## Reaction pathways for HCN on transition metal surfaces

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<td>Complete List of Authors:</td>
<td>Abdel-Rahman, Mohammed; University of Illinois at Chicago, Chemistry Feng, Xu; Virginia Polytechnic Institute and State University, Chemistry Muir, Mark; University of Illinois at Chicago, Chemistry Ghale, Kushal; Louisiana State University, Department of Chemical Engineering Xu, Ye; Louisiana State University, Department of Chemical Engineering Trenary, Michael; University of Illinois at Chicago, Chemistry</td>
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</table>
Reaction pathways for HCN on transition metal surfaces

Mohammed Abdel-Rahmana, Xu Fenga, Mark Muirb, Kushal Ghaleb, Ye Xud, and Michael Trenaryab

The adsorption and decomposition of HCN on the Pd(111) and Ru(001) surfaces have been studied with reflection absorption infrared spectroscopy and density functional theory calculations. The results are compared to earlier studies of HCN adsorption on the Pt(111) and Cu(100) surfaces. In all cases the initial adsorption at low temperatures gives rise to a ν(C-H) stretch peak at ~ 3300 cm⁻¹, which is very close to the gas phase value indicating that the triple CN bond is retained for the adsorbed molecule. When the Pd(111) surface is heated to room temperature, the HCN is converted to the aminocarbyne species, CNH₂, which was also observed on the Pt(111) surface. DFT calculations confirm the high stability of CNH₂ on Pd(111), and suggest a bi-molecular mechanism for its formation. When HCN on Cu(100) is heated, it desorbs without reaction. In contrast, no stable intermediates are detected on Ru(001) as the surface is heated, indicating that HCN decomposes completely to atomic species.

1. Introduction

The adsorption and reactions of hydrogen cyanide on transition metal surfaces have been widely studied. These studies have been motivated in part by the relevance of the surface chemistry of molecules containing CN bonds to various areas of heterogeneous catalysis. At a more fundamental level, as a relatively small molecule that is isoelectronic with the prototypical molecular adsorbate CO, HCN offers an opportunity for a detailed mapping of its bonding structure and reaction pathways by both experimental and theoretical methods. Here we present a study that combines surface vibrational spectroscopy with density functional theory calculations of HCN interaction with the Pd(111) and Ru(001) surfaces. The present study was motivated in part by the marked contrast in the reported structure and reactions of HCN on Pd(111) with those on Pt(111). Kordesch et al. observed a vibrational loss with high resolution electron energy loss spectroscopy (HREELS) at 1540 cm⁻¹ following HCN adsorption on Pd(111) at 300 K.¹ ² This frequency is characteristic of a C≡N double bond from which they concluded that HCN bonds to the surface in a di-σ configuration with the C≡N bond parallel to the surface. A NEXAFS study confirmed this orientation for the CN bond.¹

In a series of papers³ ⁸, we have used the technique of reflection absorption infrared spectroscopy (RAIRS) to investigate the structure and reactions of HCN on Pt(111). At a temperature of 85 K, we found that HCN adsorbs molecularly with the axis oriented perpendicularly to the surface. This was based on the strong similarity of the infrared spectrum of the absorbed molecule to that of gas phase HCN. In particular, the CH stretch of HCN on Pt(111) was observed at 3298-3000 cm⁻¹, compared to values of 3311-3312 cm⁻¹ in the gas phase⁹,¹⁰ and 3305-3306 cm⁻¹ in an argon matrix.¹¹, ¹² As the CH stretch frequency is a sensitive indicator of the hybridization on the C atom, the observed value indicates that the adsorbed molecule retains a CN triple bond. The CN stretch is very weak for HCN on Pt(111), which is also characteristic of the gas phase and matrix-isolated molecule. For HCN adsorbed with a perpendicular orientation, the CH and CN stretches would be surface IR allowed but the bending mode would be forbidden. The latter occurs at 712 cm⁻¹ in the gas phase⁹,¹⁰, which was below the low wavenumber cut-off in our RAIRS studies. However, we detected a peak at 1311 cm⁻¹ that we assigned to the overtone of the bending fundamental. These spectral characteristics of HCN adsorbed at low temperature on Pt(111) led us to conclude that the molecule bonds to a Pt atom through the nitrogen lone pair in a perpendicular orientation.

When HCN is adsorbed on Pt(111) at low temperature and then warmed to 300 K, pronounced changes are observed in the RAIR spectra. The bands associated with HCN are replaced with ones at 3363, 1567, and 1323 cm⁻¹, which were assigned to an NH₂ symmetric stretch, a NH₂ scissor mode, and a C≡N stretch, respectively, of an aminocarbyne (CNH₂) species.³ These assignments were supported by observing isotopic shifts after adsorbing H₁²C₁⁴N and H₁²C₁⁵N. Subsequent density

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³ Department of Chemistry, University of Illinois at Chicago, 845 W Taylor Street, Chicago, IL 60607 USA.
⁴ Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA.
© Electronic Supplementary Information (ESI) available: Addition RAIR spectra for HCN isotopologues on Pd(111); TPRS results for HCN on Pd(111).
function theory calculations based on small Pt cluster models of the Pt(111) surface were used to accurately simulate the observed RAIR spectrum and isotopic shifts of aminocarbyne on Pt(111). Other theoretical calculations showed that aminocarbyne is a stable species on Pt(111) and that it bonds with the CN axis perpendicular to the surface. In independent work, aminocarbyne has also been identified as a stable intermediate on R(111) in the decomposition of methyl amine and azomethane.

