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Low-Energy Structures of Ligand Passivated Si Nanoclusters: Theoretical Investigation of Si_2L_4 and $Si_{10}L_{16}$ (L = H, CH_3, OH, and F)

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The influence of the ligands H, CH_3, OH, and F on the preferred geometric structure of passivated silicon nanoclusters was investigated by ab initio density functional calculations. $Si_{10}L_{16}$ has enough ligands to allow the silicon core to form the bulk Si like structure often anticipated to be present in silicon nanoparticles. Our calculations confirm that H and CH_3 ligands do favor being uniformly spread over the Si core to form the expected passivated nanoparticle structures. However, we find the more electronegative F or OH ligands to more strongly favor forming SiL_3 groups thereby causing the bulk Si like analog to be appreciably higher in energy. Similar structural trends were also found when comparing the relative energies of L_2SiSiL_2 against $LSiSiL_3$ with the same series of ligands L. The calculations suggest that to theoretically understand the properties, such as the bright photoluminescence, of passivated Si nanoclusters is going to require a model which takes into account the appropriate structural features of the particle.

Introduction

In the past two decades, there has been tremendous interest in the optical properties of silicon nanoclusters. Unlike bulk Si, which is an indirect gap semiconductor, porous Si[1] initially and then Si nanoclusters[2] later were found to exhibit a bright photoluminescence which has the promise of being developed into a Si-based optoelectronic device. The origin of the bright photoluminescence is still not completely understood and various models have been proposed ranging from quantum confinement in the nanometer sized Si crystallites[3,4] to the role played by some type of surface defect.[5] Presumably, in a practical optoelectronic device, the nanometer sized particles present in both porous Si and Si nanoclusters need to be passivated by some air stable ligand. Wolkin et al. found that the energy of the photoluminescence of H-passivated porous Si rapidly undergoes red shifts of up to 1 eV on exposure to oxygen.[5] One difficulty with any attempt at theoretical modeling the photoluminescence is the challenge of experimentally measuring the exact atomic composition and arrangement of the atoms forming the Si nanocluster. As a consequence, some of the recent high level quantum mechanical-based calculations on Si nanoclusters passivated by different surface atoms essentially assume that the Si_x core to be a fragment of a bulk Si latticelike structure.[6,7] Perhaps some support for the likelihood of the Si nanocluster favoring a bulk Si like core is provided by the recent report of the experimental synthesis and structure determination of sila-adamantane:[8] a molecule which contains a Si_{10} cluster core with a bulk Si like structure capped by 12 methyl and 4 trimethyl silyl groups. However, the purpose of this paper is to present the results from our recent calculations which show that the most stable geometric arrangement of Si atoms in a nanocluster are dependent on the ligand which is used to passivate the cluster surface. This is an important observation because the optical properties of the Si nanocluster should be dependent on the Si core structure. We obtain the low-energy cluster structures using a global optimization strategy which we have recently developed for clusters with Si_xH_y[9,10] and Si_xF_y[11] stoichiometries. The advantage of the global optimization procedure is that many different cluster structures are systematically investigated without utilizing any preconceived notions about the anticipated most stable cluster structure. Our approach contrasts with local geometry optimization procedures which use a bulk Si like structure as the initial guess. The local geometry optimization will almost certainly converge to a local minimum with the same the bulk Si like structure but now with the internuclear distances optimized, even when other cluster structures exist which are appreciably lower in energy.

