

## Competition and Selectivity in the Reaction of Nitriles on Ge(100)-2×1

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**Abstract:** We have experimentally investigated bonding of the nitrile functional group (R-C≡N:) on the Ge(100)-2×1 surface with multiple internal reflection infrared spectroscopy. Density functional theory calculations are used to help explain trends in the data. Several probe molecules, including acetonitrile, 2-propenenitrile, 3-butenitrile, and 4-pentenenitrile, were studied to elucidate the factors controlling selectivity and competition on this surface. It is found that acetonitrile does not react on the Ge(100)-2×1 surface at room temperature, a result that can be understood with thermodynamic and kinetic arguments. A [4+2] cycloaddition product through the conjugated  $\pi$  system and a [2+2] C=C cycloaddition product through the alkene are found to be the dominant surface adducts for the multifunctional molecule 2-propenenitrile. These two surface products are evidenced, respectively, by an extremely intense  $\nu(\text{C}=\text{C}=\text{N})$ , or ketenimine stretch, at 1954  $\text{cm}^{-1}$  and the  $\nu(\text{C}=\text{N})$  stretch near 2210  $\text{cm}^{-1}$ . While the non-conjugated molecules 3-butenitrile and 4-pentenenitrile are not expected to form a [4+2] cycloaddition product, both show vibrational modes near 1954  $\text{cm}^{-1}$ . Additional investigation suggests that 3-butenitrile can isomerize to 2-butenitrile, a conjugated nitrile, before introduction into the vacuum chamber, explaining the presence of the vibrational modes near 1954  $\text{cm}^{-1}$ . Pathways directly involving only the nitrile functional group are thermodynamically unfavorable at room temperature on Ge(100)-2×1, demonstrating that this functional group may prove useful as a vacuum-compatible protecting group.

### I. Introduction

Due to its position at the boundary between traditional microelectronics and the realm of organic materials, functionalization of group IV semiconductor surfaces has garnered considerable attention in the past 5 years, and applications in the areas of molecular electronics, biological recognition, and reagentless micropatterning have been proposed.<sup>1-3</sup> If many of these concepts are to become technologically feasible, however, the creation of an ordered and selectively grown layer will likely be required.<sup>4</sup> To attain this goal, a precise understanding of the kinetic and thermodynamic factors that control surface reactions will be of paramount importance. Several studies in recent years have aimed to illuminate these governing principles, particularly on the technologically relevant (100) surfaces of Si and Ge.<sup>5-24</sup>

Past work on Si(100)-2×1 has highlighted the high reactivity of this surface toward many organic functional groups. In several instances, the facility with which reactions occur on this surface leads to nonselective bonding of multifunctional compounds.<sup>21</sup> Because of low reaction barriers, the reaction pathways of different functional groups of a molecule can all compete, and, hence, an assortment of surface products is usually formed. However, recent work by Wang and co-workers<sup>21</sup> has highlighted Ge(100)-2×1 as a possible solution to the nonselective bonding seen on Si(100)-2×1. The Ge-C bond strength is 7-9 kcal/mol weaker than that of its silicon analogue, as calculated

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for 1,3-butadiene on the Si(100)-2x1 and Ge(100)-2x1 surfaces,<sup>25</sup> and this difference alters the thermodynamics and kinetics of surface reactions. These changes may allow a multifunctional molecule to bond in a more selective manner, leaving an anisotropic monolayer with specific moieties unreacted.

To engineer the desired surface functionality, it will also be necessary to successively attach additional organic monolayers to a previously deposited layer. This type of second layer attachment chemistry will require that a reactive moiety be available after the deposition of the initial organic monolayer. Although reactions of a number of functional groups, such as alkenes, carbonyls, and amines, have been shown to occur on bare Si(100)-2x1 and Ge(100)-2x1 surfaces, attachment of subsequent organic monolayers has proven difficult. To date, only simple hydrogenation,<sup>26</sup> bromination,<sup>27</sup> and imide coupling<sup>28</sup> have been reported in a vacuum. Since the functional groups that are expected to be reactive in second layer reactions, such as amines and carbonyls, also react directly with the bare semiconductor surface, the challenge is to protect these groups during the deposition of the initial layer. We will show that the nitrile functional group will not bond directly with Ge(100)-2x1 and can be thought of as a vacuum-compatible protecting group. Subsequent conversion of the remaining nitrile to an amine via in situ hydrogenation may open the doorway to second layer attachment.

The reconstructed Si(100)-2x1 and Ge(100)-2x1 surfaces are known to possess a shared surface structure and similar electronic properties.<sup>29</sup> After proper preparation, both surfaces form rows of dimers, each with a strong  $\sigma$  bond and a weak  $\pi$  bond.<sup>30</sup> These surface dimers possess some of the characteristics of classic alkenes from organic chemistry and provide a highly ordered template of reactive sites. Diels-Alder,<sup>5-7</sup> [2+2] cycloaddition,<sup>8-10</sup> and 1,2-dipolar addition<sup>31</sup> products occurring through the surface dimers on Si(100)-2x1 and Ge(100)-2x1 have all been demonstrated experimentally.

Due to solid state electronic effects, specifically 1-D band structure requirements, the surface dimers tilt out of the surface plane.<sup>29</sup> Si surface dimers are dynamically tilting on the picosecond time scale at room temperature,<sup>32</sup> while Ge surface dimers are statically buckled.<sup>33</sup> The recessed atom, known as the “down atom”, donates significant electronic charge to the protruding or “up atom”. The down atom is hence electrophilic, and the up atom is nucleophilic.<sup>22</sup> This electronic structure, which gives rise to a diradical or zwitterionic character, makes possible another group of surface reactions with parallels in solution phase chemistry. For example, dative bonding, the donation of a molecule’s lone pair to the electrophilic dimer atom, has been observed for ammonia,<sup>11,12</sup> methylamines,<sup>13-16</sup> cyclic amines,<sup>34-37</sup> ketones,<sup>19-21</sup> and water<sup>22</sup> on Si(100)-2x1

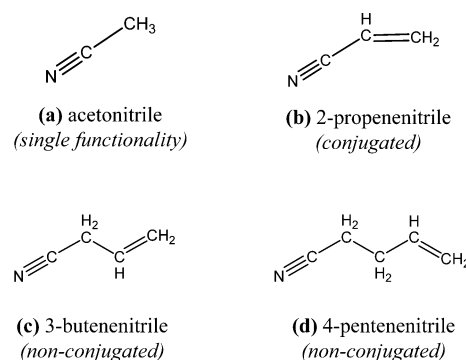


Figure 1. Nitrile-containing probe molecules investigated in this study.

