

# Interactions of alkylamines with the silicon (001) surface\*

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The interactions of primary, secondary, and tertiary alkylamines with the Si(001) surface have been investigated using x-ray/ultraviolet photoelectron spectroscopy, Fourier transform infrared spectroscopy and scanning tunneling microscopy. Experimental and computational results show that alkylamines bond to the surface through the nitrogen atom. Primary alkylamines such as hexylamine bond to the surface by breaking only one N–H bond. Secondary alkylamines such as dimethylamine and *N*-methylpentylamine cleave only the N–H bond, leaving the N–C bonds intact. Tertiary alkylamines, such as trimethylamine and *N,N*-dimethylbutylamine, can form stable dative-bonded adducts on the surface that are characterized by very high N(1s) binding energies of 402.2 eV. The ability to form dative-bonded adducts between tertiary alkylamines and Si(001) stems from the capability of electron transfer from nitrogen to the surface. Our results show that this charge exchange controls the propensity for N–H vs N–C bond cleavage. © 2002 American Vacuum Society. [DOI: 10.1116/1.1490381]

## I. INTRODUCTION

Interactions of organic molecules with the Si(001) surface have drawn a great deal of attention because of their technological importance in molecular electronics and biosensors.<sup>1,2</sup> The Si(001) surface has a unique (2×1) reconstruction structure in which pairs of atoms bond together to form Si=Si dimers. This bonding within dimers can be described in terms of a strong  $\sigma$  and a weak  $\pi$  bond,<sup>3–5</sup> analogous to the C=C bonds of organic alkenes and the Si=Si bonds of silenes.

While recent studies of interactions of organic alkenes with the Si(001) surface have suggested that electron donation from C=C  $\pi$  orbitals to the surface plays an important role in controlling the overall reaction,<sup>6–10</sup> molecules that contain nitrogen atoms are of particular interest because the N lone-pair electrons are potentially good electron donors. Previous studies of adsorption of ammonia on Si(001) have indicated that ammonia bonds to the surface through the nitrogen atom, cleaving a N–H bond and producing chemisorbed H atoms and NH<sub>2</sub> fragments.<sup>11–18</sup> Computational studies have shown that this reaction proceeds through a mechanism in which the nitrogen lone-pair electrons interact with one Si atom of a Si=Si dimer via a transient dative bond, which in turn weakens the N–H bond and leads to dissociative adsorption.<sup>19,20</sup> A similar process has been proposed for aniline (C<sub>6</sub>H<sub>5</sub>–NH<sub>2</sub>), which also interacts with Si(001) via cleavage of one N–H bond, leaving chemisorbed Si–NH(C<sub>6</sub>H<sub>5</sub>) fragments and chemisorbed H atoms.<sup>21–24</sup> In order to focus on the role of nitrogen lone-pair electrons during the reaction, we have selected several alkylamines for study. Our results demonstrate that the formation of dative-bonded intermediates plays an important role in controlling the overall reaction pathways.

## II. EXPERIMENT

All experiments reported here were performed in several different ultrahigh vacuum (UHV) chambers, each having base pressure of  $<1 \times 10^{-10}$  Torr. Clean, well-ordered Si(001)-(2×1) surfaces were prepared by high-temperature annealing to  $>1100$  °C in UHV.<sup>25</sup> Highly doped samples were used for the x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling microscopy (STM) experiments, while lightly doped samples were used in the Fourier transform infrared (FTIR) experiments. The surfaces were characterized by several techniques. XPS data were obtained using a Physical Electronics system with monochromatized Al K $\alpha$  radiation (1486.6 eV), described previously.<sup>21</sup> UPS data were obtained using a VG ultraviolet (UV) lamp with helium(I) radiation (21.2 eV); the Fermi level was determined by measuring the UPS spectrum of the tantalum clip on the sample holder. FTIR absorption spectra were obtained using a multiple internal reflection prism and a Mattson RS-1 FTIR spectrometer coupled to an UHV chamber through BaF<sub>2</sub> windows with a liquid nitrogen-cooled InSb detector. Direct observation of adsorbed molecules was achieved using a homemade UHV STM. Images were obtained at sample bias of  $-2.0$  V, utilizing a tunneling current of 20 pA.