The previous work arguing that HCN adsorbs on Pd(111) at 300 K with a CN double bond parallel to the surface did not consider the possibility of reaction to form a new chemical entity, such as CNH$_2$. The present study is designed to determine if HCN displays qualitatively different behaviour on Pt(111) and Pd(111), as suggested by past studies. By observing with RAIRS small isotopic shifts with $^{13}$C and $^{15}$N substitution, we show that CNH$_2$ does indeed form on Pd(111). Furthermore, our DFT calculations suggest that CNH$_2$ can form at very low temperatures and is stable to 350 K on Pd(111), just as it is on Pt(111).

On the Ru(001) surface, no RAIR peaks are observed after annealing the surface to temperatures of 150 K or higher. From this observation, we conclude that HCN dissociates completely to atomic H, C, and N. At the other extreme of reactivity, on Cu(100), HCN was found to desorb molecularly without reaction. Based on the similarity of the low temperature and low coverage RAIR spectra for HCN on Pt(111), Pd(111), Ru(001) and Cu(100), we conclude that HCN can adsorb in a common metastable form on these surfaces that is independent of its subsequent reactive chemistry.

2. Experimental

The experiments on Pd(111) were conducted in a ultrahigh vacuum (UHV) chamber equipped for RAIRS, temperature programed reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). The apparatus as well as the details of the crystal mounting and cleaning procedures are described in a recent publication. The Ru(001) experiments were conducted in a separate UHV chamber equipped for RAIRS, TPRS, Auger electron spectroscopy and LEED. This apparatus and the crystal mounting and cleaning procedure are described elsewhere.

Hydrogen cyanide was synthesized using the method of Hagans et al. In which potassium cyanide was reacted with H$_2$SO$_4$(aq). Natural abundance KCN was purchased from Aldrich Chemical Company with a quoted purity of 97%. $^{13}$C$_2$H$_4$N and $^{15}$C$_2$H$_4$N were synthesized using the same procedure with $^{13}$C$_4$N and $^{15}$C$_4$N, which were purchased from Cambridge Isotope Laboratories with quoted purities of 99 and 98%, respectively. The purity of the HCN gases was checked with mass spectrometry and no impurities were detected.

3. Computational Methods

Self-consistent, periodic DFT calculations were performed using the Vienna Ab Initio Simulations Package (VASP v5.2 and above) with the optB86b Van der Waals (vdW) functional developed by Klimček et al. and as well as the GGA-RPBE functional for comparison. Core electrons were described by the projector augmented wave (PAW) method and the Kohn-Sham valence states (including Pd(4d5s); Ru(4d5s); N(2s2p); C(2s2p); and H(1s)) were expanded in a plane wave basis set up to a cutoff energy of 500 eV. The electronic states were smeared using a first-order Methfessel-Paxton scheme with a temperature of 0.075 eV. All total energies were extrapolated back to 0 K.

The lattice constants were calculated to be 3.906 Å for Pd and 2.704/4.259 Å for Ru using the optB86b vdW functional, in close agreement with measured values (3.92 Å and 2.70/4.266 Å, respectively). In comparison, the RPBE lattice constant for Pd is 3.941 Å. The fcc(111) and hcp(001) facets were each modeled using a four-layer slab with a (2×2) surface unit cell, and the Brillouin zone was sampled on a 7×7×1 Monkhorst-Pack k-point mesh, respectively. A vacuum space of ~16 Å was included in the z direction to minimize interactions of neighboring images, together with electrostatic decoupling in the z direction. The top two layers of metal atoms were fully relaxed, with the bottom two fixed at bulk positions. Geometric optimization (i.e. structural relaxation) was converged to 0.01 eV/Å for each relaxed degree of freedom. Energy-minimized states were verified to have no imaginary frequencies except for upright HCN.

Adsorption energies were calculated as $\Delta E = E_{\text{total}} - E_{\text{slab}} - E_{\text{mol}}$, where $E_{\text{total}}$, $E_{\text{slab}}$, and $E_{\text{mol}}$ are the energies of the surface with the adsorbate, the clean surface without any adsorbate, and the adsorbate molecule isolated in the gas phase in a neutral state (closed-shell or radical), respectively. A more negative $\Delta E$ therefore corresponds to stronger adsorption. The minimum-energy reaction path for an elementary step and the transition state (TS) associated with it were determined using the climbing-image nudged elastic band (CI-NEB) method and the dimer method. The activation energy was calculated as $E_a = E_{TS} - E_{IS}$, where IS and TS denote the initial state and transition state, respectively. Each TS was verified to possess only one vibrational mode with negative curvature in the direction of the bond being broken or formed. The transition state search was converged to 0.03 eV/Å for each relaxed degree of freedom.

