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A Theoretical Study of the Interaction of Ammonia with Silicon Trimer

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Theoretical calculations are reported for the interaction potential of $Si_3 + NH_3$. The existence of loosely bound physisorbed states separated by sizable barriers from more tightly bound states more akin to dissociative chemisorption is predicted. These findings correspond to experimental results on this system which suggest ammonia desorbs intact from small silicon clusters, a behavior expected for physisorbed species. Qualitative explanations using frontier molecular orbital theory help explain the differences between the interaction of ammonia with small clusters and bulk silicon.

I. Introduction

One of the gifts that Raphy Levine brings to the study of molecular reaction dynamics is an ability to find model systems that provide key ideas in several ways. The chemistry of small gas-phase clusters presents one such area where the ability to compare behaviors between these small systems and bulk surface chemistry extends understanding beyond the system itself. Inevitably, gas-phase nanoclusters have been subjected to a variety of chemical interrogations.[1−5] While some of these studies have been used to infer structural information about the clusters, others have been carried out to compare reactivity of the clusters with bulk surfaces. The number of elements whose cluster chemistry has been studied is wide-ranging, and silicon clusters provide some of the most intriguing observations. For example, while many metallic clusters show reactivity that rapidly approaches the limit shown by bulk surface chemistry,[1] silicon clusters often react substantially different than bulk silicon surfaces.[2,6]

The reaction of ammonia on silicon is one example of these differences. For the bulk surface the use of ammonia for chemical vapor deposition (CVD) of silicon nitride and oxynitride films has led to a number of theoretical[7,8] and experimental[6,9−12] studies. This reaction shows sensitivity to several experimental details, such as surface symmetry and reconstruction, but dissociative chemisorption is regularly evident,[6] unless the experiment is carried out at low temperatures.[9] For small silicon clusters, Jarrold and co-workers found evidence that ammonia dissociates intact,[13,14] a result that is different than the preponderance of bulk surface chemistry.[10−12] Smalley and co-workers[15,16] have also studied this reaction, and there has been some controversy over issues such as magic numbers, cluster sizes that are relatively inert under the reaction conditions obtained. This controversy arises with clusters, notably larger than the trimer we have studied here. Other reactions on silicon clusters, such as that of oxygen,[17] also find unusual trends.

Theoretical studies of silicon clusters have been primarily directed at structural issues and predicting reactivity in more general terms.[18,19] For example, investigations of various isomers of larger clusters, such as Si_{10}, have proposed that bimodal reactivity observations are due to the reaction of different clusters. This theme has been further explored from an experimental perspective, classifying cluster structures as either prolate or oblate and separating the reactivity patterns of these two classes.[20] Mixed silicon and oxygen clusters have been studied,[21,22] but these investigations focus on minima of the potential energy surface after the oxygen is already incorporated with the cluster.

In this work we have carried out electronic structure calculations to elucidate the interaction potential for the reaction $Si_3 + NH_3$. Twenty-two stationary points were found on the surface including local minima and transition states. While not an exhaustive description of the potential surface, these points allow us to characterize the probable molecular reaction dynamics this system undergoes. In particular, our calculations show the probable existence of loosely bound adducts, akin to physisorption that are separated by a sizable barrier from more stable structures that resemble dissociative chemisorption. These observations correlate with observed experimental data and also extrapolate relatively well to bulk surface chemistry and its differences to the nanocluster chemistry. Additional qualitative insight connecting these systems can be garnered using frontier molecular orbital theory arguments. We organize our presentation as follows. Calculational methods are presented in section II, and results of the electronic structure calculations are given in section III. The concluding discussion is given in section IV.

II. Methods of Calculation

For the electronic structure calculations, we employed effective core potentials (ECP) for the nitrogen and silicon atoms. The ECP that we used are the compact effective potentials of Stevens, Basch, and Krauss (SBK).[23] These have been shown to provide results in very good agreement with analogous all-electron calculations, while reducing the computational effort by eliminating the explicit treatment of chemically inactive core electrons.

