Bull. Chem. Soc. Jpn., 74, 817—825 (2001)

NH_3 Dissociative Adsorption on Si(100)-(2×1) Surface: A B3LYP Quantum Chemical Cluster Model Study

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(Received September 28, 2000)

Dissociative adsorption of ammonia on the Si(100)-(2×1) surface has been investigated using the hybrid density functional B3LYP method and the Si_9H_{12} one-dimer cluster model of the surface. The adsorption geometries and the reaction energetics from NH_3(a) to NH_2(a) and H(a) have been studied with Si basis sets varying from the standard all electron 6-31G(d) to the LanL2DZ with effective core potential, while keeping NH_3 basis sets as 6-31G(d,p) in all cases. It was found that B3LYP/LanL2DZ is a reasonable level of theory for the calculations of not only the geometries, but also the reaction energetics. This provides a cost-effective way to extend the size of the Si cluster models and to study in details the energetics of the whole reaction path. Based on the experimental and theoretical results available, we recommend an "optimal" bond geometry of NH_2(a) and H(a) on the Si(100)-(2×1) surface to be: Si–Si (symmetric dimer) 2.42 Å, Si–N 1.75 Å, Si–H 1.50 Å, N–H 1.01 Å, Si–Si–N 115°, Si-N-H 118°, Si–Si–H 111°, H–N–H 109°. The calculated results on the reaction energetics are in general agreement with the experimental findings as well as the previous theoretical ones.

Ammonia adsorption on silicon(100) has been the subject of numerous investigations due to its importance in the technological applications of silicon nitride. Silicon nitride films under atomic-order-thickness control can be applied to resonant tunnelling barriers and very thin gate insulators, which are necessary for the next generation of ultra-large-scale integrated circuits.[1,2]

Various experimental techniques have been employed to elucidate the adsorption geometries,[3–5] electronic structures,[6–9] vibrational interactions,[5,10] as well as reaction energetics[3,10,11] of the NH_3/Si(100) system. Although controversies still exist, the majority of results point toward the picture that at room temperature ammonia molecule dissociatively adsorbs over one Si dimer to produce an NH_2(a) and a H(a), which in turn passivate the surface dangling bonds to prevent NH_2(a) from further dissociation. Such formed species are found to be stable up to ~600 K.[4,5,8,10] The temperature programmed desorption (TPD) experiments predicted that the activation energy for the associative desorption of NH_3 is around 46 kcal mol^{-1}.[4]

Based on the ESDIAD (electron-stimulated desorption ion angular distributions) results and the EELS (electron energy loss spectroscopy) results, Dresser et al.[4] and Fujisawa et al.[5] independently proposed that the Si–NH_2 group is in a trigonal pyramidal geometry. These two studies, however, differ significantly in the predicted values of the Si–Si–N and Si–N–H angles. Dresser et al. supposed the Si–Si–N and Si–N–H angles be 125° and 106.8° respectively,[4] while Fujisawa et al. gave values of 110° and 120°.[5] A recent scanned-energy mode photoelectron diffraction (PhD) study provided quantitative determination of the key structural parameters of the Si–NH_2 group.[3] The Si–N bond length was found to be 1.73 ± 0.08 Å, with the bond angle relative to the surface normal being 21° ± 4°. This corresponds to a Si–Si–N angle of 111° ± 4°, assuming a symmetric Si–Si dimer bond.[3] Unfortunately, no direct information on the N–H and Si–H bonds could be deduced from this technique, due to the absence of the H core level.[3]

So far, only a few theoretical investigations have been reported on the NH_3/Si(100) system.[12–16] In the early 1990s, Zhou et al. performed the atom superposition and electron delocalization-molecular orbital (ASED-MO) and the discrete variational Xα (DV-Xα) calculations with cluster models,[12] and Moriarty and Smith performed the slab-modified intermediate neglect of differential overlap (Slab-MINDO) molecular orbital calculations.[13] The results of these two calculations differ in various aspects. The Si–N bond length and Si–N bond angle relative to the surface normal are 2.04 Å and 25° by ASED-MO and 1.707 Å and 22.7° by Slab-MINDO, while the Si–H bond length and Si–H bond angle relative to the surface normal are 1.38 Å and 25° by ASED-MO and 1.52 Å and 19.5° by Slab-MINDO.[12,13] On one hand, Slab-MINDO found that the NH_2 molecular plane makes an angle of 168.2° with the Si–N bond, predicting a nearly planar Si–NH_2 configuration.[13] On the other hand, ASED-MO gave the Si–N–H angle of 105°, supporting the experimentally deduced trigonal pyramidal geometry.[12] The observed difference has been attributed to the neglect of both surface and subsurface relaxations in the cluster model calculations of Zhou et al.[13]

More recently, three new calculations at the state of the art level appeared, among which there is one cluster model calculation using the ab initio CASSCF/MRSDCI (complete active space self-consistent field/multireference single and double ex-

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citation configuration interaction) method[14] and two slab model calculations with the density-functional theory (DFT) of the local density approximation (LDA)[15] or the generalized gradient approximation (GGA).[16] These three calculations all predicted the Si–N bond length of ~1.75 Å. The Si–N bond angles relative to the surface normal are, however, 24°,[14] 10°,[15] and 28°,[16] a spread of up to 18°. The Si–N–H angles from the GGA and the CASSCF calculations are 146° [16] and 117.7°.[14]

The detailed energetics from NH_3(g) to NH_2(a) and H(a) over one Si dimer has been predicted by the MRSDCI/Cluster and the GGA/Slab models.[14,16] The dissociation was found to involve a barrierless molecular chemisorption of NH_3(g), followed by an activated N–H bond cleavage of NH_3(a) to form NH_2(a) and H(a). The molecular adsorption energy was predicted to be 33 kcal mol^{-1} by MRSDCI[14] and 28 kcal mol^{-1} by GGA.[16] The activation energy was found to be around 15 kcal mol^{-1} by both methods.[14,16] The whole reaction energetics is 75 kcal mol^{-1} by MRSDCI,[14] 46 kcal mol^{-1} by GGA[16] and 100 kcal mol^{-1} by LDA.[15]

In the present work, we present a hybrid density functional B3LYP cluster model calculation on the dissociative adsorption of ammonia over a single dimer site on the Si(100) surface. The adsorption geometries and reaction energetics are compared critically with the available theoretical and experimental results on this system. Attention has been paid to the validity of the employment of the pseudopotential method so as to find out a cost-effective way to expand the silicon cluster model and to study in details the whole ammonia dissociation reaction mechanism over the silicon surface.

