Clusters

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Received: April 4, 1997; In Final Form: May 8, 1997<sup>Ⓢ</sup>

The interaction of a water molecule with Si,  $\text{Si}_2$ , and  $\text{Si}_7$  clusters is studied using local-spin-density (LSD) functional theory, with and without exchange-correlation gradient corrections. Water binds to a Si atom in a triplet state, with a binding energy of 0.704 eV, while it does not bind stably to  $\text{Si}_2$ , forming a metastable singlet state  $\text{Si-Si-OH}_2$  cluster, whose dissociation into  $\text{Si}_2 + \text{H}_2\text{O}$  involves a barrier. Water binds weakly to  $\text{Si}_7$ . Binding in the ionized species is much stronger. In all cases binding is through formation of a Si-O bond, with a partial donation of charge from the oxygen, accompanied by the development of a large dipole moment.

## 1. Introduction

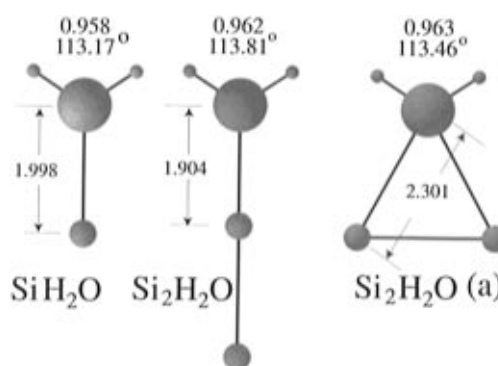
The geometries, electronic structure, energetics, and reactivity of small silicon clusters have been the subject of increasing theoretical and experimental research efforts.<sup>1</sup> These studies include investigations of bare  $\text{Si}_n$  clusters, whose structures and properties are found to be different from those of the bulk material, as well as binding of atoms to such clusters (see e.g. recent investigations of  $\text{Si}_n\text{Na}$ ,  $n \leq 10$ , clusters<sup>2</sup>).

In this Letter we report on local-spin-density (LSD) functional calculations, with and without exchange-correlation gradient corrections (xcg), of the binding of a water molecule to Si,  $\text{Si}_2$ , and  $\text{Si}_7$  clusters ( $\text{Si}_7$  was chosen because in the range of cluster size with up to 10 atoms, it exhibits the lowest electron affinity and binding energy<sup>3</sup> to Na). Our study shows that at the LSD-xcg level  $\text{H}_2\text{O}$  binds to a Si atom with a binding energy  $E_b = 0.704$  eV, while it does not bind stably to  $\text{Si}_2$  (forming a metastable  $\text{Si}_2\text{H}_2\text{O}$  cluster, whose dissociation into  $\text{Si}_2 + \text{H}_2\text{O}$  with an exothermicity of 0.18 eV involves an activation barrier). Water binds very weakly ( $E_b = 0.025$  eV) to  $\text{Si}_7$ . On the other hand, binding in the ionized species, *i.e.*  $(\text{SiH}_2\text{O})^+$ ,  $(\text{Si}_2\text{H}_2\text{O})^+$ , and  $(\text{Si}_7\text{H}_2\text{O})^+$ , is much stronger, *i.e.* 2.606, 0.879, and 0.118 eV, respectively. In all cases binding is via formation of a Si-O bond, with partial charge donation from the oxygen atom leading to the development of significant dipole moments.

## 2. Method

In calculations of the total energies and structural optimizations, we have used the Born–Oppenheimer (BO) local-spin-density (LSD) functional molecular dynamics (MD), (BO-LSD-MD) method,<sup>4</sup> where the motion of the ions is confined to the ground state BO electronic potential energy surface calculated concurrently via the Kohn–Sham (KS)-LSD method. In these calculations we have employed nonlocal norm-conserving pseudopotentials<sup>5</sup> for the valence electrons of the silicon and oxygen atoms (s, p, and d components for Si and s, p for O), and a local pseudopotential was used for the hydrogens.<sup>4</sup>

As discussed in detail elsewhere,<sup>4</sup> in our method, no supercells (*i.e.*, periodic replica of the ionic system) are used, thus allowing studies of charged and multipolar clusters in an accurate and straightforward manner. In structural optimizations, using a conjugate gradient method, and in dynamical simulations, the Hellmann–Feynman forces on the ions are evaluated between each optimization or MD step, involving iterative solution of