Below, we present the relative energies computed using ab initio density functional calculations for different locally optimized $Si_{10}L_{16}$ clusters with the monodentate passivating

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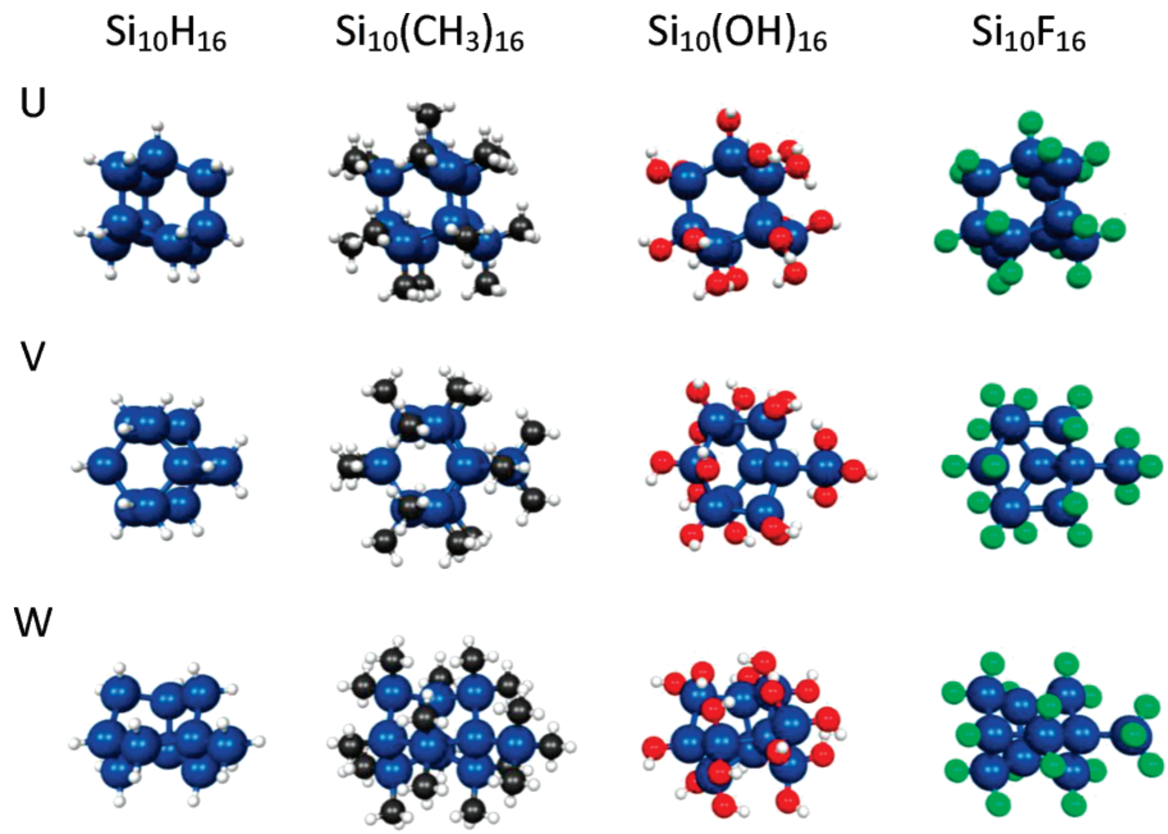

Figure 1. Locally optimized $Si_{10}L_{16}$ structures with L = H, CH_3, OH, F. The U clusters contains a Si_{10} core with a bulk Si like arrangements and is the $Si_{10}H_{16}$ global minimum. Clusters V and W can be derived from U by the shift of a $=SiL_2$ to a $\equiv SiL$ to form a $\equiv Si-SiL_3$ group.