All alkylamines were obtained from Aldrich and had 99% purity. Freeze–pump–thaw cycles were performed to remove all dissolved gases prior to dosing. The purity of each compound was verified in the vacuum chamber using an *in situ* mass spectrometer. The molecules were introduced into the UHV chamber using a variable leak valve. The chamber pressure was used as an indicator of overall dosage, however actual exposures at the surface are higher. All exposures are expressed as nominal exposures, in units of langmuirs (L), where  $1 \text{ L} = 1 \times 10^{-6}$  Torr s.

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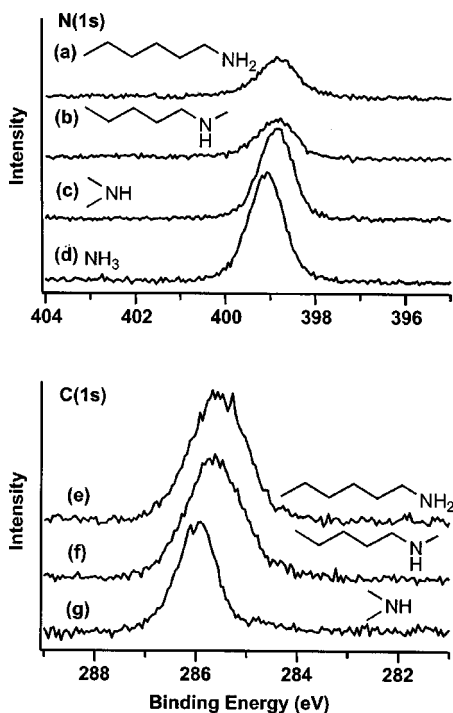


FIG. 1. XPS spectra of Si(001) surfaces exposed to different molecules at 300 K: (a) N(1s), hexylamine, (b) N(1s), *N*-methylpentylamine, (c) N(1s), dimethylamine, (d) N(1s), ammonia, (e) C(1s), hexylamine, (f) C(1s), *N*-methylpentylamine, and (g) C(1s), dimethylamine.

### III. RESULTS AND DISCUSSION

#### A. Bonding of primary and secondary alkylamines

Because our experiments show that the behavior of primary and secondary alkylamines is quite similar, we present the results for these two types of molecules together. Figure 1 shows N(1s) XPS data obtained after Si(001) samples at 300 K were saturated (10 L exposure) by hexylamine [ $\text{CH}_3(\text{CH}_2)_5\text{NH}_2$ ], *N*-methylpentylamine (MPA) [ $\text{CH}_3(\text{CH}_2)_4\text{NHCH}_3$ ], and dimethylamine (DMA) [ $(\text{CH}_3)_2\text{NH}$ ]. Each spectrum shows a single, narrow peak at 398.9 eV with a full width at half maximum (FWHM) of 0.9 eV. The narrow width suggests that in each case there is only a chemically distinguishable form of nitrogen on the surface, and the nearly identical N(1s) binding energies indicate that the environment is nearly the same in all three compounds. For comparison, we also obtained an XPS spectrum of a Si(001) surface saturated by ammonia; the resulting N(1s) spectrum [Fig. 1(d)] again shows a single narrow peak, but with a slightly higher binding energy at 399.1 eV. Previous studies have established that ammonia reacts with the Si(001) surface via cleavage of a N–H bond, and produces chemisorbed H atoms and  $\text{NH}_2$  fragments.<sup>11–18,26</sup> The 398.9 eV N(1s) binding energy observed for hexylamine, MPA and DMA is close to the 398.5–399.1 eV N(1s) binding energies of dissociatively adsorbed ammonia,<sup>12,15,26</sup> pyrrolidine,<sup>21</sup> and aniline<sup>21,22</sup> on Si(001) surfaces. Thus it is likely that hexylamine, MPA and DMA also bond with cleavage of a N–H or N–C bond, leaving the N atom with a coordination number of 3.