1. Computational Details

Bulk Si possesses the structure of diamond, where each Si atom is tetrahedrally coordinated. Cutting-out a surface will create some dangling bonds. It is now generally accepted that the ideal Si(100) surface with two dangling bonds per surface atom will undergo a (2×1) reconstruction with pairs of surface atoms moving together to form surface dimers. The simplest cluster model for a single surface dimer is known as Si_9H_{12} (Fig. 1a), where hydrogen atoms are used to terminate the unphysical dangling bonds at the subsurface silicon atoms.[14,25,34–38] In this model, there are two surface layer Si atoms representing the dimer, four second layer Si atoms, two third layer Si atoms, and one fourth layer Si atom. Each NH_3 molecule will attack one Si atom of the silicon dimer, forming a molecular adsorption state of NH_3/Si_9H_{12} (Fig. 1b), which will undergo dissociation to form NH_2–H/Si_9H_{12} (Fig. 1d), through a transition state (TS) of $NH_2\cdots H/Si_9H_{12}$ (Fig. 1c). The complete geometry optimization (with no constrained degree of freedom) is done using analytical gradients and second derivatives. The augmented Hessian method was used to search for the TS. The matrix of second derivatives is calculated at each critical point to verify that it is a true minimum or first-order saddle point.

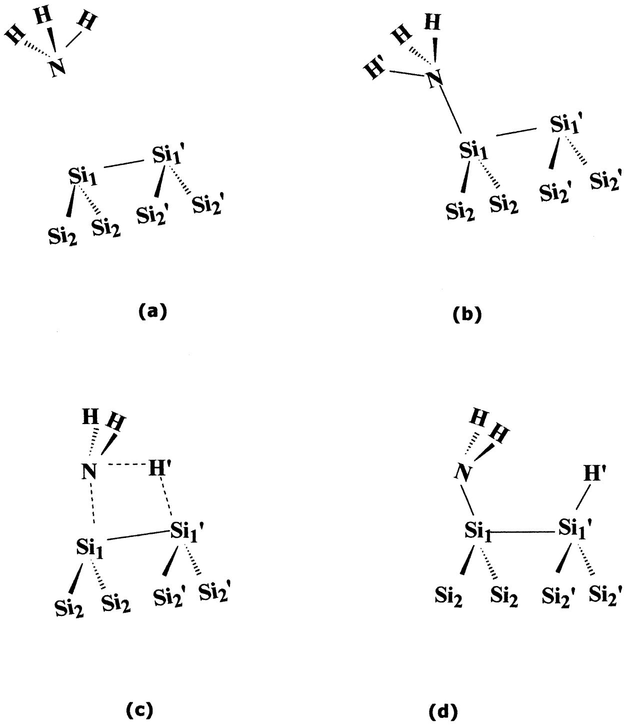

Fig. 1. Schematic representation of (a) free adsorbate NH_3 and Si_9H_{12} single dimer model cluster; (b) molecular adsorption state of NH_3/Si_9H_{12}; (c) transition state of $NH_2\cdots H/Si_9H_{12}$; (d) dissociative adsorption state of NH_2–H/Si_9H_{12}. Only Si atoms in the top two layers of Si_9H_{12} model cluster are shown. The optimized geometries are practically in C_s symmetry.

The basis set used for adsorbate NH_3 is the standard 6-31G(d,p) (double-zeta plus d and p polarization functions on N and H, respectively).[17] For the surface cluster Si_9H_{12}, we have used several basis sets. The first one is 6-31G(d).[17,18] The other two are the standard basis set of LanL2DZ and the LanL2DZ(d) basis set with one d polarization function of 0.3247[14] being added for all Si atoms.[18] The notation LanL2DZ stands for the standard D95 double-zeta basis sets for the terminal hydrogen atoms[19] and the Hay and Wadt's effective core potential (ECP) along with double-zeta valence basis sets for Si atoms.[20] The ECP employed reduces the number of electrons per Si atom from 14 to 4. But its applicability to describe the geometries, and more importantly, the reaction energetics in this kind of system remains to be verified.

The theoretical method employed is B3LYP.[21] It consists of the Slater exchange, the Hartree–Fock exchange, the exchange function of Becke,[21] the correlation functional of Lee–Yang–Par,[22] and the correlation functional of Vosco–Wilk–Nusair.[23] The contribution of each energy to the B3LYP energy expression was fitted empirically on a reference set of molecules.[21] The hybrid B3LYP method has been reported to provide excellent descriptions of various reaction profiles, especially in geometries, heats of reactions, barrier heights and vibrational analyses.[24] In particular, Nachtigall et al. found that the B3LYP functional gives a close agreement with their quadratic CI calculations in the study of hydrogen desorption from the monohydride phase of Si(100)-(2×1) surface.[25]

All calculations are carried out with Gaussian 98 suite of programs.[26] The spin multiplicities in all the systems calculated here are equal to 1.

