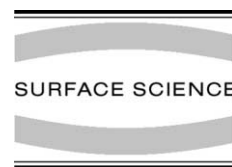




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The role of Pi-conjugation in attachment of organic molecules to the silicon (001) surface

Michael P. Schwartz, Robert J. Hamers *

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, USA

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Abstract

We have investigated the role of conjugation in attachment of multifunctional organic molecules to the Si(001) surface. The model molecules we have chosen are acrylonitrile ($\text{CH}_2=\text{CHC}\equiv\text{N}$) and allyl cyanide ($\text{CH}_2=\text{CHCH}_2\text{C}\equiv\text{N}$) due to the electron-withdrawing nature of the cyano group. X-ray photoelectron spectroscopy shows that significant difference in primary binding configuration exists. Infrared spectroscopy establishes that acrylonitrile attaches to the Si(001) surface primarily through a mechanism involving the cyano group, leading to a novel keteneimine structure that is evidenced by characteristic strong infrared absorbance at 1985 cm^{-1} . Allyl cyanide adsorbs in a way that principally utilizes the vinyl portion of the molecule, leading mainly to alkane infrared absorbance below 3000 cm^{-1} . These results show that conjugation can play an important role in controlling product distribution when attaching multifunctional organic molecules to the Si(001) surface.

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1. Introduction

The fabrication of well-defined interfaces between silicon and organic materials has attracted a great deal of attention over the last several years due to emerging applications in new microelectronics technologies [1,2] and for linking microelectronics with biological molecules [3]. While there are many approaches to making organic interfaces to silicon, recent studies have focused on establishing links between the chemistry of silicon surfaces and the chemistry of other compounds known from organic or inorganic chemistry.

The bare Si(001) surface is composed of highly ordered arrays of reactive Si=Si dimers which are analogous to the C=C bonds of alkenes and Si=Si bonds of silenes. However, there are two important differences between surface dimers and alkenes or silenes. The first difference is that the bonds between the Si=Si dimers and the underlying bulk are not planar; thus, the intrinsic hybridization of the surface dimers is somewhere between sp^2 and sp^3 . Secondly, the Si dimers are able to tilt out of the surface plane; this leads to charge transfer between the two atoms and contributes some zwitterionic character to the dimer [4].

One consequence of the unique geometric and electronic structure of Si=Si dimers is that many reactions can occur on the Si(001) surface that would not be facile in analogous solution-phase

* Corresponding author. Tel.: +1-608-262-6371; fax: +1-608-262-0453.

E-mail address: rjhamers@facstaff.wisc.edu (R.J. Hamers).

reactions. For example, alkenes will react readily with the Si(001) surface, forming stable, highly-ordered overlayers with a four-member ring at the organic–inorganic interface [5–8], even though the analogous reactions in solution are typically very slow and are formally forbidden in a high-symmetry geometry [9,10]. Computational studies have shown that the reaction pathway for these surface reactions involves formation of a low-symmetry intermediate in which the electron-rich alkene (C=C) group interacts with one end of a Si=Si dimer, where the π^* orbital has its greatest state density [8,10]. Thus, the initial interaction involves electron donation from the alkene to the Si surface [8]. The importance of the ability of the Si(001) surface to act as a facile electron acceptor has been further confirmed in recent studies showing that amines can form stable dative-bonded adducts involving electron donation from the N atom “lone pair” to one Si atom of the Si=Si dimer [11,12].

These results suggest that it may be possible to control the manner in which unsaturated molecules react with the Si(001) surface by adding electron-withdrawing groups to the molecule. The cyano group (C≡N) is strongly electron-withdrawing [13], and reactions of this group with other unsaturated molecules typically only occur under harsh conditions [14]. A very recent study concluded that acetonitrile (CH₃C≡N) and acrylonitrile (CH₂=CH–C≡N) molecules interact with the Si(001) surface via the cyano group, leading to a four-member ring involving two Si atoms and a CN group [15,16]. However, the explicit role of *conjugation* was not addressed. Here, we focus on two nearly identical molecules. Acrylonitrile and allyl cyanide (CH₂=CHCH₂C≡N) each contain one vinyl (C=C) and one nitrile (C≡N) group. However, in acrylonitrile these two groups are conjugated, while in allyl cyanide the presence of an additional methylene (–CH₂–) spacer interrupts conjugation. In acrylonitrile the conjugation of the bonds leads to an alternative “resonance structure”, depicted in Fig. 1a. The resonance structure leads to a shift in electron density towards the nitrogen end of the molecule, making the nitrile group more electron-rich than the nitrile end of the

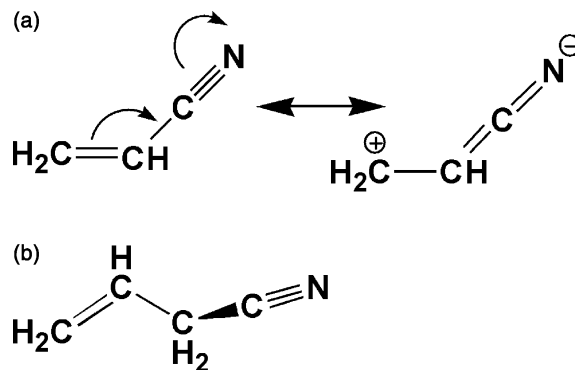


Fig. 1. Representation of (a) two resonance structures of acrylonitrile and (b) allyl cyanide.

allyl cyanide molecule. In addition to a shift in electron density, conjugation of the nitrile group to the vinyl group induces polarization of the C=C bond [17]. Fig. 1b depicts the allyl cyanide molecule. Here, the absence of conjugation is expected to make the two functional groups behave essentially independently.