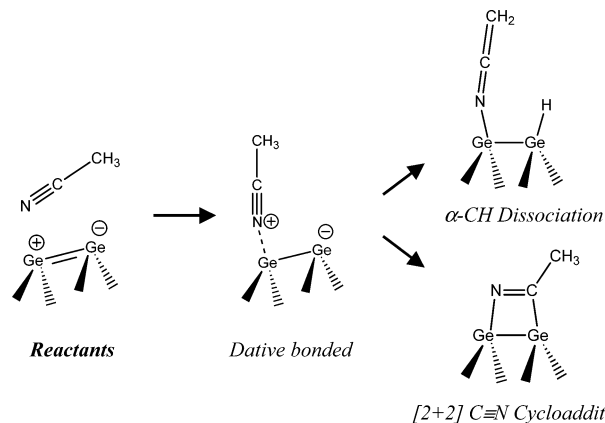


Figure 2. Possible reaction pathways for acetonitrile on Ge(100)-2x1.

and/or Ge(100)-2x1. Some of these molecules dative bond initially and then undergo subsequent surface reaction to form a thermodynamically more favorable product. For instance, hydrogen abstraction by the surface has been observed as a subsequent reaction with ammonia and some methylamines on Si(100)-2x1.<sup>11,13,14</sup>

In this work, we explore the bonding of the nitrile-containing organic molecules shown in Figure 1 on the Ge(100)-2x1 surface. The nitrile functional group consists of an  $sp$  hybridized carbon atom triply bonded to nitrogen. The nonbonding molecular orbital (MO) or lone pair of the nitrile originates on the nitrogen atom and is directed away from but parallel to the orthogonal  $\pi$  bonds of the  $C\equiv N$  bond. Furthermore, the electronegative nitrogen atom creates a highly polarized charge distribution in the direction  $\delta^+C\equiv N\delta^-$ .

Examination of organic reactions studied previously on Si(100)-2x1 and Ge(100)-2x1 leads one to predict that acetonitrile, a simple saturated nitrile, may bond in the configurations shown in Figure 2. A [2+2] cycloaddition product across the  $\pi$  bonds of the nitrile, referred to as a [2+2]  $C\equiv N$  cycloaddition, as well as a dative bond between the nitrogen lone pair and electrophilic dimer atom, are possible. Furthermore,  $\alpha$ -CH dissociation may also occur. Wang and co-workers recently showed that  $\alpha$ -CH dissociation, a reaction analogous to the pericyclic “ene” reaction from classic organic chemistry, is the predominant reaction pathway for acetone on Ge(100)-2x1.<sup>20</sup> The electron-withdrawing nature of the highly polarized  $\delta^+C=O\delta^-$  functional group, in the case of acetone,

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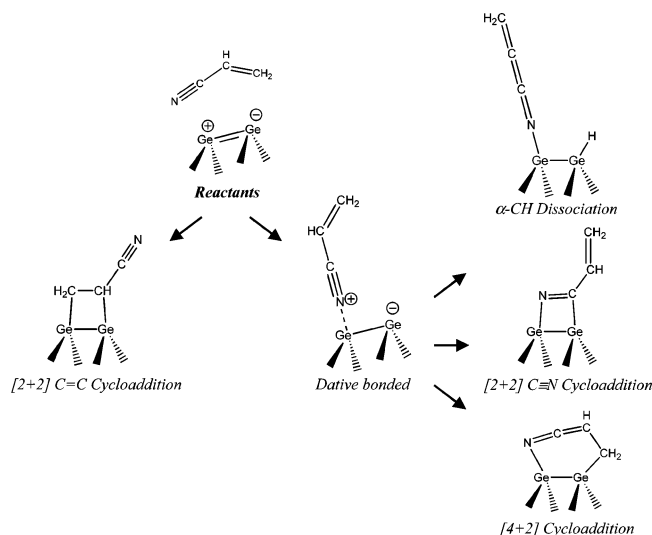
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**Figure 3.** Possible reaction pathways for 2-propenenitrile on Ge(100)–2×1.

weakens the  $\alpha$ -CH bond. Because these hydrogen atoms are acidic, they are more easily transferred to the nucleophilic dimer atom after the molecule initially adsorbs in a weakly bound dative-bonded state. Acetonitrile is chemically related to acetone because both molecules contain a methyl substituted carbon atom that is  $\pi$  bonded to a more electronegative atom containing one or more lone pairs. Thus, their reactivity toward the Ge(100)–2×1 surface is expected to be similar.

The multifunctional molecules, 2-propenenitrile, 3-butenitrile, and 4-pentenitrile, are studied to understand the competition and selectivity of the Ge(100)–2×1 surface. In addition to the possible surface adducts for acetonitrile, which include the dative bond, [2+2] C≡N cycloaddition product, and  $\alpha$ -CH dissociation product, multifunctionality may enable other competing pathways. As illustrated in Figure 3, a conjugated nitrile such as 2-propenenitrile may also react to form a hetero-Diels–Alder, or [4+2] cycloaddition product, similar to that seen for ethylvinylketone.<sup>20</sup> A [2+2] cycloaddition solely through the alkene  $\pi$  bond, referred to as a [2+2] C=C cycloaddition, is also possible.

## II. Experimental and Computational Details

All reactions were completed under ultrahigh vacuum conditions in a reactor described previously.<sup>38</sup> Infrared spectra were collected in a multiple internal reflection (MIR) geometry by employing a Fourier transform infrared (FTIR) spectrometer equipped with a narrow-band mercury–cadmium–telluride (MCT) detector. Trapezoidally shaped Ge crystals (1 × 20 × 50 mm, 45° beveled edges) were heated via a resistive tungsten heater and cooled by heat exchange with a liquid nitrogen coldfinger. A thin molybdenum plate was placed between the tungsten heater and crystal to minimize adsorption onto the uncleaned back face of the crystal. The Ge(100)–2×1 surface was prepared by Ar<sup>+</sup> sputtering at room temperature (7  $\mu$ A, 0.5 kV) followed by annealing to 875 K for 5 min, a procedure that has been shown to provide the proper 2 × 1 surface reconstruction.<sup>9</sup> In addition to LEED, a comparison of measured infrared spectra of saturated hydrogen-terminated surfaces with spectra from the literature<sup>39</sup> allowed us to verify that the proper surface reconstruction was achieved. To record infrared

spectra of the unreacted molecules, several multilayers were condensed at temperatures near 115 K. All spectra shown were corrected for baseline instabilities.