ligands L = H, CH_3, OH, F. We choose the relatively small $Si_{10}L_{16}$ cluster because it is computationally tractable for high level quantum chemistry calculations while being large enough that the Si_{10} core can exhibit representative features of a bulk Si like structure. All of the U structures in Figure 1 contain a Si_{10} core with bulk Si like structure where each Si atom is tetrahedrally coordinated by either three or two other Si atoms and one or two ligands L. As expected, our earlier work confirmed that structure U is the $Si_{10}H_{16}$ global minimum.[9,10] Previously, we have also found global minima with bulk Si like structures for $Si_{14}H_{20}$ and $Si_{18}H_{24}$ where the number of H atoms included in these clusters ensure that each Si atom is tetrahedrally coordinated by four neighboring atoms.[9,10] Not surprisingly, we found very different global minima for the $Si_{10}H_{14}$, $Si_{14}H_{18}$, and $Si_{18}H_{22}$ series with stoichiometries where two H atoms are removed from the clusters which have the bulk Si like structure. Each Si still prefers being coordinated by four neighbors, but this can only be accomplished by rearranging the Si core so it no longer has the bulk Si like structure.[9,10] When we tried to extend the Si_xH_y global optimization strategy to Si_xF_y clusters, we found that $Si_{10}F_{16}$ preferred to form structure A shown in Figure 2 which is very different from the bulk Si like structure U.[11] Our calculations suggested that this new structural type is preferred because the highly electronegative F atoms like to form terminal SiF_3 groups rather than be evenly distributed over the available surface sites on the Si_{10} core. On the basis of an electronegativity argument, a CH_3 passivating ligand should be expected to produce clusters with Si core structures similar to those found for the Si_xH_y clusters, whereas the high O atom electronegativity means the OH ligand should favor low-energy structures with Si cores similar to those found for the $Si_{10}F_{16}$ clusters. Unfortunately, the present calculations are not able to provide any insight into the role of ligand size in controlling structure nor to indicate the likely structures for silicon clusters passivated by a bidentate ligands such as oxygen atoms.

The paper is organized as follows. The next section outlines the computational method. Results and discussion of the various low-energy Si_2L_4 and $Si_{10}L_{16}$ structures are presented in section 3. Concluding remarks are given in final section of the paper.

Computational Method

Ab initio density functional calculations were performed on clusters with Si_2L_4 and $Si_{10}L_{16}$ stoichiometries with L = H, CH_3, OH, and F. The $Si_{10}L_{16}$ cluster structures considered in this manuscript were selected from the three lowest energy structures U, V, and W shown in Figure 1 found in the global optimization of $Si_{10}H_{16}$[9,10] and from the four lowest energy structures A, B, C, and D shown in Figure 2 determined in the $Si_{10}F_{16}$ global optimization.[11] The cluster global optimizations (CGA) were performed using a genetic algorithm which operates directly on the Cartesian coordinates of the atoms composing the clusters. An initial population of typically 100 clusters is randomly generated and locally optimized. The fitter, lower energy, clusters are then mated to produce an offspring population of locally optimized structures. The CGA effectively lets good structural features present in a cluster to be passed onto succeeding generations until the global minimum is found. Since the CGA requires a very large number of energy calculations, the CGA uses a reparametrized AM1 semiempirical method for prescreening the relative energies of the Si_xH_y and Si_xF_y clusters prior to performing any ab initio calculations.

The actual $Si_{10}L_{16}$ structures and relative energies reported here were obtained by starting from a previously optimized $Si_{10}H_{16}$ or $Si_{10}F_{16}$ structure[9−11] and replacing either all of the H or all of the F atoms with a new ligand L = H, CH_3, OH, F