In this paper, we have explored the adsorption of acrylonitrile and allyl cyanide to the Si(001) surface to understand whether or not conjugation will lead to significant changes in attachment chemistry compared to a non-conjugated molecule. We have observed significant differences in attachment of acrylonitrile to Si(001) at 300 K compared to previously reported results at 110 K [16], and have shown that conjugation does play an important role in attachment of multifunctional molecules to the silicon surface.

2. Experimental

The experiments described here were performed in two separate ultrahigh vacuum (UHV) chambers, each with a base pressure $< 1 \times 10^{-10}$ Torr. X-ray photoelectron spectroscopy (XPS) was used to characterize chemical composition and oxidation states while Fourier transform infrared spectroscopy using a multiple internal reflection geometry (MIR-FTIR) was used to determine the vibrational modes present for the adsorbed species.

2.1. Si(001) samples

All experiments were carried out using Si(001) samples that were rinsed in methanol for 15 min followed by exposure to ozone for 15 min to remove contamination due to residual organic species. After introduction to the UHV chamber, samples were outgassed overnight at 850 K and then annealed to 1400 K to remove the oxide layer, producing a clean, well-ordered (2×1)-reconstructed Si(001) surface [18]. XPS experiments were carried out using low-resistivity ($0.004 \Omega \text{cm}$) Si(001) wafers (Wacker Chemitronics). Multiple internal-reflection FTIR experiments were carried out using high-resistivity ($15 \Omega \text{cm}$), B-doped, double polished wafers oriented to the (001) surface within $\pm 0.5^\circ$ (Wacker Chemitronics). The edges of the Si wafers used for MIR-FTIR experiments were polished 45° from the (001) plane to create a prism with large (001) faces that could be used for the MIR geometry [19,20].

2.2. Techniques

XPS measurements were performed using a physical electronics system with a monochromatized Al K_α source and a hemispherical analyzer with a 16-channel detector array. The Si(2p) and N(1s) regions were probed using a pass energy of 11.75 eV and the C(1s) region was probed using a pass energy of 5.85 eV for both molecules. A Shirley background correction [21] was performed on the XPS data, followed by fitting to Voigt (Gaussian–Lorentzian convolution) peak shapes using the IGOR software package (Wavemetrics). The quality of fit was determined by using a reduced χ^2 statistical analysis. In order to correct for band-bending effects, all peaks were adjusted using the bulk Si(2p) peaks which were assumed to have values of 99.4 and 100.0 eV for the Si(2p) $_{3/2}$ and Si(2p) $_{1/2}$ lines, respectively. The C(1s) and N(1s) peaks were then adjusted by the same amount as the Si(2p) peaks.

MIR-FTIR experiments were performed using a Mattson RS-1 FTIR spectrometer which was coupled into the narrow edge of a clean, polished Si sample (~ 20 mm length) through BaF₂ win-

dows. An InSb detector was used to collect the IR light, and the entire optical path was purged with nitrogen. Spectra of the pure liquids were collected using a Nicolet 740 FTIR with a triglycine sulfate (TGS) detector. All FTIR spectra were collected at 4 cm^{-1} resolution.

2.3. Chemicals

Acrylonitrile (99+% purity) and allyl cyanide (98% purity) were purchased from Aldrich and further purified using several freeze-pump-thaw cycles. Purity was verified using in situ mass spectroscopy.

3. Results

3.1. Acrylonitrile XPS

Fig. 2a and c show the XPS spectra of a silicon surface that has been exposed to 10 L (5×10^{-8} Torr, 200 s) acrylonitrile at 300 K. Fig. 2a shows that the N(1s) spectrum for acrylonitrile attached to the Si(001) surface can be fit to two peaks ($\chi^2 = 1.24$): a dominant peak at 398.9 eV (FWHM = 0.92 eV, relative area ~ 0.91) and a minority peak at 397.8 eV (FWHM = 0.79 eV, relative area ~ 0.09). Based on the N(1s) XPS data, we can conclude that there are at least two chemically distinguishable N species on the Si(001) surface after exposure to saturation coverage of acrylonitrile.

Fig. 2c shows that the C(1s) region for saturation coverage of acrylonitrile on Si(001) can be fit to two peaks at 284.4 eV (FWHM = 0.99 eV) and 285.7 eV (FWHM = 1.58 eV) with $\chi^2 = 1.14$, and a relative peak area ratio of 1/1.66. A FWHM value of 1.58 suggests that the peak at 285.7 eV may consist of C atoms in different chemical environments. Attempts to fit the C(1s) spectrum for acrylonitrile to three peaks had little effect on the χ^2 value, and therefore we feel that fitting to two peaks is justified. Based on the C(1s) XPS data, we can conclude that there are at least two chemically distinguishable C species on the Si(001) surface after exposure to saturation coverage of acrylonitrile.