**Figure 1.** Geometries for neutral  $\text{SiH}_2\text{O}$  and  $\text{Si}_2\text{H}_2\text{O}$  clusters. For  $\text{Si}_2\text{H}_2\text{O}$  the ground state and a higher energy isomer (denoted as  $\text{Si}_2\text{H}_2\text{O}$  (a)) are shown. The energy of the isomer is 0.025 eV higher at the xcg level (0.038 eV at LSD level). The Si–O and O–H bond lengths and the  $\angle(\text{HOH})$  angles are indicated.

the KS-LSD equations. This ensures that the ionic trajectories are followed on the BO potential energy surface. Both LSD calculations and calculations including exchange<sup>6</sup>-correlation<sup>7</sup> gradient corrections (xcg) have been performed (the xcg calculations were performed in the post-LSD mode, PLSD; *i.e.*, the gradient corrections were evaluated using the charge densities and optimized geometries obtained via the LSD calculations). A plane-wave cutoff of 62 Ry was employed in the calculations. The pseudopotentials<sup>5</sup> core radii,  $r_c$ , are  $r_c^{\text{s,p,d}}(\text{Si}) = 2.10a_0$ ,  $r_c^{\text{s}}(\text{H}) = 0.95a_0$ , and  $r_c^{\text{s,p,d}}(\text{O}) = 1.45a_0$ , where s, p, d denote the angular momentum components. For both Si and O the highest angular momentum component of the pseudopotential is chosen as the local part.

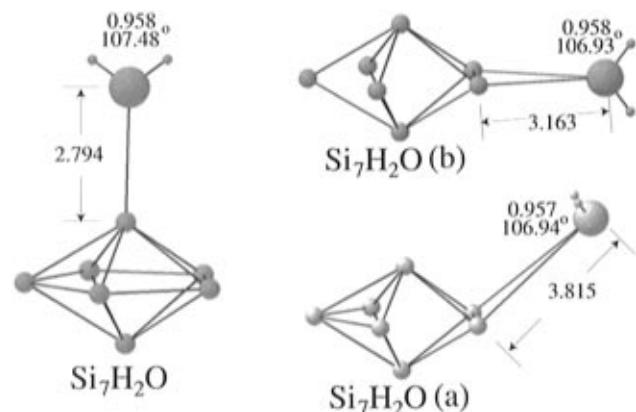
## 3. Results

The optimal structures of  $\text{SiH}_2\text{O}$ ,  $\text{Si}_2\text{H}_2\text{O}$ , and  $\text{Si}_7\text{H}_2\text{O}$  (for the dimer and heptamer clusters higher energy isomers are also shown) are displayed in Figures 1 and 2, and the corresponding geometrical parameters are given in Table 1. The main result is that in the optimal binding geometries the  $\text{H}_2\text{O}$  molecule binds through formation of a Si–O bond which lies in the plane of the  $\text{H}_2\text{O}$  molecule; the bridge binding geometries (see  $\text{Si}_2\text{H}_2\text{O}$  (a) in Figure 1 and also  $\text{Si}_7\text{H}_2\text{O}$  (a, b) in Figure 2) are less stable (see also Table 2). The Si–O bond lengths in the ground-state  $\text{SiH}_2\text{O}$ ,  $\text{Si}_2\text{H}_2\text{O}$ , and  $\text{Si}_7\text{H}_2\text{O}$  are 1.998, 1.904, and 2.794 Å compared to 1.479 Å of the double bond in SiO (the experimental value<sup>8</sup> is 1.510 Å), and the Si–Si bond in  $\text{Si}_2\text{H}_2\text{O}$  is

<sup>Ⓢ</sup> Abstract published in *Advance ACS Abstracts*, June 15, 1997.

**TABLE 1: Bond Lengths (Å) and Bond Angles  $\theta = \angle(\text{H}-\text{O}-\text{H})$  (deg), in  $\text{Si}_n\text{H}_2\text{O}$ ,  $n = 0, 1, 2$ , and 7**

$\text{Si}_n\text{H}_2\text{O}/n =$	0	1	2	2a	7	7a	7b
$r_{\text{Si}-\text{O}}$		1.998	1.904	2.301	2.794	3.815	3.163
$r_{\text{O}-\text{H}}$	0.954	0.958	0.962	0.963	0.958	0.957	0.958
$\theta$	105.993	113.166	113.809	113.464	107.475	106.936	106.926



**Figure 2.** Geometries for neutral  $\text{Si}_7\text{H}_2\text{O}$  clusters. In addition to the ground state, two isomers are shown denoted as (a) and (b). The energy of the a isomer is higher than that of the ground-state configuration (xcg) by 0.057 eV (0.013 eV using LSD), and that of the b isomer is higher (xcg) by 0.144 eV (0.138 eV using LSD). The Si-O and O-H bond lengths and the  $\angle(\text{HOH})$  angles are indicated.