2. Calculation Results and Discussions

2.1 Geometrical Features. A. Free Adsorbate NH_3 and Single Dimer Model Cluster Si_9H_{12}: Table 1 summarizes the important geometric features of the free adsorbate NH_3 and the single dimer model cluster Si_9H_{12} (See Fig. 1a). NH_3 is in the C_{3v} symmetry. Our B3LYP/6-31G(d,p) calculations provide the N–H bond length of 1.018 Å and $\angle$HNH angle of 105.7°. These values agree well with the experimental ones (N–H = 1.012 Å and $\angle$HNH = 106.7°),[27] as well as those from CASSCF calculations of Fattal et al. (N–H = 1.028 Å and $\angle$HNH = 106.4°),[14] GGA calculations of Lee and Kang (N–H = 1.030 Å and $\angle$HNH = 106.2°)[16] and LDA calculations of Miotto et al. (N–H = 1.05 Å and $\angle$HNH = 104°).[15] We have also optimized the geometry of the NH_2 radical with multiplicity = 2. The N–H bond are found to be 1.033 Å along with the $\angle$HNH = 101.8°. The corresponding experimental/theoretical values of GGA are N–H = 1.024/1.049 Å and $\angle$HNH = 103.3°/102.1°, respectively.[15,27] Our B3LYP/6-31G(d,p) calculated dissociation energy from NH_3 to NH_2 + H is 112.0 kcal mol^{-1}, which is also in good agreement with the experimental value of 108 kcal mol^{-1}.[27]

As for the geometric structures of the bare Si(100) surface, there exist numerous experimental[28–33] as well as theoretical investigations.[13–16,34–38] The most intriguing subjects are whether the surface dimers are symmetric (unbuckled) or asymmetric (buckled) and whether the bond lengths of the surface dimers are longer or shorter than the Si–Si distances (2.352 Å) in the bulk. Both symmetric and asymmetric dimers are observed by STM (scanning tunneling microscopy).[28] The estimated dimer bond length and the buckling angle from different experiments differ significantly (e.g. Jayaram et al. 2.2 Å/5.6°,[29] Jedrecy et al. 2.32 Å/7.4°,[30] Holland et al. 2.47 Å/8.4°,[31] Felici et al. 2.67 Å/20° [32]). A recent room temperature LEED (low-energy electron diffraction) investigation estimated a dimer bond length of 2.24 ± 0.08 Å.[33] They predicted that the vertical separation between the top-layer dimer atoms is 0.72 ± 0.05 Å and the tilt angle of the dimer is 19 ± 2°. The formation of Si dimers induces distortion in deeper Si layers, most notably a buckling in the third and fourth layers by 0.34 and 0.25 Å, respectively.[33] This lends certain supports to our employment of the full optimization algorithm without any restriction on the four-layer single dimer cluster model Si_9H_{12}.

Theoretically determined values of the dimer bond and the buckling angle depend critically on the theoretical methods employed (i.e., DFT, GVB, CI, etc.), the ways of modeling (i.e. Slab or cluster models; the presumed periodic symmetry of a slab model or the size of a cluster model), the basis sets used, and the constraints imposed on the systems of optimizations.[14–16,33–37] CASSCF/Cluster-model calculations of Fattal et al. gave a symmetric dimer with the dimer bond length of 2.421 Å.[14] The very recent ab initio multi-reference configuration interaction calculations with cluster models also did not find an asymmetric structure.[35] On the contrary, Yang and Kang obtained a buckled dimer of 14.9° (the buckling angle) and 2.291 Å (the dimer bond length) with B3LYP/6-31G(d) based on a three-dimer model of $Si_{21}H_{20}$.[34] GGA/Slab-model calculations of Lee and Kang predicted a buckled dimer with the dimer bond length of 2.337 Å and the tilt of dimer of 18.2° for the p(2×1) reconstruction.[16] These two values stemmed from the LDA/Slab calculations of Miotto et al. are 2.25 Å and 16°, respectively.[15] Our B3LYP/6-31G(d) optimizations lead to the dimer bond length of 2.225 Å and the buckling angle of 4.9°. These could be considered as in good agreement with the

Table 1. Geometric Parameters for the Free Adsorbate NH_3 and Si_9H_{12} Single Dimer Model Cluster
Bond lengths are in Amstrong (Å) and bond angles are in degree (°). The number in square brackets is No. of Reference.

		Present work:$^{a)}$		CASSCF/	LDA/	GGA/		Expl: NH_3 [27]	
		B3LYP/6-31G(d,p)/		Cluster	Slab	Slab		and Si(100)-(2×1)	
	6-31G(d)	LanL2DZ(d)	LanL2DZ	[14]	[15]	[16]	[29$^{d)}$]	[33$^{e)}$]	[33$^{f)}$]
N–H	1.018	1.018	1.018	1.028	1.030	1.012	1.012	1.012	1.012
H–N–H	105.7	105.7	105.7	106.4	106.4	106.7	106.7	106.7	106.7
Si_1–Si_1'	2.225	2.190	2.213	2.421	2.25	2.337$^{c)}$	2.20	2.181	2.280
Si_1–Si_2	2.342	2.321	2.348	2.364	2.33		2.41	2.282	2.215
Si_1'–Si_2'	2.353	2.321	2.348	2.364	2.39		2.50	2.432	2.476
Si2–Si_1–Si_1'	110.2	106.8	107.1				109	120.8	107.3
Si_2'–Si_1'–Si_1	102.6	106.7	107.1				105	89.0	90.7
Si_2–Si_1–Si_2	116.8	115.5	113.7	107.5			105	114.6	120.2
Si2′–Si_1'–Si_2'	113.8	115.5	113.7	107.5			100	104.3	101.7
$\alpha_1$$^{b)}$	4.90	0.06	0.04	0.0	16	18.2$^{c)}$	5.6	18.4	18.7
$\alpha_2$$^{b)}$	0.85	0.01	0.03	0.0			0.6	0.16	0.00

a) In the present work, B3LYP is employed. The basis sets used for NH_3 is 6-31G(d,p); while those for Si_9H_{12} model cluster are 6-31G(d), LanL2DZ(d) and LanL2DZ. C_s symmetry is approximately maintained.

b) Buckling angles for the first layer of dimer (α_1) and the second layer Si atoms (α_2) are calculated relative to the terminal hydrogens at the fifth layer.

c) The values are for the asymmetric p(2×1) phase of Si(100).

d) Values calculated based on Table 1 of Ref. 29.