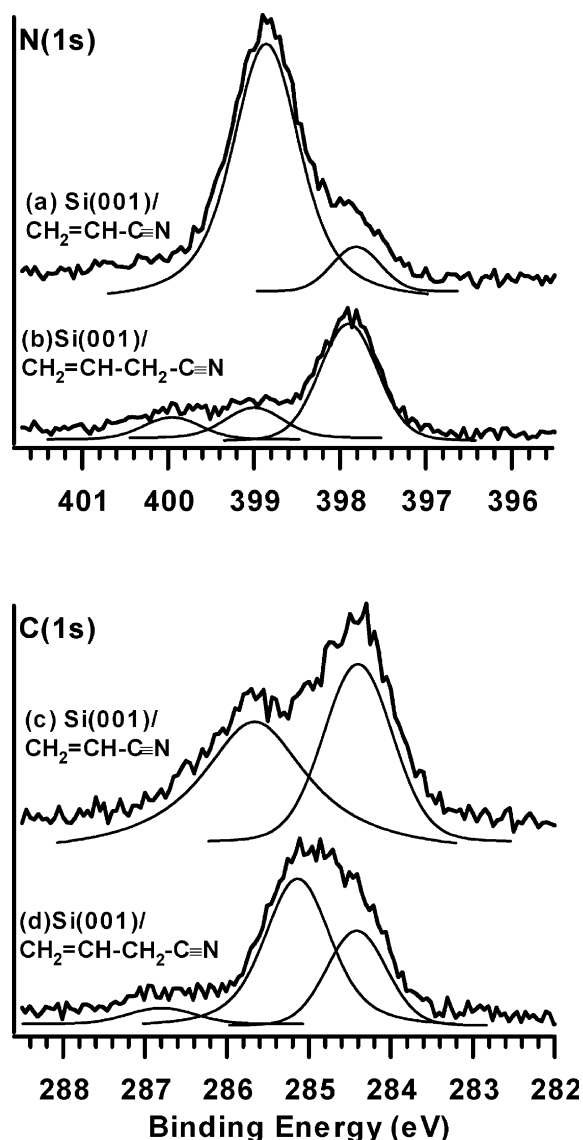


Fig. 2. XPS spectra of a Si(001) surface after exposure to molecules of interest. (a) N(1s), acrylonitrile. (b) N(1s), allyl cyanide. (c) C(1s), acrylonitrile. (d) C(1s), allyl cyanide.

3.2. Allyl cyanide XPS

Fig. 2b and d show the XPS spectra for a Si(001) sample that has been exposed to 5 L (5×10^{-8} Torr, 100 s) allyl cyanide at 300 K. Evaluation of the N(1s) spectrum in Fig. 2b shows that in addition to the 397.9 eV peak that is rep-

resentative of the primary bonding species (relative area ~ 0.70), there are minority peaks at 399.0 eV (relative area ~ 0.17) and 400.0 eV (relative area ~ 0.13). Each of these peaks have a width of 0.79 eV FWHM; this narrow width suggests that each N(1s) XPS peak represents a single bonding configuration. A χ^2 value of 0.92 indicates that the N(1s) spectrum for attached allyl cyanide is well represented by three peaks, meaning that there are at least three distinguishable N species present on the Si(001) surface.

Fig. 2d shows that the C(1s) XPS spectrum of Si(001) exposed to allyl cyanide is characterized by peaks at 284.4 eV (FWHM = 0.86 eV, relative area ~ 0.31), 285.1 eV (FWHM = 0.95 eV, relative area ~ 0.64), and a weak intensity peak at 286.8 eV (FWHM = 0.96 eV, relative area ~ 0.05). The C(1s) XPS spectrum for allyl cyanide/Si(001) has a $\chi^2 = 0.85$ eV. Based on the C(1s) XPS spectrum, we can conclude that there are at least three distinguishable C species present for saturation exposure allyl cyanide on the Si(001) surface.

3.3. Acrylonitrile FTIR

In order to identify the specific chemical species that are present on the Si(001) surface, FTIR spectra were also acquired. Fig. 3a shows the FTIR spectrum of a Si(001) surface that has been exposed to 3 L (1×10^{-8} Torr, 300 s) acrylonitrile at 300 K. Further exposure beyond 3L did not lead to any changes in the FTIR spectrum, and thus we conclude that the spectrum in Fig. 3a is representative of a self-terminating monolayer of acrylonitrile adsorbed to the Si(001) surface. The FTIR spectrum in Fig. 3a is characterized by a very strong absorbance at 1985 cm^{-1} , a weak peak at 2218 cm^{-1} , and several weak to medium peaks at 2556 , 2617 , 2898 , 3008 , 3028 , 3087 , 3145 , and 3347 cm^{-1} .

The first important feature of the FTIR spectrum for acrylonitrile/Si(001) is the striking peak at 1985 cm^{-1} . The peak at 1985 cm^{-1} has an absorbance of 0.033 while the next largest peak at 2898 cm^{-1} has an absorbance of 4.2×10^{-4} , $\sim 80 \times$ smaller. An evaluation of characteristic group frequency tables indicates that cumulated double

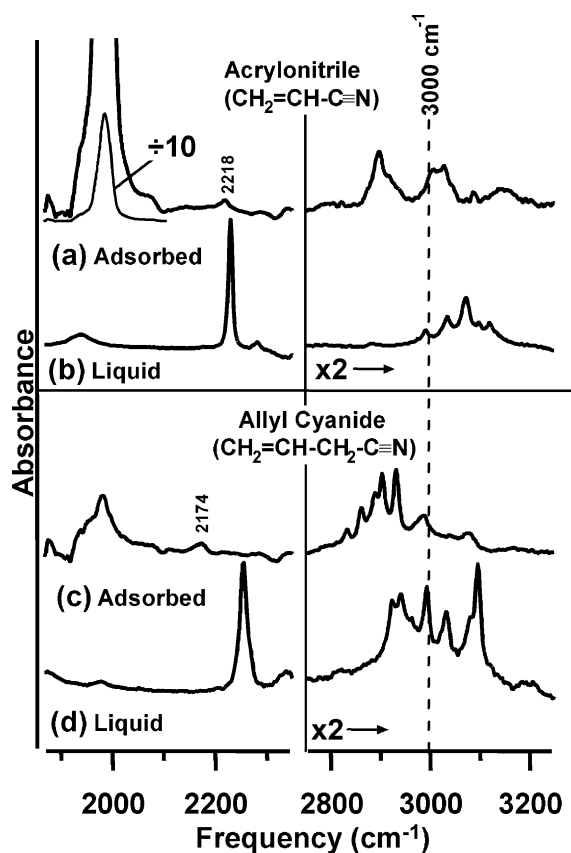


Fig. 3. FTIR spectra for molecular monolayers and pure liquids. (a) Saturation coverage acrylonitrile monolayer on Si(001) surface. (b) Liquid acrylonitrile. (c) Saturation coverage allyl cyanide monolayer on Si(001) surface. (d) Liquid allyl cyanide.