TABLE I. Peak area ratios and saturation N coverages of various alkylamines on Si(001).

	$\text{NH}_3$	Hexylamine	MPA	DMA	TMA	DMBA
$A_{\text{N}1s}/A_{\text{Si}2p}$	3.35	1.54	1.24	2.51	1.59	1.58
$A_{\text{C}1s}/A_{\text{Si}2p}$	...	1.53	1.56	1.01	0.98	1.92
N coverage (ML)	0.5	0.23	0.19	0.37	0.24	0.24

Since there is little difference in electronegativity between H and C, it cannot be easily determined from the N(1s) spectra alone whether hexylamine, MPA, and DMA cleave N–H or N–C bonds (or both) when adsorbing to the Si(001) surface. Analysis of the C(1s) spectra clarifies the situation. Figures 1(e)–1(g) show corresponding C(1s) spectra for hexylamine, MPA, and DMA, respectively. The C(1s) spectra for hexylamine and MPA are almost identical, each exhibiting a single broad peak at 285.6 eV (FWHM = 1.3 eV). The C(1s) spectrum of DMA [Fig. 1(g)] shows a single sharp, narrow peak at 286.0 eV (FWHM = 0.9 eV). During adsorption, cleavage of a N–C bond would be expected to produce methyl fragments bonded to the silicon surface (i.e., Si–CH<sub>3</sub> species), which we have shown in separate experiments yields a C(1s) peak at 284.1 eV.<sup>27</sup> However, all C(1s) binding energies shown in Figs. 1(e)–1(g) are more than 1.5 eV higher than this value. Because silicon (Pauling electronegativity = 2.1) is a better electron donor than nitrogen (electronegativity = 3.0) and C (electronegativity = 2.5), carbon atoms bonded to a N or C atom are normally expected to have a higher binding energy than those bonded to Si. Thus, the XPS data suggest that these alkylamines adsorb to Si(001) by cleaving a N–H bond, thus producing Si–NH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> for hexylamine, Si–N(CH<sub>3</sub>)(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> for MPA, and Si–N(CH<sub>3</sub>)<sub>2</sub> for DMA on the surface.

Quantitative information about surface coverage can be obtained based on analysis of the peak area. Previous studies have established that the saturation N coverage is ~0.5 monolayer (ML) for ammonia (1 nitrogen atom per Si=Si dimer).<sup>28</sup> Since all XPS experiments for ammonia and alkylamines here were performed under one consistent set of conditions, we can estimate the surface coverage of alkylamines by comparing the peak area ratios ( $A_{\text{N}1s}/A_{\text{Si}2p}$ ) of the alkylamines with that of ammonia. As listed in Table I, analysis of the N(1s) peak area yields  $A_{\text{N}1s}/A_{\text{Si}2p}$  ratios of 1.54 for hexylamine, 1.24 for MPA, and 2.51 for DMA. By comparing the  $A_{\text{N}1s}/A_{\text{Si}2p}$  ratio of 3.35 for ammonia, we can determine that the N saturation coverages of hexylamine, MPA, and DMA are about 0.23, 0.19 and 0.37 ML, respectively, with an error of  $\pm 0.03$  ML. The saturation coverages for hexylamine and MPA are almost the same within the range of error, and are only about half that of DMA. The difference in saturation coverage can be attributed to the different sizes of these molecules. Since the larger molecule (hexylamine or MPA) has approximately half the saturation coverage of DMA, we can conclude that the carbon chain of hexylamine or MPA creates some steric block of surface