e) Values calculated based on the FHI data of Table 1 in Ref. 33.

f) Values calculated based on the ICM data of Table 1 in Ref. 33.

experimental results of Jayaram et al., based on the transmission electron diffraction investigation.[29] LanL2DZ and LanL2DZ(d) predict a symmetric dimer, even though the dimer bond lengths (2.213 and 2.190 Å, respectively, with and without d polarization function being added to the Si atoms) are quite close to the 6-31G(d) value. Although the energy difference between the symmetric and the unsymmetric dimer is small (e.g. 0.05 $\mathrm{kcal\,mol^{-1}}$ as predicted by Konecny and Doren[38]), it is believed that buckling will create nucleophilic sites and electrophilic sites at the dimer and is, therefore, of chemical significance.[36–38] However, the methodology employed here clearly underestimated the buckling, as compared to the most recent experimental results.[32,33]

B. Molecular Adsorption State of NH_3/Si_9H_{12}: When an ammonia molecule approaches the surface dimer, it reaches a local potential minimum of a molecular adsorption state (See Fig. 1b). One N–H bond of NH_3 is in the same plane of the dimer bond, while the dimer bond bisects the angle between the other two N–H bonds of NH_3, giving an essential C_s symmetry of the system. In fact, the C_s symmetry is basically maintained throughout the whole dissociation reaction, even though no symmetry restriction is imposed in our calculations. This is in accordance with the finding of Fattal et al.[14] Both CASSCF/Cluster-model and GGA/Slab-model calculations located the molecular adsorption states.[14,16] It is interesting, however, to notice that the hydrogen in the N–H bond paralleling to the dimer bond is in the "*trans*" conformation with respect to N–Si–Si in Fig. 1a of Lee and Kang;[16] while this hydrogen is in the "*cis*" conformation, as shown in Fig. 2b of Fattal et al.[14] Our optimized geometries are in accordance with the GGA/slab-model results of Lee and Kang.[16] B3LYP/LandL2DZ(d) (For simplicity, we omit the basis sets for NH_3, as they are always kept in 6-31G(d,p) in all calculations.) predicts that the "*trans*" conformation is 0.39 $\mathrm{kcal\,mol^{-1}}$ more stable than the "*cis*" conformation.

In the molecular adsorption state, the ammonia molecule is only slightly perturbed, with the N–H bond lengths being elongated by 0.004 Å and the H–N–H angles α_1 and α_2 being enlarged by 1 and 3° (See Fig. 1b and Table 2). The Si–N bond is found to be around 2.0 Å with the Si–Si–N angle of 104°. These findings are in good agreement with those of Lee and Kang, who observed the Si–N bond length of 2.08 Å and the Si–Si–N angle of 109°.[16] Fattal et al. reported the same value of Si–N bond length of 2.003 Å, but their Si–Si–N angle is considerably smaller, being at 91.8°.[14] Our optimized Si–Si–N angle in the "*cis*" conformation is around 103°.

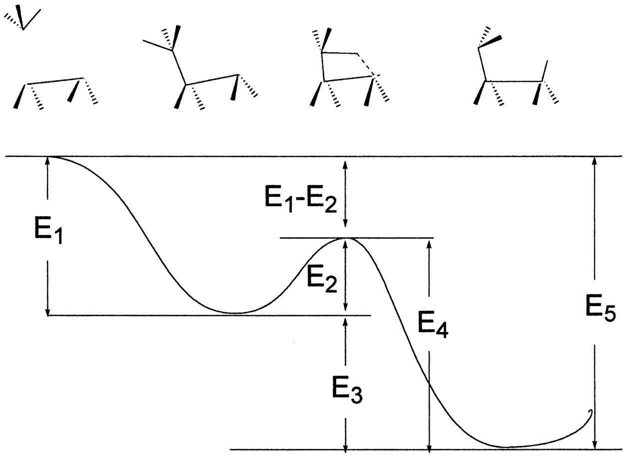

Fig. 2. Reaction profile for the molecular and dissociative adsorption of NH_3 onto a single silicon dimer of the Si(100)-(2×1) surface.

Table 2. Geometric Parameters for the Molecular Adsorption State of NH_3/Si_9H_{12}

Bond lengths are in Amstrong (Å) and bond angles are in degree (°). The number in square brackets is No. of Reference.

	Present work: B3LYP/6-31G(d,p)/			CASSCF/Cluster	GGA/Slab
	6-31G(d)	LanL2DZ(d)	LanL2DZ	[14]	[16]
N–H	1.022	1.022	1.022	1.028	1.04
N–H′	1.021	1.022	1.022	1.028	1.04
H–N–H	106.9	106.8	106.7	106.4	
H–N–H′	108.6	108.8	108.7	106.4	
Si_1–N	2.013	1.996	2.011	2.003	2.08
Si_1–N–H	109.0	108.7	108.8		127
Si_1–N–H′	114.4	114.8	115.1	100.5	
N–Si_1–Si_1'	104.6	104.6	103.6	91.8	109
H′–N–Si_1–Si_1'	179.7	180.0	175.1	0.0	180
Si_1–Si_1'	2.360	2.318	2.382	2.502	2.41
Si_1–Si_2	2.363	2.337	2.363	2.372	
Si_1'–Si_2'	2.396	2.361	2.413	2.400	
Si_2–Si_1–Si_1'	115.2	114.4	114.0	115.2	
Si_2'–Si_1'–Si_1	93.2	94.9	95.1	94.6	
Si_2–Si_1–Si_2	108.3	108.6	108.4	106.6	
Si_2'–Si_1'–Si_2'	96.7	98.1	97.7	99.5	
α_1	14.9	13.0	12.5		12
α_2	5.0	4.1	3.6		

Table 3. Geometric Parameters for the Transition State of $NH_2\cdots H/Si_9H_{12}$
Bond lengths are in Amstrong (Å) and bond angles are in degree (°).