bonds ($X=Y=Z$) absorb between $1800\text{--}2000\text{ cm}^{-1}$, but that very few other species are found in this region. For example, overtones are commonly found in the $1800\text{--}2000\text{ cm}^{-1}$ region, but these peaks are usually quite weak [22]. Previous studies have found that silicon-keteneimine species absorb in the $2000\text{--}2040\text{ cm}^{-1}$ region [23,24], and are characterized by “very strong” $C=C=N$ absorption [23]. Thus, the IR spectrum suggests that keteneimine species might also be produced by adsorption of acrylonitrile on the Si(001) surface.

In addition to the peak at 1985 cm^{-1} , there is a very weak absorbance at 2219 cm^{-1} which is within the $C\equiv N$ stretching region, and several

peaks in the C–H stretching region ($\sim 2800\text{--}3200\text{ cm}^{-1}$). The peak at 2898 cm^{-1} is within the region typically associated with C–H stretching of saturated hydrocarbon species ($\sim 2800\text{--}3000\text{ cm}^{-1}$), while peaks at 3008 , 3028 , 3087 , and 3145 cm^{-1} are in the region usually associated with C–H stretching of unsaturated hydrocarbon species ($\sim 3000\text{--}3200\text{ cm}^{-1}$).

Fig. 3b shows the FTIR spectrum for liquid acrylonitrile. This spectrum is characterized by a strong $C\equiv N$ absorbance at 2230 cm^{-1} and several strong $C=C\text{--}H$ stretching peaks at 3034 , 3073 , and 3119 cm^{-1} , in good agreement with previously assigned spectra [25]. Several weak FTIR peaks are also observed and have been attributed previously to combination bands [25].

A comparison of FTIR spectra between liquid acrylonitrile (Fig. 3b) and acrylonitrile/Si(001) (Fig. 3a) shows several very distinct changes upon adsorption. First, the disappearance of the $C\equiv N$ stretching peak at 2230 cm^{-1} for the liquid spectrum corresponds to the appearance of a very strong peak at 1985 cm^{-1} for acrylonitrile/Si(001), indicating that the nitrile portion of the acrylonitrile molecule is involved in attachment to the Si(001) surface. Second, while liquid acrylonitrile shows FTIR peaks almost exclusively above 3000 cm^{-1} due to the $C=C\text{--}H$ absorbance of the intact molecule (as well as a combination band), a peak at 2898 cm^{-1} (within the alkane C–H stretching region) appears after attachment to the Si(001) surface. The formation of a peak at 2898 cm^{-1} after adsorption of acrylonitrile to the Si(001) surface indicates that the vinyl group is involved in attachment. Finally, after attachment of acrylonitrile to the Si(001) surface, there are new peaks at 2616 and 3347 cm^{-1} (not shown) that are not present in the liquid spectrum. The peak at 2616 cm^{-1} is in a region where few organic species typically absorb. The peak at 3347 cm^{-1} is in a region that can be associated with --NH stretching, but is a weak intensity peak, and may be due to a combination band. Based on a comparison between liquid acrylonitrile and acrylonitrile/Si(001), we can conclude that the acrylonitrile molecule is significantly perturbed upon attachment to the Si(001) surface.

3.4. Allyl cyanide FTIR

Fig. 3c shows the spectrum for a Si(001) surface exposed to 5 L (5×10^{-8} Torr, 100 s) allyl cyanide at 300 K. Further exposure beyond 5 L did not lead to any changes in the FTIR spectrum, and thus we conclude that the spectrum in Fig. 3c is representative of a self-terminating monolayer of allyl cyanide adsorbed to the Si(001) surface. Peaks at 1982, 2173, 2833, 2861, 2889, 2903, 2931, 2988, 3039, and 3076 cm^{-1} characterize the spectrum for attached allyl cyanide. The peak at 1982 cm^{-1} is within the region associated with cumulated double bonds ($\text{X}=\text{Y}=\text{Z}$ species). The small peak at 2174 cm^{-1} is near the region associated with $\text{C}\equiv\text{N}$ stretching. A previous study has shown $-\text{C}\equiv\text{N}$ stretches for silicon-nitrile species to be located below 2200 cm^{-1} [26], suggesting that there may be cyano groups either directly attached to the surface or interacting in some other way. The C–H stretching region is characterized mostly by peaks in the saturated C–H stretching range (2800–3000 cm^{-1}), with only very small absorbance in the unsaturated region (above 3000 cm^{-1}).

Fig. 3d shows the FTIR spectrum for liquid allyl cyanide. This spectrum is characterized by a strong $\text{C}\equiv\text{N}$ absorbance at 2255 cm^{-1} and several medium-strong C–H stretching peaks, in good agreement with previously assigned peaks [27].