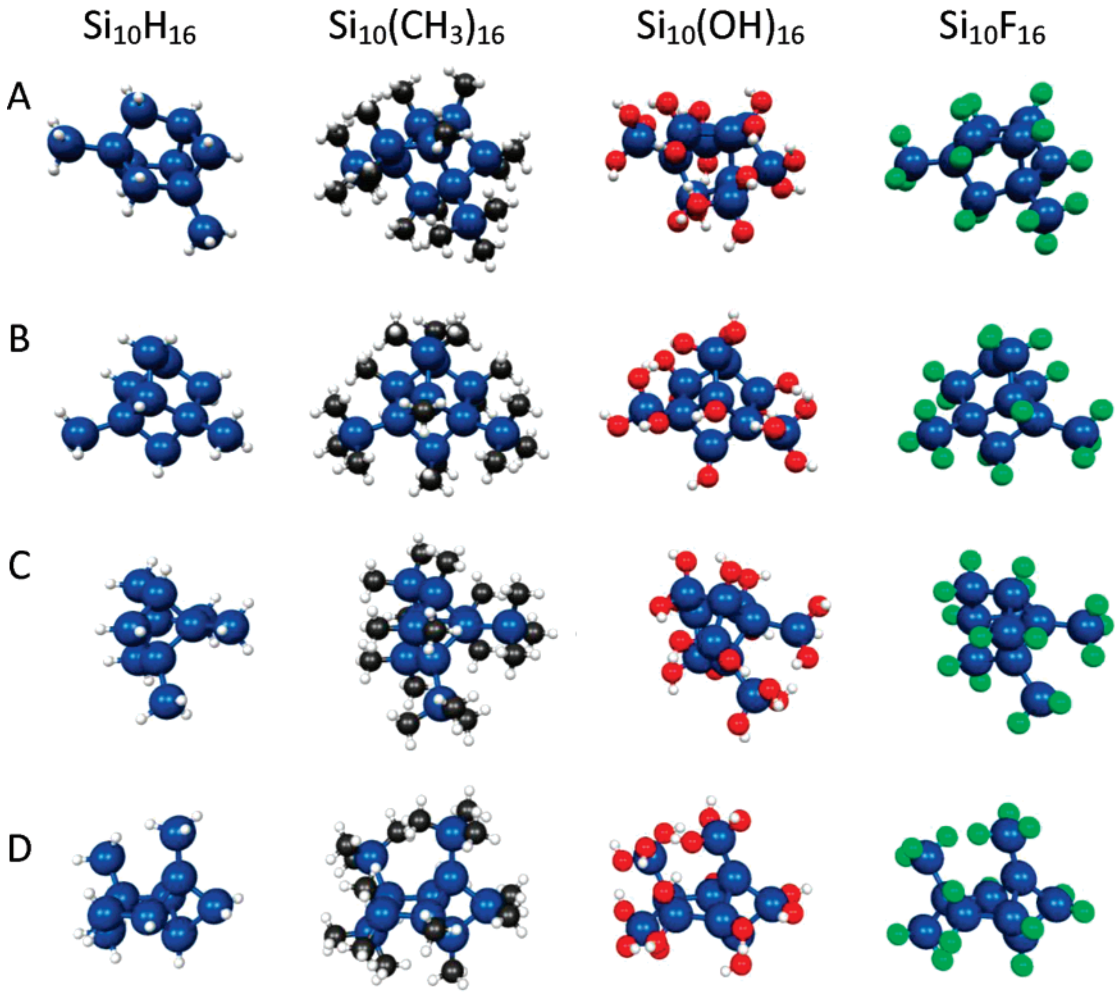

Figure 2. Locally optimized $Si_{10}L_{16}$ structures with L = H, CH_3, OH, F derived from the low-energy structures found in the global optimization of $Si_{10}F_{16}$. Structures A−C consist of a Si_8 core and 2 SiL_3 groups, and structure D has a Si_7 core and three SiL_3 groups.

and performing a local geometry optimization using B3LYP/6-31G(d) density functional calculations[12−14] computed by the PC GAMESS computer program.[15,16] The $Si_{10}H_{16}$ and $Si_{10}F_{16}$ optimized structures and relative energies are essentially the same as those we obtained previously using a slightly different basis set.[9−11] Finding the lowest energy structures for the $Si_{10}(OH)_{16}$ and $Si_{10}(CH_3)_{16}$ clusters is more challenging than for $Si_{10}H_{16}$ and $Si_{10}F_{16}$ owing to the OH and CH_3 ligands being able to form several different conformers on the same Si_{10} core framework. For this reason, five initial geometries for the $Si_{10}(OH)_{16}$ and $Si_{10}(CH_3)_{16}$ clusters were generated for each Si_{10} core type by replacing either all of the H or all of the F atoms in the optimized $Si_{10}H_{16}$ and $Si_{10}F_{16}$ clusters with OH or CH_3 groups where the SiOH or one of SiCH planes were orientated at a randomly selected angle relative to the cluster framework. Frequency calculations at the B3LYP/6-31G(d) level were performed to verify that the geometry optimizations converged to a true local minimum, and we include the vibrational zero point energy (ZPE) in the resulting cluster relative energies. Some second-order perturbation theory (MP2) calculations were performed on the Si_2L_4 clusters to check that the B3LYP/6-31G(d) calculations gave consistent relative energies for the different clusters.