		B3LYP/6-31G(d,p)/	
	6-31G(d)	LanL2DZ(d)	LanL2DZ
N–H	1.020	1.020	1.020
N–H′	1.402	1.385	1.408
H–N–H	108.5	108.5	108.1
H–N–H′	114.2	114.4	114.5
Si_1–N	1.881	1.874	1.894
Si_1–N–H	117.1	117.0	116.4
Si_1–N–H′	84.2	83.9	86.0
N–Si_1–Si_1'	85.8	86.6	84.4
H′–N–Si_1–Si_1'	0.0	0.0	0.0
Si_1'–H′	1.842	1.855	1.839
H′–Si_1'–Si_1	62.4	62.2	63.8
Si_1–Si_1'	2.373	2.345	2.384
Si_1–Si_2	2.353	2.328	2.352
Si_1'–Si_2'	2.374	2.348	2.380
Si_2–Si_1–Si_1'	109.6	109.3	109.3
Si_2'–Si_1'–Si_1	101.0	101.3	101.3
Si_2–Si_1–Si_2	113.5	113.0	113.0
Si_2'–Si_1'–Si_2'	104.0	104.2	104.2
α_1	9.2	7.8	8.0
α_2	3.7	2.8	3.2

The substrate cluster, Si_9H_{12}, experiences a relatively larger geometric change during the adsorption, as compared to the adsorbate NH_3. The Si–Si dimer bond lengths are enlarged by 4.9% for 6-31G(d), 5.8% for LanL2DZ(d) and 7.6% for LanL2DZ. The corresponding values are 3.1% for GGA/Slab-model16 and 3.3% for CASSCF/Cluster-model.[14] As is clearly seen from Fig. 2 of Fattal et al., adsorption induces or enhances the dimer buckling.[14] In a similar case of H_2O adsorption on Si(100)-(2×1), Konecny and Doren reported that molecular adsorption of water increases the buckling angle from 9.6° to 16.4°.38 We find that the buckling angles are 14.9° for 6-31G(d), 13.0° for LanL2DZ(d) and 12.5° for LanL2DZ. Actually, the second layer, which is essentially symmetric in the bare surface cluster, is also buckled due to the molecular adsorption of NH_3. The buckling angles are 5.0° for 6-31G(d), 4.1° for LanL2DZ(d) and 3.6° for LanL2DZ. This is understandable, as the interaction between the molecular NH_3 and the Si dimer should be mainly electrostatic, as in the case of H_2O/Si(100).[38] These interactions are enhanced by an increase in the buckling angle, which increases the charge polarization of the surface dimer. It is interesting to see that Lee and Kang observed a decrease of the buckling angle from the bare substrate of 18.2° to the NH_3 molecular adsorption of 12°.[16]

C. Transition State of $NH_2\cdots H/Si_9H_{12}$: So far, no detailed geometric parameters for the transition state of NH_2...H/Si_9H_{12} have been reported. Figure 1c and Table 3 summarize our optimized TS geometries. In the TS, one of the N–H bonds of NH_3 is coplanar with the Si–Si dimer bond, with a dihedral angle H–N–Si–Si of 0.0°. The Si–N bond lengths are 1.881 Å for 6-31G(d), 1.874 Å for LanL2DZ(d) and 1.894 Å for LanL2DZ, with a clear contribution of the covalent bonding. The coplanar N–H bonds are somewhat stretched, being 1.402 Å for 6-31G(d), 1.385 Å for LanL2DZ(d) and 1.408 Å for LanL2DZ, which leads to the partial formation of Si–H bonds at 1.842 Å for 6-31G(d), 1.855 Å for LanL2DZ(d) and 1.839 Å for LanL2DZ. As compared with the geometries of the molecular states, the dimer bond lengths are further enlarged, being 2.363 Å for 6-31G(d), 2.338 Å for LanL2DZ(d) and 2.366 Å for LanL2DZ. The buckling angles of the first dimer layer and the second layer are reduced to 9.18° and 3.70° for 6-31G(d), 7.84° and 2.81° for LanL2DZ(d) and 8.02° and 3.16° for LanL2DZ. Generally speaking, the geometric parameters produced by the ECP/basis sets of LanL2DZ are in good agreement with those from the all-electron basis sets.

D. Dissociative Adsorption State of NH_2–H/Si_9H_{12}: Our optimized geometric parameters for the dissociative adsorption state of NH_2–H/Si_9H_{12} are presented in Table 4 and Fig. 1d. Previous experimental as well as theoretical calculation results are also included in Table 4 for comparison. As is shown in Fig. 1d, the optimized geometries agree well with the ESDIAD results of Dresser et al.,[4] EELS results of Fujisawa et al.[5] and the scanned-energy mode PhD study of Franco et al.,[3] supporting the conclusion that the Si–NH_2 group is in a trigonal pyramidal geometry with the hydrogens on the NH_2(a) group pointing inward toward the dimer bond and upward away from the surface. The previous theoretical calculations gave the same picture,[12,14–16] with the exception of the MINDO/Slab-model calculations of Moriarty and Smith, which predicted a nearly planar Si–NH_2 configuration.[13]

Dresser et al.[4] and Fujisawa et al.[5] have assumed the un-

Table 4. Geometric Parameters for the Dissociative Adsorption State of NH_2–H/Si_9H_{12}
Bond lengths are in Amstrong (Å) and bond angles are in degree (°). The number in square brackets is No. of Reference.