FTIR spectra show that distinct changes in the allyl cyanide molecule have occurred upon attachment. First, chemisorption leads to nearly complete attenuation of the large $\text{C}\equiv\text{N}$ stretching peak at 2255 cm^{-1} ; the attenuation of this peak indicates that the cyano group is involved in attachment of most molecules. The decrease at 2255 cm^{-1} is accompanied by the appearance of a medium intensity peak at 1982 cm^{-1} and a weak absorbance at 2174 cm^{-1} . There is also a very significant change in the C–H stretching region. While liquid allyl cyanide is characterized by several strong saturated (C–C–H) and unsaturated (C=C–H) peaks, allyl cyanide/Si(001) shows only very weak absorbance in the unsaturated region (above 3000 cm^{-1}). The fact that FTIR absorption due to C–H stretching is found almost exclusively below 3000 cm^{-1} , with only a small amount of

absorbance in the 3000–3100 cm^{-1} region, indicates that the C=C bond for allyl cyanide has been perturbed for most of the molecules upon attachment to the Si(001) surface.

4. Possible binding configurations

4.1. Majority acrylonitrile configuration

Evaluation of the XPS data for acrylonitrile attached to the Si(001) surface shows several important pieces of information. First, since there are two peaks present at 397.8 ($\sim 10\%$ area) and 398.9 eV ($\sim 90\%$ area) in the N(1s) XPS spectrum (Fig. 2a), we can conclude that there are at least two bonding configurations, with $\sim 90\%$ of the molecules adsorbed such that the nitrogen atoms are in a similar chemical environment.

N-containing molecules in highly unsaturated environments tend to have exceptionally high N(1s) binding energies [16,28–30] that are expected to decrease upon saturation or interaction with the Si(001) surface due to increased electron density around the N atom. A study of HCN on Si(001) showed that adsorbed $\text{HC}=\text{NH}$, $\text{HC}=\text{N}$ and intact $\text{C}\equiv\text{N}$ species resulted in an ~ 1.5 eV decrease of the N(1s) binding energy compared to the intact molecule, indicating that interaction of a nitrile group with the Si(001) surface increases electron density around the N atom [28]. Similarly, an evaluation of the N(1s) XPS spectrum for acrylonitrile/Si(001) shows that each peak is shifted by at least 1.0 eV compared to intact nitrile containing molecules [16,28–30], indicating that the N atom of acrylonitrile is also in a more electron-rich environment after interaction with the Si(001) surface and that the nitrile group is perturbed for all adsorbed species.

Evaluation of the C(1s) XPS region reveals additional information about acrylonitrile attached to the Si(001) surface. Due to electron donation from Si to C (Pauling electronegativity of 1.90 vs. 2.55 for Si vs. C), alkane C atoms are found to be lower in binding energy when attached to Si atoms (284.0–284.5 eV) compared to those attached only to only C and H atoms (284.8–285.0 eV) [31,32]. The presence of a low binding energy

peak of 284.4 eV suggests that there are C atoms directly attached to the Si(001) surface for acrylonitrile/Si(001). Similarly, C=C peaks have been reported at 285.4–286.4 eV [16,31,33]. The presence of a peak at 285.7 eV suggests that C=C bonds are also present on a Si(001) surface exposed to acrylonitrile.

Evaluation of the FTIR spectra for liquid and adsorbed acrylonitrile reveals several chemical details about the Si(001) bonded species. First, the complete attenuation of the C≡N stretch at 2230 cm⁻¹ for liquid acrylonitrile (Fig. 3b) along with the formation of a striking peak at 1985 cm⁻¹ after attachment (Fig. 3a) indicates that bonding to the surface involves the C≡N portion of the molecule. Since combination bands are typically weak, it is very unlikely that the intense peak at 1985 cm⁻¹ is due to a combination band. While the C≡N modes of nitriles are typically found in the 2200–2260 cm⁻¹ region [22], bonding to Si would be expected to lower the vibrational frequency, as evidenced by the fact that a C≡N vibrational mode as low as 2165 cm⁻¹ for a molecule containing the Si–C≡N group, shown in Fig. 4, has been reported [26]. Since this is shifted 180 cm⁻¹ from the value we observe, we conclude that that peak at 1985 cm⁻¹ does not arise from a nitrile species.

Examination of infrared frequency tables indicates that the only species that are likely to give rise to strong absorption between 1800–2000 cm⁻¹ are those associated with cumulated double bonds (X=Y=Z) [22]. Several keteneimine species (C=C=N) have been found to have strong IR absorbance between 2012 and 2057 cm⁻¹ (4.89–

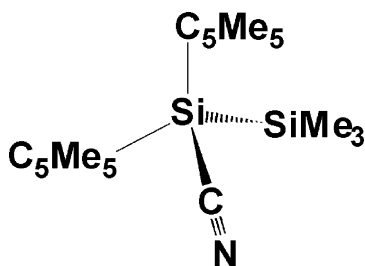


Fig. 4. Schematic structure of Bis(pentamethylcyclopentadienyl)ciano(trimethylsilyl)silane, which has an infrared C≡N stretching vibration at 2165 cm⁻¹ [26].

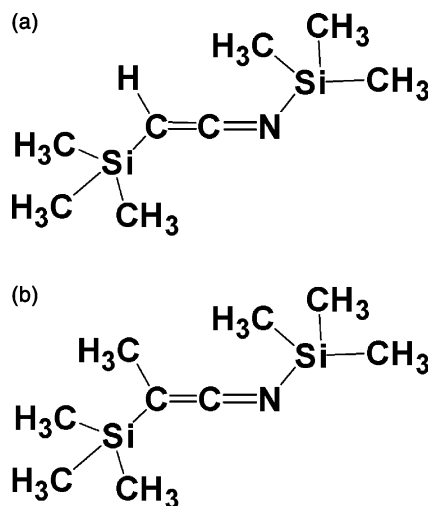


Fig. 5. Structures of two molecules with silicon keteneimine groups. (a) Trimethylsilylketene–trimethylsilylimine, C=C=N absorbance at 2028 cm⁻¹ [23]. (b) Methyltrimethylsilyl-*N*-trimethylsilylketeneimine, C=C=N absorbance at 2000 cm⁻¹ [24].

