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

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The interaction of a water molecule with Si, Si$_2$, and 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 Si$_2$, forming a metastable singlet state Si–Si–OH$_2$ cluster, whose dissociation into Si$_2$ + H$_2$O involves a barrier. Water binds weakly to 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.[1] These studies include investigations of bare 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 Si$_n$Na, $n \leq 10$, clusters[2]).

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, Si$_2$, and Si$_7$ clusters (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[3] to Na). Our study shows that at the LSD-xcg level H$_2$O binds to a Si atom with a binding energy E_b = 0.704 eV, while it does not bind stably to Si$_2$ (forming a metastable Si$_2$H$_2$O cluster, whose dissociation into Si$_2$ + H$_2$O with an exothermicity of 0.18 eV involves an activation barrier). Water binds very weakly (E_b = 0.025 eV) to Si$_7$. On the other hand, binding in the ionized species, *i.e.* (SiH$_2$O)$^+$, (Si$_2$H$_2$O)$^+$, and (Si$_7$H$_2$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,[4] 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[5] 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.[4]

As discussed in detail elsewhere,[4] 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
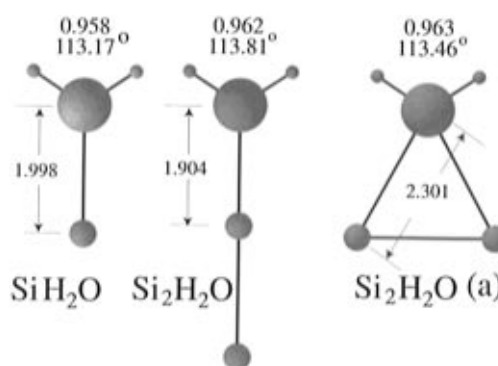
Figure 1. Geometries for neutral SiH$_2$O and Si$_2$H$_2$O clusters. For Si$_2$H$_2$O the ground state and a higher energy isomer (denoted as SiH$_2$O (a)) are shown. The energy of the isomer is 0.025 eV higher at the xcg level (0.038 eV at LSD level). The Si–O and O–H bond lengths and the $\angle$(HOH) 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[6]-correlation[7] 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[5] core radii, r_c, are $r_c^{s,p,d}$(Si) = 2.10a_0, r_c^s(H) = 0.95a_0, and $r_c^{s,p}$(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 SiH$_2$O, Si$_2$H$_2$O, and Si$_7$H$_2$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 H$_2$O molecule binds through formation of a Si–O bond which lies in the plane of the H$_2$O molecule; the bridge binding geometries (see Si$_2$H$_2$O (a) in Figure 1 and also Si$_7$H$_2$O (a, b) in Figure 2) are less stable (see also Table 2). The Si–O bond lengths in the ground-state SiH$_2$O, Si$_2$H$_2$O, and Si$_7$H$_2$O are 1.998, 1.904, and 2.794 Å compared to 1.479 Å of the double bond in SiO (the experimental value[8] is 1.510 Å), and the Si–Si bond in Si$_2$H$_2$O is

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TABLE 1: Bond Lengths (Å) and Bond Angles $\theta = \angle(\text{H}-\text{O}-\text{H})$ (deg), in Si_nH_2O, $n = 0, 1, 2$, and 7

$Si_nH_2O/n =$	0	1	2	2a	7	7a	7b
r_{Si-O}		1.998	1.904	2.301	2.794	3.815	3.163
r_{O-H}	0.954	0.958	0.962	0.963	0.958	0.957	0.958
θ	105.993	113.166	113.809	113.464	107.475	106.936	106.926

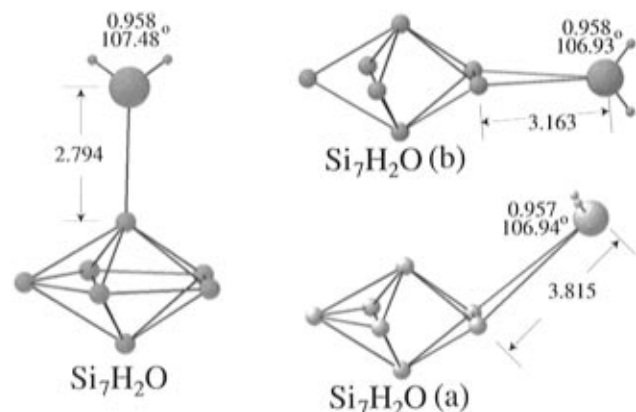**Figure 2.** Geometries for neutral Si_7H_2O clusters. In additional to the ground state, two isomers are shown denoted as (a) and (b). The energy of the a isomer is higher than that of the ground-state configuration (xcg) by 0.057 eV (0.013 eV using LSD), and that of the b isomer is higher (xcg) by 0.144 eV (0.138 eV using LSD). The Si−O and O−H bond lengths and the $\angle$(HOH) angles are indicated.

