

# Adsorption of Phenyl Isothiocyanate on Si(001): A 1,2-Dipolar Surface Addition Reaction

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The adsorption of phenyl isothiocyanate (PITC) on silicon (001) surfaces has been investigated using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, scanning tunneling microscopy (STM), and ab initio calculations. The experimental evidence shows that adsorption onto the Si surface occurs in a highly selective manner, through the N=C=S group and not through the benzene ring. Both experimental and theoretical evidence suggests that the adsorption involves the interaction of the N and C atoms of the N=C=S group with the Si=Si dimer, forming a four-member Si<sub>2</sub>NC ring at the interface. This process leaves the aromatic ring nearly unperturbed and is analogous to a 1,2-dipolar addition reaction. Theoretical calculations confirm that this is the most stable product.

## I. Introduction

The adsorption of organic molecules on silicon surfaces is of great technological importance.<sup>1</sup> The ability to form an ordered organic adlayer on silicon presents an advance that opens opportunities for several fields, such as microelectronics and biosensing. Of particular interest in this respect is the Si(001) surface, which undergoes a reconstruction involving a pairing of surface atoms into dimers.<sup>2</sup> These dimers are formally held together with a double bond, suggesting that the chemistry of Si(001) may be similar to the chemistry of organic alkenes. The adsorption of the two simplest unsaturated hydrocarbons, ethylene and acetylene, on Si(001) has been extensively studied.<sup>3–10</sup> Ethylene adsorbs onto Si(001) so that the C=C  $\pi$  bond and the Si=Si  $\pi$  bond break, forming two new Si–C  $\sigma$  bonds. Initially, acetylene was also thought to bond in a fashion similar to that of ethylene, but recent evidence suggests that acetylene's adsorption behavior is more complex.<sup>11</sup> Recently, the adsorption behavior of more complex alkenes has also received a great deal of attention. Several examples of [2 + 2] cycloaddition reactions, in which the double bond of the organic molecule reacts with the double bond between the Si atoms to form a four-member Si<sub>2</sub>C<sub>2</sub> ring, have been reported.<sup>12–16</sup> In addition, molecules that contain at least two conjugated double bonds have been shown to adsorb via a [4 + 2] ("Diels–Alder") reaction.<sup>17–20</sup> Moreover, certain molecules adsorb via both cycloaddition processes, and some studies have investigated the competition between the [2 + 2] and [4 + 2] pathways in the adsorption process.<sup>17</sup> Finally, recent investigations have shown that these cycloaddition reactions on the Si(001) surface are not limited solely to alkenes. We have demonstrated the possibility of a cycloaddition reaction involving a N=N bond,<sup>21</sup> while White et al. have shown that a C=O bond may also undergo a [2 + 2] addition on Si(001).<sup>22</sup>

The high reactivity of alkenes toward the dimers on the Si(001) surface is unexpected, because the [2 + 2] reactions in solution-phase chemistry are formally symmetry forbidden.<sup>23</sup> The reactions of alkenes with the Si surface dimers are thought to be so facile because they proceed through a low-symmetry

intermediate.<sup>7</sup> To improve our understanding of the reactivity of unsaturated compounds with the Si(001) surface, we have investigated the adsorption of phenyl isothiocyanate, C<sub>6</sub>H<sub>5</sub>–N=C=S (PITC). This molecule has the potential to adsorb on the surface in several different configurations. Benzene adsorbs quite readily on Si(001), although the exact adsorption geometry is the subject of debate.<sup>24–31</sup> By analogy, then, PITC may adsorb to Si(001) via the phenyl ring. Additionally, the N=C and C=S double bonds each present an opportunity for a [2 + 2] cycloaddition reaction with the Si dimers. Solution-phase organic reactions have shown that PITC will undergo a cycloaddition reaction with an alkene via the N=C group,<sup>32,33</sup> while sulfonyl-PITC will react with an alkene via the C=S moiety.<sup>33</sup> The reactions reported in the literature also demonstrate that PITC will undergo a cycloaddition reaction via the N=C=S group.<sup>32</sup> Finally, PITC may adsorb onto Si(001) by forming a five-member ring that involves the formation of two new  $\sigma$  bonds, one Si–N bond and one Si–S bond. This 1,3-dipolar addition has been predicted theoretically,<sup>34</sup> but we were unable to find any reports of this type of reaction in the literature. Thus, the N=C=S group also presents several possibilities for reaction of PITC with the Si dimers on Si(001). Clearly, the PITC molecules have several possible adsorption pathways. Here, we present strong evidence that a 1,2-dipolar addition is the preferred adsorption geometry.

## II. Experimental Section

The adsorption of phenyl isothiocyanate (PITC) on Si(001) at 300 K was investigated using several methods: X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), scanning tunneling microscopy (STM), and ab initio calculations. Individually, each of these methods reveals a specific subset of information about the adsorbate–surface system. When taken together, the results from the four techniques provide a comprehensive picture of the adsorption process.

All of the experiments described here were performed in ultrahigh vacuum (UHV) chambers having base pressures of  $< 1 \times 10^{-10}$  Torr. The Si(001) samples were cut from n-type wafers (Wacker Chemitronic), degreased in methanol, and

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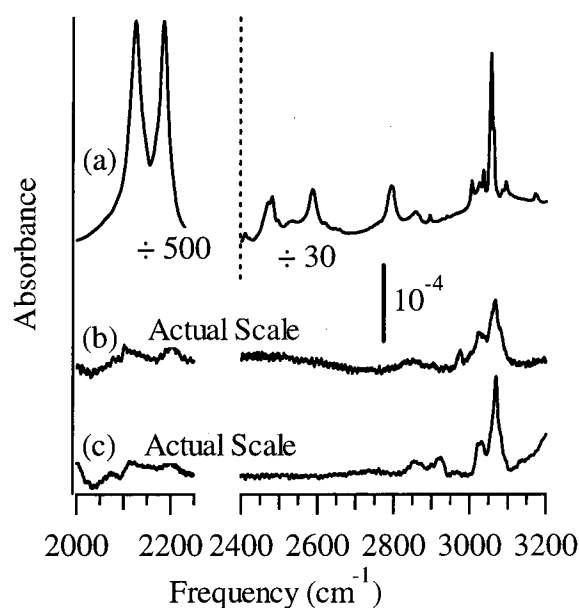
cleaned of residual carbon contamination by exposure to ozone for  $\sim 10$  min. Highly doped crystals ( $< 0.1$  ohm cm, Sb-doped) were used for the XPS and STM experiments, while lightly doped ( $> 5$  ohm cm, B-doped) crystals were used for the IR experiments. Once in a vacuum, the Si samples were degassed at  $\sim 850$  K overnight. The samples were then heated to 1400 K to remove the oxide layer, leaving a clean Si(001) surface. This procedure has been shown to produce the clean, well-ordered ( $2 \times 1$ ) reconstructed Si(001) surface.<sup>35</sup>

Phenyl isothiocyanate (PITC) was obtained at 99.5% purity (Aldrich). It was further purified by several freeze–pump–thaw cycles. The PITC was introduced into the chamber through a variable leak valve, and its purity was checked with in situ mass spectrometers in each UHV chamber. Deuterated PITC was obtained at 98.9% purity (CDN Isotopes). The supplier specified greater than 99.7% D atom purity, as determined by NMR. The deuterated compound was also further purified by several freeze–pump–thaw cycles, after which its purity was verified by in situ mass spectrometry. Methyl isothiocyanate (MITC) was obtained at 99% purity (Fluka). At room temperature, MITC is a solid. To further purify the MITC, it was heated in a vacuum, the resulting vapor was pumped away, and the liquid was allowed to re-solidify. Several cycles of this process were repeated to achieve contaminant-free MITC, as verified by in situ mass spectrometry.