Results and Discussion

In all of these local geometry optimizations with the different ligands, we found that the same basic Si_{10} core framework was always maintained. For each of the specific Si_{10} frameworks, we found the different $Si_{10}(CH_3)_{16}$ starting geometries always converged to the same local minimum in the geometry optimization. Whereas, the local optimization of the $Si_{10}(OH)_{16}$ clusters for each specific Si_{10} framework produced several different local minima with different H-bonding networks between neighboring OH groups on the clusters. The present calculations are consistent with our previous global optimization results: the lowest energy $Si_{10}H_{16}$ cluster (structure U) having a bulk Si like structure and the $Si_{10}F_{16}$ global minimum being one of the three close in energy A, B, or C structures containing small Si_3 or Si_4 rings.[9−11] Obviously, it is much less certain whether we have obtained the lowest energy structures for $Si_{10}(CH_3)_{16}$ and $Si_{10}(OH)_{16}$, and one goal of our future work is to develop a global optimization technique which can correctly treat these types of clusters. The resulting optimized $Si_{10}L_{16}$ cluster structures and their relative energies are discussed in more detail below. However, it appears the major structural differences which occur when H or CH_3 are the cluster passivating ligand versus the more electronegative OH and F ligands are essentially illustrated by comparing the relative energies of the locally optimized $L_2Si{=}SiL_2$ and $L_3Si{-}SiL$ geometries, and these are discussed first.

Si_2L_4. Figure 3 shows the structures of locally optimized $L_2Si{=}SiL_2$ and $L_3Si{-}SiL$, and Table 1 lists their relative energies, where for each ligand type L the lowest energy structure in Table 1 is taken to have the zero reference energy. Since one purpose

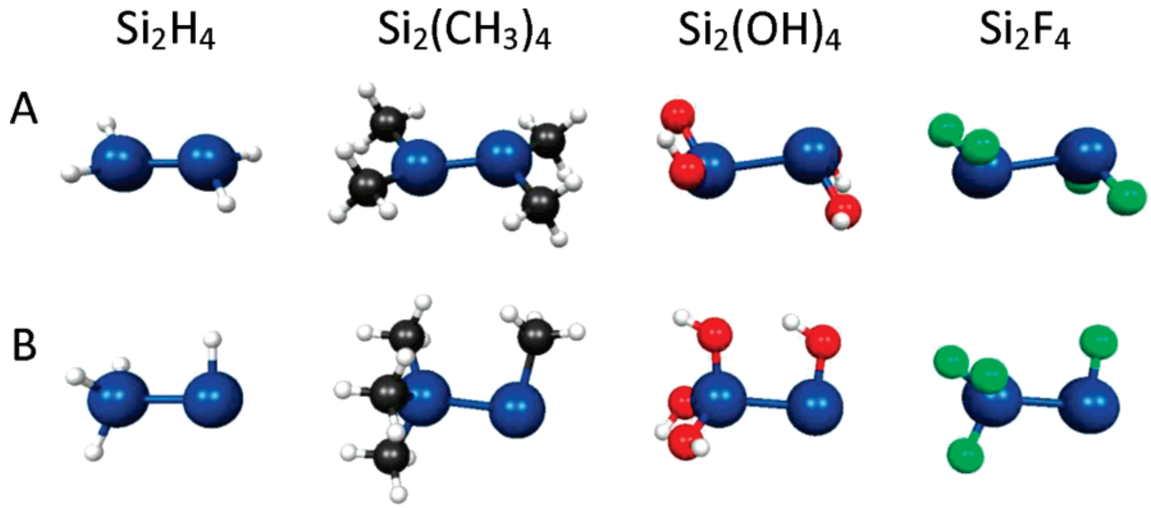

Figure 3. Locally optimized Si_2F_4 structures with L = H, CH_3, OH, F.