The simulated IR spectra of surface adsorbates were calculated using the Atomic Simulation Environment. The vibrational modes and frequencies were calculated from a finite difference approximation of the dynamical matrix, and the IR intensities were calculated from a finite difference approximation of the gradient of the dipole moment in the z direction. The magnitude of the displacement was 0.01 Å in each relaxed degree of freedom. The zero-point energies (ZPE) were calculated from the vibrational frequencies ($\nu$) of a molecule as:
4. Results

4.1 RAIR spectra

The changes in the RAIR spectra for increasing exposure of HCN to Ru(001) at 90 K are shown in Fig. 1. Similar behaviour was observed on Pd(111) and Pt(111). For the highest exposures, HCN forms a multilayer and the spectra are similar to those reported previously for solid HCN. As a linear triatomic molecule, HCN has three fundamentals: the CH and CN stretches and the bending mode. At the lowest exposure, only the CH stretch at 3297 cm\(^{-1}\) is observed. As the exposure increases, it changes from a single-sharp peak in the 0.1 L spectrum, to a broader pair of peaks 3233 and 3129 cm\(^{-1}\) after a 5 L exposure. In the solid, HCN forms linear chains of hydrogen-bonded molecules and the strong red-shift and broadening of the CH stretch is consistent with the formation of hydrogen bonds in the multilayer. For the multilayer, the bending fundamental at 845 cm\(^{-1}\) is by far the most intense. The CN stretch, seen at 2101 cm\(^{-1}\) in the 5.0 L spectrum, is notably weak relative to the other fundamentals for gas and solid phase HCN and for HCN in an Ar matrix and is thus an intrinsic characteristic of the molecule. The CH stretch at 3297 cm\(^{-1}\) is close to the value of gas phase HCN\(^3\) at 3312 and of HCN in an Ar matrix\(^11, 12\) at 3305-3306 cm\(^{-1}\). As this value is indicative of the hybridization of the carbon atom, it follows that the adsorbed HCN retains a CN triple bond. The spectra at low coverages are thus most consistent with an HCN molecule bonded through the nitrogen lone pair with the axis perpendicular to the surface. With this orientation, the bending mode would not be surface IR allowed. However, the overtone of the bend would be allowed, and peaks assigned to it were observed at 1311-1323 cm\(^{-1}\) on Pt(111)\(^6\) and at 1395 on Cu(100). No peak clearly attributable to the bending overtone is observed for low coverages on Ru(001), although there are broad but weak features in this spectral region.

Upon annealing the HCN covered Ru(001) surface to 150 K and above, all peaks disappear from the RAIR spectrum. We interpret this as indicating complete dissociation to atomic species. A distinctly different change is seen in the RAIR spectra of HCN on Pd(111), as shown in Fig. 2. After exposing the Pd(111) surface at 90 K to 1.0 L of H\(^{12}\)C\(^{14}\)N, two peaks are seen at 1641 and 3301 cm\(^{-1}\). These are assigned to molecularly adsorbed HCN. As for HCN on Ru(001), the value of the CH stretch is indicative of an sp-hybridized carbon atom, thus implying a triple CN bond.

\[
E_{ZPE} = \frac{1}{2} \sum_i h \nu_i
\]
The assignment of the peak at 1641 cm$^{-1}$ is less straightforward. In solid HCN,$^{33-35}$ the overtone of the bending mode occurs at 1621-1632 cm$^{-1}$ whereas it is at 1427 cm$^{-1}$ in an Ar matrix$^{12}$ and at 1412 cm$^{-1}$ in gas phase HCN.$^{37}$ For HCN on Pt(111) and Cu(100), we assigned peaks at 1311 and 1395 cm$^{-1}$ to the bending overtone.$^{3,6}$ The peak observed at 1641 cm$^{-1}$ in Fig. 2 could be plausibly assigned to the bending overtone, but this frequency is also consistent with a CN double bond stretch. One way to distinguish between these two possibilities is through isotopic shifts. Table 1 compares the values of the HCN bending modes and CN stretch modes of gas phase HCN and of CNH$_2$ on Pt(111) upon substitution with $^{13}$C and $^{15}$N along with the ratio of the shifted frequencies. As the values of the bending overtone for the $^{13}$C and $^{15}$N isotopologues of HCN in an Ar matrix are not available in the literature, the frequencies given in Table 1 are simply twice the fundamentals given by Nakagawa and Morino.$^{10}$ With ratios of 0.9872 and 0.9884 upon $^{13}$C and $^{15}$N substitution, the peak on Pd(111) shows shifts similar to those seen on Pt(111) for the peak assigned to the bending mode overtone, despite the rather different frequencies (1641 vs 1311 cm$^{-1}$). Moreover, these shifts are notably different from what is seen for the CN bond stretch of gas phase HCN or of CNH$_2$ on Pt(111), where the bond-order is between one and two. We therefore assign the 1641 cm$^{-1}$ peak for HCN adsorbed at low temperature on Pd(111) to the overtone of the bending mode. This mode would be surface IR allowed for an upright HCN orientation, although the bending fundamental would not be allowed. While a wavenumber value of 1641 cm$^{-1}$ is consistent with a C=$\text{N}$ stretch, a C=N double bond implying sp$^2$ hybridization on the carbon atom is not consistent with the high value of the CH stretch peak at 3301 cm$^{-1}$.

Fig. 3. RAIR spectra of 1.0 L H$^{12}$C$^{14}$N taken at 90 K after annealing for one minute at the indicated temperatures.

Fig. 4. A comparison of RAIR spectra taken at 90 K for each isotope after annealing at 300 K for one minute.
Table 1: Wavenumber (cm$^{-1}$) positions of infrared peaks of HCN isotopologues and ratios (in parentheses) of positions relative to H$^{12}$C$^{14}$N.