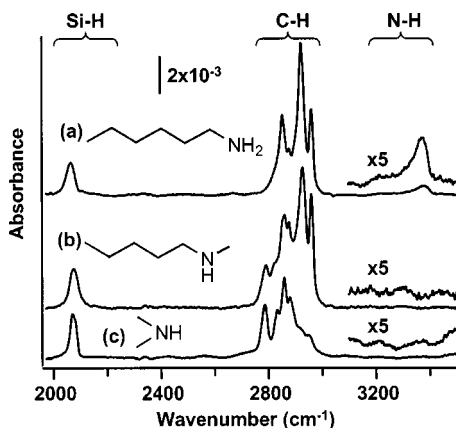


FIG. 2. FTIR spectra of Si(001) surfaces exposed to different molecules at 300 K: (a) 10 L of hexylamine, (b) 10 L of *N*-methylpentylamine, and (c) 10 L of dimethylamine.

sites, but that the organic chain is likely directed away from the surface. The corresponding analysis for C(1s) peaks is consistent with that for N(1s) peaks. The  $A_{C\ 1s}/A_{Si\ 2p}$  ratio of hexylamine is almost the same as that of MPA, but is  $\sim 1.5$  times that of DMA because both hexylamine and MPA have three times more C atoms in one molecule but only half the number of molecules on the surface compared with DMA. Table I also includes data for tertiary alkylamines that will be discussed later.

More information about the propensity toward N–H vs N–C bond cleavage can be obtained from infrared spectra. Figure 2 shows infrared spectra of Si(001) surfaces exposed to 10 L of hexylamine, MPA, or DMA at 300 K. Each spectrum shows a strong, sharp peak in the Si–H stretching region, peaking at  $2066\text{ cm}^{-1}$  for hexylamine and at  $2072\text{ cm}^{-1}$  for MPA and DMA.<sup>29</sup> Worth noting is that the Si–H vibration is nearly the same intensity for all three molecules, even though MPA and DMA are secondary amines and hexylamine is a primary amine. Each spectrum has large peaks in the  $2750\text{--}3000\text{ cm}^{-1}$  region, in which C–H vibrations of saturated molecules are typically found. However, no intensity is observed in the  $3000\text{--}3100\text{ cm}^{-1}$  region where alkene-like (i.e., C=C–H) vibrations are typically found. Finally, in the N–H region, a small peak is observed at  $3379\text{ cm}^{-1}$  for hexylamine, but there is no significant N–H vibration detected from chemisorbed MPA or DMA. These FTIR data indicate that bonding of MPA and DMA is accompanied by cleavage of the N–H bond, with the H atoms bonding to the Si surface and giving rise to the Si–H vibrations observed at  $2072\text{ cm}^{-1}$ . For hexylamine, however, the data indicate that adsorption involves only cleavage of *one* of its two N–H bonds. One H atom bonds to the Si surface and produces the Si–H mode at  $2066\text{ cm}^{-1}$ , while the Si–NH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> species produces  $3379\text{ cm}^{-1}$  N–H vibration. The observation that primary amines cleave only one N–H bond upon adsorption is consistent with previous results for aniline (C<sub>6</sub>H<sub>5</sub>–NH<sub>2</sub>) (Ref. 21) as well as with data for ammonia that indicate that the Si–NH<sub>2</sub> group is the principal surface species.<sup>28</sup>

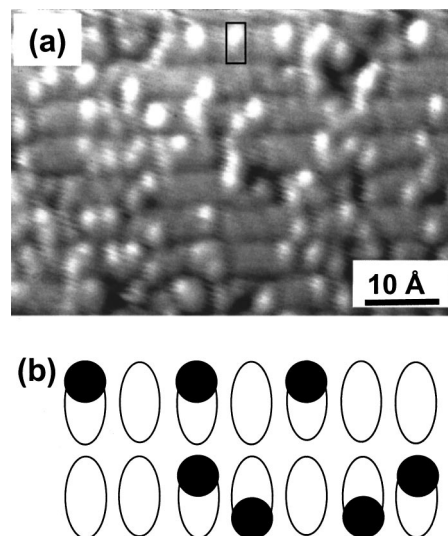


FIG. 3. (a) STM image of a clean Si(001) surface exposed to 0.05 L of dimethylamine with a sample bias voltage of  $-2.0\text{ V}$  and a tunneling current of  $20\text{ pA}$ . A single Si=Si dimer with an adsorbed molecule is outlined. (b) Schematic illustration showing the location of adsorbed molecules with respect to the underlying dimers.