X-ray photoelectron spectroscopy data were obtained using a Physical Electronics system with monochromatized Al K $\alpha$  radiation. Because the X-ray source is monochromatized, this instrument has the capability for very high resolution. To increase surface sensitivity and minimize emission from bulk silicon, the sample was oriented so that the detection angle for the photoelectrons was  $65^\circ$  from the surface normal. The data presented here were obtained using a pass energy of 5.85 eV in the hemispherical analyzer. This setting was found to provide a good compromise between signal intensity and resolution sufficient to distinguish adsorbate atoms in different chemical environments. To distinguish between true chemical shifts and band-bending effects, the Si(2p) peaks were always measured and used as an internal standard. All spectra reported here have been adjusted to yield a constant 99.4 eV binding energy for the bulk Si 2p<sub>3/2</sub> line. The same shift (typically  $< 0.2$  eV) was then applied to the binding energies of the C(1s), N(1s), and S(2s) peaks to ensure that shifts in the binding energies reported here are due solely to changes in the local chemical environment.

The XPS data are fit by a commercial software package (Wavemetrics). Because the identification of the chemical species that comprise each XPS feature is dependent upon this fitting procedure, a reliable method of ascertaining the number of individual peaks is necessary. A fit parameter, the so-called reduced  $\chi^2$ , is used to determine when the fit is a good representation of the data.<sup>16</sup> A reduced  $\chi^2$  of less than or equal to 1.0 indicates that the fit is statistically equivalent to the data. Our fitting procedure iteratively increases the number of individual peaks until the reduced  $\chi^2$  is less than or equal to 1, thereby achieving good fit quality with the minimal number of statistically justifiable peaks.

Direct imaging of the surface and adsorbed PITC molecules was achieved using a home-built UHV scanning tunneling microscope (STM). All STM images were obtained with a sample bias of  $-2.5$  V and a tunneling current of 200 pA. Fourier transform infrared (FTIR) absorption spectra were collected using multiple internal-reflection geometry. The IR radiation was produced and collected by a Mattson RS-1 FTIR spectrometer, was coupled to the vacuum chamber through a



**Figure 1.** FTIR spectra of PITC adsorbed on Si(001) at 300 K. The upper trace (a) shows the spectrum for multilayers of PITC. The middle trace (b) shows the data for the monolayer with the IR electric field polarization along the dimer axis, and the lower trace (c) shows the data for the monolayer with the electric field polarization perpendicular to the dimer axis and perpendicular to the surface plane.

pair of BaF<sub>2</sub> windows, and was detected using either an InSb or a HgCdTe detector. A polarizer was used to define the polarization of the IR light with respect to the surface plane. For the FTIR experiments, two types of Si wafers were used: Si(001) samples, and samples that were miscut by  $4^\circ$  from the (001) direction. The miscut causes steps to be two atomic layers high, so that the rows of dimers run the same direction across the entire sample.<sup>36</sup> By varying the direction of polarization of the IR light, we are thus able to determine the orientation of certain bonds with respect to the dimers.

### III. Results

**A. FTIR Data.** Figure 1 shows FTIR data taken after exposing a  $4^\circ$ -miscut Si(001) sample to PITC. As will be discussed below, the upper trace (a) was obtained by condensing multilayers of PITC on Si(001) at 130 K. The lower two spectra were obtained by exposing a 300 K surface to 20 L (1 L  $\equiv$  Langmuir  $\equiv 10^{-6}$  Torr s) of PITC. The middle trace (b) shows the absorbance of the sample using s-polarized light with the electric field vector of the incident light parallel to the Si=Si dimer bond axis. The lower trace (c) shows the absorbance using p-polarized light. In this case, the electric field vector has one component perpendicular to the surface plane and one perpendicular to the dimer axis. Chabal has shown that in the multiple internal reflection (MIR) geometry, the sensitivity to vibrations is nearly equal for all three components (two in surface plane, one perpendicular to surface).<sup>37</sup> For comparison, Table 1 shows our experimental values and the results of a previous vibrational analysis of PITC in the liquid phase.<sup>38</sup> The peaks at 2110 and 2200  $\text{cm}^{-1}$  can be assigned to the N=C=S symmetric and asymmetric stretches. Also in this spectral region, apparent in Figure 1b, is a weak peak at 2073  $\text{cm}^{-1}$ , which can be attributed to either a N=C=S mode or to a Si–H stretching mode. To assess quantitatively the amount of any possible C–H bond dissociation upon adsorption, however, we performed this same experiment with deuterated PITC, as will be discussed below. The strong peaks at 3032 and 3069  $\text{cm}^{-1}$  are attributed to

**TABLE 1: Vibrational Frequencies of Multilayer PITC, Adsorbed PITC, and Literature Values<sup>a</sup>**

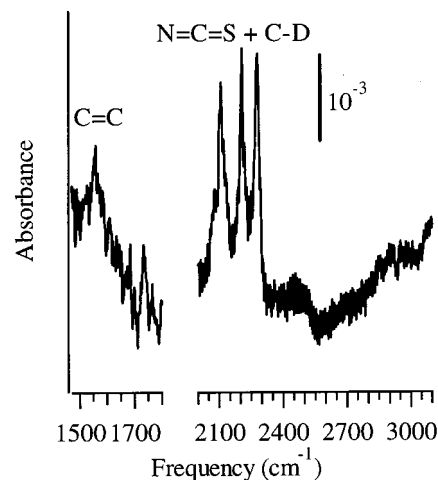
vibrational frequencies (cm <sup>-1</sup> )			
PITC multilayer	PITC liquid phase (from ref 38)	PITC monolayer	
		p-polarized	s-polarized
2124	2115, fundamental NCS stretch	2112	2101
2184	2180, fundamental NCS stretch	2203	2200
2330	2312, overtone		
2410	2415 combination band		
2480	2475, overtone		
2585	2560, overtone		
2794	2750 combination band		
2859	2850, combination band, C–C stretch and C–N stretch	2854	2849
2925	2930, combination band, 2 C=C stretches	2924	
2975	2968, combination band, 2 C=C stretches		2968
3005		obscured	obscured
3025		3022	3021
3035	fundamental C–H stretch	3032	3034
3056	3055, 3079, fundamental C–H stretches	3069	3067
3094	3100, fundamental C–H stretch	3097, shoulder	3095, shoulder
3171	3185, overtone		

<sup>a</sup> Literature values have an estimated uncertainty of  $\pm 15$  cm<sup>-1</sup>; current values have an estimated uncertainty of  $\pm 2$  cm<sup>-1</sup>.

fundamental C–H stretches of the aromatic ring. While these peaks are too high in frequency to arise from alkane-like C–H stretches (which typically appear at 2850 cm<sup>-1</sup> to 3000 cm<sup>-1</sup>),<sup>13,21,39</sup> the bottom, p-polarized spectrum does show small peaks at 2924 and 2968 cm<sup>-1</sup>. However, these values are nearly identical to those previously assigned (2930, 2968 cm<sup>-1</sup>) to C=C combination bands of the aromatic ring. While the possibility of some small fraction of secondary products cannot be ruled out, our infrared data indicates that the benzene ring remains intact and nearly unperturbed after adsorption.