	Present work:$^{a)}$			CASSCF	LDA	GGA	ASED	MINDO/	Expl.
	B3LYP/6-31G(d,p)/			/Cluster	/Slab	/Slab	/Cluster	Slab	
	6-31G(d)	LanL2DZ(d)	LanL2DZ	[14]	[15]	[16]	[12]	[13]	[3]
N–H	1.013	1.013	1.014	1.025	1.05	1.03	1.14	1.020	
H–N–H	110.2	109.8	109.2	108.9	105			106.2	
Si$_1$–N	1.752	1.745	1.775	1.768	1.75	1.76	2.04	1.707	1.73$^{a)}$
Si$_1$–N–H	118.4	117.9	116.5	117.7		146	105	168.2	
N–Si$_1$–Si$_1'$	120.1	120.0	120.1	114.0	102	118	115	114.9	111$^{a)}$
Si$_1'$–H′	1.494	1.481	1.477	1.516	1.51	1.51	1.38	1.522	
H′–Si$_1'$–Si$_1$	113.8	113.8	113.4	110.7	104	110	115	107.3	
Si$_1$–Si$_1'$	2.416	2.395	2.421	2.496	2.36	2.44		2.419	2.8$^{a)}$
Si$_1$–Si$_2$	2.369	2.345	2.369	2.370	2.38			2.340$^{b)}$	
Si$_1'$–Si$_2'$	2.367	2.343	2.364	2.366	2.31			2.301$^{b)}$	
Si$_2$–Si$_1$–Si$_1'$	103.5	103.5	104.0					103.4$^{b)}$	
Si2′–Si$_1'$–Si$_1$	105.5	105.4	105.3					106.8$^{b)}$	
Si$_2$–Si$_1$–Si$_2$	105.3	105.1	104.8	106.5				110.3$^{b)}$	
Si$_2'$–Si$_1'$–Si$_2'$	105.3	105.3	104.9	105.8				113.1$^{b)}$	
α_1	0.3	0.6	0.6		−1.9	0	0$^{a)}$	−2.2	0$^{a)}$

a) Si dimers are assumed to be symmetric. No relaxations are allowed in the substrate cluster.
b) Values calculated according to coordinates of Table 2 in Ref. 13
c) Based on the PhD spectra [Ref. 3], the Si–N bond length is determined to be 1.73 ± 0.08 Å and the bond angle relative to the surface normal is 21 ± 4°. The dimer is believed to be symmetric. The estimated titled angle is 8 ± 8° and the dimer bond length is 2.8 ± 1.7Å.

changed N–H bond length and H–N–H angle in the analyses of the adsorption structures. This assumption has been supported by the LDA/Slab-model calculations of Miotto et al., where the N–H bond length and the H–N–H angle in NH_2(a) were found to be exactly the same as those in the free NH_3.[15] Fattal et al., however, predicted that the N–H bond length would contract slightly (by 0.003 Å) and the H–N–H angle would expand somewhat (by 2.5°).[14] Our results are in support of those of Fattal et al.[14] We obtain a N–H bond contraction of around 0.005 Å and a H–N–H angle expansion of around 4°. It is interesting to notice that the N–H bond length should expand by 0.012 Å and the H–N–H angle should contract by 3.4°, if one compares the experimental geometry of free NH_2 radical with that of free NH_3.[27]

Dresser et al. has deduced a Si–N bond length of 1.71 Å.[4] This was confirmed by the recent scanned-energy mode PhD study of Franco et al., where the Si–N bond length was found to be 1.73 ± 0.08 Å.[3] This bond length can be compared favorably with the Si–N bond length in tri-silylamine ($(SiH_3)_3N$; Si–N: 1.738 ± 0.020 Å[39]). Previous theoretical results are in agreement with the experimental findings (i.e., 1.707 Å, Moriarty and Smith;[13] 1.75 Å, Miotto et al.;[15] 1.76 Å, Lee and Kang;[16] 1.768 Å, Fattal et al.[14]), with the exception of 2.04 Å of Zhou et al.[12] Our optimized Si–N bond lengths are 1.751 Å for 6-31G(d), 1.745 Å for LanL2DZ(d) and 1.773 Å for LanL2DZ.

There is no direct experimental result on the bond distance of Si–H. The calculated values are 1.522 Å, Moriarty and Smith;[13] 1.516 Å, Fattal et al.;[14] 1.51 Å, Miotto et al.;[15] 1.51 Å, Lee and Kang,[16] with the result of Zhou et al. being considerably smaller (1.38 Å[12]). Our optimized Si–H bond lengths are 1.494 Å for 6-31G(d), 1.481 Å for LanL2DZ(d) and 1.477 Å for LanL2DZ. The experimental Si–H bond length in SiH4 is 1.480 Å.[27] The Si–H bond angles found in the previous calculations are 25°, Zhou et al.;[12] 19.5°, Moriarty and Smith;[13] 20.7°, Fattal et al.;[14] 16°, Miotto et al.;[15] 20°, Lee and Kang,[16] relative to the surface normal. Our optimized values are 23° for all three kinds of basis sets.

There seems no consensus on the Si–N bond angle relative to the surface normal. For Si–N bond angle, Dresser et al. supposed a value of 35°;[4] Fujisawa et al. argued for 20°;[5] and Franco et al. reported 21 ± 4°.[3] Two recent slab-model calculations gave values of 10° by LDA[15] and 28° by GGA,[16] differing by 18°. The others are 25° by ASED-MO,[12] 23° by Slab-MINDO[13] and 24° by CASSCF.[14] Our optimized values are 30° for all three kinds of basis sets. Our calculations indicate that the Si–N bond angle is sensitive to the rotation of the NH_2 group. While rotating NH_2 by the Si–N axis experiences only a barrier of 1.2 kcal mol^{-1}, the change of the Si–N bond angle could be more than 10°.

There also exist significant differences in the predicted values of the Si–N–H angle. Dresser et al. supposed a Si–N–H angle of 106.8°,[4] the same as that of the H–N–H angle in the free NH_3; Fujisawa et al., however, suspected a value of 120°.[5] Early calculations of ASED-MO gave a Si–N–H angle of 105°,[12] supporting the assumption of Dresser et al., while Slab-MINDO calculations led to a nearly planar Si–NH_2 configuration with a Si–N–H angle of 168.2°.[13] Agreement is not

Table 5. Reaction Energetics for the Molecular and Dissociative Adsorption of NH_3 onto a Single Silicon Dimer of the Si(100)-(2×1) Surface

E_1 is the desorption energy from the molecular state to the gas phase. E_2 is the activation energy to overcome from the molecular state to the dissociative state. E_5 is the activation energy of the associated desorption of NH_3. E_4 is the depth of the dissociative adsorption well and E_3 measures the relative stability of the molecular state and dissociative state. All energies are in kcal mol^{-1}. The number in square brackets is No. of Reference.