5.00 μm) [34,35] and previous work has shown that keteneimine-silicon species have very strong C=C=N absorption peaks between 2000 and 2040 cm⁻¹ [23,24]. Fig. 5 shows two examples of silicon-keteneimine molecules. Trimethylsilylketene–trimethylsilylimine, shown in Fig. 5a, has an IR absorption at 2028 cm⁻¹ (4.94 μm) [23] while methyltrimethylsilyl-*N*-trimethylsilylketeneimine, shown in Fig. 5b, has an IR absorbance at 2000 cm⁻¹ [24]. Comparison of the molecules in Fig. 5a and b shows that IR peak location for a keteneimine species can be significantly changed (28 cm⁻¹ in this case) with only a small change in molecular structure; thus, the 15 cm⁻¹ shift that we observe for acrylonitrile/Si(001) compared with what was observed for the molecule shown in Fig. 5b is reasonable. Therefore, we conclude that the predominant bonding configuration for acrylonitrile on the Si(001) surface is also a keteneimine species.

Fig. 6 shows several potential products in which acrylonitrile interacts with the Si(001) surface to form a keteneimine. The C(1s) XPS spectrum shows that C–Si and C=C species are both present on the Si(001) surface after attachment of acrylonitrile, and each is present for the configurations

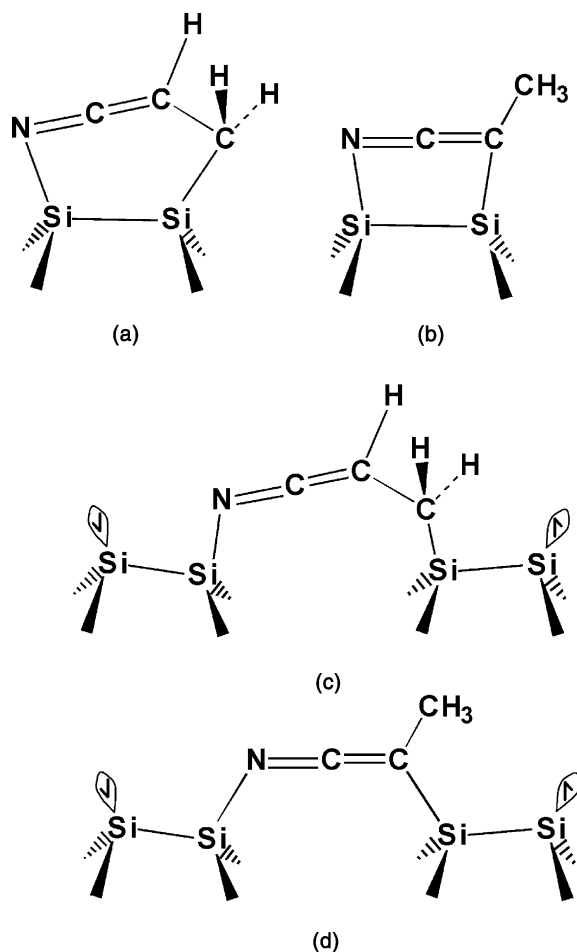


Fig. 6. Four possible bonding configurations for acrylonitrile on Si(001). (a) Formation of a keteneimine species over a single dimer without C–H cleavage. (b) Formation of a keteneimine species over a single dimer involving intramolecular H-atom transfer. (c) Formation of a keteneimine species between dimer rows without C–H cleavage. (d) Formation of a keteneimine species between dimer rows involving intramolecular H-atom transfer.

shown in Fig. 6a–d. However, the products in Fig. 6b and d would not be expected to have unsaturated =CH species present, and the FTIR spectra show evidence for significant C–H absorbance due to alkane and alkene groups. Therefore, based on the presence of alkane and alkene species, along with the presence of a large FTIR peak at 1985 cm⁻¹, we conclude that chemical species similar to those shown in Fig. 6a and c are likely to be the

dominant binding configuration for acrylonitrile attached to the Si(001) surface.

4.2. Minority acrylonitrile configurations

The presence of two N(1s) XPS peaks (Fig. 2a) indicates that there is at least one minority bonding configuration for acrylonitrile/Si(001). The presence of several widely scattered peaks in the unsaturated C–H stretching region, a small peak within the nitrile region at 2219 cm⁻¹, and a peak at 3344 cm⁻¹ (not shown) that is in the region where N–H species have been shown to absorb [28,36] makes it difficult to conclusively assign the minority configuration(s). However, while the minority species are difficult to assign, they represent a small fraction of the overall surface product (~10% based on relative peak areas of the N(1s) spectrum).

4.3. Majority allyl cyanide configuration

The presence of FTIR peaks mainly below 3000 cm⁻¹ for allyl cyanide attached to the Si(001) surface suggests that for the majority of adsorbed molecules, there are no longer C=C–H species present. Furthermore, the presence of a C(1s) XPS peak at 284.4 eV, which is similar to a previously reported C–Si species [31,32] indicates that C atoms are involved in attachment of allyl cyanide to the Si(001) surface. One way in which C atoms could be directly involved in attachment of allyl cyanide to Si(001) could be through direct interaction of the π -bond (from the vinyl group) of allyl cyanide with two electrons of a surface dimer, resulting in a four-member Si₂C₂ species as shown in Fig. 7a. Similar reactions have been observed for several alkene species [5,8,37–40]. Based on the presence of primarily unsaturated C–C bonds, coupled with evidence for C–Si bonds, we conclude that the vinyl group is involved in attachment of allyl cyanide to the Si(001) surface for the majority of the adsorbed molecules.