**TABLE 2: Energy Difference,  $\Delta_{\text{st}}$  (eV), between Singlet and Triplet States, Calculated as the Difference between the Total Ground-State Energies of the Two States<sup>a</sup>**

$\text{Si}_n/n =$	1	2
$\Delta_{\text{st}}(\text{LSD})$	0.717	0.459
$\Delta_{\text{st}}(\text{xcg})$	0.809	0.568
exp	0.781 <sup>b</sup>	

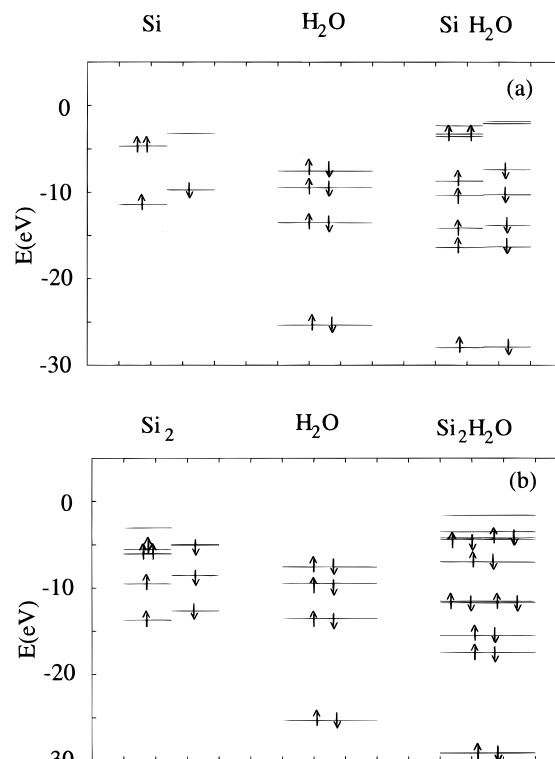
$\text{Si}_n\text{H}_2\text{O}/n =$	1	2
$\Delta_{\text{st}}(\text{LSD})$	0.667	-0.179
$\Delta_{\text{st}}(\text{xcg})$	0.841	-0.010

<sup>a</sup> A positive value corresponds to a triplet ground state and a negative one when the ground state is a singlet. <sup>b</sup> Reference 9.

2.049 Å compared to 2.128 Å in  $\text{Si}_2$ , where the experimental value<sup>8</sup> is 2.245 Å.

Both the Si atom and the bare  $\text{Si}_2$  cluster are in a triplet ground-state configuration (see Figure 3, where the KS-LSD energy levels are shown, and Table 2). The singlet to triplet splitting is equal to  $\Delta_{\text{st}} = 0.809$  for Si (compared to a measured value<sup>9</sup> of 0.781 eV) and  $\Delta_{\text{st}} = 0.568$  eV for  $\text{Si}_2$ ; all other neutral  $\text{Si}_n$  with  $n \geq 3$  clusters are in a singlet ground electronic state.<sup>1</sup> Interestingly,  $\text{SiH}_2\text{O}$  remains in the triplet configuration (see LSD Kohn-Sham levels in Figure 3a), which is energetically preferred over the singlet state by 0.841 eV. On the other hand, the (thermodynamically metastable)  $\text{Si}_2\text{H}_2\text{O}$  cluster is in the singlet configuration (see Figure 3b) with the triplet state energy higher by 0.010 eV (see Table 2). Additionally, the bonding of  $\text{H}_2\text{O}$  to the silicon atom and clusters involves donation of partial charge from the oxygen to the silicon, creating significant dipole moments (see Table 3), with the dipole (in the ground-state configurations) directed along the Si-O bond and lying in the plane of the  $\text{H}_2\text{O}$  molecule. In this context we note that the vertical and adiabatic ionization potentials (vIP and aIP, see Table 4) of Si and  $\text{Si}_2$  are lowered markedly upon binding to  $\text{H}_2\text{O}$ , and to a lesser extent for the  $\text{Si}_7$  cluster. In all these clusters the small values of the reorganization energy,  $E_{\text{R}} = \text{vIP} - \text{aIP}$ , reflect rather small structural changes as the ionized clusters relax to their optimal ground-state geometries.