To determine the local symmetry of adsorbed molecules, STM experiments were performed. Figure 3(a) shows a STM image of a clean Si(001) surface exposed to 0.05 L DMA. The image was obtained with a sample bias voltage of  $-2.0\text{ V}$  and a tunneling current of  $20\text{ pA}$ . The dimer rows and individual dimers are clearly seen. Bright round-shaped protrusions are observed and appear to be similar to one another in what appears to be a unique bonding configuration. Since under these imaging conditions adsorbed H atoms are known to appear as surface depressions, we attribute the bright features to N(CH<sub>3</sub>)<sub>2</sub> groups. Clearly all bright protrusions are located on one side of the Si=Si dimers, as illustrated in Fig. 3(b), indicating the N(CH<sub>3</sub>)<sub>2</sub> species bonds to *one* silicon atom of the dimer.

## B. Bonding of tertiary alkylamines

While both primary and secondary alkylamines undergo complete dissociation upon adsorption, tertiary alkylamines behave very differently. Figure 4 shows XPS spectra of Si(001) samples at 300 K exposed to 2 L of trimethylamine (TMA) [(CH<sub>3</sub>)<sub>3</sub>N] and *N,N*-dimethylbutylamine (DMBA) [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>2</sub>]. The N(1s) XPS spectra of TMA [Fig. 4(a)] and of DMBA [Fig. 4(b)] both show two peaks at 402.2 and 398.9 eV, with the 402.2 eV peak the major one. While the C(1s) spectrum of TMA [Fig. 4(c)] is dominated by a single sharp peak at 286.9 eV, the C(1s) spectrum of DMBA [Fig. 4(d)] shows a broad peak from 284.5 to 286.9 eV.

The most striking result shown in Fig. 4 is the presence of N(1s) and C(1s) peaks at very high binding energies. In particular, the 402.2 eV N(1s) binding energy is 2 eV higher than the 400.2 eV value observed for physisorbed TMA on Au.<sup>30</sup> We recently showed that the high 402.2 eV binding energy of TMA on Si(001) arises from the fact that it bonds

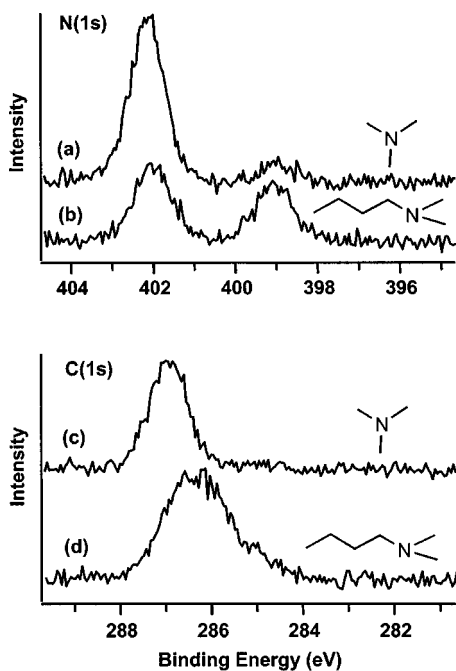


FIG. 4. XPS spectra of Si(001) surfaces exposed to 2 L of trimethylamine and *N,N*-dimethylbutylamine at 300 K, respectively. (a) N(1s), trimethylamine, (b) N(1s), *N,N*-dimethylbutylamine, (c) C(1s), trimethylamine, and (d) C(1s), *N,N*-dimethylbutylamine.

to the surface and forms a quaternary, dative-bonded adduct in which the N atom transfers its electron density to the Si=Si dimer, leaving behind a very electron-deficient N atom.<sup>27</sup> Likewise, the smaller N(1s) feature at 398.9 eV is almost identical to that observed in primary and secondary alkylamines, leading us to attribute it to Si–N(CH<sub>3</sub>)<sub>2</sub> species formed via N–C bond cleavage. The data in Fig. 4 show that DMBA yields peaks at similar energies, but with a markedly increased tendency toward N–C bond cleavage. From the XPS spectra it is not possible to determine whether the methyl group or the butyl group is cleaved, but it is likely that both will be cleaved with nearly equal probability.