The energy-optimized shared-exponent from 4-31G Gaussian basis sets of Cundari and Stevens[24] was used for nitrogen and

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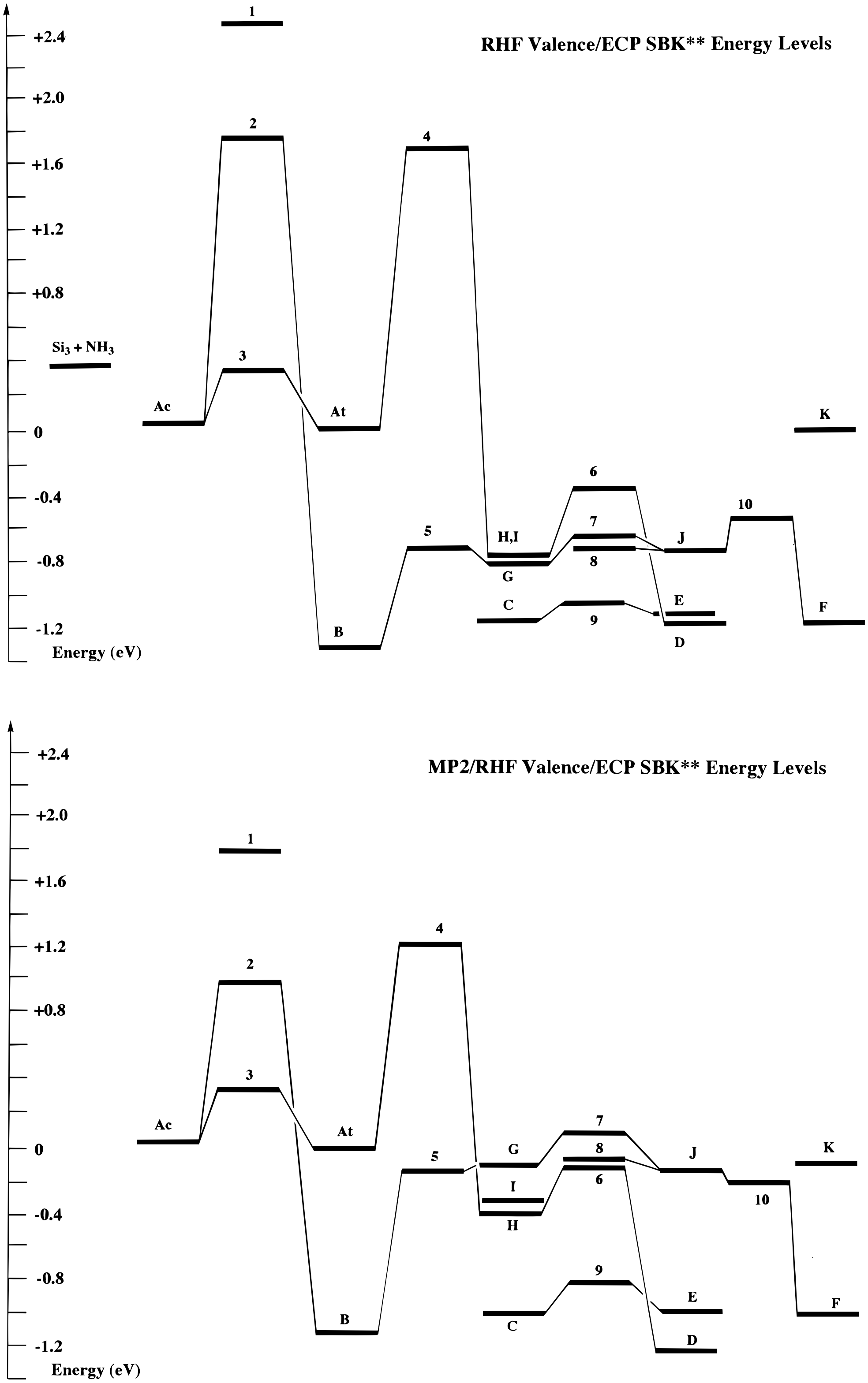

Figure 1. Energy levels of the stationary points determined on the potential energy surface for Si_3-NH_3. Part a (top) shows the energies for the optimized HF level structures, while part b (bottom) shows the same structures with single-point MP2 corrections. Minimum-energy paths between transition states and local minima are indicated as well.

silicon centers and a 4-31G basis for hydrogen.[25] The basis set was augmented by one diffuse d function on each N or Si center, with exponents 0.80 and 0.395, respectively. The importance of including d orbitals on these atoms for the correct prediction of structures has been stressed previously,[26] and our study supports those observations, though we do not present any of the results obtained with out d orbitals on silicon. To the hydrogen basis was added a p orbital with exponent 1.1.