As seen from Table 4, the  $\text{H}_2\text{O}$  molecule binds rather strongly



**Figure 3.** LSD Kohn-Sham levels (in unit of electronvolts). In (a) those for Si,  $\text{H}_2\text{O}$ , and  $\text{SiH}_2\text{O}$  are shown, and in (b) we display those for  $\text{Si}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{Si}_2\text{H}_2\text{O}$ . In each case the spin up (left) and down (right) levels and their occupations are shown (cases where they are degenerate are indicated by a longer horizontal line). Note that Si and  $\text{Si}_2$  are both in a triplet state, while  $\text{SiH}_2\text{O}$  is in a triplet state and  $\text{Si}_2\text{H}_2\text{O}$  is a singlet.

to a single Si atom ( $E_{\text{b}} = 0.704$  eV). The binding is much weaker to the dimer and heptamer, where for the latter  $E_{\text{b}} = 0.025$  eV. For  $\text{Si}_2\text{H}_2\text{O}$  we find a metastable state, where the LSD-xcg calculations indicate exothermic dissociation into  $\text{Si}_2 + \text{H}_2\text{O}$  (with a release of 0.181 eV for the more stable isomer of  $\text{Si}_2\text{H}_2\text{O}$ ), in a process which involves an activation barrier. On the other hand, the binding energies increase significantly in the ionized  $\text{Si}_n\text{H}_2\text{O}^+$  clusters, which are all well bound. The favorable (endothermic) dissociation channel for the ionized clusters is  $\text{Si}_n\text{H}_2\text{O}^+ \rightarrow \text{Si}_n^+ + \text{H}_2\text{O}$  (see  $E_{\text{b}+}$  in Table 4), rather than  $\text{Si}_n\text{H}_2\text{O}^+ \rightarrow \text{Si}_n + \text{H}_2\text{O}^+$  (see  $E_{+b}$  in Table 4).

Finally, several other reactions are worth commenting on: (i) the exothermicity of the dissociation reaction,  $\text{SiH}_2\text{O} \rightarrow \text{SiO} + \text{H}_2$ , is calculated at the xcg level to be 2.548 eV (compared to 2.230 eV using LSD), and that of  $\text{Si} + \text{H}_2\text{O} \rightarrow \text{SiO} + \text{H}_2$  is 3.252 eV at the xcg level (3.179 eV using LSD), compared to a derived experimental value<sup>10,11</sup> of 3.154 eV; (ii) the exothermicity of the reaction  $\text{Si}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{SiO} + 2\text{H}_2$  is 0.103 eV calculated at the xcg level (0.085 eV using LSD), compared with a derived experimental value<sup>10,11</sup> of 0.108 eV; (iii) the reaction of a silicon atom with  $\text{SiH}_2\text{O}$  to form the metastable  $\text{Si}_2\text{H}_2\text{O}$  cluster (*i.e.*,  $\text{Si} + \text{SiH}_2\text{O} \rightarrow \text{Si}_2\text{H}_2\text{O}$ ) is thermodynamically favorable with an exothermicity (xcg) of 2.828 eV (3.420 eV at the LSD level). Consequently, if quenched prior to dissociation (into  $\text{Si}_2 + \text{H}_2\text{O}$ ), this reaction could allow generation of  $\text{Si}_2\text{H}_2\text{O}$  clusters.

**TABLE 3: Dipole Moment  $\mu$  (in D), Angle  $\alpha$  between the Dipole Moment and the Line Connecting the Center of Mass of  $\text{Si}_n$  and O, and the Effective Charge  $q$  (electron) =  $\mu/d$ , Where  $d$  Is the Distance between Center of Mass of  $\text{Si}_n$  and O in the  $\text{Si}_n\text{H}_2\text{O}$  Clusters**

$\text{Si}_n\text{H}_2\text{O}/n =$	0	1	2	2a	7	7a	7b
$\mu$	1.688	4.443	6.681	2.601	3.358	1.337	2.998
$\alpha$		0.0	0.0	0.0	0.4	88.5	0.8
$q$		0.522	0.536	0.301	0.195	0.063	0.153

**TABLE 4: Total Energy (per Atom),  $E^{(n)}/n$ , and Atomization Energy (per Atom),  $E_a$ , of  $\text{Si}_n$ ; Vertical (vIP) and Adiabatic (aIP) Ionization Energies of  $\text{Si}_n$  and  $\text{Si}_n\text{H}_2\text{O}$  Clusters and  $E_R = \text{vIP} - \text{aIP}$ ; Energies of Several Reactions<sup>a</sup>**