The IR spectrum of PITC in the liquid phase has been carefully studied.<sup>38</sup> To compare more closely our results with the known vibrational spectrum of PITC, we obtained a FTIR spectrum of multilayers of PITC on Si(001). This was achieved by cooling the sample to 130 K and exposing it to 60 L of PITC. The spectrum thus obtained is shown in Figure 1a. The most striking feature is the very strong absorption between 2000 and 2200 cm<sup>-1</sup> by the N=C=S stretches. Such intense N=C=S vibrational transitions, dwarfing the C–H stretches, are also characteristic of PITC in the liquid phase<sup>38</sup> and other isothiocyanates,<sup>40–43</sup> and the vibrations of molecules containing intact N=C=S groups are so intense that combination bands are easily observed in the region from 2400 to 2900 cm<sup>-1</sup>.<sup>38</sup> In contrast, however, Figure 1a shows that the first monolayer of chemisorbed PITC yields only weak absorption in this region. A measurement of the integrated area in the N=C=S and C–H spectral regions in the multilayer and in the monolayer PITC shows that the “normalized” area ratio  $A_{\text{NCS}}/A_{\text{C-H}}$  is 100 times smaller for the first monolayer than for multilayer films. This observation clearly shows that the N=C=S group is involved in the binding of PITC to Si(001). In contrast, the features in the C–H region for adsorbed monolayer and multilayer PITC are nearly the same. In particular, all three spectra show the intense C–H stretch near 3060 cm<sup>-1</sup>. Note that all the features present in the multilayers of PITC and the adsorbed PITC are in very good agreement with the literature values.

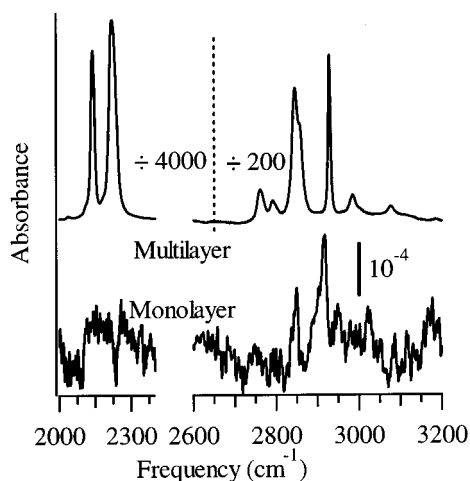
Quantitative analysis of the intensity of any Si–H spectral features is a useful means of assessing any partial cleavage of C–H bonds, because H atoms produced by C–H bond cleavage typically bond to the Si surface. However, the Si–H features typically observed at 2080 cm<sup>-1</sup> overlap somewhat with the N=C=S features. To ensure correct identification of any possible Si–H vibrations, we performed a FTIR experiment in which a Si(001) surface was dosed with d<sub>5</sub>-PITC, and searched



**Figure 2.** FTIR spectrum of d<sub>5</sub>-PITC adsorbed on Si(001) at 300 K. The incident light was not polarized for this spectrum.

for the appearance of any Si–D vibrations. As shown in Figure 2, the FTIR spectrum of Si(001) exposed to d<sub>5</sub>-PITC shows only a single peak at 1558 cm<sup>-1</sup>. A peak near this frequency, 1575 cm<sup>-1</sup>, was previously assigned to a C=C stretching mode of liquid PITC.<sup>38</sup> After correcting for the small shift in the C=C frequency anticipated due to the D atoms, this is in nearly perfect agreement with the 1558 cm<sup>-1</sup> we observe. To ensure that the 1558 cm<sup>-1</sup> peak did not arise from a Si–D vibration, we also prepared a D–Si–Si–D “monodeuteride”-terminated Si(001) surface by passing >30 L of D<sub>2</sub> over a hot W filament located close to the sample. This resulted in a peak at 1525 cm<sup>-1</sup> with an integrated area of 0.23 cm<sup>-1</sup>, in good agreement with previous observations of D-terminated Si(111) surfaces.<sup>44</sup> On the basis of the absence of any 1525 cm<sup>-1</sup> peak in our d<sub>5</sub>-PITC spectrum, the signal-to-noise of the baseline in this region, and the known absorbance of 1 monolayer of D atoms, we are able to establish that no more than 2% of the surface is covered with deuterium atoms. This in turn demonstrates that adsorption of PITC onto Si(001) occurs with little or no cleavage of C–H bonds.

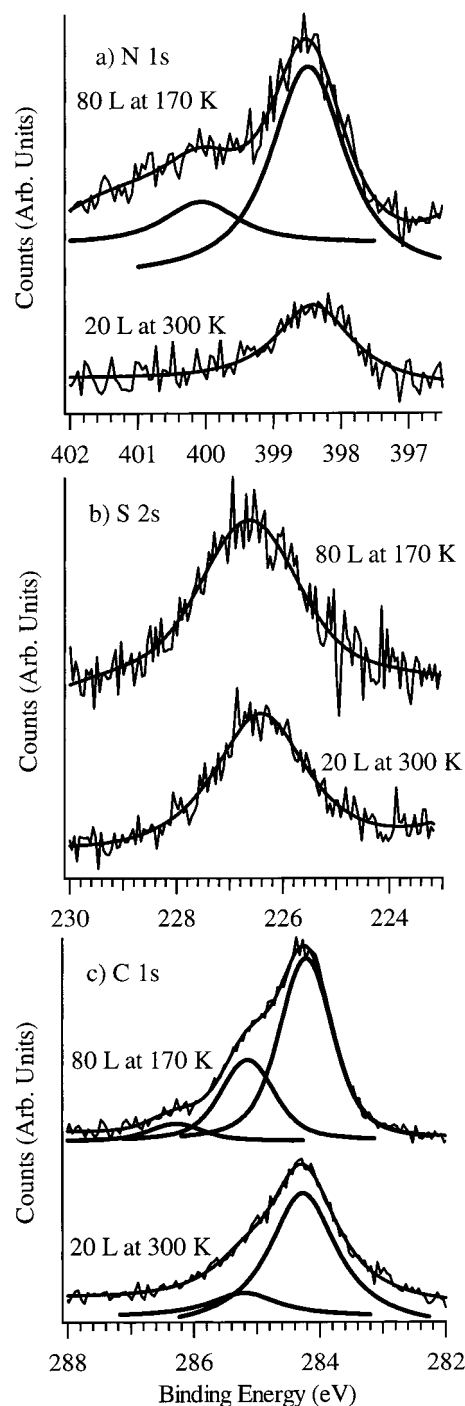
To provide a comparison to PITC, we also obtained FTIR spectra for methyl isothiocyanate (MITC) adsorbed on Si(001). Figure 3a shows the vibrational spectrum for MITC multilayers grown by exposing a 130 K Si(001) sample to 180 L of MITC. As was the case with the PITC, the N=C=S stretching peaks



**Figure 3.** FTIR spectrum of monolayer coverage of MITC compared with multilayer coverage. The N=C=S absorption decreases by a factor of 400 relative to the C-H absorption. The incident light was not polarized for these spectra.

between 2000 and 2200  $\text{cm}^{-1}$  are by far the most intense. These data are in excellent agreement with the reported IR spectrum of solid MITC.<sup>40,41</sup> The FTIR data for a 300 K Si(001) sample exposed to 20 L of MITC are shown in Figure 3b. The most noticeable change between Figure 3, parts a and 3, once again, is the large decrease in N=C=S intensity for monolayer MITC, as compared to the multilayer film. Relative to the integrated area under the C-H region, the integrated area under the N=C=S region decreases in intensity by a factor of approximately 400 between the multilayer MITC and the monolayer MITC. Additionally, the monolayer of MITC shows no detectable feature in the region between 2000 and 2100  $\text{cm}^{-1}$ , indicating that MITC does not undergo C-H bond cleavage during adsorption. Because the MITC is not expected to adsorb to Si(001) via an intact methyl group, then, these data, suggest that MITC, like PITC, adsorbs to Si(001) via the N=C=S group.