Acetonitrile (Fisher Scientific, 99.9%), 2-propenenitrile (Aldrich, 99+%), 3-butenitrile (Aldrich, 98%), and 4-pentenitrile (Fisher Scientific, 98%) are liquid under ambient conditions, and transfer to sample vials was completed under N<sub>2</sub> purge. Each compound was purified by several freeze–pump–thaw cycles before exposure to the crystal surface via a variable leak valve. An in situ quadrupole mass spectrometer confirmed the molecular identity and purity of each compound after introduction to the chamber. Surface exposures were measured in Langmuirs (1 Langmuir = 10<sup>–6</sup> Torr s), and dosing was performed by backfilling the chamber to a particular pressure for a specified period of time. The stated pressures were not corrected for ion gauge sensitivity.

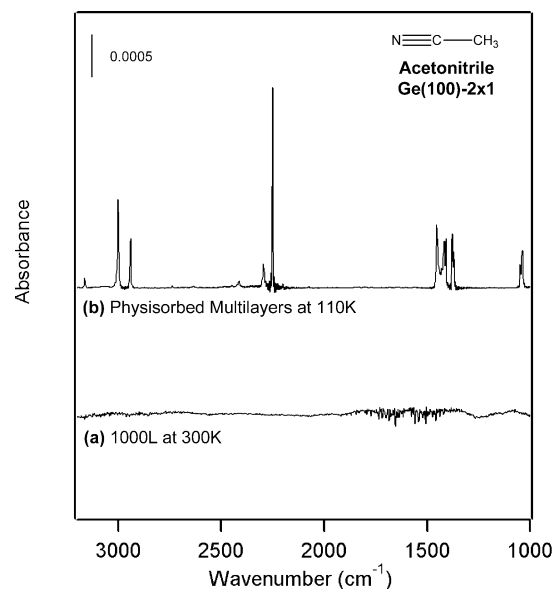
Electronic structure calculations were completed with the Gaussian 98 software package<sup>40</sup> using Becke3 Lee–Yang–Parr (B3LYP) three-parameter density functional theory.<sup>41</sup> The B3LYP functional is composed of the Lee–Yang–Parr and VWN correlation functionals<sup>42,43</sup> in addition to the Becke hybrid gradient-corrected exchange functional.<sup>44</sup> Previous studies of B3LYP indicate that it provides predictive results for similar systems<sup>10,13,24,25,37,45</sup> and is in good agreement when experimental results are available.<sup>13,24,46</sup> Geometries of important local minima and transition states on the potential energy surface were calculated with the polarized double- $\zeta$ , 6-31G(d) basis set without geometrical constraints followed by a single point calculation at the 6-31G(d) geometry with the more accurate, triple- $\zeta$ , 6-311++G(2df,pd) basis set. Local minima and transition states were verified with frequency calculations of the optimized structure with the 6-31G(d) basis set. All reported energies were zero-point corrected.

Because of the predominantly localized bonding of group IV (100)–2×1 semiconductor surfaces, we modeled the Ge(100)–2×1 surface as a dimer cluster. Most frequently, Si(100)–2×1 is modeled with a Si<sub>9</sub>H<sub>12</sub> cluster where the top two Si atoms compose the surface dimer. The remaining seven Si atoms compose three subsurface layers which are hydrogen terminated to preserve the sp<sup>3</sup> hybridization of the bulk diamond lattice. Because the time requirement for DFT methods scales approximately as order  $N^3$ , where  $N$  is the number of electrons in the system, a Ge<sub>9</sub>H<sub>12</sub> cluster calculation would take approximately 10 times longer than the analogous Si<sub>9</sub>H<sub>12</sub> calculation. What previously required 1 week of computing time for a Si<sub>9</sub>H<sub>12</sub> cluster would require more than 2 months to complete with a Ge<sub>9</sub>H<sub>12</sub> cluster, an increase that makes calculations computationally expensive and ultimately prohibitive. Interestingly, calculations at the B3LYP/6-311++G(2df,pd) level of theory for 1,3-butadiene cycloaddition products on a Ge<sub>2</sub>Si<sub>7</sub>H<sub>12</sub> cluster, where the two dimer atoms are replaced with Ge, result in a binding energy within 1–2 kcal/mol of that found with the Ge<sub>9</sub>H<sub>12</sub> cluster.<sup>15,25</sup> DFT is used in our study to explain experimental trends, and the Ge<sub>2</sub>Si<sub>7</sub>H<sub>12</sub> cluster provides an acceptable model for this purpose.

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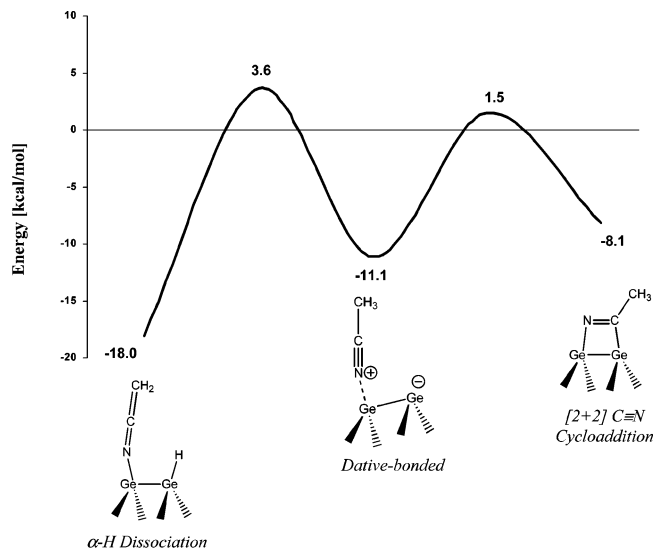


**Figure 4.** Infrared spectra of acetonitrile on Ge(100)-2x1: (a) 1000 L at 300 K; (b) multilayers (scaled) at 110 K.

### III. Results and Discussion

**A. Acetonitrile.** Before examining multifunctional molecules, for which competing reactions make identification of the surface adducts more challenging, it is instructive to first understand acetonitrile, a simple saturated nitrile. Acetonitrile ( $C_2H_3N$ ) consists of a nitrile group with a single methyl substituent. It has already been shown experimentally by others that acetonitrile bonds to the Si(100)-2x1 surface via a [2+2]  $C\equiv N$  cycloaddition at 110 K,<sup>47</sup> and previous theoretical calculations found a reaction pathway occurring through a dative-bonded precursor state.<sup>48</sup> In contrast to the results on Si(100)-2x1, we find in the present study that acetonitrile does not bond to the Ge(100)-2x1 surface at room temperature, even at doses as large as 1000 L.