Quantitative measurement of the N(1s) peak intensities again shows that the saturation N coverage is 0.24 ML for both TMA and DMBA (about one molecule per two dimers), as listed in Table I. The presence of a hydrocarbon tail has little effect on the saturation coverage. As expected from their stoichiometries, the corresponding analysis for C(1s) peaks shows DMBA has a  $A_{C\ 1s}/A_{Si\ 2p}$  ratio twice that of TMA.

While XPS provides detailed information about the core levels of the molecules, UPS provides complementary information about the valence levels. Figure 5 shows UPS spectra of a clean Si(001) surface and the same surface after saturation by TMA. The spectrum of the clean surface [Fig. 5(a)] clearly shows surface states of the Si=Si dimers 0.65 eV below the Fermi energy.<sup>31,32</sup> After a nominal exposure of 20 L of TMA, the intensity of the peaks associated with the dimer states decreases substantially [Fig. 5(b)], indicating the dimers are directly involved in the interaction with TMA molecules. However, even after 20 L exposure (far exceeding

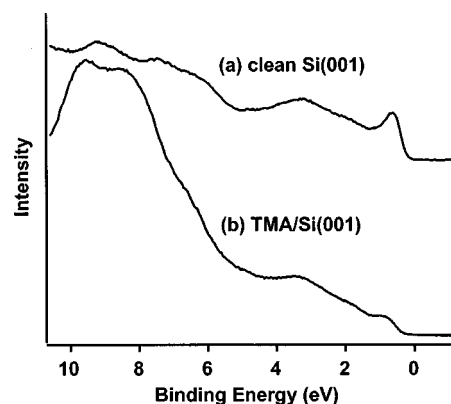


FIG. 5. UPS spectra of a (a) clean Si(001) surface and (b) the same surface exposed to 20 L of trimethylamine at 300 K.

the “saturation” value), some residual intensity is observed in this region. Adsorption of TMA also causes large changes in the spectrum in the 4.5–9.5 eV range, with two large peaks visible at 8.5 and 9.5 eV. Assignment of these peaks is complicated by the fact that the XPS data show that TMA undergoes some dissociation. Other experiments (not shown) show that the Al *K*α x-ray source has no significant effect on the sample; the He (I) UV source enhances the dissociation. Previous photoelectron studies of gas-phase TMA have shown that the N lone pair gives rise to a peak 8.5 eV below the Fermi energy  $E_F$ .<sup>33,34</sup> Similarly, previous studies of adsorption of ammonia on Si(001) have shown that physisorbed ammonia gives rise to a peak at ~6.7 eV and dissociatively bonded ammonia (i.e., Si–NH<sub>2</sub> species) at ~5.0 eV due to the N lone pair.<sup>12</sup> Since our XPS data for a 20 L exposure of TMA show significant dissociative bonding as well as dative bonding (spectrum not shown), the features in the 4.5–9.5 eV region probably arise from the N lone pair of the dissociative-bonded products or from new states of the silicon surface due to the bonding of TMA.