**B. XPS Data.** Figure 4 shows XPS spectra taken of Si(001) samples at 300 K and at 170 K that were exposed to PITC. When the surface temperature was 300 K, exposure to more than 20 L of PITC did not result in any further increase in N, S, or C XPS signals. However, when the sample was cooled to  $\sim 170$  K, continued exposure produced an increase in signal, which we attribute to a physisorbed layer. Panel (a) shows the N(1s) region. The lower curve shows saturation coverage at 300 K, whereas the upper curve is the spectrum obtained by exposing a 170 K Si(001) sample to 80 L of PITC. Adsorption at 300 K yields a single peak centered at a binding energy of 398.4 eV. The fit, as shown by the dark line, yields a reduced  $\chi^2$  of 0.9, indicating that the inclusion of more than a single peak in the fit is not justified statistically. This result suggests that the PITC molecules adsorb in a configuration such that the N atoms are all in a chemically indistinguishable environment. In contrast, adsorption at 170 K produces two distinct peaks. Fitting to two peaks is justified by a decrease in the reduced  $\chi^2$  decreases from 1.3 to 0.9 as the number of fitted peaks is increased from 1 to 2. The larger peak has a binding energy of 398.5 eV, identical (within experimental error) to that observed for PITC adsorbed at 300 K. We therefore assign this peak to N atoms of the chemisorbed layer. The second peak at 400.2 eV, which is not present at 300 K, is attributed to N atoms from physisorbed PITC. These data show that the N(1s) binding energy decreases by 1.7 eV upon bonding of PITC to the Si(001) surface; for comparison, the N(1s) binding energy of  $\text{NH}_3$  decreases by 1.6 eV in going from a physisorbed state (400.1 eV) to a chemi-

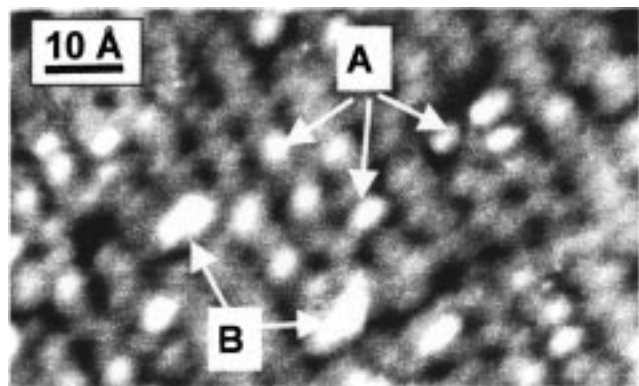


**Figure 4.** XPS data of PITC adsorbed on Si(001) at 170 and 300 K. Shown are the data, the fit to the data, and where more than one peak is present, the individual peaks.

sorbed state with direct Si-N bond formation (398.5 eV).<sup>45</sup> Thus, our data strongly indicates that adsorption of PITC involves direct Si-N bond formation.

Figure 4b shows the S(2s) region. Although the S(2p) peak is often used as the primary sulfur peak in XPS analysis, we are not able to use the S(2p) peak for quantitative studies because it overlaps with a plasmon loss peak from the Si(2p) region.<sup>46</sup> The S(2s) peak is less intense and broader than the S(2p) peak. The lower curve shows the spectrum obtained after saturation coverage at 300 K, whereas the upper curve shows the spectrum obtained by exposing a 170 K Si(001) sample to 80 L of PITC. The fit of the lower curve to a single peak at 226.4 eV and fwhm of 2.4 eV results in a reduced  $\chi^2$  of 0.98. Fitting the S(2s)





**Figure 5.** STM image of Si(001) at 300 K exposed to 0.01 L of PITC. The image was acquired at a sample bias of  $-2.5$  V and a tunneling current of 200 pA.

data for physisorbed PITC (Figure 4b) to a single peak yields a reduced  $\chi^2$  of 0.86 (fwhm = 2.7 eV), indicating that fitting to larger numbers of peaks is not justifiable statistically. Furthermore, fitting to two peaks produced only a negligible further decrease, to  $\chi^2 = 0.85$ . Thus, we find only a 0.2 eV shift to 226.6 and a  $\sim 25\%$  increase in integrated S(2s) intensity upon formation of a physisorbed layer. This slight broadening and small shift of 0.2 eV can arise from a variety of factors such as thickness-dependent changes in final-state relaxation processes and are smaller than those anticipated for direct Si–S bond formation. Thus, our sulfur XPS data suggests that sulfur atoms are not directly involved in the bonding of PITC onto Si(001).

Figure 4c displays the C(1s) XPS data. The data for 300 K adsorption are best fit by two peaks at 284.3 and 285.2 eV, which results in a reduced  $\chi^2$  of 0.76. In contrast, fitting to a single peak results in a reduced  $\chi^2$  of 3.6. Therefore, we conclude that fitting the C(1s) data to two distinct peaks is statistically justifiable. The ratio of the areas of the larger peak to the smaller peak is  $5.8 \pm 0.6$ . Because the PITC molecule contains 7 C atoms, our observation of two types of C atoms with relative populations of 6:1 supports intact molecular adsorption.

The C(1s) XPS data for the 170 K adsorption of PITC are shown in the upper trace of Figure 4c. Fitting these data to 2 peaks yields a reduced  $\chi^2$  of 1.2, whereas fitting to 3 peaks results in a reduced  $\chi^2$  of 0.8. The peaks at binding energies of 286.3, 285.1, and 284.2 eV have area ratios of 11:5:1, respectively. Because of the number of C atoms in the PITC molecule, direct interpretation of these data is difficult. The binding energies of 285.1 and 284.2 eV are, within experimental error, identical to those observed for the two C species at 300 K (285.2 and 284.3 eV). Compared with monolayer adsorption, the monolayer plus physisorbed film at 170 K shows greater intensity in the higher binding energy peaks at 286.3 and 285.2 eV. This in turn suggests that direct binding of PITC to Si(001) lowers the binding energy of the 1s electrons of some of the C atoms.