$n$	0	1	2	2a	7
	$\text{Si}_n$				
$E^{(n)}/n$	102.802	104.816			107.075
$E^{(n)}/n(\text{xcg})$	103.836	105.687			107.646
$E_a$		2.024			4.283
$E_a(\text{xcg})$		1.857			3.808
vIP	8.329	8.017			8.142
aIP	8.329	7.907			7.930
$E_R$	0.000	0.110			0.212
vIP(xcg)	8.461	8.035 <sup>b</sup>			8.170
aIP(xcg)	8.461	7.935			7.875
$E_R(\text{xcg})$	0.000	0.100			0.295
	$\text{Si}_n\text{H}_2\text{O}$				
vIP	13.330	6.601	7.068	7.263	7.805
aIP	13.197	6.460	6.962	7.138	7.761
$E_R$	0.133	0.161	0.106	0.125	0.044
vIP(xcg)	13.026	6.659	6.951	7.149	7.829
aIP(xcg)	12.934	6.559	6.876	6.850	7.795
$E_R(\text{xcg})$	0.092	0.100	0.075	0.299	0.034
$\text{Si}_n + \text{H}_2\text{O} \rightarrow \text{Si}_n\text{H}_2\text{O}$ : $E_b = -E(\text{Si}_n\text{H}_2\text{O}) + [E(\text{Si}_n) + E(\text{H}_2\text{O})]$		0.949	0.321	0.283	0.201
$E_b$		0.704	-0.181	-0.207	0.025
$E_b(\text{xcg})$					
$\text{Si}_n\text{H}_2\text{O}^+ \rightarrow \text{Si}_n^+ + \text{H}_2\text{O}$ : $E_{b+} = [E(\text{Si}_n^+) + E(\text{H}_2\text{O})] - E(\text{Si}_n\text{H}_2\text{O}^+)$		2.818	1.266	1.051	0.370
$E_{b+}$		2.606	0.879	0.649	0.118
$E_{b+}(\text{xcg})$					
$\text{Si}_n\text{H}_2\text{O}^+ \rightarrow \text{Si}_n + \text{H}_2\text{O}^+$ : $E_{+b} = [E(\text{Si}_n) + E(\text{H}_2\text{O}^+)] - E(\text{Si}_n\text{H}_2\text{O}^+)$		7.686	6.556	6.341	5.638
$E_{+b}$		7.080	5.877	5.647	5.176
$E_{+b}(\text{xcg})$					

<sup>a</sup> Results are given for both LSD and LSD-xcg calculations. All values in electronvolts. <sup>b</sup> The measured value is bracketed between 7.9 and 8.1 eV; see ref 12.

#### 4. Summary

In this brief note we reported on the binding characteristics of  $\text{H}_2\text{O}$  to  $\text{Si}_n$  ( $n = 1, 2, 7$ ) clusters, calculated through local-spin-density (LSD) functional theory, with and without exchange-correlation gradient corrections. The main findings may be summarized as follows:

(i)  $\text{H}_2\text{O}$  binds to a Si atom in a triplet state with a binding energy of 0.704 eV, forms a metastable singlet  $\text{Si}_2\text{H}_2\text{O}$  complex,

and binds weakly (0.025 eV) to  $\text{Si}_7$ . The binding energies in the ionized hydrated clusters are much higher (2.606, 0.879, and 0.118 eV, respectively).

(ii)  $\text{H}_2\text{O}$  binding to  $\text{Si}_n$  clusters involves formation of a Si–O bond with partial donation of charge from the oxygen atom, leading to the development of significant dipole moments. In the ground-state configurations, the Si–O bond is in the plane of the  $\text{H}_2\text{O}$  molecule. The ionization potentials of the hydrated Si atom and  $\text{Si}_n$  clusters are much smaller than that of  $\text{H}_2\text{O}$  and smaller than those of the bare  $\text{Si}_n$  species.

(iii) The reaction of a Si atom with  $\text{SiH}_2\text{O}$ , *i.e.*,  $\text{Si} + \text{SiH}_2\text{O} \rightarrow \text{Si}_2\text{H}_2\text{O}$ , to form the metastable  $\text{Si}_2\text{H}_2\text{O}$  cluster is exothermic by 2.828 eV, and thus, if quenched before dissociation into  $\text{Si}_2 + \text{H}_2\text{O}$  (through a barrier), it may lead to the formation of  $\text{Si}_2\text{H}_2\text{O}$ .

**Acknowledgment.** Useful conversations with J.L. Gole are gratefully acknowledged. This research is supported by the Department of Energy and the Air Force Office of Scientific Research. Calculations were performed at the National Energy Research Scientific Computing Center, Lawrence Berkeley National Laboratory, and the Georgia Institute of Technology Center for Computational Materials Science.

#### References and Notes

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