These data, displayed in Figure 4a, show no measurable absorption over the  $\nu(C-H)$ ,  $\nu(C\equiv N)$ ,  $\nu(C=N)$ , and  $\nu(Ge-H)$  stretching regions. This result can be understood by examining the structure of the postulated [2+2]  $C\equiv N$  cycloaddition and  $\alpha$ -CH dissociation products shown in Figure 2. The [2+2]  $C\equiv N$  cycloaddition product exhibits  $sp^2$  hybridization due to the remaining  $\pi$  bond between the carbon and nitrogen. Although this highly strained surface structure is observed for acetonitrile<sup>47</sup> and benzonitrile<sup>49</sup> on Si(100)-2x1, it is expected to be unstable on Ge(100)-2x1 at room temperature due to the weaker bonds that germanium forms with carbon.<sup>21</sup> The other pathway, an  $\alpha$ -CH dissociation reaction, would create a linear  $C=C=N$  group, known as a ketenimine, on the surface. Similar to allenes, ketenimines are cumulated dienes because they contain an  $sp^2$  hybridized carbon and nitrogen atom doubly bonded to the same  $sp$  hybridized carbon. Because of the weak electronic structure associated with the orthogonal  $\pi$  bonds of this functional group, the  $\alpha$ -CH dissociation product is also expected to possess a weak binding energy. Weak binding energies allow for reversible desorption, and both the [2+2]  $C\equiv N$  cycloaddition and the



**Figure 5.** Critical points on the potential energy surface of acetonitrile on Ge(100)-2x1.

$\alpha$ -CH dissociation product will likely not be observed at room temperature. These intuitive arguments alone can explain why acetonitrile is not observed experimentally with IR spectroscopy; however, additional evidence can be gleaned with DFT calculations.

Figure 5 details a partial potential energy surface of important local minima and transition states calculated for the reaction of acetonitrile on a Ge(100)-2x1 model dimer cluster. Acetonitrile first passes through a dative-bonded precursor state, shown in the center of the diagram, before continuing to the final surface products. The binding energy of the dative-bonded state of the nitrile functional group, at -11 kcal/mol, is approximately 9 kcal/mol weaker than that of an amine.<sup>15</sup> This difference can be explained by the hybridization of the nitrogen atom. The nitrogen atom of the nitrile is  $sp$  hybridized and has considerably more  $s$  character than the  $sp^3$  hybridized carbon atom of an amine. The increased  $s$  character of the nitrile diminishes the electron donor strength and leads to a weaker dative bond.<sup>50</sup>

Investigation of the two pathways leading from the dative-bonded precursor state to the [2+2]  $C\equiv N$  cycloaddition and  $\alpha$ -CH dissociation products reveals why no reaction products are observed for acetonitrile at room temperature. As expected, the binding energy of the [2+2]  $C\equiv N$  cycloaddition is weak (-8.1 kcal/mol), and a first-order kinetic analysis with a preexponential factor of  $10^{13} s^{-1}$ , believed to be a good approximation for these systems,<sup>51</sup> yields a surface lifetime on the order of  $10^{-7} s$ . This is extremely short when compared to the time scale of our spectroscopic measurements, which is on the order of  $10^2 s$ . The  $\alpha$ -CH dissociated product is 10 kcal/mol more stable than the [2+2]  $C\equiv N$  cycloaddition, resulting in a surface lifetime of nearly 1 s; however, this is still relatively short when compared to the time scale of our measurements. Furthermore, the activation barrier is 3.6 kcal/mol above the vacuum level (14.7 kcal/mol above the dative-bonded state) and would be difficult to surmount at room temperature, if one assumes even minimal energy accommodation after the molecule initially adsorbs in the dative-bonded state.

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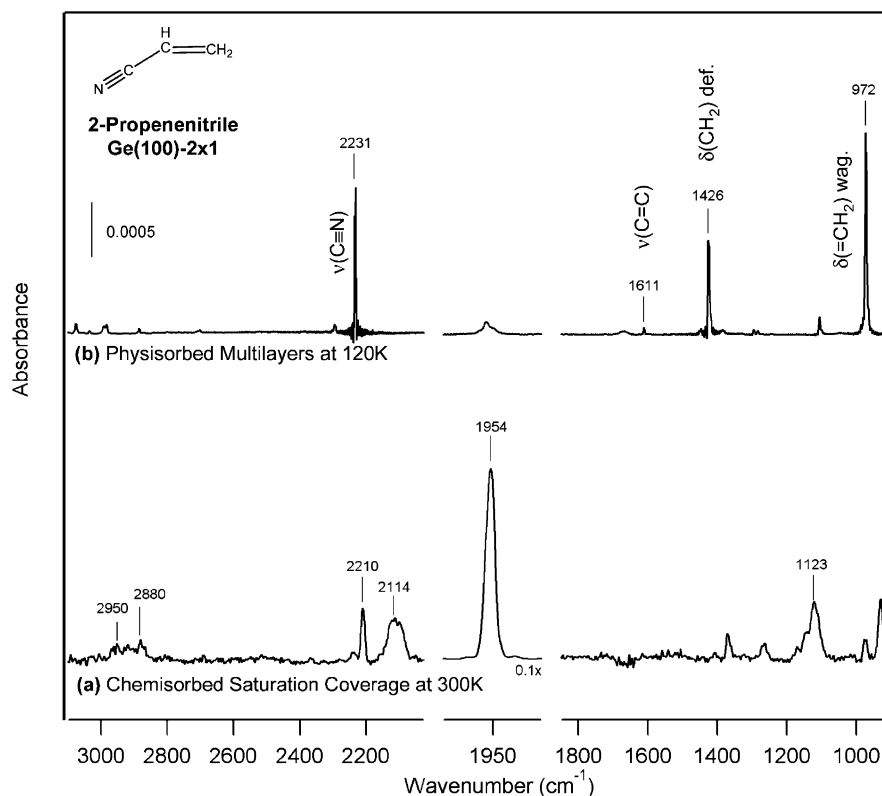
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**Figure 6.** Infrared spectra of 2-propenenitrile on Ge(100)–2×1: (a) 40 L at 300 K; (b) multilayers (scaled) at 120 K.