<table>
<thead>
<tr>
<th>Mode, Isotopologue</th>
<th>Pd(111) (exp.)</th>
<th>Pd(111) (calc.)</th>
<th>Pt(111) (exp.)</th>
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<td>1317</td>
<td>1290</td>
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<td>(0.9751)</td>
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<td>1337</td>
<td>1312</td>
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<td>$\delta$(NH$_2$), $^{12}$C$^{13}$N</td>
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<td>(0.9926)</td>
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<td>1506</td>
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<tr>
<td>$\delta$(NH$_2$), $^{12}$C$^{14}$N</td>
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<td>1514</td>
<td>1499</td>
</tr>
<tr>
<td>$\delta$(NH$_2$), $^{12}$C$^{13}$N</td>
<td>(0.9936)</td>
<td>(0.9934)</td>
<td>(0.9949)</td>
</tr>
</tbody>
</table>

The RAIR spectra in Fig. 2 shows that as the HCN covered Pd(111) surface is heated, the peaks associated with adsorbed HCN are replaced by a new set of peaks, the most prominent of which is at 1562 cm$^{-1}$ in the 250 and 300 K spectra. In the 150 K spectrum the reaction is incomplete with some adsorbed HCN still present as indicated by the CH stretch at 3295 cm$^{-1}$. The spectra in Fig. 2 were obtained with 4096 scans, requiring approximately 16 minutes per spectrum. While this reduces the noise level, it also can lead to some mis-cancellations between the background and sample spectra leading to artefacts. The peaks that are labelled in Fig. 2 are reproducible, while other features, such as the peaks at about 3400 cm$^{-1}$ in the 200 K spectrum and 1500 cm$^{-1}$ in the 250 K spectrum, are not.

Table 2. Peak positions for the $\nu$(CN) and $\delta$(NH$_2$) modes of CNH$_2$ on Pd(111) (experimental and calculated) and Pt(111) (experimental) and ratios, in parentheses, of the positions relative to those of $^{12}$C$^{14}$H$^{15}$N$_2$.

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<tr>
<th>Mode, Isotopologue</th>
<th>Pd(111) (exp.)</th>
<th>Pd(111) (calc.)</th>
<th>Pt(111) (exp.)</th>
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<td>1290 (0.9978)</td>
<td>1290 (0.9751)</td>
<td>1303 (0.9939)</td>
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<tr>
<td>$\nu$(CN), $^{12}$C$^{13}$N$_2$</td>
<td>1303 (0.9939)</td>
<td>1290 (0.9751)</td>
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<tr>
<td>$\nu$(CN), $^{12}$C$^{14}$N$_2$</td>
<td>(0.9936)</td>
<td>(0.9934)</td>
<td>(0.9949)</td>
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The most significant changes occur in the lower wavenumber range and Fig. 3 shows spectra from 1150 to 1750 cm$^{-1}$, which were obtained with 1024 scans, which eliminates some of the artefacts seen with 4096 scans in Fig. 2. As before, the 150 K anneal causes the 1646 cm$^{-1}$ peak to disappear and be replaced by peaks at 1562 and 1359 cm$^{-1}$. The 1359 cm$^{-1}$ peak is accompanied by a weak feature at about 1390 cm$^{-1}$ in the 150 K spectrum, and this region shows some possible structure in the 200 K spectrum, which may be indicative of incomplete conversion of HCN to CNH$_2$. The spectra show little change from 200 to 350 K, demonstrating the stability of CNH$_2$ on the Pd(111) surface.

The assignment of the CNH$_2$ peaks seen in Fig. 3 is aided by repeating the experiment with H$^{13}$C$^{14}$N and H$^{13}$C$^{15}$N and spectra with these isotopologues analogous to those of Fig. 3 are given in the supplementary information. Fig. 4 shows a comparison of the spectra obtained starting with H$^{12}$C$^{14}$N, H$^{13}$C$^{14}$N and H$^{13}$C$^{15}$N. Table 2 lists the wavenumber values for the $\nu$(CN) and $\delta$(NH$_2$) modes for CNH$_2$ on Pd(111) along with the corresponding values for CNH$_2$ on Pt(111). The fact that the peak at 1564 cm$^{-1}$ shifts to 1554 upon $^{15}$N substitution but to only 1562 cm$^{-1}$ with $^{13}$C substitution clearly reveals that this is a $\delta$(NH$_2$) mode, rather than a C=N stretch. The large shift of the peak at 1354 to 1342 cm$^{-1}$ with $^{15}$N substitution and to 1328 cm$^{-1}$ with $^{13}$C substitution clearly indicates that it is a CN stretch mode. The similar positions and isotopic shifts of the peaks on Pd(111) and Pt(111) indicates that the same species, aminocarbene (CNH$_2$), forms on both surfaces.

4.2 Computational results

4.2.1 Adsorption of surface intermediates

To help elucidate the mechanism of the decomposition of HCN on Pd(111), we first modelled and calculated various possible intermediates based on prior work on this and similar systems by us and other groups. Table 3 lists and compares their adsorption energies ($\Delta E_{ads}$) calculated using the RPBE and optB86b functionals. Fig. 5 shows the optimized molecular structures of these species. Molecular images in this figure and those below are created using VESTA.38

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**Table 1** Wavenumber (cm$^{-1}$) positions of infrared peaks of HCN isotopologues and ratios (in parentheses) of positions relative to H$^{12}$C$^{14}$N.