### C. Theoretical calculations

To better understand the behavior of alkylamines that interact with the Si(001) surface, we calculated the energies of various amine-silicon adducts using the GAUSSIAN'98 program.<sup>35</sup> The results reported here were performed using density functional theory with the 6-31+G\* basis set and the Becke3LYP hybrid density functional.<sup>36</sup> The Si<sub>9</sub>H<sub>12</sub> cluster was used to simulate the Si(001) surface; this cluster has seven “bulk-like” Si atoms and has two more “surface-like” Si atoms in a dimer configuration similar to that of a single dimer on the Si(001) surface, and has been used extensively in previous studies.<sup>8,20,37–39</sup>

The molecular bonding of TMA and the dissociative bonding of DMA are readily explained by these computational results. As shown in Fig. 6(a), the quaternary-bonded TMA-Si(001) adduct has energy 104 kJ/mol lower than the separated reactants, but dissociation to produce Si–N(CH<sub>3</sub>)<sub>2</sub> and chemisorbed methyl groups (on the same dimer) is 248 kJ/mol lower in energy than the separated reactants. Thus,

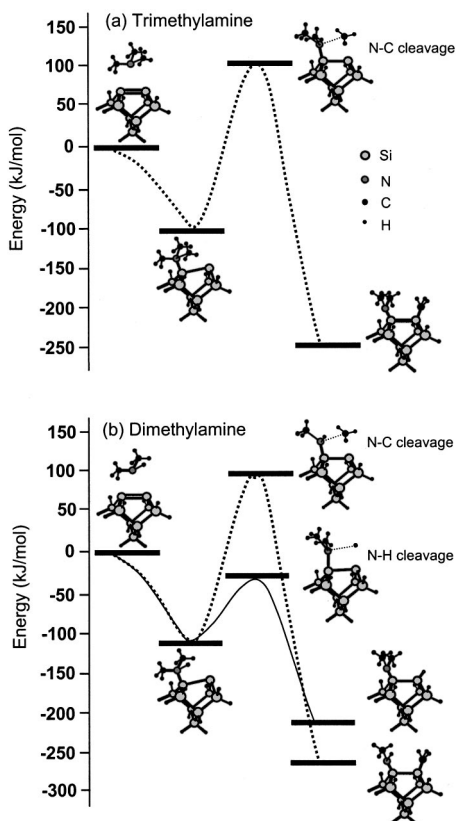


FIG. 6. Energy diagrams that represent  $\text{Si}_9\text{H}_{12}$  clusters plus free molecules, dative-bonded transient intermediates and final products obtained from calculations. (a) Trimethylamine reacting with the  $\text{Si}_9\text{H}_{12}$  cluster. (b) Dimethylamine reacting with the  $\text{Si}_9\text{H}_{12}$  cluster.

thermodynamics clearly favor dissociation. However, the high-symmetry transition state involved in cleaving a N–C bond to produce  $\text{Si–N}(\text{CH}_3)_2$  and  $\text{Si–CH}_3$  species leads to a barrier 107 kJ/mol higher than the energy of the separated reactants. Consequently, the TMA–Si(001) molecular complex is only metastable toward dissociation, but the barrier is sufficiently large that the molecularly bonded adduct can be easily observed at room temperature. Analogous calculations for DMA [Fig. 6(b)] show that the molecularly bonded adduct is 113 kJ/mol lower in energy than the separated reactants. The final products of N–C bond cleavage ( $\text{Si–NHCH}_3$  and  $\text{Si–CH}_3$  species) are 263 kJ/mol lower than the reactants, while those produced by N–H bond cleavage [ $\text{Si–N}(\text{CH}_3)_2$  and  $\text{Si–H}$  species] are only 212 kJ/mol lower than the reactants. However, while the transition state for N–C cleavage is again high (96 kJ/mol above the reactants), the transition state for N–H cleavage is 27 kJ/mol below the energy of the separate reactants. Thus, for DMA, the calculations predict that dissociation should occur in a facile manner via N–H bond cleavage; the molecular configuration, although a likely transient intermediate, is not likely to be observed at room temperature. Similar conclusions have been reached in previous computational studies of ammonia<sup>19,20</sup> and in a very recent study of methylamines<sup>39</sup> interacting with the Si(001) surface.