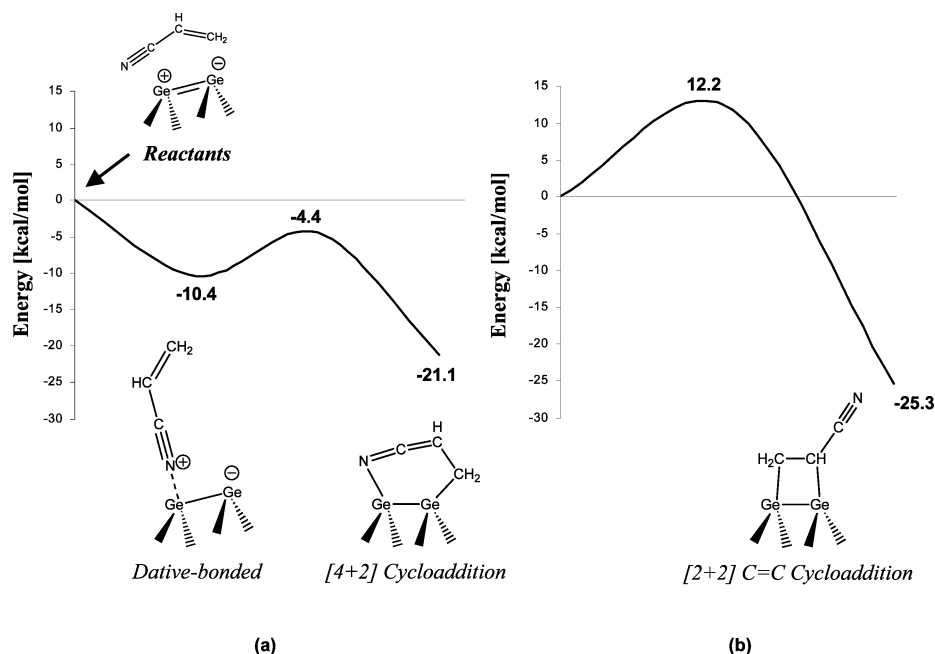
**B. 2-Propenenitrile.** The multifunctional molecule 2-propenenitrile ( $C_3H_3N$ , common name: acrylonitrile) can be employed to investigate competition and selectivity on the Ge(100)–2×1 surface. Unlike acetonitrile, 2-propenenitrile is found to form adsorbed surface species at room temperature. Experimental results for a Ge(100)–2×1 surface saturated with 2-propenenitrile at room temperature are illustrated in Figure 6a. The dominant feature of the infrared spectrum is an extremely intense and broad (fwhm =  $24\text{ cm}^{-1}$ ) absorption peak at  $1954\text{ cm}^{-1}$ , scaled by  $0.1\times$  relative to the rest of the spectrum. In fact, the integrated intensity of the peak at  $1954\text{ cm}^{-1}$  far exceeds any other IR mode seen in our previous investigations of organic reactions on group IV semiconductors. This peak falls squarely in the  $\nu(\text{Ge}-\text{H})$  stretch spectral region, but comparison to a fully saturated Ge–H surface indicates that it is far too intense and broad for this to be the correct assignment. The condensed phase IR peak seen near  $1962\text{ cm}^{-1}$  in Figure 6b, which is a weak combination band resulting from the low frequency  $\rho_w(\text{C}=\text{CRH})$  and  $\rho_w(\text{C}=\text{CH}_2)$  wagging modes of the free molecule,<sup>52</sup> is in close proximity to the  $1954\text{ cm}^{-1}$  peak. However, because combination bands arising from chemisorbed surface products are usually weak in intensity, the multilayer peak at  $1962\text{ cm}^{-1}$  cannot account for the strong peak observed at  $1954\text{ cm}^{-1}$  for the surface adduct. Rather, we conclude that this feature corresponds to a cyclic ketenimine stretch. It is known from organic chemistry that the ketenimine functional group possesses a large transition dipole moment, and  $\nu_a(\text{C}=\text{C}=\text{N})$  asymmetric stretching modes are usually found between  $1950$  and  $2100\text{ cm}^{-1}$ .<sup>53–55</sup> We further conclude that

the peak arises from a [4+2] cycloaddition product because it is the only postulated adduct that exhibits a ketenimine functionality. In addition, using a typical scaling factor of 0.96 for the 6-31G(d) basis set,<sup>56</sup> we found that the calculated ketenimine frequency for this surface product is within  $10\text{ cm}^{-1}$  of that observed experimentally. Our finding of a [4+2] cycloaddition or hetero-Diels-Alder product for 2-propenenitrile is supported by the results of recent studies on Si(100)–2×1<sup>57,58</sup> and Si(111)–7×7.<sup>59</sup>

The peak detected near  $2210\text{ cm}^{-1}$  (Figure 6a) is close to the  $\nu(\text{C}\equiv\text{N})$  stretch observed at  $2231\text{ cm}^{-1}$  for the condensed phase IR spectrum of 2-propenenitrile (Figure 6b). Thus, we assign this peak to a  $\nu(\text{C}\equiv\text{N})$  stretch, indicating the presence of the [2+2] C=C cycloaddition product because it is the only adduct (Figure 3) where the nitrile functional group remains intact. Conjugated nitriles usually exhibit  $\nu(\text{C}\equiv\text{N})$  stretching absorption peaks near  $2230\text{ cm}^{-1}$  as compared to  $2250\text{ cm}^{-1}$  for their saturated counterparts (i.e., acetonitrile) because of electron delocalization effects.<sup>60</sup> When 2-propenenitrile bonds to form a [2+2] C=C cycloaddition product, the alkene saturates, and the surface product is no longer conjugated (Figure 3). Following this argument, the remaining  $\nu(\text{C}\equiv\text{N})$  would be expected to blue-shift closer to that of saturated nitriles, but the measured peak is actually red-shifted relative

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**Figure 7.** Critical points on the potential energy surface of 2-propenenitrile on Ge(100)-2×1 for experimentally observed surface products: (a) [4+2] cycloaddition product; (b) [2+2] C=C cycloaddition product.

to the multilayer. However, while it is known that the  $\nu(\text{C}\equiv\text{N})$  is insensitive to different organic substituents,<sup>60</sup> the presence of a nearby inorganic atom can substantially red-shift the nitrile stretching frequency. In fact, a comparison of experimentally determined nitrile stretching frequencies for gas-phase acetonitrile ( $\text{CH}_3\text{CN}$ ) and germyl cyanide ( $\text{GeH}_3\text{CN}$ ) reveals a  $62\text{ cm}^{-1}$  red-shift.<sup>61</sup> Therefore, we believe that the observed red-shift is likely a proximity effect between the nitrile functional group in the product and the germanium dimer atoms to which the molecule bonds.

The experimental results for acetonitrile on Ge(100)-2×1 suggest that the [2+2] C≡N cycloaddition and  $\alpha$ -CH dissociation products will not be observed for 2-propenenitrile, a conclusion that is confirmed by the spectral data (Figure 6a). Alkene and imine absorption peaks, appearing between  $1600$  and  $1675\text{ cm}^{-1}$ , which should be present for the [2+2] C≡N cycloaddition product, are not observed. The  $\alpha$ -CH dissociation reaction would form a heterocumulene ( $\text{C}=\text{C}=\text{C}=\text{N}$ ) surface product (Figure 3). Cumulenes are functional groups that contain two or more adjacent double bonds that have a cumulated structure. In fact, many heterocumulenes can only be observed under cryogenic conditions and are normally not isolable.<sup>53</sup> Absence of this product is evidenced by lack of a strong heterocumulene peak above  $2150\text{ cm}^{-1}$ .<sup>54</sup> The  $\nu(\text{Ge}-\text{H})$  spectral region, which could provide additional support as to the lack of the  $\alpha$ -CH dissociation reaction, is obscured by the strong cyclic ketenimine absorption feature.