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<th>Pt(111) (exp.)</th>
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<td>1430 (0.9917)</td>
<td>1440 (0.9986)</td>
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<tr>
<td>$\nu$(CN), gas$^{10}$</td>
<td>2097</td>
<td>2063 (0.9838)</td>
<td>2064 (0.9838)</td>
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<td>1303 (0.9939)</td>
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<tr>
<td>$\nu$(CN), $^{12}$H, Pt(111)$^3$</td>
<td>1332</td>
<td>1290 (0.9751)</td>
<td>1312 (0.9917)</td>
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</tbody>
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**Table 2.** Peak positions for the $\nu$(CN) and $\delta$(NH$_2$) modes of CNH$_2$ on Pd(111) (experimental and calculated) and Pt(111) (experimental) and ratios, in parentheses, of the positions relative to those of $^{12}$C$^{14}$H$^{15}$N$_2$.

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<th>Pt(111) (exp.)</th>
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<td>$\nu$(CN), $^{12}$C$^{14}$N$_2$</td>
<td>(0.9808)</td>
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<td>$\nu$(CN), $^{12}$C$^{13}$N$_2$</td>
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<td>$\nu$(CN), $^{12}$C$^{14}$N$_2$</td>
<td>(0.9987)</td>
<td>(0.9980)</td>
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<tr>
<td>$\nu$(CN), $^{12}$C$^{14}$N$_2$</td>
<td>(0.9936)</td>
<td>(0.9934)</td>
<td>(0.9949)</td>
</tr>
</tbody>
</table>
The preferred adsorption sites of several of the species, including di-σ HCN, CN, and atomic H, are consistent with those previously reported by Herron et al. CN, CNH, and CNH₂ all preferentially adsorb in upright geometries on the threefold fcc site. We have not found any stable geometry for CN adsorbed on Pd(111) in which the C-N bond is parallel to the surface, in agreement with Herron et al. and contradicting Kordesch et al. Bader analysis indicates that the C atom in CN carries a charge of +0.56 e whereas the N atom carries -0.93 e, making the CN group overall negatively charged. Cis- and trans-HCNH are included as potential intermediates to CNH₂. The cis isomer binds through both C and N in the bridge-top geometry, whereas the trans isomer binds through C on the top site only. Atomic N and H prefer to adsorb on the fcc site, whereas atomic C prefers to adsorb on the hcp threefold site. The RPBE adsorption energies of CN, N, and C are noticeably more negative than those reported by Herron et al., which were calculated self-consistently in PW91 and non-self-consistently in RPBE. Non-self-consistent calculations may be insufficient for describing the strong chemical bonding between the C or N and Pd.

The fact that the molecular adsorption of upright HCN is not exothermic according to RPBE appears to be inconsistent with its facile reactivity on this surface. A recent study by Hensley et al. finds that the contribution of vdW energies to adsorption on transition metal surfaces becomes significant when the values of RPBE $\Delta E_{ads}$ fall roughly below 70% of the corresponding ones for optB86b. Based on the adaptive sum method introduced by Hensley et al., we conclude that the optB86b values more closely reflect the actual heats of adsorption for the intermediates on Pd(111) (see Table S1), although over-binding to some extent by optB86b is expected.

Table 3: DFT-calculated minimum-energy configurations and associated adsorption energies ($\Delta E_{ads}$, in eV) of various molecular and atomic intermediates in HCN decomposition on Pd(111), in comparison with available DFT and experimental literature values.

<table>
<thead>
<tr>
<th>Species</th>
<th>Preferred site</th>
<th>$\Delta E_{ads}$</th>
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<th>Exp. lit.</th>
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<td></td>
<td></td>
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<td>optB86b-vdW</td>
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<tr>
<td>HCN upright</td>
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<td>-0.56</td>
<td>-0.39 2</td>
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<tr>
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Each adsorbate is located on a (2×2) surface unit cell at 1/4 ML coverage. $\Delta E_{ads}$ is with respect to each adsorbate in gas phase and is non-ZPE corrected. “br” stands for bridge site.

1 From Ref. 39
2 From Ref. 42
3 per unit of HCN or CN.
4 From Ref. 43

Thus the low-temperature HCN desorption features observed by Guo et al., from which they deduced a maximum desorption barrier of 9.1 kcal/mol (the $\alpha_3$ state), most likely corresponded to desorption from the upright HCN state present in a saturated HCN adlayer because the value is consistent with the optB86b $\Delta E_{ads}$ of -0.56 eV (-13 kcal/mol) for upright HCN. The subsequent investigation of the decomposition pathway is conducted based on the optB86b results.
4.2.2 Simulated infrared spectra of intermediates

The IR spectra for various H_xCN intermediates have been simulated and compiled in Fig. 6, which include only the fundamental modes but not overtones. The most prominent features include the $\delta$(NH$_2$) mode of CNH$_2$ (1538 cm$^{-1}$) and the $\nu$(CH) mode of upright HCN (3366 cm$^{-1}$). They are in line with the assignment of 1564 cm$^{-1}$ to CNH$_2$ and 3301 cm$^{-1}$ to HCN.