TABLE 2: Energy Difference, Δ_{st} (eV), between Singlet and Triplet States, Calculated as the Difference between the Total Ground-State Energies of the Two States[a]

$Si_n/n =$	1	2
Δ_{st}(LSD)	0.717	0.459
Δ_{st}(xcg)	0.809	0.568
exp	0.781[b]	

$Si_nH_2O/n =$	1	2
Δ_{st}(LSD)	0.667	−0.179
Δ_{st}(xcg)	0.841	−0.010

[a] A positive value corresponds to a triplet ground state and a negative one when the ground state is a singlet. [b] Reference 9.

2.049 Å compared to 2.128 Å in Si_2, where the experimental value[8] is 2.245 Å.

Both the Si atom and the bare 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 $\Delta_{st} = 0.809$ for Si (compared to a measured value[9] of 0.781 eV) and $\Delta_{st} = 0.568$ eV for Si_2; all other neutral Si_n with $n \geq 3$ clusters are in a singlet ground electronic state.[1] Interestingly, SiH_2O remains in the triplet configuration (see LSD Kohn−Sham levels in Figure 3a), which is energetically prefered over the singlet state by 0.841 eV. On the other hand, the (thermodynamically metastable) Si_2H_2O 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 H_2O 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 H_2O molecule. In this context we note that the vertical and adiabatic ionization potentials (vIP and aIP, see Table 4) of Si and Si_2 are lowered markedly upon binding to H_2O, and to a lesser extent for the Si_7 cluster. In all these clusters the small values of the reorganization energy, $E_R = \text{vIP} - \text{aIP}$, reflect rather small structural changes as the ionized clusters relax to their optimal ground-state geometries.

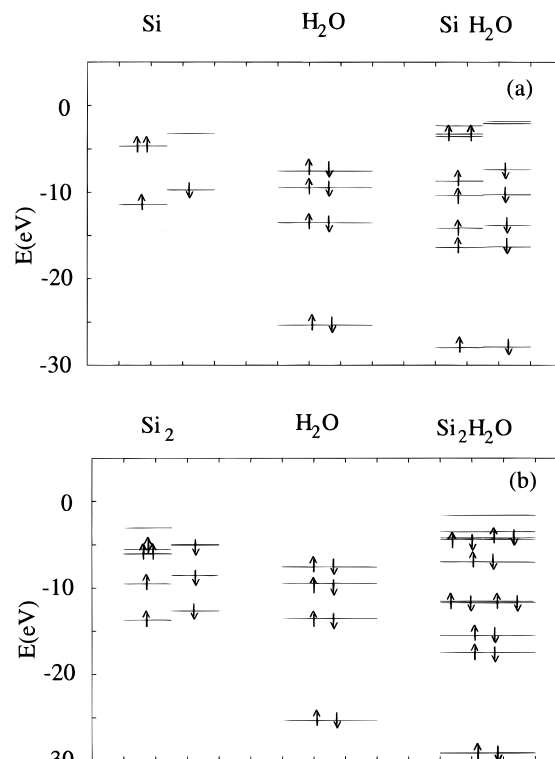As seen from Table 4, the H_2O molecule binds rather strongly

Figure 3. LSD Kohn−Sham levels (in unit of electronvolts). In (a) those for Si, H_2O, and SiH_2O are shown, and in (b) we display those for Si_2, H_2O, and Si_2H_2O. 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 Si_2 are both in a triplet state, while SiH_2O is in a triplet state and Si_2H_2O is a singlet.

to a single Si atom ($E_b = 0.704$ eV). The binding is much weaker to the dimer and heptermer, where for the latter $E_b = 0.025$ eV. For Si_2H_2O we find a metastable state, where the LSD-xcg calculations indicate exothermic dissociation into $Si_2 + H_2O$ (with a release of 0.181 eV for the more stable isomer of Si_2H_2O), in a process which involves an activation barrier. On the other hand, the binding energies increase significantly in the ionized $Si_nH_2O^+$ clusters, which are all well bound. The favorable (endothermic) dissociation channel for the ionized clusters is $Si_nH_2O^+ \rightarrow Si_n^+ + H_2O$ (see E_{b+} in Table 4), rather than $Si_nH_2O^+ \rightarrow Si_n + H_2O^+$ (see E_{+b} in Table 4).