The [4+2] and [2+2] C=C cycloaddition adducts are the only products that we have identified from the spectrum in Figure 6a. Assuming that these are the only significant surface species, it is possible to approximate their relative surface coverage. DFT calculations show that the stretching frequency of the cyclic ketenimine (from the [4+2] product) should be 3.5 times as intense as that of the nitrile (from the [2+2] C=C product). Therefore, using integrated intensities from the IR

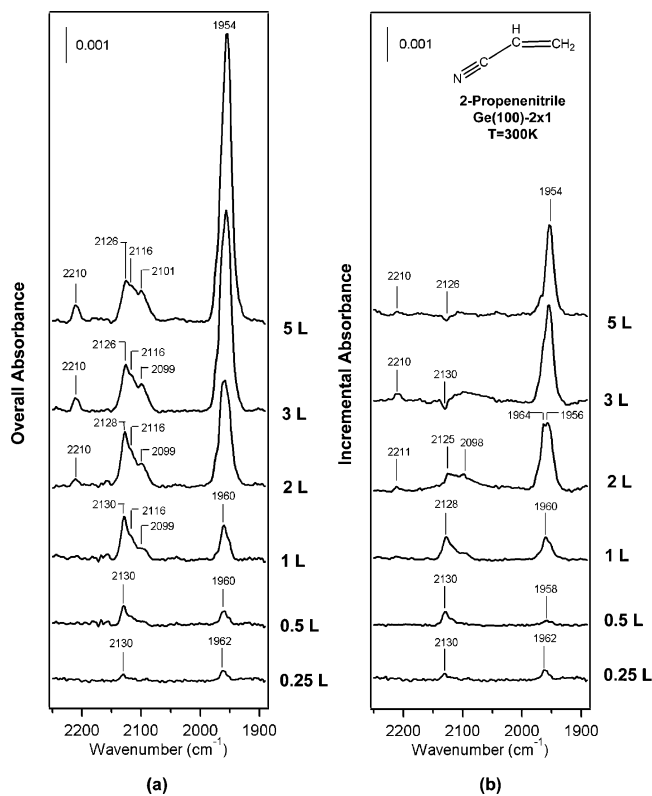
spectrum, we can estimate that the [4+2] and [2+2] C=C cycloaddition surface products are present in a 10:1 ratio and *the cyclic ketenimine is the majority surface adduct*.

Simplified potential energy surfaces of the two dominant reaction pathways of 2-propenenitrile on Ge(100)-2×1 are displayed in Figure 7. 2-Propenenitrile is expected to pass through a dative-bonded precursor state before forming the [4+2] cycloaddition product as shown in Figure 7a. In contrast to the analogous reaction with ethylvinylketone, this reaction with 2-propenenitrile is found to be activated with respect to the precursor state, a difference attributed to the highly strained nature of the cyclic ketenimine surface adduct. The [2+2] C=C cycloaddition pathway does not pass through the dative-bonded precursor state and is activated with a barrier  $12.2\text{ kcal/mol}$  above the vacuum level, as shown in Figure 7b. We find that the transition state for the [2+2] C=C cycloaddition pathway is a weakly bound  $\pi$  complex analogous to that first reported by Liu and Hoffman,<sup>62</sup> although Choi and Gordon later proposed this structure to be an artifact of a single-configurational wavefunction calculation.<sup>10</sup> Nonetheless, these relative energetics for the two competing pathways, in which one reaction is activated and the other unactivated, are in qualitative agreement with the intensity data discussed above and suggest that the [4+2] cycloaddition product will dominate over the [2+2] C=C cycloaddition product.

Coverage-dependent IR spectra of 2-propenenitrile, displayed in Figure 8, provide evidence for interdimer bonded products and help to explain the origin of the spectral features observed between  $2100$  and  $2130\text{ cm}^{-1}$ . Overall spectra, which are ratioed to the clean surface spectrum, are shown in Figure 8a for a range of surface exposures. These data are also plotted as incremental spectra, which are each ratioed to the previous spectrum, in Figure 8b. In the following analysis, the spectral regions of  $1954$ – $1962\text{ cm}^{-1}$ ,  $2100$ – $2130\text{ cm}^{-1}$ , and  $2210\text{ cm}^{-1}$  will be treated separately.

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**Figure 8.** Coverage-dependent infrared spectra of 2-propenenitrile on Ge(100)-2 $\times$ 1 at 300 K: (a) overall, ratioed to the clean surface; (b) incremental, ratioed to the previous dose.

We begin with the asymmetric ketenimine stretch near 1962  $\text{cm}^{-1}$ . The peak appears at low surface coverage, and its intensity increases with exposure. A red-shift to 1954  $\text{cm}^{-1}$  and appearance of shoulders are visible in the overall spectra (Figure 8a), but inspection of the incremental spectra at 2 L (Figure 8b) reveals that multiple peaks are present. Similar to the scanning tunneling microscope observations of norbornadiene<sup>63</sup> and benzene<sup>64</sup> in bonding configurations that bridge multiple surface dimers on Si(100)-2 $\times$ 1, we speculate that these closely spaced absorption peaks are spectral evidence of interdimer [4+2] cycloaddition products for 2-propenenitrile on Ge(100)-2 $\times$ 1. At low surface coverages, where vacant, adjacent dimers are readily available, one would expect substantial interdimer bonding. Molecules eventually must bond to a single dimer as adjacent surface sites become occupied. Thus, the peaks near 1964 and 1956  $\text{cm}^{-1}$  may correspond to interdimer and single dimer [4+2] cycloaddition products, respectively.

The set of peaks between 2100 and 2130  $\text{cm}^{-1}$  in Figure 8 are currently unassigned because these frequencies do not correspond with any molecular vibrations that might arise from the expected reaction products illustrated in Figure 3. However, alkyne (C $\equiv$ C) and isonitrile ( $-\text{N}\equiv\text{C}$ ) stretching frequencies also fall in this spectral region,<sup>60</sup> and we cannot rule out the possibility of a complex pathway leading to surface adducts exhibiting these functionalities. Additionally, the shoulders and shifts that occur with increasing coverage are similar to those of the ketenimine peaks near 1960  $\text{cm}^{-1}$ , leading us to speculate

that these two spectral regions are possibly related. Thus, another explanation for the origin of the 2100–2130  $\text{cm}^{-1}$  peaks is Fermi resonance or combination bands arising from low-frequency bending modes coupling with the strong ketenimine modes.