**C. STM Images.** Figure 5 shows a STM image of 300 K Si(001) exposed to 0.01 L of PITC, taken at  $-2.5$  V bias and 200 pA tunneling current. At this low coverage, the molecules may be imaged in their “preferred” adsorption geometry, without steric hindrances present at higher coverages. The image shows a single type of feature, labeled “A”, that we attribute to adsorbed PITC molecules. These features appear to be confined to the space occupied by a single Si=Si dimer of the surface. However, the maximum of each feature is slightly offset from the center of the underlying dimer, located slightly closer to one of the two underlying Si atoms in each dimer. Closer examination suggests that the direction of this sideways shift is

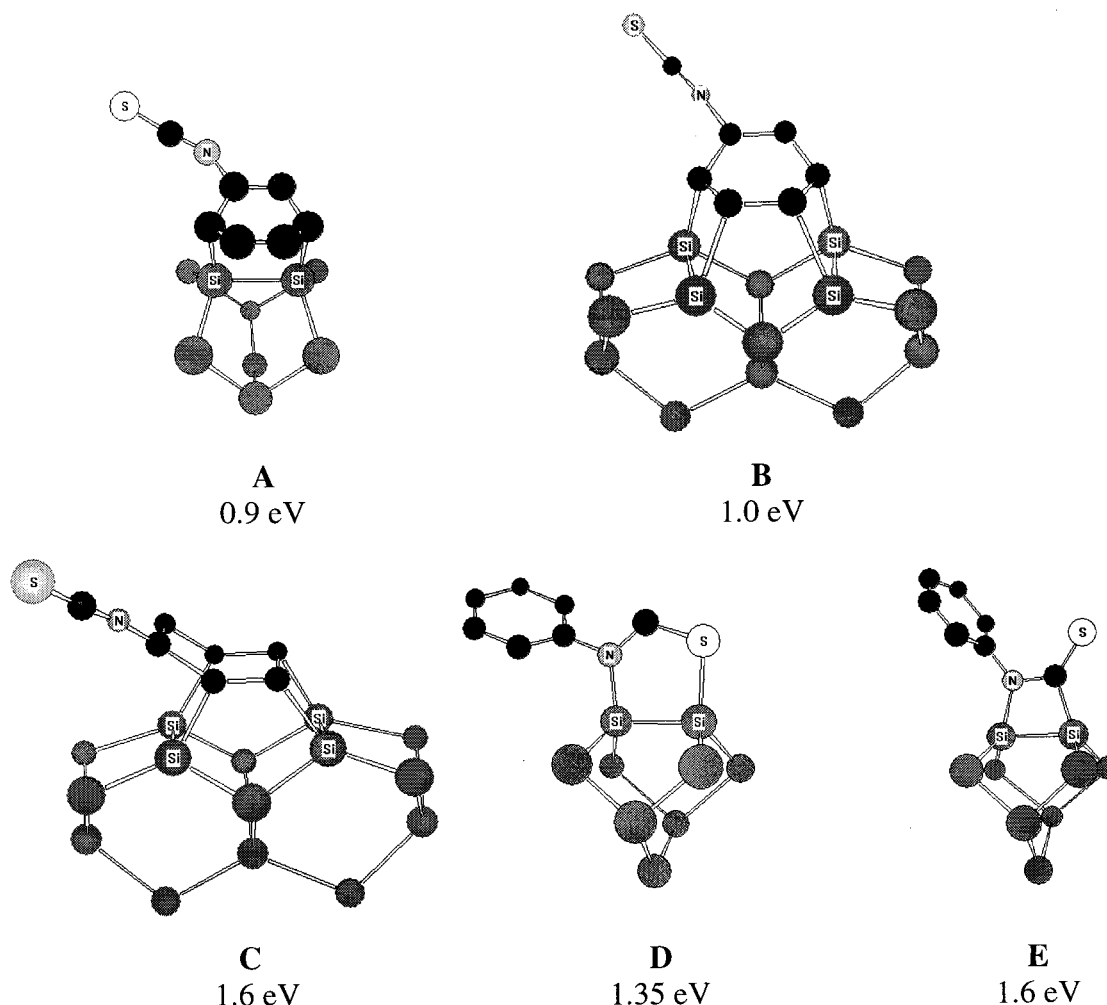
random, indicating that the apparent loss of symmetry does not result from an asymmetric STM tip but rather arises from the true representation of the adsorption configuration of PITC. In repeated STM experiments, we also found that PITC also interacts strongly with the STM tip, and that after exposure to PITC the STM tips would occasionally deposit globular material, such as those labeled “B” in Figure 5, onto the sample. Exposures greater than 1 L resulted in STM images that showed large irregular features. Other work in this laboratory has found that sulfur-containing compounds interact strongly with the STM tip. We postulate that PITC also reacts with the W tip and decomposes. The resulting decomposition products are deposited onto the sample during scanning, thereby preventing us from using STM to observe the Si(001) surface when it is completely covered by PITC.

**D. Ab Initio Calculations.** To understand the energetics of binding of PITC on Si(001), we performed ab initio calculations using Gaussian 98<sup>47</sup> for a PITC molecule adsorbed onto 9-atom and 15-atom Si clusters. The 9-atom cluster is identical to that used in several previous studies,<sup>7,18,37</sup> and has one exposed Si=Si dimer. The 15-atom cluster is an extension of this to include two surface dimers. In both clusters, Si atoms at the cluster edges were terminated with H atoms to provide full coordination for all atoms except those forming the surface dimer. Calculations were performed using the Becke3LYP hybrid density functional and the 6-31+G\* basis set.<sup>7,18,48</sup> Molecular binding energies were obtained by placing the molecule of interest near the appropriate cluster in a geometry close to that anticipated for the different final structures, and then allowing all atomic positions to adjust to find local minimum in energy. The energy of the optimized free cluster and of the optimized free molecule were subtracted from the total energy of this combined cluster to yield a net binding energy. No constraints were placed during any of the geometry optimizations. Although the absolute values of the adsorption energies may have systematic errors, differences in binding energies between various configurations are still expected to provide the correct ordering of energies for the various configurations.<sup>18</sup>

We investigated five different binding configurations. Three of these configurations involve binding through the benzene ring and are analogous to the lowest-energy binding configurations of benzene, and two configurations are unique to the isothiocyanate group of PITC. A comparison of the calculated binding configurations and their associated adsorption energies is shown in Figure 6.

Configurations A–C involve bonding through the benzene ring. In these three configurations there are different isomers possible depending on whether the isothiocyanate group is on the C atoms directly bonded to the Si surface. Although multiple isomers were not investigated for each geometry, lower-level calculations indicated changes in bonding energy of no more than 0.1 eV depending on the position of the NCS group.

Structure A involves adsorption through the benzene ring at the (1,4) positions and is analogous to that obtained from a [4 + 2] cycloaddition reaction onto a single Si dimer. For this configuration we obtain a binding energy of 0.9 eV; this binding energy is nearly identical to the value of 0.88 eV reported by Wolkow for benzene in a similar configuration.<sup>29</sup> Structures B and C involve PITC bonded to two dimers and are analogous to the “twisted bridge” and “tight bridge” configurations previously investigated for benzene on Si(001). We find that PITC bonded into the “twisted bridge” configuration has a binding energy of 1.0 eV, while PITC bonded into the “tight



**Figure 6.** Three possible adsorption geometries for PITC on Si(001). Shown are the results of the energy optimization of the ab initio calculations. Also given are the calculated binding energies of the configurations. For clarity, the H atoms are not displayed. The C atoms are black, and the other atoms are labeled, except for the Si cluster, in which only the two Si atoms of each surface dimer are labeled.

bridge" configuration has a binding energy of 1.6 eV. These energies compare quite favorably with the values of 0.91 and 1.49 eV reported by Wolkow et al. for benzene adsorbed into the same configurations.