Reaction of allyl cyanide with Si(001) solely through the vinyl group would be expected to leave intact C≡N groups on the surface, which should in turn lead to significant absorbance in the nitrile stretching region of the FTIR spectrum.

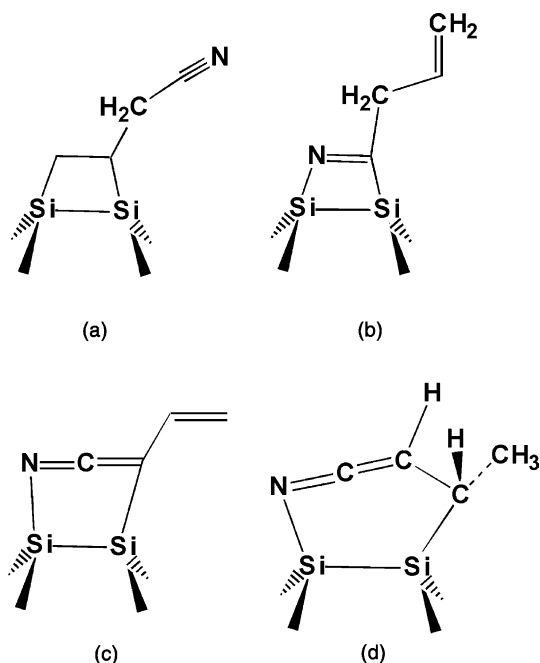


Fig. 7. Possible bonding configurations for allyl cyanide on Si(001). (a) Attachment through the vinyl group to form a four-member Si₂C₂ ring. (b) Attachment through the nitrile group to form a four-member Si₂C=N ring. (c) and (d) Products with keteneimine structure.

The absence of a peak between 2200 and 2300 cm⁻¹ (nitrile stretching region) suggests that the cyano group is perturbed due to interaction with the Si(001) surface for the majority of adsorbed molecules. This interaction may explain the unusually low N(1s) binding energy at 397.9 eV for the majority configuration of allyl cyanide/Si(001). The exact nature of possible interaction of the cyano group with the surface cannot be determined based on the presented evidence, but may result from further reaction, dissociation, or charge transfer effects with a neighboring dimer.

4.4. Minority allyl cyanide configuration

Fig. 7 shows several possible binding configurations for allyl cyanide/Si(001). Based on analysis of the N(1s) XPS spectrum, ~70% of adsorbed molecules give rise to a binding energy of 397.9 eV. In addition to the primary peak at 397.9 eV in the N(1s) XPS spectrum, there are two minority peaks

at 399.0 (~17% area) and 400.0 eV (~13% area). The presence of a peak at 399.0 eV in the N(1s) XPS spectrum along with an FTIR peak at 1982 cm⁻¹ for adsorbed allyl cyanide, each of which is very similar to peaks observed for acrylonitrile/Si(001), indicates that ~17% of the minority species are a keteneimine. Fig. 7c and d shows two possible keteneimine products that could be formed when allyl cyanide adsorbs to the Si(001) surface. There is not enough evidence to determine the nature of the species that gives rise to the peak at 400.0 eV, although this peak is within the range of previously reported nitrile N(1s) XPS peaks [16,28–30].

While adsorption of allyl cyanide to the Si(001) surface is somewhat complicated, it is clear that the vinyl group is involved for the majority of the attached molecules. The presence of at least three chemical species on a Si(001) surface exposed to allyl cyanide complicates interpretation of the data. A reaction pathway that forms a four-member ring through reaction of the vinyl group with a Si dimer would be one possible explanation for the identity of the majority species, but further interaction through the nitrile group likely occurs. The important conclusion that can be made based on the FTIR and XPS results is that while attachment of allyl cyanide to the Si(001) surface involves the vinyl group for the majority of adsorbed molecules, interaction of the cyano group is also observed.

4.5. Comparison between acrylonitrile and allyl cyanide

There are several pieces of information that we have presented to show that acrylonitrile and allyl cyanide interact with the Si(001) surface in very different ways. First, a large difference in the N(1s) binding energy for the dominant configuration indicates that the most favored reaction pathway leaves N atoms in very different chemical environments for acrylonitrile vs. allyl cyanide. This is further supported by the pronounced difference in the C(1s) XPS spectra. Next, the FTIR spectra show that significant alkane and alkene species are present for acrylonitrile/Si(001), while allyl cyanide/Si(001) yields almost exclusively alkane

species. Finally, evaluation of the FTIR and XPS data indicates that acrylonitrile forms primarily a keteneimine structure when attached to Si(001), while a keteneimine is only a minority product for allyl cyanide. The conclusion from this information is that structural differences between acrylonitrile and allyl cyanide lead to very different products when adsorbed to the Si(001) surface.

5. Mechanism

The above data show that acrylonitrile and allyl cyanide interact with the Si(001) surface in a significantly different way. These differences can be attributed to two primary effects resulting from the differences in conjugation. The first is the difference in mechanical flexibility between the free molecules. The presence of a methylene ($-\text{CH}_2-$) group in the allyl cyanide molecule provides it with greater mechanical flexibility, since there is likely to be little barrier to rotation about the adjacent C–C bonds. In contrast, the presence of conjugation in the allyl cyanide molecule makes it quite rigid, since the additional stabilization energy resulting from conjugation is only attained when the $\text{C}\equiv\text{N}$ and $\text{C}=\text{C}$ groups are coplanar. Qualitatively, one might expect that allyl cyanide would have the ability to adopt a different range of bonding configurations than acrylonitrile due to the increased flexibility provided by the ($-\text{CH}_2-$) spacer.