The mode near 2210  $\text{cm}^{-1}$  originates from a  $\nu(\text{C}\equiv\text{N})$  stretch stemming from the [2+2] C=C cycloaddition product. This mode does not become distinguishable from the noise until 2 L, and we ascribe its slow growth to the high activation barrier associated with this pathway.

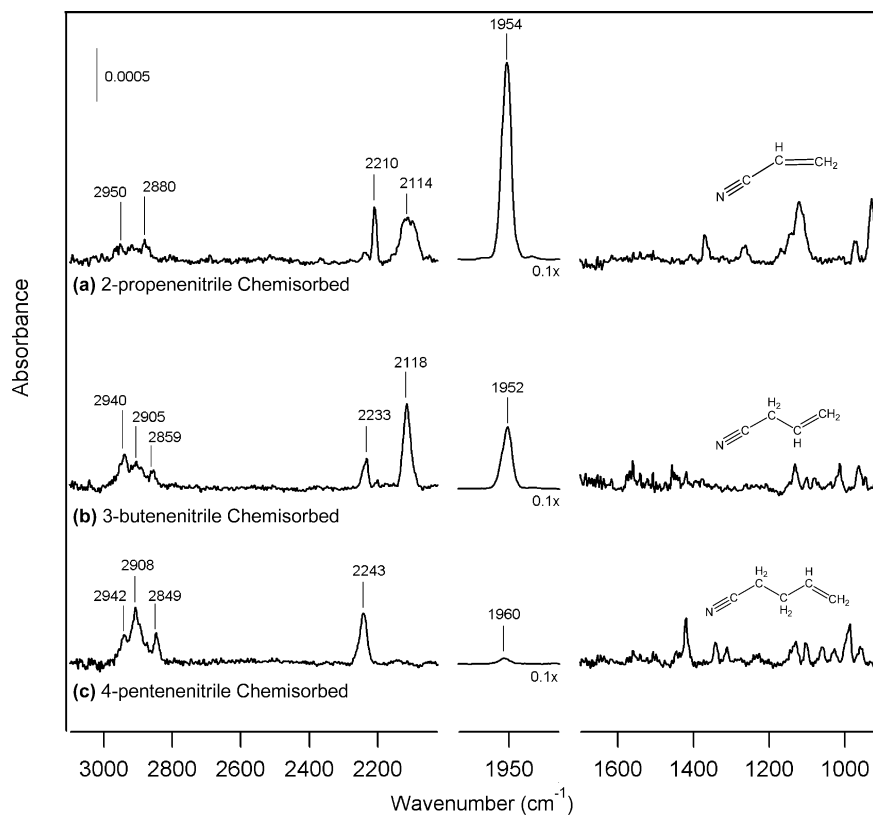
**C. 3-Butenenitrile.** Reaction of the non-conjugated molecule 3-butenitrile ( $\text{C}_4\text{H}_5\text{N}$ , common name: allyl cyanide) on Ge(100)-2 $\times$ 1 is expected to form a relatively simple product distribution. Because the C=C and C $\equiv$ N bonds are not conjugated, this molecule is not expected to form a [4+2] cycloaddition product. In addition, experimental results from acetonitrile and 2-propenenitrile indicate that the [2+2] C $\equiv$ N cycloaddition product will not be stable. Hence, the  $\alpha$ -CH dissociated and [2+2] C=C cycloaddition products are the only expected surface adducts. Note that we cannot rule out the  $\alpha$ -CH dissociation pathway for 3-butenitrile, even though this product is not observed for acetonitrile and 2-propenenitrile. Although the energetics for these molecules were unfavorable, it is anticipated that in 3-butenitrile the linear ketenimine conjugated with the vinyl alkene in the product will increase electron delocalization, resulting in a higher binding energy.

Figure 9 compares the IR spectra for 2-propenenitrile, 3-butenitrile, and 4-pentenenitrile saturated Ge(100)-2 $\times$ 1 surfaces at room temperature. As in Figure 6a, the spectral region between 1900 and 2000  $\text{cm}^{-1}$  is scaled 0.1 $\times$  relative to the rest of the spectrum. In contradiction to the preceding analysis, Figure 9b shows that a strong mode at 1952  $\text{cm}^{-1}$  is still observed for 3-butenitrile. This peak is in close proximity to the cyclic ketenimine absorption peak characteristic of the 2-propenenitrile [4+2] cycloaddition product, and we believe that a cyclic ketenimine is in fact present on the surface. However, as will be discussed in the following section, the cyclic ketenimine is likely a result of an isomerization from 3-butenitrile to 2-butenitrile *before* introduction to the reaction chamber.

The 2233  $\text{cm}^{-1}$  nitrile stretch in 3-butenitrile, indicative of a [2+2] C=C cycloaddition, is blue-shifted 23  $\text{cm}^{-1}$  relative to its position for 2-propenenitrile. This shift brings it significantly closer, but still red-shifted relative to the condensed phase  $\nu(\text{C}\equiv\text{N})$  peaks usually seen near 2250  $\text{cm}^{-1}$  for saturated nitriles. This trend agrees with the previously postulated idea that the red-shift away from 2250  $\text{cm}^{-1}$  results from a proximity effect between the germanium dimer atoms on the surface and the nitrile functional group in the product. The additional methylene group in 3-butenitrile further separates the nitrile from the surface and reduces the observed red-shift. Although experimental infrared data are not available for compounds with different alkyl chain spacings between the germyl ( $-\text{GeH}_3$ ) and nitrile ( $-\text{C}\equiv\text{N}$ ) functional groups, we performed preliminary DFT calculations to investigate this trend. The results are in accord with our explanation and show that for the gas-phase molecules  $\text{GeH}_3\text{CN}$ ,  $\text{GeH}_3(\text{CH}_2)\text{CN}$ , and  $\text{GeH}_3(\text{CH}_2)_2\text{CN}$ , the nitrile stretching frequency is red-shifted relative to that of acetonitrile by 48, 21, and 12  $\text{cm}^{-1}$ , respectively.

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**Figure 9.** Saturation coverage infrared spectra of (a) 2-propenenitrile, (b) 3-butenitrile, and (c) 4-pentenenitrile on Ge(100)-2×1 at 300 K.