TABLE 1: Relative B3LYP (MP2) energies with B3LYP ZPE corrections for L_2SiSiL_2 and L_3SiSiL where all energies are in kcal/mol

	Si_2H_4	$Si_2(CH_3)_4$	$Si_2(OH)_4$	Si_2F_4
L_2SiSiL_2	0.0	0.0	7.9 (11.6)	6.8 (11.4)
L_3SiSiL	4.7 (6.9)	4.5 (4.7)	0.0	0.0

of these calculations is to simulate the major structural features found in $Si_{10}L_{16}$ clusters, we have not considered structures, such as where a L atom bridges the 2 Si atoms, which are also known to be low in energy for the Si_2L_4 stoichiometry but not in the larger clusters.[17,18] As a validation for the B3LYP energy values used to estimate the relative energies of the different structural types, we include in parenthesis in Table 1 the energies obtained using MP2/6-31G(d) calculations augmented with B3LYP zero point energy corrections. The Si_2H_4 and Si_2F_4 relative energies are also consistent with our earlier calculations[11] and in work by others[17,18] performed using larger basis sets and higher quality CCSD(T) calculations. Our calculations show that L = H or CH_3 favor the formation of the ethylene analog $L_2Si{=}SiL_2$ whereas L = OH or F result in the $L_3Si{-}SiL$ having lower energy. In all four ethylene analogs $L_2Si{=}SiL_2$, the two Si atoms do not strictly form a π bond, and instead, a nonplanar equilibrium structure with C_{2h} symmetry is formed. Valencia et al. have also found that F favors forming similar asymmetrical structures in the $Si_2H_{6-x}F_x$ series of molecules using B3LYP/6-311++G(d,P) calculations.[19] They compute $SiF_2H{-}SiH_3$, $SiF_3{-}SiH_3$, and SiF_3SiFH_2 to be 7, 10, and 3 kcal/mol more stable than $SiFH_2{-}SiFH_2$, $SiF_2H{-}SiFH_2$, and $SiF_2H{-}SiF_2H$, respectively. The electrostatic stabilization gained from interacting with the highly polar SiF bond is probably the driving force for why a second or third F atom prefers to bind to a Si atom which is already bonded to at least one other F atom. The two $Si_2(OH)_4$ optimized structures are influenced by both the O atom electronegativity and by steric effects due to a H bond network formed between OH groups located either on the same Si atom or on neighboring Si atoms. Presumably, like for Si_2F_4, the large O electronegativity results in the $(HO)_3SiSiOH$ structure being the most stable. However, as a consequence of the ligands H bonding to each other $(HO)_3SiSiOH$ has an eclipsed conformer, whereas the L on the two different Si atoms in all the other L_3SiSiL structures are staggered relative to each other.

$Si_{10}L_{16}$. The ZPE corrected B3LYP/6-31G(d) relative energies for the $Si_{10}L_{16}$ clusters with the different ligands L are summarized in Table 2. The zero reference in Table 2 is taken from either the U or the A $Si_{10}L_{16}$ cluster which has lowest energy. Consistent with our global optimization studies,[9,10] the lowest energy $Si_{10}H_{16}$ cluster U has a bulk Si like structure where each of the four $\equiv$SiH groups form three Si−Si bonds with the six available $=SiH_2$ groups. The next two low-energy V and W structures are related to the $Si_{10}H_{16}$ global minimum by a shift of a $=SiH_2$ unit to one of the available $\equiv$SiH positions to form $\equiv Si{-}SiH_3$. In structure V, a $=SiH_2$ is transferred to an adjacent $\equiv$SiH, while in W the $=SiH_2$ is transferred to a $\equiv$SiH on the opposite side of the cluster. The resulting Si_9 core in V and W must have some strain due to the reduction in some of the Si atoms ring sizes, and consequently the $Si_{10}H_{16}$ energy in both clusters is raised by around 4 kcal/mol.