Structures D and E involve bonding of PITC to the surface through the  $\text{N}=\text{C}=\text{S}$  moiety. Structure D involves the formation of a five-member ring between the N, C, and S atoms of PITC and the two atoms of the Si dimer and yields a calculated binding energy of 1.35 eV. Finally, Structure E shows a four-member ring between the N and C atoms of the PITC molecule and the two Si atoms of the dimer and has a calculated binding energy of 1.6 eV. The primary result of our calculated binding energies is that binding through the NCS group (structures D, E) is almost equal in energy to binding through the benzene ring via the "tight-bridge" configuration. In reality, we may expect that the calculations may overestimate the energy involved in binding in the tight-bridge and twisted-bridge configurations because the energy minimization of these structures shows substantial distortion of the silicon cluster in order to achieve bonding to two dimers. Since a real lattice is more rigid, we expect that bonding through the NC group should in fact be slightly more favorable than binding into the tight-bridge configuration.

#### 4. Discussion

**A. Adsorption Geometry.** We expect PITC to have several distinct adsorption possibilities. Our data indicate that PITC

adsorbs onto Si(001) molecularly, with minimal dissociation. Furthermore, the FTIR spectra show that, upon adsorption, the  $\text{N}=\text{C}=\text{S}$  feature is greatly reduced, whereas the C–H features are essentially unchanged. These data indicate that PITC binds to Si(001) through the  $\text{N}=\text{C}=\text{S}$  group. Additionally, the XPS data demonstrate that N and C, but not S, are involved in the binding of the molecule to the Si surface. The discussion below presents these results in greater detail and proposes an adsorption configuration that is best supported by the experimental data.

Dissociative adsorption is not consistent with our data. Quantitative analysis of the very small Si–H intensity observed in our FTIR data indicates that fewer than 2% of PITC molecules undergo C–H bond scission upon adsorption. Furthermore, a dissociative adsorption process in which the C–N bond between the benzene ring and the  $\text{N}=\text{C}=\text{S}$  group is cleaved is unlikely for the following reason. This process would be expected to leave a  $\text{N}=\text{C}=\text{S}$  group bound through the N atom to a dimer. Silicon tetraisothiocyanate,  $\text{Si}(\text{NCS})_4$ , displays a very large  $\text{N}=\text{C}=\text{S}$  absorption feature,<sup>49</sup> so the absence of this absorption feature in Figure 1 is inconsistent with the presence of a  $\text{Si}-\text{N}=\text{C}=\text{S}$  surface species. Finally, the vibrational features at  $2854\text{ cm}^{-1}$  (p-polarized) and  $2849\text{ cm}^{-1}$  (s-polarized) observed in the monolayer PITC have been assigned previously as a combination band from a C=C stretch and the C–N stretch at  $2850\text{ cm}^{-1}$  in liquid PITC.<sup>38</sup> Observation of these peaks in our monolayer spectra indicates that the C–N

**TABLE 2: N(1s) Binding Energies for Several N-Containing Molecules Adsorbed on Si(001)**

molecule	N(1s) binding energy (eV)
3-pyrroline, <sup>51</sup> C <sub>2</sub> N-Si	398.3
PITC chemisorbed	398.4
NH <sub>3</sub> <sup>45</sup> H <sub>2</sub> N-Si Chemisorbed	398.5
azo- <i>tert</i> -butane <sup>21</sup> C-N-(N,Si)	399.0
3-pyrroline, <sup>51</sup> C <sub>2</sub> NH	399.2
NH <sub>3</sub> <sup>45</sup> physisorbed	400.1
PITC physisorbed	400.2
azobenzene physisorbed Ph-N=N-Ph	400.8

bond is intact after adsorption. We therefore rule out a dissociative adsorption process involving C-N bond cleavage.

While dissociative adsorption has been ruled out, several possibilities for molecular adsorption must still be considered. First, PITC may adsorb through the benzene ring, as benzene itself is known to adsorb molecularly.<sup>29,31,50</sup> However, FTIR spectra of benzene adsorbed on Si(001) obtained in our laboratory<sup>50</sup> and elsewhere<sup>29</sup> show rather significant differences from our spectra of PITC. In contrast, the data shown in Figure 1 and the comparison in Table 1 demonstrates that the C-H vibrational frequencies we observe for monolayer PITC are very close to those observed for PITC multilayers and for PITC in the liquid phase. The lack of significant change in the C-H stretching region suggests that PITC adsorption does not occur via the benzene ring.

Finally, PITC may adsorb through the N=C bond, the C=S bond, or the N=C=S group to form a five-member ring. Previous studies of aromatic<sup>38</sup> and nonaromatic isothiocyanate compounds<sup>40-43</sup> as well as our data for multilayers of PITC and MITC (Figures 1 and 2) uniformly show N=C=S stretching vibrations that are much more intense than the C-H stretching region. Our FTIR data clearly show that adsorption onto Si(001) dramatically decreases the vibrational intensities in N=C=S spectral region, while leaving the C-H region almost unchanged. Thus, our FTIR data strongly suggest that PITC adsorbs onto Si(001) by a reaction involving only the N=C=S group, through either the N=C bond, or the C=S bond, or through both bonds.

The FTIR data for MITC provide strong support for this conclusion. Because we see no evidence for C-H bond dissociation during MITC adsorption, we conclude that MITC can only bind to the Si(001) surface through the N=C=S group. MITC shows a significant decrease in N=C=S intensity upon adsorption, just as PITC does. We therefore believe that the decrease in N=C=S absorption for both adsorbed MITC and adsorbed PITC is due to similar adsorption processes for the two molecules. Specifically, both compounds adsorb onto Si(001) in some manner via the N=C=S group.

Bonding through the isothiocyanate group is also strongly supported by the XPS data. The observation of a single, sharp N(1s) peak for monolayer PITC indicates that the N atoms are in indistinguishable chemical environments. When compared with the binding energy of 400.2 for a physisorbed layer, the binding energy of 398.4 eV for monolayer PITC shows that the binding energy of the N(1s) decreases by 1.8 eV upon adsorption onto the surface. The large magnitude of this shift strongly suggests direct bonding to an electron-donating element such as Si, and suggests that upon bonding to the surface, N breaks its  $\pi$  bond to C and forms a new  $\sigma$  bond to the silicon surface. As shown in Table 2, the 398.3 N(1s) eV binding energy for PITC chemisorbed on Si(001) is in good agreement with results for similar molecules in which a N atoms are known to be bonded directly to the Si surface.<sup>51</sup>

The XPS data for C are much more difficult to interpret. The number of C atoms in a PITC molecule, 7, makes assignment of XPS peaks to specific C atoms ambiguous. However, the data in Figure 4c show that the chemisorbed monolayer lacks the high binding energy feature at 286.3 and has a decrease in the relative intensity of the peak at 285.2 eV compared with the peak at 284.3 eV. These decreases in C(1s) binding energy again suggest direct bonding of at least one C atom directly to Si. Our data suggest that more than one C atom may show a measurable core-level shift during chemisorption. A shift in one C atom can be accounted for via direct bonding of the N=C=S group to the surface. Furthermore, some additional shifts of other carbon atoms, particularly the aromatic C atom bonded to the isothiocyanate N atom, might be expected due to loss of the conjugation with the isothiocyanate group.