Di-$\sigma$ HCN is expected to be essentially undetectable with RAIRS due to the lack of any strong mode. CNH, and cis- and trans- HCNH have several modes with moderate IR intensities. The $\nu$(CN) mode of adsorbed CN is calculated to have a very weak intensity and a frequency of 1922 cm$^{-1}$, in agreement with the HREELS assignment of 1910 cm$^{-1}$ by Kordesch et al. to CN.$^1$

We have also simulated IR spectra for isotopically labelled CNH$_2$ coadsorbed with CN (Fig. 7), for reasons that will become clear below. The two modes visible in Fig. 7 are the $\delta$(NH$_2$) and $\nu$(CN) of CNH$_2$. As can be seen, the isotopic shifts seen in Fig. 4 are closely captured by the computational results in Fig. 7, which further confirms the assignment of 1564 cm$^{-1}$ and 1354 cm$^{-1}$ (Fig. 4) to CNH$_2$.

4.2.3 Reaction pathways for HCN decomposition on Pd(111)

We have explored a number of possible reaction pathways to explain the reactivity of HCN following its deposition on Pd(111), including the nature of the hydrogenation/dehydrogenation steps that are operative at cryogenic temperatures. Two minimum-energy reaction pathways are depicted in Figs. 8 and 9, one uni-molecular (Fig. 8) and the other bi-molecular (Fig. 9). The minimum-energy uni-molecular
mechanism for the formation of CNH₂ consists of the steps listed in Table 4, corresponding to what is depicted in Fig. 8. The upright HCN state, which vibrational analysis indicates to be unstable according to RPBE but which does represent a shallow minimum on the potential energy surface according to opt86b, is predicted to convert to the di-σ state with an essentially zero barrier as an isolated molecule (Fig. 8, Table 4). This suggests that the upright state cannot exist on the surface except under high coverage conditions where its isomerization is sterically hindered.

The minimum energy uni-molecular mechanism does not proceed through HCNH as an intermediate, unlike what was previously proposed by Gómez-Díaz and López for CNH₂ formation on Pt(111). Similar to the energetics that they reported, the uni-molecular hydrogenation/dehydrogenation steps have significant kinetic barriers. Even with ZPE corrections included, the size of the activation energies for the last 3 steps is clearly inconsistent with the observed formation of CNH₂ at a temperature as low as 150 K, which implies a maximum barrier of ca. 0.4 eV.

We use the semi-classically corrected harmonic transition state theory (SC-HTST) formulated by Fermann et al. to estimate the contribution of quantum tunnelling to the reactivity of the last hydrogenation step, which has the highest barrier of the four steps. The eigenvalue of the imaginary mode is found to be 1032 cm⁻¹, which corresponds to a crossover temperature of 239 K. On the other hand, 1.20 eV corresponds to a peak reaction temperature of 462 K, based on Redhead analysis for a second-order rate process with initial coverage of 1 ML and a heating rate of 2 K/s. Therefore, we conclude that quantum tunnelling does not play a significant role in promoting the uni-molecular mechanism for CNH₂ formation.

Alternatively, we have explored whether bi-molecular interaction can facilitate the formation of CNH₂, and found it to be possible. The bi-molecular mechanism (Fig. 9), which to our knowledge has not been proposed before for HCN on transition metals, consists of the steps listed in Table 5. All steps except one involve two (or two units of) HCN or its derivatives reacting with each other. The pathway begins with an upright HCN coupling via its C atom to the N atom of a di-σ HCN, yielding a dimer state ((HCN)₂). This species is reminiscent of the known HCN trimer, s-triazine, and its formation is consistent with the tendency of HCN to polymerize due to its possession of both a nucleophilic N and an electrophilic C. This step has a small barrier of 0.17 eV, the last 3 steps is clearly inconsistent with the observed formation of CNH₂ at a temperature as low as 150 K, which implies a maximum barrier of ca. 0.4 eV.

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The pathway produces coadsorbed CNH and CN, which stabilize each other (by 0.22 eV, with ZPE, same below) and is slightly more stable than a pair of coadsorbed CNH (by 0.22 eV, with ZPE, same below) and is more stable than CNH (by 0.04 eV). On an isolated basis, as indicated by the dashed lines in Fig. 9, CNH is more stable than CNH on Ru(001). Multiple species in the same state are calculated at infinite separation.

The pathway that we have found for CNH₂ formation on Pd(111) from HCN allows new insights into the previously published studies on this system. The HREELS results are similar to what we observe but the assignments were quite different. For a 0.1 L HCN exposure to Pd(111) at 300 K, loss peaks were observed at 1290 and 1540 cm⁻¹, which given the HREELS resolution of 65 cm⁻¹, are close to our values of 1354 and 1564 cm⁻¹. They also found that the expected peak in the CH/NH stretch region was too weak to observe for low exposures at 300 K. They assigned their 1540 cm⁻¹ peak to the HCN bend, with the CH/NH stretch mode of CNH₂ and assign the CNH bend to the HCN bend, with the CH/NH stretch mode of CNH₂. We therefore conclude that the 300 K HREELS data is better assigned to CNH₂ than to a di-σ bonded CNH species. Other earlier observations are also consistent with CNH₂ on Pd(111). For example, it was noted that the same spectra were obtained from HCN adsorption as from the hydrogenation of CN produced from the dissociation of cyanogen. On Pt(111), we showed that CN produced from cyanogen dissociation is kinetically more facile than HCN desorption will be the subject of a future study. We note that H₂ desorption is known to occur at lower temperature on Cu(100) than on Pd(111). Thus monitoring H₂ desorption in a TPD study of HCN on Cu(100), which has not been performed to our knowledge, would provide more definitive evidence that HCN does not dissociate on Cu(100).