	E_1	E_2	E_1-E_2	E_3	E_4	E_5
CASSCF/MRSDCI/Cluster model [14]	33	15	18	42	57	75
GGA/Slab model [16]: 1/2NH_3/Si(100)-p(2×2)	28	16	12	18	34	46
1 NH_3/Si(100)-p(2×2)	25	14	11	21	35	46
1 NH_3/Si(100)-p(2×1)	16					45
LDA/Slab model [15]: 1NH_3/Si(100)-p(2×1)						100
Present work[a)]: B3LYP/6-31G(d,p)/6-31G(d)	27.0	18.5	8.5	30.7	49.2	57.7
/LanL2DZ(d)	25.6	17.2	8.5	30.5	48.1	56.5
/LanL2DZ	23.2	16.7	6.5	26.6	43.6	50.1
/LanL2DZ(+d)	25.1	16.7	8.3	31.3	48.0	56.3
Exptl.	19[b)]	15[b)]	4[11]	36[b)]	42	46[4]

a) In the present work, optimizations are performed with B3LYP. The basis sets used for NH_3 is 6-31G(d,p); while those for Si_9H_{12} model cluster are 6-31G(d), LanL2DZ(d) and LanL2DZ. The notation LanL2DZ(+d) stands for a single point B3LYP calculation with the d polarization function being added to the Si atoms at the corresponding LanL2DZ optimized geometry.

b) Values calculated by assuming the dissociative activation energy E_2 of 15 kcal mol^{-1}.

reached in the recent first principle calculations. The Si–N–H angles from GGA and CASSCF calculations are 146° and 117.7°.[14,16] We obtain Si–N–H angles of 118.4° for 6-31G(d), 117.9° for LanL2DZ(d) and 116.5° for LanL2DZ, supporting the result of Fattal et al.[14]

It is generally agreed, both experimentally and theoretically, that dissociation adsorption of NH_2 and H passivates the dangling bonds of the surface dimer, which results in an elongation of Si–Si dimer bond and quenches the dimer buckling. Our calculations show that the buckling angle is practically zero in the dissociative adsorption state of NH_3 and the Si–Si dimer bond length is elongated by 9% with respect to that in the free substrate cluster.

In summary of all the experimental and theoretical findings,[3–5,12–16] we recommend an "optimal" bond geometry of NH_2(a) and H(a) on the Si(100)-(2×1) surface to be: Si–Si (symmetric dimer) 2.42 Å, Si–N 1.75 Å, Si–H 1.50 Å, N–H 1.01 Å, Si–Si–N 115°, Si–N–H 118°, Si–Si–H 111°, and H–N–H 109°.

2.2 Reaction Energetics. Early ASED-MO/DV-Xa calculations of Zhu et al. predicted that NH_3 can dissociate to NH_2 and H with no activation barrier.[12] This result seems to be in agreement with the experimental finding that NH_3 can dissociate at a temperature as low as 90 K.[7,8] As the surface reconstruction is known to play an important role in the chemistry of silicon, the reliability of the calculations of Zhu et al., which totally ignored the surface reconstructions,[12] should be limited. Recently, more sophisticated methods, CASSCF/MRSDCI/Cluster model and GGA/Slab model, have been employed to explore the detailed energetics from NH_3(g) to NH_2(a) and H(a) over one Si dimer.[14,16] The dissociation was found to involve a barrierless molecular chemisorption of NH_3(g) followed by an activated N–H bond cleavage of NH_3(a) to form NH_2(a) and H(a). This was confirmed by the very recent molecular beam experiments of Takaoka and Kusunoki.[11] Based on the measured angular distribution of the scattered NH_3 molecules, it was concluded that the adsorption of NH_3 follows a trapping-mediated mechanism. The trapped molecular NH_3 is in thermal equilibrium with the surface, either desorbing into the gas phase or adsorbing into the dissociative adsorption state (NH_2 + H) (See Fig. 2). Our calculated reaction profiles are in general agreement with the findings of Fattal et al., Lee and Kang and Takaoka and Kusunoki.[11,14,16]

Figure 2 illustrates the potential energy along the reaction path. The numerical results are summarized in Table 5. E_1 is the desorption energy from the molecular state to the gas phase. E_2 is the activation energy to overcome from the molecular state to the dissociative state. E_1-E_2 is determined by the equilibrium between the adsorption and desorption, which has been estimated by Takaoka and Kusunoki to be 4.0 ± 0.4 kcal mol^{-1}.[11] There are, unfortunately, no direct experimental data of E_1 and E_2. Fattal et al. gave E_2 of 15 kcal mol^{-1}, based on their MRSDCI/cluster model calculation.[14] Assuming this value to be correct, the "experimental" value of E_1 should be around 19 kcal mol^{-1}, which is much smaller than the theoretical value 33 kcal mol^{-1} of Fattal et al.[14] Lee and Kang, based on their GGA/Slab model calculations, estimated an activation energy E_2 of 16 or 14 kcal mol^{-1} at the coverage of 1/2 NH_3 or one NH_3 per Si dimer at Si(100)-p(2×2), respectively.[16] The corresponding E_1 is 28 or 25 kcal mol^{-1},[16] giving E_1-E_2 of 12 or 11 kcal mol^{-1} at the half or full coverage of NH_3. Our calculated values of E_1 are 27.0 kcal mol^{-1} for 6-31G(d), 25.6 kcal mol^{-1} for LanL2DZ(d), 23.2 kcal mol^{-1} for LanL2DZ and 25.1 kcal mol^{-1} for LanL2DZ(+d). The notation LanL2DZ(+d) stands for a single point B3LYP calculation, with the d polarization function being added to the Si atoms at the corresponding LanL2DZ optimized geometry. It is worthy of notice that LanL2DZ(+d) gives basically the same energetics as LanL2DZ(d) does. Our E_2 values of are18.5 kcal mol^{-1} for 6-31G(d), 17.2 kcal mol^{-1} for LanL2DZ(d), 16.7 kcal mol^{-1} for LanL2DZ and 16.7 kcal mol^{-1} for LanL2DZ(+d), giving E_1-E_2 of 6.5–8.5 kcal mol^{-1} for the different basis sets, which is in reasonable agreement with the experimental value of Takaoka and Kusunoki.[11]