The important conclusion from the calculations for TMA

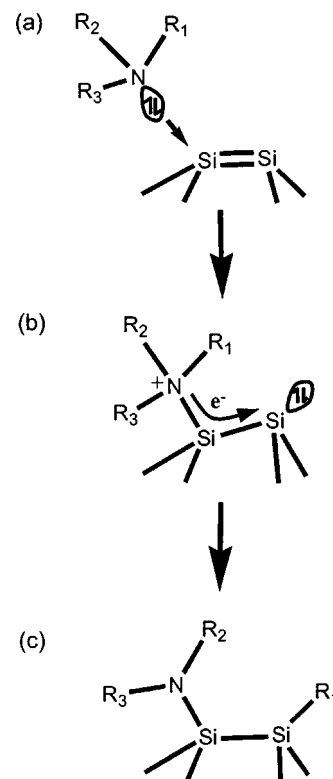


FIG. 7. Illustration of the reaction pathway of alkylamines with the Si(001) surface.

and DMA is that for secondary amines such as DMA, cleavage of a N–C bond is favored by the overall thermodynamics, but it involves a high activation barrier. Consequently, cleavage of the N–H bond is favored because it involves a lower barrier even though final products are slightly less stable energetically. For TMA, however, there is no N–H bond to break; consequently, the dative-bonded adduct is in a rather deep energetic potential minimum, and cleavage of the N–C bond occurs only slowly.

#### D. Reaction pathway

Based on our experimental results, we believe that the insights gleaned from the theoretical calculations for TMA and DMA can be extended to other amines, and lead to the general reaction pathway shown in Fig. 7. When an alkylamine reacts with the Si(001) surface, the electron-rich N atom interacts with one silicon atom of the Si=Si dimer [Fig. 7(a)], and forms a dative-bonded adduct. The adduct is stabilized because the electron density donated from the N to the Si=Si dimer can largely be transferred to the other Si atom of the dimer [Fig. 7(b)]. We propose that if the alkylamine is primary or secondary (at least one of the  $R_1$ ,  $R_2$  and  $R_3$  is the H atom, for example,  $R_1$  is H), the increase of positive charge on the N atom preferentially weakens the N–H bond, so dissociation occurs through the N–H bond cleavage [Fig. 7(c)]. After breaking one N–H bond, the N atom reestablishes its conventional coordination number of 3, making further cleavage of N–H or N–C bonds much more difficult. However, if the alkylamine is tertiary, the

dative-bonded intermediates are stabilized by the electron-donating alkane groups. This produces a higher energy barrier for breaking a N–C than a N–H bond and allows the dative-bonded adducts to persist at room temperature.

From these studies, it is clear that N lone-pair electrons control the overall reaction pathway. In particular, the fact that primary amines cleave only one N–H bond is a direct consequence of the charge exchange that accompanies formation of the initial dative-bonded complex. Formation of dative bonds between the tertiary alkylamine with Si(001) results in electron density being transferred from the nitrogen atom of the tertiary alkylamine to the surface. Electron transfer modifies the electronic structure of surface silicon atoms and thus probably will bring new properties to the surface. In fact, our recent studies have shown that the adsorption of TMA onto one Si atom allows the other Si atom within the same Si=Si dimer to interact with BF<sub>3</sub>, and form an unusual TMA-Si–Si–BF<sub>3</sub> electron donor–acceptor complex.<sup>40</sup>

#### IV. CONCLUSION

The adsorption of primary, secondary and tertiary alkylamines on the Si(001) surface was systematically studied by XPS, UPS, FTIR, and STM. Our results have shown that alkylamines bond to the surface by the nitrogen atom. Primary alkylamines, such as hexylamine, bond to the surface by breaking only one N–H bond. In a similar way, secondary alkylamines such as dimethylamine and *N*-methylpentylamine only cleave the N–H bond during adsorption, leaving the N–C bonds intact. More important, tertiary alkylamines, trimethylamine and *N,N*-dimethylbutylamine can form stable dative-bonded adducts on the surface and are characterized by very high XPS N(1s) binding energies of 402.2 eV. Our results indicate that the overall behavior of amines on Si(001) surfaces is controlled by the formation of the dative-bonded intermediate.

#### ACKNOWLEDGMENT

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