5. Discussion

The pathway that we have found for CNH₂ formation on Pd(111) from HCN allows new insights into the previously published studies on this system. The HREELS results are similar to what we observe but the assignments were quite different. For a 0.1 L HCN exposure to Pd(111) at 300 K, loss peaks were observed at 1290 and 1540 cm⁻¹, which given the HREELS resolution of 65 cm⁻¹, are close to our values of 1354 and 1564 cm⁻¹. They also found that the expected peak in the CH/NH stretch region was too weak to observe for low exposures at 300 K. They assigned their 1540 cm⁻¹ peak to the HCN bend, with the assumption that it was stiffened upon adsorption. In a separate study by the same authors, the HCN bend position was assigned to an HREELS peak at 1355 cm⁻¹. These values are essentially at the same position, within the margin of error, as the peaks that we observe at 1354 and 1564 cm⁻¹ and assign to the δ(NH₃) and ν(CN) modes of CNH₂. We therefore conclude that the 300 K HREELS data is better assigned to CNH₂ than to a di-σ bonded CNH species. Other earlier observations are also consistent with CNH₂ on Pd(111). For example, it was noted that the same spectra were obtained from HCN adsorption as from the hydrogenation of CN produced from the dissociation of cyanogen. On Pt(111), we showed that CN produced from cyanogen dissociation is kinetically more facile than HCN desorption will be the subject of a future study. We note that H₂ desorption is known to occur at lower temperature on Cu(100) than on Pd(111). Thus monitoring H₂ desorption in a TPD study of HCN on Cu(100), which has not been performed to our knowledge, would provide more definitive evidence that HCN does not dissociate on Cu(100).
readily hydrogenated to CNH$_2$, and it follows that the same reaction occurs on Pd(111).\textsuperscript{48}

The orientation of the CN bond of the proposed di-σ bonded HCN was investigated with NEXAFS and the data indicated that the CN bond was parallel to the surface.\textsuperscript{1} For the adsorbed diatomic molecules CO, NO, and CN, the NEXAF spectra at the N 1s edge show a sharp π resonance at the threshold and a broader σ resonance at higher photon energy. The α/π intensity ratio depends on the angle ($\theta_\alpha$) between the surface normal and the electric field vector and is much larger for CO and NO than it is for CN. As the former are bonded perpendicular to the surface, it was concluded that CN was bonded parallel to the surface. They then argued that because the NEXAFS results for HCN resembled the results for CN, that the CN bond of HCN was also parallel to the surface. This is in contrast to our findings that HCN exposure at room temperature leads to both CN and CNH$_2$ on the surface. Although we do not detect adsorbed CN experimentally, the calculations indicate that it is oriented perpendicular to the surface, as is the CN bond of CNH$_2$. The calculations imply that di-σ bonded HCN should be a stable intermediate with the CN axis parallel to the surface, but there is no evidence for it from our RAIR spectra. Similar considerations would apply to an angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) study.\textsuperscript{49} Spectra obtained after annealing to 200 K an HCN layer adsorbed at 110 K should have produced a mixture of CN and CNH$_2$. The resulting ARUP spectra display four distinct peaks and their angular dependencies were carefully characterized. However, the discussion indicated that there was some ambiguity in interpreting the results in terms of di-σ bonded HCN with the CN bond parallel to the surface. While it is difficult to reconcile the results from NEXAFS and ARUPS with our results using RAIRS, it is possible that the former techniques detect species that are invisible to the latter.

Our findings can also provide new insights into the reaction chemistry of HCN on Pd(111) as studied with TPRS by Guo et al.\textsuperscript{42} Following an HCN exposure of 2.6×10$^{15}$ molecules/cm$^2$ at a surface temperature of 87 K, three desorption products were observed: HCN, H$_2$, and CO$_2$. Multilayer HCN was observed to desorb as two peaks ($\alpha_1$ and $\alpha_2$) at 118 and 131 K and monolayer HCN as a peak ($\alpha_1$) at 150 K. A single higher temperature HCN desorption peak ($\beta_1$) was observed at 400 K. The latter was accompanied by reaction limited H$_2$ desorption ($\beta_2$). A desorption-limited H$_2$ peak ($\beta_1$) was observed at lower temperatures, with the exact temperature depending on HCN exposure. Cyanogen desorption was observed in the temperature range of 500 to 750 K. No surface carbon or nitrogen was detected with Auger electron spectroscopy after cyanogen desorption, indicating that the CN bond remains intact throughout the reaction pathway. Our limited TPRS results roughly matched those of Guo et al.,\textsuperscript{42} although we were unable to detect cyanogen desorption, which was almost certainly due to a lower sensitivity in our TPRS experiments compared to theirs.