Even though the  $\alpha$ -CH dissociated product for 3-butenitrile is likely more stable than its acetonitrile and 2-propenenitrile analogues, due to increased electron delocalization, the infrared spectrum (Figure 9b) is ambiguous and provides no conclusive evidence as to the presence or absence of this product. The stretching vibration for a linear ketenimine formed in an  $\alpha$ -CH dissociation reaction is expected to be considerably blue-shifted with respect to the cyclic ketenimine stretch due to the release of strain. Although an infrared mode is observed at 2118  $\text{cm}^{-1}$ , we believe that this peak is not a linear ketenimine absorption because it coincides with the set of peaks between 2100 and 2130  $\text{cm}^{-1}$  for 2-propenenitrile, which cannot form a surface adduct with a linear ketenimine. The  $\nu(\text{Ge}-\text{H})$  stretch region is again obscured due to the intense cyclic ketenimine mode. We also do not see evidence for a  $\nu(\text{C}=\text{C})$  stretching mode around 1650  $\text{cm}^{-1}$ , which would be present for the  $\alpha$ -CH dissociated product, but these modes tend to be weak and could be difficult to observe in this surface species. We do observe a weak absorption peak near 3042  $\text{cm}^{-1}$ , typical of terminal alkene  $\nu(=\text{CH}_2)$  stretches.<sup>65</sup> However, the peak is difficult to distinguish from the noise in that region, and, furthermore, presence of an alkene  $\nu(=\text{CH})$  stretch in the surface adduct could result from a [4+2] cycloaddition product in addition to the  $\alpha$ -CH dissociated product.

**D. 3-Butenenitrile Isomerization.** In this section, we will address the unexpected cyclic ketenimine stretching mode, characteristic of a [4+2] cycloaddition product, that was observed for 3-butenitrile. For a cyclic ketenimine to occur with 3-butenitrile, a shift of the double bond from the 3 to 2 position would allow a [4+2] cycloaddition product to form.

Because electron delocalization results in stabilization and an overall energy reduction, there is a thermodynamic driving force for such a conversion of 3-butenitrile to 2-butenitrile. However, previous theoretical work by Dubnikova and co-workers<sup>66</sup> shows that this transformation, which involves the intramolecular transfer of an acidic hydrogen atom from the  $\alpha$ -carbon to the  $\gamma$ -carbon via a resonance stabilized carbanion intermediate, has a substantial barrier of 75 kcal/mol that is likely insurmountable at room temperature. In fact, gas-phase experimental studies of this isomerization reaction are probed at temperatures exceeding 1200 K.<sup>67</sup> In contrast, our data show an intense ketenimine mode for 3-butenitrile at room temperature, although it is weaker than that for 2-propenenitrile at saturation coverage.

We investigated 4-pentenenitrile, a non-conjugated nitrile with a longer alkyl chain spacing between the nitrile and alkene functionality, in an attempt to further reduce the probability of isomerization via intramolecular hydrogen transfer. The barrier to hydrogen transfer along this molecular backbone would be expected to be significantly greater because the additional methylene spacer would prevent the intermediates from being resonance stabilized.<sup>68</sup> However, similar to 2-propenenitrile and 3-butenitrile, this molecule also showed a peak near 1960  $\text{cm}^{-1}$ , as shown in Figure 9c.

A comparison of the surface coverage dependence for 2-propenenitrile (Figure 8) and 3-butenitrile (not shown) provides important insight into the origin of these apparently anomalous cyclic ketenimine peaks. Unlike 2-propenenitrile, the

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coverage dependence data for 3-butenitrile show that the cyclic ketenimine peak appears only at higher surface exposures. This coverage study was completed by filling the stainless steel gas handling manifold with an initial volume of 3-butenitrile with each successive dose drawing from this initial volume of gas. The fact that only higher doses show the cyclic ketenimine stretching mode suggests that some percentage of the 3-butenitrile is isomerizing to 2-butenitrile *before* introduction into the reaction chamber. In other words, the stainless steel of the gas handling manifold may be acting as a reaction catalyst for the isomerization of 3-butenitrile to 2-butenitrile.

To further investigate this possibility, we recorded several multilayer spectra of 3-butenitrile (not shown), after different residence times in the gas handling system. A strong peak at  $2250\text{ cm}^{-1}$  and a small peak at  $2219\text{ cm}^{-1}$ , characteristic of a  $\nu(\text{C}\equiv\text{N})$  stretching mode for a saturated and unsaturated nitrile, respectively, are present at 0 h. As the gas residence time increases, the peak near  $2220\text{ cm}^{-1}$  continues to grow in, until, at 48 h, its intensity is one-half that of the saturated  $\nu(\text{C}\equiv\text{N})$  peak at  $2250\text{ cm}^{-1}$ . Several previous infrared investigations of 3-butenitrile also report the presence of a weak mode near  $2220\text{ cm}^{-1}$ . Durig et al.<sup>69</sup> and Verma et al.<sup>70</sup> both ascribe this peak to a combination band, but these authors disagree as to the contributing fundamental modes. However, Griffith et al. provide spectral evidence that the peak near  $2220\text{ cm}^{-1}$  is a direct result of 2-butenitrile,<sup>71</sup> leading us to conclude that the cyclic ketenimine surface adduct forms as a *direct result of the isomerization of 3-butenitrile to 2-butenitrile in the gas handling manifold before introduction to the chamber.*

#### IV. Conclusions

We have studied the competition and selectivity of several nitrile-containing compounds on the  $\text{Ge}(100)\text{-}2\times 1$  surface.

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A combination of MIR-FTIR and DFT was employed to identify surface products and predict pathways. Our studies show that acetonitrile does not react at room temperature on  $\text{Ge}(100)\text{-}2\times 1$  because both the  $\alpha\text{-CH}$  dissociation and  $[2+2]\text{ C}\equiv\text{N}$  reactions have high barriers and low binding energies. The use of multifunctional molecules to investigate competition and selectivity provided interesting results as well. The conjugated molecule 2-propenenitrile primarily forms a  $[4+2]$  cycloaddition surface product in addition to a small percentage of  $[2+2]\text{ C=C}$  cycloaddition product.

The fact that the nitrile functional group does not directly react with the  $\text{Ge}(100)\text{-}2\times 1$  surface to give a  $[2+2]\text{ C}\equiv\text{N}$  cycloaddition product further highlights the possible benefits of the enhanced thermodynamic selectivity observed with this surface. Because this functional group can remain unreacted, it would be available for second layer reaction chemistry. It is known that compared to ketones or amines, for example, nitriles are relatively unreactive with other organic functional groups. However, conversion of the nitrile via in situ hydrogenation, which can be performed in UHV, creates an amine. The amine, in principle, could then be reacted with a strong electrophile in vacuum, ultimately leading to ordered layer by layer growth of organic functionalized surfaces. We are currently investigating the feasibility of such a method in our laboratory.

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