Finally, several other reactions are worth commenting on: (i) the exothermicity of the dissociation reaction, $SiH_2O \rightarrow SiO + H_2$, is calculated at the xcg level to be 2.548 eV (compared to 2.230 eV using LSD), and that of $Si + H_2O \rightarrow SiO + H_2$ is 3.252 eV at the xcg level (3.179 eV using LSD), compared to a derived experimental value[10,11] of 3.154 eV; (ii) the exothermicity of the reaction $Si_2 + 2H_2O \rightarrow 2SiO + 2H_2$ is 0.103 eV calculated at the xcg level (0.085 eV using LSD), compared with a derived experimental value[10,11] of 0.108 eV; (iii) the reaction of a silicon atom with SiH_2O to form the metastable Si_2H_2O cluster (i.e., $Si + SiH_2O \rightarrow Si_2H_2O$) 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 $Si_2 + H_2O$), this reaction could allow generation of Si_2H_2O clusters.

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TABLE 3: Dipole Moment μ (in D), Angle α between the Dipole Moment and the Line Connecting the Center of Mass of Si_n and O, and the Effective Charge q (electron) = μ/d, Where d Is the Distance between Center of Mass of Si_n and O in the Si_nH_2O Clusters

$Si_nH_2O/n =$	0	1	2	2a	7	7a	7b
μ	1.688	4.443	6.681	2.601	3.358	1.337	2.998
α		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 Si_n; Vertical (vIP) and Adiabatic (aIP) Ionization Energies of Si_n and Si_nH_2O Clusters and E_R = vIP − aIP; Energies of Several Reactions[a]

n	0	1	2	2a	7
			Si_n		
$E^{(n)}/n$		102.802	104.816		107.075
$E^{(n)}/n$(xcg)		103.836	105.687		107.646
E_a			2.024		4.283
E_a(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[b]		8.170
aIP(xcg)		8.461	7.935		7.875
E_R(cxg)		0.000	0.100		0.295
			Si_nH_2O		
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(xcg)	0.092	0.100	0.075	0.299	0.034
$Si_n + H_2O \rightarrow Si_nH_2O$: $E_b = -E(Si_nH_2O) + [E(Si_n) + E(H_2O)]$					
E_b		0.949	0.321	0.283	0.201
E_b(xcg)		0.704	−0.181	−0.207	0.025
$Si_nH_2O^+ \rightarrow Si_n^+ + H_2O$: $E_{b+} = [E(Si_n^+ + E(H_2O)] − E((Si_nH_2O^+)$					
E_{b+}		2.818	1.266	1.051	0.370
E_{b+}(xcg)		2.606	0.879	0.649	0.118
$Si_nH_2O^+ \rightarrow Si_n + H_2O^+$: $E_{+b} = [E(Si_n) + E(H_2O^+)] − E((Si_nH_2O)^+)$					
E_{+b}		7.686	6.556	6.341	5.638
E_{+b}(xcg)		7.080	5.877	5.647	5.176

[a] Results are given for both LSD and LSD-xcg calculations. All values in electronvolts. [b] 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 H_2O to 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) H_2O binds to a Si atom in a triplet state with a binding energy of 0.704 eV, forms a metastable singlet Si_2H_2O complex, and binds weakly (0.025 eV) to Si_7. The binding energies in the ionized hydrated clusters are much higher (2.606, 0.879, and 0.118 eV, respectively).

(ii) H_2O binding to 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 H_2O molecule. The ionization potentials of the hydrated Si atom and Si_n clusters are much smaller than that of H_2O and smaller than those of the bare Si_n species.

(iii) The reaction of a Si atom with SiH_2O, *i.e.*, Si + SiH_2O → Si_2H_2O, to form the metastable Si_2H_2O cluster is exothermic by 2.828 eV, and thus, if quenched before dissociation into Si_2 + H_2O (through a barrier), it may lead to the formation of Si_2H_2O.

References and Notes

(1) Wei, Siqing; Barnett, R. N.; Landman, U. *Phys. Rev.* **1997**, *B55*, 7935 and refs 1−32 cited therein.

(2) See ref 1 and ref 30−32 therein.

(3) See Figures 7 and 8 and Table 2 in ref 1.

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(11) While the experimental atomization energies for SiO and H_2 are well established, a spread of values is given for H_2O, and a larger spread of values for Si_2. In our estimation of the experimental reaction energies, we have used an atomization energy of 9.584 eV for H_2O and a "concensus value" of 3.10 eV for Si_2 (see ref 10).

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