In contrast to the results obtained following HCN exposures at 87 K, high HCN exposures with the Pd(111) surface at 300 K led to the formation of a (HCN)$_x$ polymeric species.\textsuperscript{42} Upon heating, (HCN)$_x$ decomposes to liberate HCN ($\beta_1$ HCN) at temperatures as high as 800 K. The amount of $\beta_2$ HCN desorbing following 300 K exposures is much greater than observed following low temperature exposures and increases linearly with HCN exposure, indicating that it forms a multilayer polymer. Although we did not explore such a polymeric species in this study, our computational results suggesting a mechanism involving HCN dimers also reflects the tendency of the HCN molecule to form bonds with itself.

Our results can provide new insights into the origin of the $\beta_1$ HCN and $\beta_1$ and $\beta_2$ H$_2$ peaks observed by Guo et al.\textsuperscript{42} We can associate the $\beta_1$ H$_2$ peak with the decomposition of the (HCN)$_2$ dimer to produce CNCHN + H, with the H atom stable on the surface until the recombinative H$_2$ desorption temperature is reached. Guo et al.\textsuperscript{42} found that for the lowest exposures to the Pd(111) crystal at 300 K, $\beta_2$ H$_2$ occurs at 375 K and $\beta_1$ HCN at 510 K. As these peaks are associated with reaction-limited desorption, and from RAIRS we observed the disappearance of CNH$_2$ for annealing temperatures above 300 K, the simplest conclusion is that $\beta_1$ HCN and $\beta_2$ H$_2$ are associated with CNH$_2$ decomposition. We further assume that at low coverages, CNH$_2$ decomposes by the reverse of the unimolecular mechanism to produce H, which immediately desorbs as $\beta_2$ H$_2$ and adsorbed CNH. The latter is then assumed to be stable to higher temperatures, but eventually desorbs as $\beta_1$ HCN. As the coverage increases, intermolecular interactions change the energetics of various steps such that the $\beta_1$ HCN and $\beta_2$ H$_2$ peaks moved closer together as the coverage increased to the point where both molecules desorbed at the same temperature of 400 K.

The experimental evidence for an upright bonding configuration for HCN on Pd(111) at low temperatures is quite clear from the RAIR spectra. When van der Waals contributions are included with the optB86b-vdW functional, an isolated, weakly bound but stable upright HCN is obtained from DFT. However, the upright HCN can be stabilized in the presence of a neighbouring di-σ bonded HCN (Fig. 9). This is only consistent with the experimental RAIRS results if we assume that the peaks of di-σ bonded HCN are too weak to observe. The calculated spectra imply that this would be the case. Similarly, although the experimentally implied pathway involves adsorbed CN, DFT indicates that it would likely be undetectable with RAIRS. The calculations predict two strong RAIRS peaks for the CNH intermediate, but these peaks are not observed in the experiments for HCN on Pd(111). However, on Pt(111), a peak was observed at 3348 cm$^{-1}$, the intensity of which rose and fell as HCN was converted to CNH$_2$, and was therefore attributed to the NH stretch of CNH. This peak was not accompanied by an observable CN stretch, in contrast to the DFT prediction in Fig. 6. Also, the position of the experimental 3348 cm$^{-1}$ peak fell between that of the CH stretch of adsorbed HCN and the NH stretch of CNH$_2$ whereas DFT implies that the NH stretch of CNH$_2$ would lie above the NH stretch of CNH$_2$. Coincidently, the NH stretch of CNH$_2$ is calculated to be at the same value as the CH stretch of upright HCN, which is not observed in the experimental spectra. The calculations predict moderately intense peaks for both cis- and trans-HCNH, but no
peaks assignable to these species are observed with RAIRS, implying that HCNH is not a stable intermediate.

6. Conclusions
The initial adsorption of HCN on Cu(100), Pt(111), Pd(111), and Ru(001) at temperatures below 100 K is characterized by a relatively sharp CH stretch at about 3300 cm⁻¹. This value is close to that of the gas phase and is characteristic of a CN triple bond. This implies that this peak corresponds to an HCN molecule that does not bond in a way that involves rehybridization of the carbon atom. The overall spectral characteristics indicate that this form of HCN bonds to these surfaces through the nitrogen lone pair and is oriented with the molecular axis perpendicular to the surface. The DFT calculations imply that an upright HCN would be stabilized through interaction with a neighbouring HCN molecule bonded with the CN axis parallel to the surface. Both the experimental and calculated RAIR spectra, including isotopic shifts, with the CN axis parallel to the surface. The overall spectral characteristics indicate that this form of HCN bonds to these surfaces through the nitrogen lone pair and is oriented with the molecular axis perpendicular to the surface. The DFT calculations imply that an upright HCN would be stabilized through interaction with a neighbouring HCN molecule bonded with the CN axis parallel to the surface. Both the experimental and calculated RAIR spectra, including isotopic shifts, demonstrate that CNH₂ forms on Pd(111). The RAIR spectra of CNH₂ on Pd(111) are almost identical to the spectra on Pt(111). The DFT calculations indicate that a bi-molecular mechanism for formation of CNH₂ from HCN with low barriers is available that can explain the observation of CNH₂ at relatively low temperatures. However, the bi-molecular mechanism involves intermediates that are not detected with RAIRS.

Conflicts of interest
There are no conflicts to declare.

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References


Two HCN molecules, adsorbed at 85 K in an upright orientation, react to form the aminocarbyne species, \( \text{CNH}_2 \), on Pd(111) when the surface is heated to 200 K.