E_5 is the activation energy of the associated desorption of NH_3, which is at about 46 kcal mol^{-1} as determined by the TPD measurement of Dresser et al.[4] GGA/Slab model calculations of Lee and Kang provided the best theoretical estimation of E_5 of 46 kcal mol^{-1}.[16] This value is overestimated by LDA (100 kcal mol^{-1} [15]) and MRSDCI (75 kcal mol^{-1} [14]). Our calculated E5's are around 56 kcal mol^{-1}.

If one assumes that E_2 equals 15 kcal mol^{-1}, all the other values, E_1, E_3 and E_4 shown in Fig. 2, can be deduced easily. We summarize these values in Table 5 and denote them all as the experimental results.[39] E_4 is the depth of the dissociative adsorption well and E_1 is that of the molecular adsorption well. E_3 measures the relative stability of the molecular state and dissociative state. The "experimental" values of E_3 and E_4 are 27 and 42 kcal mol^{-1}. The GGA/Slab model results at half coverage are 18 and 34 kcal mol^{-1}, underestimating the relative stability of the dissociative state by 9 kcal mol^{-1}, while the MRSDCI/Cluster model results are 42 and 57 kcal mol^{-1}, overestimating the stability of the dissociative state relative to the molecular state by 15 kcal mol^{-1}. Our calculated values for E_3 are 30.7 kcal mol^{-1} for 6-31G(d), 30.5 kcal mol^{-1} for LanL2DZ(d), 26.6 kcal mol^{-1} for LanL2DZ and 31.3 kcal mol^{-1} for LanL2DZ(+d); while E_4 are 49.2 kcal mol^{-1} for 6-31G(d), 48.1 kcal mol^{-1} for LanL2DZ(d), 43.6 kcal mol^{-1} for LanL2DZ and 48.3 kcal mol^{-1} for LanL2DZ(+d), in an average error of 4 kcal mol^{-1} as compared with the experimental values.

In general, we would like to conclude that the methodology employed here is capable of reproducing the whole energetics, in addition to the geometric parameters and the vibrational interactions at the surface.[41] In a similar system of CO/Si(100)-(2×1), Bacalzo et al. concluded that B3LYP/LanL2DZ is good for prediction of geometric parameters, but is not sufficient to describe the energetics.[42] The difference between our and their methodologies is that we have kept the basis sets for the adsorbate molecule always at 6-31G(d,p) and only replaced the basis sets for the substrate clusters with LanL2DZ. It should be their reduction of the quality of the adsobate basis sets that worsens the reaction energetics.

All the present theoretical calculations predicted an activation energy around 15 kcal mol^{-1}. This may indicate that the reaction path for NH_3 dissociation over a single dimer is not feasible below room temperature. There would exist other reaction paths with low or no activation barrier in order to account for the experimentally observed ammonia dissociation at a temperature as low as 90 K.[7,8] Actually, recent theoretical calculations even suggested that the single dimer model, Si_9H_{12}, is not adequate at all to the modeling of the Si(100) surface.[34,35] It is therefore mandatory to find out a cost-effective way to expand the silicon cluster model and to study in details the whole ammonia dissociation reaction mechanism over the silicon surface. We believe that B3LYP/LanL2DZ(+d), with adsorbate basis sets being 6-31G(d,p), will behave even better for larger cluster models, as the Schrödinger equation is solved variationally, and the increase of the total number of basis functions of the system should, in principle, improve the quality of the solution.

3. Concluding Remarks

In the present work, we present a hybrid density functional B3LYP cluster model calculation of the dissociative adsorption of ammonia over a single dimer site on the Si(100) surface. The adsorption geometries and the reaction energetics from NH_3(g) to NH_2(a) and H(a) have been studied with Si basis sets varying from the standard all electron 6-31G(d) to the LanL2DZ with effective core potential, while keeping NH_3 basis sets as 6-31G(d,p) in all cases. The results are compared critically with the available theoretical and experimental findings on this system. It was found that B3LYP/LanL2DZ is a reasonable level of theory for the calculations of not only the geometries, but also the reaction energetics. This provides a cost-effective way to extend the size of the Si cluster models and to study the energetics of the whole reaction path.

In summary of all the experimental and theoretical findings, we recommend an "optimal" bond geometry of NH_2(a) and H(a) on the Si(100)-(2×1) surface to be: Si–Si (symmetric dimer) 2.42 Å, Si–N 1.75 Å, Si–H 1.50 Å, N–H 1.01 Å, Si–Si–N 115°, Si–N–H 118°, Si–Si–H 111°, and H–N–H 109°.

Our calculations support the recent molecular beam experimental results that the adsorption of NH_3 follows a trapping-mediated mechanism. Based on the results with the 6-31G(d) basis sets for the substrate clusters, the depth of the molecular adsorption well is estimated to be around 27.0 kcal mol^{-1} (E_1), while that of the dissociative adsorption well is around 49.2 kcal mol^{-1} (E_4), indicating that the dissociative adsorption state is 30.7 kcal mol^{-1} (E_3) more stable than the molecular adsorption state. The 6-31G(d) estimated dissociation activation energy is 18.5 kcal mol^{-1} (E_2), with an (E_1-E_2) of 8.5; while the calculated activation energy of the association desorption of NH_3 is found to be around 57.7 kcal mol^{-1}. All these results are in general agreement with the experimental as well as the previous theoretical findings.

This work is supported by "Research for the Future" Program from the Japan Society for the Promotion of Science, Natural Science Foundation of China, Educational Ministry of China, and Fok Ying Tung Education Foundation.

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