Molecular structures and transition-state (TS) geometries for 22 stationary points on the potential energy surface were determined at the single-configuration HF self-consistent field (SCF) level. TS geometries were optimized such that the rms

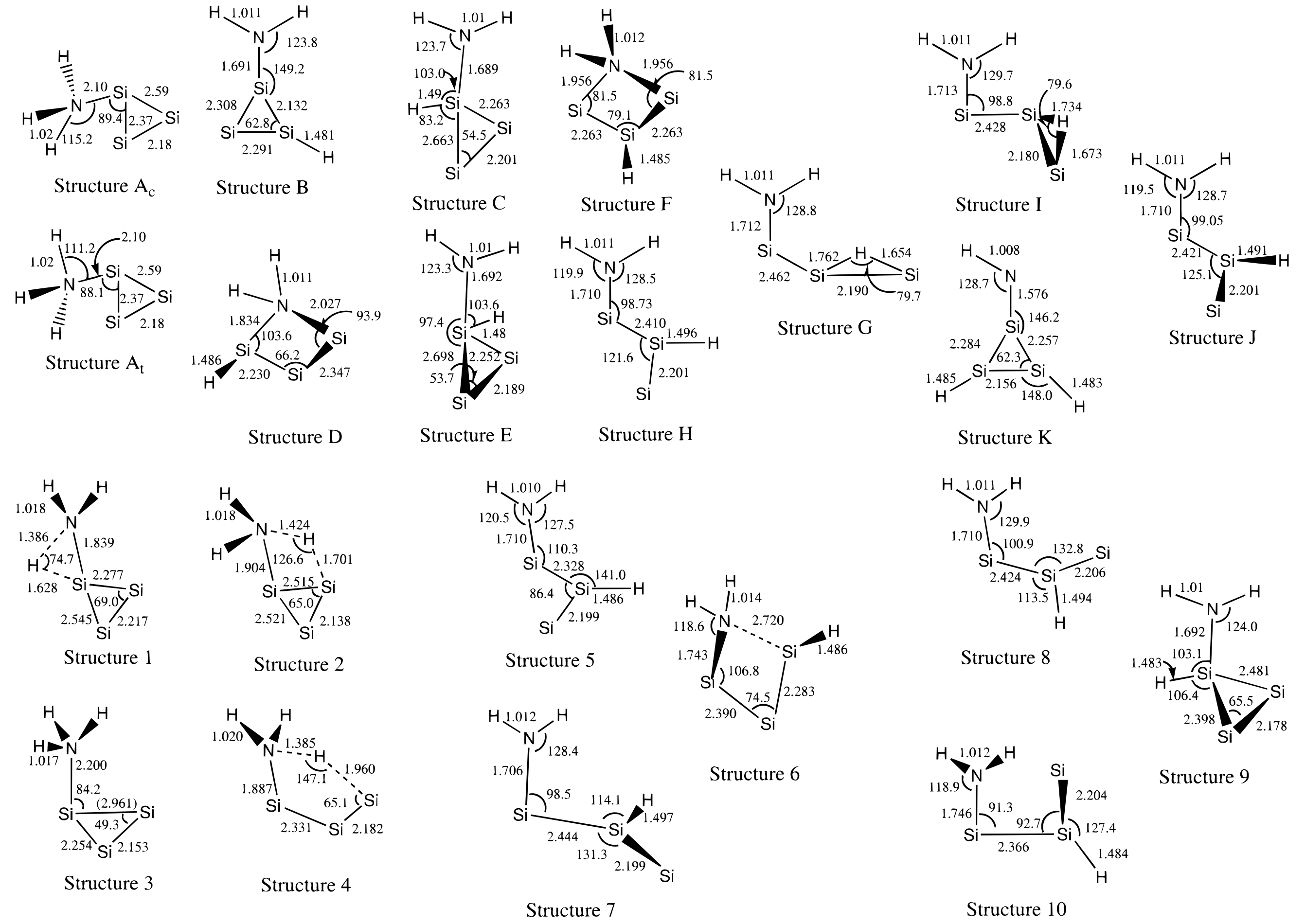

Figure 2. Structures for the 22 stationary points on the potential energy surface characterized in this work. Local minima are indicated by letters. and saddle points are designated by numbers. All structures are optimized at the RHF/ECP SBK** level of calculation and confirmed as either minima or transition states by Hessian calculations.

energy gradient with respect to internal coordinates was less than 0.1 cm^{-1}/bohr. Local minima geometries were located in a fashion similar to within 2 cm^{-1}/bohr or better.