TABLE 2: $Si_{10}L_{16}$ B3LYP/6-31G(d) relative energies including ZPE corrections in kcal/mol where the zero energy is taken with respect to either the U or the A cluster depending on which structure has lowest energy

	$Si_{10}H_{16}$	$Si_{10}(CH_3)_{16}$	$Si_{10}(OH)_{16}$	$Si_{10}F_{16}$
U	0.0	0.0	31.7	29.6
V	4.3	0.8	12.5	12.7
W	4.5	0.8	12.2	11.9
A	13.3	0.5	0.0	0.0
B	13.2	0.7	5.1	1.6
C	12.9	2.6	−1.5	1.1
D	25.9	11.6	3.5	6.1

Likewise, Table 2 shows cluster A to be the lowest energy $Si_{10}F_{16}$ cluster in agreement with our previous global optimization results.[11] Indeed, for $Si_{10}F_{16}$, cluster A is 30 kcal/mol lower in energy than the bulk Si like cluster U and this demonstrates that in the $Si_{10}F_{16}$ cluster there is a very strong preference for forming SiF_3 groups. All of the different low-energy structures can be related to the bulk Si like structure U through the same type of transfer process $=SiF_2 + \equiv SiF \rightarrow \equiv Si{-}SiF_3$ as described for structures V and W above. Structure A contains two of these SiF_3 groups and a remaining Si_8 core which can no longer form a bulk Si like framework. The gain in energy obtained by forming the two SiF_3 groups in cluster A must outweigh the energy expense of forming five and even four membered Si rings in the Si_8 core. Structures B and C have the same Si_8 core as cluster A but have the SiF_3 groups located at different $\equiv$SiF positions. Hence, the A, B, and C structures are all very close in energy, but because of using the 6-31G(d) basis in the present calculations, we obtain the B and C relative energies reversed from our previous results.[11] By considering the $Si_{10}H_{16}$ A, B, and C relative energies in Table 2, the ring strain in the Si_8 core must be around 10 kcal/mol. Clusters A, B, and C have the two SiF_3 groups bound to a Si atom which binds with three other Si atoms in the Si_8 core. Structure D contains three SiF_3 groups but with two of the groups bound to the same Si atom, and consequently, it has a Si_7 cluster core. Thus, the Si_7 core in cluster D must consist of smaller Si ring sizes than in A−C thereby raising the $Si_{10}F_{16}$ relative energy by 5 kcal/mol. Nonetheless, structure D is still a lot lower in energy than the bulk Si like structure U. Further evidence that when F is used as passivating ligand for Si clusters there will be a strong preference for forming SiF_3 groups is shown by the relative energies for the $Si_{10}F_{16}$ clusters V and W which have only one $\equiv$SiSiF$_3$ unit but which are both still much lower in energy than cluster U. This suggests that in larger clusters a bulk Si like core could exist provided it is passivated by SiF_3 groups rather than simply F atoms.