The XPS data for S in chemisorbed PITC show a single peak at 226.4 eV binding energy, indicating that the S atoms are chemically indistinguishable. When PITC is physisorbed, a single peak is still observed, but its binding energy is shifted 0.2 eV upward, from 226.4 (monolayer) to 226.6 eV (monolayer plus physisorbed) and broadens by about 0.3 eV. The slight increase in binding energy, 0.2 eV, is approximately equal to the experimental error in the binding energies. In previous studies of other double-bonded species on silicon, we have found that bonding directly to silicon decreases binding energies by 1.8 eV for N=N bonds (azo-*tert*-butane N(1s))<sup>21</sup> and 1.4–1.6 eV for C=C bonds (3-pyrroline and cyclopentene C(1s)).<sup>51</sup> Thus, we believe that the very small (0.2 eV) shift observed for sulfur with PITC indicates that the S atoms are not bonded directly to Si. We attribute the 0.2 eV decrease to the fact that breaking the N=C bond and donation of electron density from Si to C also donates some electron density to S and decreases the S(2s) binding energy.

The FTIR and XPS data, then, suggest an adsorption geometry in which the PITC molecule undergoes a cycloaddition reaction with the Si dimer via the N=C bond of the isothiocyanate group. This cycloaddition product is expected to have the phenyl group protruding out over one end of the dimer and the S atom over the opposite end of the same dimer. Although a detailed interpretation of the STM images cannot yet be performed, the general features of the STM images are consistent with this structure. In particular, the protrusions observed in STM are confined to the width of one dimer, but are asymmetrically located toward one side of the dimer. In contrast, we would expect that bonding into the tight-bridge or twist-bridge configurations would reveal features that were at least the width of two dimers, since binding in these configurations is expected to significantly alter the electronic structure of the two adjacent dimers to which the molecule is bonded. Because stable STM images were obtained only at negative sample bias, reflecting the spatial distribution of filled electronic states, it is likely that our images reflect either the location of the C=S bond or the benzene ring. However, we have recently shown that even completely saturated surface groups without electronic states directly accessible to tunneling can appear as protrusions,<sup>52</sup> so that detailed interpretation is not yet possible.

Our *ab initio* calculations also indicate that the binding configuration with a four-member ring between the Si dimer and the N and C atoms of the isothiocyanate group, Structure E in Figure 6, is the most stable adsorption geometry. Slightly higher in energy is Structure D, a five-member ring between the Si dimer and the N, C, and S atoms of the isothiocyanate group. The STM images cannot distinguish between these two geometries, but the XPS data are consistent with the first picture,



because they indicate that N and C, but not S, are directly involved in binding PITC to the Si dimer.

On the basis of the FTIR and XPS data, STM images, and ab initio calculations, we believe that PITC adsorbs onto Si(001) in a manner analogous to a [2 + 2] cycloaddition reaction between the  $\pi$  bond of the Si dimer and the N=C  $\pi$  bond of the isothiocyanate group. Because the N=C bond is polar, this cycloaddition reaction is not labeled a [2 + 2] cycloaddition but rather is known as a 1,2-dipolar addition. We therefore conclude that the most plausible adsorption configuration is one in which the N=C bond of the isothiocyanate group undergoes a 1,2-dipolar cycloaddition reaction with the Si dimer to form Structure E. This cycloaddition product is also consistent with the known solution-phase reaction of PITC with an alkene to form a four-member ring.<sup>33</sup> We note that this structure will produce a high density of benzene rings on the surface. The underlying order of the dimers does not translate into exact ordering of the overlayer, but the benzene rings are held in position with respect to the dimer axis.

**B. Comparison with Other Cycloaddition Processes on Si(001).** A surprising and important result of this work is the observation that little, if any, PITC adsorbs to Si(001) via the benzene ring. Previous studies of benzene<sup>29,30,53</sup> and several other aromatic and nonaromatic conjugated systems<sup>11,19,20</sup> show that these molecules react quite readily with the dimers of Si(001), often involving multiple reaction pathways. The specificity displayed by PITC, then, is different from the adsorption behavior of other systems.

For simple alkenes, our recent work suggests that [2 + 2] cycloaddition reactions of alkenes on silicon surfaces are facile because they occur through a low-symmetry pathway that is essentially a nucleophilic attack by the electron-rich alkene at the electron-poor region at the ends of the Si=Si dimers, where the (unoccupied)  $\pi^*$  antibonding orbital has its maximum state density.<sup>17</sup> Dimers on Si(001) can readily tilt, with a concurrent transfer of charge between the two atoms that makes the “down” atom electron-deficient and positively charged,<sup>35,54,55</sup> further enhancing the possible importance of electrostatic interactions between the electron-rich alkene and the electron-poor “down” atom of the tilted dimer. Indeed, recent high-level calculations show that for reactions of alkenes with Si(001) the nucleophilic attack by the alkene is facilitated by the dimer tilting, leading to a transition state that involves a strong interaction between the incident alkene and the “down” atom of the tilted surface dimers.<sup>56</sup>

For conjugated dienes such as 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene, adsorption can occur via a [2 + 2] reaction involving only one C=C bond or via a [4 + 2] “Diels-Alder” reaction involving both double bonds of the molecule. While for both these molecules the [4 + 2] adduct is predicted to be more stable by  $\sim 0.7$  eV,<sup>18</sup> experimental studies have shown that a significant fraction (20%–35%) bind via a [2 + 2] cycloaddition pathway.<sup>17</sup> Both experiments<sup>17</sup> and recent high-level ab initio calculations<sup>56</sup> show that the barrier to conversion between these products is large, so that the product distributions of conjugated dienes are locked in during the initial adsorption.

The aromatic nature of benzene leads to significantly different behavior. In this case multiple adsorption products have been observed, but the barrier between interconversion is small enough that changes in product distributions can be observed on time scales of minutes to hours to ultimately produce almost exclusively one stable bonding geometry.<sup>29,30,57</sup> This facile conversion between benzene binding sites can be attributed to the fact that the aromatic nature of benzene leads to significantly

smaller adsorption energies (than comparable nonaromatic systems) and adsorption–desorption behavior that is almost completely reversible.

In light of the adsorption of unsaturated molecules on Si(001), our results for PITC are quite unique. Based on the observed behavior of benzene, the highly specific product distribution we observe may occur via an initial adsorption into multiple sites that are able to undergo subsequent conversion into the most stable geometry (analogous to benzene). On the other hand, kinetic processes during initial adsorption might strongly favor binding through the N=C=S group. Because the N=C bonding region is electron-rich, PITC could undergo an electrostatically driven reorientation in order to bring the N=C=S group, rather than the benzene ring, closest to the surface. Dimer tilting could facilitate a strong electrostatic attraction between the N=C region of PITC and the positively charged “down” atom of a tilted Si dimer. Considering these electrostatic arguments, it is plausible that a PITC molecule approaching the Si surface is “steered” so that the N atom moves toward one end of a Si dimer.

## V. Conclusions

We have investigated a prototypical 1,2-dipolar addition reaction on a Si(001) surface. Our results show that PITC and MITC adsorb molecularly on Si(001) through a 1,2-dipolar addition reaction to form a four-member ring between the two Si atoms of a dimer and the N and C atoms of the isothiocyanate groups. Unlike many other surface reactions of molecules containing multiple functional groups, adsorption of PITC onto Si(001) occurs in a highly selective way, with little or no bonding through the aromatic ring. This high degree of selectivity suggests that isothiocyanate linkages may provide a useful means for attachment of various other organic substituents to the Si(001) surface in a selective manner.