Numerical Hessians were performed at each of the stationary points, thus verifying their status as either local minima or TS. While more time-consuming than analytic Hessians, this technique provides the dipole derivative tensor and certainly verifies whether stationary points are local minima or saddle points. Minimum-energy paths (MEP)[27] which connect TS to local minima were calculated using the Gonzales−Schlegel (GS2) second-order method.[28] A number of the transition states under consideration lie at positions on the potential energy surface with small curvature in the direction of the MEP, as evidenced by relatively modest negative eigenvalues in the Hessian computed at those TS. Such circumstances require some care in performing the initial steps away from the TS into the MEP if the reaction pathway is to be reliable. We found the GS2 procedure quite adept at handling, in an automated fashion, the construction of MEP for difficult instances such as we encountered and use that method for all MEP calculations.

Second-order perturbation theory (MP2)[29] energy corrections were computed at the RHF optimized geometries. All calculations were performed with GAMESS.[30]

III. Discussion of Results

The energy levels corresponding to 22 symmetry distinct stationary points of the RHF potential energy surface of NH_3Si_3 are shown schematically in Figure 1. The geometries of the 22 structures are given in Figure 2. On the left of the diagram, the sum of the energies for the separated ammonia and silicon trimer fragments is indicated. Local minima are indicated by letters, and saddle point structures are indicated by numbers.

The **At** and **Ac** levels correspond to two orientations of NH_3 physisorbed on Si_3. These geometries possess C_s symmetry, with N, one H, and all Si atoms coplanar. The c and t subscripts indicate that the coplanar H is “cis” or “trans” with respect to the second-nearest Si atom. The shortest silicon−silicon bond length is shared by the silicon pair of atoms that are not directly involved in the dative bond. The **At** structure is 0.015 eV lower in energy than the **Ac** structure, and its energy is taken as the reference point energy in this diagram.

There are three saddle point structures that could influence the dissociation of NH_3 to $NH_2 + H$ on the silicon trimer. The geometries of these transition states are given by structures **1**, **2**, and **4** in Figure 2. As is clear from the energy level diagram (Figure 1), the barriers to dissociation are relatively large along the indicated MEP. The highest energy pathway (through **1**) leads to structure **C** with a hydrogen attached to the silicon already bonded to the nitrogen, a 1,2 transfer. This pathway seems unlikely to compete with the two lower energy transition states (**1** and **4**) for 1,3 hydrogen transfer. With MP2 energy corrections, our calculations predict the barriers to be 0.96, 1.22, and 1.78 eV above the **At** energy.

The planar structure resulting from the 1,3 proton transfer through **2** is designated as **B**. It lies lowest in energy on the RHF potential surface of all the structures treated presently.