The second contributing effect can be the differences in the spatial distribution of the electron density. In acrylonitrile, conjugation leads to significant electron transfer from the vinyl group to the cyano group, which can be depicted by the resonance structure in Fig. 1a. In contrast, for allyl cyanide, the $-\text{CH}_2-$ group effectively separates the electronic properties of the $\text{C}=\text{C}$ and $\text{C}\equiv\text{N}$ groups. Consequently, in allyl cyanide the $\text{C}=\text{C}$ and $\text{C}\equiv\text{N}$ groups are essentially independent of one another.

Fig. 8 illustrates possible routes to forming the keteneimine species through interaction of an acrylonitrile molecule with a Si=Si dimer. We note that recent studies of organic amines have shown that these compounds can form stable dative-

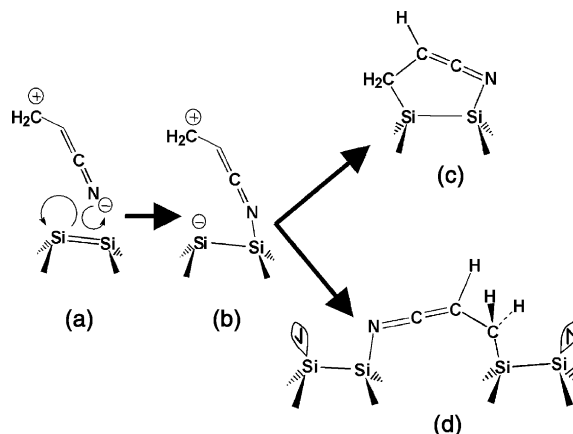


Fig. 8. Two possible mechanisms for formation of a keteneimine species through the interaction of an acrylonitrile molecule with the Si(001) surface.

bonded adducts in which the N atom donates its electron density to one atom of the Si=Si dimer, and this electron density is in part transferred to the other “non-bonded” Si atom [11,12]. In the case of acrylonitrile, conjugation leads to increased electron density on the N atom (Fig. 8a), which in turn is expected to enhance its ability to react with a Si=Si dimer. Formation of a bond between the N atom and one Si atom would lead to an intermediate state like that shown in Fig. 8b, which is somewhat analogous to the charge distribution observed experimentally and theoretically for the organic amines interacting with Si(001) [11, 12]. With acrylonitrile, the positively-charged CH_2 group could then link to the Si surface, either on the same dimer (Fig. 8c), or by linking to another dimer in an adjacent row (Fig. 8d). Preliminary scanning tunneling microscopy experiments indicate that acrylonitrile bonds between rows, lending support for the configuration shown in Fig. 8d [41]. The formation of keteneimine species has been observed previously in the reaction of $\text{SiH}(\text{CH}_3)_3$ and other similar molecules with $(\text{CF}_3)_2\text{C}=\text{C}(\text{C}\equiv\text{N})_2$ to form $(\text{CF}_3)_2\text{CH}-\text{C}(\text{CN})=\text{C}=\text{N}-\text{SiMe}_3$ [42].

While in the case of acrylonitrile the overall reaction appears to involve a very strong interaction between the two functional groups, in the case of allyl cyanide the bonding of the vinyl group and

the cyano group to the surface might be expected to be independent, or even competitive. The low frequency of the C–H vibrations (below 3000 cm^{-1}) indicates that the C–H species of the majority of allyl cyanide molecules involve sp^3 -hybridized carbons; this in turn indicates that the vinyl groups interact strongly with the surface for most adsorbed molecules. Yet, the FTIR spectrum for allyl cyanide/Si(001) shows no $\text{C}\equiv\text{N}$ stretching peak, even though the spectrum has good signal-to-noise ratio in the appropriate spectral region. Thus, we conclude that most allyl cyanide molecules *also* react with the surface through the cyano group. Since the methylene group provides the molecule with a high degree of flexibility, it is plausible that the molecule might be able to initially link to the surface through either group, and that the other group may react subsequently. It is impossible to determine whether the $\text{C}=\text{C}$ or the $\text{C}\equiv\text{N}$ group of allyl cyanide reacts first, but it is evident that both groups are involved in the reaction. FTIR and XPS results also show that there is a minority amount of a keteneimine species for allyl cyanide/Si(001), which shows that conjugation is not a necessary element in the formation of keteneimines on Si(001).

Finally, our results for acrylonitrile attachment to the Si(001) surface at 300 K are quite different from what was observed in another recent study of the adsorption of acrylonitrile to the Si(001) surface at low temperature (110 K) [16]. In particular, the previous work did not observe or report the keteneimine structure. Since those experiments were performed at lower temperature, it is possible that the behavior may be strongly temperature-dependent. Further studies will be needed to fully understand these differences in behavior.

6. Conclusions

The adsorption of two molecules with the same functional groups, acrylonitrile and allyl cyanide, to the Si(001) surface leads to significantly different binding configurations as a result of the differences in electron conjugation. The overall product distributions appear to be consistent with the emerging picture that the reaction pathways

are controlled by the charge exchange with the Si(001) surface. Our results show that conjugation has a major effect on the product distribution for attachment of organic molecules to the Si(001) surface. The formation of a novel keteneimine species on the Si(001) surface has also been shown for the first time.

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