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## References and Notes

- (1) Yates, J. T., Jr. *Science* **1998**, 279, 335–336.
- (2) Appelbaum, J. A.; Baraff, G. A.; Hamann, D. R. *Phys. Rev. B* **1976**, 14, 588.
- (3) Cheng, C. C.; Wallace, R. M.; Taylor, P. A.; Choyke, W. J.; Yates, J. T., Jr. *J. Appl. Phys.* **1990**, 67, 3693–3699.
- (4) Craig, B. I. *Surf. Sci.* **1995**, 329, 293–294.
- (5) Huang, C.; Widdra, W.; Weinberg, W. H. *Surf. Sci. Lett.* **1994**, 315, 953.
- (6) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, 117, 4082–4092.
- (7) Liu, H.; Hamers, R. J. *J. Am. Chem. Soc.* **1997**, 119, 7593–7594.
- (8) Mayne, A. J.; Cataldi, T. R. I.; Knall, J.; Avery, A. R.; Jones, T. S.; Pinheiro, L.; Hill, H. A. O.; Briggs, G. A. D.; Pethica, J. B.; Weinberg, W. H. *Far. Discuss. R. Soc.* **1992**, 94, 199.
- (9) Mayne, A. J.; Avery, A. R.; Knall, J.; Jones, T. S.; Briggs, G. A. D.; Weinberg, W. H. *Surf. Sci.* **1993**, 284, 247.
- (10) Yoshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *J. Chem. Phys.* **1987**, 87, 7332.
- (11) Yates, J. T., Jr. Private communication.
- (12) Hovis, J. S.; Lee, S.; Liu, H.; Hamers, R. J. *J. Vac. Sci. Technol. B* **1997**, 15, 1153–1158.
- (13) Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1997**, 101, 9581–9585.
- (14) Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1998**, 102, 687–692.
- (15) Liu, H.; Hamers, R. J. *To Be Published*.
- (16) Liu, H. Surface Chemistry of Unsaturated Organic Molecules on Si(001) Surfaces. Ph.D. Thesis, University of Wisconsin-Madison, 1998.
- (17) Hovis, J. S.; Liu, H.; Hamers, R. J. *J. Phys. Chem. B* **1998**, 102, 6873–6879.



- (18) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098–11099.
- (19) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, *119*, 11100–11101.
- (20) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Chem. Phys.* **1998**, *108*, 4599–4606.
- (21) Ellison, M. D.; Hovis, J. S.; Liu, H.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 8510–8518.
- (22) Armstrong, J. L.; Pylant, E. D.; White, J. M. *J. Vac. Sci. Technol. A* **1998**, *16*, 123–130.
- (23) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.
- (24) Birkenheuer, U.; Gutdeutsch, U.; Rösch, N. *Surf. Sci.* **1998**, *409*, 213–228.
- (25) Borovsky, B.; Krueger, M.; Ganz, E. *Phys. Rev. B* **1998**, *57*, R4269–R4272.
- (26) Craig, B. I. *Surf. Sci.* **1993**, *280*, L279–L284.
- (27) Gokhale, S.; Trischberger, P.; Menzel, D.; Widdra, W.; Dröge, H.; Steinrück, H.-P.; Birkenheuer, U.; Gutdeutsch, U.; Rösch, N. *J. Chem. Phys.* **1998**, *108*, 5554–5564.
- (28) Jeong, H. D.; Ryu, S.; Lee, Y. S.; Kim, S. *Surf. Sci.* **1995**, *344*, L1226–L1230.
- (29) Lopinski, G. P.; Fortier, T. M.; Moffatt, D. J.; Wolkow, R. A. *J. Vac. Sci. Technol. A* **1998**, *16*, 1037–1042.
- (30) Self, K. W.; Pelzel, R. I.; Owen, J. H. G.; Yan, C.; Widdra, W.; Weinberg, W. H. *J. Vac. Sci. Technol. A* **1998**, *16*, 1031–1036.
- (31) Taguchi, Y.; Fujisawa, M.; Takaoka, T.; Okada, T.; Nishijima, M. *J. Chem. Phys.* **1991**, *95*, 6870–6876.
- (32) Reddy, C. K.; Reddy, P. S. N.; Ratnam, C. V. *Ind. J. Chem.* **1987**, *26B*, 882–883.
- (33) Schaumann, E.; Bauch, H.-G.; Sieveking, S.; Adiwidjaja, G. *Chem. Ber.* **1982**, *115*, 3340–3352.
- (34) Doren, D. J. Private communication.
- (35) Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B* **1986**, *34*, 5343.
- (36) Chadi, J. D. *Phys. Rev. Lett.* **1987**, *59*, 1691–1694.
- (37) Chabal, Y. J. *Surf. Sci. Rep.* **1988**, *8*, 211.
- (38) Stephenson, C. V.; Coburn, W. C., Jr.; Wilcox, W. S. *Spectrochim. Acta* **1961**, *17*, 933–946.
- (39) Hamers, R. J.; Hovis, J. S.; Lee, S.; Liu, H.; Shan, J. *J. Phys. Chem. B* **1997**, *101*, 1489–1492.
- (40) Durig, J. R.; Sullivan, J. F.; Heusel, H. L. *J. Mol. Struct.* **1983**, *100*, 241–257.
- (41) Durig, J. R.; Sullivan, J. F.; Durig, D. T.; Craddock, S. *Can. J. Chem.* **1985**, *63*, 2000–2006.
- (42) Ham, N. S.; Willis, J. B. *Spectrochim. Acta* **1960**, *16*, 279–301.
- (43) Sjogren, C. E.; Klaeboe, P. J. *J. Mol. Struct.* **1983**, *100*, 433–452.
- (44) Luo, H.; Chidsey, C. E. D.; Chabal, Y. Infrared Spectroscopy of Covalently Bonded Species on Silicon Surfaces: Deuterium, Chlorine, and Cobalt Tetracarbonyl. *Science and Technology of Semiconductor Surface Preparation*; San Francisco, CA, 1997.
- (45) Bozso, F.; Avouris, P. *Phys. Rev. B* **1988**, *38*, 3937–3942.
- (46) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, 1992.
- (47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, P. S.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Rev. D.4*; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (48) Lee, C.; Wang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (49) Schnell, E.; Wersin, G. *Monatsh. Chem.* **1961**, *92*, 647–653.
- (50) Hovis, J. S. Unpublished data.
- (51) Liu, H.; Hamers, R. J. *Surf. Sci.* **1998**, *416*, 354–362.
- (52) Padowitz, D. F.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 8541–8545.
- (53) Lopinski, G. P.; Moffatt, D. J.; Wolkow, R. A. *Chem. Phys. Lett.* **1998**, *282*, 305–312.
- (54) Ihm, J.; Cohen, M. L.; Chadi, D. J. *Phys. Rev. B* **1980**, *21*, 4592–4599.
- (55) Wolkow, R. A. *Phys. Rev. Lett.* **1992**, *68*, 2636–2639.
- (56) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.*, submitted.
- (57) Wolkow, R. A.; Lopinski, G. P.; Moffatt, D. J. *Surf. Sci. Lett.* **1998**, *416*, L1107–L1113.