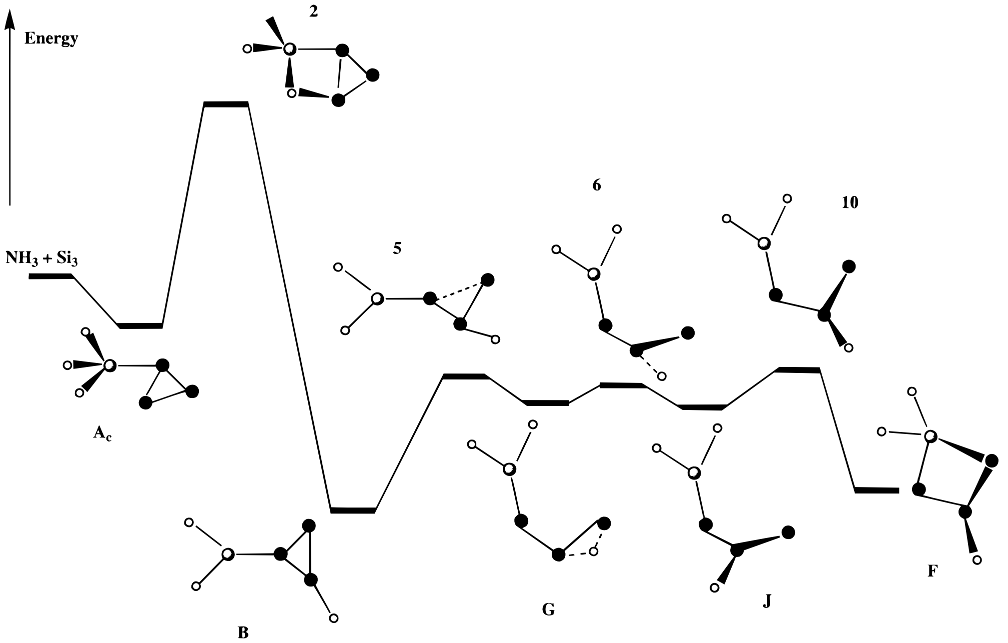

Figure 3. A sample reaction path for the interaction of ammonia with silicon trimer. The loosely bound physisorbed state (A) must overcome a large barrier (2) to undergo dissociative chemisorption. Once this barrier is traversed many possible local minima are readily accessed. In this example the final destination is a four-member ring, where NH_2 has inserted into a Si−Si bond.

When MP2 single-point energy calculations are included, however, a second structure, designated as **D**, becomes lower in energy. The relative energy ordering of these two structures could alter again upon optimization at the MP2 level, but the general scheme of the reaction dynamics would not be altered by this information. Features of the MEP proceeding from **2** to **B** indicate a low-energy rearrangement followed by a N−H bond breakage which appears as a rather abrupt event on the MEP.

The competing 1,3 proton transfer requires the ammonia fragment to swing out of the plane of the silicon trimer and ultimately leads to another structure that does not maintain the closed Si_3 triangle. We designate the resulting structure for this dissociation pathway as **G**. It has the interesting feature that the migrating hydrogen moves to a bridging site at the 3,4 position. Bridged structures for Si_2H_2 have been previously investigated.[31] It is worth noting that the presence of the diffuse d orbitals used to augment the silicon basis set is required in order for this structure to appear on the calculated potential energy surface. A second structure, structure **I**, is similar to **G** in exhibiting a monobridged feature but lies slightly higher in energy.

We did not locate a transition state that one might expect to lie on the MEP between **At** and **Ac**, which would represent the barrier to NH_3 rotation (NSi_3 coplanar). This torsional motion is only slightly hindered, so gradients along this direction were difficult to minimize to a saddle point. Nonetheless, the distinction between **At** and **Ac** is probably not significant when considered relative to the sizable activation energy required for the ammonia decomposition along the MEP through **2** or **4**. However, we have characterized an out-of-plane rotation of NH_3 which connects **Ac** to **At** through structure **3**. It is reasonable to expect that the rotation of NH_3 would occur with a lower barrier than this out of plane distortion. Structure **3** may be important when one considers the motions of physisorbed ammonia on silicon surfaces, as the out-of-plane distortion might resemble a precursor for surface hopping in extended systems.

Those isomers whose energy levels lie below **At** in Figure 1 all correspond to single proton-transfer products NH_2Si_3H, with the exception of the isomer **K** which is a planar two-proton-transfer product in which the relocated hydrogen atoms are attached equatorially at the vertexes of the silicon ring. The remaining energy levels are separated into two tiers, with one group at roughly −0.7 eV with respect to the **At** energy, and another group in the vicinity of −1.3 eV. Broadly speaking, the group of structures belonging to the upper tier, structures **G**−**I**, **5**−**8**, and **10**, have the common feature that the ring has at least partially opened, as seen in Figure 2. This set of chainlike structures all lie very close in energy to each other, with no substantial barriers to rearrangements. With one exception (for a transition state), all of the structures in this upper tier of energy levels have geometries in which the reacted proton is bonded to the middle of the chain, i.e., the second silicon (from the nitrogen atom) at position 3. Of course, for **G** and **I** the hydrogen atom is bridged to the third silicon at position 4 as well. It is interesting to note that the present calculations have not been able to identify a MEP directly from the H-bridged structures to a chain isomer and that neither of the characterized 1,3 proton transfer MEPs leads directly to a chain structure. The majority of geometrical differences in this tier of structures results primarily from low-energy rotations of the NH_2 group about the closest silicon atom.

In contrast, the lower tier of energy levels, structures **B**−**F** and **9**, correspond to silicon trimer rings and to two four-membered rings. It is not particularly surprising that instances where the closed trimer structure is maintained lie at lower energies than where it is not. Much of the theory of magic numbers in silicon clusters is associated with the minimization of “dangling bonds”, unfulfilled silicon atom valencies.[14−19] This tier of structure has the general feature of removing dangling bonds by forming ring structures.