The $Si_{10}(OH)_{16}$ clusters show very similar relative energy trends as the $Si_{10}F_{16}$ clusters. However, the identification of the lowest energy $Si_{10}(OH)_{16}$ conformer is made more difficult by the OH ligands being able to form a H bond network on the cluster surface. As noted above, we locally optimized each $Si_{10}(OH)_{16}$ cluster type by starting from the corresponding $Si_{10}F_{16}$ cluster and replacing each F atom with an OH group chosen to have some random orientation. In the local optimizations, we found several different H-bonding networks between the OH groups being formed on the Si cluster surface which range in energy by as much as a 8 kcal/mol. change. The $Si_{10}(OH)_{16}$ relative energies listed in Table 2 are taken from the OH orientation which produces the lowest energy. Not all of the OH ligands in $Si_{10}(OH)_{16}$ are close enough to a neighboring OH group to be able to form a H bond, but as expected, the lowest energy conformer for each cluster type always has the most H bonds. Obviously, the present strategy does not guarantee finding the $Si_{10}(OH)_{16}$ global minimum or even if we have found the lowest energy OH conformation for each $Si_{10}(OH)_{16}$ structural type. Perhaps as a consequence of a more favorable H-bond network cluster C has the lowest energy structure being 1.5 kcal/mol lower in energy than cluster A. Similarly, structure D, which has three $Si(OH)_3$ groups and probably the most strained Si_7 core, is still able to form enough H bonds to produce a structure which is lower in energy than cluster B. The trend that the relative energies of clusters A−D are less than clusters V and W and that structure U has highest energy for both the $Si_{10}(OH)_{16}$ and the $Si_{10}F_{16}$ suggests a consistent energy ordering for the $Si_{10}(OH)_{16}$ clusters has been obtained. Thus, we can make the useful observation that the most stable Si clusters passivated by OH will favor the presence of $Si(OH)_3$ groups, and the Si core will not simply have a bulk Si like structure. We anticipate other O containing passivating ligands, such as a methoxide group, to also favor forming $Si(OCH_3)_3$ like groups, although the lack of H bonding will influence the relative energy ordering of the different structures. The $Si_{10}(OH)_{16}$ results also suggest that a Si cluster passivated by an oxide layer should be expected to have a Si core structure quite different to a bulk Si like structure.

Consistent with the C atom electronegativity, the relative energies in Table 2 for the different $Si_{10}(CH_3)_{16}$ clusters show that the Si core favors forming a bulk Si structure. The lack of H bonding between neighboring methyl groups makes the local optimization of the $Si_{10}(CH_3)_{16}$ clusters much more straight forward than for the $Si_{10}(OH)_{16}$ clusters. The geometry optimization always produced the same final $Si_{10}(CH_3)_{16}$ structure type even though the initial cluster geometries had different random orientations of the CH_3 groups. Surprisingly, we find the energy spread for the $Si_{10}(CH_3)_{16}$ structures U, V, W, A, B, and C to be only 2.6 kcal/mol and much smaller than we have found for any of the other ligands. We speculate that this is because there is some steric crowding between nearest neighboring CH_3 ligands in the U structure which gets relieved with the presence of one $Si(CH_3)_3$ group in structures V and W and the two $Si(CH_3)_3$ groups in the A−C structures. The reduction in the CH_3 steric crowding compensates for Si ring strain present in the Si_9 and Si_8 cores. The ring strain energy of Si_7 core in the D $Si_{10}(CH_3)_{16}$ cluster must be much higher and is not compensated by forming three $Si(CH_3)_3$ groups. Our results for the $Si_{10}(CH_3)_{16}$ cluster are interesting in view of the recent report of the synthesis and structure of sila-adamantane.[8] The close energy spacings for the different $Si_{10}(CH_3)_{16}$ structures suggest that there may be several different sila-adamantane conformers close in energy. The amount of steric crowding between CH_3 ligands will increase on larger Si nanoclusters because of their surface being flatter than for the Si_{10} core. Thus, the sila-adamantane structure[8] may be a consequence of trying to reduce the CH_3 steric crowding by having CH_3 and $Si(CH_3)_3$ groups around the Si_{10} core.

Conclusions

This work illustrates that the lowest energy structure of passivated Si nanoclusters is sensitive to the type of ligands used to passivate the particle. Ligands with electronegativities similar to that of Si give rise to low-energy structures where the ligand is uniformly dispersed over the Si core surface. Providing there are enough ligands, the Si core in the lowest energy structure resembles a bulk Si like fragment. However, more bulky low electronegativity ligands, such as CH_3 may experience static crowding on a Si_{10} core resulting in structures containing $Si(CH_3)_3$ groups to be only a few kcal/mol higher in energy than the cluster with a bulk Si like core. The more electronegative ligands have a strong preference for forming SiL_3 groups, and this tendency eliminates the likelihood of the Si atoms at the nanocluster surface to have a bulk Si like arrangement. Work is in progress to determine how the optical properties of Si nanoclusters are affected by different passivating ligands and the influence from the resulting preferred lowest energy cluster structure.

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