The **K** isomer is the only product resulting from two proton transfers that we consider here. It lies only 0.085 eV in energy below the chemisorbed state **At** and 0.66 eV above the closest HSi_3NH_2 energy level, so it is unlikely to compete as a destination for dissociative behavior. A treatment of the energetics of silylene and its isomers by Truong and Gordon[32] indicates that $HSiNH_2$ is the global minimum on the $SiNH_3$

potential energy surface, with H_2SiNH lying 0.78 eV higher in energy than $HSiNH_2$. Similarly, the present findings suggest that decomposition to NH_2Si_3H will be favored over $NHSi_3H_2$.

To consider the broad features of this potential energy hypersurface, we consider an example reaction path, depicted in Figure 3. There is nothing particularly special about this path, except that several saddle points have been characterized along it. Along this path, and presumably others, there is a physisorbed-like state with ammonia interacting molecularly with the silicon cluster. After overcoming a sizable energy barrier, 1,3 hydrogen transfer may occur leading to a process resembling dissociative chemisorption. This process is substantially exothermic, enough so that the initial local minimum reached after traversing the barrier is not likely to be the only one visited. In the example shown a series of ring-opening states and hydrogen migration ultimately leads to a four-membered ring with NH_2 inserting into the silicon trimer. All of these latter processes may occur based only on the exothermicity of the chemisorption process. This example path does not show a second hydrogen transfer. We have not been able to locate any saddle points for such a process, and the product, $NHSi_3H_2$, is likely to be significantly less stable than those local minima shown in the example path.

Considering these results in light of experimental studies of clusters and of bulk surface chemistry provides some useful insight. The existence of a sizable barrier between the physisorbed states, **At** and **Ac**, and lower energy states that resemble dissociative chemisorption products corroborates the possibility that experimental conditions exist where the intact dissociation of ammonia is favored. Nonetheless, the lower energy dissociative states could be accessed under different experimental conditions giving rise to observations more akin to bulk properties. The energy clustering of these dissociative states with one hydrogen migration favored may indicate that small silicon clusters resemble 7 × 7 Si(111) in their chemical reactivity.[9] We must admit the possibility, however, that these states are favored because of the relatively small number of Si atoms in our system.

IV. Conclusions

We have reported on electronic structure calculations for the interaction of ammonia with a silicon trimer as a representative potential energy surface for silicon cluster chemistry. We have identified 22 stationary points on the RHF potential surface. While this is not an exhaustive survey of the possible structures and improvements to the structural and energy predictions that can be expected through optimization with correlated wave functions, we expect it is sufficient to provide several useful characterizations.

First, the existence of states that resemble physisorption of intact ammonia on the silicon cluster provides important corroboration of experimental observation of intact desorption of ammonia from silicon clusters.[2] This behavior in clusters stands in contrast to most bulk surface studies.[10−12] Consideration of frontier molecular orbital arguments helps to rationalize this difference further. The pertinent frontier orbitals in cluster chemistry, particularly for small silicon clusters, show unfavorable energy gaps to allow facile dissociative reactivity of the ammonia. Because the smaller clusters are highly unsaturated, a state not energetically conducive for silicon, the LUMO needed to interact with the ammonia lone pair HOMO is too high in energy. By contrast, surface reconstruction on bulk silicon provides surface states that interact favorably with these orbitals.

Second, while there are states that show molecular ammonia interacting with silicon clusters, they are not favored in terms of the total energy. States in which one hydrogen atom transfers to a silicon are generally lower in energy than the molecular adsorbed states. For this single hydrogen-transfer state, those that retain a ring structure for the silicon trimer are more stable than cases where the ring is opened or partially opened. Double hydrogen transfer is not favored for this system. All of these states are separated by a large barrier from the molecularly absorbed states.

Finally, some structures located on the potential energy surface show bridging hydrogen atoms. These structures are not a surprise in light of similar results for silaacetylene.[31] Current experiments are not directed toward observation of this level of structural detail. It should be noted, however, that the vibrational frequencies of such bridging hydrogens are distinct from more conventional Si−H single bonds,[31] so appropriate spectroscopies, if developed, could confirm the existence of this type of structure. The signal from bridged hydrogen would be small but not buried beneath the nonbridged hydrogen signal.

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